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UNIVERSITÉ DE MONTRÉAL

STEADY-STATE MODELING OF NUTRIENT TRANSFORMATIONS IN ACTIVATED SLUDGE TREATMENT OF PULP AND PAPER WASTEWATER

LUCY ELLEN COTTER

DÉPARTMENT DE GÉNIE CHIMIQUE

ÉCOLE POLYTECHNIQUE DE MONTRÉAL

MÉMOIRE PRÉSENTÉ EN VUE DE L'OBTENTION

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CE MÉMOIRE INTITULÉ :

STEADY-STATE MODELING OF NUTRIENT TRANSFORMATIONS IN ACTIVATED SLUDGE TREATMENT OF PULP AND PAPER WASTEWATER

présenté par : <u>COTTER Lucy Ellen</u>

en vue de l'obtention du diplôme de: <u>Maîtrise ès sciences appliquées</u>

a été dûment accepté par le jury d'examen constitué de:

M. <u>PERRIER MICHEL</u>, Ph.D., président

M. <u>STUART PAUL</u>, Ph.D., membre et directeur de recherche

M. <u>PALUMBO JAMES</u>, M.S., membre

A generous heart, kind speech,
and a life of service and
compassion are the things which
renew humanity.

- Buddha

Dedication

For my shiny, shiny family
Anne & Tony
Kate, Moira, Danielle & Loretta,
for your laughter, generosity
& magnanimity

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Résumé

Les eaux usées de l'industrie papetière sont souvent carencées en nutriments, typiquement en azote et en phosphore, tandis que ces éléments sont normalement retrouvés en quantité suffisante ou en excès des besoins des microorganismes des boues activées dans les eaux usées municipales. Le contrôle du dosage de l'azote et du phosphore supplémentaires peut entraîner une réduction de coûts ainsi qu'une opportunité de réduire les concentrations des nutriments à l'effluent final. Ce dernier avantage est non négligeable considérant les exigences de rejet de plus en plus sévères imposées par les autorités environnementales ou gouvernementales. Plusieurs types de procédés pâte et papier et de procédés du traitement des eaux usées existent. Ce mémoire présent une étude de cas d'une usine papetière de type PTM-papier journal intégré : la méthodologie utilisée dans cette étude est applicable de façon générale pour l'industrie papetière.

La caractérisation des eaux usées a été effectuée pour l'effluent d'une usine papetière de type PTM-papier journal intégré, par des méthodologies systématiques et bien-acceptées. La méthodologie utilisée dans cette étude, du traitement rigoureux des données, de la détection des régimes pseudo-permanents, le développement des bilans de masse et l'utilisation d'un modèle basé sur ASM1 qui a été développé pour l'industrie papetière, donne un aperçu des transformations des nutriments qui se passent dans un réacteur de boues activées de type complètement-mélangé (CM) de temps de rétention hydraulique court .

La caractérisation de l'affluent a permis de souligner les différences majeures de la détermination des fractions de la DCO entre les eaux usées municipales et les eaux usées de l'industrie papetière. Le calage du modèle basé sur ASM a été extrêmement difficile pour la gamme entière des conditions du procédé ; les paramètres cinétiques modifiés individuellement ont été utilisés, avec une évolution des taux des réactions de la nitrification et de la dénitrification avec le temps. L'usine a déjà mis en place une boucle de contrôle de rapport sur le dosage des nutriments, avec un contrôle de type rétroaction (feed-back) sur les concentrations des nutriments à l'effluent, et l'utilisation d'un modèle basé sur ASM sera mis en place comme une couche additionnelle de contrôle.

Abstract

Pulp and paper wastewater is often deficient in readily available macronutrients, typically nitrogen and phosphorus, whereas municipal wastewater usually contains adequate or excess quantities of these nutrients in relation to the requirements of the activated sludge microorganisms. The control of supplemental nitrogen and phosphorus dosing represents a cost reduction opportunity as well as an opportunity to reduce nutrient concentrations in the final effluent discharge, which are increasingly prescribed by environmental or governmental authorities. A wide range of pulp and paper and wastewater treatment process configurations exist industry-wide. This thesis presents a case study of an integrated TMP-newsprint mill; the methodology of the study is practical and broadly applicable.

Wastewater characterisation was carried out on a pulp and paper mill effluent for an integrated TMP-newsprint mill according to well-accepted systematic methodologies. The methodology used in this study, of rigorous data treatment, detection of pseudo-steady states, development of mass

balances and the use of a pulp and paper-specific ASM1-based model, has demonstrated important insights into the nutrient transformations occurring in a well-mixed (CSTR) short-retention time AST wastewater treatment plant.

The wastewater characterisation methods highlighted major differences between the determination of COD fractions in pulp and paper wastewater and those in municipal wastewater. Calibration of the ASM-based model was exceedingly difficult for the entire range of process conditions; individually adjusted kinetic parameters were used, with an evolution of the nitrification-denitrification process rates over time. The use of the ASM-based model saturation functions as an indicator of the actual plant operating regime and of nutrient deficiency in the biomass are proposed as potentially powerful tools for the plant operators. The mill has already implemented upstream ratio control of nutrient dosing with feed-back of residual concentrations, and the proposed use of the ASM-based model will be implemented as an additional layer of control.

Condensé en français

INTRODUCTION

Les eaux usées de l'industrie papetière sont souvent carencées en nutriments, typiquement en azote et en phosphore, tandis que ces éléments sont normalement retrouvés en quantité suffisante ou en excès des besoins des microorganismes des boues activées dans les eaux usées municipales. Le contrôle du dosage de l'azote et du phosphore supplémentaires peut entraîner une réduction de coûts ainsi qu'une opportunité de réduire les concentrations des nutriments à l'effluent final. Ce dernier avantage est non négligeable considérant les exigences de rejet de plus en plus sévères imposées par les autorités environnementales ou gouvernementales.

MÉTHODOLOGIE

La méthodologie globale du projet comporte plusieurs étapes, incluant la compilation de dimensions des équipements et de données de conception de l'usine ainsi que des données en continu et discrètes du laboratoire venant du système automatique de collecte de données (PI). De plus, des mesures additionnelles de la caractérisation des eaux usées ont été effectuées au laboratoire de l'usine et au laboratoire de l'université selon les méthodes standardisées [2]. Ces données ont été traitées afin de les synchroniser pour tenir compte du temps de rétention hydraulique des bassins aérés, d'exclure les conditions anormales du procédé tel que les arrêts de l'usine, et d'identifier les scenarios de régime pseudo-permanent qui ont varié en durée de 6 heures jusqu'à 32 heures [3]. Les données ainsi traitées ont, par la suite, été réconciliées par un bilan de masse pour chaque scenario de régime pseudo-permanent avant d'être intégrées à un modèle basé sur ASM (modèle de boues activées standardisé).

La caractérisation des eaux usées a été effectuée pour l'effluent d'une usine papetière de type PTM-papier journal intégré, par des méthodologies systématiques et bien-acceptées. Les scenarios de régime pseudo-permanent ont été utilisés conjointement avec la caractérisation des eaux usées et avec un modèle basé sur ASM1 développé pour l'industrie papetière afin d'évaluer les transformations des nutriments en régime permanent dans le traitement des eaux usées de cette industrie. Le modèle basé sur ASM1 a tenu compte de la nature des eaux usées de l'industrie papetière y compris la carence possible en nutriments.

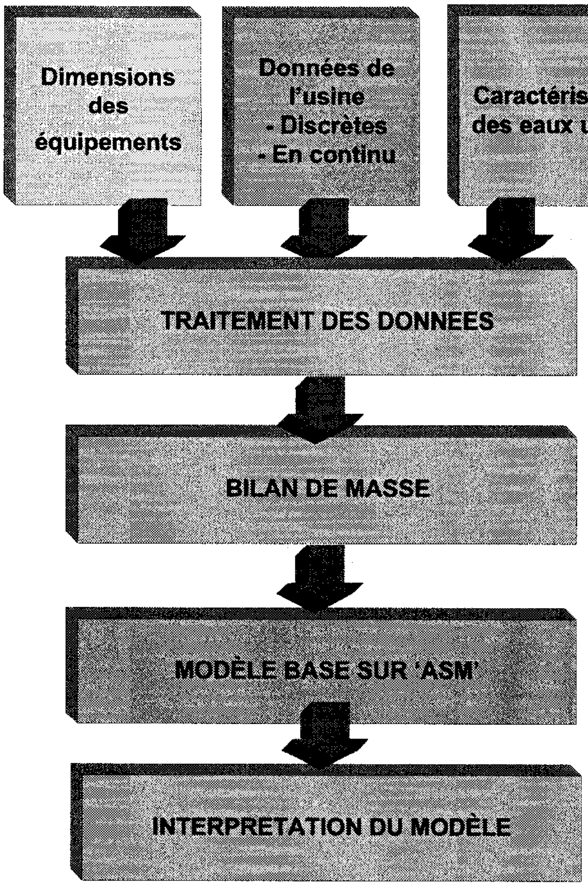

Figure 1: Méthodologie du projet

RÉSULTATS

La caractérisation de l'affluent a permis de souligner les différences entre les eaux usées municipales et les eaux usées de l'industrie papetière. Cette caractérisation requiert du travail additionnel si les modèles basés sur ASM y seront appliqués de manière générale. La concentration de DCO totale, et possiblement la taille relative des fractions de DCO, peuvent varier dans le temps (pendant une journée), ce qui se traduit en un défi pour l'application d'un modèle basé sur ASM à un réacteur de type complètement mélangé (CM) qui a un temps de rétention hydraulique court.

Il est possible d'utiliser un modèle basé sur ASM pour modéliser le traitement des eaux usées de l'industrie papetière, pendant que le système de traitement et la population de microorganismes sont stables. Il est extrêmement difficile de modéliser les petites variations des concentrations des nutriments lorsque les procédés biologiques de nitrification partielle et dénitrification partielle varient avec le temps et varient en réponse aux changements de la caractérisation de l'affluent et du temps de rétention des boues.

Les résultats du modèle basé sur ASM ont été interprétés de manière approfondie et des stratégies de contrôle ont été proposées. L'usine a déjà mis en place une boucle de contrôle de rapport sur le dosage des nutriments, avec un contrôle de type rétroaction (feed-back) sur les concentrations des nutriments à l'effluent, et l'utilisation d'un modèle basé sur ASM sera mis en place comme une couche additionnelle de contrôle. Tandis que plusieurs types de procédés pâte et papier et de procédés du traitement des eaux usées existent, la méthodologie et le modèle basé sur ASM utilisés dans cette étude sont applicables de façon générale pour l'industrie papetière, et ils représentent la fine pointe de la technologie pour l'industrie.

CONCLUSIONS

Les contributions les plus importantes de ces travaux sont les suivantes:

- Le traitement systématique des données permet l'identification des économies possibles pour l'usine à partir des bilans de masse et de la comparaison entre les rapports de DBO_5 : N : P de l'usine et ceux des autres usines ;

- La modélisation des eaux usées de l'industrie papetière permet l'identification des transformations des nutriments dans le traitement des eaux ; et
- Le modèle basé sur ASM a été interprété de manière approfondie et des stratégies de contrôle ont été proposées

Les points suivants énumèrent quelques opportunités de recherche pour l'avenir:

- La caractérisation standardisée des affluents de l'industrie papetière, incluant la détermination des différences entre les fractions de la DCO, en particulier entre les fractions S_S, X_S et X_I ;
- Une caractérisation à court terme des affluents de l'industrie papetière afin d'évaluer la variation des fractions de la DCO ; et
- La validation de l'hypothèse qu'un modèle basé sur ASM pourrait être utilisé pour prédire une carence en nutriments dans la biomasse avant que celle-ci puisse être mesurée dans la concentration résiduelle des nutriments à l'effluent.

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Notation and Abbreviations

References: [4, 5]

Symbol	***Definition***	***Units***
α	Alpha-factor: ratio of wastewater to clean water K_La	-
A	Area	m^2
AMT	Accepted Modern Technology	-
AOR	Actual oxygen requirement	kg O_2/h
AOX	Adsorbable organic halogen compounds	mg AOX/L
APMP	Alkaline-peroxide mechanical pulping	-
APP	Ammonium polyphosphate	-
ASB	Aerated stabilisation basin (lagoon)	-
AST	Activated sludge treatment	-
ASM1	Activated Sludge Model no 1 by IAWPRC	-
ATP	Adenosine triphosphate	-
β	Beta-factor: ratio of wastewater to clean water C_{O2S}	-
b	Decay rate constant	d^{-1}

Symbol	***Definition***	***Units***
b_A	Autotrophic decay rate	d^{-1}
BAS	Biofilm-activated sludge process (MBBR + AST)	-
BAT	Best available techniques	-
BATEA	Best Available Technology Economically Achievable	-
BCOD	Biodegradable COD	mg COD/L
b_H	Heterotrophic decay rate	d^{-1}
bio-P	Biological phosphorus removal (process)	-
BKM	Bleached Kraft mill (process)	-
BNR	Biological nutrient removal (process)	-
BOD	Biological oxygen demand	mg BOD/L
BODfilt	BOD measured after sample is filtered to 1.0µm (BOD of filtrate)	mg BOD/L
BOD_i	Accumulated oxygen demand for biological growth after i days	mg BOD/L
BODinf	Accumulated oxygen demand after a very long time (infinite, uBOD)	mg BOD/L
BODmeas	Measured BOD	mg BOD/L

Symbol	***Definition***	***Units***
BODsed	BOD measured after sample has settled	mg BOD/L
BODs	BOD measured after sample is filtered to 0.1μm (BOD of filtrate), some literature uses filtrate of 0.45μm	mg BOD/L
BODtot	BOD measured on raw sample (non-filtered)	mg BOD/L
C_A	Concentration of species A (nominally substrate)	mg/L
$C_{A,S}$	Saturation concentration of species A	mg/L
CAC	Citric acid cycle	-
CN	Carbon-nitrogen library	-
CNP	Carbon-nitrogen-phosphorus library	-
COD	Chemical oxygen demand – oxygen equivalent required for complete oxidation of all organic material and all chemically-oxidizable material	mg COD/L
fCOD	COD measured after sample is filtered to 1.0μm (COD of filtrate)	mg COD/L
sCOD	COD measured after sample is filtered to 0.1μm (COD of filtrate), some	mg COD/L

Symbol	***Definition***	***Units***
	literature uses filtrate of 0.45µm	
tCOD	COD measured on raw sample (total, non-filtered)	mg COD/L
CRISP-DM	Cross Industry Standard Process for Data Mining	-
CSTR	Continuously stirred tank reactor	-
CTMP	Chemithermomechanical pulp (process)	-
DCS	Distributed control system	-
D_L	Diffusivity (diffusion constant)	$cm^2/s = 10^4\ m^2/s$
DNA	Deoxyribonucleic acid	-
DO	Dissolved oxygen	mg O_2/L
DRP	dissolved reactive phosphorus (ortho-phosphate plus may include some polyphosphates hydrolysed during test)	mg P/L
DTPA	Diethylene triamine pentaacetic acid (chelating agent)	-
E_a	Activation energy for reaction	J/mol
e(t)	Controller error signal	-
ECF	Elemental chlorine free	-

Symbol	***Definition***	***Units***
EDTA	Ethylenediamine tetraacetic acid (chelating agent)	-
FADH	Flavin adenine dinucleotide	-
ϕ_{BOD}	Characterisation: correction factor for cell decay	mg COD/ mg BOD
f_{BOD}	Modelling: Ratio of BOD5: ultimate BOD	mg BOD/ mg BOD
F/M	Food-to-microorganism rate	g COD/g VSS
fxii	Fraction of biomass present as intra-cellular dissolved inorganics	mg COD/mg COD
g	Acceleration due to gravity	m/s^2
HMW	High molecular weight	-
HRT	Hydraulic Retention Time (volume/ volumetric flow rate)	m^3/ m^3/day
H_S	Henry's Law constant	mg O_2/L. kPa
IAWPRC	International Association on Water Pollution Research and Control, now IWA	-
IAWQ	International Association on Water Quality, now IWA	-

Symbol	***Definition***	***Units***
i_{CV}	Elemental oxygen required for every gram of biomass consumed in an oxidation process	mg O_2/mg wastewater
ISE	Ion-selective electrode	-
i_{NXB}	Nitrogen fraction of COD in biomass, X_B	g N/ g COD
i_{NXU}	Nitrogen fraction of COD in unbiodegradable particulates from cell decay, X_U	g N / g COD
i_{PXB}	Phosphorus fraction of COD in biomass, X_B	g P/ g COD
i_{PXU}	Phosphorus fraction of COD in unbiodegradable particulates from cell decay, X_U	g P / g COD
IWA	International Water Association	-
J	Mass Flux	kg/m^2.day
k_a	Specific ammonification rate	m^3/g COD. day
k_A	Reaction constant specific to species A	*
K_A	Saturation constant of species A	mg/L
K_C	Controller gain	-
K_d	Endogenous decay coefficient	g VSS/g VSS.d

Symbol	***Definition***	***Units***
k_h	Maximum specific hydrolysis rate	g COD/g cell COD.d
k_L	Mass transfer coefficient	m/d
K_La	Overall mass transfer coefficient	d^{-1}
K_{NA}	Ammonia half saturation constant (autotrophic)	g NH4-N/ m^3
K_{NO}	Nitrate half saturation constant	g NO 3-N/ m^3
K_{OA}	Oxygen half saturation constant (autotrophic)	g O_2/m^3
K_{OH}	Oxygen half saturation constant (heterotrophic)	g O_2/m^3
K_P	Phosphorus half saturation constant	g P/m^3
K_{SH}	Half saturation constant for assimilation of carbon	g COD/m^3
k_T	Arrhenius temperature coefficient (also θ_T used in different formation of the equation)	$^{\circ}C^{-1}$
K_X	Hydrolysis half saturation constant	g COD/g cell COD
LMW	Low molecular weight	-
μ	Kinematic viscosity	kg/m.s

Symbol	***Definition***	***Units***
μ_A	Autotrophic maximum specific growth rate	d^{-1}
μ_H	Heterotrophic maximum specific growth rate	d^{-1}
μ_{MAX}	Maximum growth rate	d^{-1}
MBBR	Moving bed biofilm reactor	-
MBR	Membrane bioreactor (process)	-
MCRT	Mean cell residence time	d
MF	Microfiltration	-
MFC	Machine finish coated paper	-
MLSS	Mixed liquor suspended solids	g VSS/L
N	Nitrogen	mg N/L
NADH	Nicotinamide adenine dinucleotide	-
NF	Nanofiltration	-
NH_4^+-N NH_{3+4}	Ammonia nitrogen	mg N/L
NO_x NO_{2+3}	Nitrate plus nitrite nitrogen	mg N/L
η_g	Correction factor for anoxic growth of	-

Symbol	***Definition***	***Units***
	heterotrophs (denitrification)	
η_h	Correction factor for anoxic hydrolysis	-
ODE	Ordinary differential equations	-
OTE	Oxygen transfer efficiency	%
p	Controller output signal	-
$\overline{p}$	Bias steady state value, controller output signal	-
P	Phosphorous	mg P/L
PAO	Phosphorus accumulating organisms	-
PC	Primary clarifier	-
PFR	Plug flow reactor	-
PHB	Polyhydroxybutyrate	-
PI	Plant information (data system)	-
PO_4-P	Ortho-phosphate phosphorus	mg P/L
p_{O2}	Partial pressure of oxygen in the gas phase	kPa
Q	Volumetric flow rate	m^3/d
Θ	Mean hydraulic retention time	d

Symbol	***Definition***	***Units***
ρ	Density	kg/m^3
ρ_i	Rate of process i (bacterial growth, decay etc)	kg COD/m^3.d
R	Gas constant	J/mol.K
r	Particle radius	m
r_A	Rate of production of species A	kg/m^3.s
RAS	Recycled activated sludge (stream)	-
RBC	Rotating biological contactors (process)	-
Re	Reynolds number	-
Redox	Reduction-oxidation	-
RNA	Ribonucleic acid	-
RO	Reverse osmosis	-
S_0	Substrate (BOD_5) concentration in influent	mg BOD_5/L
S_{ALK}	Alkalinity	mol CaCO3/L
SBR	Sequential batch reactor (process)	-
S_e	Substrate (BOD_5) concentration in effluent	mg BOD_5/L
S_I	Soluble inert organic material	mg COD/L

Symbol	***Definition***	***Units***
S_{ND}	Soluble organically bound nitrogen	mg N/L
S_{NH}	Ammonium nitrogen	mg N/L
S_{NO}	Nitrate nitrogen	mg N/L
S_O	Dissolved oxygen	mg -COD/L
SOTE	Standard oxygen transfer efficiency	%
S_{PD}	Soluble organically bound phosphorus	mg P/L
SRT	Sludge retention time	day
S_S	Soluble organic biodegradable material	mg COD/L
SVI	Sludge volume index	mL/g
τ	Normalised time	-
τ_I	Controller integral time	s
τ_D	Controller derivative time	s
t	Time	s
T	Temperature	ºC
TCA	Tricarboxylic acid cycle	-
TKN	Total Kjeldahl Nitrogen (sum of ammonia nitrogen and organic nitrogen)	mg N/L

Symbol	***Definition***	***Units***
TMP	Thermomechanical pulp (process)	-
TN	Total nitrogen	mg N/L
TOC	Total organic nitrogen	mg N/L
TP	Total phosphorus	mg P/L
TSS	Total suspended solids	mg TSS/L
TUDP	Delft University of Technology	-
UF	Ultrafiltration	-
UV	Ultraviolet	-
V	Volume	m^3
v	Velocity	m/s
v_0	maximum theoretical settling velocity	m/day
v_i	settling velocity	m/day
v_{max}	maximum practical settling velocity	m/day
VSS	Volatile suspended solids	mg VSS/L
v_t	Terminal velocity	m/s
w	Manipulated variable	-
WAS	Waste activated sludge (stream)	-
WERF	Water Environment Research	-

Symbol	***Definition***	***Units***
	Foundation	
WWTP	Wastewater treatment plant	-
x	Measured variable	-
X	VSS concentration in the aeration basin	g VSS/L
X_{BA}	Autotrophic biomass	mg COD/L
X_{BH}	Heterotrophic biomass	mg COD/L
XCOD	Particulate COD	mg COD/L
X_I	Particulate inert organic material	mg COD/L
X_{II}	Particulate inert inorganic material	mg COD/L
X_{ND}	Particulate organic nitrogen	mg N/L
X_{PD}	Particulate organic phosphorus	mg P/L
X_S	Particulate organic biodegradable material	mg COD/L
X_U	Unbiodegradable particulates from cell decay	mg COD/L
Y	Yield of biomass per unit substrate consumed	g VSS/g BOD_5
Y_A	Autotrophic yield	g cell COD/g N
Y_H	Heterotrophic yield	g cell COD/g SS

Symbol	***Definition***	***Units***
Y_{OBS}	Observed yield	g VSS/g BOD_5
Y_{TH}	Theoretical yield	g VSS/g BOD_5
y_m	Controller input signal	-
y_{SP}	Controller set point	-

*Dependent on reaction order

List of Appendices

Thesis Organisation

This thesis is organised into sections, the first section (A) contains a critical review of literature, the second section (B) contains the research thesis, which is organised into seven chapters containing background on the case study mill, gaps in the body of knowledge, objectives and hypotheses, the study methodology, results and discussion including the presentation of two published articles, a summary of error and sensitivity analyses, conclusions, recommendations and contributions to the body of knowledge. Raw data, calculations and detailed information are presented in the eight appendices, which are organised in the same order as the thesis chapters.

SECTION A

LITERATURE REVIEW

1. Wastewater Treatment in the Pulp and Paper Industry[1]

1.1. Historic Development

The pulp and paper industry is one of the world's oldest manufacturing industries, with historic evidence of paper making occurring in ancient Egypt and China [6]. The world-wide pulp and paper industry in 2005 produced 25.2 million (metric) tonnes of wood pulp, 6.7 thousand tonnes of printing and writing papers and 7.8 million tonnes of newsprint [7]. Pulp and paper mill effluent is typically discharged into a water body such as a river, lake or ocean. Secondary or biological treatment to remove the organic load and suspended solids discharged to the water body became popular during the 1980's and 1990's, particularly in Canada and Scandinavian countries [8].

1.2. Driving Factors for Research

Water pollution is a concern for most industrialised nations, and government regulation often drives the spending by industry on the infrastructure required to abate such pollution. Water pollution is a significant social cost of industry to society.

Wastewater treatment is considered to be a component of the so-called triple bottom line for industrial sites nowadays; however it does not constitute part of their core operations and as such, is often viewed as an unnecessary cost. With wastewater treatment plant installations in the order of $34 to $44 million capital cost (AST system, 1997 cost estimates), and operating costs in the order of $3.5 to $6 million per year, there is a genuine incentive to

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[1] Greater detail on the literature review is presented in Appendix 1.

reduce operating costs related to the wastewater treatment plant [9]. The incentive is even greater if a reduction in operating costs aligns with a better quality effluent, as is potentially the case with the reduction of nutrient addition to the process.

1.3. North American context

Much of North America could be considered as water-rich, especially when compared to other countries such as Spain or Australia, where annual precipitation is a fraction of that in Canada. The fresh water in North America is to a large extent land-locked in inland lakes. In Canada, the total land area of the country 9 984 670 km^2 consists of 91% land and 9% fresh water [10]. The Great Lakes system (Superior, Michigan, Huron, Erie and Ontario) have a combined surface area of 245 000 km^2, of which approximately one third is Canadian territory [11]. The inland freshwater situation in North America is comparable that in Norway, Sweden and Finland, where freshwater covers 5.5%, 9.7% and 11.3% of the total land respectively [12-14]. The freshwater system of the Great Lakes poses international regulation issues, similar to those of many rivers in Europe [15]. In Canada, much of the fresh water is inaccessible for human use, as 85% of the population lives within 300 km of the Canadian-US border, and 60% of the fresh water flows north towards the Artic Ocean [16, 17].

World-wide regulations referring to pulp and paper mill effluent discharge are listed in Appendix 1 according to the country where they have been implemented. Experience with these regulations has been documented for pulp and paper mills [18, 19]. Regulations vary from the end-of-pipe concentration or total loading, to the receiving water impact-based limits, and set out the minimum standards for the industry. Site-specific discharge permits are being developed world-wide to further manage the requirements of specific receiving waters.

1.4. Environmental Benchmarks

A number of environmental benchmarking systems are available that can be used to gauge the performance of mill operations or as guidelines for designing future installations. The main ones discussed here are the European Best Available Techniques (BAT), the Australian Accepted Modern Technology (AMT) and the North American Best Available Control Technology (BACT) or Best Available Technology Economically Achievable (BATEA)[2]. Recent proposals concerning new pulp mill projects have resulted in detailed guidelines and environmental impact assessments, which consolidate much of the world-wide environmental benchmarking for the pulp and paper industry, in particular for kraft pulp mills [20, 21].

1.5. Characteristics of wastewater

There has been extensive research in the area of municipal wastewater treatment, which can be attributed to the necessity of treatment in all regions of the world and the extensive implementation of secondary treatment systems. Domestic (raw) wastewater contaminants consist principally of organic carbon compounds, as does pulp and paper wastewater and other industrial wastewaters which are presented in Table 1 below [22, 23]. Certain other industrial wastewaters, such as those from mining and petrochemical processing, consist of inorganic pollutants or complex organic pollutants such as aromatic compounds, which are toxic in high concentrations to microorganisms and may render the wastewater unsuitable for biological treatment processes [24, 25]. A discussion of

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[2] Best available technology economically available is referred to as BAT in the literature, but will be referred to as BATEA here for clarity.

wastewater characteristics, concentrating on the similarities and differences between domestic and pulp and paper wastewaters, is made below. It is assumed that municipal wastewaters consist entirely of domestic wastewater; i.e. combinations of domestic and industrial wastewaters are not considered.

Table 1: Wastewater characteristics: industrial & domestic [22, 23]

Parameters (mg/L)	***Agro industries***				***Domestic***
	Tannery	***Poultry processing***	***Textile***	***Dairy***	
Total COD	2,285	2,490	2,400	1,410	430
Soluble COD	1,298	1,770	1,700	1,075	170
TSS	770	418	500	190	350
TKN	160	343	35	63	47
Total P	6	30	34	7	8

1.5.1. Municipal vs. pulp and paper wastewater

Typical characteristics of primary treated pulp mill wastewaters from a bleached kraft mill (BKM), a thermomechanical mill (TMP) and a linerboard mill were presented by Slade *et al.* [26]. The pulp mill wastewater characteristics can be compared with the wastewater characterisation carried out for a municipal wastewater treatment plant in the Netherlands, as presented in the right-hand column of Table 2 [27]. From the data in Table 2, it can be seen that pulp mill primary treated wastewater contains a relatively high strength load in terms of COD and BOD concentrations and relatively deficient in the nutrients nitrogen and phosphorus when compared to primary treated municipal wastewater.

Table 2: Pulp mill and municipal primary treated wastewater characteristics [26, 27]

Parameter	*BKM*	*TMP*	*Linerboard*	*Municipal (average)*
COD tot (mg/L)	490 – 590	2,200 – 3,300	1,040 – 1,450	604
COD sol (mg/L)	430 – 480	1,540 – 2,240	890 – 1,250	241 [a]
BOD_5 (mg/L)	150 – 190	1,000 – 1,460	510 – 880	246
TSS (mg/L)	10 – 115	240 – 400	70 – 150	309
VSS (mg/L)	10 – 80	230 – 390	70 – 120	
TN (mg/L)	1.1 – 1.7	5.5 – 10.9	4.4 – 6.4	69
TN_{sol} (mg/L)	0.8 – 0.9	2.3 – 3.7	2.6 – 3.6	
NH_4^+-N (mg/L)	ND [b]	0.1 – 0.6	0.03 – 0.06	53
NO_x (mg/L)	0.07 – 0.08	0.0 – 0.1	1.4 – 2.0	0.1
TP (mg/L)	0.6	2.9 – 5.8	0.9 – 1.4	8.4
DRP (mg/L) [c]	0.5	1.4 – 3.7	0.05 – 0.15	5.2
BOD_5: N	100:0.6 – 100:0.7	100:0.5 – 100:1	100:0.9	
BOD_5: P	100:0.4	100:0.3 – 100:0.4	100:0.15	
pH	7.9 – 8.0	4.8 – 5.3	5.1 – 7.0	

a - CODsol represents soluble COD in the filtrate of a 0.45μm filtered sample;

b - ND = not determined;

c - DRP = dissolved reactive phosphorus (ortho-phosphate plus may include some polyphosphates hydrolysed during testing).

1.5.2. Variability

1.5.2.1. Flow

Municipal wastewater flows vary on a diurnal (24 hour) cycle, typically with very low flow overnight and peak flows in the morning and evening, the exact time of which is dependent on the residence time in the wastewater collection sewer system and possibly the socio-economic demographics of the population [28]. There is also variability between weekdays and weekends, with lower peak flows seen on weekends [28, 29]. These flow variations occur over a period of hours. The magnitude of the flow variation is typically two-fold over the course of the day, and four-fold annually [30, 31].

1.5.2.2. Bulk organic load

The strength or (COD or BOD_5) concentration of pulp and paper wastewater can be significantly larger than that found in municipal wastewater. Comparing data presented in Table 1 and Table 2 above, the chemical oxygen demand (COD) can be used as one indication of the magnitude of the organic load on the effluent treatment plant. The total COD concentration in the BKM effluent is comparable to that in a municipal influent, whereas that from the TMP or linerboard mill is 2 to 3 times as high. Also, the soluble COD in the pulp and paper mill effluents makes up 68 to 88% of the total COD, whereas it makes up only 40% of the municipal influent.

1.5.2.3. Temperature

The temperature of pulp and paper mill wastewater is typically in the range of 40 to 55°C, depending on the mill processes [32], whereas the temperature of municipal wastewater is nominally in the range of 20 to 35°C, dependent on the residence time and temperature in the sewer system. Pulp and paper wastewater temperatures can be as low as 10ºC in northern Canada, due to the extremely low ambient temperatures [33]. Steam is sometimes injected into the wastewater to ensure stable treatment plant operation. As discussed in section 2.3.1.1 below, microorganisms in the biological treatment stage operate most efficiently at a particular temperature range, for example 20 - 35ºC for mesophilic bacteria [34]. This often necessitates wastewater cooling for pulp and paper mill effluents in order to operate the treatment plant efficiently. Some research has been done regarding the use of thermophilic bacteria in wastewater treatment [34], including treatment of pulp and paper mill whitewater streams [35, 36].

Both pulp and paper and municipal wastewater demonstrate a notable variation in temperature between summer and winter seasons. The magnitude of this variation is dependent on the exposure of the wastewater to ambient conditions, either in open channels or open tanks, such as a balancing tank, selector or lagoon. The effects of heat loss due to low ambient temperatures in cold climates are considerable due to the high dependency of chemical reaction kinetics and oxygen solubility on temperature [37].

1.5.3. Biodegradability

As discussed in greater detail in sections 2.3.1 and 3.1, microorganisms consume organic carbon in order to grow and reproduce. A compound is considered 'biodegradable' if it can be decomposed or consumed by an organism, particularly by bacteria [38]. The rate at which microorganisms can consume organic carbon is determined by, amongst other things, the size and structure of the organic carbon molecule [39], and can be tested for using a standard 5- or 7-day biological oxygen demand (BOD) test [40]. A high concentration of toxic substances in the wastewater will inhibit the activity of the microorganisms in the treatment process, as well as having an adverse effect on the receiving water.

1.5.3.1. Molecular weight distribution of organic carbon

Organic material is released in the effluent streams of the CTMP process from the impregnation stage, bleaching and chip washing and screening processes [41]. This organic material can be described as lignin, carbohydrates, 'extractives'[3], and low molecular weight compounds such as acetic acid, methanol and formic acid [41]. The distribution of the molecular weight of organic carbon (COD) in CTMP pulp wastewater can be seen in Figure 2 below [41].

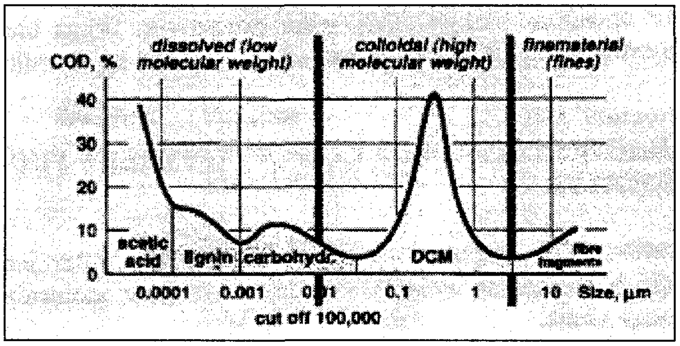

Figure 2: COD molecular size distribution, CTMP effluent [41]

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[3] 'Extractives' refers to the waxes, fats, non-volatile hydrocarbons and resin (pitch) related compounds extracted from wood using solvent extraction, in this case DCM extraction carried out using dichloromethane as the solvent [42]

Within the dissolved organic compounds region, the total organic carbon (TOC) for an integrated TMP-newsprint mill, before and after biological treatment with a trickling filter process, is presented in Figure 3 according to molecular weight [43]. This chart implies that the lower molecular weight fractions are removed at the highest rate by bacterial metabolic processes [43]. The increase in TOC removal for the higher molecular weight fractions can be interpreted as significant hydrolysis occurring over biological treatment [43].

These results are consistent with those found in another study of the biodegradability of effluent from two bleached kraft mill effluent, one hardwood and one softwood [39]. The latter study found that lower molecular weight organic carbon, less than or equal to 960 Daltons, was preferentially removed by biological treatment and that the most effective biological treatment occurred for organic carbon with a molecular weight less than 300 Daltons [39]. Another study of four bleached kraft mills further fractionated the mill effluent into 'low molecular weight (LMW) adsorbable' and 'LMW non-adsorbable', 'high molecular weight (HMW) hydrolysable' and 'HMW non-hydrolysable' [44]. These fractions were interpreted as corresponding to carbohydrates (HMW hydrolysable), lignin (HMW non-hydrolysable), methanol and carboxylic acids (for example, LMW) [44].

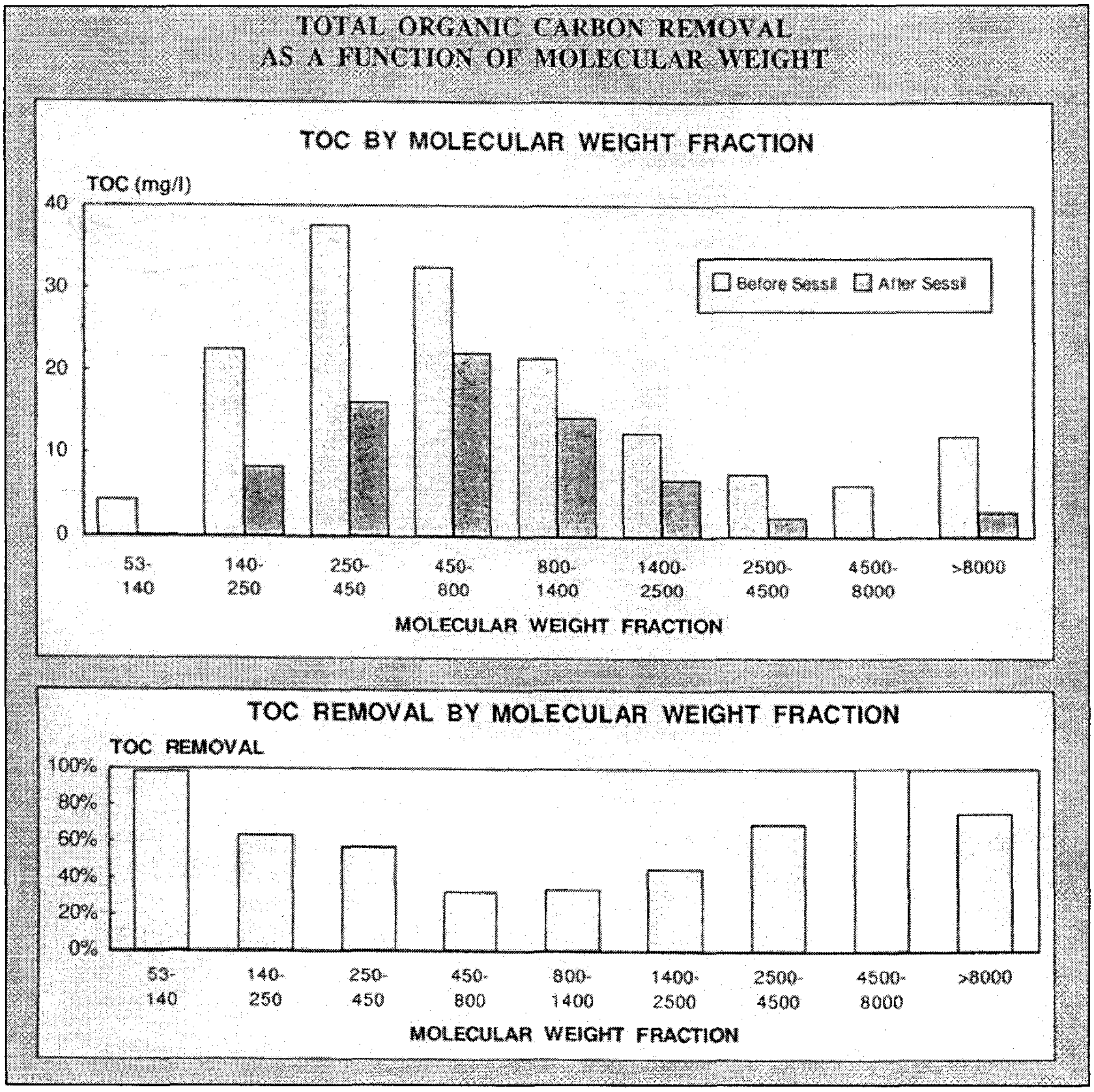


Figure 3: Total organic carbon (TOC) removal by trickling filter process according to molecular weight [43]

The particle size distribution for municipal wastewater, industrial food processing wastewater and agricultural swine waste primary and secondary effluent is presented in Figure 4. In terms of the first row of graphs, graphs (a), (e) and (i), it is clear that the COD in the primary effluent is more broadly distributed at a much lower concentration for the municipal wastewater than for either of the other wastewaters.

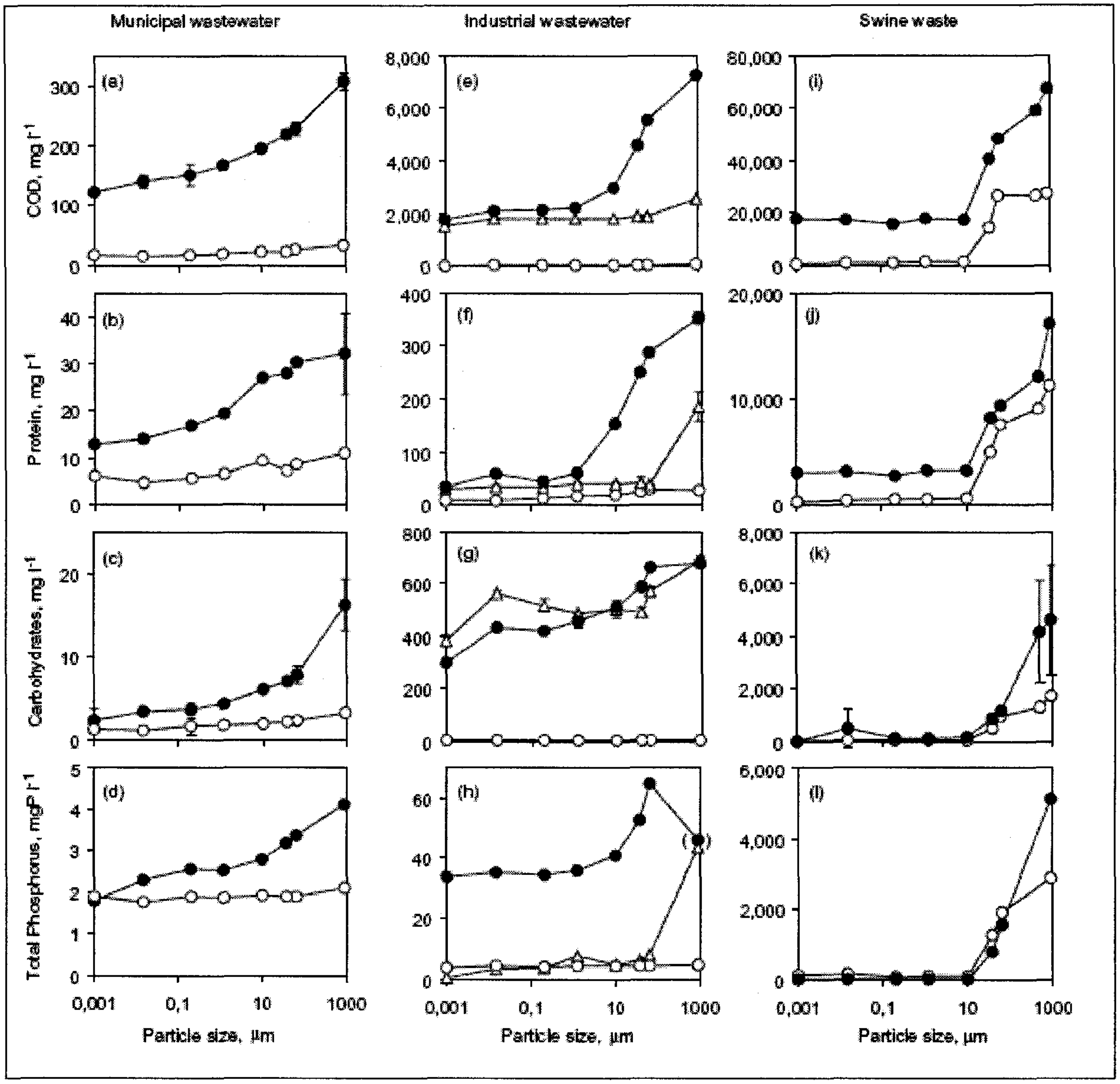


Figure 4: Particle size distribution for municipal, industrial food processing and swine waste (● = primary effluent, ○ = secondary effluent) [45]

Comparing Figure 2, Figure 3 and Figure 4, it can be seen that pulp and paper wastewater contains higher concentrations and fractions of longer, less readily degradable molecules than municipal wastewater. In particular, the peak of colloidal material which occurs in Figure 2 between the particle sizes of 0.1μm and 1μm corresponds to up to 40% of the COD load for the pulp and paper mill [41]. Any such peak is notably absent from the municipal wastewater COD distribution.

1.5.3.2. Toxicity

Toxicity refers to the "potential for a test constituent to cause adverse effects on living organisms" [45]. For municipal wastewater, toxicity is commonly caused by the final effluent ammonia, nitrate or nitrite concentration [45]. The presence of pathogens or pharmaceuticals that have not been removed during the treatment process may also cause adverse effects on the receiving water ecosystem [45, 46]. For pulp and paper effluent, toxicity is commonly associated with the fatty acids, resin acids, chlorinated phenols, monoterpenes and high hydrogen peroxide concentrations [25, 32, 47]. Resin acids are diterpenoid carboxylic acids found in softwood extractives, in the treatment plant these are less readily available for bacteria than other carbon sources [48].

1.5.4. Nutrient load and type

The importance of the nutrients in the influent to the secondary treatment plant is to supply the microorganisms with enough nutrients to achieve an adequate removal of organic carbon. Municipal wastewater provides a "good nutrient balance" [49], whereas pulp and paper mill effluent typically has a higher organic load and a negligible nutrient concentration, which results in a deficiency of nutrient with respect to the biological requirements of the biomass [50, 51]. For the purposes of the following discussion, the term 'nutrient deficient' can be used to describe a deficiency with respect to the biological requirements of the biomass such that the nutrient concentration is growth-limiting, and therefore the organic load (BOD) consumed in the process is not the maximum possible [49].

The nutrient load in municipal and pulp and paper wastewater was presented in Table 2 above. These data show that the nutrient load to the treatment plant from these sources is different in magnitude and nature. A recap is presented in Table 3 below. If the reactive, or assimilable, forms of nutrients are in the ammonia and ortho-phosphate fractions, it is clear from Table 2 that pulp and paper wastewater has very low concentrations of these nutrients available.

Table 3: Nutrient load recap, municipal and pulp and paper primary treated effluent [26, 27]

Parameter	***Municipal (average)***	***TMP***
BOD_5 (mg/L)	245.5	1,000 – 1,460
TN (mg/L)	68.8	5.5 – 10.9
NH_4^+-N (mg/L)	53.4	0.1 – 0.6
NO_x (mg/L)	0.1	0.0 – 0.1
TP (mg/L)	8.4	2.9 – 5.8
PO_4 (mg/L)	5.2	1.4 – 3.7*

* DRP

Nutrients are thus added to pulp and paper wastewaters as supplemental nutrients [50]. Due to the operating cost of purchasing these chemicals, it is in the mills' interest to minimise the quantity of nutrients added to the process, ensuring adequate nutrients for biomass growth while minimizing excess nutrient addition. It is also in the mills' interest to minimise the quantity of nutrients that are present in the final effluent discharged to the receiving environment, in order to avoid eutrophication and to adhere to government regulation. A number of control strategies have been implemented in the pursuit of these goals [51-53].

This section of the literature review has presented some of the history of wastewater treatment, the driving forces behind research, the North American context, world-wide environmental benchmarks and some of the similarities and differences between municipal and pulp and paper wastewater characteristics. The following sections of the literature review will develop these concepts, particularly in relation to modelling of the activated sludge process in pulp and paper wastewater treatment.

2. Activated Sludge Treatment

2.1. Wastewater Treatment Plant

Biological wastewater treatment was developed in the nineteenth century in the form of septic tanks, and by 1913 the activated sludge process was developed concurrently by Ardern and Lockett in Manchester, England and by Clark in Massachusetts, United States [54]. The following is a discussion of some of the unit operations and unit processes of a typical industrial wastewater treatment plant, as shown in Figure 5.

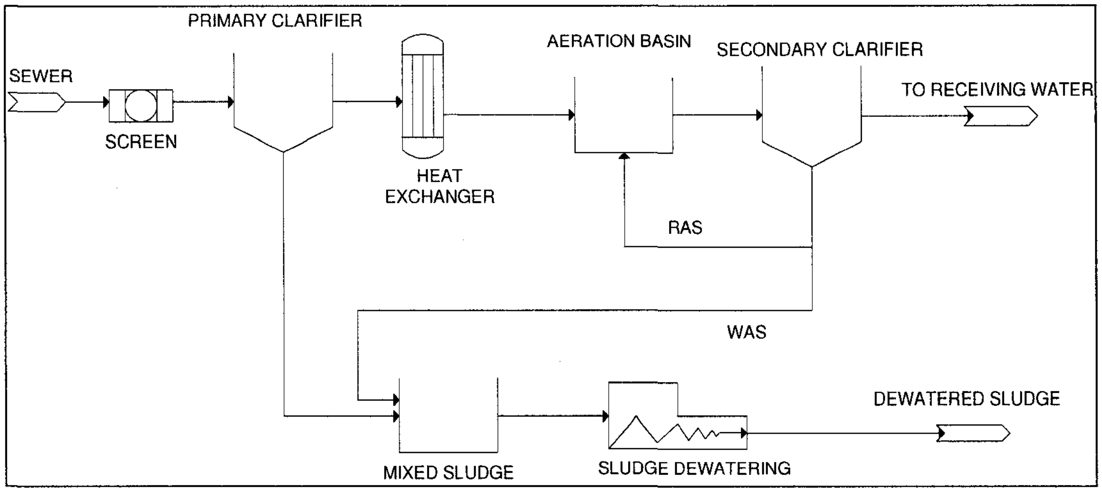


Figure 5: Typical wastewater treatment plant process (basic)

2.1.1. Secondary Treatment

Secondary treatment generally refers to the combination of a biological treatment stage and a solids separation stage that follow the primary clarification or floatation stage. Biological treatment is used to remove soluble organic matter from the wastewater and the solids separation stage is used to remove biomass and other insoluble organic solids from the wastewater [55].

2.1.1.1. Biological Treatment

Two major categories of biological treatment exist: suspended growth systems and attached growth systems.

2.1.1.1.1. Suspended growth system

Suspended growth systems rely upon the exocellular excretion of polysaccharide to form a floc or agglomeration of microorganisms, as well as the recycling of microorganisms within the system in order to maintain the bacterial population [45, 56]. Floc formation is discussed further under section 2.3.1. The aeration system or another mixing system is used to maintain the suspension of bacteria in the wastewater. Bacteria are removed from the solids separation unit and returned to the aeration basin via the recycled activated sludge (RAS) stream or wasted via the waste activated sludge (WAS) stream, not necessarily with the same solids concentration. The majority of modern suspended solids treatment systems consist of either an activated sludge treatment system or an aerated stabilisation basin.

Activated Sludge Treatment (AST)

The activated sludge treatment system consists of a basin or tank in which a population of "active" bacteria are used to consume organic matter [45]. Many systems employ a selector; refer to section 2.2.2 for further discussion. A continuously operating AST basin can be modelled as a plug flow or continuously stirred tank reactor depending on the reactor configuration; refer to section 2.2.1 for further discussion. A batch-type reactor has also been developed, called a sequential batch reactor (SBR). Process configurations have been developed to take advantage of anoxic and anaerobic basins to promote nitrogen removal via the nitrification and denitrification processes and biological phosphorus removal (bio-P) via luxury phosphorus uptake, which can be advantageous for municipal wastewater [56]. Any combination of these processes is referred to as biological nutrient removal (BNR). A two-stage AST system was implemented to treat a paper mill effluent using nitrification and denitrification processes, which resulted in higher organic load removal efficiency than a single stage process [57]. Denitrification was also implemented at an ammonia-based sulphite mill in Canada [58].

Activated sludge systems are reasonably compact in size which results in little if any heat loss from the basin and a short hydraulic retention time. The AST system is relatively easy to control since aeration, recycle and wasting flow rates can be measured and controlled.

Aerated Stabilisation Basin (ASB)

An aerated stabilisation basin system consists of a pond or lagoon which can be fully aerobic or facultative: aerobic, anoxic and anaerobic in layers. The ASB can usually be modelled as a combination of plug flow and continuously stirred reactor tanks. The basin is often constructed of earth rather than concrete, and many have irregular shapes leading to complex hydraulic characteristics. Aeration is often achieved using surface aerators in aerobic or facultative ASBs. If not mechanically aerated, aeration and mixing in the ASB relies upon wind action [45]. Nitrification can be achieved in an ASB with a very long residence time, and then usually only during the summer months [59].

The ASB undergoes significant recycle of nutrients and lysed bacteria from the sediment in the basin, referred to as benthal feedback [60]. This recycling manifests itself as a lower nutrient demand for the same organic load than the equivalent AST system [60, 61]. It has also been seen that some pulp and paper ASB systems can operated without any supplementary nutrient addition, which is due to sufficient nutrient internal recycling and nitrogen fixation [51, 62, 63]. Solids separation can occur in non-aerated, non-mixed areas such as quiescent zones. If the quiescent zone becomes anaerobic, this can also lead to nutrient release [60]. Effluent from the ASB can contain algae [45].

The aerated stabilisation basin has a relatively large surface area which results in greater heat losses to atmosphere from the water surface than an AST system for an equal organic removal rate, and a long hydraulic retention time [45]. This makes the ASB process particularly suitable for treatment of effluent from Kraft mills which generally have a hotter effluent, although it is also employed at a few TMP and paper mills in Canada [64]. The ASB can be relatively difficult to control since internal recycling is not measurable or controllable, although some external controlled solids recycling has been installed [45].

2.1.1.1.2. Attached growth systems

Attached growth or fixed-film systems depend upon microorganisms that are attached or fixed to some media across which the wastewater is passed [45]. Systems such as the trickling filter and the packed bed treatment systems use a stationary media-biomass and percolate the wastewater over the biomass. Other systems such as the rotating biological contactors (RBC) move a disc of media and biomass through the stationary wastewater.

The advantages of these systems include their suitability for warm climates, the low energy requirements and their low operating costs, which is primarily due to a lack of mechanical aeration.

2.1.1.2. Solids separation

Solids separation in the secondary treatment stage is usually achieved using a clarifier, which is commonly designed based on a circular clarifier equipped with a scraping (rake) or suction-type solids removal [45]. Other clarifier types include rectangular clarifiers equipped with travelling flights or bridge solids removal, tray clarifiers, tube and lamella settlers and intrachannel clarifiers [45].

The purpose of the secondary clarifier is the clarification of the wastewater, which involves the sedimentation of the bacterial flocs, as well as the thickening of sludge, which involves compaction of the sludge in the base of the clarifier [45, 65]. The thickening of the sludge occurs in the base of the clarifier, which is designed to accommodate a certain period of storage of the sludge, even during peak load conditions [45, 66]. In a circular clarifier, a centre well may be employed to promote flocculation and the dispersion of energy (momentum) of the inlet flow [66].

2.1.2. Tertiary Treatment

Tertiary treatment may be required to treat the effluent from the secondary treatment due to particular obligations of a discharge permit or regulations, which may include nutrient concentrations or toxicity testing. Besides the treatment processes described here, tertiary treatment processes include sand/gravel granular medium filters, air stripping, breakpoint chlorination, ion exchange, activated carbon adsorption, chemical oxidation, volatization and gas-stripping [45]. These processes have been applied to paper mill effluent following secondary treatment using the activated sludge process [67, 68].

2.1.2.1. Chemical precipitation

Chemical precipitation is often used to remove phosphorus using calcium, aluminium and iron salts, which is discussed further in section 3.1.5.5. Precipitation is more effective for phosphorus in the form of ortho-phosphate than organic phosphorus or polyphosphates, therefore chemical addition would usually occur following secondary treatment [45]. The use of lime for process pH control may lead to inadvertent phosphorus precipitation and interference with other coagulant chemicals [69, 70].

2.1.2.2. Membrane technologies

Membrane technologies consist of pressurised wastewater being driven through a polysulfone- or cellulose acetate-based membrane of a determined porosity: microfiltration (MF) refers to a porosity of 1,000 to 5,000 Angstroms (1Å = 1×10^{-10} m), ultrafiltration (UF) refers to a porosity of 50 to 500 Angstroms, nanofiltration (NF) refers to a porosity of 5 to 20 Angstroms and reverse osmosis (RO) refers to a porosity of 1 to 10 Angstroms [71, 72]. The pressure required to drive the water through the membrane increases with decreasing porosity whereas the quality of the water increases with increasing porosity, up to the RO process which removes ions or deionises water [71]. Wastewater would usually be pre-filtered prior to applying the RO process in order to minimise membrane fouling and energy requirements [71].

2.2. AST Design: Current Configurations & Developing Technology

The following is a discussion of theory behind the main components of a traditional continuous AST unit: the reactor, the selector, the oxygen transfer system, the mixing system and the clarifier, as well as some of the areas of technology being developed on an industrial scale.

2.2.1. Chemical Reactors

Continuously fed chemical reactors can be characterised as idealised plug flow reactors (PFR) or continuously stirred tank reactors (CSTR), or any combination thereof. Other mass transfer systems that involve chemical reactions such as packed beds and fluidised beds can be used to describe biological reactors such as attached growth systems, these will not be discussed further here [55].

2.2.1.1. Plug Flow Reactor (PFR)

A plug flow reactor, also known as a tubular or piston reactor, is characterised by flow only in the longitudinal direction, perfect radial mixing (perpendicular to flow) and zero axial mixing (parallel to flow) [55]. Each cross section of the reactor is assumed to have a uniform velocity and concentration [55]. Resolving the steady state mass balance for this reactor demonstrates that the concentration of a reactant is distance dependent (in the direction of the reactor length) [55].

2.2.1.2. Continuously Stirred Tank Reactor (CSTR)

A continuously stirred tank reactor, also known as a well-mixed reactor, is perfectly mixed and therefore the contents of the entire tank are spatially uniform in concentration, temperature and reaction rate [73]. This is to say that the contents of the influent are instantly transformed by the chemical reaction in the tank, and the concentration of a species in the tank is equal to the concentration of that species in the effluent. The name 'chemostat' is sometimes used to describe a well mixed activated sludge process; the term comes from the microbiology field and refers to a well mixed biological reactor maintained at steady state by continuous overflow [74].

2.2.1.3. Non-Ideal Reactors

No actual reactor will behave exactly according to the idealised models described above. Therefore a combination of the PFR and CSTR is often used to represent constructed reactors. It should be noted that an infinite number of CSTRs in series will produce the same reaction model as a single PFR for a given reactor volume [45]. Reasons for non-ideal behaviour include non-ideal mixing conditions such as non-uniform mixing in CSTRs and excess axial mixing in PFRs, which can be produced by aeration systems [55].

2.2.1.4. Reactor residence time

The residence time of a reactor can be determined from a pulse or step change in concentration of an inert tracer, such as lithium or a coloured dye, the concentration of which can be measured easily throughout the basin or at the effluent. By analysing the effluent concentration of the tracer, a reactor can be characterised as a PFR, CSTR or a combination thereof.

2.2.1.5. Reaction Kinetics

A chemical reaction can be classified as homogeneous if it involves only one phase (gas, liquid, solid) or heterogeneous if it involves more than one phase, reversible or irreversible, and according to the order of the reaction rate equation [73]. The reaction rate equation has the general form of:

$$-r_A = [k_A][f(C_A, C_B....)]$$

where $-r_A$ is the rate of consumption of A, k_A is the reaction constant specific to species A, and C_A is the concentration of species A [73]. Generally only irreversible reactions are considered in wastewater applications.

The specific reaction constant, k_A, is temperature dependent [73]. This temperature dependency is commonly described using the Arrhenius relationship:

$$k_A = B.e^{-E_a/RT}$$

where B is a constant, E_a represents the activation energy for the reaction, R is the gas constant (8.314 J/mol.K) and T is the temperature [73].

2.2.2. AST Selector

The purpose of a selector is to 'select' or encourage the growth of floc forming microorganisms, especially over and above the growth of filamentous bacteria which cause problems such as those described in section 3.2.5.2 [45]. This is achieved by having a mixing zone for the RAS and wastewater that is separate and upstream of the rest of the reactor [56]. The selector may or may not be aerated, depending on the desired process configuration [56].

The selector process is based on the notion that certain desirable bacteria are capable of more rapid uptake and storage of soluble substrate than their filamentous counterparts [56, 75]. This uptake and storage is typically seen in plug flow reactors where there is a gradient in the carbon concentration over time or space [76, 77]. The selector exploits this notion, rendering the activated sludge basin into a famine zone and the selector into the feast zone for the bacteria [56].

2.2.3. Oxygen Transfer System

Aeration tanks with a depth of 8 to 12 m are described as 'deep', whereas those of 4 to 6 m depth were previously standard depth [78]. The depth of the aeration system has an effect on the oxygen transfer system.

2.2.3.1. Oxygen requirement

Oxygen is required under aerobic conditions for bacterial consumption of organic substrate, as described in section 2.3.1.2 and 3.1.3. Oxygen is also required for the nitrification reactions and for cell reproduction and maintenance processes [45], and therefore the quantity of actual oxygen required (AOR) can be predicted [79].

2.2.3.2. Oxygen solubility

The solubility of oxygen in water is governed by Henry's Law if no chemical reaction is taking place [80]. Henry's Law states that the concentration of a species is proportional to the partial pressure of the species in the gas phase (air) above the liquid.

2.2.3.3. Oxygen diffusion

Oxygen or air is supplied to wastewater processes in the gaseous form. Mass transfer by the process of diffusion can be generally described by Fick's Law [73, 80]. The mass transfer of oxygen from the gaseous phase to the liquid phase is understood to be governed by a two-film diffusion process, which takes into consideration eddy diffusion in the liquid as well as molecular diffusion at the gas-liquid interface. Mass transfer is further simplified by assuming that the driving force of the concentration gradient occurs and is limited across the thickness y_L of the film in the liquid [80, 81], which is thought to be true for gases that are sparingly soluble in the liquid phase such as oxygen in water [45].

2.2.3.4. Aeration systems

Industrial aeration systems use either air or pure oxygen to provide adequate oxygen for the microbial consumption of organic substrate. The types of aeration include surface aerators, submerged aerators and mechanical aeration [45]. The type of air diffusion devices ranges from fine-pore diffusers to jet aerators which rely on venturi effects and sparge-injection devices [45]. Surface aerators or mechanical aerators that rely on the dispersion of water droplets in the air above a basin or lagoon are not suitable for cold climates where the surface and droplets will freeze over.

2.2.4. Mixing System

A mixing system is required if the aeration basin is required to be of the CSTR type reactor. The degree of mixing required depends on the geometry of the basin and the type and distribution of the aeration system in an aerobic process [45].

2.2.5. Clarifier Hydraulics

A clarifier theoretically acts hydraulically like multiple completely mixed reactors in series, although the fluid dynamics occurring in the clarifier are quite complex [82-86]. In fact, a centre well may be added to circular clarifiers in order to dissipate the energy (momentum) of the inlet flow as well as to promote flocculation [66]. “Readily settleable” solids settle quickly in the primary clarifier; flocculation of colloidal material is increased with increasing detention time in the clarifier [45]. A secondary clarifier is used to store a certain quantity of sludge, and therefore can be separated into two or more layers, such as the clarification zone and the thickening zone, since each layer theoretically acts hydraulically like multiple mixed reactors in series [87]. Even then, there are often differences between the theoretical and the actual hydraulic behaviour in the clarifier; this can be attributed to short-circuiting, dead spaces or non-ideal flow behaviour due to mixing, density and temperature currents [82, 84, 88, 89].

2.2.6. Clarifier settling & thickening

In addition to the complex hydraulics present in the clarifier, additional processes occur in the clarifier which can be described as by settling and thickening mechanisms, by which solids separation is achieved. This was described briefly in section 2.1.1.2. The formation of flocs is described further in section 2.3.1.3.

Gravity settling of an ideal particle can be described by the Stokes equation for a small sphere falling from rest in a viscous fluid [90]. The activated sludge that arrives at the secondary clarifier has a broad distribution of particle sizes, a municipal example of which has major peaks at 0.5 to 5.0µm and 25 to 1,600µm which represent primary particles and flocs respectively [91]. It was found that the settling of the activated sludge did not settle strictly in accordance with Stokes law, but enhanced settling for small sized primary particles occurred, which was attributed to the fact that the flocs collected the primary particles during settling, accurately described as flocculation [91]. Flocculation is aided by the presence of a centre well, by deeper tanks such that the sludge blanket is relatively low, by inboard weirs, good hydraulic distribution, low overflow rates and minimum mixed liquor suspended solids concentrations at the inlet to the secondary clarifier [91]. Flocculation is also improved by good floc formation, which includes reducing the shear forces placed on the flocs by the aeration system in the aeration basin [91].

A blanket of sludge is allowed to form in the base of the secondary clarifier, which serves to thicken and compact the sludge as well as store some biomass that is then recycled to the aeration basin in the RAS stream or wasted in the WAS stream. The thickening of the sludge blanket is commonly measured using the sludge volume index (SVI). The SVI reflects a number of possible events occurring in the sludge blanket including a high concentration of filamentous bacteria and a high zooglea bound water content [92]. The height of the sludge blanket can be controlled by adjusting the RAS and WAS rates.

2.2.7. AST Technology: Developing

Development in the AST process for pulp and paper wastewater application has recently focussed on two main areas: reducing sludge production and reducing the physical space required for the unit processes. Development in the arena of municipal wastewater application has been focussed on nutrient removal processes as well as those mentioned; however these are not usually applicable to pulp and paper wastewaters and will not be discussed further here. Zero effluent pulp and paper mills are discussed here as a technological development, although it eliminates the use of a wastewater treatment plant *per se*.

2.2.7.1. Moving Bed Biofilm Reactor (MBBR)

Traditional activated sludge technology has consisted of suspended growth aerated basin or lagoons, or fixed growth trickling filters, for example. Recent developments have seen the combination of these technologies in order to take advantage of the desirable attributes of both.

The MBBR technology places carrier elements inside a well mixed tank, the carrier elements provide a surface area for fixed growth to establish [93]. A MBBR process was demonstrated to be effective for integrated newsprint mill effluent [93]. A combination of the MBBR technology and conventional AST technology, called the biofilm-activated sludge process (BAS), has been implemented at multiple pulp and paper mills [94].

2.2.7.2. Low sludge production

With sludge treatment comprising up to 60% of the wastewater treatment plant operating costs, there is a significant incentive to reduce the quantity of sludge produced or find alternative treatment processes for the sludge [95]. Options exist for changes to the wastewater treatment process that would reduce the overall quantity of sludge produced, these include extended aeration, membrane bioreactors, low sludge process and anoxic/oxic zone treatment amongst others [95]. Alternatives for treatment of the sludge produced include incineration, vitrification, gasification, super critical water oxidation, aerobic and anaerobic digestions amongst others [95].

2.2.7.3. Mechanical lysis of sludge

Lysis, as discussed in section 3.1.2.6, describes the rupture of the cell wall, which results in death for a single cell organism, as well as the release of the cell contents into the wastewater media [55]. The extended aeration process is essentially an activated sludge process with a very long sludge age or residence time, which allows the process to operate with endogenous respiration, as described in section 3.1.2.5 [96]. Mechanical lysis of the WAS stream has been explored as a way to improve the extended aeration process and avoid variations in growth and decay rates, while avoiding the incur of costs associated with physical-chemical lysis [97].

2.2.7.4. Reduced and zero-effluent mills

Pulp and paper mills use a relatively large quantity of water, although this quantity has been reduced in recent years in terms of water per tonne of paper produced [98]. Recycling of biologically treated wastewater back to the mill has been studied [99]. A reduction in mill effluent due to cleaner processing within the integrated bleached Kraft mill led to the production of a nutrient deficient wastewater and necessitated phosphorus dosing in one ASB treatment plant [100].

Some mills have implemented zero-effluent operating regimes, which involve closing water loops within the mills, the effects of which include increasing the concentration of dissolved organic and inorganic substances [98]. Mills often require some type of wastewater treatment inside the mill in order to act as a 'kidney' to purge these dissolved compounds [98].

2.3. AST Operation

The operation of an AST process requires a balance between many parameters in order to provide the optimal growth conditions for the microorganisms in the AST, and efficient solids removal to provide a high quality effluent. The following is a discussion of the microorganisms commonly found in the AST and the growth pressures on the organisms.

2.3.1. Microbiology

The basis of the Activated Sludge Treatment process is the 'active sludge' or microorganisms that consume the carbonaceous substrate contained in the influent to the wastewater treatment plant. Transformation mechanisms for carbon and other nutrients are discussed in greater detail in section 3.1. This section will introduce the microorganisms that constitute the activated sludge.

2.3.1.1. Psychrophilic, Mesophilic, Thermophilic

Microorganisms used in the biological treatment stage operate most efficiently at a particular temperature, for example 20 - 35ºC for mesophilic bacteria, as discussed in section 2.3.1.1 [34]. The possible temperature range for growth of different classes of organisms and their optimum growth temperature range is described in Table 4 below [45].

Table 4: Classification organism growth rates according to temperature [45]

Temperature class	*Temperature range*	*Optimum range*
Psychrophilic	10 – 30ºC	12 – 18ºC

Temperature class	*Temperature range*	*Optimum range*
Mesophilic	20 – 50ºC	25 – 40ºC
Thermophilic	35 – 75ºC	55 – 65ºC

2.3.1.2. Aerobic, Anaerobic, Facultative

Microorganisms can be classed according to the type(s) of metabolism that they use in order to consume substrate to reproduce and maintain their cellular material. Some organisms can tolerate non-optimal oxygen conditions, as seen in Table 5 below [101].

Table 5: Classification organism metabolism & oxygen relationships [101]

Oxygen class	*Sub-group*	*Relationship to oxygen*	*Metabolism*
Aerobic	Obligate	Required	Aerobic respiration
	Facultative	Not required, but growth better with oxygen	Aerobic, anaerobic respiration, fermentation
	Microaerophilic	Required at levels less than atmospheric	Aerobic respiration
Anaerobic	Aerotolerant	Not required, growth is not better if oxygen is present	Fermentation
	Obligate	Harmful or lethal	Fermentation, anaerobic respiration

2.3.1.3. Floc formation

A floc is an aggregate of particles that can be formed via two mechanisms: microflocculation or perikinetic flocculation by the random movement of the particles (Brownian motion) and macroflocculation or orthokinetic flocculation by velocity gradients and gravitational settling [45]. In the activated sludge process, microorganisms form flocs larger than primary particles, usually in the size range of 50 to 200μm [45]. Although the mechanisms are not fully understood, it is thought that filamentous bacteria form the backbone of these flocs, and the extracellular polysaccharide secreted by microorganisms forms bridges that allows the floc to grow [56]. Formation of the floc is key to the performance of the activated sludge process since a well-formed floc will settle easily in the secondary clarifier and produce a clear effluent. Problems with floc formation include high concentrations of filamentous bacteria which produce a floating or bulking effect, and high shear on the flocs which produce small 'pin' flocs which do not settle easily [56]. Substrate is adsorbed (biosorption) onto the floc and then assimilated into the microorganism cells [102]. Sorption occurs in the selectors where the returned sludge (RAS) is mixed with the wastewater [103].

2.3.1.4. Floc population

A diverse population of microorganisms is desirable in the floc: bacteria, fungi, protozoa and metazoa [56]. A typical floc contains 15 to 20% exocellular polymers on a suspended solids basis [56]. A diverse population in the floc ensures that the activated sludge can adapt to changes in their environment and/or substrate [104]. The substrate and nutrient concentration in the wastewater can affect the selection of different microorganisms [105, 106].

2.3.1.5. Growth rates

The rate of bacteria growth, ρ_{GROWTH}, can be described using the following equation [104]:

$$\rho_{GROWTH} = \mu_{MAX} \cdot f(C_A).X_B$$

where μ_{MAX} represents the maximum specific growth rate, $f(C_A)$ is a function of the substrate concentration, C_A, which describes the growth kinetics and X_B is the concentration of the biomass [104].

The growth kinetics function $f(C_A)$ can be modelled with equations such as the Michaelis-Menten and Monod equations which consider that the rate of substrate removal is limited by the concentration of the dissolved substrate [45]. The Monod equation is used to model the relationship between the concentration of the substrate and the rate of growth of the microorganism [107] cited in [75]:

$$f(C_A) = \frac{C_A}{K_A + C_A}$$

where K_A is the saturation constant and C_A represents the concentration of the growth limiting substrate [75]. The growth limiting substrate can be the carbonaceous substrate or it can be another nutrient required for growth.

A first order kinetic equation is sometimes used to describe bacterial growth, and is often used to describe the rate of the bacterial decay process, for example [104]:

$$\rho_{DECAY} = b.X_B$$

where b is the decay rate constant and X_B represents the concentration of the biomass [104].

2.3.2. Growth pressures

The optimal growth and substrate removal conditions for the microorganisms in the activated sludge are subject to a number of pressures on the microorganisms. These growth pressures include dissolved oxygen levels, pH, concentration of nutrients and substrate available, temperature and toxicity as discussed previously [108].

2.4. Process Control

2.4.1. Basic Control Theory

Process control for continuous processes is based on a controlled or manipulated variable ‘w’, a measured variable ‘x’ and a set point for ‘x’ [109]. An algorithm is required to relate the control variable to the difference between the measured value for x and its set point [109].

A feedback controller reacts to process disturbances and a feed forward controller reacts before the process is disturbed [109]. Figure 6 below shows the simplest form of a boiler level control loop for (a) feed back flow control and (b) feed forward flow control, where FE is a flow element and LE is a level element, which are the measured variables [109].

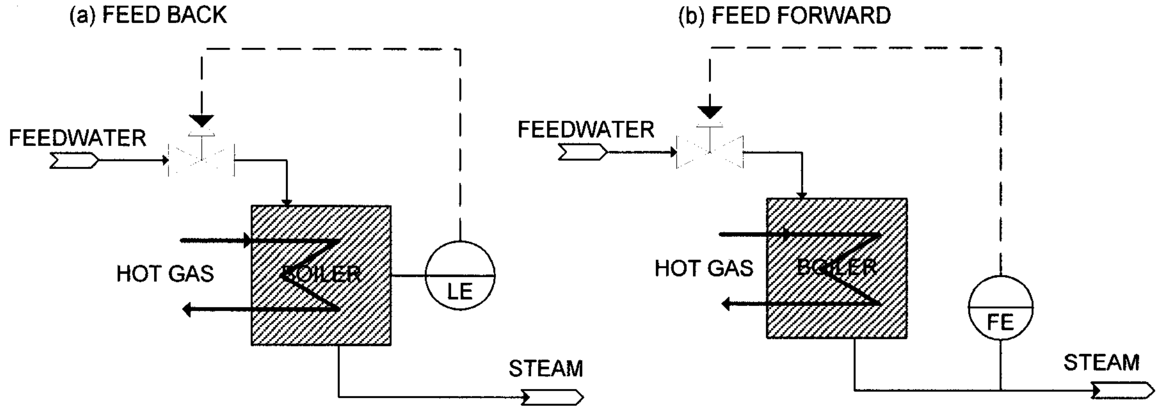


Figure 6: Control loops: (a) feedback and (b) feed forward [109]

2.4.2. AST Control

Control of an AST system is complex and involves many control loops. AST process control is commonly achieved using one or more of the following strategies listed in Table 6, which correspond to growth pressures as discussed in section 2.3.2. In addition to the control loops and strategies presented below, the configuration of the process also addresses growth pressures: hydraulic retention times, temperature, types of microorganisms, type and biodegradability of substrate.

Table 6: Common AST control strategies & corresponding growth pressures [31, 108]

Control loop	*Control Strategies*	*Growth Pressure*
Sludge wasting (WAS)	Sludge age F/M ratio MLSS Microscopic findings	F/M ratio
Sludge recycle (RAS)	Clarifier sludge depth RAS suspended solids Overall solids balance HRT secondary clarifier	F/M ratio
Dissolved oxygen	Automatic/manual Constant aeration rate	Dissolved oxygen
Chemical addition	Constant dosing rate Proportional to flow Influent short-term BOD or COD	Nutrients pH Toxicity Types of

Control loop	*Control Strategies*	*Growth Pressure*
	Nutrient residual Nutrient balance WAS nutrient content Influent/effluent pH Toxicity tests Microscopic findings SVI	microorganisms
Flow or load equalisation	Equalisation basin Pumping rate/ level control	Hydraulic retention times F/M ratio

2.4.2.1. Knowledge-based control

Given the empirical nature of some wastewater characteristics, empirically determined control strategies are sometimes employed in wastewater treatment. A 'holistic health index' was employed to account for the floc morphology (form and structure), floc activity, floc nutrient and floc settleability in multiple pulp and paper activated sludge treatment plants [110]. The index takes into account various on-line and laboratory measurements from multiple locations in the plant [110].

In terms of control of nutrient residuals and nutrient dosing, a simplified [111] and an advanced control strategy were employed at a municipal recirculating BNR plant, implementing a 'STAR' or Superior Tuning and Reporting system [112]. This advanced control is possible due to on-line nutrient fraction measurements as well as on-line dissolved oxygen and flow rate measurements [112].

A dynamic process simulation based on the ASM models (discussed in section 5) was used for the purposes of operator training, process operation observation and process operation prediction at a municipal wastewater treatment plant [113].

3. Carbon & Nutrient Transformation Mechanisms

Microbiological activity is the basis of the activated sludge process, through which the removal of organic matter from wastewater is achieved. The following is a review of the mechanisms via which this activity occurs and may be controlled, starting with activity at the molecular level and progressing to the design and operation of a large scale plant.

Microorganisms consume organic carbon in order to grow and reproduce. By definition [114], a nutrient is "any element or compound necessary for or contributing to an organism's metabolism, growth, or other functioning". The essential nutrient in the growth and reproduction of microorganisms is carbon, followed by oxygen, nitrogen and phosphorus. These four elements are the major constituents of the nucleotide molecule, from which DNA is constructed, and are therefore vital for the growth and reproduction of cells.

Other substances that are essential for cellular growth include macronutrients: hydrogen, sulphur, potassium, magnesium, calcium and sodium, micronutrients: boron, chromium, cobalt, copper, iron, manganese, molybdenum, nickel, selenium, tungsten, vanadium and zinc, and growth factors: vitamins, amino acids, purines and pyrimidines [101].

For further details on the microbiology of the AST process, refer to section 2.3.1. The discussion below applies generally to both prokaryotic and eukaryotic cells, and is in some cases specific to prokaryotic cells; this includes bacteria and blue-green algae, which are important for aerobic wastewater treatment.

3.1. Cell pathways (Micro level)

The term metabolism describes all biochemical functions of a cell. A cell's metabolic reactions or pathways can be further described as catabolic, the breaking down of complex organic molecules (polymers to monomers, for example) which releases energy, or anabolic, the building up of complex organic molecules (monomers to polymers, for example) which consumes energy. Some processes participate in both catabolic and anabolic processes; these are referred to as amphibolic.

The cellular processes for microorganisms are generally categorised as cell respiration, reproduction or cellular maintenance processes. Respiration consumes substrate (carbohydrate, lipid or protein) to produced energy. Reproductive processes consume energy to produce molecules such as DNA and RNA. Cellular maintenance processes consume energy to resynthesise molecules such as proteins or nucleic acids. The biomass that is produced per unit of substrate consumed by the bacteria is referred to as the yield [55].

These cellular pathways can be represented by oxidation-reduction (Redox) reactions in that they involve the exchange of electrons. In a fully aerobic environment, the electron acceptor will be oxygen, in anoxic or anaerobic environments the electron acceptor may be an inorganic or organic compound. Aerobic bacteria can be further categorised by the type of electron donor and source of carbon that they use in their redox reactions, as detailed in Table 7. The redox half reactions for carbon and each nutrient will be detailed in the following sections.

Table 7: Classification of bacteria according to redox reactions [55]

Bacteria	***Electron Donor***	***Carbon source***	***Example***
Heterotrophic	Organic carbon	Organic carbon	Floc-formers, Denitrifiers
Autotrophic	Inorganic compounds	Carbon dioxide	Nitrifiers

3.1.1. Cell transport

The transport of biodegradable carbon sources across the cell membrane occurs via facilitated enzyme transport [70]. Transport of inorganic assimilable nutrients across the cell membrane occurs via diffusion [70].

3.1.2. Carbon

3.1.2.1. Cell respiration

Carbon is broken down or catabolized from long-chain carbohydrate, protein and lipid molecules into monosaccharides, amino acids, fatty acids and glycerol. The term disaccharide refers to a carbohydrate of two monosaccharide units, polypeptide refers to molecule of two or more amino acids, protein refers to a molecule of fifteen or more amino acids, a nucleoside is a molecule that incorporates one monosaccharide and one nucleic acid monomer, a nucleotide is a phosphate ester of a nucleoside [101].

3.1.2.2. Assimilation

Assimilation describes the reduction of an inorganic compound for use as a nutrient source, such as the nitrate, sulphate or carbon dioxide molecules [101]. Usually only the quantity of inorganic compound required for growth purposes is reduced in assimilative metabolism [101]. This is in contrast with the reduction of the same molecules for use as electron acceptors in energy metabolism, which is referred to as dissimilative metabolism [101].

The catabolism of high molecular weight molecules is of great importance to microorganisms, as only low molecular weight molecules are easily assimilated into the cell [55]. Microorganisms excrete extracellular enzymes to carry out catabolic processes on the high molecular weight molecules in the wastewater media; these processes are grouped under the umbrella term ‘hydrolysis’ in wastewater modelling [55].

3.1.2.3. Cell reproduction (growth/ cell synthesis)

The energy produced by the respiration process in the form of the ATP molecule can be used in cellular reproductive processes. For single cell organisms such as bacteria, the cycle of cell reproduction results in the reproduction of an independent organism and can be described by its two phases: interphase and mitosis [115].

3.1.2.4. Cell maintenance

The energy produced by the respiration process in the form of the ATP molecule can also be used in cellular maintenance processes. Processes such as spontaneous movement (motility), osmotic regulation, molecular transport and maintenance of ionic gradients are described as mechanical maintenance processes [55]. Processes such as the resynthesis of cell walls, flagella, cell membrane, proteins or nucleic acids are described as chemical maintenance processes [55].

Maintenance energy requirements are generally considered to be independent of the microorganism growth rate, despite some evidence to the contrary [55].

3.1.2.5. Endogenous respiration

Up to this point, discussions of respiration processes have assumed that a carbonaceous substrate and an electron donor are provided to the cell via the wastewater media. In the case where the concentration or availability of these externally provided (exogenous) substrates is decreased, a microorganism will decrease the rate of cell reproduction (growth) in order to maintain the rate of cell maintenance [55]. If the exogenous substrate is further decreased to below the level required for cell maintenance processes, the microorganism will start to consume substrate that is stored inside the cell itself: this process is referred to as endogenous respiration [55]. The form of stored substrate varies from glycogen to amino acids or proteins, depending on the microorganism and the form of substrate previously available to it [55]. If the concentration or availability of the exogenous substrate is reduced to zero, and if all endogenous substrate is consumed, the microorganism will become dormant or die [55].

3.1.2.6. Cell lysis

Some of the cell maintenance and cell reproduction processes involve the hydrolysis of cell walls by autolysins enzymes, prior to the resynthesis of the walls or the production of a new cell [55]. If the regulation of this process is interrupted or lost, the cell wall may rupture, which is referred to as cell lysis [55].

The result of cell lysis for a single cell organism is death, as well as the release of the cell contents into the wastewater media [55]. Enzymes present in the media will hydrolyse most of the cell walls and cell membranes, which renders them available for assimilation by other microorganisms [55]. Some of the cell contents are difficult to hydrolyse and are considered to be cell debris [55].

3.1.2.7. Predation

The microbiological population in an activated sludge process is usually very diverse, and the higher microorganisms such as protozoa will feed on the bacteria in the media [55]. This process is referred to as predation.

3.1.3. Oxygen

An activated sludge process can be described as aerobic, anoxic or anaerobic: these terms are used to describe the level or type of oxygen available to bacteria, and are often used to describe the bacteria themselves. In terms of the oxygen available to bacteria, aerobic describes the condition where dissolved elemental oxygen is available to bacteria at a level that is not limiting to the bacterial growth rate [55]. Anoxic describes the condition where oxygen is available in the form of nitrite (NO_2^-) or nitrate (NO_3^-) [55]. Anaerobic describes the process condition where no oxygen is available in any form, and the electron acceptors are usually carbon dioxide or sulphate [55]. Aerobic processes are the most efficient in terms of biomass growth per unit of substrate consumed, with anoxic the next efficient and anaerobic the least efficient process [55].

3.1.4. Nitrogen

Nitrogen plays two important roles in the activated sludge process, one as an electron acceptor in terms of nitrate and nitrite in anoxic processes, and one as a nutrient form required for bacteria growth and maintenance processes. These roles are accomplished via the following processes.

3.1.4.1. Ammonification

Nitrogen present in the wastewater media in the form of organic compounds, such as amino acids, is released during the catabolism of these compounds [55]. These catabolic processes include deamination and hydrolysis reactions, amongst others. This is the only way that organic nitrogen can be transformed into a form of nitrogen available to microorganisms [55].

3.1.4.2. Assimilation

Ammonia nitrogen is the most easily assimilated form of nitrogen for a microorganism. Nitrate can be assimilated, but requires extra energy for the reduction step from the +V oxidation state to the –III oxidation state [55].

3.1.4.3. Cell synthesis

The cell synthesis process requires nitrogen due to the fact that the DNA and RNA molecules both contain nitrogen. The use of ammonia requires less energy than the use of nitrate, as discussed above, therefore nitrate will only be used as the nitrogen source for cell synthesis if no ammonia is present [55].

3.1.4.4. Nitrification

Nitrification is the process by which ammonia nitrogen is reduced to nitrite and then to nitrate, which occurs under aerobic conditions. This process is carried out by both heterotrophic and autotrophic bacteria, but is usually attributed to autotrophic bacteria, in particular the those of the *Nitrosomonas* and *Nitrobacter* genera [55]. These bacteria can use organic carbonaceous substrate, but the quantity is usually so small that it is ignored and carbon dioxide is used to represent the carbon source for this process [55]. Nitrification can occur at the floc exterior [45].

3.1.4.5. Denitrification

Denitrification is the process by which nitrate nitrogen is reduced to elemental nitrogen gas, which occurs under anoxic conditions, and is also called 'dissimilative nitrate reduction' [101]. This process is carried out by heterotrophic bacteria and therefore requires an organic carbon substrate: the substrate may be provided by an exogenous source in the wastewater media or by an endogenous source [60]. Denitrification can occur at the floc interior [45].

3.1.4.6. Atmospheric fixation

Atmospheric fixation describes the phenomenon whereby atmospheric nitrogen gas is reduced to ammonia, which typically occurs using heterotrophic diazotroph bacteria under aerobic, anaerobic or microaerophilic conditions [26, 116]. This has been shown to be a significant transformation of nitrogen in large bodies of water such as aerated lagoons or aerated stabilisation basins (ASB) [26, 116]. However, it is thought that the amount of nitrogen fixed by bacteria in an aerated basin with a relatively short residence time is insignificant.

3.1.4.7. Gaseous stripping

Ammonia (NH_3) exists in solution in equilibrium with ammonium ions (NH_4^+) and hydroxide ions (OH^-) [60]. The removal of ammonia can be achieved by raising the pH of the wastewater media, which converts all ammonium ions to ammonia (NH_3), and then providing adequate air-water surface area to strip the ammonia gas from the solution [60].

3.1.4.8. Cell lysis

As discussed previously, cell lysis is a process that involves the bursting of the microorganism cell wall and results in the release of organic matter, including organic nitrogen. This material may undergo ammonification (deamination and hydrolysis) and then be assimilated into the biomass as a source of nitrogen [117], although it is likely that some material will remain difficult to degrade.

3.1.5. Phosphorus

Phosphorus plays an important role in the activated sludge process as a nutrient form required for bacteria growth and maintenance processes. The manner by which this role is accomplished is described in the following processes, along with the processes used to accomplish phosphorus removal related to meeting final effluent quality requirements.

3.1.5.1. Phosphatification

Analogous to ammonification for nitrogen, it has been postulated that the phosphorus present in the wastewater media in the form of organic compounds, such as lipids or polyphosphates, is released during the catabolism of these compounds [118, 119]. These catabolic processes include β-oxidation and hydrolysis reactions, amongst others. This is the only way that organic phosphorus or polyphosphates can be transformed into a form of phosphorus available to microorganisms [118].

3.1.5.2. Assimilation

Ortho-phosphate is the most easily assimilated form of phosphorus for a microorganism [60]. Other forms of phosphorus must be hydrolysed to the ortho-phosphate form, which is less efficient than using ortho-phosphate available [60].

3.1.5.3. Cell synthesis

The cell synthesis process requires phosphorus due to the fact that the DNA and RNA molecules both contain phosphorus, as do the energy storing molecules of ATP and NADPH and structural molecules such as phospholipids [70].

3.1.5.4. Biological Phosphorus Removal (Bio-P)

The biochemical process called biological phosphorus removal (Bio-P) requires an anaerobic zone upstream of the aerobic zone. Under anaerobic conditions, the phosphorus accumulating organisms (PAO) will release any phosphate they are storing and store readily-biodegradable carbon and energy in the form of polyhydroxybutyrate (PHB) [120]. Under the subsequent aerobic conditions, the PAO's will use the PHB for energy and growth, and internally accumulate phosphate in excess of their biological requirements, which is referred to as luxury uptake [120]. This process can be combined with the nitrification-denitrification processes to produce a biological nutrient removal (BNR) process [45].

The biological phosphorus removal process has been shown to produce a final effluent with a [total] phosphorus concentration of 1 to 2 mg/L, and thus it is not considered to be an advantage for pulp and paper wastewater treatment [50].

3.1.5.5. Precipitation

Phosphorus can be chemically precipitated using a number of chemicals, notably calcium, aluminium and iron, which form insoluble cation phosphate precipitates [60]. Chemical precipitation is often combined with either the sedimentation occurring in the secondary clarifier, which is referred to a simultaneous phosphorus elimination, or with the Bio-P process, which is referred to as simultaneous precipitation [121]. The precipitation chemicals can be added in the aeration basin if there is an excess of phosphorus, but would usually be added in the secondary clarifier in pulp and paper wastewater treatment to eliminate the residual phosphorus after biological treatment.

3.1.5.6. Cell lysis

As discussed previously, cell lysis is a process that involves the bursting of the microorganism cell wall and results in the release of organic matter, including organic phosphorus. This material may undergo phosphatification (β-oxidation and hydrolysis) and then be assimilated into the biomass as a source of phosphorus, although it is likely that some material will remain difficult to degrade.

3.2. Bulk processes (Macro level)

The operation of an AST plant requires observation, measurement and control of bulk processes. At this macro level, it is not possible to observe the reactions occurring at the cell level. The phenomena that are observed often require interpretation of skilled operators and management of gross parameters. This section will describe the macro implications of the reactions described above.

3.2.1. Transport Processes

Many of the reactions described above depend upon the provision of dissolved carbon, oxygen, nitrogen or phosphorus to the bacteria. In order for these molecules to arrive at the cell wall of the bacteria, it is necessary that they diffuse through the wastewater media, and then that they are adsorbed onto the floc: these processes are described below.

3.2.1.1. Diffusion

The diffusion of oxygen is described in section 2.2.3.3.

3.2.1.2. Floc sorption

The sorption of substrate onto the floc is described in section 2.3.1.3.

3.2.2. Yield

The term 'yield' refers to the quantity of biomass produced per unit of substrate consumed [45], as described by the equation [119]:

$$\frac{1}{Y} Substrate + \frac{1-Y}{Y} O_2 \rightarrow Biomass$$

Substrate can be measured in units of BOD_5 or COD, and therefore the units of yield can be in g VSS/g BOD5 or g VSS/g COD.

3.2.2.1. Microbial Decay

The term 'microbial decay' has been used as a catch-all to describe the processes that result in an observed yield that is less than the theoretical yield, including predation [55].

3.2.2.2. Viable Biomass

As discussed previously, volatile suspended solids (VSS) is not necessarily a good indicator of the viability or activity of the biomass in a system [122]. Alternate measurements of the active biomass include cellular ATP [123].

3.2.3. Nitrification

The maximum growth rate of nitrifying bacteria is much lower than that of heterotrophic bacteria [55]. If a process is operated with a long sludge age, the nitrifying bacteria have a much greater opportunity to develop, whereas conditions that encourage rapid growth will cause the decline of the nitrifying bacteria population [55].

The yield of nitrifying bacteria is less than that of heterotrophic bacteria, which manifests as a minimal impact on the overall suspended solids concentration of the mixed liquor in the activated sludge process [55].

3.2.4. Denitrification

Symptoms of unintentional denitrification include poor settling in the secondary clarifier, due to the gaseous nitrogen formed in the flocs. Denitrification in the secondary clarifier would require a significant concentration of nitrate to be present in the outlet of the aeration basin, and that the oxygen concentration be less than 1 mg/L [40, 60].

3.2.5. Nutrient requirements for stable AST operation

The quantity of nutrients required for biological wastewater treatment is based on the composition of a typical bacterial cell, which has a generic formula of $C_{12}H_{87}O_{23}N_{12}P$ or a simplified formula of $C_5H_7NO_2$ if including the macronutrients [45]. These formulas are used to generate the mass ratio of

BOD_5:N:P of 100:5:1 that is often used as a measure that nutrient concentration in a wastewater is adequate for biological growth [45].

As mentioned in section 2.3.1.5, a low concentration of nutrients can have a limiting effect on the biological growth, according to the Monod kinetic relation [124]. It is for this reason, and to avoid a nutrient deficiency as described below, that nutrients are often added in surplus [50]. The detectable presence of bio-available nutrient residuals in the final effluent is used as an indication that adequate nutrients are present in the biological treatment process unit [60]. Stable AST operation is seen with low variation in flow rate and organic load to the treatment plant [50]. Sludge age and temperature influence the actual macronutrient requirements, with lower sludge yields and therefore lower nutrient requirements in warmer temperatures [56, 125].

3.2.5.1. Nutrient mixtures

The major nutrients added to pulp and paper wastewater for the purposes of biological treatment are nitrogen and phosphorus. There are a few different easily assimilable forms of these nutrients that can easily be added to the process, notably urea and ammonium hydroxide for nitrogen; phosphoric acid for phosphorus [126]. Ammonium polyphosphate (APP) has been found to be readily hydrolysable, with complete depolymerisation within 100 minutes [126]. Improvements in settleability (SVI) were reported using a nutrient mixture that included a yeast extract and micronutrients: iron, potassium, magnesium, molybdenum, zinc, copper, manganese, cobalt, nickel, selenium, boron, vanadium and tungsten, as well as nitrogen and phosphorus [127]. Lysed waste activated sludge (WAS) was also investigated as a source of nutrients for the AST process [126].

3.2.5.2. Nutrient requirements: different AST technology

Conventional AST technology results in approximately equal nutrient concentrations in the final effluent and the wasted sludge for the treatment of Kraft pulp mill effluent [128]. Other AST technologies such as the low-loaded AST, low sludge production and MBBR plus AST process configuration result in higher nutrient concentrations in the wasted sludge than the final effluent [128]. This result implies that alternative AST technologies offer the opportunity to reduce the nutrient concentration in the final effluent further than that achieved by conventional AST technology.

3.2.5.3. Nutrient deficiency: effects

The effects of nutrient deficiency include accelerated growth of filamentous bacteria which manifests as a sludge that is difficult to settle and high solids concentration is seen in the final effluent [60]. Nutrient deficiency can also lead to filamentous bulking events, production of viscous exocellular material (polysaccharide), or production of foaming exocellular material [56]. Overproduction of exocellular material is a significant problem for pulp and paper wastewaters deficient in phosphorus [70].

3.3. Nutrient addition control strategies

Nutrient addition control strategies are determined primarily by the desired result and subsequently by the desired accuracy, precision and complexity of the process control. The possible purpose or results desired include the minimisation of effluent concentrations of organic pollutants and nutrients (BOD, N, P) or the minimisation of nutrient dosage quantities, whilst maintaining stable process operation and efficient BOD removal [53].

The major benefit of feed-forward control is the ability of the control loop to react swiftly to changes in influent quality, for example to load or flow variations [129]. Feed-back control reacts less efficiently to process upset conditions, but has the advantage of greater accuracy of control [129].

3.3.1. Constant (manual) dosing

The most simple nutrient addition control is to dose the nutrient, nitrogen or phosphorus, in a constant flow rate [130]. This could theoretically be done without any measurement of nitrogen or phosphorus content of any stream. Constant dosing is inferior to automated control since it does not respond to changes in the process [131].

3.3.2. Proportional to flow

A nutrient addition rate proportional to effluent flow rate may be applicable for municipal wastewater treatment, however for pulp and paper mill effluent, the concentration of organic load may vary with constant flow rate: this control strategy is not considered appropriate for pulp and paper wastewater treatment [132].

3.3.3. BOD_5:N:P ratio (Ratio control)

The BOD_5:N:P mass ratio of 100:5:1 has its origins in the dry-basis contents by weight of a typical bacterial cell, and the assumption that bacterial cells require the macronutrients nitrogen and phosphorus in proportion to the composition of cell biomass, as described in section 3.2.5. [45]. For pulp and paper wastewater treatment using AST technology, BOD_5:N:P ratios have been reported for stable plant operation from 100:3.5:0.6 [50] to lower limits suggested for BOD_5:N of 100:2.5 to 100:4.5 and BOD_5:P of 100:0.4 to 100:0.6 [51, 52]. Zero supplemental phosphorus was added to a pulp mill effluent with successful stable AST operation [52], and zero nutrient addition has been implemented successfully for pulp and paper ASB operations, which is due to sufficient nutrient internal recycling [51, 62, 63].

Ratio control can be based on a BOD_5:N:P mass ratio, which translates to control of nutrient dosing flow rate in proportion to the measured BOD load in the incoming mill effluent. This control relies on the accurate on-line measurement of BOD or a substitute for BOD. A number of substitutes and combination of parameters including BOD_1, total organic carbon (TOC), COD, conductivity, pH and TSS were tested on Kraft mill effluent with a particular focus on upset conditions, with mixed results [133]. Conductivity has been used successfully as a surrogate for organic load [132]. In terms of on-line instrumentation, one study considered TOC as the best surrogate in comparison with respirometry [134]. Instrumentation is discussed further in section 4.1.

3.3.4. Nutrient residual (Feedback control)

In municipal wastewater treatment plants, chemicals are dosed based on the ammonia and phosphate residuals in the final effluents for processes involving denitrification and chemical precipitation of phosphate [131]. This approach has also been implemented for pulp and paper wastewater for both ASB and AST treatment processes [60]. Reported residual levels in the final effluent range from 0.5 to 1.5 mg NH_3-N/L and 0.25 to 1.0 mg PO_4-P/L [60], as discussed further in section 3.5. One of the problems with this method of control is that the control loop can only react slowly to an upset in influent to the wastewater treatment [8].

If the *aim of nutrient control is to minimise the residual nitrogen and* phosphorus in the final effluent, it should be noted that the majority of total nitrogen is present in the suspended solids, indicating it is bound in the biomass, and indicating the importance of solids separation to nutrient control [51, 135].

3.3.5. Modified nutrient control

Feed back control based on effluent nutrient residuals is also used for pulp and paper mills in Finland with an ongoing assessment of the nutrient balance over the wastewater treatment plant in an attempt to minimise changes in the nutrient levels throughout the treatment process [53]. An expert control system incorporating on-line measurements, control software and predictive modelling has been trialled at a number of full-scale pulp mill wastewater treatment plants [136, 137]. A combination of ratio and feed back control was implemented for a fine paper mill effluent and resulted in a reduction of final effluent nutrient concentrations as well as a reduction of supplemental nutrient addition to the process [138].

3.3.6. Respirometric-based control

A method for the detection and quantification of a nutrient deficient state for sludge from a pulp and paper activated sludge process was developed [139]. The implementation of this methodology for the control of nutrient dosing to the process has been proposed [139].

3.4. Control implementation

The successful implementation of nutrient control depends on a number of criteria, not least the equipment used in the control loop. Instrumentation for measurement of nutrient fractions is discussed further in section 4.1.

3.4.1. Control equipment

Important aspects of control equipment to consider for full-scale implementation of nutrient control include the capacity of the actuators and pumps, the presence of basic control loops such as dissolved oxygen control, definition of the control performance goal measurement time period, and quality assurance of the equipment [129]. The control equipment should also be installed in appropriate locations and reaction to the measurements should be made within a time frame appropriate to the process time scale [129].

3.4.2. Control implementation

An appropriate implementation strategy should be planned for automated or semi-automated controls. A period of monitoring followed by manual control and then control automation allows operators to develop their intuition and become familiar with the control loop [129]. Keeping the control strategy simple facilitates a rapid adaptation to its use [131].

3.5. Effluent discharge

As discussed in section 3.3.4, the concentration of nutrients in the final effluent discharge can be used to control the addition of supplemental nutrients to pulp and paper wastewater treatment. The following is a discussion of the achievable limits of final effluent pollutant and nutrient concentrations and the quality of receiving waters.

3.5.1. Achievable limits

Final effluent discharge is regulated in most countries in terms of the concentration of pollutants that can be discharged. A summary of regulated and typical concentrations of BOD_5, TSS, COD and AOX is presented in Table 8 below in units of kg per tonne production [140].

Table 8: Final effluent discharge concentrations BOD_5, TSS, COD, AOX in kg/tonnes production [140]

Country	*BOD_5*	*TSS*	*COD*	*AOX*
New Zealand	1.75	4.0	12.2	0.34
Canada	7.5	11.25	-	1.5 (0)
USA	2.73	4.41	45.6	0.623
Indonesia	8.5	8.5	29.75	-
Japan	13.7	13.9	17.6	-
Sweden	-	-	10 – 15	0.1 – 0.2
Finland	-	-	65 (15)	1.0 (HW) 2.0 (SW)
France	3.9 (SW) 2.6 (HW)	6.5	65(SW) 32.5(HW)	1.0 (HW) 2.0 (SW)
Brazil	1.3 – 6.5	1.4 – 60	4.6 – 45	0.2 – 1.0

HW = Hardwood SW = softwood

In terms of bio-available nutrient discharge, the concentration of ammonia and ortho-phosphate in the final effluent that are achievable, commonly seen and seen during very stable AST operation for pulp and paper wastewater treatment plants are presented in the first three rows of Table 9 below [50]. These values correspond to the medians found in a survey of 135 pulp and paper facilities, as indicated the final two rows of Table 9 [141].

Table 9: Final effluent discharge concentrations NH_3-N, PO_4-P (mg/L) [50, 141]

Measurement	*NH_3-N*	*PO_4-P*	*TP*	*Comments*
Mean	1 mg/L	1 mg/L	-	Achievable
Maximum	10 mg/L	5 mg/L	-	Commonly seen
Optimised Max	7 mg/L	0.5 mg/L	-	Very stable operation
Survey Mean	1.91 mg/L	-	1.31 mg/L	
Survey Median	1.0 mg/L	-	0.82 mg/L	

It was found that gradually lowering the phosphorus dosing in steps facilitated the establishment of lower limits of final effluent phosphorus concentration for a particular pulp and paper activated sludge wastewater treatment system without causing process upsets, and was a better approach than solely analysing past operating data [142].

3.5.2. Receiving water quality

The implementation of Canadian regulations on the discharge of effluent from pulp and paper mills in 1992 resulted in many mills installing secondary treatment plants and changing from chlorine bleaching to chlorine dioxide bleaching (elemental chlorine free, ECF)[143]. Studies conducted on the receiving waters of a number of mills indicated that the environmental effect of the mills may be reduced since these changes, although the studies were not conclusive and the authors recommended further work to include a refinement of the parameters to be measured in environmental monitoring [143]. A methodology for environmental monitoring and decision making was proposed for new mills in Australia [144]. Receiving water quality was found to be dependent on the differences in seasonal flow rates in the receiving river for one bleached Kraft mill, in that the relatively higher winter river flow rates provided greater dilution for the mill effluent [145].

3.6. Relevance to upstream process (mill)

The correct measurement of physical, chemical and microbiological parameters in the pulp and paper mill wastewater allows the correct identification of the constituents and flow of the wastewater, and the realisation of a site-wide nutrient balance. These tools may be used to identify design and/or operational changes in the production areas which would be advantageous to the operation of the wastewater treatment plant, or evaluate proposed changes in the production areas for their influence on the wastewater treatment plant.

3.6.1. Identification of sources of wastewater flow and components

Measurement of contaminants and wastewater flow at the inlet to the wastewater treatment plant allows control of the plant, as discussed in section 3.3, and modelling of the plant, as discussed in section 5.5.

Identification of the upstream sources of the contaminants and wastewater flow allows a more holistic or site-wide approach to the management of wastewater. It is possible to reduce the site water usage, reduce the flow or change the characteristics of the influent wastewater to the treatment plant, by managing the sources of contaminants and flow [146]. A study of a particular mill may show that separate treatment of wastewater from different areas of the mill would be beneficial, or that recycling or closing water loops within or between production areas may be advantageous. The correct identification of the constituents of the wastewater from a pulp and paper mill can potentially be achieved using the measurement techniques discussed in section 4.1. In particular, the identification of sources of nutrients can allow effective management of nutrients on a site-wide basis.

4. Data Measurement, Collection & Processing

The way in which data is measured, collected and processed influences both the results of further data analysis as well as the conclusions that can be drawn from those results. The following is a discussion of methods used to measure, collect and process data, predominantly in the wastewater industry but also in other chemical engineering fields.

4.1. Data Measurement

It is important to take note of how reliable the measurement results are for each instrument or test method. A number of definitions from the Standard Methods are reiterated in Table 29 [147].

Table 10: Glossary of statistical terms *[147] **[148]

Accuracy * (trueness)	The combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to a true value
Bias* (error)	Consistent deviation of measured values from the true value, caused by systematic errors in a procedure
Calibration	The method by which the trueness of the instrument is verified
Drift	The change in trueness of the instrument over time
Reproducibility* (precision)	Measure of the degree of agreement among replicate analyses of a sample, usually expressed as the standard deviation

Repeatability**	Refers to precision obtainable by the same technician under the same conditions (intra-laboratory), compared to reproducibility which refers to precision obtainable by different technicians under different conditions (inter-laboratory)

The ideal measurement would combine low bias with high reproducibility, minimal calibration required and minimal drift found during calibration. The precision and bias are noted for each measurement where known. The bias of measurements is dependent on the laboratory's interpretation of the test method as well as the method itself.

There are various types of measurement or sampling regimes. For simplicity, a number of definitions from the Standard Methods and other references are reiterated in Table 30.

Table 11: Measurement type definition *[147] **[134] †[149] ‡[150]

Grab / Catch*	A sample collected at a particular time and place, usually representative of only the composition of the source at that time and place. Can be interpreted as representative of process changes based on operator knowledge.
Composite*	A mixture of grab samples collected at the same sampling point at different times ('time-composite'), often used for 24-hour averages
Integrated*	A mixture of grab samples collected from various sampling points at the same moment in time, generally used for analysing the receiving water
Real-time**	Little or no delay between the time the sample is taken and results

	being available (short measurement interval), usually electronically via DCS
On-line†	A continuously measuring probe, can be located in-situ or in a side stream (data usually collected electronically via DCS)
In-line†	Instrument located directly in the media, direct contact with the wastewater sample (whether the sample is in-situ or pumped to/ through analyser)
In-situ‡	Installed directly in the process (tank, basin, pipe, channel)

One benefit of composite samples is that they account for large variations in flow rates, which is often the case in mill drains [47].

4.1.1. Benefits & Issues with in-situ measurements

The benefits of in-situ measurements include a reduction in daily labour efforts as well as an overall improved compliance with discharge limits [129, 131]. While previously constructed wastewater plants may be over-designed to compensate for a lack of real time data, in-situ measurements offer an advantage for upgrading facilities [151].

The major issue with in-situ measurements is the quality assurance of the data, particularly the calibration of instruments. The construction of control charts has been suggested to visualise and shift, drift or gross errors in instrument data, which also allows operators to evaluate the need for recalibration of instruments [152].

4.1.2. Measurement Methods

The basis of measurement of traditional process attributes such as flow rate, pH, temperature, tank levels and conductivity are standard; that of wastewater characteristics such as colour, dissolved oxygen, solids content and BOD are also generally well understood [45, 153]. The bases of the major measurement methods proposed for the measurement of nutrient fractions are presented here.

4.1.2.1. Ion-selective electrode (ISE): NO3 & NH4

The potential or voltage is measured between two electrodes, one reference electrode and one measurement electrode [129, 150, 154]. Previously the measurement electrode was separated from the wastewater by an ultrafiltration (UF) membrane; this has now been replaced by a specific ion-binding membrane [154]. The measurement electrode experiences some cross-sensitivity disturbances from ions with properties similar to the measurement ion [154].

When the gas-sensitive NH_4^+ ISE is used, the pH of the wastewater sample is raised in order to push the ammonia-ammonium equilibrium towards NH_4^+, and therefore all ammonia or ammonium in the sample is measured as a gas [151].

4.1.2.2. UV-Vis Spectroscopy: COD, sCOD, NOx

A spectrometer measures the absorbance of light; it is usually measured in the ultraviolet range (200 – 400 nm) or the UV and visible light range (200 nm – 750 nm) [155]. Some instruments measure single wavelengths, usually at 254 nm as it has been shown that TOC and COD have correlations to the UV absorption at 254 or 260 nm [151]. A full-spectrum measurement is preferable, as the species are more easily distinguished, which results in a more accurate calibration [155].

This is an indirect method, and relies on the initial and on-going calibration of the instrument against laboratory measurements [155]. Calibration for BOD measurement relies on the accuracy of BOD measurements, which is not assured [45]. Automated cleaning systems are available and advantageous; compressed air or mechanical (physical wiping) methods are offered by different suppliers.

4.1.2.3. Photometric / Colorimetric methods (Automated Wet Chemistry): NH_4, NO_2, NO_3, PO_4

The term 'on-line analyser' is often used for these instruments, as well as for the thermal oxidation instruments, and it refers to the fact that the wastewater sample may be pumped from the process to the analyser unit, which allows multiple sampling points for a single analytical unit [151].

The common factor in these instruments is that one or more chemical reagents are added to the wastewater sample and a chemical reaction occurs. The resultant product is analysed for light absorption photometrically: colour intensity is assumed to correlate to concentration [151]. The units require intensive attention from both maintenance and operation personnel, and the chemical reagent costs are significant [151]. However, this is the only standard method of measuring ortho-phosphate. Filtration of the wastewater sample is usually required to reduce interference of solids, and newer technologies use an ion-specific membrane to minimise interference [156].

4.1.2.4. Thermal oxidation: TP, TN, TOC

These instruments rely on the total oxidation (digestion) of the wastewater sample to one parameter, which is then measured by various techniques. The oxidation may be realised using high temperature catalytic conversion or chemical addition plus oxidation by UV light and moderate temperatures, or mineralisation for nitrogen [151, 157, 158]. In the case of TOC, the final oxidation product is carbon dioxide, for TP it is ortho-phosphate and for TN it is nitrate [151, 157, 158]. Carbon dioxide concentration is then measured using an infrared analyser, ortho-phosphate concentration is measured using photometric methods and nitrate concentration is measured using spectophotometry [151, 157, 158]. The wastewater sample usually requires filtration and pH adjustment, and sometimes dilution [151]. The measurement interval is short considering the complexity of the measurement [134].

4.1.2.5. Respirometry

A respirometer is a miniaturised reactor, in which the oxygen uptake rate is measured over time given a quantity of wastewater and a seed of microorganisms [151]. The unit usually operates batch-wise, although one on-line calculations based on dissolved oxygen concentration and air flow rate was studied [159]. The results must be analysed and interpreted in order to achieve data related to biodegradation kinetics, stoichiometric coefficients and parameters used in biological modelling, such as the Activated Sludge Models (ASM) established by the International Water Association (IWA, formerly IAWQ) [151, 160].

Respirometry is considered as a good method to determine these parameters and coefficients, the measuring frequency is limited to 7 to 10 minutes [160]. The method demands some expertise and time, and a permanent in-line installation would require intensive attention from both maintenance and operation personnel.

4.1.3. Comparison of instrument types

A classification of instrument types in terms of response time and measuring frequency is presented in Table 12 [161]. This type of classification allows a comparison of non-alike measurement types.

Table 12: Measurement types categorised by response time & measurement frequency [161]

Category	*A*	*B_0*	*B_1*	*C_0*	*C_1*	*D*
Measurements	**MLSS** **Turbidity** **Ammonia** (ISE) **NOx** (ISE) **NOx** (UV) **COD** (UV-Vis) **sCOD** (UV-Vis) **Flowrate** **Water level** **Temperature** **pH** **Oxygen** **Sludge height**	**Ammonia** (Gas-sensitive) **NOx** (UV)	**Ammonia** (Photometric) **Nitrate** (Photometric) **Nitrite** (Photometric) **Phosphate** (Photometric)	**Ammonia** (Gas-sensitive) **NOx** (UV)	**Ammonia** (Photometric) **Nitrate** (Photometric) **Nitrite** (Photometric) **Phosphate** (Photometric)	**COD** (thermal oxidation & photometric) **TOC** (thermal oxidation & IR detection) **TN** (thermal oxidation & IR or chemiluminescence) **TP** (thermal oxidation & photometric) **Respirometer** **Titration biosensor** (alkalinity)
Filtration	-	Fast	Fast	Slow	Slow	-
Response Time (min)	1	10	10	20	20	30
Measuring Interval (min)	0	0	5	0	5	30

4.2. Data Processing: Continuous Data

4.2.1. Data Collection

Data is collected at Papier Masson using a Foxboro distributed control system (DCS). The data is transmitted from the DCS to an advanced workstation where an exception deviation filter is applied in order to reduce the quantity of data transmitted further. The data is then sent to the mill network, from which the PI system compresses and archives data. The scan rate for data is generally 0.5 to 1 second in the DCS and 10 seconds in the PI system.

The exception deviation filter dead-band, data compression and storage, date extraction and interpolation techniques are discussed in Appendix 1.

4.2.1.1. Instrument details

The following attributes are set in the configuration for each instrument:

- Span
- Zero
- Compression deviation (recording limit/ dead-band for compression)
- Exception deviation (recording limit/ dead-band for transmission)

Visual inspection of the compressed data over a particular time range can indicate whether the compression deviation is set too high or too low for a particular instrument.

4.2.2. Data Preparation & Treatment

The preparation, cleaning or pre-processing of data requires a great deal of effort. Steps in data preparation include removal of abnormal operating conditions such as mill shuts or low production periods, the identification and removal of outliers, and filtering noise in the data [162]. Outliers are those data points that deviate greatly from all other data points [163]. On-line data cleaning and pre-processing has been studied [163].

4.2.3. Steady State Identification

The detection of steady state conditions can be achieved by selecting a window or time period of data and performing an steady state identification exercise [164]. The steady state identification exercise can consist of a variety of analysis, from a moving average plus data variance limits, or other statistical tests on the data average, variance or regression [164]. In all cases, the term ‘steady state’ is used to describe a time period at which the plant is operating in a stable fashion; the term ‘stable operation’ could equally be used.

4.3. Pulp and paper wastewater measurements, data treatment & modelling

4.3.1. Pulp and paper wastewater measurements

Typical frequency of measurements of pulp and paper wastewater streams is outlined in Table 13 below. The frequency of measurements made for operations monitoring is often daily, while operations control requires a shorter frequency of measurement, and measurements made for regulatory compliance may be daily but require the greater accuracy associated with an accredited laboratory. Laboratory measurements are often grab samples while the samples sent to accredited laboratories for compliance are usually composite samples.

Table 13: Pulp & paper wastewater measurement frequency (typical)

Measurement	*Frequency*	*Location*	*Purpose*
COD NH_4 NO_3 PO_4 TSS	Daily	AST inlet	Monitoring
COD DO Temperature	On-line	AST inlet	Control
SVI TSS VSS	Daily	AST outlet	Monitoring
NH_4 NO_3 PO_4	Daily	Final Effluent	Monitoring
BOD_5 TSS COD	Daily	Final Effluent	Regulatory compliance

4.3.2. Data treatment & modelling

The data treatment process necessarily calculates an average value of measured values, whether it be a minute average of on-line measurements made at a frequency of 15 seconds, or hourly average of measurements made every minute. In pulp and paper modelling, a number of approaches have been used. Daily, weekly and yearly averaged data has been used in pulp and paper wastewater modelling research, as detailed in Table 14.

Table 14: Pulp & paper wastewater measurement average data used for modelling

Measurement	***Frequency***	***Average used for modelling***	***Reference***
COD BOD TSS N P Flow	Daily	Yearly	[4]
BOD COD fractions P fractions N fractions	Two occasions 8 days apart	Averaged	
BOD COD fractions P fractions N fractions	Three consecutive days	Averaged	[119]
COD BOD TSS		Yearly	

Measurement	***Frequency***	***Average used for modelling***	***Reference***
Batch reactor tests for COD fractions	Two occasions in triplicate	Averaged triplicates	[165]
COD BOD TSS	Daily or twice daily during a 4-year period	Daily (Yearly used for mass balances)	[166]
Batch reactor tests			[139, 167-169]

5. Modelling: Activated Sludge Models (ASM)

The benefit of modelling of a wastewater treatment plant is at least two-fold: to facilitate a deep understanding of current operating regimes, and to enable the amelioration of the process operation, the results of which may include new design projects. A model is a powerful tool which can save both money and time for an operator or process designer. It is important to understand the principles upon which the model was developed and the limitations of the model, since any model is constructed to reflect reality only within certain constraints.

5.1. Background

The history of the development of models that represent the Activated Sludge process is very well expressed in an article by Gujer [170]. Suffice to say that the modelling of AST processes developed in 1964 by Downing, Painter and Knowles, and Wuhrmann led to development work by Gujer himself and by the University of Cape Town (UCT) led by Marais during the late 1970s. World-wide modelling work culminated in 1982 in the formation of a task group by the then International Association on Water Pollution Research and Control (IAWPRC), who developed the matrix notation for dynamic modelling that was more accessible than the previous FORTRAN programming [170]. The matrix represents the Monod model of biological processes which occur in the AST [171] cited in [172].

The first Activated Sludge Model (ASM) developed by the IAWPRC taskforce was aptly named ASM1. The stated purpose of the taskforce was "to review existing models and... to reach a consensus concerning the simplest one having the capability of realistic predictions of the performance of single sludge systems carrying out carbon oxidation, nitrification and denitrification"[173]. The matrix bearing his name originated in Petersen's 1965 publication "Chemical Reaction *Analysis*" [174] *cited in* [172, 173, 175], and is a systematic representation of the stoichiometric and kinetic relationships between the system components and the biological processes. The system components may include the wastewater COD fractions, the biomass fractions, nutrient fractions, oxygen or alkalinity, according to established standards [5].

The ASM model was further developed to include biological phosphorus uptake and the associated denitrification process (ASM2, ASM2d), and to include the storage of substrate under concentration gradient conditions (ASM3) [173, 176].

5.2. *Mathematical Modelling*

The beauty of the ASM models is that they make every effort to apply mechanistic models whilst remaining as simple as possible, and all this in order to represent biological processes which are occurring in a microbiological population that is populated by a complex mixture of microorganisms. The key to understanding the ASM models is that they represent bulk processes observed, and not necessarily each of the processes that are occurring at a microscopic level inside the floc, such as those described in section 3.1 of this literature review, a model of which would be impossible to calibrate.

The ASM models can be described as "dynamic, lumped-parameter, grey-box models including nonlinear reaction terms"[119]. Each of these designations is discussed in Appendix 1.

5.3. *Modelling Methodology*

The following is a discussion of the general methodology involved in modelling a process such as wastewater treatment.

5.3.1. Build, Calibrate, Validate

The methodology described in *Petersen et al.* will form the basis for this modelling exercise [177]. This methodology, depicted in Figure 7, is widely accepted and reiterated in many articles [169, 176, 178-182]. The inputs to the model will include design and operational data for the specific plant, as well as the characterisation of each sub-model: the hydraulic, settling and biochemical model, the latter will require an evaluation or estimation of kinetic and stoichiometric parameters [177].

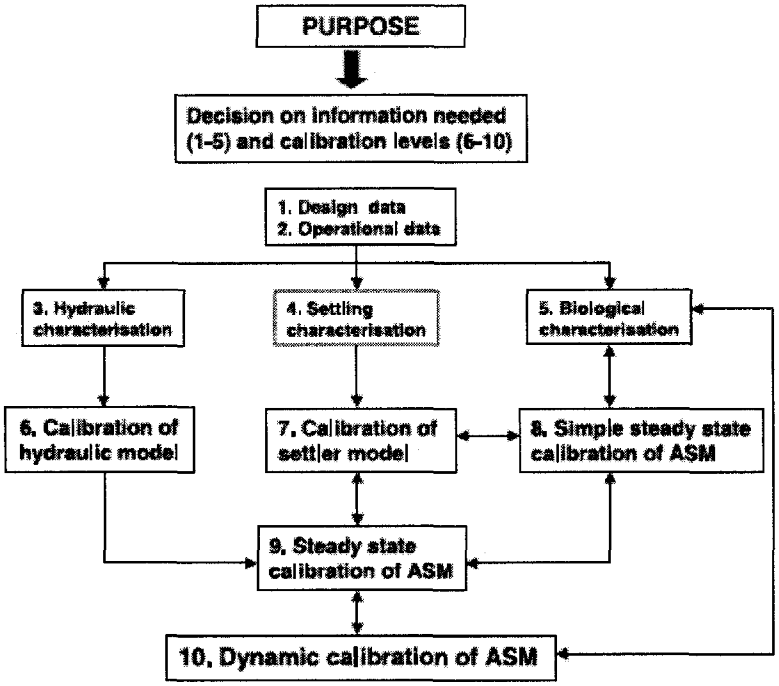


Figure 7: Modelling Methodology, from *Petersen et al.*[177]

One of the most important steps in this methodology is to specify the purpose of the model, and the intended calibration level [183]. The term 'calibration' refers to "the selection of values for the kinetic and stoichiometric coefficients of a mathematical model" [172].

According to common data mining methodologies, calibration could also be referred to as the use of a training or learning dataset to construct a model using a supervised algorithm [184]. In this case, the next step in such a methodology is to use a previously unused data set, the validation dataset, to validate the model that has been built. This validation step is included in the comprehensive generalised simulation guidelines presented by Langergraber *et al.* [179], as shown in Figure 8. Hulsbeek *et al.* recommend using a distinct data set, say from a different season, for the validation data set [185]. Langergraber *et al* suggest a short period, say of four days, of independent monitoring for use as the validation data set [179]. Sreckovic's experience with a limited data set indicates the division of the data set into a calibration and a validation set, based on extreme outlier values and variation of the data, is sufficient [166]. Furthermore, Sreckovic reiterates the calibration process four times in order to avoid a local minimum in his calibration algorithm [166].

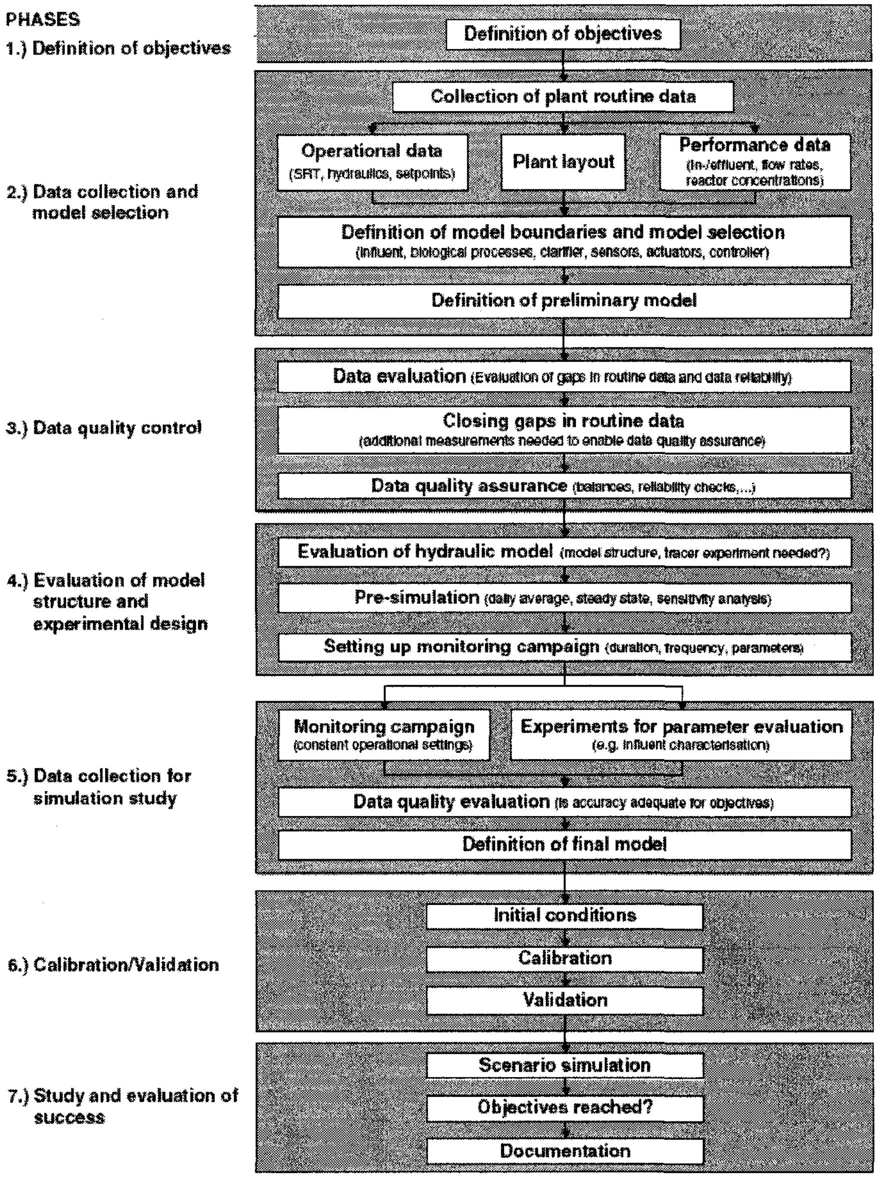
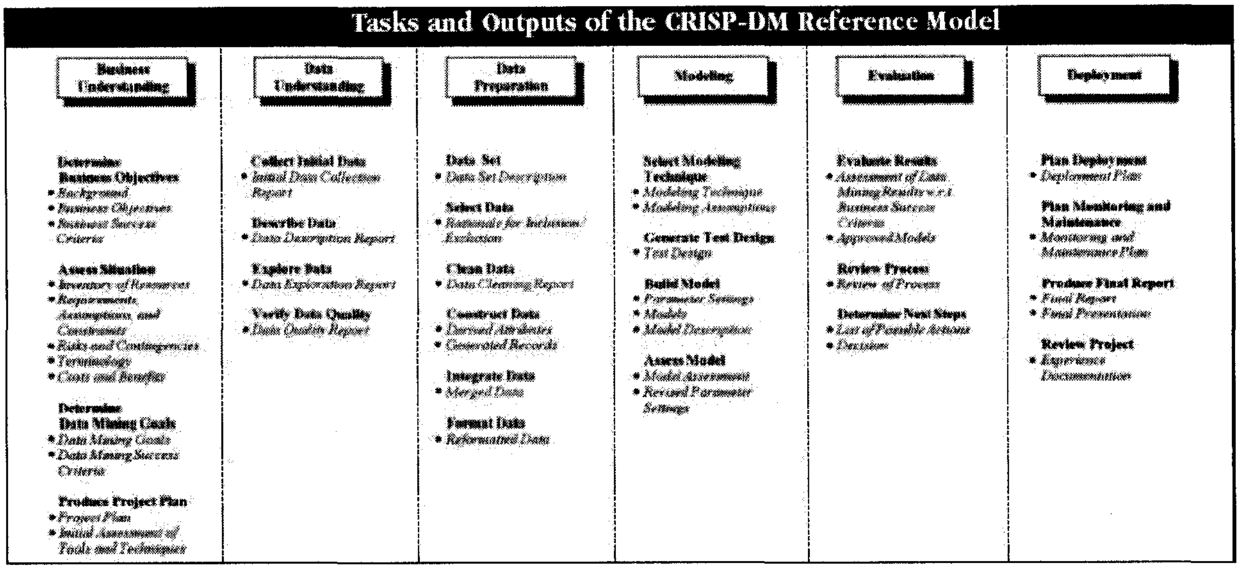


Figure 8: Simulation guidelines, *Langergraber et al.*[179]

The context of modelling in the overall data mining exercise is demonstrated by the CRISP-DM methodology [186], which includes data preparation, data collection as discussed in the previous data collection section, and presented in Figure 9.



Tasks and Outputs of the CRISP-DM Reference Model

Business Understanding	Data Understanding	Data Preparation	Modeling	Evaluation	Deployment
Determine Business Objectives • *Background* • *Business Objectives* • *Business Success Criteria* **Assess Situation** • *Inventory of Resources* • *Requirements, Assumptions, and Constraints* • *Risks and Contingencies* • *Terminology* • *Costs and Benefits* **Determine Data Mining Goals** • *Data Mining Goals* • *Data Mining Success Criteria* **Produce Project Plan** • *Project Plan* • *Initial Assessment of Tools and Techniques*	**Collect Initial Data** • *Initial Data Collection Report* **Describe Data** • *Data Description Report* **Explore Data** • *Data Exploration Report* **Verify Data Quality** • *Data Quality Report*	**Data Set** • *Data Set Description* **Select Data** • *Rationale for Inclusion/ Exclusion* **Clean Data** • *Data Cleaning Report* **Construct Data** • *Derived Attributes* • *Generated Records* **Integrate Data** • *Merged Data* **Format Data** • *Reformatted Data*	**Select Modeling Technique** • *Modeling Technique* • *Modeling Assumptions* **Generate Test Design** • *Test Design* **Build Model** • *Parameter Settings* • *Models* • *Model Description* **Assess Model** • *Model Assessment* • *Revised Parameter Settings*	**Evaluate Results** • *Assessment of Data Mining Results w.r.t. Business Success Criteria* • *Approved Models* **Review Process** • *Review of Process* **Determine Next Steps** • *List of Possible Actions* • *Decision*	**Plan Deployment** • *Deployment Plan* **Plan Monitoring and Maintenance** • *Monitoring and Maintenance Plan* **Produce Final Report** • *Final Report* • *Final Presentation* **Review Project** • *Experience Documentation*

Figure 9: CRISP-DM Methodology [186]

5.3.2. Modelling effort

The construction of a model of a wastewater treatment plant can be characterised by the effort required for the process simulator, as presented in Figure 8 below [187].

Table 15: Modelling effort & deliverables [187]

Modelling effort & deliverables	***Low effort***	***High effort***
Person-hours (order of magnitude)	Tens to hundreds of hours	Thousands of hours
Modelled Layout	Simplified representation of the plant focusing on liquid line processes	Complete representation of the plant including liquid and solids processing and parallel process lines

Modelling effort & deliverables	***Low effort***	***High effort***
Data	Existing data only, focus on average plant performance	Sampling and monitoring program designed specifically for model calibration and evaluation – including stress testing and dynamic event monitoring
Calibration	Based on one or two pseudo-steady-state events (average performance over a period of time with relatively consistent influent and stable operation)	Numerous steady-state and dynamic calibrations over a wide range of plant operating conditions. Kinetic and stoichiometric parameters identified using, for example, respirometry
Evaluation	Limited (if any) formal evaluation of model calibration using independent data sets	Formal evaluation using multiple independent data sets that represent a wide range of plant operating conditions
Plant Analysis	Steady-state analysis of a few key scenarios	A wide-ranging analysis of plant layout and operations under existing and future loading conditions. Optimization of planned upgrades and operation

5.3.3. Modelling Challenges & Risks

As discussed previously, a model is one representation of reality, not necessarily the only possible representation. With respect to the modelling methodology discussed, it is important to recognise that many model parameters are fit to the data and assumed to be constant – this is particularly true of the ASM model kinetic and stoichiometric parameters discussed below [188]. Alternatives to the ASM models exist, such as the suggested model based on F/M ratio rather than substrate concentration [188].

One problem that has been highlighted with the ASM models in particular is that two parameter sets may produce the same model result [166]. Sreckovic reports that this problem, termed 'identifiability' of the model, requires a dynamic sensitivity analysis of the model [166].

5.4. Model Components

The overall wastewater treatment plant model is made up of a hydraulic model, a settling model and a biological model (ASM), and for each of these model components a number of variations exist.

5.4.1. Hydraulic Model

5.4.1.1. Biological Reactor

The hydraulic model is specific to the type of reactor process unit selected, whether it is a continuously stirred-tank reactor (CSTR), a plug-flow reactor (PFR) or sequencing batch reactor (SBR) type of suspended growth reactor, or an attached growth reactor such as a trickling filter or a rotating biological contactor (RBC)[189]. The modelled reactor should take into consideration the real-life degree of dead space or short-circuiting, and the degree to which the actual reactor fits the idealised reactor model [189], including any non-equal flow splits [182].

The theory behind CSTR and PFR engineering is presented in section 2.2.1. The hydraulic models included in the GPS-$X^{®}$ simulation environment follow this theory exactly (refer to equations 2.1 to 2.4 in [189]).

5.4.1.2. Clarifiers

The hydraulic model for the primary or secondary clarifiers is based on the geometry of the clarifier (rectangular, circular, conical etc), plus the settling model selected [189].

5.4.2. Settling Model

The settling model can range from physical settling only (non-reactive) to physical settling plus some biological reactions (reactive). The settling models available in the GPS-$X^{®}$ simulation environment include a point settler (zero-dimensional and non-reactive), a one-dimensional non-reactive model and a one-dimensional reactive model [189]. The reactive models are reliant on the biological model chosen for the upstream activated sludge process to determine the possible reactions that could occur in the secondary clarifier [189].

5.4.3. Biological Model

There are currently four main ASM models available: ASM1, ASM2, ASM2d and ASM3. The main differences between each model are the biochemical processes which are included in each model. *Gernaey et al.* present an excellent review of the differences between the ASM models, as well as other activated sludge models available, a summary of which is presented in Table 16 [176]. All models include the removal of organic carbon

Table 16: Summary of activated sludge model biochemical processes [176]

Model	*Processes included*	*Reference*
ASM1	Nitrification, denitrification, Death regeneration (not electron acceptor depending), Hydrolysis (electron acceptor depending)	[190]
ASM2	Nitrification, denitrification, Death regeneration (not electron acceptor depending), Hydrolysis (electron acceptor depending), Biological Phosphorus removal (bio-P), Lysis of Phosphorus accumulating organisms (PAO), Fermentation, chemical phosphorus removal	[191]
ASM2d	Nitrification, denitrification, Death regeneration (not electron acceptor depending), Hydrolysis (electron acceptor depending) Biological Phosphorus removal (bio-P), Denitrifying PAO, Lysis of Phosphorus accumulating organisms (PAO), Fermentation, chemical phosphorus removal	[192]
ASM3	Nitrification, denitrification, Endogenous respiration (electron acceptor	[193]

Model	***Processes included***	***Reference***
	depending), Hydrolysis (not electron acceptor depending)	
ASM3 bio-P	Nitrification, denitrification, Endogenous respiration (electron acceptor depending), Hydrolysis (not electron acceptor depending) Biological Phosphorus removal (bio-P), Denitrifying PAO, Lysis of Phosphorus accumulating organisms (PAO)	[194]
Barker & Dold	Nitrification, denitrification, Death regeneration (not electron acceptor depending), Hydrolysis (electron acceptor depending) Biological Phosphorus removal (bio-P), Denitrifying PAO, Lysis of Phosphorus accumulating organisms (PAO), Fermentation	[195]
TUDP (Delft University of Technology)	Nitrification, denitrification, Death regeneration (not electron acceptor depending), Hydrolysis (electron acceptor depending) Biological Phosphorus removal (bio-P), Denitrifying PAO, Lysis of Phosphorus accumulating	[196]

Model	***Processes included***	***Reference***
	organisms (PAO), Fermentation	

Considering only the ASM models, ASM2 and ASM2d models incorporate the biological phosphorus removal processes that are outlined in *Comeau et al.* [120]. These processes are now well established and installed in municipal effluent treatment plants, however only one installation for pulp and paper effluent treatment is known [197].

One of the main differences between ASM1 and ASM3 is that ASM3 incorporates aerobic storage of the organic carbon, which is typically seen in plug flow reactors where there is a gradient in the carbon concentration over time or space [76, 77, 198-200]. In order to model this storage step, it was mathematically necessary to de-couple the death regeneration fate of the lysed bacteria found in ASM1, and the endogenous respiration model was therefore incorporated into ASM3, which can be seen in Figure 10 [176].

The applicability of these models specifically for pulp and paper wastewater is discussed in detail in section 5.7.2.

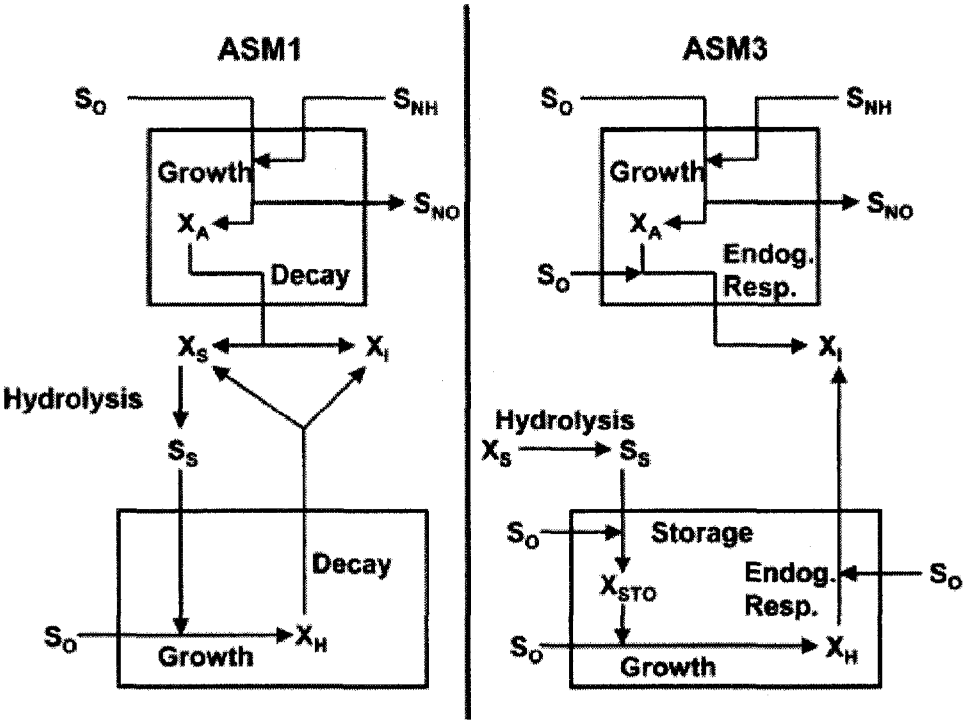


Figure 10: ASM1 vs ASM3 Processes [176]

5.4.3.1. Kinetics

The ASM models are constructed using kinetic parameters that are applicable for the range of 10ºC to 20ºC or 25°C, with ASM2 to ASM3 using the Arrhenius temperature relationship [173, 176]. This is potentially a significant limitation to these models, as the kinetic growth and inhibition rates are highly temperature dependent and the temperature of pulp and paper effluent is normally above 30°C. It can be assumed that kinetic parameters increase with increasing temperature for the same type of microbiological population; they should be measured for a particular microbiological population if a large temperature difference exists such as that between 10ºC and 40ºC [4].

In some of the ASM models, the growth rate of bacteria can be nutrient limited, although not in ASM1[176]. The presence of toxic substances can be inhibitory to the growth of bacteria and to the rate of nitrification, although the latter is not considered specifically in ASM1 [176].

5.4.3.2. Stoichiometry

The ASM models are all based on a chemical oxygen demand (COD) balance, as discussed in section 5.5.1. The models therefore require information on the chemical composition of the biomass or cellular matter, in order to complete this material balance. This information is represented by the ratio between COD to volatile suspended solids (VSS), or BOD to total suspended solids (TSS), or a combination thereof [189]. These ratios may be estimated from the theoretical chemical components of cellular matter or calculated from site data, as they will probably vary according to the bacterial population and wastewater composition.

5.5. ASM Model Basis

5.5.1. Chemical Oxygen Demand (COD) Material Balance

Chemical Oxygen Demand (COD) was chosen as the basis of the material balances in the ASM model due to the total conservation of mass, compared to total organic carbon (TOC), and for the rapidity of measurement, compared to biological oxygen demand (BOD_5 or BOD_7) [189].

5.5.2. Chemical Oxygen Demand (COD) Fractionation

COD is fractionated into the state variables, denoted by 'X' for particulate and 'S' for soluble, the definition of which is the filtrate that passes through either 0.45µm or 0.1µm filter paper [183]. Table 17 is a list of COD fractions that can be included in the ASM models using the CNPIP (carbon-nitrogen-phosphorus industrial pollutant) library [189]. As discussed in the next section, not all of the fractions are required for all models. A simple COD fractionation is presented in Figure 26.

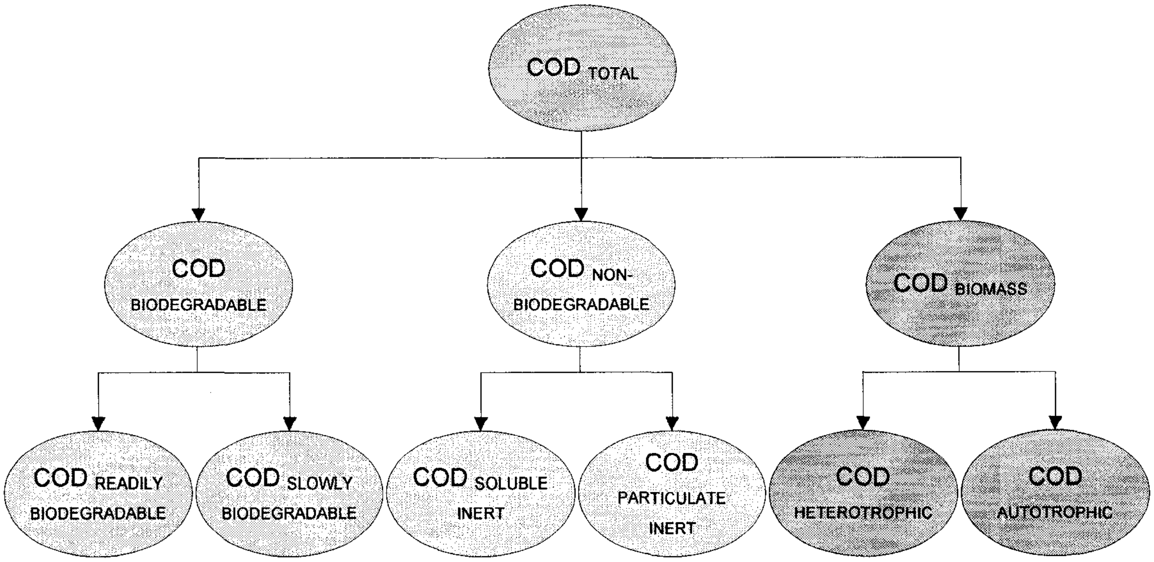


Figure 11: COD Fractionation, simple [183]

5.5.3. Nitrogen and Phosphorus

Nitrogen and phosphorus can also be fractionated and included in mass balance calculations, according to the biological model selected. Table 17 includes the largest range of possible fractions that can be included in the ASM models, which are graphically represented in Figure 28 and Figure 27.

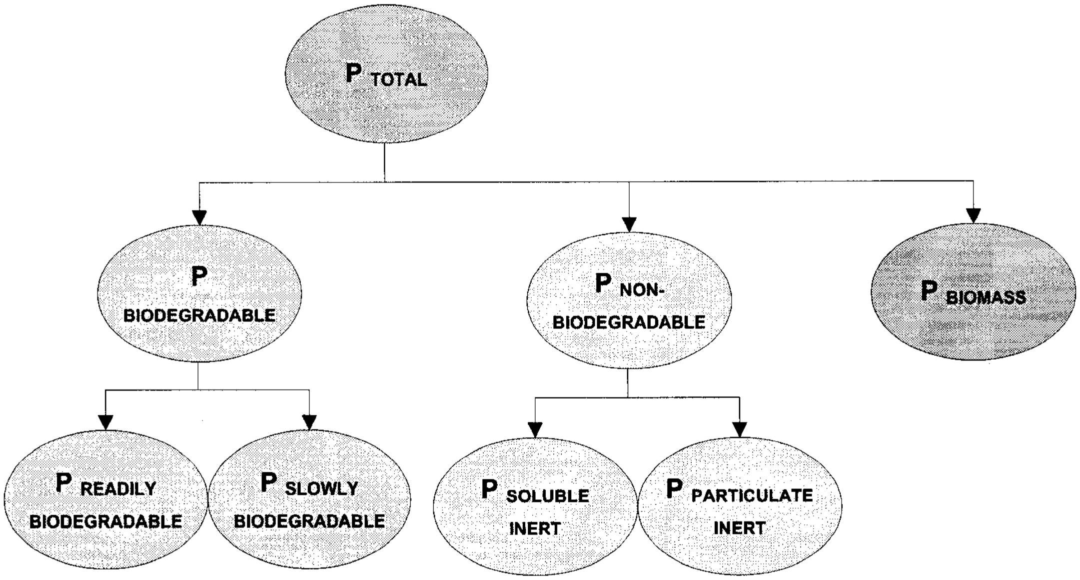


Figure 12: Phosphorus Fractionation

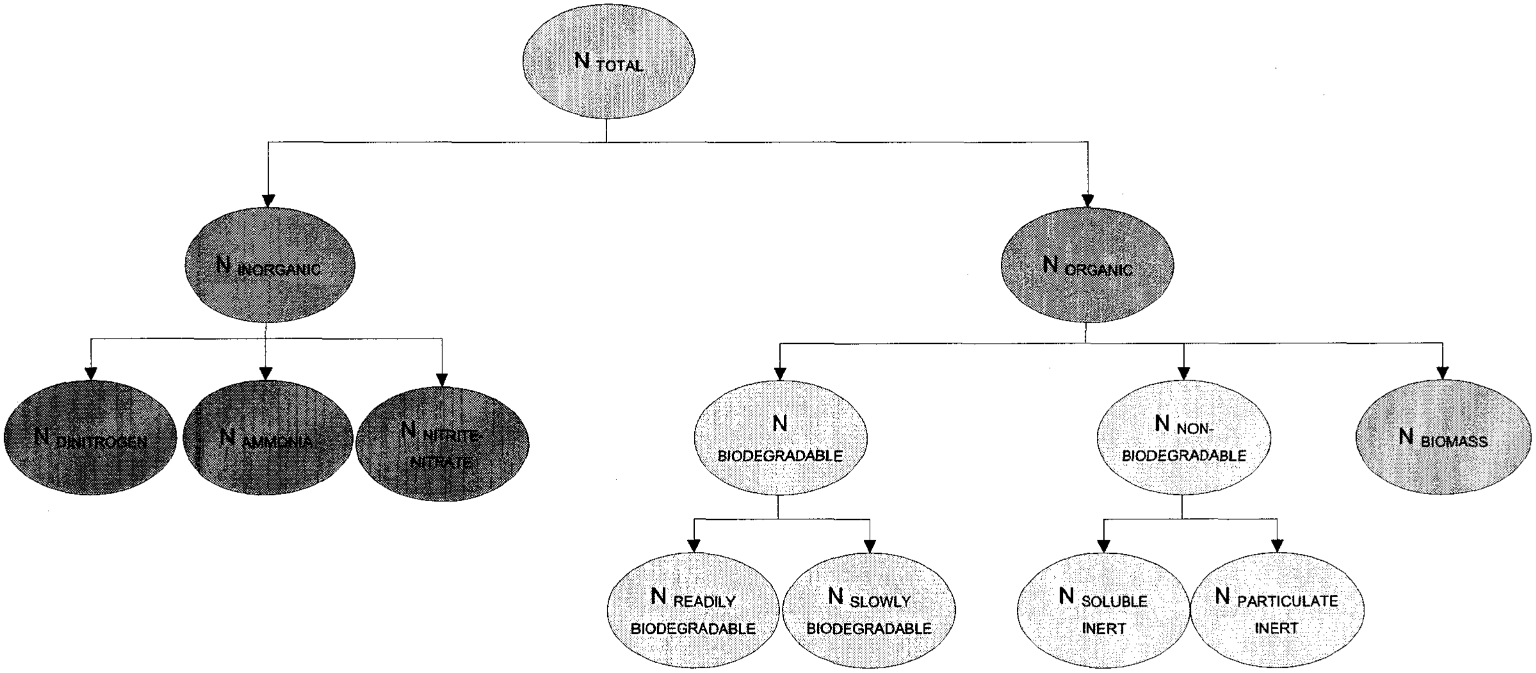


Figure 13: Nitrogen Fractionation

Table 17: Example of State Variables (CNPIP Library), From Hydromantis Inc Technical Reference [189]

#	*Symbol*	*State Variable*	*Units*
1	S_I	Soluble inert organics	g COD/ m^3
2	S_S	Readily biodegradable (soluble) substrate	g COD/ m^3
3	X_I	Particulate inert organics	g COD/ m^3
4	X_S	Slowly biodegradable (stored, particulate) substrate	g COD/ m^3
5	X_{BH}	Active heterotrophic biomass	g COD/ m^3
6	X_{BA}	Active autotrophic biomass	g COD/ m^3
7	X_U	Unbiodegradable particulates from cell decay	g COD/ m^3
8	S_O	Dissolved oxygen	g O_2/ m^3
9	S_{NO}	Nitrate and nitrite N	g N/ m^3
10	S_{NH}	Free and ionized ammonia	g N/ m^3
11	S_{ND}	Soluble biodegradable organic nitrogen (in S_S)	g N/ m^3
12	X_{ND}	Particulate biodegradable organic nitrogen (in X_S)	g N/ m^3
13	X_{PM}	Polyphosphate accumulating biomass	g COD/ m^3
14	X_{BT}	Poly-hydroxy-alkanoates (PHA)	g COD/ m^3
15	X_{PP}	Stored polyphosphate	g P/ m^3
16	S_{LF}	Volatile fatty acids	g COD/ m^3
17	S_P	Soluble phosphorus	g P/ m^3

#	**Symbol**	**State Variable**	**Units**
18	S_{ALK}	Alkalinity	mole / m^3
19	S_{NN}	Dinitrogen	g N/ m^3
20	S_{NI}	Soluble unbiodegradable organic nitrogen (in S_I)	g N/ m^3
21	S_F	Fermentable readily biodegradable substrate	g COD/ m^3
22	X_{GLY}	Stored glycogen	g COD/ m^3
23	X_{PPR}	Stored polyphosphate (releasable)	g P/ m^3
24	X_{MEOH}	Metal-hydroxides	g / m^3
25	X_{MEP}	Metal-phosphate	g / m^3
26	X_{STO}	Cell internal storage product	g COD/ m^3
27	X_{II}	Inert inorganic suspended solids	g COD/ m^3
28	S_{ZA}	Soluble component "a"	Not set
43	X_{ZA}	Particulate component "a"	Not set

5.5.4. Alkalinity and pH

The ASM models incorporate a balance of alkalinity, which is the measure of the buffering capacity of a solution in equivalent moles of calcium carbonate [201]. The Water Quality Association glossary makes the analogy of pH to temperature as alkalinity would be the heat capacity of a substance [201]. The ASM models assume the pH is constant and near neutral, they do not take into consideration the effect of pH on the biochemical processes [173].

5.5.5. Temperature

The ASM models do not include a heat and energy balance.

5.6. *Simulation environment*

A number of commercial simulation environments have been built using the ASM model components, notably GPS-X® by Hydromantis, WEST® by Hemmis and Biowin® by Envirosim, the latter includes elemental mass balances.

The following is a glossary of terms, taken from the *Hydromantis Inc Entry Level Guide* [202] and *Technical Reference* [189].

Table 18: GPS-X® glossary of terms [202]

Term	*Meaning*	*Example*
State Variable	Define the state of the system	X_S
Composite Variable	Calculated from state variables (& other constants)	VSS, TKN
Initial Conditions	Initial numeric value for wastewater composition, kinetic and stoichiometric parameters, used to find steady state	
Library	A collection of state variables that can be used in conjunction with an influent model and ASM model to build the appropriate biological model in GPS-X	CN, CNP
Influent Model	A representation of organic, nitrogen and phosphorus fractions in the influent	'States'

5.6.1. Simulation Basis

The basis of the GPS-X® simulator is a material balance over each of the state variables in the ASM model over each of the process units, taking into account the flow rates in and out of the process unit as well as the generation or consumption rate specified [202]. The state variables are predominantly COD, oxygen and nutrient fractions, as seen in Table 17.

5.6.2. Influent Model (Influent Advisor)

The GPS-X simulator allows the entry of influent COD, nitrogen, phosphorus and solids fractions in a number of ways. The simulator Influent Advisor spreadsheet demonstrates the links between user input values and state and composite variables. A summary of differences between the influent models is listed in Table 19 below.

Table 19: Influent model attributes [189]

Model	***Attributes***
BOD based	Use if BOD data is available and COD data not available Relies on f_{ss}: ratio of soluble substrate to ultimate BOD
COD fractions	Complicated calculation of N and P fractions Allows direct input of state variables via data file
States	Use if full wastewater characterisation has been carried out in reality
TSS COD	XCOD is calculated from TSS via VSS

5.6.3. Library

The choice of library is fairly simple: the CN library contains only COD, oxygen and nitrogen fractions; the CNP library contains phosphorus fractions as well. The exact fractions included in any model are dependent on the ASM model, library and influent model chosen. The IP libraries add industrial pollutant fractions to either the CN or CNP libraries. The industrial pollutants are user-defined fractions. These fractions can be used as proxies for other COD or nutrient fractions, as they are in the construction of the ASM-PP model (see section 5.8).

5.6.4. Composite Variable Calculation

The model calculates the composite variables from the state variables using certain ratios, so-called 'stoichiometric constants'[4], as illustrated in Appendix 1 [189].

5.6.5. Calculation Basis

The steady state solver in the GPS-X simulator detects a steady state convergence when the sum of derivatives of state variables falls below the 'iteration termination criteria', which has a default value of 10.0 [189]. Two other parameters that can have a significant effect on the steady state solver are the 'contract constant' and 'expand constant' which regulate the size of the steps taken by the steady state solver between iterations [189]. The default numerical solver integration method is the Runge-Kutta-Felberg method [189].

5.6.6. Alkalinity and pH

The GPS-X simulator conducts an alkalinity balance in accordance with the ASM models.

5.6.7. Temperature

The GPS-X simulator does not include a heat balance.

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[4] Although these constants are often ratios of solids to COD, which are not strictly stoichiometric. The term stoichiometric refers to the quantity of reactants required to produce a quantity of products in a chemical reaction.

5.7. Wastewater & Biomass Characterisation

5.7.1. COD and Nutrient Fractions

In order to satisfy the requirements of the ASM model COD balance and the simulator state variable material balance, a wastewater characterisation should be completed on various wastewater streams. This comprises of a characterisation of the carbonaceous (COD) fractions, nitrogen fractions and phosphorus fractions in the wastewater and sludge, as well as the settling and thickening properties of the sludge [203]. A large amount of the data required is normally collected by the treatment plant or mill, however the COD fractionation and some other parameters may require additional measurement campaigns.

There have been many published methods of carrying out these wastewater characterisations, predominantly for municipal (domestic) wastewater [203-210]. A thorough review of wastewater COD fraction characterisation for pulp and paper wastewaters is presented in a Paprican report [183], many of which require respirometry and are based on the methods established for municipal wastewater. Many methods have been established, for example a rapid physical-chemical method to determine the readily biodegradable soluble COD (S_S) fraction [211], and complete guidelines in the Netherlands for a simplified COD fractionation for modelling purposes [1]. A nitrogen fractionation characterisation for pulp and paper wastewater was completed by Jarvinen for both chemical and mechanical mill wastewaters [135]. Schnell used the BOD to COD ratio to indicate the biodegradability of the wastewater [32].

A wastewater characterisation based on ASM1 fractions was carried out at the Hylte pulp and paper mill at Hyltebruk, Sweden [4, 119]. This mill consists of TMP, groundwood and wastepaper pulp (including a de-inking plant) and newsprint paper production. The effluent treatment plant consists of trickling filters and anaerobic rectors upstream of the activated sludge treatment. In short, the configuration of this mill and its effluent treatment plant is far from simple.

5.7.2. Kinetic and stoichiometric parameters

Similarly to the wastewater characterisation of COD and nutrient fractions, a number of methods have been established for the determination of kinetic and stoichiometric parameters for use with the ASM models [183, 210, 212, 213]. Again, many of these methods are based on respirometry [183, 213]. Some of the kinetic and stoichiometric parameters can be determined during the wastewater characterisation exercise, some are based on theoretical calculations and others rely on experimental data found in the literature. The basis of these parameters is presented in Table 20 below. All values are quoted at 20ºC.

Table 20: Basis of calculations, kinetic & stoichiometric parameters

Parameter		Calculation/ Basis	Value(s)	Units
i_{CV}	XCOD / VSS (biomass)	$C_5H_7NO_2+5O_2 \rightarrow 5CO_2+NH_3+2H_2O$ $\frac{160gO_2}{113gC_5H_7NO_2}=1.42\ gO_2/gC_5H_7NO_2$	1.48	g COD/ g VSS
f_{BOD}	BOD5 / BOD ultimate ratio	Wastewater characterisation [1] BOD_{total}/ BOD_5 for (PI) Primary clarifier influent & (PE) Primary Effluent Estimated at 0.66 for municipal wastewater	PI: **0.18 – 0.28** PE: **0.21 – 0.23**	g BOD/ g BOD
i_{XBN}	N content of active biomass	Typical cell composition $C_5H_7NO_2$ [173] $\frac{14gN}{113gC_5H_7NO_2}\cdot\frac{113gC_5H_7NO_2}{160gO_2}$	0.086	g N / g COD
i_{XUN}	N content of endogenous / inert mass	Estimated to be less than i_{XBN} [173]	0.06	g N / g COD
i_{XBPP}	P content of active biomass	Estimated to be 0.02 g P / g COD [173]	0.021	g P / g COD
i_{XUPP}	P content of	Estimated to be 0.01 g P / g COD [173]	0.021	g P / g

Parameter		Calculation/ Basis	Value(s)	Units
	endogenous / inert mass			COD
f_P	Fraction of biomass leading to particulate products‡	Observed fraction is approximately 20% [173] For recycled process [173]: $f_{P,OBS} = \frac{f_P}{1 - Y_H(1 - f_P)}$	(f_U) 0.08	g COD / g COD
Y_H	Heterotrophic yield (active biomass) ‡	Stoichiometric equations of a COD balance for substrate (acetate), which gives an yield of [45]; $\frac{0.42 gVSS}{gCODsubstrate} \cdot \frac{1.48 gCODcells}{gVSS} = \frac{0.622 gCODcells}{gCODsubstrate}$ Observed yield typically lower (0.3 – 0.5) than the maximum yield constant Y_{MAX} (0.6 – 0.65) [104] Observed in range 0.46 – 0.69 [173]	0.666	g COD / g COD
Y_A	Autotrophic yield (active biomass) ‡	4.33 g O_2 required/g NO_3-N formed [173]	0.24	g COD / g N
μ_H	Heterotrophic maximum specific growth rate‡	Estimated to be 3.0 -13.2 d^{-1}, dependent on wastewater and process configuration [173]	6.0	d^{-1}

Parameter		**Calculation/ Basis**	**Value(s)**	**Units**
		Determined to be 9.0 d^{-1} [4]		
K_S	Readily biodegradable substrate half saturation…‡	Estimated to be 10 -180 g biodegradable COD/ m^3 [173]	20.0	g COD / m^3
K_{OH}	Oxygen half saturation *coefficient*‡	'Typical value' [173]	0.2	g O_2 / m^3
K_{NO}	Nitrate half saturation coefficient‡	'Typical value' [173]	0.5	g N / m^3
η_g	Anoxic growth factor‡	Estimated to be 0.6 – 1.0, higher values for aerobic sewers [173]	0.8	-
b_H	Heterotrophic decay rate‡	Determined to be 0.930 d^{-1} [4]	0.62	d^{-1}
μ_A	Autotrophic maximum specific growth rate‡	Literature values 0.34 – 0.65 d^{-1} [173]	0.8	d^{-1}
K_{NH}	Ammonia half saturation coefficient for autotrophic…‡	'Typical value' [173]	1.0	g N / m^3

Parameter		Calculation/ Basis	Value(s)	Units
b_A	Autotrophic decay rate‡	'Typical value' [173]	0.2	d^{-1}
K_{OA}	Oxygen half saturation coefficient for autotrophic…‡	'Typical value' [173]	0.4	g O_2 / m^3
k_h	Maximum specific hydrolysis rate‡	'Typical value' [173]	3.0	d^{-1}
K_X	Slowly biodegradable substrate half saturation…‡	'Typical value' [173]	0.03	g COD / g COD
η_h	Anoxic hydrolysis factor‡	Estimated in the region of 0.4 [173]	0.4	-
k_a	Ammonification rate‡	'Typical value': neutral pH domestic wastewater [173]	0.08	m^3 / g COD / d
K_P	Phosphorus half saturation constant	Estimated at 0.01 for ASM2d [173]	0.01	g P / m^3

PI = Primary Influent, PE = Primary Effluent

*As defined by the modified Petersen matrix

**Theoretical values used

†Calculated from wastewater characterisation

‡ Values used for pulp and paper wastewater modelling by *Bolmstedt* [4]

A summary of some kinetic and stoichiometric parameters found for municipal wastewaters is presented in Table 21 below [214]. The temperature coefficients, k_T, listed are based on an Arrhenius-type correction of kinetic parameters at temperature T, using the maximum growth rate with a base temperature of 20ºC as an example [214]:[5]

$$\mu_{MAX,T} = \mu_{MAX,20oC}.\exp(k_T(T-20))$$

Table 21: Municipal wastewater kinetic & stoichiometric characterisation studies (ASM1) [214]

Kinetic & Stoichiometric parameters		Range	Unit
Stoichiometry			
Readily biodegradable COD (fraction)	S_S	0.20 – 0.23	-
Slowly biodegradable COD (fraction)	X_S	0.50 – 0.60	-
Heterotrophic growth			
Yield	Y_H	0.57 – 0.64	-
Maximal growth rate	μ_{MAX}	2.5 – 4.0	d^{-1}
Temperature coefficient	k_T	0.07	$ºC^{-1}$
Saturation constant	K_H	5 – 20	$gCOD/m^3$
Hydrolysis			
Hydrolysis rate	k_h	1.5 - 55	d^{-1}
Temperature coefficient	k_T	0.03 – 0.07	$ºC^{-1}$
Saturation constant	K_X	0.02 – 10	-
Temperature coefficient	k_T	0	$ºC^{-1}$
Decay of biomass			

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[5] Arrhenius equation may also have the form $\mu_T = \mu_{20ºC}*(\theta)^{T-20}$, a θ value of 1.04 gives approximately the same doubling of the parameter for every 10ºC rise in temperature as for a k_T value of 0.07 $ºC^{-1}$.

Kinetic & Stoichiometric parameters		Range	Unit
Inert particulate products	X_U	0.08 – 0.10	-
Inert particulate COD in feed	X_I	5 – 15	gCOD/m^3
Decay rate	b_h	0.50 – 0.58	d^{-1}
Temperature coefficient	k_T	0.07	ºC^{-1}

5.8. ASM-PP: Pulp and Paper ASM model

5.8.1. ASM-PP model basis

The aim of this thesis is to use an existing ASM model, with modifications if appropriate, not to invent a new model or basis of modelling. A pulp and paper-specific modified ASM1 model was constructed by Brault, entitled the ASM-PP model [118]. On the basis of the information and references presented in Table 26, the ASM-PP is based on the ASM1 model. The modifications to ASM1 are presented in Table 27 in the form of the Petersen matrix, modifications are shown in red. The interpretation of the Petersen matrix is discussed further in section 5.8.3.

The ASM2 and ASM2d models will not be discussed further, since there is usually no biological phosphorus removal process in pulp and paper wastewater treatment plants, and none occurs in the case study mill.

Although some variations made in ASM3 do improve the fit of the mechanistic model to reality, such as the detail relating to the decay and intra-cellular processes, they also increase the complexity of the model. In keeping with the aim of the IAWPRC taskforce, the ASM-PP model aims to be the simplest model possible, and results have shown that the simpler decay processes of ASM1 provide an adequate model of pulp and paper effluent [118].

Barañao and Hall provide convincing arguments to use ASM3 for pulp and paper wastewater, given their assertion that "storage of readily biodegradable substrate is dominant" in their case study wastewater treatment plant [169]. However an equally persuasive argument is presented by Insel *et al.* that industrial wastewaters contain high fractions of slowly biodegradable COD, which renders the hydrolysis process the most significant mechanism [23]. In addition to the latter theory, a molecular weight distribution characterisation of TMP effluent upstream and downstream of a biological treatment plant shows significant hydrolysis of high molecular weight total organic carbon fractions [43]. It has also been shown that hydrolysis is a significant process in activated sludge treatment of pulp and paper effluent [23, 43].

In contrast, the storage of readily biodegradable substrate is seen in incidences where there is a gradient in substrate concentration in space or time [76, 77, 198-200], which is theoretically not the case in a well aerated, CSTR reactor. Particularly in this case study, the selector includes aeration and recirculation pump mixing, and is considered a CSTR reactor itself, therefore it does not provide a plug-flow design necessary to provide the feast-famine conditions required for storage of soluble COD [200]. It is hypothesised that the presence of feast-famine conditions results in out-competition of storage-incapable bacteria by the storage-capable bacteria [200]. There may be storage-capable bacteria present in the case study activated sludge population, however the storage biological process is not considered since the feast-famine conditions are assumed to be insignificant.

The limitation of biomass growth rates due to nutrient concentration, specifically ammonia-nitrogen and ortho-phosphate concentration, is considered necessary for pulp and paper wastewater; various combinations of this theory have been used in previous studies [4, 119, 166]. These studies combined the ASM-based model with higher organisms (protozoa), luxury phosphorus uptake and a double (sum) Monod switching function for ortho-phosphate [119], and temperature, pH and spill of an inhibitory substance (hydrogen peroxide) [166].

The state variable included in the ASM-PP model are presented in Table 22 [118]. As previously discussed, the 'industrial pollutant' fractions in the CNPIP library are used as proxies for the added fractions due to requirements of the software available.

It is assumed that lysis of cellular material results in particulate COD and nutrient fractions but not soluble nutrient fractions (i.e. soluble nutrients are immediately readily available in fractions S_P, S_{NH} or S_{NO}). This assumption is necessary given the lack of simple characterisation method to determine the soluble inert cellular material resulting from biomass lysis. One reference for pulp and paper wastewater measured the residual soluble cellular material as 0.057 mg COD/ mg total COD in the influent [206].

It is further assumed that the particulate nutrient fractions are accounted for in the X_{ND} (and X_{PD}) fraction and that the nutrient fractions relating to particulate inerts from cell decay, X_U, and to particulate biomass, X_{BH} and

X_{BA}, are composite variables (X_{NU}, X_{PU}, X_{NB}, and X_{PB}). This is to say that X_{NU} is a constant fraction of X_U, and is unchanged by process described by the Petersen matrix.

Table 22: ASM-PP State Variables [118]

#	*Symbol*	*State Variable*	*Units*
1	S_I	Soluble inert organics	g COD/ m^3
2	S_S	Readily biodegradable (soluble) substrate	g COD/ m^3
3	X_I	Particulate inert organics	g COD/ m^3
4	X_S	Slowly biodegradable (stored, particulate) substrate	g COD/ m^3
5	X_{BH}	Active heterotrophic biomass	g COD/ m^3
6	X_{BA}	Active autotrophic biomass	g COD/ m^3
7	X_U	Particulate inerts from cell decay (fraction)	g COD/ m^3
8	S_O	Dissolved oxygen	g O_2/ m^3
9	S_{NH}	Free and ionized ammonia	g N/ m^3
10	S_{NO}	Nitrate and nitrite N	g N/ m^3
11	S_{ND}	Soluble biodegradable organic nitrogen (in influent and from hydrolysis of X_{ND})	g N/ m^3
12	X_{ND}	Particulate biodegradable organic nitrogen (in influent and from biomass decay)	g N/ m^3
13	S_P	Soluble phosphorus (ortho-phosphates in influent and from phosphatification (hydrolysis of X_{PD}))	g P/ m^3
14	X_{PD}	Particulate biodegradable organic phosphorus (in influent and from biomass decay)	g P/ m^3

#	Symbol	State Variable	Units
15	S_{PD}	Soluble biodegradable organic phosphorus (in influent and from hydrolysis of X_{PD})	g P/ m^3
16	X_{II}	Inert inorganic suspended solids	g/m^3
17	S_{NN}	Dinitrogen	g N/ m^3
18	S_{ALK}	Alkalinity	mole / m^3

Table 23: ASM-PP Model composite variables [118]

#	Symbol	State Variable	Units
18	X_{NB}	Particulate active biomass nitrogen (in X_{BH}, X_{BA})	g N/ m^3
19	X_{NU}	Particulate nitrogen from cell decay inerts (in X_U)	g N/ m^3
20	X_{PB}	Particulate active biomass phosphorus (in X_{BH}, X_{BA})	g P/ m^3
21	X_{PU}	Particulate phosphorus from cell decay inerts (in X_U)	g P/ m^3

5.8.2. State variables relating to pulp & paper wastewater

The ASM-PP fractions can be related to known wastewater characteristics of pulp and paper wastewater according to Table 24 below. The biodegradability of resin acids has been related to the family of resin acid: pimaric or abietic [215]. Values of these state variables that have been experimentally evaluated or fit in a model for pulp and paper wastewater are presented in Table 25 below. Unfortunately there have been very few studies of this kind for pulp and paper wastewater, therefore only a small sample size exists for comparison.

Table 24: ASM state variables related to pulp & paper wastewater [168, 215]

Fraction	***COD form***
S_S	Softwood extractives: Volatile fatty acids (VFA) Fatty acid esters Resin acids (Abietic) [215]*
X_S	Lignin Colloidal fibrous material (Hemi-cellulose & cellulose)
S_I	Lignin Resin acids (Pimaric) [215]*
X_I	Large fibres with attached colloidal material

* See further work on dehydroabietic acid (DHA) [216]; and on compounds found in bleach plant effluents [217]

It is theoretically possible to divide the components of wood, hemi-cellulose, cellulose and lignin, into the X_S and X_I fractions is estimated based on the relative molecular weights of each class of compounds. However, it is not likely that hemi-cellulose and cellulose would be present in their pure form in the effluent, particularly in the effluent from a TMP plant: they would be present as fibrous material. Lignin is known to cause the colour of pulp and paper wastewater [218], and can therefore be attributed to both the slowly biodegradable and inert soluble fractions, X_S and S_I. The division of lignin into these two fractions would be dependent upon how the large molecules are cleaved, whether they are cleaved into small chains (slowly biodegradable) or not (inert).

Table 25: ASM state variables values for pulp & paper primary treated wastewaters (influent) [165, 169]

Fraction	***ASM influent state variable value***					
Pulp & Paper Process	*TMP/RCF (1993, 1994)*	*CTMP*	*BKM, BKM/TMP*	*BKM*	*CTMP*	*Municipal (ASM3 default)*
S_S	0.15, 0.29	0.49	0.24, 0.44	0.42	0.28	0.43
S_I	0.093, 0.082	0.14	0.36, 0.32	0.33	0.33	0.13
X_S	0.64, 0.54	0.30	0.42, 0.23	0.11	0.34	0.33
X_I	0.12, 0.088	0.07	0.07, 0.03	0.14	0.05	0.11
Reference	[165]	[169]	[168]	PAPRO work *cited in* [169]	[166]	[169]

5.8.3. ASM development

5.8.3.1. Temperature

The commercially available ASM1 model software includes the ability to model kinetic parameters based on the Arrhenius temperature-dependency model. An alternative temperature dependency was suggested and used by Sreckovic [166], based on experimentally determined behaviour of biomass in response to deviation from their acclimatised optimal temperature. It is considered that this complexity is not required for the ASM-PP model; it could be considered for future work.

5.8.3.2. Nutrient transformations

The ASM1 model is based on the use of ammonia nitrogen as the nitrogen source for all bacterial growth. The Mantis model incorporates processes for the use of both ammonia and nitrate-nitrogen as the nitrogen source for bacterial growth. It is considered that this complexity is not required for the ASM-PP model; it could be considered for future work.

All ASM models present nitrification as a one-step process and do not include a state variable for nitrite. Modelling nitrification as a two-step process could be considered for future work.

Table 26: ASM-PP reasoning & references

Process	***Pulp and Paper***	***ASM1***	***ASM3***	***ASM-PP***
Growth rate limitations	Nutrient limited [51, 60]	Neither ammonia nor phosphate considered [173]	Ammonia considered as limiting, phosphate not considered [173]	Both ammonia and phosphate considered as possibly limiting, under different operating conditions
Biomass decay	Release of lysed nutrients strongly related to decay	Death regeneration [173]	Endogenous respiration [173]	Death-regeneration
Storage of readily biodegradable substrate	Dependent on reactor type (CSTR, PFR)	Not considered [173]	Considered [173] Pertinent to concentration gradient [76, 77, 198-200]	Not considered for CSTR
Hydrolysis of slowly biodegradable substrate	Hydrolysis limiting step in organic carbon consumption	Considered, important [173]	Less significant than for ASM1, storage is more	Limiting step

Process	***Pulp and Paper***	***ASM1***	***ASM3***	***ASM-PP***
	[23, 43]		important [173]	
Ammonification of soluble organic nitrogen	Organic nitrogen content of wood varies with season [219]	Organic nitrogen concentration dependent [173]	Influent contains fixed fraction of organic nitrogen [173]	Organic nitrogen concentration dependent
Hydrolysis of entrapped organic nitrogen	Organic nitrogen content of wood varies with season [219]	Organic nitrogen concentration dependent [173]	Not considered [173]	Organic nitrogen concentration dependent
Phosphatification	Process by which soluble organic P is converted into ortho-phosphate for growth	Not considered [173]	Not considered [173]	Considered
Heterotrophic anoxic growth	Dependent on reactor aeration, dead space	Considered [173]	Considered [173]	Not considered due to fully aerated basin

Table 27: ASM-PP Petersen matrix (modifications from ASM1 shown in red) [58]

	Component (i) →	1	2	3	4	5	6	7	8	9
	↓ Process (j)	S_I	S_S	X_I	X_S	X_{BH}	X_{BA}	X_U	S_O	S_{NH}
1	Aerobic heterotrophic growth		$-\frac{1}{Y_H}$			1			$-\left(\frac{1-Y_H}{Y_H}\right)$	$-i_{XBN}$
2	Anoxic heterotrophic growth		$-\frac{1}{Y_H}$			1				$-i_{XBN}$
3	Aerobic autotrophic growth						1		$-\left(\frac{4.57-Y_A}{Y_A}\right)$	$-i_{XBN}-\frac{1}{Y_A}$
4	Heterotrophic degradation				$1-f_U$	-1		f_U		
5	Autotrophic degradation				$1-f_U$		-1	f_U		
6	Ammonification									1
7	Hydrolysis of X_S		1		-1					
8	Hydrolysis of X_{ND}									
9	Phosphatification									
10	Hydrolysis of X_{PD}									

	Component (i) →	10	11	12	13	14	15	16	17	18
	↓ Process (j)	S_{NO}	S_{ND}	X_{ND}	S_P	X_{PD}	S_{PD}	X_{II}	S_{NN}	S_{ALK}
1	Aerobic heterotrophic growth				$-i_{XBP}$					$-i_{XBN}/14$
2	Anoxic heterotrophic growth	$-\left(\frac{1-Y_H}{2.86*Y_H}\right)$			$-i_{XBP}$				$\left(\frac{1-Y_H}{2.86*Y_H}\right)$	$\left(\frac{1-Y_H}{14*2.86*Y_H}\right)-i_{XBN}/14$
3	Aerobic autotrophic growth	$-\frac{1}{Y_A}$			$-i_{XBP}$					$-\frac{i_{XBN}}{14}-\frac{1}{7*Y_A}$
4	Heterotrophic degradation			$i_{XBN}-f_U*i_{XUN}$		$i_{XBP}-f_U*i_{XUP}$				
5	Autotrophic degradation			$i_{XBN}-f_U*i_{XUN}$		$i_{XBP}-f_U*i_{XUP}$				
6	Ammonification		-1							1/14
7	Hydrolysis of X_S									
8	Hydrolysis of X_{ND}		1	-1						
9	Phosphatification				1		-1			
10	Hydrolysis of X_{PD}					-1	1			

	Component (i) → ↓ Process (j)	Reaction rate (ρj)
1	Aerobic heterotrophic growth	$\mu_H\left(\frac{S_S}{K_{SH}+S_S}\right)\left(\frac{S_O}{K_{OH}+S_O}\right)\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_P}{K_P+S_P}\right)X_{BH}$
2	Anoxic heterotrophic growth	$\mu_H\left(\frac{S_S}{K_{SH}+S_S}\right)\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_P}{K_P+S_P}\right)\eta_g X_{BH}$
3	Aerobic autotrophic growth	$\mu_A\left(\frac{S_O}{K_{OA}+S_O}\right)\left(\frac{S_{NH}}{K_{NA}+S_{NH}}\right)\left(\frac{S_P}{K_P+S_P}\right)X_{BA}$
4	Heterotrophic degradation	$b_H X_{BH}$
5	Autotrophic degradation	$b_A X_{BA}$
6	Ammonification	$k_a S_{ND} X_{BH}$
7	Hydrolysis of X_S	$k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)\left[\left(\frac{S_O}{K_{OH}+S_O}\right)+\eta_h\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{BH}$
8	Hydrolysis of X_{ND}	$k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)\left[\left(\frac{S_O}{K_{OH}+S_O}\right)+\eta_h\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{BH}\left(\frac{X_{ND}}{X_S}\right)$
9	Phosphatification	$k_p S_{PD} X_{BH}$
10	Hydrolysis of X_{PD}	$k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)\left[\left(\frac{S_O}{K_{OH}+S_O}\right)+\eta_h\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{BH}\left(\frac{X_{PD}}{X_S}\right)$

SECTION B

RESEARCH THESIS

1. Case study background: Site & Process

1.1. Papier White Birch, Masson division, Pulp and Paper Mill

The Papier White Birch, Masson division, pulp and paper mill is located in Gatineau, Québec, and consists of a single line thermo-mechanical pulping (TMP) process followed by a single newsprint paper machine.

Papier White Birch procure the chip furnish for the pulp mill, which consists of up to 8% hardwood and 92% softwood. The softwood furnish, predominantly pine, is further divided into high density and low density chips. The pulping process is the world's largest single line TMP pulping process, producing over 740 BDt/d with high consistency primary and secondary refiners (36 MW motors each), three low consistency tertiary refiners, and a single rejects refiner. Sodium hydrosulphite is added to the pulp for brightness prior to storage of the pulp.

The paper machine incorporates a vertical headbox, a three-roll press, a four-roll calendar and an in-line winder and re-winder. The finishing plant is located in a separate building, linked to the paper machine via a horizontal roll conveyor. The 8.4 metre wide paper machine runs at 1320 m/min, producing newsprint predominantly from 100% TMP pulp.

Very small quantities of chemicals containing nitrogen and phosphorus are added to the site boiler for the purposes of controlling deposits and corrosion. The concentration of these chemicals in the effluent under normal operating conditions is very low and originates from the continuous boiler blowdown.

1.2. Wastewater Treatment Plant

The secondary wastewater treatment plant at the Papier White Birch site was constructed in 1995. It is physically located approximately 400 metres from the boilers. From January 2007, the mill has operated the wastewater treatment plant remotely. The operator monitors the performance of the plant remotely from the boiler house, and therefore the mill automated various measurements. Notably, a filtered chemical oxygen demand (fCOD) and multiple total suspended solids (TSS) meters were installed.

Municipal wastewater is sent to the municipal sewer for off-site treatment. Storm-water from roof run-off, landfill leachate and chip pile run-off are treated on site, 60% of all other storm-water run-off bypasses the treatment plant.

1.2.1. Process configuration

The wastewater plant process configuration encompasses coarse screening (mechanical bar screen), primary treatment (clarification), two activated sludge treatment (AST) basins operating in parallel, and two secondary clarifiers operating in parallel. The influent is cooled during summer months; this is not required during winter. An emergency basin is available for use under process upset conditions or for spills. The process does not incorporate an equalisation basin, neutralisation tank or tertiary treatment.

Each AST structure includes a selector section and submerged venturi (jet) aerators in a well-mixed basin. The secondary treatment process was originally designed by CH2M Hill, and the AST basins are oversized for the current influent from the mill due to process modifications to the pulp and paper mills. Anecdotally, the plant can operate with a single basin; however the basins are very close to the water table (aquifer), and need to contain water for most of the year in order to maintain structural integrity.

Nutrients are dosed into the RAS stream in the form of urea and phosphoric acid.

Primary and secondary sludge flows are mixed without any upstream dewatering. The mixed primary and secondary sludge is treated via a gravity table pre-thickener and then a belt press. The dewatered sludge is stored for a maximum of 8 to 12 hours prior to disposal by composting and agricultural land-spreading.

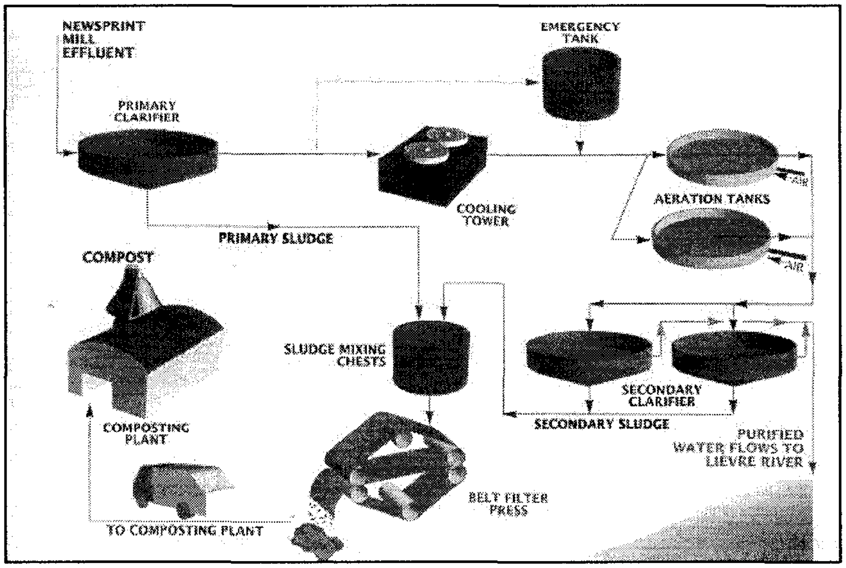

Figure 14: Papier White Birch Wastewater Treatment Plant Configuration (courtesy Papier White Birch)

1.2.2. Current Operating Strategy

It should be noted that any automated controls mentioned in this section are likely to have a long damping due to the long residence times between measurement points.

1.2.2.1. Primary Clarifier

Primary treatment consists of a gravity clarifier with conventional centre feed. No polymer is dosed to the clarifier.

1.2.2.2. Neutralisation

Fresh water entering site from the Lièvre River has an alkalinity of approximately 50 to 60 ppm. Sodium hydrosulphite is added to the pulp for brightness, and this causes some formation of sulphides, including hydrogen sulphide (H_2S), in the primary clarifier, some volatile fatty acids are also present in the influent - all of which affect the pH.

At the effluent treatment plant, pH is controlled at two points via the addition of 50% sodium hydroxide (caustic soda, NaOH). Coarse pH control is carried out via dosing upstream of the primary influent, at the mill drain close to the paper machine, and measurement immediately upstream of the primary clarifier, for which the pH set point is approximately 6.5. Finer pH control is conducted via dosing in the distribution pit to the AST selectors, and measurement in the selectors, for which the pH set point is in the range of 6.3 to 6.6. The operator modifies the set point for this control on a weekly basis, and control is weighted largely on the flow rate at the primary clarifier inlet.

1.2.2.3. Emergency Basin

Influent flows to the primary clarifier will be sent to the emergency basin via actuated control valves according to the site procedure. This procedure includes spills of listed chemicals and oils greater than 200 L in quantity. Operators have a 10 minute window of opportunity in which to divert flow. Particular attention is paid to spills of biocide. The emergency basin has no aeration or mixing control and the contents of the basin can only be sent to the AST basins via gravity or emptied via vacuum truck. The basin is used very infrequently; it was used 8 times in 2006. Reasons for diverting flow into the basin include for maintenance of other basins at the treatment plant. The point of diversion is upstream of the primary clarifier.

1.2.2.4. Cooling

During the months of May to September, evaporative cooling towers are used to lower the temperature of the primary clarifier effluent by up to 10ºC based on a flow rate of 20 000 L/min. Spray nozzles were removed from the cooling towers due to frequent blockages, and these may be reinstalled to increase the surface area of water droplets and thus the heat transfer capacity of the towers, if required. The outlet of the cooling towers will alarm at 39ºC. During 2006, the primary clarifier effluent had an average temperature of 35ºC in winter and an average temperature of 45ºC in summer.

1.2.2.5. Activated Sludge Treatment

Current nutrient control is a constant rate dosage for both chemicals: urea and phosphoric acid. The laboratory technician carries out a chemical oxygen demand (COD) measurement in the influent to the wastewater treatment plant once per day, and the nutrient dosage rate is modified based on the results of this test. Previously, the plant operator did this test and adjusted the nutrient dosage rate more often.

The actual set point for the nutrient dosage is manually set according to nutrient residuals found during discrete laboratory nutrient testing for ammonia and nitrate nitrogen and ortho-phosphate, and further verified against a ratio between COD and nutrient requirements. This ratio was not necessarily held constant historically (discussed further in the data description section). This control is not automated, and depends largely on operator process knowledge. The temperature of the nitrogen (urea) tank is monitored to avoid crystallisation at temperatures less than 18ºC.

The flow rate of air to each AST basin is not controlled. There are three air blowers available, the plant normally operates with a single blower and the operator can manually start up a second blower (there is no automated start up control). Dissolved oxygen (DO) is measured continuously in one selector and one aeration basin; the number of blowers used is generally controlled in order to maintain a DO concentration of approximately 3 mg/L in the AST selectors and 1.5 mg/L in the AST basins. Aeration is delivered to the selectors and the basins via jet aeration. The selector is very well mixed and is not compartmentalised.

1.2.2.6. Secondary Clarifier

The two secondary clarifiers are suction-type clarifiers.

No polymer is dosed into the secondary clarifiers.

The sludge age is approximately 6 to 7 days, based on AST mixed liquor suspended solids (MLSS) of approximately 2000 mg/L.

The sludge wasting rate (WAS) is controlled according to the MLSS in the AST basin. The mill is investigating the possibility of controlling the WAS based on the secondary clarifier sludge inventory.

The sludge recirculation rate (RAS) is controlled proportional to the final effluent flow rate, and furthermore manually modified according to the sludge density and sludge volume index (SVI) measurements. The mill has developed this strategy in order to maintain a sludge blanket height as constant as possible in the clarifiers, and has found that the final effluent flow rate is the best measurement variable (due to near constant flow rate during normal operation). The RAS is returned to the AST selector.

1.2.2.7. Sludge Treatment

The flow rate of mixed primary and secondary sludge to the vibrating screen, gravity table and the belt press is controlled according to the WAS control (described above). The press speed is controlled according to the WAS rate, as well as to maintain an average sludge dryness between 25% and 27%, although the dryness is acceptable as low as 20%.

A cationic flocculant polymer is dosed into the sludge press inlet, the flow rate of which is manually set by the operator.

1.2.2.8. Operational problems

Operational problems experienced during the year 2006 can be characterised by a rise in COD (by approximately 600 mg/L at the primary clarifier inlet) as well as a rise in secondary sludge production, both of which occur during the winter months. Dewatered sludge dryness drops during this period, due to the higher secondary biological sludge content, but is normally maintained above 20% dryness. The mill does see some hydrogen sulphide formation in the primary clarifier.

Remedial actions taken include increasing the dissolve oxygen, nutrients and polymer dosing rates.

It usually takes approximately two sludge ages for sludge quality to return to normal following an operational problem (10 to 15 days).

1.2.2.9. Operations Monitoring

The following parameters are monitored on a regular basis by the mill in order to supervise operation and to assist operators in making informed decisions regarding control of the plant.

1.2.2.9.1. Microscopic Analysis

The microbiological population in the ASTs are monitored on a daily basis using a phase-contrast microscope and camera. In particular, higher organism forms such as filamentous bacteria and protozoa, as well as the general state of floc formation are monitored by the operator, as changes in the population size of these bacteria usually give a good indication of any change in process conditions. The mill has sent samples in the past to an independent consultant on a monthly basis, who reported on the microbiological population in more detail.

1.2.2.9.2. Toxicity Testing

Acute toxicity testing is conducted on the final effluent as per the provincial and federal regulations: daphnia, *Daphnia magna*, and rainbow trout, *Oncorhynchus mykiss*.

1.2.3. Plant Design Data

The following is a list of current plant design data which was used to model the wastewater treatment plant.

Table 28: Plant Design Data

Process Unit	***Parameter***	***Design Value***	***Reference****
Primary Clarifier 150-030	Volume	10 000m^3	Arrangement Drawing 9077-501-002
	Diameter	55 m	
	Side Water Depth	4.5 m	
Emergency Basin 150-209	Volume	10 000m^3	P&ID 601
	Diameter	36 m	
	Side Water Depth	10 m	
Aeration Basin (each) 150-201, 150-202	Volume	16 800 m^3	P&ID 602
	Diameter	47.8 m	
	Side Water Depth	10 m	
Aeration Selector (each) 150-203, 150-204	Volume	1 000 m^3	P&ID 602
	Side Water Depth	10 m	
Secondary Clarifier (each) 150-205, 150-207	Volume	5 000m^3	Dwg 136 Dwg 137
	Diameter	36 m	
	Side Water Depth	4.5 m	
Cooling Tower 150-296 150-294, 150-295	Temperature Drop (effluent side)	[10 ºC]	P&ID 601
	Based on flow rate	62 620 m^3/d [43 500 m^3/d]	
	Fan power (each)	50 hp (37 kW)	

Process Unit	***Parameter***	***Design Value***	***Reference*****
Sludge Mixing Tank 150-250	Volume	180 m^3	P&ID 604
Dry Sludge Silo 150-240	Volume	200 m^3	P&ID 605
Sludge Belt Press 150-244A	Mass flow rate Outlet	[50 tonne/day]	
	Dryness outlet	27%	
	Ratio primary: secondary sludge	30:70 [70:30]	
Urea Storage Tank 1 150-216	Volume	40 m^3	P&ID 606
Urea Storage Tank 2 150-220	Volume	40 m^3	P&ID 606
Caustic Storage Tank 150-285	Volume	40 m^3	P&ID 606
Phosphoric Acid Tank 150-215	Volume	40 m^3	P&ID 606

*Current operating values may be different to original design given the changes made to the pulp and paper processes upstream. Where known, current operating values are shown in square brackets and will be used for modelling purposes.

**See also Hydraulic Profile drawing A0-BPR-50-06-610

2. Gaps in the body of knowledge, Objectives, Hypothesis

2.1. Gaps in the body of knowledge

From the literature review, gaps in the body of knowledge have been identified. These gaps are:

1. No systematic methodology has been proposed which, based on objectively determined near-steady state conditions, can be used to develop mechanistic models that assist in the understanding of the particular nutrient transformations of interest to pulp and paper mills AST operation.

2. Control of supplemental nutrient dosing to pulp and paper wastewater treatment plants is often achieved using simple feedback control, and by feed-forward ratio control in a few cases [138]. Knowledge-based expert systems have seldom been used for control of nutrient dosing in AST systems. One expert control system incorporating on-line measurements, control software and predictive modelling has been trialled at a number of full-scale pulp mill wastewater treatment plants and is no longer in use [136, 137], another has been proposed for respirometric-based control of nutrient addition [139]. There may be an opportunity to used mechanistic modelling as the basis for an automatic strategy for the rate of nutrient addition and nutrient residual control.

3. A mechanistic model developed for municipal wastewater treatment, such as the ASM models, provides a powerful tool to model the biochemical transformations occurring in the AST process. ASM models have been modified previously for the application to pulp and paper wastewater and nutrient deficiency [4, 119, 166, 220]; however they have not been used in conjunction with rigorous-determined steady state data. There is a need to produce a systematic methodology that would allow mills to propose an ASM model adaptation for the biochemical nutrient transformations particular to their pulp and paper effluent treatment, including nitrification and denitrification processes.

2.2. *Objectives*

The overall project objective of this project is:

To propose a nutrient addition and operating strategy based on an ASM-based model that incorporates reliable process data

The two sub-objectives of this project are:

1. ASM-based modelling for pulp & paper

To use an ASM-based model to model a pulp and paper wastewater plant, including the nutrient transformations occurring, especially nitrification-denitrification.

2. Operating strategy

To propose a nutrient addition and operating strategy incorporating an ASM-based model of pulp and paper wastewater.

2.3. Hypotheses

The overall project hypothesis of this project is:

Incorporating reliable process data into an ASM-based model provides practical information such that ASTs can be better operated with regards to nutrient control.

The two sub-hypothesis of this project are:

1. ASM-based modelling for pulp & paper

It is feasible to use an ASM-based model to model a pulp and paper wastewater treatment plant including nutrient transformations, by taking into account nutrient uptake regimes, especially nitrification-denitrification.

2. Operating strategy

An ASM-based model of a pulp and paper wastewater plant can be interpreted and used to form the basis of a nutrient addition and operating strategy.

3. Methodology

3.1. Overall Methodology

The project methodology outlined in Figure 15 encompasses data collection of the mill physical design data, of continuous and discrete laboratory data from the mill PI system, and additional wastewater characterization measurements carried out at the mill laboratory and at the university laboratory according to Standard Methods [2]. This data was then treated to synchronize data over the hydraulic retention time of the AST basins, to exclude abnormal process conditions such as mill shuts, and to identify pseudo-steady state scenarios which varied in duration from 6 hours to 32 hours [3]. The treated data was further reconciled by mass balances for each pseudo-steady state prior to inclusion in an ASM-based model.

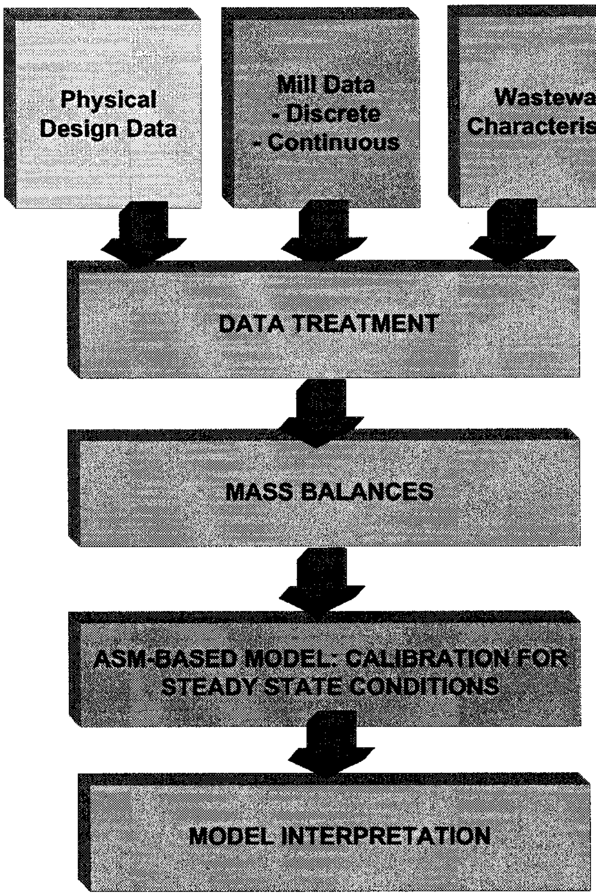

Figure 15: Project methodology

3.2. Data Collection

Data has been collected and stored/ warehoused on site historically in two forms: laboratory experiments in the Production Quality database and on-line instrumentation data in the Osisoft 'PI' system. The data housed in these two sources will be discussed separately in the following sections.

3.2.1. Glossary

3.2.1.1. Measurement evaluation

It is important to take note of how reliable the measurement results are for each instrument or test method. A number of definitions from the Standard Methods are reiterated in Table 29 [2].

Table 29: Glossary of statistical terms *[2] **[148]

Accuracy * (trueness)	The combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to a true value
Bias* (error)	Consistent deviation of measured values from the true value, caused by systematic errors in a procedure
Calibration	The method by which the trueness of the instrument is verified
Drift	The change in trueness of the instrument over time
Reproducibility* (precision)	Measure of the degree of agreement among replicate analyses of a sample, usually expressed as the standard deviation
Repeatability**	Refers to precision obtainable by the same technician under the same conditions (intra-laboratory), compared to reproducibility which refers to precision obtainable by different technicians under different conditions (inter-laboratory)

The ideal measurement would combine low bias with high reproducibility, minimal calibration required and minimal drift found during calibration. The precision and bias are noted for each measurement where known. The bias of measurements is dependent on the laboratory's interpretation of the test method as well as the method itself, and this element of the bias will be investigated in the Error Analysis section 5.

3.2.1.2. *Measurement type*

There are various types of measurement or sampling regimes. For simplicity, a number of definitions from the Standard Methods and other references are reiterated in Table 30.

Table 30: Measurement type definition *[2] **[134] †[149] ‡[150]

Grab / Catch*	A sample collected at a particular time and place, usually representative of only the composition of the source at that time and place. Can be interpreted as representative of process changes based on operator knowledge.
Composite*	A mixture of grab samples collected at the same sampling point at different times ('time-composite'), often used for 24-hour averages
Integrated*	A mixture of grab samples collected from various sampling points at the same moment in time, generally used for analysing the receiving water
Real-time**	Little or no delay between the time the sample is taken and results being available (short measurement interval), usually electronically via DCS
On-line†	A continuously measuring probe, can be located in-situ or in a side stream (data usually collected electronically via DCS)
In-line†	Instrument located directly in the media, direct contact with the wastewater sample (whether the sample is in-situ or pumped to/ through analyser)

In-situ‡	Installed directly in the process (tank, basin, pipe, channel)

One benefit of composite samples is that they account for large variations in flow rates, which is often the case in mill drains [47].

3.2.2. Production Quality Database

The Production Quality Database is a Microsoft Access database in which lab technicians and machine operators register the results from their experiments on a daily or shift-wise basis. Mill personnel have different levels of access to the database, to read or record data. The effluent treatment plant test results were formerly entered by the plant operator and the lab technician. Since 2 December 2006, a fewer number of tests are completed by the lab technician, who records the results directly in the database. Table 31 lists the production quality tag numbers for laboratory measurements, the associated measurement location and type, which were used in this study.

Table 31: Effluent Treatment Plant Production Quality tags (PVX, LAB.EFF)

#	*Tag*	*Measurement Type*	*Measurement Location*	#	*Tag*	*Measurement Type*	*Measurement Location*
1	MP3.DCOT	COD	Paper Machine	29	SBA.SVI	Sludge volume index	AST Tanks
2	PTM.DCOT	COD	TMP plant	30	SBA.NNH4	Ammonia-N	AST Tanks Outlet
3	EEP.MES	TSS	Primary Inlet	31	SBA.OPO4	Ortho-Phosphate	AST Tanks Outlet
4	ECP.DEBI	Flow rate	Primary Inlet	32	SBA.NNO3	Nitrate-N	AST Tanks Outlet
5	ESP.DCOS	COD soluble	Primary Outlet	33	SBA.SSV3	SSV-30	AST Tanks Outlet
6	ESP.MES	TSS	Primary Outlet	34	CSE.VOBO	Sludge blanket	Secondary Clarifier East
7	SCP.DB5T	BOD_5	Primary Outlet	35	CSO.VOBO	Sludge blanket	Secondary Clarifier West
8	BOP.MES	TSS	Primary Sludge	36	RAE.MES	TSS	RAS Secdary Clarifier East
9	SS.OXYG	Dissolved Oxygen	South AST Selector	37	RAO.MES	TSS	RAS Secdary Clarifier West
10	SN.OXYG	Dissolved Oxygen	North AST Selector	38	WAE.MES	TSS	WAS Secdary Clarifier East
11	ES.DCOS	COD soluble	Inlet AST Selector	39	WAO.MES	TSS	WAS Secdary Clarifier West
12	SSN.DCOS	COD soluble	Outlet Selector	40	POL.CONC	Concentration	Chemical Dosing

#	*Tag*	*Measurement Type*	*Measurement Location*	#	*Tag*	*Measurement Type*	*Measurement Location*
			North			(polymer)	
13	SSS.DCOS	COD soluble	Outlet Selector South	41	BOM.MES	TSS	Mixed Sludge
14	BA.MICRO	Microscopy	AST Tanks	42	BOM.BPBM	% primary sludge	Mixed Sludge
15	BA.N	Nitrogen Flow rate	AST Tanks	43	BOM.FE	Ferric sulphate flow rate	Mixed Sludge
16	BA.NDCO	Nitrogen/ tonne COD	AST Tanks	44	BOM.POLY	Polymer flow rate	Mixed Sludge
17	BA.NAOH	NaOH Flow rate	AST Tanks	45	BOM.PH	pH	Mixed Sludge
18	BA.P	Phosphorus Flow rate	AST Tanks	46	BPS.SICC	Sludge dryness	Sludge press
19	BAN.MES	TSS	North AST Tank	47	BPS.ICC	Sludge dryness	Sludge press/ silo
20	BAN.OXYG	Dissolved Oxygen	North AST Tank	48	EF.DCOT	COD total	Final Effluent
21	BA.TRHH	Hydraulic Retention Time	AST Tanks	49	EEF.DCOT	COD total	Final Effluent
22	BAS.MES	TSS	South AST Tank	50	EF.MES	TSS	Final Effluent
23	BAS.OXYG	Dissolved Oxygen	South AST Tank	51	EF.MESV	VSS	Final Effluent
24	SBA.PH	pH	AST Tanks Outlet	52	EF.PH	pH	Final Effluent

#	Tag	Measurement Type	Measurement Location	#	Tag	Measurement Type	Measurement Location
25	SBA.MES	TSS	AST Tanks Outlet	53	EF.NNH4	Ammonia-N	Final Effluent
26	SBA.MESV	VSS	AST Tanks Outlet	54	EF.OPO4	Ortho-Phosphate	Final Effluent
27	SBA.TSUO	TSUO	AST Tanks Outlet	55	EF.NNO3	Nitrate-N	Final Effluent
28	BA.TSUO	TSUO	AST Tanks				

3.2.2.1. Experiments: Detail & Protocols

The following is a discussion of the experiments that were regularly completed by mill personnel, for which results were entered into the Production Quality Database.

Chemical Oxygen Demand (COD)

The COD test protocol uses pre-prepared ampules of reagents supplied by HACH, each ampule contains chromic acid (K_2CrO_4), sulphuric acid (H_2SO_4), silver sulphate ($AgSO_4$), mercury sulphate ($HgSO_4$) and demineralised water. The test requires the preparation of a control ampule with distilled water only, and the wastewater samples separately, using distilled water to dilute if necessary. The ampules are heated to 150ºC for two hours, cooled and the absorbance of light through each ampule is measured using a spectrophotometer at 620 nm, using the control to zero the spectrophotometer. This method is generally referred to as the HACH method 435 (0 to 1500 ppm COD). It is similar to the Standard Method 5220(D) Closed Reflux, Colorimetric Method [2].

Soluble COD is considered by the mill to be the COD of the filtrate that passes through a Pall Type A/E glass fibre filter of porosity 1.0µm (considered elsewhere to be the filtered COD). The sample from the primary clarifier outlet is always filtered, the final effluent sample is sometimes filtered and sometime allowed to decant.

The testing campaign also measured the COD of the filtrate that passes through a Pall-Gelman Supor polyethersulfone membrane of porosity 0.1µm.

The bias of the test method is not reported. The precision of the test method is reported by HACH to be +/- 18 mg/L for the 0 to 1500 ppm COD range.

Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS): P50.801

For the TSS and VSS test protocols, a Pall Type A/E glass fibre filter of porosity 1.0µm is prepared by drying it to 105ºC during at least 2 hours, washing with distilled water a number of times and then further drying at 550ºC for 15 minutes.

The TSS test protocol requires the residue remaining on a Pall Type A/E glass fibre filter of porosity 1.0µm to be dried at 105ºC. The weight of the dried residue divided by the wastewater sample volume gives the TSS value in milligrams per litre (mg/L). This protocol corresponds to the Standard Method 2540(D) Total Suspended Solids Dried at 103 – 105ºC [2].

The residue from the TSS test is dried further at 550ºC for 15 to 20 minutes. The difference between this final residue weight and the weight measured after drying at 105ºC divided by the wastewater sample volume gives the VSS value. This protocol corresponds to the Standard Method 2540(E) Fixed and Volatile Solids Ignited at 550ºC [2].

The precision of the TSS test method is reported to be 33% at 15 mg/L, 10% at 242 mg/L and 0.76% at 1707 mg/L [2]. The bias of the TSS test method at one laboratory is reported to be 2.8 mg/L [2]. The precision of the VSS test is reported to be 6.47% at 170 mg/L [2]. The bias of the VSS test method is not reported.

Oxygen uptake rate (OUR & SOUR): P50.802

The OUR test protocol requires a wastewater (mixed liquor) sample is well aerated (usually to 7.5 mg/L). The dissolved oxygen (DO) concentration in the sample is then measured over time using an oxygen-sensitive YSI 5905 BOD probe electrode for a period of 10 minutes whilst the sample is agitated. The rate of oxygen consumption per hour is the OUR value; the average OUR is recorded. The OUR divided by the sample VSS is equal to the specific oxygen uptake rate, or SOUR. This protocol corresponds to Standard Methods 2710(B) Oxygen Consumption Rate/(1) Probe with an oxygen-sensitive electrode [2].

The precision of this test method has not been determined, and bias is not applicable [2].

Ammonia and nitrate nitrogen: P50.805

The ammonia-nitrogen test protocol uses an ammonia (NH_3) ion selective electrode (ISE) to test for the total ammonia (NH_3 plus NH_4^+). The addition of 2 mL ISA Ammonia pH adjusting solution, containing sodium hydroxide (NaOH) and methanol, to approximately 100 mL of the filtered wastewater sample raises the pH, ensuring all NH_4^+ ammonium ions are converted to ammonia NH_3. The reading of the ISE is taken at the lowest point that it reaches before starting to increase. A calibration curve generated by the laboratory is used to translate the ISE reading from the electrode into an ammonia-nitrogen (N-NH3) concentration. This protocol corresponds to Standard Method 4500-NH3(F) Ammonia Selective Electrode Method [2].

The nitrate in the wastewater sample is then reduced by the addition of titanium (III) chloride to ammonium ions, and once the ISE reading reaches a high value (200mV) excess sodium hydroxide (ISA) is added to covert the ammonium ions to ammonia, and the ISE measurement is recorded at the lowest point. The ISE is resaturated in an ammonium standard solution between each reading. This protocol corresponds to Standard Method 4500-NO3(G) Titanous Chloride Reduction Method [2].

The precision of the ammonia test method is reported to be between 2.2% and 3.8% at ammonia concentrations between 0.13 and 1.0 mg NH3-N/L [2]. The expected precision of the nitrate test method is reported to be 3.0% [2]. The bias of the test methods is not reported.

Ortho-phosphate

The ortho-phosphate test protocol uses the addition of ascorbic acid ($C_6H_8O_6$), potassium pyrosulphate ($K_2S_2O_7$) and sodium molybdate (Na_2MoO_4) to a filtered wastewater sample to produce the molybdenum blue coloured complex with ortho-phosphate. The light absorbance of the coloured complex and that of a wastewater blank are measured at a wavelength of 890 nm in a spectrophotometer. The wastewater blank and sample are sometimes diluted if necessary, since the range of the spectrophotometer is 0 to 0.90 mg PO_4-P/L. This method is generally referred to as the HACH method 496. It is similar to the Standard Method 4500-P(E) Ascorbic Acid Method [2]. No hydrolysis or digestion is performed prior to the ortho-phosphate test, which indicates that the phosphorus fraction measured in this test is dissolved reactive phosphorus.

The precision of the phosphate Standard Methods test method is reported to be between 4.0% and 9.1% over the ortho-phosphate concentration range 0.1 to 7.0 mg PO4-P/L [2]. The bias of the test method is reported to be between 4.4 and 10% for the same concentration range [2]. The precision of the test method is not reported by HACH.

Dissolved Oxygen

Dissolved oxygen is measured in the aerated basin and aerated selectors once per day using a luminescent type HACH dissolved oxygen probe (LDO). The luminescent dissolved oxygen unit operates based on oxygen quenching luminophores, or more specifically on the "dynamic fluorescence quenching of a luminophore (luminescent dye molecule) by oxygen" [2]. These instruments use a platinum based luminophore that is excited by blue light and emits red light; the duration of red-light emittance correlates to the concentration of dissolved oxygen. This method is reported to correspond to ASTM method D888-05 (ASTM Standards volumes 11.01 and 11.02).

The accuracy of the DO meters is reported by the supplier to be +/- 0.2% of the span, the span of the instrument is 0 to 20.0 mg/L, therefore the accuracy is +/- 0.04 mg/L or less. The repeatability of the DO meters is reported by the supplier to be +/-0.5% of the span, or +/-0.1mg/L.

Settling rate (SSV-30): P50.807

The settling rate protocol requires a wastewater (mixed liquor) sample from the outlet of the aerated basins is agitated and allowed to settle in a one-litre 'settlometer': a cylinder with marked volume graduations. The sample is allowed to settle for a duration of 30 minutes, at which time the level of the settled sludge is recorded. This protocol corresponds to Standard Method m Settled Sludge Volume (manual agitation) [2].

The precision of this test method has not been determined, and bias is not applicable [2].

Sludge Volume Index (SVI)

The SVI is calculated from the SSV-30 value and the TSS of the mixed liquor from the aerated basin, according to the following equation:

$$SVI = \frac{SSV_{30}}{TSS_{AERATION\_BASIN}}$$

This protocol corresponds to Standard Method 2710(D) Sludge Volume Index [2].

The precision of this test method is dependent on the precision of the constituent measurements, and bias is not applicable [2].

Sludge blanket height

The sludge blanket height in the secondary clarifiers is measured manually once per day by the operator using a Sludge Judge gauge, which consists of a transparent cylinder closed at one end by a check valve and float valve. The sludge blanket height is measured when the clarifier suction mechanism is approximately 90º to the walkway where the measurement is taken.

The precision and bias of this test method are not reported.

Sludge dryness - Press

The sludge dryness is measured for dried sludge using a sample of 12 to 15 grams taken from the back (outlet) of the sludge press, which is dried using a Sartorius dome MA30 moisture analyser for a duration of 60 minutes at 130 ºC.

The precision and bias of this test method are not reported.

Sludge dryness – Primary sludge, RAS, WAS, Mixed Liquor

The dryness of the primary sludge, RAS and WAS stream samples is measured using a sample of approximately 40 mL, which is dried using an OHAUS MB45 moisture analyser at 130 ºC, until the sample weight changes less than 0.001g per 30 seconds, typically for a duration of at least 60 minutes.

The Mixed liquor, RAS and WAS dryness are generally used by the plant operator to approximate the TSS value obtained by the laboratory. In this study the laboratory TSS values will be used and these three dryness parameters will not be considered further.

The precision and bias of this test method are not reported.

Polymer concentration: P50.809

The concentration of polymer is determined by evaporation of the water in a sample heated to 105ºC for a duration of 4 hours.

The precision and bias of this test method are not reported.

3.2.2.2. Measurement type

The following Table 32 describes the type of sample taken for each the test methods discussed above.

Table 32: Plant Production Quality test method measurement type

Test Method	*Measurement Type*
COD, TSS, VSS, OUR, SOUR, NH4, NO3, PO4, DO, SSV-30, SVI, sludge blanket height, sludge dryness, RAS dryness, WAS dryness, polymer concentration	Grab Composite: Final Effluent

3.2.3. External Laboratories

Papier White Birch engages accredited external laboratories to perform testing required to meet federal and provincial governmental regulations.

3.2.3.1. Experiments: Detail

The parameters measured by these laboratories are listed in Table 33, along with the provincial Quebec (MA) and federal Canadian (EPS) governmental test method. The precision and bias reported for each test method are listed in Table 34.

Table 33: External laboratory experiments

Measurement Type	*Gov. Method*	*Standard Method*	*Measurement Location*
BOD_5	MA.315-DBO 1.1	5210(B)	Final Effluent[1]
TSS	-	2540(D)	Final Effluent[1]
COD	-	5220(C)	Final Effluent
Oil & grease (C_{10}-C_{50})	MA.400-Hyd.1.0	5520	Final Effluent

Measurement Type	***Gov. Method***	***Standard Method***	***Measurement Location***
Fatty Acids & Resin Acids	MA. 414 -Aci-g-r 1.0	5560	Final Effluent
Trace Metals: Aluminium, Copper, Nickel, Lead, Zinc	MA.200-Met.1.0	3111(B) & (D)	Final Effluent
Microbiology characterisation	-	9000	Aerated Basin & Selectors
Toxicity[2]: Daphnia Rainbow trout	EPS 1/RM/14 EPS 1/RM/13	-	Final Effluent

1 – Previously but no longer measured at inlet to primary clarifier

2 – *Daphnia magna*, *Oncorhynchus mykiss*

It should be noted that the microbiological characterisation such as differentiation and counting follow a number of test methods that have been described in the literature [2, 56], however there is an element of subjectivity with respect to the labels 'dominant', 'common', 'rare' etc given to particular micro-organisms. This type of work requires some experience and expertise in the domain.

Table 34: External laboratories: test precision and bias reported

Measurement Type	***Detection Limit****	***Precision***		***Bias***	***Ref.***
		Reproducibility	***Repeatability***	***Relative error*****	
BOD_5	0.7 mg/L	6.25 % at 3.2 mg/L	2.24 % at 223 mg/L	11.4%	[221]

Measurement Type	***Detection Limit****	***Precision***		***Bias***	***Ref.***
		Reproducibility	***Repeatability***	***Relative error****	
TSS		33% at 15 mg/L 10% at 242 mg/L 0.76% at 1707 mg/L		2.8 mg/L (one lab)	[2]
COD		5.6% at 195 mg/L 4.8% at 208 mg/L		Not known	[2]
Oil & grease	0.1 mg/L	5.2% at 5 mg/L 8.1% at 16 mg/L	5.2% at 250 mg/L	0% at 5 mg/L	[222]
Fatty Acids & Resin Acids	15µg/L	Between 0 and 56% at 100 µg/L[1]	14% at 1.78 mg/L[2] 11% at 2.62 mg/L[3]	Between 1.6 and 76% at 100 µg/L[1]	[223]
Trace Metals Aluminium Copper Nickel Lead Zinc	4 µg/L 1 µg/L 0.5 µg/L 0.7 mg/L 2.9 µg/L	2.3% at 44 µg/L 2.6% at 151 µg/L 4.0% at 5 µg/L 1.4% at 13.9 µg/L 1.6% at 64 µg/L	7.9% at 630 µg/L 6.1% at 3.3 mg/L 7.4% at 2.7 mg/L 8.3% at 240 µg/L 6.5% at 930 µg/L	5.5% 6.4% 10% 2.1% 3.8%	[224]
Microbiology characterisation	Sample photographs provided, difficult to quantify precision or bias				[56]

Measurement Type	Detection Limit*	Precision		Bias	Ref.
		Reproducibility	Repeatability	Relative error**	
Toxicity: Daphnia Rainbow trout	Laboratory conducts tests against known concentrations of reference samples				[225-227]

*Quebec environmental test methods differentiate between detection and quantification limits; the detection limit is quoted here

**Quebec environmental test methods quote a relative error under ‘accuracy’

1 – Individual fatty acid and resin acids, **2** – Total fatty acids, **3** – Total resin acids

3.2.3.2. Measurement type

The following Table 35 describes the type of sample taken for each the test methods discussed above.

Table 35: External Laboratories test method measurement type

Test Method	*Measurement Type*
Microbiology characterisation	Grab
BOD_5, TSS, COD, Oil & grease, Trace metals, Toxicity, Fatty acids & resin acids	Composite (24 hour)

3.2.4. PI System

The Osisoft PI system is described as a Real-time Performance Management (RtPM) Platform between the Programmable Logic Controllers (PLCs), Distributed Control Systems (DCS), Laboratory Information Systems (LIMS), Supervisory Control and Data Acquisition systems (SCADA), and other IT systems on site. Table 36 lists the PI tag numbers for on-line measurements, the associated measurement location and type, which were used in this study.

Table 36: Effluent Treatment Plant PI Tags

	Tag #	Measurement Type	Measurement Location		Tag #	Measurement Type	Measurement Location
1	50FY6030.PNT	Flow rate	Mill drain[1]	27	50AI5241.PNT	TSS	Aerated Basin Outlet
2	50FI5720.PNT	Flow rate	Landfill leachate	28	50FIC5105.MEAS	RAS Flow rate	#1 Secondary Clarifier
3	50AIC6035.MEAS	pH	Mill drain	29	50FIC5106.MEAS	RAS Flow rate	#2 Secondary Clarifier
4	50FI5006.PNT	Flow rate	Primary Inlet	30	50FIC5101.MEAS	WAS Flow rate	#1 Secondary Clarifier
5	50TI5003.PNT	Temperature	Primary Inlet	31	50FIC5100.MEAS	WAS Flow rate	#2 Secondary Clarifier
6	50AI5001.PNT	pH	Primary Inlet	32	50FI5420.MEAS	Flow rate	Nitrogen Addition to RAS
7	50AI5002.PNT	Conductivity	Primary Inlet	33	50FFIC5470.MEAS	Flow rate	Phosphorus Addition to RAS
8	50AI4037.PNT	TSS	Primary Inlet	34	50FI5440.PNT	Flow rate	NaOH Addn to Primary Accepts
9	50TI5075.PNT	Temperature	Primary Accepts	35	50FFY5447.OUT	Flow rate	NaOH Addition to sludge
10	50AIC5053.MEAS	COD	Primary Accepts	36	50FI6036.PNT	Flow rate	NaOH Addition to

	Tag #	Measurement Type	Measurement Location		Tag #	Measurement Type	Measurement Location
							Mill Drain
11	50AI5060.PNT	TSS	Primary Accepts	37	50LI5425.PNT	Level	Nitrogen Tank (216)
12	50AI5054.PNT	Conductivity	Primary Accepts Pit	38	50LI5405.PNT	Level	Nitrogen Tank (220)
13	50FIC4150.MEAS	Flow rate	Primary Sludge	39	50LI5445.PNT	Level	NaOH Tank
14	50LI5005.PNT	Level	Emergency Basin	40	50LI5480.PNT	Level	Phosphorus Tank
15	50TI5068.PNT	Temperature	South AST Selector	41	50FFIC5210.MEAS	Flow rate	Polymer to sludge
16	50AI5066.PNT	pH	South AST Selector	42	50TI5426.PNT	Temperature	Urea
17	50AIC5067.MEAS	Dissolved Oxygen	South AST Selector	43	50FY5400D.PNT	Ratio (Calc)	Ratio Phosphorus-COD
18	50TI5071.PNT	Temperature	North AST Selector	44	50FY5420D.PNT	Ratio (Calc)	Ratio Nitrogen-COD
19	50AI5069.PNT	pH	North AST Selector	45	50LI5230.PNT	Level	Mixed Sludge Tank
20	50AIC5070.MEAS	Dissolved Oxygen	North AST Selector	46	50FIC5235.MEAS	Flow rate	Mixed Sludge Tank
21	50TI5074.PNT	Temperature	North AST Tank	47	50LI5335.PNT	Level	Sludge Silo
22	50AI5072.PNT	pH	North AST Tank	48	50FI4040.PNT	Flow rate	Final Effluent

	Tag #	Measurement Type	Measurement Location		Tag #	Measurement Type	Measurement Location
23	50AIC5073.MEAS	Dissolved Oxygen	North AST Tank	49	50TI4060.PNT	Temperature	Final Effluent
24	50TI5065.PNT	Temperature	South AST Tank	50	50AI4050.PNT	pH	Final Effluent
25	50AI5063.PNT	pH	South AST Tank	51	50AI4045.PNT	Conductivity	Final Effluent
26	50AIC5064.MEAS	Dissolved Oxygen	South AST Tank	52	50AI4038.PNT	TSS	Final Effluent

1 – Mill drain specified ‘Corridor THR’, très haute rendement (high yield sulphite), former pulping process

3.2.4.1. On-line Instrumentation: Detail

The following is a discussion of the on-line testing equipment for which results are recorded into the PI system.

Flow rate

Flow rates are measured on-line in the effluent treatment plant in the locations and using the instruments indicated in Table 37.

Table 37: Flow meters location, type, size & supplier

	Location	*Type*	*Diameter*	*Make*
1	Mill drain	Parshall Flume[1]	-	-
2	Landfill leachate to treatment	Magnetic	300 mm	ABB
4	Inlet Primary Clarifier	Magnetic	500 mm	ABB-1430
13	Primary Sludge	Magnetic	150 mm	ABB-3111
28-29	RAS from #1 and #2 Sdry Clrfs	Magnetic	300 mm	ABB-1430
30-31	WAS from #1 and #2 Sdry Clrfs	Magnetic	100 mm	ABB-3111
32	Nitrogen Addition to RAS	Mass	25 mm	Micro motion[2]
33	Phosphorus Addition to RAS	Mass	25 mm	Micro motion[2]
34	NaOH Addn to Prm Clr Apt	Magnetic	6 mm	ABB-1472
35	NaOH Addition to sludge	Dosing Pump[3]	-	Neptune-EC5004

	Location	***Type***	***Diameter***	***Make***
36	NaOH Addition to Mill Drain	Magnetic	6 mm	ABB-1419
41	Polymer Addition to sludge	Magnetic	25 mm	ABB-3111
46	Mixed sludge to press	Magnetic	200 mm	ABB-3111
48	Final Effluent	Parshall Flume[4]	610 mm	E&H- FHB20

1 – Bubble pipe in Parshall Flume constructed circa 1930

2 - Model CMF025H520NC 'Elite'

3 - Electronic stroke controller-positioner

4 - Level meter in Parshall Flume, E&H: Endress & Hauser

The Primary Clarifier Inlet flow meter is volumetrically validated by external consultants once per year. The total difference between the change in volume in the primary clarifier and the inlet flow meter was 9.6% in 2006. This methodology does not take into account the volume occupied by the centre well structure.

The Final Effluent Parshall Flume is validated by operators on a daily basis, as well as once per year by external consultants using a propeller-type current meter and a bubbler level meter. The difference between the theoretical volume of water in the Parshall Flume and test meter in the 2006 test was 2.0%, the difference between the level meter and test meter was 3.2%.

The mill drain Parshall Flume is no longer validated, and has not been at least since the TMP plant started operating in July, 2000.

The accuracy of the ABB magnetic flow meters is reported by the supplier to be 1% of the flow rate at best, and less accurate at a flow rate less than 10% of the full scale calibration. The accuracy of the Micromotion mass flow meters is reported by the supplier to be 0.1% of the flow plus or minus a function of the meter's zero stability (approximately 0.15% for a mass flow rate of 0.3 kg/min), the repeatability is reported to be 0.05% of the flow plus or minus a function of the meter's zero stability. The positioning accuracy of the Neptune stroke positioner is reported by the supplier to be 1.5%.

pH

pH is measured on-line in the effluent treatment plant in the locations and using the instruments indicated in Table 38. The ISE type probe is a site standard and incorporates automatic temperature compensation.

Table 38: pH meter location, type & supplier

	Location	*Type*	*Make*
3	Mill drain	ISE	Rosemount-396R
6	Inlet Primary Clarifier	ISE	Rosemount-396R
16-19	Aeration Selector (south & north)	ISE	Rosemount-396R
22-25	Aeration Basin (south & north)	ISE	Rosemount-396R
50	Final Effluent (2 off)	ISE	Rosemount-396R

The instrument is reported by the supplier to have 97% linearity over the pH range 2 to 12. The instrument is calibrated using a two-point calibration at pH 4.0 and 10.0.

Temperature

Temperature is measured on-line in the effluent treatment plant in the locations and using the instruments indicated in Table 39. The spring-loaded platinum RTD is a site standard.

Table 39: Thermometer location, type & supplier

	Location	*Type*	*Make*
5	Primary Clarifier Inlet	RTD	Rosemount
9	Primary Clarifier Accepts	RTD	Rosemount
15-18	Aeration Selector (south & north)	RTD	Rosemount
21-24	Aeration Basin (south & north)	RTD	Rosemount
42	Urea	RTD	Rosemount
49	Final Effluent	RTD	Rosemount

The repeatability of the thermometers is reported by the supplier to be +/-0.05% or 0.13ºC. The accuracy of the thermometers is reported by the supplier to be between +/-0.30ºC and +/-0.80ºC over the temperature range 0ºC to 100ºC.

Dissolved Oxygen

Dissolved oxygen is measured on-line in the effluent treatment plant in the locations and using the instruments indicated in Table 40.

Table 40: Dissolved Oxygen meter location, type & supplier

	Location	*Type*	*Make*
20	North AST Selector (repeated South)	Luminescent	HACH

	Location	*Type*	*Make*
26	South AST Tank (repeated North)	Luminescent	HACH

The basis of measurement for the LDO probes is described in section 0.

The accuracy of the DO meters is reported by the supplier to be +/- 0.2% of the span, the span of the instrument is 0 to 20.0 mg/L, therefore the accuracy is +/- 0.04 mg/L or less. The repeatability of the DO meters is reported by the supplier to be +/-0.5% of the span, or +/-0.1mg/L.

Conductivity

Conductivity is measured on-line in the effluent treatment plant in the locations and using the instruments indicated in Table 41.

Table 41: Conductivity meter location, type & supplier

	Location	*Type*	*Make*
7	Primary Inlet	AC-Resistivity	Rosemount-228
12	Primary Accepts Pit	AC-Resistivity	Rosemount-228
51	Final Effluent	AC-Resistivity	Rosemount-228

The accuracy of the conductivity meters is reported by the supplier to be +/- 0.5% of full scale at 25ºC, or +/-10mS. The repeatability of the conductivity meters is reported by the supplier to be +/-0.25% of full scale, or +/-5mS.

Level

Level is measured on-line in the effluent treatment plant in the locations and using the instruments indicated in Table 42.

Table 42: Level meter location, type & supplier

	Location	*Type*	*Make*
14	Emergency Basin	Ultrasonic	Milltronics (Siemens)
37	Urea Tank (216)	Differential Pressure	Rosemount-1151
38	Urea Tank (220)	Differential Pressure	Rosemount-1151
39	Caustic (NaOH) Tank	Differential Pressure	Rosemount-1151
40	Phosphorus Tank	Differential Pressure	Rosemount-1151
45	Mixed Sludge Tank	Ultrasonic	Milltronics (Siemens)
47	Sludge Silo	Guided wave radar	Endress & Hauser-RMP332

The accuracy of the Rosemont DP cell level meters is reported by the supplier to be +/- 0.075% of the upper range limit, or +/- 15 mm over the calibrated span. The error associated with changes in temperature for these units is reported by the supplier to be +/- 56 mm per 56ºC change. The accuracy of the Milltronics ultrasonic meter is reported by the supplier to be +/-0.25% of the full scale, or +/-25 mm. The accuracy of the Endress & Hauser guided wave radar is reported by the supplier to be +/- 1% of the full scale. The repeatability of this unit is reported by the supplier to be +/- 0.2% full scale.

TSS

Total Suspended Solids are measured on-line in the effluent treatment plant in the locations and using the instruments indicated in Table 43.

Table 43: TSS meter location, type & supplier

	Location	*Type*	*Make*
8	Primary Clarifier Inlet	Backlight scattering	HACH
11	Primary Clarifier Outlet	Backlight scattering	HACH
27	Outlet Aerated Basins	Backlight scattering	HACH
52	Final Effluent	Backlight scattering	HACH

The Solitax sc unit operates based on dual beam infrared scattered light absorption detection at 90º to the transmitted light source (turbidity) and a backscatter photoreceptor at 140º to the light source (suspended solids) [228].

The accuracy of the TSS meters is reported by the supplier to be less than 5% of the reading for suspended solids. The repeatability of the meters is reported by the supplier to be less than 3% of the reading. The meter detection limit is 1 mg/L suspended solids and the range of the meter is from 1 mg/L to 50,000 mg/L [228].

COD

Chemical Oxygen Demand is measured on-line in the effluent treatment plant in the locations and using the instruments indicated in Table 44.

Table 44: COD meter location, type & supplier

	Location	*Type*	*Make*
10	Primary Clarifier Inlet	UV Absorbance	HACH

The UVAS Plus (2 mm) unit operates based on the absorbance of ultraviolet light at 254 nm, using dual beam technology over a 2mm path length, according to DIN 38404 C3. The unit compensates for suspended solids content at a wavelength of 550 nm. The instrument has been calibrated over the range 0 to 1500 m^{-1}, which corresponds to measure filtered chemical oxygen demand (fCOD) in the range of 0 to 2944 mg/L according to the site-specific correlation developed at the mill.

The precision and accuracy of the instrument are reported by the supplier to be 3% + 0.5 m^{-1}, the repeatability of the instrument is reported to be 2% + $0.5m^{-1}$. The Pearson's R^2 value for the site-specific correlation developed at the mill is 0.69.

Ratio (Calculated)

The ratio of nutrient addition to COD in the primary clarifier accepts is calculated on-line in the effluent treatment plant using the instruments indicated in Table 45.

Table 45: Nutrient: COD ratios & calculation

	Ratio Type	*Calculation*
43	Phosphorus-COD	Phosphoric acid addition [L/min] x 0.3938/ COD
44	Nitrogen-COD	Urea addition [L/min] x 0.266 / COD

The ratios are based on the COD measured with the aforementioned UVAS Plus on-line COD meter. The calculations are listed below, the origins of which are the specific gravity and concentration certified by the suppliers; the concentration is certified as phosphorus pentoxide and as nitrogen respectively for each of the chemicals.

Calculation 1: Phosphoric Acid

$$
\begin{aligned}
& Flowrate\_P[kg\_P/\min] \\
& = Phosphoric\ \_acid_{ADDED}[L\_H_3PO_4/\min] \\
& \times density[kg/L] \\
& \times concentrat\ ion[\%w/w] \\
& \times molar\_weight\_ratio[kg\_P/kg\_H_3PO_4] \\
& = L\_H_3PO_4/\min \times 1.660 kg/L \times 75\% w/w \times 31/98 \\
& = L\_H_3PO_4/\min \times 0.3938
\end{aligned}
$$

Calculation 2: Urea

$$
\begin{aligned}
& Flowrate\_N[kg\_N/\min] \\
& = Urea_{ADDED}[L\_(NH_2)_2CO/\min] \\
& \times density[kg/m^3] \\
& \times concentrat\ ion[\%w/w] \\
& \times molar\_weight\_ratio[kg\_N/kg\_(NH_2)_2CO] \\
& = L\_N/\min \times 1.14 kg/L \times 50\% w/w \times 28/60 \\
& = L\_(NH_2)_2CO/\min \times 0.266
\end{aligned}
$$

3.2.4.2. *Measurement type*

The following Table 46 describes the type of sample taken for each the test methods discussed above.

Table 46: PI system test method measurement type

Test Method	*Measurement Type*
Flow, DO, pH, temperature, conductivity, level	On-line, in-situ, real-time
TSS, COD	In-line, real-time

3.2.5. Wastewater Characterisation (Analytical Procedures)

In addition to the data collection described above, a wastewater characterisation was carried out in accordance with the methodology presented by Roeleveld and Van Loosdrecht [1], as well as nutrient fraction measurements. This entailed additional experimental testing, as described herein.

3.2.5.1. *Site laboratory experiments*

COD, sCOD (filtered)

Unfiltered samples were collected from the inlet and outlet of the primary clarifier, the outlet of the aeration basins, the final effluent, the RAS and the WAS streams. The COD protocol HACH #435 was carried out on the unfiltered samples with suitable dilution of the sample to render it in the range of 0 to 1500 mg/L COD.

Samples were also filtered using a Pall-Gelman Supor hydrophilic polytheresulfone membrane of porosity 0.1µm (part no. 60310). Filtered samples were then tested according to the HACH #435 protocol.

The bias of the test method is not reported. The precision of the test method is reported by HACH to be +/- 18 mg/L for the 0 to 1500 ppm COD range.

TSS, VSS

Unfiltered samples were collected from the inlet and outlet of the primary clarifier, the outlet of the aeration basins, the final effluent, the RAS and the WAS streams. The Standard Methods 2540(D) and 2540(E) were applied to the unfiltered samples [2].

The precision of the TSS test method is reported to be 33% at 15 mg/L, 10% at 242 mg/L and 0.76% at 1707 mg/L [2]. The bias of the TSS test method at one laboratory is reported to be 2.8 mg/L [2]. The precision of the VSS test is reported to be 6.47% at 170 mg/L [2]. The bias of the VSS test method is not reported.

The limit of detection of solids using this gravimetric methodology has been reported as 3 mg/L, and the limit of quantification as 11 mg/L, if a sample of 200 mL is used [229].

3.2.5.2. External laboratory experiments

The following experiments were performed by the technicians Denis Bouchard and Francisc Ardelean in the Environmental Laboratory of the Civil, Geological and Mining Engineering Department of the Polytechnique, Montreal.

Continuous $BOD_{1\text{-}28}$

Unfiltered samples were collected from the inlet and outlet of the primary clarifier, the outlet of the aeration basins, the final effluent, the RAS and the WAS streams. Nitrification inhibitory agent 2-chloro-6-(trichloromethyl)pyridine (TCMP), also known as HACH formula 2533, was added at the moment of preparation for analysis (not time of sampling), as were nutrients. Analysis was carried out using the 'BODTrak' instrument. This protocol corresponds to the Standard Method 5210 Biochemical Oxygen Demand (D) continuous oxygen uptake [2].

The BOD of the seed was also measured however no nitrification inhibitory agent was added to the seed since the seed used (HACH PN#2471200) contains no nitrifying bacteria.

The precision of this test method is reported to be 5% for a BOD concentration of 50 to 100 mg/L and 3% for "more concentrated samples" [2]. The bias of this test method cannot be determined [2].

Nutrient digestions: TKN, TP

Unfiltered samples were digested according to Standard Methods 4500-Norg (B) Macro-Kjeldahl Method [2] slightly modified in accordance with the US EPA method 365.4.

The recovery of the Macro-Kjeldahl test method is reported to be between 84.3% and 113% over the organic nitrogen concentration range 0.5 to 20 mg N_{org}-N/L [2]. The precision of the test method is reported to be between 0 and 41.7% for the same concentration range [2].

Soluble nutrients: NO3, NH4, PO4

Samples were filtered using a Pall-Gelman Supor hydrophilic polytheresulfone membrane of porosity 0.1µm (part no. 60310). Filtered samples were then tested according to the Standard Methods 4500-NH3(H) Flow injection analysis, 4500-NO3(F) Automated cadmium reduction method and 4500-P(F) Automated ascorbic acid reduction method.

The recovery of the ammonia test method is reported to be between 88% and 125% at ammonia concentrations between 0 and 0.8 mg NH3-N/L [2]. The precision of this test method is reported to be between 0 and 1.9% for the same concentration range [2].

The precision of the nitrate test method is reported to be between 4.1% and 26.3% at nitrate concentrations between 0.029 and 2.48 mg $NO3^-$-N/L [2]. The bias of this test method is reported to be between 2.69 and 18.1% for the same concentration range [2].

The precision of the phosphate test method is reported to be 4.4% at an average ortho-phosphate concentration of 0.340 mg PO4-P/L [2]. The bias of the test method is reported to be between 6.2% for the same concentration [2].

Quality control

Samples were filtered on-site for the nitrate, ammonia and ortho-phosphate tests. Samples were sent to the Polytechnique laboratory in an insulated container with ice packs. Due to this packaging method, and the fact that the samples were processed within 24 hours, it is considered reasonable to assume that the sample results are representative of the nutrient and BOD concentrations present in the mill process. Any delay between sampling and analysis introduces the possibility of a gross error in experiment results.

The following experiments were performed in collaboration with technician Sébastian Houle in the Environmental Laboratory of the Civil, Geological and Mining Engineering Department of the Polytechnique, Montreal.

3.2.5.3. On-line instrumentation

The following instrumentation was installed in collaboration with John Meunier Inc, Montreal.

Ammonia

The Amtax SC HACH instrument was installed, sampling from the final effluent of the wastewater treatment plant. The unit admits one sample filtered to 0.15µm every 5 minutes, adjusts the pH to convert all ammonium ions (NH_4^+) to gaseous ammonia (NH_3) and measures the concentration of gaseous ammonia using a gas-sensitive electrode (ammonia-specific). The membrane on the electrode allows only the NH_3 gas molecule to pass through, and the change in colour of the indicator reagent is correlated to a change in pH. The change in colour measured is periodically calibrated to known standards of ammonia (standard concentrations of 1 mg N/L and 10 mg N/L).

This method is similar to Standard Method 4500-NH3(F) Ammonia-Selective Electrode Method in application of the potentiometric principle, although it applies an additional step for the conversion of ammonium ions to ammonia gas and uses a colorimetric measurement instead of direct pH measurement. The supplier reports that there is no transformation of any nitrite or nitrate in the sample, nor do they interfere with the measurement of ammonia; amines, mercury and silver could interfere. The unit incorporates automatic calibration and cleaning cycles.

The precision of the test method is reported by the supplier to be 2% or +/- 0.05 mg NH4-N/L. The accuracy of the test method is reported by the supplier to be 3% or +/- 0.05 mg NH4-N /L. The range of measurement is 0.05 to 20 mg NH4-N/L, and the limit of detection of the instrument is 0.05 mg NH4-N/L.

Phosphate (Dissolved, Reactive)

The Phosphax SC HACH instrument was installed, sampling from the final effluent of the wastewater treatment plant. The unit admits one sample filtered to 0.15µm every 5 minutes, vanadate-molybdate is added to form vanadomolybdophosphoric acid with any ortho-phosphate present, a yellow compound of which the light absorbance is measured via colorimetry. The supplier reports that interference with the measurement of ortho-phosphate is possible from fluoride, thorium, bismuth, thiosulphate, thiocyanate or sulphide. This method corresponds to Standard Method 4500-P(C) Vanadomolybdophosphoric Acid Colorimetric Method. The unit incorporates an automatic cleaning cycle.

The precision of the test method is reported by the supplier to be 2% or +/- 0.05 mg PO4-P/L. The accuracy of the test method is reported by the supplier to be 2% or +/- 0.05 mg PO4-P/L. The range of measurement is 0.05 to 15 mg PO4-P/L, and the limit of detection of the instrument is 0.05 mg PO4-P/L.

3.3. Data Preparation

The following methodology was applied to the raw data for the purpose of data description and steady state detection. It should be noted that the purpose of this project is to model the steady state operation of the wastewater treatment plant, and this has a direct influence on the methodology implemented in this case: an alternative methodology would be applied in the case of dynamic modelling. The methodology is developed for steady state detection using continuously recorded data, such as that recorded on-line in the PI system. Discrete data, such as grab samples and laboratory tests on composite samples will be prepared to describe steady states once they have been detected. In all cases, the term 'steady state' is used to describe a time period at which the plant is operating in a stable fashion; the term 'stable operation' could equally be used.

3.3.1. Continuously Measured Data Preparation & Steady State Detection

The description 'continuously measured' can be applied to data that represents the measurements taken by instruments located in-line or in-situ, and often represents data that is recorded in real-time on-line, as defined in Table 30 previously. These are the definitions that will be used from here on.

Although a number of methods to detect steady state have been published [230], the time constants of the wastewater treatment plant are much longer than the processes considered in the literature, and the published methods are generally inappropriate for the wastewater process for this reason. In wastewater literature, Barker and Dold recommend that three to four sludge ages be used as the time period for steady state attainment [231], however this does not appear to be practical for the case study. As discussed in section 3.3.1.1, the hydraulic and solids retention times for this process are in the order of hours, the influent flow rate to the plant can change in the order of minutes and the organic load seen in the aeration basin can change in the order of hours.

In practice, the flow rates and organic load from the mill varies such that it is appropriate to set limits for key measured parameters in order to detect near steady state conditions. The choice of key parameters is explored below.

3.3.1.1. Process Time Characteristics

It is important to note that the time constants that characterise the flow and solids retention in the wastewater treatment system are considerably longer than those of many other processes, for example pulp and paper processes such as pulp refining. The following time characteristics can be evaluated using daily average data in order to determine the order of magnitude of the constants.

Hydraulic Retention Time (HRT) = $\frac{V_{BASIN}}{Q_{INFLUENT}}$

Mean Cell Residence Time (MCRT) =
Solids Retention Time (SRT)
Sludge Age

$$\frac{V_{AERATION\ BASIN} \cdot X_{AERATION\ BASIN}}{Q_{EFFLUENT} \cdot X_{EFFLUENT} + Q_{WAS} \cdot X_{WAS}}$$

Where Q represents volumetric flow rate, X represent volatile suspended solids concentration and V represents tank volume, assuming an ideal continuously-stirred tank reactor (CSTR).

A clarifier theoretically acts hydraulically like a series of continuously mixed reactors (tanks-in-series), as discuss in the literature review. The HRT can be calculated using the entire clarifier volume, which is called the theoretical or ideal HRT and assumes one completely mixed reactor. For a primary clarifier in a municipal wastewater treatment plant, this is typically from 1 to 3 hours [45]. This retention time applies to the dissolved, dispersed or suspended organic load, solids and nutrient concentrations that do not settle but flow to the effluent of the clarifiers. The basins operate via gravity overflow, which results in a near-instantaneous conveyance of flow through the basin network.

Table 47 below presents the process time constants for this case study. The HRT for the aerated selector and basins take into account the RAS flow, the calculated HRT without the RAS flow is shown in brackets for the selector. The theoretical HRT for the clarifiers is included in this table, based on the full clarifier volume and one completely mixed reactor. The HRT for each process unit was not quantified using a tracer test.

Table 47: Wastewater process time characteristics (2006 flow data)

Time Characteristic	***Basin***	***Typical Range (PML)***
HRT	Primary Clarifier	8 - 9 hours
HRT	AST Selector	50 – 65 minutes [90 – 110 min]
HRT	Aerated Basins	15 – 18 hours
HRT	Secondary Clarifier	5 - 6 hours
MCRT	Aerated Basin	5 – 9 days

3.3.1.2. Choice of key parameters

Using the information previously specified for the precision and bias of each instrument, a qualitative judgement of each instrument was constructed for the purpose of choosing the most appropriate measurement from each group of measurements to use in the steady state detection exercise. For example, out of all of the flow meters, it is preferable to use the flow meter that has the highest precision and lowest bias, which would be the final effluent flow meter.

Table 48: Qualitative evaluation of instrumentation for choice of key parameters

#	*Type*	*Location*	*Accuracy*	*Verification*	*Score*
1	FE	Mill drain	L	0	0
2	FE	Landfill leachate to treatment	H	L	2
4	FE	Inlet Primary Clarifier	H	H	7
13	FE	Primary Sludge	H	M	5
28-29	FE	RAS from #1 and #2 Sdry Clrfs	H	M	5
30-31	FE	WAS from #1 and #2 Sdry Clrfs	H	M	5
32	FE	Nitrogen Addition to RAS	H	M	5
33	FE	Phosphorus Addition to RAS	H	M	5
34	FE	NaOH Addn to Prm Clr Apt	H	M	5
35	FE	NaOH Addition to sludge	H	L	2

#	Type	Location	Accuracy	Verification	Score
36	FE	NaOH Addition to Mill Drain	H	L	2
41	FE	Polymer Addition to sludge	H	M	5
46	FE	Mixed sludge to press	H	M	5
48	FE	Final Effluent	H	VH	10
3	pH	Mill drain	H	H	7
6	pH	Inlet Primary Clarifier	H	H	7
16-19	pH	Aeration Selector (S & N)	H	H	7
22-25	pH	Aeration Basin (S & N)	H	H	7
50	pH	Final Effluent (2 off)	H	H	7
5	TE	Primary Clarifier Inlet	H	H	7
9	TE	Primary Clarifier Accepts	H	H	7
15-18	TE	Aeration Selector (S & N)	H	H	7
21-24	TE	Aeration Basin (S & N)	H	H	7
42	TE	Urea	H	H	7
49	TE	Final Effluent	H	H	7
20	DO	North AST Selector	H	H	7
26	DO	South AST Tank	H	H	7

#	Type	Location	Accuracy	Verification	Score
7	CD	Primary Inlet	H	H	7
12	CD	Primary Accepts Pit	H	H	7
51	CD	Final Effluent	H	H	7
14	LE	Emergency Basin	M	M	5
37	LE	Urea Tank (216)	H	M	7
38	LE	Urea Tank (220)	H	M	7
39	LE	Caustic (NaOH) Tank	H	M	7
40	LE	Phosphorus Tank	H	M	7
45	LE	Mixed Sludge Tank	M	M	5
47	LE	Sludge Silo	M	M	5
8	TSS	Primary Clarifier Inlet	M	M	5
11	TSS	Primary Clarifier Outlet	M	M	5
27	TSS	Outlet Aerated Basins	M	M	5
52	TSS	Final Effluent	M	M	5
10	COD	Primary Clarifier Inlet	M	M	5

For many of these instrument types, there is little difference between the accuracy and verification at different instrument locations. It is clear however that it would be preferable to use the information from the final effluent flow meter than other flow meters. Due to the lack of differentiation between the other types of instruments, it is considered reasonable to use the instrument closes to the inlet of the aeration basin, and those in the aeration basin itself where available, since the aerated selector and basin are the main reactors in the process and therefore of the most interest for further modelling work.

The key parameters chosen and their typical values are presented in Table 49.

Table 49: Steady State Detection Key Parameters

Key Parameter	*Location*	*Typical Value*
Flow rate	Final Effluent	25,000 L/min
Temperature	Aerated Basin Selector Inlet	36ºC
TSS	Aerated Basin Selector Inlet	1,000 mg/L
COD	Aerated Basin Selector Inlet	1,500 m^{-1}
DO	AST Basin	2.0 mg/L
pH	AST Basin	6.3
Flow rate	RAS 1 & 2	7,000 L/min
Chemical Addition Rate	Nitrogen	2.0 L/min
Chemical Addition Rate	Phosphorus	0.3 L/min

3.3.1.3. Time period for average data

The aim of this step is to determine if it is reasonable to use data averaged over a time period greater than the smallest time period over which data is recorded, which would reduce computing time required for steady state detection. For this purpose, it is considered reasonable to use a rolling or running average to represent each set of data. Applying this type of average is useful to exclude the effects of the short-term variability of the instrument reading whilst retaining the true process information, especially since the purpose of its application does not include analysis of the system dynamics.

The decision criterion for establishing the correct time period for the rolling average for each key parameter is based on comparing the standard deviation for different time periods over a particular data set. The data set chosen for this purpose was the week-long period between midnight 9 February and midnight 13 February, 2007. This data set was chosen for the following reasons: it does not include any mill shuts, and it is long enough that a rolling average time period in the order of multiple hours can be evaluated. For each instrument, the running average was inspected for the time periods 10 minutes, 30 minutes, 1 hour, 2 hours and 4 hours. A summary of the average standard deviation for each key parameter over these time periods can be found below in Table 50.

Table 50: Standard Deviation of Rolling Averages, multiple time periods, 9 February to 13 February 2007

Key Parameter		***Standard deviation***				
	Units	***10 min***	***30 min***	***1 hour***	***2 hours***	***4 hours***
Flow rate – Final Effluent	L/min	11.1	12.5	12.9	13.2	13.4
Temperature	ºC	0.0051	0.0068	0.0077	0.0084	0.0091
TSS	mg/L	2.8	3.2	3.6	4.2	5
COD	m^{-1}	0.7	1.1	1.4	1.9	2.5
DO	mg/L	0.0073	0.0077	0.0080	0.0082	0.0085

Key Parameter		Standard deviation				
	Units	10 min	30 min	1 hour	2 hours	4 hours
pH	-	1.00E-05	1.70E-05	2.40E-05	3.50E-05	4.90E-05
Flow rate – RAS 1	L/min	6.45	6.63	6.68	6.71	6.75
RAS 2		6.00	6.24	6.32	6.36	6.39
Nitrogen Addition Rate	L/min	0.00441	0.00460	0.00469	0.00477	0.00483
Phosphorus Addition Rate	L/min	1.10E-05	1.90E-05	2.70E-05	3.80E-05	5.40E-05

The results displayed in Table 50 demonstrate that the standard deviation increases with increasing time period, as would be expected. However the increase is not significant given the typical values in Table 49, as demonstrated by expressing the standard deviations from Table 50 as a percentage of the average for the same period as presented below in Table 51.

Table 51: Standard Deviation as a percentage of Rolling Averages, multiple time periods, 9 February to 13 February 2007

Key Parameter		Standard deviation (% of average)				
	Units	10 min	30 min	1 hour	2 hours	4 hours
Flow rate – Final Effluent	L/min	0.0625	0.0704	0.0726	0.0743	0.0754
Temperature	ºC	0.0142	0.0189	0.0214	0.0233	0.0253
TSS	mg/L	0.280	0.320	0.360	0.420	0.500

Key Parameter		***Standard deviation (% of average)***				
	Units	***10 min***	***30 min***	***1 hour***	***2 hours***	***4 hours***
COD	m^{-1}	0.0467	0.0733	0.0933	0.127	0.167
DO	mg/L	0.365	0.385	0.400	0.410	0.425
pH	-	1.59E-04	2.70E-04	3.81E-04	5.56E-04	7.78E-04
Flow rate – RAS 1	L/min	0.0921	0.0947	0.0954	0.0959	0.0964
RAS2	L/min	0.0857	0.0891	0.0903	0.0909	0.0913
Nitrogen Addition Rate	L/min	0.221	0.230	0.235	0.239	0.242
Phosphorus Addition Rate	L/min	1.00E-05	1.73E-05	2.45E-05	3.45E-05	4.91E-05

Based on the results in Table 50 and Table 51 above, it is evident that there is very little change in two process parameters: pH and the phosphorus addition rate. These two parameters are so stable that they cannot be used to determine steady state; the remaining seven key parameters will be used.

On visual inspection of plotted data, the difference between the time periods of the rolling averages is apparent. Taking the example of a 12 hour period on 9 February 2007 for the final effluent flow rate, Figure 16 presents the rolling averages for multiple time periods. It is clear that process information is lost for the time period of 4 hours, and even for 2 hours. The original process data is smoothed to such an extent that the flow rate peak occurring at approximately 3pm presents as a much smaller peak for the 2 hour time period and is smoothed even further for the 4 hour time period, which delays the peak until approximately 4pm. In contrast, the 10 minute time period retains almost all detail of the data, and the 30 minute time period retains a great deal of the detail. It is considered that the 1 hour time period represents a reasonable compromise between the need exclude the effects of the short-term variability of the instrument reading whilst retaining enough detail to represent the true process information. The rolling average for the final effluent flow rate using a 1 hour time period is shown in Figure 17 below.

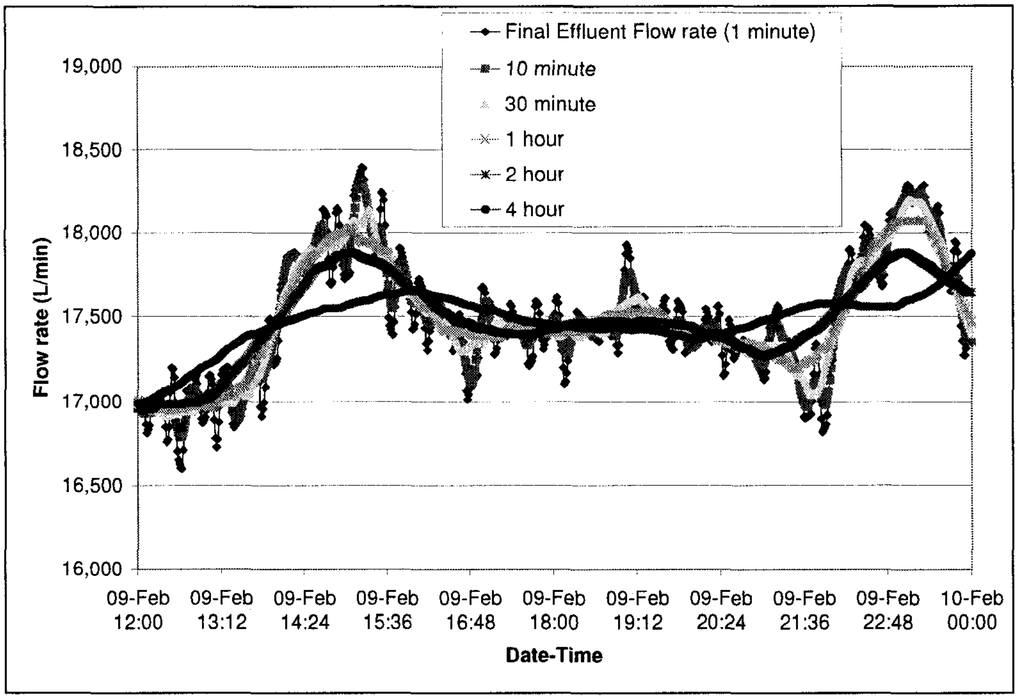

Figure 16: Final Effluent Flow rate rolling averages, multiple time periods, 12 hour duration 9 February 2007

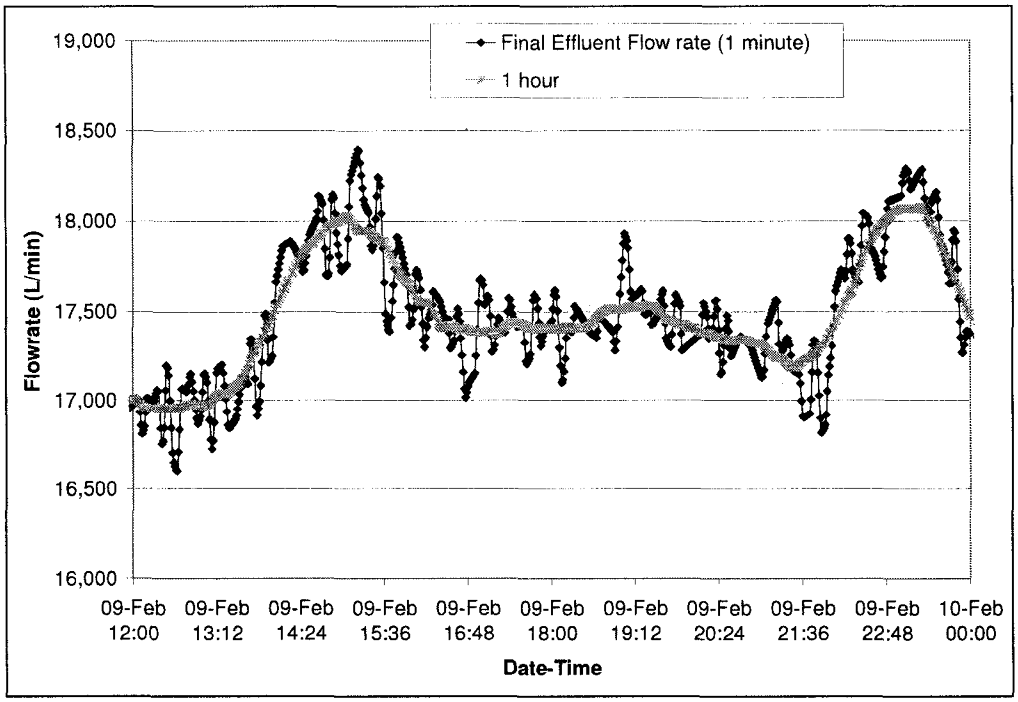

Figure 17: Final Effluent Flow rate, rolling average, 1 hour time period, 12 hour duration 9 February 2007

The time period deemed to be the most reasonable using visual inspection of the time periods of 10 minutes, 30 minutes, 1 hour, 2 hours and 4 hours was found to be 1 hour for each of the key variables. This time period has not been optimised, and that could constitute further work in the future.

3.3.1.4. Compensation for residence times in basins (synchronisation)

According to the fact that there is a time delay between each of the measurement points due to the residence times in each clarifier, aerated basin and selector, the data should be treated to reflect this: the observations for the final effluent would be moved into the past by a number of hours and so on, so that a single process condition is described for each case. This synchronisation would be applied to solids and nutrient concentrations, but it is not necessary to synchronise the flow rate data, as discussed in section 3.3.1.1 above.

The key parameters chosen for the purposes of steady-state detection are all measured at the inlet of the selector and at the aerated basins. Given the residence time in the selector is approximately one hour, and that the period of steady state detection is six hours (see section 3.3.1.6), it is not considered necessary to synchronise the data for this steady state detection exercise (synchronisation of data across the aerated basin (16 hours) was carried out for the purposes of the nutrient balance). In the event that the HRT's of the basins were quantified using a tracer test, the data could easily be synchronised, and this could constitute further work in the future.

3.3.1.5. Mill shuts

The TMP plant and the paper machine routinely shut down for operational and maintenance purposes, sometimes independently of each other. These shuts have a direct impact on the flow and organic load that is sent to the effluent treatment plant. For the purposes of steady state modelling, the data collected while the machine Fan Pump (52II152_234) is off (motor current below 58 Amps) or while the TMP plant (38PTM_OPER) is not operating will be excluded from further investigation, as demonstrated in Figure 18 below.

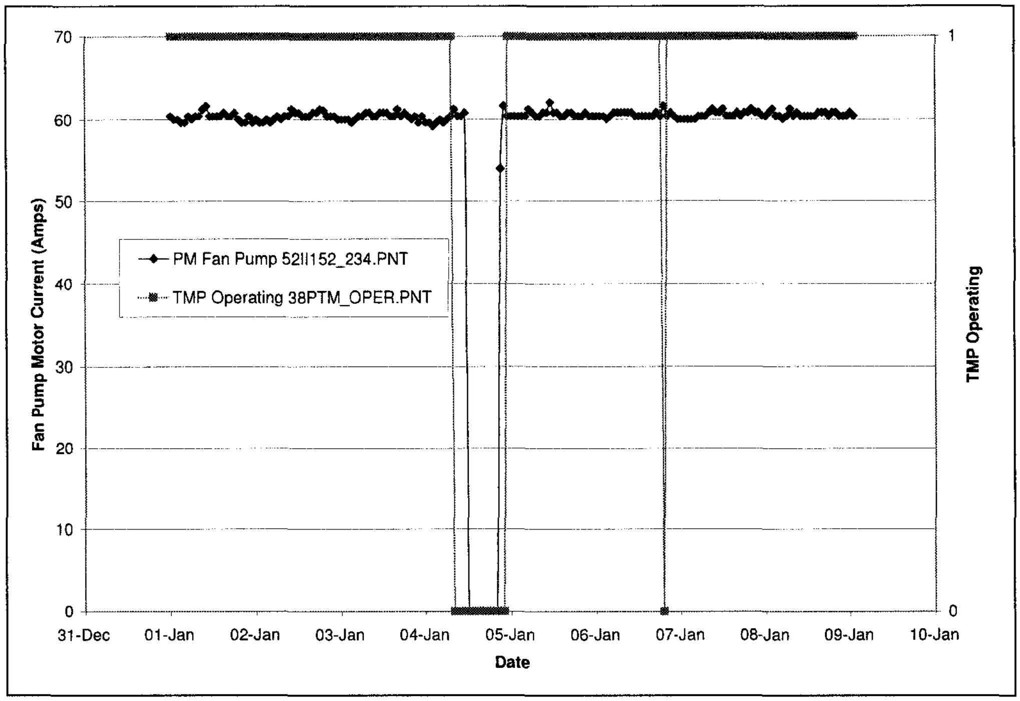

Figure 18: Mill Shut January 2006

3.3.1.6. Detection of near-steady-state operation

The use of the rolling average in the detection of steady state was discussed in section 3.3.1.3. Once the appropriate time period is established for each of the key parameters, the derivative of this rolling average is taken. A zero value of this derivative indicates the rate of change of the parameter is zero, and therefore can be interpreted as a steady-state. For this exercise, the absolute values of the derivative are considered, which disregards the direction of change.

The criterion to determine if a parameter is at near-steady-state has been chosen to be if the derivative of the 1-hour rolling average of the parameter is within a certain percentiles of values for that month. The percentiles and the equivalent percentage of the variable are listed below in Table 52.

Table 52: Near-steady-state determination,
parameter derivative of rolling average 95th percentiles (% of variable)

Key Parameter		***Upper bound = 95th percentile (% of variable)***			
	Units	***February***	***March***	***April***	***May***
Flow rate – Final Effluent	L/min	0.137	0.140	0.139	0.138
Temperature	ºC	0.00280	0.00322	0.00340	0.00505
TSS	mg/L	0.115	0.161	0.880	0.202
COD	m^{-1}	0.0388	0.0384	0.0466	0.0505
DO	mg/L	0.339	0.347	0.397	0.6980
Flow rate – RAS 1	L/min	0.138	0.141	0.140	0.137
RAS 2	L/min	0.138	0.141	0.140	0.140
Nitrogen Addition Rate	L/min	0.0359	0.0496	0.121	0.147

In order to determine near-steady-state behaviour for the entire system, the derivate of the rolling average of every key parameter should all be within their respective percentiles, for a certain duration. By investigating the number of steady state cases, in minutes, for each of the four months in 2007 for which data was collected, the appropriate duration for this exercise was selected. As demonstrated by the data in Table 53, the wastewater treatment plant operation was more stable in April and May than in the earlier months. Based on this data, the most appropriate duration is six hours, since this gives the longest duration possible while maintaining a reasonable percentage (nominally 10%) of steady state cases in the later months with which further work will be completed.

Table 53: Percentage of steady state cases, four months data February to May 2007

Duration of steady state cases (hours)	***Percentage of steady state cases (%)***			
	February	***March***	***April***	***May***
1	48	36	44	39
2	26	19	30	29
3	11	9	21	22
4	4	3	16	17
5	1	0.8	13	13
6	**0.3**	**0**	**10**	**10**
7	0	0	8	8
8	0	0	6	7
Total minute timestamps in month after data preparation	37,000	40,151	38,569	41,288

An example of one near-steady-state operating regime is seen in Figure 19 below, where the flow rates for the final effluent and the two RAS streams, as well as the TSS and COD are shown on the left-hand primary axis. The temperature, dissolved oxygen and nitrogen addition flow rate are shown on the right-hand secondary axis.

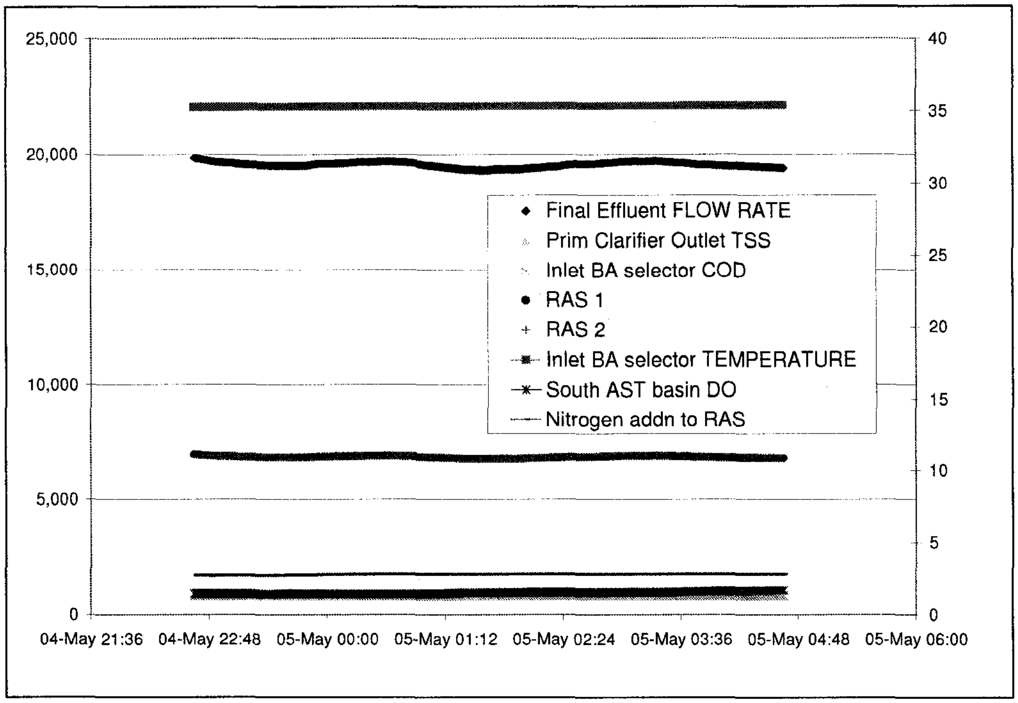

Figure 19: Example of one near-steady-state, duration 6 hours, 4 May 2007, all key parameters

3.3.1.7. Regroupment of measurements

Measurements are physically taken in a number of locations in a wastewater treatment plant. For the purpose of modelling, it is necessary to group the measurements at the inlet and outlet of each basin. Based on the assumption of continuously-stirred (CSTR) aerated basins and selectors, it is reasonable to assume that concentrations measured at the outlet of the basin are constant throughout the entire volume of the basin, and vice versa. Presented below in Table 54 is a re-grouped list of measured parameters.

Table 54: Regrouped measurements

Location	*Measurements*
Mill Drain	Flow rate

Location	***Measurements***
Inlet Primary Clarifier	Temperature, pH, Conductivity, TSS
Outlet Primary Clarifier (accepts) Inlet Aerated Basin Selector	Nutrient addition to RAS, RAS Flowrate Temperature, pH, COD, TSS, Conductivity
Outlet Aerated Basin Selector Inlet Aerated Basin	Temperature, pH, DO
Outlet Aerated Basins Inlet Secondary Clarifiers	Temperature, pH, DO TSS, VSS, NH4, PO4, NO3, TSUO,
Outlet Secondary Clarifiers Final Effluent	Flow rate, COD, TSS, VSS, NH4, PO4, NO3 Temperature, pH, Conductivity, TSS
Primary Sludge	Flow rate
Secondary Sludge	RAS Flow rate, WAS Flow rate, TSS
Mixed Sludge	Tank level, flow rate, percentage primary sludge, TSS
Nutrient, Polymer, NaOH Tanks	Tank Levels, Flow rates, C:N:P ratio

The purpose of these groups of data is to use in further modelling work. The data will be averaged over each of the steady states detected. It should be noted that some of the continuous on-line measurements were not available for the entire time period investigated; they have been included where available.

3.3.1.8. Step-wise methodology

The methodology described above can be summarised, as per the steps in Figure 20. This methodology is intended to render the data ready for description and to identify a number of near steady state operation regimes for further modelling exercises.

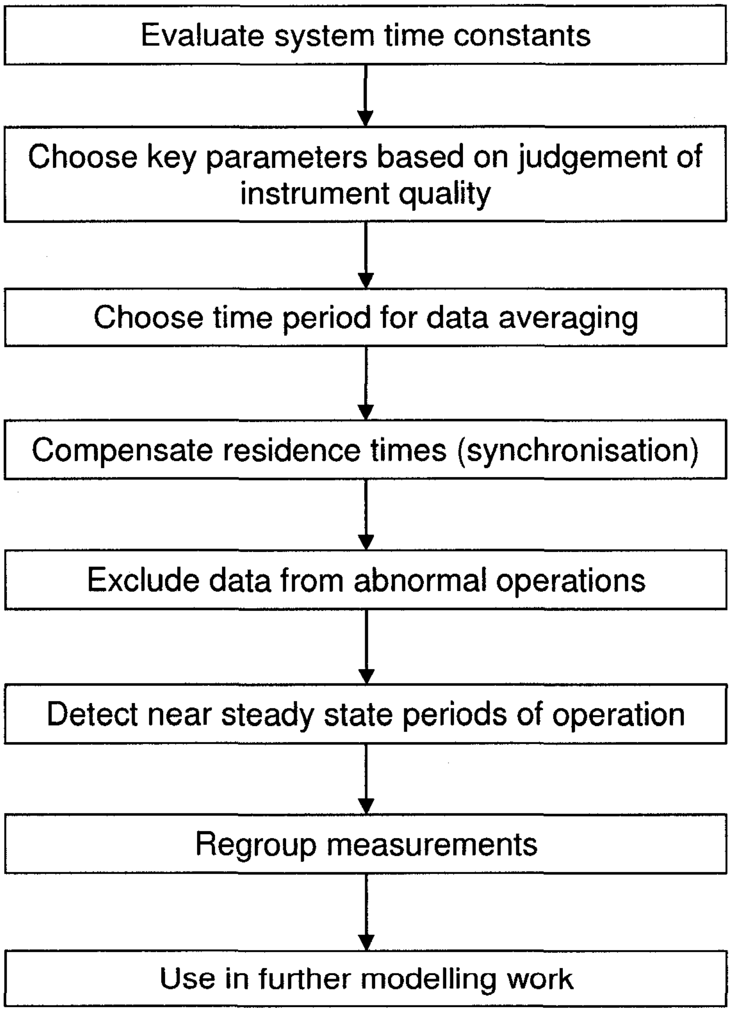

Figure 20: Data preparation step-wise methodology: steady state detection

3.3.2. Discrete Data Preparation

In contrast to continuously recorded data, ‘discrete data’ will be used to describe the data collected from grab samples and composite samples, laboratory testing that is recorded once per day or per shift.

Discrete data will not be used to detect steady state. The following methodology is proposed for the purposes of preparing the discrete data for use in further modelling work.

3.3.2.1. Steady states detected

Steady states detected according to the continuous data preparation shall be the only time periods considered for further modelling work.

3.3.2.2. Data extrapolation

Discrete data is collected according to the schedules of the laboratory technicians and plant operators (now boiler operators), usually but not always once per 8, 12 or 24 hours. It is reasonable to linearly extrapolate the discrete data over a time period of 24 hours, when taking into consideration the time constants of the process and the fact that the data investigated originates only from steady state operation. Variables that are not measured for a duration longer than 24 hours shall be evaluated on a case-by-case basis, investigating the behaviour of other process variables over the time period as well as the sensitivity of the variable itself.

3.3.2.3. Step-wise methodology

The methodology described above can be summarised, as per the steps in Figure 21. This methodology is intended to render the data ready for further modelling exercises.

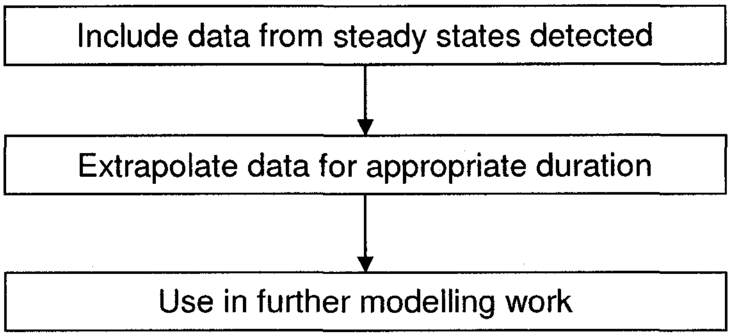

Figure 21: Data preparation step-wise methodology: discrete data

3.3.3. Data Reconciliation

Reconciliation was required for some data, notably for the flow rate of phosphorus addition to the process and for the total suspended solids in the inlet to the AST. The reconciliation methods and results are discussed in the appropriate sections, as presented in Table 55 below.

Table 55: Data reconciliation cross-references

Data Reconciliation	*Methodology*	*Results*
Phosphorus Addition Flow rate	B.3.4 Mass balances/ Phosphorus	B.5.1 Mass balances/ Phosphorus
TSS inlet AST	B.3.5.1 Process simulation development/ Simulator environment/ Influent advisor/ Solids	B.5.3.6 Process Simulation Parameter Specification/ Steady state cases (TSS)

3.4. Wastewater Characterisation

The wastewater characterisation required for the purposes of modelling the AST process could have been carried out according to various methodologies developed and published in the literature. It was carried out in accordance with the methodology presented by Roeleveld and Van Loosdrecht [1], as well as nutrient fraction measurements based on Standard Methods, as described in the Data Collection section.

3.4.1. Experimental Methodology

The wastewater characterisation methodology is presented by Roeleveld and Van Loosdrecht [1], based on the physical-chemical testing which has been established by the Dutch Foundation for Applied Water Research (STOWA), and has been widely used in the Netherlands for the aeration basin of municipal wastewater treatment plants. The COD and nutrient fractionation experiments are somewhat simplified compared to the more elaborate methods seen elsewhere in the literature, however they adequately address the requirements of this modelling exercise.

3.4.1.1. COD Fractions

STOWA method

The methodology presented below is a reiteration of the guidelines presented by Roeleveld and Van Loosdrecht for the influent to the aeration basin

[1].

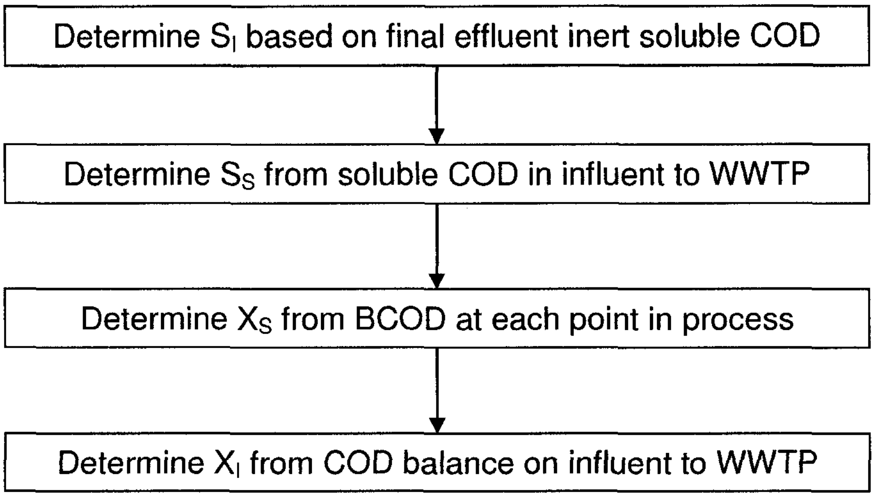

Figure 22: COD fraction characterisation methodology [1]

The first order rate constant of BOD versus time, k_{BOD}, is determined by conducting a linear regression with the least squares method on the influent (to a particular basin or process unit). The equation used in this regression is:

$$BOD_{total} = \frac{1}{1 - e^{-k_{BOD}t}} BOD_{OBS}$$

Rearranging this gives an equation in the exponential form *y= **m**.exp(**c**x)*:

$$\left(1 - \frac{BOD_{OBS}}{BOD_{total}}\right) = -me^{-k_{BOD}t}$$

An exponential trendline can be fitted to this curve and a goodness of fit is indicated by the Pearson's R^2 value. By systematically varying the value of

BOD_{total}, the value of BOD_{total} and k_{BOD} can be optimised for the highest R^2 value and a 'm' value as close to 1 as possible.

The biodegradable COD (BCOD) is then determined according to the following equation, using the correction factor f_{BOD} to account for inert COD generated in biomass lysis[6]. A f_{BOD} in the range of 0.1 to 0.2 is suggested for municipal wastewater treatment [1].

$$BCOD = \frac{1}{1 - f_{BOD}} BOD_{total}$$

The wastewater characteristics for the influent wastewater are then converted to ASM1 fractions according to Table 56 below [1]. For this methodology, the influent and effluent soluble COD refers to the COD measured in the filtrate from a 0.1µm filter, 'effluent' refers to the final effluent from the wastewater treatment plant and 'influent' refers to the influent to the aeration basin [1]. For one case, the soluble COD was estimated from total COD and the COD fractionation data since no soluble fraction measurement was available.

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[6] The correction factor f_{BOD} takes into account the "interaction of growth and decay of biomass" during the BOD measurement in the laboratory [1]. These BOD measurements are carried out using a standardised biomass seed. Therefore the correction factor can be assumed to be similar for municipal and industrial wastewater BOD measurements.

Table 56: ASM1 COD fraction calculations (inlet aeration basin)

ASM1 Fraction	***Calculation (inlet aeration basin)***
S_I	$= 0.9 \times COD_{effluent,\ soluble} - 1.5 \times BOD_{5,\ effluent}$[7]
S_S	$= COD_{influent,\ soluble} - S_I$
X_S	$= BCOD - S_S$
X_I	$= COD_{influent,\ total} - S_I - S_S - X_S$
X_{BH}	$= 0$
X_{BA}	$= 0.1$

This method assumes that there is no generation of soluble inert (unbiodegradable) COD in the process, which is contradicted by the ASM-PP model (refer to S_U fraction) [232].

ALTERNATIVE METHODS

A thorough discussion of alternative methods for calculating the wastewater characterisation are presented in the 2003 WERF report [232]. A number of these methods were applied in addition to the STOWA method above, in order to verify the results of the STOWA method. This was considered necessary due to the sensitivity of the model and model results to the wastewater characterisation.

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[7] The correction factors '0.9' and '1.5' account for "residual biodegradable organics in the effluent" [232]. For example, '0.9' signifies that 90% of the soluble effluent COD is present as S_I and the remaining 10% is present as S_S.

Soluble inert (unbiodegradable) fraction (S_I)

This fraction can be considered to be 100% of the soluble COD in the final effluent, where 'soluble' refers to the COD present in either a 0.45μm filtered sample or a pre-flocculated sample [232].

Particulate inert (unbiodegradable) fraction (X_I)

The theoretical volatile suspended solids in the mixed liquor can be calculated and compared to the measured value for a number of X_I fractions in order to estimate the true X_I value [232]. The development of this equation is presented in Appendix 2.

$$X_{VSS} = \frac{Q.COD_{T,Influent}.\theta_X}{f_{CV}.V}\left[\frac{\left(1 - f_{SI} - f_{XI}\right).Y_H}{1 + b_H\theta_X}\left(1 + f.b_H\theta_X\right) + f_{XI}\right]$$

Where X_{VSS} is the mixed liquor VSS concentration (mg/L), Q is the influent flow rate (L/d), $COD_{T,Influent}$ is the total COD concentration in the influent (mg/L), θ_X is the sludge age (d), V is the reactor volume (L), Y_H is the heterotroph yield coefficient (0.66 mg COD/ mg COD), b_H is the steady state theory endogenous decay rate (temperature dependent, 0.24 d^{-1} at 20ºC), ***f*** is the steady state theory endogenous residue fraction (0.2 mg VSS/ mg VSS), f_{CV} is the mixed liquor solids COD to VSS ratio (measured mill value used: 1.63 mg COD/ mg VSS), f_{XI} is the fraction of total influent COD which is particulate unbiodegradable, and f_{SI} is the fraction of total influent COD which is soluble unbiodegradable [232].

(Soluble) readily biodegradable fraction (S_S)

The oxygen uptake rate (OUR) can be measured during an aerobic batch reactor (bioassay) experiment, using a completely mixed reactor set-up of wastewater seeded with mixed liquor [232]. An idealised set of results are shown in Figure 23 below can be interpreted in terms of the cumulative OUR or area under the curve: area 1 corresponds to the mass of oxygen consumed during the oxidation of readily biodegradable COD (S_S), area 2 corresponds to the mass of oxygen consumed during nitrification, area 3 corresponds to the mass of oxygen consumed during the oxidation of slowly biodegradable COD (X_S) and the remaining area corresponds to the oxygen consumed during endogenous respiration [232].

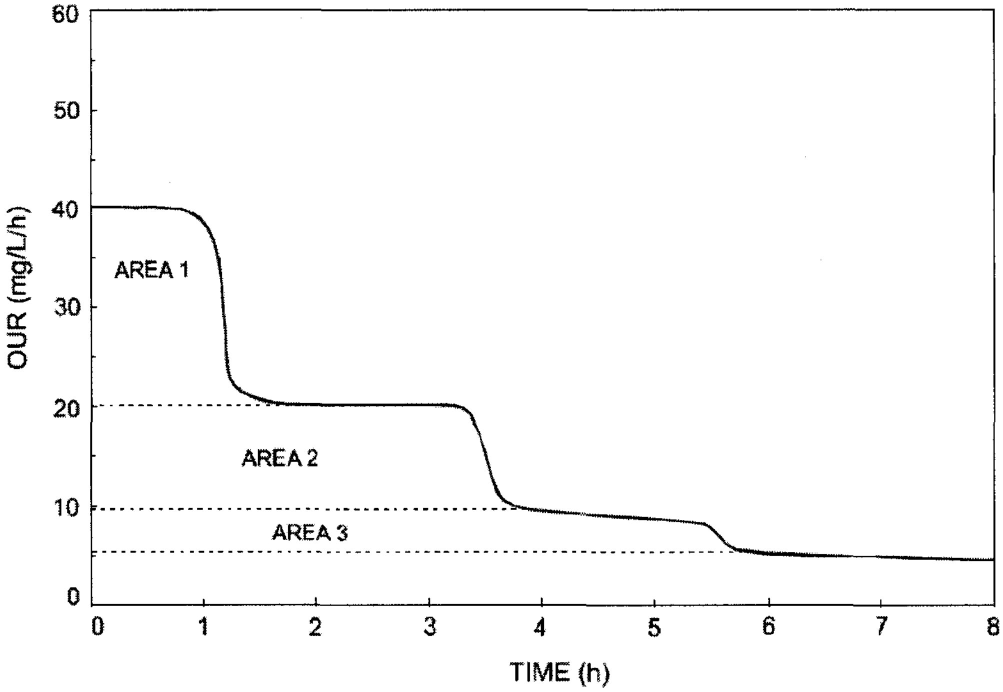

Figure 23: Oxygen uptake rate (OUR) during aerobic batch reactor experiment [232]

The concentration S_S is then calculated according to the equation [232]:

$$S_S = \left(\frac{M_O}{1 - Y_H} \right) \left(\frac{V_{SL} - V_{WW}}{V_{WW}} \right)$$

Where M_O is the mass of oxygen consumed per liter batch test volume (mg O_2/L), Y_H is the heterotrophic yield coefficient (0.66 mg cell COD/ mg substrate COD), V_{SL} is the volume of activated sludge mixed liquor used in test and V_{WW} is the volume of wastewater used in test [232].

(Particulate) slowly biodegradable fraction (X_S)

This fraction can be determined from the COD balance in the influent [232]:

$$X_S = COD_{influent,\,total} - S_I - S_S - X_I$$

It is also proposed to adapt the oxygen uptake rate (OUR) results during an aerobic batch reactor (bioassay) experiment, using a completely mixed reactor set-up of wastewater seeded with mixed liquor [232], to determine the ultimate BOD as the sum of the readily biodegradable fraction (S_S) plus the slowly biodegradable fraction (X_S), as per Figure 23 above.

3.4.1.2. Nutrient Fractions

Nitrogen

The nitrogen fractions were determined according to the following relations [45]:

$$N_{ORG} = TKN - NH_{3+4}$$

$$TN = TKN + NO_3$$

Where TKN represents the Total Kjeldahl Nitrogen, TN represents the total nitrogen and N_{ORG} represents the organic nitrogen. No nitrite measurements were made, nitrite concentration is assumed to be zero in all cases.

Phosphorus

The phosphorus fractions were determined according to the following relation [45]:

$$TP = P_{ORG} + P_{POLYPHOSPHATE} + PO_4$$

Where TP represents the total phosphorus and P_{ORG} represents the organic phosphorus.

3.4.1.3. Solids

The solids fractions were determined according to the following relations [45]:

TSS = VSS + FSS

VSS = Active biomass + dead biomass + inert organic matter

FSS = Inert inorganic matter

3.5. Mass Balances

Mass balances were conducted over the major process units: the aerated selector and basin as well as the primary and secondary clarifiers. The mass balances were used to calculate unknown parameter values; data reconciliation was not carried out on all of the process measurements as this is not considered necessary for the purpose of the project. The phosphorus and solids mass balances are described by Meijer *et al.* [27], and the COD and nitrogen mass balances are described by Barker and Dold [231]. These mass balances were carried out on data prepared according to the steady stated detection and data preparation methodology described in section 3.3.

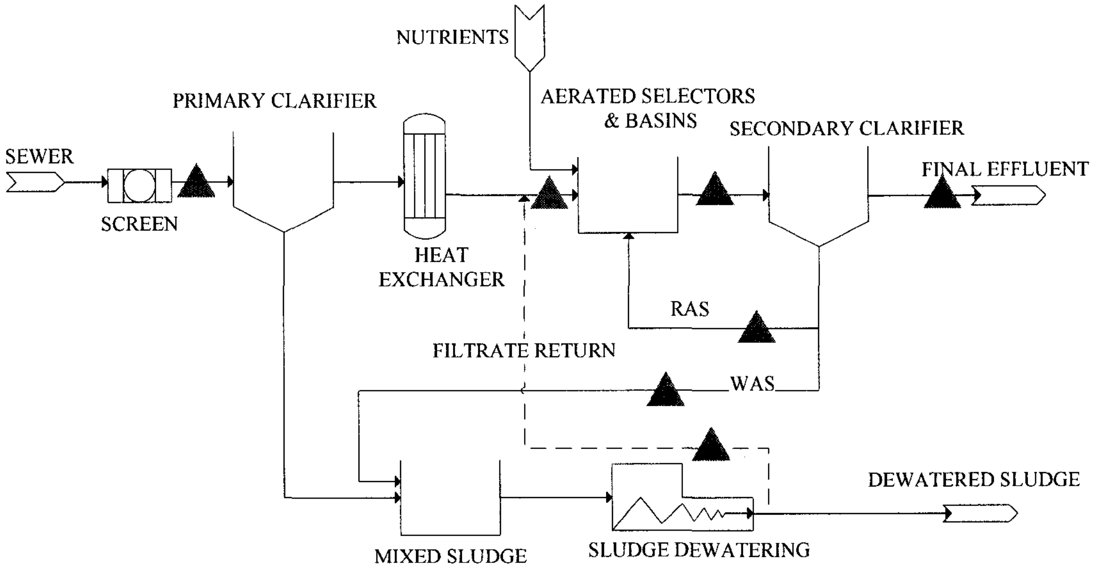

Figure 24: Wastewater plant configuration and sampling points (▲)

3.5.1. Flow

The volumetric flow balances were carried out over activated sludge selector, basin, primary and secondary clarifiers, according to the equations:

AST and Secondary Clarifier:	$Q_{AST\text{-}inlet}$	$= Q_{Effluent} + Q_{WAS}$
Primary Clarifier:	$Q_{PC\text{-}inlet}$	$= Q_{PC\text{-}outlet} + Q_{PC\text{-}sludge}$
Press Filtrate return:	$Q_{AST\text{-}inlet}$	$= Q_{PC\text{-}outlet} + Q_{Press\text{-}Filtrate}$

A volumetric flow balance is considered valid assuming water is incompressible, temperature is constant and therefore density is not changing, and assuming zero evaporation in the basins.

The point of the inlet to the AST selector is specified to be downstream of the press filtrate return and upstream of the addition of nutrients. The flow rates of the nutrient additions are assumed to be insignificant since they are so small compared to the wastewater flows, and are therefore not considered in the above flow balance equations.

3.5.2. Phosphorus

Phosphorus, unlike COD and nitrogen, does not transform into any gaseous phases in the wastewater process, and therefore the phosphorus mass balance can be closed [27]. As proposed by Meijer *et al.*, the phosphorus mass balance was performed first due to the simplicity of the balance and transformation mechanisms [27]. The phosphorus mass balances presented in the article in Appendix 4 were based on a ratio of total phosphorus in the WAS stream to that in the RAS stream of 2.9 mg TP/mg TP. However, this approach resulted in zero total phosphorus concentration in the RAS and WAS streams in cases of phosphorus deficiency, which is unlikely due to the fact that biomass growth would be severely limited by the complete lack of phosphorus which would result in reduced BOD or COD removal, which in fact was not observed. Instead, the total phosphorus in the RAS and WAS streams were determined to be a ratio of total phosphorus to total suspended solids from the average wastewater characterisation work. These ratios are:

Total Phosphorus

$P_{WAS} / X_{WAS} = 0.0101$ mg TP/ mg TSS

$P_{RAS} / X_{RAS} = 0.0113$ mg TP/ mg TSS

The total phosphorus balance over the secondary clarifier was then calculated according to the equation:

Total Phosphorus

$$P_{AST\text{-}BASIN} * (Q_{AST\text{-}inlet} + Q_{RAS}) = P_{effluent} * Q_{effluent} + P_{WAS} * Q_{WAS} + P_{RAS} * Q_{RAS}$$

The ortho-phosphate is measured daily in the AST basin and in the final effluent. From these measurements and the phosphorus fractionation, the total phosphorus concentration in the final effluent stream can be estimated. The average ratio of ortho-phosphate to total phosphorus was determined to be 0.821 mg PO_4/mg TP in the final effluent.

The total phosphorus balance over the aerated selector, basin and secondary clarifier was calculated according to the equation:

Total Phosphorus

$$P_{AST\text{-}inlet} * Q_{AST\text{-}inlet} = P_{Effluent} * Q_{Effluent} + P_{WAS} * Q_{WAS}$$

The concentration of the phosphoric acid added to the aerated selector is a fixed percentage of the total flow rate, 75%w/w or 0.394 kg P/L, the minimum concentration as specified by the chemical supplier.

The total phosphorus balance over the return of the press filtrate to the outlet of the primary clarifier was calculated according to the equation:

Total Phosphorus

$$\begin{aligned} P_{AST\text{-}inlet} * Q_{AST\text{-}inlet} &= P_{PC\text{-}outlet} * Q_{PC\text{-}outlet} + P_{Press\text{-}Filtrate} * Q_{Press\text{-}Filtrate} \\ &\quad + P_{ADDN} * Q_{ADDN} \end{aligned}$$

The total phosphorus concentration for the press filtrate was estimated from a single composite grab sample, 9.8 mg/L. This sample was assumed to correspond to the average wastewater fractionation, where the average total phosphorus in the WAS stream was determined to be 143 mg P/L, and a ratio from the average wastewater fractionation to the WAS total phosphorus was calculated for each steady state case, using the value of 0.0635 mg TP filtrate/ mg TP WAS.

The total phosphorus balance over the primary clarifier was calculated according to the equation:

Total Phosphorus

$$P_{PC\text{-}inlet} {}^{*}Q_{PC\text{-}inlet} = P_{PC\text{-}outlet} {}^{*}Q_{PC\text{-}outlet} + P_{P\text{-}Sludge} {}^{*}Q_{P\text{-}Sludge}$$

The total phosphorus concentration in the primary clarifier inlet stream was assumed to be equal to that in the outlet of the primary clarifier, which was essentially the case in the phosphorus fractionation measurements. The total phosphorus concentration in the primary clarifier outlet was assumed to be constant and equal to the average determined in the wastewater fractionation, due to a lack of other data. The mill laboratory does not test regularly for any form of phosphorus in this stream. This assumption is deemed to be reasonable given the magnitude of total phosphorus in this stream (primary clarifier outlet) is approximately 10% to 20% of the total phosphorus entering the aerated selector, and the variation in total phosphorus in the phosphoric acid addition, RAS and filtrate streams is assumed to be greater than the variation in the total phosphorus from the mill at steady state conditions.

3.5.3. Solids

The total suspended solids (TSS) balance over the secondary clarifier was calculated according to the equation:

Solids

$$\begin{aligned} X_{\text{AST-BASIN}} {}^*(Q_{\text{AST-inlet}} + Q_{\text{RAS}}) &= X_{\text{effluent}} {}^* Q_{\text{effluent}} + X_{\text{WAS}} {}^* Q_{\text{WAS}} + X_{\text{RAS}} {}^* Q_{\text{RAS}} \\ &= X_{\text{effluent}} {}^* Q_{\text{effluent}} + X_{\text{RAS}} (3.25 {}^* Q_{\text{WAS}} + Q_{\text{RAS}}) \end{aligned}$$

The TSS data from the on-line instrument available was used for the final effluent values. At the inlet to the AST basin, the TSS data from the mill laboratory was considered to be more trustworthy than that from the on-line instrument based and so the laboratory data was used for this point in the process.

The average ratio of the total suspended solids concentration in the RAS stream to that in the WAS stream is 3.25 (excluding the highest and lowest measured values, n=8 between 6 March and 22 May, 2007). Using this relation, the equation can be simplified and solved for all streams.

3.5.4. Carbon (COD)

The chemical oxygen demand (COD) balance was carried out according to the methodology outlined by Barker and Dold [231].

Since the secondary clarifier is the only basin in the system that is possibly not fully aerated, a mass balance of the nitrates in and out of this basin will determine whether denitrification is occurring. The mass of nitrate denitrified in the secondary clarifier is calculated from the laboratory nitrate measurements:

Nitrate denitrified

$$M_{denit,\ Total} = M_{Nitrate,\ effluent} - M_{nitrate,\ AST\text{-}outlet}$$
$$= N_{Nitrate,\ effluent} {}^{*} Q_{effluent} - N_{Nitrate,\ AST\text{-}outlet} {}^{*} Q_{AST\text{-}outlet}$$

The mass of COD in the effluent is calculated:

COD

$$M_{COD,\ effluent} = S_{T,effluent} {}^{*} Q_{effluent}$$

The mass of COD in the WAS stream is calculated:

COD

$$M_{COD,\ WAS} = f_{CV} {}^{*} X_{VSS,\ WAS} {}^{*} Q_{WAS}$$

The index f_{CV} represents a theoretical value of COD/VSS according to the stoichiometric equation[45]:

$$C_5H_7NO_2 + 5O_2 \longrightarrow 5CO_2 + NH_3 + 2H_20$$

$$M_W = 113 \qquad M_W = 160$$

$$COD = 160/113 = 1.42 \text{ mg } O_2/\text{mg } C_5H_7NO_2$$

The actual stoichiometry of the biomass may differ from the theoretical $C_5H_7NO_2$ for a number of reasons, not least because the biomass is a complex mixture of organisms. The value of 1.48 mg COD/mg VSS has been shown to be a good approximation over a range of sludge ages and wastewater characterisations [231].

A simplified chemical equation is used to describe nitrification [231] :

$$NH_4^+ \quad + \quad 2O_2 \quad \longrightarrow \quad NO_3^- \quad + \quad 2H^+ \quad + H_20$$

$M_W = 18 \qquad M_W = 64$

COD = 64/14 = 4.57 mg NO_3 formed/mg NH_4^+ consumed

The mass of nitrate formed by nitrification is calculated:

Nitrate - Nitrification

$$M_{NIT} \approx (N_{Nitrate,\ effluent} {}^*Q_{effluent} + M_{denit,\ Total})$$

The mass of oxygen consumed by nitrification is calculated:

Oxygen Demand - Nitrification

$$M_{OD,\ NIT} = 4.57 \, {}^*(N_{Nitrate,\ effluent} {}^*Q_{effluent} + M_{denit,\ Total})$$

The total mass of COD oxidised in the aerated basins and selectors is calculated:

COD

$$M_{COD,\ aer} = O_T{}^*V{}^*24 - 4.57 \, {}^*(N_{Nitrate,\ effluent} {}^*Q_{effluent} + M_{denit,\ Total})$$

Where O_T represents the total oxygen utilisation rate (per hour) and V represents the volume of the aerated selectors and basins. This equation is based on the difference between the oxygen utilization rate and the theoretical oxygen usage via the nitrification and denitrification reactions. The total oxygen utilisation rate (OUR) is calculated as the lab-determined (measured once per day) specific oxygen utilisation rate (SOUR) multiplied by the volatile suspended solids in the activated sludge (MLVSS).

The COD consumed by denitrification is calculated:

COD

$$M_{COD,\ denit} = 2.86 * M_{denit,\ Total}$$

The factor of 2.86 comes from the calculation by electron equivalent half reactions that the transfer of one electron equivalent requires the reduction of 1/4 mole of oxygen or 1/5 mole of nitrate [231]. Multiplying through by their respective molecular weights results in the equivalency of one gram of nitrate-nitrogen to 2.86 grams of oxygen. This assumes that the denitrified nitrate is completely transformed into nitrogenous gas and no intermediate species are produced [231].

The total mass of COD oxidized in the system is calculated:

COD

$$M_{COD,\ oxidised} = M_{COD,\ denit} + M_{COD,\ aer}$$

The total mass of COD output from the system is calculated:

COD

$$\text{Output COD} = M_{COD,\ effluent} + M_{COD,\ WAS} + M_{COD,\ oxidised}$$

The total mass of COD input to the system is calculated:

COD

$$\text{Input COD} = S_{T,\text{influent}} * Q_{\text{influent}}$$

The percentage that the COD mass balance is correct is calculated:

COD

$$\%\ \text{Balance COD} = \frac{\text{Output COD}}{\text{Input COD}} * 100$$

3.5.5. Nitrogen

The mass of nitrate in the final effluent is calculated:

Nitrate

$$M_{\text{Nitrate, effluent}} = N_{\text{Nitrate, effluent}} * Q_{\text{effluent}}$$

The ratio of the average TKN concentration to that of ammonia-nitrogen in the final effluent stream was determined to be 4.36 (excluding the highest and lowest measured values, n=6 between 23 January and 15 May, 2007). Using this relation, the mass of TKN in the final effluent is calculated from the on-line ammonia concentration:

TKN

$$M_{\text{TKN, effluent}} = 4.36 * N_{\text{NH4, effluent}} * Q_{\text{effluent}}$$

The mass of nitrogen in the WAS stream is estimated:

Total Nitrogen

$$M_{N,\,WAS} = f_N * X_{WAS} * Q_{WAS}$$

Where f_N of 0.1 mg N/ mg VSS is considered reasonable over a range of sludge ages for municipal sludges. A range of 3% to 6% nitrogen content of activated sludge has been seen for pulp and paper wastewaters [53].

The total mass of nitrogen output from the system is calculated:

Total Nitrogen

$$\text{Output N} = M_{\text{Nitrate, effluent}} + M_{\text{TKN, effluent}} + M_{N,\,WAS} + M_{\text{denit, Total}}$$

The total mass of nitrogen input to the system is calculated:

Total Nitrogen

$$\text{Input N} = S_{N,\text{influent}} * Q_{\text{influent}} + \mathbf{S_{urea}} * \mathbf{Q_{urea}}$$

Which explicitly incorporates the addition of nitrogen in the form of urea. The total nitrogen concentration in the inlet to the AST basins was assumed to be constant and equal to the average determined in the wastewater fractionation, due to a lack of other data, 5.67 mg N/L (n = 7 between 7 February and 15 May 2007). The mill laboratory does not test regularly for any form of nitrogen in this stream.

The percentage that the total nitrogen mass balance is correct is calculated:

Total Nitrogen

$$\% \text{ Balance TN} = \frac{\text{Output TN}}{\text{Input TN}} * 100$$

3.6. Modelling

3.6.1. Process Simulation Development

As discussed in the literature review, the overall wastewater treatment plant model is made up of a hydraulic model, a settling model and a biological model (ASM). The following is a discussion of the development of the appropriate combination of model elements for the case study pulp and paper mill effluent treatment plant. The ASM-P model developed by *Brault et al.* forms the basis of the biological model as referenced below [118]. The hydraulic model and the settling model were developed as specified in the GPS-X software.

All parameters in **bold** are specified for a particular steady state operating regime, as defined by the data preparation methodology. These cases will be presented in section 4.

Operating costs were not evaluated using GPS-X as part of this project. As such, the oxygen transfer parameters are of little significance except for the DO controller set point and the PI controller settings.

3.6.1.1. Definition of model boundaries

The boundaries of the model were chosen to be from the AST selector inlet to the outlet of the AST, as per Figure 25 below. This choice was made due to the fact that the wastewater characterisation carried out for the ASM model applies to the primary clarified effluent; the characterisation applies to the inlet to the AST selectors. Without detailed characterisation data on the primary sludge, it is considered unnecessary for the purposes of this study to model the solids dewatering. During the course of the study, it was neither possible nor practical to develop a suitable secondary clarifier settling model for pulp and paper wastewater.

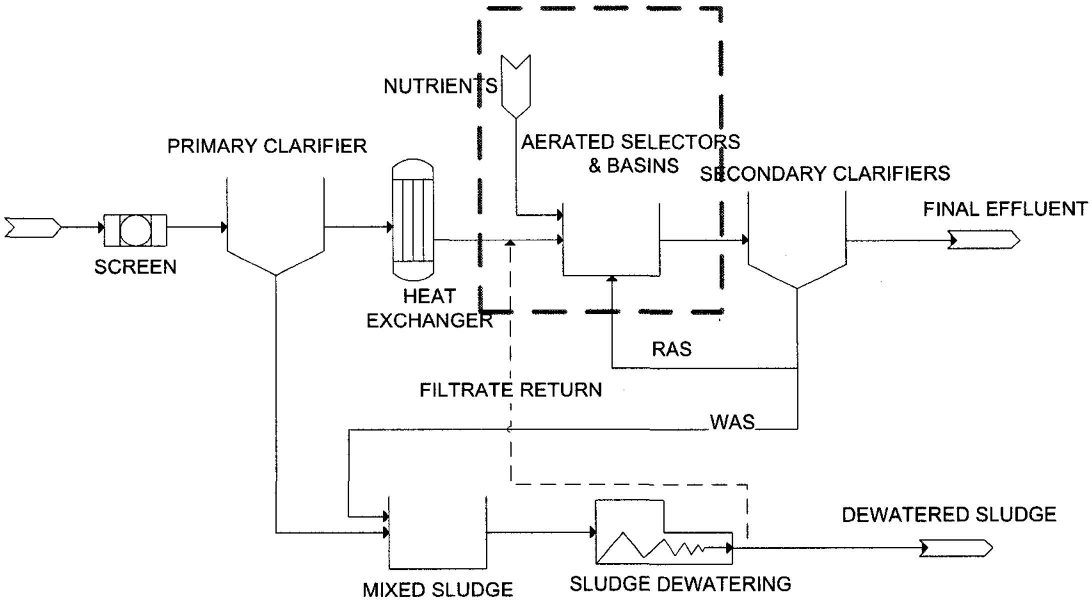

Figure 25: Model boundaries

3.6.2. Temperature

The temperature is set using the model Options/ General Data/ System/ Input parameters/ Physical/ Liquid temperature, plus entering an Arrhenius coefficient (nominally 1.04 $^{\circ}C^{-1}$) for all kinetic parameters in the 'Model Variables' worksheet of the model. This liquid temperature is reset for each steady state, and is generally in the range of 30 – 36ºC. These temperatures are outside the range normally catered to by the ASM models: the temperature-dependent terms *must* be calibrated taking this into account, particularly the kinetic terms.

3.6.3. Model parameters

The design and default parameters used in the model are listed in Appendix 5, including the parameters for each of the process units for the hydraulic and biological models. The settling model was chosen to be a point settler model as discussed previously.

3.6.4. Simulator Environment

3.6.4.1. Simulator Calculation Method

As discussed in the literature review, the GPS-X software uses numerical methods to calculate the mass balance over each of the process units in the layout. Using the Runge-Kutta-Felberg integration method, the software solves for liquid flows first followed by state variables. The balances are conducted by cutting the RAS stream and sequentially calculating the flow through each process unit for each iteration. A 'derivative' is produced for each state variable in each process unit and each layer in the reactive clarifier model. The derivative is equal to the difference between the value of the state variable from one iteration to the next. The absolute sum of all derivatives is used as the termination criteria for the steady-state solver: this sum has mixed units as a function of the state variables in the model.

Modelling of ASM models can produce more than one solution for a given process, Petersen matrix and initial conditions. It is therefore possible that the software will find more than one solution, that a local optimum may exist.

Hydromantis uses three levels of testing of the GPS-X software. The first level is the testing that ACSL provides for their mathematical solutions software. The second level is continuity mass balance testing over each new process model that Hydromantis conducts. The third level of testing incorporates various case studies for municipal and industrial sites that Hydromantis conducts with respect to calibrating kinetic parameters. Hydromantis is also party to the International Water Association (IWA) and the C.O.S.T. benchmark systems which provide an international standard of ASM model simulation.

3.6.4.2. Model Developer

The ASM1 model was modified in the Model Developer spreadsheet for the GPS-X program. The following is a brief description of the steps taken to produce the ASMPP model from the ASM1 model, according to information in the Hydromantis instruction manual [233].

Petersen Matrix modifications

Modifications to the Petersen Matrix are presented in red in Table 58. These modifications were presented as the ASMPP model by *Brault et al.* [118], plus the inclusion of the intracellular dissolved inorganics, the denitrification process, the anoxic growth of heterotrophs and therefore the S_{NN} dinitrogen fraction. The following assumptions have been made:

- Growth of autotrophs and heterotrophs: any and all bacterial growth may be limited by the concentration of soluble phosphorus and ammonia nitrogen;
- Nitrification and denitrification can occur;
- Soluble biodegradable organic phosphorus can become available via the process of 'phosphatification' and 'hydrolysis of entrapped organic phosphorus', processes analogous to the 'ammonification' and 'hydrolysis of entrapped organic nitrogen' processes included in the ASM1 model; and
- Intracellular dissolved inorganics that precipitate in the VSS-TSS test are identified as a fraction fxii of the active biomass [234].

It is necessary to modify the kinetic rate equations in order to correspond to the modifications made in the Petersen matrix.

State variables, stoichiometric & kinetic parameters

Each of the twenty-six state variables in the ASM-PP model are entered into the model developer as model variables, with appropriate symbols, units, diffusion constants and an initial value in the activated sludge. The model variables are listed in Appendix 5. The relationships between the COD and nutrient fractions are presented in Figure 26, Figure 27 and Figure 28.

The fraction added to the original model must be entered under a substitute or proxy that is included in the CNPIP library. A list of the proxy used is presented in Table 57 below.

Table 57: State variable proxies used CNPIP library

#	*Symbol*	*Proxy*	*State Variable*
14	X_{PD}	X_{ZA}	Particulate biodegradable organic phosphorus (in influent and from biomass decay)
15	S_{PD}	S_{ZA}	Soluble biodegradable organic phosphorus (in influent and from hydrolysis of X_{PD})

Composite variables

The state variables added to the ASM model must be included in the calculation of composite variables. The necessary modifications to the composite variable calculation are presented in Appendix 5.

Table 58: ASM-P Petersen matrix (modifications from ASM1 shown in red)

	Component (i) →	1	2	3	4	5	6	7	8	9
	↓ Process (j)	S_I	S_S	X_I	X_S	X_{BH}	X_{BA}	X_U	S_O	S_{NH}
1	Aerobic heterotrophic growth		$-\frac{1}{Y_H}$			1			$-\left(\frac{1-Y_H}{Y_H}\right)$	$-i_{XBN}$
2	Anoxic heterotrophic growth		$-\frac{1}{Y_H}$			1				$-i_{XBN}$
3	Aerobic autotrophic growth						1		$-\left(\frac{4.57-Y_A}{Y_A}\right)$	$-i_{XBN} - \frac{1}{Y_A}$
4	Heterotrophic degradation				$1-f_U$	-1		f_U		
5	Autotrophic degradation				$1-f_U$		-1	f_U		
6	Ammonification									1
7	Hydrolysis of X_S		1		-1					
8	Hydrolysis of X_{ND}									
9	Phosphatification									
10	Hydrolysis of X_{PD}									

	Component (i) → **↓ Process (j)**	10 S_{NO}	11 S_{ND}	12 X_{ND}	13 S_P	14 X_{PD}	15 S_{PD}	16 X_{II}	17 S_{NN}	18 S_{ALK}
1	Aerobic heterotrophic growth				$-i_{XBP}$					$-i_{XBN}/14$
2	Anoxic heterotrophic growth	$-\left(\frac{1-Y_H}{2.86*Y_H}\right)$			$-i_{XBP}$				$\left(\frac{1-Y_H}{2.86*Y_H}\right)$	$\left(\frac{1-Y_H}{14*2.86*Y_H}\right)-i_{XBN}/14$
3	Aerobic autotrophic growth	$-\frac{1}{Y_A}$			$-i_{XBP}$					$-\frac{i_{XBN}}{14}-\frac{1}{7*Y_A}$
4	Heterotrophic degradation			$i_{XBN}-f_U*i_{XUN}$		$i_{XBP}-f_U*i_{XUP}$				
5	Autotrophic degradation			$i_{XBN}-f_U*i_{XUN}$		$i_{XBP}-f_U*i_{XUP}$				
6	Ammonification		-1							1/14
7	Hydrolysis of X_S									
8	Hydrolysis of X_{ND}		1	-1						
9	Phosphatification				1		-1			
10	Hydrolysis of X_{PD}					-1	1			

	Component (i) → ↓ Process (j)	Reaction rate (ρj)
1	Aerobic heterotrophic growth	$\mu_H\left(\frac{S_S}{K_{SH}+S_S}\right)\left(\frac{S_O}{K_{OH}+S_O}\right)\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_P}{K_P+S_P}\right)X_{BH}$
2	Anoxic heterotrophic growth	$\mu_H\left(\frac{S_S}{K_{SH}+S_S}\right)\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_P}{K_P+S_P}\right)\eta_g X_{BH}$
3	Aerobic autotrophic growth	$\mu_A\left(\frac{S_O}{K_{OA}+S_O}\right)\left(\frac{S_{NH}}{K_{NA}+S_{NH}}\right)\left(\frac{S_P}{K_P+S_P}\right)X_{BA}$
4	Heterotrophic degradation	$b_H X_{BH}$
5	Autotrophic degradation	$b_A X_{BA}$
6	Ammonification	$k_a S_{ND} X_{BH}$
7	Hydrolysis of X_S	$k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)\left[\left(\frac{S_O}{K_{OH}+S_O}\right)+\eta_h\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{BH}$
8	Hydrolysis of X_{ND}	$k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)\left[\left(\frac{S_O}{K_{OH}+S_O}\right)+\eta_h\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{BH}\left(\frac{X_{ND}}{X_S}\right)$
9	Phosphatification	$k_p S_{PD} X_{BH}$
10	Hydrolysis of X_{PD}	$k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)\left[\left(\frac{S_O}{K_{OH}+S_O}\right)+\eta_h\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{BH}\left(\frac{X_{PD}}{X_S}\right)$

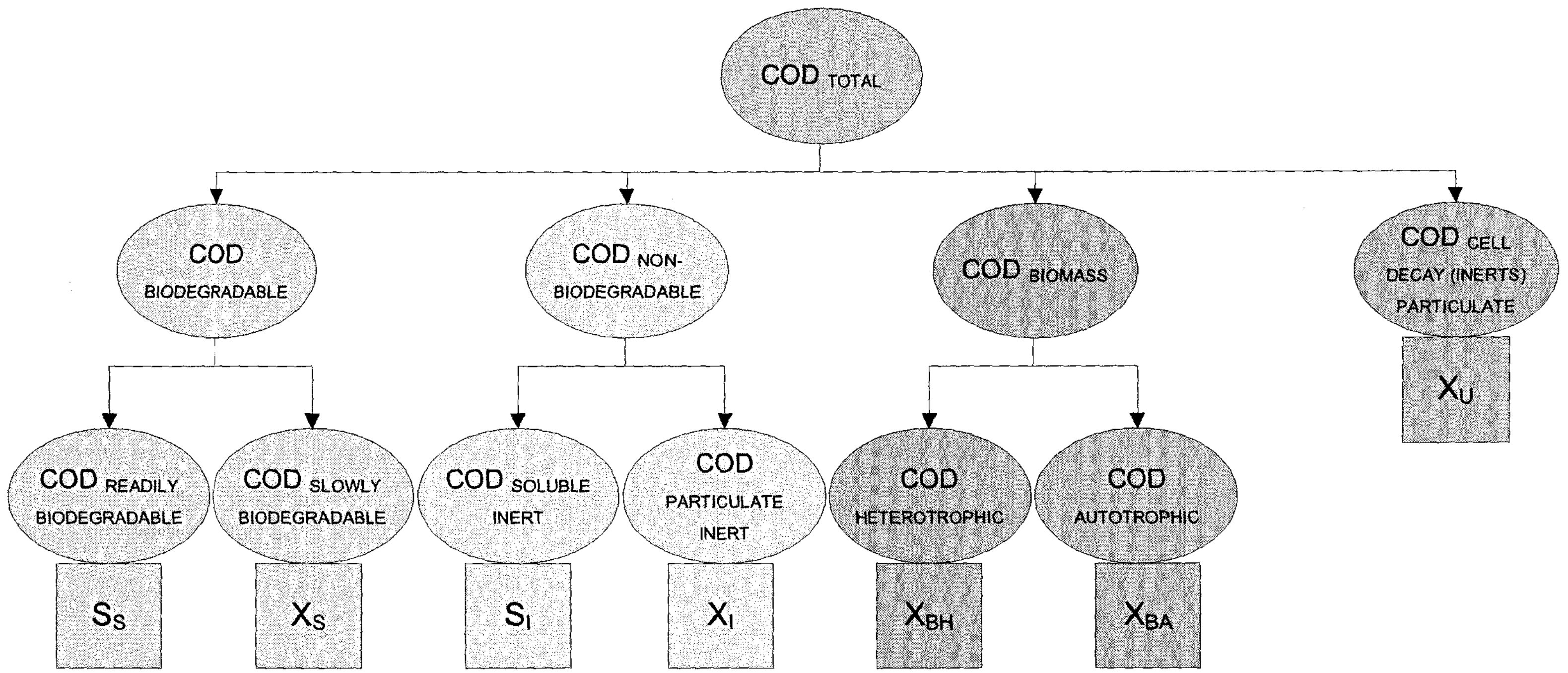

Figure 26: COD Fractionation, simple & modified [118, 183]

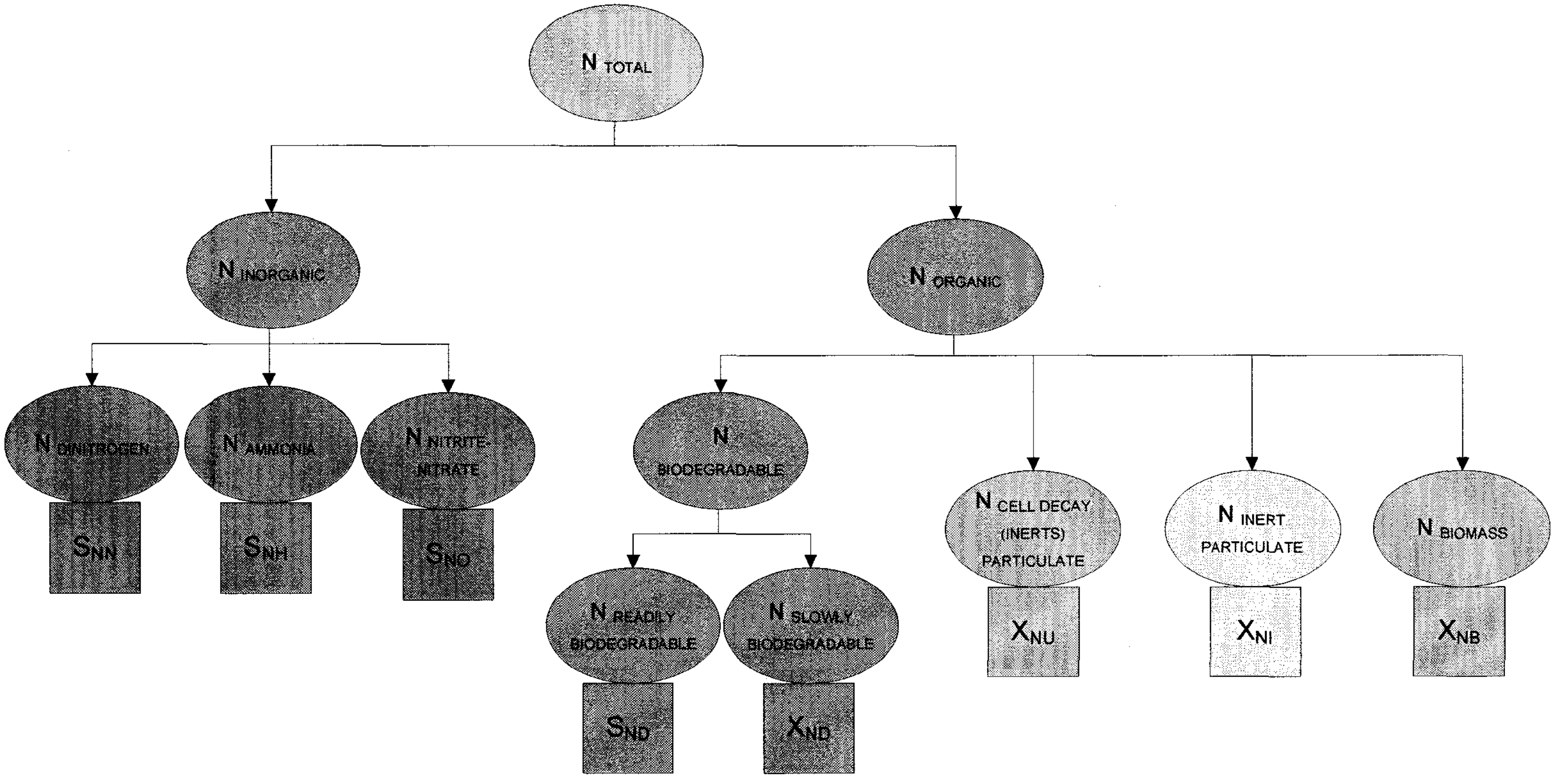

Figure 27: Nitrogen Fractionation, detailed & modified [118, 172]

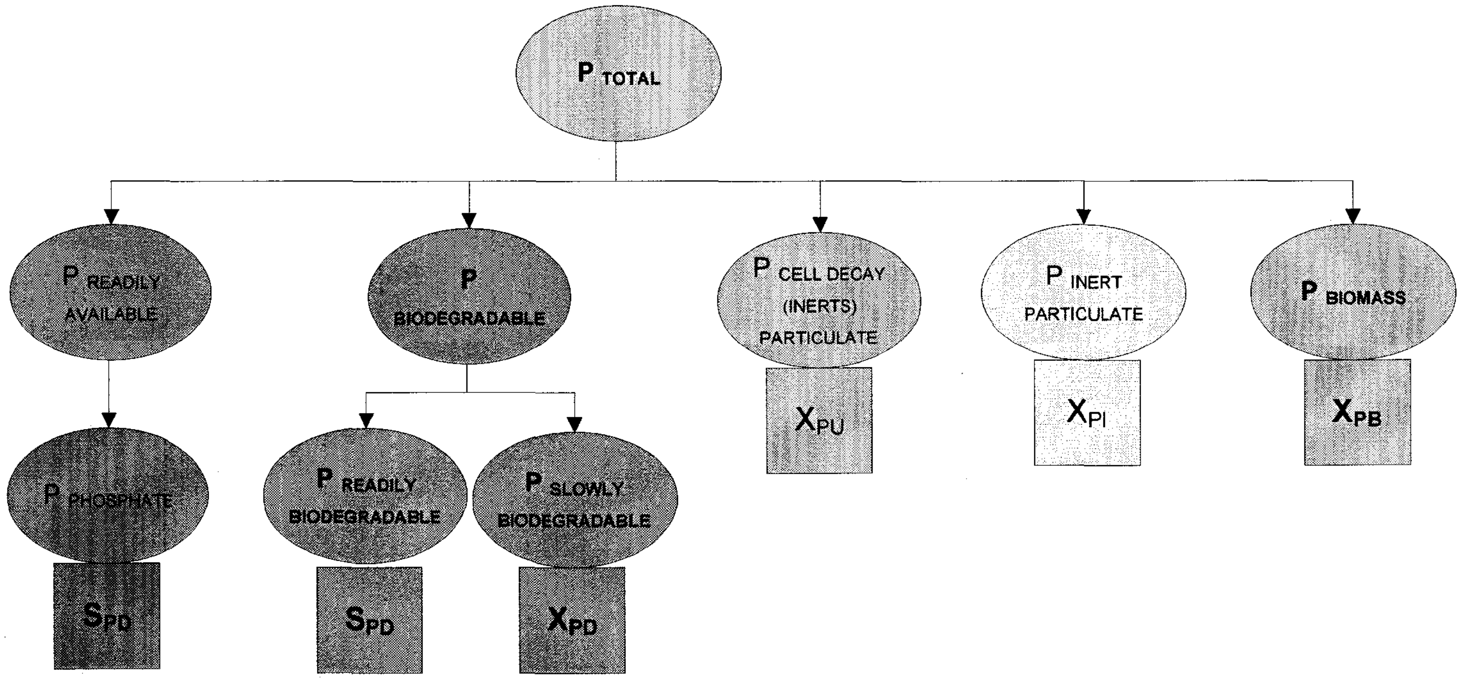

Figure 28: Phosphorus Fractionation, detailed & modified [118]

3.6.4.3. *Influent Advisor*

Parameters that change value for each steady state are listed in Appendix 3. A full list of parameter values and the determination methods are presented in Appendix 5.

COD

The 'States' version of the influent characterisation is used in GPS-X for simplicity, as it corresponds best with the experimental fractionation carried out. This is applicable since a full wastewater characterisation has been carried out.

Solids

The measured total suspended solids plus the average wastewater solids fractionation is used for all steady states. The inert inorganic suspended solids fraction X_{II} is calculated as the difference between the TSS and the VSS in the influent: this is zero in all cases.

As discussed in the literature review, the ratio of BOD_5 to ultimate BOD, f_{BOD}, is calculated from the wastewater characterisation exercise for the influent to the AST selectors. The result from the wastewater characterisation, 0.24, is notably different from the value calculated for each steady state via the on-line COD measurement and a $COD:BOD_5$ mass ratio determined by the mill (2.36). The latter value is supported by external laboratory data and is therefore the value used for each steady state.

As discussed in Appendix 2, the X_{II} fraction of inert inorganic material is equal to zero in the AST influent stream for all steady states. However, the solids fractionation work highlighted a difference between the VSS and TSS concentrations in the mixed liquor: 125 mg FSS/L on average. From the steady state data, the mixed liquor measurement for all steady states demonstrates a difference between the TSS and VSS measurements. For the purposes of modelling, it is necessary that the origin of this solids fraction is identified. Work by Ekama *et al.* highlights that 15% of the content of ordinary heterotrophic organisms is present as inert inorganic salts (mg ISS/mg VSS), or X_{II}, which precipitate during the VSS-TSS test procedure [234]. Given that the active biomass content of the VSS concentration has been measured at approximately 25% (mg active biomass/ mg VSS) for pulp and paper wastewater [220] this results in 4% mg ISS/mg VSS. It can therefore be assumed that the 5% of mixed liquor TSS concentration that is unaccounted for by VSS is present as X_{II} originating from these inert inorganic salts. This can be taken into account in the model by calculating the X_{II} fraction as a state variable, as a fraction fxii of the active biomass. The value of the fraction fxii is based on the following calculation:

$$f_{xii} = \frac{X_{II}}{VSS} * \frac{VSS}{Active\_biomass} = \frac{0.052}{0.25} = 0.208$$

Nutrients

The average values of the measured nutrient fractionation are used for all steady states. The concentration of nitrogen gas in the influent is assumed to be zero (S_{NN}). Likewise, the fractions of particulate active biomass nitrogen (X_{NB}) and particulate nitrogen from cell decay inerts (X_{NU}) are assumed to be zero in the influent.

The fractions of particulate active biomass phosphorus (X_{PB}) and particulate phosphorus from cell decay inerts (X_{PU}) are assumed to be zero in the influent. The fraction of particulate biodegradable organic phosphorus (X_{PD})

is assumed to account for the balance of the particulate organic phosphorus measured in the AST influent, which is close to zero. Other fractions were calculated from wastewater characterisation data, the details are presented in Appendices 2 and 5.

3.6.4.4. Library

The choice of library of state variables depends on the intended use of the model. This model considers the transformations of nutrients and therefore it is essential that the library of state variables includes phosphorus as well as the basic library of carbon and nitrogen fractions. It is also necessary to include the 'industrial pollutant' library, as this allows the creation and modification of both soluble and particulate fractions such as those in the ASMPP model listed in Table 57.

3.6.5. Calibration & Validation

As discussed in the literature review, there are many precedents for the calibration of ASM models. The following is based on that presented in the WERF report [232]. Hulsbeek *et al.* recommend using a completely distinct data set for the validation data set [185].

Table 59: Calibration process & parameters (general order)

Step	*Process*	*Parameters*	*Target*
1	Plant configuration & model modification	Design parameters ASMPP model	-
2	Specify steady-state data	Steady-state parameters: Temperature, influent etc	-
3	Soluble inert balance	S_I	Effluent S_I

Step	*Process*	*Parameters*	*Target*
4	Suspended Solids	WAS, settling parameters	Effluent TSS
5	Inert suspended solids	ISS	Effluent VSS
6	Solids wasting	WAS flow	WAS flow
7	Organic load removal	ASMPP model	BOD Removal
8	Nitrification	Autotrophic growth rate	Effluent NH_4
9	Particulate inert balance	Influent X_I	MLVSS, OUR
10	Secondary settling	Settling parameters	RAS TSS
11	Nutrient transformations	ASMPP model	Effluent NH4, NO3, PO4

3.6.6. Sensitivity Analysis

A sensitivity analysis will be completed by varying a number of parameters in the model and quantifying how the model reacts to these changes.

4. Publication Executive Summary

4.1. *Presentation of publications*

The following papers are presented in Appendix 4.2 and 4.3 respectively and were submitted to and/or published in peer-reviewed international scientific journals:

- Cotter, L., Brault, J. M. & Stuart, P. R. (2008) Steady state modelling of nutrient transformations in activated sludge treatment of pulp and paper wastewater, *Water Research*

- Cotter, L., Lemire, D, Bigelow, J. & Stuart, P. R. (2008) Pulp and paper wastewater: Activated sludge modeling and control strategies, *Tappi Journal*

The following paper, also presented in Appendix 4.1, was presented at a peer-reviewed international conference:

- Cotter, L., Brault, J. M., Lemire, D., Bussière, S. & Stuart, P. R. (2007) Nutrient, COD and solids mass balances for pulp & paper activated sludge wastewater treatment plants: the practical benefits for a TMP mill. *TAPPI Engineering, Pulping & Environmental Conference*. Jacksonville, Florida.

4.2. *Links between publications*

The peer-reviewed international conference paper in Appendix 4.1 presents the results of the systematic data treatment process and mass balances, which highlighted unwanted nutrient transformations occurring in the AST selectors, basins and the secondary clarifiers. The potential cost savings on supplemental nutrient addition associated with these processes was estimated at $13,000 annually. Comparison of calculated BOD_5:N:P mass ratios with those reported in the literature indicate a possible saving estimated at $85,000 annually.

The results from the data treatment process and mass balances were used in conjunction with an ASM-based model developed for pulp and paper wastewater, presented in the article submitted for a peer-reviewed international journal, presented in Appendix 4.2. The ASM-based model took into consideration the nutrient deficient nature of pulp and paper wastewater.

The influent characterisation of pulp and paper wastewater highlighted significant differences between this wastewater and municipal wastewater, which warrants further work if the ASM-based models are to be applied to this industry. Pulp and paper wastewater total COD concentration, and possibly the relative size of the COD fractions, can vary significantly over the course of a day, which represents a challenge in terms of applying the ASM-based model for a well-mixed (CSTR) AST plant with a short retention time. It is possible to use an ASM-based model to model the wastewater treatment plant at a pulp and paper mill, when the plant is operating in a stable manner with a stable microbiological population. It is extremely difficult to model small changes in nutrient concentrations when the partial nitrification-denitrification processes vary over time and in response to changes in the influent characterisation and sludge retention time.

The results from the ASM-based model were further interpreted and control strategies were proposed in the article submitted for a peer-reviewed international journal, presented in Appendix 4.3. The overall methodology used in this study, of rigorous data treatment, detection of pseudo-steady states, development of mass balances and individually calibrated scenarios, demonstrated important insights into the nutrient transformations occurring in a well-mixed (CSTR) short-retention time AST wastewater treatment plant.

The use of the ASM-based model for the control of dosing of supplemental nitrogen and phosphorus or for the control of process operations such as the WAS flow rate have been proposed as possible control strategies to meet nutrient residual concentrations. The mill has already implemented ratio control of nutrient dosing with feed-back of residual concentrations, and the proposed use of the ASM-based model will be implemented as an additional layer of control. While a large range of pulp and paper process wastewater treatment configurations exist, the methodology and the ASM-based modeling used in this study are broadly applicable to the industry and represent state of the art technology application in the industry.

4.3. Synthesis

The objective of this synthesis is to summarise and discuss the most pertinent results of the work done in this study, using the previously outlined methodology.

4.3.1. Overall methodology

The project methodology outlined in Figure 29 encompasses data collection of the mill physical design data, of continuous and discrete laboratory data from the mill PI system, and additional wastewater characterisation measurements carried out at the mill laboratory and at the university laboratory according to Standard Methods. This data was then treated to synchronise data over the hydraulic retention time of the AST basins, to exclude abnormal process conditions such as mill shuts, and to identify pseudo-steady state scenarios which varied in duration from 6 hours to 32 hours. The treated data was further reconciled by mass balances for each pseudo-steady state prior to inclusion in an ASM-based model.

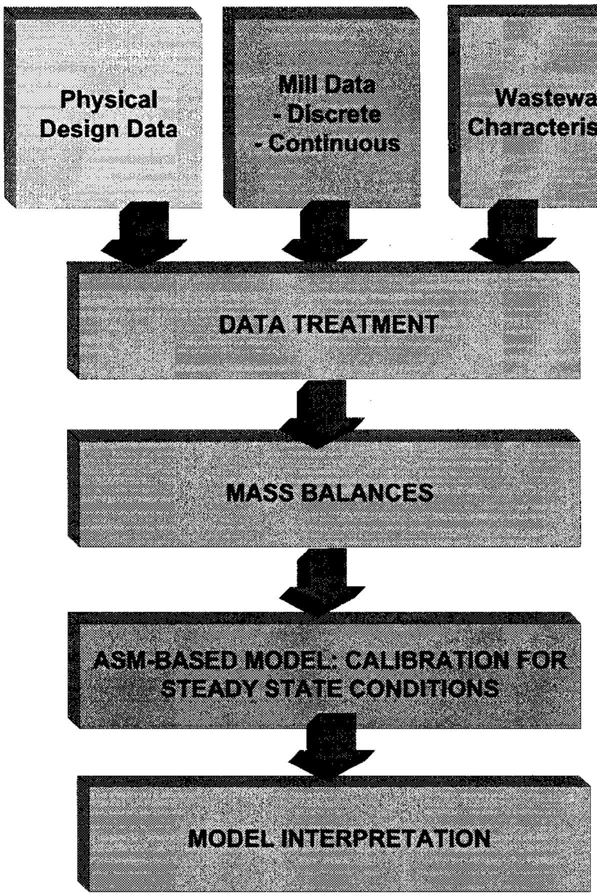

Figure 29: Project methodology

4.3.2. Wastewater characterisation

Nutrient, solids and COD fractionation were carried out on process streams on a number of occasions during a four month period; the sampling points are indicated by triangles in Figure 30. The sample filtration for the COD fractionation was carried out using a Pall-Gelman Supor polyethersulfone membrane of porosity 0.1µm to determine soluble COD (sCOD), and a Pall Type A/E glass fiber filter of porosity 1.0µm to determine filtered COD (fCOD). The testing methods used were Standard Methods plus the HACH method for COD. Regarding the on-line measurements, the on-line UV COD meter was calibrated on site to COD filtered using a Pall Type A/E glass fiber filter of porosity 1.0µm. The samples for both of the nutrient residual measurements in the final effluent are filtered to 0.15µm. Filtering wastewater using such a fine filter is designed to exclude the effect of organic nutrients in residual biomass; it was found that different filter porosities gave different results.

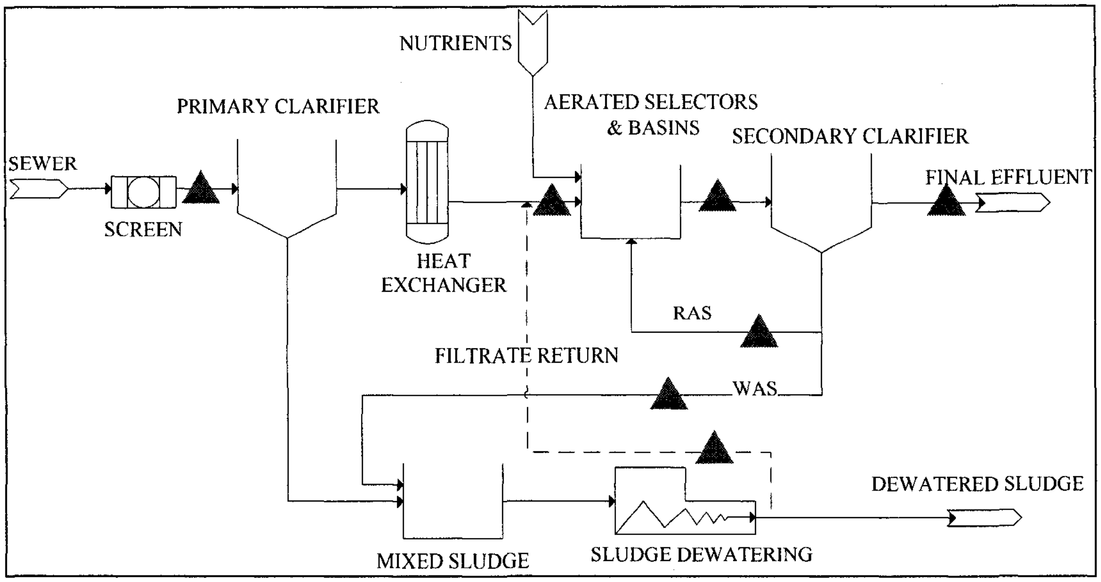

Figure 30: Wastewater treatment plant process and sampling points (▲)

The results of these fractionation tests are presented in Table 60 to Table 63, in terms of the average values and ranges of measured variables. These wastewater characterization results are separate and distinct from the steady state calculations that follow.

Table 60: Solids fractionation results - averages

Stream	*VSS (mg/L)*		*TSS(mg/L)*	
	Average	*Range*	*Average*	*Range*
PC Inlet	1,211	216 – 5,637	1,222	212 – 5,703
AST Inlet	194	113 – 286	190	86 – 288
AST Outlet	2,016	1,722 – 2,616	2,140	1,806 – 2,758
Final Effluent	16	8 – 39	15	3 – 40
RAS	4,205	3,410 – 5,100	4,462	3,612 – 5,404
WAS	12,772	9,100 – 15,468	13,567	9,717 – 16,351

Table 61: Phosphorus fractionation results - averages

Stream	*PO4-P (mgP/L)*		*TP (mgP/L)*	
	Average	***Range***	***Average***	***Range***
PC Inlet	0.32	0.04 – 0.5	0.81	0.3 – 1.2
AST Inlet	0.26	0.03 – 0.4	1.07	0.9 – 1.3
AST Outlet	0.76	0.04 – 2.0	23.4	19.0 – 31.3
Final Effluent	0.81	0.03 – 1.8	1.0	0.2 – 2.4
RAS	1.29	0.2 – 2.1	49.5	41.6 – 56.8
WAS	3.91	2.0 – 5.8	143	95.7 – 194.0
Press Filtrate	4.69	-	9.09	-

Table 62: Nitrogen fractionation results - averages

Stream	NO_3 *(mg N/L)*		NH_{3+4} *(mg N/L)*		N_{ORG} *(mg N/L)*		*TN (mg N/L)*	
	Avg	***Range***	***Avg***	***Range***	***Avg***	***Range***	***Avg***	***Range***
PC Inlet	0.18	0 – 0.9	0.01	0 – 0.1	5.85	1.9 – 11.9	6.03	1.9 – 11.9
AST Inlet	0.03	0 – 0.1	0.03	0 – 0.1	5.61	3.5 – 10.6	5.67	3.5 – 10.6
AST Outlet	0.73	0 – 4.6	1.6	0 – 6.6	154	143 – 202	156	148 – 202
Final Effluent	1.04	0.01 – 4.7	0.8	0 – 3.6	3.3	2.7 – 5.9	5.1	3.8 – 9.1
RAS	0.02	0 – 0.1	1.1	0.6 – 3.6	328	284 – 380	329	288 – 381
WAS	0.03	0 – 0.1	2	0.5 – 3.5	958	685 – 1206	960	686 – 1208
Press Filtrate	0.057	-	3.87	-	38.9	-	42.9	-

Table 63: COD fractionation results - averages

Stream	*sCOD (mg/L)*		*fCOD (mg/L)*		*CODt (mg/L)*	
	Avg	***Range***	***Avg***	***Range***	***Avg***	***Range***
PC Inlet	1,297	1,134 – 1,638	1,658	1,538 – 1,744	3,602	3,396 – 3,840
AST Inlet	1,096	924 – 1,258	1,628	1,308 – 1,818	1,918	1,130 – 2,180
AST Outlet	83	66 – 105	99	80 – 119	3,399	3,060 – 3,685
Final Effluent	81	66 – 94	91	70 – 109	110	79 – 135
RAS	86	76 – 110	99	85 – 122	8,504	7,000 – 10,464
WAS	179	136 – 268	249	180 – 325	40,000	31,806 – 46,686
Press Filtrate	457	-	505	-	1676	

4.3.3. Steady state detection

Process steady states were established by evaluating the derivative of a number of key measured variables in the aerated selector and aerated basin, according to the methodology outlined in Figure 31. Data synchronization was not necessary for steady state detection since all key parameters were located within one hour residence time from each other whereas the steady state duration was set to be greater than six hours. Non-flow data were synchronized between the aerated selector and the outlet of the aerated basin, using the basin residence time of approximately 16 hours, for the purpose of the nutrient, COD and solids mass balances. The 32 steady states detected range in duration from six to thirty-two hours; the data were averaged over the duration of each steady state for further analysis.

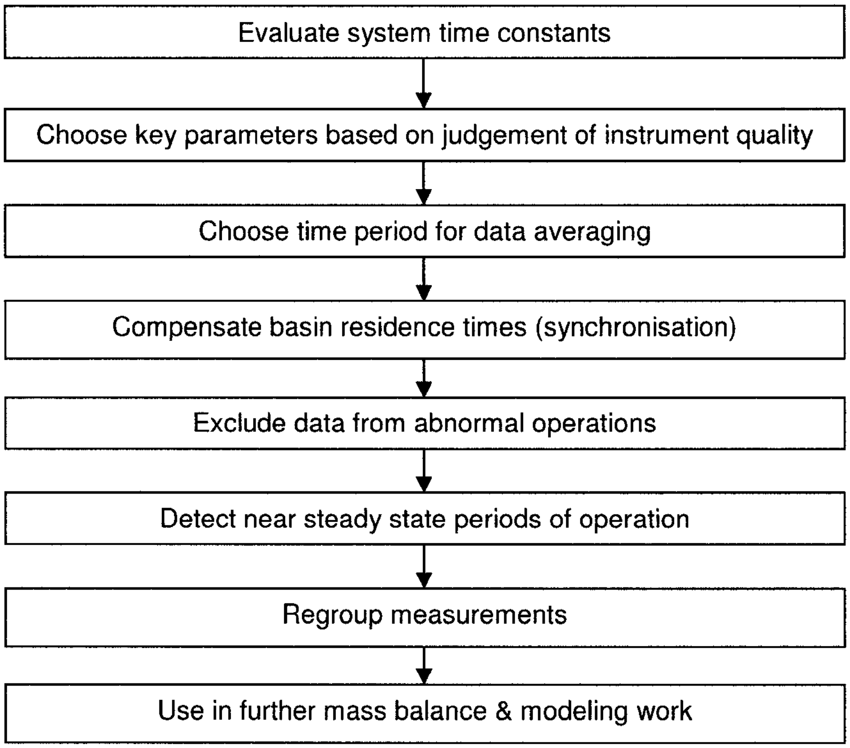

Figure 31: Data preparation step-wise methodology: steady state detection

4.3.4. Mass balances

Mass balances were conducted over the major process units including the aerated selector and basin, as well as the primary and secondary clarifiers. The mass balances were used to calculate unknown parameter values. The phosphorus and solids mass balances were developed by Meijer *et al.* [27], and the COD and nitrogen mass balances were developed by Barker and Dold [231]. A volumetric flow balance is considered valid assuming water density does not change, and assuming negligible evaporation in the basins. Phosphorus, unlike COD and nitrogen, does not transform into gaseous forms in the wastewater process, and therefore the phosphorus mass balance can be closed [27]. As proposed by Meijer *et al.*, the phosphorus mass balance was performed first due to the simplicity of the balance and transformation mechanisms [27].

4.3.4.1. Phosphorus

The mass balance of total phosphorus over the secondary clarifier results in the calculated mass flow rate of total phosphorus in the WAS and RAS streams. There are operational conditions where the phosphorus concentration in the aerated basin is zero. It can be assumed that the activated sludge is phosphorus-deprived during these periods, and therefore bacterial growth is phosphorus-limited.

4.3.4.2. Nitrogen

The nitrogen balances were carried out over the AST and secondary clarifier. The average percentage balance of the calculations was 106%.

Denitrification

The secondary clarifier is considered to be the only basin that is not fully aerated and where sufficient nitrates may be present for denitrification to potentially occur. A mass balance of nitrates over the secondary clarifier for the steady states was conducted using the laboratory-measured nitrate concentrations in the final effluent and the outlet of the aerated basins. This balance shows that denitrification did occur under some process operation conditions. This mass balance assumes that denitrified nitrate is completely transformed into nitrogen gas and no intermediate species are produced [231]. This mass of nitrate represents nitrogen that has been added to the process but was not used for its intended purpose (bacterial growth), and is therefore considered an unnecessary cost to the plant operation.

Nitrification

Similarly, the mass of nitrogen produced via the nitrification process in the aerated selectors and basins was calculated, assuming that the influent to the wastewater treatment plant contains negligible nitrates. This mass of nitrate represents nitrogen that has been added to the process and not used for its intended purpose, however also represents excess oxygen utilization and therefore excess aeration, all of which represent unnecessary costs to the plant operation.

4.3.4.3. Solids

The jet aeration system in the aerated selectors and aerated basins provides both aeration and mixing; high aeration rates risk shearing the flocs and potentially reducing the solids removal performance in the secondary clarifiers, which in turn would result in higher nutrient discharge in the final effluent. Higher aeration also promotes nitrification which consumes supplemental nitrogen unnecessarily. The solids removal across the secondary clarifier was calculated for each of the steady states, the results range from 94% to 100%. This data confirms that the process achieves good solids removal in the secondary clarifier. The relationship between lower solids removal performance and process operation will be investigated further.

4.3.4.4. COD

The COD balances were carried out over the AST and secondary clarifier. The average COD removal is 93%. The average percentage balance of the calculations was 75%, which refers to the ratio of mass flow rate output to mass flow rate input of COD to the secondary treatment system for each steady state process condition. In this context, output COD refers to oxidized COD as well as COD in the final effluent and the WAS stream. Reasons suggested that the COD balance may not be 100% include that there may be denitrification occurring that consumes more carbonaceous substrate than accounted for [231].

4.3.4.5. BOD$_5$:N:P mass ratios

The ratios calculated from the steady state data are presented in Figure 32. A range of ratios have been found in stably operated pulp and paper wastewater plants. The average BOD$_5$:N:P ratio for the steady states was found to be 100: 5.4: 0.6. For nitrogen, this is 116% higher than the lower limit from the literature (100:2.5) and 20% higher than the upper limit from the literature (100:4.5). For phosphorus, this is 49% higher than the lower limit from the literature (100:0.4) and equal to the upper limit from the literature (100:0.6).

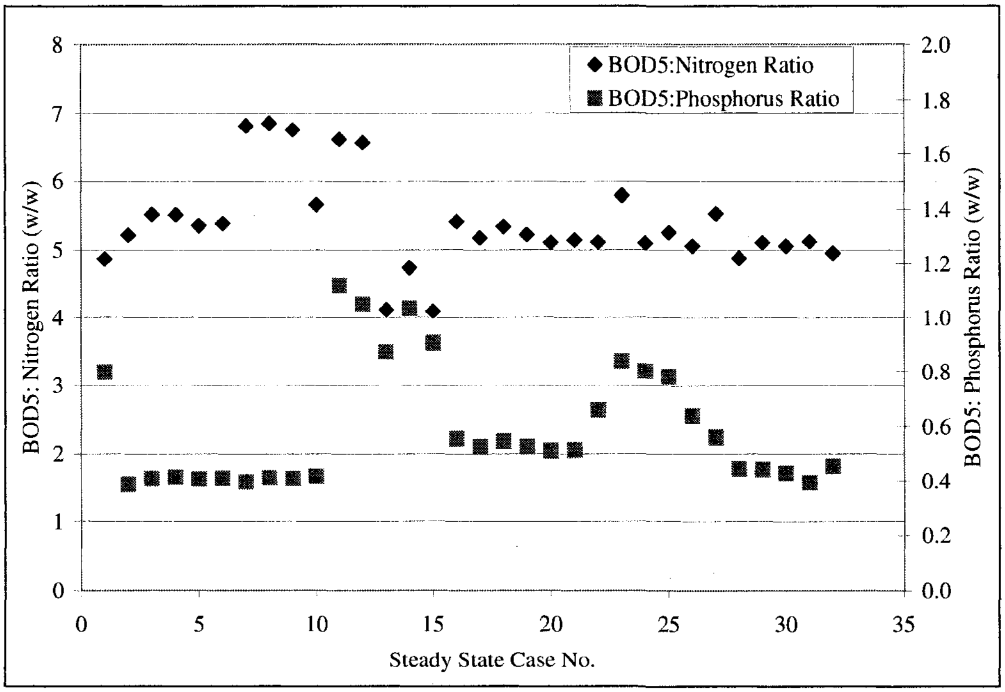

Figure 32: BOD$_5$:N:P mass ratios

4.3.4.6. Cost savings

Based on the nutrient balances outlined above, the supplemental nutrients added to the pulp and paper wastewater treatment plant are not only assimilated into microorganisms in order to remove carbonaceous substrate and allow microorganisms to carry out reproductive and maintenance activities, but also the nitrogen added is being transformed through the biochemical processes of nitrification and denitrification. This wastewater plant is not designed to take advantage of these processes, and they are not desirable since they consume resources in the form of aeration and ammonia-nitrogen.

The cost savings associated with the unnecessary nitrogen addition that resulted in nitrification and denitrification biochemical processes are estimated to be in the order of $13,000 annually, depending on the operation of the wastewater plant. This does not take into account the additional savings on aeration associated with the extent that nitrification is occurring.

As seen in the discussion of the BOD_5:N:P ratios, it is possible to maintain stable AST operation for high BOD removal and simultaneous nutrient minimization or optimization, which may lead to lower ratios. The cost savings are estimated to be in the range of $85,000 annually, with respect to the possible reduction in dosing of urea and phosphoric acid.[8] It should be noted that not all pulp and paper wastewater treatment plants will operate successfully with the same BOD_5:N:P ratio, the ratio is dependent on the upstream pulp and paper process. The nature and source of nutrients and organic load in the wastewater itself can vary depending on the combination and variation in upstream process operation

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[8] This calculation is based on the average difference between the operating BOD_5:N:P mass ratio compared to the minimum and maximum ratios from the literature, considering either nitrogen or phosphorus, not the combination of the two. The value of $85,000 refers to the savings possible using the difference between the operating and the minimum literature ratio for phosphoric acid as well as the difference between the operating and the maximum literature ratio for urea. The calculation is based on the 32 steady states found during the four month data collection period and assumes that the same range and proportion of BOD_5:N:P mass ratios, and thus the same average ratios, would be found during a full year of operation. The calculation does not include the capital cost of installation of new instrumentation or control equipment.

[47]. Laboratory scale activated sludge plants have been operated successfully with zero phosphorus addition for pulp mill effluent [52], and full scale aerated stabilization basins have operated successfully with zero nutrient addition [62]. Operation of the wastewater treatment plant will also vary with a high dependence on season and process cooling, since the kinetics of the biological processes are highly sensitive to temperature.

The major cost saving associated with reduced nutrient addition is the saving associated with the purchase of the chemicals themselves. There would also be cost and energy savings associated with reduced aeration requirements if the nitrification biochemical process is eliminated. Certainly at the mill studied, the change to remote operation of the wastewater plant has resulted in reduced operating costs. This adjustment is being assisted through the use of on-line instrumentation, and could be further assisted through the regular assessment and use of nutrient, solids and COD balances. A regular mass balance assessment could indicate when nitrification or denitrification processes were occurring and corrective action could be taken quickly thereafter.

4.3.5. Modelling

A better understanding of the biological processes in pulp and paper treatment plants can be gained using the Activated Sludge Models (ASM) developed for the municipal wastewater industry. Wastewater characterisations of pulp and paper wastewater from other ASM-based studies are presented in Table 25. These studies cover a broad range of pulp and paper processes as well as a range of wastewater treatment plant processes. The study results range from “good agreement with plant operating data“ [165] to “a poor model response for the effluent COD and suspended solids concentrations” [235]. Some interesting characterisation and modelling work was conducted for the Hylte mill in Sweden [4, 119], which has unusual pulp and paper and wastewater process configurations and is therefore not included in the comparison in Table 25.

Table 64: Fractionation of pulp & paper primary effluents

Pulp & Paper Process	***WWTP Process***	**SRT**	**HRT**	***Fraction***				***Reference***
				S_S	S_I	X_S	X_I	
	Units	*d*	*h*	*mg COD/mg total COD*				
TMP/RCF (1993, 1994)	*ASB*	20 - 29	50	0.15, 0.29	0.093, 0.082	0.64, 0.54	0.12, 0.088	[165]
BKM	*ASB*		82	0.42	0.33	0.11	0.14	[167]†
CTMP	*Plug-flow AST**	6.5	4.7	0.49	0.14	0.3	0.07	[169]
CTMP	*Plug-flow AST**	6.5	4.7	0.28	0.33	0.34	0.05	[166]
BKM, BKM/TMP	*UNOX***		6.5 – 7	0.24, 0.44	0.36, 0.32	0.42, 0.23	0.07, 0.03	[168]
Municipal (ASM3 default)	-			0.43	0.13	0.33	0.11	[169]
TMP	*CSTR AST*	4 – 6	16	0.47 – 0.52	0.02 – 0.07	0.12 – 0.34	0.12 – 0.34	This study (range by alternative methods)

†*cited in* [169]

*5 x CSTR's in series approximates a plug-flow AST

**UNOX: high-oxygen AST, 3 x CSTR's in series, pseudo-plug flow

The ASM models consist of mechanistic lumped-parameter models, which are used to describe the overall biological reactions occurring in an activated sludge system. This approach works well for long retention time processes, such as aerated stabilisation basins (ASB) or lagoon systems [59], but it does not take into account local conditions nor reactions occurring on a microscopic scale within the biological flocs. Modelling of a well-mixed (CSTR) AST with a relatively short retention time (approximately 16 hours) for industrial wastewater represents a significant challenge for the application of the ASM models.

The wastewater characterisations included in Table 25 and in many other studies [1] assume a constant influent wastewater characterisation in terms of the fraction of each COD component (S_I, S_S, X_I, and X_S) with respect to time. The influent to a wastewater treatment plant at a pulp and paper mill varies significantly over the course of a day, in terms of total COD concentration, as seen in Figure 33, which presents the minute average total COD measured by an on-line UV instrument at the inlet of the AST. This graph demonstrates the variation possible on a day when the paper machine shut down between 7am and 2.30pm and the TMP plant shut down between 7am and 6pm, with a maximum COD of 1670 mg COD/L and a minimum COD of 1190 mg COD/L, not including instrument noise.

The variation of each COD component as a fraction of the total COD has not been measured in pulp and paper wastewater during the course of a day. However, it can be reasonably assumed that variation exists and is attributable to changes in the mill production rate and grades, variations in the readily biodegradable methanol and 'lights' present in condensate streams sent to effluent from the energy recovery process, variations in slowly biodegradable lignin and cellulose in fibre-rich streams sent to effluent from the whitewater or other storage tanks, and variations in the quantity of wash-up chemicals sent to effluent when the mill plant is shut down for maintenance.

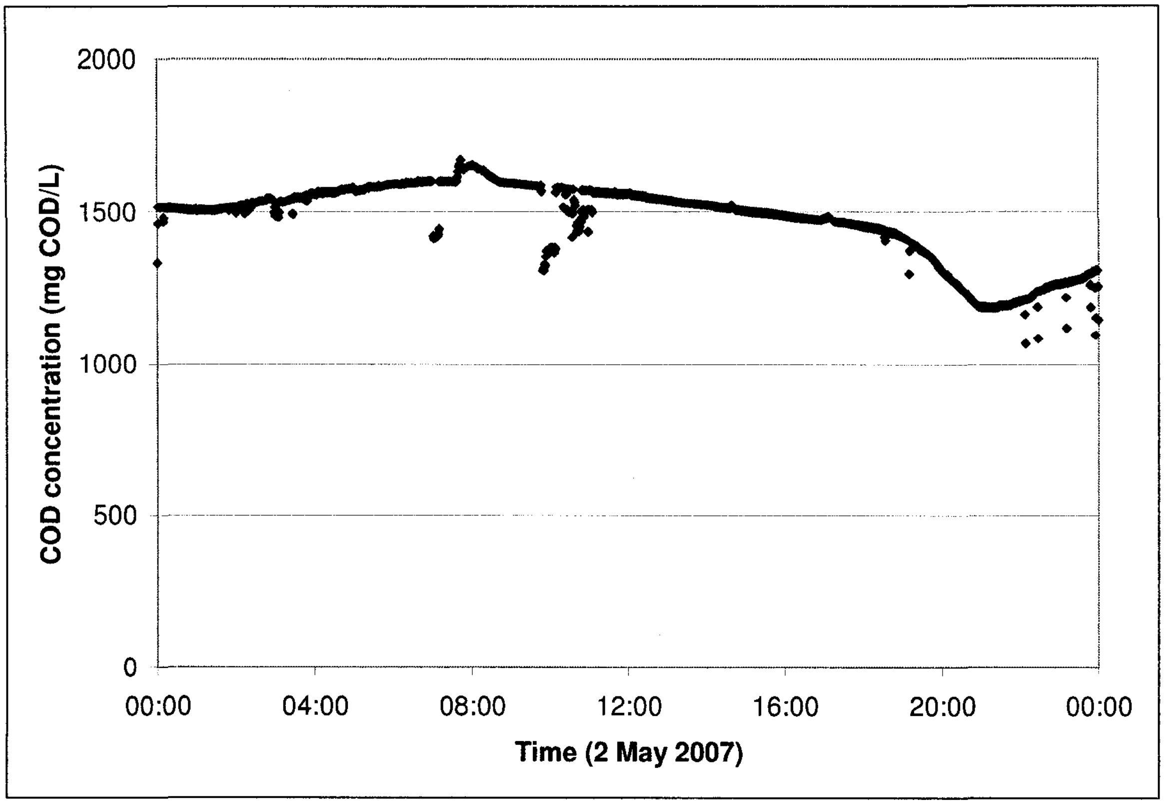

Figure 33: Total COD primary effluent, minute average data (on-line data), 2 May 2007

The results of steady state modelling carried out using experimental and mill data are presented and an interpretation of the nutrient transformations occurring in the activated sludge treatment of pulp and paper wastewater is proposed. The methodology employed includes meticulous data treatment, the identification of disparate operating conditions, and the development of a calibration process applied to each operating condition that accounts for varying nutrient transformation conditions.

4.3.5.1. Biological Model

The biological model presented by Brault *et al.* (2006, 2008) is a hybrid model developed for pulp and paper wastewater based on ASM1. ASM1 was chosen as the basis of the model in part because hydrolysis has been shown to be a significant process in the activated sludge treatment of industrial wastewater, and for pulp and paper effluent in particular [23, 43], whereas ASM3 places more emphasis on storage of readily biodegradable substrate than hydrolysis.

The major modifications to the ASM1 model include:

1. The incorporation of nutrient limitation to bacterial growth rates via the addition of a Monod switching function for both ammonia-nitrogen and phosphate-phosphorus;
2. The addition of a 'phosphatification' process by which soluble organic phosphorus is converted into ortho-phosphates for growth, analogous to the ammonification process;
3. The addition of hydrolysis of organic phosphorus, analogous to the hydrolysis of organic nitrogen;
4. The addition of a 'particulate biodegradable organic phosphorus' fraction (X_{PD}), analogous to the nitrogen fraction X_{ND}, and the addition of a 'soluble biodegradable organic phosphorus' fraction (S_{PD}), analogous to the nitrogen fraction S_{ND};
5. The consideration of nutrient fractions of nitrogen and phosphorus relating to particulate inerts, X_I, from cell decay, X_U, and to particulate biomass, X_{BH} and X_{BA}, as constant fractions of their respective COD fractions (X_{NU}, X_{PU}, X_{NB}, and X_{PB}); and
6. The omission of nutrient fractions of nitrogen and phosphorus relating to the COD fractions S_I, S_S and X_S due to the extremely low concentrations found for pulp and paper wastewater (see results section for details).

The modifications (1) to (4) were made due to the fact that pulp and paper wastewater is known to be deficient in readily available macronutrients, typically nitrogen and phosphorus, in relation to the requirements of the microorganisms used in an activated sludge treatment process to consume organic substrate in the wastewater [50, 51]. The limitation of biomass growth rates due to nutrient concentration, specifically ammonia-nitrogen and ortho-phosphate concentration, is considered necessary for pulp and paper wastewater; various combinations of this theory have been used in previous studies [4, 119, 166]. The modifications

(5) and (6) were made due to the measured nutrient concentrations in the primary effluent and in the mixed liquor.

4.3.5.2. Influent Characterisation

Experimental wastewater characterisation results are presented below, followed by mass balance results and model results.

28-day BOD Analysis

It was found that the BOD respirometry test results for a 10-day period were not sufficient to adequately fit a curve to the data; the BOD curve had not sufficiently approached the ultimate BOD concentration. It was for this reason that the BOD respirometry work was conducted for a 28-day period; this duration gave a better approximation of the ultimate BOD concentration. The results for the primary effluent are presented here; final results only are presented for the influent to the primary clarifier.

The BOD respirometry results were consistent between the three test sets. The results are depicted in Figure 34 for primary effluent; a single curve is shown in Figure 34 for the purpose of clarity. The curves were corrected for the seed BOD and for a number of small process shocks that occurred to all samples between day 15 and day 27. All curves showed no signs of impediment or inhibition at the beginning of the test, which indicates that the seed did not require time to acclimatise to toxicity in the wastewater.

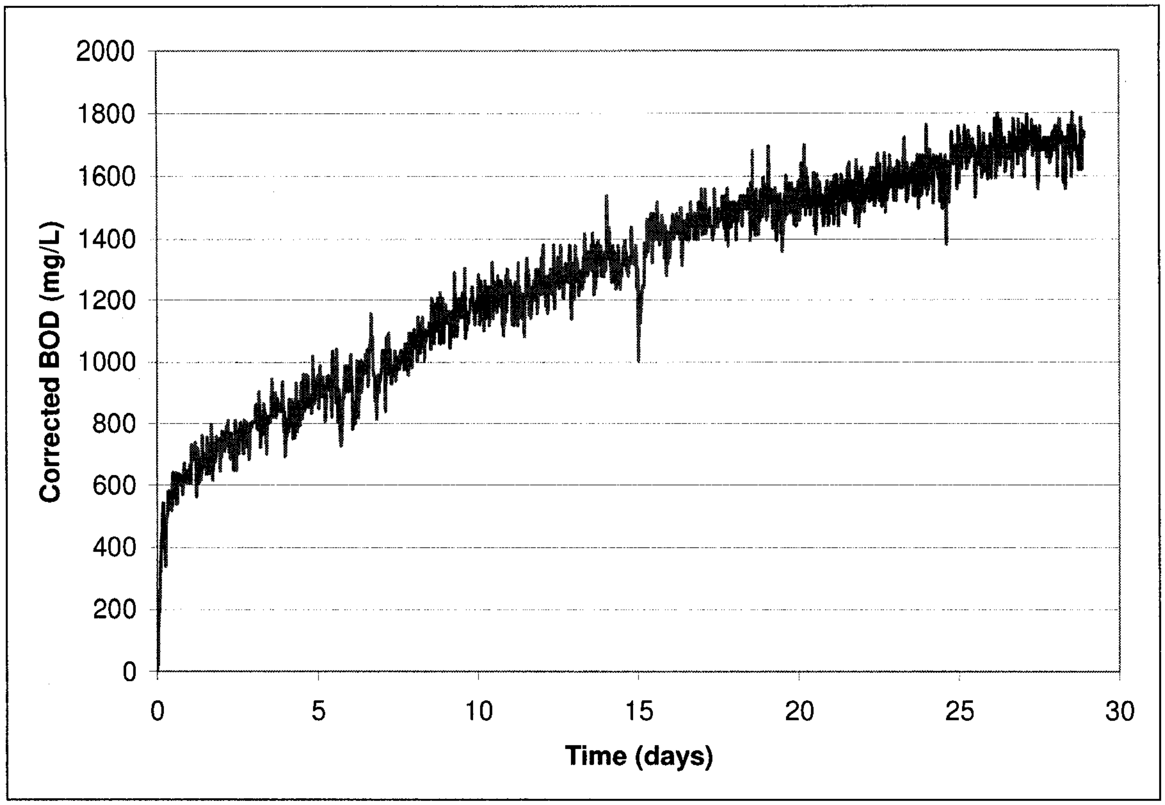

Figure 34: Primary effluent BOD1-28, single curve, corrected BOD

None of the curves displayed the expected asymptotic behaviour that is seen in municipal wastewater [1], in fact, they all appear to be steadily rising. This indicates that a large proportion of the organic substrate is slowly biodegradable; it is only a matter of how slowly it degrades. This is further expressed as the first order rate constant of BOD versus time, k_{BOD}, which was found to be between 0.051 and 0.057 d^{-1} for the primary effluent in this study, compared to 0.15 to 0.8 d^{-1} found for municipal wastewater having undergone primary treatment [1]. Current work by NCASI on the final effluent of pulp and paper mills indicates that the carbonaceous BOD measurement of that stream required 120 to 150 days for the BOD to approach an asymptote [236]; the COD in this stream corresponds to the soluble inert S_I fraction.

While the average BOD_5 concentration in the primary effluent, 426 mg/L, is comparable to the average concentration data for a municipal primary treated effluent, 246 mg/L [27], the total BOD_5 load in the pulp and paper wastewater, 12,660 kg/d, is much larger than the municipal load of 1,680 kg/d.

Primary Effluent Wastewater Characterisation

The combination of the above continuous BOD and the COD measurement data is used to convert the COD fractions into the ASM1 wastewater fractions, the results of which are summarised in Table 65. The BOD_5 reported by the external laboratory in the final effluent for the sample date was 8 mg/L. The correction factor ϕ_{BOD} represents the inert COD generated in biomass lysis during the BOD test. Modification of the correction factor ϕ_{BOD} between the recommended values of 0.1 to 0.2 results in variation in only the X_S and X_I fractions (not presented). It was found that a ϕ_{BOD} of 0.087 was necessary in the primary effluent in order to arrive at a positive X_I value for one of the data sets, which is particularly small. In two of the primary effluent data sets, the total BOD calculated is larger or very close to the total COD measured, which renders it difficult to solve for a reasonable ϕ_{BOD} value and obtain a positive X_I fraction.

Table 65: ASM1 wastewater characteristics (mg COD/L),
ϕ_{BOD} = (BCOD – BOD_{28}) / BCOD = 0.15

Stream	S_I	S_S	X_S	X_I	***COD total***
Raw Influent Average	79	1,249	786	916	3,030
Primary Effluent Average	79	1,201	1,220	ND (-340)	2,160

Where ND = not determined, calculation method results in negative X_I concentration, which is not possible.

The methodology employed to determine biodegradable COD (BCOD) is "almost intrinsically subject to inaccuracy (10 to 20%)", according to its authors [1]. From the results in Table 65, this wastewater characterisation methodology is not considered to be suitable for pulp and paper wastewater, due to the fact that this wastewater does not display any asymptotic behaviour during long-term BOD experiments, indicating that the distinction between the slowly biodegradable X_S fraction and the rapidly biodegradable S_S fraction is not as clear for pulp and paper wastewater as it is for municipal wastewater.

Primary Effluent Wastewater Characterisation for Pseudo-steady states

It was decided that the wastewater characterisation for the purposes of modelling work should be based on measurable parameters available for each pseudo-steady state scenario. For this purpose, methods from the 2003 WERF report [232] were used, namely:

- Soluble inert (unbiodegradable) fraction (S_I) **:** 100% of the final effluent soluble COD, calculated using the daily laboratory total COD concentration values multiplied by the average fraction of soluble to total COD in the final effluent from the wastewater characterisation work;
- (Soluble) readily biodegradable fraction (S_S): the difference between the influent soluble COD and S_I concentration, calculated using the on-line COD in the primary effluent multiplied by the average fraction of soluble to total COD in the primary effluent from the wastewater characterisation work;
- Particulate inert (unbiodegradable) fraction (X_I): derived from mass balances, fxi is calculated as a function of mixed liquor VSS, influent flow rate, influent total COD, sludge age, reactor volume, heterotroph yield coefficient, endogenous decay rate, endogenous residue fraction, mixed liquor solids COD to VSS ratio, soluble unbiodegradable COD fraction, plus the first step of model calibration to the measured mixed liquor TSS concentration; and

- (Particulate) slowly biodegradable fraction (X_S): determined from the COD balance in the primary effluent: $X_S = COD_{influent, total} - S_I - S_S - X_I$
  It is important to note for pulp and paper wastewater that the X_S fraction may contain large soluble slowly biodegradable substrate such as lignin, and therefore the 'particulate' label is not entirely appropriate.

The results of this characterisation for all 22 steady state events are presented in Figure 35, including the calibrated particulate inert X_I fraction (fxi). It is clear from Figure 35 that the fraction of the rapidly biodegradable COD, fss, and the fraction of the soluble inert COD, fsi, are reasonably constant throughout the data set: fsi varies from 0.022 to 0.068; fss varies from 0.47 to 0.52. The particulate inert fraction fxi is calculated as a function of sludge retention time, and for this reason there is a larger range of fxi values, from 0.12 to 0.34, and fxs calculated as the balance of total COD varies from 0.12 to 0.34. This characterisation method, while suitable for the modelling exercise, indicates that the distinction between the slowly biodegradable X_S fraction and the particulate inert X_I fraction is not as clear for pulp and paper wastewater as it is for municipal wastewater, and that the particulate inert components (large fibres with attached colloidal material) may be biodegradable to some extent for a longer sludge retention time.

The ASM1 wastewater characteristics of the primary effluent are generally comparable to those found for pulp and paper wastewater: S_I of 0.14 to 0.36, S_S of 0.24 to 0.49, X_S of 0.11 to 0.42, and X_I of 0.03 to 0.14 [169], as well as those for municipal wastewater found in the literature: S_I of 0.03 to 0.10, S_S of 0.09 to 0.42, X_S of 0.1 to 0.48, and X_I of 0.23 to 0.50 [1].

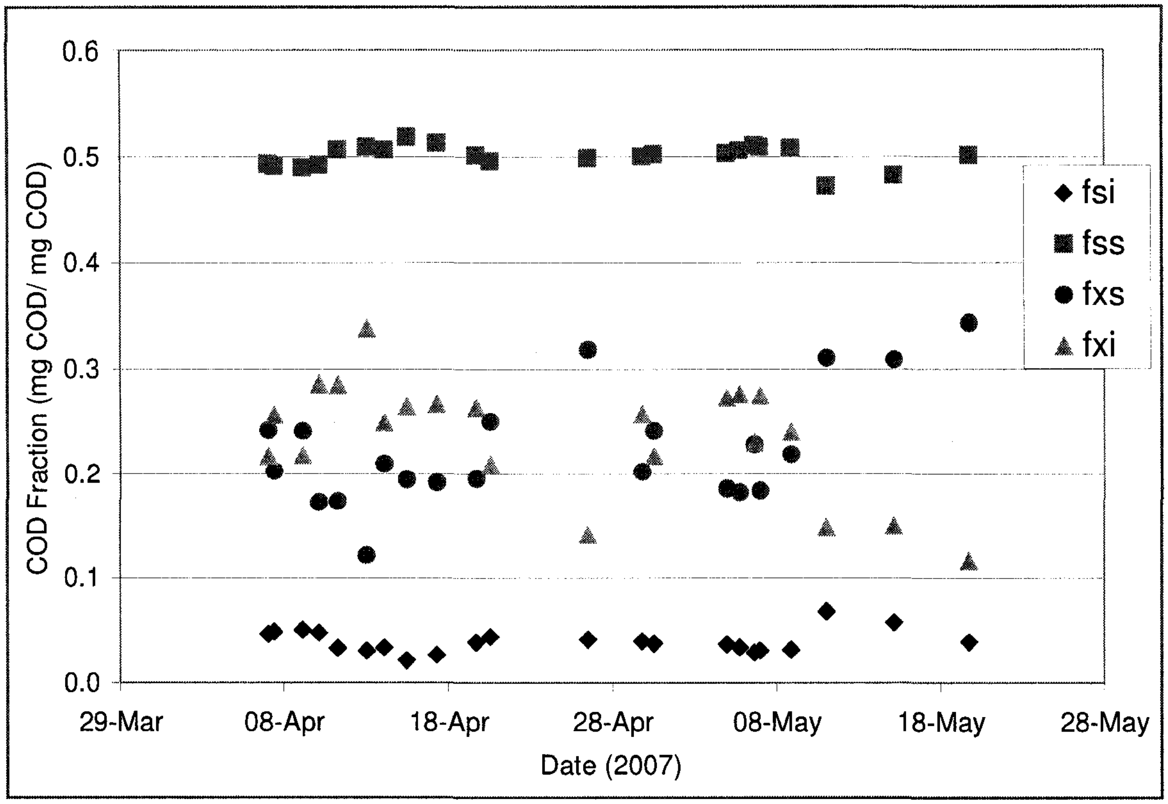

Figure 35: Steady state wastewater characterisation - Xi calibrated to mixed liquor total suspended solids

4.3.5.3. Biological Model

Nutrient fractions & transformations

A number of wastewater ratios were calculated from the wastewater characterisation experimental data, details of which are summarised in Table 66. As described elsewhere [220], the nutrient fractions in the mixed liquor were determined using the theoretical nutrient concentrations in the biomass (inxb = 0.086 mg N/mg COD, ipxb = 0.016 mg P/mg COD), an assumed concentration in the cell decay COD fraction X_U (inxu = 0.06 mg N/mg COD, ipxu = 0.015 mg P/mg COD), and the remainder nutrient concentrations attributed to the particulate inert COD fraction X_I (inxi = 0.03 mg N/mg COD, ipxi = 0.0016 mg P/mg COD). The inxi and ipxi concentrations in the mixed liquor fit well those measured in the primary effluent stream, if all organic nutrients in the primary effluent are attributed to the X_I fraction.

Table 66: Wastewater measured ratios summary

Location	***Parameter or Ratio***	***Units***	***Measured Range***	***ASM1, ASM2, ASM3 default values***	***Model uses:***
Influent	Organic nitrogen to total COD ratio	mg N/ mg COD	0.0016 – 0.0093	0.01 – 0.04	Zero nutrient concentration: insi, inss, inxs inxi = 0.03*
Influent	Organic phosphorus to total COD ratio	mg P/ mg COD	0.00025 - 0.00085	0 – 0.01	Zero nutrient concentration: ipsi, ipss, ipxs ipxi = 0.0016*
Influent	f_{CV} (particulate COD to VSS ratio)	mg XCOD/ mg VSS	1.93 – 2.64	2.2	Calculate for each steady state $f_{CV} = \frac{XCOD}{VSS} = \frac{X_I + X_S}{VSS}$
Influent	X_{II}	mg COD/L	0		Zero concentration
Influent	f_{BOD} (BOD_5: BODu)	mg BOD/ mg COD	PI: 0.18 – 0.28 PE: 0.21 – 0.23	0.66	Calculate for each steady state $f_{BOD} = \frac{BOD_5}{S_S + X_S}$
Mixed	Organic nitrogen to	mg N/	0.049 –	0.086	inxbh = inxba = 0.086

Location	Parameter or Ratio	Units	Measured Range	ASM1, ASM2, ASM3 default values	Model uses:
liquor	COD ratio	mg COD	0.058		inxu = 0.06 inxi = 0.03
Mixed liquor	Organic phosphorus to COD ratio	mg P/ mg COD	0.0064 - 0.0101	0.02	ipxbh = ipxba = 0.016 ipxu = 0.015 ipxi = 0.0016
Mixed liquor	f_{CV} (particulate COD to VSS ratio)	mg XCOD/ mg VSS	1.34 – 1.85	1.48	Average value: 1.63 mg XCOD/mg VSS
Mixed liquor	X_{II}	mg COD/L	X_{II} = 5%TSS		fxii = 0.208†

(PI) Primary Influent, (PE) Primary Effluent

†Calculated from: Average mixed liquor xii = 0.052*vss; active biomass = 0.25*vss‡; xii = 0.052/0.25*(active biomass)

‡ Approximately 25% of MLVSS is present as active biomass [237]

*inxi(primary effluent) = inxi(mixed liquor), ipxi(primary effluent) = ipxi(mixed liquor), all influent nutrients attributed to X_I fraction

Mass balances

The experimental, on-line and physical data collected were treated and mass balances were produced for each of the pseudo-steady state scenarios identified [3]. The volumetric flow balance and phosphorus balances were calculated from measurements and close 100% [27]. The COD balances close 85% on average for these 22 pseudo-steady states, the nitrogen balances close 93% on average, following a standard methodology that includes nitrification and denitrification processes [231]. Data reconciliation was conducted for the supplemental phosphorus dosing measurement and total suspended solids measurements at the AST inlet. The resulting mass balances provide a rigorously-determined basis for further modelling work.

Measurement accuracy, repeatability, measurement redundancy, and process variation were evaluated for mill on-line and laboratory measurements. The propagation of measurement and process uncertainty through the mass balances was also evaluated; however, it is not possible to ever reproduce the exact process conditions that generated the mill on-line data. When measuring bulk process conditions such as the dissolved oxygen concentration and temperature in the AST basin and inferring small changes in nutrient concentrations or reaction rates, the uncertainty at each data point is expected to be large and variable. The uncertainty of reaction rates has therefore not been evaluated.

Calibrated pseudo-steady states

The ASM1-based model was calibrated to measured data for each pseudo-steady state scenario developed using the mass balance results. The development of the calibration methodology is described below.

Phosphorus

It was found that the hydrolysis of organic phosphorus and phosphatification processes are necessary to model the nutrient transformations occurring in the AST. Without these two processes, the model demonstrated a severe bacterial growth limitation due to low ortho-phosphate phosphorus concentrations.

Solids

The model includes a point-settler secondary clarifier model due to the difficulties encountered in calibrating the existing settling models for pulp and paper solids. Sludge age or sludge retention time is therefore calculated using the volume of solids in the mixed liquor, excluding the volume of solids in the secondary clarifier, and the nutrient transformations in the secondary clarifier are not modelled. This is a limitation encountered when simplifying reality with a model.

The calibration of the X_I fraction was carried out systematically for a range of heterotrophic yield (Y_H) and heterotrophic decay (b_H) values. The heterotrophic yield value of 0.666 g COD/g COD and the heterotrophic decay value of 0.50 d^{-1} were found to fit the measured data best. The heterotrophic decay value is in agreement with that found in recent research of a similar pulp and paper wastewater treatment plant [220].

Carbonaceous substrate (BOD) removal

Once the solids balance had been established, the models were found to be very sensitive to three parameters: the heterotrophic maximum growth rate, μ_H, the autotrophic maximum growth rate, μ_A, and the anoxic growth factor, η_g. The heterotrophic maximum growth rate, μ_H, was set at a value of 18 d^{-1}, which gave good results for BOD removal ($\mu_A = 0.5$, $\eta_g = 0.08$) for the data sets where nitrate residuals were measured (where partial nitrification-denitrification is obviously occurring). This μ_H value is in agreement with that found in recent research of a similar pulp and paper wastewater treatment plant [220].

Nitrogen

The concentrations of ammonia, nitrate, and ortho-phosphate at the outlet of the AST were used as the calibration criteria for the nutrient transformations.

A uniform model capable of describing the entire data set was extensively investigated but was not found. Two possible scenarios can be proposed to explain the residual nitrates and ammonia measured at the outlet of the AST: (A) partial nitrification-denitrification is occurring, and subsequently the rate of nitrification diminishes, or (B) partial nitrification-denitrification is occurring, and subsequently the rate of denitrification increases. The proposed models were calibrated according to scenario (A), but it was not possible to evaluate scenario (B) with any great accuracy; given the already low-to-zero autotrophic maximum growth rates, the range of anoxic growth correction factors that reasonably fit the measured data is quite large.

Two models that each describe a part of the nutrient residual data were investigated. The model results are compared to the measured nutrient residual data in Figure 36. Model 1 refers to the situation where partial nitrification-denitrification is occurring ($\mu_A = 0.5\ d^{-1}$, $\eta_g = 0.08$, $k_a = 0.08$, $k_p = 0.08$, $b_H = 0.62$) and Model 2 refers to the situation where nitrification is not occurring ($\mu_A = 0$, $\eta_g = 0$, $k_a = 0.025$, $k_p = 0.08$, $b_H = 0.50$). It is clear that two disparate process conditions, zero nitrification and partial nitrification-denitrification, can each be modelled by a uniform model, but in fact a uniform model does not describe the entire data set in this study. For this reason, the kinetic parameters that describe nutrient transformations were adjusted for each individual pseudo-steady state.

Once the heterotrophic maximum growth rate was determined, the autotrophic maximum growth rate, μ_A, and the anoxic growth factor, η_g, were calibrated for individual pseudo-steady state cases. The range of values investigated for each case was 0 to 1.0 d^{-1} for μ_A and 0 to 0.1 for η_g, which were used to calibrate the nitrate concentration at the AST outlet. The ammonification rate, k_a, was used to further calibrate the ammonia concentration at the AST outlet. The half saturation constant for the assimilation of nitrogen for autotrophs, K_{NA}, was reduced to a value of 0.05 g COD/m^3 for all model calibration work in order to allow the nitrification process to proceed at low ammonia concentrations.

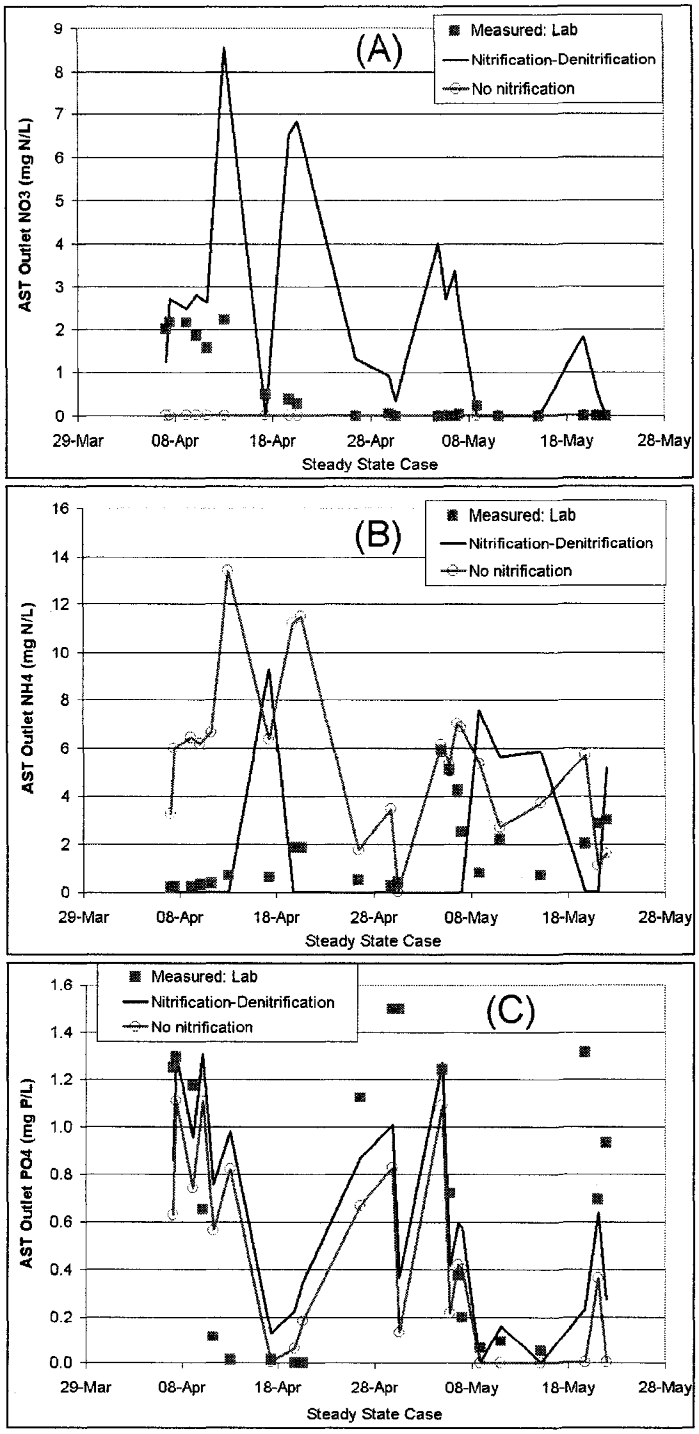

Figure 36: Uniform model approach, AST outlet nutrient residuals measured & modelled (a) Nitrate (b) Ammonia (c) Phosphate

The proposed model was calibrated for each pseudo-steady state case; the parameters of which are presented in Table 67 in comparison with selected values from the literature, ranging from the ASM default parameters to studies on pulp and paper wastewater. Two of the parameters that were used to calibrate each case, μ_A and ka, were found to have values generally lower than those found in the literature, although ka was found to have a large range of values in this study. Many of the parameters listed in Table 67 are default parameters that were investigated but found not to be sensitive in this model. It should be noted that the calibrated solution for each pseudo-steady state is not necessarily a unique solution due to the nature of the ASM model. The individually adjusted kinetic parameters for each scenario are listed in Table 68. As previously stated, for the later scenarios, given the already low-to-zero autotrophic maximum growth rates, the range of anoxic growth correction factors that reasonably fit the measured data is quite large. So while an anoxic correction factor of zero may fit the measured data, laboratory analysis is required to validate this value.

Table 67: Kinetic & stoichiometric parameters: calibrated model

Parameter	*Symbol*	*Units*	*Literature Values*	*Literature References*	*Model (Range)*
Individually adjusted kinetic parameters					
Autotrophic maximum growth rate	μ_A	1/d	0.8 15* 0.4	**1** **2** **3**	**0.05 – 0.30**
Correction factor for anoxic growth of	η_g	-			**0 – 0.7**

Parameter	***Symbol***	***Units***	***Literature Values***	***Literature References***	***Model (Range)***
heterotrophs (denitrification)					
Specific ammonification rate	k_a	m^3/g COD. d	0.08 0.07 0.003-0.004	**1** **2** **7**	**0.009 – 0.4**
Specific phosphatification rate	k_p	m^3/g COD. d	0.03 – 0.8	**7**	**0.029 – 0.4**
Constant kinetic parameters					
Heterotrophic maximum growth rate	μ_H	1/d	6 39 2.3 – 4.79	**1** **2** **4**	18
Heterotrophic decay rate	b_H	1/d	0.62 0.5 – 0.58 0.13	**1** **3** **5**	0.50
Autotrophic decay rate	b_A	1/d	0.05 0.29	**1** **2**	0.04
Yield of heterotrophic biomass growth	Y_H	g COD/ g COD	0.67 0.44, 0.62 0.76	**1** **6** **5**	0.666
Yield of autotrophic biomass growth	Y_A	g COD/ g N	0.24 0.3	**1** **2**	0.24
Correction factor for anoxic hydrolysis	η_h	-			0.40

Parameter	***Symbol***	***Units***	***Literature Values***	***Literature References***	***Model (Range)***
Half saturation constant for assimilation of carbon (heterotrophs)	K_{SH}	g COD /m³	20 158 5	**1** **2** **3**	20
Phosphorus half saturation constant (heterotrophic)	K_{PH}	mg P/L			0.01
Phosphorus half saturation constant (autotrophic)	K_{PA}	mg P/L			0.01
Half saturation constant for assimilation of nitrogen (heterotrophs)	K_{NH}	g COD /m³			0.05
Half saturation constant for assimilation of nitrogen (autotrophs)	K_{NA}	g COD /m³	1 2.7	**1** **2**	0.05
Maximum specific hydrolysis rate	k_h	g COD /g cell COD.d	3 7.9 8.1	**1** **2** **5**	3
Hydrolysis half saturation constant	K_X	g COD /g cell COD	0.03 0.5	**1** **2**	0.03

Parameter	***Symbol***	***Units***	***Literature Values***	***Literature References***	***Model (Range)***
Oxygen half saturation constant (autotrophic)	K_{OH}	g O_2/m^3			0.20
Oxygen half saturation constant (heterotrophic)	K_{OA}	g O_2/m^3			0.40

* Unconstrained optimal model solution, not measured value

References:

1: [173]
2: [166]
3: [214]
4: [165]
5: [169]
6: [168]
7: [220]

Table 68: Individually adjusted kinetic parameters: calibrated model

Scenario	μ_A	η_g	k_a	k_p
1	0.18	0.04	0.10	0.40
2	0.17	0.08	0.13	0.40
3	0.16	0.07	0.09	0.40
4	0.16	0.08	0.06	0.03
5	0.20	0.09	0.40	0.04

Scenario	μ_A	η_g	k_a	k_p
6	0.14	0.17	0.07	0.06
7	0.30	0.18	0.20	0.30
8	0.11	0.30	0.04	0.18
9	0.11	0.45	0.05	0.09
10	0.08	0.70	0.05	0.40
11	0.12	0.50	0.07	0.40
12	0.05	0	0.03	0.40
13	0.08	0	0.02	0.17
14	0.05	0	0.02	0.40
15	0.05	0	0.01	0.07
16	0.05	0	0.01	0.05
17	0.05	0	0.01	0.08
18	0.05	0	0.02	0.08
19	0.05	0	0.01	0.08
20	0.05	0	0.01	0.40
21	0.05	0	0.08	0.40
22	0.05	0	0.05	0.40

The nutrient residuals for nitrate, ammonia, and phosphate found from the individually adjusted kinetic parameter model are compared to the measured values in Figure 37. The modelled nitrogen residuals are found to fit very well to the measured data, while the modelled phosphate residuals fit less well, which is understandable given the existence of three parameters to describe the nitrogen transformation processes, μ_A, η_g and k_a, compared to one parameter, k_p, to describe the phosphorus transformation processes. There is also more uncertainty associated with the phosphoric acid dosing rate calculated in the mass balances compared to the measured urea dosing rate due to the quality of measured data available.

It should be noted that the pseudo-steady state cases 9:06pm 8 May and 3:52am 15 May have poor modelled BOD removal due to phosphorus deficiency, with modelled BOD residuals of 77 mg BOD/L and 60 mg BOD/L, respectively. This indicates that either the calculated phosphoric addition rate from the mass balances is inadequate or that phosphorus previously stored by the biomass became available, in addition to the phosphorus calculated in the mass balances.

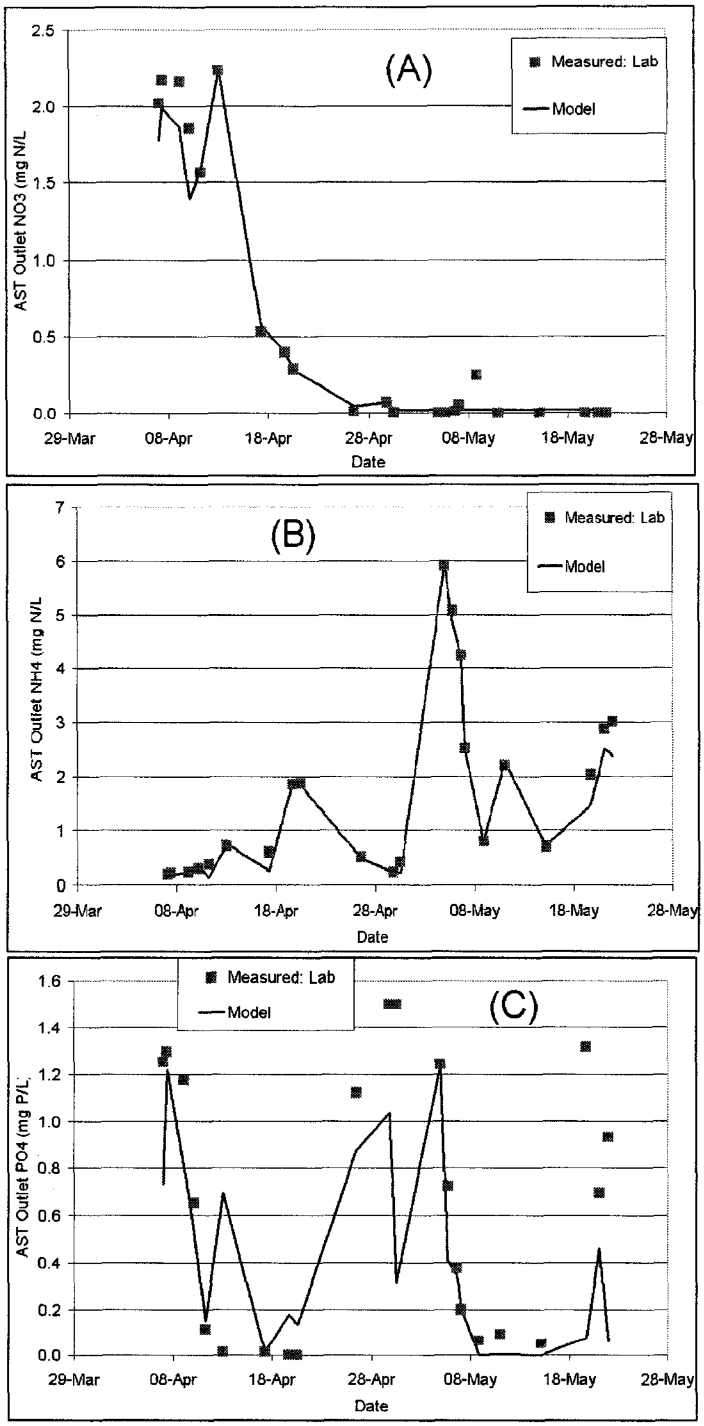

Figure 37: Individually adjusted kinetic parameter approach, AST outlet nutrient residuals measured & modelled (a) Nitrate (b) Ammonia (c) Phosphate

The autotrophic maximum growth rate, μ_A, the anoxic growth factor, η_g, the ammonification rate, ka, and the phosphatification rate were compared to influent COD fractions and process operating conditions such as the sludge retention time, dissolved oxygen concentration, temperature, and sludge volume index. No obvious trends were observed.

The nitrification and denitrification reactions are influenced by the dissolved oxygen concentration, the ammonia concentration, the temperature and the sludge retention time, the latter due to the fact that the maximum autotrophic growth rate is significantly lower than the maximum heterotrophic growth rate [55]. If a process is operated with a long sludge age, the nitrifying bacteria have a much greater opportunity to develop, whereas conditions that encourage rapid growth will cause the decline of the nitrifying bacteria population [55]. The yield of nitrifying bacteria is less than that of heterotrophic bacteria, which manifests as a minimal impact on the overall suspended solids concentration of the mixed liquor in the activated sludge process [55].

Nitrification is carried out by both heterotrophic and autotrophic bacteria, but is usually attributed to autotrophic bacteria, in particular those of the *Nitrosomonas* and *Nitrobacter* genera [55]. These bacteria can use an organic carbonaceous substrate, but the quantity is usually so small that it is ignored and carbon dioxide is used to represent the carbon source for this process [55]. Nitrification is modelled in the ASM1-based model as a one-step process, which can be described by the simplified overall nitrification equation as follows [231]:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + 2H_2O$$

Denitrification is carried out by heterotrophic bacteria and therefore requires an organic carbon substrate; the substrate may be provided by an exogenous source in the wastewater media or by an endogenous source [60]. An overall equation for denitrification, using methanol as the carbon substrate, is given by Buckley (2001):

$$6NO_3^- + 5CH_3OH \longrightarrow 3N_2 + 5CO_2 + 7H_2 + H_2O + 6OH^-$$

Investigation of the nitrification, denitrification, and ammonification rates with respect to the AST selector dissolved oxygen concentration, ammonia concentration, temperature, and sludge retention time was expected to show some correlations. However, there are no obvious trends between the process rates and these process operating conditions.

Investigation of process conditions one to two sludge ages prior to the drop in nitrate residual concentrations was expected to yield some insight into the change in nitrification rate. From inspection of six months of unfiltered data of the nitrate residuals, shown in Figure 38, it is clear that the process suffered a minor temperature shock during the first week of May when the WWTP cooling towers were turned on and the temperature dropped approximately 5ºC. This event would be expected to slow the rate of nitrification; however, the nitrate residual concentration had begun to decrease almost 2 weeks earlier. The dashed lines in Figure 38 demarcate the period of time that was modelled, which starts amid already rising nitrate residual concentrations and rising temperatures.

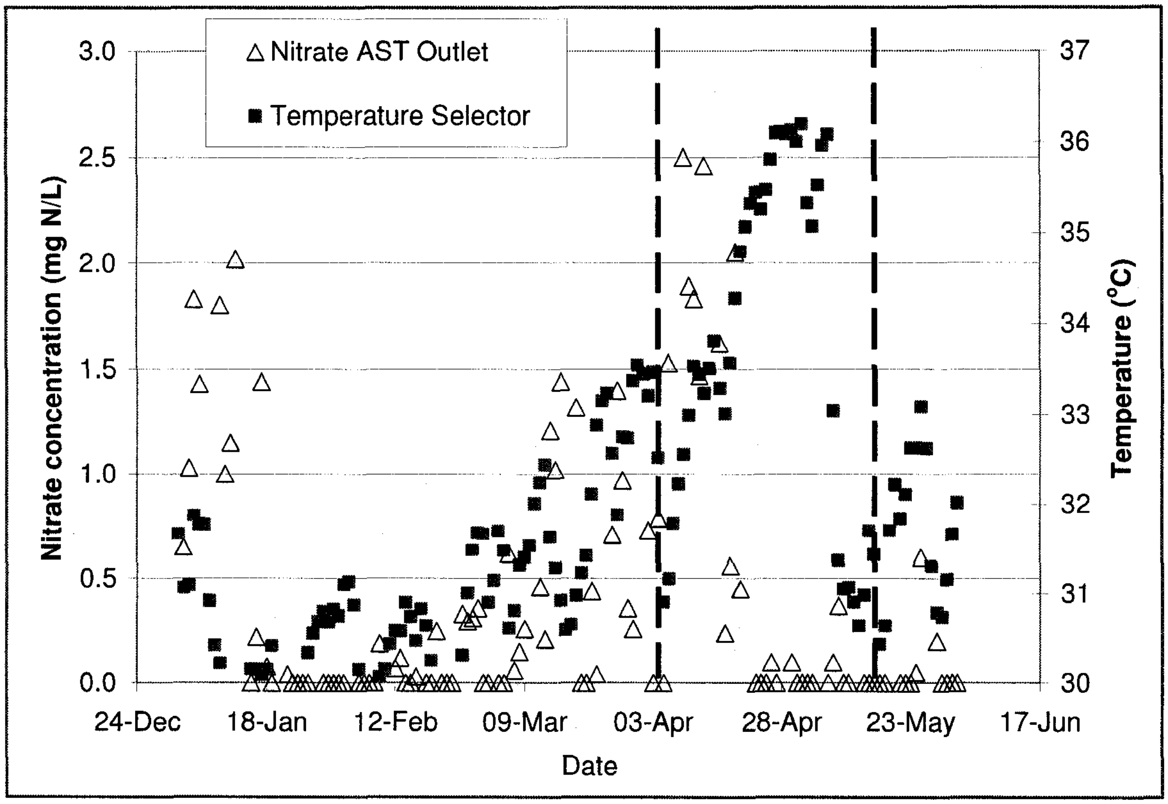

Figure 38: Six months of nitrate data (unfiltered) vs. temperature, section between dashed lines (---) represents modelled time period

Returning to the calibrated primary effluent wastewater characterisation, represented in Figure 35, it is possible that a step change in the relative values of the X_I fraction and X_S fraction caused the response in the nitrate residual. However, inspection of six months of nitrate residual concentration data in comparison with the calculated fraction of slowly biodegradable influent COD fraction fxs and in comparison with the sludge retention time does not show any correlation. As seen in Figure 39, there is a significant spread of data.

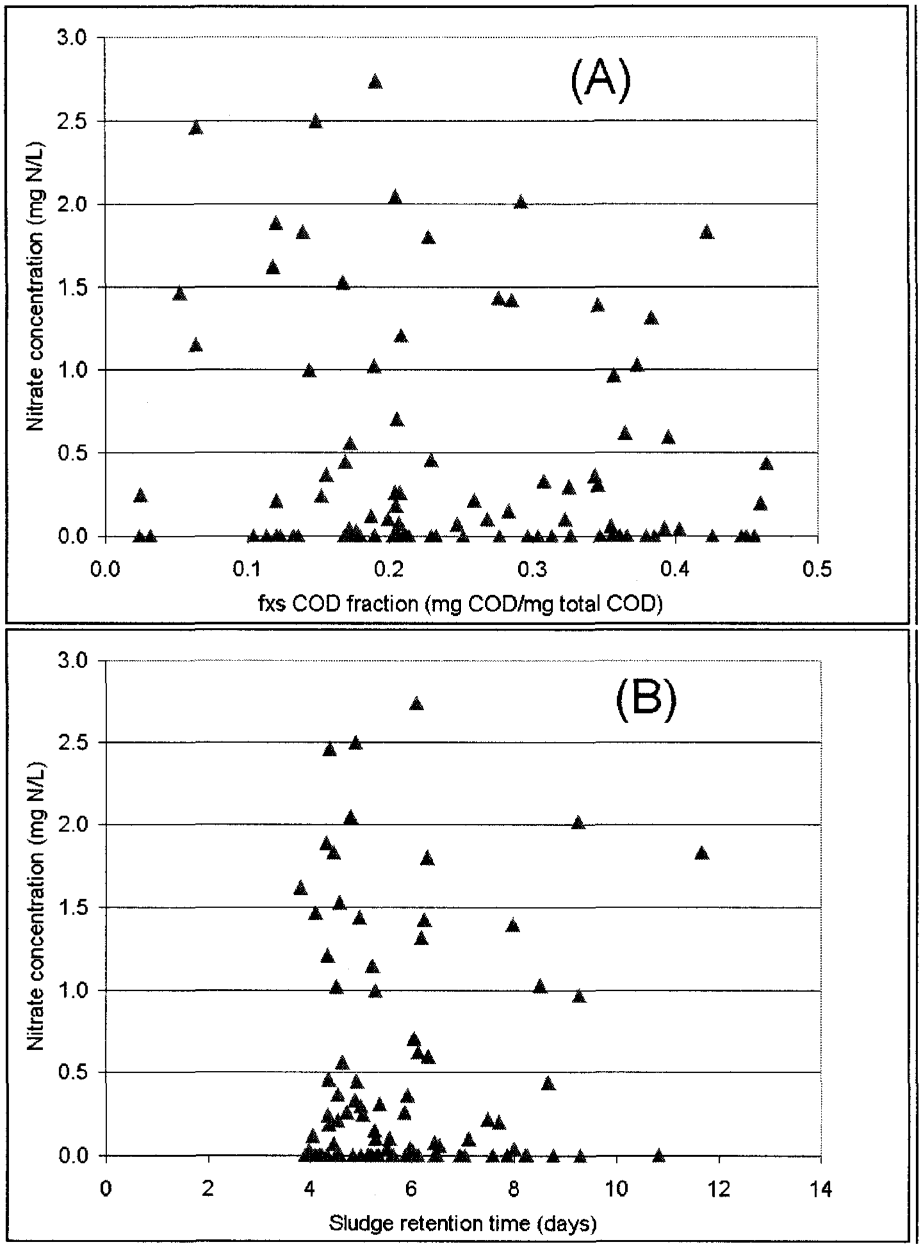

Figure 39: Six months nitrate data (untreated data) vs. (a) biomass fraction of slowly biodegradable influent COD (fxs, mg COD/mg total COD), (b) sludge retention time (days)

It is possible that the nitrification process became inhibited due to toxic substances in the primary effluent, and this is the reason that the nitrification rate diminished with time in the modelled time period. Inspection of six months of unfiltered nitrate residual concentration data in comparison with the AST inlet pH and in comparison with the AST inlet conductivity does not show any correlation. As seen in Figure 40, there is a significant spread of data.

An investigation of the modelled time period only, shown in Figure 41 (a), reveals a relationship between the nitrate concentration and the pH, which does not correspond to the general relationship between pH and the rate of nitrification. Generally in municipal systems, the rate of nitrification is optimal in the pH range of 7.5 to 8.0, and may be at only 10 to 20% of the optimal rate in the pH range of 5.8 to 6.0 [45]. Conductivity was relatively stable during this period, between 150 to 190 µS. Figure 41 (b) demonstrates the change of nitrate concentration (left-hand axis) and primary effluent pH (right-hand axis) over time; an evolution of both occurs over the modelled time period. The downward arrow indicates a high pH event in the primary influent on 30 April: a pH of 10.2 was recorded in both the mill drain and in the primary influent. A pH adjustment at the primary clarifier resulted in a pH of 6.3 in the primary effluent.

It is possible that organic toxic substances, such as polymers from the paper machine, were present in the primary effluent [238] but were unmeasured by either pH or conductivity. High BOD concentrations in the final effluent were not observed for any scenario indicating that no inhibition of carbonaceous substrate removal occurred.

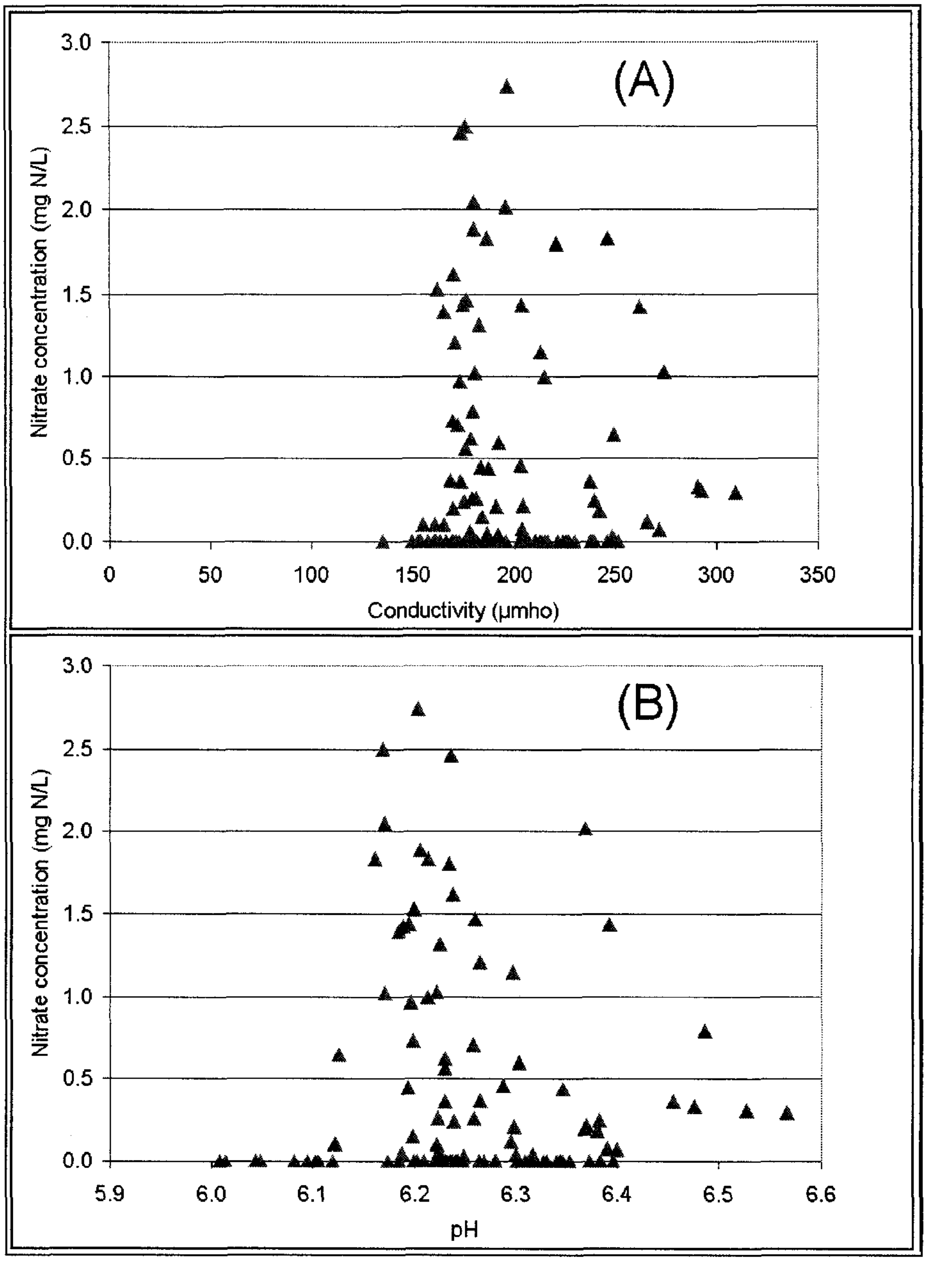

Figure 40: Six months of nitrate data (untreated data) vs. (a) Conductivity (µmho), (b) pH

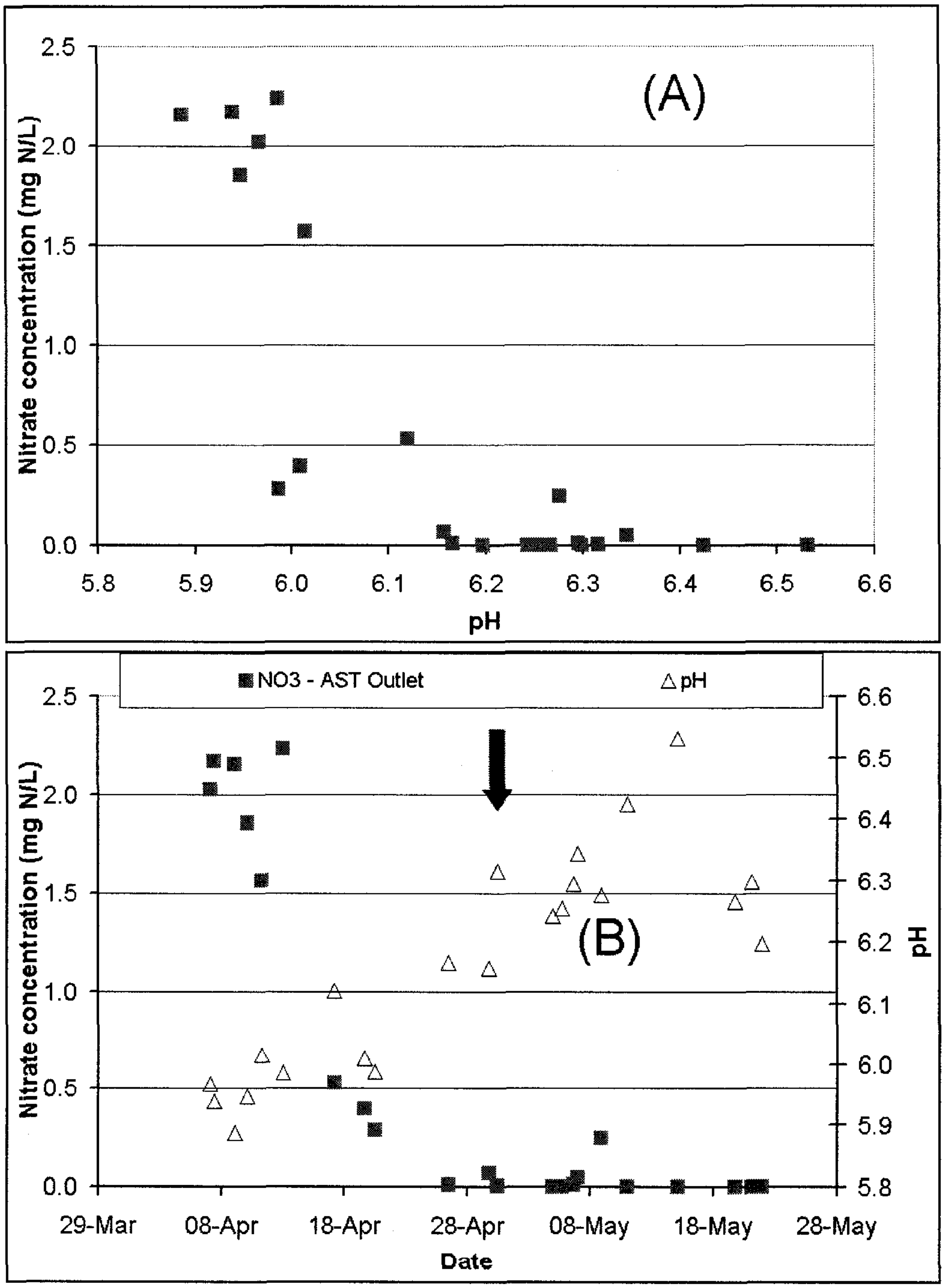

Figure 41: (a) Nitrate concentration vs. pH, (b) Nitrate concentration (left-hand axis), pH (right-hand axis) over modelled time period, downward arrow indicates high pH event in primary influent

Discussion

Modelling and influent characterisation of pulp and paper wastewater has presented a significant challenge to researchers over the past 10 to 15 years, with experiences ranging from "good agreement with plant operating data" [165] to "a poor model response for the effluent COD and suspended solids concentrations" [235]. Modifications to the ASM models for this industry include nutrient-limited growth [4, 119, 166, 220], predatory biomass [119], optimised model calibration [166], kinetic parameter measurements [168, 169], and phosphatification [220]. The wastewater characterisation is believed to offer the mill the opportunity to assess the impact of the sludge retention time on the slowly biodegradable X_S and particulate inert X_I fractions of the primary effluent, which would allow them to assess whether the primary effluent COD is removed via biological mechanisms (X_S) or physical settling in the secondary clarifier (X_I).

The two-model approach used in this study was found to reasonably model either the process regime including partial nitrification-denitrification, or the zero-nitrification process regime, but not the transition between the two process regimes. The goodness of fit of each of these models to the measured data can be described by the Pearson's R^2 and the chi-squared statistics, listed in Table 69, used to compare modelled to measured nutrient residual data (a R^2 and/or chi-squared value of 1 is considered to be a good fit of modelled to measured data). Restricting the range of each model improves the goodness of fit of each model. Future work includes estimating and interpreting the ammonification rate for the zero-nitrification process regime.

Table 69: Goodness of fit, 2-model approach & individually adjusted kinetic parameter approach (SS = pseudo-steady state cases)

Model	***Data set***	***R^2 Nitrate***	***R^2 Ammonia***	***R^2 Phosphate***
1:With nitrification-denitrification	Full	0.01	0.12	0.24
	First 6 SS	0.29	0.16	0.10
2: No nitrification-denitrification	Full	0	0.08	0.18
	Last 13 SS	0.24	0	0.20
Individually adjusted kinetic parameter model	Full	0.98	0.98	0.42
Model	***Data set***	***χ^2 Nitrate***	***χ^2 Ammonia***	***χ^2 Phosphate***
1:With nitrification-denitrification	Full	0	0	0
	First 6 SS	0	0.30	0.84
2: No nitrification-denitrification	Full	0	0	0
	Last 13 SS	0.01	1.00	0
Individually adjusted kinetic parameter model	Full	1.00	1.00	0

The adjustment of kinetic parameters for individual pseudo-steady states provides one plausible non-unique model solution to the measured data. The step-wise calibration of the nitrification-denitrification and phosphatification reaction rates provides a goodness of fit to the measured data that can be described by the Pearson's R^2 and the chi-squared statistic, listed in Table 69, when comparing modelled to measured nutrient residual data. The goodness of fit of the individually adjusted kinetic parameter model is far superior to the uniform model approach, particularly for the nitrate and ammonia residual concentrations. This individual adjustment of kinetic parameters methodology is in contrast to the optimised calibration techniques used by Sreckovic (2001), which resulted in some unlikely reaction rates, such as a maximum autotrophic growth rate μ_A of 15 d^{-1} (unconstrained optimal model solution). The implications of the individually adjusted kinetic parameters will be investigated in further work.

Pulp and paper wastewater influent can be highly variable in the short term compared to municipal wastewater; however, the biomass' environment does not change as quickly as the influent due to the residence time of the well-mixed (CSTR) selectors and AST basins. The microbiology of the AST system is believed to be determined to a certain extent by the conditions in the selectors in terms of which bacteria out-compete others. It is thought that the conditions in the selectors will also therefore determine the nutrient transformations that occur in the AST system to a certain degree. The overall sludge retention time (SRT) of the system will also play a role since the nitrifying bacteria generally require a longer time to establish the population and can be washed out of the system at short SRTs. The fact that the nitrification-denitrification process rates did not correlate to any of the process conditions was unexpected and is further evidence of the difficulty of modelling partial nitrification and denitrification reactions.

This case study was focussed on a pulp and paper wastewater treatment plant consisting of very well-mixed selectors and AST basins. Every AST system is unique in its hydraulic, settling, and biological behaviour; some AST basins may experience dead zones or pockets of sludge deposition, depending on the aeration and mixing systems employed. The methodology presented in this study is broadly applicable to AST systems, independently of the particular details of the treatment plant.

4.3.6. Control Strategies

4.3.6.1. Control strategies implemented

Since the start of this study, the mill has implemented a number of changes to its control strategy, including an upstream BOD5:N:P ratio control in conjunction with feed-back residual monitoring and monitoring of the mixed liquor biological population. The upstream ratio is based on a target BOD5:N:P mass ratio for the dosage of both supplemental nutrient chemicals: urea and phosphoric acid. The ratios are calculated based on the COD measured with the UV on-line COD meter. The ratios are also a function of the nutrient solution specific gravity and concentration, as well as the wastewater COD: BOD5 ratio. At this mill, the COD: BOD5 ratio has been established over the 12 months of 2006 to be 2.36, with a standard deviation of 0.33, during normal plant operation using BOD5 and filtered COD measurements in the inlet to the aerated basins. This control is currently in the phase of having the upstream BOD5:N:P ratio control automated.

The mill has found this control strategy works very well, particularly when the mixed liquor suspended solids, F/M ratio, and sludge age are relatively constant. The mill has found the final effluent on-line nutrient residual instruments to be reliable and to require little operation or maintenance from mill personnel. The regular analysis of the biological population provides important insights into the occurrence of partial nitrification-denitrification and biological predatory behavior, particularly predation of nitrifiers, that has been otherwise unmeasured by nutrient residuals.

4.3.6.2. Further model results

The following is a presentation of an additional level of the modelling results with the view to establishing a control strategy for the dosing of supplemental nutrients and for the operation of the pulp and paper wastewater process.

Extensive model results are presented elsewhere [239]. The following is a presentation of an additional level of interpretation of those results, with the view to establishing control strategies for the dosing of supplemental nutrients and for the operation of the pulp and paper wastewater process. The model and results are based on the specific case study mill; however, the methodology is broadly applicable.

Figure 42 presents the phosphorus and ammonia saturation functions as calculated using the ASM-based model for the selectors. The saturation function indicates whether each nutrient is present in sufficient quantities (function approaches 1) or is deficient relative to the biological requirements of the microorganisms modeled (function approaches zero). The comparison of the ammonia and the phosphorus saturation function for each pseudo-steady state indicates which nutrient is relatively deficient. Monitoring the relative values of these saturation functions on a regular basis could be very useful for plant operators in order to determine which of the two supplemental nutrients is in short supply for the biomass to complete efficient BOD removal.

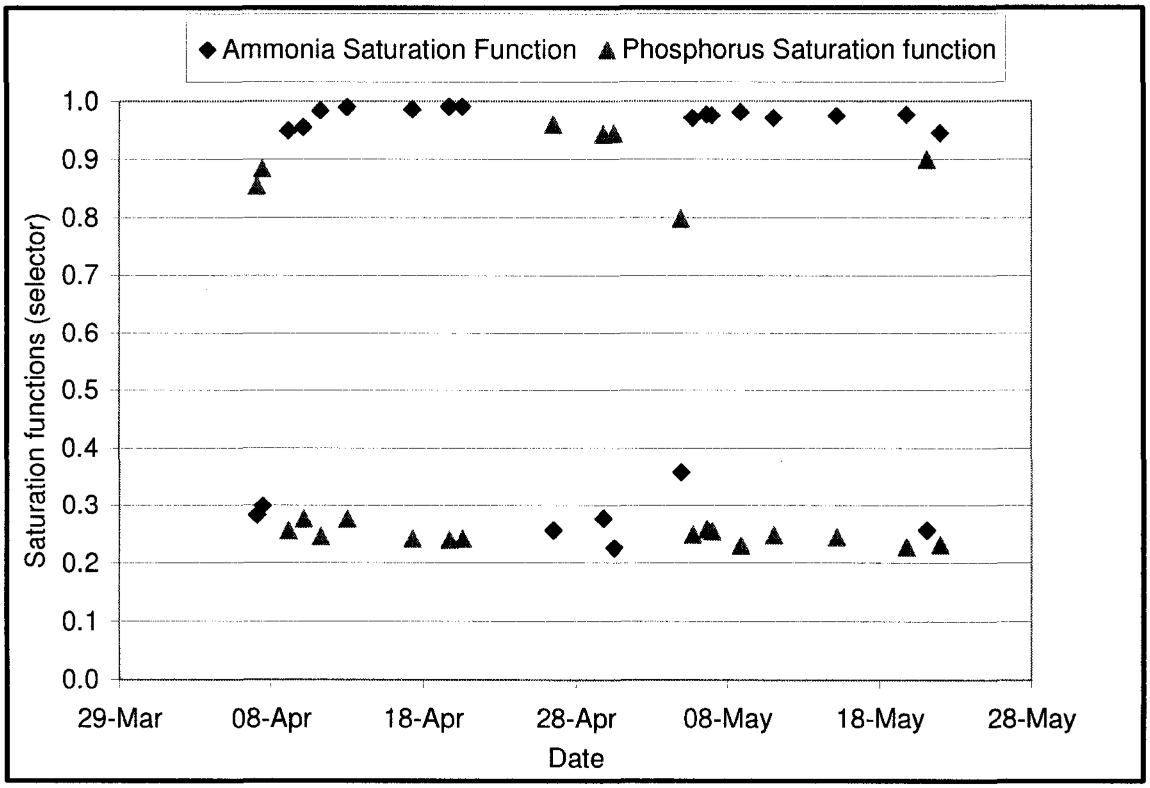

Figure 42: Phosphorus & Ammonia saturation functions (selector), model calculated

Figure 43 presents the measured residual phosphate concentration at the AST outlet (left-hand axis) compared to the phosphorus saturation functions in the selector (right-hand axis). The saturation function is a function of the nutrient concentration at the AST outlet, so there is by definition a correlation between the saturation function and the nutrient concentration. In the case of phosphorus, the saturation function fell to a value below 0.3 (dashed arrow A) prior to a fall in the ortho-phosphate concentration (dashed arrow B) in the AST outlet. This suggests that the model could be used to predict an imminent nutrient deficient state prior to the exhibition of symptoms such as low nutrient residuals. This would be an extremely useful tool for plant operators to monitor on a regular basis. This hypothesis requires validation with further data treatment, mass balance, and modeling endeavors.

In the case of nitrogen, the saturation function and nutrient residual relationships can be divided into different operating regimes: (1) nitrification, (2) nitrogen deficiency and (3) zero-nitrification, as presented in Figure 44. In previous work, no correlation was found between nitrification-denitrification reaction rates and process conditions such as dissolved oxygen concentrations, influent ammonia concentrations, temperature, sludge retention time, pH and conductivity. If such a correlation did exist, it could be combined with the model saturation function to predict which nitrogen operating regime was occurring in the AST. According to the results of this study, the nitrate and ammonia residual concentrations indicate the nitrification and zero-nitrification operating regimes, and the saturation function indicates nitrogen deficiency. The transition from nitrification to zero-nitrification is not predicted by the saturation function alone; this transition is one of the most difficult scenarios for modeling of partial nitrification-denitrification processes in this AST.

The implications of using the proposed control strategies are significant for the mill. An operator could potentially use a calibrated pseudo-steady state model to determine the actual operating regime of the plant, in terms of nitrification-denitrification processes as well as the relative nutrient deficiency of nitrogen and phosphorus. Using a model to predict nutrient-deficient events or to identify which nutrient is deficient can have a large impact for mills, especially those operating under nutrient-stressed conditions, which can produce filamentous bulking events or excursions from nutrient residual discharge limits. The proposed nutrient control strategies require further validation; however an example case is used to demonstrate the value for the mill.

In the pseudo-steady state case from 13 April, nitrate residuals are present, plus the ammonia saturation function is approaching one, therefore the operator could determine that nitrification-denitrification is occurring in the plant. The operator would then take steps to limit the unwanted nitrification-denitrification processes, such as reducing the ammonia dosed to the process by reducing the BOD5:N ratio control. Comparing the ammonia and phosphate saturation functions for this pseudo-steady state, it is also apparent that phosphorus is the nutrient in relative deficiency, therefore the operator could increase the BOD5:P ratio control. These steps should be implemented subject to satisfying other aspects of the wastewater treatment plant operations (i.e., well-settling sludge in the secondary clarifier, appropriate mixed liquor suspended solids, F/M ratio). Reducing the nutrient dosing flow rate to the treatment plant represents significant cost savings for the mill, as mentioned previously. The operational control strategies implemented at each mill may vary depending on the plant configuration, dosing locations and operating regimes; however the methodology is broadly applicable.

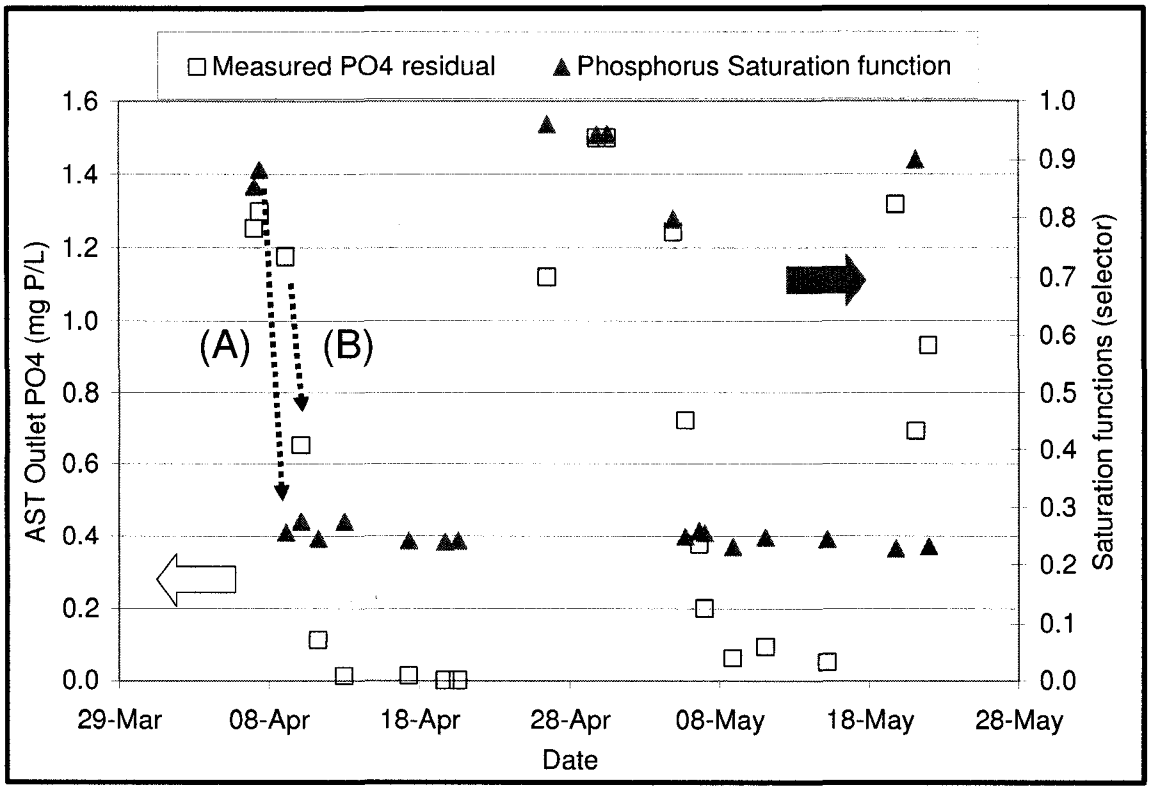

Figure 43: Measured & modeled AST outlet phosphate residuals (right-hand axis) vs. phosphorus saturation function (left-hand axis)

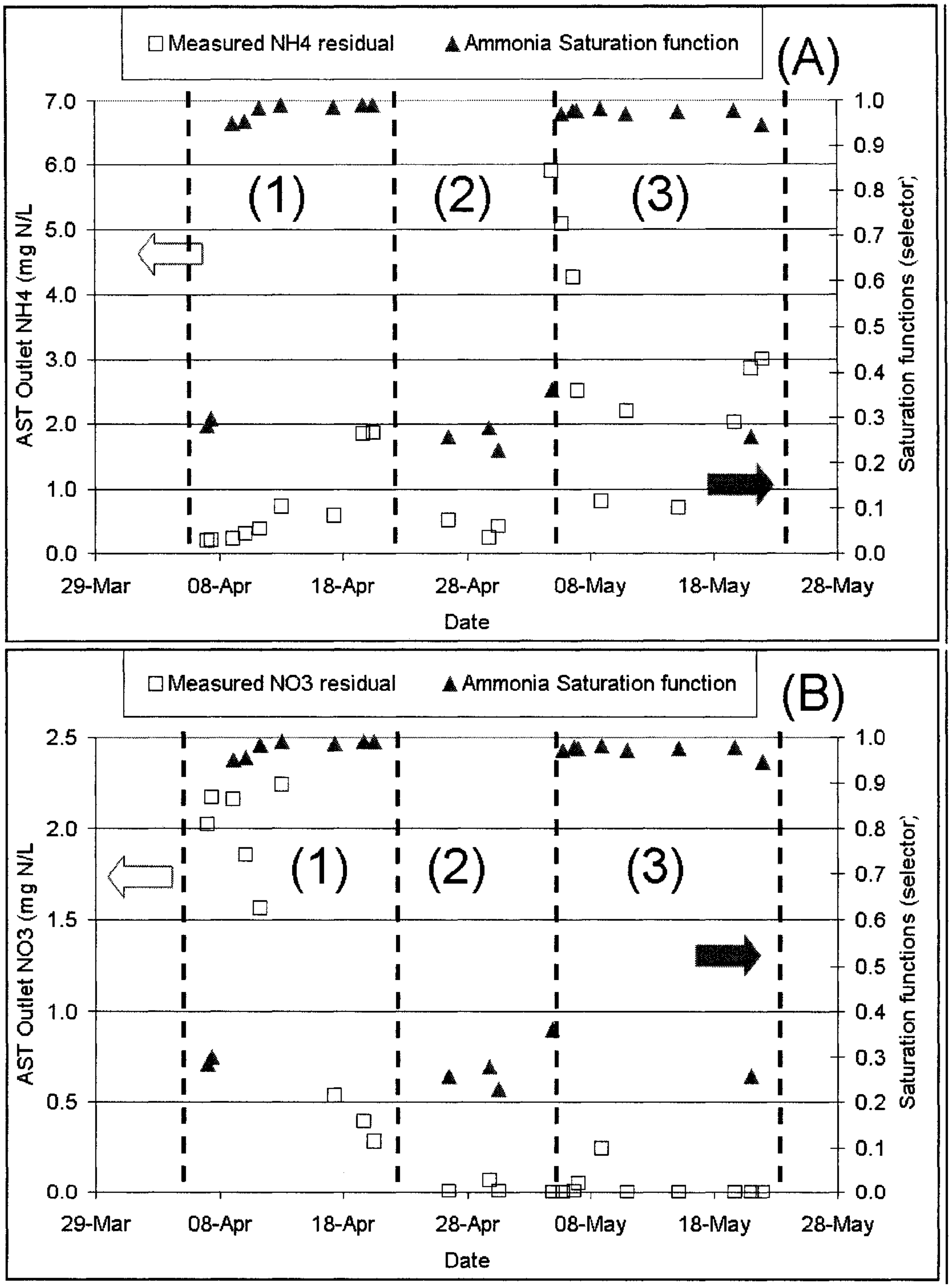

Figure 44: Measured & modeled AST outlet (a) ammonia residuals and (b) nitrate residuals (right-hand axis) vs. ammonia saturation function (left-hand axis), process regimes indicated: (1) Nitrification, (2) Nitrogen deficiency, (3) No nitrification

4.4. Conclusion

This chapter presents the application of a systematic methodology for the implementation of an ASM-based model for pulp and paper wastewater and for the potential integration of this model into an advanced control strategy for the control of nutrient dosing and nutrient residuals. First, the collected data was systematically processed and treated in order to identify pseudo-steady state events. Mass balances were used to reconcile the data for each pseudo-steady state event, the mass balance calculations highlighted that unwanted nitrification and denitrification were occurring for some process conditions. The potential cost savings on supplemental nutrient addition associated with these processes is estimated at $13,000 annually. Comparison of calculated BOD5:N:P mass ratios with those reported in the literature indicate a possible saving estimated at $85,000 annually.

Second, a wastewater characterisation for an ASM-based model was conducted for each pseudo-steady state event. Given the fact that this pulp and paper mill has straightforward wastewater treatment processes (single line CSTR) and an effluent from a single pulping process (TMP), it is unlikely that ASM-based models in their current state can be broadly applied to the pulp and paper industry. The influent characterisation of pulp and paper wastewater highlights significant differences between this industrial wastewater and municipal wastewater, which warrants further work if the ASM-based models are to be applied to this industry.

Third, an ASM-based model developed for pulp and paper wastewater was applied for each pseudo-steady state event. ASM-based models have been developed for the treatment of pulp and paper industrial wastewater that take into consideration its nutrient-deficient nature as well as nutrient transformations such as the hydrolysis of organic phosphorus and the phosphatification reaction.

It is feasible to use an ASM-based model to model the wastewater treatment plant at a pulp and paper mill, when the plant is operating in a stable manner with a stable microbiological population. It is extremely difficult to model small changes in nutrient concentrations when the partial nitrification-denitrification processes vary over time and in response to changes in the influent characterisation and sludge retention time. The short-term variability of pulp and paper mill effluent is much greater than that of municipal wastewater, as can be seen by the wide range of Primary Effluent COD concentration, flow rates, dissolved oxygen concentration, sludge retention times and possible Primary Effluent characterisation fractions. This variability results in stresses to the microbial population and therefore unpredicted changes in the local nutrient transformations occurring in an AST system operating with partial nitrification-denitrification.

Fourth, the use of the ASM-based model saturation functions as an indicator of the actual plant operating regime and of nutrient deficiency in the biomass requires validation and is potentially a powerful tool for the plant operators. The mill has already implemented upstream ratio control of nutrient dosing with feed-back of residual concentrations, and the proposed use of the ASM-based model will be implemented as an additional layer of control. While a large range of pulp and paper process wastewater treatment configurations exist, the methodology and the ASM-based modeling used in this study are broadly applicable to the industry and represent state of the art technology application.

The methodology used in this study, of rigorous data treatment, detection of pseudo-steady states, development of mass balances, and individually calibrated scenarios, has demonstrated important insights into the nutrient transformations occurring in a well-mixed (CSTR) short-retention time AST wastewater treatment plant.

5. Analyses

5.1. Error Analysis

The following is an analysis of the uncertainty or error that is associated with individual quantitative scientific observations, with repeated quantitative measurements and that associated with variation in the process itself. Raw data and calculation results are presented in Appendix 6 related to the following: the error related to laboratory experiments conducted for solids, nutrients and COD concentrations in the wastewater, the on-line measurements from instruments installed at the mill site, the propagation of uncertainties through calculations [240], a discussion of repeatability of laboratory experiments, a discussion of measurement redundancy, the propagation of process variation and a discussion of the results and sources of uncertainty.

As previously discussed, there are a number of terms commonly used to describe the uncertainty associated with measurements. A number of definitions from the Standard Methods are reiterated in Table 70 [2]. Although there is a difference in the definition of 'error' and 'uncertainty', they will be used interchangeably in this study according to the definition of 'uncertainty'.

Table 70: Glossary of statistical terms *[2] **[148] †[241]

Accuracy * (trueness)	The combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to a true value

Bias*	Consistent deviation of measured values from the true value, caused by systematic errors in a procedure
Calibration	The method by which the trueness of the instrument is verified
Drift	The change in trueness of the instrument over time
Error†	The difference between an individual result and the true value
Reproducibility* (precision)	Measure of the degree of agreement among replicate analyses of a sample, usually expressed as the standard deviation
Repeatability**	Refers to precision obtainable by the same technician under the same conditions (intra-laboratory), compared to reproducibility which refers to precision obtainable by different technicians under different conditions (inter-laboratory)
Uncertainty†	The dispersion of the values that could reasonably characterise the results of an analytical procedure and defined sample type, expressed as a range of values

The ideal measurement would combine low bias with high reproducibility, minimal calibration required and minimal drift found during calibration. The precision and bias are noted for each measurement where known. The bias of measurements is dependent on the laboratory's interpretation of the test method as well as the method itself.

Figure 45 below demonstrates the interaction between accuracy, repeatability and reproducibility [148]. Figure 45 (a) presents the case that is neither accurate nor precise where both systematic and random errors are present; Figure 45 (b) presents a precise but inaccurate case where systematic error is present but random error is controlled; and Figure 45 (c) presents an accurate and precise case where both random and systematic errors are controlled [148]. If the results of any of the cases (a) to (c) could be reproduced a number of times, this would be a repeatable or reproducible result, depending on whether the results were from a single or multiple technicians/laboratories.

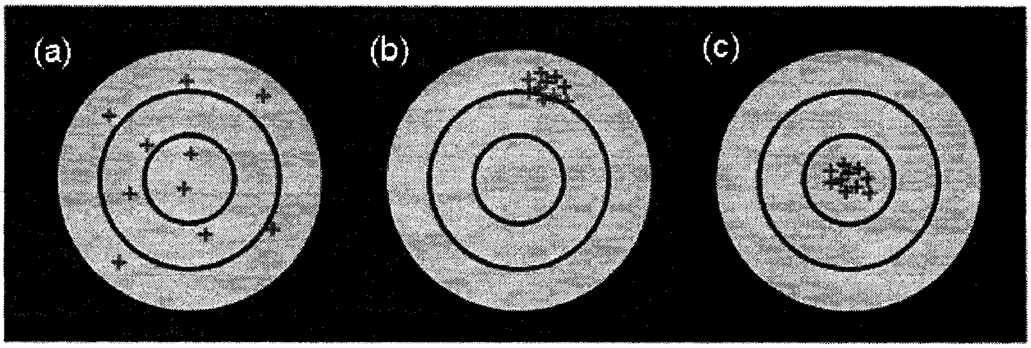

Figure 45: Interaction of accuracy, repeatability and reproducibility [148]

As described in the Eurachem-CITAC guide, “knowledge of the uncertainty implies increased confidence in the validity of a measurement result” [241], which is the purpose of identifying and quantifying the sources of uncertainty in the analytical and on-line measurements as well as the calculations that rely on these measurements.

5.1.1. Propagation of Uncertainty

5.1.1.1. Measurement Uncertainty

The propagation of uncertainty from the measured values to calculated values must be quantified in order to ascertain the uncertainty related to calculation results, such as mass balances. The propagation of uncertainty can be calculated according to the rules presented in Table 71 below [242].

Table 71: Propagation of uncertainty rules: measurement uncertainty [242]

Calculation	*Measurement Uncertainty*
$A = B + C$ or $A = B - C$	$\Delta A = \Delta B + \Delta C$
$A = B \times C$ or $A = B / C$	$\frac{\Delta A}{\lvert A\rvert} = \frac{\Delta B}{\lvert B\rvert} + \frac{\Delta C}{\lvert C\rvert}$
$A = B^C$ where C is any number	$\frac{\Delta A}{\lvert A\rvert} = \lvert C\rvert \cdot \frac{\Delta B}{\lvert B\rvert}$
$A = \ln(x)$, e^x or any function with extremum	$\Delta A = \frac{A_{MAX} - A_{MIN}}{2}$

5.1.1.2. Process Variation

The propagation of uncertainty from the process variation, reported as standard deviation, to calculated values must be quantified in order to ascertain the uncertainty related to calculation results, such as mass balances. The propagation of uncertainty can be calculated according to the rules presented in Table 72 below [240]. These rules are based on the premise that the variation of the process parameters can be described by a normal distribution. It is assumed that ratios and concentrations derived from laboratory or wastewater characterisation work that are used in calculations do not vary during the steady state condition: the following describes the measured variation in process parameters only.

Table 72: Propagation of uncertainty rules: process variation (normal distribution) [240]

Calculation	*Process Uncertainty*
A = q (x, y)	$\sigma^2_A = \left(\frac{\delta q}{\delta x}.\sigma_x\right)^2 + \left(\frac{\delta q}{\delta y}.\sigma_y\right)^2$
A = B + C or A = B – C	$\sigma^2_A = \sigma^2_B + \sigma^2_C$
A = B x C or A = B / C	$\frac{\sigma^2_A}{A^2} = \frac{\sigma^2_B}{B^2} + \frac{\sigma^2_C}{C^2}$
A = B x C where C is any constant number	$\sigma^2_A = (C.\ \sigma_B)^2$

5.1.2. Measurement Accuracy & Process Variation

The following is a summary of the uncertainty calculations relating to the mass balance results, reported individually as the measurement accuracy and as the process variation. Details are presented in Appendix 6.

Generally, measurement accuracy is considered to be the more conservative of the two uncertainties calculated. The process variation uncertainty demonstrates how close each pseudo-steady state is to actual steady state. Nevertheless, the magnification of uncertainty through calculations renders some parameters more or less certain for the same steady state.

5.1.2.1. Flow rates

Accuracy and process variation values were calculated for the flow mass balance results, which are presented in Table 73 below.

Table 73: Flow rate: mass balance results: average calculated accuracy & process variation (%)

Average	***Inlet Primary Clarifier***	***Outlet Primary Clarifier***	***Primary Sludge***	***Press Filtrate***	***AST Inlet***	***WAS***	***RAS***	***Final Effluent***
Accuracy	1.0%	1.0%	1.0%	68.6%	2.0%	1.0%	1.0%	2.0%
Process variation	0.20%	0.21%	1.98%	5.23%	0.07%	0.09%	0.12%	0.08%

5.1.2.2. Phosphorus

Accuracy and process variation values were calculated for the phosphorus mass balance results, which are presented in Table 74 below.

Table 74: Phosphorus: mass balance results: calculated accuracy & process variation (%)

Average	***Inlet Primary Clarifier***	***Outlet Primary Clarifier***	***Primary Sludge***	***Press Filtrate***	***PO4 Add (meas)***	***AST Inlet***	***WAS***	***RAS***	***Final Effluent***
Accuracy	265%	269%	1.1%	33.9%	0.8%	30.6%	33.2%	16.5%	14.9%
Process variation	0.20%	0.20%	1.98%	5.23%	0.06%	0.90%	1.05%	0.33%	0.08%

5.1.2.3. Solids

Accuracy and process variation values were calculated for the solids mass balance results, which are presented in Table 75 below.

Table 75: Solids: mass balance results: calculated accuracy & process variation (%)

Average	***Inlet Primary Clarifier***	***Outlet Primary Clarifier***	***Primary Sludge***	***AST Outlet***	***WAS***	***RAS***	***Final Effluent***
Accuracy	*10.5%*	*3.0%*	*13.0%*	*2.7%*	*23.9%*	*6.9%*	*7.0%*
Process variation	0.20%	0.21%	0.24%	0.06%	1.05%	0.33%	20.4%

5.1.2.4. COD

Accuracy and process variation values were calculated for the COD mass balance results, which are presented in Table 76 below.

Table 76: COD: mass balance results: calculated accuracy & process variation (%)

Average	***Input COD***	***Output COD***		
	AST Inlet	***COD Oxidised***	***WAS***	***Final Effluent***
Accuracy	14.8%	6.6%	32.8%	17.8%
Process variation	*0%*	*0.001%*	*0%*	*0.076%*

5.1.2.5. Nitrogen

Accuracy and process variation values were calculated for the nitrogen mass balance results, which are presented in Table 77 below. A large source of uncertainty in the calculation of the TKN in the final effluent is the fact that the ammonia concentrations from which it is calculated are very small, often smaller than the limit of detection of the on-line instrument. This leads to a large relative uncertainty in the measured value: an uncertainty of 0.05 mg/L relative to a measurement of 0.02 mg/L is a relative uncertainty of 250%, for example.

Table 77: Total Nitrogen: mass balance results: calculated accuracy & process variation (%)

Average	***Input Nitrogen***		***Output Nitrogen***			
	AST Inlet	***Urea***	***NO3 Denitrified***	***WAS***	***NO3 Final Effluent***	***TKN Final Effluent***
Accuracy	*2.9%*	*1.03%*	*13.1%*	*10.0%*	*5.0%*	*200%*
Process variation	*0.07%*	*0.61%*	*0.19%*	*0%*	*0.05%*	*0.07%*

5.1.2.6. Influent Characterisation

As discussed by Roeleveld and Van Loosdrecht [1], there is inherently a 10 to 20% uncertainty (inaccuracy) associated with the calculation of the ASM fractions via the STOWA methodology, and the error is compounded in the XI fraction using this method.

Accuracy values were calculated for the influent characterisation results, which are presented in Table 78 below. A large source of uncertainty in the calculation of the S_I influent fraction is the magnitude of the accuracy of the COD measurement (+/- 18 mg COD/L) compared to the magnitude of the measurement itself in the final effluent (80 mg COD/L), and furthermore the compounding of this relative uncertainty in the measurements used to construct the ratio of soluble to total COD concentration in the final effluent. Repeatability experiments carried out on the filtered COD (1.0μm) in the final effluent suggest that the precision of the measurement is much smaller than the accuracy calculated here.

The uncertainty of the X_S fraction is also extremely high, due to the compounding of the uncertainty associated with each of the other fractions.

Table 78: Influent characterisation results: calculated accuracy & process variation (% of concentration)

Average	***Nutrients***		***Carbonaceous fractions***			
	Urea	***Phosphoric Acid***	S_I	S_S	X_I	X_S
Accuracy	*2.99%*	*14.1%*	*253%*	*59.7%*	*131%*	*1240%*

The ortho-phosphate and ammonia-nitrogen balances over the contributing streams to the AST Inlet are presented in Appendix 3. Again, a large source of uncertainty in the phosphorus balance is related to the accuracy of measurement of the press filtrate flow rate.

5.1.3. Measurement Precision: Repeatability

A summary of repeatability testing for mill laboratory tests is presented in Appendix 6. Each parameter was tested 10 times on a single sample by the same person. Variation in experimental repeatability is expressed as the standard deviation as a percentage of the average value.

It is clear that the variation in repeatability is much smaller as a percentage of the average value for test parameters with large absolute values, such as the COD and solids concentrations of the RAS and WAS streams. In comparison, the test parameters with small absolute values, such as the COD and solids concentrations of the final effluent stream, suffer from higher relative variation in experimental repeatability. With regards to the ortho-phosphate concentration, this premise appears to be reversed, but in fact it holds due to the fact that the sample from the aeration basin outlet is diluted 10 times, and therefore the absolute value of the instrument reading for this sample is much smaller than that found for the final effluent test. Overall the experimental repeatability of these tests appears to be reasonable, generally less than 10% of the test average. One exception to this is the oxygen uptake rate (OUR) experiment, for which there is a slightly larger variation in repeatability, 12%.

Given the repeatability of these tests is generally reasonable, these parameters can be discarded as major sources of uncertainty.

5.1.4. Measurement Redundancy

Measurement redundancy is used in this context to describe a parameter that was evaluated using two or more analytical. In this study, the only parameters where this information is available is the ammonia nitrogen and the ortho-phosphate in the final effluent for those steady states where the on-line instrumentation was installed.

From Figure 46 below, it is clear that there is little correlation between the on-line ammonia concentration and the laboratory measurement. In this case, the on-line measurements were used in the mass balances due to the fact that the laboratory method was impossible to repeat more than once per day due to electrode saturation, and therefore there was less confidence in the laboratory method. The on-line instrument also self-calibrates against known standard concentrations on a regular basis and there was more confidence in these results.

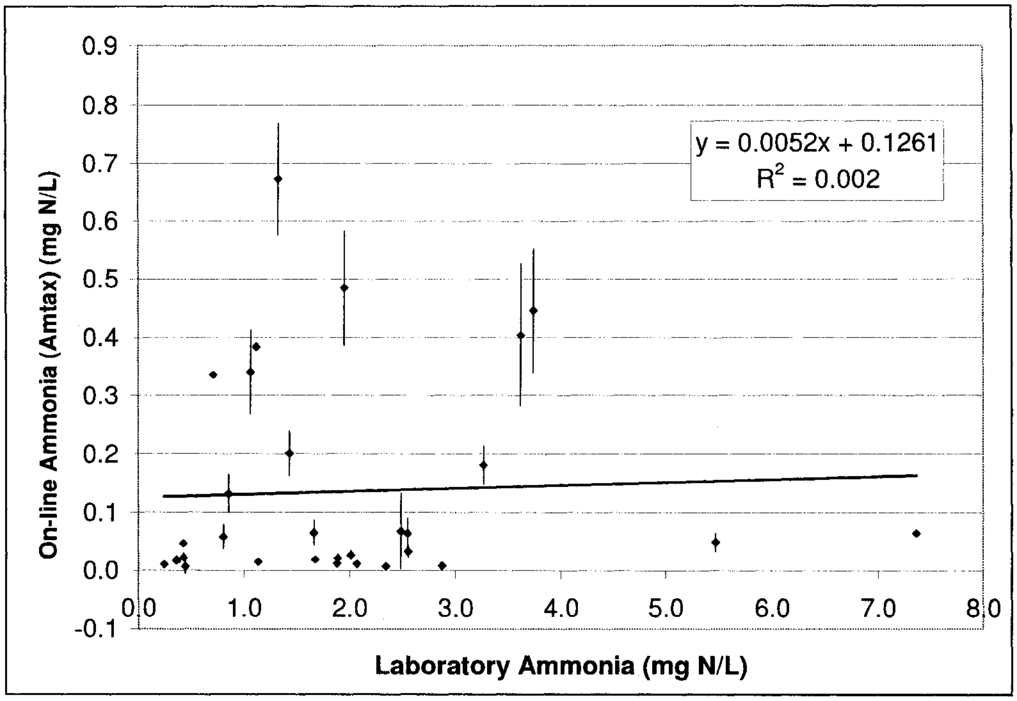

Figure 46: Measurement redundancy - final effluent ammonia (mg N/L), error bars represent one standard deviation above & below average

In contrast, from Figure 47 below, it is clear that there is a statistically significant correlation between the ortho-phosphate measured in the laboratory and that measured on-line, for the steady state data used in the mass balances. Anecdotally, mill personnel have extended this correlation and use the correlation to verify the on-line results with the laboratory results.

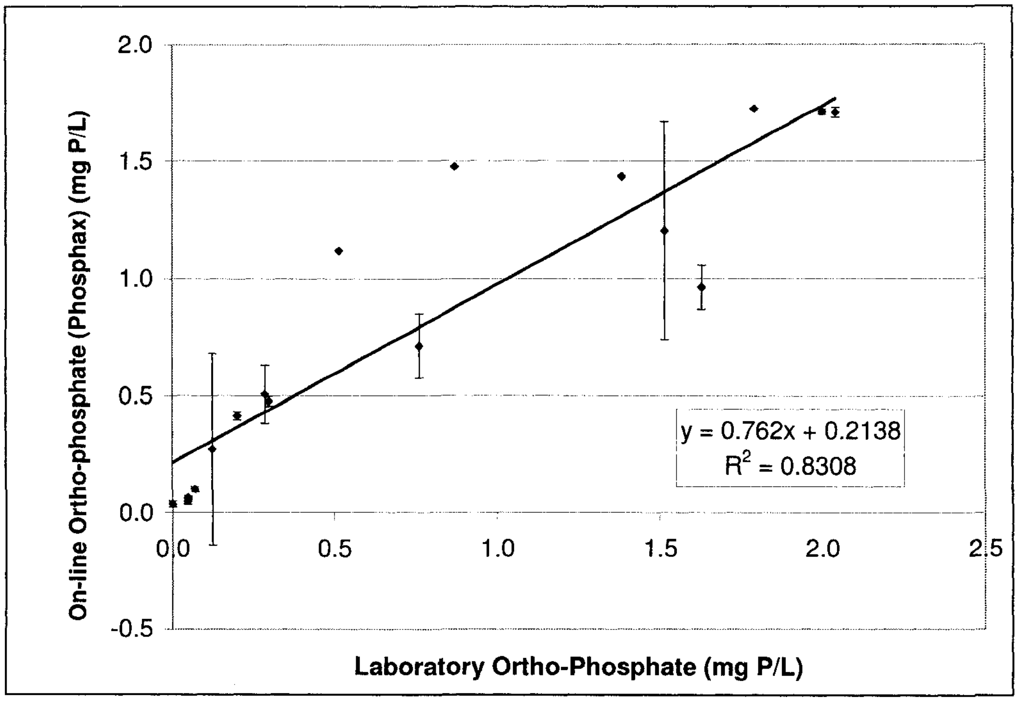

Figure 47: Measurement redundancy - final effluent ortho-phosphate (mg P/L), error bars represent one standard deviation above & below average

5.1.5. Measurement Bias, Gross error (systematic error)

The bias of a measurement can only be assessed when the true value of a measurement is known, which was not the case for any of the experiments carried out in this study.

In two cases, it was determined that data from measured parameters was not reliable, namely the measured phosphoric acid dosing flow rate and the TSS measured at the outlet of the primary clarifier (two steady state cases). In both of these cases, a judgement was made on the confidence in each of the data sources, and the source thought to be more reliable was used. In both cases, the data that was thought to contain a systematic error was identified and not used in further calculations.

Possible sources of systematic error include the miscalibration or lack of calibration of flow meters and other on-line instruments. However, the instrumentation personnel at the site were vigilant and proactive with regards to instrument calibration, so this is not thought to be a major issue.

Another possible source of gross error in the flow rate calculations is the assumption that volume is a conserved quantity, which comes from the assumptions that water is incompressible, temperature is constant (therefore density is not changing) and zero evaporation occurs in the basins.

Apart from the cases discussed above, it is difficult to quantify systematic error in measurements used in this study.

5.1.6. Discussion

The following is a discussion of results from the error analysis and of the possible sources of uncertainty.

5.1.6.1. Results

Usually in a continuous dynamic process one might expect the variation in the process signal to be much greater than the uncertainty related to the measurement of the process parameters. The results above show that this is generally not the case for steady states detected in the effluent treatment plant of this pulp and paper plant, in fact the opposite is generally true. The small variations in the process signals can be attributed to the fact that the mass balances were carried out on steady states.

There are a small number of process parameters which display a relatively large variation in the process signal, notably the final effluent TSS. This large variation in process signal can be attributed to the large variation of the final effluent TSS concentration for a number of steady states. The error bars in Figure 48 below represent one standard deviation above and below the average TSS value for each of the steady states. There are at least six steady states for which the TSS concentration is far from steady state. It is this variation that propagates through the mass balance calculations. The origin of the signal variation is most likely to be a build-up of algae in the instrument tank where the TSS instrument is located, which was washed periodically by the operator.

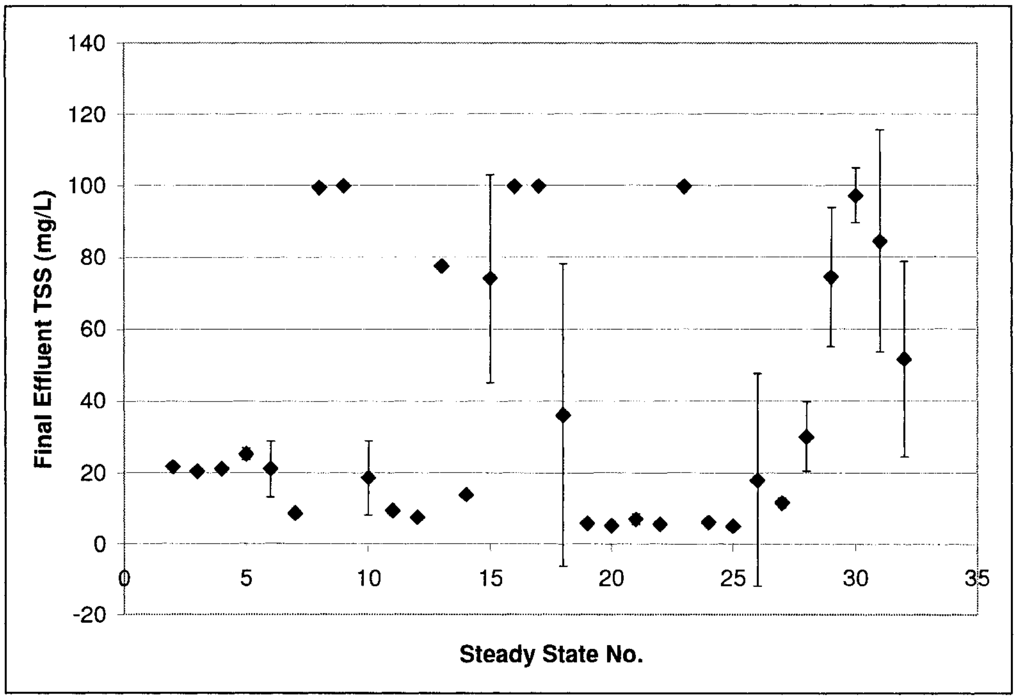

Figure 48: Final Effluent TSS (mg/L), error bars represent one standard deviation above & below average

It is usual for error to compound or magnify in the variables that are calculated from other measurements, as it does for the press filtrate flow rate. This is not to say that the uncertainty of 69% is desirable; it is suggested that further work include the continuous measurement of the flow rate and regular measurement of other variables in the press filtrate stream in order to reduce the uncertainty relating to the measurements in this stream.

It is also suggested that further work include more regular measurement of the nutrient fractions: measurements for each and every steady state would completely avoid the need to use average data or ratios from the wastewater characterisation work.

5.1.6.2. Sources of uncertainty

According to the Eurachem-CITAC guide, common sources of uncertainty relating to analytical experimental methods include sampling, storage conditions, instrument effects, reagent purity, assumed stoichiometry, measurement conditions, sample effects, computational effects, blank corrections, operator effects and random effects [241].

Sources of uncertainty that were not considered in this study could be identified using data reconciliation, by creating redundancy through calculations throughout the mass balances [230].

5.2. Sensitivity Analysis

The following is a summary of the results of a sensitivity analysis that was conducted on the calibrated models, using steady state number two as an example of process conditions that included partial nitrification-denitrification.

5.2.1.1. Sensitivity Analysis Parameters

A range of parameters, including kinetic, stoichiometric and influent parameters, were investigated during the sensitivity analysis. The full range of parameters are listed in Table 79. The parameters were generally varied between 50% and 150% of their calibrated value and the response in model output variables was recorded as a percentage of the calibrated model value, details are presented in Appendix 7.

Table 79: AST Parameters varied during sensitivity analysis

Parameter	***Symbol***	***Units***
Biomass nitrogen fraction	Inxb	mg N/mg COD
Cell decay products nitrogen fraction	Inxu	mg N/mg COD
Particulate inerts nitrogen fraction	Inxi	mg N/mg COD
Biomass phosphorus fraction	Ipxb	mg P/mg COD
Cell decay products phosphorus fraction	Ipxu	mg P/mg COD
Particulate inerts phosphorus fraction	Ipxi	mg P/mg COD
Heterotrophic maximum growth rate	μ_H	1/d
Autotrophic maximum growth rate	μ_A	1/d
Correction factor for anoxic growth of heterotrophs (denitrification)	η_g	-
Heterotrophic decay rate	b_H	1/d
Autotrophic decay rate	b_A	1/d
Yield of heterotrophic biomass growth	Y_H	g COD/ g SS
Yield of autotrophic biomass growth	Y_A	g COD/ g N
Half saturation constant for assimilation of carbon (heterotrophs)	K_{SH}	g COD /m^3
Phosphorus half saturation constant (heterotrophic)	K_{PH}	mg P/L
Phosphorus half saturation constant (autotrophic)	K_{PA}	mg P/L
Half saturation constant for assimilation of nitrogen	K_{NH}	g COD /m^3

Parameter	***Symbol***	***Units***
(heterotrophs)		
Half saturation constant for assimilation of nitrogen (autotrophs)	K_{NA}	g COD /m^3
Maximum specific hydrolysis rate	k_h	g COD /g cell COD.d
Hydrolysis half saturation constant	K_X	g COD /g cell COD
Specific ammonification rate	k_a	m^3/g COD. d
Specific phosphatification rate	k_p	m^3/g COD. d
Half saturation constant for oxygen (heterotrophs)	K_{OH}	g O_2 /m^3
Half saturation constant for oxygen (autotrophs)	K_{OA}	g O_2 /m^3
Temperature		ºC
Dissolved oxygen: selector		mg O_2/L
Dissolved oxygen: AST basin		mg O_2/L
Influent NH_4 concentration		mg N/L
Influent PO_4 concentration		mg P/L
Influent S_I concentration		mg COD/L
Influent S_S concentration		mg COD/L
Influent X_I concentration		mg COD/L
Influent X_S concentration		mg COD/L
fxii fraction		mg COD/mg COD

5.2.1.2. Sensitivity Analysis Results

A number of parameters were determined to be highly sensitive, in terms of the change in the output parameters mixed liquor suspended solids and the

AST outlet nutrient concentrations, as presented in Table 80. The mixed liquor suspended solids were not found to be highly sensitive for any of the parameters varied, which is thought to be attributable to the fact that the solids balance and COD balance were already calibrated.

Table 80: Sensitivity analysis results

Parameter	***Symbol***	***Units***	***Sensitive output parameters***
Biomass nitrogen fraction	inxb	mg N/mg COD	NH4, NO3
Cell decay products nitrogen fraction	inxu	mg N/mg COD	NO3
Biomass phosphorus fraction	ipxb	mg P/mg COD	NH4, NO3
Cell decay products phosphorus fraction	ipxu	mg P/mg COD	NH4, NO3
Autotrophic maximum growth rate	μ_A	1/d	NH4, NO3
Correction factor for anoxic growth of heterotrophs (denitrification)	η_g	-	NO3
Heterotrophic decay rate	b_H	1/d	NH4, NO3, PO4
Yield of heterotrophic biomass growth	Y_H	g COD/ g SS	NH4, NO3, PO4
Half saturation constant for assimilation of nitrogen (autotrophs)	K_{NA}	g COD /m³	NH4
Half saturation constant for oxygen (autotrophs)	K_{OA}	g O_2 /m³	NH4
Temperature		ºC	NH4, NO3, PO4
Dissolved oxygen: AST basin		mg O_2/L	NH4, NO3

Parameter	***Symbol***	***Units***	***Sensitive output parameters***
Influent NH_4 concentration		mg N/L	NO3
Influent PO_4 concentration		mg P/L	NH4, NO3, PO4
Influent S_S concentration		mg COD/L	NH4, NO3, PO4
Influent X_S concentration		mg COD/L	NH4, NO3, PO4

5.2.1.3. Sensitivity Analysis Discussion

The most sensitive kinetic and stoichiometric parameters were determined to be:

- Biomass and cell decay nutrient fractions;
- Autotrophic maximum growth rate;
- Correction factor for anoxic growth of heterotrophs;
- Heterotrophic decay rate;
- Heterotrophic yield;
- Half saturation constant for assimilation of nitrogen (autotrophs); and
- Half saturation constant for oxygen (autotrophs).

The most sensitive physical and influent parameters were determined to be:

- Temperature;
- Dissolved oxygen (AST basin);
- Influent nutrient concentrations; and
- Influent biodegradable COD concentrations (S_S and X_S).

Variation in kinetic and stoichiometric parameters related to nutrient transformations affected the nutrient residuals by changing the extent of the nitrification, denitrification, ammonification, phosphatification and hydrolysis of organic nutrient processes. There is no experimental evidence to support modification of kinetic and stoichiometric parameters, this should form part of future work for pulp and paper wastewater modelling.

6. General Discussion

The control of nutrient residual concentrations for the purposes of economic savings and for reduction of nutrient discharges to the receiving waters is an important issue for pulp and paper mills. The availability of vast amounts of on-line data at the mill offers the opportunity to make use of advanced analysis and process simulation tools in order to add an additional layer of control to the mill's existing nutrient addition control strategy.

Data treatment

The frequency of measurements and the averaging of data relating to the characterisation of wastewater and other inputs into ASM-based models previously investigated for pulp and paper wastewater have been inadequate to describe the nutrient transformations occurring in the activated sludge treatment process for this industry. As detailed in the literature review, some models used yearly averages of daily measurements. The concentrations of nutrients present in the wastewater effluent are so small that the variations in these concentrations are relatively large, and averaging this data over a year is inadequate to capture variations in the nutrient concentrations. This study presents a rigorous data treatment methodology that reconciles the measured and calculated data via pseudo-steady state detection and mass balances.

ASM-based model

The ASM models were developed for municipal wastewater and the authors of these models do not claim that they are applicable for industrial wastewater. The application of an ASM-based model for pulp and paper wastewater in this study was ambitious from the outset. Influent wastewater characterisation methods are very well developed for municipal wastewater, and this study offers recommendations for future work on the definition of the wastewater components for the pulp and paper industry thought to be required for further use of the ASM-based models for this industry. The ASM models offer a potentially powerful tool for industrial wastewater treatment modelling.

The use of individually calibrated models for each pseudo-steady state is unorthodox in the world of municipal wastewater modelling, however it has offered insight into the required modifications to the Petersen matrix and multiple nutrient addition and operating strategies were derived from the modelling results. The evolution of partial nitrification-denitrification reaction rates over time is consistent with microbiological observations of pulp and paper wastewater biomass over time, which is possibly very different to the evolution of municipal wastewater reaction rates. The ASM models are lumped parameter models and as such, they do not address local conditions at the floc level, which may be required for wastewater treatment plants with partial nitrification-denitrification reactions.

The exclusion of the secondary clarifier from the model was necessary from a practical point of view, and should have minimal impact on the nutrient transformations occurring in the AST selectors and basins, although this remains to be verified. Existing clarifier models do not predict reaction to nutrient deficient events such as filamentous bulking.

The case study mill's AST is extremely well-mixed and the assumption of no dead zones or sludge deposits is correct for this mill, this assumption should be verified for other mills. Similarly, the case study mill incorporates selectors in each of the AST basins and this may not be applicable for all mills. This latter point is particularly important since it is believed that the majority of the microbiological response to the mill effluent occurs in the selector under competition for the carbonaceous substrate. Plants without a selector or with plug-flow type reactors will experience different nutrient transformations and the ASM-based model should be modified accordingly prior to implementation.

The practical application of a model using individually calibrated models is very different to the application of a uniform model: the individually calibrated model must be calibrated for each scenario as the nitrification-denitrification and phosphatification rates evolve. In as such, the individually calibrated model can be used as an indicator of the actual plant operating regime and of nutrient deficiency in the biomass, which are very practical applications for the mill. However, the individually calibrated model cannot be used in the current form as a uniform predictive model due to the evolution of the nutrient transformations with time. It is possible that the model requires a greater degree of complexity in order to fully describe the evolution of nutrient transformations over time, which was outside the scope of this study.

The uncertainty associated with the influent characterisation inputs into the ASM-based model are relatively large, and further work is required to characterise the wastewater influent over a longer time period in an effort to reduce the uncertainty associated with this data. Nevertheless, the application of the model as a tool to detect the actual plant operating regime or to detect nutrient deficiency, to be validated over a larger data set, is broadly applicable. An ASM-based model developed for any specific wastewater treatment plant configuration and process has the potential to provide the mill with these nutrient control tools.

Operating strategies

The proposed operating strategies are heuristic in that they are based on the observational analysis of the modelling results of the case study mill, not explicitly optimised or analysed via mathematical algorithms. In the case of heuristic control strategies, the implementation at the mill should be that of a manual control loop to complement the existing mill nutrient control strategy. The regular and long-term use of the ASM-based model by the mill is likely to increase experience and confidence in the heuristic control strategy, which could be adapted to evolving conditions in the wastewater treatment plant.

The potential implementation of the proposed control strategies is two-fold. The switching functions calculated in the model could be monitored on a daily basis and a rule could be developed by the mill as to whether they increase or decrease nutrient dosing. Again, increased use of the control strategy is likely to develop it further and instil confidence from the plant operators. A single calibrated pseudo-steady state model could be used by the mill to determine if reducing the nutrient dosing is likely to result in a biomass nutrient-deficiency which would result in decreased plant efficiency in terms of BOD removal, or if it may result in increased or decreased unwanted nitrification and denitrification reactions. The use of the ASM-based models for pulp and paper wastewater is still in a stage of development, and the use of the model as an automated control technique is not suggested.

7. Conclusions & Recommendations

7.1. Contributions to the body of knowledge

ASM-based model

The ASM-based model was used to model each of the pseudo-steady state events, taking into account the nutrient transformations occurring in the AST treatment system including nitrification-denitrification.

Operating strategy

The ASM-based model was interpreted and used to form the basis of the proposed nutrient addition and operating strategies.

Overall

The incorporation of reliable process data into an ASM-based model provides practical information such that ASTs can be better operated with regards to nutrient control.

7.2. Future work

Data collection & treatment

The data treatment process could be further developed to take into consideration the optimisation of synchronisation of data over tank residence times. The automation of the data treatment process would also allow the regular assessment and use of nutrient, solids and COD balances. Continuous measurement of the flow rate and regular measurement of other variables in the press filtrate stream is suggested in order to reduce the uncertainty relating to the measurements in this stream.

Wastewater characterisation

Significant differences exist between pulp and paper wastewater and municipal wastewater, which warrants further work if the ASM-based models are to be applied to this industry. In particular, the definition of the differences between the rapidly and slowly biodegradable fractions, S_S and X_S, and between the particulate inert and slowly biodegradable fractions, X_I and X_S, are not distinct for pulp and paper wastewater. Further work in this area should include long-term BOD testing on the primary effluent, primary influent and final effluent streams, from multiple mills of differing pulp and paper process configurations (Kraft, TMP etc) if possible.

A more regular measurement of the nutrient fractions is also suggested, measurements for each and every pseudo-steady state event would completely avoid the need to use average data or ratios from the wastewater characterisation work.

ASM-based model

ASM-based models could be further developed to include a heat and energy balance, which may be important for the pulp and paper industry as the effluent is generally hotter than municipal wastewater. Also, modelling nitrification as a two step process could be incorporated into the Petersen matrix, which would be particularly applicable for mills that measure nitrite in their effluent.

Modelling pulp and paper wastewater is still in the development stage, and more experimental evidence is required to support modification of kinetic and stoichiometric parameters. Nevertheless, future work will include estimating and interpreting the ammonification rate for the zero-nitrification process regime.

Operating strategies

The implementation of the proposed nutrient addition and operating strategies is suggested for the case study mill as a manual control in addition to existing nutrient addition strategies. Technology transfer to the mill and implementation of the proposed nutrient addition and operating strategies will occur in a step-wise fashion, allowing for the operators to adapt to the new strategies over time.

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Table of Contents

APPENDIX 1
Literature Review

1. Wastewater Treatment in the Pulp and Paper Industry

1.1. Historic Development

Collection of wastewater in a sewer or drainage system began as early as 2500 to 1500 B.C. in Crete and the Indus Valley, now Pakistan, and was well developed by the time of the Roman empire [1]. Biological wastewater treatment was developed in the nineteenth century in the form of septic tanks, and by 1913 the activated sludge process was developed concurrently by Ardern and Lockett in Manchester, England and by Clark in Massachusetts, United States [2]. Litigation between researchers and developers in the two countries delayed the widespread implementation of the process until the patent and royalty litigation was settled in favour of Activated Sludge Ltd of Britain in 1934 [3].

The pulp and paper industry is one of the world's oldest manufacturing industries, with historic evidence of paper making occurring in ancient Egypt and China [4]. The world-wide pulp and paper industry in 2005 produced 25.2 million (metric) tonnes of wood pulp, 6.7 thousand tonnes of printing and writing papers and 7.8 million tonnes of newsprint [5]. Pulp and paper mill effluent is typically discharged into a water body such as a river, lake or ocean. Secondary or biological treatment to remove the organic load and suspended solids discharged to the water body became popular during the 1980's and 1990's, particularly in Canada and Scandinavian countries [6].

The unit processes required for biological and physical-chemical wastewater treatment are discussed in depth in section 2.1.

1.2. Driving Factors for Research

Water pollution is a concern for most industrialised nations, and government regulation often drives the spending by industry on the infrastructure required to abate such pollution. Water pollution is a significant social cost of industry to society.

Eutrophication is defined as the process by which plant life proliferation causes reduced dissolved oxygen content (becomes eutrophic), in waters rich in nutrients [7]. While high organic load to receiving waters can promote plant life proliferation, the term eutrophication is typically used to refer to waters rich in nitrogen and phosphorus [8]. Phosphorus in particular is linked to eutrophication, as it is understood to be the growth-limiting nutrient in lakes where algae can fix nitrogen from the air [9]. The consequences of eutrophication include algal blooms and the decrease of fish stocks, which reduce the use of waterways [8]. Eutrophication occurs in localised areas such as lakes and rivers, as well as on a large scale such as in the Baltic and North Seas [10].

Wastewater treatment is considered to be a component of the so-called triple bottom line for industrial sites nowadays; however it does not constitute part of their core operations and as such, is often viewed as an unnecessary cost. With wastewater treatment plant installations in the order of $34 to $44 million capital cost (AST system, 1997 cost estimates), and operating costs in the order of $3.5 to $6 million per year, there is a genuine incentive to reduce operating costs related to the wastewater treatment plant [11]. The incentive is even greater if a reduction in operating costs aligns with a better quality effluent, as is potentially the case with the reduction of nutrient addition to the process.

1.3. North American context

Much of North America could be considered as water-rich, especially when compared to other countries such as Spain or Australia, where annual precipitation is a fraction of that in Canada. The fresh water in North America is to a large extent land-locked in inland lakes. In Canada, the total land area of the country 9 984 670 km^2 consists of 91% land and 9% fresh water [12]. The Great Lakes system (Superior, Michigan, Huron, Erie and Ontario) have a combined surface area of 245 000 km^2, of which approximately one third is Canadian territory [13]. The inland freshwater situation in North America is comparable that in Norway, Sweden and Finland, where freshwater covers 5.5%, 9.7% and 11.3% of the total land respectively [14-16]. The freshwater system of the Great Lakes poses international regulation issues, similar to those of many rivers in Europe [17]. In Canada, much of the fresh water is inaccessible for human use, as 85% of the population lives within 300 km of the Canadian-US border, and 60% of the fresh water flows north towards the Artic Ocean [18, 19].

World-wide regulations referring to pulp and paper mill effluent discharge are listed in Table 1 according to the country where they have been implemented. Experience with these regulations has been documented for pulp and paper mills [20, 21]. Regulations vary from the end-of-pipe concentration or total loading, to the receiving water impact-based limits, and set out the minimum standards for the industry. Site-specific discharge permits are being developed world-wide to further manage the requirements of specific receiving waters.

Table 1: Pulp and paper effluent discharge regulations by country [22]

Country	*Major Regulation**	*Year*	*Regulated Parameters*	*Documents available*
European Union	EU IPPC-directive 96/61/EC Best Available Techniques in the Pulp & Paper Industry	2001	COD, BOD TSS, AOX TP, TN, Flow	eippcb.jrc.es
Finland	Finnish Environmental Protection Act (EPA)	2000 2004	As per BAT**	environment.fi
Sweden	Swedish Environmental Code	1999	As per BAT**	internat. naturvardsverket.se
Norway	Environmental Impact Assessment (EIA) regulations	1999 2005	As per BAT**	regjeringen.no
Canada	Pulp and Paper Effluent Regulations (Fisheries Act) Canadian EPA	1992 2004	BOD, TSS, Acute toxicity Dependent on mill & receiving water study	ec.gc.ca/nopp/ PandP/ en/index.cfm
USA	US Federal Water Pollution Control Act (Clean Water Act) Water Quality Act Effluent Guidelines Pulp & Paper Great Lakes Legacy Act	1977 1987 1998 2002	Total Maximum Daily Load (TMDL) Dependent on mill & receiving water study	epa.gov
Australia	State-based EPA	1970 1993 1986	Dependent on mill & receiving water study	epa.vic.gov.au epa.sa.gov.au epa.qld.gov.au
New Zealand	Environment Act Resource Management Act	1986 1991	Dependent on mill & receiving water study	mfe.govt.nz

*Some provincial/county/state/territory legislation may exist to complement the major regulation, which represents the federal legislation or guidelines in most cases presented here.

**BAT refers to the European Best Available Techniques

1.4. Environmental Benchmarks

A number of environmental benchmarking systems are available that can be used to gauge the performance of mill operations or as guidelines for designing future installations. The main ones discussed here are the European Best Available Techniques (BAT), the Australian Accepted Modern Technology (AMT) and the North American Best Available Control Technology (BACT) or Best Available Technology Economically Achievable (BATEA)[1]. Recent proposals concerning new pulp mill projects have resulted in detailed guidelines and environmental impact assessments, which consolidate much of the world-wide environmental benchmarking for the pulp and paper industry, in particular for kraft pulp mills [23, 24].

The European Commission published the Integrated Pollution Prevention and Control (IPPC) directive in 2001 which outlines Best Available Techniques, defined as "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole" [25]. This document outlines the processes and the resulting air and water emission levels that are currently achievable with BAT, and is used as a reference for members of the EU. Table 2 below includes a summary of the BAT water emission levels for a bleached kraft pulp mill and an integrated newsprint mill, as an example of the BAT information available. BAT specifies a range of values for each parameter since each site uses different processes and different feedstock, the quality and quantity of raw materials required for different paper grades is site-dependent, and the size of the site has an impact on the effluent quality it can achieve [25]. The 2001 BAT document is currently under revision (2006 to 2007).

Table 2: EU BAT bleached kraft mill & integrated mechanical pulp and paper mill [25]

Mill	*Flow*	*COD*	*BOD*	*TSS*	*AOX*	*TN*	*TP*
	m^3/t	*kg/t*	*kg/t*	*kg/t*	*kg/t*	*kg/t*	*kg/t*
Bleached kraft pulp	30 - 50	8 - 23	0.3 - 1.5	0.6 - 1.5	< 0.25	0.1 - 0.25	0.01 - 0.03
Integrated mechanical pulp and paper mill	12 - 20	2.0 - 5.0	0.2 - 0.5	0.2 - 0.5	< 0.01	0.04 - 0.1	0.0004 - 0. 01

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[1] Best available technology economically available is referred to as BAT in the literature, but will be referred to as BATEA here for clarity.

TN refers to total nitrogen, TP refers to total phosphorus and AOX refers to adsorbable organic halogen compounds.

Accepted Modern Technology (AMT) is defined in the Tasmanian State Policy on Water Quality Management and Draft Environment Protection Policy (Air Quality) as a "technology which has a demonstrated capacity to achieve the desired emission concentration in a cost-effective manner, takes account of cost-effective engineering and scientific developments and pursues opportunities for waste minimisation" [23]. In July 2006, the Draft Integrated Impact Statements for a pulp mill being proposed by the company Gunns, in Australia, was submitted under these Tasmanian AMT guidelines.

EKONO Inc maintains a database in which mills across Europe, North and South America enter their own environmental data for benchmarking purposes [21]. Benchmarking environmental limits across geographical areas has highlighted some fundamental differences between regions, such as typical effluent flows and loads between North America and the Scandinavian countries [21]. These differences are indicative of the different regulations and evolution of the pulp and paper industries world-wide.

1.5. Characteristics of wastewater

There has been extensive research in the area of municipal wastewater treatment, which can be attributed to the necessity of treatment in all regions of the world and the extensive implementation of secondary treatment systems. Domestic wastewater contaminants consist principally of organic carbon compounds, as does pulp and paper mill wastewater, as do many other industrial wastewaters such as those from animal slaughter, dairy processes and textile processes, which are presented in Table 3 below [26, 27]. This fact results in the applicability of secondary wastewater treatment processes to municipal as well as pulp and paper industrial wastewaters, although the processes must be adapted for the unique nature of the organic carbon load in different wastewater sources. Certain other industrial wastewaters, such as those from mining and petrochemical processing, consist of inorganic pollutants or complex organic pollutants such as aromatic compounds, which can be toxic in high concentrations to microorganisms and may render the wastewater unsuitable for biological treatment processes [28, 29]. A discussion of wastewater characteristics, concentrating on the similarities and differences between domestic and pulp and paper wastewaters, is made below. It is assumed that municipal wastewaters consist entirely of domestic wastewater; i.e. combinations of domestic and industrial wastewaters are not considered.

Table 3: Wastewater characteristics: industrial & domestic (mg /L) [26, 27]

Parameters (mg/L)	*Agro industries*				*Domestic*
	Tannery	*Poultry processing*	*Textile*	*Dairy*	
Total COD	2,285	2,490	2,400	1,410	430
Soluble COD	1,298	1,770	1,700	1,075	170
TSS	770	418	500	190	350
TKN	160	343	35	63	47
Total P	6	30	34	7	8

1.5.1. Municipal vs. pulp and paper wastewater

Typical characteristics of primary treated pulp mill wastewaters from a bleached kraft mill (BKM), a thermomechanical mill (TMP) and a linerboard mill were presented by Slade *et al.* [30]. The pulp mill wastewater characteristics can be compared with the wastewater characterisation carried out for a municipal wastewater treatment plant in the Netherlands, as presented in the right-hand column of Table 4 [31]. From the data in Table 4, it can be seen that pulp mill primary treated wastewater contains a relatively high strength load in terms of COD and BOD concentrations and relatively deficient in the nutrients nitrogen and phosphorus when compared to primary treated municipal wastewater.

Table 4: Pulp mill and municipal primary treated wastewater characteristics [30, 31]

Parameter	*BKM*	*TMP*	*Linerboard*	*Municipal (average)*
COD tot (mg/L)	490 – 590	2,200 – 3,300	1,040 – 1,450	604
COD sol (mg/L)	430 – 480	1,540 – 2,240	890 – 1,250	241 [a]
BOD_5 (mg/L)	150 – 190	1,000 – 1,460	510 – 880	246
TSS (mg/L)	10 – 115	240 – 400	70 – 150	309
VSS (mg/L)	10 – 80	230 – 390	70 – 120	
TN (mg/L)	1.1 – 1.7	5.5 – 10.9	4.4 – 6.4	69
TN_{sol} (mg/L)	0.8 – 0.9	2.3 – 3.7	2.6 – 3.6	
NH_4^+-N (mg/L)	ND [b]	0.1 – 0.6	0.03 – 0.06	53

Parameter	BKM	TMP	Linerboard	Municipal (average)
NO_x (mg/L)	0.07 – 0.08	0.0 – 0.1	1.4 – 2.0	0.1
TP (mg/L)	0.6	2.9 – 5.8	0.9 – 1.4	8.4
DRP (mg/L) [c]	0.5	1.4 – 3.7	0.05 – 0.15	5.2
BOD_5: N	100:0.6 – 100:0.7	100:0.5 – 100:1	100:0.9	
BOD_5: P	100:0.4	100:0.3 – 100:0.4	100:0.15	
pH	7.9 – 8.0	4.8 – 5.3	5.1 – 7.0	

a - CODsol represents soluble COD in the filtrate of a 0.45μm filtered sample;
b - ND = not determined;
c - DRP = dissolved reactive phosphorus (ortho-phosphate plus may include some polyphosphates hydrolysed during testing).

1.5.2. Variability

1.5.2.1. Flow

Municipal wastewater flows vary on a diurnal (24 hour) cycle, typically with very low flow overnight and peak flows in the morning and evening, the exact time of which is dependent on the residence time in the wastewater collection sewer system and possibly the socio-economic demographics of the population [32]. There is also variability between weekdays and weekends, with lower peak flows seen on weekends [32, 33]. These flow variations occur over a period of hours. The magnitude of the flow variation is typically two-fold over the course of the day, and four-fold annually [34, 35]. This is demonstrated by the peaking factors typically used for municipal wastewater, from the average daily maximum month (ADMM) to the annual average daily (ADD) flows, from the maximum daily (MD) to ADD flows, from the peak hour (PH) to ADD flows, as presented in Table 5 below [34]. Modelling of rainfall and sewer flows can be used to predict flows to the municipal wastewater treatment system, which could aid operating stability [36].

Table 5: Municipal wastewater peaking factors [34]

Parameter	ADMM:AAD	MD:AAD	PH:AAD
Flow	1.15	1.40	2.14
BOD_5 Loading	1.40	2.00	3.44
TSS Loading	1.50	2.00	4.00

Parameter	***ADMM:AAD***	***MD:AAD***	***PH:AAD***
TKN Loading	1.40	2.00	3.44

Pulp and paper wastewater flows vary on a much shorter time scale, in the order of minutes. The average ratio of daily maximum to daily average flow is 1.25 for kraft (chemical) mills and 1.28 for mechanical mills, the average ratio of monthly maximum to monthly average flow is 1.14 for kraft (chemical) mills and 1.13 for mechanical mills [37]. This data indicates that there is not a statistically significant difference between these peaking factors for different types of mills.

While large flow variations are a challenge for wastewater treatment plant design at paper mills, it is less of an issue at continuous pulp mills [10]. At two integrated kraft mills, the major sources of wastewater flow are found to be from non-closed loops around paper machines, pulp dryers and from the spent pulping and bleaching liquors being washed to drain [38]. It was found that the age of the process technology had a large influence on the flow rate of wastewater from the bleaching process [38].

For both municipal and industrial wastewater, rain events can have a significant impact on the flow arriving at the treatment plants [39]. This effect can be considerable for municipal treatment plants, depending on the size of the catchment area and if all stormwater enters the same (combined) sewer or is treated in the same plant as sanitation wastewater [39]. Pulp and paper mills often collect and treat contaminated stormwater such as that from chip pile and landfill leachate, and rainwater from building roofs.

Municipal wastewater may undergo some transformations while it is in the sewer pipeline on the way to the treatment plant, since the residence time in the pipe can be extremely long during the transportation process [40]. These in-sewer transformations are sometimes referred to 'transport' processes, which describes transformations that include mixing, advection-dispersion, biodegradation, sedimentation, re-suspension, erosion and deposition [41]. Municipal sewer systems also suffer from infiltration of groundwater and exfiltration (leakage) of wastewater [39] .

Some municipal and pulp and paper mills employ strategies such as a 'balancing' or flow equalisation, which is achieved using a tank located upstream or downstream of the primary clarifier that equalizes flow variations [39]. Pulp and paper mills often use an off-line tank to deal with flow or concentration peaks. The equalization tank or retention basin design volume is calculated from the time-dependent mass and average flow rates [39], which may be a few hours of nominal influent flow. This may result in long hydraulic retention times during low-flow conditions if the tank is in-line with other process units. Municipal wastewater plants taking combined sewers use stormwater models to size their retention basins, commonly for half an hour or one hour of extreme stormwater flow [42]. To make use of such a tank risks the development of malodorous anaerobic conditions, therefore aeration of the tank contents may form part of the design [35].

Another strategy sometimes employed in municipal wastewater treatment plants is the installation of smaller volume tank designed to store the 'first-flush' of stormwater [43]. The first-flush was traditionally thought to be a period during which a high concentration of suspended solids were washed into the treatment plant with stormwater runoff, although it has been debated whether or not this first-flush actually exists [44].

1.5.2.2. Bulk organic load

The strength or (COD or BOD_5) concentration of pulp and paper wastewater can be significantly larger than that found in municipal wastewater. Comparing data presented in Table 3 and Table 4 above, the chemical oxygen demand (COD) can be used as one indication of the magnitude of the organic load on the effluent treatment plant. The total COD concentration in the BKM effluent is comparable to that in a municipal influent, whereas that from the TMP or linerboard mill is 2 to 3 times as high. Also, the soluble COD in the pulp and paper mill effluents makes up 68 to 88% of the total COD, whereas it makes up only 40% of the municipal influent.

In municipal wastewater, the variation in concentration of pollutants in the raw effluent is small compared to the variation in flow rate, and it is therefore the variation in flow rate that dominates the plant dynamics [31].

1.5.2.3. Temperature

The temperature of pulp and paper mill wastewater is typically in the range of 40 to 55°C, depending on the mill processes [45], whereas the temperature of municipal wastewater is nominally in the range of 20 to 35°C, dependent on the residence time and temperature in the sewer system. Pulp and paper wastewater temperatures can be as low as 10ºC in northern Canada, due to the extremely low ambient temperatures [37]. Steam is sometimes injected into the wastewater to ensure stable treatment plant operation. As discussed in section 2.3.1.1 below, microorganisms in the biological treatment stage operate most efficiently at a particular temperature range, for example 20 - 35ºC for mesophilic bacteria [46]. This often necessitates wastewater cooling for pulp and paper mill effluents in order to operate the treatment plant efficiently. Some research has been done regarding the use of thermophilic bacteria in wastewater treatment [46], including treatment of pulp and paper mill whitewater streams [47, 48].

Both pulp and paper and municipal wastewater demonstrate a notable variation in temperature between summer and winter seasons. The magnitude of this variation is dependent on the exposure of the wastewater to ambient conditions, either in open channels or open tanks, such as a balancing tank, selector or lagoon. The effects of heat loss due to low ambient temperatures in cold climates are considerable due to the high dependency of chemical reaction kinetics and oxygen solubility on temperature [49].

1.5.3. Biodegradability

As discussed in greater detail in sections 2.3.1 and 3.1, microorganisms consume organic carbon in order to grow and reproduce. A compound is considered 'biodegradable' if it can be decomposed or consumed by an organism, particularly by bacteria [50]. The rate at which microorganisms can consume organic carbon is determined by, amongst other things, the size and structure of the organic carbon molecule [51], and can be tested for using a standard 5- or 7-day biological oxygen demand (BOD) test [52]. A high concentration of toxic substances in the wastewater will inhibit the activity of the microorganisms in the treatment process, as well as having an adverse effect on the receiving water.

1.5.3.1. Molecular weight distribution of organic carbon

Organic material is released in the effluent streams of the CTMP process from the impregnation stage, bleaching and chip washing and screening processes [53]. This organic material can be described as lignin, carbohydrates, 'extractives'[2], and low molecular weight compounds such as acetic acid, methanol and formic acid [53]. The distribution of the molecular weight of organic carbon (COD) in CTMP pulp wastewater can be seen in Figure 1 below [53].

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[2] 'Extractives' refers to the waxes, fats, non-volatile hydrocarbons and resin (pitch) related compounds extracted from wood using solvent extraction, in this case DCM extraction carried out using dichloromethane as the solvent [54]

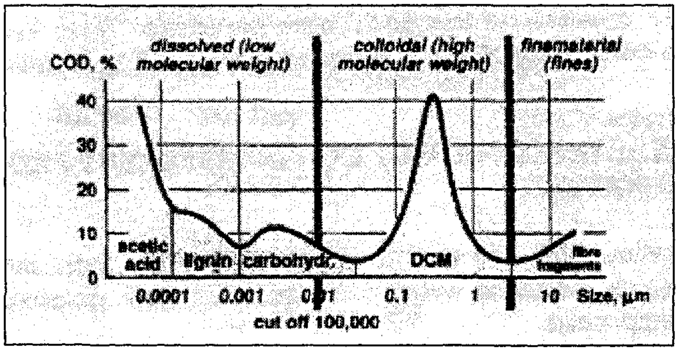


Figure 1: COD molecular size distribution, CTMP effluent [53]

Within the dissolved organic compounds region, the total organic carbon (TOC) for an integrated TMP-newsprint mill, before and after biological treatment with a trickling filter process, is presented in Figure 2 according to molecular weight [55]. This chart implies that the lower molecular weight fractions are removed at the highest rate by bacterial metabolic processes [55]. The increase in TOC removal for the higher molecular weight fractions can be interpreted as significant hydrolysis occurring over biological treatment [55].

These results are consistent with those found in another study of the biodegradability of effluent from two bleached kraft mill effluent, one hardwood and one softwood [51]. The latter study found that lower molecular weight organic carbon, less than or equal to 960 Daltons, was preferentially removed by biological treatment and that the most effective biological treatment occurred for organic carbon with a molecular weight less than 300 Daltons [51]. Another study of four bleached kraft mills further fractionated the mill effluent into 'low molecular weight (LMW) adsorbable' and 'LMW non-adsorbable', 'high molecular weight (HMW) hydrolysable' and 'HMW non-hydrolysable' [56]. *These fractions were interpreted as* corresponding to carbohydrates (HMW hydrolysable), lignin (HMW non-hydrolysable), methanol and carboxylic acids (for example, LMW) [56].

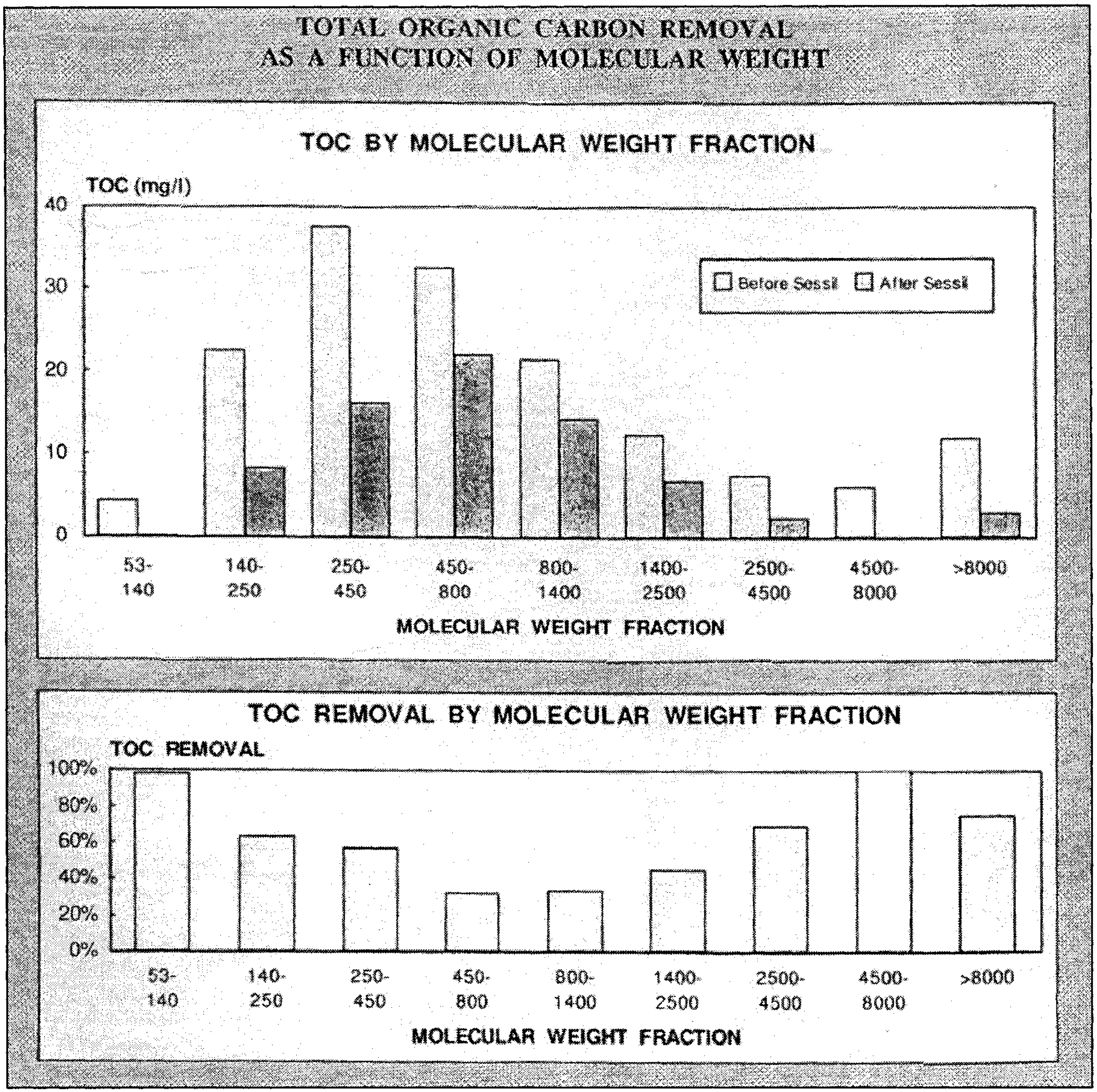


Figure 2: Total organic carbon (TOC) removal by trickling filter process according to molecular weight [55]

The particle size distribution for municipal wastewater, industrial food processing wastewater and agricultural swine waste primary and secondary effluent is presented in Figure 3. In terms of the first row of graphs, graphs (a), (e) and (i), it is clear that the COD in the primary effluent is more broadly distributed at a much lower concentration for the municipal wastewater than for either of the other wastewaters.

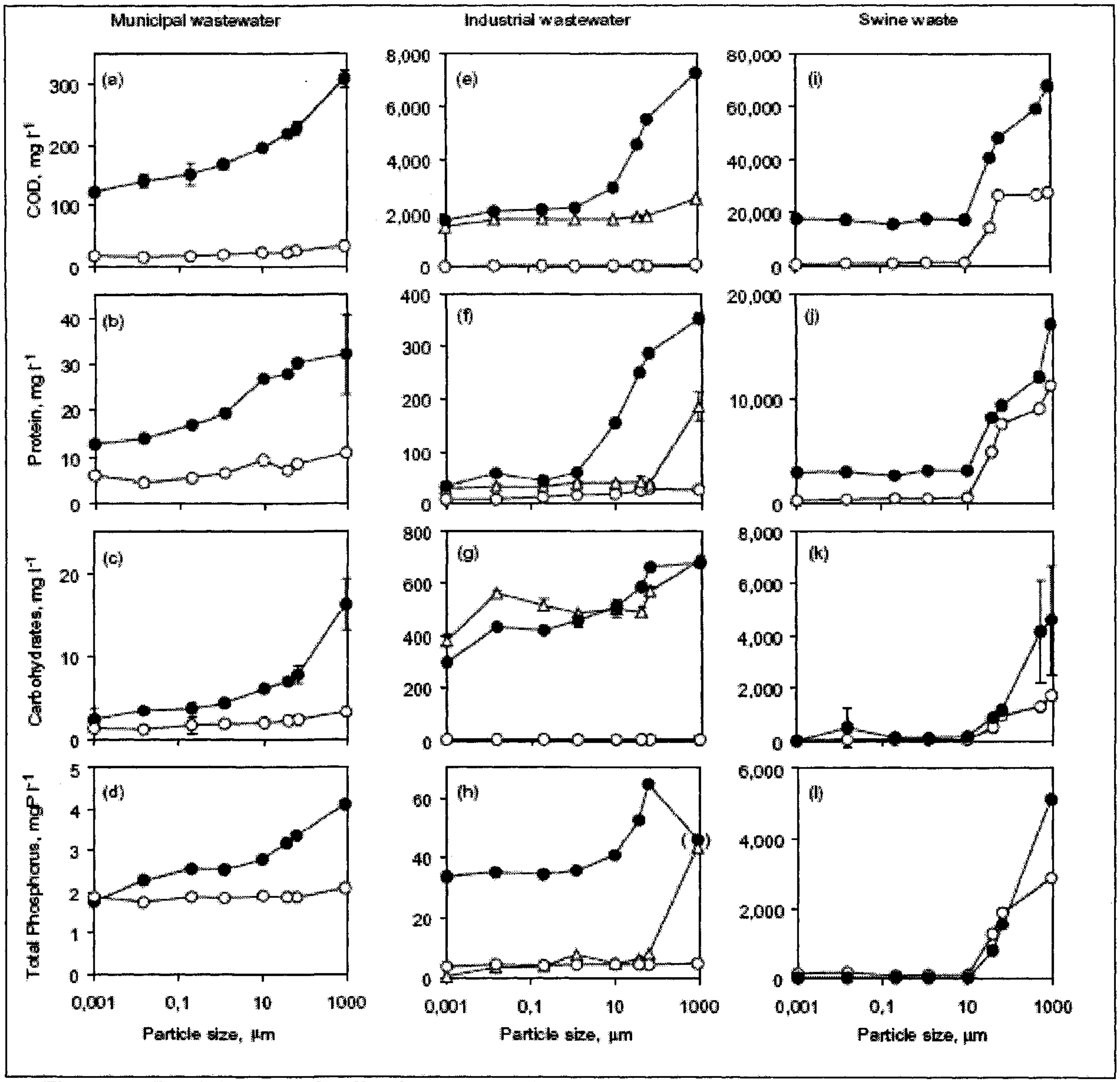


Figure 3: Particle size distribution for municipal, industrial food processing and swine waste (• = primary effluent, ○ = secondary effluent) [57]

Comparing Figure 1, Figure 2 and Figure 3, it can be seen that pulp and paper wastewater contains higher concentrations and fractions of longer, less readily degradable molecules than municipal wastewater. In particular, the peak of colloidal material which occurs in Figure 1 between the particle sizes of 0.1µm and 1µm corresponds to up to 40% of the COD load for the pulp and paper mill [53]. Any such peak is notably absent from the municipal wastewater COD distribution.

1.5.3.2. Toxicity

Toxicity refers to the "potential for a test constituent to cause adverse effects on living organisms" [39]. For municipal wastewater, toxicity is commonly caused by the final effluent ammonia, nitrate or nitrite concentration [39]. The presence of pathogens or pharmaceuticals that have not been removed during the treatment process may also cause adverse effects on the receiving water ecosystem [39, 58]. For pulp and paper effluent, toxicity is commonly associated with the fatty acids, resin acids, chlorinated phenols, monoterpenes and high hydrogen peroxide concentrations [29, 38, 45]. Resin acids are diterpenoid carboxylic acids found in softwood extractives, in the treatment plant these are less readily available for bacteria than other carbon sources [59]. A small quantity of resin acids are typically transferred from the chips to the effluent during the chip washing and pulping processes, the majority remains in the pulp stream and some is thought to degrade or be transferred to the steam produced in the refiners [60]. Figure 4 shows the molecular structure of resin acids commonly found in Canadian softwood pulp mill effluents [61]. It was found that nitrogen concentration (ammonia) played a critical role in the removal of resin acids in CTMP effluent [59].

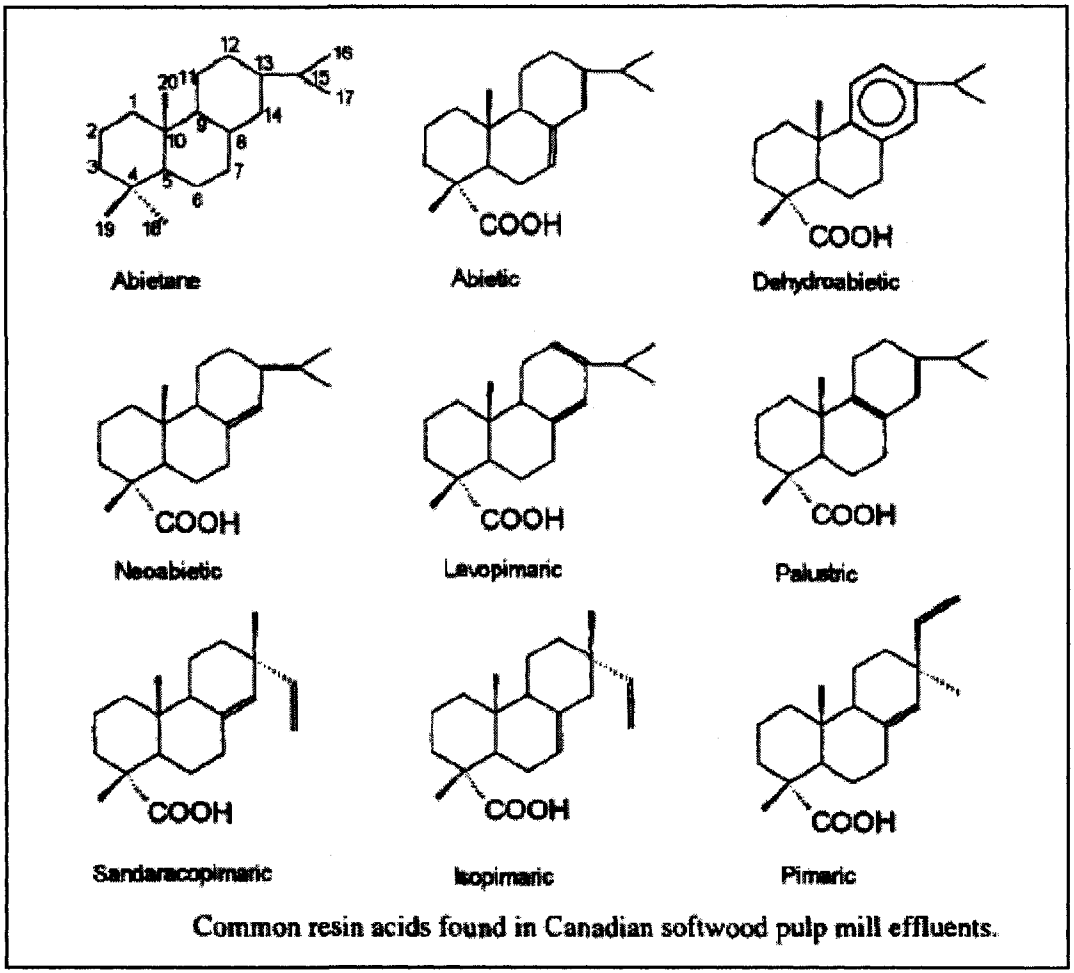


Figure 4: Common resin acids found in Canadian softwood pulp mill effluents [61]

1.5.4. Nutrient load and type

The importance of the nutrients in the influent to the secondary treatment plant is to supply the microorganisms with enough nutrients to achieve an adequate removal of organic carbon. Municipal wastewater provides a "good nutrient balance" [62], whereas pulp and paper mill effluent typically has a higher organic load and a negligible nutrient concentration, which results in a deficiency of nutrient with respect to the biological requirements of the biomass [10, 63]. For the purposes of the following discussion, the term 'nutrient deficient' can be used to describe a deficiency with respect to the biological requirements of the biomass such that the nutrient concentration is growth-limiting, and therefore the organic load (BOD) consumed in the process is not the maximum possible [62].

The nutrient load in municipal and pulp and paper wastewater was presented in Table 4 above. These data show that the nutrient load to the treatment plant from these sources is different in magnitude and nature. A recap is presented in Table 6 below. If the reactive, or assimilable, forms of nutrients are in the ammonia and ortho-phosphate fractions, it is clear from Table 4 that pulp and paper wastewater has very low concentrations of these nutrients available.

Table 6: Nutrient load recap, municipal and pulp and paper primary treated effluent [30, 31]

Parameter	***Municipal (average)***	***TMP***
BOD_5 (mg/L)	245.5	1,000 – 1,460
TN (mg/L)	68.8	5.5 – 10.9
NH_4^+-N (mg/L)	53.4	0.1 – 0.6
NO_x (mg/L)	0.1	0.0 – 0.1
TP (mg/L)	8.4	2.9 – 5.8
PO_4 (mg/L)	5.2	1.4 – 3.7*

* DRP

Nutrients are thus added to pulp and paper wastewaters as supplemental nutrients [10]. Due to the operating cost of purchasing these chemicals, it is in the mills' interest to minimise the quantity of nutrients added to the process, ensuring adequate nutrients for biomass growth while minimizing excess nutrient addition. It is also in the mills' interest to minimise the quantity of nutrients that are present in the final effluent discharged to the receiving environment, in order to avoid eutrophication and to adhere to government regulation. A number of control strategies have been implemented in the pursuit of these goals [63-65].

Cell metabolic processes are described in section 3.1, the nutrient requirements for stable AST operation, including growth-limiting kinetics, are described in section 3.2.5 and the source of nutrients in the pulp and paper mills is described in section 3.6.1.

This section of the literature review has presented some of the history of wastewater treatment, the driving forces behind research, the North American context, world-wide environmental benchmarks and some of the similarities and differences between municipal and pulp and paper wastewater characteristics. The following sections of the literature review will develop these concepts, particularly in relation to modelling of the activated sludge process in pulp and paper wastewater treatment.

2. Activated Sludge Treatment

2.1. Wastewater Treatment Plant

Biological wastewater treatment was developed in the nineteenth century in the form of septic tanks, and by 1913 the activated sludge process was developed concurrently by Ardern and Lockett in Manchester, England and by Clark in Massachusetts, United States as discussed in section 1.1 [2]. The following is a discussion of the unit operations and unit processes of a typical industrial wastewater treatment plant, as shown in Figure 5.

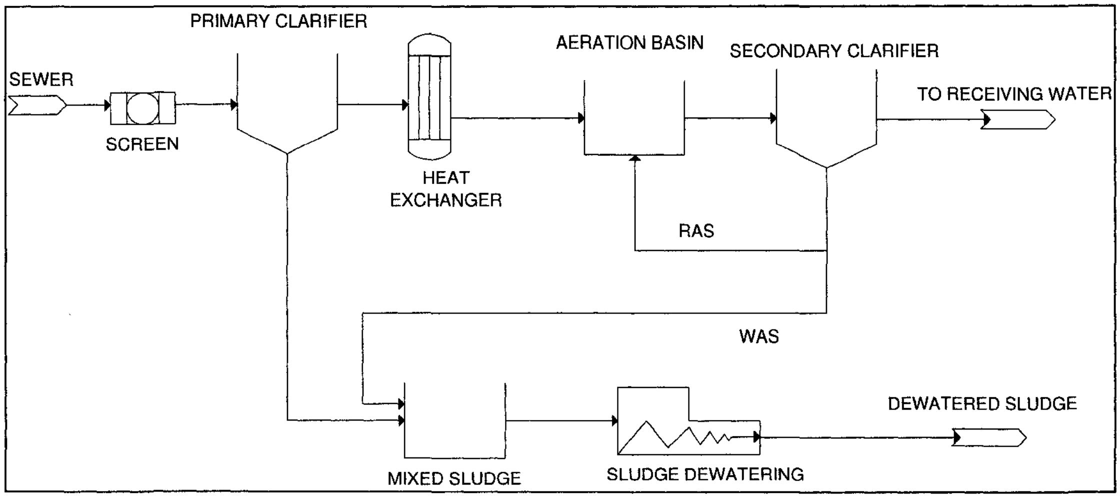


Figure 5: Typical wastewater treatment plant process (basic)

2.1.1. Coarse & Fine Screening

Effluent is often treated prior to arriving at the primary treatment in order to remove large and/or heavy pieces of trash, as well as fine contaminants such as sand and grit, the purpose of which is to protect downstream equipment [39]. Coarse screening can be achieved using equipment such as bar screens, comminution (grinding), rotating disc or drum screens [39]. Fine screening can be achieved using equipment such as gravity, aerated, vortex or centrifugal grit removal [39]. These screening steps generally removes inorganic insoluble matter [66].

2.1.2. Flow Equalisation

A wastewater treatment plant is one of the few processes where the influent flow rate to the process is not controlled, which is due to the fact that the wastewater treatment plant must accept and treat all flow that arrives. The variation in flow that does arrive at the treatment plant can be attenuated or dampened to some degree using a large tank upstream of the treatment plant to 'equalise' flow and solids loading to the plant [39]. The benefits of flow equalisation include more effective biological treatment and solids removal processes, due to the avoidance of shock loads to the process [39].

2.1.3. Surge Storage

A large tank or pond may be available for unexpected surges in flow, such as a large spill or extraordinary storm water flow. This tank allows for diversion of flows upstream and/or downstream of the primary treatment, and allows for the reintroduction of the contents of the tank to the treatment system. This is more common in industrial wastewater treatment where production shut-down would cause a large short-term flow to the wastewater treatment plant.

2.1.4. Primary Treatment

The purpose of primary treatment is to remove settleable and floatable solids relatively quickly prior to further treatment [39, 67]. A clarifier is often employed, and these can be designed based on gravity settling, high-rate settling, with or without lamella (inclined) plates, or using dissolved air floatation (DAF) technology [39]. Gravity settling relies upon a liquid-solid mixture being in a quiescent or motionless state, which is not perfectly true in a continuous process [39].

Coagulant chemicals such as aluminium and iron salts or organic polymers are often added to the primary clarifier in order to aid the speed and fraction of solids settling, which is referred to as advanced or enhanced primary treatment [39].

The benefit of primary treatment is the avoidance of the expense of biological treatment of solids that are relatively easy to settle, and not necessarily biodegradable, such as wood fibres, fillers, coating pigments, shives, ash and sand [25]. Settled solids are removed from the primary treatment stage, referred to as primary sludge, for further treatment either separate to or mixed with sludge produced in the secondary treatment stage. The primary treatment stage generally removes organic insoluble matter [66].

2.1.5. Wastewater cooling

Heat exchangers are often required to cool the wastewater prior to biological treatment, particularly for industrial wastewater such as pulp and paper wastewater. This is due to the fact that the microorganisms in the biological treatment stage operate most efficiently at a particular temperature, for example 20 - 35ºC for mesophilic bacteria, as discussed in section 2.3.1.1 [46]. Wastewater from the pulp and paper mill can be in the range of 40 – 55ºC [45]. The effects of heat loss due to low ambient temperatures in cold climates are considerable due to the high dependency of chemical reaction kinetics and oxygen solubility on temperature [49].

2.1.6. Secondary Treatment

Secondary treatment generally refers to the combination of a biological treatment stage and a solids separation stage. Biological treatment is used to remove soluble organic matter from the wastewater and the solids separation stage is used to remove biomass and other insoluble organic solids from the wastewater [66].

2.1.6.1. Biological Treatment

Two major categories of biological treatment exist: suspended growth systems and attached growth systems.

2.1.6.1.1. Suspended growth system

Suspended growth systems rely upon the exocellular excretion of polysaccharide to form a floc or agglomeration of microorganisms, as well as the recycling of microorganisms within the system in order to maintain the bacterial population [39, 68]. Floc formation is discussed further under section 2.3.1. The aeration system or another mixing system is used to maintain the suspension of bacteria in the wastewater. Bacteria are removed from the solids separation unit and returned to the aeration basin via the recycled activated sludge (RAS) stream or wasted via the waste activated sludge (WAS) stream, not necessarily with the same solids concentration. The majority of modern suspended solids treatment systems consist of either an activated sludge treatment system or an aerated stabilisation basin.

Activated Sludge Treatment (AST)

The activated sludge treatment system consists of a basin or tank in which a population of "active" bacteria are used to consume organic matter [39]. Many systems employ a selector; refer to section 2.2.2 for further discussion. A continuously operating AST basin can be modelled as a plug flow or continuously stirred tank reactor depending on the reactor configuration; refer to section 2.2.1 for further discussion. A batch-type reactor has also been developed, called a sequential batch reactor (SBR). Process configurations have been developed to take advantage of anoxic and anaerobic basins to promote nitrogen removal via the nitrification and denitrification processes and biological phosphorus removal (bio-P) via luxury phosphorus uptake, which can be advantageous for municipal wastewater [68]. Any combination of these processes is referred to as biological nutrient removal (BNR). A two-stage AST system was implemented to treat a paper mill effluent using nitrification and denitrification processes, which resulted in higher organic load removal efficiency than a single stage process [69]. Denitrification was also implemented at an ammonia-based sulphite mill in Canada [70].

Activated sludge systems are reasonably compact in size which results in little if any heat loss from the basin and a short hydraulic retention time. The AST system is relatively easy to control since aeration, recycle and wasting flow rates can be measured and controlled.

Aerated Stabilisation Basin (ASB)

An aerated stabilisation basin system consists of a pond or lagoon which can be fully aerobic or facultative: aerobic, anoxic and anaerobic in layers. The ASB can usually be modelled as a combination of plug flow and continuously stirred reactor tanks. The basin is often constructed of earth rather than concrete, and many have irregular shapes leading to complex hydraulic characteristics. Aeration is often achieved using surface aerators in aerobic or facultative ASBs. If not mechanically aerated, aeration and mixing in the ASB relies upon wind action [39]. Nitrification can be achieved in an ASB with a very long residence time, and then usually only during the summer months [71].

The ASB undergoes significant recycle of nutrients and lysed bacteria from the sediment in the basin, referred to as benthal feedback [72]. This recycling manifests itself as a lower nutrient demand for the same organic load than the equivalent AST system [9, 72]. It has also been seen that some pulp and paper ASB systems can operated without any supplementary nutrient addition, which is due to sufficient nutrient internal recycling and nitrogen fixation [63, 73, 74]. Solids separation can occur in non-aerated, non-mixed areas such as quiescent zones. If the quiescent zone becomes anaerobic, this can also lead to nutrient release [72]. Effluent from the ASB can contain algae [39].

The aerated stabilisation basin has a relatively large surface area which results in greater heat losses to atmosphere from the water surface than an AST system for an equal organic removal rate, and a long hydraulic retention time [39]. This makes the ASB process particularly suitable for treatment of effluent from Kraft mills which generally have a hotter effluent, although it is also employed at a few TMP and paper mills in Canada [75]. The ASB can be relatively difficult to control since internal recycling is not measurable or controllable, although some external controlled solids recycling has been installed [39].

Other suspended growth processes

There are many other suspended growth systems, notably the sequencing batch reactor (SBR), oxidation ditch, deep shaft reactor, aerobic and anaerobic digestion [39].

2.1.6.1.2. Attached growth systems

Attached growth or fixed-film systems depend upon microorganisms that are attached or fixed to some media across which the wastewater is passed [39]. Systems such as the trickling filter and the packed bed treatment systems use a stationary media-biomass and percolate the wastewater over the biomass. Other systems such as the rotating biological contactors (RBC) move a disc of media and biomass through the stationary wastewater.

The advantages of these systems include their suitability for warm climates, the low energy requirements and their low operating costs, which is primarily due to a lack of mechanical aeration.

2.1.6.1.3. Other biological systems

There are many other forms of biological wastewater treatment, notably the combination of suspended and attached growth process such as the membrane bioreactor (MBR), and processes that mimic naturally occurring wastewater treatment such as slow-rate, rapid infiltration, constructed wetlands, marshes, floating aquatic plant systems [39].

2.1.6.2. Solids separation

Solids separation in the secondary treatment stage is usually achieved using a clarifier, which is commonly designed based on a circular clarifier equipped with a scraping (rake) or suction-type solids removal [39]. Other clarifier types include rectangular clarifiers equipped with travelling flights or bridge solids removal, tray clarifiers, tube and lamella settlers and intrachannel clarifiers [39].

The purpose of the secondary clarifier is the clarification of the wastewater, which involves the sedimentation of the bacterial flocs, as well as the thickening of sludge, which involves compaction of the sludge in the base of the clarifier [39, 76]. The thickening of the sludge occurs in the base of the clarifier, which is designed to accommodate a certain period of storage of the sludge, even during peak load conditions [39, 77]. In a circular clarifier, a centre well may be employed to promote flocculation and the dispersion of energy (momentum) of the inlet flow [77].

Coagulant chemicals such as aluminium and iron salts or synthetic organic polymers are often added to the secondary clarifier in order to aid the speed and fraction of solids settling [68]. The use of inorganic coagulants increases the volume of the sludge, whereas organic polymers do not [68]. The chemicals are often added to the influent to the clarifier in the inner well to allow sufficient mixing prior to gravity settling.

A suction-type clarifier can operate at a lower sludge blanket height compared to a rake-type scraper clarifier under the same operating conditions, which results in lower solids carry-over to the final effluent for the suction-type clarifier [78].

The RAS and WAS streams may be removed from different levels in the clarifier, which results in different solids concentrations in each stream. This must be taken into account in mass balance or modelling exercises, the idealised mass balance does not take this into account.

2.1.7. Tertiary Treatment

Tertiary treatment may be required to treat the effluent from the secondary treatment due to particular obligations of a discharge permit or regulations, which may include nutrient concentrations or toxicity testing. Besides the treatment processes described below, tertiary treatment processes include sand/gravel granular medium filters, air stripping, breakpoint chlorination, ion exchange, activated carbon adsorption, chemical oxidation, volatization and gas-stripping [39]. These processes have been applied to paper mill effluent following secondary treatment using the activated sludge process [79, 80].

2.1.7.1. Polishing Ponds

A lagoon or pond located downstream of the secondary treatment plant can be used to 'polish' the effluent, this is usually an aerobic pond used primarily to decant suspended solids [39].

2.1.7.2. Chemical precipitation

Chemical precipitation is often used to remove phosphorus using calcium, aluminium and iron salts, which is discussed further in section 3.1.5.5. Precipitation is more effective for phosphorus in the form of ortho-phosphate than organic phosphorus or polyphosphates, therefore chemical addition would usually occur following secondary treatment [39]. The use of lime for process pH control may lead to inadvertent phosphorus precipitation and interference with other coagulant chemicals [81, 82].

2.1.7.3. Membrane technologies

Membrane technologies consist of pressurised wastewater being driven through a polysulfone- or cellulose acetate-based membrane of a determined porosity: microfiltration (MF) refers to a porosity of 1,000 to 5,000 Angstroms (1Å = 1×10^{-10} m), ultrafiltration (UF) refers to a porosity of 50 to 500 Angstroms, nanofiltration (NF) refers to a porosity of 5 to 20 Angstroms and reverse osmosis (RO) refers to a porosity of 1 to 10 Angstroms [25, 83]. The pressure required to drive the water through the membrane increases with decreasing porosity whereas the quality of the water increases with increasing porosity, up to the RO process which removes ions or deionises water [83]. Wastewater would usually be pre-filtered prior to applying the RO process in order to minimise membrane fouling and energy requirements [83].

2.2. AST Design: Current Configurations & Developing Technology

The following is a discussion of theory behind the main components of a traditional continuous AST unit: the reactor, the selector, the oxygen transfer system, the mixing system and the clarifier, as well as some of the areas of technology being developed on an industrial scale.

2.2.1. Chemical Reactors

Continuously fed chemical reactors can be characterised as idealised plug flow reactors (PFR) or continuously stirred tank reactors (CSTR), or any combination thereof. Other mass transfer systems that involve chemical reactions such as packed beds and fluidised beds can be used to describe biological reactors such as attached growth systems, these will not be discussed further here [66].

2.2.1.1. Plug Flow Reactor (PFR)

A plug flow reactor, also known as a tubular or piston reactor, is characterised by flow only in the longitudinal direction, perfect radial mixing (perpendicular to flow) and zero axial mixing (parallel to flow) [66]. Each cross section of the reactor is assumed to have a uniform velocity and concentration [66]. Resolving the steady state mass balance for this reactor demonstrates that the concentration of a reactant is distance dependent (in the direction of the reactor length) [66].

2.2.1.2. Continuously Stirred Tank Reactor (CSTR)

A continuously stirred tank reactor, also known as a well-mixed reactor, is perfectly mixed and therefore the contents of the entire tank are spatially uniform in concentration, temperature and reaction rate [84]. This is to say that the contents of the influent are instantly transformed by the chemical reaction in the tank, and the concentration of a species in the tank is equal to the concentration of that species in the effluent.

The CSTR mass balance for component A is as follows [66]:

Accumulation = Rate in - Rate out + Generation

$$V\frac{dC_A}{dt} = Q_o C_{AO} - QC_A + r_A V$$

where V is the volume of the reactor, C_A is the concentration of species A, r_A is the rate of production of species A, Q_o is the inlet flow rate, Q is the outlet flow rate. Although molar balances could be used, mass balances are traditionally used in wastewater engineering, which results in a reaction rate r_A with units of mass per volume per time [39]. Rearranging for influent flow rate equal to effluent flow rate, $Q_o = Q$, gives:

$$-r_A = \frac{Q}{V}(C_{AO} - C_A)$$

The suitable rate equation can then be substituted for r_A depending on the reaction kinetics, as discussed in section 0. For example, a first order reaction rate is represented by $r_A = -k_A C_A$, which gives a first order ordinary linear differential equation [39]:

$$\frac{dC}{dt} + \left(k_A + \frac{Q}{V}\right)C_A = \frac{Q}{V}C_{AO}$$

The mass balance can also be solved for steady state conditions based on zero accumulation and inlet flow rate equal to outlet flow rate, $Q_o = Q$, as follows [39]:

$$0 = Q_o C_{AO} - QC_A - k_A CV$$

$$C_A = \frac{C_{AO}}{1 + k_A\left(\frac{V}{Q}\right)}$$

The name 'chemostat' is sometimes used to describe a well mixed activated sludge process; the term comes from the microbiology field and refers to a well mixed biological reactor maintained at steady state by continuous overflow [85].

2.2.1.3. *Non-Ideal Reactors*

No actual reactor will behave exactly according to the idealised models described above. Therefore a combination of the PFR and CSTR is often used to represent constructed reactors. It should be noted that an infinite number of CSTRs in series will produce the same reaction model as a single PFR for a given reactor volume [39].

Reasons for non-ideal behaviour include non-ideal mixing conditions such as non-uniform mixing in CSTRs and excess axial mixing in PFRs, which can be produced by aeration systems [66].

2.2.1.4. *Reactor residence time*

The residence time of a reactor can be determined from a pulse or step change in concentration of an inert tracer, such as lithium or a coloured dye, the concentration of which can be measured easily throughout the basin or at the effluent. By analysing the effluent concentration of the tracer, a reactor can be characterised as a PFR, CSTR or a combination thereof. In Figure 6, Figure 7, Figure 8 and Figure 9 below, C_A represents the tracer concentration; t represents time and τ represents the mean residence time.

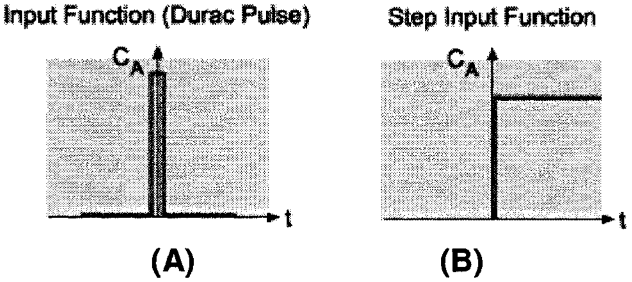
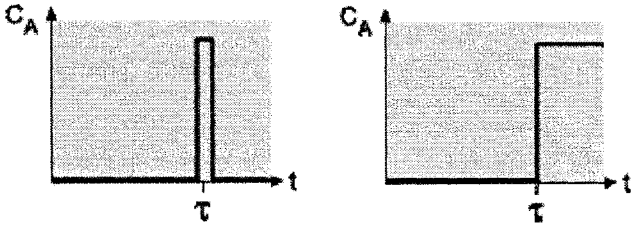


Figure 6: Tracer input functions (A) Pulse, (B) Step change [86]

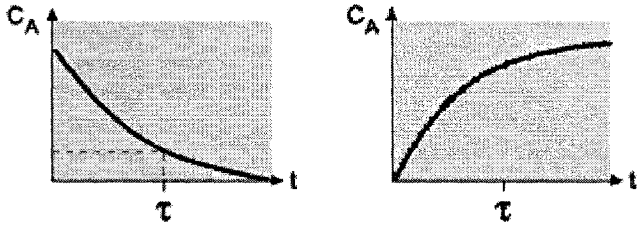
If the reactor operates as a plug flow reactor, a pulse tracer test would result in an effluent concentration profile with a pulse at one point in time, the hydraulic retention time. A step change tracer input would result in a step change at the HRT for a PFR.



(A) **(B)**

Figure 7: Tracer response functions Plug-flow reactor (A) Pulse, (B) Step change [86]

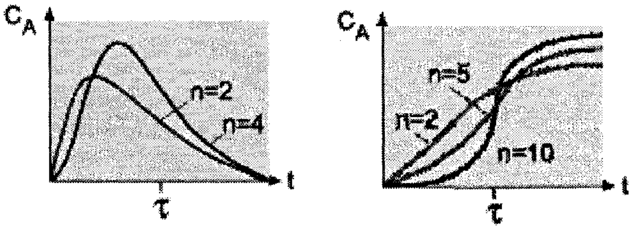
If the reactor operates as a completely mixed reactor, a pulse tracer test would result in an effluent concentration profile with an instantaneous initial concentration peak which then decreases quickly to asymptote at zero. A step change tracer input would result in an initial zero concentration which then increases quickly to an asymptote.



(A) **(B)**

Figure 8: Tracer response functions Continuously stirred tank reactor (A) Pulse, (B) Step change [86]

Multiple CSTRs in series are used to model flow conditions that are somewhere between those of the ideal PFR or CSTR. If the reactor operates as multiple CSTRs in series, a pulse tracer test would result in an effluent concentration profile with a characteristic peak, neither instantaneous nor a pulse. A step change tracer input would result in an increasing concentration of the tracer, which increases more rapidly at the hydraulic retention time as the number of tanks in series (n) increases.



(A) (B)

**Figure 9: Tracer response functions Multiple CSTRs in series (A) Pulse, (B) Step change,
n = number of reactors in series [86]**

2.2.1.5. Reaction Kinetics

A chemical reaction can be classified as homogeneous if it involves only one phase (gas, liquid, solid) or heterogeneous if it involves more than one phase, reversible or irreversible, and according to the order of the reaction rate equation [84]. The reaction rate equation has the general form of:

$$-r_A = [k_A].[f(C_A, C_B....)]$$

where $-r_A$ is the rate of consumption of A, k_A is the reaction constant specific to species A, and C_A is the concentration of species A [84]. Generally only irreversible reactions are considered in wastewater applications.

The specific reaction constant, k_A, is temperature dependent [84]. This temperature dependency is commonly described using the Arrhenius relationship:

$$k_A = B.e^{-E_a/RT}$$

where B is a constant, E_a represents the activation energy for the reaction, R is the gas constant (8.314 J/mol.K) and T is the temperature [84].

The order of the reaction is said to be the power to which the concentration of the species is raised [84]. For example a reaction with a reaction rate of the form $-r_A=k_A.C_A.C_B^2$ is said to be a first order reaction with respect to species A and second order with respect to species B; the overall order of the reaction is the sum of the order of each species which would be third order in this case.

The reaction rate order can be related to the stoichiometry of the chemical reaction, which is called an elementary rate law or an elementary reaction, such as the oxidation of nitric oxide [84]:

$$2NO + O_2 \rightarrow 2NO_2$$
$$-r_{NO} = k_{NO}C_{NO}^2C_{O_2}$$

The reaction rate is determined from experimental observation in all cases [84].

The reaction rate for the growth of microorganisms is discussed in section 2.3.1.6.

2.2.2. AST Selector

The purpose of a selector is to 'select' or encourage the growth of floc forming microorganisms, especially over and above the growth of filamentous bacteria which cause problems such as those described in section 3.2.5.2 [39]. This is achieved by having a mixing zone for the RAS and wastewater that is separate and upstream of the rest of the reactor [68]. The selector may or may not be aerated, depending on the desired process configuration [68].

The selector process is based on the notion that certain desirable bacteria are capable of more rapid uptake and storage of soluble substrate than their filamentous counterparts [68, 87]. This uptake and storage is typically seen in plug flow reactors where there is a gradient in the carbon concentration over time or space [88, 89]. The selector exploits this notion, rendering the activated sludge basin into a famine zone and the selector into the feast zone for the bacteria [68]. The bacteria that thrive in an aerobic selector have been shown include amorphous zoogloeal colonies [68] and are thought to include floc-forming bacteria [90]. In order to promote plug-like flow, a well-mixed selector would consist of multiple compartments to reduce longitudinal mixing [68]. Industrial wastewater such as that from the pulp and paper process typically has a larger substrate concentration than a municipal wastewater, and therefore a larger substrate gradient across the selector, which allows the use of well-mixed selectors [91].

2.2.3. Oxygen Transfer System

Aeration tanks with a depth of 8 to 12 m are described as 'deep', whereas those of 4 to 6 m depth were previously standard depth [92]. The depth of the aeration system has an effect on the oxygen transfer system, as discussed below.

2.2.3.1. Oxygen requirement

Oxygen is required under aerobic conditions for bacterial consumption of organic substrate, as described in section 2.3.1.2 and 0. Oxygen is also required for the nitrification reactions and for cell reproduction and maintenance processes [39], and therefore the quantity of actual oxygen required (AOR) can be predicted using the following equations [93]:

$$AOR_{total} = AOR_{carbon} + AOR_{nitrificat\ ion}$$

$$AOR_{carbon} = \frac{Q(r_{BOD} - 1.42 * Y)(S_O - S_e) + (1.42 * K_d)XV}{1000 * 24}$$

$$AOR_{nitrificat\ ion} = \frac{4.57 * Q * TKN_O \left({}^{P_N}\!/_{100} \right)}{1000 * 24}$$

Where Q represents the wastewater flow rate, Y represents the yield of biomass per unit substrate consumed (kg VSS/kg BOD_5), S_O represents the BOD_5 concentration in the influent, S_e represents the BOD_5 concentration in the effluent, K_d represents the endogenous decay coefficient (g VSS/g VSS.d), X represents the VSS concentration in the aeration basin, V represents the total basin volume, 1.42 represents the oxygen equivalent of the biomass (kg O_2/kg VSS), TKN_O represents the influent TKN concentration (mg N/L), P_N represents the percentage of nitrification occurring and 4.57 represents the weight of oxygen consumed per weight of nitrate formed by nitrification [93].

2.2.3.2. Oxygen solubility

The solubility of oxygen in water is governed by Henry's Law if no chemical reaction is taking place [94]. Henry's Law states that the concentration of a species is proportional to the partial pressure of the species in the gas phase (air) above the liquid, which can be expressed for oxygen as:

$$C_{O_2S} = H_S p_{O_2}$$

where C_{O2S} is the saturation concentration of oxygen, H_S is Henry's Law constant and p_{O2} is the partial pressure of oxygen in the gas phase [94]. Henry's Law constant, H_S, is a function of temperature and contaminants in the liquid phase (water) [94]. There are a number of configurations of Henry's Law, and the constant has also been expressed as k_H, but this may cause confusion with the reaction constant therefore the nomenclature of H_S will be used.

2.2.3.3. *Oxygen diffusion*

Oxygen or air is supplied to wastewater processes in the gaseous form. Mass transfer by the process of diffusion can be generally described by Fick's Law:

$$J = -D_L A \frac{dC}{dx}$$

where J is the mass flux or mass of a species transported per unit area per unit time, D_L is the diffusivity or diffusion constant and A is the cross-sectional area across which mass is transferred ignoring edge effects (assuming an infinite area of mass transfer) [84, 94].

The mass transfer of oxygen from the gaseous phase to the liquid phase is understood to be governed by a two-film diffusion process, which takes into consideration eddy diffusion in the liquid as well as molecular diffusion at the gas-liquid interface. Mass transfer is further simplified by assuming that the driving force of the concentration gradient occurs and is limited across the thickness y_L of the film in the liquid [94, 95], which is thought to be true for gases that are sparingly soluble in the liquid phase such as oxygen in water [39]. The mass transfer coefficient, k_L, can be expressed as a function of the diameter of the oxygen or air bubble and the depth of the aeration tank [96]. The diffusion model is still further simplified to measurable parameters using an overall mass transfer coefficient, K_La and the saturation concentration $C_{A,S}$ [94]:

$$\frac{dC_A}{dt} = K_L a\left(C_{A,S} - C_{A,X}\right)$$

The overall mass transfer coefficient, K_La is a function of temperature, which can be modelled using an Arrhenius-type equation [39]. K_La is also influenced by contaminants in the wastewater that accumulate at the gas-liquid interface and modify the interface, such as antifoamer and dissolved organics [95]. The saturation concentration $C_{A,S}$ is a function of temperature and the concentration of dissolved solutes [95].

2.2.3.4. *Aeration systems*

Industrial aeration systems use either air or pure oxygen to provide adequate oxygen for the microbial consumption of organic substrate. The types of aeration include surface aerators, submerged aerators and mechanical aeration [39]. The type of air diffusion devices ranges from fine-pore diffusers to jet aerators which rely on venturi effects and sparge-injection devices [39]. Surface aerators or mechanical aerators that rely on the dispersion of water droplets in the air above a basin or lagoon are not suitable for cold climates where the surface and droplets will freeze over.

Models of oxygen transfer in wastewater make use of empirical factors to take into account the ratio of the overall mass transfer coefficient, K_La, and the saturation concentration of oxygen, C_{O2S}, measured in pure water and that measured in a particular wastewater: the alpha and beta factors respectively [39]. The difference between the field conditions and standard conditions is taken into consideration using a combination of the alpha and beta factors as well as the Arrhenius-type compensation for temperature effects [39]. In addition to these empirical factors, the oxygen transfer efficiency (OTE) takes into account the particular aeration system installed, and is measured at standard conditions (SOTE) for commercially available equipment [39]. Fouling of aeration devices can also be taken into account [39].

2.2.4. Mixing System

A mixing system is required if the aeration basin is required to be of the CSTR type reactor. The degree of mixing required depends on the geometry of the basin and the type and distribution of the aeration system in an aerobic process [39].

2.2.5. Clarifier Hydraulics

A clarifier theoretically acts hydraulically like multiple completely mixed reactors in series, although the fluid dynamics occurring in the clarifier are quite complex [78, 97-100]. In fact, a centre well may be added to circular clarifiers in order to dissipate the energy (momentum) of the inlet flow as well as to promote flocculation [77]. “Readily settleable” solids settle quickly in the primary clarifier; flocculation of colloidal material is increased with increasing detention time in the clarifier [39]. A secondary clarifier is used to store a certain quantity of sludge, and therefore can be separated into two or more layers, such as the clarification zone and the thickening zone, since each layer theoretically acts hydraulically like multiple mixed reactors in series [101]. Even then, there are often differences between the theoretical and the actual hydraulic behaviour in the clarifier; this can be attributed to short-circuiting, dead spaces or non-ideal flow behaviour due to mixing, density and temperature currents [78, 97, 102, 103].

The hydraulics of clarifiers was investigated using pure water only, which is more relevant for primary clarifiers since flow in secondary clarifiers is noticeably influenced by density currents [100]. Solving momentum and mass transfer equations using a finite-volume method, assuming steady-state, incompressible flow and uniform density for axisymmetrical centrally-fed circular clarifiers results in computed velocity streamlines such as those depicted in Figure 10 below for a radial section of the clarifier, which does not take into account swirl produced by the scraping or suction sludge removal mechanism [100]. The inlet is on the left hand side and the effluent weir is on the right hand side of the diagram. A sill physically existed in the test case clarifier, between the inner sludge collection zone and the outer shallower zone, which is modelled in Figure 10 as a reduced sill height due to increased sludge volume resulting in both sections of the clarifier base having a 1:12 slope [100].

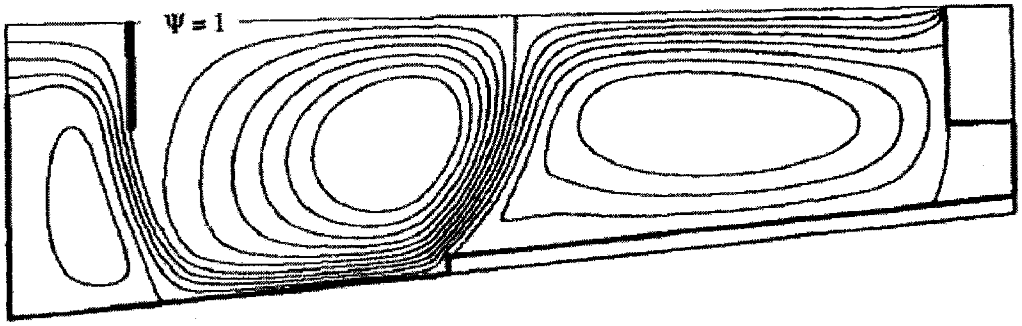


Figure 10: Finite-volume method computed velocity streamlines (no swirl effect) [100]

As discussed in section 2.2.1.4, the residence time distribution of the basin can be determined using a tracer test. The results of a pulse tracer test and calculations are shown as normalised tracer effluent concentration, C, over initial tracer concentration, C_O, versus normalised time, τ, over the mean hydraulic retention time, Θ, in Figure 11 and Figure 12 below. These tracer response curves demonstrate that the clarifier operates as tanks-in-series or multiple CSTRs in series. There is some short-circuiting, as indicated by the delay before the first appearance of the tracer, at normalised time 0.1 to 0.15.

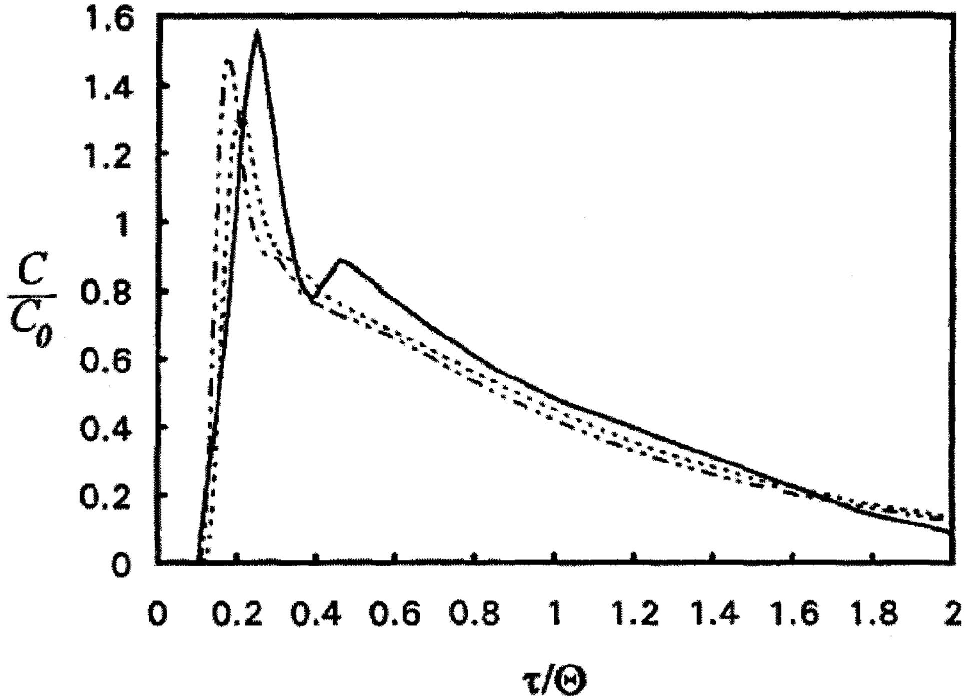


Figure 11: Clarifier tracer test results – no swirl effect: from McCorquodale's (1976) Experiments (—), Computation 58 x 80 grid (- - - -), Computation 64 x 122 Grid (— - - —) [100]

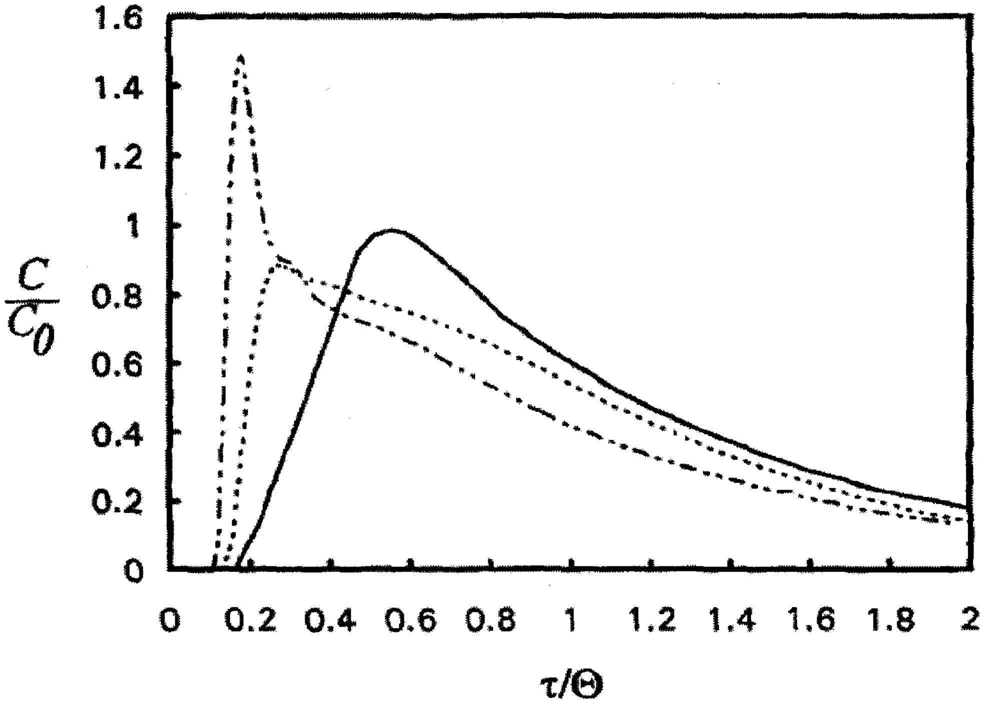


Figure 12: Clarifier tracer test results – with swirl effect: from McCorquodale's (1976) Experiments (—), Computation (- - - -), no swirl computation (— - - —) [100]

2.2.6. Clarifier settling & thickening

In addition to the complex hydraulics present in the clarifier, additional processes occur in the clarifier which can be described as by settling and thickening mechanisms, by which solids separation is achieved. This was described briefly in section 2.1.6.2. The formation of flocs is described further in section 2.3.1.4.

Gravity settling of an ideal particle can be described by the Stokes equation for a small sphere falling from rest in a viscous fluid [104]:

$$v_t = \frac{2}{9}\frac{r^2(\rho_s - \rho)g}{\mu}$$

Where v_t represents the terminal velocity, r is the particle radius, ρ_S represents the density of the particle (solid), ρ represents the fluid density, μ represents the fluid viscosity and g represents the acceleration due to gravity. This equation describes the balance of buoyant and kinetic forces by gravitational forces and is valid for a Reynolds number less than 0.1 [104].

The activated sludge that arrives at the secondary clarifier has a broad distribution of particle sizes, a municipal example of which has major peaks at 0.5 to 5.0µm and 25 to 1,600µm which represent primary particles and flocs respectively [105]. It was found that the settling of the activated sludge did not settle strictly in accordance with Stokes law, but enhanced settling for small sized primary particles occurred, which was attributed to the fact that the flocs collected the primary particles during settling, accurately described as flocculation [105]. Flocculation is aided by the presence of a centre well, by deeper tanks such that the sludge blanket is relatively low, by inboard weirs, good hydraulic distribution, low overflow rates and minimum mixed liquor suspended solids concentrations at the inlet to the secondary clarifier [105]. Flocculation is also improved by good floc formation, which includes reducing the shear forces placed on the flocs by the aeration system in the aeration basin [105].

A blanket of sludge is allowed to form in the base of the secondary clarifier, which serves to thicken and compact the sludge as well as store some biomass that is then recycled to the aeration basin in the RAS stream or wasted in the WAS stream. The thickening of the sludge blanket is commonly measured using the sludge volume index (SVI). The SVI reflects a number of possible events occurring in the sludge blanket including a high concentration of filamentous bacteria and a high zooglea bound water content [106]. The height of the sludge blanket can be controlled by adjusting the RAS and WAS rates.

2.2.7. AST Technology: Developing

Development in the AST process for pulp and paper wastewater application has recently focussed on two main areas: reducing sludge production and reducing the physical space required for the unit processes. Development in the arena of municipal wastewater application has been focussed on nutrient removal processes as well as those mentioned; however these are not usually applicable to pulp and paper wastewaters and will not be discussed further here. Zero effluent pulp and paper mills are discussed here as a technological development, although it eliminates the use of a wastewater treatment plant *per se*.

2.2.7.1. Moving Bed Biofilm Reactor (MBBR)

Traditional activated sludge technology has consisted of suspended growth aerated basin or lagoons, or fixed growth trickling filters, for example. Recent developments have seen the combination of these technologies in order to take advantage of the desirable attributes of both.

The MBBR technology places carrier elements inside a well mixed tank, the carrier elements provide a surface area for fixed growth to establish [107]. A MBBR process was demonstrated to be effective for integrated newsprint mill effluent [107]. A combination of the MBBR technology and conventional AST technology, called the biofilm-activated sludge process (BAS), has been implemented at multiple pulp and paper mills [108].

2.2.7.2. Low sludge production

With sludge treatment comprising up to 60% of the wastewater treatment plant operating costs, there is a significant incentive to reduce the quantity of sludge produced or find alternative treatment processes for the sludge [109]. Options exist for changes to the wastewater treatment process that would reduce the overall quantity of sludge produced, these include extended aeration, membrane bioreactors, low sludge process and anoxic/oxic zone treatment amongst others [109]. Alternatives for treatment of the sludge produced include incineration, vitrification, gasification, super critical water oxidation, aerobic and anaerobic digestions amongst others [109].

2.2.7.3. Mechanical lysis of sludge

Lysis, as discussed in section 3.1.2.6, describes the rupture of the cell wall, which results in death for a single cell organism, as well as the release of the cell contents into the wastewater media [66]. The extended aeration process is essentially an activated sludge process with a very long sludge age or residence time, which allows the process to operate with endogenous respiration, as described in section 3.1.2.5 [110]. Mechanical lysis of the WAS stream has been explored as a way to improve the extended aeration process and avoid variations in growth and decay rates, while avoiding the incur of costs associated with physical-chemical lysis [111].

2.2.7.4. Reduced and zero-effluent mills

Pulp and paper mills use a relatively large quantity of water, although this quantity has been reduced in recent years in terms of water per tonne of paper produced [112]. Recycling of biologically treated wastewater back to the mill has been studied [113]. A reduction in mill effluent due to cleaner processing within the integrated bleached Kraft mill led to the production of a nutrient deficient wastewater and necessitated phosphorus dosing in one ASB treatment plant [114].

Some mills have implemented zero-effluent operating regimes, which involve closing water loops within the mills, the effects of which include increasing the concentration of dissolved organic and inorganic substances [112]. Mills often require some type of wastewater treatment inside the mill in order to act as a 'kidney' to purge these dissolved compounds [112].

2.3. AST Operation

The operation of an AST process requires a balance between many parameters in order to provide the optimal growth conditions for the microorganisms in the AST, and efficient solids removal to provide a high quality effluent. The following is a discussion of the microorganisms commonly found in the AST and the growth pressures on the organisms.

2.3.1. Microbiology

The basis of the Activated Sludge Treatment process is the 'active sludge' or microorganisms that consume the carbonaceous substrate contained in the influent to the wastewater treatment plant. Transformation mechanisms for carbon and other nutrients are discussed in greater detail in section 3.1. This section will introduce the microorganisms that constitute the activated sludge.

2.3.1.1. Psychrophilic, Mesophilic, Thermophilic

Microorganisms used in the biological treatment stage operate most efficiently at a particular temperature, for example 20 - 35ºC for mesophilic bacteria, as discussed in section 2.3.1.1 [46]. The possible temperature range for growth of different classes of organisms and their optimum growth temperature range is described in Table 7 below [39].

Table 7: Classification organism growth rates according to temperature [39]

Temperature class	*Temperature range*	*Optimum range*
Psychrophilic	10 – 30ºC	12 – 18ºC
Mesophilic	20 – 50ºC	25 – 40ºC
Thermophilic	35 – 75ºC	55 – 65ºC

2.3.1.2. Aerobic, Anaerobic, Facultative

Microorganisms can be classed according to the type(s) of metabolism that they use in order to consume substrate to reproduce and maintain their cellular material. Some organisms can tolerate non-optimal oxygen conditions, as seen in Table 8 below [115].

Table 8: Classification organism metabolism & oxygen relationships [115]

Oxygen class	*Sub-group*	*Relationship to oxygen*	*Metabolism*
Aerobic	Obligate	Required	Aerobic respiration
	Facultative	Not required, but growth better with oxygen	Aerobic, anaerobic respiration, fermentation
	Microaerophilic	Required at concentration levels less than atmospheric	Aerobic respiration
Anaerobic	Aerotolerant	Not required, growth is not better if oxygen is present	Fermentation
	Obligate	Harmful or lethal	Fermentation, anaerobic respiration

2.3.1.3. Eukaryote, Prokaryote

Microorganisms can be classed according to their cellular structure. The significant difference between the major classes of organisms is the presence or lack of a membrane-enclosed nucleus: a eukaryote has a membrane-enclosed nucleus and a prokaryote does not [115]. Other important differences are listed in Table 9 below. With respect to wastewater treatment, simple bacteria are Prokaryotes and higher organisms such as protozoa and rotifers are Eukaryotes: higher organisms usually prey on the simple organisms as well as the substrate, and are hence described as predatory [39].

Table 9: Cell structure characteristics (✓ = present, × = absent) [115]

Characteristic	*Prokaryote*	*Eukaryote*
Phylogenetic groups	Bacteria, Archaea	Eukarya: Algae, fungi, protozoa, plants, animals
Nuclear membrane	×	✓
DNA	Single molecule, not complexed with histone	Linear, usually complexed with histones
Division	No mitosis	Mitosis
Reproduction	No meiosis, fragmentary process, unidirectional	Regular process, meiosis,
Internal membranes	Relatively simple	Complex
Membranous organelles	×	✓

Characteristic	Prokaryote	Eukaryote
Cytoplasm cell walls	✓ in most	✓ in most (× in animals & most protozoa)
Flagella movement	Flagella rotate, single type of protein	Flagella or cilia, do not rotate
Size	Generally small, usually < 2µm in diameter	Generally larger, 2 to > 100µm diameter

2.3.1.4. Floc formation

A floc is an aggregate of particles that can be formed via two mechanisms: microflocculation or perikinetic flocculation by the random movement of the particles (Brownian motion) and macroflocculation or orthokinetic flocculation by velocity gradients and gravitational settling [39]. In the activated sludge process, microorganisms form flocs larger than primary particles, usually in the size range of 50 to 200µm [39]. Although the mechanisms are not fully understood, it is thought that filamentous bacteria form the backbone of these flocs, and the extracellular polysaccharide secreted by microorganisms forms bridges that allows the floc to grow [68]. Formation of the floc is key to the performance of the activated sludge process since a well-formed floc will settle easily in the secondary clarifier and produce a clear effluent. Problems with floc formation include high concentrations of filamentous bacteria which produce a floating or bulking effect, and high shear on the flocs which produce small 'pin' flocs which do not settle easily [68]. Substrate is adsorbed (biosorption) onto the floc and then assimilated into the microorganism cells [116]. Sorption occurs in the selectors where the returned sludge (RAS) is mixed with the wastewater [117].

2.3.1.5. Floc population

A diverse population of microorganisms is desirable in the floc: bacteria, fungi, protozoa and metazoa [68]. A typical floc contains 15 to 20% exocellular polymers on a suspended solids basis [68]. A diverse population in the floc ensures that the activated sludge can adapt to changes in their environment and/or substrate [118]. The substrate and nutrient concentration in the wastewater can affect the selection of different microorganisms [90, 119]. An analysis of seven bleached Kraft mills worldwide found substantial differences in the bacterial composition of their biological wastewater treatment systems [120].

2.3.1.6. Growth rates

The rate of bacteria growth, ρ_{GROWTH}, can be described using the following equation [118]:

$$\rho_{GROWTH} = \mu_{MAX} \cdot f(C_A).X_B$$

where μ_{MAX} represents the maximum specific growth rate, $f(C_A)$ is a function of the substrate concentration, C_A, which describes the growth kinetics and X_B is the concentration of the biomass [118].

The growth kinetics function $f(C_A)$ can be modelled with equations such as the Michaelis-Menten and Monod equations which consider that the rate of substrate removal is limited by the concentration of the dissolved substrate [39]. The Monod equation is used to model the relationship between the concentration of the substrate and the rate of growth of the microorganism [121] cited in [87]:

$$f(C_A) = \frac{C_A}{K_A + C_A}$$

where K_A is the saturation constant and C_A represents the concentration of the growth limiting substrate [87]. The growth limiting substrate can be the carbonaceous substrate or it can be another nutrient required for growth.

A first order kinetic equation is sometimes used to describe bacterial growth, and is often used to describe the rate of the bacterial decay process, for example [118]:

$$\rho_{DECAY} = b.X_B$$

where b is the decay rate constant and X_B represents the concentration of the biomass [118].

2.3.2. Growth pressures

The optimal growth and substrate removal conditions for the microorganisms in the activated sludge are subject to a number of pressures on the microorganisms. These growth pressures include dissolved oxygen levels, pH, concentration of nutrients and substrate available, temperature and toxicity as discussed previously [122]. The following is a discussion of two additional growth pressures: the F/M ratio and the retention time in the aeration basin, as measured by MCRT.

2.3.2.1. Food to microorganism (F/M) ratio

The food to microorganism (F/M) ratio is defined as [123]:

$$F/M = \frac{QC_O}{V_{AST} X_{AST}}$$

Where Q is the effluent volumetric flow rate, C_O is the substrate (BOD or COD) concentration in the influent, V is the volume of the aeration basin and X is the volatile suspended solids concentration in the aeration basin. The F/M ratio can be used to operate an activated sludge plant [123], as it indicates the loading of substrate per unit biomass in the aeration basin.

As the F/M ratio decreases, microorganism growth rates may become limited by substrate concentration. As the F/M ratio increases, microorganism growth rates may not be limited by the substrate concentration, in which case more dissolved oxygen and nutrients may be required to facilitate higher growth rates.

2.3.2.2. Mean cell residence time (MCRT)

The mean cell residence time (MCRT) for an ideal continuously-stirred tank reactor (CSTR) is defined as:

$$MCRT = \frac{V_{AST} X_{AST}}{Q_{effluent} X_{effluent} + Q_{WAS} X_{WAS}}$$

Where $Q_{effluent}$ and Q_{WAS} represent the volumetric flow rate, $X_{effluent}$ and X_{WAS} represent volatile suspended solids concentration in the final effluent and WAS streams respectively. The volume of the secondary sedimentation basins are sometimes included with the volume of the AST basins in this calculation [124]. Using the volatile suspended solids concentration for both the MCRT and F/M calculations is problematic in that the VSS measurement does not account for the activity of the biomass [124]. The MCRT can be used to operate an activated sludge plant in combination with the specific growth rate of an organism, as these parameters indicate whether the biomass has had enough time in the process to establish itself and will grow more rapidly than it is removed from the process [124].

2.4. Process Control

2.4.1. Basic Control Theory

Process control for continuous processes is based on a controlled or manipulated variable 'w', a measured variable 'x' and a set point for 'x' [125]. An algorithm is required to relate the control variable to the difference between the measured value for x and its set point [125].

A feedback controller reacts to process disturbances and a feed forward controller reacts before the process is disturbed [125]. Figure 13 below shows the simplest form of a boiler level control loop for (a) feed back flow control and (b) feed forward flow control, where FE is a flow element and LE is a level element, which are the measured variables [125].

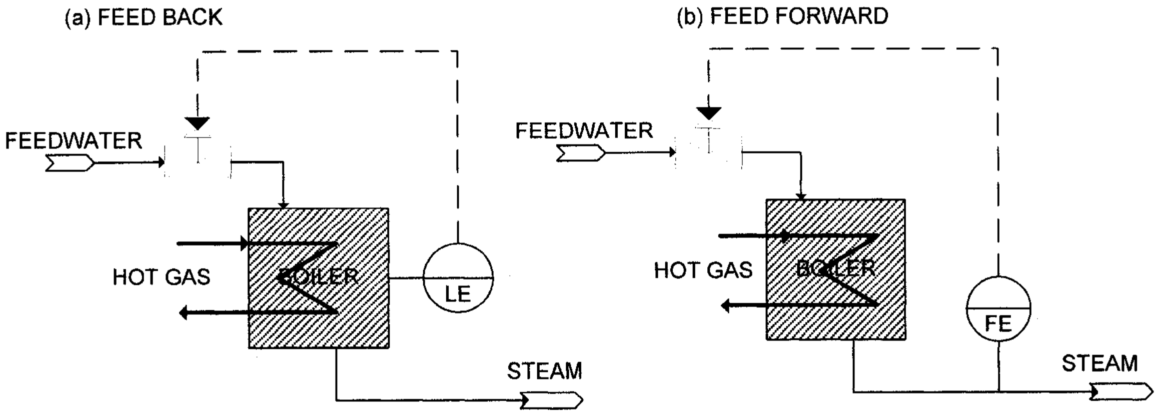


Figure 13: Control loops: (a) feedback and (b) feed forward [125]

2.4.1.1. *Feed back control*

The error signal or function is the difference between the measured variable and its set point, according to the equation [125]:

$$e(t) = y_{sp}(t) - y_m(t)$$

The error signal is then related to the output signal p according to a relationship, usually proportional, integral or derivative, as visualised in Figure 14 below.

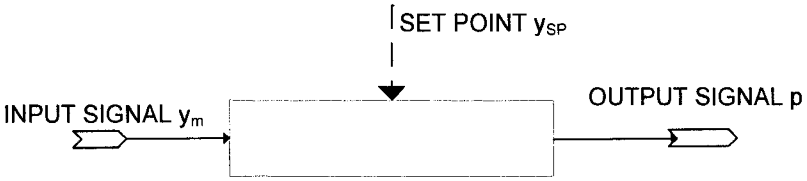


Figure 14: Feedback controller schematic [125]

Further details of these relationships are listed in Table 10 below, where K_C represents the controller gain, τ_I represents the integral time, τ_D represents the derivative time, and $\bar{p}$ represents the bias steady state value of p [125]. The benefit of additional complexity of control is the corresponding increase in accuracy and reduced response time.

Table 10: Controller output signal: ideal P, PI, PID feedback controllers [125]

Characteristic	*Output signal p(t)*

Characteristic	Output signal p(t)
Proportional (P)	$\bar{p} + K_C e(t)$
Proportional, Derivative (PD)	$\bar{p} + K_C\left(e(t) + \frac{1}{\tau_I}\int_0^t e(t^*)dt^*\right)$
Proportional, Derivative, Integral (PID)	$\bar{p} + K_C\left(e(t) + \frac{1}{\tau_I}\int_0^t e(t^*)dt^* + \tau_D \frac{de(t)}{dt}\right)$

2.4.1.2. Feed forward control

Feed forward control is possible when disturbance variables can be measured on-line [125]. A comparison of feed forward and feedback controls, and their combination, for effluent treatment plants have been carried out [126, 127].

2.4.2. AST Control

Control of an AST system is complex and involves many control loops. AST process control is commonly achieved using one or more of the following strategies listed in Table 11, which correspond to growth pressures as discussed in section 2.3.2. In addition to the control loops and strategies presented below, the configuration of the process also addresses growth pressures: hydraulic retention times, temperature, types of microorganisms, type and biodegradability of substrate.

Table 11: Common AST control strategies & corresponding growth pressures [35, 122]

Control loop	Control Strategies	Growth Pressure
Sludge wasting (WAS)	Sludge age F/M ratio MLSS Microscopic findings	F/M ratio
Sludge recycle (RAS)	Clarifier sludge depth RAS suspended solids Overall solids balance HRT secondary clarifier	F/M ratio
Dissolved oxygen	Automatic/manual	Dissolved oxygen

Control loop	***Control Strategies***	***Growth Pressure***
	Constant aeration rate	
Chemical addition	Constant dosing rate Proportional to flow Influent short-term BOD or COD Nutrient residual Nutrient balance WAS nutrient content Influent/effluent pH Toxicity tests Microscopic findings SVI	Nutrients pH Toxicity Types of microorganisms
Flow or load equalisation	Equalisation basin Pumping rate/ level control	Hydraulic retention times F/M ratio

2.4.2.1. Knowledge-based control

Given the empirical nature of some wastewater characteristics, empirically determined control strategies are sometimes employed in wastewater treatment. A 'holistic health index' was employed to account for the floc morphology (form and structure), floc activity, floc nutrient and floc settleability in multiple pulp and paper activated sludge treatment plants [128]. The index takes into account various on-line and laboratory measurements from multiple locations in the plant [128].

In terms of control of nutrient residuals and nutrient dosing, a simplified [129] and an advanced control strategy were employed at a municipal recirculating BNR plant, implementing a 'STAR' or Superior Tuning and Reporting system [130]. This advanced control is possible due to on-line nutrient fraction measurements as well as on-line dissolved oxygen and flow rate measurements [130].

A dynamic process simulation based on the ASM models (discussed in section 5) was used for the purposes of operator training, process operation observation and process operation prediction at a municipal wastewater treatment plant [131].

3. Carbon & Nutrient Transformation Mechanisms

Microbiological activity is the basis of the activated sludge process, through which the removal of organic matter from wastewater is achieved. The following is a review of the mechanisms via which this activity occurs and may be controlled, starting with activity at the molecular level and progressing to the design and operation of a large scale plant.

Microorganisms consume organic carbon in order to grow and reproduce. By definition [132], a nutrient is "any element or compound necessary for or contributing to an organism's metabolism, growth, or other functioning". The essential nutrient in the growth and reproduction of microorganisms is carbon, followed by oxygen, nitrogen and phosphorus. These four elements are the major constituents of the nucleotide molecule (refer to Figure 15), from which DNA is constructed, and are therefore vital for the growth and reproduction of cells.

Other substances that are essential for cellular growth include macronutrients: hydrogen, sulphur, potassium, magnesium, calcium and sodium, micronutrients: boron, chromium, cobalt, copper, iron, manganese, molybdenum, nickel, selenium, tungsten, vanadium and zinc, and growth factors: vitamins, amino acids, purines and pyrimidines [115].

For further details on the microbiology of the AST process, refer to section 2.3.1. The discussion below applies generally to both prokaryotic and eukaryotic cells, and is in some cases specific to prokaryotic cells; this includes bacteria and blue-green algae, which are important for aerobic wastewater treatment.

3.1. Cell pathways (Micro level)

The term metabolism describes all biochemical functions of a cell. A cell's metabolic reactions or pathways can be further described as catabolic, the breaking down of complex organic molecules (polymers to monomers, for example) which releases energy, or anabolic, the building up of complex organic molecules (monomers to polymers, for example) which consumes energy. Some processes participate in both catabolic and anabolic processes; these are referred to as amphibolic.

The cellular processes for microorganisms are generally categorised as cell respiration, reproduction or cellular maintenance processes. Respiration consumes substrate (carbohydrate, lipid or protein) to produced energy.

Reproductive processes consume energy to produce molecules such as DNA and RNA. Cellular maintenance processes consume energy to resynthesise molecules such as proteins or nucleic acids. The biomass that is produced per unit of substrate consumed by the bacteria is referred to as the yield [66].

These cellular pathways can be represented by oxidation-reduction (Redox) reactions in that they involve the exchange of electrons. In a fully aerobic environment, the electron acceptor will be oxygen, in anoxic or anaerobic environments the electron acceptor may be an inorganic or organic compound. Aerobic bacteria can be further categorised by the type of electron donor and source of carbon that they use in their redox reactions, as detailed in Table 12. The redox half reactions for carbon and each nutrient will be detailed in the following sections.

Table 12: Classification of bacteria according to redox reactions [66]

Bacteria	***Electron Donor***	***Carbon source***	***Example***
Heterotrophic	Organic carbon	Organic carbon	Floc-formers, Denitrifiers
Autotrophic	Inorganic compounds	Carbon dioxide	Nitrifiers

3.1.1. Cell transport

The transport of biodegradable carbon sources across the cell membrane occurs via facilitated enzyme transport [82]. Transport of inorganic assimilable nutrients across the cell membrane occurs via diffusion [82].

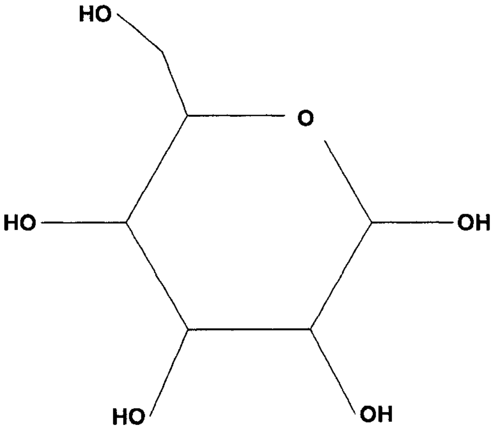
3.1.2. Carbon

3.1.2.1. Cell respiration

Carbon is broken down or catabolized from long-chain carbohydrate, protein and lipid molecules into monosaccharides, amino acids, fatty acids and glycerol. Refer to Figure 15 for the chemical structures of these molecules. The term disaccharide refers to a carbohydrate of two monosaccharide units, polypeptide refers to molecule of two or more amino acids, protein refers to a molecule of fifteen or more amino acids, a nucleoside is a molecule that incorporates one monosaccharide and one nucleic acid monomer, a nucleotide is a phosphate ester of a nucleoside [115].

<table>
<tr><th>Monomer</th><th>Polymer</th></tr>
<tr><td>

Monosaccharide (glucose)



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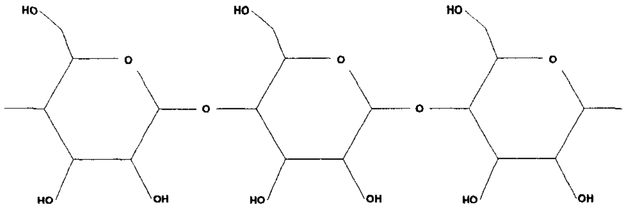
Carbohydrate (polysaccharide)



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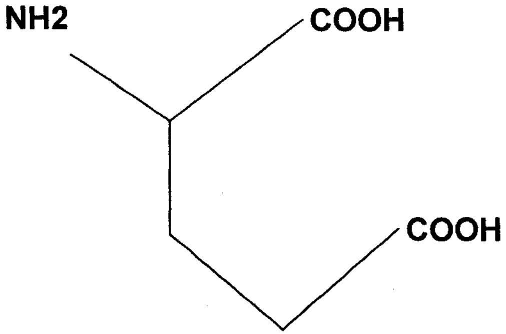
Amino Acid (glutamine)



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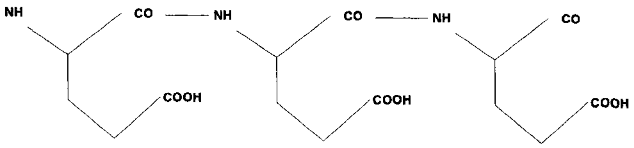
Protein (polypeptide)



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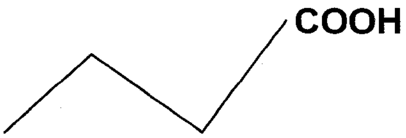
Fatty Acid (saturated, butanoic)



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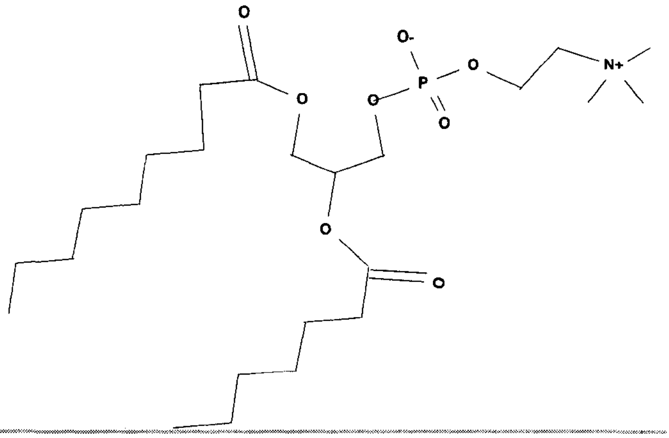
Lipid (glycerolipid)



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</table>

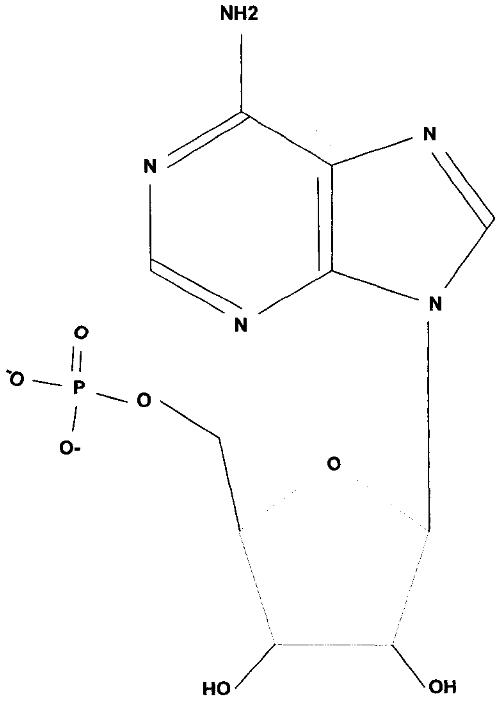
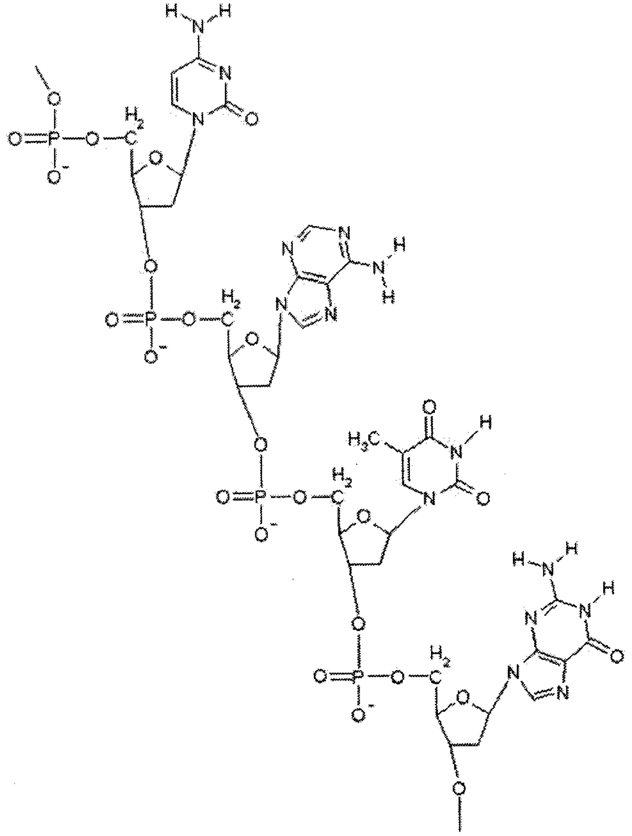
Monomer	***Polymer***
Nucleotide (Adenosine monophosphate) 	DNA (Deoxyribonucleic acid) 

Figure 15: Structure of important carbon-containing molecules

The major catabolic pathways include glycolysis for carbohydrates, deamination for proteins, and the β-oxidation pathway for lipids. In all cases, hydrolysis takes part in the overall reactions. The resultant molecules are converted to the Acetyl-CoA or pyruvate molecules, which then participate in the tricarboxylic acid (TCA) cycle, which is also called the Krebs cycle or citric acid cycle (CAC) [115].

The CAC cycle provides predecessors for other metabolic processes, and is therefore an amphibolic process. Starting with pyruvate, the CAC cycle results in the production of 1 molecule of adenosine triphosphate (ATP), 4 molecules of reduced nicotinamide adenine dinucleotide (NADH), 1 molecule of reduced flavin adenine dinucleotide (FADH) and 3 molecules of carbon dioxide (CO_2) per molecule of pyruvate consumed [115]. The NADH and FADH molecules are oxidised participating in the electron transport chain producing 3 molecules of ATP per molecule of NADH and 2 molecules of ATP per molecule of FADH [115]. The overall process is summarised in Figure 16.

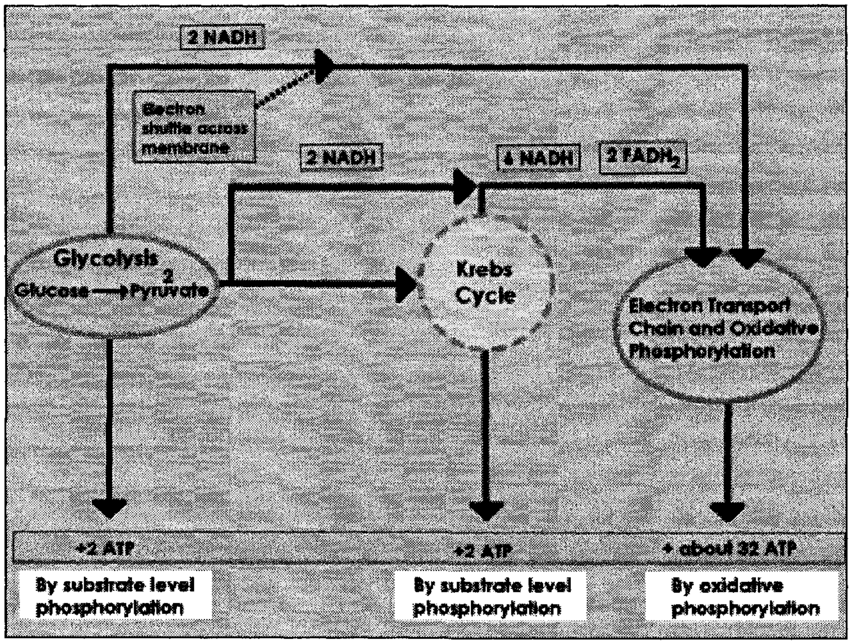


Figure 16: Cell metabolism summary [133]

3.1.2.2. Assimilation

Assimilation describes the reduction of an inorganic compound for use as a nutrient source, such as the nitrate, sulphate or carbon dioxide molecules [115]. Usually only the quantity of inorganic compound required for growth purposes is reduced in assimilative metabolism [115]. This is in contrast with the reduction of the same molecules for use as electron acceptors in energy metabolism, which is referred to as dissimilative metabolism [115].

The catabolism of high molecular weight molecules is of great importance to microorganisms, as only low molecular weight molecules are easily assimilated into the cell [66]. Microorganisms excrete extracellular enzymes to carry out catabolic processes on the high molecular weight molecules in the wastewater media; these processes are grouped under the umbrella term 'hydrolysis' in wastewater modelling [66].

3.1.2.3. Cell reproduction (growth/ cell synthesis)

The energy produced by the respiration process in the form of the ATP molecule can be used in cellular reproductive processes. For single cell organisms such as bacteria, the cycle of cell reproduction results in the reproduction of an independent organism and can be described by its two phases: interphase and mitosis [133].

3.1.2.4. Cell maintenance

The energy produced by the respiration process in the form of the ATP molecule can also be used in cellular maintenance processes. Processes such as spontaneous movement (motility), osmotic regulation, molecular transport and maintenance of ionic gradients are described as mechanical maintenance processes [66]. Processes such as the resynthesis of cell walls, flagella, cell membrane, proteins or nucleic acids are described as chemical maintenance processes [66].

Maintenance energy requirements are generally considered to be independent of the microorganism growth rate, despite some evidence to the contrary [66].

3.1.2.5. Endogenous respiration

Up to this point, discussions of respiration processes have assumed that a carbonaceous substrate and an electron donor are provided to the cell via the wastewater media. In the case where the concentration or availability of these externally provided (exogenous) substrates is decreased, a microorganism will decrease the rate of cell reproduction (growth) in order to maintain the rate of cell maintenance [66]. If the exogenous substrate is further decreased to below the level required for cell maintenance processes, the microorganism will start to consume substrate that is stored inside the cell itself: this process is referred to as endogenous respiration [66]. The form of stored substrate varies from glycogen to amino acids or proteins, depending on the microorganism and the form of substrate previously available to it [66]. If the concentration or availability of the exogenous substrate is reduced to zero, and if all endogenous substrate is consumed, the microorganism will become dormant or die [66].

3.1.2.6. Cell lysis

Some of the cell maintenance and cell reproduction processes involve the hydrolysis of cell walls by autolysins enzymes, prior to the resynthesis of the walls or the production of a new cell [66]. If the regulation of this process is interrupted or lost, the cell wall may rupture, which is referred to as cell lysis [66].

The result of cell lysis for a single cell organism is death, as well as the release of the cell contents into the wastewater media [66]. Enzymes present in the media will hydrolyse most of the cell walls and cell membranes, which renders them available for assimilation by other microorganisms [66]. Some of the cell contents are difficult to hydrolyse and are considered to be cell debris [66].

3.1.2.7. Predation

The microbiological population in an activated sludge process is usually very diverse, and the higher microorganisms such as protozoa will feed on the bacteria in the media [66]. This process is referred to as predation.

3.1.2.8. Redox reactions

The redox half reactions for various organic electron donors (heterotrophic) are as follows [66]:

Domestic wastewater (empirical formula):

$$\frac{1}{50}C_{10}H_{19}O_3N+\frac{9}{25}H_2O\longrightarrow\frac{9}{50}CO_2+\frac{1}{50}NH_4^+ +\frac{1}{50}HCO_3^- +H^+ +e^-$$

Proteins:

$$\frac{1}{66}C_{16}H_{24}O_5N_4+\frac{27}{66}H_2O\longrightarrow\frac{8}{33}CO_2+\frac{2}{33}NH_4^+ +\frac{31}{33}H^+ +e^-$$

Carbohydrates:

$$\frac{1}{4}CH_2O+\frac{1}{4}H_2O\longrightarrow\frac{1}{4}CO_2+H^+ +e^-$$

Lipids:

$$\frac{1}{46}C_8H_{16}O+\frac{15}{46}H_2O\longrightarrow\frac{4}{23}CO_2+H^+ +e^-$$

The redox half reactions for various inorganic electron donors (autotrophic) are as follows [66]: (See also Nitrification, section 3.1.4.4)

Sulphur:

$$\frac{1}{6}S+\frac{2}{3}H_2O\longrightarrow\frac{1}{6}SO_4^{2-}+\frac{4}{3}H^+ +e^-$$

Iron:

$$Fe^+\longrightarrow Fe^{+3}+e^-$$

A typical bacterial cell has a generic formula of $C_{12}H_{87}O_{23}N_{12}P$ or a simplified formula of $C_5H_7NO_2$ if including the macronutrients [39]. The oxidation of the bacterial cell can be described according to the equation [134]:

$$C_5H_7NO_2 + 5O_2 + H^+ \longrightarrow 5CO_2 + 2H_2O + NH_4^+$$

Taking into account the molecular weights of the biomass (113 g/g-mol) and of oxygen gas (32 g/g-mol), 1.42 grams of elemental oxygen is required for every gram of biomass consumed in an oxidation process [134].

Similarly, the oxidation of domestic wastewater can be described by the equation [134]:

$$C_{18}H_{19}NO_9 + \frac{35}{2}O_2 + H^+ \longrightarrow 18CO_2 + 18H_2O + NH_4^+$$

Taking into account the molecular weights of the domestic wastewater (393 g/g-mol) and of oxygen gas (32 g/g-mol), 1.42 grams of elemental oxygen is also required for every gram of domestic wastewater consumed in an oxidation process [134].

3.1.3. Oxygen

An activated sludge process can be described as aerobic, anoxic or anaerobic: these terms are used to describe the level or type of oxygen available to bacteria, and are often used to describe the bacteria themselves. In terms of the oxygen available to bacteria, aerobic describes the condition where dissolved elemental oxygen is available to bacteria at a level that is not limiting to the bacterial growth rate [66]. Anoxic describes the condition where oxygen is available in the form of nitrite (NO_2^-) or nitrate (NO_3^-) [66]. Anaerobic describes the process condition where no oxygen is available in any form, and the electron acceptors are usually carbon dioxide or sulphate [66]. Aerobic processes are the most efficient in terms of biomass growth per unit of substrate consumed, with anoxic the next efficient and anaerobic the least efficient process [66].

The redox half reaction for oxygen as an electron acceptor is [66]:

$$\frac{1}{2}H_2O \longrightarrow \frac{1}{4}O_2 + H^+ + e^-$$

3.1.4. Nitrogen

Nitrogen plays two important roles in the activated sludge process, one as an electron acceptor in terms of nitrate and nitrite in anoxic processes, and one as a nutrient form required for bacteria growth and maintenance processes. These roles are accomplished via the following processes.

3.1.4.1. Ammonification

Nitrogen present in the wastewater media in the form of organic compounds, such as amino acids, is released during the catabolism of these compounds [66]. These catabolic processes include deamination and hydrolysis reactions, amongst others. This is the only way that organic nitrogen can be transformed into a form of nitrogen available to microorganisms [66].

3.1.4.2. Assimilation

Ammonia nitrogen is the most easily assimilated form of nitrogen for a microorganism. Nitrate can be assimilated, but requires extra energy for the reduction step from the +V oxidation state to the –III oxidation state [66].

3.1.4.3. Cell synthesis

The cell synthesis process requires nitrogen due to the fact that the DNA and RNA molecules both contain nitrogen. The use of ammonia requires less energy than the use of nitrate, as discussed above, therefore nitrate will only be used as the nitrogen source for cell synthesis if no ammonia is present [66]. The redox half reactions for nitrogen required for cell synthesis are as follows [66]:

Ammonia

$$\frac{1}{20}C_5H_7O_2N+\frac{9}{20}H_2O\longrightarrow\frac{1}{5}CO_2+\frac{1}{20}HCO_3^-+\frac{1}{20}NH_4^++H^++e^-$$

Nitrate

$$\frac{1}{28}C_5H_7O_2N+\frac{11}{28}H_2O\longrightarrow\frac{1}{28}NO_3^-+\frac{5}{28}CO_2+\frac{29}{28}H^++e^-$$

3.1.4.4. Nitrification

Nitrification is the process by which ammonia nitrogen is reduced to nitrite and then to nitrate, which occurs under aerobic conditions. This process is carried out by both heterotrophic and autotrophic bacteria, but is usually attributed to autotrophic bacteria, in particular the those of the *Nitrosomonas* and *Nitrobacter* genera [66]. These bacteria can use organic carbonaceous substrate, but the quantity is usually so small that it is ignored and carbon dioxide is used to represent the carbon source for this process [66]. Nitrification can occur at the floc exterior [39].

The equations that describe nitrification are as follows [52]:

Nitritation:

$$2NH_3 + 3O_2 \xrightarrow{Nitrosomonas} 2NO_2^- + 2H^+ + 2H_2O$$

Nitratation:

$$2NO_2^- + O_2 \xrightarrow{Nitrobacter} 2NO_3^-$$

A simplified overall nitrification equation is [135]:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + 2H_2O$$

Taking into account the molecular weights of nitrogen (14 g/g-mol) and 2 moles of oxygen gas (64 g/2g-mol), 4.57 grams of elemental oxygen is required for every gram of nitrate-nitrogen produced in the nitrification process [135].

The redox half reactions for nitrogen compounds as electron donors are as follows [66]:

Ammonia:

$$\frac{1}{6}NH_4^+ + \frac{1}{3}H_2O \longrightarrow \frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^-$$

$$\frac{1}{8}NH_4^+ + \frac{3}{8}H_2O \longrightarrow \frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^-$$

Nitrite:

$$\frac{1}{2}NO_2^- + \frac{1}{2}H_2O \longrightarrow \frac{1}{2}NO_3^- + H^+ + e^-$$

3.1.4.5. *Denitrification*

Denitrification is the process by which nitrate nitrogen is reduced to elemental nitrogen gas, which occurs under anoxic conditions, and is also called 'dissimilative nitrate reduction' [115]. This process is carried out by heterotrophic bacteria and therefore requires an organic carbon substrate: the substrate may be provided by an exogenous source in the wastewater media or by an endogenous source [72]. Denitrification can occur at the floc interior [39].

The equation for denitrification, using methanol as the carbon substrate, is as follows [72]:

$$6NO_3^- + 5CH_3OH \longrightarrow 3N_2 + 5CO_2 + 7H_2 + H_2O + 6OH^-$$

Assuming that denitrification proceeds to nitrate as the final product and no intermediates are produced, the quantity of oxygen required for the denitrification process can be calculated according to the theoretical half equations [135]:

$$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- \longrightarrow \frac{1}{10}N_2 + \frac{3}{5}H_2O$$

$$\frac{1}{4}O_2 + H^+ + e^- \longrightarrow \frac{1}{2}H_2O$$

Taking into account the molecular weights of nitrogen (14 g/g-mol) and of oxygen gas (32 g/g-mol), 2.86 grams of elemental oxygen is required for every gram of nitrate-nitrogen consumed in the denitrification process [135].

The redox half reaction for nitrogen as an electron acceptor is as follows [66]:

Nitrate

$$\frac{1}{10}N_2 + \frac{3}{5}H_2O \longrightarrow \frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^-$$

3.1.4.6. Atmospheric fixation

Atmospheric fixation describes the phenomenon whereby atmospheric nitrogen gas is reduced to ammonia, which typically occurs using heterotrophic diazotroph bacteria under aerobic, anaerobic or microaerophilic conditions [30, 136]. This has been shown to be a significant transformation of nitrogen in large bodies of water such as aerated lagoons or aerated stabilisation basins (ASB) [30, 136]. However, it is thought that the amount of nitrogen fixed by bacteria in an aerated basin with a relatively short residence time is insignificant.

The equation for nitrogen fixation is [115]:

$$N_2 + 8e^- + 8H^+ + (18-24)ATP$$
$$\xrightarrow{Nitrogenase-enzyme} 2NH_3 + H_2 + (18-24)ADP + (18-24)P_i$$

3.1.4.7. Gaseous stripping

Ammonia (NH_3) exists in solution in equilibrium with ammonium ions (NH_4^+) and hydroxide ions (OH^-), according to the following equilibrium equation where $NH_3 \bullet H_2O$ represents the ammonia gas-water combination [72]:

$$NH_3 + H_2O \Leftrightarrow NH_3 \bullet H_2O \Leftrightarrow NH_4^+ + OH^-$$

The removal of ammonia can be achieved by raising the pH of the wastewater media, which converts all ammonium ions to ammonia (NH_3), and then providing adequate air-water surface area to strip the ammonia gas from the solution [72].

3.1.4.8. Cell lysis

As discussed previously, cell lysis is a process that involves the bursting of the microorganism cell wall and results in the release of organic matter, including organic nitrogen. This material may undergo ammonification (deamination and hydrolysis) and then be assimilated into the biomass as a source of nitrogen [137], although it is likely that some material will remain difficult to degrade.

3.1.5. Phosphorus

Phosphorus plays an important role in the activated sludge process as a nutrient form required for bacteria growth and maintenance processes. The manner by which this role is accomplished is described in the following processes, along with the processes used to accomplish phosphorus removal related to meeting final effluent quality requirements.

3.1.5.1. Phosphatification

Analogous to ammonification for nitrogen, it has been postulated that the phosphorus present in the wastewater media in the form of organic compounds, such as lipids or polyphosphates, is released during the catabolism of these compounds [134, 138]. These catabolic processes include β-oxidation and hydrolysis reactions, amongst others. This is the only way that organic phosphorus or polyphosphates can be transformed into a form of phosphorus available to microorganisms [138].

3.1.5.2. Assimilation

Ortho-phosphate is the most easily assimilated form of phosphorus for a microorganism [72]. Other forms of phosphorus must be hydrolysed to the ortho-phosphate form, which is less efficient than using ortho-phosphate available [72].

3.1.5.3. Cell synthesis

The cell synthesis process requires phosphorus due to the fact that the DNA and RNA molecules both contain phosphorus, as do the energy storing molecules of ATP and NADPH and structural molecules such as phospholipids [82].

3.1.5.4. Biological Phosphorus Removal (Bio-P)

The biochemical process called biological phosphorus removal (Bio-P) requires an anaerobic zone upstream of the aerobic zone. Under anaerobic conditions, the phosphorus accumulating organisms (PAO) will release any phosphate they are storing and store readily-biodegradable carbon and energy in the form of polyhydroxybutyrate (PHB) [139]. Under the subsequent aerobic conditions, the PAO's will use the PHB for energy and growth, and internally accumulate phosphate in excess of their biological requirements, which is referred to as luxury uptake [139]. This process can be combined with the nitrification-denitrification processes to produce a biological nutrient removal (BNR) process [39].

The biological phosphorus removal process has been shown to produce a final effluent with a [total] phosphorus concentration of 1 to 2 mg/L, and thus it is not considered to be an advantage for pulp and paper wastewater treatment [10].

3.1.5.5. Precipitation

Phosphorus can be chemically precipitated using a number of chemicals, notably calcium, aluminium and iron, which form insoluble cation phosphate precipitates [72]. Chemical precipitation is often combined with either the sedimentation occurring in the secondary clarifier, which is referred to a simultaneous phosphorus elimination, or with the Bio-P process, which is referred to as simultaneous precipitation [140]. The precipitation chemicals can be added in the aeration basin if there is an excess of phosphorus, but would usually be added in the secondary clarifier in pulp and paper wastewater treatment to eliminate the residual phosphorus after biological treatment.

The mechanism of chemical precipitation of iron phosphate has been described by the following steps: precipitation of solids $FePO_4$ and $Fe(OH)_3$, coprecipitation of ferric-oxo-hydroxo-phosphate complexes, formation of soluble ferric-phosphate and ferric-hydroxide complexes, formation of organic side products and adsorption of phosphate ions, organic dissolved phosphorus on ferric hydroxide flocs and coagulation/flocculation of primary precipitate colloidal particles and of organic colloidal phosphorus [141, 142].

For a synthetic wastewater, precipitation of calcium phosphate is most efficient at a pH of 11, and most efficient for both aluminium phosphate and iron (ferric) phosphate at a pH of 6 [143]. At municipal wastewater treatment facilities a final effluent total phosphorus discharge on a monthly average basis of 0.2 mg/L was achieved with additional chemical use, this also resulted in an increase in sludge quantity and a change in sludge properties dependent on the chemical precipitant used [144]. At pulp and paper mills, final effluent total phosphorus concentrations of 1.2 to 4.0 mg/L have been achieved using techniques to reduce the quantity of phosphorus added to the treatment system, which did not meet the target limit of 1.0 mg/L [145, 146].

The non-readily-biodegradable high molecular weight molecules present in biologically treated pulp mill effluents are a hindrance to the precipitation of phosphorus [10].

3.1.5.6. Cell lysis

As discussed previously, cell lysis is a process that involves the bursting of the microorganism cell wall and results in the release of organic matter, including organic phosphorus. This material may undergo phosphatification (β-oxidation and hydrolysis) and then be assimilated into the biomass as a source of phosphorus, although it is likely that some material will remain difficult to degrade.

3.2. Bulk processes (Macro level)

The operation of an AST plant requires observation, measurement and control of bulk processes. At this macro level, it is not possible to observe the reactions occurring at the cell level. The phenomena that are observed often require interpretation of skilled operators and management of gross parameters. This section will describe the macro implications of the reactions described above.

3.2.1. Transport Processes

Many of the reactions described above depend upon the provision of dissolved carbon, oxygen, nitrogen or phosphorus to the bacteria. In order for these molecules to arrive at the cell wall of the bacteria, it is necessary that they diffuse through the wastewater media, and then that they are adsorbed onto the floc: these processes are described below.

3.2.1.1. Diffusion

The diffusion of oxygen is described in section 2.2.3.3.

3.2.1.2. *Floc sorption*

The sorption of substrate onto the floc is described in section 2.3.1.4.

3.2.2. Yield

The term 'yield' refers to the quantity of biomass produced per unit of substrate consumed [39], as described by the equation [134]:

$$\frac{1}{Y} Substrate + \frac{1-Y}{Y} O_2 \rightarrow Biomass$$

Substrate can be measured in units of BOD_5 or COD, and therefore the units of yield can be in g VSS/g BOD5 or g VSS/g COD. The observed yield takes into account the substrate consumed for the purpose of cell synthesis (S_1) as well as for cell maintenance purposes (S_2), as described by the equation [134]:

$$Y_{OBS} = \frac{\Delta X}{\Delta S_1 + \Delta S_2}$$

The theoretical yield can therefore be described by the equation [134]:

$$Y_{TH} = \frac{\Delta X}{\Delta S_1}$$

3.2.2.1. *Microbial Decay*

The term 'microbial decay' has been used as a catch-all to describe the processes that result in an observed yield that is less than the theoretical yield, including predation [66]. The rate of endogenous decay, k_d, is related to the observed and theoretical yield by the following equation [147]:

$$Y_{OBS} = \frac{Y_{TH}}{1 + k_d SRT}$$

Where SRT represents the sludge retention time (days).

3.2.2.2. *Viable Biomass*

As discussed previously, volatile suspended solids (VSS) is not necessarily a good indicator of the viability or activity of the biomass in a system [124]. Alternate measurements of the active biomass include cellular ATP [148].

3.2.3. Nitrification

The maximum growth rate of nitrifying bacteria is much lower than that of heterotrophic bacteria [66]. If a process is operated with a long sludge age, the nitrifying bacteria have a much greater opportunity to develop, whereas conditions that encourage rapid growth will cause the decline of the nitrifying bacteria population [66].

The yield of nitrifying bacteria is less than that of heterotrophic bacteria, which manifests as a minimal impact on the overall suspended solids concentration of the mixed liquor in the activated sludge process [66].

3.2.4. Denitrification

Symptoms of unintentional denitrification include poor settling in the secondary clarifier, due to the gaseous nitrogen formed in the flocs. Denitrification in the secondary clarifier would require a significant concentration of nitrate to be present in the outlet of the aeration basin, and that the oxygen concentration be less than 1 mg/L [52, 72].

3.2.5. Nutrient requirements for stable AST operation

The quantity of nutrients required for biological wastewater treatment is based on the composition of a typical bacterial cell, which has a generic formula of $C_{12}H_{87}O_{23}N_{12}P$ or a simplified formula of $C_5H_7NO_2$ if including the macronutrients [39]. These formulas are used to generate the mass ratio of BOD_5:N:P of 100:5:1 that is often used as a measure that nutrient concentration in a wastewater is adequate for biological growth [39].

As mentioned in section 2.3.1.6, a low concentration of nutrients can have a limiting effect on the biological growth, according to the Monod kinetic relation [149]. It is for this reason, and to avoid a nutrient deficiency as described below, that nutrients are often added in surplus [10]. The detectable presence of bio-available nutrient residuals in the final effluent is used as an indication that adequate nutrients are present in the biological treatment process unit [72]. Stable AST operation is seen with low variation in flow rate and organic load to the treatment plant [10]. Sludge age and temperature influence the actual macronutrient requirements, with lower sludge yields and therefore lower nutrient requirements in warmer temperatures [68, 150].

3.2.5.1. Nutrient mixtures

The major nutrients added to pulp and paper wastewater for the purposes of biological treatment are nitrogen and phosphorus. There are a few different easily assimilable forms of these nutrients that can easily be added to the process, notably urea and ammonium hydroxide for nitrogen; phosphoric acid for phosphorus [151]. Ammonium polyphosphate (APP) has been found to be readily hydrolysable, with complete depolymerisation within 100 minutes [151]. Improvements in settleability (SVI) were reported using a nutrient mixture that included a yeast extract and micronutrients: iron, potassium, magnesium, molybdenum, zinc, copper, manganese, cobalt, nickel, selenium, boron, vanadium and tungsten, as well as nitrogen and phosphorus [152]. Lysed waste activated sludge (WAS) was also investigated as a source of nutrients for the AST process [151].

3.2.5.2. Nutrient requirements: different AST technology

Conventional AST technology results in approximately equal nutrient concentrations in the final effluent and the wasted sludge for the treatment of Kraft pulp mill effluent [153]. Other AST technologies such as the low-loaded AST, low sludge production and MBBR plus AST process configuration result in higher nutrient concentrations in the wasted sludge than the final effluent [153]. This result implies that alternative AST technologies offer the opportunity to reduce the nutrient concentration in the final effluent further than that achieved by conventional AST technology.

3.2.5.3. Nutrient deficiency: effects

The effects of nutrient deficiency include accelerated growth of filamentous bacteria which manifests as a sludge that is difficult to settle and high solids concentration is seen in the final effluent [72]. Nutrient deficiency can also lead to filamentous bulking events, production of viscous exocellular material (polysaccharide), or production of foaming exocellular material [68]. Overproduction of exocellular material is a significant problem for pulp and paper wastewaters deficient in phosphorus [82].

3.3. Nutrient addition control strategies

Nutrient addition control strategies are determined primarily by the desired result and subsequently by the desired accuracy, precision and complexity of the process control. The possible purpose or results desired include the minimisation of effluent concentrations of organic pollutants and nutrients (BOD, N, P) or the minimisation of nutrient dosage quantities, whilst maintaining stable process operation and efficient BOD removal [65].

The major benefit of feed-forward control is the ability of the control loop to react swiftly to changes in influent quality, for example to load or flow variations [126]. Feed-back control reacts less efficiently to process upset conditions, but has the advantage of greater accuracy of control [126].

3.3.1. Constant (manual) dosing

The most simple nutrient addition control is to dose the nutrient, nitrogen or phosphorus, in a constant flow rate [154]. This could theoretically be done without any measurement of nitrogen or phosphorus content of any stream.

Constant dosing is inferior to automated control since it does not respond to changes in the process [155].

3.3.2. Proportional to flow

A nutrient addition rate proportional to effluent flow rate may be applicable for municipal wastewater treatment, however for pulp and paper mill effluent, the concentration of organic load may vary with constant flow rate: this control strategy is not considered appropriate for pulp and paper wastewater treatment [156].

3.3.3. BOD_5:N:P ratio (Feed forward control)

The BOD_5:N:P mass ratio of 100:5:1 has its origins in the dry-basis contents by weight of a typical bacterial cell, and the assumption that bacterial cells require the macronutrients nitrogen and phosphorus in proportion to the composition of cell biomass, as described in section 3.2.5. [39]. For pulp and paper wastewater treatment using AST technology, BOD_5:N:P ratios have been reported for stable plant operation from 100:3.5:0.6 [10] to lower limits suggested for BOD_5:N of 100:2.5 to 100:4.5 and BOD_5:P of 100:0.4 to 100:0.6 [63, 64]. Zero supplemental phosphorus was added to a pulp mill effluent with successful stable AST operation [64], and zero nutrient addition has been implemented successfully for pulp and paper ASB operations, which is due to sufficient nutrient internal recycling [63, 73, 74].

Feed forward control can be based on a BOD_5:N:P mass ratio, which translates to control of nutrient dosing flow rate in proportion to the measured BOD load in the incoming mill effluent. This control relies on the accurate on-line measurement of BOD or a substitute for BOD. A number of substitutes and combination of parameters including BOD_1, total organic carbon (TOC), COD, conductivity, pH and TSS were tested on Kraft mill effluent with a particular focus on upset conditions, with mixed results [157]. Conductivity has been used successfully as a surrogate for organic load [156]. In terms of on-line instrumentation, one study considered TOC as the best surrogate in comparison with respirometry [158]. Instrumentation is discussed further in section 4.1.

3.3.4. Nutrient residual (Feedback control)

In municipal wastewater treatment plants, chemicals are dosed based on the ammonia and phosphate residuals in the final effluents for processes involving denitrification and chemical precipitation of phosphate [155]. This approach has also been implemented for pulp and paper wastewater for both ASB and AST treatment processes [72]. Reported residual levels in the final effluent range from 0.5 to 1.5 mg NH_3-N/L and 0.25 to 1.0 mg PO_4-P/L

[72], as discussed further in section 3.5. One of the problems with this method of control is that the control loop can only react slowly to an upset in influent to the wastewater treatment [6].

If the aim of nutrient control is to minimise the residual nitrogen and phosphorus in the final effluent, it should be noted that the majority of total nitrogen is present in the suspended solids, indicating it is bound in the biomass, and indicating the importance of solids separation to nutrient control [63, 159].

3.3.5. Modified nutrient control

Feed back control based on effluent nutrient residuals is also used for pulp and paper mills in Finland with an ongoing assessment of the nutrient balance over the wastewater treatment plant in an attempt to minimise changes in the nutrient levels throughout the treatment process [65]. An expert control system incorporating on-line measurements, control software and predictive modelling has been trialled at a number of full-scale pulp mill wastewater treatment plants [160, 161]. A combination of feed forward and feed back control was implemented for a fine paper mill effluent and resulted in a reduction of final effluent nutrient concentrations as well as a reduction of supplemental nutrient addition to the process [162].

3.3.6. Respirometric-based control

A method for the detection and quantification of a nutrient deficient state for sludge from a pulp and paper activated sludge process was developed [163]. The implementation of this methodology for the control of nutrient dosing to the process has been proposed [163].

3.4. Control implementation

The successful implementation of nutrient control depends on a number of criteria, not least the equipment used in the control loop. Instrumentation for measurement of nutrient fractions is discussed further in section 4.1.

3.4.1. Control equipment

Important aspects of control equipment to consider for full-scale implementation of nutrient control include the capacity of the actuators and pumps, the presence of basic control loops such as dissolved oxygen control, definition of the control performance goal measurement time period, and quality assurance of the equipment [126]. The control equipment should also be installed in appropriate locations and reaction to the measurements should be made within a time frame appropriate to the process time scale [126].

3.4.2. Control implementation

An appropriate implementation strategy should be planned for automated or semi-automated controls. A period of monitoring followed by manual control and then control automation allows operators to develop their intuition and become familiar with the control loop [126]. Keeping the control strategy simple facilitates a rapid adaptation to its use [155].

3.5. Effluent discharge

As discussed in section 3.3.4, the concentration of nutrients in the final effluent discharge can be used to control the addition of supplemental nutrients to pulp and paper wastewater treatment. The following is a discussion of the achievable limits of final effluent pollutant and nutrient concentrations and the quality of receiving waters.

3.5.1. Achievable limits

Final effluent discharge is regulated in most countries in terms of the concentration of pollutants that can be discharged. A summary of regulated and typical concentrations of BOD_5, TSS, COD and AOX is presented in Table 13 below in units of kg per tonne production [164].

Table 13: Final effluent discharge concentrations BOD_5, TSS, COD, AOX in kg/tonnes production [164]

Country	***BOD_5***	***TSS***	***COD***	***AOX***
New Zealand	1.75	4.0	12.2	0.34
Canada	7.5	11.25	-	1.5 (0)
USA	2.73	4.41	45.6	0.623
Indonesia	8.5	8.5	29.75	-
Japan	13.7	13.9	17.6	-
Sweden	-	-	10 – 15	0.1 – 0.2
Finland	-	-	65 (15)	1.0 (HW) 2.0 (SW)
France	3.9 (SW) 2.6 (HW)	6.5	65(SW) 32.5(HW)	1.0 (HW) 2.0 (SW)
Brazil	1.3 – 6.5	1.4 – 60	4.6 – 45	0.2 – 1.0

HW = Hardwood SW = softwood

In terms of bio-available nutrient discharge, the concentration of ammonia and ortho-phosphate in the final effluent that are achievable, commonly seen and seen during very stable AST operation for pulp and paper wastewater treatment plants are presented in the first three rows of Table 14 below [10]. These values correspond to the medians found in a survey of 135 pulp and paper facilities, as indicated the final two rows of Table 14 [165].

Table 14: Final effluent discharge concentrations NH_3-N, PO_4-P (mg/L) [10, 165]

Measurement	***NH_3-N***	***PO_4-P***	***TP***	***Comments***
Mean	1 mg/L	1 mg/L	-	Achievable
Maximum	10 mg/L	5 mg/L	-	Commonly seen
Optimised Max	7 mg/L	0.5 mg/L	-	Very stable operation
Survey Mean	1.91 mg/L	-	1.31 mg/L	
Survey Median	1.0 mg/L	-	0.82 mg/L	

It was found that gradually lowering the phosphorus dosing in steps facilitated the establishment of lower limits of final effluent phosphorus concentration for a particular pulp and paper activated sludge wastewater treatment system without causing process upsets, and was a better approach than solely analysing past operating data [145].

3.5.2. Receiving water quality

The implementation of Canadian regulations on the discharge of effluent from pulp and paper mills in 1992 resulted in many mills installing secondary treatment plants and changing from chlorine bleaching to chlorine dioxide bleaching (elemental chlorine free, ECF)[166]. Studies conducted on the receiving waters of a number of mills indicated that the environmental effect of the mills may be reduced since these changes, although the studies were not conclusive and the authors recommended further work to include a refinement of the parameters to be measured in environmental monitoring [166]. A methodology for environmental monitoring and decision making was proposed for new mills in Australia [167]. Receiving water quality was found to be dependent on the differences in seasonal flow rates in the receiving river for one bleached Kraft mill, in that the relatively higher winter river flow rates provided greater dilution for the mill effluent [168].

3.6. Relevance to upstream process (mill)

The correct measurement of physical, chemical and microbiological parameters in the pulp and paper mill wastewater allows the correct identification of the constituents and flow of the wastewater, and the realisation of a site-wide nutrient balance. These tools may be used to identify design and/or operational changes in the production areas which would be advantageous to the operation of the wastewater treatment plant, or evaluate proposed changes in the production areas for their influence on the wastewater treatment plant.

3.6.1. Identification of sources of wastewater flow and components

Measurement of contaminants and wastewater flow at the inlet to the wastewater treatment plant allows control of the plant, as discussed in section 3.3, and modelling of the plant, as discussed in section 5.5.

Identification of the upstream sources of the contaminants and wastewater flow allows a more holistic or site-wide approach to the management of wastewater. It is possible to reduce the site water usage, reduce the flow or change the characteristics of the influent wastewater to the treatment plant, by managing the sources of contaminants and flow [169]. A study of a particular mill may show that separate treatment of wastewater from different areas of the mill would be beneficial, or that recycling or closing water loops within or between production areas may be advantageous.

Site-wide surveys of two mills in New Zealand were used to identify the sources of organics, inorganics, solids, nutrients, trace organics and acute toxicity [38]. The study highlighted, for the Kinleith Kraft-NSSC integrated pulp and paper mill, the major source of nitrogen was condensate wastewater and the major source of phosphorus was the D-stage and first open acid stage of the bleaching sequence [38]. Other sources of phosphorus and nitrogen molecules in pulp and paper mills include black liquor and residual lignin, and process additives such as defoamers, biocides, chelants, wet and dry strength additives, dyes and pigments [9]. A characterisation of the nitrogen fractions present in both chemical and mechanical pulp and paper mill wastewater was carried out which showed very low levels of inorganic nitrogen present [159]. Some organic nitrogen was present in mill effluent as chelating agents EDTA and DTPA, which were used for hydrogen peroxide stage pulp bleaching [159].

The major sources of wastewater flow were found to be from non-closed loops around paper machines, pulp dryers and from the spent pulping and bleaching liquors [38]. The modernity of the process technology had a large influence on the flow rate of wastewater from the bleaching process [38].

All process areas contributed approximately an equal percentage of the overall soluble COD to the treatment plant, at both mill sites (process areas defined in the study) [38]. The major contributor to the COD load at an integrated alkaline-peroxide mechanical pulping and machine finish coated paper mill (APMP-MFC) was the pulp impregnation pressate streams [45].

The bleaching sequence in a Kraft mill had a significant impact on the biodegradability of the effluent, in particular the biodegradation and removal of adsorbable organic halide compounds (AOX)[170].

The correct identification of the constituents of the wastewater from a pulp and paper mill can potentially be achieved using the measurement techniques discussed in section 4.1. In particular, the identification of sources of nutrients can allow effective management of nutrients on a site-wide basis.

4. Data Measurement, Collection & Processing

The way in which data is measured, collected and processed influences both the results of further data analysis as well as the conclusions that can be drawn from those results. The following is a discussion of methods used to measure, collect and process data, predominantly in the wastewater industry but also in other chemical engineering fields.

4.1. Data Measurement

It is important to take note of how reliable the measurement results are for each instrument or test method. A number of definitions from the Standard Methods are reiterated in Table 15 [171].

Table 15: Glossary of statistical terms *[171] **[172]

Accuracy * (trueness)	The combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to a true value
Bias* (error)	Consistent deviation of measured values from the true value, caused by systematic errors in a procedure
Calibration	The method by which the trueness of the instrument is verified
Drift	The change in trueness of the instrument over time
Reproducibility* (precision)	Measure of the degree of agreement among replicate analyses of a sample, usually expressed as the standard deviation
Repeatability**	Refers to precision obtainable by the same technician under the same conditions (intra-laboratory), compared to reproducibility which refers to precision obtainable by different technicians under different conditions (inter-laboratory)

The ideal measurement would combine low bias with high reproducibility, minimal calibration required and minimal drift found during calibration. The precision and bias are noted for each measurement where known. The bias of measurements is dependent on the laboratory's interpretation of the test method as well as the method itself.

There are various types of measurement or sampling regimes. For simplicity, a number of definitions from the Standard Methods and other references are reiterated in Table 16.

Table 16: Measurement type definition *[171] **[158] †[173] ‡[174]

Grab / Catch*	A sample collected at a particular time and place, usually representative of only the composition of the source at that time and place. Can be interpreted as representative of process changes based on operator knowledge.
Composite*	A mixture of grab samples collected at the same sampling point at different times ('time-composite'), often used for 24-hour averages
Integrated*	A mixture of grab samples collected from various sampling points at the same moment in time, generally used for analysing the receiving water
Real-time**	Little or no delay between the time the sample is taken and results being available (short measurement interval), usually electronically via DCS
On-line†	A continuously measuring probe, can be located in-situ or in a side stream (data usually collected electronically via DCS)
In-line†	Instrument located directly in the media, direct contact with the wastewater sample (whether the sample is in-situ or pumped to/ through analyser)
In-situ‡	Installed directly in the process (tank, basin, pipe, channel)

One benefit of composite samples is that they account for large variations in flow rates, which is often the case in mill drains [38].

4.1.1. Benefits of in-situ measurements

The benefits of in-situ measurements include a reduction in daily labour efforts as well as an overall improved compliance with discharge limits [126, 155]. While previously constructed wastewater plants may be over-designed to compensate for a lack of real time data, in-situ measurements offer an advantage for upgrading facilities [175].

4.1.2. Issues with in-situ measurements

The major issue with in-situ measurements is the quality assurance of the data, particularly the calibration of instruments. The construction of control charts has been suggested to visualise and shift, drift or gross errors in instrument data, which also allows operators to evaluate the need for recalibration of instruments [176].

4.1.3. Measurement Methods

The basis of measurement of traditional process attributes such as flow rate, pH, temperature, tank levels and conductivity are standard; that of wastewater characteristics such as colour, dissolved oxygen, solids content and BOD are also generally well understood [39, 177]. The bases of the major measurement methods proposed for the measurement of nutrient fractions are presented here.

4.1.3.1. Ion-selective electrode (ISE): NO3 & NH4

The potential or voltage is measured between two electrodes, one reference electrode and one measurement electrode [126, 174, 178]. Previously the measurement electrode was separated from the wastewater by an ultrafiltration (UF) membrane; this has now been replaced by a specific ion-binding membrane [178]. The measurement electrode experiences some cross-sensitivity disturbances from ions with properties similar to the measurement ion [178].

When the gas-sensitive NH_4^+ ISE is used, the pH of the wastewater sample is raised in order to push the ammonia-ammonium equilibrium towards NH_4^+, and therefore all ammonia or ammonium in the sample is measured as a gas [175].

4.1.3.2. UV-Vis Spectroscopy: COD, sCOD, NOx

A spectrometer measures the absorbance of light; it is usually measured in the ultraviolet range (200 – 400 nm) or the UV and visible light range (200 nm – 750 nm) [179]. Some instruments measure single wavelengths, usually at 254 nm as it has been shown that TOC and COD have correlations to the UV absorption at 254 or 260 nm [175]. A full-spectrum measurement is preferable, as the species are more easily distinguished, which results in a more accurate calibration [179].

This is an indirect method, and relies on the initial and on-going calibration of the instrument against laboratory measurements [179]. Calibration for BOD measurement relies on the accuracy of BOD measurements, which is not assured [39]. Automated cleaning systems are available and advantageous; compressed air or mechanical (physical wiping) methods are offered by different suppliers.

4.1.3.3. Photometric / Colorimetric methods (Automated Wet Chemistry): NH_4, NO_2, NO_3, PO_4

The term 'on-line analyser' is often used for these instruments, as well as for the thermal oxidation instruments, and it refers to the fact that the wastewater sample may be pumped from the process to the analyser unit, which allows multiple sampling points for a single analytical unit [175].

The common factor in these instruments is that one or more chemical reagents are added to the wastewater sample and a chemical reaction occurs. The resultant product is analysed for light absorption photometrically: colour intensity is assumed to correlate to concentration [175]. The units require intensive attention from both maintenance and operation personnel, and the chemical reagent costs are significant [175]. However, this is the only standard method of measuring ortho-phosphate. Filtration of the wastewater sample is usually required to reduce interference of solids, and newer technologies use an ion-specific membrane to minimise interference [180].

4.1.3.4. Thermal oxidation: TP, TN, TOC

These instruments rely on the total oxidation (digestion) of the wastewater sample to one parameter, which is then measured by various techniques. The oxidation may be realised using high temperature catalytic conversion or chemical addition plus oxidation by UV light and moderate temperatures, or mineralisation for nitrogen [175, 181, 182]. In the case of TOC, the final oxidation product is carbon dioxide, for TP it is ortho-phosphate and for TN it is nitrate [175, 181, 182]. Carbon dioxide concentration is then measured using an infrared analyser, ortho-phosphate concentration is measured using photometric methods and nitrate concentration is measured using spectophotometry [175, 181, 182]. The wastewater sample usually requires filtration and pH adjustment, and sometimes dilution [175].

These instruments are supplied as either bench-top or on-line analysers. The measurement interval is short considering the complexity of the measurement [158].

4.1.3.5. Respirometry

A respirometer is a miniaturised reactor, in which the oxygen uptake rate is measured over time given a quantity of wastewater and a seed of microorganisms [175]. The unit usually operates batch-wise, although one on-line calculations based on dissolved oxygen concentration and air flow rate was studied [183]. The results must be analysed and interpreted in order to achieve data related to biodegradation kinetics, stoichiometric coefficients and parameters used in biological modelling, such as the Activated Sludge Models (ASM) established by the International Water Association (IWA, formerly IAWQ) [175, 184].

Respirometry is considered as a good method to determine these parameters and coefficients, the measuring frequency is limited to 7 to 10 minutes [184]. The method demands some expertise and time, and a permanent in-line installation would require intensive attention from both maintenance and operation personnel.

4.1.4. Comparison of instrument types

A classification of instrument types in terms of response time and measuring frequency is presented in Table 17 [185]. This type of classification allows a comparison of non-alike measurement types.

Table 17: Measurement types categorised by response time & measurement frequency [185]

Category	*A*	B_0	B_1	C_0	C_1	*D*
Measurements	**MLSS** **Turbidity** **Ammonia** (ISE) **NOx** (ISE) **NOx** (UV) **COD** (UV-Vis) **sCOD** (UV-Vis) **Flowrate** **Water level** **Temperature** **pH** **Oxygen** **Sludge height**	**Ammonia** (Gas-sensitive) **NOx** (UV)	**Ammonia** (Photometric) **Nitrate** (Photometric) **Nitrite** (Photometric) **Phosphate** (Photometric)	**Ammonia** (Gas-sensitive) **NOx** (UV)	**Ammonia** (Photometric) **Nitrate** (Photometric) **Nitrite** (Photometric) **Phosphate** (Photometric)	**COD** (thermal oxidation & photometric) **TOC** (thermal oxidation & IR detection) **TN** (thermal oxidation & IR or chemiluminescence) **TP** (thermal oxidation & photometric) **Respirometer** **Titration biosensor** (alkalinity)
Filtration	-	Fast	Fast	Slow	Slow	-
Response Time (min)	1	10	10	20	20	30
Measuring Interval (min)	0	0	5	0	5	30

4.2. *Data Processing: Continuous Data*

4.2.1. Data Collection

Data is collected at Papier Masson using a Foxboro distributed control system (DCS). The data is transmitted from the DCS to an advanced workstation where an exception deviation filter is applied in order to reduce the quantity of data transmitted further. The data is then sent to the mill network, from which the PI system compresses and archives data. The scan rate for data is generally 0.5 to 1 second in the DCS and 10 seconds in the PI system.

4.2.1.1. Exception deviation filter

An exception deviation dead-band is defined for each instrument, as a percentage of the instrument span. If a subsequent data point is within this dead-band, no change is recorded. This is to say that the data point will be recorded with the same value as the previous data point. As shown in Figure 17 below, although the value of data point 2 is different from that of data point 1, it will be recorded with the same value. Only when the instrument registers a data point outside of the dead-band, such as data point 3, will the recorded value change. The configuration of the site PI system has been carried out to ensure that the exception deviation filter is twice as small as the filter applied for data compression, thus ensuring that the stored data

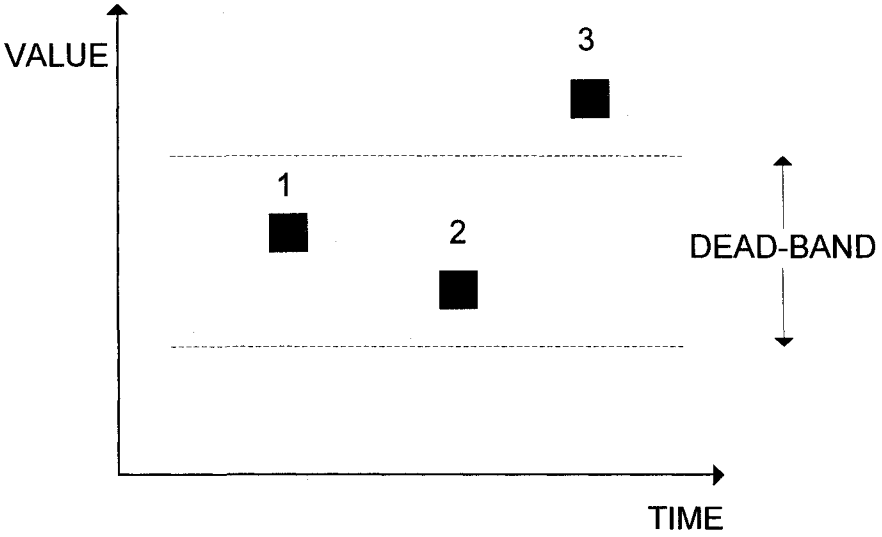


Figure 17: Data collection exception deviation filter dead-band

4.2.2. Data Compression & Storage

Data compression was traditionally required due to the cost of data storage, which is debatably no longer a large cost today [186]. Compression can be useful when sending large quantities of data via telecommunications (internet, telemetry) or satellite [186, 187] and is very useful to increase the efficiency of data extraction. The purpose of data compression is to store the least amount of data while maintaining the required level of information [188]. The extent of data compression should suit the intended purpose of the data, whether it be daily average site production or high resolution dynamic process control [187]. Data compression actually entails the compression of data into a matrix of raw data and coefficients, as well as the reconstruction of data into the original time domain from the compression matrix [186].

4.2.2.1. Compression methods

The following is a brief and non-exhaustive discussion of compression methods commonly used in the process industries, including with the 'swinging door' compression method which is applied in the PI system at Papier Masson. These are all direct compression methods except for the wavelet method which is a transform method; transform methods require a batch of data for compression whereas direct methods are applied to each data point and a decision is made as the data is recorded [186]. Direct methods use very little computation to achieve a simple compression of data, transform methods are more complex but no data is lost in the transform process [188].

Boxcar (Hale & Sellars) [189]

Much like dead-band filtering, the boxcar compression algorithm records a data point once the difference between a data point and the previously recorded data point is greater or equal to a ‘recording limit’ [188, 190]. This method is considered useful for long steady state periods, but is not considered effective if there is a linear drift in measurements or a change between periods of steady state [188, 190].

Backward slope (Hale & Sellars) [189]

Improving on the boxcar algorithm, the recording limit is predicted according to the slope of the previous two data points for this backward slope algorithm [188, 190]. The new data point is recorded only if it lies outside of the predicted recording limit [188, 190]. This algorithm does not deal well with noisy data [190].

Swinging door compression (Bristol) [191]

A modification of the backward slope algorithm, the recording limit is predicted according to the slope between one previous data point and the current data point [188, 190, 191]. This method attempts to maintain the longest straight trend line possible, however it does not deal with outliers [190].

Wavelet transform

A linear transform usually compresses the data by creating vector components that describe the data, a number of which will have near-zero coefficients [188]. If these near-zero coefficients are discarded, a higher level of compression or compaction can be achieved with some loss of information [188]. The wavelet transform relies upon the division of a signal into its frequency components and treating each frequency according to a corresponding time resolution: high time resolution for high signal frequencies, low time resolution for low signal frequencies [186]. Wavelet transforms exist for continuous and discrete data [188] and is considered superior to other transforms such as Laplace or Fourier transforms for the purposes of data compression [186].

4.2.2.2. Data extraction

Data can be extracted from the PI system in at least two forms: compressed or non-compressed data. All compressed data has been subjected to the swinging door compression method, as described above. When compressed or archived data is extracted, only the stored data is listed, which may be any number of points for a given time range. All non-compressed data is linearly interpolated between archived (compressed) data points, when these are extracted.

Interpolation

Data can be interpolated between data points according to a linear relationship or a step-change relationship, as demonstrated in Figure 18 below. The effects of the choice are seen when searching for data values in between recorded data points, which is likely to always be the case since the time stamp of recorded data is determined to the order of seconds.

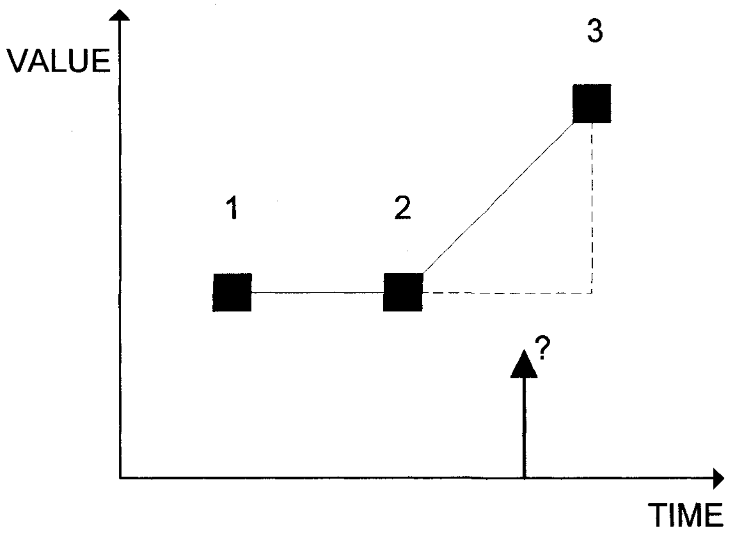


Figure 18: Data interpolation

4.2.2.3. Instrument details

The following attributes are set in the configuration for each instrument:

- Span
- Zero
- Compression deviation (recording limit/ dead-band for compression)
- Exception deviation (recording limit/ dead-band for transmission)

Visual inspection of the compressed data over a particular time range can indicate whether the compression deviation is set too high or too low for a particular instrument.

Table 18: Effluent Treatment Plant PI Tags

	Tag #	***Measurement Type***	***Measurement Location***	***Span***	***Compensation Deviation***	***Units***	***Compensation Deviation (% Span)***
1	50FI4235.PNT	Flow rate	Fresh water (site)	6,000	6	L/min	0.1
2	50AI6035.PNT	pH	Corridor THR	24	0.024	pH	0.1
3	50FI5006.PNT	Flow rate	Primary Inlet	60,010	60	L/min	0.1
4	50TI5003.PNT	Temperature	Primary Inlet	70	0.07	ºC	0.1
5	50AI5001.PNT	pH	Primary Inlet	24	0.024	pH	0.1
6	50AI5002.PNT	Conductivity	Primary Inlet	5,010	5	µmho	0.1
7	50AI4037.PNT	TSS	Primary Inlet	5,000	10	mg/L	0.2
8	50TI5075.PNT	Temperature	Primary Accepts	70	0.07	ºC	0.1
9	50AIC5053.MEAS	COD	Primary Accepts	3,000	3	mg/L	0.1
10	50AI5060.PNT	TSS	Primary Accepts	300	0.03	mg/L	0.01
11	50AI5054.PNT	Conductivity	Primary Accepts Pit	5,010	5	µmho	0.1
12	50FIC4150.MEAS	Flow rate	Primary Sludge	4,010	4	L/min	0.1
13	50LI5005.PNT	Level	Emergency Basin	110	0.11	%	0.1
14	50TI5068.PNT	Temperature	South AST Selector	70	0.07	ºC	0.1
15	50AI5066.PNT	pH	South AST Selector	24	0.024	pH	0.1
16	50AIC5067.MEAS	Dissolved Oxygen	South AST Selector	18	0.018	mg/L	0.1
17	50TI5071.PNT	Temperature	North AST Selector	70	0.07	ºC	0.1
18	50AI5069.PNT	pH	North AST Selector	24	0.024	pH	0.1
19	50AIC5070.MEAS	Dissolved Oxygen	North AST Selector	18	0.018	mg/L	0.1
20	50TI5074.PNT	Temperature	North AST Tank	70	0.07	ºC	0.1
21	50AI5072.PNT	pH	North AST Tank	24	0.024	pH	0.1

	Tag #	***Measurement Type***	***Measurement Location***	***Span***	***Compensation Deviation***	***Units***	***Compensation Deviation (% Span)***
22	50AIC5073.MEAS	Dissolved Oxygen	North AST Tank	18	0.018	mg/L	0.1
23	50TI5065.PNT	Temperature	South AST Tank	70	0.07	ºC	0.1
24	50AI5063.PNT	pH	South AST Tank	24	0.024	pH	0.1
25	50AIC5064.MEAS	Dissolved Oxygen	South AST Tank	18	0.018	mg/L	0.1
26	50FIC5105.MEAS	RAS Flowrate	#1 Secondary Clarifier	30,010	30	L/min	0.1
27	50FIC5106.MEAS	RAS Flowrate	#2 Secondary Clarifier	30,010	30	L/min	0.1
28	50FIC5101.MEAS	WAS Flowrate	#1 Secondary Clarifier	4,010	4	L/min	0.1
29	50FIC5100.MEAS	WAS Flowrate	#2 Secondary Clarifier	4,010	4	L/min	0.1
30	50FI5420.MEAS	Flow rate	Nitrogen Addition to RAS	20	0.02	L/min	0.1
31	50FI5400.MEAS	Flow rate	Phosphorus Addition to RAS	15	0.015	L/min	0.1
32	50FI5440.PNT	Flow rate	NaOH Addn to Primary Accepts	20	0.02	L/min	0.1
33	50FFY5447.OUT	Flow rate	NaOH Addition to sludge	110	0.11	%	0.1
34	50FI6036.PNT	Flow rate	NaOH Addition to Corridor Thr	35	0.035	L/min	0.1
35	50LI5425.PNT	Level	Nitrogen Tank	110	0.11	%	0.1
36	50LI5405.PNT	Level	Phosphorus Tank	110	0.11	%	0.1
37	50LI5445.PNT	Level	NaOH Tank	110	0.11	%	0.1
38	50LI5480.PNT	Level	Ferric Sulfate Tank	110	0.11	%	0.1
39	50FFIC5210.MEAS	Flow rate	Polymer to sludge	80	0.08	L/min	0.1

	Tag #	***Measurement Type***	***Measurement Location***	***Span***	***Compensation Deviation***	***Units***	***Compensation Deviation (% Span)***
40	50TI5426.PNT	Temperature	Urea	50	0.05	ºC	0.1
41	50FY5400D.PNT	Ratio (Calc)	Ratio Phosphorus-COD	21	0.021	L/min	0.1
42	50FY5420D.PNT	Ratio (Calc)	Ratio Nitrogen-COD	21	0.021	L/min	0.1
43	50LI5230.PNT	Level	Mixed Sludge Tank	110	0.11	%	0.1
44	50FIC5235.MEAS	Flow rate	Mixed Sludge Tank	5,010	5	L/min	0.1
45	50LI5335.PNT	Level	Sludge Silo	110	0.11	%	0.1
46	50FI4040.PNT	Flow rate	Final Effluent	60,010	60	L/min	0.1
47	50TI4060.PNT	Temperature	Final Effluent	70	0.007	ºC	0.01
48	50AI4050.PNT	pH	Final Effluent	14	0.0014	pH	0.01
49	50AI4045.PNT	Conductivity	Final Effluent	1,000	0.1	µmho	0.01
50	50AI4038.PNT	TSS	Final Effluent	410	0.41		0.1

4.2.3. Data Preparation & Treatment

The preparation, cleaning or pre-processing of data requires a great deal of effort. Steps in data preparation include removal of abnormal operating conditions such as mill shuts or low production periods, the identification and removal of outliers, and filtering noise in the data [192]. Outliers are those data points that deviate greatly from all other data points [193]. On-line data cleaning and pre-processing has been studied [193].

4.2.4. Steady State Identification

The detection of steady state conditions can be achieved by selecting a window or time period of data and performing an steady state identification exercise [194]. The steady state identification exercise can consist of a variety of analysis, from a moving average plus data variance limits, or other statistical tests on the data average, variance or regression [194].

4.3. Pulp and paper wastewater measurements, data treatment & modelling

4.3.1. Pulp and paper wastewater measurements

Typical frequency of measurements of pulp and paper wastewater streams is outlined in Table 19 below. The frequency of measurements made for operations monitoring is often daily, while operations control requires a shorter frequency of measurement, and measurements made for regulatory compliance may be daily but require the greater accuracy associated with an accredited laboratory. Laboratory measurements are often grab samples while the samples sent to accredited laboratories for compliance are usually composite samples.

Table 19: Pulp & paper wastewater measurement frequency (typical)

Measurement	*Frequency*	*Location*	*Purpose*
COD NH_4 NO_3 PO_4 TSS	Daily	AST inlet	Monitoring
COD DO Temperature	On-line	AST inlet	Control

Measurement	***Frequency***	***Location***	***Purpose***
SVI TSS VSS	Daily	AST outlet	Monitoring
NH_4 NO_3 PO_4	Daily	Final Effluent	Monitoring
BOD_5 TSS COD	Daily	Final Effluent	Regulatory compliance

4.3.2. Data treatment & modelling

The data treatment process necessarily calculates an average value of measured values, whether it be a minute average of on-line measurements made at a frequency of 15 seconds, or hourly average of measurements made every minute. In pulp and paper modelling, a number of approaches have been used. Daily, weekly and yearly averaged data has been used in pulp and paper wastewater modelling research, as detailed in Table 20.

Table 20: Pulp & paper wastewater measurement average data used for modelling

Measurement	***Frequency***	***Average used for modelling***	***Reference***
COD BOD TSS N P Flow	Daily	Yearly	[195]
BOD COD fractions P fractions N fractions	Two occasions 8 days apart	Averaged	
BOD COD fractions P fractions N fractions	Three consecutive days	Averaged	[134]

Measurement	***Frequency***	***Average used for modelling***	***Reference***
COD BOD TSS		Yearly	
Batch reactor tests for COD fractions	Two occasions in triplicate	Averaged triplicates	[196]
COD BOD TSS	Daily or twice daily during a 4-year period	Daily (Yearly used for mass balances)	[197]
Batch reactor tests			[163, 198-200]

5. Modelling: Activated Sludge Models (ASM)

The benefit of modelling of a wastewater treatment plant is at least two-fold: to facilitate a deep understanding of current operating regimes, and to enable the amelioration of the process operation, the results of which may include new design projects. A model is a powerful tool which can save both money and time for an operator or process designer. It is important to understand the principles upon which the model was developed and the limitations of the model, since any model is constructed to reflect reality only within certain constraints.

5.1. Background

The history of the development of models that represent the Activated Sludge process is very well expressed in an article by Gujer [201]. Suffice to say that the modelling of AST processes developed in 1964 by Downing, Painter and Knowles, and Wuhrmann led to development work by Gujer himself and by the University of Cape Town (UCT) led by Marais during the late 1970s. World-wide modelling work culminated in 1982 in the formation of a task group by the then International Association on Water Pollution Research and Control (IAWPRC), who developed the matrix notation for dynamic modelling that was more accessible than the previous FORTRAN programming [201]. The matrix represents the Monod model of biological processes which occur in the AST [202] cited in [203].

The first Activated Sludge Model (ASM) developed by the IAWPRC taskforce was aptly named ASM1. The stated purpose of the taskforce was "to review existing models and... to reach a consensus concerning the simplest one having the capability of realistic predictions of the performance of single sludge systems carrying out carbon oxidation, nitrification and denitrification"[204]. The matrix bearing his name originated in Petersen's 1965 publication "Chemical Reaction *Analysis*" [205] *cited in* [203, 204, 206], and is a systematic representation of the stoichiometric and kinetic relationships between the system components and the biological processes. The system components may include the wastewater COD fractions, the biomass fractions, nutrient fractions, oxygen or alkalinity, according to established standards [207].

The ASM model was further developed to include biological phosphorus uptake and the associated denitrification process (ASM2, ASM2d), and to include the storage of substrate under concentration gradient conditions (ASM3) [204, 208].

5.2. Mathematical Modelling

The beauty of the ASM models is that they make every effort to apply mechanistic models whilst remaining as simple as possible, and all this in order to represent biological processes which are occurring in a microbiological population that is populated by a complex mixture of microorganisms. The key to understanding the ASM models is that they represent bulk processes observed, and not necessarily each of the processes that are occurring at a microscopic level inside the floc, such as those described in section 3.1 of this literature review, a model of which would be impossible to calibrate.

The ASM models can be described as "dynamic, lumped-parameter, grey-box models including nonlinear reaction terms"[134]. Each of these designations is discussed below.

5.2.1. Steady State, Dynamic, Adaptive

The definition of steady state according to chemical engineering reference texts is the state at which all terms in the mass balance are constant: the sum of the rate of change of generation, accumulation, consumption and flow of mass in or out of the system is zero [104]. In one process simulator, this is expressed as the state where "none of the state variables change over time" [209].

A simulator may require a steady state model run to produce the initial values for the dynamic model [209]. The convergence parameters are set in the model and determine the level of precision, and the number of iterations permitted to achieve that precision, for the process variables [210]. Understanding the manner by which the mathematical model arrives at the steady state or dynamic simulation is important, and will be discussed further in the project methodology section.

A 'dynamic' simulation refers to the fact that the model responds to changes in the influent to the wastewater treatment plant, using either the steady state model or other inputs for the initial values [210]. The dynamic simulation should be run in a repeating sequence in order to determine whether it converges or diverges over time [209].

In reality, a microbiological population as diverse as that found in activated sludge basins adapts to current process conditions. Within the bounds of reality, there are a very large number of combinations of process conditions that may result in adequate process performance. A model that is updated according to current process conditions, perhaps using on-line process data, is referred to as an adaptive model [203]. A continuously updated model would be of great benefit to plant operators if, for instance, the purpose of the model is to predict out of compliance events.

5.2.2. Lumped-Parameter, Distributed

A lumped parameter model assumes that the partial differential equations required to fully describe mass, momentum and heat transport phenomena, such as those found in Bird, Stewart and Lightfoot [104], can be simplified to ordinary differential equations (ODE) [203]. This assumption is based on the hypothesis that the composition of the process flow does not change with respect to distance in terms of heat, mass and momentum, within a certain 'isotropic' region [203].

A spatially distributed model could theoretically be used to model a physical system [206], although this higher degree of precision would require more parameters to be evaluated, and the incremental increase in accuracy would not necessarily merit the effort involved in that evaluation.

Lindblom uses the example of the lumped parameter reactor outlet concentration of a continuously stirred-tank reactor (CSTR), compared to a distributed (distance-based) reactor concentration in an ideal plug-flow reactor [134]. The lumped parameter assumption is reasonable [206] and forms part of the 'complexity compromise' made when modelling a real-life physical system [211].

It should be noted that the model simulator uses numerical calculations and iterations to solve the ODEs, it does not attempt to find an analytical solution to the equations [209].

5.2.3. Black Box-White Box (Statistical-Mechanistic, Stochastic-Deterministic)

The term 'mechanistic' refers to the fact that the model uses prior knowledge of the process and microbiology in order to relate input values to modelled outputs, and for this reason the model is widely applicable for different operating regimes and conditions, within the model limitations [195]. A mechanistic model may also be called a deterministic model [212] or a white-box model [134].

In contrast, a statistical model, or black-box or stochastic model, refers to a model that represents observed behaviour between the inputs and outputs of a process, with no consideration for the theoretical principals that govern the process. These types of models do not allow interpretation of the cause and effect relationships between parameters, yet they are useful for predicting an output for a given input if no insight is desired.

A grey-box model, as indicated by Lindblom [134], refers to the fact that the ASM models are based on a combination of mass balances (black-box) plus Monod-type expressions (white-box), which is typical of real-life process models since science is after all a description of nature.

5.2.4. Linear, Non-Linear Reaction

A chemical or biochemical reaction could be described as linear if the rate of change in concentration of the reactants or products were a linear relationship. Bacterial growth and inhibition biochemical reactions occurring in the AST system are commonly described by the Monod kinetics term, which is a highly non-linear function [134].

5.3. Modelling Methodology

The following is a discussion of the general methodology involved in modelling a process such as wastewater treatment.

5.3.1. Build, Calibrate, Validate

The methodology described in *Petersen et al.* will form the basis for this modelling exercise [213]. This methodology, depicted in Figure 19, is widely accepted and reiterated in many articles [200, 208, 214-218]. The inputs to the model will include design and operational data for the specific plant, as well as the characterisation of each sub-model: the hydraulic, settling and biochemical model, the latter will require an evaluation or estimation of kinetic and stoichiometric parameters [213].

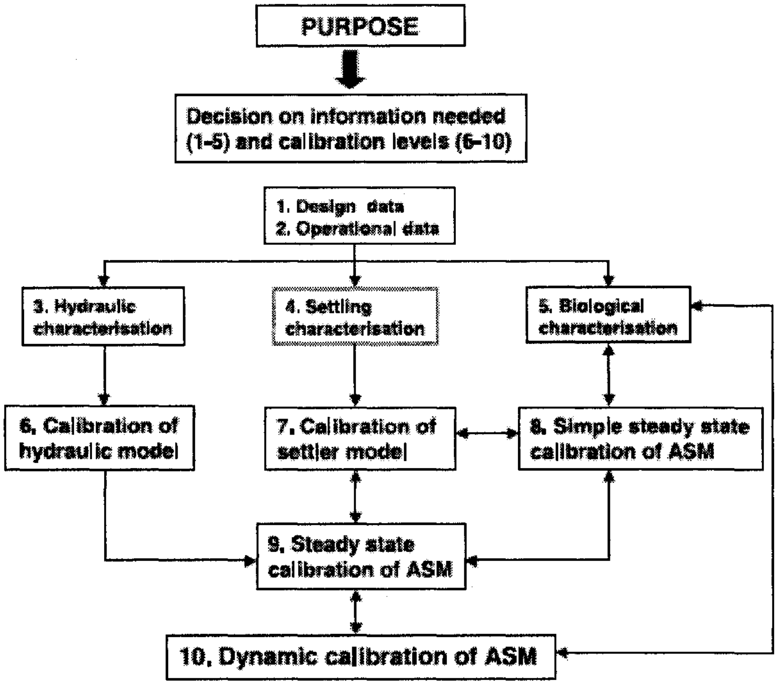


Figure 19: Modelling Methodology, from *Petersen et al.*[213]

One of the most important steps in this methodology is to specify the purpose of the model, and the intended calibration level [219]. The term 'calibration' refers to "the selection of values for the kinetic and stoichiometric coefficients of a mathematical model" [203].

According to common data mining methodologies, calibration could also be referred to as the use of a training or learning dataset to construct a model using a supervised algorithm [220]. In this case, the next step in such a methodology is to use a previously unused data set, the validation dataset, to validate the model that has been built. This validation step is included in the comprehensive generalised simulation guidelines presented by Langergraber *et al.* [215], as shown in Figure 20. Hulsbeek *et al.* recommend using a distinct data set, say from a different season, for the validation data set [221]. Langergraber *et al* suggest a short period, say of four days, of independent monitoring for use as the validation data set [215]. Sreckovic's experience with a limited data set indicates the division of the data set into a calibration and a validation set, based on extreme outlier values and variation of the data, is sufficient [197]. Furthermore, Sreckovic reiterates the calibration process four times in order to avoid a local minimum in his calibration algorithm [197].

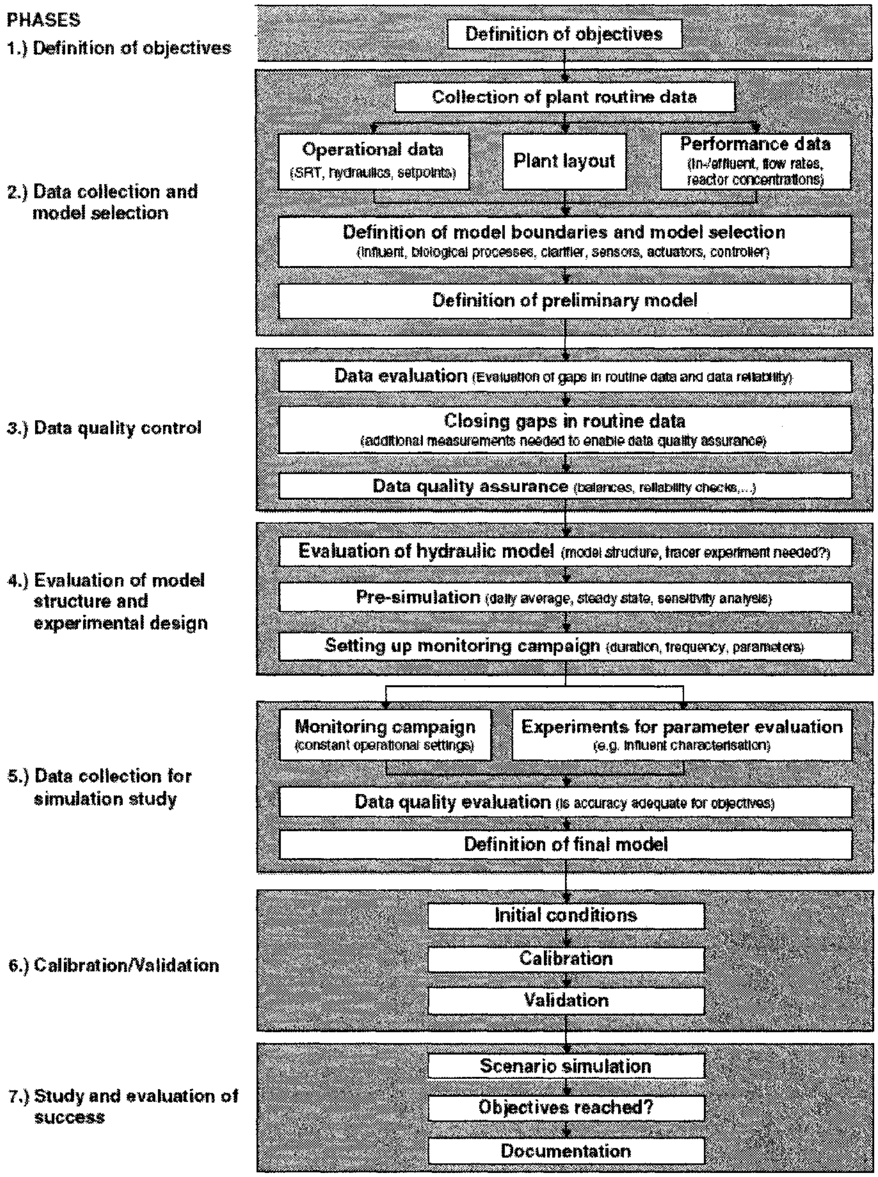


Figure 20: Simulation guidelines, *Langergraber et al.*[215]

The context of modelling in the overall data mining exercise is demonstrated by the CRISP-DM methodology [222], which includes data preparation, data collection as discussed in the previous data collection section, and presented in Figure 21.

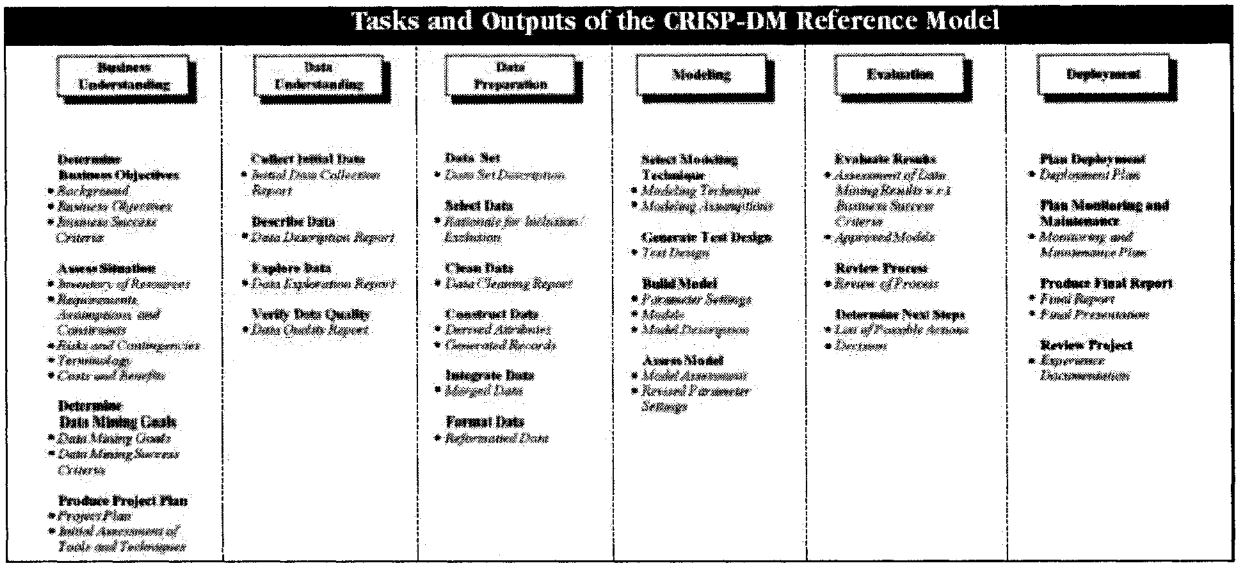


Figure 21: CRISP-DM Methodology [222]

5.3.2. Modelling effort

The construction of a model of a wastewater treatment plant can be characterised by the effort required for the process simulator, as presented in Figure 20 below [223].

Table 21: Modelling effort & deliverables [223]

Modelling effort & deliverables	***Low effort***	***High effort***
Person-hours (order of magnitude)	Tens to hundreds of hours	Thousands of hours
Modelled Layout	Simplified representation of the plant focusing on liquid line processes	Complete representation of the plant including liquid and solids processing and parallel process lines
Data	Existing data only, focus on average plant performance	Sampling and monitoring program designed specifically for model calibration and evaluation – including stress testing and dynamic event monitoring
Calibration	Based on one or two pseudo-steady-state events (average performance over a period of time with relatively consistent	Numerous steady-state and dynamic calibrations over a wide range of plant operating conditions. Kinetic and

Modelling effort & deliverables	***Low effort***	***High effort***
	influent and stable operation)	stoichiometric parameters identified using, for example, respirometry
Evaluation	Limited (if any) formal evaluation of model calibration using independent data sets	Formal evaluation using multiple independent data sets that represent a wide range of plant operating conditions
Plant Analysis	Steady-state analysis of a few key scenarios	A wide-ranging analysis of plant layout and operations under existing and future loading conditions. Optimization of planned upgrades and operation

5.3.3. Modelling Challenges & Risks

As discussed previously, a model is one representation of reality, not necessarily the only possible representation. With respect to the modelling methodology discussed, it is important to recognise that many model parameters are fit to the data and assumed to be constant – this is particularly true of the ASM model kinetic and stoichiometric parameters discussed below [224]. Alternatives to the ASM models exist, such as the suggested model based on F/M ratio rather than substrate concentration [224].

One problem that has been highlighted with the ASM models in particular is that two parameter sets may produce the same model result [197]. Sreckovic reports that this problem, termed 'identifiability' of the model, requires a dynamic sensitivity analysis of the model [197].

5.4. Model Components

The overall wastewater treatment plant model is made up of a hydraulic model, a settling model and a biological model (ASM), and for each of these model components a number of variations exist.

5.4.1. Hydraulic Model

5.4.1.1. Biological Reactor

The hydraulic model is specific to the type of reactor process unit selected, whether it is a continuously stirred-tank reactor (CSTR), a plug-flow reactor

(PFR) or sequencing batch reactor (SBR) type of suspended growth reactor, or an attached growth reactor such as a trickling filter or a rotating biological contactor (RBC)[210]. The modelled reactor should take into consideration the real-life degree of dead space or short-circuiting, and the degree to which the actual reactor fits the idealised reactor model [210], including any non-equal flow splits [218].

The theory behind CSTR and PFR engineering is presented in section 2.2.1. The hydraulic models included in the GPS-X® simulation environment follow this theory exactly (refer to equations 2.1 to 2.4 in [210]).

5.4.1.2. Clarifiers

The hydraulic model for the primary or secondary clarifiers is based on the geometry of the clarifier (rectangular, circular, conical etc), plus the settling model selected [210].

5.4.2. Settling Model

The settling model can range from physical settling only (non-reactive) to physical settling plus some biological reactions (reactive). The settling models available in the GPS-X® simulation environment include a point settler (zero-dimensional and non-reactive), a one-dimensional non-reactive model and a one-dimensional reactive model [210]. The reactive models are reliant on the biological model chosen for the upstream activated sludge process to determine the possible reactions that could occur in the secondary clarifier [210].

The point settler model is an idealised physical settling model, where the clarifier is treated as a single layer. A mass balance is carried out based on the solids content of the inlet and outlet streams of the clarifier, based only on the solids separation.

The one-dimensional physical settling models in GPS-X® are based on a mass balance carried out on each layer, based on the bulk liquid flow and gravity settling between each layer, for a total of 10 layers [210].

The secondary clarifier model includes a correlation with the sludge volume index (SVI) that is not included in the primary clarifier model [210].

5.4.3. Biological Model

There are currently four main ASM models available: ASM1, ASM2, ASM2d and ASM3. The main differences between each model are the biochemical processes which are included in each model. *Gernaey et al.* present an excellent review of the differences between the ASM models, as well as other activated sludge models available, a summary of which is presented in Table 22 [208]. All models include the removal of organic carbon

Table 22: Summary of activated sludge model biochemical processes [208]

Model	***Processes included***	***Reference***
ASM1	Nitrification, denitrification, Death regeneration (not electron acceptor depending), Hydrolysis (electron acceptor depending)	[225]
ASM2	Nitrification, denitrification, Death regeneration (not electron acceptor depending), Hydrolysis (electron acceptor depending), Biological Phosphorus removal (bio-P), Lysis of Phosphorus accumulating organisms (PAO), Fermentation, chemical phosphorus removal	[226]
ASM2d	Nitrification, denitrification, Death regeneration (not electron acceptor depending), Hydrolysis (electron acceptor depending) Biological Phosphorus removal (bio-P), Denitrifying PAO, Lysis of Phosphorus accumulating organisms (PAO), Fermentation, chemical phosphorus removal	[227]
ASM3	Nitrification, denitrification, Endogenous respiration (electron acceptor depending), Hydrolysis (not electron acceptor depending)	[228]
ASM3 bio-P	Nitrification, denitrification, Endogenous respiration (electron acceptor depending), Hydrolysis (not electron acceptor depending) Biological Phosphorus removal (bio-P), Denitrifying PAO, Lysis of Phosphorus accumulating organisms (PAO)	[229]
Barker & Dold	Nitrification, denitrification, Death regeneration (not electron acceptor depending), Hydrolysis (electron acceptor depending) Biological Phosphorus removal (bio-P), Denitrifying PAO, Lysis of Phosphorus accumulating organisms (PAO), Fermentation	[230]
TUDP	Nitrification, denitrification,	[231]

Model	***Processes included***	***Reference***
(Delft University of Technology)	Death regeneration (not electron acceptor depending), Hydrolysis (electron acceptor depending) Biological Phosphorus removal (bio-P), Denitrifying PAO, Lysis of Phosphorus accumulating organisms (PAO), Fermentation	

Considering only the ASM models, ASM2 and ASM2d models incorporate the biological phosphorus removal processes that are outlined in *Comeau et al.* [139]. These processes are now well established and installed in municipal effluent treatment plants, however only one installation for pulp and paper effluent treatment is known [232].

One of the main differences between ASM1 and ASM3 is that ASM3 incorporates aerobic storage of the organic carbon, which is typically seen in plug flow reactors where there is a gradient in the carbon concentration over time or space [88, 89, 233-235]. In order to model this storage step, it was mathematically necessary to de-couple the death regeneration fate of the lysed bacteria found in ASM1, and the endogenous respiration model was therefore incorporated into ASM3, which can be seen in Figure 22 [208].

The applicability of these models specifically for pulp and paper wastewater is discussed in detail in section 5.7.2.

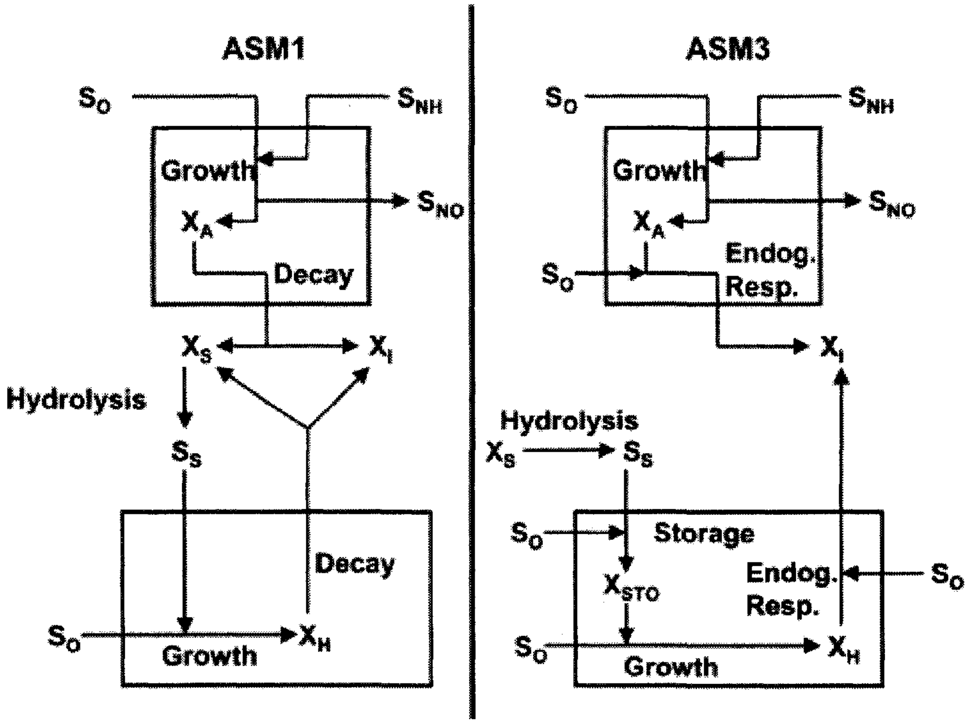


Figure 22: ASM1 vs ASM3 Processes [208]

5.4.3.1. Kinetics

The ASM models are constructed using kinetic parameters that are applicable for the range of 10ºC to 20ºC or 25°C, with ASM2 to ASM3 using the Arrhenius temperature relationship [204, 208]. This is potentially a significant limitation to these models, as the kinetic growth and inhibition rates are highly temperature dependent and the temperature of pulp and paper effluent is normally above 30°C. It can be assumed that kinetic parameters increase with increasing temperature for the same type of microbiological population; they should be measured for a particular microbiological population if a large temperature difference exists such as that between 10ºC and 40ºC [195].

In some of the ASM models, the growth rate of bacteria can be nutrient limited, although not in ASM1[208]. The presence of toxic substances can be inhibitory to the growth of bacteria and to the rate of nitrification, although the latter is not considered specifically in ASM1 [208].

5.4.3.2. Stoichiometry

The ASM models are all based on a chemical oxygen demand (COD) balance, as discussed in section 5.5.1. The models therefore require information on the chemical composition of the biomass or cellular matter, in order to complete this material balance. This information is represented by the ratio between COD to volatile suspended solids (VSS), or BOD to total suspended solids (TSS), or a combination thereof [210]. These ratios may be estimated from the theoretical chemical components of cellular matter or calculated from site data, as they will probably vary according to the bacterial population and wastewater composition.

5.5. ASM Model Basis

5.5.1. Chemical Oxygen Demand (COD) Material Balance

Chemical Oxygen Demand (COD) was chosen as the basis of the material balances in the ASM model due to the total conservation of mass, compared to total organic carbon (TOC), and for the rapidity of measurement, compared to biological oxygen demand (BOD_5 or BOD_7) [210].

5.5.2. Chemical Oxygen Demand (COD) Fractionation

COD is fractionated into the state variables, denoted by 'X' for particulate and 'S' for soluble, the definition of which is the filtrate that passes through either 0.45µm or 0.1µm filter paper [219]. Table 23 is a list of COD fractions that can be included in the ASM models using the CNPIP (carbon-nitrogen-phosphorus industrial pollutant) library [210]. As discussed in the next section, not all of the fractions are required for all models. A simple COD fractionation is presented in Figure 23.

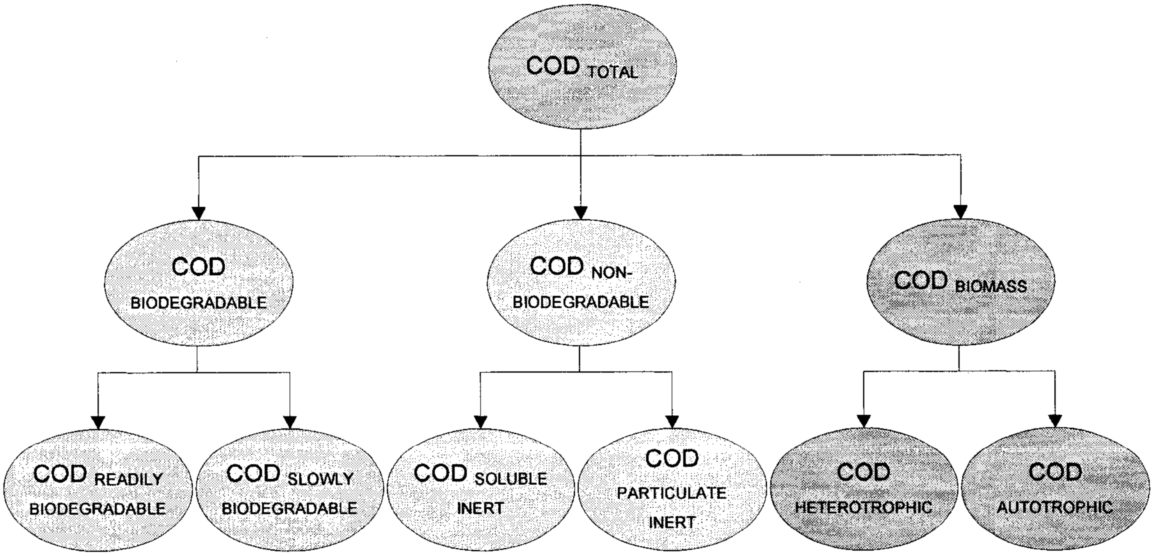


Figure 23: COD Fractionation, simple [219]

5.5.3. Nitrogen and Phosphorus

Nitrogen and phosphorus can also be fractionated and included in mass balance calculations, according to the biological model selected. Table 23 includes the largest range of possible fractions that can be included in the ASM models, which are graphically represented in Figure 24 and Figure 25.

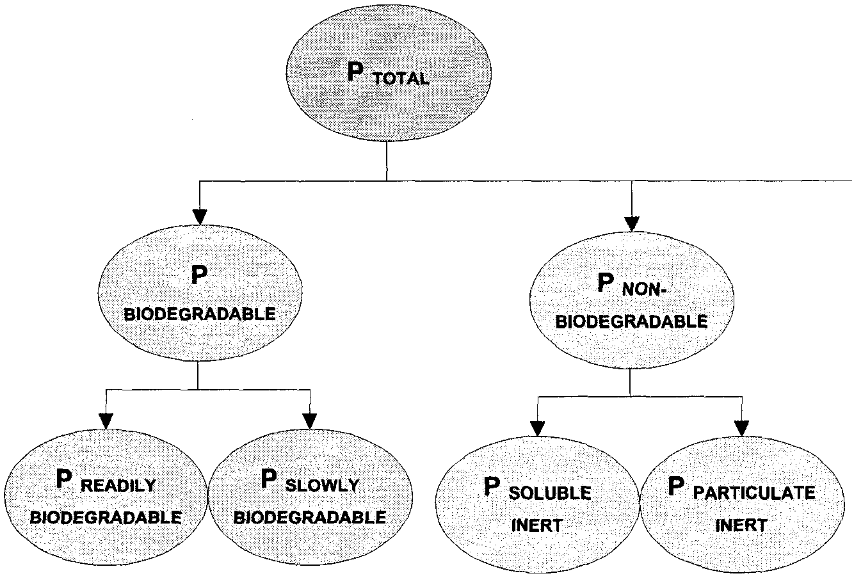


Figure 24: Phosphorus Fractionation

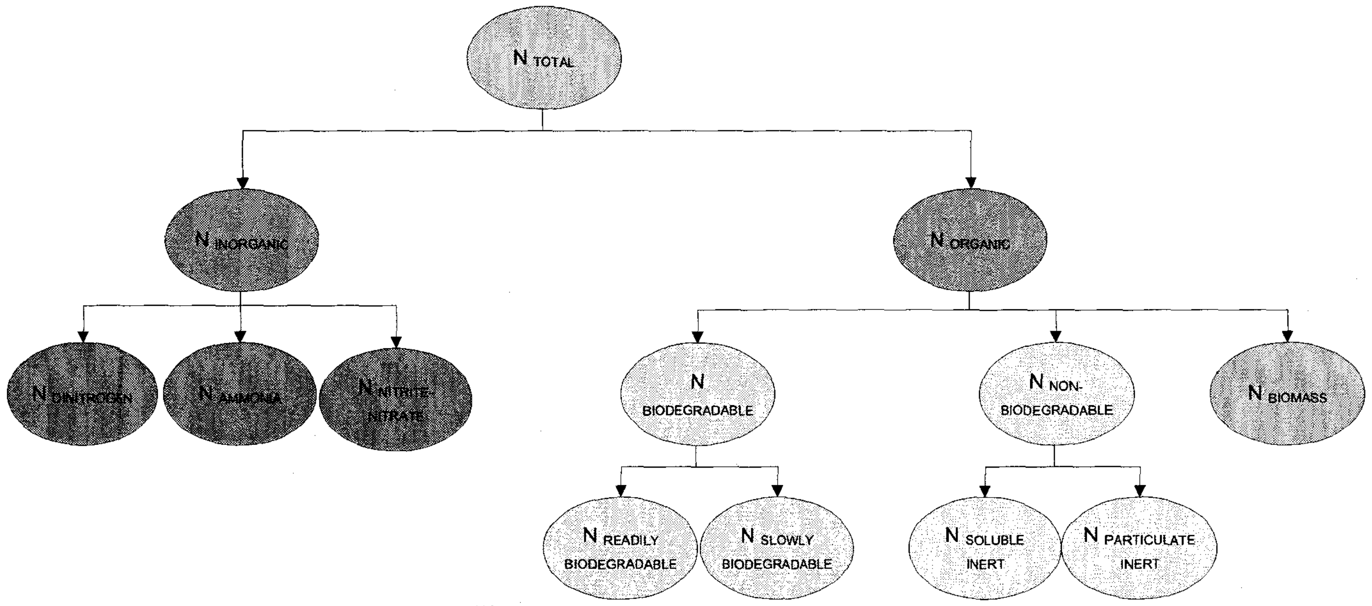


Figure 25: Nitrogen Fractionation

Table 23: Example of State Variables (CNPIP Library), From Hydromantis Inc Technical Reference [210]

#	Symbol	State Variable	Units
1	S_I	Soluble inert organics	g COD/ m^3
2	S_S	Readily biodegradable (soluble) substrate	g COD/ m^3
3	X_I	Particulate inert organics	g COD/ m^3
4	X_S	Slowly biodegradable (stored, particulate) substrate	g COD/ m^3
5	X_{BH}	Active heterotrophic biomass	g COD/ m^3
6	X_{BA}	Active autotrophic biomass	g COD/ m^3
7	X_U	Unbiodegradable particulates from cell decay	g COD/ m^3
8	S_O	Dissolved oxygen	g O_2/ m^3
9	S_{NO}	Nitrate and nitrite N	g N/ m^3
10	S_{NH}	Free and ionized ammonia	g N/ m^3
11	S_{ND}	Soluble biodegradable organic nitrogen (in S_S)	g N/ m^3
12	X_{ND}	Particulate biodegradable organic nitrogen (in X_S)	g N/ m^3
13	X_{PM}	Polyphosphate accumulating biomass	g COD/ m^3
14	X_{BT}	Poly-hydroxy-alkanoates (PHA)	g COD/ m^3
15	X_{PP}	Stored polyphosphate	g P/ m^3
16	S_{LF}	Volatile fatty acids	g COD/ m^3
17	S_P	Soluble phosphorus	g P/ m^3
18	S_{ALK}	Alkalinity	mole / m^3
19	S_{NN}	Dinitrogen	g N/ m^3
20	S_{NI}	Soluble unbiodegradable organic nitrogen (in S_I)	g N/ m^3
21	S_F	Fermentable readily biodegradable substrate	g COD/

#	Symbol	State Variable	Units
			m^3
22	X_{GLY}	Stored glycogen	g COD/ m^3
23	X_{PPR}	Stored polyphosphate (releasable)	g P/ m^3
24	X_{MEOH}	Metal-hydroxides	g / m^3
25	X_{MEP}	Metal-phosphate	g / m^3
26	X_{STO}	Cell internal storage product	g COD/ m^3
27	X_{II}	Inert inorganic suspended solids	g COD/ m^3
28	S_{ZA}	Soluble component "a"	Not set
43	X_{ZA}	Particulate component "a"	Not set

5.5.4. Alkalinity and pH

The ASM models incorporate a balance of alkalinity, which is the measure of the buffering capacity of a solution in equivalent moles of calcium carbonate [236]. The Water Quality Association glossary makes the analogy of pH to temperature as alkalinity would be the heat capacity of a substance [236]. The ASM models assume the pH is constant and near neutral, they do not take into consideration the effect of pH on the biochemical processes [204].

5.5.5. Temperature

The ASM models do not include a heat and energy balance.

5.6. Simulation environment

A number of commercial simulation environments have been built using the ASM model components, notably GPS-X® by Hydromantis, WEST® by Hemmis and Biowin® by Envirosim, the latter includes elemental mass balances.

These simulation environments provide a useful interface between the model and the operator or process engineer. They could potentially interface with other process simulators such as CADsim Plus® by Aurel or IDEAS® simulation by Andritz, which model pulp and paper processes.

The following is a glossary of terms, taken from the *Hydromantis Inc Entry Level Guide* [209] and *Technical Reference* [210].

Table 24: GPS-X® glossary of terms [209]

Term	***Meaning***	***Example***
State Variable	Define the state of the system	X_S
Composite Variable	Calculated from state variables (& other constants)	VSS, TKN
Initial Conditions	Initial numeric value for wastewater composition, kinetic and stoichiometric parameters, used to find steady state	
Library	A collection of state variables that can be used in conjunction with an influent model and ASM model to build the appropriate biological model in GPS-X	CN, CNP
Influent Model	A representation of organic, nitrogen and phosphorus fractions in the influent	'States'

5.6.1. Simulation Basis

The basis of the GPS-X® simulator is a material balance over each of the state variables in the ASM model over each of the process units, taking into account the flow rates in and out of the process unit as well as the generation or consumption rate specified [209]. The state variables are predominantly COD, oxygen and nutrient fractions, as seen in Table 23.

5.6.2. Influent Model (Influent Advisor)

The GPS-X simulator allows the entry of influent COD, nitrogen, phosphorus and solids fractions in a number of ways. The simulator Influent Advisor spreadsheet demonstrates the links between user input values and state and composite variables. A summary of differences between the influent models is listed in Table 25 below.

Table 25: Influent model attributes [210]

Model	***Attributes***
BOD based	Use if BOD data is available and COD data not available Relies on f_{SS}: ratio of soluble substrate to ultimate BOD
COD fractions	Complicated calculation of N and P fractions Allows direct input of state variables via data file
States	Use if full wastewater characterisation has been carried out

Model	Attributes
	in reality
TSS COD	XCOD is calculated from TSS via VSS

Given the fact that VSS in pulp and paper wastewater includes fibre content as well as biomass, which differs significantly from municipal wastewater, it is not considered reasonable to use the TSS COD influent model for pulp and paper wastewater.

Due to the fact that a wastewater characterisation has been carried out for the case study mill in terms of COD fractions, the simplest influent model to use is the States model.

5.6.3. Library

The choice of library is fairly simple: the CN library contains only COD, oxygen and nitrogen fractions; the CNP library contains phosphorus fractions as well. The exact fractions included in any model are dependent on the ASM model, library and influent model chosen.

An advanced nitrogen library also exists, called the C2N library. This library includes fractions for nitrogen associated with inert fractions, as well as nitrite-nitrogen, which is associated with process models that model nitrification as a two-step process.

The IP libraries add industrial pollutant fractions to either the CN or CNP libraries. The industrial pollutants are user-defined fractions. These fractions can be used as proxies for other COD or nutrient fractions, as they are in the construction of the ASM-PP model (see section 5.8).

5.6.4. Composite Variable Calculation

The model calculates the composite variables from the state variables using certain ratios, so-called 'stoichiometric constants'[3], as illustrated in Figure 26, Figure 27 and Figure 28 below [210].

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[3] Although these constants are often ratios of solids to COD, which are not strictly stoichiometric. The term stoichiometric refers to the quantity of reactants required to produce a quantity of products in a chemical reaction.

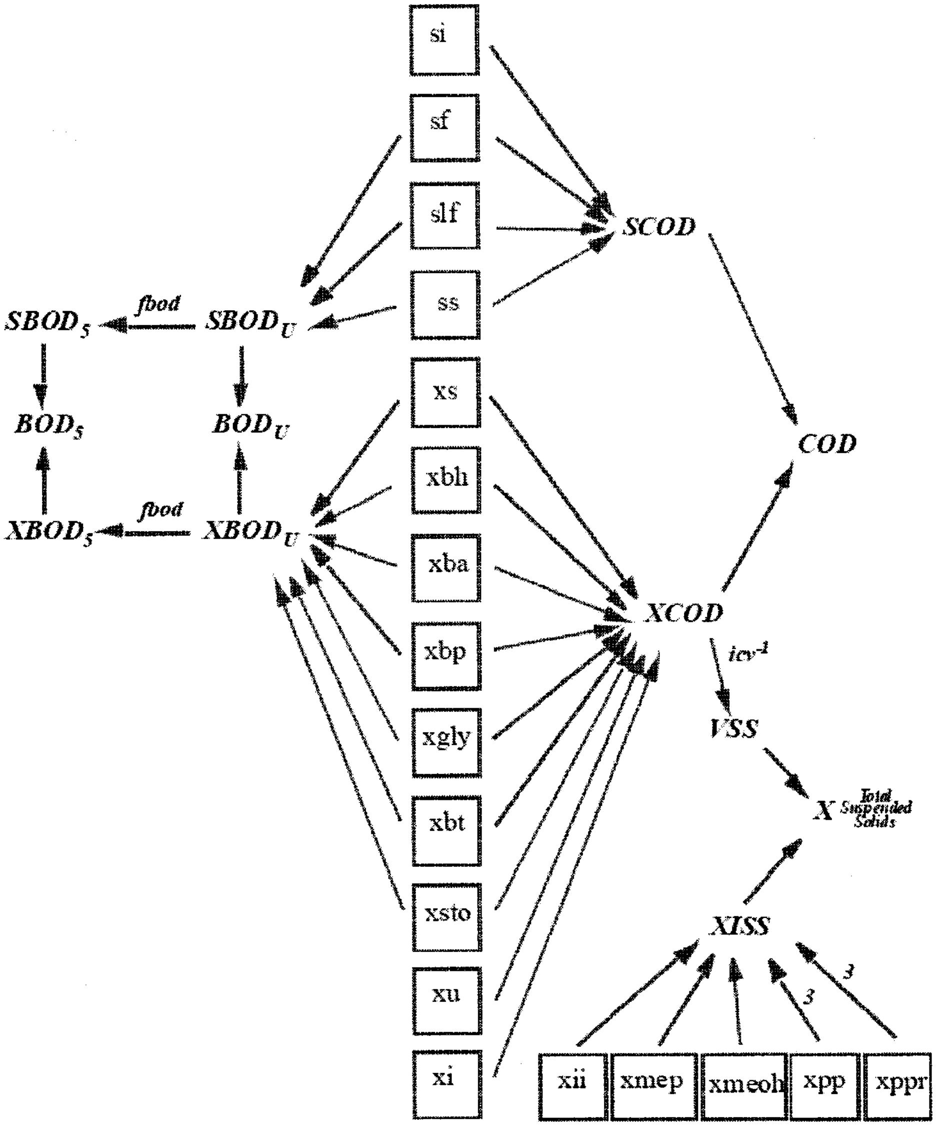

Figure 26: CNP Library state and composite variables: COD [210][4]

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[4] Note that a summation operator is implied at converging arrows, and indices sitting on an arrow indicate a multiplication operator (default of 1).

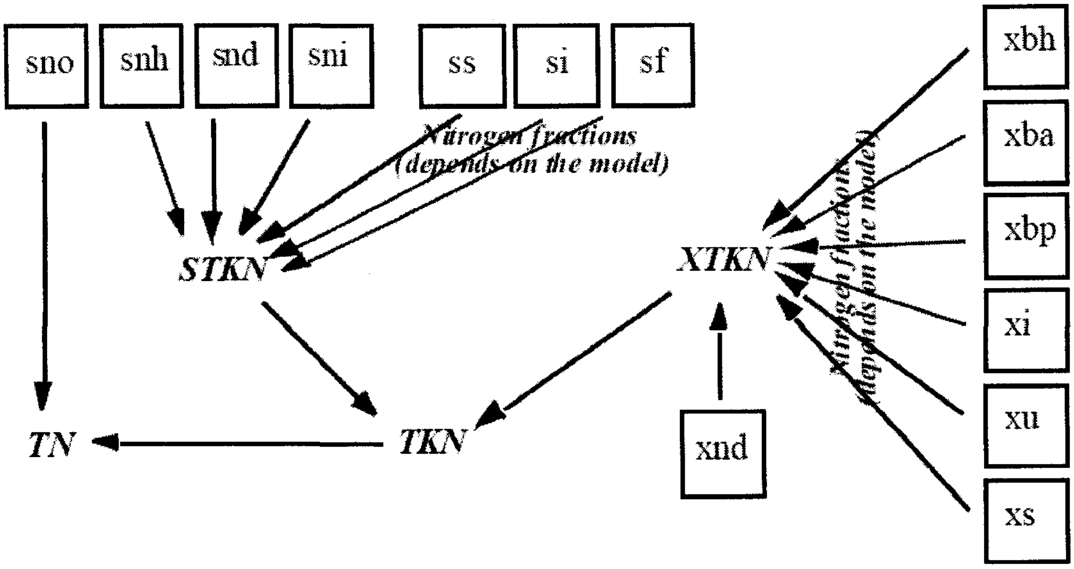

Figure 27: CNP Library state and composite variables: Nitrogen [210]

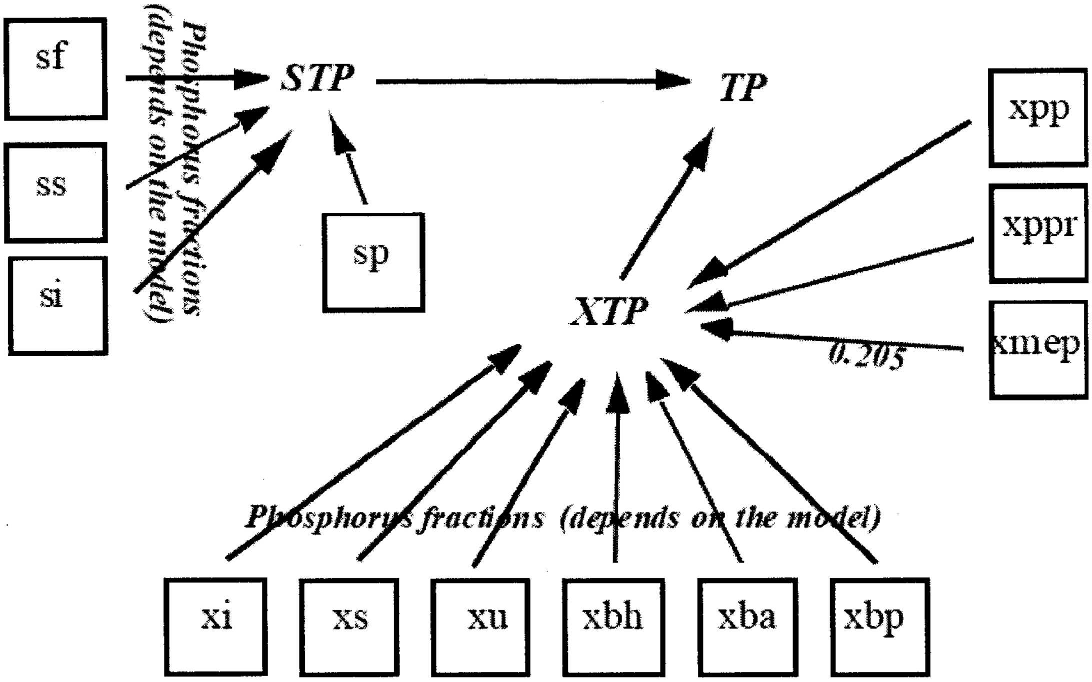

Figure 28: CNP Library state and composite variables: phosphorus [210]

5.6.5. Calculation Basis

The steady state solver in the GPS-X simulator detects a steady state convergence when the sum of derivatives of state variables falls below the 'iteration termination criteria', which has a default value of 10.0 [210]. Two other parameters that can have a significant effect on the steady state solver are the 'contract constant' and 'expand constant' which regulate the size of the steps taken by the steady state solver between iterations [210]. The default numerical solver integration method is the Runge-Kutta-Felberg method [210].

5.6.6. Alkalinity and pH

The GPS-X simulator conducts an alkalinity balance in accordance with the ASM models.

5.6.7. Temperature

The GPS-X simulator does not include a heat balance.

5.7. Wastewater & Biomass Characterisation

5.7.1. COD and Nutrient Fractions

In order to satisfy the requirements of the ASM model COD balance and the simulator state variable material balance, a wastewater characterisation should be completed on various wastewater streams. This comprises of a characterisation of the carbonaceous (COD) fractions, nitrogen fractions and phosphorus fractions in the wastewater and sludge, as well as the settling and thickening properties of the sludge [237]. A large amount of the data required is normally collected by the treatment plant or mill, however the COD fractionation and some other parameters may require additional measurement campaigns.

There have been many published methods of carrying out these wastewater characterisations, predominantly for municipal (domestic) wastewater [237-244]. A thorough review of wastewater COD fraction characterisation for pulp and paper wastewaters is presented in a Paprican report [219], many of which require respirometry and are based on the methods established for municipal wastewater. Many methods have been established, for example a rapid physical-chemical method to determine the readily biodegradable soluble COD (S_S) fraction [245], and complete guidelines in the Netherlands for a simplified COD fractionation for modelling purposes [246]. A nitrogen fractionation characterisation for pulp and paper wastewater was completed by Jarvinen for both chemical and mechanical mill wastewaters [159].

Schnell used the BOD to COD ratio to indicate the biodegradability of the wastewater [45].

A wastewater characterisation based on ASM1 fractions was carried out at the Hylte pulp and paper mill at Hyltebruk, Sweden [134, 195]. This mill consists of TMP, groundwood and wastepaper pulp (including a de-inking plant) and newsprint paper production. The effluent treatment plant consists of trickling filters and anaerobic rectors upstream of the activated sludge treatment. In short, the configuration of this mill and its effluent treatment plant is far from simple.

A wastewater characterisation based on ASM1 fractions was carried out for the effluent of a bleached Kraft mill [199]. Another modelling exercise carried out using the ASM1 model as the basis of modelling fit the wastewater fraction parameters under constrained and non-constrained conditions, and compared the results to the bleached Kraft mill results [197].

5.7.2. Kinetic and stoichiometric parameters

Similarly to the wastewater characterisation of COD and nutrient fractions, a number of methods have been established for the determination of kinetic and stoichiometric parameters for use with the ASM models [219, 244, 247, 248]. Again, many of these methods are based on respirometry [219, 248]. Some of the kinetic and stoichiometric parameters can be determined during the wastewater characterisation exercise, some are based on theoretical calculations and others rely on experimental data found in the literature. The basis of these parameters is presented in Table 26 below. All values are quoted at 20ºC.

Table 26: Basis of calculations, kinetic & stoichiometric parameters

Parameter		***Calculation/ Basis***	***Value(s)***	***Units***
i_{CV}	XCOD / VSS (biomass)	$C_5H_7NO_2 + 5O_2 \rightarrow 5CO_2 + NH_3 + 2H_2O$ $\frac{160 gO_2}{113 gC_5H_7NO_2} = 1.42\ gO_2/gC_5H_7NO_2$	1.48	g COD/ g VSS
f_{BOD}	BOD5 / BOD ultimate ratio	Wastewater characterisation [246] BOD_{total}/ BOD_5 for (PI) Primary influent & (PE) Primary effluent Estimated at 0.66 for municipal wastewater	PI: **0.18 – 0.28** PE: **0.21 – 0.23**	g BOD/ g BOD
i_{XBN}	N content of active biomass	Typical cell composition $C_5H_7NO_2$ [204] $\frac{14 gN}{113 gC_5H_7NO_2} \cdot \frac{113 gC_5H_7NO_2}{160 gO_2}$	0.086	g N / g COD
i_{XUN}	N content of endogenous / inert mass	Estimated to be less than i_{XBN} [204]	0.06	g N / g COD
i_{XBPP}	P content of active biomass	Estimated to be 0.02 g P / g COD [204]	0.021	g P / g COD
i_{XUPP}	P content of endogenous / inert mass	Estimated to be 0.01 g P / g COD [204]	0.021	g P / g COD
f_P	Fraction of biomass leading to particulate products‡	Observed fraction is approximately 20% [204] For recycled process [204]: $f_{P,OBS} = \frac{f_P}{1 - Y_H(1 - f_P)}$	(f_U) 0.08	g COD / g COD

Parameter		Calculation/ Basis	Value(s)	Units
Y_H	Heterotrophic yield (active biomass) ‡	Stoichiometric equations of a COD balance for substrate (acetate), which gives an yield of [39]; $\frac{0.42gVSS}{gCODsubstrate}\cdot\frac{1.48gCODcells}{gVSS}=\frac{0.622gCODcells}{gCODsubstrate}$ Observed yield typically lower (0.3 – 0.5) than the maximum yield constant Y_{MAX} (0.6 – 0.65) [118] Observed in range 0.46 – 0.69 [204]	0.666	g COD / g COD
Y_A	Autotrophic yield (active biomass) ‡	4.33 g O_2 required/g NO_3-N formed [204]	0.24	g COD / g N
μ_H	Heterotrophic maximum specific growth rate‡	Estimated to be 3.0 -13.2 d^{-1}, dependent on wastewater and process configuration [204] Determined to be 9.0 d^{-1} [195]	6.0	d^{-1}
K_S	Readily biodegradable substrate half saturation…‡	Estimated to be 10 -180 g biodegradable COD/ m^3 [204]	20.0	g COD / m^3
K_{OH}	Oxygen half saturation coefficient‡	'Typical value' [204]	0.2	g O_2 / m^3
K_{NO}	Nitrate half saturation coefficient‡	'Typical value' [204]	0.5	g N / m^3
η_g	Anoxic growth factor‡	Estimated to be 0.6 – 1.0, higher values for aerobic sewers [204]	0.8	-

Parameter		Calculation/ Basis	Value(s)	Units
b_H	Heterotrophic decay rate‡	Determined to be 0.930 d^{-1} [195]	0.62	d^{-1}
μ_A	Autotrophic maximum specific growth rate‡	Literature values 0.34 – 0.65 d^{-1} [204]	0.8	d^{-1}
K_{NH}	Ammonia half saturation coefficient for autotrophic…#	‘Typical value’ [204]	0.05	g N / m^3
b_A	Autotrophic decay rate‡	‘Typical value’ [204]	0.2	d^{-1}
K_{OA}	Oxygen half saturation coefficient for autotrophic…‡	‘Typical value’ [204]	0.4	g O_2 / m^3
k_h	Maximum specific hydrolysis rate‡	‘Typical value’ [204]	3.0	d^{-1}
K_X	Slowly biodegradable substrate half saturation…‡	‘Typical value’ [204]	0.03	g COD / g COD
η_h	Anoxic hydrolysis factor‡	Estimated in the region of 0.4 [204]	0.4	-

Parameter		Calculation/ Basis	Value(s)	Units
k_a	Ammonification rate‡	‘Typical value’: neutral pH domestic wastewater [204]	0.08	m^3 / g COD / d
K_P	Phosphorus half saturation constant	Estimated at 0.01 for ASM2d [204]	0.01	g P / m^3

PI = Primary Influent, PE = Primary Effluent
*As defined by the modified Petersen matrix
**Theoretical values used
†Calculated from wastewater characterisation
‡ Values used for pulp and paper wastewater modelling by *Bolmstedt* [195]
# ASM2d typical value for ammonia as a nutrient

A summary of some kinetic and stoichiometric parameters found for municipal wastewaters is presented in Table 27 below [249]. The temperature coefficients, k_T, listed are based on an Arrhenius-type correction of kinetic parameters at temperature T, using the maximum growth rate with a base temperature of 20ºC as an example [249]:[5]

$$\mu_{MAX,T} = \mu_{MAX,20oC}.\exp(k_T(T-20))$$

Table 27: Municipal wastewater kinetic & stoichiometric characterisation studies (ASM1) [249]

Kinetic & Stoichiometric parameters		Range	Unit
Stoichiometry			
Readily biodegradable COD (fraction)	S_S	0.20 – 0.23	-
Slowly biodegradable COD (fraction)	X_S	0.50 – 0.60	-
Heterotrophic growth			
Yield	Y_H	0.57 – 0.64	-
Maximal growth rate	μ_{MAX}	2.5 – 4.0	d^{-1}
Temperature coefficient	k_T	0.07	ºC^{-1}
Saturation constant	K_H	5 – 20	gCOD/m^3
Hydrolysis			
Hydrolysis rate	k_h	1.5 - 55	d^{-1}
Temperature coefficient	k_T	0.03 – 0.07	ºC^{-1}
Saturation constant	K_X	0.02 – 10	-
Temperature coefficient	k_T	0	ºC^{-1}
Decay of biomass			
Inert particulate products	X_U	0.08 – 0.10	-
Inert particulate COD in feed	X_I	5 – 15	gCOD/m^3
Decay rate	b_h	0.50 – 0.58	d^{-1}
Temperature coefficient	k_T	0.07	ºC^{-1}

5.8. ASM-PP: Pulp and Paper ASM model

5.8.1. ASM-PP model basis

The aim of this thesis is to use an existing ASM model, with modifications if appropriate, not to invent a new model or basis of modelling. A pulp and paper-specific modified ASM1 model was constructed by Brault, entitled the ASM-PP model [138]. On the basis of the information and references

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[5] Arrhenius equation may also have the form $\mu_T = \mu_{20^{\circ}C}*(\theta)^{T-20}$, a θ value of 1.04 gives approximately the same doubling of the parameter for every 10ºC rise in temperature as for a k_T value of 0.07 ºC^{-1}.

presented in Table 33, the ASM-PP is based on the ASM1 model. The modifications to ASM1 are presented in Table 34 in the form of the Petersen matrix, modifications are shown in red. The interpretation of the Petersen matrix is discussed further in section 5.8.3.

The ASM2 and ASM2d models will not be discussed further, since there is usually no biological phosphorus removal process in pulp and paper wastewater treatment plants, and none occurs in the case study mill.

Although some variations made in ASM3 do improve the fit of the mechanistic model to reality, such as the detail relating to the decay and intra-cellular processes, they also increase the complexity of the model. In keeping with the aim of the IAWPRC taskforce, the ASM-PP model aims to be the simplest model possible, and results have shown that the simpler decay processes of ASM1 provide an adequate model of pulp and paper effluent [138].

Barañao and Hall provide convincing arguments to use ASM3 for pulp and paper wastewater, given their assertion that "storage of readily biodegradable substrate is dominant" in their case study wastewater treatment plant [200]. However an equally persuasive argument is presented by Insel *et al.* that industrial wastewaters contain high fractions of slowly biodegradable COD, which renders the hydrolysis process the most significant mechanism [27]. In addition to the latter theory, a molecular weight distribution characterisation of TMP effluent upstream and downstream of a biological treatment plant shows significant hydrolysis of high molecular weight total organic carbon fractions [55]. It has also been shown that hydrolysis is a significant process in activated sludge treatment of pulp and paper effluent [27, 55].

In contrast, the storage of readily biodegradable substrate is seen in incidences where there is a gradient in substrate concentration in space or time [88, 89, 233-235], which is theoretically not the case in a well aerated, CSTR reactor. Particularly in this case study, the selector includes aeration and recirculation pump mixing, and is considered a CSTR reactor itself, therefore it does not provide a plug-flow design necessary to provide the feast-famine conditions required for storage of soluble COD [235]. It is hypothesised that the presence of feast-famine conditions results in out-competition of storage-incapable bacteria by the storage-capable bacteria [235]. There may be storage-capable bacteria present in the case study activated sludge population, however the storage biological process is not considered since the feast-famine conditions are assumed to be insignificant.

The limitation of biomass growth rates due to nutrient concentration, specifically ammonia-nitrogen and ortho-phosphate concentration, is considered necessary for pulp and paper wastewater; various combinations of this theory have been used in previous studies [134, 195, 197]. These studies combined the ASM-based model with higher organisms (protozoa), luxury phosphorus uptake and a double (sum) Monod switching function for ortho-phosphate [134], and temperature, pH and spill of an inhibitory substance (hydrogen peroxide) [197].

The state variable included in the ASM-PP model are presented in Table 28 [138]. As previously discussed, the 'industrial pollutant' fractions in the CNPIP library are used as proxies for the added fractions due to requirements of the software available.

It is assumed that lysis of cellular material results in particulate COD and nutrient fractions but not soluble nutrient fractions (i.e. soluble nutrients are immediately readily available in fractions S_P, S_{NH} or S_{NO}). This assumption is necessary given the lack of simple characterisation method to determine the soluble inert cellular material resulting from biomass lysis. One reference for pulp and paper wastewater measured the residual soluble cellular material as 0.057 mg COD/ mg total COD in the influent [240].

It is further assumed that the particulate nutrient fractions are accounted for in the X_{ND} (and X_{PD}) fraction and that the nutrient fractions relating to particulate inerts from cell decay, X_U, and to particulate biomass, X_{BH} and X_{BA}, are composite variables (X_{NU}, X_{PU}, X_{NB}, and X_{PB}). This is to say that X_{NU} is a constant fraction of X_U, and is unchanged by process described by the Petersen matrix.

Table 28: ASM-PP State Variables [138]

#	*Symbol*	***State Variable***	***Units***
1	S_I	Soluble inert organics	g COD/ m^3
2	S_S	Readily biodegradable (soluble) substrate	g COD/ m^3
3	X_I	Particulate inert organics	g COD/ m^3
4	X_S	Slowly biodegradable (stored, particulate) substrate	g COD/ m^3
5	X_{BH}	Active heterotrophic biomass	g COD/ m^3
6	X_{BA}	Active autotrophic biomass	g COD/ m^3

#	Symbol	State Variable	Units
7	X_U	Particulate inerts from cell decay (fraction)	g COD/ m^3
8	S_O	Dissolved oxygen	g O_2/ m^3
9	S_{NH}	Free and ionized ammonia	g N/ m^3
10	S_{NO}	Nitrate and nitrite N	g N/ m^3
11	S_{ND}	Soluble biodegradable organic nitrogen (in influent and from hydrolysis of X_{ND})	g N/ m^3
12	X_{ND}	Particulate biodegradable organic nitrogen (in influent and from biomass decay)	g N/ m^3
13	S_P	Soluble phosphorus (ortho-phosphates in influent and from phosphatification (hydrolysis of X_{PD}))	g P/ m^3
14	X_{PD}	Particulate biodegradable organic phosphorus (in influent and from biomass decay)	g P/ m^3
15	S_{PD}	Soluble biodegradable organic phosphorus (in influent and from hydrolysis of X_{PD})	g P/ m^3
15	X_{II}	Inert inorganic suspended solids	g/m^3
16	S_{NN}	Dinitrogen	g N/ m^3
17	S_{ALK}	Alkalinity	mole / m^3

Table 29: ASM-PP Model composite variables [138]

#	Symbol	State Variable	Units
18	X_{NB}	Particulate active biomass nitrogen (in X_{BH}, X_{BA})	g N/ m^3
19	X_{NU}	Particulate nitrogen from cell decay inerts (in X_U)	g N/ m^3
20	X_{PB}	Particulate active biomass phosphorus (in X_{BH}, X_{BA})	g P/ m^3
21	X_{PU}	Particulate phosphorus from cell decay inerts (in X_U)	g P/ m^3

5.8.2. State variables relating to pulp & paper wastewater

The ASM-PP fractionation of state variables is presented visually in Figure 29, Figure 30 and Figure 31. These fractions can be related to known wastewater characteristics of pulp and paper wastewater according to Table 30 below. The biodegradability of resin acids has been related to the family of resin acid: pimaric or abietic [60]. Values of these state variables that have been experimentally evaluated or fit in a model for pulp and paper wastewater are presented in Table 32 below. Unfortunately there have been very few studies of this kind for pulp and paper wastewater, therefore only a small sample size exists for comparison.

Table 30: ASM state variables related to pulp & paper wastewater [60, 199]

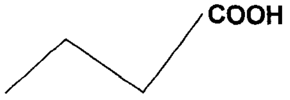
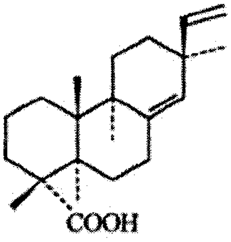
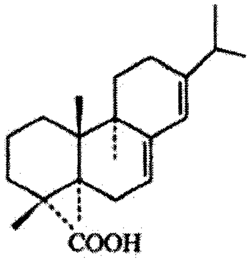
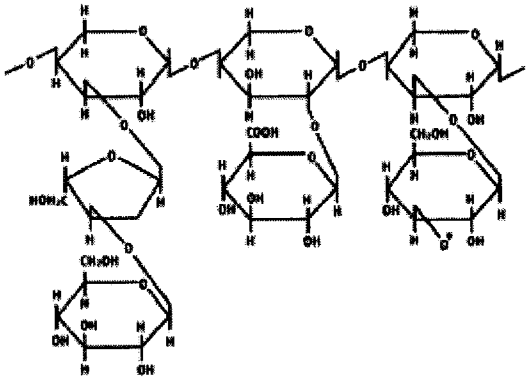
Fraction	*COD form*
S_S	Softwood extractives: Volatile fatty acids (VFA) Fatty acid esters Resin acids (Abietic) [60]*
X_S	Lignin Colloidal fibrous material (Hemi-cellulose & cellulose)
S_I	Lignin Resin acids (Pimaric) [60]*
X_I	Large fibres with attached colloidal material

* See further work on dehydroabietic acid (DHA) [250]; and on compounds found in bleach plant effluents [251]

It is theoretically possible to divide the components of wood, hemi-cellulose, cellulose and lignin, into the X_S and X_I fractions is estimated based on the relative molecular weights of each class of compounds as presented in Table 31 below. However, it is not likely that hemi-cellulose and cellulose would be present in their pure form in the effluent, particularly in the effluent from a TMP plant: they would be present as fibrous material. Lignin is known to cause the colour of pulp and paper wastewater [252], and can therefore be attributed to both the slowly biodegradable and inert soluble fractions, X_S and S_I. The division of lignin into these two fractions would be dependent upon how the large molecules are cleaved, whether they are cleaved into small chains (slowly biodegradable) or not (inert).

Table 31: Molecular weight & structure of hydrocarbons commonly found in wood

Compound class	*Molecular Weight Range (g/mol)*	*Compound structure*
Extractives	< 10,000	Volatile fatty acids

Compound class	***Molecular Weight Range (g/mol)***	***Compound structure***
		 Resin acids [253]  **Pimaric acid**  **Abietic acid**
Hemi-cellulose	32,000	Glucose, Mannose, Galactose, Xylose & Arabinose-based [254] *cited in* [199], branched structure $(C_6H_{10}O_5)_n$ n = ***200*** 
Cellulose	97,000 – 2,400,000	Glucose-based, linear structure $(C_6H_{10}O_5)_n$ n = ***600 – 1,500***

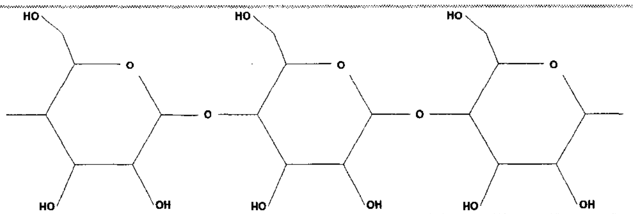
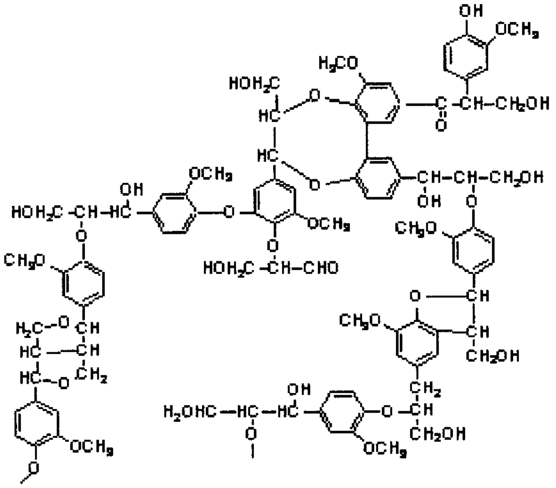
Compound class	***Molecular Weight Range (g/mol)***	***Compound structure***
		
Lignin	> 10,000	Phenol-based [255] 

Table 32: ASM state variables values for pulp & paper primary treated wastewaters (influent) [196, 200]

Fraction	***ASM influent state variable value***					
Pulp & Paper Process	*TMP/RCF (1993, 1994)*	*CTMP*	*BKM, BKM/TMP*	*BKM*	*CTMP*	*Municipal (ASM3 default)*
S_S	0.15, 0.29	0.49	0.24, 0.44	0.42	0.28	0.43
S_I	0.093, 0.082	0.14	0.36, 0.32	0.33	0.33	0.13
X_S	0.64, 0.54	0.30	0.42, 0.23	0.11	0.34	0.33
X_I	0.12, 0.088	0.07	0.07, 0.03	0.14	0.05	0.11
Reference	[196]	[200]	[199]	PAPRO work *cited in* [200]	[197]	[200]

Table 33: ASM-PP reasoning & references

Process	***Pulp and Paper***	***ASM1***	***ASM3***	***ASM-PP***
Growth rate limitations	Nutrient limited [63, 72]	Neither ammonia nor phosphate considered [204]	Ammonia considered as limiting, phosphate not considered [204]	Both ammonia and phosphate considered as possibly limiting, under different operating conditions
Biomass decay	Release of lysed nutrients strongly related to decay	Death regeneration [204]	Endogenous respiration [204]	Death-regeneration
Storage of readily biodegradable substrate	Dependent on reactor type (CSTR, PFR)	Not considered [204]	Considered [204] Pertinent to concentration gradient [88, 89, 233-235]	Not considered for CSTR
Hydrolysis of slowly biodegradable substrate	Hydrolysis limiting step in organic carbon consumption [27, 55]	Considered, important [204]	Less significant than for ASM1, storage is more important [204]	Limiting step
Ammonification of soluble organic nitrogen	Organic nitrogen content of wood varies with season [256]	Organic nitrogen concentration dependent [204]	Influent contains fixed fraction of organic nitrogen [204]	Organic nitrogen concentration dependent
Hydrolysis of entrapped organic nitrogen	Organic nitrogen content of wood varies with season [256]	Organic nitrogen concentration dependent [204]	Not considered [204]	Organic nitrogen concentration dependent

Process	***Pulp and Paper***	***ASM1***	***ASM3***	***ASM-PP***
Phosphatification	Process by which soluble organic P is converted into ortho-phosphate for growth	Not considered [204]	Not considered [204]	Considered
Heterotrophic anoxic growth	Dependent on reactor aeration, dead space	Considered [204]	Considered [204]	Not considered due to fully aerated basin

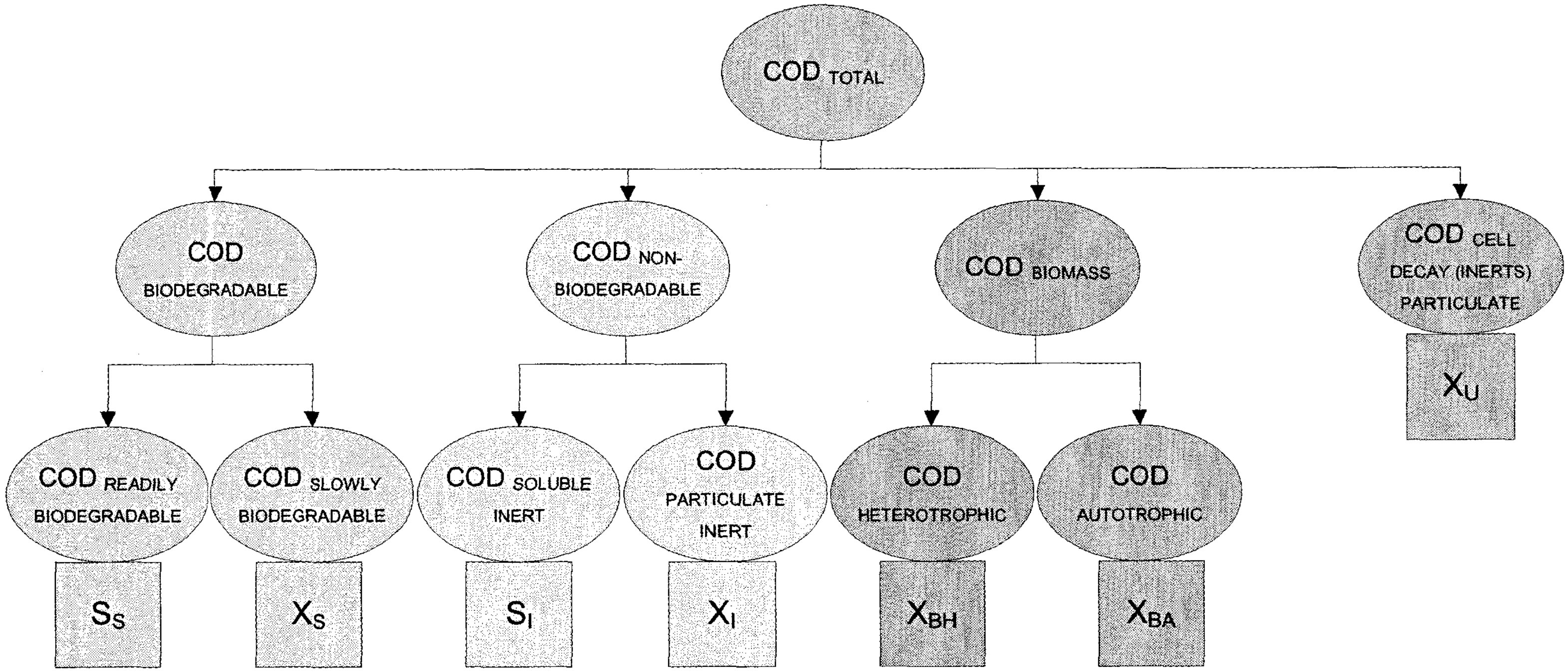


Figure 29: COD Fractionation, simple & modified [138, 219]

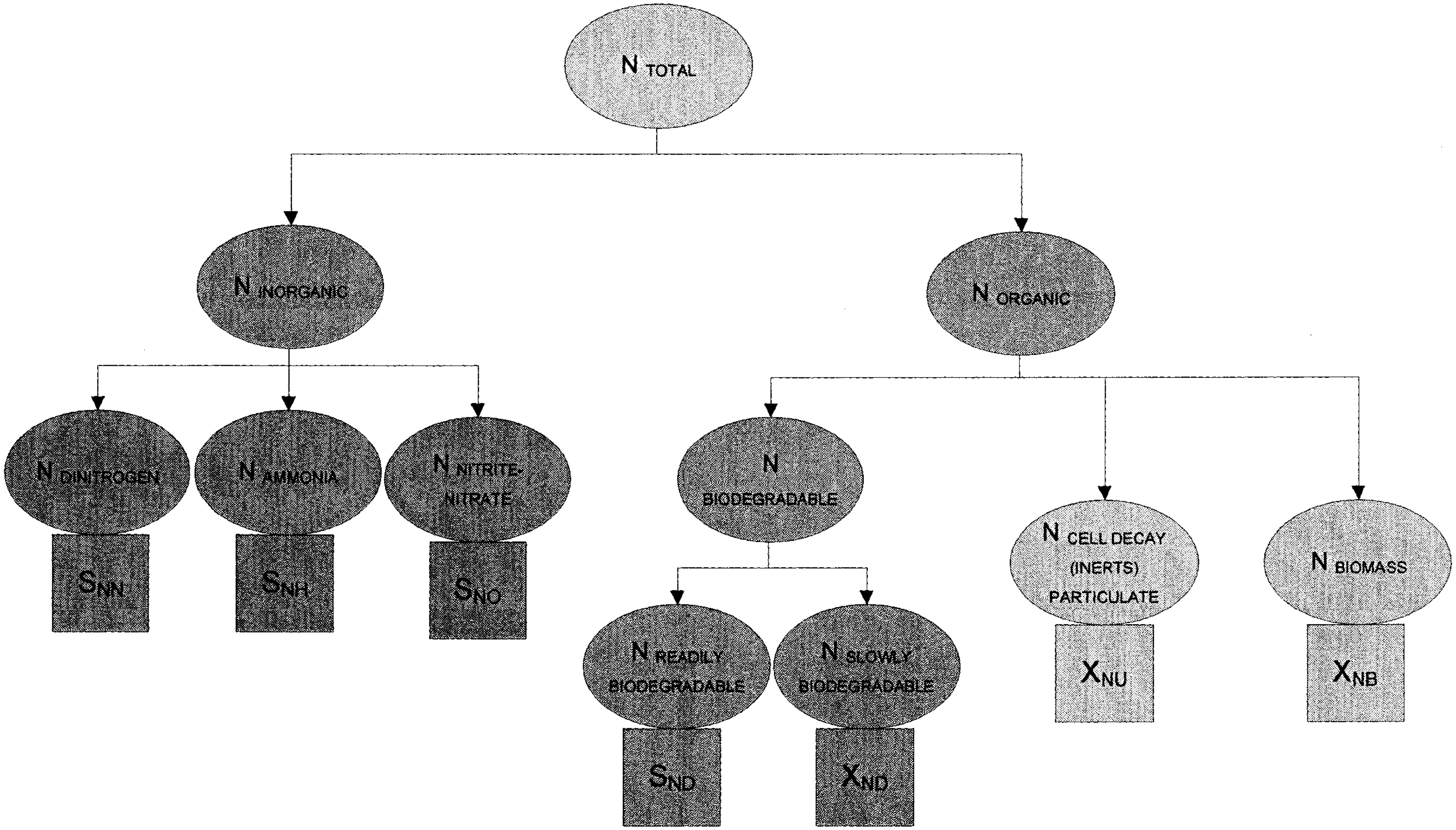


Figure 30: Nitrogen Fractionation, detailed & modified [138, 203]

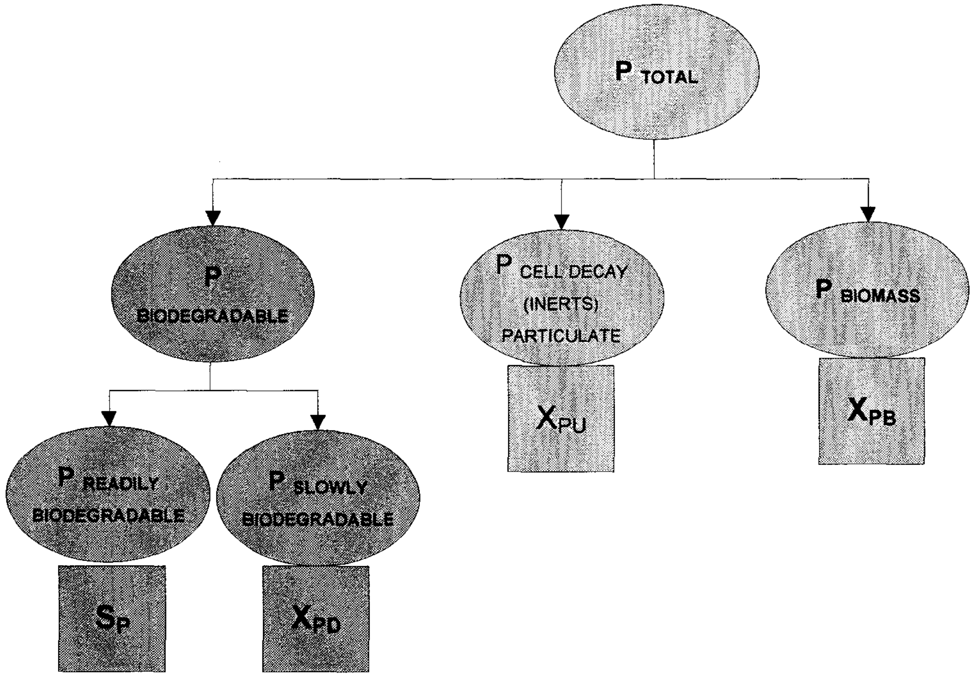


Figure 31: Phosphorus Fractionation, detailed & modified [138]

Table 34: ASM-PP Petersen matrix (modifications from ASM1 shown in red) [58]

	Component (i) → ↓ Process (j)	1 S_I	2 S_S	3 X_I	4 X_S	5 X_{BH}	6 X_{BA}	7 X_U	8 S_O	9 S_{NH}
1	Aerobic heterotrophic growth		$-\frac{1}{Y_H}$			1			$-\left(\frac{1-Y_H}{Y_H}\right)$	$-i_{XBN}$
2	Anoxic heterotrophic growth		$-\frac{1}{Y_H}$			1				$-i_{XBN}$
3	Aerobic autotrophic growth						1		$-\left(\frac{4.57-Y_A}{Y_A}\right)$	$-i_{XBN}-\frac{1}{Y_A}$
4	Heterotrophic degradation				$1-f_U$	-1		f_U		
5	Autotrophic degradation				$1-f_U$		-1	f_U		
6	Ammonification									1
7	Hydrolysis of X_S		1		-1					
8	Hydrolysis of X_{ND}									
9	Phosphatification									
10	Hydrolysis of X_{PD}									

	Component (i) → ↓ Process (j)	10 S_{NO}	11 S_{ND}	12 X_{ND}	13 S_P	14 X_{PD}	15 S_{PD}	16 X_{II}	17 S_{NN}	18 S_{ALK}
1	Aerobic heterotrophic growth				$-i_{XBP}$					$-i_{XBN}/14$
2	Anoxic heterotrophic growth	$-\left(\frac{1-Y_H}{2.86*Y_H}\right)$			$-i_{XBP}$				$\left(\frac{1-Y_H}{2.86*Y_H}\right)$	$\left(\frac{1-Y_H}{14*2.86*Y_H}\right)-i_{XBN}/14$
3	Aerobic autotrophic growth	$-\frac{1}{Y_A}$			$-i_{XBP}$					$-\frac{i_{XBN}}{14}-\frac{1}{7*Y_A}$
4	Heterotrophic degradation			$i_{XBN}-f_U*i_{XUN}$		$i_{XBP}-f_U*i_{XUP}$				
5	Autotrophic degradation			$i_{XBN}-f_U*i_{XUN}$		$i_{XBP}-f_U*i_{XUP}$				
6	Ammonification		-1							1/14
7	Hydrolysis of X_S									
8	Hydrolysis of X_{ND}		1	-1						
9	Phosphatification				1		-1			
10	Hydrolysis of X_{PD}					-1	1			

	Component (i) → ↓ Process (j)	Reaction rate (ρj)
1	Aerobic heterotrophic growth	$\mu_H\left(\frac{S_S}{K_{SH}+S_S}\right)\left(\frac{S_O}{K_{OH}+S_O}\right)\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_P}{K_P+S_P}\right)X_{BH}$
2	Anoxic heterotrophic growth	$\mu_H\left(\frac{S_S}{K_{SH}+S_S}\right)\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_P}{K_P+S_P}\right)\eta_g X_{BH}$
3	Aerobic autotrophic growth	$\mu_A\left(\frac{S_O}{K_{OA}+S_O}\right)\left(\frac{S_{NH}}{K_{NA}+S_{NH}}\right)\left(\frac{S_P}{K_P+S_P}\right)X_{BA}$
4	Heterotrophic degradation	$b_H X_{BH}$
5	Autotrophic degradation	$b_A X_{BA}$
6	Ammonification	$k_a S_{ND} X_{BH}$
7	Hydrolysis of X_S	$k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)\left[\left(\frac{S_O}{K_{OH}+S_O}\right)+\eta_h\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{BH}$
8	Hydrolysis of X_{ND}	$k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)\left[\left(\frac{S_O}{K_{OH}+S_O}\right)+\eta_h\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{BH}\left(\frac{X_{ND}}{X_S}\right)$
9	Phosphatification	$k_p S_{PD} X_{BH}$
10	Hydrolysis of X_{PD}	$k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)\left[\left(\frac{S_O}{K_{OH}+S_O}\right)+\eta_h\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{BH}\left(\frac{X_{PD}}{X_S}\right)$

5.8.3. ASM development

5.8.3.1. Temperature

The commercially available ASM1 model software includes the ability to model kinetic parameters based on the Arrhenius temperature-dependency model. An alternative temperature dependency was suggested and used by Sreckovic [197], based on experimentally determined behaviour of biomass in response to deviation from their acclimatised optimal temperature. It is considered that this complexity is not required for the ASM-PP model; it could be considered for future work.

5.8.3.2. Nutrient transformations

The ASM1 model is based on the use of ammonia nitrogen as the nitrogen source for all bacterial growth. The Mantis model incorporates processes for the use of both ammonia and nitrate-nitrogen as the nitrogen source for bacterial growth. It is considered that this complexity is not required for the ASM-PP model; it could be considered for future work.

All ASM models present nitrification as a one-step process and do not include a state variable for nitrite. Modelling nitrification as a two-step process could be considered for future work.

5.8.3.3. Death-regeneration model

A methodology was developed by Dold to calculate the sludge production of an activated sludge treatment plant, based on the sludge age of the system [257]. This methodology can be applied to calculate the theoretical oxygen and nutrient requirements for cell synthesis, as a function of sludge age of the system. The application of the methodology to pulp and paper activated sludge treatment systems requires a modification separating the fraction of nitrogen (and phosphorus) in each of the particulate fractions [258].

The Dold methodology was demonstrated in detail for the endogenous respiration model (ASM3) and the death-regeneration model (ASM1) [257]; the latter would be appropriate for use with this study since the ASM--PP model is based on the ASM1 model. This methodology relies upon the definition of a COD fraction X_E, which represents the endogenous residue produced by the decay of biomass (formerly included in the X_I fraction) [257]. The benefit of using this X_E fraction is that decayed biomass will theoretically contain the same fraction of nutrients (nitrogen and phosphorus) that the active biomass contained, whereas the X_I fraction may have a significantly different fraction of nutrients – particularly for an industrial wastewater such as pulp and paper wastewater.

The death-regeneration model assumes that active heterotrophic biomass die at a rate proportional to the concentration of the biomass, and that the products of this decay process are an endogenous residue (in the XI fraction) and some 'lysed' biodegradable substrate (in the X_S fraction) [257].

5.8.4. Petersen Matrix Interpretation

The Petersen matrix, such as that depicted in Table 34, represents both the process rate equation, p_j, and the rate of transformation or mass balance for each individual fraction (state variable) in the system [204].

Taking the first process in the ASM-PP model, aerobic heterotrophic growth, as an example, the process rate equation p_1, is presented in the right hand column of Table 34:

$$p_1 = \mu_H \left(\frac{S_S}{K_S + S_S} \right) \left(\frac{S_O}{K_O + S_O} \right) \left(\frac{S_{NH}}{K_{NH} + S_{NH}} \right) \left(\frac{S_P}{K_P + S_P} \right) X_{BH}$$

The 'system reaction term', r_i, relates the process rate equations to each of the state variables according to the relation [204]:

$$r_i = \sum_j v_{ij} p_j$$

Where v_{ij} represents the stoichiometric coefficients and p_j represents the process rates [204].

Taking the soluble substrate, S_S as an example, the rate of reaction for this state variable is [204]:

$$\begin{aligned} r_{S_S} &= 1 \cdot p_6 - \frac{1}{Y_H} \cdot p_1 \\ &= k_h \left(\frac{X_S / X_{BH}}{K_X + X_S / X_{BH}} \right) \left(\frac{S_O}{K_{OH} + S_O} \right) X_{BH} \\ &\quad - \frac{1}{Y_H} \mu_H \left(\frac{S_S}{K_S + S_S} \right) \left(\frac{S_O}{K_O + S_O} \right) \left(\frac{S_{NH}}{K_{NH} + S_{NH}} \right) \left(\frac{S_P}{K_P + S_P} \right) X_{BH} \end{aligned}$$

This last equation is a mass balance for the component S_S; a similar mass balance is constructed for each state variable in the system from the Petersen matrix in the process simulation environment.

APPENDIX 2
Wastewater Characterisation

2.1. *Wastewater Characterisation*

The wastewater characterisation was conducted according to the methodology outlined in the thesis: the following results were found.

2.1.1. Raw Data

Table 35: Wastewater Characterisation COD & Solids Raw Data (mg COD/L, mg TSS/L, mg VSS/L)

Date	Location	TSS	VSS	sCOD	fCOD	COD total	Date	Location	TSS	VSS	sCOD	fCOD	COD total
08-Feb	Primary Effluent	157	170		1820	2410	13-Feb	Primary effluent	198	214		2174	2606
08-Feb	AST Effluent	2125	2009		150	3768	13-Feb	AST Effluent	2196	2084		142	3988
08-Feb	RAS	4421	4173		158	>6600	13-Feb	RAS	4820	4565		66	8816
08-Feb	Final Effluent	16	29		144	176	13-Feb	Final Effluent	24	26		42	88
20-Feb	Primary Influent	470	483		278	1132	27-Feb	Primary Influent	946	936		2258	>6600
20-Feb	Primary Effluent	86	113		1740	2068	27-Feb	Primary effluent	170	179		1998	2524
20-Feb	AST Effluent	2147	2034		104	3676	27-Feb	AST Effluent	1974	1836		120	3352
20-Feb	RAS	4075	3831		112	7264	27-Feb	RAS	4536	4226		130	7728
20-Feb	Final Effluent	3	8		104	116	27-Feb	Final Effluent	17	18		122	146
06-Mar	Primary Influent	1065	1068		2160	4456	13-Mar	Primary Influent	212	216		1662	2224
06-Mar	Primary Effluent	180	187		1894	2430	13-Mar	Primary effluent	148	161		1928	2466
06-Mar	AST Effluent	2125	1988		244	3448	13-Mar	AST Effluent	2172	2012		78	3856
06-Mar	RAS	4526	4283		196	7704	13-Mar	RAS	4616	4360		88	9184
06-Mar	WAS	15904	14918		240	>13200	13-Mar	WAS	15094	14276		230	33000
06-Mar	Final Effluent	10	12		94	102	13-Mar	Final Effluent	10	12		90	124
20-Mar	Primary Influent	868	876		2096	3672	27-Mar	Primary Influent	968	976		2010	4004
20-Mar	Primary Effluent	133	145		1834	2190	27-Mar	Primary effluent	192	190		1520	1938
20-Mar	AST Effluent	1806	1722		98	2992	27-Mar	AST Effluent	2179	2056		109	3712
20-Mar	RAS	3858	3660		100	6560	27-Mar	RAS	4816	4520		151	9344
20-Mar	WAS	16351	15468		286	51956	27-Mar	WAS	11980	11292		346	37944
20-Mar	Final Effluent	15	17		118	82	27-Mar	Final Effluent	21	22		94	98
03-Apr	Primary Influent	858	864	1140		3840	17-Apr	Primary Influent	847	842	1134	1538	3396
03-Apr	Primary Effluent	213	213	968		2098	17-Apr	Primary effluent	217	215	960	1574	2108
03-Apr	AST Effluent	2271	2155	75		3760	17-Apr	AST Effluent	2081	1991	66	81	3360
03-Apr	RAS	5073	4798	83		9992	17-Apr	RAS	4306	4092	79	86	7928

Date	Location	TSS	VSS	sCOD	fCOD	COD total	Date	Location	TSS	VSS	sCOD	fCOD	COD total
03-Apr	WAS	9717	9100	153		31806	17-Apr	WAS	13580	12771	136	180	41044
03-Apr	Final Effluent	40	39	78		135	17-Apr	Final Effluent	10	11	66	70	79
24-Apr	Primary Influent	897	845	1254	1638	3472	01-May	Primary Influent	892	855	1376	1730	3748
24-Apr	Primary Effluent	212	210	924	1308	1862	01-May	Primary effluent	263	254	1240	1628	2180
24-Apr	AST Effluent	2002	1890	70	80	3584	01-May	AST Effluent	1961	1811	84	103	3060
24-Apr	RAS	3612	3410	76	85	10464	01-May	RAS	4076	3790	92	117	7000
24-Apr	WAS	13048	12258	161	207	41478	01-May	WAS	14349	13430	268	325	41292
24-Apr	Final Effluent	11	11	82	90	104	01-May	Final Effluent	22	20	87	102	127
08-May	Primary Influent	5703	5637	656	842	21452							
08-May	Primary Effluent	288	286	1296	1800	2386							
08-May	AST Effluent	2758	2616	90	90	3584							
08-May	RAS	5404	5100	99	113	9496							
08-May	Final Effluent	10	10	80	80	96							
15-May	Mill Drain	372	367	1060	1470	2340	22-May	Primary Influent	985	981	1240	1744	3712
15-May	Primary Influent	942	930	1638	1640	3444	22-May	Primary effluent	232	231	1228	1818	2072
15-May	Primary Effluent	181	179	1258	1810	2156	22-May	AST Effluent	2004	1854	98	114	3096
15-May	AST Effluent	2207	2077	105	119	3608	22-May	RAS	3945	3736	110	122	7112
15-May	RAS	4645	4386	78	87	8528	22-May	WAS	15230	14428	175	293	46686
15-May	WAS	12081	11434	183	238	37696	22-May	Final Effluent	6	8	94	109	111
15-May	Final Effluent	13	11	76	82	102							

Table 36: Wastewater Characterisation Nutrients Raw Data (mg P/L, mg N/L)

Stream	***Primary Influent***			***Primary Effluent***			***AST Effluent***			***Final Effluent***			***RAS***			***WAS***		
23-Jan-07																		
o-PO4							1.29	1.29		0.970	0.972							
TP							20.9	21		1.120	1.160							
TKN-N							124	121		1.100	0.930							
NH4-N							0.164	0.154		0.090	0.090							
NO3-N							0.076	0.075		0.022	0.018							
07-Feb-07																		
o-PO4				0.202	0.274		2.18	2.17		2.160	2.150		2.3	2.3				

Stream	Primary Influent			Primary Effluent			AST Effluent			Final Effluent			RAS			WAS		
TP				0.971	0.955		25.8	25.7		2.780	2.920		57.2	56.1				
TKN-N				3.36	3.32		144.0	144.0		4.080	4.080		336.0	327.0				
NH4-N				0.05	0.05		0.880	0.870		1.030	1.040		0.850	0.830				
NO3-N				0.046	0.031		0.111	0.113		0.046	0.045		0.009	0.006				
20-Feb-07																		
o-PO4	0.035	0.035		0.279	0.28		2.01	2.03		1.690	1.690		2.1	2.1				
TP	0.274	0.342		1.18	1.23		31.5	31.1		2.070	2.670		56.6	56.9				
TKN-N	1.92	1.84		5.12	4.83		170.0	166.0		6.050	7.810		289.0	286.0				
NH4-N	<,01	<,01		0.06	0.06		4.640	4.670		3.620	3.600		3.5	3.6				
NO3-N	<,005	<,005		0.117	0.119		0.031	0.036		0.015	0.018		<,005	<,005				
06-Mar-07																		
o-PO4	0.4440	0.4340		0.352	0.349		0.644	0.643		0.777	0.778		1.71	1.71		5.75	5.86	
TP	1.0200	1.4400		1.28	1.23		24.9	25.0		0.218	0.222		55.5	56.5		194	194	
TKN-N	7.0700	5.9800		5.35	4.71		153.0	152.0		3.560	2.950		319.0	319.0		1100	1100	
NH4-N	0.0500	0.0570		0.074	0.072		0.034	0.035		0.109	0.112		0.6	0.6		3	3	
NO3-N	0.1480	0.1480		0.059	0.059		0.849	0.851		1.480	1.480		<,005	<,005		<,005	<,005	
20-Mar-07																		
o-PO4	0.344	0.268	0.332	0.402	0.375		1.51	1.48	1.48	1.750	1.750	1.79	1.75	1.76	1.74	5.44	5.49	5.39
TP	0.640	1.130		0.91	1		20.0	19.6		1.780	1.860		41.60	41.60		161	166	
TKN-N	8.100	5.300		7.58	8.02		143.0	143.0		4.250	4.570		317	311		1180	1235.00	
NH4-N	<,05	<,05	<,05	<,05	<,05		0.115	0.111	0.114	0.147	0.171	0.175	0.58	0.57	0.56	1.81	1.66	1.94
NO3-N	<,005	<,005	0.006	<,005	<,005		4.68	4.60	4.59	4.790	4.720	5	0.11	0.12	0.13	<,005	0.01	0.01
03-Apr-07																		
o-PO4	0.292	0.29	0.3	0.035	0.033	0.034	0.339	0.339	0.341	0.542	0.535	0.536	1.58	1.59	1.58	3.44	3.44	3.45

Stream	**Primary Influent**			**Primary Effluent**			**AST Effluent**			**Final Effluent**			**RAS**			**WAS**		
TP	0.48	0.676		0.992	n.a.		24.3	25.8		0.849	0.911		51.5	53.2		95.60	95.70	
TKN-N	11.7	12.1		10.7	10.4		196	208		5.730	6.160		376	386		679	692	
NH4-N	<,05	<,05	<,05	<,05	<,05	<,05	<,05	<,05	<,05	<,05	<,05	<,05	0.58	0.58	0.58	0.52	0.52	0.52
NO3-N	<,05	<,05	<,05	<,05	<,05	<,05	0.08	0.08	0.09	1.010	1.010	1.01	<,05	<,05	<,05	0.06	0.06	0.07
17-Apr-07																		
o-PO4	0.302	0.296	0.299	0.126	0.127	0.127	0.041	0.04	0.041	0.047	0.042	0.042	0.38	0.38	0.38	2.83	2.84	2.84
TP	0.861	0.942		0.986	1.18		20	20		0.310	0.379		44.1	42.1		139	136	
TKN-N	3.77	3.98		4.2	4.39		157	162		2.910	2.730		353.00	349.00		1033	998	
NH4-N	<,05	<,05	<,05	<,05	<,05	<,05	0.065	0.066	0.065	0.119	0.117	0.117	0.60	0.59	0.60	2.47	2.47	2.46
NO3-N	0.155	0.156	0.16	0.08	0.08	0.08	0.263	0.266	0.262	2.050	2.050	2.06	<,05	<,05	<,05	0.06	0.06	0.07
15-May-07																		
o-PO4	0.491	0.481	0.474	0.363	0.363	0.361	0.043	0.045	0.043	0.031	0.028	0.027	0.229	0.229	0.230	2.020	2.020	2.020
TP	0.881	1		0.955	0.858		18.6	19.4		0.221	0.304		46.7	46.8		125	125	
TKN-N	4.28	4.27		3.68	3.31		148	154		3.980	3.810		319	321		791	792	
NH4-N	<,05	<,05	<,05	<,05	<,05	<,05	0.661	0.66	0.654	1.130	1.130	1.02	1.140	1.140	1.140	3.400	3.350	3.450
NO3-N	0.086	0.095	0.091	<,005	<,005	<,005	<,005	<,005	<,005	0.008	0.007	0.008	<,005	<,005	<,005	0.029	0.031	0.033

Stream	**Press Filtrate**		
30-May-07			
o-PO4	4.69	4.7	4.69
TP	9.16	9.01	
TKN-N	44.10	41.50	
NH4-N	3.76	3.93	3.93
NO3-N	0.055	0.059	0.057

2.1.2. COD & BOD fractionation

2.1.2.1. Raw BOD respirometry

The BOD respirometry test were conducted during a 28 day period for samples taken on 31 October, 2007: the Primary influent, the Primary effluent and Final effluent were composite samples collected over a 24 hour period (midnight to midnight). It should be noted that the Primary effluent sample may contain landfill leachate and/or chip pile run-off.

Table 37 below summarises the BOD on each day in the 28 day test period for the two sampling points upstream and downstream of the primary clarifier, which are also represented in Figure 32 and Figure 33. Ten day test period measurements carried out on samples taken during the period of February to May 2007 did not produce adequate results as they did not sufficiently approach the ultimate BOD concentration.

Table 37: BOD respirometry results 31 October 2007 (mg BOD/L)

Stream	*Primary Influent*			*Primary effluent*		
	1	*2*	*3*	*1*	*2*	*3*
BOD$_1$	17	197	87	227	327	167
BOD$_2$	184	344	194	174	194	194
BOD$_3$	172	392	202	382	302	302
BOD$_4$	262	402	192	352	332	272
BOD$_5$	302	522	452	492	392	452
BOD$_6$	272	552	382	442	422	482
BOD$_7$	444	744	514	594	474	534
BOD$_8$	471	738	513	580	624	545
BOD$_9$	511	778	453	640	604	645
BOD$_{10}$	570	877	552	799	723	783
BOD$_{11}$	630	897	432	759	783	763
BOD$_{12}$	605	973	587	894	798	719
BOD$_{13}$	645	933	567	874	758	699
BOD$_{14}$	583	950	745	952	816	837
BOD$_{15}$	392	879	474	501	465	406
BOD$_{16}$	568	915	589	657	460	821
BOD$_{17}$	522	1049	724	691	595	856
BOD$_{18}$	524	1052	786	593	717	918

Stream	Primary Influent			Primary effluent		
	1	2	3	1	2	3
BOD$_{19}$	619	993	769	794	864	999
BOD$_{20}$	665	1198	774	899	829	1085
BOD$_{21}$	601	1095	871	976	846	1121
BOD$_{22}$	728	1141	818	842	952	1048
BOD$_{23}$	686	1220	816	921	991	1166
BOD$_{24}$	682	1235	771	1096	986	1082
BOD$_{25}$	696	1289	745	1150	1000	976
BOD$_{26}$	673	1187	863	1008	998	993
BOD$_{27}$	741	1375	771	1136	986	1141
BOD$_{28}$	780	1334	850	1175	1105	1280

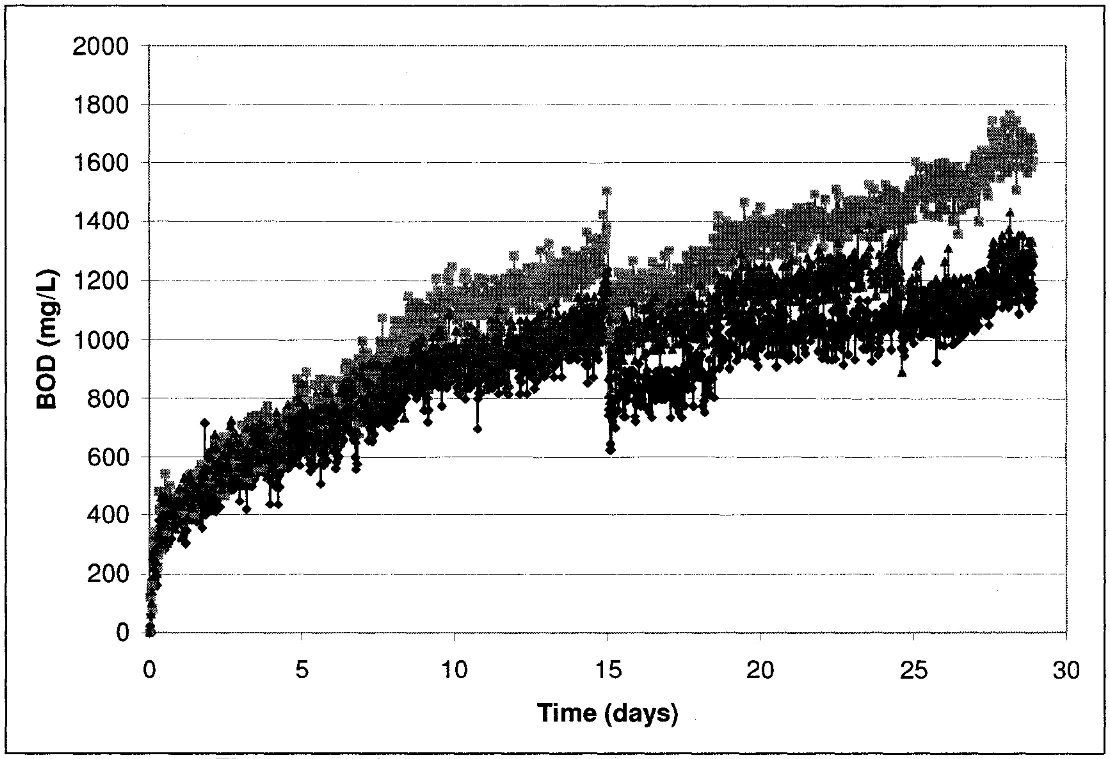


Figure 32: Primary Influent BOD1-28 31 October 2007

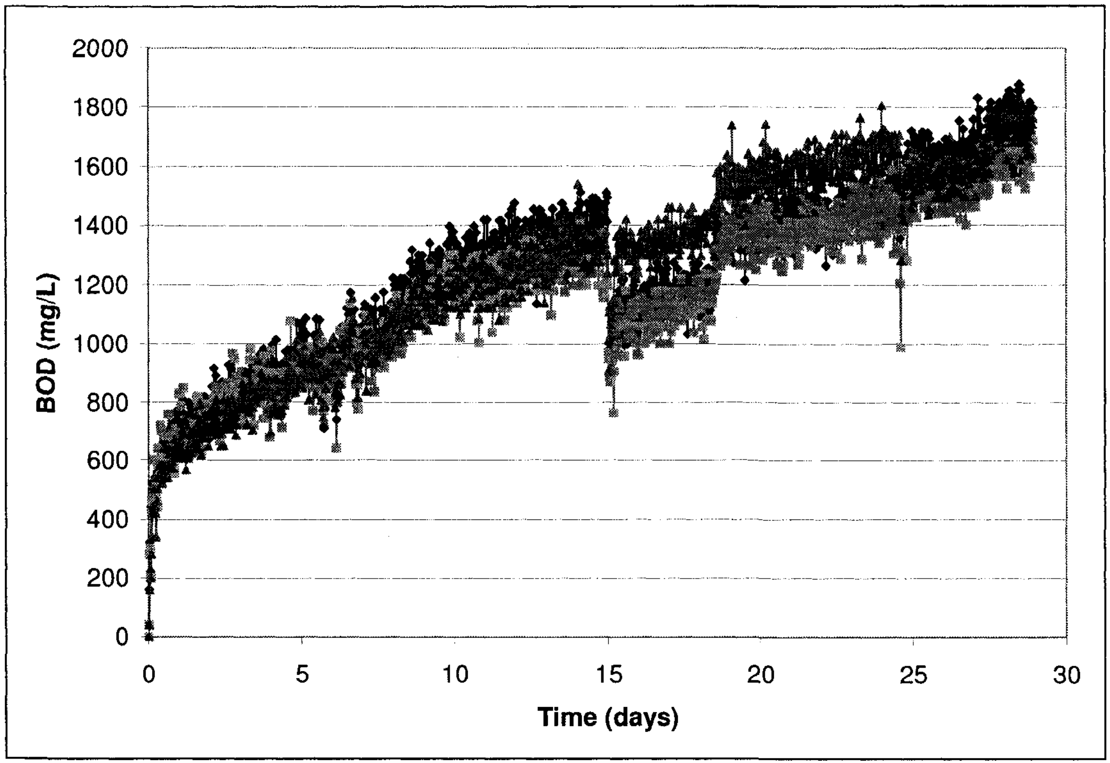


Figure 33: Primary effluent BOD1-28 31 October 2007

For each of the complete BOD datasets, which had time steps of 29 minutes, an exponential curve was fitted to the following relation and the parameters BOD_{total} and k_{BOD} were optimised with respect to the Pearson's R^2 of the coefficient of the exponential curve *y= **m**.exp(**c**x)*, where 'm' was forced to be equal to 1. In all cases, the curve was transposed vertically in order to fit the data, which corresponds to a curve of the form *y= **m**.exp(**c**x) + **a***

$$1-\frac{BOD_{OBS}}{BOD_{total}} = -e^{-k_{BOD}t}$$

Subsequently, the biodegradable COD fraction (BCOD) was calculated according to the correction factor ϕ_{BOD} to account for inert COD generated in biomass lysis. The Table 38 below presents the fitted parameters resulting from this exercise as well as the Pearson's R^2 value for the fitted trendline and the coefficient of the exponential curve 'm'.

Table 38: BOD respirometry fitted parameters ($\phi_{BOD} = 0.15$)

Stream	BOD_{total}	k_{BOD}	R^2	*'m'*	ϕ_{BOD}	***BCOD***
Units	mg BOD/L	d^{-1}	-	-	mg COD/ mg BOD	mg COD/L
Primary Influent						
PI1	1320	0.060	0.795	1	0.15	1553
PI2	1750	0.070	0.924	1	0.15	2059
PI3	1520	0.054	0.830	1	0.15	1788
Primary effluent						
PE1	1910	0.058	0.800	1	0.15	2247
PE2	1780	0.061	0.874	1	0.15	2094
PE3	2050	0.053	0.921	1	0.15	2412

Results were calculated for a range of ϕ_{BOD} values, which influences only the BCOD value (of those presented in Table 38) and the ASM wastewater characterisation fractions.

2.1.2.2. Corrected BOD respirometry

The raw BOD respirometry data was corrected to take into account the shock to the system on day 15 to 18, plus other disturbances to the experiment. Table 39 below summarises the corrected BOD on each day in the 28 day test period for the two sampling points upstream and downstream of the primary clarifier, which are also represented in Figure 34 and Figure 35.

Table 39: Corrected BOD respirometry results 31 October 2007 (mg BOD/L)

Stream	***Primary Influent***			***Primary effluent***		
	1	***2***	***3***	***1***	***2***	***3***
BOD_1	17	197	87	227	327	167
BOD_2	184	344	194	174	194	194
BOD_3	172	392	202	382	302	302
BOD_4	262	402	192	352	332	272
BOD_5	302	522	452	492	392	452
BOD_6	272	552	382	442	422	482
BOD_7	444	744	514	594	474	534
BOD_8	471	738	513	580	624	545
BOD_9	511	778	453	640	604	645

Stream	Primary Influent			Primary effluent		
	1	2	3	1	2	3
BOD_{10}	570	877	552	799	723	783
BOD_{11}	630	897	432	759	783	763
BOD_{12}	605	973	587	894	798	719
BOD_{13}	645	933	567	874	758	699
BOD_{14}	583	950	745	952	816	837
BOD_{15}	647	1,049	554	859	718	506
BOD_{16}	823	1,085	669	1,015	713	921
BOD_{17}	777	1,219	804	1,049	848	956
BOD_{18}	779	1,222	866	951	970	1,018
BOD_{19}	802	1,103	769	1,031	952	959
BOD_{20}	848	1,308	774	1,136	917	1,045
BOD_{21}	784	1,205	871	1,213	934	1,081
BOD_{22}	911	1,251	818	1,079	1,040	1,008
BOD_{23}	869	1,330	816	1,158	1,079	1,126
BOD_{24}	865	1,345	771	1,333	1,074	1,042
BOD_{25}	879	1,344	903	1,271	1,051	1,077
BOD_{26}	856	1,242	1,021	1,129	1,049	1,094
BOD_{27}	924	1,430	929	1,257	1,037	1,242
BOD_{28}	889	1,265	902	1,215	1,072	1,259

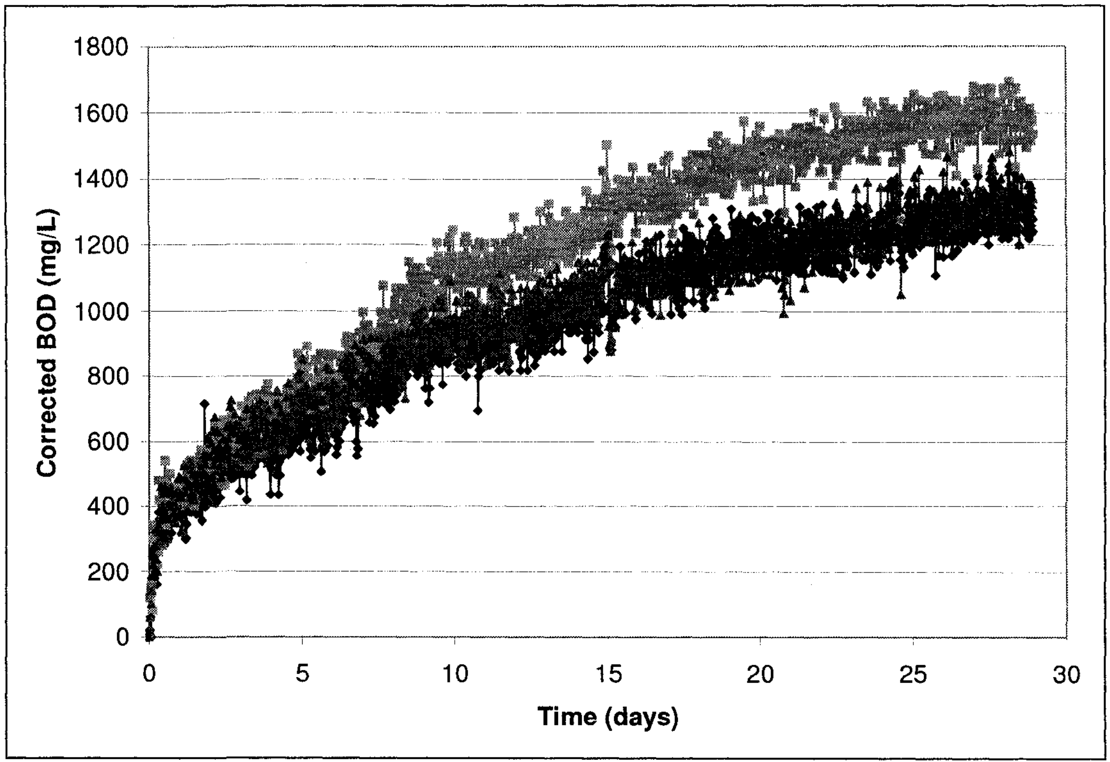


Figure 34: Corrected Primary Influent BOD1-28 31 October 2007

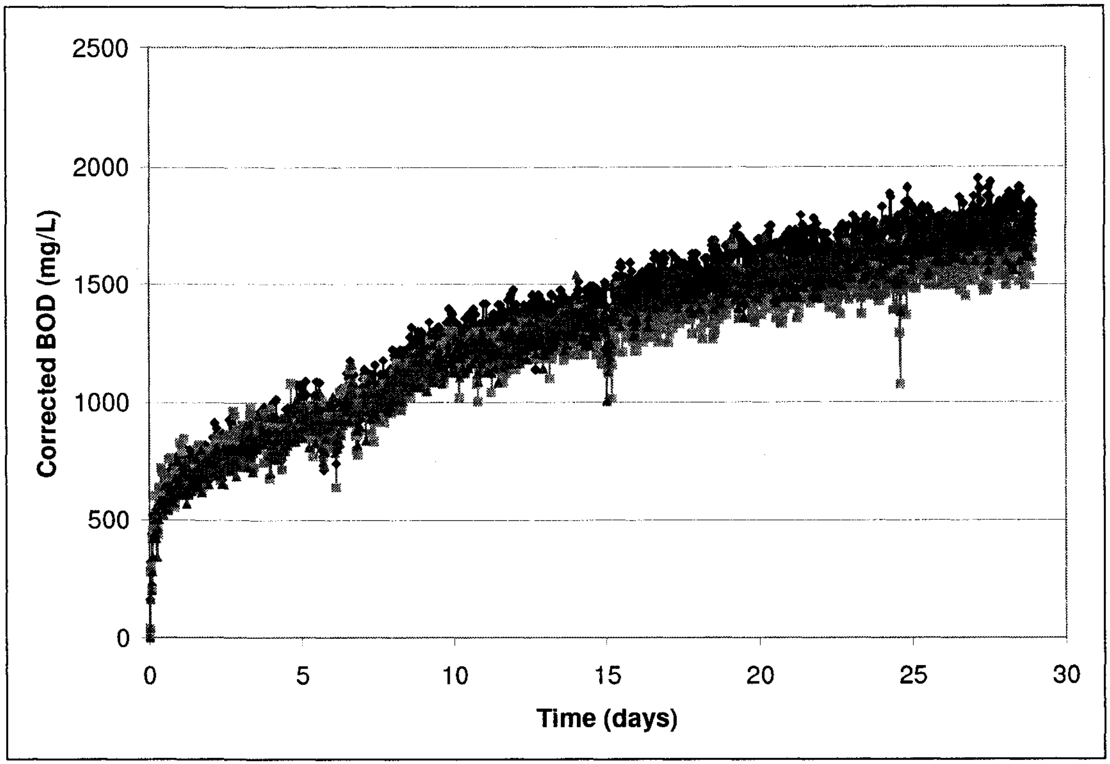


Figure 35: Corrected Primary effluent BOD1-28 31 October 2007

Table 40 below presents the fitted parameters resulting from the data fitting exercise as well as the Pearson's R^2 value for the fitted trendline and the coefficient of the exponential curve 'm'.

Table 40: Corrected BOD respirometry fitted parameters ($\phi_{BOD} = 0.15$)

Stream	***BOD$_{total}$***	***k_{BOD}***	***R^2***	***'m'***	***ϕ_{BOD}***	***BCOD***
Units	mg BOD/L	d^{-1}	-	-	mg COD/ mg BOD	mg COD/L
Primary Influent						
PI1	1,690	0.047	0.929	1.0	0.15	1,988
PI2	1,850	0.070	0.955	1.0	0.15	2,176
PI3	1,650	0.050	0.925	1.0	0.15	1,941
Primary effluent						
PE1	2,175	0.056	0.942	1.0	0.15	2,559
PE2	1,900	0.057	0.909	1.0	0.15	2,235
PE3	2,100	0.051	0.950	1.0	0.15	2,471

The corrected BOD respirometry results are those used for the ASM influent characterisation.

2.1.2.3. COD measurements

It should be noted that the aforementioned methodology calls for use of the soluble COD fraction measured in the influent and effluent as measured in the filtrate from a 0.1µm filter. It was not possible to measure the soluble COD fraction prior to 3 April 2007 due to the laboratory equipment available. Therefore a number of COD fractionations were conducted after this date, the results of which are presented in Table 41 below. The terms 'sCOD' refers to soluble COD (filtrate 0.1µm), 'fCOD' refers to filtered COD (filtrate 1.0µm), 'CODt' refers to total COD (non-filtered), 'CODcol' refers to the colloidal COD which is the difference between the measured soluble COD and filtered COD, and 'pCOD' refers to the particulate COD which is the difference between the measured filtered COD and the total COD.

COD experiments prior to 17 April 2007 occasionally resulted in a small quantity of residue in the base of the test tubes. This indicated an incomplete oxidation, and the subsequent samples (those results presented) were further diluted in order to obtain full oxidation within the 2-hour test.

Table 41: Soluble, filtered and total COD fractionation (mg COD/L, fractions)

Stream	***Measured***			***Fractions***			
	sCOD	***fCOD***	***CODt***	***sCOD***	***CODcol***	***pCOD***	***CODt***
17-Apr-07							
Prim In	1134	1538	3396	0.33	0.12	0.55	1.0
AST In	960	1574	2108	0.46	0.29	0.25	1.0
AST Out	66	81	3360	0.020	0.0045	0.98	1.0
Final Eff	66	70	79	0.84	0.051	0.11	1.0
RAS	79	86	7928	0.010	0.00088	0.99	1.0
WAS	136	180	41044	0.0033	0.0011	1.00	1.0
24-Apr-07							
Prim In	1254	1638	3472	0.36	0.11	0.53	1.0
AST In	924	1308	1862	0.50	0.21	0.30	1.0
AST Out	70	80	3584	0.020	0.0028	0.98	1.0
Final Eff	82	90	104	0.79	0.077	0.13	1.0
RAS	76	85	10464	0.0073	0.00086	0.99	1.0
WAS	161	207	41478	0.0039	0.0011	1.00	1.0
01-May-07							
Prim In	1376	1730	3748	0.37	0.094	0.54	1.0

Stream	Measured			Fractions			
	sCOD	fCOD	CODt	sCOD	CODcol	pCOD	CODt
AST In	1240	1628	2180	0.57	0.18	0.25	1.0
AST Out	84	103	3060	0.027	0.0062	0.97	1.0
Final Eff	87	102	127	0.69	0.118	0.20	1.0
RAS	92	117	7000	0.013	0.0036	0.98	1.0
WAS	268	325	41292	0.0065	0.0014	0.99	1.0
15-May-07							
Mill Drain	1060	1470	2340	0.45	0.175	0.37	1.0
Prim In	1638	1640	3444	0.48	0.001	0.52	1.0
AST In	1258	1810	2156	0.58	0.26	0.16	1.0
AST Out	105	119	3608	0.029	0.0039	0.97	1.0
Final Eff	76	82	102	0.75	0.059	0.20	1.0
RAS	78	87	8528	0.009	0.0011	0.99	1.0
WAS	183	238	37696	0.0049	0.0015	0.99	1.0
22-May-07							
Prim In	1240	1744	3712	0.33	0.136	0.53	1.0
AST In	1228	1818	2072	0.59	0.28	0.12	1.0
AST Out	98	114	3096	0.032	0.0052	0.96	1.0
Final Eff	94	109	111	0.85	0.135	0.02	1.0
RAS	110	122	7112	0.015	0.0017	0.98	1.0
WAS	175	293	46686	0.0037	0.0025	0.99	1.0
30-May-07							
Press Filtrate	457	505	1676	0.27	0.029	0.70	1.0

An analysis of the COD fractionation results leads to the summary presented in Table 42 below.

Table 42: Summary COD fractionation (mg COD/L, fractions)

Stream	Measured			Fractions			
	sCOD	fCOD	CODt	sCOD	CODcol	pCOD	CODt
Average							
Prim In	1,297	1,658	3,602	0.36	0.10	0.54	1.0
Primary effluent	1,096	1,628	1,918	0.57	0.28	0.15	1.0
AST Out	83	99	3,399	0.024	0.0048	0.97	1.0
Final Eff	81	91	110	0.73	0.092	0.17	1.0
RAS	86	99	8,504	0.0102	0.00154	0.99	1.0

Stream	Measured			Fractions			
	sCOD	fCOD	CODt	sCOD	CODcol	pCOD	CODt
WAS	179	249	40,000	0.0045	0.0017	0.99	1.0
Standard Deviation							
Prim In	189	83	187				
Primary effluent	161	209	402				
AST Out	16	18	271				
Final Eff	10	16	20				
RAS	13	18	1,455				
WAS	46	60	4,942				

2.1.2.4. ASM1 wastewater characteristics (STOWA method)

The combination of the above corrected BOD respirometry and the COD measurement data is used to convert the COD fractions into the ASM1 wastewater fractions, the results of which are summarised in Table 43 below. The BOD_5 reported by the external laboratory in the final effluent for 31 October 2007 was 8 mg/L.

Table 43: ASM1 wastewater characteristics (mg COD/L) (ϕ_{BOD} = 0.15)

Stream	S_I	S_S	X_S	X_I	COD total
Primary Influent					
1	79	1,249	739	963	3,030
2	79	1,249	927	775	3,030
3	79	1,249	692	1,010	3,030
Average	79	1,249	786	916	3,030
Primary effluent					
1	79	1,201	1,358	-478	2,160
2	79	1,201	1,034	-154	2,160
3	79	1,201	1,269	-389	2,160
Average	79	1,201	1,220	-340	2,160

Modification of the correction factor ϕ_{BOD} results in variation in only the X_S and X_I fractions, some of which are presented in Table 44 below.

Table 44: ASM1 wastewater characteristics (mg COD/L) (ϕ_{BOD} = 0.15)

Stream	$\phi_{BOD} = 0.1$		$\phi_{BOD} = 0.15$		$\phi_{BOD} = 0.20$	
	X_S	X_I	X_S	X_I	X_S	X_I
Primary Influent						
1	628	1,073	739	963	863	839
2	806	896	927	775	1,063	639
3	584	1,118	692	1,010	813	889
Average	673	1,029	786	916	913	789
Primary effluent						
1	1,216	-336	1,358	-478	1,518	-638
2	910	-30	1,034	-154	1,174	-294
3	1,132	-252	1,269	-389	1,424	-544
Average	1,086	-206	1,220	-340	1,372	-492

In order to obtain a positive X_I fraction in one of the data sets for the Primary effluent, it is necessary to use a correction factor ϕ_{BOD} of 0.087, which is particularly small. In two of the Primary effluent data sets, the total BOD calculated is larger or very close to the total COD measured, which renders it nearly impossible to solve for ϕ_{BOD} to obtain a positive X_I fraction.

An analysis of the ASM1 characterisation using ϕ_{BOD} of 0.15 results leads to the fraction summary presented in Table 45 below.

Table 45: ASM1 wastewater characteristics, fractions relative to COD total (ϕ_{BOD} = 0.15)

Stream	S_I	S_S	X_S	X_I
Primary Influent				
1	0.03	0.41	0.24	0.32
2	0.03	0.41	0.31	0.26
3	0.03	0.41	0.23	0.33
Average	0.03	0.41	0.26	0.30
Primary effluent				
1	0.04	0.56	0.63	-0.22
2	0.04	0.56	0.48	-0.07
3	0.04	0.56	0.59	-0.18
Average	0.04	0.56	0.57	-0.16

2.1.2.5. Alternative methods

Soluble inert (unbiodegradable) fraction (S_I)

The soluble COD concentration in the final effluent was calculated using the daily laboratory total COD concentration values multiplied by the average fraction of soluble to total COD in the final effluent from the wastewater characterisation work. The alternative methodology uses 100% of this value as the S_I concentration, expressed as a fraction of the total COD at the inlet to the AST (primary effluent plus press filtrate) in Table 46, Table 47 and Table 49 below.

Particulate inert (unbiodegradable) fraction (X_I)

The theoretical volatile suspended solids in the mixed liquor can be calculated and compared to the measured value for a number of X_I fractions in order to estimate the true X_I value [259]. The X_I fraction was varied from 0.05 to 0.40 in order to determine the most suitable X_I value for each steady state, as presented in Table 46, Table 47 and Table 49 below. The endogenous decay rate (b_H) is temperature dependent and the mixed liquor COD to solids ratio of 1.63 mg XCOD/ mg VSS was used (average of measured wastewater characterisation work). The sludge retention time was calculated using the formula in Appendix C of the 2003 WERF report [259].

The development of the equation used to calculate the X_I fraction is presented here, adapted slightly from the endogenous respiration model presented by Dold *et al.* [257] for the death regeneration model of ASM1.

A mass balance on sludge over a well-mixed reactor is given by:

Accumulation = Input – Output + Production by reaction – Loss by reaction – Loss by wastage

For steady state, accumulation is equal to zero.

$$V.\frac{dX_{BH}}{dt} = 0 = 0 - 0 + Y.Q(S_{INF} - S_{EFF}) - b.X_{BH}.V - \frac{X_{BH}.V}{\theta_X}$$

$$V.X_{BH} = \frac{Y.Q.(S_{INF} - S_{EFF}).\theta_X}{1 + b.\theta_X}$$

$$MX_{BH} = \frac{Y.M\Delta S.\theta_X}{1 + b.\theta_X} = MS_{T,INF}.(1 - f_{SI} - f_{XI}).\frac{Y.\theta_X}{1 + b.\theta_X}$$

Where MX_{BH} = mass of X_{BH} in the system (mg COD)
$M\Delta S$ = mass of substrate removed per day (mg COD/d)

A steady state mass balance on the decay products X_U at steady state is given by:

$$V.\frac{dX_U}{dt}=0=0-0+f_U.b.X_{BH}.V-0-\frac{X_U.V}{\theta_X}$$

$$V.X_U = f_U.b.\theta_X.V.X_{BH}$$

$$MX_U = f_U.b.\theta_X.MX_{BH} = MS_{T,INF}.(1-f_{SI}-f_{XI}).f_U.b.\theta_X.\frac{Y.\theta_X}{1+b.\theta_X}$$

Where MX_U = mass of X_U in the system (mg COD)

The mass of inert particulate matter from the influent can be expressed in VSS units also:

$$MX_I = MS_{T,INF}.f_{XI}.\theta_X$$

Where MX_I = mass of X_I in the system (mg COD)

The overall mass of volatile solids in the system is the sum of the three masses determined above:

$$MX_V = MX_{BH} + MX_U + MX_I$$

$$= MS_{T,INF}.\theta_X.\left\{\frac{Y.(1-f_{SI}-f_{XI})}{1+b.\theta_X}.(1+f_U.b.\theta_X)+f_{XI}\right\}$$

The concentration of VSS in the mixed liquor can be expressed as:

$$X_{VSS}=\frac{Q.COD_{T,Influent}.\theta_X}{f_{CV}V}\left[\frac{(1-f_{SI}-f_{XI}).Y_H}{1+b_H\theta_X}(1+f.b_H\theta_X)+f_{XI}\right]$$

And the f_{XI} fraction can be expressed as:

$$f_{XI} = \frac{\dfrac{X_{VSS}V.f_{CV}}{Q.COD_{T,Influent}.\theta_X} + (f_{SI} - 1)\left(\dfrac{Y_H.(1 + f_U.b_H\theta_X)}{1 + b_H\theta_X}\right)}{1 - \left(\dfrac{Y_H.(1 + f_U.b_H\theta_X)}{1 + b_H\theta_X}\right)}$$

Where X_{VSS} is the mixed liquor VSS concentration (mg/L), Q is the influent flow rate (L/d), $COD_{T,Influent}$ is the total COD concentration in the influent (mg/L), θ_X is the sludge age (d), V is the reactor volume (L), Y_H is the heterotroph yield coefficient (0.66 mg COD/ mg COD), b_H is the steady state theory endogenous decay rate (temperature dependent, 0.24 d^{-1} at 20ºC), f_U is the steady state theory endogenous residue fraction (0.2 mg VSS/ mg VSS), f_{CV} is the mixed liquor solids COD to VSS ratio (measured mill value used: 1.63 mg COD/ mg VSS), f_{XI} is the fraction of total influent COD which is particulate unbiodegradable, and f_{SI} is the fraction of total influent COD which is soluble unbiodegradable [259].

(Soluble) readily biodegradable fraction (S_S)

The oxygen uptake rate (OUR) can be measured during an aerobic batch reactor (bioassay) experiment, using a completely mixed reactor set-up of wastewater seeded with mixed liquor [259]. This test method may be interesting for the mill to use in order to update the wastewater characterisation on a regular basis, perhaps every 3 to 6 months, since it takes considerably less time than the 28 day BOD tests. However, these experiments did not work out.

(Particulate) slowly biodegradable fraction (X_S)

This fraction can be determined from the COD balance in the influent [259]:

$$X_S = COD_{influent,\ total} - S_I - S_S - X_I$$

Given the fact that this calculation relies upon the value of the SS concentration, this fraction will not be reported in the summary.

Table 46: Alternative methods: ASM1 wastewater characteristics (mg COD/L)

Stream	S_I	X_I	*COD total*
Primary effluent	101	< 108	2,160

Table 47: Alternative methods: ASM1 wastewater characteristics, fractions relative to COD total

Stream	S_I	X_I	COD total
Primary effluent	0.047	< 0.05	2,160

2.1.2.6. Further modelling work

Using a mixture of the STOWA and alternative calculation methods, the wastewater characterisation used in further modelling work is presented in Table 48 and Table 49 below.

Table 48: ASM1 COD fraction calculations (inlet aeration basin)

ASM1 Fraction	Calculation (inlet aeration basin)
S_I	$= COD_{effluent,\ soluble}$
S_S	$= COD_{influent,\ soluble} - S_I$
X_I	= Alternative WERF method Plus first step calibration
X_S	$= COD_{influent,\ total} - S_I - S_S - X_I$
X_{BH}	$= 0$
X_{BA}	$= 0$

Table 49: Alternative methods: ASM fractions for pseudo-steady state cases (mg COD/mg COD), Primary effluent

Steady State No.	S_I	S_S	X_I	X_S	Total COD (mg COD/L)
1	109	1,199	1,112	0	2,420
2	97	1,021	363	588	2,068
3	100	1,005	447	493	2,045
4	110	1,066	423	577	2,177
5	105	1,076	570	432	2,183
6	73	1,111	521	485	2,190
7	64	1,056	610	341	2,070
8	68	1,052	778	174	2,072
9	71	1,053	712	244	2,079
10	71	1,066	435	531	2,103
11	43	1,019	381	522	1,964

Steady State No.	S_I	S_S	X_I	X_S	Total COD (mg COD/L)
12	52	999	397	496	1,945
13	76	979	369	528	1,953
14	85	949	267	611	1,912
15	86	1,024	137	806	2,052
16	79	993	358	553	1,983
17	77	1,013	300	626	2,017
18	75	1,014	416	509	2,014
19	70	1,044	424	523	2,061
20	68	1,196	373	702	2,340
21	72	1,186	579	490	2,326
22	72	1,142	445	587	2,245
23	151	1,046	226	792	2,216
24	124	1,027	246	732	2,129
25	84	1,079	168	820	2,152
26	105	1,149	0	1,066	2,321
27	109	1,156	0	1,075	2,339
28	116	1,042	0	984	2,141
29	121	1,101	0	1,038	2,260
30	124	1,057	0	1,004	2,185
31	125	1,048	0	997	2,171
32	104	1,084	0	1,010	2,198

2.1.3. Nutrient fractionation

2.1.3.1. Nitrogen fractions

The nitrogen fractions of nitrate, ammonia and total Kjeldahl nitrogen (TKN) were measured for various sample points. No measurement of nitrite was made. The total nitrogen and organic nitrogen fractions were calculated from the measured values, and are presented in Table 50 below. The sludge press was shut on 20 February, and therefore there was no WAS flow on this day and no sample could be taken.

Table 50: Nitrate, ammonia, organic and total nitrogen fractions (mg N/L)

Stream	*NO_3*	*$NH4_{+4}$*	*N_{ORG}*	*TN*
20-Feb-07				
Prim In	0	0	1.88	1.88
Primary effluent	0.12	0.06	4.92	5.09
AST Out	0.034	4.66	163.3	168.0
Final Eff	0.017	3.61	3.32	6.95
RAS	0	3.56	283.9	287.5
06-Mar-07				
Prim In	0.15	0.054	6.47	6.67
Primary effluent	0.059	0.073	4.96	5.09
AST Out	0.85	0.035	152.5	153.4
Final Eff	1.48	0.11	3.14	4.74
RAS	0	0.647	318.4	319
WAS	0	3.47	1097	1100
20-Mar-07				
Prim In	0	0.006	6.7	6.7
Primary effluent	0	0	7.8	7.80
AST Out	4.62	0.11	143	148
Final Eff	4.72	0.16	4.25	9.13
RAS	0.12	0.57	313	314
WAS	0.0075	1.80	1206	1208
03-Apr-07				
Prim In	0	0	11.9	11.9
Primary effluent	0	0	10.55	10.55
AST Out	0.083	0	202	202
Final Eff	1.01	0	5.95	6.96
RAS	0	0.577	380.4	381
WAS	0.063	0.5267	685.0	685.6
17-Apr-07				
Prim In	0	0.023	3.85	3.88
Primary effluent	0	0	4.30	4.30
AST Out	0.264	0.065	159.4	159.6
Final Eff	2.05	0.118	2.70	3.83
RAS	0	0.60	350	351
WAS	0.063	2.47	1013	1016
15-May-07				
Prim In	0.907	0	4.275	5.18

Stream	NO_3	$NH4_{+4}$	N_{ORG}	TN
Primary effluent	0	0	3.495	3.50
AST Out	0	6.583	144.4	151.0
Final Eff	0.0077	1.0933	2.80	3.90
RAS	0	1.14	318.8	320
WAS	0.031	3.4	788.1	791.5
30-May-07				
Press Filtrate	0.057	3.87	38.9	42.9

An analysis of the nitrogen fractionation results leads to the summary presented in Table 51 below.

Table 51: Summary nitrogen fractionation (mg N/L, fractions)

Stream	Measured				Fractions			
	NO_3	$NH4_{+4}$	N_{ORG}	TN	NO_3	$NH4_{+4}$	N_{ORG}	TN
Average								
Prim In	0.2	0.014	5.8	6.0	0.03	0.03	0.94	1.0
Primary effluent	0.03	0.026	5.61	5.67	0.01	0.01	0.98	1.0
AST Out	0.8	1.6	153.8	156.0	0.005	0.01	0.980	1.0
Final Eff	1.2	0.8	3.3	5.1	0.22	0.36	0.438	1.0
RAS	0.02	1.1	328.0	329.2	0	0.0035	0.996	1.0
WAS	0.03	2.3	957.7	960.0	0	0.0025	0.997	1.0
Standard Deviation								
Prim In	0.4	0.021	3.5	3.4				
Primary effluent	0.05	0.033	2.6	2.6				
AST Out	1.6	2.6	23.2	20.2				
Final Eff	1.6	1.2	1.4	2.1				
RAS	0.04	1.1	30.5	32.6				
WAS	0.03	2.3	216.2	216.6				

2.1.3.2. Phosphorus fractions

The phosphorus fractions of ortho-phosphate and total phosphorus were measured for various sample points. The difference between the two measurements is assumed to represent the polyphosphate and organic phosphate fraction, as represented in Table 52 below. The measurements made on the final effluent on the 6 March resulted in an ortho-phosphate concentration higher than the total phosphorus concentration. In this case, the polyphosphate and organic phosphorus fraction is assumed to be zero, and the two results for the other fractions remain.

Table 52: Ortho-phosphate, polyphosphate and organic phosphate, and total phosphorus fractions (mg P/L)

Stream	PO_4	$PolyP + P_{ORG}$	TP
20-Feb-07			
Prim In	0.035	0.27	0.31
Primary effluent	0.28	0.93	1.21
AST Out	2.02	29.3	31.3
Final Eff	1.69	0.68	2.37
RAS	2.1	54.7	56.8
06-Mar-07			
Prim In	0.439	0.79	1.23
Primary effluent	0.35	0.90	1.26
AST Out	0.64	24.3	25.0
Final Eff	0.78	0	0.22
RAS	1.71	54.8	56.5
WAS	5.81	188	194
20-Mar-07			
Prim In	0.34	0.54	0.89
Primary effluent	0.39	0.57	0.96
AST Out	1.49	18.3	19.8
Final Eff	1.76	0.057	1.82
RAS	1.75	39.9	41.6
WAS	5.44	158.1	163.5
03-Apr-07			
Prim In	0.29	0.28	0.58
Primary effluent	0.034	0.96	0.99
AST Out	0.34	24.7	25.1
Final Eff	0.54	0.34	0.88
RAS	1.58	50.8	52.4
WAS	3.44	92.2	95.7
17-Apr-07			
Prim In	0.299	0.60	0.90
Primary effluent	0.127	0.96	1.08
AST Out	0.0407	20.0	20.0
Final Eff	0.0437	0.30	0.34
RAS	0.387	42.7	43.1

Stream	***PO_4***	***PolyP + P_{ORG}***	***TP***
WAS	2.837	134.7	137.5
15-May-07			
Prim In	0.482	0.458	0.940
Primary effluent	0.362	0.544	0.906
AST Out	0.044	18.95	19
Final Eff	0.029	0.233	0.262
RAS	0.229	46.52	46.75
WAS	2.02	122.98	125
30-May-07			
Press Filtrate	4.69	4.39	9.08

An analysis of the phosphorus fractionation results leads to the summary presented in Table 53 below.

Table 53: Summary phosphorus fractionation (mg P/L, fractions)

Stream	***Measured***			***Fractions***		
	PO_4	***PolyP + P_{ORG}***	***TP***	***PO_4***	***PolyP + P_{ORG}***	***TP***
Average						
Prim In	0.3	0.5	0.81	0.39	0.61	1.0
Primary effluent	0.3	0.8	1.1	0.24	0.76	1.0
AST Out	0.8	22.6	23.4	0.0327	0.97	1.0
Final Eff	0.8	0.2	1.0	0.821	0.18	1.0
RAS	1.3	48.2	49.5	0.0260	0.97	1.0
WAS	3.9	139.2	143.13	0.0273	0.97	1.0
Standard Deviation						
Prim In	0.2	0.2	0.3			
Primary effluent	0.1	0.2	0.1			
AST Out	0.8	4.3	4.7			
Final Eff	0.8	0.4	0.9			
RAS	0.8	6.2	6.6			
WAS	1.6	36.2	37.5			

2.1.4. Solids fractionation

The solids fractions of volatile (VSS) and total suspended solids (TSS) were measured for various sample points; the fixed suspended solids (FSS) is calculated from the difference between these two fractions. The measurement results are presented in Table 54 below. The measurements made on the primary influent on 3 April, as well as the final effluent on the 17 April and 22 May resulted in a VSS concentration higher than the TSS concentration. In this case, the fixed solids fraction is assumed to be zero, and the two results for the other fractions remain. The sludge press was shut on 8 May, and therefore there was no WAS flow on this day and no sample could be taken.

Table 54: VSS, FSS and TSS solids fractions (mg solids/L)

Stream	*VSS*	*FSS*	*TSS*
03-Apr-07			
Prim In	864	0	858
AST In	213	0	213
AST Out	2155	116	2271
Final Eff	39	1	40
RAS	4798	275	5073
WAS	9100	617	9717
17-Apr-07			
Prim In	842	5	847
AST In	215	2	217
AST Out	1991	90	2081
Final Eff	11	0	10
RAS	4092	214	4306
WAS	12771	809	13580
24-Apr-07			
Prim In	845	52	897
AST In	210	2	212
AST Out	1890	112	2002
Final Eff	11	0	11
RAS	3410	202	3612
WAS	12258	790	13048
01-May-07			
Prim In	855	37	892
AST In	254	9	263
AST Out	1811	150	1961
Final Eff	20	2	22
RAS	3790	286	4076
WAS	13430	919	14349
08-May-07			
Prim In	5637	66	5703
AST In	286	2	288
AST Out	2616	142	2758
Final Eff	10	0	10
RAS	5100	304	5404
15-May-07			

Stream	VSS	FSS	TSS
Mill Drain	367	5	372
Prim In	930	12	942
AST In	179	2	181
AST Out	2077	130	2207
Final Eff	11	2	13
RAS	4386	259	4645
WAS	11434	647	12081
22-May-07			
Prim In	981	4	985
AST In	231	1	232
AST Out	1854	150	2004
Final Eff	8	0	6
RAS	3736	209	3945
WAS	14428	802	15230

An analysis of the solids fractionation results leads to the summary presented in Table 55 below. It should be noted that the average VSS concentration is larger than the average TSS concentration for both the Primary effluent and the Final Effluent streams.

Table 55: Summary solids fractionation (mg solids/L, fractions)

Stream	Measured			Fractions		
	VSS	FSS	TSS	VSS	FSS	TSS
Average						
Prim In	1211	11.7	1222	0.99	0.01	1.0
Primary effluent	194.3	0	190.3	1.0	0	1.0
AST Out	2016	125	2140	0.94	0.06	1.0
Final Eff	15.9	0	15.2	1.0	0	1.0
RAS	4205	257	4462	0.94	0.06	1.0
WAS	12772	795	13567	0.94	0.06	1.0
Standard Deviation						
Prim In	1413	0	1431			
Primary effluent	46.4	0.2	54.8			
AST Out	226	4	234			
Final Eff	8.5	0.4	9.4			
RAS	483	6	510			
WAS	2009	36	2121			

2.1.5. Wastewater ratios: modelling

Various ratios of nutrients, solids, BOD and COD are required for modelling purposes with the ASM models. A number of these were determined from experimental data listed in this appendix. The calculations are presented below, primarily for fractions in the influent and in the mixed liquor (in the selectors and AST basins).

2.1.5.1. Influent

Nutrients: insi, inss, inxi, inxs, ipsi, ipss, ipxi, ipxs

The organic nitrogen and organic phosphorus concentrations in the Primary effluent were calculated for each of the wastewater characterisations. These concentrations are expressed as organic nutrient concentration per total COD concentration in Table 56 below, and compared to the range of default values from ASM2 and ASM3 for the influent fractions S_S, S_I, X_S and X_I [204]. It is clear that the calculated range is 8 to 25 times smaller than the upper ASM default values in the case of nitrogen, and 22 to 40 times smaller in the case of phosphorus. There is no trend in the measured fractions with respect to time (R^2 = 0.028 for nitrogen, R^2=0.014 for phosphorus), as presented in Figure 36.

Based on this data, the further modelling work will assume a zero value for each of the nutrient content of the influent fractions S_S, S_I, and X_S. The nutrient fraction of X_I in the influent will be the same as the fraction determined for the mixed liquor in section 2.1.5.2.

Table 56: Wastewater fractions Primary effluent: nutrient content

Nutrient	*Calculated Range*	*Range of ASM2, ASM3 default values [204]*
Organic Nitrogen (mg TN/ mg total COD)	0.0016 – 0.0050	0.01 – 0.04
Organic Phosphorus (mg TP/ mg total COD)	0.00025 - 0.00046	0 – 0.01

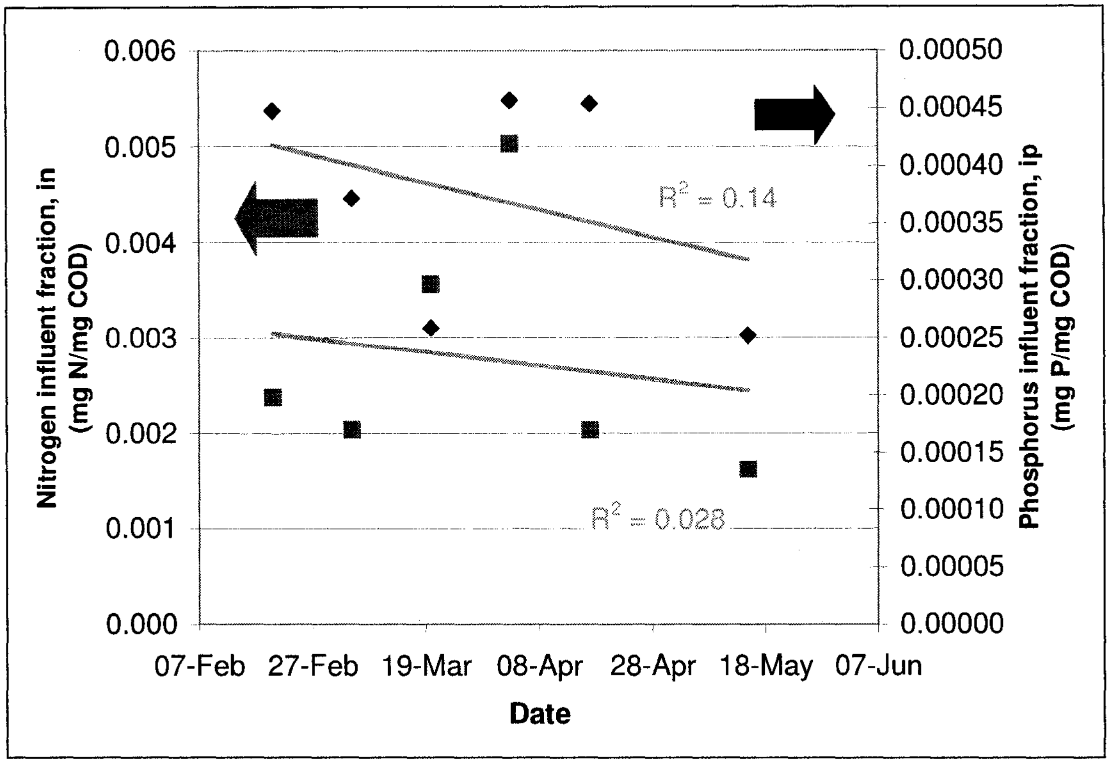


Figure 36: Influent organic nutrient fractions measured (mg N/mg COD, mg P/mg COD)

Solids: f_{CV}

The ratio of particulate COD (XCOD) to influent volatile suspended solids (VSS) was calculated for each of the wastewater characterisations. These concentrations are expressed as particulate COD concentration per VSS concentration in Table 57 below, and compared to the default values from ASM1, f_{CV}. The calculated range is 12% smaller to 20% larger than the ASM1 default value. There is no statistically significant trend in the measured f_{CV} fractions with respect to time ($R^2 = 0.59449$) as presented in Figure 37.

Table 57: Wastewater fractions mixed liquor: solids ratio f_{CV}

Ratio	***Calculated Range***	***ASM1 default value [204]***
f_{CV} (mg XCOD/ mg VSS)	1.93 – 2.64	2.2

Based on this data, the further modelling work will calculate the f_{CV} ratio for the influent for each steady state, based on the equation:

$$f_{CV,INFLUENT} = \frac{XCOD}{VSS} = \frac{X_I + X_S}{VSS}$$

This calculation is possible due to the fact that the biomass fractions X_{BH} and X_{BA}, and the cell decay fraction X_U are assumed to be zero in the influent.

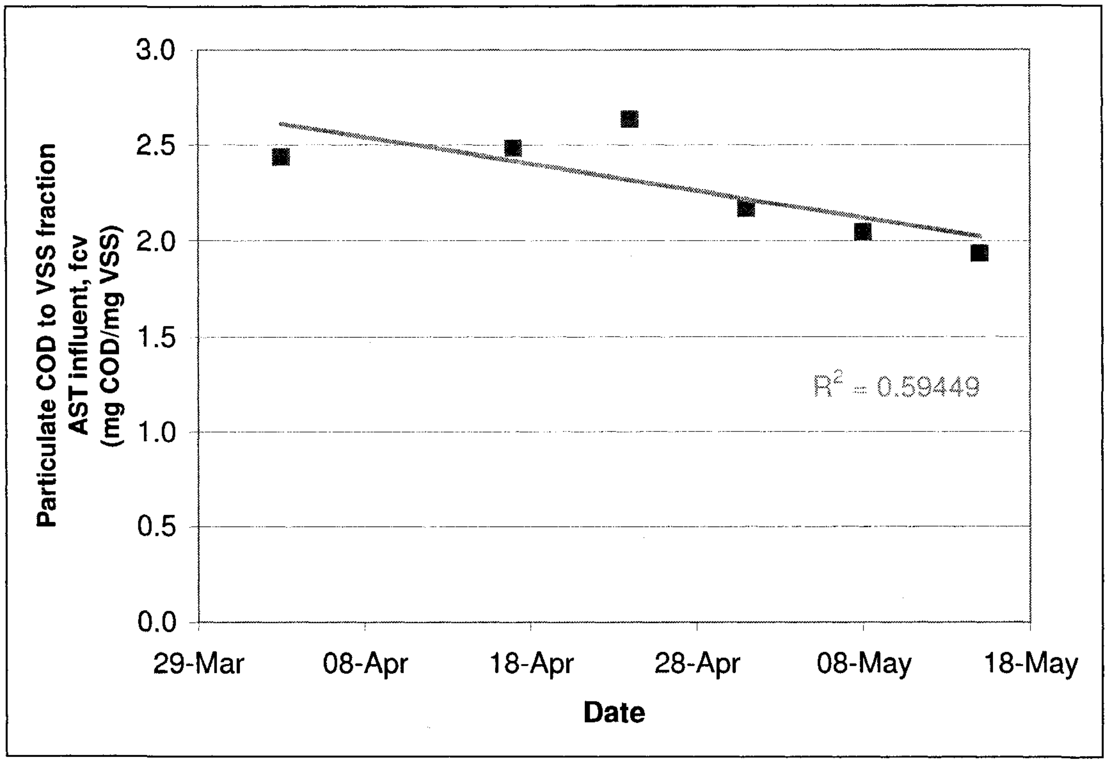


Figure 37: Influent particulate COD to VSS fractions measured (mg COD/mg VSS)

Solids: X_{II}

As noted in the solids fractionation section 2.1.4 of this appendix, the average VSS concentration in the Primary effluent is higher than the average TSS concentration. Inspection of the individual wastewater characterisations reveals that the VSS concentration in the Primary effluent is generally within 2 mg/L of the TSS concentration, once it is 9 mg/L less than the TSS concentration. Based on this data, it is reasonable to assume that the X_{II} fraction of inert inorganic material is equal to zero in this Primary effluent stream. This assumption will be applied to all pseudo-steady state cases.

2.1.5.2. Mixed liquor

Nutrients: inxb, ipxb

The organic nitrogen and organic phosphorus concentrations in the AST effluent were calculated for each of the wastewater characterisations, according to the following calculations:

Typical micro-organism cell stoichiometry: $C_{60}H_{87}O_{23}N_{12}P$ [39]

$$\text{N content of cell} = \frac{\text{Molecular weight (N)} \times n(\text{N})}{\text{Molecular weight (cell)}} = \frac{14 \times 12 \text{ g N/mol}}{1374 \text{ g VSS/mol}} = 0.12 \text{ gN/g VSS}$$

$$\text{P content of cell} = \frac{\text{Molecular weight (P)} \times n(\text{P})}{\text{Molecular weight (cell)}} = \frac{31 \times 1 \text{ g P/mol}}{1374 \text{ g VSS/mol}} = 0.023 \text{ gP/g VSS}$$

$$\text{Theoretical COD} = (2{*}n(\text{C}) + 0.5{*}n(\text{H}) - n(\text{O}) - 1.5{*}(\text{N})){*}32/2 = 1960 \text{ g COD/mol}$$

$$\text{Theoretical COD / VSS} = \frac{1960 \text{ g COD/mol}}{1374 \text{ g VSS/mol}} = 1.43 \text{ g COD/ g VSS}$$

$$\text{Theoretical N content of cell} = \frac{0.12 \text{ g N/g VSS}}{1.43 \text{ g COD/g VSS}} = 0.086 \text{ g N/g COD}$$

$$\text{Theoretical P content of cell} = \frac{0.023 \text{ g P/g VSS}}{1.43 \text{ g COD/g VSS}} = 0.016 \text{ g P/g COD}$$

$\therefore$ inxbh = inxba = 0.086 g N/g COD, ipxbh = ipxba = 0.016 g P/g COD

Nutrient fractions of cell decay products are estimated to be slightly less than the nutrient fractions of the biomass [204].

$\therefore$ inxu = 0.06 g N/g COD, ipxu = 0.015 g P/g COD

The volatile suspended solids measured in the mixed liquor can be divided into fractions of biomass and non-biomass, using the fact that approximately 25% of mixed liquor in a pulp and paper AST wastewater treatment plant is active biomass [260]. The measured average mixed liquor COD/VSS of

1.63 g COD / g VSS is then used to solve for the COD/VSS ratio of the non-biomass component of the measured VSS:

VSS = biomass + non-biomass
1.63 g COD/g VSS = 25 % *1.43 g COD/g VSS + 75% *(COD/VSS non-biomass)

$\therefore$COD/VSS of non-biomass = 1.70 g COD/g VSS

Using the average mixed liquor VSS of 1962 mg VSS/L, the measured VSS can be divided into fractions of biomass, cell decay products and inerts. Modelling results estimate the ratio of particulate inert (X_I) to particulate inert plus cell decay products ($X_I + X_U$) in the mixed liquor as 0.21 g COD/g COD. This is used in further calculations.

VSS = biomass + inerts + cell decay products
1962 mg VSS/L = 25%*1962 mg VSS/L +
0.79*(75%*1962 mg VSS/L) + 0.21*(75%*1962 mg VSS/L)
1962 mg VSS/L = 491 mg VSS/L + 1167 mg VSS/L + 305 mg VSS/L

Measurements of the organic nitrogen in the mixed liquor can be related to the relative components of the measured VSS:
N content of biomass = 0.12 g N/g VSS * 491 g VSS/L = 60 g N/L
N content of cell decay products
= 0.06 g N/g COD * 305 g VSS/L * 1.70 g COD/g VSS
= 31 g N/L

N content of inerts = Measured organic N – N(biomass) – N(cell decay products)
= 153 g N/L – 60 g N/L – 31 g N/L
= 62 g N/L

$$\text{N fraction of inerts} = \frac{62 \text{ g N/L}}{1167 \text{ g VSS/L}} = 0.053 \text{ g N/g VSS}$$

$$= \frac{0.053 \text{ g N/g VSS}}{1.70 \text{ g COD/g VSS}} = 0.03 \text{ g N/g COD}$$

Similarly, the phosphorus fraction of inerts was determined to be 0.015 g P/g COD.

∴inxi = 0.03 g N/g COD, ipxi = 0.0016 g P/g COD

These concentrations are expressed as organic nutrient concentration per total COD concentration in Table 58 below, and compared to the range of default values from ASM1 for nitrogen and from ASM2 and ASM3 for phosphorus, in the biomass fraction X_B. The calculated range is 32 to 43% smaller than the ASM1 default value in the case of nitrogen and 49 to 68% smaller than the ASM2d and ASM3 default values in the case of phosphorus. There is no trend in the measured fractions of organic nitrogen divided by VSS with respect to time (R^2 = 0.1025); however there is a statistically significant linear trend in the measured fractions of organic phosphorus divided by VSS with respect to time (R^2 = 0.8263), as presented in Figure 38. An average value was assumed for the

Table 58: Wastewater fractions mixed liquor: nutrient content (mg N/mg COD, mg P/mg COD)

COD Fraction	***Nutrient***	***Symbol***	***Calculated or assumed value***	***ASM1 (N), ASM2d & ASM2 (P) default values [204]***
Biomass	N	inxbh inxba	0.086	0.07 - 0.086
Cell decay products	N	inxu	0.06	0.06
Particulate inerts	N	inxi	0.03	0.02 - 0.03
Slowly biodegradable	N	inxs	0	0.04
Soluble inert	N	insi	0	0.01
Soluble biodegradable	N	inss	0	0.03
Biomass	P	ipxbh ipxba	0.016	0.02 – 0.021
Cell decay products	P	ipxu	0.015	0.02
Particulate inerts	P	ipxi	0.0016	0.01
Slowly biodegradable	P	ipxs	0	0.01
Soluble inert	P	ipsi	0	0 – 0.01
Soluble biodegradable	P	ipss	0	0.01

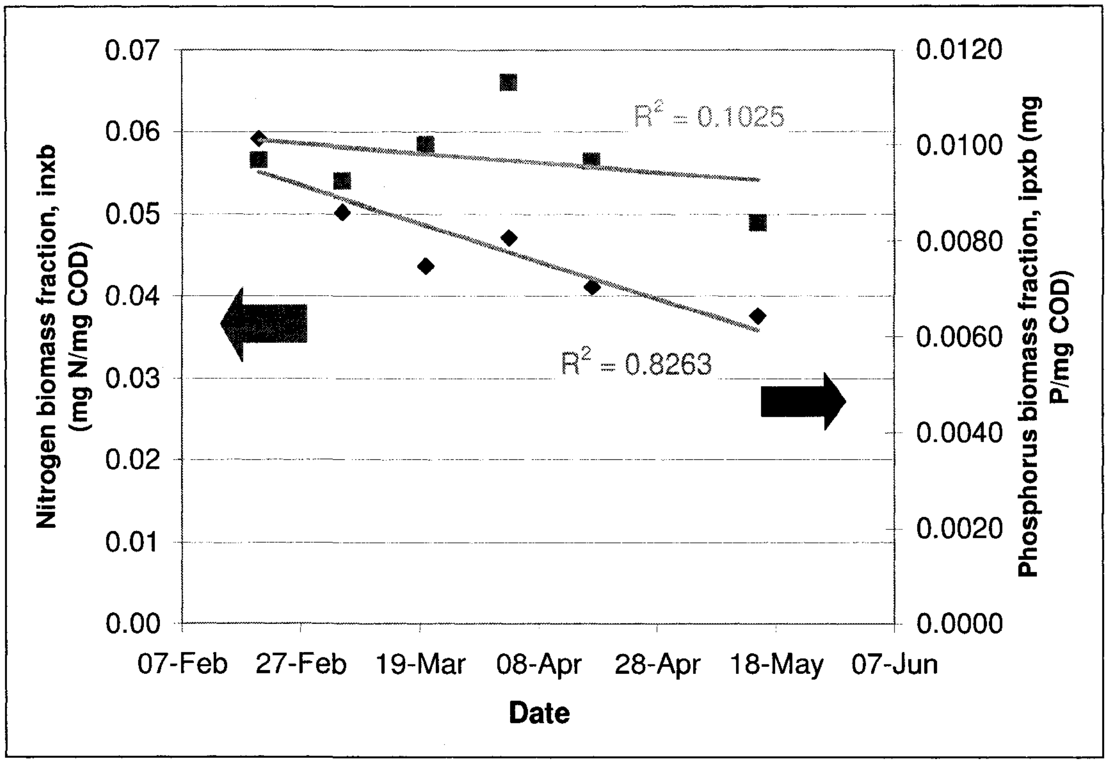


Figure 38: Nutrient biomass fractions measured (mg N/mg COD, mg P/mg COD)

Solids: f_{CV}

The ratio of particulate COD (XCOD) to mixed liquor volatile suspended solids (VSS) was calculated for each of the wastewater characterisations. These concentrations are expressed as particulate COD concentration per VSS concentration in Table 59 below, and compared to the default values from ASM1, f_{CV}. The calculated range is 10% smaller to 25% larger than the ASM1 default value. There is no trend in the measured f_{CV} fractions with respect to time ($R^2 = 0.09589$) as presented in Figure 39.

Based on this data, the further modelling work will assume an average value (1.63) for the f_{CV} ratio for the mixed liquor. This takes into account the effect exerted by larger particles such as lignin which are included in both the COD and VSS measurements but are not biomass: the COD to VSS ratio of lignin is 2.04 for a chemical composition of $C_{10}H_{12}O_3$.

Table 59: Wastewater fractions mixed liquor: solids ratio f_{CV}

Ratio	***Calculated Range***	***ASM1 default value [204]***
f_{CV} (mg XCOD/ mg VSS)	1.34 – 1.85	1.48

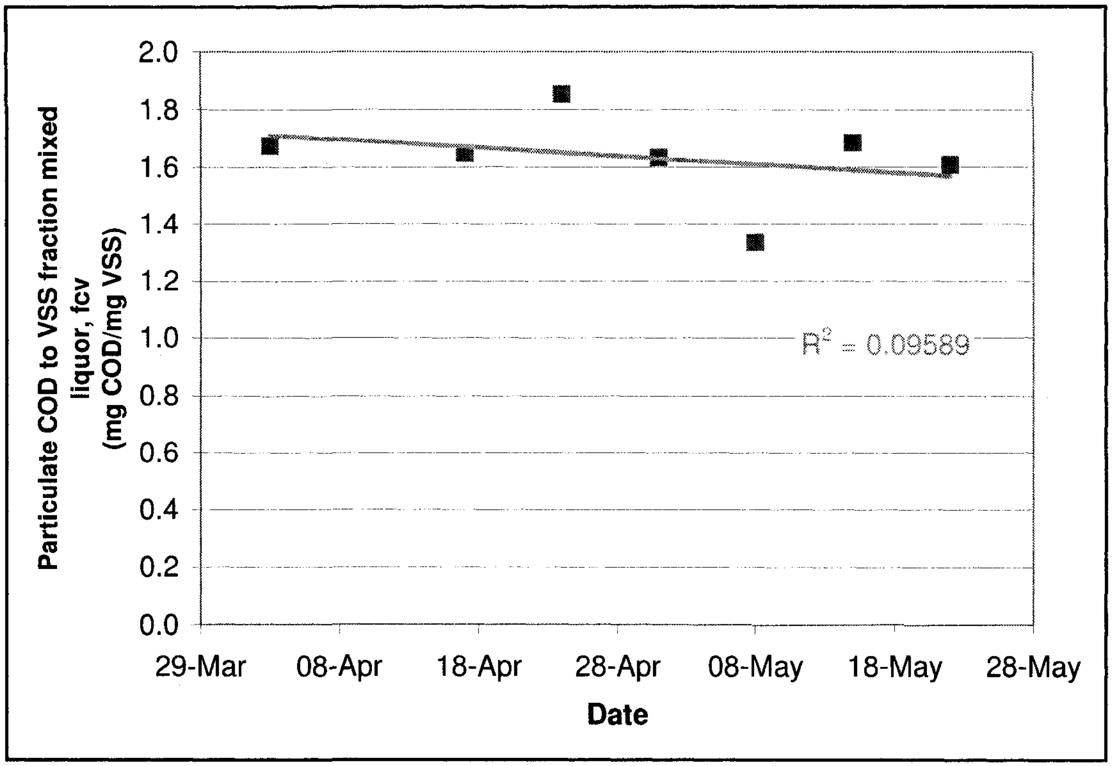


Figure 39: Mixed liquor particulate COD to VSS fractions measured (mg COD/mg VSS)

Solids: X_{II}

As noted above, the X_{II} fraction of inert inorganic material is equal to zero in the Primary effluent stream for all pseudo-steady state cases. However, the solids fractionation work highlighted a difference between the VSS and TSS concentrations in the mixed liquor: 125 mg FSS/L on average in the AST outlet. From the steady state data, the mixed liquor measurement for all pseudo-steady state cases demonstrates a difference between the TSS and VSS measurements. For the purposes of modelling, it is necessary that the origin of this solids fraction is identified. Work by Ekama *et al.* highlights that 15% of the content of ordinary heterotrophic organisms is present as inert inorganic salts (mg ISS/mg VSS), or X_{II}, which precipitate during the VSS-TSS test procedure [261]. Given that the active biomass content of the VSS concentration has been measured at approximately 25% (mg active biomass/ mg VSS) for pulp and paper wastewater [262] this results in 4%

mg ISS/mg VSS. It can therefore be assumed that the 5% of mixed liquor TSS concentration that is unaccounted for by VSS is present as X_{II} originating from these inert inorganic salts. This can be taken into account in the model by calculating the X_{II} fraction as a state variable, as a fraction fxii of the active biomass.

2.1.6. Results & Discussion

2.1.6.1. COD & BOD fractionation

BOD respirometry (STOWA method)

It was found that the BOD respirometry test results for a 10 day period were not sufficient to adequately fit a curve to the data: the BOD curve had not sufficiently approached the ultimate BOD concentration. It was for this reason that the BOD respirometry work was conducted for a 28 day period, this duration gave a better approximation of the ultimate BOD concentration.

The BOD respirometry results are consistent in the same order of magnitude between the three test sets. The results are depicted below in Figure 40 for primary influent and Figure 41 for Primary effluent; all curves are corrected for the seed BOD. All curves show no signs of impediment or inhibition at the beginning of the test, which indicates that the seed did not require time to acclimatise to toxicity in the wastewater. However, all samples suffered a shock around day 15; the data was corrected prior to conducting the curve-fitting exercise that calculated the wastewater characterisation.

None of the curves definitively display asymptotic behaviour, which was expected and is seen in municipal wastewater [246], in fact they all appear to be steadily rising. This indicates that a large proportion of the organic substrate is slowly biodegradable; it is only a matter of how slowly it degrades. This is further expressed as the first order rate constant of BOD versus time, k_{BOD}, which was found to be between 0.051 and 0.057 d^{-1} for the Primary effluent in this study, compared to 0.15 to 0.8 d^{-1} found for municipal primary treated wastewater [246]. Ultimate BOD is generally reproducible, but varies by approximately 200 to 275 mg BOD/L for both samples in this study, which is a large variability.

While the average BOD_5 concentration in the Primary Effluent, 426 mg/L, is comparable to the average concentration data for a municipal primary treated effluent, 246 mg/L [31], the total BOD_5 load in the pulp and paper wastewater, 12,660 kg/d, is much larger than the municipal load of 1,680 kg/d. A comparison between the study data and other pulp and paper wastewaters is detailed in Table 32 below.

Furthermore, the absolute value of BOD_{total} for the primary influent was lower to equal that of the Primary effluent. This can be interpreted in one of two ways: either the addition of press filtrate in the Primary effluent sample causes a rise in the BOD of that stream; or the concentration of biodegradable organic substrate has been slightly increased (strengthened) over the primary clarifier process unit via the removal of the primary sludge stream. Given the relatively large variability in the value of BOD_{total}, the difference between the primary influent to the Primary effluent is slight.

The main purpose of this BOD data is for use in the ASM1 characterisation, discussed below.

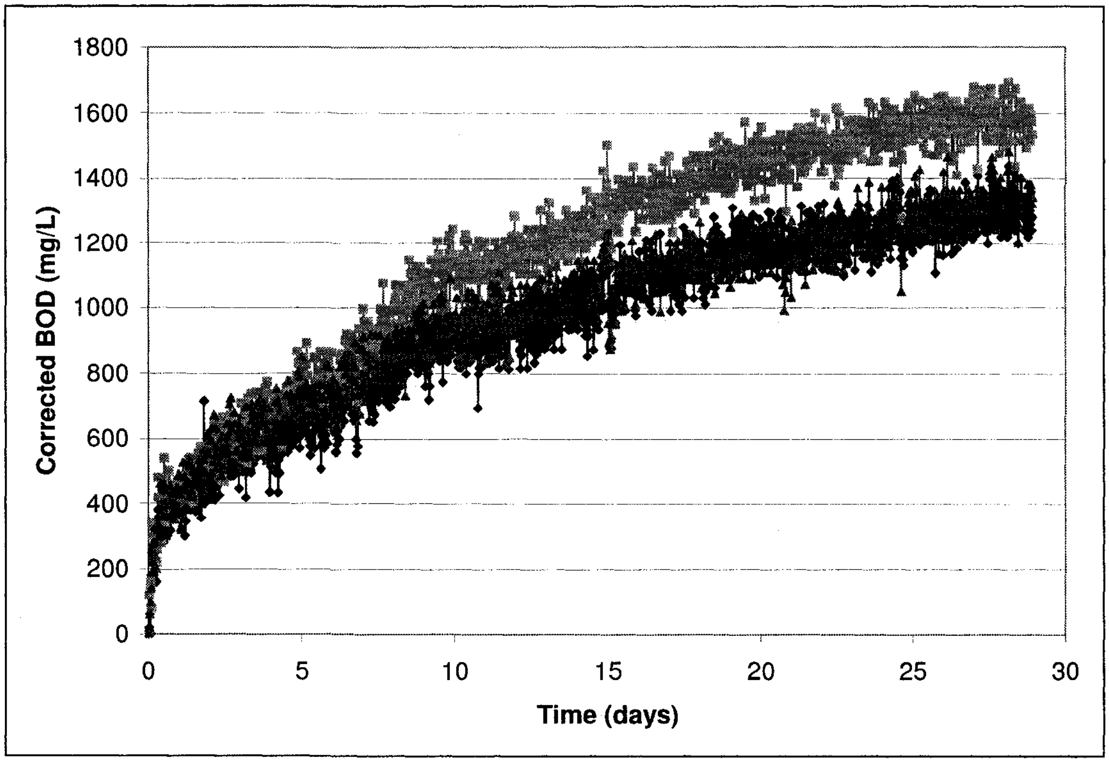


Figure 40: Corrected Primary Influent BOD1-28 31 October 2007

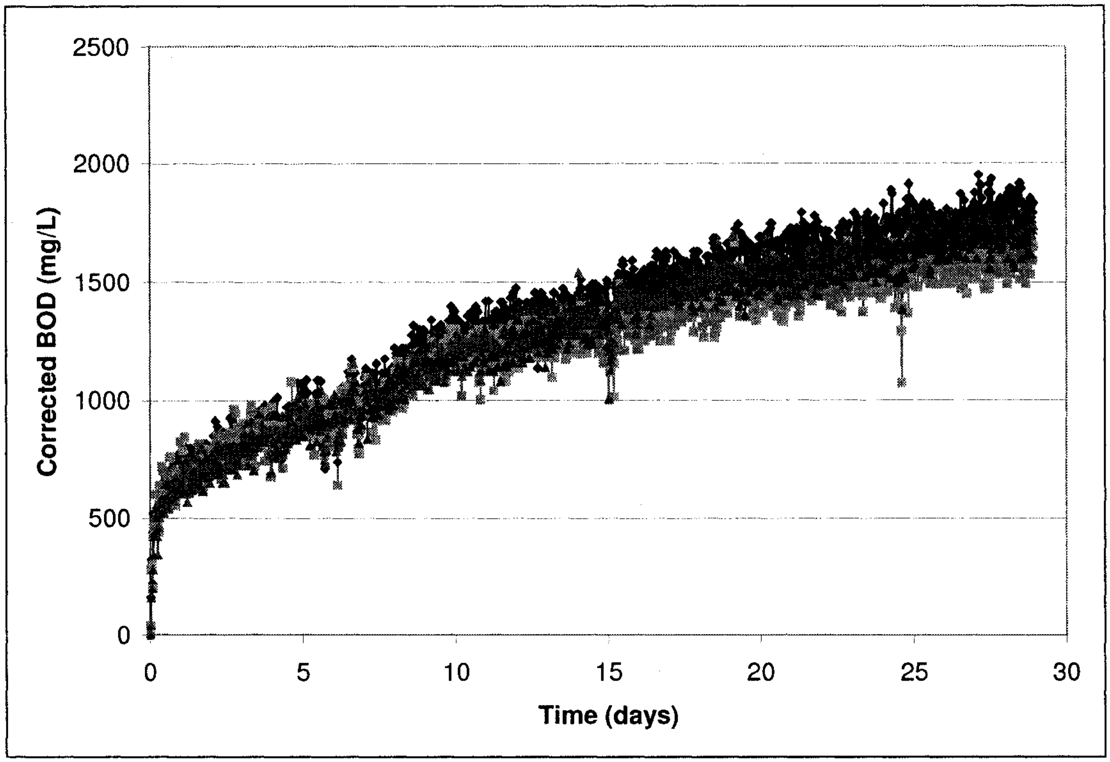


Figure 41: Corrected Primary effluent BOD1-28 31 October 2007

Table 60: BOD values for pulp & paper primary effluent (mg/L) [200]

Parameter	***Primary treated effluent***			
Pulp & Paper Process	*TMP*	*TMP*	*Default ASM1*	*Municipal**
BOD_5 (kg/d)	12,660	18,450**		1,680
BOD_5: BODu	0.21 – 0.23		0.66	0.81 – 0.97
BODu: BOD_5	4.4 – 4.8		1.5	1.0 – 1.2
k_{BOD} (d^{-1})	0.051 – 0.057			0.15 – 0.80
XCOD:MLVSS	1.34 – 1.85		1.48	
Reference	Current study	[30]**	[204]	[31, 200, 246]

*BOD_{total} in this case is BOD_{10}

**Assumed flowrate of 15,000 m3/d wastewater

COD measurements (STOWA method)
The COD fractionation data, in particular the average fractions, are very informative. Colloidal COD, being the difference between the COD measured in the samples filtered to 0.1µm and 0.45µm, is a significant fraction of the inlet to the primary clarifier as well as the inlet to the AST basins: on average 10% and 28% of the total COD respectively. The AST outlet as well as the RAS and WAS streams are almost entirely made up of particulate COD, which can be interpreted as a high fraction of biomass. The final effluent has a very high soluble COD fraction, 73%, which indicates good solids removal across the secondary clarifier. The increase in the soluble and colloidal COD fractions from the inlet to the primary clarifier to the inlet of the AST basins also indicates good solids removal across the primary clarifier. These results can be seen in Figure 42 below.

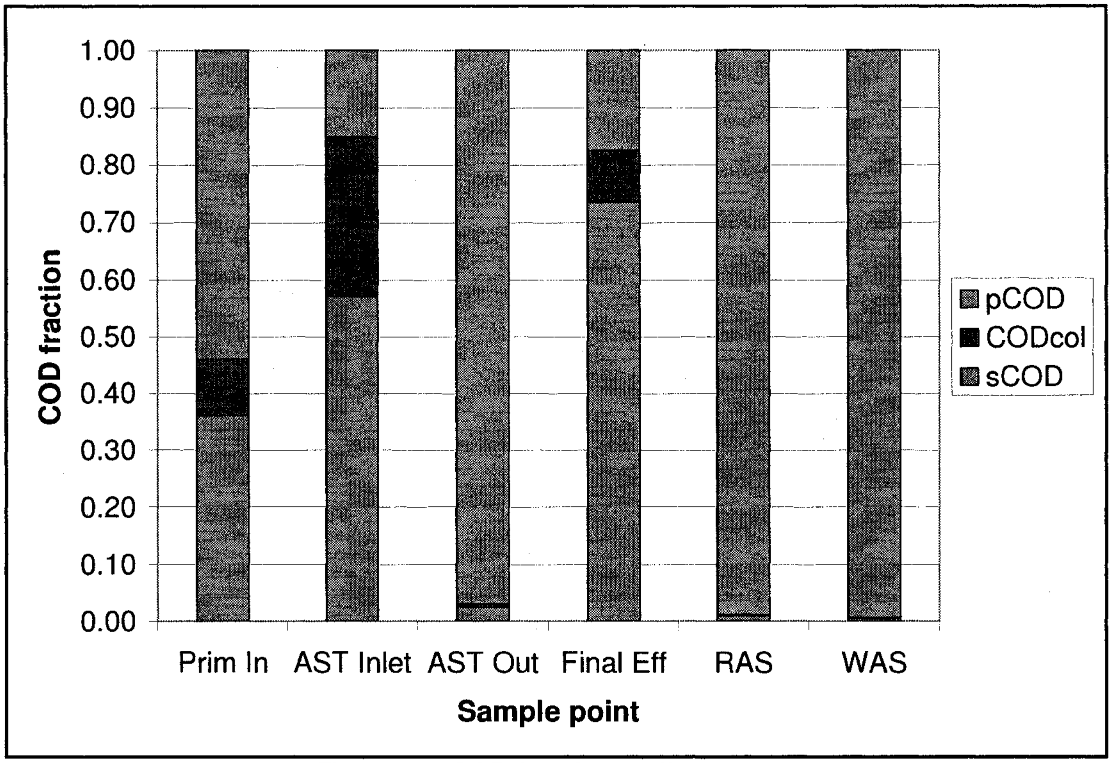


Figure 42: COD fractions, all streams

In terms of the absolute COD concentrations as illustrated by the average data, it is interesting to note the decrease in total COD concentration across the primary clarifier and the subsequent increase in total COD concentration across the AST basins, which corresponds to the sedimentation occurring in the primary clarifier and the generation of COD in the form of biomass in the AST basins.

In terms of the standard deviation of the average COD data, the standard deviation ranges from 5% (colloidal COD, inlet primary clarifier) to 26% (soluble COD, WAS stream). The standard deviation is generally in the vicinity of 15 to 20% for the different COD fractions. This dispersion of data is not insignificant, and should be taken into account when discussing results dependent on the COD measurements.

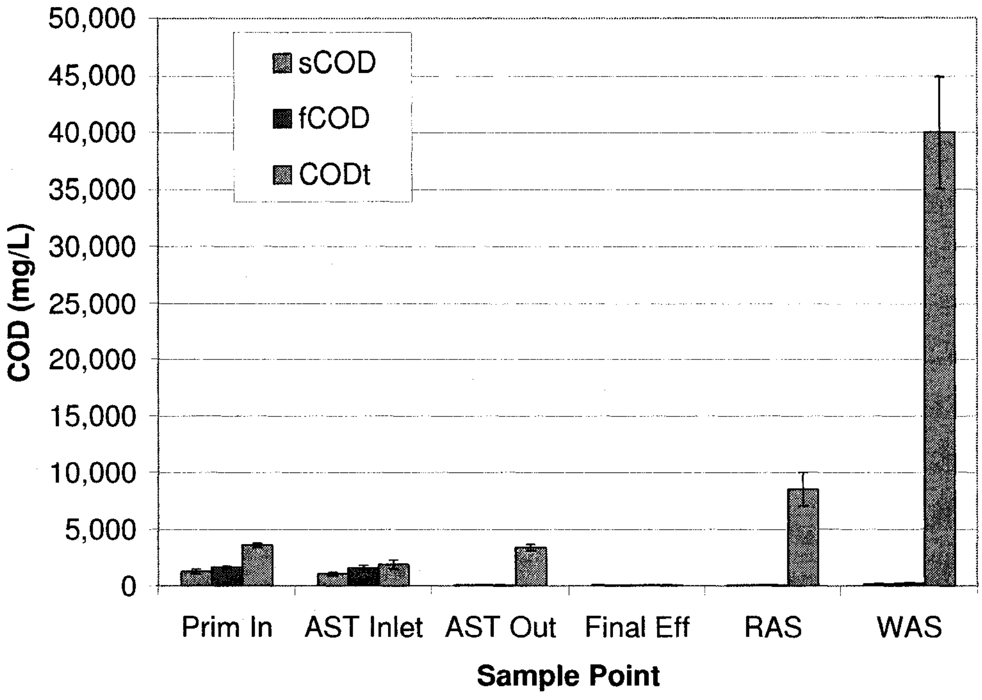


Figure 43: Measured COD (mg/L), error bars represent one standard deviation

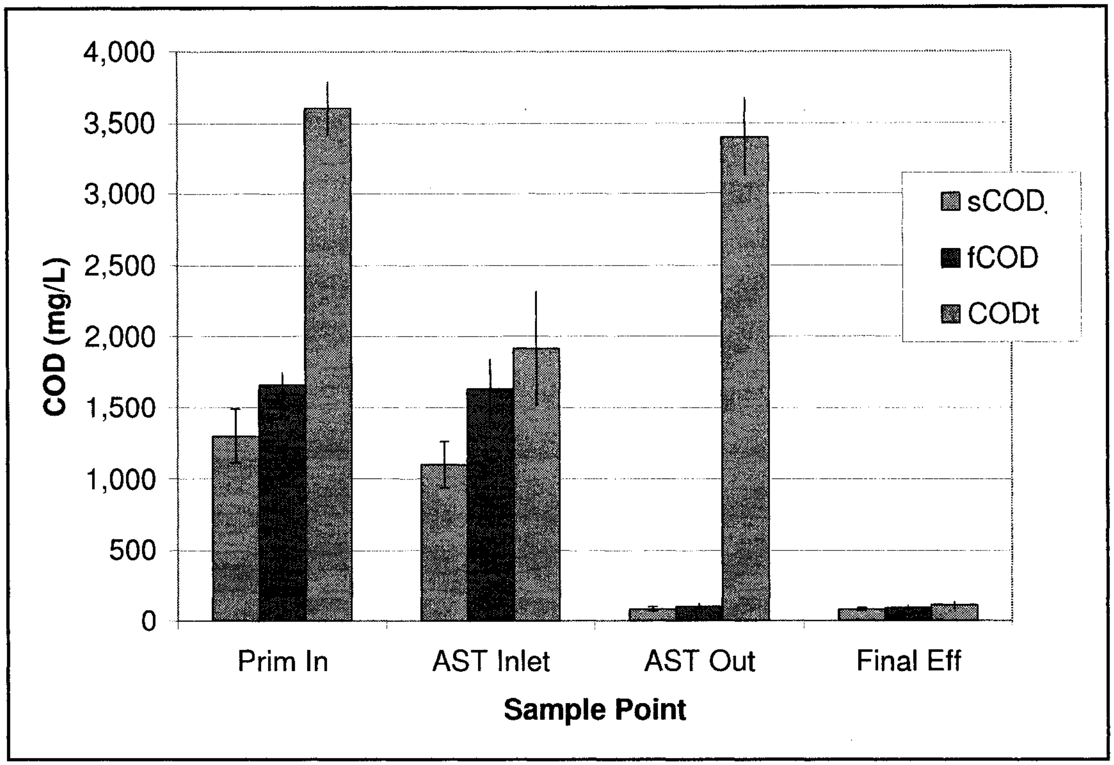


Figure 44: Measured COD (magnified) (mg/L), error bars represent one standard deviation

ASM1 wastewater characteristics (STOWA method)

The combination of the above BOD respirometry and the COD measurement data is used to convert the COD fractions into the ASM1 wastewater fractions, the results of which are summarised in Table 61 below. The BOD_5 reported by the external laboratory in the final effluent for 31 October 2007 was 8 mg/L.

Table 61: ASM1 wastewater characteristics (mg COD/L) (ϕ_{BOD} = 0.15)

Stream	S_I	S_S	X_S	X_I	COD total
Primary Influent					
1	79	1,249	739	963	3,030
2	79	1,249	927	775	3,030
3	79	1,249	692	1,010	3,030
Average	79	1,249	786	916	3,030
Primary effluent					
1	79	1,201	1,358	-478	2,160
2	79	1,201	1,034	-154	2,160

Stream	S_I	S_S	X_S	X_I	***COD total***
3	79	1,201	1,269	-389	2,160
Average	79	1,201	1,220	-340	2,160

Modification of the correction factor ϕ_{BOD} results in variation in only the X_S and X_I fractions, some of which are presented in Table 44 below.

Table 62: ASM1 wastewater characteristics (mg COD/L) (ϕ_{BOD} = 0.1, 0.15, 0.2)

Stream	$\phi_{BOD} = 0.1$		$\phi_{BOD} = 0.15$		$\phi_{BOD} = 0.20$	
	X_S	X_I	X_S	X_I	X_S	X_I
Primary Influent						
1	628	1,073	739	963	863	839
2	806	896	927	775	1,063	639
3	584	1,118	692	1,010	813	889
Average	673	1,029	786	916	913	789
Primary effluent						
1	1,216	-336	1,358	-478	1,518	-638
2	910	-30	1,034	-154	1,174	-294
3	1,132	-252	1,269	-389	1,424	-544
Average	1,086	-206	1,220	-340	1,372	-492

In order to maintain a zero or positive calculated fraction for X_I, it was necessary to modify the correction factor ϕ_{BOD}, which is used to account for inert COD generated by biomass lysis [246]. While the recommended range of ϕ_{BOD} for municipal wastewater is 0.1 to 0.2, it was found that a ϕ_{BOD} of 0.087 was necessary in the Primary effluent in order to arrive at a positive X_I value, for in one of the data sets, which is particularly small. In two of the Primary effluent data sets, the total BOD calculated is larger or very close to the total COD measured, which renders it nearly impossible to solve for ϕ_{BOD} to obtain a positive X_I fraction.

An analysis of the ASM1 characterisation using ϕ_{BOD} of 0.15 results leads to the fraction summary presented in Table 45 below.

Table 63: ASM1 wastewater characteristics, fractions relative to COD total (ϕ_{BOD} = 0.15)

Stream	S_I	S_S	X_S	X_I
Primary Influent				
1	0.03	0.41	0.24	0.32
2	0.03	0.41	0.31	0.26
3	0.03	0.41	0.23	0.33
Average	0.03	0.41	0.26	0.30
Primary effluent				
1	0.04	0.56	0.63	-0.22
2	0.04	0.56	0.48	-0.07
3	0.04	0.56	0.59	-0.18
Average	0.04	0.56	0.57	-0.16

The ASM1 wastewater characteristics of the inlet to the AST basins are generally comparable to those for found for pulp and paper wastewater: S_I of 0.14 to 0.36, S_S of 0.24 to 0.49, X_S of 0.11 to 0.42 and X_I of 0.03 to 0.14 [200], as well as those municipal wastewater found in the literature: S_I of 0.03 to 0.10, S_S of 0.09 to 0.42, X_S of 0.1 to 0.48 and X_I of 0.23 to 0.50 [246]. This confirms the previous assumption that the wastewater characterisation methodology should be applied to the influent to the AST basins.

The methodology employed to determine BCOD is "almost intrinsically subject to inaccuracy (10 to 20%)" according to its authors [246].

Alternative methods

A thorough discussion of alternative methods for calculating the wastewater characterisation are presented in the 2003 WERF report [259]. A number of these methods were applied in addition to the STOWA method above, in order to verify the results of the STOWA method. This was considered necessary due to the sensitivity of the model and model results to the wastewater characterisation.

Soluble inert (unbiodegradable) fraction (S_I)

The soluble COD concentration in the final effluent was calculated using the daily laboratory total COD concentration values multiplied by the average fraction of soluble to total COD in the final effluent from the wastewater characterisation work. The alternative methodology uses 100% of this value as the S_I concentration, expressed as a fraction of the total COD at the inlet to the AST (primary effluent plus press filtrate) in Table 46 and Table 47 below.

Particulate inert (unbiodegradable) fraction (X_I)

The theoretical volatile suspended solids in the mixed liquor can be calculated and compared to the measured value for a number of X_I fractions in order to estimate the true X_I value [259], as presented in Table 46 and Table 47 below.

(Soluble) readily biodegradable fraction (S_S)

The oxygen uptake rate (OUR) can be measured during an aerobic batch reactor (bioassay) experiment, using a completely mixed reactor set-up of wastewater seeded with mixed liquor [259]. The results are not presented as they are thought to incorporate a large systematic error.

This test method is certainly very interesting for the mill to use in order to update the wastewater characterisation on a regular basis, every 3 to 6 months, since it takes considerably less time than the 28 day BOD tests.

(Particulate) slowly biodegradable fraction (X_S)

This fraction can be determined from the COD balance in the influent [259]:

$$X_S = COD_{influent,\ total} - S_I - S_S - X_I$$

Given the fact that this calculation relies upon the value of the S_S concentration and that that fraction is thought to incorporate a large systematic error, the calculation will also contain an error in this case.

Unfortunately the test that determined the S_S fraction did not demonstrate a clearly delineated X_S fraction. Therefore this fraction will not be reported in the summary.

Table 64: Alternative methods: ASM1 wastewater characteristics (mg COD/L)

Stream	S_I	X_I	*COD total*
Primary effluent	101	< 108	2,160

Table 65: Alternative methods: ASM1 wastewater characteristics, fractions relative to COD total

Stream	S_I	X_I	*COD total*
Primary effluent	0.047	< 0.05	2,160

Further modelling work

Given the inherent inaccuracy associated with the determination of the wastewater fractions, in further modelling exercises, the Primary effluent will be modelled using the slightly modified fractionation presented in Table 48 and Figure 45 below, which combine the STOWA and alternative calculation methods.

Table 66: ASM1 COD fraction calculations (inlet aeration basin)

ASM1 Fraction	*Calculation (inlet aeration basin)*
S_I	$= COD_{\text{effluent, soluble}}$
S_S	$= COD_{\text{influent, soluble}} - S_I$
X_I	= Alternative WERF method Plus first step calibration
X_S	$= COD_{\text{influent, total}} - S_I - S_S - X_I$
X_{BH}	$= 0$
X_{BA}	$= 0$

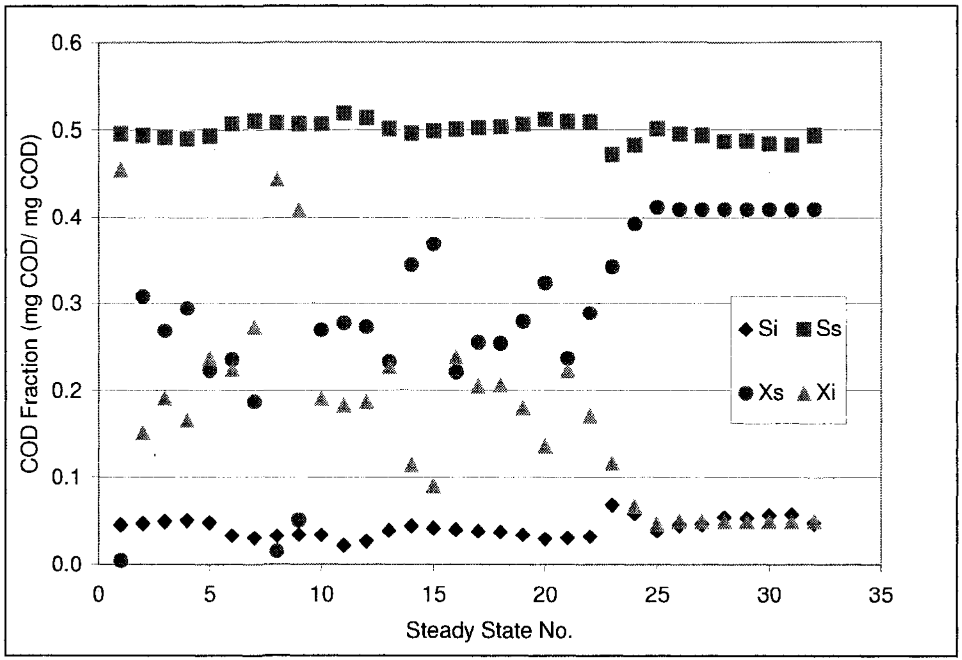


Figure 45: Steady state wastewater characterisation: for further modelling work

2.1.6.2. Nutrient fractionation

Nitrogen

The majority of the nitrogen present in all streams is in the form of organic nitrogen, which is assumed to originate from the pulp and paper process for the influent to the primary clarifier and to the AST basin, and to be associated with biomass in all other streams. This can be seen in Figure 46 below.

It is important to note that the standard deviation associated with the measurement of the nitrogen fractions ranges from 10% (total nitrogen, RAS) to 250% (nitrate, RAS). It can be concluded from this that it is very difficult to accurately measure some nitrogen fractions, particularly as the absolute concentration nears the limit of detection of the experimental test methods employed.

Generally, the concentration of nitrate was found to be quite low in all streams on all dates that samples were taken. The hypothesis that nitrification-denitrification processes are negligible in the treatment of pulp and paper wastewater will be considered in the use of the ASM models.

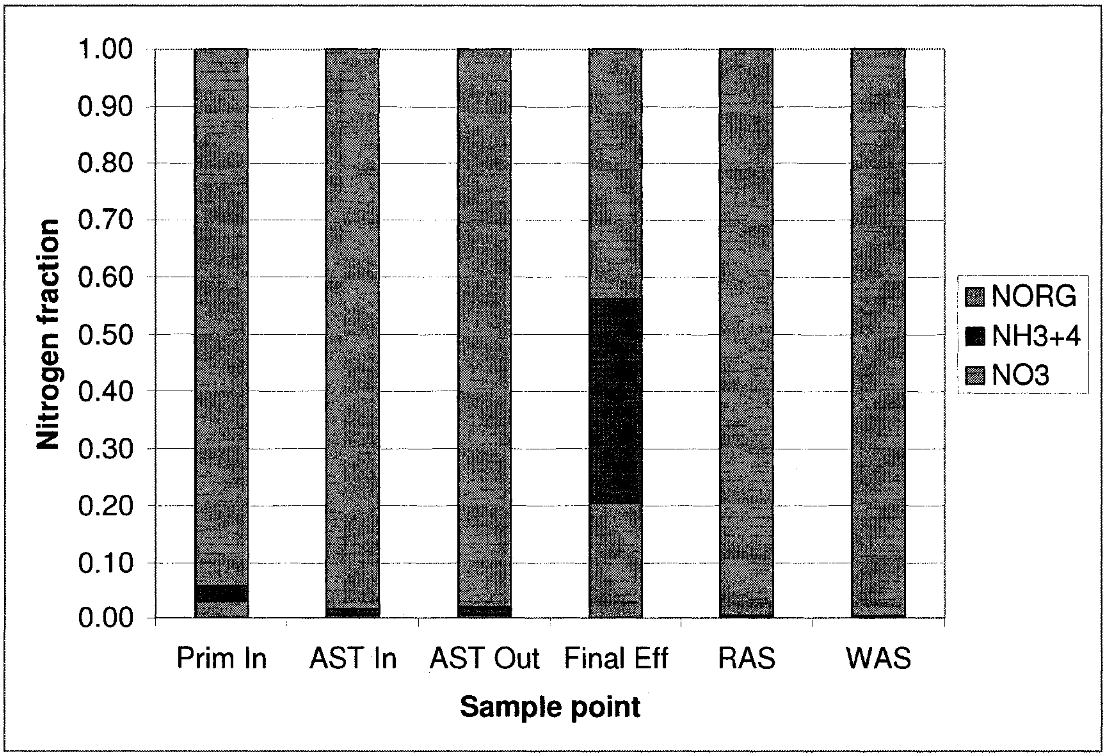


Figure 46: Nitrogen fractions

Phosphorus

The majority of phosphorus present in most streams is in the form of polyphosphate and organic phosphorus, with the exception of the final effluent which contains 82% phosphate. This can be seen in Figure 47 below.

As with the nitrogen fractions, the standard deviation associated with the measurement of the phosphorus fractions ranges from 13% (total phosphorus, RAS) to 250% (polyphosphate and organic phosphorus, final effluent). It can be concluded from this that it is very difficult to accurately measure some phosphorus fractions, particularly as the absolute concentration nears the limit of detection of the experimental test methods employed.

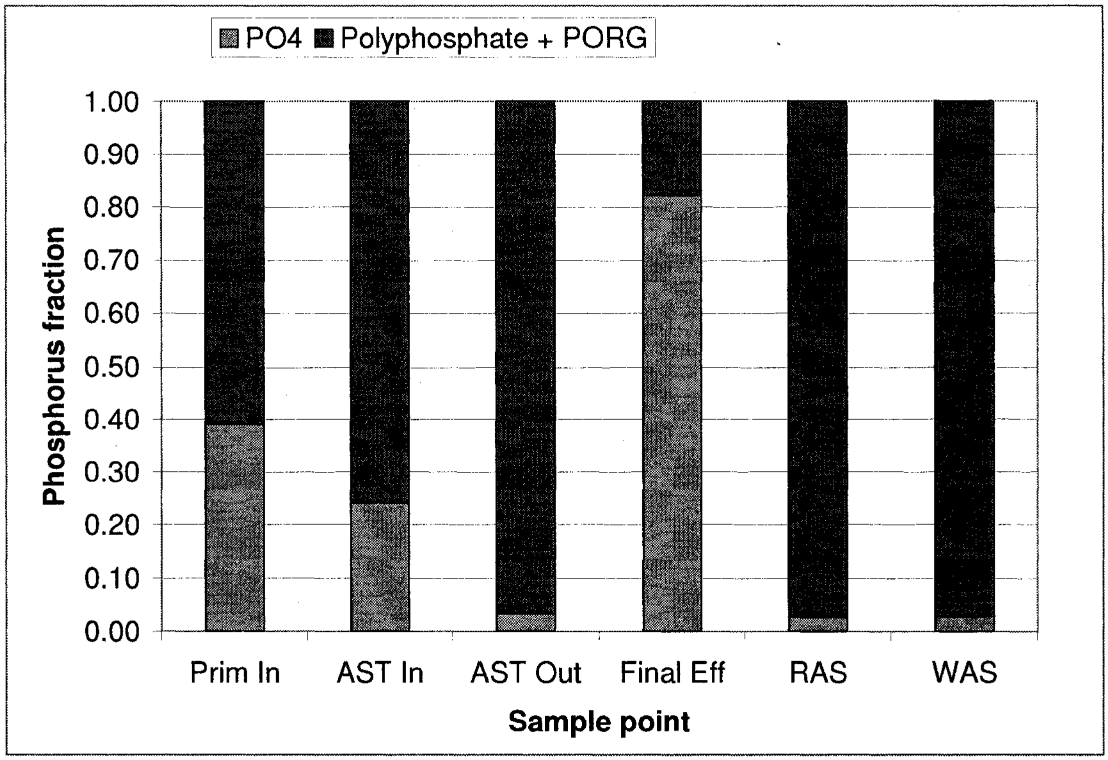


Figure 47: Phosphorus fractions

2.1.6.3. Steady state detection

Steady state detection was carried out according to the methodology outlined in the methodology section. While this steady state detection is based on key essentially independent parameters, it is useful to evaluate the behaviour of other process variables for the duration of each steady state. In particular, the behaviour of the on-line nutrients is of interest since nutrient dosing is, and will be based on these parameters. The rate at which nutrient dosing occurred will also be evaluated.

Nutrients: Nutrient dosing

Nitrogen

In terms of the behaviour of the nitrogen dosing rate during each steady state, it is clear from Figure 48 that the dispersion of data is very narrow for each steady state. In this diagram, the error bars represent one standard deviation from the average value. This result is to be expected since the nitrogen (urea) addition rate was used as one of the key parameters for steady state detection.

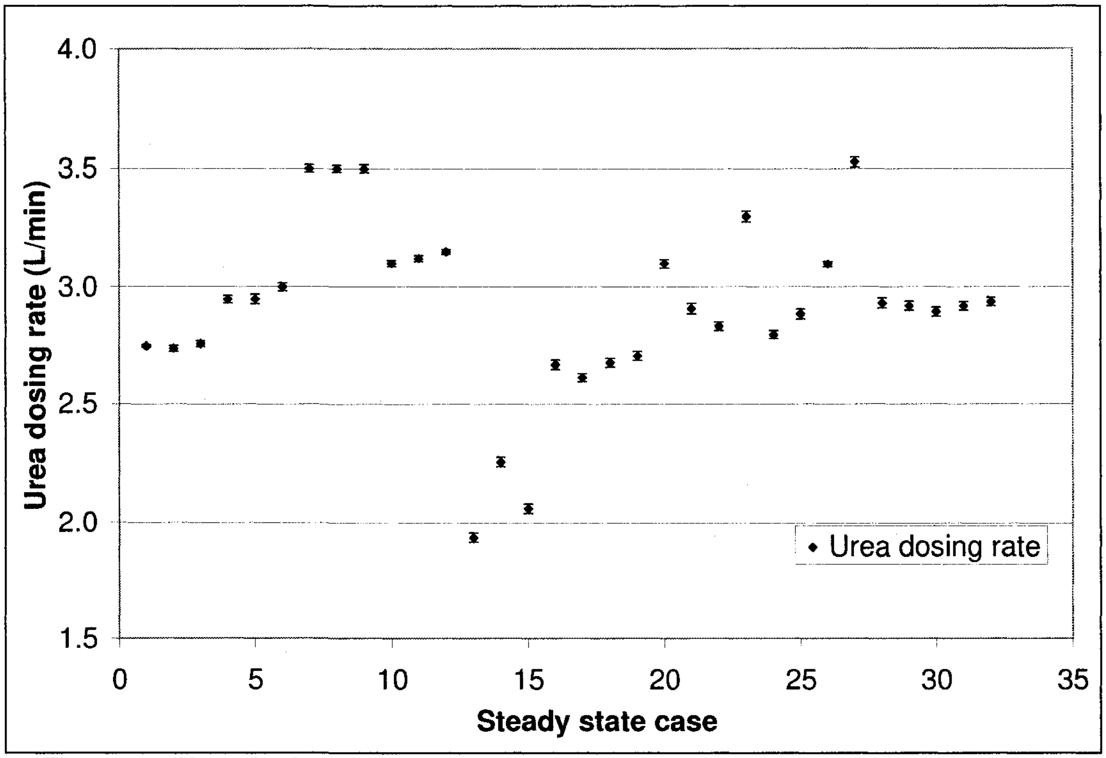


Figure 48: Urea dosing rate (L/min), error bars represent one standard deviation

Phosphorus

In terms of the behaviour of the phosphorus dosing rate during each steady state, it is clear from Figure 49 that the dispersion of data is extremely narrow for each steady state. In this diagram, the error bars represent one standard deviation from the average value. These results are consistent with the fact that the phosphorus (phosphoric acid) addition rate was determined to vary too little to even be used as one of the key parameters for steady state detection.

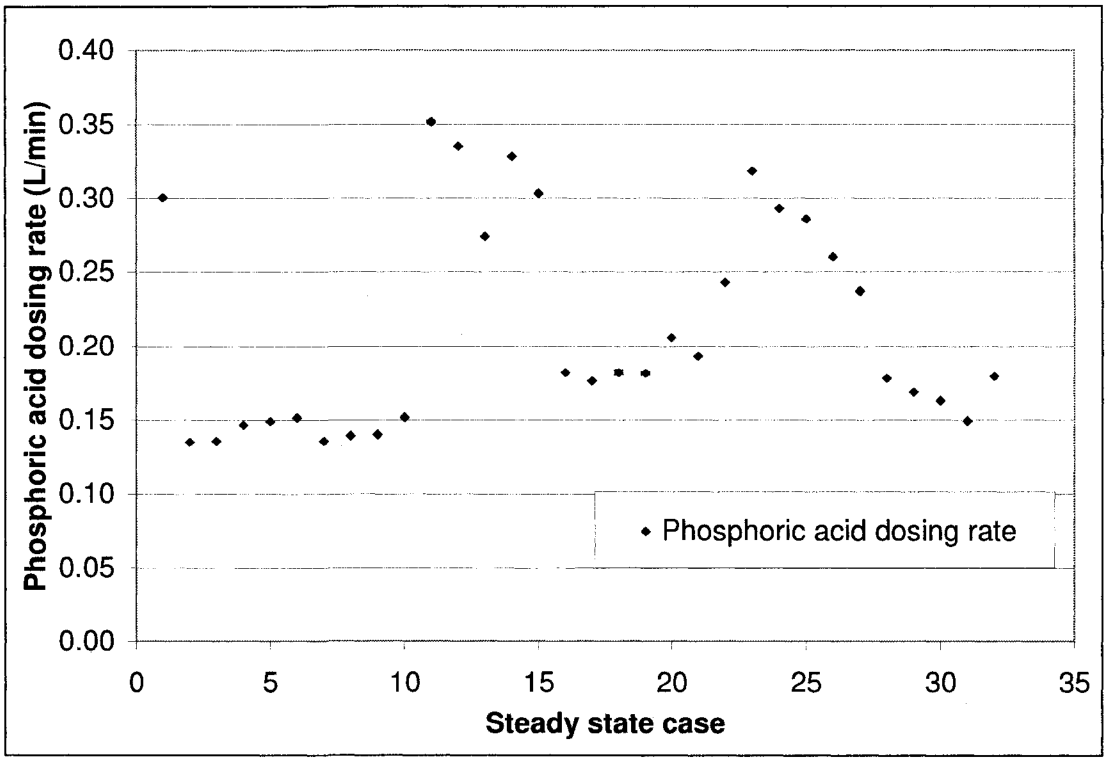


Figure 49: Phosphoric acid dosing rate (L/min), error bars represent one standard deviation

Final effluent nutrient residuals

Ammonia (Amtax)

The on-line measurements made with the Amtax instrument are represented in Figure 50 below, where the error bars represent one standard deviation above and below the average for each steady state. It is clear that there are at least 6 steady state conditions for which the ammonia measurement in the final effluent is not necessarily at steady state. The origin of the signal variation is most likely to be a build-up of algae in the instrument tank where the ammonia instrument is located, which was washed periodically by the operator.

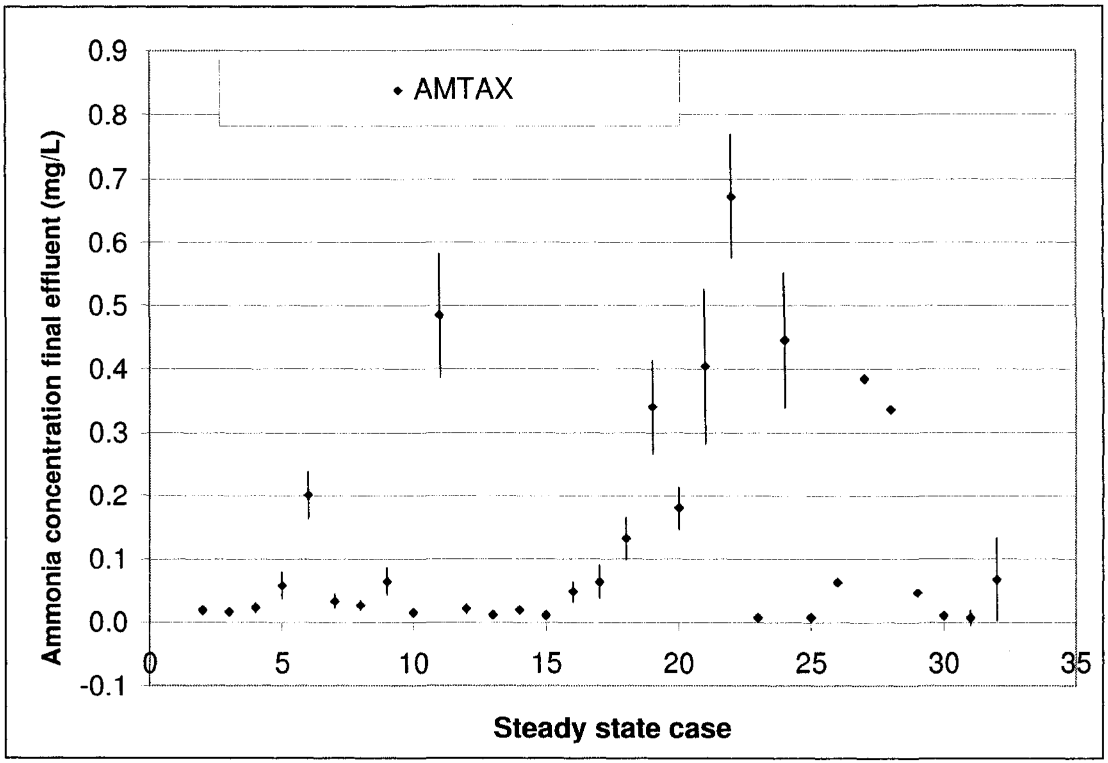


Figure 50: Final effluent ammonia concentration (mg N/L), error bars represent one standard deviation

Phosphorus

The on-line measurements made with the Phosphax instrument are represented in Figure 51 below, where the error bars represent one standard deviation above and below the average for each steady state. It is clear that there are at least 2 steady state conditions for which the ortho-phosphate measurement in the final effluent is not necessarily at steady state. The origin of the signal variation is most likely to be a build-up of algae in the instrument tank where the phosphorus instrument is located, which was washed periodically by the operator.

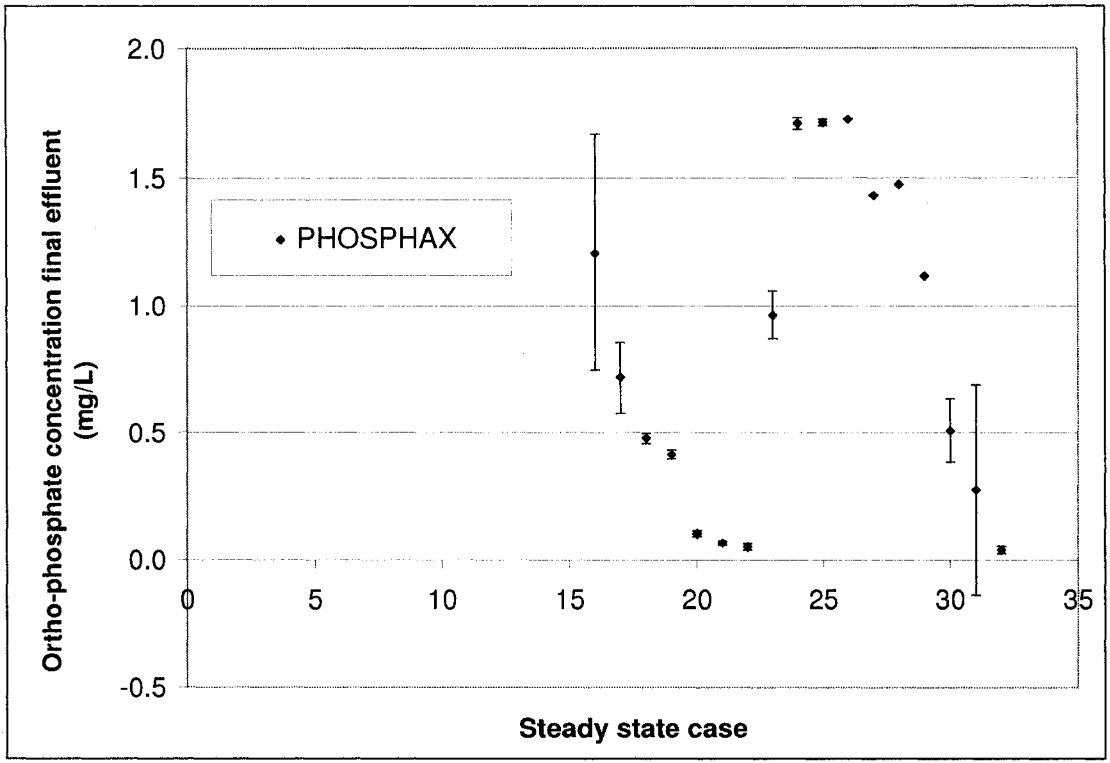


Figure 51: Final effluent ortho-phosphate concentration (mg P/L), error bars represent one standard deviation

APPENDIX 3
Mass Balance

3.1. Mass Balance

3.1.1. Raw Data

3.1.1.1. Flow

The results of the 32 steady states flow balances are shown in Table 67 below.

Table 67: Flow balance results (L/min)

Inlet Primary Clarifier	*Outlet Primary Clarifier*	*Primary Sludge*	*Press Filtrate*	*AST Inlet*	*WAS*	*RAS*	*Final Effluent*
17,468	17,167	301	1,525	18,692	1,200	12,243	17,492
18,856	18,482	375	1,366	19,848	650	13,438	19,198
18,154	17,762	392	1,305	19,067	650	12,891	18,417
18,291	17,916	375	1,068	18,984	650	12,833	18,333
18,770	18,470	300	1,178	19,648	800	13,193	18,848
18,939	18,679	260	1,021	19,700	750	13,265	18,950
18,437	18,227	210	1,051	19,278	787	12,943	18,490
18,321	18,046	275	1,389	19,435	1,000	12,904	18,435
18,509	18,234	275	1,238	19,471	1,000	12,928	18,471
19,332	19,057	275	1,061	20,118	800	13,522	19,318
17,794	17,535	259	1,202	18,737	700	12,626	18,037
18,264	18,014	250	1,019	19,033	714	12,822	18,319
17,846	17,571	275	969	18,540	641	12,528	17,899
18,432	18,182	250	1,066	19,248	641	13,025	18,607
18,199	17,970	229	1,091	19,060	559	12,948	18,501
18,420	18,220	200	1,553	19,773	680	13,365	19,093
18,547	18,338	210	1,400	19,738	624	13,378	19,114
18,462	18,262	200	1,379	19,641	680	13,272	18,961
18,678	18,478	200	1,242	19,721	679	13,330	19,041
19,389	19,190	199	1,125	20,315	751	13,694	19,564
18,167	17,920	247	976	18,896	840	12,637	18,056
18,391	18,141	250	1,062	19,203	840	12,855	18,363
19,169	18,879	290	873	19,752	721	13,321	19,031

Inlet Primary Clarifier	**Outlet Primary Clarifier**	**Primary Sludge**	**Press Filtrate**	**AST Inlet**	**WAS**	**RAS**	**Final Effluent**
19,163	18,873	290	1,006	19,880	721	13,412	19,159
18,972	18,685	287	761	19,446	680	13,135	18,766
19,710	19,409	300	470	19,880	541	13,537	19,339
20,374	20,083	291	979	21,062	500	14,393	20,562
20,878	20,532	346	534	21,066	437	14,440	20,629
18,894	18,533	360	649	19,182	451	13,110	18,731
19,523	19,154	369	513	19,667	450	13,452	19,217
19,539	19,164	375	810	19,973	420	13,688	19,553
20,094	19,718	375	180	19,898	321	13,704	19,578

3.1.1.2. Phosphorus

The results of the 32 steady states total phosphorus balances are shown in Table 68 below. These results represent the methodology described in the methodology section.

It is important to note that a single composite sample was available for the total phosphorus in the press filtrate, due to the lack of sample points in this stream. For this reason, the sample data taken on 30 May 2007 is assumed to correlate to the average WAS data, and the concentration of the filtrate phosphorus and nitrogen contents are assumed to vary in proportion to those average concentrations found for the WAS stream. This assumption is essential to completing the mass balances since the nutrient concentrations and the flow rate of the press filtrate are not normally measured.

With respect to the primary clarifier, the concentration of phosphorus in the inlet to the primary clarifier is assumed to be equal to the average concentration determined in the wastewater characterisation. A further assumption is made that the concentration of total phosphorus in the primary sludge is equal to the concentration in the inlet and outlet of the primary clarifier. These assumptions are necessary due to the lack of measurements at the outlet of the clarifier and at the primary sludge.

It is important to note that these mass balances do not close perfectly between the primary clarifier and the inlet to the AST basin. The phosphorus balance should close 100%, since no phosphorus can be generated within the AST basin.

It is thought that the addition rate of phosphoric acid is the most likely source of error due to the fact that the dosing rate is extremely low and the control equipment is oversized for this low flow rate. The level in the phosphoric acid dosing tank was used to try to confirm either the calculated or the measured phosphoric acid dosing rate, without success. The flow rate calculated from the tank level data differed from the measured flow rate value by 150% on average, and differed from the mass balance calculated flow rate value by 184% on average. Due to the lack of supporting data, the calculated phosphoric acid dosing rate will be used in further modelling exercises. Furthermore, in cases of phosphorus deficiency beyond the quantity of phosphoric acid addition to the process, the mass balance over the primary clarifier has been modified in order to close the phosphorus balance 100% in all cases.

Table 68: Total phosphorus balance results (kg P/d)

Inlet Primary Clarifier	*Outlet Primary Clarifier*	*Primary Sludge*	*Press Filtrate*	*PO4 Add (meas)*	*PO4 Add (calc)*	*AST Inlet (no RAS)*	*AST Outlet*	*WAS*	*RAS*	*Final Effluent*
20	20	0.4	21	170	243	284	1,204	262	920	22
22	21	0.4	20	77	161	203	1,295	154	1,093	49
21	21	0.5	20	77	161	202	1,253	154	1,051	47
21	21	0.4	16	83	160	197	1,243	154	1,046	43
22	21	0.3	17	84	174	212	1,248	183	1,036	29
22	22	0.3	15	86	152	189	1,281	180	1,092	10
21	21	0.2	15	77	146	182	1,207	181	1,025	1
21	21	0.3	18	79	168	207	1,119	206	911	2
22	21	0.3	16	80	164	200	1,081	198	881	2
22	22	0.3	14	86	136	173	1,159	170	986	3
21	20	0.3	16	199	110	146	1,034	143	888	3
21	21	0.3	13	190	114	148	1,046	146	899	2
21	20	0.3	13	155	121	154	1,045	133	890	22
21	21	0.3	13	186	138	172	1,032	123	860	49
21	21	0.3	14	172	124	158	1,032	110	873	49
21	21	0.2	21	103	152	193	1,157	143	964	51
22	21	0.2	19	100	120	160	1,152	135	992	26

Inlet Primary Clarifier	*Outlet Primary Clarifier*	*Primary Sludge*	*Press Filtrate*	*PO4 Add (meas)*	*PO4 Add (calc)*	*AST Inlet (no RAS)*	*AST Outlet*	*WAS*	*RAS*	*Final Effluent*
21	21	0.2	19	103	119	160	1,165	150	1,005	10
22	21	0.2	18	103	122	162	1,206	155	1,045	7
23	22	0.2	17	117	143	182	1,310	180	1,128	2
21	21	0.3	14	109	156	191	1,168	189	978	1
21	21	0.3	14	138	141	176	1,095	175	919	1
22	22	0.3	11	180	162	195	1,087	141	892	54
22	22	0.3	13	166	176	211	1,118	142	908	69
22	22	0.3	9	162	167	198	1,075	132	877	66
23	23	0.3	6	147	137	166	1,067	105	901	61
24	23	0.3	12	134	110	146	1,093	96	948	50
24	24	0.4	6	101	82	112	1,032	81	920	31
22	22	0.4	7	96	67	96	887	79	791	17
23	22	0.4	6	92	59	87	879	77	792	10
23	22	0.4	9	85	45	76	883	72	807	4
23	23	0.4	2	102	35	60	938	60	878	0

3.1.1.3. *Ortho-phosphate*

An ortho-phosphate mass balance was conducted over the streams contributing to the AST Inlet stream for further modelling work. The mass balance was based on the ratios of ortho-phosphate to total phosphorus determined for the press filtrate and the primary effluent streams, presented in Appendix 6, as well as the concentration of phosphorus in the calculated phosphoric acid addition stream, which was assumed to be completely available as ortho-phosphate.

The ortho-phosphorus balance over the return of the press filtrate to the outlet of the primary clarifier was calculated according to the equation:

Ortho-Phosphorus

$$O\text{-}P_{AST\text{-}inlet} * Q_{AST\text{-}inlet} = (0.2410 * TP_{PC\text{-}outlet} * Q_{PC\text{-}outlet}) + (0.5166 * TP_{Press\text{-}Filtrate} * Q_{Press\text{-}Filtrate}) + O\text{-}P_{ADDN} * Q_{ADDN}$$

The results of the ortho-phosphate balance are presented here in Table 69 in units of concentration (mg P/L) and load (kg P/d).

Table 69: Ortho-phosphate balance results

PO4 Add (calc)		***Press Filtrate***		***Outlet Primary Clarifier***		***AST Inlet***	
mg P/L	*kg P/d*	*mg P/L*	*kg P/d*	*mg P/L*	*kg P/d*	*mg P/L*	*kg P/d*
393,608	242.9	4.98	10.9	0.19	4.8	9.61	258.6
393,608	160.7	5.39	10.6	0.19	5.2	6.17	176.4
393,608	161.4	5.40	10.1	0.19	5.0	6.43	176.5
393,608	160.1	5.40	8.3	0.19	5.0	6.34	173.4
393,608	173.7	5.20	8.8	0.19	5.2	6.63	187.7
393,608	152.1	5.45	8.0	0.19	5.2	5.83	165.3
393,608	146.0	5.25	7.9	0.19	5.1	5.73	159.0
393,608	168.2	4.68	9.3	0.19	5.1	6.52	182.6
393,608	163.7	4.52	8.0	0.19	5.1	6.31	176.9
393,608	136.3	4.83	7.4	0.19	5.3	5.15	149.0
393,608	110.1	4.66	8.0	0.19	4.9	4.56	123.0
393,608	113.6	4.64	6.8	0.19	5.0	4.58	125.4
393,608	121.1	4.71	6.6	0.19	4.9	4.97	132.6
393,608	138.0	4.38	6.7	0.19	5.1	5.40	149.8
393,608	124.0	4.47	7.0	0.19	5.0	4.96	136.1
393,608	151.6	4.78	10.7	0.19	5.1	5.88	167.3
393,608	119.6	4.91	9.9	0.19	5.1	4.74	134.7
393,608	119.1	5.02	9.9	0.19	5.1	4.74	134.2
393,608	122.2	5.19	9.3	0.19	5.2	4.81	136.7
393,608	142.9	5.46	8.8	0.19	5.4	5.37	157.1
393,608	155.9	5.13	7.2	0.19	5.0	6.18	168.1
393,608	141.1	4.74	7.2	0.19	5.1	5.55	153.4
393,608	162.2	4.44	5.6	0.19	5.3	6.08	173.1
393,608	176.1	4.48	6.5	0.19	5.3	6.56	187.8
393,608	166.9	4.42	4.8	0.19	5.2	6.32	177.0
393,608	137.2	4.41	3.0	0.19	5.4	5.09	145.6
393,608	110.5	4.36	6.1	0.19	5.6	4.03	122.2
393,608	82.3	4.22	3.2	0.19	5.8	3.01	91.3
393,608	67.4	4.00	3.7	0.19	5.2	2.76	76.3

PO4 Add (calc)		Press Filtrate		Outlet Primary Clarifier		AST Inlet	
mg P/L	kg P/d	mg P/L	kg P/d	mg P/L	kg P/d	mg P/L	kg P/d
393,608	58.9	3.90	2.9	0.19	5.4	2.37	67.1
393,608	45.3	3.90	4.5	0.19	5.4	1.92	55.2
393,608	34.8	4.24	1	0	5.5	1.44	41

3.1.1.4. Solids

The results of the 32 steady states total suspended solids balances are shown in Table 70 below. With respect to the primary clarifier, the concentration of solids in the inlet and the outlet of the primary clarifier are assumed to be equal to the respective average concentrations determined in the wastewater characterisation.

Table 70: Total Suspended Solids balance results (kg TSS/d)

Inlet Primary Clarifier	Outlet Primary Clarifier	Primary Sludge	AST Outlet	WAS	RAS	Final Effluent
30,287	4,730	25,558	108,461	26,039	81,667	756
32,695	5,092	27,603	112,865	15,255	97,009	601
31,476	4,894	26,582	109,152	15,308	93,301	543
31,714	4,936	26,778	108,735	15,304	92,873	558
32,545	5,089	27,456	110,802	18,144	91,967	690
32,838	5,146	27,691	115,312	17,821	96,914	577
31,967	5,022	26,945	109,204	18,001	90,974	229
31,767	4,972	26,795	103,932	20,392	80,899	2,640
32,092	5,024	27,068	100,548	19,677	78,214	2,657
33,519	5,250	28,268	104,923	16,849	87,557	517
30,853	4,831	26,022	93,252	14,211	78,798	244
31,667	4,963	26,704	94,438	14,453	79,788	197
30,942	4,841	26,101	94,198	13,152	79,050	1,997
31,958	5,009	26,949	88,967	12,220	76,377	370
31,554	4,951	26,603	90,398	10,895	77,528	1,974
31,937	5,020	26,917	102,434	14,153	85,537	2,744
32,159	5,052	27,106	104,116	13,345	88,022	2,748

Inlet Primary Clarifier	*Outlet Primary Clarifier*	*Primary Sludge*	*AST Outlet*	*WAS*	*RAS*	*Final Effluent*
32,010	5,032	26,979	105,061	14,859	89,218	984
32,386	5,091	27,295	108,289	15,378	92,752	159
33,618	5,287	28,331	118,104	17,846	100,112	145
31,500	4,937	26,563	105,738	18,766	86,791	181
31,888	4,998	26,889	99,045	17,335	81,563	147
33,237	5,202	28,036	95,891	13,942	79,214	2,736
33,226	5,200	28,026	94,829	14,083	80,578	168
32,895	5,148	27,747	91,063	13,109	77,821	133
34,174	5,348	28,826	90,875	10,389	79,987	499
35,326	5,533	29,793	93,970	9,507	84,121	342
36,200	5,657	30,543	90,556	8,029	81,636	891
32,759	5,106	27,653	80,120	7,858	70,255	2,007
33,850	5,277	28,573	80,687	7,653	70,345	2,689
33,878	5,280	28,598	81,134	7,152	71,603	2,379
34,840	5,433	29,407	85,309	5,933	77,921	1,456

3.1.1.5. Carbon (COD)

The results of the 32 steady states total COD balances are shown in Table 71 below.

Table 71: Total COD balance results (kg COD/d)

Input COD	*Output COD*		
AST Inlet	*COD Oxidised*	*WAS*	*Final Effluent*
51,081	12,316	36,558	3,750
46,358	15,944	21,268	3,655
44,026	16,145	21,342	3,629
46,659	17,879	21,336	3,972
48,433	15,938	25,296	3,865
48,720	15,966	24,845	2,728
45,068	14,053	25,096	2,309
45,467	11,308	28,430	2,462

Input COD	Output COD		
AST Inlet	**COD Oxidised**	**WAS**	**Final Effluent**
45,712	9,748	27,432	2,566
47,764	13,631	23,490	2,692
41,555	14,231	19,812	1,504
41,794	14,694	20,150	1,871
40,884	17,333	18,336	2,681
41,565	14,229	17,036	3,090
44,172	15,380	15,190	3,104
44,274	13,925	19,731	2,973
44,961	13,658	18,605	2,889
44,669	13,685	20,715	2,782
45,891	14,707	21,439	2,632
53,670	13,716	24,881	2,628
49,635	12,991	26,163	2,547
48,687	12,856	24,168	2,581
49,419	13,972	19,437	5,656
47,787	15,976	19,634	4,647
47,247	15,071	18,276	3,108
52,098	20,511	14,484	3,992
55,636	19,125	13,254	4,387
50,926	17,060	11,193	4,684
48,953	15,693	10,955	4,431
48,519	14,832	10,669	4,665
48,954	14,273	9,971	4,797
49,381	14,381	8,271	3,989

3.1.1.6. Nitrogen

The results of the 32 steady states total nitrogen balances are shown in Table 72 below.

Table 72: Total Nitrogen balance results (kg N/d)

Input Nitrogen		***Output Nitrogen***			
AST Inlet	***Urea***	***NO3 Denitrified***	***WAS***	***NO3 Final Effluent***	***TKN Final Effluent***
153	1,038	0	2,470	0.08	0
162	1,035	19	1,437	78	2.3
156	1,042	20	1,442	80	1.9
155	1,113	9	1,442	90	2.6
160	1,114	0	1,709	89	6.9
161	1,132	0	1,679	86	24
157	1,321	39	1,696	65	3.8
159	1,321	23	1,921	64	3.1
159	1,321	12	1,854	64	7.5
164	1,170	0	1,587	66	1.8
153	1,179	7.5	1,339	10	55
155	1,189	5.5	1,361	7	2.4
151	731	0	1,239	137	1.3
157	853	3.2	1,151	0	2.2
156	777	0.31	1,026	0	1.3
161	1,009	0	1,333	0	5.8
161	987	0	1,257	0	7.7
160	1,012	0.39	1,400	0	16
161	1,023	2.4	1,449	0	41
166	1,170	12	1,681	0	22
154	1,098	0	1,768	0	46
157	1,069	0	1,633	0	77
161	1,246	0	1,313	0	0.89
162	1,057	0	1,327	0	54
159	1,089	0	1,235	0	0.90
162	1,169	11	979	0	7.7
172	1,332	26	896	1.3	50
172	1,107	16	756	4.4	44
157	1,103	8.6	740	5.9	5.5

Input Nitrogen		***Output Nitrogen***			
AST Inlet	***Urea***	***NO3 Denitrified***	***WAS***	***NO3 Final Effluent***	***TKN Final Effluent***
161	1,093	4.6	721	7.3	1.3
163	1,102	1.7	674	8.0	0.84
163	1,110	0	559	0	8.3

3.1.1.7. Ammonia-nitrogen

An ammonia-nitrogen mass balance was conducted over the streams contributing to the AST Inlet stream for further modelling work. The mass balance was based on the ratio of ammonia-nitrogen to total nitrogen determined for the primary effluent stream, presented in Appendix 6, as well as the concentration of nitrogen in the urea measured addition stream, which was assumed to be completely available as ammonia-nitrogen.

The ammonia-nitrogen balance over the return of the press filtrate to the outlet of the primary clarifier was calculated according to the equation:

Ammonia-Nitrogen

$$S_{NH4,\ AST\text{-}inlet} \ {}^{*}Q_{AST\text{-}inlet} = S_{NH4,\ PC\text{-}outlet\&Press\text{-}filtrate} \ {}^{*}Q_{PC\text{-}outlet\&Press\text{-}filtrate} + \mathbf{S}_{\mathbf{urea}} \ {}^{*}\mathbf{Q}_{\mathbf{urea}}$$

The results of the ammonia-nitrogen balance are presented here in Table 73 in units of concentration (mg N/L) and load (kg N/d).

Table 73: Ammonia-nitrogen balance results

Urea Addition		***Outlet Primary Clarifier & Press Filtrate***		***AST Inlet***	
mg N/L	kg N/d	mg N/L	kg N/d	mg N/L	kg N/d
262,200	1,038	0.026	0.70	38.6	1,039
262,200	1,035	0.026	0.75	36.2	1,035
262,200	1,042	0.026	0.72	38.0	1,043
262,200	1,113	0.026	0.71	40.7	1,114
262,200	1,114	0.026	0.74	39.4	1,114
262,200	1,132	0.026	0.74	39.9	1,133
262,200	1,321	0.026	0.73	47.6	1,322
262,200	1,321	0.026	0.73	47.2	1,322
262,200	1,321	0.026	0.73	47.1	1,322

Urea Addition		***Outlet Primary Clarifier & Press Filtrate***		***AST Inlet***	
mg N/L	kg N/d	mg N/L	kg N/d	mg N/L	kg N/d
262,200	1,170	0.026	0.76	40.4	1,171
262,200	1,179	0.026	0.71	43.7	1,179
262,200	1,189	0.026	0.72	43.4	1,190
262,200	731	0.026	0.70	27.4	732
262,200	853	0.026	0.72	30.8	854
262,200	777	0.026	0.72	28.3	778
262,200	1,009	0.026	0.74	35.4	1,009
262,200	987	0.026	0.74	34.7	988
262,200	1,012	0.026	0.74	35.8	1,012
262,200	1,023	0.026	0.74	36.0	1,024
262,200	1,170	0.026	0.76	40.0	1,170
262,200	1,098	0.026	0.71	40.4	1,099
262,200	1,069	0.026	0.72	38.7	1,070
262,200	1,246	0.026	0.74	43.8	1,246
262,200	1,057	0.026	0.75	36.9	1,057
262,200	1,089	0.026	0.73	38.9	1,090
262,200	1,169	0.026	0.75	40.9	1,170
262,200	1,332	0.026	0.79	43.9	1,333
262,200	1,107	0.026	0.79	36.5	1,108
262,200	1,103	0.026	0.72	39.9	1,103
262,200	1,093	0.026	0.74	38.6	1,094
262,200	1,102	0.026	0.75	38.3	1,103
262,200	1,110	0.026	0.75	38.7	1,110

3.1.2. Results & Discussion

There appears to be a cyclical nature to some of the mass balance data, particularly the phosphorus mass balance. While the data does not represent a continuous time series, the steady states are in chronological order, and this cyclical nature is evident in the time series in Figure 52, which also demonstrates that the majority of the steady state cases occurred within the months of April and May 2007, with only one steady state case in

February. For convenience sake, the rest of the results will be presented according to the steady state number on the horizontal axis.

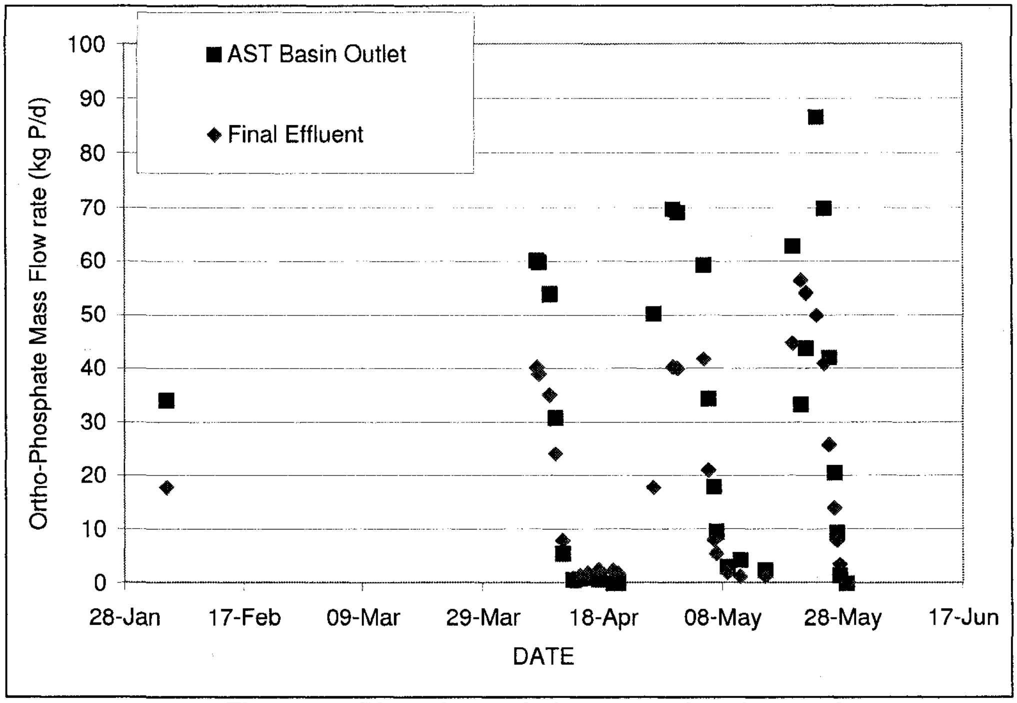


Figure 52: Phosphorus balance results: time series

3.1.2.1. *Flow*

The flow rate mass balance is based on the measured flow rates for the final effluent, RAS and WAS streams. Each steady state balance closes 100% and no data reconciliation has been carried out on the data. This flow rate data is used as the basis of each of the nutrient, COD and solids mass balances. The data is presented in Figure 53 and Figure 54 below.

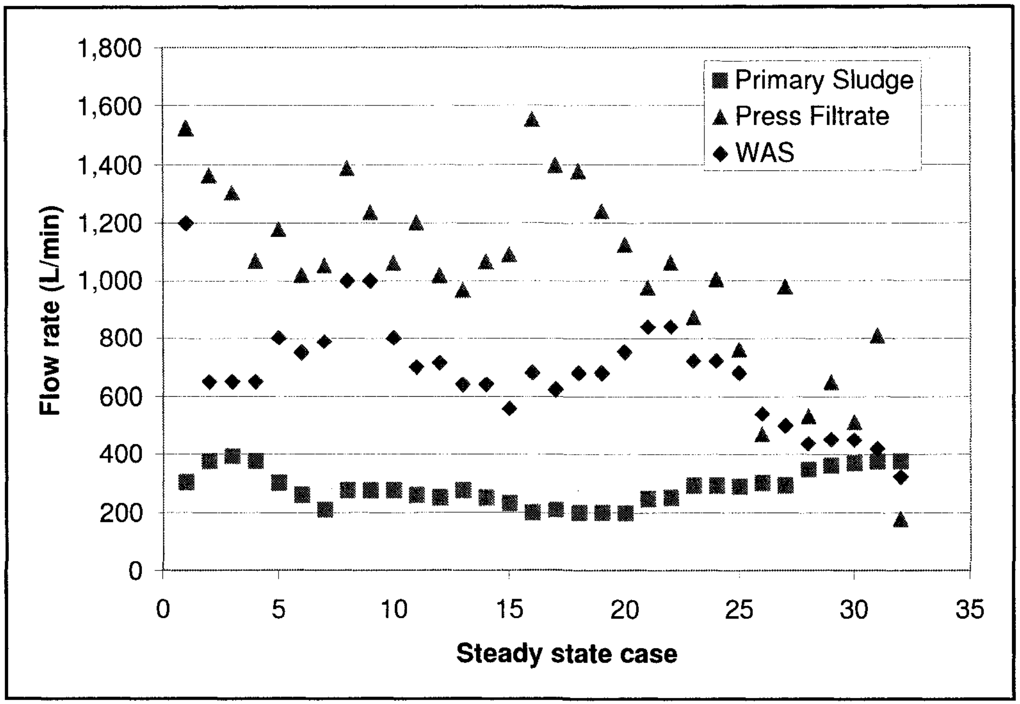


Figure 53: Flow balance data, low range (L/min)

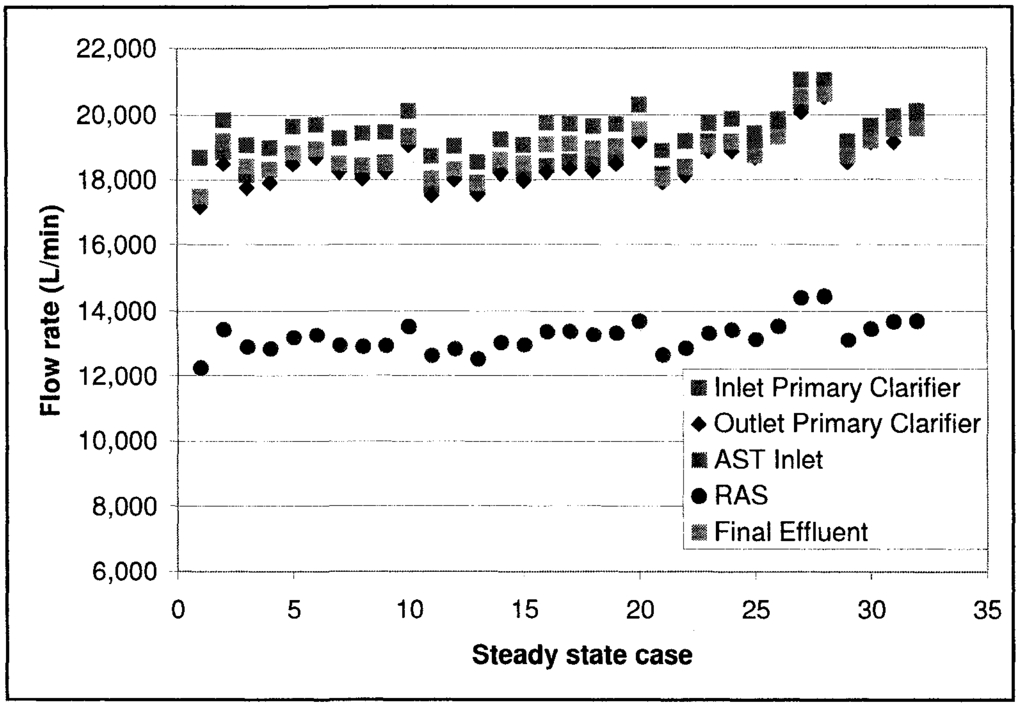


Figure 54: Flow balance data, high range (L/min)

3.1.2.2. *Phosphorus*

The fact that the mass balances do not close between the primary clarifier and the inlet to the AST basin can be attributed to the fact that the mass balance around the primary clarifier is based on:

- average wastewater characterisation data;
- the data at the final effluent is based on daily composite samples which are analysed at the site laboratory; and
- the quantity of phosphate added to the process is based on a controlled flow rate which is suspected to be poorly controlled.

In short, the data originates from a variety of sources, and the data has not been reconciled to take into account the relative reliability of each source.

Of the total phosphorus in the AST basin outlet, an average of 3.2% is present as ortho-phosphate, in the final effluent stream an average of 82% of the total is present as ortho-phosphate. Ortho-phosphate is the most easily assimilated form of phosphorus for a microorganism [72]. Other forms of phosphorus must be hydrolysed to the ortho-phosphate form, which is less efficient for the microorganisms than using ortho-phosphate available [72].

The total phosphorus in the press filtrate is a not significant source of phosphorus to the AST basins, accounting for up to 10% of the total phosphorus arriving at the AST inlet excluding the RAS stream, or approximately 1% of the total phosphorus to the AST inlet including the RAS stream. Figure 55 below demonstrates the relative contribution to total phosphorus from each of the streams into the inlet of the AST selectors, as percentages on the right-hand axis of the total phosphorus load (kg P/d) on the left-hand axis. This data makes use of the calculated phosphorus addition rate of phosphoric acid (not the measured value). Figure 56 below demonstrates the equivalent idea for ortho-phosphate, assuming all phosphoric acid added to the process is available as ortho-phosphate, and assuming average wastewater characterisation fractions (ortho-phosphate to total phosphorus) for the other streams.

The phosphoric acid addition becomes a much larger percentage of the phosphorus arriving at the AST selectors when the ortho-phosphate form is considered, in comparison to the total phosphorus form where the RAS stream provides the majority.

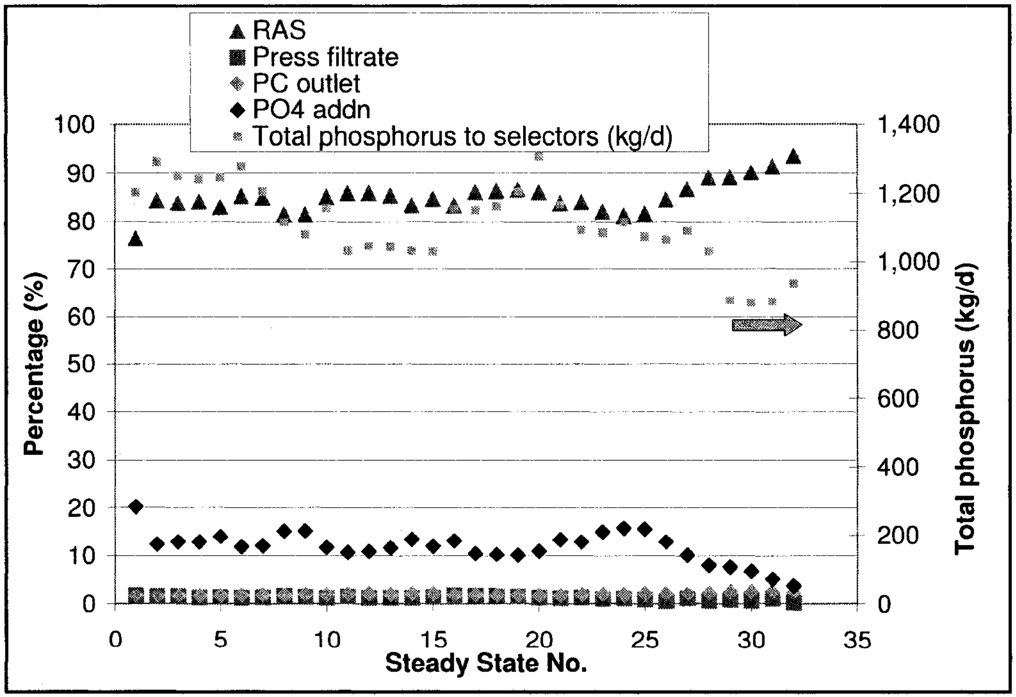


Figure 55: Total phosphorus to AST selectors (including RAS) (% right-hand axis, kg P/d left-hand axis)

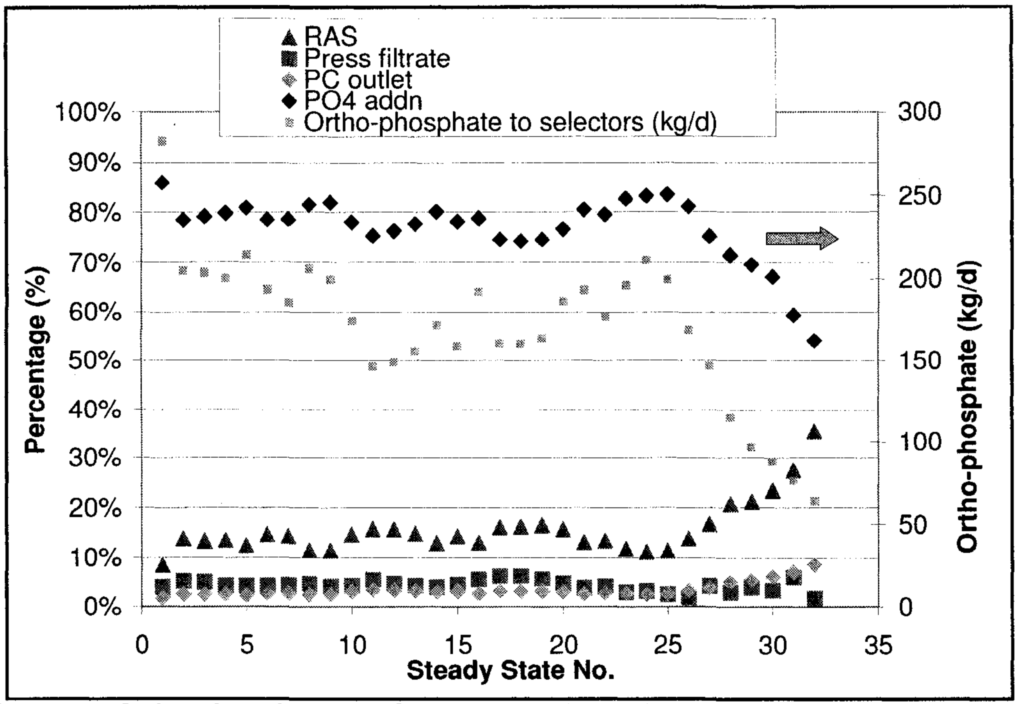


Figure 56: Ortho-phosphate to AST selectors (including RAS) (% right-hand axis, kg P/d left-hand axis)

3.1.2.3. Solids

The solids balance over the primary clarifier indicates good solids removal, 85%, based on the average wastewater characterisation data. There is no evaluation of the settleability or nature of these solids, although it can be noted from the wastewater characterisation that 99% to 100% of the total suspended solids concentrations in both the inlet and outlet of the primary clarifier are present as volatile suspended solids.

3.1.2.4. Carbon (COD)

The COD balances were carried out over the AST and secondary clarifier, as presented in Figure 57 below. The average percentage balance of the calculations was 75%, which refers to the ratio of mass flow rate output to mass flow rate input of COD to the secondary treatment system for each steady state process condition.

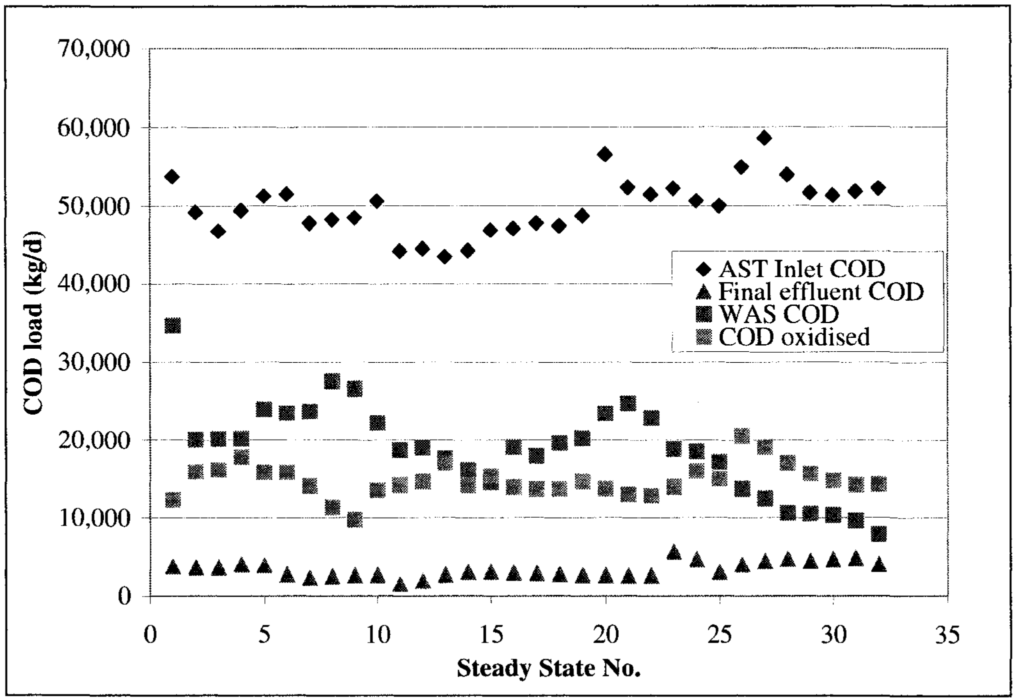


Figure 57: COD mass flow rates (kg COD/d), Secondary Treatment

3.1.2.5. Nitrogen

The nitrogen balances were carried out over the AST and secondary clarifier. The average percentage balance of the calculations was 106%. As discussed previously, both nitrification and denitrification were found to occur for some steady state conditions.

The total nitrogen in the press filtrate is a not significant source of nitrogen to the AST basins, accounting for up to 8% of the total nitrogen arriving at the AST inlet excluding the RAS stream, or approximately 1% of the total nitrogen to the AST inlet including the RAS stream. Figure 58 below demonstrates the relative contribution to total nitrogen from each of the streams into the inlet of the AST selectors, as percentages on the right-hand axis of the total nitrogen load (kg/d) on the left-hand axis. Figure 59 below demonstrates the equivalent idea for ammonia-nitrogen, assuming all urea added to the process is available as ammonia, and assuming average wastewater characterisation fractions for the other streams.

The urea addition becomes a much larger percentage of the phosphorus arriving at the AST selectors when the ammonia-nitrogen form is considered, in comparison to the total nitrogen form where the RAS stream provides the majority.

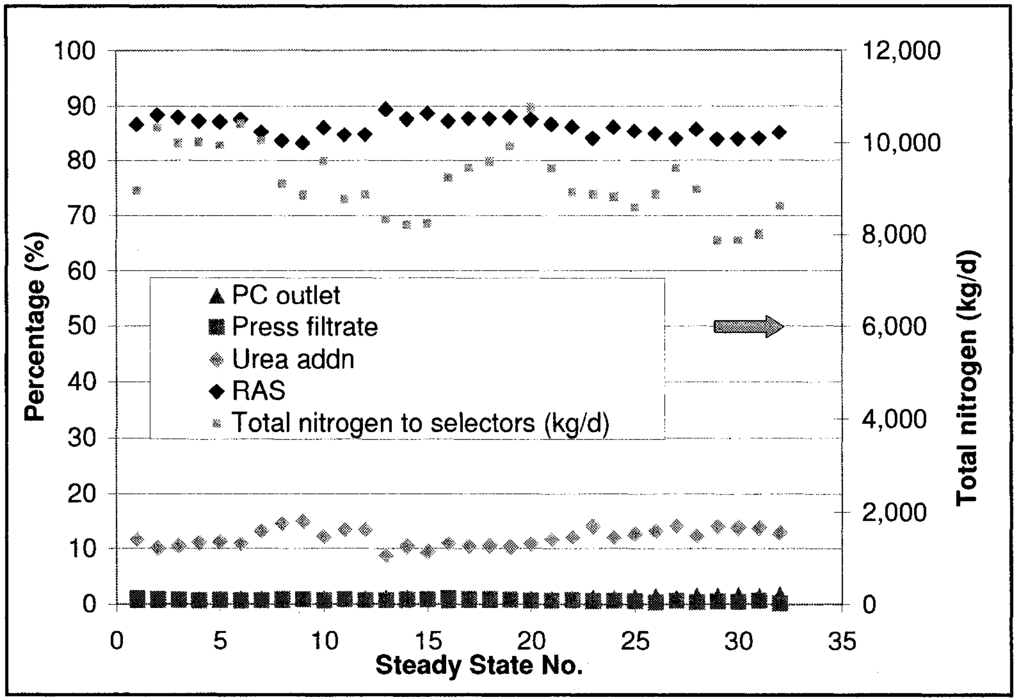


Figure 58: Total nitrogen to AST selectors (including RAS) (%, kg N/d left-hand axis)

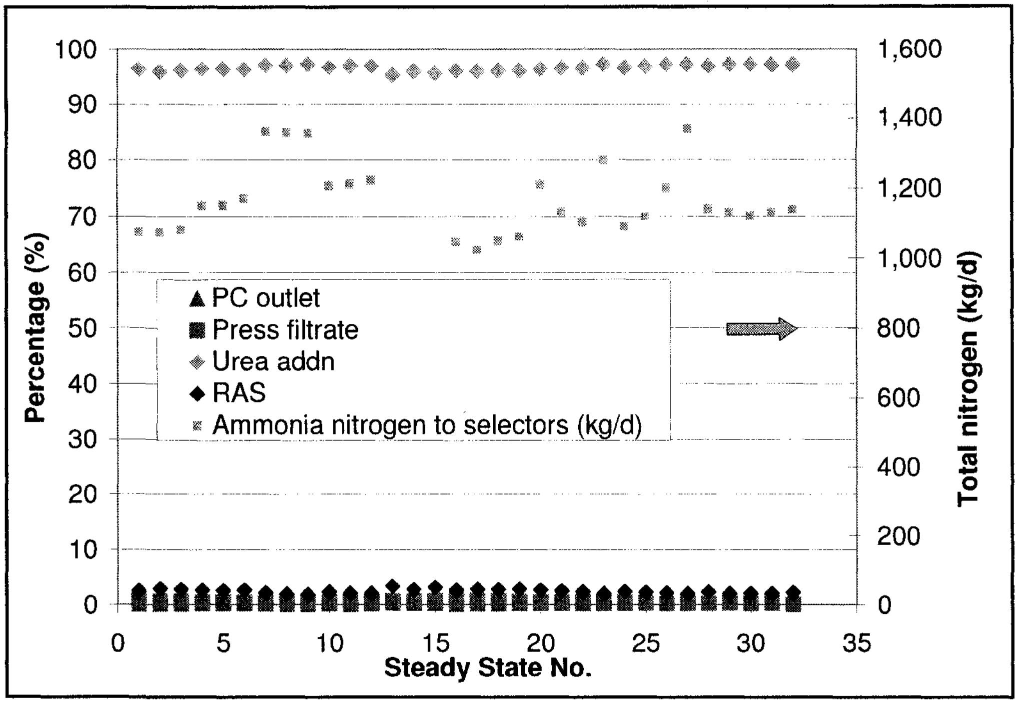


Figure 59: Ammonia nitrogen to AST selectors (including RAS) (%, kg N/d left-hand axis)

The quantity of nitrate formed due to the nitrification process can also be related to selector temperature, Figure 60, to the selector dissolved oxygen, Figure 61, and to the ammonia residual in the final effluent, Figure 62. There appears to be some correlation between the mass of nitrate formed and both of the first two process parameters, temperature and dissolved oxygen, and possibly an inverse correlation with the latter process parameter, final effluent ammonia concentration, each of which corresponds to theoretical knowledge of the nitrification process.

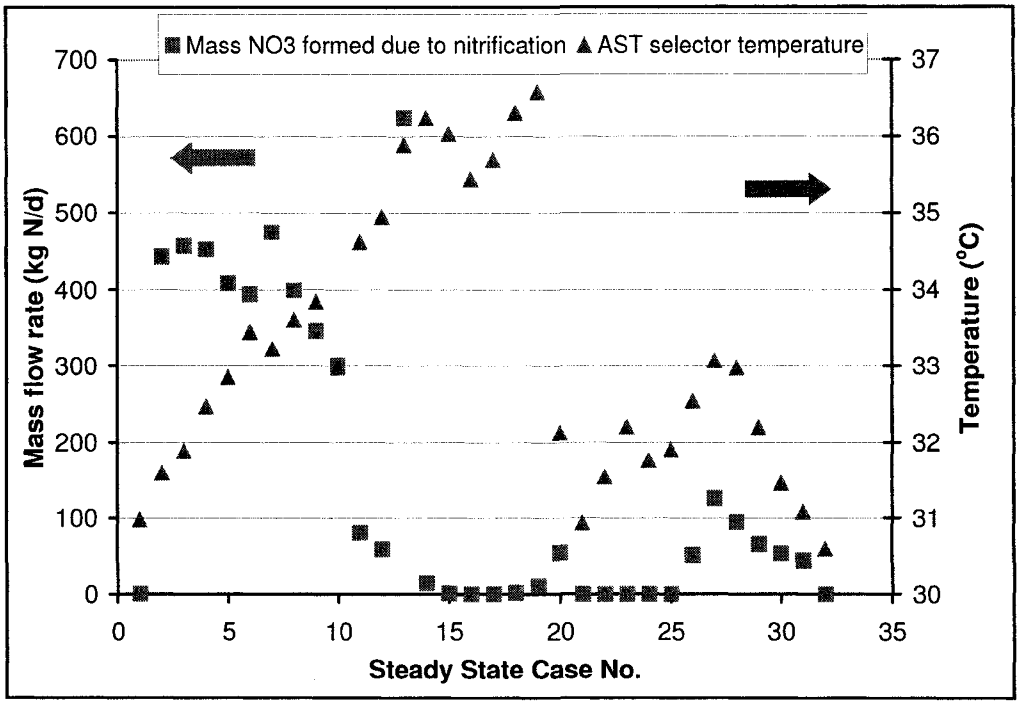


Figure 60: Nitrate formed due to nitrification vs. temperature

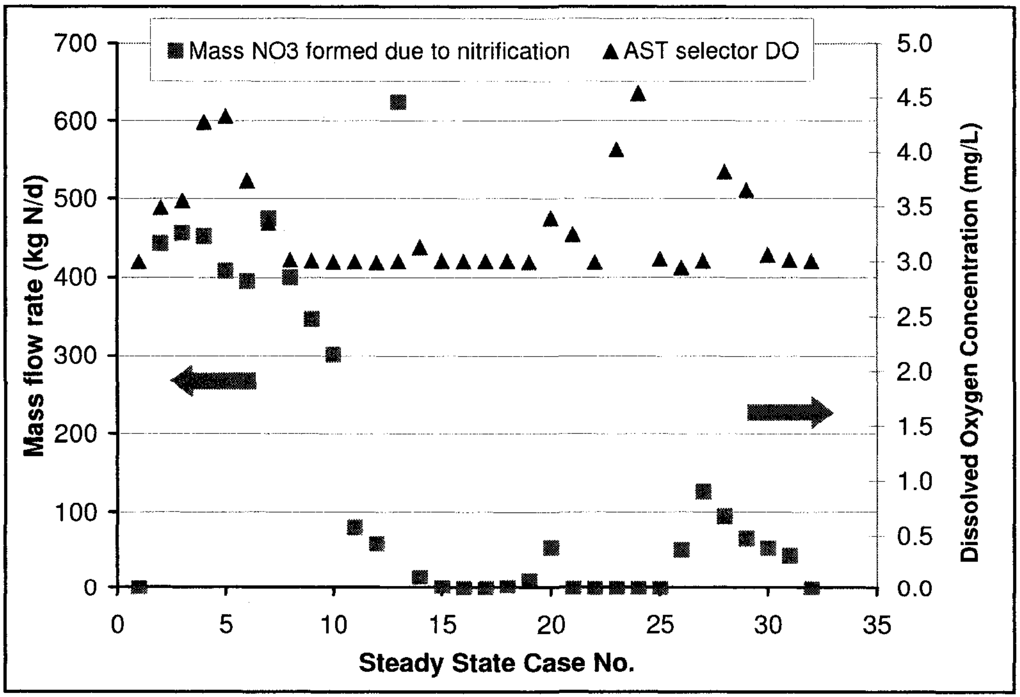


Figure 61: Nitrate formed due to nitrification vs. dissolved oxygen concentration

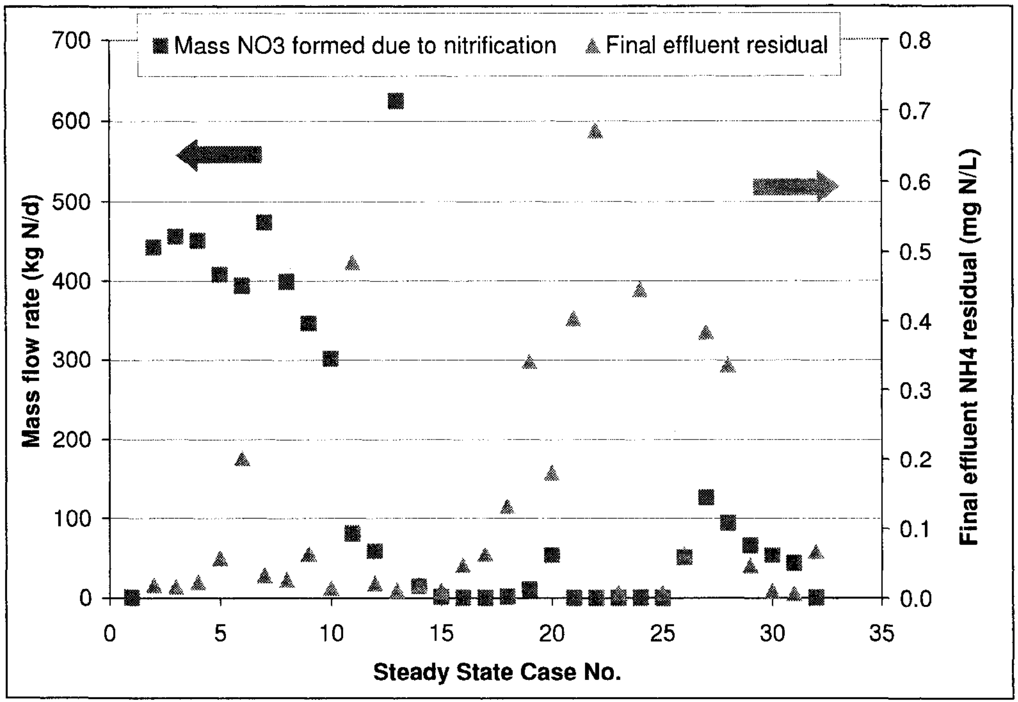


Figure 62: Nitrate formed due to nitrification vs. ammonia residual in final effluent

3.1.3. Process Simulation Parameter Specification

In addition to the measurements and calculations previously discussed, a number of steady state measurements must be specified for the process simulation, and they are described herein.

3.1.3.1. Steady State Cases

The concentration of nitrogen in the urea dosing flow is 0.262 kg N/L (262,000 mg N/L) and the concentration of phosphorus in the phosphoric acid dosing flow is 0.394 kg P/L (394,000 mg P/L). As noted in section 3.1.1.2, the phosphoric acid dosing rate is the calculated rate from the mass balance.

Table 74: Steady state cases flow rate, dissolved oxygen and SVI data for model (RAS, WAS total flow rate)

Steady state Case No.	*Temp*	*Influent Flow rate*	*Urea flow rate*	*Influent N conc**	*Phosphoric acid flow rate**	*Influent PO4 conc**	*Aerated selector DO set point*	*Aerated basins DO set point*	*RAS pumped rate*	*WAS underflow flow*	*Sludge volume index*
Units	*ºC*	*L/min*	*L/min*	*mg N/L*	*L/min*	*mg P/L*	*mg O_2/L*	*mg O_2/L*	*L/min*	*L/min*	*mL/g*
1	31.0	18,692	2.75	38.6	0.43	9.61	3.00	2.35	12,243	1200	208
2	31.6	19,848	2.74	36.2	0.28	6.17	3.49	0.99	13,438	650	140
3	31.9	19,067	2.76	38.0	0.28	6.43	3.55	0.99	12,891	650	124
4	32.5	18,984	2.95	40.7	0.28	6.34	4.28	1.00	12,833	650	119
5	32.9	19,648	2.95	39.4	0.31	6.63	4.33	1.01	13,193	800	137
6	33.5	19,700	3.00	39.9	0.27	5.83	3.74	1.00	13,265	750	159
7	33.2	19,278	3.50	47.6	0.26	5.73	3.35	1.00	12,943	787	170
8	33.6	19,435	3.50	47.2	0.30	6.52	3.02	1.11	12,904	1000	179
9	33.8	19,471	3.50	47.1	0.29	6.31	3.01	1.20	12,928	1000	186
10	33.0	20,118	3.10	40.4	0.24	5.15	3.00	1.18	13,522	800	184
11	34.6	18,737	3.12	43.7	0.19	4.56	3.00	1.20	12,626	700	175
12	34.9	19,033	3.15	43.4	0.20	4.58	2.99	1.31	12,822	714	198
13	35.9	18,540	1.94	27.4	0.21	4.97	3.00	1.79	12,528	641	190
14	36.2	19,248	2.26	30.8	0.24	5.40	3.13	1.03	13,025	641	173
15	36.0	19,060	2.06	28.3	0.22	4.96	3.01	1.26	12,948	559	183
16	35.4	19,773	2.67	35.4	0.27	5.88	3.00	1.73	13,365	680	210
17	35.7	19,738	2.61	34.7	0.21	4.74	3.00	1.54	13,378	624	206

Steady state Case No.	***Temp***	***Influent Flow rate***	***Urea flow rate***	***Influent N conc****	***Phosphoric acid flow rate****	***Influent PO4 conc****	***Aerated selector DO set point***	***Aerated basins DO set point***	***RAS pumped rate***	***WAS underflow flow***	***Sludge volume index***
Units	***ºC***	***L/min***	***L/min***	***mg N/L***	***L/min***	***mg P/L***	***mg O_2/L***	***mg O_2/L***	***L/min***	***L/min***	***mL/g***
18	36.3	19,641	2.68	35.8	0.21	4.74	3.00	1.35	13,272	680	202
19	36.6	19,721	2.71	36.0	0.22	4.81	3.00	1.16	13,330	679	200
20	32.1	20,315	3.10	40.0	0.25	5.37	3.40	1.45	13,694	751	219
21	30.9	18,896	2.91	40.4	0.28	6.18	3.25	1.46	12,637	840	271
22	31.5	19,203	2.83	38.7	0.25	5.55	2.99	1.66	12,855	840	190
23	32.2	19,752	3.30	43.8	0.29	6.08	4.02	1.01	13,321	721	184
24	31.8	19,880	2.80	36.9	0.31	6.56	4.54	1.06	13,412	721	168
25	31.9	19,446	2.88	38.9	0.29	6.32	3.02	2.94	13,135	680	145
26	32.5	19,880	3.10	40.9	0.24	5.09	2.95	1.27	13,537	541	128
27	33.1	21,062	3.53	43.9	0.19	4.03	3.01	1.13	14,393	500	109
28	33.0	21,066	2.93	36.5	0.15	3.01	3.82	0.99	14,440	437	91
29	32.2	19,182	2.92	39.9	0.12	2.76	3.65	1.01	13,110	451	83
30	31.5	19,667	2.89	38.6	0.10	2.37	3.06	1.09	13,452	450	79
31	31.1	19,973	2.92	38.3	0.08	1.92	3.01	1.71	13,688	420	75
32	30.6	19,898	2.94	38.7	0.06	1.44	3.00	1.17	13,704	321	79

*As calculated from the ortho-phosphate and ammonia-nitrogen mass balances

Table 75: Steady state cases target outputs

Steady state Case No.	AST MLSS	AST MLVSS	WAS TSS	RAS TSS	AST Outlet NH4	AST Outlet NO3	AST Outlet PO4	Final Effluent COD	Final Effluent TSS	Final Effluent VSS	Final Effluent NH4	Final Effluent NO3	Final Effluent PO4
Units	mg TSS/L	mg VSS/L	mg TSS/L	mg TSS/L	mg N/L	mg N/L	mg P/L	mg COD/L	mg TSS/L	mg VSS/L	mg N/L	mg N/L	mg P/L
1	2,435	2,319	15,066	4,632	0.45	0	0.76	149	30	30	0	0	0.70
2	2,355	2,192	16,305	5,013	0.191	2.02	1.25	132	22	22	0.019	2.80	1.45
3	2,372	2,221	16,347	5,026	0.216	2.17	1.30	137	20	20	0.016	3.02	1.47
4	2,373	2,255	16,346	5,026	0.231	2.16	1.18	150	21	21	0.023	3.41	1.33
5	2,343	2,233	15,744	4,841	0.310	1.86	0.65	142	25	25	0.058	3.29	0.89
6	2,429	2,310	16,501	5,074	0.38	1.57	0.11	100	21	21	0.201	3.16	0.29
7	2,354	2,238	15,876	4,881	0.717	2.24	0.013	87	9	9	0.033	2.44	0.033
8	2,232	2,126	14,160	4,354	1.18	1.88	0.017	93	99	99	0.026	2.41	0.053
9	2,155	2,056	13,664	4,201	1.46	1.63	0.020	96	100	100	0.065	2.40	0.066
10	2,166	2,073	14,625	4,497	0.595	0.53	0.014	97	19	19	0.015	2.37	0.086
11	2,065	1,962	14,096	4,334	1.85	0.39	0	58	9	9	0.485	0.39	0.088

Steady state Case No.	AST MLSS	AST MLVSS	WAS TSS	RAS TSS	AST Outlet NH4	AST Outlet NO3	AST Outlet PO4	Final Effluent COD	Final Effluent TSS	Final Effluent VSS	Final Effluent NH4	Final Effluent NO3	Final Effluent PO4
Units	mg TSS/L	mg VSS/L	mg TSS/L	mg TSS/L	mg N/L	mg N/L	mg P/L	mg COD/L	mg TSS/L	mg VSS/L	mg N/L	mg N/L	mg P/L
12	2,059	1,956	14,054	4,321	1.87	0.28	0	71	7	7	0.021	0.28	0.063
13	2,106	2,000	14,251	4,382	0.514	0.01	1.12	104	77	77	0.011	5.30	0.69
14	1,914	1,818	13,244	4,072	0.242	0.07	1.50	115	14	14	0.019	0	1.50
15	1,961	1,857	13,524	4,158	0.421	0	1.50	117	74	74	0.011	0	1.50
16	2,147	2,051	14,455	4,444	5.91	0	1.24	108	100	100	0.048	0	1.52
17	2,183	2,092	14,860	4,569	5.08	0	0.72	105	100	100	0.064	0	0.76
18	2,217	2,126	15,183	4,668	4.25	0	0.38	102	36	36	0.132	0	0.30
19	2,275	2,173	15,716	4,832	2.51	0.05	0.20	96	6	6	0.340	0	0.20
20	2,412	2,286	16,512	5,077	0.795	0.25	0.063	93	5	5	0.181	0	0.07
21	2,329	2,251	15,513	4,770	2.20	0	0.095	98	7	7	0.405	0	0.05
22	2,145	2,049	14,330	4,406	0.703	0	0.052	98	6	6	0.673	0	0.05
23	2,013	1,890	13,43	4,130	2.02	0	1.32	206	100	100	0.007	0	1.63

Steady state Case No.	**AST MLSS**	**AST MLVSS**	**WAS TSS**	**RAS TSS**	**AST Outlet NH4**	**AST Outlet NO3**	**AST Outlet PO4**	**Final Effluent COD**	**Final Effluent TSS**	**Final Effluent VSS**	**Final Effluent NH4**	**Final Effluent NO3**	**Final Effluent PO4**
Units	*mg TSS/L*	*mg VSS/L*	*mg TSS/L*	*mg TSS/L*	*mg N/L*	*mg N/L*	*mg P/L*	*mg COD/L*	*mg TSS/L*	*mg VSS/L*	*mg N/L*	*mg N/L*	*mg P/L*
			1										
24	1,978	1,871	13,570	4,172	2.86	0	0.69	168	6	6	0.446	0	2.04
25	1,941	1,851	13,382	4,114	3.00	0	0.93	115	5	5	0.008	0	2.00
26	1,889	1,793	13,346	4,103	0.787	0.24	1.80	143	18	18	0.064	0	1.79
27	1,841	1,748	13,200	4,059	0.988	0.54	1.37	148	12	12	0.385	0.05	1.38
28	1,771	1,682	12,769	3,926	0.701	0.41	0.82	158	30	30	0.336	0.15	0.87
29	1,723	1,636	12,103	3,721	0.502	0.31	0.44	164	74	74	0.047	0.22	0.51
30	1,692	1,607	11,811	3,631	0.373	0.25	0.20	169	97	97	0.010	0.26	0.28
31	1,674	1,589	11,815	3,633	0.303	0.20	0.03	170	84	84	0.007	0.28	0.12
32	1,763	1,674	12,842	3,949	0.999	0	0	141	52	52	0.068	0	0

APPENDIX 4
Published Articles

APPENDIX 4.1
Published Article 1

Nutrient, COD and solids mass balances for pulp and paper activated sludge wastewater treatment plants: the practical benefits for a TMP mill

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Abstract

Nutrient, COD and solids mass balances were conducted for an activated sludge treatment (AST) plant of an integrated TMP-newsprint mill, and the costs for nutrient addition (nitrogen and phosphorus) were evaluated. An interpretation of the nutrient transformation phenomena occurring in each of the major unit processes is presented, as well as an overview of the differences between municipal and pulp and paper effluent treatment with respect to nutrient transformation. The use of the activated sludge models (ASM) initially developed for municipal wastewater to model nutrient transformations is discussed. The practical benefits and cost savings for the

mill through better control of nutrient addition have been estimated at between CAN$13,000 and $85,000 annually.

Introduction

Nutrient limits are increasingly common in pulp and paper mill effluent discharge permits, making the control of nitrogen and phosphorus an important objective at an increasing number of mills. There are also cost reduction opportunities due to reductions in nutrient consumption, and the avoidance of potential capital cost for tertiary nutrient removal technologies. Activated sludge treatment (AST) plants have been installed in many pulp and paper mills for wastewater treatment, and it is the goal of this project to explore nutrient transformations in these systems.

Understanding and controlling nutrient discharge levels is complex, being a function of the raw effluent characteristics (biodegradability, variability), the AST system design (mixing characteristics, aeration technology), and perhaps most importantly, system operation including the nutrient addition control strategy. Modeling of pulp and paper treatment plants using the Activated Sludge Models (ASM) developed for the municipal wastewater industry offers the opportunity to improve the understanding of the biological treatment plant. Practical benefits that may arise from the modeling work include the development and implementation of a nutrient addition control strategy, with the possibility for automated nutrient dosing control. The emphasis of this work was to understand the nutrient transformations occurring in the AST plant with the longer-term objective of implementing a simple and practical control strategy.

In this paper, we present the results of nutrient, solids and COD mass balances carried out using current data and we review the practical benefits for a pulp and paper mill using modeling to better understand the operation of its wastewater treatment plant.

Background

Mill Process

The White Birch Papers pulp and paper mill is located in Gatineau, Québec, and consists of a single line thermo-mechanical pulping (TMP) process followed by a single newsprint paper machine. The pulping process is the world's largest single line TMP pulping process, producing over 740 ODt/d. The pulp is bleached using sodium hydrosulphite prior to storage. The paper machine produces newsprint predominantly from 100% TMP pulp.

The secondary wastewater treatment plant was constructed in 1995, and since January 2007, the mill has operated the wastewater treatment plant remotely from the boiler house. In order to assist with this change, the mill has automated various measurements. Notably, a UV chemical oxygen demand (COD) and multiple total suspended solids (TSS) meters were installed, as well as on-line residual nutrient measurements.

The wastewater plant process configuration (see Figure 63 below) encompasses coarse screening (mechanical bar screen), primary clarifiers, two selectors and AST basins operating in parallel, and two secondary clarifiers operating in parallel. The influent is cooled during summer months; this is not required during winter. An emergency basin is available for use under process upset conditions or for spills. The process does not incorporate an equalization basin, neutralization tank or tertiary treatment. Sanitary wastewater from the site is sent to the municipal sewer for off-site treatment. Storm water from roof run-off, landfill leachate and chip pile run-off are treated.

Each AST line has submerged venturi (jet) aerators in a well-mixed basin. The AST basins are oversized for the current influent from the mill due to process modifications to the pulp and paper mills. Nutrients are dosed into the inlet of the aerated selector in the form of urea and phosphoric acid. Primary and secondary sludge flows are mixed without any upstream dewatering. The mixed primary and secondary sludge is treated via a gravity table pre-thickener followed by a belt press. The dewatered sludge is stored for a maximum of 8 to 12 hours prior to disposal by composting and agricultural land-spreading.

Municipal vs. pulp & paper wastewater treatment

Domestic (raw) wastewater contaminants consist principally of organic carbon compounds, as does pulp and paper wastewater and other industrial wastewaters [26, 27]. Certain other industrial wastewaters, such as those from mining and petrochemical processing, consist of inorganic pollutants or complex organic pollutants such as aromatic compounds, which are toxic in high concentrations to microorganisms which may render the wastewater unsuitable for biological treatment processes [28].

On the other hand, municipal wastewater and its treatment is inherently different to that of pulp and paper wastewater in many ways, not least being the fact that pulp and paper wastewater often lacks readily available macronutrients such as nitrogen and phosphorus whereas municipal wastewater typically contains these nutrients in excess of the requirements of microorganisms used to consume the organic load in the wastewater. For municipal wastewaters, this has required the development of the biological nutrient removal (BNR) processes such as nitrification-denitrification and biological phosphorus (bio-P) removal.

Typical characteristics of primary treated pulp mill wastewaters from a bleached kraft mill (BKM), a thermomechanical mill (TMP) and a linerboard mill were presented by Slade *et al.* [30]. The pulp mill wastewater characteristics can be compared with the wastewater characterisation carried out for a municipal wastewater treatment plant in the Netherlands, as presented in the right-hand column of Table 76 [31]. From the data in Table 76, it can be seen that pulp mill primary treated wastewater contains a relatively high load in terms of COD and BOD concentrations and relatively deficient in the nutrients nitrogen and phosphorus when compared to primary treated municipal wastewater.

Table 76: Pulp mill and municipal primary treated wastewater characteristics [30, 31]

Parameter	***BKM***	***TMP***	***Linerboard***	***Municipal (average)***
COD tot (mg/L)	490 – 590	2,200 – 3,300	1,040 – 1,450	604
COD sol (mg/L)	430 – 480	1,540 – 2,240	890 – 1,250	241 [a]
BOD_5 (mg/L)	150 – 190	1,000 – 1,460	510 – 880	246
TSS (mg/L)	10 – 115	240 – 400	70 – 150	309
VSS (mg/L)	10 – 80	230 – 390	70 – 120	
TN (mg/L)	1.1 – 1.7	5.5 – 10.9	4.4 – 6.4	69
TN_{sol} (mg/L)	0.8 – 0.9	2.3 – 3.7	2.6 – 3.6	
NH_4^+-N (mg/L)	ND [b]	0.1 – 0.6	0.03 – 0.06	53
NO_x (mg/L)	0.07 – 0.08	0.0 – 0.1	1.4 – 2.0	0.1
TP (mg/L)	0.6	2.9 – 5.8	0.9 – 1.4	8.4
DRP (mg/L) [c]	0.5	1.4 – 3.7	0.05 – 0.15	5.2
BOD_5: N	100:0.6 – 100:0.7	100:0.5 – 100:1	100:0.9	
BOD_5: P	100:0.4	100:0.3 – 100:0.4	100:0.15	

Parameter	***BKM***	***TMP***	***Linerboard***	***Municipal (average)***
pH	7.9 – 8.0	4.8 – 5.3	5.1 – 7.0	

a - CODsol represents soluble COD in the filtrate of a 0.45μm filtered sample;
b - ND = not determined;
c - DRP = dissolved reactive phosphorus.

Nutrient addition and control

The BOD_5:N:P mass ratio of 100:5:1 has its origins in the dry-basis contents by weight of a typical bacterial cell, and the assumption that bacterial cells require the macronutrients nitrogen and phosphorus in proportion to the composition of cell biomass [39]. Sludge age and temperature influence the actual macronutrient requirements [68]. For pulp and paper wastewater treatment using AST technology, BOD_5:N:P ratios have been reported for stable plant operation from 100:3.5:0.6 [10] to lower limits suggested for BOD_5:N of 100:2.5 to 100:4.5 and BOD_5:P of 100:0.4 to 100:0.6 [63, 64]. Assuming the influent from the mill is nutrient deficient, that the activated sludge process has a short enough residence time that nitrogen fixation and cell lysis provide inadequate nutrient, then the nutrient requirements for the aerated basin must be met by the addition of supplemental nutrients.

Nutrient addition strategies are determined primarily by the desired result and subsequently by the desired accuracy, precision and complexity of the process. Possible desired results include the minimisation of effluent concentrations (BOD_5, N, P) or the minimisation of nutrient dosage quantities, whilst maintaining stable process operation and efficient BOD removal [65]. The major benefit of feed-forward control is the ability of the control loop to react swiftly to changes in influent quality, for example to load or flow variations [126]. Feed-back control reacts less efficiently to process upset conditions, but has the advantage of greater accuracy of control [126].

Current nutrient control at this mill is feed-forward based on a target BOD_5:N:P mass ratio for the dosage for both nutrient supplemental chemicals: urea and phosphoric acid. The ratios are calculated on the COD measured with the UV on-line COD meter. The ratios are also a function of the nutrient solution specific gravity and concentration, as well as the wastewater COD: BOD_5 ratio. At this mill, the COD: BOD_5 ratio has been established over the 12 months of 2006 to be 2.36 with a standard deviation of 0.33, during normal plant operation for BOD_5 and filtered COD measured in the inlet to the aerated basins.

The purpose of the installation of the on-line nutrient residual measurements for ammonia-nitrogen and ortho-phosphate is to add an element of feed-back control to the existing feed-forward nutrient control strategy. One ion-sensitive electrode ammonia-nitrogen (NH4-N) and one colorimetric ortho-phosphate (PO4-P) instrument were installed in the final effluent to monitor nutrient residuals.

Overdosing nutrients to the activated sludge process is both costly and can potentially cause eutrophication or toxicity if the nutrient concentrations in the discharged effluent are high enough. There are also adverse effects of under-dosing nutrients; in particular nutrient deficiency can lead to filamentous bulking events, production of viscous exocellular material (polysaccharide), or production of foaming exocellular material [68]. These types of process upsets can lead to poorly settling sludge which may lead to increased nutrient concentrations in the final effluent, or may require additional chemical dosing. The costs associated with these events are not insignificant.

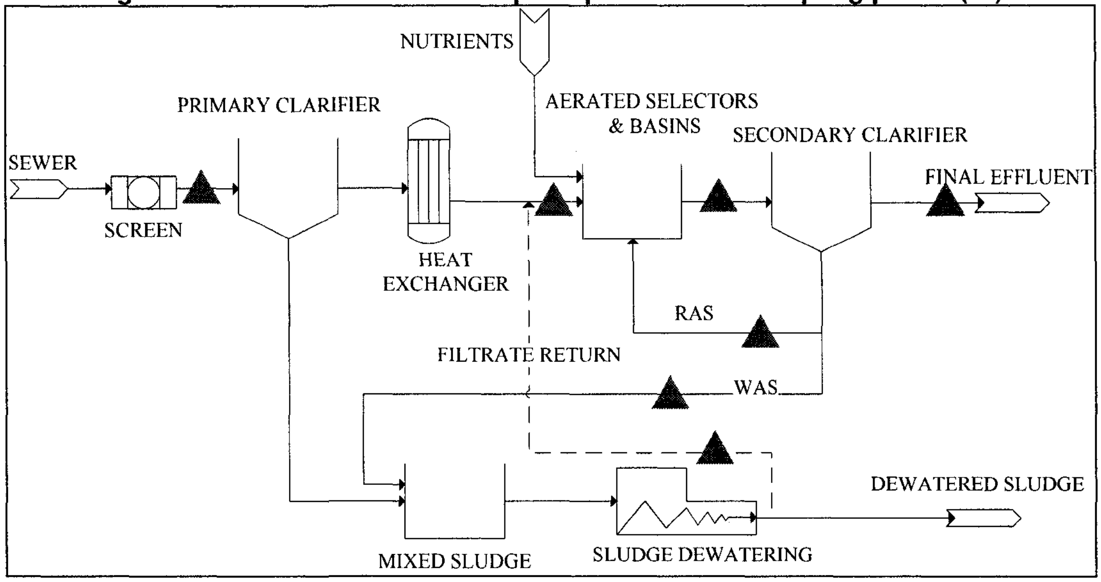
Methodology

Nutrient measurements

On-line measurements were installed at the final effluent for ammonia-nitrogen (NH4-N) and ortho-phosphate (PO4-P). Comparisons were conducted between laboratory measurements and the on-line measurements, and the operators eventually had an equal or greater confidence in the on-line instruments than the laboratory instruments.

Nutrient, solids and COD fractionation were carried out on process streams on a number of occasions during a four month period; the sampling points are indicated by triangles in Figure 63. The sample filtration for the COD fractionation was carried out using a Pall-Gelman Supor polyethersulfone membrane of porosity 0.1µm to determine soluble COD (sCOD), and a Pall Type A/E glass fiber filter of porosity 1.0µm to determine filtered COD (fCOD). The testing methods used were Standard Methods plus the HACH method for COD. Regarding the on-line measurements, the on-line UV COD meter was calibrated on site to COD filtered using a Pall Type A/E glass fiber filter of porosity 1.0µm. The samples for both of the nutrient residual measurements in the final effluent are filtered to 0.15µm. Filtering wastewater using such a fine filter is designed to exclude the effect of organic nutrients in residual biomass; it was found that different filter porosities gave different results.

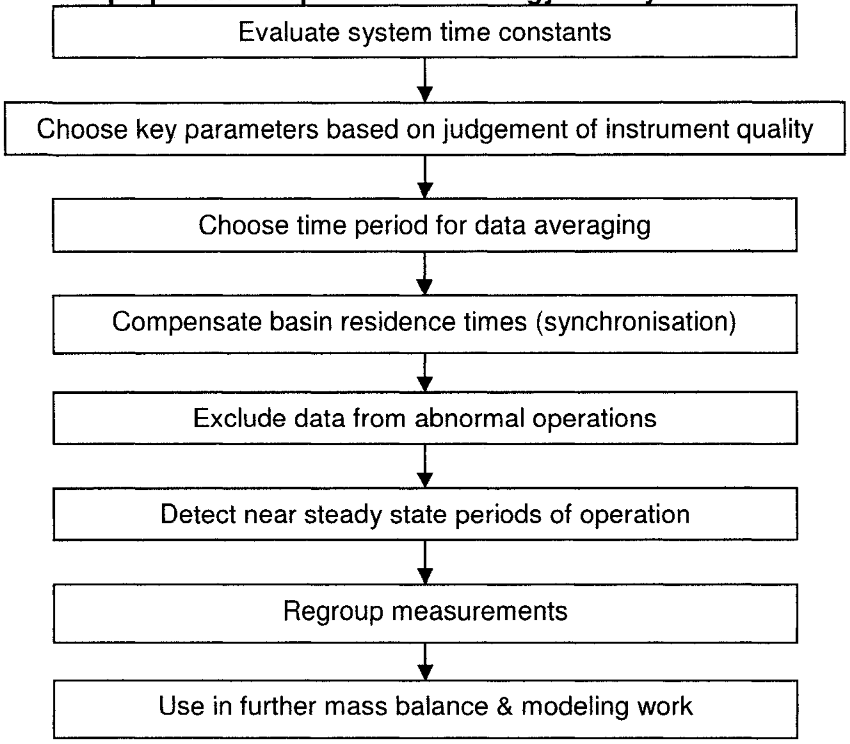
Figure 63: Wastewater treatment plant process and sampling points (▲)



Nutrient balances

Process steady states were established by evaluating the derivative of a number of key measured variables in the aerated selector and aerated basin, according to the methodology outlined in Figure 64. Data synchronization was not necessary for steady state detection since all key parameters were located within one hour residence time from each other whereas the steady state duration was set to be greater than six hours. Non-flow data were synchronized between the aerated selector and the outlet of the aerated basin, using the basin residence time of approximately 16 hours, for the purpose of the nutrient, COD and solids mass balances. The 32 steady states detected range in duration from six to thirty-two hours; the data were averaged over the duration of each steady state for further analysis.

Figure 64: Data preparation step-wise methodology: steady state detection



Mass balances were conducted over the major process units including the aerated selector and basin, as well as the primary and secondary clarifiers. The mass balances were used to calculate unknown parameter values. The phosphorus and solids mass balances were developed by Meijer *et al.* [31], and the COD and nitrogen mass balances were developed by Barker and Dold [135]. A volumetric flow balance is considered valid assuming water density is not changing, and assuming negligible evaporation in the basins. Phosphorus, unlike COD and nitrogen, does not transform into gaseous forms in the wastewater process, and therefore the phosphorus mass balance can be closed [31]. As proposed by Meijer *et al.*, the phosphorus mass balance was performed first due to the simplicity of the balance and transformation mechanisms [31].

Results

Wastewater characterisation results

Nutrient, solids and COD fractionation, or wastewater characterization, tests were carried out on process streams on a number of occasions during the four month period; tests were conducted on the press filtrate on a single occasion. The results of these fractionation tests are presented in Table 77 to Table 80, in terms of the average values and ranges of measured variables. These wastewater characterization results are separate and distinct from the steady state calculations that follow.

Table 77: Solids fractionation results - averages

Stream	***VSS (mg/L)***		***TSS(mg/L)***	
	Average	***Range***	***Average***	***Range***
PC Inlet	1,211	216 – 5,637	1,222	212 – 5,703
AST Inlet	194	113 – 286	190	86 – 288
AST Outlet	2,016	1,722 – 2,616	2,140	1,806 – 2,758
Final Effluent	16	8 – 39	15	3 – 40
RAS	4,205	3,410 – 5,100	4,462	3,612 – 5,404
WAS	12,772	9,100 – 15,468	13,567	9,717 – 16,351

Table 78: Phosphorus fractionation results - averages

Stream	***PO4-P (mgP/L)***		***TP (mgP/L)***	
	Average	***Range***	***Average***	***Range***
PC Inlet	0.32	0.04 – 0.5	0.81	0.3 – 1.2
AST Inlet	0.26	0.03 – 0.4	1.07	0.9 – 1.3
AST Outlet	0.76	0.04 – 2.0	23.4	19.0 – 31.3
Final Effluent	0.81	0.03 – 1.8	1.0	0.2 – 2.4
RAS	1.29	0.2 – 2.1	49.5	41.6 – 56.8
WAS	3.91	2.0 – 5.8	143	95.7 – 194.0
Press Filtrate	4.69	-	9.09	-

Table 79: Nitrogen fractionation results - averages

Stream	***NO_3 (mg N/L)***		***NH_{3+4} (mg N/L)***		***N_{ORG} (mg N/L)***		***TN (mg N/L)***	
	Average	***Range***	***Average***	***Range***	***Average***	***Range***	***Average***	***Range***
PC Inlet	0.18	0 – 0.9	0.01	0 – 0.1	5.85	1.9 – 11.9	6.03	1.9 – 11.9
AST Inlet	0.03	0 – 0.1	0.03	0 – 0.1	5.61	3.5 – 10.6	5.67	3.5 – 10.6
AST Outlet	0.73	0 – 4.6	1.6	0 – 6.6	154	143 – 202	156	148 – 202
Final Effluent	1.04	0.01 – 4.7	0.8	0 – 3.6	3.3	2.7 – 5.9	5.1	3.8 – 9.1
RAS	0.02	0 – 0.1	1.1	0.6 – 3.6	328	284 – 380	329	288 – 381
WAS	0.03	0 – 0.1	2	0.5 –	958	685 –	960	686 –

Stream	NO_3 (mg N/L)		NH_{3+4} (mg N/L)		N_{ORG} (mg N/L)		TN (mg N/L)	
	Average	Range	Average	Range	Average	Range	Average	Range
				3.5		1206		1208
Press Filtrate	0.057	-	3.87	-	38.9	-	42.9	-

Table 80: COD fractionation results - averages

Stream	sCOD (mg/L)		fCOD (mg/L)		CODt (mg/L)	
	Average	Range	Average	Range	Average	Range
PC Inlet	1,297	1,134 – 1,638	1,658	1,538 – 1,744	3,602	3,396 – 3,840
AST Inlet	1,096	924 – 1,258	1,628	1,308 – 1,818	1,918	1,130 – 2,180
AST Outlet	83	66 – 105	99	80 – 119	3,399	3,060 – 3,685
Final Effluent	81	66 – 94	91	70 – 109	110	79 – 135
RAS	86	76 – 110	99	85 – 122	8,504	7,000 – 10,464
WAS	179	136 – 268	249	180 – 325	40,000	31,806 – 46,686
Press Filtrate	457	-	505	-	1676	

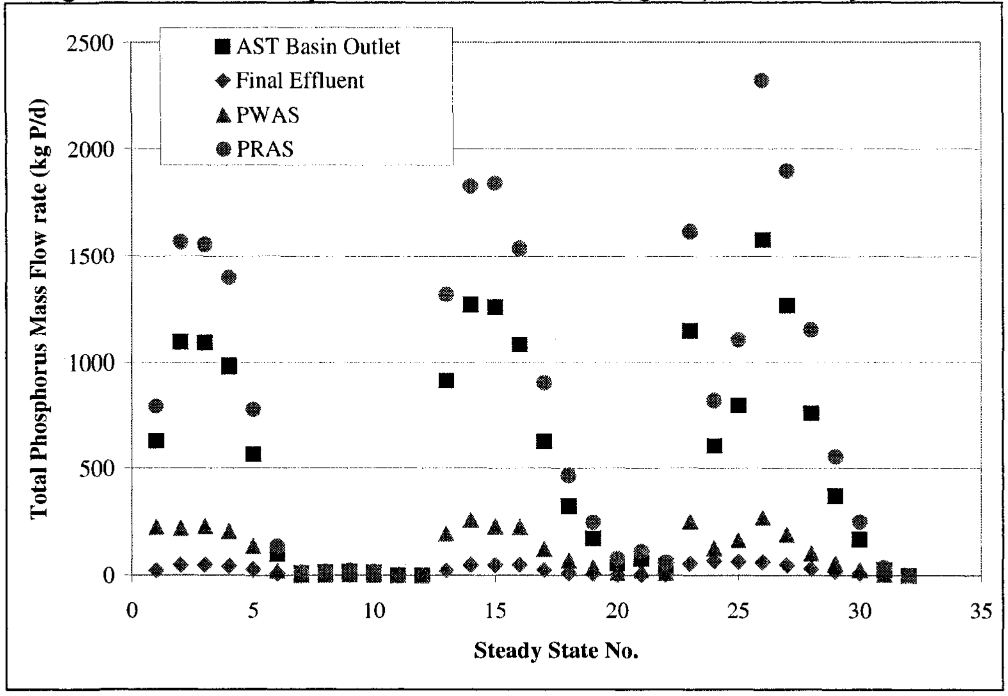
It should be noted that the average VSS for the final effluent and inlet to the AST selector are both higher than the average TSS results, as seen in Table 77. For both of these sample points, all the solids in the stream consist of biomass. It is assumed that the VSS measurement represents the fiber content at the inlet to the primary clarifier since there is no biomass re-circulated to this point in the process.

Mass balance results

Phosphorus

The mass balance of total phosphorus over the secondary clarifier results in the calculated mass flow rate of total phosphorus in the WAS and RAS streams, as illustrated in Figure 65. The ratio of the average total phosphorus concentration in the WAS stream to that in the RAS stream is 2.9. There are operational conditions where the phosphorus concentration in the aerated basin and the sludge streams is zero. It can be assumed that the activated sludge is phosphorus-deprived during these periods, and therefore bacterial growth is phosphorus-limited.

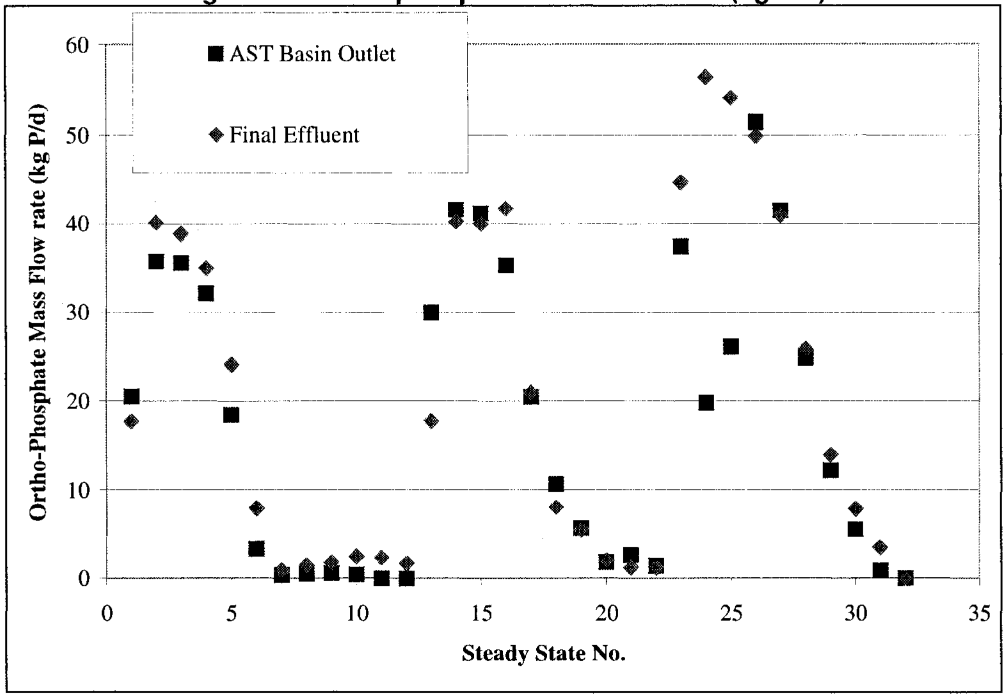
Figure 65: Total Phosphorus mass flow rates (kg P/d), Secondary Clarifier



Of the total phosphorus in the AST basin outlet, an average of 3.2% is present as ortho-phosphate, whereas in the final effluent stream an average of 82% of the total is present as ortho-phosphate. Microorganisms can most easily assimilate the ortho-phosphate form of phosphorus [72]. Other forms of phosphorus must be hydrolyzed to the ortho-phosphate form, which is less efficient for the microorganisms than using ortho-phosphate available [72].

Figure 66 shows that the phosphorus load of the RAS stream closely follows that of the AST basin outlet, as can be expected since the majority of phosphorus content in the AST basin outlet is due to organic phosphorus or polyphosphates, which are associated with the biomass, and the content of the RAS stream is essentially biomass. The phosphorus load in the RAS and WAS stream are equal in terms of the concentration of phosphorus per unit biomass, calculated using the VSS concentration in each stream. Figure 65 shows that nearly 100% of the ortho-phosphate present in the outlet of the AST basin is carried through to the final effluent; this residual is now measured using on-line instrumentation. This data indicates good solids removal in the secondary clarifier, as discussed in the solids mass balance section further on.

Figure 66: Ortho-phosphate mass flow rate (kg P/d)



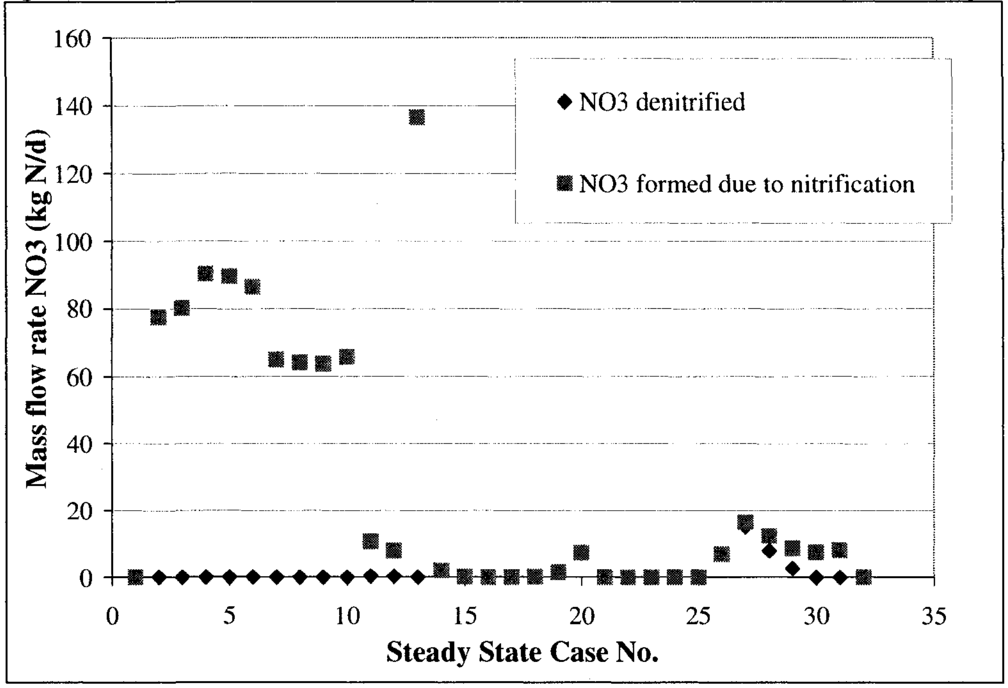
Denitrification

The secondary clarifier is considered to be the only basin that is not fully aerated and where sufficient nitrates may be present for denitrification to potentially occur. A mass balance of nitrates over the secondary clarifier for the steady states was conducted using the laboratory-measured nitrate concentrations in the final effluent and the outlet of the aerated basins. This balance shows that denitrification did occur under some process operation conditions, as illustrated in Figure 67. This mass balance assumes that denitrified nitrate is completely transformed into nitrogen gas and no intermediate species are produced [135]. This mass of nitrate represents nitrogen that has been added to the process but was not used for its intended purpose (bacterial growth), and is therefore considered an unnecessary cost to the plant operation.

Nitrification

Similarly, the mass of nitrogen produced via the nitrification process in the aerated selectors and basins was calculated, assuming that the influent to the wastewater treatment plant contains negligible nitrates. This mass of nitrate represents nitrogen that has been added to the process and not used for its intended purpose, however also represents excess oxygen utilization and therefore excess aeration, all of which represent unnecessary costs to the plant operation.

Figure 67: Mass nitrate formed by nitrification and mass nitrate denitrified (kg/d)

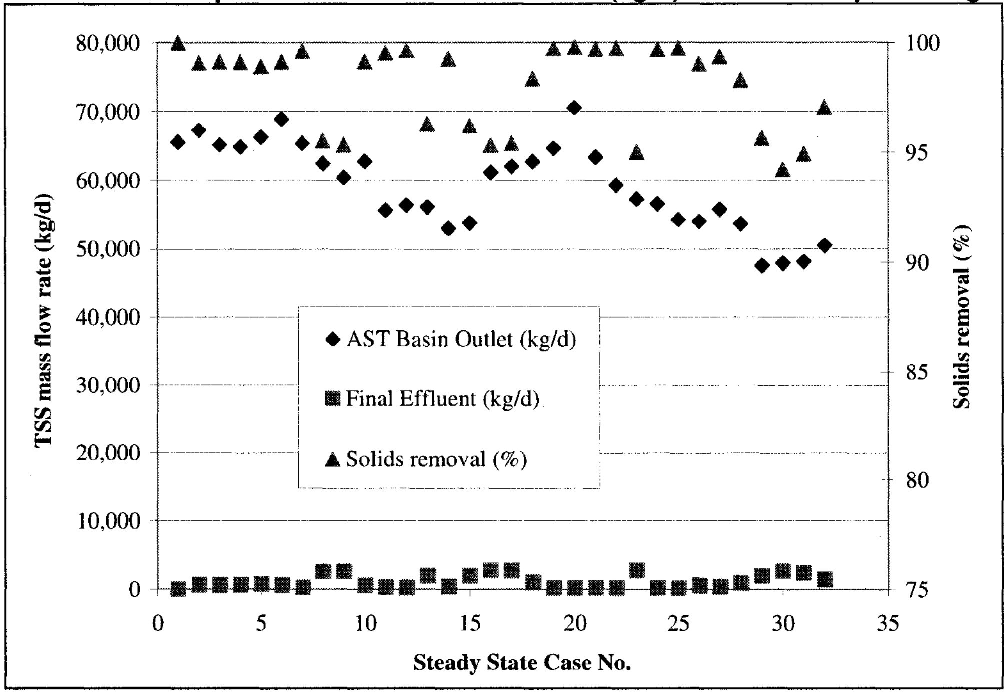


It appears from Figure 67 that the nitrification occurring in earlier steady state cases has been brought under control. This may be due to the increase in process knowledge and the continuing calibration of on-line instruments that occurred during this period. In order to maintain this situation, a better understanding of the nutrient transformations that result in these biochemical processes is desired by mill personnel.

Solids mass balance

The jet aeration system in the aerated selectors and aerated basins provides both aeration and mixing; high aeration rates risk shearing the flocs and potentially reducing the solids removal performance in the secondary clarifiers, which in turn would result in higher nutrient discharge in the final effluent. Higher aeration also promotes nitrification which consumes supplemental nitrogen unnecessarily. The solids removal across the secondary clarifier was calculated for each of the steady states, the results range from 94% to 100%, as shown on the left-hand axis in Figure 68. This data confirms that the process achieves good solids removal in the secondary clarifier. The relationship between lower solids removal performance and process operation will be investigated further.

Figure 68: Total suspended solids mass flow rates (kg/d) and removal percentage (%)



COD balance

The COD balances were carried out over the AST and secondary clarifier. The average COD removal is 93%. The average percentage balance of the calculations was 75%, which refers to the ratio of mass flow rate output to mass flow rate input of COD to the secondary treatment system for each steady state process condition. In this context, output COD refers to oxidized COD as well as COD in the final effluent and the WAS stream. Reasons suggested that the COD balance may not be 100% include that there may be denitrification occurring that consumes more carbonaceous substrate than accounted for [135].

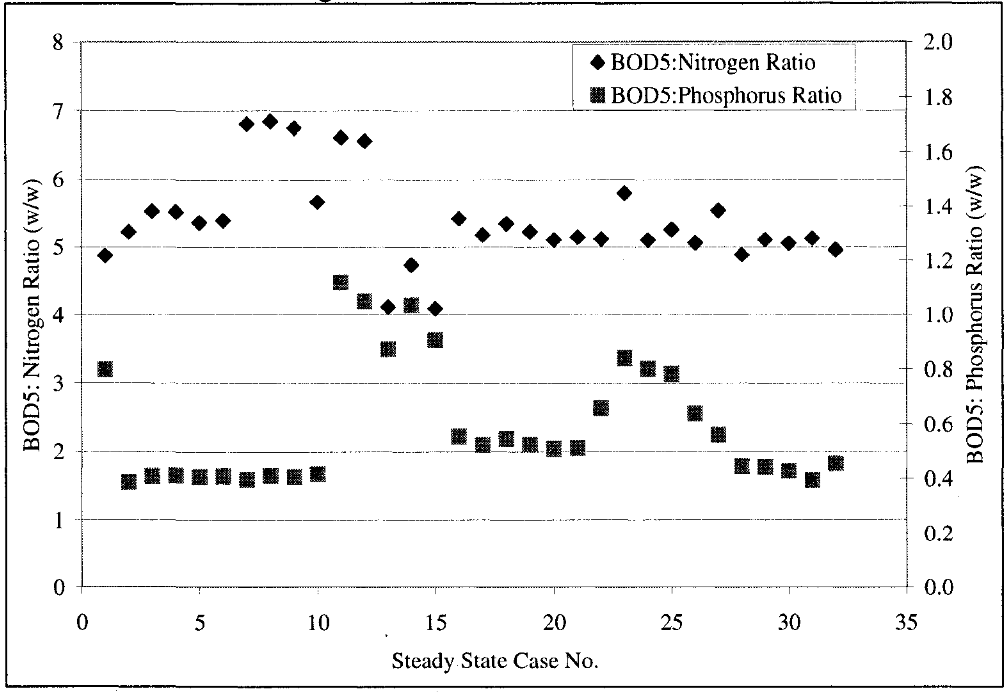
Nitrogen balance

The nitrogen balances were carried out over the AST and secondary clarifier. The average percentage balance of the calculations was 106%. From the nitrogen mass balances, the nitrogen mass flow rates from the outlet of the primary clarifier and the press filtrate return were calculated. The contribution of nitrogen of these two streams to the activated sludge treatment is of the same order of magnitude, which together contributes on average 16% of the mass flow rate of total nitrogen added through supplemental urea.

BOD$_5$:N:P mass ratios

The ratios calculated from the steady state data are presented in Figure 69. As previously discussed, a range of ratios have been found in stably operated pulp and paper wastewater plants. The average BOD$_5$:N:P ratio for the steady states was found to be 100: 5.4: 0.6. For nitrogen, this is 116% higher than the lower limit from the literature (100:2.5) and 20% higher than the upper limit from the literature (100:4.5). For phosphorus, this is 49% higher than the lower limit from the literature (100:0.4) and equal to the upper limit from the literature (100:0.6).

Figure 69: BOD5:N:P mass ratios



Discussion

Based on the nutrient balances outlined above, the supplemental nutrients added to the pulp and paper wastewater treatment plant are not only assimilated into microorganisms in order to remove carbonaceous substrate and allow microorganisms to carry out reproductive and maintenance activities, but also the nitrogen added is being transformed through the biochemical processes of nitrification and denitrification. This wastewater plant is not designed to take advantage of these processes, and they are not desirable since they consume resources in the form of aeration and ammonia-nitrogen.

Cost savings

The cost savings associated with the unnecessary nitrogen addition that resulted in nitrification and denitrification biochemical processes are estimated to be in the order of $13,000 annually, depending on the operation of the wastewater plant. This does not take into account the additional savings on aeration associated with the extent that nitrification is occurring.

As seen in the discussion of the BOD_5:N:P ratios, it is possible to maintain stable AST operation for high BOD removal and simultaneous nutrient minimization or optimization, which may lead to lower ratios. The cost savings are estimated to be in the range of $85,000 annually, with respect to the possible reduction in dosing of urea and phosphoric acid.[6] It should be noted that not all pulp and paper wastewater treatment plants will operate successfully with the same BOD_5:N:P ratio, as demonstrated by the range of values in Table 76, the ratio is dependent on the upstream pulp and paper process. The nature and source of nutrients and organic load in the wastewater itself can vary depending on the combination and variation in upstream process operation [38]. Laboratory scale activated sludge plants have been operated successfully with zero phosphorus addition for pulp mill effluent [64], and full scale aerated stabilization basins have operated successfully with zero nutrient addition [73]. Operation of the wastewater treatment plant will also vary with a high dependence on season and process cooling, since the kinetics of the biological processes are highly sensitive to temperature.

The major cost saving associated with reduced nutrient addition is the saving associated with the purchase of the chemicals themselves. There would also be cost and energy savings associated with reduced aeration requirements if the nitrification biochemical process is eliminated. Certainly at the mill studied, the change to remote operation of the wastewater plant has resulted in reduced operating costs. This adjustment is being assisted through the use of on-line instrumentation, and could be further assisted through the regular assessment and use of nutrient, solids and COD

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[6] This calculation is based on the average difference between the operating BOD_5:N:P mass ratio compared to the minimum and maximum ratios from the literature, considering either nitrogen or phosphorus, not the combination of the two. The value of $85,000 refers to the savings possible using the difference between the operating and the minimum literature ratio for phosphoric acid as well as the difference between the operating and the maximum literature ratio for urea. The calculation is based on the 32 steady states found during the four month data collection period and assumes that the same range and proportion of BOD_5:N:P mass ratios, and thus the same average ratios, would be found during a full year of operation. The calculation does not include the capital cost of installation of new instrumentation or control equipment.

balances. A regular mass balance assessment could indicate when nitrification or denitrification processes were occurring and corrective action could be taken quickly thereafter.

ASM model for pulp & paper wastewater

Activated Sludge Models (ASM) were originally developed for the municipal wastewater industry [204] and have been applied to a small number of pulp and paper cases [134, 195]. The ASM models are mathematical models that can be described as "dynamic, lumped-parameter, grey-box models including nonlinear reaction terms" [134]. ASM1 is still considered to be the "state of the art" in many studies; this model uses 8 biochemical processes including nitrification, denitrification, endogenous respiration (death-regeneration) and hydrolysis involving both heterotrophic and autotrophic bacteria [208]. These metabolic processes represent a complex set of redox (reduction-oxidation) reactions occurring at the cellular level in the activated sludge, which would be extremely difficult to solve without the mathematical model. These models offer the opportunity to improve understanding of the biological treatment plant by investigating the complex biochemical processes that are occurring in the activated sludge process.

The benefit of modeling a wastewater treatment plant is at least two-fold: to facilitate a deeper understanding of current operating regimes, and to enable the amelioration of the process operation. A deeper understanding of the nutrient transformation mechanisms with respect to the different nutrient fractions and effective nutrient control strategies can permit stable AST operation for high BOD removal and simultaneous nutrient minimization or optimization. Improved process control may include the development and implementation of an operational control strategy, with possibilities for automated nutrient dosing control.

The methodology used in this study resulted in the identification of 32 nutrient, solids and COD steady state process conditions. Each of these steady states will be used to calibrate and validate an ASM model of this wastewater treatment plant, and therefore the results of the steady state mass balances are essential to building the ASM model. Performing mass balances is a simple and effective method to ascertain the reliability of the data. This set of reliable data along with the transformations confirmed by mass balances allow the construction of a model that adds a layer of further information by calculating processes such as nutrient transformations that are not easily quantifiable by measurement in the field or laboratory.

ASM models strive to apply mechanistic algorithms while remaining as simple as possible, and represent biological processes which are occurring in a complex mixture of microorganisms. Brault presented a pulp and paper-specific modified ASM1 model entitled the ASM1-PP model [138]. Further work will be based on this model.

Conclusions

Mass balance calculations have shown that unwanted nitrification and denitrification were occurring for some process conditions. The potential cost savings on supplemental nutrient addition associated with these processes is estimated at $13,000 annually. Comparison of calculated BOD_5:N:P mass ratios with those reported in the literature indicate a possible saving estimated at $85,000 annually.

The wastewater process at this mill is operating well, with reduced nitrification and denitrification while maintaining stable operation and good removal of carbonaceous substrates. The reliability of the process has increased in part due to the operators' confidence in the on-line nutrient instruments used in the final effluent stream. Further understanding of the process operation and a more well-defined control strategy are anticipated with the future use of the ASM model.

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APPENDIX 4.2
Published Article 2

Steady state modelling of nutrient transformations in activated sludge treatment of pulp and paper wastewater

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Abstract

Pulp and paper wastewater is often deficient in readily available macronutrients, typically nitrogen and phosphorus, whereas municipal wastewater usually contains adequate or excess quantities of these nutrients in relation to the requirements of the activated sludge microorganisms. The control of supplemental nitrogen and phosphorus dosing represents a cost reduction opportunity for mills as well as an opportunity to reduce nutrient concentrations in the final effluent discharge, which are increasingly prescribed by environmental or governmental authorities.

Wastewater characterisation was carried out on a pulp and paper mill effluent for an integrated TMP-newsprint mill according to well-accepted systematic methodologies. Previously determined pseudo-steady state cases were used in conjunction with the wastewater characterisation and a pulp and paper-specific ASM1-based model to evaluate the nutrient transformations at steady state in pulp and paper wastewater treatment.

The wastewater characterisation methods highlighted major differences between the determination of COD fractions in pulp and paper wastewater and those in municipal wastewater. Calibration of the ASM-based model was exceedingly difficult for the entire range of process conditions; individually adjusted kinetic parameters are proposed, with an evolution of the nitrification-denitrification process rates over time.

Key words

Modelling, nutrients, pulp, paper, ASM, activated sludge

Abbreviations and Notations

Symbol	***Definition***	***Units***
ASB	Aerated stabilisation basin (lagoon)	-
AST	Activated sludge treatment	-
ASM1	Activated Sludge Model no 1 by IAWPRC	-
b	Decay rate constant	d^{-1}
BCOD	Biodegradable COD	mg COD/L
BKM	Bleached Kraft mill (process)	-
CSTR	Continuously stirred tank reactor	-

Symbol	***Definition***	***Units***
CTMP	Chemithermomechanical pulp (process)	-
DO	Dissolved oxygen	mg O_2/L
ϕ_{BOD}	Characterisation: correction factor for cell decay	mg COD/ mg BOD
f_{BOD}	Modelling: Ratio of BOD5: ultimate BOD	mg BOD/ mg BOD
F/M	Food-to-microorganism rate	g COD/g VSS
fxii	Fraction of biomass present as intra-cellular dissolved inorganics	mg COD/mg COD
HRT	Hydraulic Retention Time (volume/ volumetric flow rate)	m^3/ m^3/day
IAWPRC	International Association on Water Pollution Research and Control, now IWA	-
IAWQ	International Association on Water Quality, now IWA	-
i_{CV}	Elemental oxygen required for every gram of biomass consumed in an oxidation process	mg O_2/mg wastewater
k_a	Specific ammonification rate	m^3/g COD. day
K_A	Saturation constant of species A	mg/L
K_C	Controller gain	-
K_d	Endogenous decay coefficient	g VSS/g VSS.d
k_h	Maximum specific hydrolysis rate	g COD/g cell COD.d
K_{NA}	Ammonia half saturation constant (autotrophic)	g NH4-N/ m^3
K_{NO}	Nitrate half saturation constant	g NO 3-N/ m^3
K_{OA}	Oxygen half saturation constant	g O_2/m^3

Symbol	***Definition***	***Units***
	(autotrophic)	
K_{OH}	Oxygen half saturation constant (heterotrophic)	g O_2/m^3
K_P	Phosphorus half saturation constant	g P/m^3
K_{SH}	Half saturation constant for assimilation of carbon	g COD/m^3
K_X	Hydrolysis half saturation constant	g COD/g cell COD
μ_A	Autotrophic maximum specific growth rate	d^{-1}
μ_H	Heterotrophic maximum specific growth rate	d^{-1}
μ_{MAX}	Maximum growth rate	d^{-1}
MCRT	Mean cell residence time	d
MLSS	Mixed liquor suspended solids	g VSS/L
N	Nitrogen	mg N/L
NH_4^+-N NH_{3+4}	Ammonia nitrogen	mg N/L
NO_3	Nitrate nitrogen	mg N/L
η_g	Correction factor for anoxic growth of heterotrophs (denitrification)	-
η_h	Correction factor for anoxic hydrolysis	-
P	Phosphorous	mg P/L
PFR	Plug flow reactor	-
PO_4-P	Ortho-phosphate phosphorus	mg P/L
Q	Volumetric flow rate	m^3/d
RAS	Recycled activated sludge (stream)	-

Symbol	***Definition***	***Units***
S_I	Soluble inert organic material	mg COD/L
S_{ND}	Soluble organically bound nitrogen	mg N/L
S_{NH}	Ammonium nitrogen	mg N/L
S_{NO}	Nitrate nitrogen	mg N/L
S_O	Dissolved oxygen	mg -COD/L
S_{PD}	Soluble organically bound phosphorus	mg P/L
SRT	Sludge retention time	day
S_S	Soluble organic biodegradable material	mg COD/L
SVI	Sludge volume index	mL/g
TKN	Total Kjeldahl Nitrogen (sum of ammonia nitrogen and organic nitrogen)	mg N/L
TMP	Thermomechanical pulp (process)	-
TN	Total nitrogen	mg N/L
TOC	Total organic nitrogen	mg N/L
TP	Total phosphorus	mg P/L
TSS	Total suspended solids	mg TSS/L
V	Volume	m^3
VSS	Volatile suspended solids	mg VSS/L
WAS	Waste activated sludge (stream)	-
WERF	Water Environment Research Foundation	-
WWTP	Wastewater treatment plant	-
X	VSS concentration in the aeration basin	g VSS/L
X_{BA}	Autotrophic biomass	mg COD/L

Symbol	Definition	Units
X_{BH}	Heterotrophic biomass	mg COD/L
XCOD	Particulate COD	mg COD/L
X_I	Particulate inert organic material	mg COD/L
X_{II}	Particulate inert inorganic material	mg COD/L
X_{ND}	Particulate organic nitrogen	mg N/L
X_{PD}	Particulate organic phosphorus	mg P/L
X_S	Particulate organic biodegradable material	mg COD/L
X_U	Unbiodegradable particulates from cell decay	mg COD/L
Y	Yield of biomass per unit substrate consumed	g VSS/g BOD_5
Y_A	Autotrophic yield	g cell COD/g N
Y_H	Heterotrophic yield	g cell COD/g SS

References: [195, 207]

Introduction

Pulp and paper wastewater is often deficient in readily available macronutrients, typically nitrogen and phosphorus, whereas municipal wastewater usually contains adequate or excess quantities of these nutrients in relation to the requirements of the activated sludge microorganisms. The control of supplemental nitrogen and phosphorus dosing represents a cost reduction opportunity for mills as well as an opportunity to reduce nutrient concentrations in the final effluent discharge, which are increasingly prescribed by environmental or governmental authorities. Activated sludge treatment (AST) plants have been installed in many pulp and paper mills for wastewater treatment, and the emphasis of this work was to understand the nutrient transformations occurring in the AST plant with the longer-term objective of implementing a simple and practical control strategy.

A better understanding of the biological processes in pulp and paper treatment plants can be gained using the Activated Sludge Models (ASM) developed for the municipal wastewater industry. Wastewater characterisations of pulp and paper wastewater from other ASM-based studies are presented in Table 32. These studies cover a broad range of pulp and paper processes as well as a range of wastewater treatment plant processes. The study results range from “good agreement with plant operating data“ [196] to “a poor model response for the effluent COD and suspended solids concentrations” [263]. Some interesting characterisation and modelling work was conducted for the Hylte mill in Sweden [134, 195], which has unusual pulp and paper and wastewater process configurations and is therefore not included in the comparison in Table 32.

Table 81: Fractionation of pulp & paper primary effluents

Pulp & Paper Process	***WWTP Process***	**SRT**	**HRT**	***Fraction***				***Reference***
				S_S	S_I	X_S	X_I	
Units		*d*	*h*	*mg COD/mg total COD*				
TMP/RCF (1993, 1994)	*ASB*	20 - 29	50	0.15, 0.29	0.093, 0.082	0.64, 0.54	0.12, 0.088	[196]
BKM	*ASB*		82	0.42	0.33	0.11	0.14	[198]†
CTMP	*Plug-flow AST**	6.5	4.7	0.49	0.14	0.3	0.07	[200]
CTMP	*Plug-flow AST**	6.5	4.7	0.28	0.33	0.34	0.05	[197]
BKM, BKM/TMP	*UNOX***		6.5 – 7	0.24, 0.44	0.36, 0.32	0.42, 0.23	0.07, 0.03	[199]
Municipal (ASM3 default)	-			0.43	0.13	0.33	0.11	[200]
TMP	*CSTR AST*	4 – 6	16	0.47 – 0.52	0.02 – 0.07	0.12 – 0.34	0.12 – 0.34	This study (range by alternative methods)

†*cited in* [200]
*5 x CSTR’s in series approximates a plug-flow AST
**UNOX: high-oxygen AST, 3 x CSTR’s in series, pseudo-plug flow

where:

- S_I Soluble unbiodegradable (inert) organic material mg COD/L
- S_S Soluble organic biodegradable material mg COD/L
- X_I Particulate unbiodegradable (inert) organic material mg COD/L
- X_S Particulate organic biodegradable material mg COD/L

The ASM models consist of mechanistic lumped-parameter models, which are used to describe the overall biological reactions occurring in an activated sludge system. This approach works well for long retention time processes, such as aerated stabilisation basins (ASB) or lagoon systems [71], but it does not take into account local conditions nor reactions occurring on a microscopic scale within the biological flocs. Modelling of a well-mixed (CSTR) AST with a relatively short retention time (approximately 16 hours) for industrial wastewater represents a significant challenge for the application of the ASM models.

The wastewater characterisations included in Table 32 and in many other studies [246] assume a constant influent wastewater characterisation in terms of the fraction of each COD component (S_I, S_S, X_I, and X_S) with respect to time. The influent to a wastewater treatment plant at a pulp and paper mill varies significantly over the course of a day, in terms of total COD concentration, as seen in Figure 70, which presents the minute average total COD measured by an on-line UV instrument at the inlet of the AST. This graph demonstrates the variation possible on a day when the paper machine shut down between 7am and 2.30pm and the TMP plant shut down between 7am and 6pm, with a maximum COD of 1670 mg COD/L and a minimum COD of 1190 mg COD/L, not including instrument noise.

The variation of each COD component as a fraction of the total COD has not been measured in pulp and paper wastewater during the course of a day. However, it can be reasonably assumed that variation exists and is attributable to changes in the mill production rate and grades, variations in the readily biodegradable methanol and 'lights' present in condensate streams sent to effluent from the energy recovery process, variations in slowly biodegradable lignin and cellulose in fibre-rich streams sent to effluent from the whitewater or other storage tanks, and variations in the quantity of wash-up chemicals sent to effluent when the mill plant is shut down for maintenance.

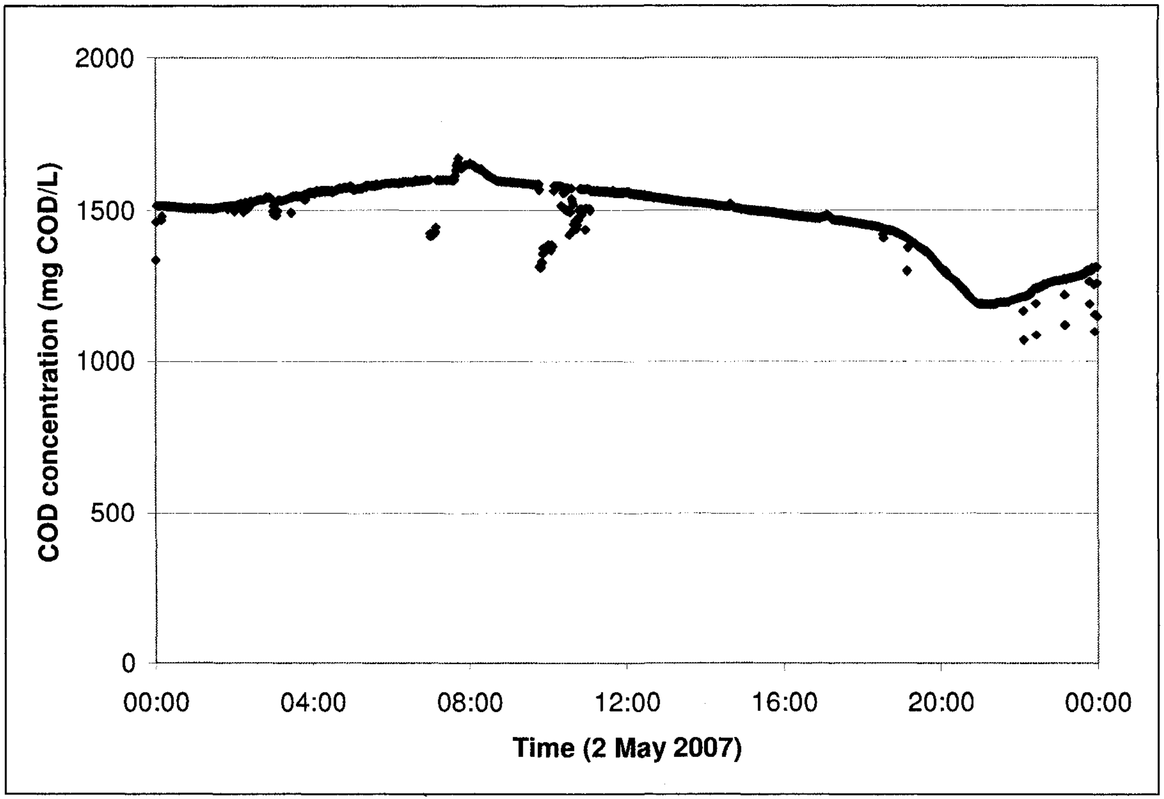

Figure 70: Total COD primary effluent, minute average data (on-line data), 2 May 2007

In this paper, the results of steady state modelling carried out using experimental and mill data are presented and an interpretation of the nutrient transformations occurring in the activated sludge treatment of pulp and paper wastewater is proposed. The methodology employed includes meticulous data treatment, the identification of disparate operating conditions, and the development of a calibration process applied to each operating condition that accounts for varying nutrient transformation conditions.

Materials and methods

White Birch Papers, Masson Division

The White Birch Papers, Papier Masson Division pulp and paper mill consists of a single line thermo-mechanical pulping (TMP) process followed by a single newsprint paper machine, producing over 680 ODt/d newsprint, predominantly from 100% TMP pulp. The secondary wastewater treatment plant was constructed in 1995, and since January 2007, the mill has operated the wastewater treatment plant remotely from the boiler house.

The wastewater plant process configuration (Figure 71) encompasses coarse screening (mechanical bar screen), one primary clarifier, two well-mixed (CSTR) aerated selectors and AST basins operating in parallel, and two secondary clarifiers operating in parallel. The influent is cooled during summer months; this is not required during winter. An emergency basin is available for use under process upset conditions or for spills. Sanitary wastewater from the site is sent to the municipal sewer for off-site treatment. Storm water from roof run-off, landfill leachate, and chip pile run-off are treated on-site in the wastewater treatment plant.

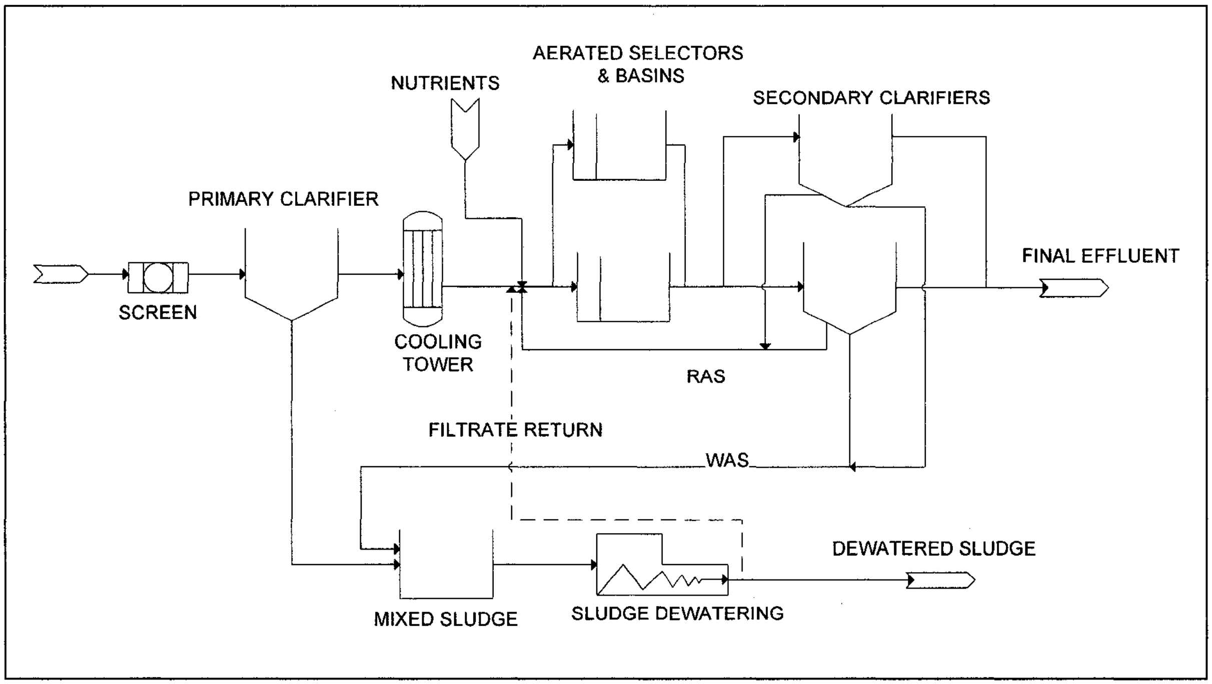

Figure 71: Wastewater treatment plant process configuration

Each AST uses submerged venturi (jet) aerators in a well-mixed basin. The AST basins are oversized for the current influent from the mill due to process modifications to the pulp and paper mill. Nutrients are dosed into the inlet of the aerated selector in the form of urea and phosphoric acid. The AST plant is not designed for nitrification; indeed this is an unwanted biochemical process as it consumes supplemental nitrogen and thus augments the operational costs of the plant.

Overall methodology

The project methodology outlined in Figure 72 encompasses data collection of the mill physical design data, of continuous and discrete laboratory data from the mill PI system, and additional wastewater characterisation measurements carried out at the mill laboratory and at the university laboratory according to Standard Methods. This data was then treated to synchronise data over the hydraulic retention time of the AST basins, to exclude abnormal process conditions such as mill shuts, and to identify pseudo-steady state scenarios that varied in duration from 6 hours to 32 hours. The treated data was further reconciled by mass balances for each pseudo-steady state prior to inclusion in an ASM-based model.

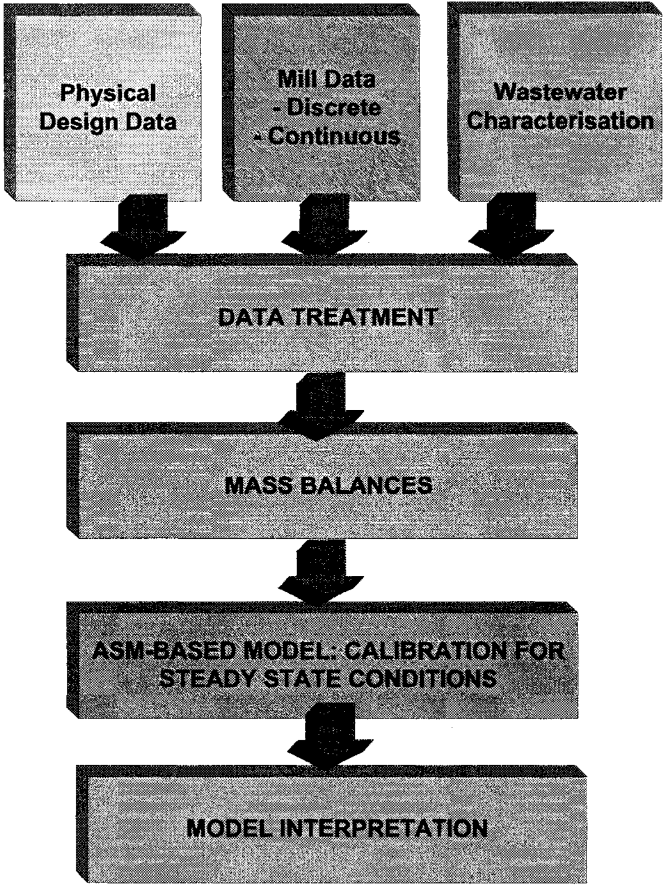

Figure 72: Project methodology

Measurements

The mill collects extensive on-line process data for the purpose of process monitoring and control, including flow rates, temperature, dissolved oxygen, pH, conductivity, as well as tank and basin levels. The mill laboratory technicians conduct daily testing on the nutrient fractions ammonia-nitrogen, nitrate-nitrogen, and ortho-phosphate according to Standard Methods [264]. Wastewater characterisation measurements (COD, solids, and nutrient fractions) were carried out on a weekly basis on-site and a fortnightly basis at the Environmental Laboratory of the Civil, Geological and Mining Engineering Department of the Polytechnique, Montreal. The experimental results of the on-site work, presented elsewhere [265], were cross-checked with Environmental Laboratory experimental results and results from the external certified laboratory used by the mill for final effluent measurements.

During 2007, the mill automated various measurements, notably by installing UV chemical oxygen demand (COD) and multiple total suspended solids (TSS) meters, as well as instruments for on-line measurement of residual nutrients in the final effluent. The Amtax SC HACH instrument analysed the ammonia-nitrogen in the final effluent using a gas-sensitive electrode (ammonia-specific) combined with a colorimetric method. This instrument calibrates daily to two known standards of ammonia (1 mg N/L and 10 mg N/L). The Phosphax SC HACH instrument analysed the ortho-phosphate in the final effluent using a vanadomolybdophosphoric acid via colorimetric method. Both instruments in the final effluent rely on a sample filtered to 0.15 μm.

A BOD-based wastewater characterisation was conducted on a number of occasions during a four-month period according to the well-accepted systematic methodology for municipal wastewater [246]. However, the results from the 10-day BOD were inconclusive and so a 28-day BOD analysis was conducted in triplicate for unfiltered samples from both the primary clarifier influent and the primary effluent using the HACH 'BODTrak' instrument. Nitrification inhibitory agent 2-chloro-6-(trichloromethyl) pyridine (TCMP), also known as HACH formula 2533, was added at the moment of preparation for analysis, as were nutrients. The BOD of the seed was also measured however no nitrification inhibitory agent was added to the seed (HACH PN#2471200) since it contains no nitrifying bacteria.

The COD protocol HACH #435 was carried out on the filtered and unfiltered samples with suitable dilution of the sample to render it in the range of 0 to 1500 mg/L COD. Samples were filtered using a Pall-Gelman Supor hydrophilic polyethersulfone membrane of porosity 0.1 μm.

Samples collected for the 28-day BOD test were 24-hour composite samples. Samples collected for the nutrient, COD and solids fractionation were grab samples except for the final effluent, which was a composite sample in all cases.

Biological Model

The biological model presented by Brault *et al.* (2006, 2008) is a hybrid model developed for pulp and paper wastewater based on ASM1. ASM1 was chosen as the basis of the model in part because hydrolysis has been shown to be a significant process in the activated sludge treatment of industrial wastewater, and for pulp and paper effluent in particular [27, 55], whereas ASM3 places more emphasis on storage of readily biodegradable substrate than hydrolysis.

The major modifications to the ASM1 model include:

1. The incorporation of nutrient limitation to bacterial growth rates via the addition of a Monod switching function for both ammonia-nitrogen and phosphate-phosphorus;
2. The addition of a 'phosphatification' process by which soluble organic phosphorus is converted into ortho-phosphates for growth, analogous to the ammonification process;
3. The addition of hydrolysis of organic phosphorus, analogous to the hydrolysis of organic nitrogen;
4. The addition of a 'particulate biodegradable organic phosphorus' fraction (X_{PD}), analogous to the nitrogen fraction X_{ND}, and the addition of a 'soluble biodegradable organic phosphorus' fraction (S_{PD}), analogous to the nitrogen fraction S_{ND};
5. The consideration of nutrient fractions of nitrogen and phosphorus relating to particulate inerts, X_I, from cell decay, X_U, and to particulate biomass, X_{BH} and X_{BA}, as constant fractions of their respective COD fractions (X_{NU}, X_{PU}, X_{NB}, and X_{PB}); and
6. The omission of nutrient fractions of nitrogen and phosphorus relating to the COD fractions S_I, S_S and X_S due to the extremely low concentrations found for pulp and paper wastewater (see results section for details).

The modifications (1) to (4) were made due to the fact that pulp and paper wastewater is known to be deficient in readily available macronutrients, typically nitrogen and phosphorus, in relation to the requirements of the microorganisms used in an activated sludge treatment process to consume organic substrate in the wastewater [10, 63]. The limitation of biomass growth rates due to nutrient concentration, specifically ammonia-nitrogen and ortho-phosphate concentration, is considered necessary for pulp and paper wastewater; various combinations of this theory have been used in previous studies [134, 195, 197]. The modifications (5) and (6) were made due to the measured nutrient concentrations in the primary effluent and in the mixed liquor.

Results

Experimental wastewater characterisation results are presented below, followed by mass balance results and model results.

28-day BOD Analysis

It was found that the BOD respirometry test results for a 10-day period were not sufficient to adequately fit a curve to the data; the BOD curve had not sufficiently approached the ultimate BOD concentration. It was for this reason that the BOD respirometry work was conducted for a 28-day period; this duration gave a better approximation of the ultimate BOD concentration. The results for the primary effluent are presented here; final results only are presented for the influent to the primary clarifier.

The BOD respirometry results were consistent between the three test sets. The results are depicted in Figure 73 for primary effluent; a single curve is shown in Figure 73 for the purpose of clarity. The curves were corrected for the seed BOD and for a number of small process shocks that occurred to all samples between day 15 and day 27. All curves showed no signs of impediment or inhibition at the beginning of the test, which indicates that the seed did not require time to acclimatise to toxicity in the wastewater.

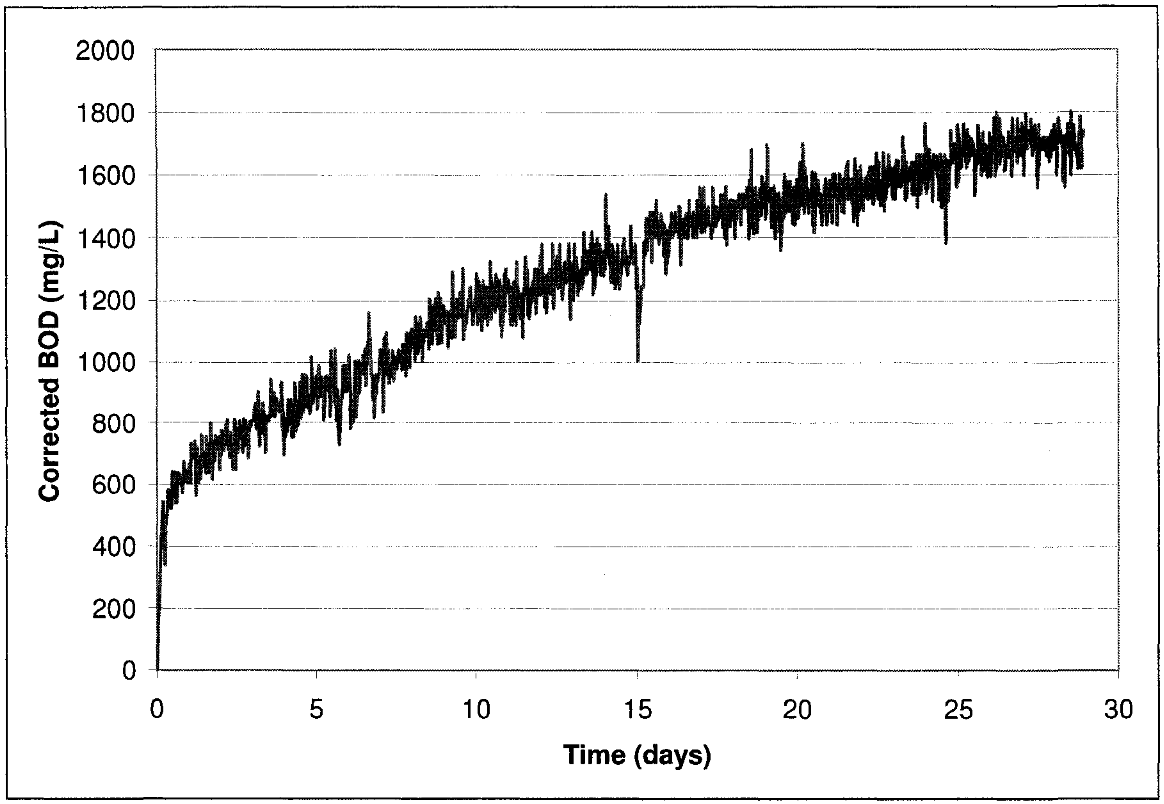

Figure 73: Primary effluent BOD1-28, single curve, corrected BOD

None of the curves displayed the expected asymptotic behaviour that is seen in municipal wastewater [246], in fact, they all appear to be steadily rising. This indicates that a large proportion of the organic substrate is slowly biodegradable; it is only a matter of how slowly it degrades. This is further expressed as the first order rate constant of BOD versus time, k_{BOD}, which was found to be between 0.051 and 0.057 d^{-1} for the primary effluent in this study, compared to 0.15 to 0.8 d^{-1} found for municipal wastewater having undergone primary treatment [246]. Current work by NCASI on the final effluent of pulp and paper mills indicates that the carbonaceous BOD measurement of that stream required 120 to 150 days for the BOD to approach an asymptote [266]; the COD in this stream corresponds to the soluble inert S_I fraction.

While the average BOD_5 concentration in the primary effluent, 426 mg/L, is comparable to the average concentration data for a municipal primary treated effluent, 246 mg/L [31], the total BOD_5 load in the pulp and paper wastewater, 12,660 kg/d, is much larger than the municipal load of 1,680 kg/d.

Primary Effluent Wastewater Characterisation

The combination of the above continuous BOD and the COD measurement data is used to convert the COD fractions into the ASM1 wastewater fractions, the results of which are summarised in Table 43. The BOD_5 reported by the external laboratory in the final effluent for the sample date was 8 mg/L. The correction factor ϕ_{BOD} represents the inert COD generated in biomass lysis during the BOD test. Modification of the correction factor ϕ_{BOD} between the recommended values of 0.1 to 0.2 results in variation in only the X_S and X_I fractions (not presented). It was found that a ϕ_{BOD} of 0.087 was necessary in the primary effluent in order to arrive at a positive X_I value for one of the data sets, which is particularly small. In two of the primary effluent data sets, the total BOD calculated is larger or very close to the total COD measured, which renders it difficult to solve for a reasonable ϕ_{BOD} value and obtain a positive X_I fraction.

Table 82: ASM1 wastewater characteristics (mg COD/L),
ϕ_{BOD} = (BCOD – BOD_{28}) / BCOD = 0.15

Stream	S_I	S_S	X_S	X_I	***COD total***
Raw Influent Average	79	1,249	786	916	3,030
Primary Effluent Average	79	1,201	1,220	ND (-340)	2,160

Where ND = not determined, calculation method results in negative X_I concentration, which is not possible.

The methodology employed to determine biodegradable COD (BCOD) is "almost intrinsically subject to inaccuracy (10 to 20%)", according to its authors [246]. From the results in Table 43, this wastewater characterisation methodology is not considered to be suitable for pulp and paper wastewater, due to the fact that this wastewater does not display any asymptotic behaviour during long-term BOD experiments, indicating that the distinction between the slowly biodegradable X_S fraction and the rapidly biodegradable S_S fraction is not as clear for pulp and paper wastewater as it is for municipal wastewater.

Primary Effluent Wastewater Characterisation for Pseudo-steady states

It was decided that the wastewater characterisation for the purposes of modelling work should be based on measurable parameters available for each pseudo-steady state scenario. For this purpose, methods from the 2003 WERF report [259] were used, namely:

- Soluble inert (unbiodegradable) fraction (S_I) : 100% of the final effluent soluble COD, calculated using the daily laboratory total COD concentration values multiplied by the average fraction of soluble to total COD in the final effluent from the wastewater characterisation work;
- (Soluble) readily biodegradable fraction (S_S): the difference between the influent soluble COD and S_I concentration, calculated using the on-line COD in the primary effluent multiplied by the average fraction of soluble to total COD in the primary effluent from the wastewater characterisation work;
- Particulate inert (unbiodegradable) fraction (X_I): derived from mass balances, fxi is calculated as a function of mixed liquor VSS, influent flow rate, influent total COD, sludge age, reactor volume, heterotroph yield coefficient, endogenous decay rate, endogenous residue fraction, mixed liquor solids COD to VSS ratio, soluble unbiodegradable COD fraction, plus the first step of model calibration to the measured mixed liquor TSS concentration; and
- (Particulate) slowly biodegradable fraction (X_S): determined from the COD balance in the primary effluent: $X_S = COD_{influent,\ total} - S_I - S_S - X_I$

  It is important to note for pulp and paper wastewater that the X_S fraction may contain large soluble slowly biodegradable substrate such as lignin, and therefore the 'particulate' label is not entirely appropriate.

The results of this characterisation for all 22 steady state events are presented in Figure 74, including the calibrated particulate inert X_I fraction (fxi). It is clear from Figure 74 that the fraction of the rapidly biodegradable COD, fss, and the fraction of the soluble inert COD, fsi, are reasonably constant throughout the data set: fsi varies from 0.022 to 0.068; fss varies from 0.47 to 0.52. The particulate inert fraction fxi is calculated as a function of sludge retention time, and for this reason there is a larger range of fxi values, from 0.12 to 0.34, and fxs calculated as the balance of total COD varies from 0.12 to 0.34. This characterisation method, while suitable for the modelling exercise, indicates that the distinction between the slowly biodegradable X_S fraction and the particulate inert X_I fraction is not as clear for pulp and paper wastewater as it is for municipal wastewater, and that the particulate inert components (large fibres with attached colloidal material) may be biodegradable to some extent for a longer sludge retention time.

The ASM1 wastewater characteristics of the primary effluent are generally comparable to those found for pulp and paper wastewater: S_I of 0.14 to 0.36, S_S of 0.24 to 0.49, X_S of 0.11 to 0.42, and X_I of 0.03 to 0.14 [200], as well as those for municipal wastewater found in the literature: S_I of 0.03 to 0.10, S_S of 0.09 to 0.42, X_S of 0.1 to 0.48, and X_I of 0.23 to 0.50 [246].

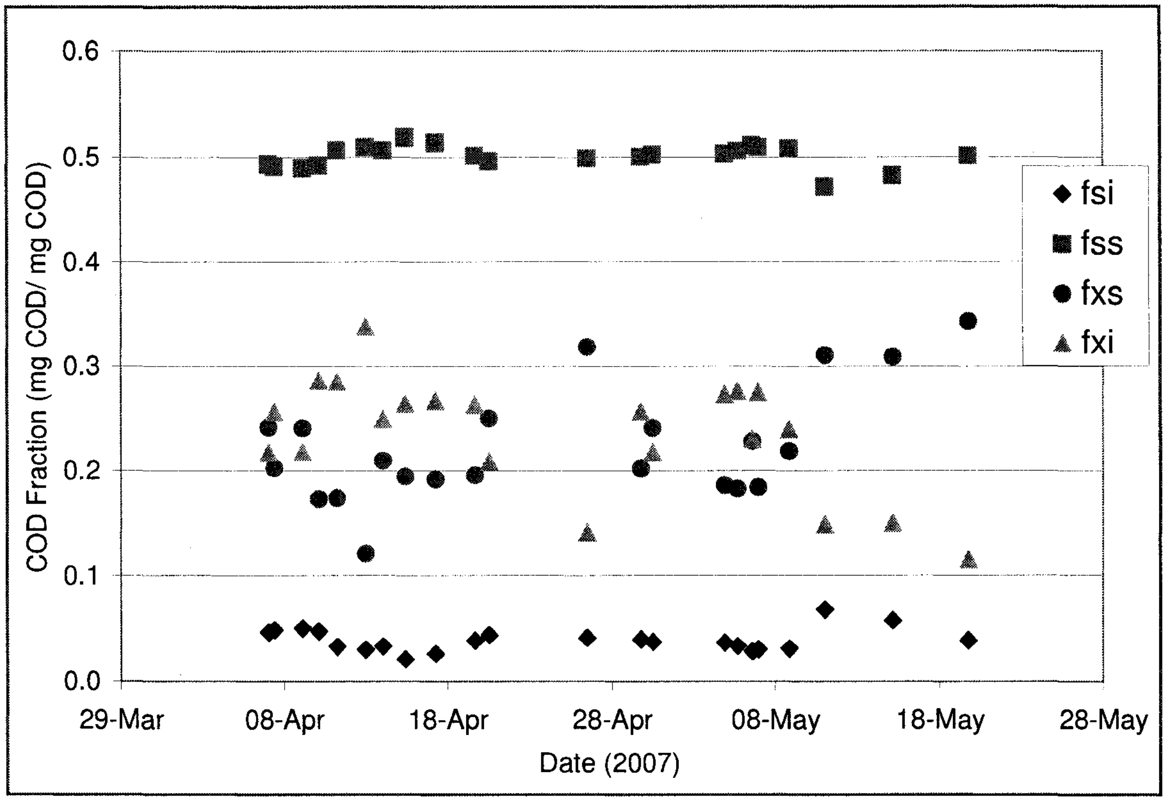

Figure 74: Steady state wastewater characterisation - Xi calibrated to mixed liquor total suspended solids

Biological Model: Nutrient fractions & transformations

A number of wastewater ratios were calculated from the wastewater characterisation experimental data, details of which are summarised in Table 100. As described elsewhere [262], the nutrient fractions in the mixed liquor were determined using the theoretical nutrient concentrations in the biomass (inxb = 0.086 mg N/mg COD, ipxb = 0.016 mg P/mg COD), an assumed concentration in the cell decay COD fraction X_U (inxu = 0.06 mg N/mg COD, ipxu = 0.015 mg P/mg COD), and the remainder nutrient concentrations attributed to the particulate inert COD fraction X_I (inxi = 0.03 mg N/mg COD, ipxi = 0.0016 mg P/mg COD). The inxi and ipxi concentrations in the mixed liquor fit well those measured in the primary effluent stream, if all organic nutrients in the primary effluent are attributed to the X_I fraction.

Table 83: Wastewater measured ratios summary

Location	*Parameter or Ratio*	*Units*	*Measured Range*	*ASM1, ASM2, ASM3 default values*	*Model uses:*
Influent	Organic nitrogen to total COD ratio	mg N/ mg COD	0.0016 – 0.0093	0.01 – 0.04	Zero nutrient concentration: insi, inss, inxs inxi = 0.03*
Influent	Organic phosphorus to total COD ratio	mg P/ mg COD	0.00025 - 0.00085	0 – 0.01	Zero nutrient concentration: ipsi, ipss, ipxs ipxi = 0.0016*
Influent	f_{CV} (particulate COD to VSS ratio)	mg XCOD/ mg VSS	1.93 – 2.64	2.2	Calculate for each steady state $f_{CV} = \frac{XCOD}{VSS} = \frac{X_I + X_S}{VSS}$
Influent	X_{II}	mg COD/L	0		Zero concentration
Influent	f_{BOD} (BOD_5: BODu)	mg BOD/ mg COD	PI: 0.18 – 0.28 PE: 0.21 – 0.23	0.66	Calculate for each steady state $f_{BOD} = \frac{BOD_5}{S_S + X_S}$
Mixed liquor	Organic nitrogen to COD ratio	mg N/ mg COD	0.049 – 0.058	0.086	inxbh = inxba = 0.086 inxu = 0.06 inxi = 0.03
Mixed liquor	Organic phosphorus to COD ratio	mg P/ mg COD	0.0064 - 0.0101	0.02	ipxbh = ipxba = 0.016 ipxu = 0.015 ipxi = 0.0016
Mixed liquor	f_{CV} (particulate COD to	mg XCOD/ mg VSS	1.34 – 1.85	1.48	Average value:

Location	***Parameter or Ratio***	***Units***	***Measured Range***	***ASM1, ASM2, ASM3 default values***	***Model uses:***
	VSS ratio)				1.63 mg XCOD/mg VSS
Mixed liquor	X_{II}	mg COD/L	X_{II} = 5%TSS		fxii = 0.208†

(PI) Primary Influent, (PE) Primary Effluent

†Calculated from: Average mixed liquor xii = 0.052*vss; active biomass = 0.25*vss‡; xii = 0.052/0.25*(active biomass)

‡ Approximately 25% of MLVSS is present as active biomass [260]

*inxi(primary effluent) = inxi(mixed liquor), ipxi(primary effluent) = ipxi(mixed liquor), all influent nutrients attributed to X_I fraction

Mass balances

The experimental, on-line and physical data collected were treated and mass balances were produced for each of the pseudo-steady state scenarios identified [265]. The volumetric flow balance and phosphorus balances were calculated from measurements and close 100% [31]. The COD balances close 85% on average for these 22 pseudo-steady states, the nitrogen balances close 93% on average, following a standard methodology that includes nitrification and denitrification processes [135]. Data reconciliation was conducted for the supplemental phosphorus dosing measurement and total suspended solids measurements at the AST inlet. The resulting mass balances provide a rigorously-determined basis for further modelling work.

Measurement accuracy, repeatability, measurement redundancy, and process variation were evaluated for mill on-line and laboratory measurements. The propagation of measurement and process uncertainty through the mass balances was also evaluated; however, it is not possible to ever reproduce the exact process conditions that generated the mill on-line data. When measuring bulk process conditions such as the dissolved oxygen concentration and temperature in the AST basin and inferring small changes in nutrient concentrations or reaction rates, the uncertainty at each data point is expected to be large and variable. The uncertainty of reaction rates has therefore not been evaluated.

Biological Model: Calibrated pseudo-steady states

The ASM1-based model was calibrated to measured data for each pseudo-steady state scenario developed using the mass balance results. The development of the calibration methodology is described below.

Phosphorus

It was found that the hydrolysis of organic phosphorus and phosphatification processes are necessary to model the nutrient transformations occurring in the AST. Without these two processes, the model demonstrated a severe bacterial growth limitation due to low ortho-phosphate phosphorus concentrations.

Solids

The model includes a point-settler secondary clarifier model due to the difficulties encountered in calibrating the existing settling models for pulp and paper solids. Sludge age or sludge retention time is therefore calculated using the volume of solids in the mixed liquor, excluding the volume of solids in the secondary clarifier, and the nutrient transformations in the secondary clarifier are not modelled. This is a limitation encountered when simplifying reality with a model.

The calibration of the X_I fraction was carried out systematically for a range of heterotrophic yield (Y_H) and heterotrophic decay (b_H) values. The heterotrophic yield value of 0.666 g COD/g COD and the heterotrophic decay value of 0.50 d^{-1} were found to fit the measured data best. The heterotrophic decay value is in agreement with that found in recent research of a similar pulp and paper wastewater treatment plant [262].

Carbonaceous substrate (BOD) removal

Once the solids balance had been established, the models were found to be very sensitive to three parameters: the heterotrophic maximum growth rate, μ_H, the autotrophic maximum growth rate, μ_A, and the anoxic growth factor, η_g. The heterotrophic maximum growth rate, μ_H, was set at a value of 18 d^{-1}, which gave good results for BOD removal ($\mu_A = 0.5$, $\eta_g = 0.08$) for the data sets where nitrate residuals were measured (where partial nitrification-denitrification is obviously occurring). This μ_H value is in agreement with that found in recent research of a similar pulp and paper wastewater treatment plant [262].

Nitrogen

The concentrations of ammonia, nitrate, and ortho-phosphate at the outlet of the AST were used as the calibration criteria for the nutrient transformations.

A uniform model capable of describing the entire data set was extensively investigated but was not found. Two possible scenarios can be proposed to explain the residual nitrates and ammonia measured at the outlet of the AST: (A) partial nitrification-denitrification is occurring, and subsequently the rate of nitrification diminishes, or (B) partial nitrification-denitrification is occurring, and subsequently the rate of denitrification increases. The proposed models were calibrated according to scenario (A), but it was not possible to evaluate scenario (B) with any great accuracy; given the already low-to-zero autotrophic maximum growth rates, the range of anoxic growth correction factors that reasonably fit the measured data is quite large.

Two models that each describe a part of the nutrient residual data were investigated. The model results are compared to the measured nutrient residual data in Figure 89. Model 1 refers to the situation where partial nitrification-denitrification is occurring (μ_A = 0.5 d^{-1}, η_g = 0.08, k_a = 0.08, k_p = 0.08, b_H = 0.62) and Model 2 refers to the situation where nitrification is not occurring (μ_A = 0, η_g = 0, k_a = 0.025, k_p = 0.08, b_H = 0.50). It is clear that two disparate process conditions, zero nitrification and partial nitrification-denitrification, can each be modelled by a uniform model, but in fact a uniform model does not describe the entire data set in this study. For this reason, the kinetic parameters that describe nutrient transformations were adjusted for each individual pseudo-steady state.

Once the heterotrophic maximum growth rate was determined, the autotrophic maximum growth rate, μ_A, and the anoxic growth factor, η_g, were calibrated for individual pseudo-steady state cases. The range of values investigated for each case was 0 to 1.0 d^{-1} for μ_A and 0 to 0.1 for η_g, which were used to calibrate the nitrate concentration at the AST outlet. The ammonification rate, k_a, was used to further calibrate the ammonia concentration at the AST outlet. The half saturation constant for the assimilation of nitrogen for autotrophs, K_{NA}, was reduced to a value of 0.05 g COD/m^3 for all model calibration work in order to allow the nitrification process to proceed at low ammonia concentrations.

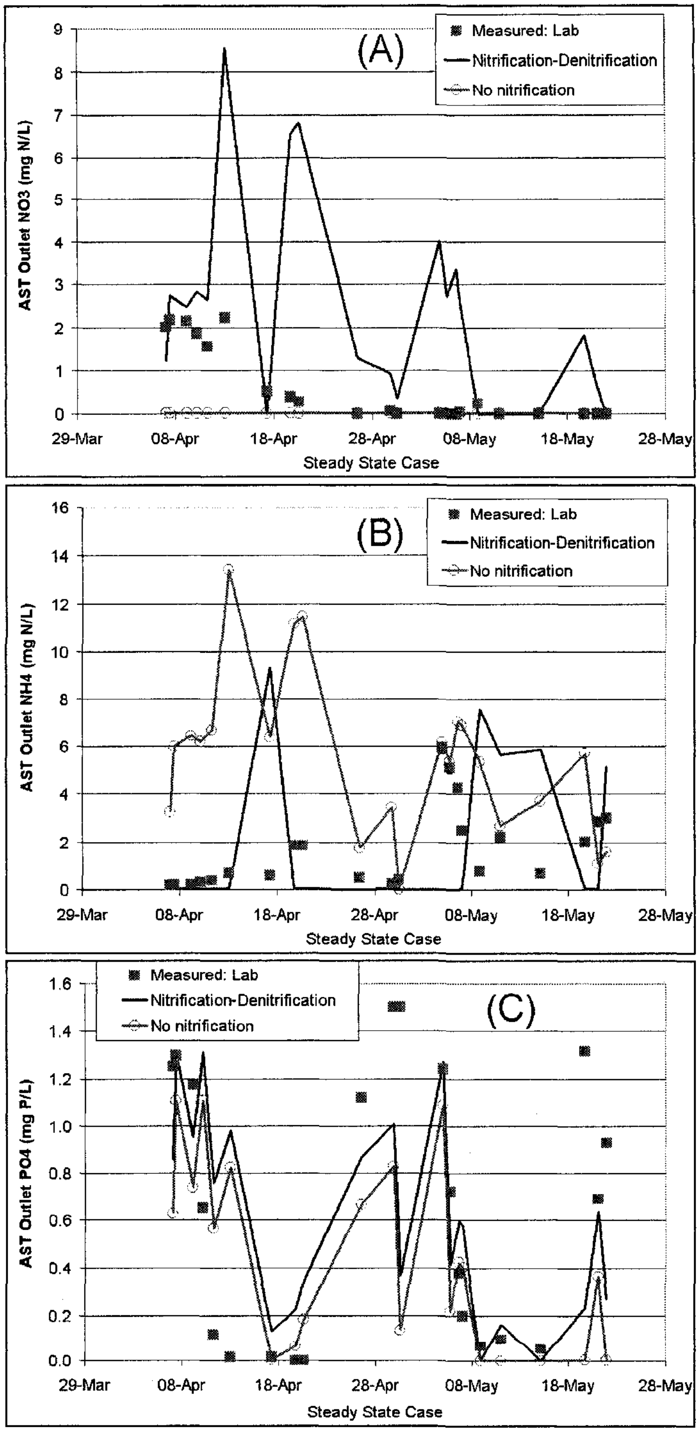

Figure 75: Uniform model approach, AST outlet nutrient residuals measured & modelled (a) Nitrate (b) Ammonia (c) Phosphate

The proposed model was calibrated for each pseudo-steady state case; the parameters of which are presented in Table 108 in comparison with selected values from the literature, ranging from the ASM default parameters to studies on pulp and paper wastewater. Two of the parameters that were used to calibrate each case, μ_A and ka, were found to have values generally lower than those found in the literature, although ka was found to have a large range of values in this study. Many of the parameters listed in Table 108 are default parameters that were investigated but found not to be sensitive in this model. It should be noted that the calibrated solution for each pseudo-steady state is not necessarily a unique solution due to the nature of the ASM model. The individually adjusted kinetic parameters for each scenario are listed in Table 85. As previously stated, for the later scenarios, given the already low-to-zero autotrophic maximum growth rates, the range of anoxic growth correction factors that reasonably fit the measured data is quite large. So while an anoxic correction factor of zero may fit the measured data, laboratory analysis is required to validate this value.

Table 84: Kinetic & stoichiometric parameters: calibrated model

Parameter	***Symbol***	***Units***	***Literature Values***	***Literature References***	***Model (Range)***
Individually adjusted kinetic parameters					
Autotrophic maximum growth rate	μ_A	1/d	0.8 15* 0.4	**1** **2** **3**	**0.05 – 0.30**
Correction factor for anoxic growth of heterotrophs (denitrification)	η_g	-			**0 – 0.7**
Specific ammonification rate	k_a	m^3/g COD. d	0.08 0.07 0.003-0.004	**1** **2** **7**	**0.009 – 0.4**
Specific phosphatification rate	k_p	m^3/g COD. d	0.03 – 0.8	**7**	**0.029 – 0.4**
Constant kinetic parameters					
Heterotrophic maximum growth rate	μ_H	1/d	6 39 2.3 – 4.79	**1** **2** **4**	18
Heterotrophic decay	b_H	1/d	0.62	**1**	0.50

Parameter	***Symbol***	***Units***	***Literature Values***	***Literature References***	***Model (Range)***
rate			0.5 – 0.58 0.13	**3** **5**	
Autotrophic decay rate	b_A	1/d	0.05 0.29	**1** **2**	0.04
Yield of heterotrophic biomass growth	Y_H	g COD/ g COD	0.67 0.44, 0.62 0.76	**1** **6** **5**	0.666
Yield of autotrophic biomass growth	Y_A	g COD/ g N	0.24 0.3	**1** **2**	0.24
Correction factor for anoxic hydrolysis	η_h	-			0.40
Half saturation constant for assimilation of carbon (heterotrophs)	K_{SH}	g COD /m^3	20 158 5	**1** **2** **3**	20
Phosphorus half saturation constant (heterotrophic)	K_{PH}	mg P/L			0.01
Phosphorus half saturation constant (autotrophic)	K_{PA}	mg P/L			0.01
Half saturation constant for assimilation of nitrogen (heterotrophs)	K_{NH}	g COD /m^3			0.05
Half saturation constant for assimilation of nitrogen (autotrophs)	K_{NA}	g COD /m^3	1 2.7	**1** **2**	0.05
Maximum specific hydrolysis rate	k_h	g COD /g cell COD.d	3 7.9 8.1	**1** **2** **5**	3
Hydrolysis half saturation constant	K_X	g COD /g cell COD	0.03 0.5	**1** **2**	0.03

Parameter	*Symbol*	*Units*	*Literature Values*	*Literature References*	*Model (Range)*
Oxygen half saturation constant (autotrophic)	K_{OH}	g O_2/m^3			0.20
Oxygen half saturation constant (heterotrophic)	K_{OA}	g O_2/m^3			0.40

* Unconstrained optimal model solution, not measured value

References:

1: [204]
2: [197]
3: [249]
4: [196]
5: [200]
6: [199]
7: [262]

Table 85: Individually adjusted kinetic parameters: calibrated model

Scenario	μ_A	η_g	k_a	k_p
1	0.18	0.04	0.10	0.40
2	0.17	0.08	0.13	0.40
3	0.16	0.07	0.09	0.40
4	0.16	0.08	0.06	0.03
5	0.20	0.09	0.40	0.04
6	0.14	0.17	0.07	0.06
7	0.30	0.18	0.20	0.30
8	0.11	0.30	0.04	0.18
9	0.11	0.45	0.05	0.09
10	0.08	0.70	0.05	0.40
11	0.12	0.50	0.07	0.40
12	0.05	0	0.03	0.40
13	0.08	0	0.02	0.17
14	0.05	0	0.02	0.40

Scenario	μ_A	η_g	k_a	k_p
15	0.05	0	0.01	0.07
16	0.05	0	0.01	0.05
17	0.05	0	0.01	0.08
18	0.05	0	0.02	0.08
19	0.05	0	0.01	0.08
20	0.05	0	0.01	0.40
21	0.05	0	0.08	0.40
22	0.05	0	0.05	0.40

The nutrient residuals for nitrate, ammonia, and phosphate found from the individually adjusted kinetic parameter model are compared to the measured values in Figure 91. The modelled nitrogen residuals are found to fit very well to the measured data, while the modelled phosphate residuals fit less well, which is understandable given the existence of three parameters to describe the nitrogen transformation processes, μ_A, η_g and k_a, compared to one parameter, k_p, to describe the phosphorus transformation processes. There is also more uncertainty associated with the phosphoric acid dosing rate calculated in the mass balances compared to the measured urea dosing rate due to the quality of measured data available.

It should be noted that the pseudo-steady state cases 9:06pm 8 May and 3:52am 15 May have poor modelled BOD removal due to phosphorus deficiency, with modelled BOD residuals of 77 mg BOD/L and 60 mg BOD/L, respectively. This indicates that either the calculated phosphoric addition rate from the mass balances is inadequate or that phosphorus previously stored by the biomass became available, in addition to the phosphorus calculated in the mass balances.

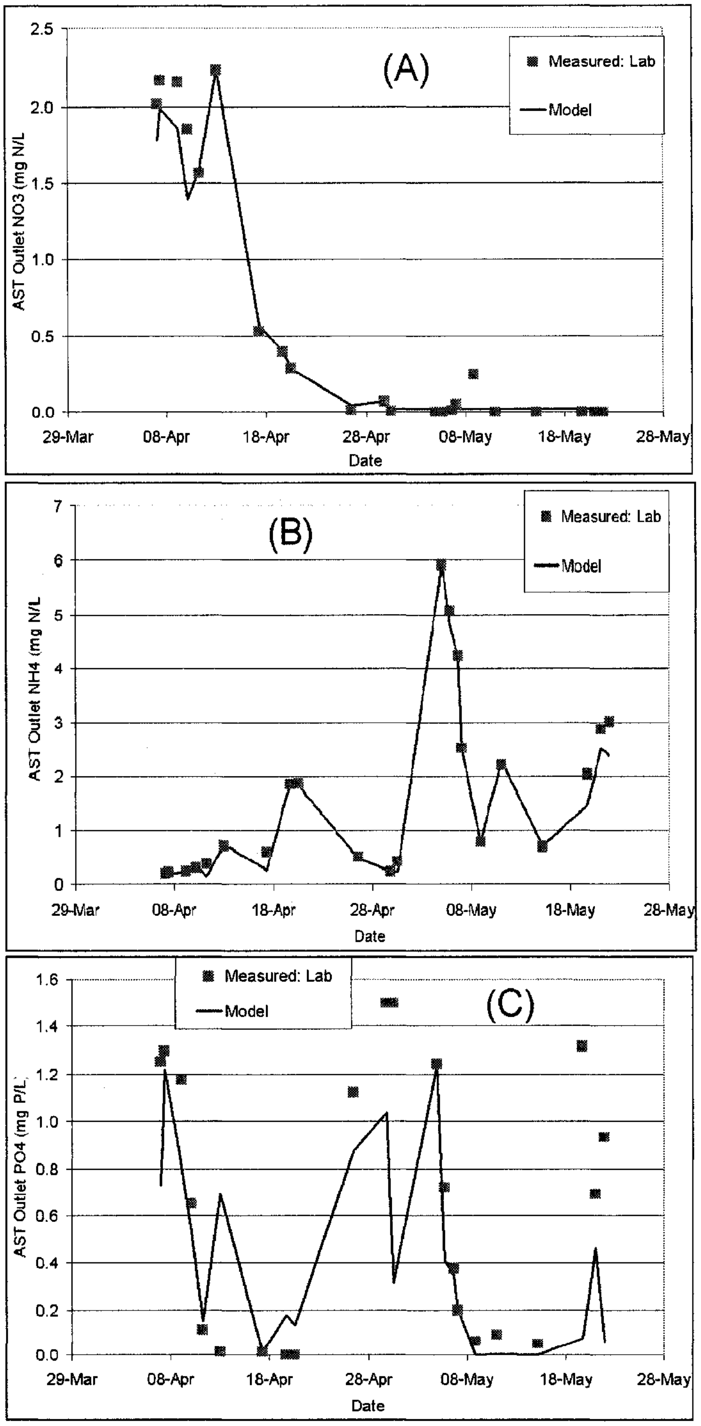

Figure 76: Individually adjusted kinetic parameter approach, AST outlet nutrient residuals measured & modelled (a) Nitrate (b) Ammonia (c) Phosphate

The autotrophic maximum growth rate, μ_A, the anoxic growth factor, η_g, the ammonification rate, ka, and the phosphatification rate were compared to influent COD fractions and process operating conditions such as the sludge retention time, dissolved oxygen concentration, temperature, and sludge volume index. No obvious trends were observed.

The nitrification and denitrification reactions are influenced by the dissolved oxygen concentration, the ammonia concentration, the temperature and the sludge retention time, the latter due to the fact that the maximum autotrophic growth rate is significantly lower than the maximum heterotrophic growth rate [66]. If a process is operated with a long sludge age, the nitrifying bacteria have a much greater opportunity to develop, whereas conditions that encourage rapid growth will cause the decline of the nitrifying bacteria population [66]. The yield of nitrifying bacteria is less than that of heterotrophic bacteria, which manifests as a minimal impact on the overall suspended solids concentration of the mixed liquor in the activated sludge process [66].

Nitrification is carried out by both heterotrophic and autotrophic bacteria, but is usually attributed to autotrophic bacteria, in particular those of the *Nitrosomonas* and *Nitrobacter* genera [66]. These bacteria can use an organic carbonaceous substrate, but the quantity is usually so small that it is ignored and carbon dioxide is used to represent the carbon source for this process [66]. Nitrification is modelled in the ASM1-based model as a one-step process, which can be described by the simplified overall nitrification equation as follows [135]:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + 2H_2O$$

Denitrification is carried out by heterotrophic bacteria and therefore requires an organic carbon substrate; the substrate may be provided by an exogenous source in the wastewater media or by an endogenous source [72]. An overall equation for denitrification, using methanol as the carbon substrate, is given by Buckley (2001):

$$6NO_3^- + 5CH_3OH \longrightarrow 3N_2 + 5CO_2 + 7H_2 + H_2O + 6OH^-$$

Investigation of the nitrification, denitrification, and ammonification rates with respect to the AST selector dissolved oxygen concentration, ammonia concentration, temperature, and sludge retention time was expected to show some correlations. However, there are no obvious trends between the process rates and these process operating conditions.

Investigation of process conditions one to two sludge ages prior to the drop in nitrate residual concentrations was expected to yield some insight into the change in nitrification rate. From inspection of six months of unfiltered data of the nitrate residuals, shown in Figure 77, it is clear that the process suffered a minor temperature shock during the first week of May when the WWTP cooling towers were turned on and the temperature dropped approximately 5ºC. This event would be expected to slow the rate of nitrification; however, the nitrate residual concentration had begun to decrease almost 2 weeks earlier. The dashed lines in Figure 77 demarcate the period of time that was modelled, which starts amid already rising nitrate residual concentrations and rising temperatures.

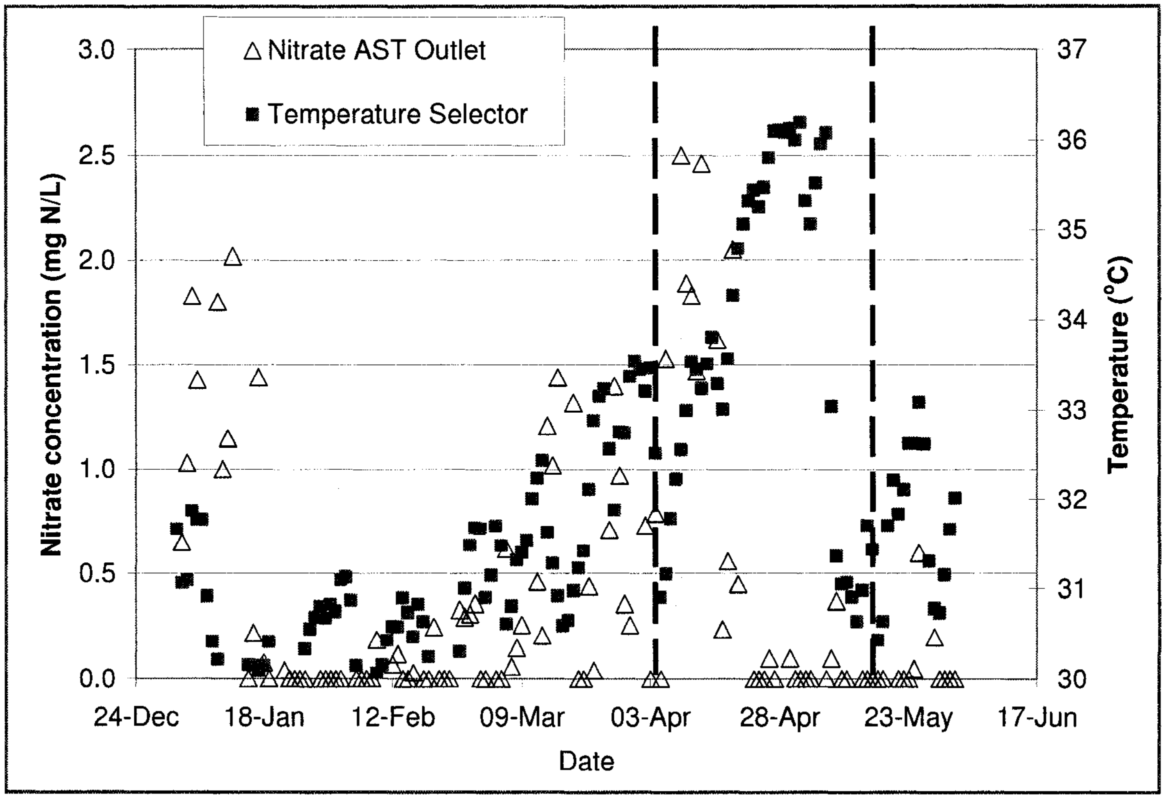

Figure 77: Six months of nitrate data (unfiltered) vs. temperature, section between dashed lines (---) represents modelled time period

Returning to the calibrated primary effluent wastewater characterisation, represented in Figure 74, it is possible that a step change in the relative values of the X_I fraction and X_S fraction caused the response in the nitrate residual. However, inspection of six months of nitrate residual concentration data in comparison with the calculated fraction of slowly biodegradable influent COD fraction fxs and in comparison with the sludge retention time does not show any correlation. As seen in Figure 78, there is a significant spread of data.

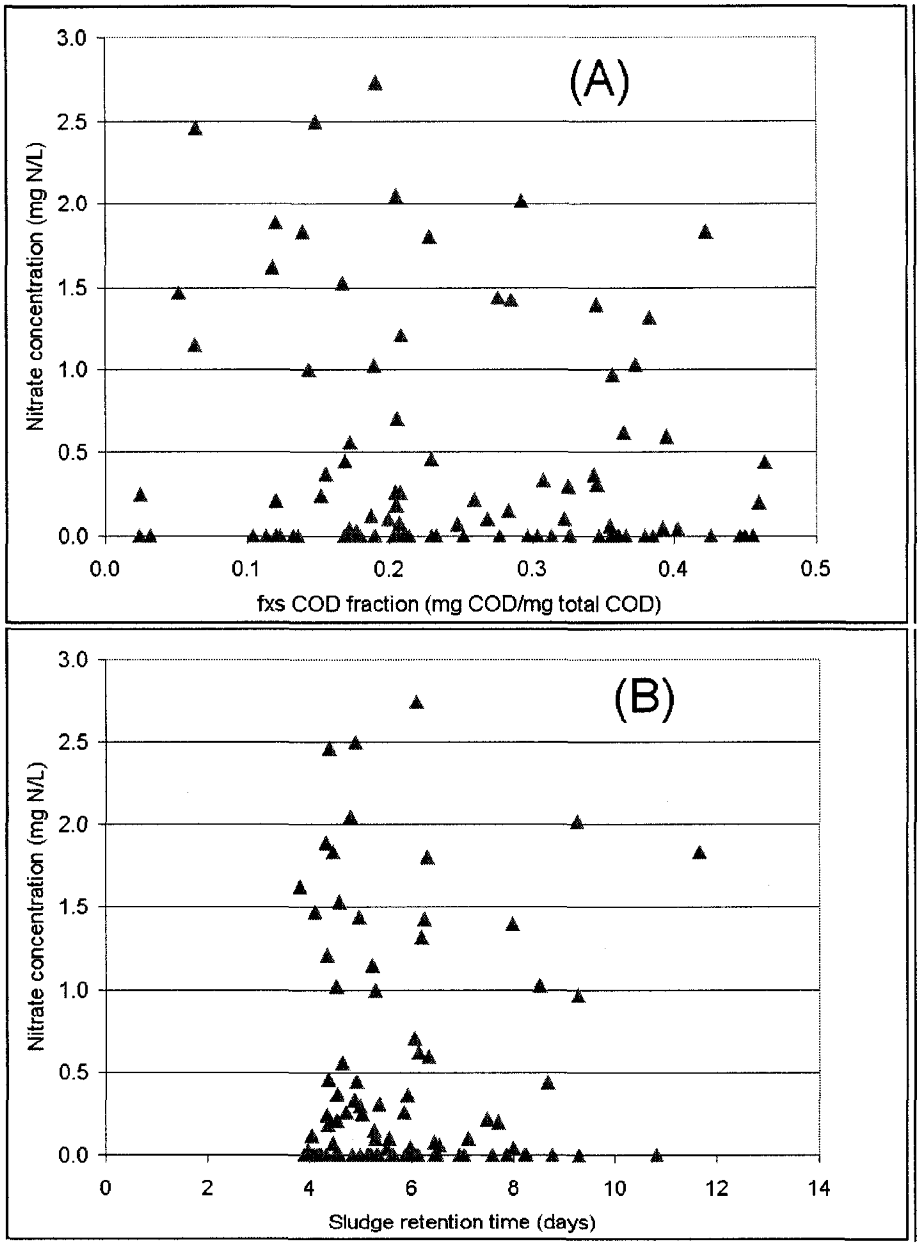

Figure 78: Six months nitrate data (untreated data) vs. (a) biomass fraction of slowly biodegradable influent COD (fxs, mg COD/mg total COD), (b) sludge retention time (days)

It is possible that the nitrification process became inhibited due to toxic substances in the primary effluent, and this is the reason that the nitrification rate diminished with time in the modelled time period. Inspection of six months of unfiltered nitrate residual concentration data in comparison with the AST inlet pH and in comparison with the AST inlet conductivity does not show any correlation. As seen in Figure 79, there is a significant spread of data.

An investigation of the modelled time period only, shown in Figure 80 (a), reveals a relationship between the nitrate concentration and the pH, which does not correspond to the general relationship between pH and the rate of nitrification. Generally in municipal systems, the rate of nitrification is optimal in the pH range of 7.5 to 8.0, and may be at only 10 to 20% of the optimal rate in the pH range of 5.8 to 6.0 [39]. Conductivity was relatively stable during this period, between 150 to 190 µS. Figure 80 (b) demonstrates the change of nitrate concentration (left-hand axis) and primary effluent pH (right-hand axis) over time; an evolution of both occurs over the modelled time period. The downward arrow indicates a high pH event in the primary influent on 30 April: a pH of 10.2 was recorded in both the mill drain and in the primary influent. A pH adjustment at the primary clarifier resulted in a pH of 6.3 in the primary effluent.

It is possible that organic toxic substances, such as polymers from the paper machine, were present in the primary effluent [267] but were unmeasured by either pH or conductivity. High BOD concentrations in the final effluent were not observed for any scenario indicating that no inhibition of carbonaceous substrate removal occurred.

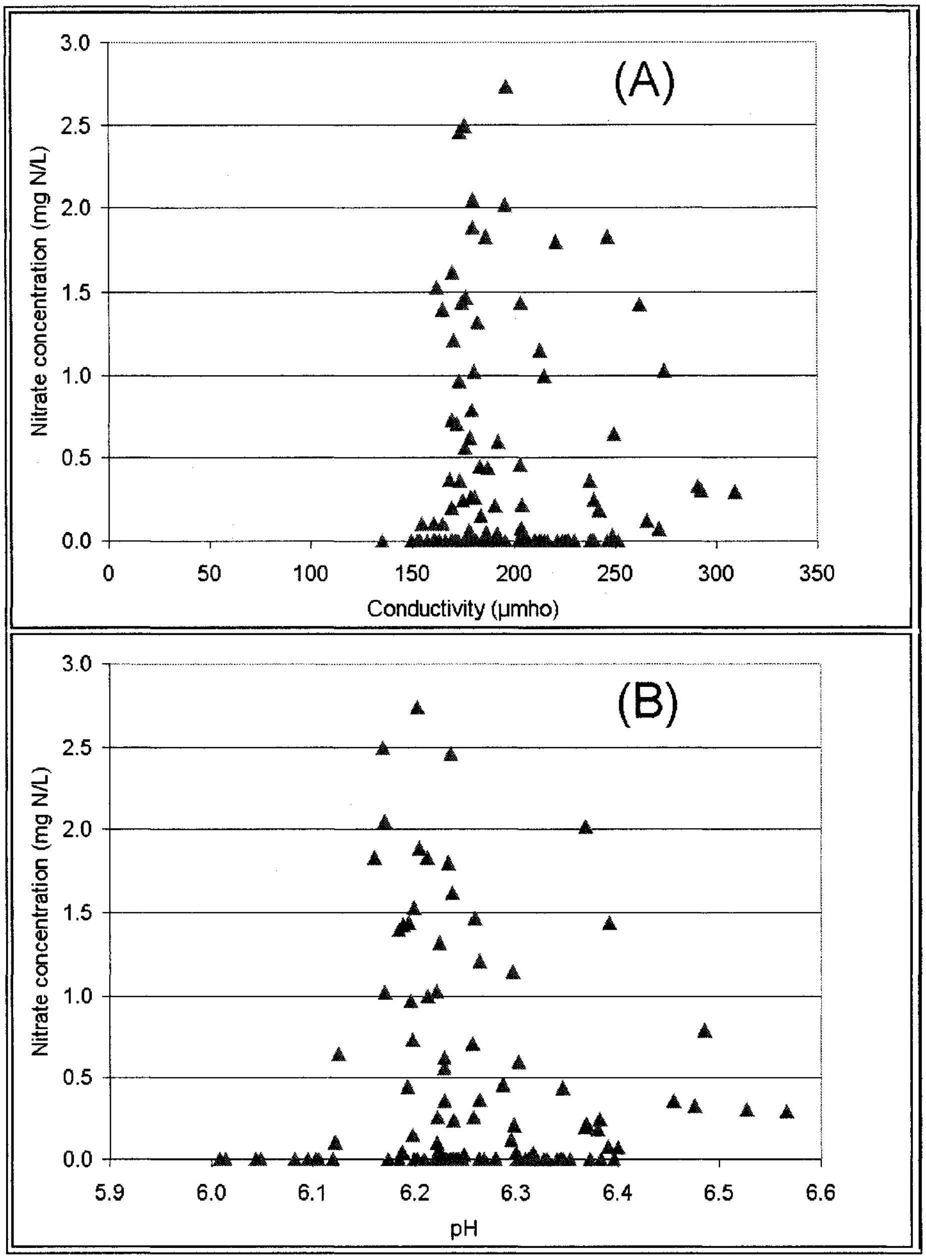

Figure 79: Six months of nitrate data (untreated data) vs. (a) Conductivity (µmho), (b) pH

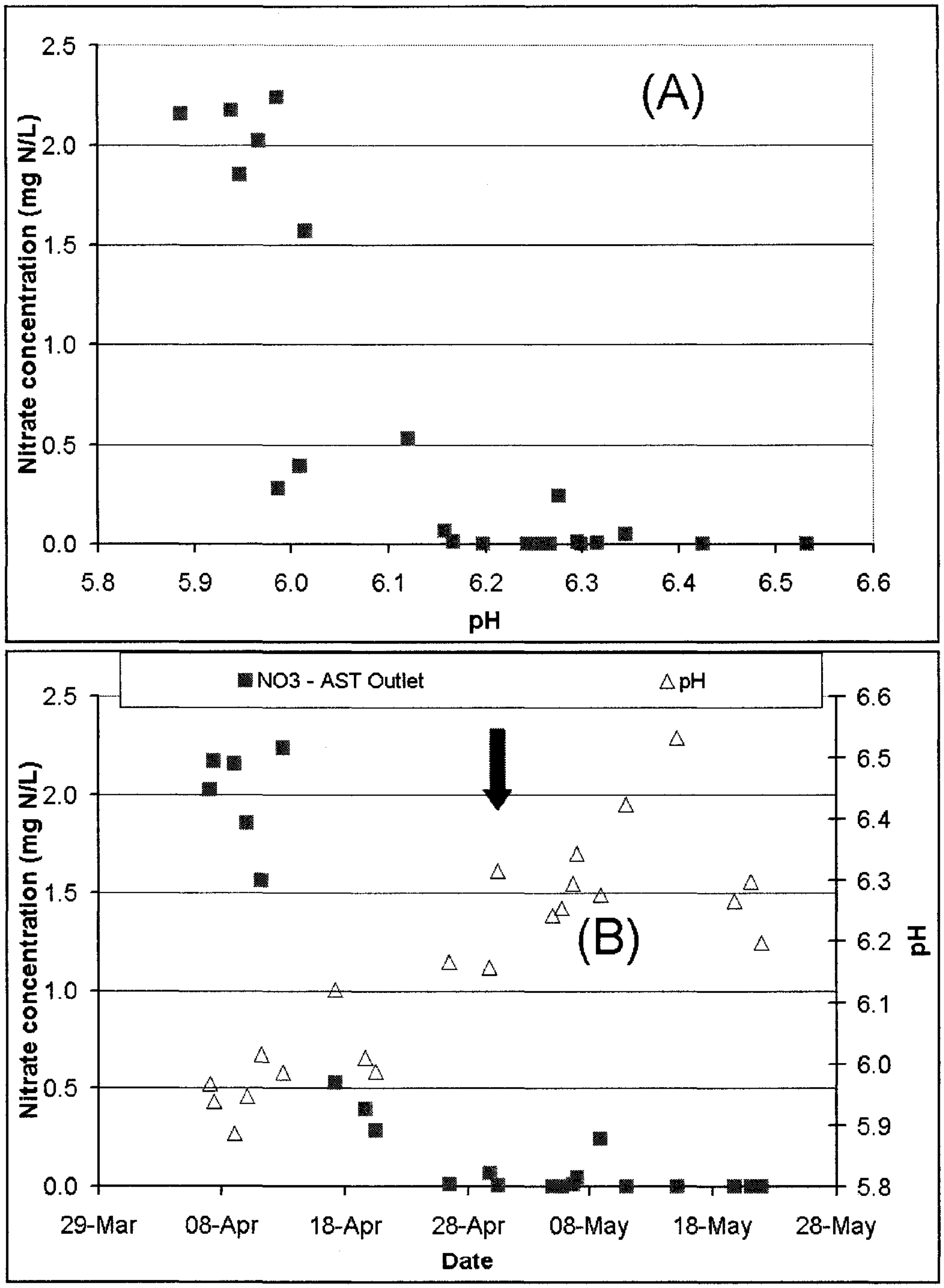

Figure 80: (a) Nitrate concentration vs. pH, (b) Nitrate concentration (left-hand axis), pH (right-hand axis) over modelled time period, downward arrow indicates high pH event in primary influent

Discussion

Modelling and influent characterisation of pulp and paper wastewater has presented a significant challenge to researchers over the past 10 to 15 years, with experiences ranging from "good agreement with plant operating data" [196] to "a poor model response for the effluent COD and suspended solids concentrations" [263]. Modifications to the ASM models for this industry include nutrient-limited growth [134, 195, 197, 262], predatory biomass [134], optimised model calibration [197], kinetic parameter measurements [199, 200], and phosphatification [262]. The wastewater characterisation is believed to offer the mill the opportunity to assess the impact of the sludge retention time on the slowly biodegradable X_S and particulate inert X_I fractions of the primary effluent, which would allow them to assess whether the primary effluent COD is removed via biological mechanisms (X_S) or physical settling in the secondary clarifier (X_I).

The two-model approach used in this study was found to reasonably model either the process regime including partial nitrification-denitrification, or the zero-nitrification process regime, but not the transition between the two process regimes. The goodness of fit of each of these models to the measured data can be described by the Pearson's R^2 and the chi-squared statistics, listed in Table 86, used to compare modelled to measured nutrient residual data (a R^2 and/or chi-squared value of 1 is considered to be a good fit of modelled to measured data). Restricting the range of each model improves the goodness of fit of each model. Future work includes estimating and interpreting the ammonification rate for the zero-nitrification process regime.

Table 86: Goodness of fit, 2-model approach & individually adjusted kinetic parameter approach (SS = pseudo-steady state cases)

Model	*Data set*	*R^2 Nitrate*	*R^2 Ammonia*	*R^2 Phosphate*
1:With nitrification-denitrification	Full	0.01	0.12	0.24
	First 6 SS	0.29	0.16	0.10
2: No nitrification-denitrification	Full	0	0.08	0.18
	Last 13 SS	0.24	0	0.20
Individually adjusted kinetic parameter model	Full	0.98	0.98	0.42

Model	**Data set**	χ^2 **Nitrate**	χ^2 **Ammonia**	χ^2 **Phosphate**
1:With nitrification-denitrification	Full	0	0	0
	First 6 SS	0	0.30	0.84
2: No nitrification-denitrification	Full	0	0	0
	Last 13 SS	0.01	1.00	0
Individually adjusted kinetic parameter model	Full	1.00	1.00	0

The adjustment of kinetic parameters for individual pseudo-steady states provides one plausible non-unique model solution to the measured data. The step-wise calibration of the nitrification-denitrification and phosphatification reaction rates provides a goodness of fit to the measured data that can be described by the Pearson's R^2 and the chi-squared statistic, listed in Table 86, when comparing modelled to measured nutrient residual data. The goodness of fit of the individually adjusted kinetic parameter model is far superior to the uniform model approach, particularly for the nitrate and ammonia residual concentrations. This individual adjustment of kinetic parameters methodology is in contrast to the optimised calibration techniques used by Sreckovic (2001), which resulted in some unlikely reaction rates, such as a maximum autotrophic growth rate μ_A of 15 d^{-1} (unconstrained optimal model solution). The implications of the individually adjusted kinetic parameters will be investigated in further work.

Pulp and paper wastewater influent can be highly variable in the short term compared to municipal wastewater; however, the biomass' environment does not change as quickly as the influent due to the residence time of the well-mixed (CSTR) selectors and AST basins. The microbiology of the AST system is believed to be determined to a certain extent by the conditions in the selectors in terms of which bacteria out-compete others. It is thought that the conditions in the selectors will also therefore determine the nutrient transformations that occur in the AST system to a certain degree. The overall sludge retention time (SRT) of the system will also play a role since the nitrifying bacteria generally require a longer time to establish the population and can be washed out of the system at short SRTs. The fact that the nitrification-denitrification process rates did not correlate to any of the process conditions was unexpected and is further evidence of the difficulty of modelling partial nitrification and denitrification reactions.

This case study was focussed on a pulp and paper wastewater treatment plant consisting of very well-mixed selectors and AST basins. Every AST system is unique in its hydraulic, settling, and biological behaviour; some AST basins may experience dead zones or pockets of sludge deposition, depending on the aeration and mixing systems employed. The methodology presented in this study is broadly applicable to AST systems, independently of the particular details of the treatment plant.

Conclusions

One of the major assumptions of the ASM models is that the microbiological population in the mixed liquor is stable. The short-term variability of pulp and paper mill effluent is much greater than that of municipal wastewater, as can be seen by the wide range of primary effluent COD concentrations, flow rates, dissolved oxygen concentrations, sludge retention times and possible primary effluent characterisation fractions. This variability results in stresses to the microbial population, and therefore leads to unpredicted changes in the local nutrient transformations occurring in an AST system operating with partial nitrification-denitrification.

One of the original aims of this study was to establish a steady state model that could predict changes in nutrient concentrations and be implemented at the mill for improved control of nutrient addition to the wastewater treatment process. Future work will include the investigation of the use of the individually adjusted kinetic parameter methodology for incorporation into a control strategy for the mill.

Given that pulp and paper mills are generally more complex than the one used in this case study, which has straightforward wastewater treatment processes (single line CSTR) and an effluent from a single pulping process (TMP), ASM-based models in their current state are unlikely to be broadly applied to the pulp and paper industry. The influent characterisation of pulp and paper wastewater highlights significant differences between this industrial wastewater and municipal wastewater, which warrants further work if the ASM-based models are to be applied to this industry. Pulp and paper wastewater total COD concentration, and possibly the relative size of the COD fractions, can vary significantly over the course of a day, which represents a challenge in terms of applying the ASM-based model for a well-mixed (CSTR) AST plant with a short retention time.

It is feasible to use an ASM-based model to model the wastewater treatment plant at a pulp and paper mill, when the plant is operating in a stable manner with a stable microbiological population. It is extremely difficult to model small changes in nutrient concentrations when the partial nitrification-denitrification processes vary over time and in response to changes in the influent characterisation and the sludge retention time.

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APPENDIX 4.3
Published Article 3

Pulp and paper wastewater: activated sludge modelling & nutrient control strategies

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Abstract

Since pulp and paper wastewater is commonly deficient in nitrogen and phosphorus, these nutrients are often added to the biological wastewater treatment process. Nutrient concentrations in mill final effluent discharge are also increasingly prescribed by environmental or governmental authorities. The control of the dosing of these nutrients represents a cost reduction opportunity as well as an opportunity to reduce the final effluent nutrient concentrations. The objective of this study is to investigate the use of ASM-based modelling in an integrated control of nutrient dosing; this paper addresses the development of a suitable ASM-based model for this purpose. A wide range of pulp and paper and wastewater treatment process configurations exist industry-wide. This paper presents a case study of an integrated TMP-newsprint mill; the methodology of the study is practical and broadly applicable.

Recent studies have demonstrated the characterization of influent and applied an ASM-based model for pulp and paper wastewater [262, 268]. The methodology used in this study, of rigorous data treatment, detection of pseudo-steady states, development of mass balances and the use of a pulp and paper-specific ASM1-based model, has demonstrated important insights into the nutrient transformations occurring in a well-mixed (CSTR) short-retention time AST wastewater treatment plant.

The use of the ASM-based model for the control of dosing of supplemental nitrogen and phosphorus, or for the control of process operations such as the WAS flow rate and nutrient dosing flow rates, is proposed as a possible control strategy to achieve desired nutrient residual concentrations. The use of the model saturation function as an advanced indicator for biomass nutrient deficiency is also proposed.

Key words

Modeling, nutrients, pulp, paper, activated sludge, wastewater treatment

Introduction

A variety of biological treatment plant processes are used in North America for the treatment of pulp and paper wastewater, including aerated stabilization basins (ASB) and activated sludge treatment (AST) plants. Most pulp and paper wastewaters are deficient in readily available macronutrients, notably nitrogen and phosphorus, which are required for biological treatment. Therefore, these nutrients are often added to the wastewater treatment process. Environmental and governmental quality requirements on the final effluent discharge to receiving waters have also become more stringent recently, particularly for nitrogen and phosphorus discharge [269]. Reductions in current levels of nitrogen and phosphorus dosing are possible while still meeting biological nutrient requirements, and represent a potential cost saving for the mill [265]. For these reasons, control of the supplemental nitrogen and phosphorus dosing to the wastewater treatment plant is an important aspect of modern mill management. The objective of this study is to investigate the use of ASM-based modelling in an integrated control of nutrient dosing; this paper addresses the development of a suitable ASM-based model for this purpose.

Nutrient addition and control

Assuming the influent from the mill is nutrient deficient, and that the activated sludge process has a short enough residence time such that nitrogen fixation and cell lysis provide inadequate nutrients, then the nutrient requirements for the aerated basin must be met by the addition of supplemental nutrients.

Nutrient addition control strategies are determined primarily by the desired result and subsequently by the desired accuracy, precision, and complexity of the process control. These objectives include the minimization of effluent concentrations of organic pollutants and nutrients (BOD, N, P), or the minimization of nutrient dosage quantities, whilst maintaining stable process operation and efficient BOD removal [65].

The BOD_5:N:P mass ratio of 100:5:1 has its origins in the dry-basis contents by weight of a typical bacterial cell, and the assumption that bacterial cells require the macronutrients nitrogen and phosphorus in proportion to the composition of cell biomass [39]. For pulp and paper wastewater treatment using AST technology, stable plant operation with a BOD_5:N:P ratio of 100:3.5:0.6 has been reported [10], and lower limits for BOD_5:N of 100:2.5 to 100:4.5 and BOD_5:P of 100:0.4 to 100:0.6 have also been suggested [63, 64]. Zero supplemental phosphorus has been added to a pulp mill effluent with successful stable AST operation [64], and zero nutrient addition has been implemented successfully for pulp and paper ASB operations, which is due to sufficient nutrient internal recycling [63, 73, 74].

Ratio control of nutrient dosing can be based on a BOD_5:N:P mass ratio, which translates to control of the nutrient dosing flow rate in proportion to the measured BOD load in the incoming mill effluent. This control relies on the accurate on-line measurement of BOD or a substitute for BOD. A number of substitutes and combinations of parameters including BOD_1, total organic carbon (TOC), COD, conductivity, pH and TSS were tested on Kraft mill effluent with a particular focus on upset conditions, with mixed results [157]. Conductivity has been used successfully as a surrogate for organic load [156]. In terms of on-line instrumentation, one study considered TOC as the best surrogate in comparison with respirometry [158].

Nutrient dosing based on the ammonia and phosphate residuals in the final effluents has also been implemented for pulp and paper wastewater for both ASB and AST treatment processes [72]. Reported residual levels in the final effluent range from 0.5 to 1.5 mg NH_3-N/L and 0.25 to 1.0 mg PO_4-P/L [72]. One of the problems with this method of control is that the control loop can only react slowly to an upset in influent to the wastewater treatment plant [6]. If the aim of nutrient control is to minimize the residual nitrogen and phosphorus in the final effluent, it should be noted that the majority of total nitrogen is present in the suspended solids, indicating it is bound in the biomass, and underlining the importance of solids separation to nutrient control [63, 159].

Feed-back control based on effluent nutrient residuals is also used for pulp and paper mills in Finland with an ongoing assessment of the nutrient balance over the wastewater treatment plant in an attempt to minimize changes in the nutrient levels throughout the treatment process [65]. An expert control system incorporating on-line measurements, control software, and predictive modeling has been trialed at a number of full-scale pulp mill wastewater treatment plants [160, 161]. A combination of upstream ratio and feed-back control was implemented for a fine paper mill effluent and resulted in a reduction of final effluent nutrient concentrations as well as a reduction of supplemental nutrient addition to the process [162]. A method for the detection and quantification of a nutrient-deficient state for sludge from a pulp and paper activated sludge process was developed [163]. The implementation of this methodology for the control of nutrient dosing to the process has been proposed [163].

Overdosing nutrients to the activated sludge process is both costly and can potentially cause eutrophication or toxicity if the nutrient concentrations in the discharged effluent are high enough. There are also adverse effects of under-dosing nutrients; in particular nutrient deficiency can lead to filamentous bulking events, production of viscous exocellular material (polysaccharide), or production of foaming exocellular material [68]. These types of process upsets can lead to poorly settling sludge which may lead to increased nutrient concentrations in the final effluent, or may require additional chemical dosing. The costs associated with these events are not insignificant.

Wastewater treatment modelling

Modeling of pulp and paper treatment plants using the Activated Sludge Models (ASM) developed for the municipal wastewater industry offers the opportunity to improve the understanding of the biological treatment plant, and to develop control strategies for the addition of nutrients to the wastewater treatment plant. These studies cover a broad range of wastewater treatment and pulp and paper processes [268]. The study results range from "good agreement with plant operating data" [196] to "a poor model response for the effluent COD and suspended solids concentrations" [263]. Some interesting characterization and modeling work was conducted for the Hylte mill in Sweden, which has unusual pulp and paper and wastewater process configurations [134, 195].

In this paper, the results of pseudo-steady state modeling carried out using experimental and mill data are summarized. In addition, control strategies for the addition of supplemental nutrients to the activated sludge treatment of pulp and paper wastewater as well as a model-based indicator for biomass nutrient deficiency are proposed. The project methodology employed includes meticulous data treatment, the identification of disparate operating conditions, and the development of a calibration process applied to each operating condition that accounts for varying nutrient transformation conditions.

Background

Mill Process

The White Birch Papers pulp and paper mill is located in Gatineau, Québec, and consists of a single line thermo-mechanical pulping (TMP) process followed by a single newsprint paper machine. The pulping process is the world's largest single line TMP pulping process, producing over 680 ODt/d. The wastewater plant process configuration is presented in Figure 81.

Since January 2007, the mill has operated the wastewater treatment plant remotely from the boiler house. In order to assist with this change, the mill has automated various measurements. Notably, one UV chemical oxygen demand (COD) and multiple total suspended solids (TSS) meters were installed, as well as one ion-sensitive ammonia-nitrogen (NH4-N) electrode and one colorimetric ortho-phosphate (PO4-P) instrument for on-line measurement of residual nutrient concentrations in the final effluent.

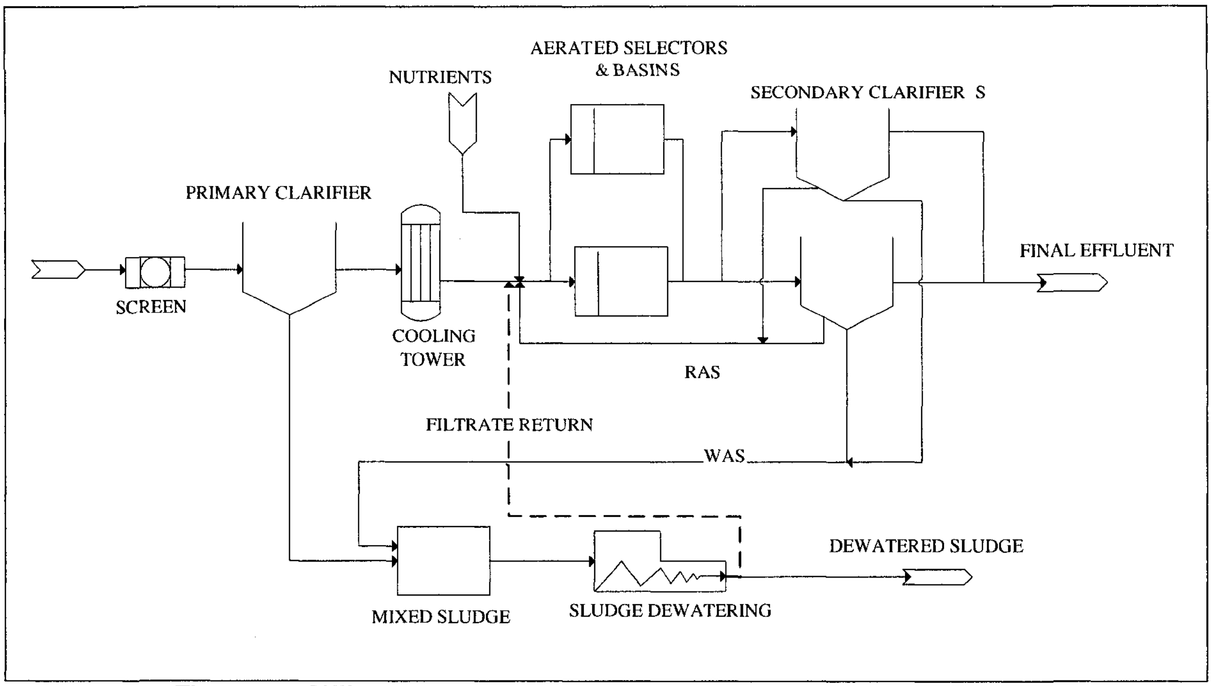

Figure 81: Mill wastewater treatment process configuration

Each AST line has submerged venturi (jet) aerators in a well-mixed basin. Nutrients are dosed into the inlet of the aerated selector in the form of urea and phosphoric acid. The mixed primary and secondary sludge is treated via a gravity table pre-thickener followed by a belt press.

Project results

The project methodology outlined in Figure 82 encompasses data collection of the mill physical design data, of continuous and discrete laboratory data from the mill PI system, and additional wastewater characterization measurements carried out at the mill laboratory and at the university laboratory according to Standard Methods [264]. This data was then treated to synchronize data over the hydraulic retention time of the AST basins, to exclude abnormal process conditions such as mill shuts, and to identify pseudo-steady state scenarios which varied in duration from 6 hours to 32 hours [265]. The treated data was further reconciled by mass balances for each pseudo-steady state prior to inclusion in an ASM-based model.

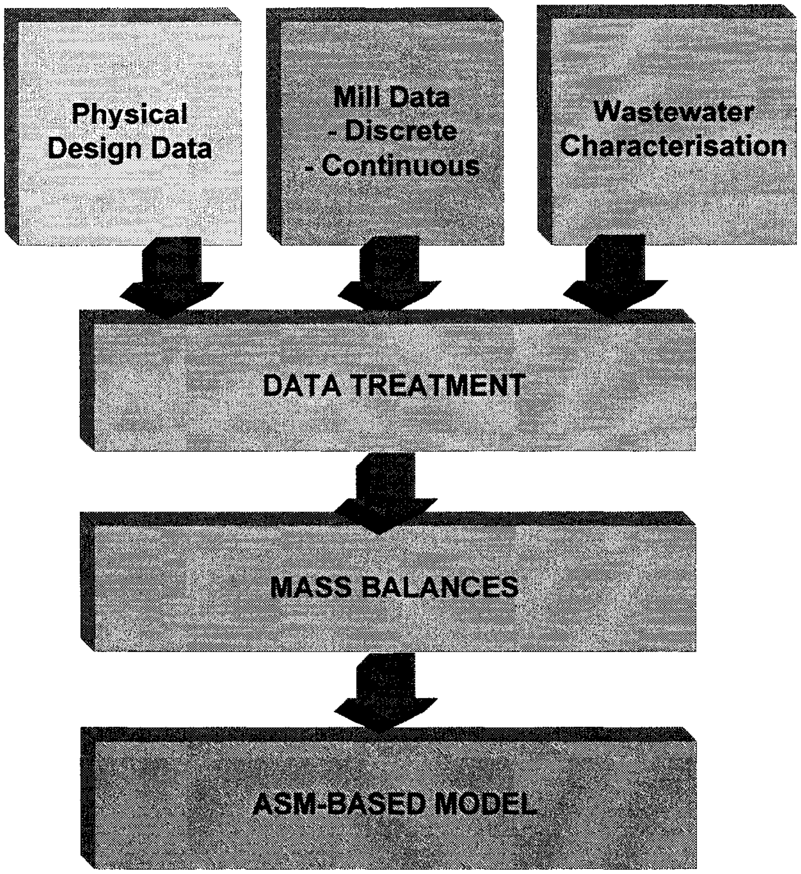

Figure 82: Project methodology

The results of the wastewater characterization and ASM-based modeling indicate that the pulp and paper wastewater is significantly different from modeled municipal wastewater, particularly in the distinction between the COD fractions: the slowly biodegradable fraction, fxs, the rapidly biodegradable fraction, fss, and the particulate inert fraction, fxi [268]. A uniform model capable of describing the entire data set was extensively investigated but was not found to be feasible. Instead, kinetic parameters were individually adjusted for the nitrification, denitrification, ammonification and phosphatification reaction rates. The phosphatification rate was found to be a function of the slowly biodegradable COD fraction, fxs. The evolution of the nitrification and denitrification reaction rates over time were thought to be attributable to changes in the microbiology, either due to a non-measured toxicity or due to subtle changes in the process conditions in the selector [268].

One of the major assumptions of the ASM models is that the microbiological population in the mixed liquor is stable. It was shown that the influent total

COD can vary significantly and it is assumed that the relative fractions of the wastewater influent can also change during the course of a day due to variations in the mill process such as changes in production grade, wash-ups and shut-downs. This variability results in changes in the microbial population and therefore changes in the minor nutrient transformations occurring in an AST system operating with partial nitrification-denitrification [268].

Results & Discussion

Control Strategies implemented

Since the start of this study, the mill has implemented a number of changes to its control strategy, including an upstream BOD_5:N:P ratio control in conjunction with feed-back residual monitoring and monitoring of the mixed liquor biological population. The upstream ratio is based on a target BOD_5:N:P mass ratio for the dosage of both supplemental nutrient chemicals: urea and phosphoric acid. The ratios are calculated based on the COD measured with the UV on-line COD meter. The ratios are also a function of the nutrient solution specific gravity and concentration, as well as the wastewater COD: BOD_5 ratio. At this mill, the COD: BOD_5 ratio has been established over the 12 months of 2006 to be 2.36, with a standard deviation of 0.33, during normal plant operation using BOD_5 and filtered COD measurements in the inlet to the aerated basins. This control is currently in the phase of having the upstream BOD_5:N:P ratio control automated.

The mill has found this control strategy works very well, particularly when the mixed liquor suspended solids, F/M ratio, and sludge age are relatively constant. The mill has found the final effluent on-line nutrient residual instruments to be reliable and to require little operation or maintenance from mill personnel. The regular analysis of the biological population provides important insights into the occurrence of partial nitrification-denitrification and biological predatory behavior, particularly predation of nitrifiers, that has been otherwise unmeasured by nutrient residuals.

Model results

Extensive model results are presented elsewhere [268]. The following is a presentation of an additional level of interpretation of those results, with the view to establishing control strategies for the dosing of supplemental nutrients and for the operation of the pulp and paper wastewater process. The model and results are based on the specific case study mill; however, the methodology is broadly applicable.

Figure 83 presents the phosphorus and ammonia saturation functions as calculated using the ASM-based model for the selectors. The saturation function indicates whether each nutrient is present in sufficient quantities (function approaches 1) or is deficient relative to the biological requirements of the microorganisms modeled (function approaches zero). The comparison of the ammonia and the phosphorus saturation function for each pseudo-steady state indicates which nutrient is relatively deficient. Monitoring the relative values of these saturation functions on a regular basis could be very useful for plant operators in order to determine which of the two supplemental nutrients is in short supply for the biomass to complete efficient BOD removal.

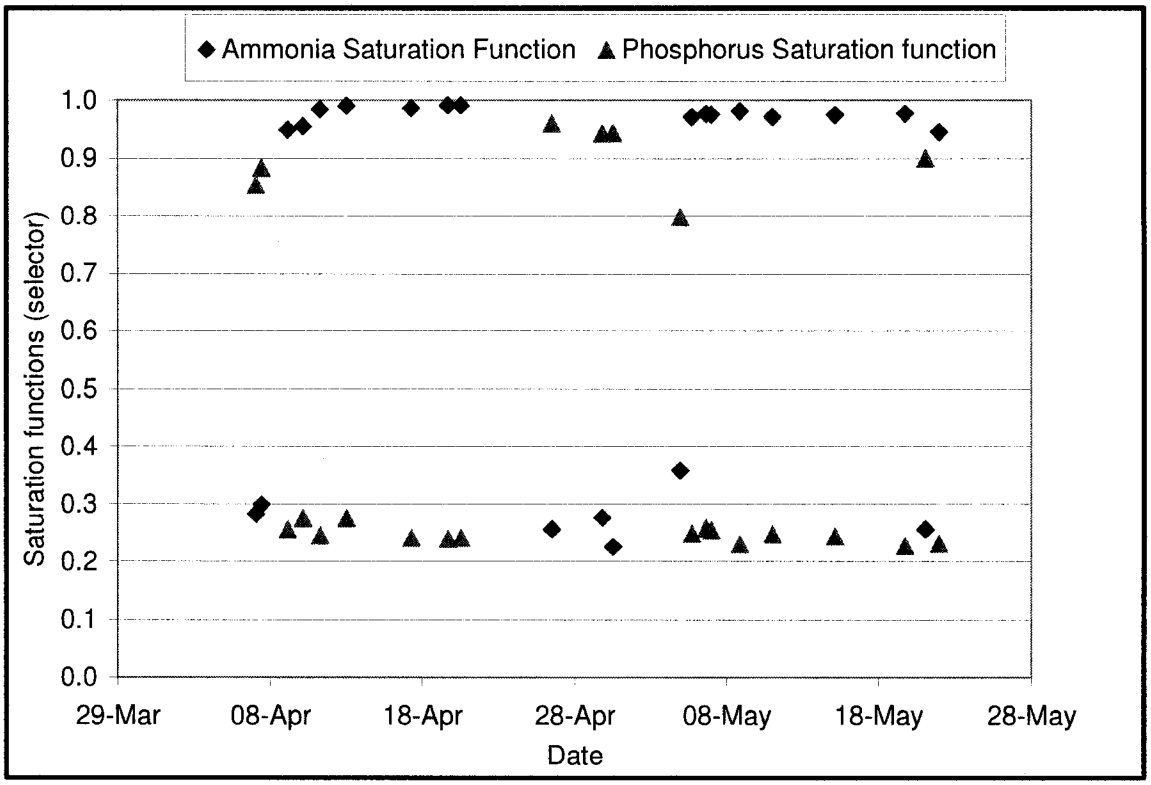

Figure 83: Phosphorus & Ammonia saturation functions (selector), model calculated

Figure 84 presents the measured residual phosphate concentration at the AST outlet (left-hand axis) compared to the phosphorus saturation functions in the selector (right-hand axis). The saturation function is a function of the nutrient concentration at the AST outlet, so there is by definition a correlation between the saturation function and the nutrient concentration. In the case of phosphorus, the saturation function fell to a value below 0.3 (dashed arrow A) prior to a fall in the ortho-phosphate concentration (dashed arrow

B) in the AST outlet. This suggests that the model could be used to predict an imminent nutrient deficient state prior to the exhibition of symptoms such as low nutrient residuals. This would be an extremely useful tool for plant operators to monitor on a regular basis. This hypothesis requires validation with further data treatment, mass balance, and modeling endeavors.

In the case of nitrogen, the saturation function and nutrient residual relationships can be divided into different operating regimes: (1) nitrification, (2) nitrogen deficiency and (3) zero-nitrification, as presented in Figure 85. In previous work, no correlation was found between nitrification-denitrification reaction rates and process conditions such as dissolved oxygen concentrations, influent ammonia concentrations, temperature, sludge retention time, pH and conductivity. If such a correlation did exist, it could be combined with the model saturation function to predict which nitrogen operating regime was occurring in the AST. According to the results of this study, the nitrate and ammonia residual concentrations indicate the nitrification and zero-nitrification operating regimes, and the saturation function indicates nitrogen deficiency. The transition from nitrification to zero-nitrification is not predicted by the saturation function alone; this transition is one of the most difficult scenarios for modeling of partial nitrification-denitrification processes in this AST.

The implications of using the proposed control strategies are significant for the mill. An operator could potentially use a calibrated pseudo-steady state model to determine the actual operating regime of the plant, in terms of nitrification-denitrification processes as well as the relative nutrient deficiency of nitrogen and phosphorus. Using a model to predict nutrient-deficient events or to identify which nutrient is deficient can have a large impact for mills, especially those operating under nutrient-stressed conditions, which can produce filamentous bulking events or excursions from nutrient residual discharge limits. The proposed nutrient control strategies require further validation; however an example case is used to demonstrate the value for the mill.

In the pseudo-steady state case from 13 April, nitrate residuals are present, plus the ammonia saturation function is approaching one, therefore the operator could determine that nitrification-denitrification is occurring in the plant. The operator would then take steps to limit the unwanted nitrification-denitrification processes, such as reducing the ammonia dosed to the process by reducing the BOD_5:N ratio control. Comparing the ammonia and phosphate saturation functions for this pseudo-steady state, it is also apparent that phosphorus is the nutrient in relative deficiency, therefore the operator could increase the BOD$_5$:P ratio control. These steps should be implemented subject to satisfying other aspects of the wastewater treatment plant operations (i.e., well-settling sludge in the secondary clarifier, appropriate mixed liquor suspended solids, F/M ratio). Reducing the nutrient dosing flow rate to the treatment plant represents significant cost savings for the mill, as mentioned previously. The operational control strategies implemented at each mill may vary depending on the plant configuration, dosing locations and operating regimes; however the methodology is broadly applicable.

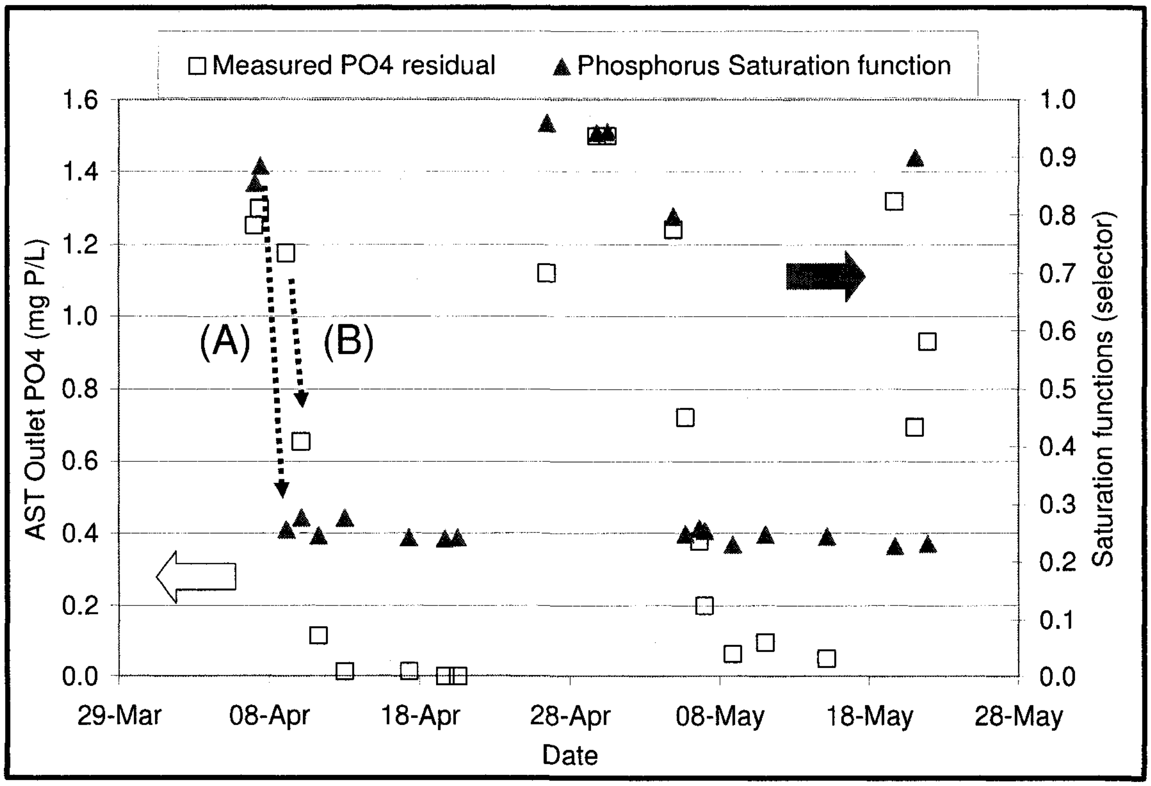

Figure 84: Measured & modeled AST outlet phosphate residuals (right-hand axis) vs. phosphorus saturation function (left-hand axis)

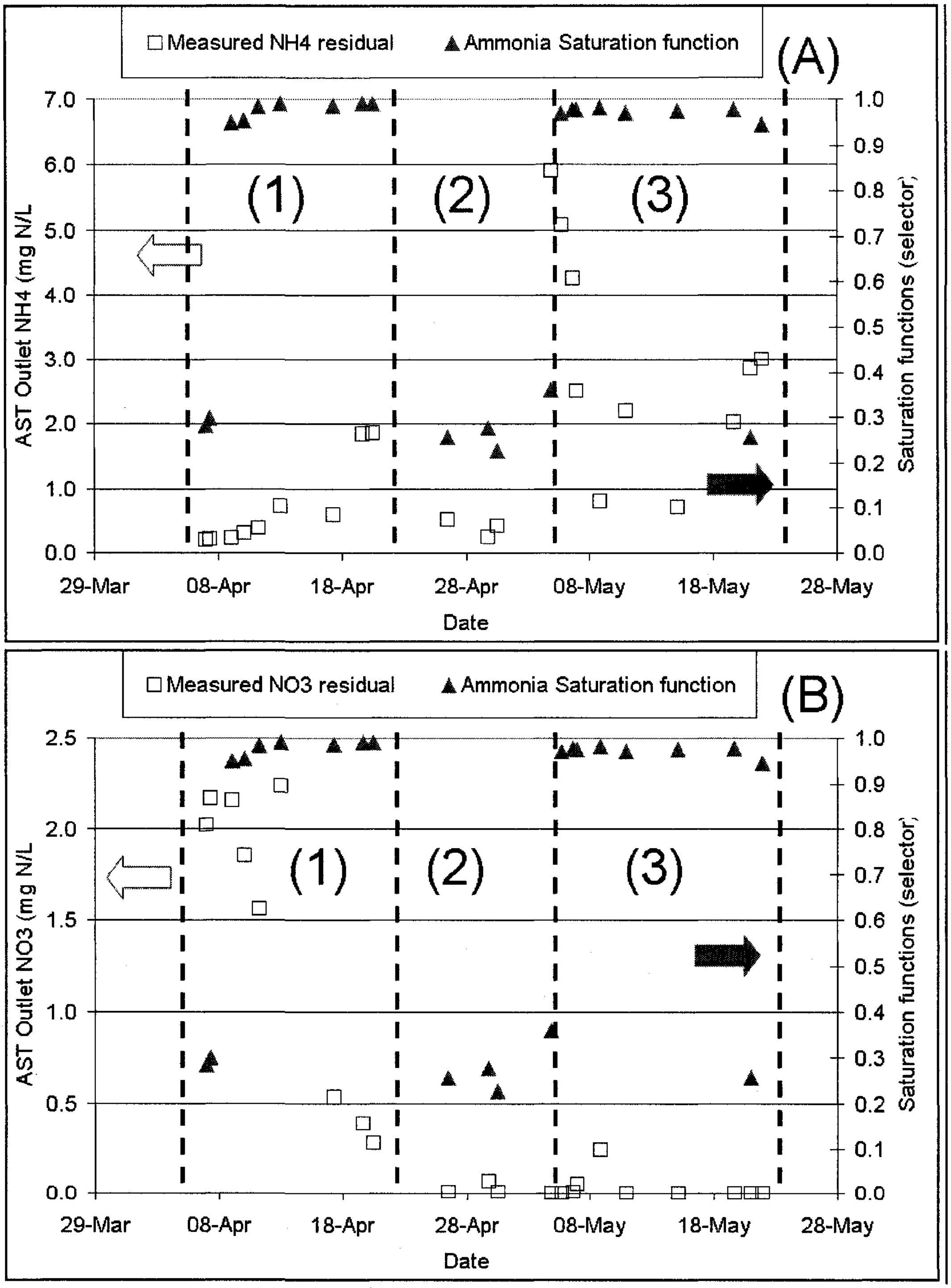

Figure 85: Measured & modeled AST outlet (a) ammonia residuals and (b) nitrate residuals (right-hand axis) vs. ammonia saturation function (left-hand axis), process regimes indicated: (1) Nitrification, (2) Nitrogen deficiency, (3) No nitrification

Conclusions

ASM-based models have been developed for the treatment of pulp and paper industrial wastewater that take into consideration its nutrient-deficient nature. Recent studies have highlighted the need for further work on the characterization of the wastewater influent and the definition of influent COD components relative to the models developed for municipal wastewater [268]. Nevertheless, the methodology used in this study, of rigorous data treatment, detection of pseudo-steady states, development of mass balances, and the use of a pulp and paper-specific ASM1-based model, has demonstrated important insights into the nutrient transformations occurring in a well-mixed (CSTR) short-retention time AST wastewater treatment plant.

The use of the ASM-based model saturation functions as an indicator of the actual plant operating regime and of nutrient deficiency in the biomass requires validation and is potentially a powerful tool for the plant operators. The mill has already implemented upstream ratio control of nutrient dosing with feed-back of residual concentrations, and the proposed use of the ASM-based model will be implemented as an additional layer of control. While a large range of pulp and paper process wastewater treatment configurations exist, the methodology and the ASM-based modeling used in this study are broadly applicable to the industry and represent state of the art technology application.

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APPENDIX 5
Modelling

5.1. *Modelling parameters*

5.1.1. Design & default parameters

The design and default parameters for the model are listed in the tables below.

5.1.1.1. Hydraulic Model

This data is entered for each process unit operation under the Physical, Operational or Consistency menu.

Aerated Selectors

The Aerated Selectors are modelled as continuously-stirred tank reactor (CSTR) units, as detailed in Table 87. The aerated selectors and basins are considered to be deep tanks in GPS-X, since they are deeper than 8 metres. The jet aerators are a Mass Transfer Systems (MTS) design, using MT4JM jet aeration nozzles.

Table 87: Aerated selectors hydraulic model parameters (each)

Data Type	*Parameter*	*Value*
Physical	Maximum volume	1000 m^3
Operational	Aeration method	Diffused Air
	Specify oxygen transfer by	Using a DO controller
	Beta factor (for DO saturation)*	0.95
	Temperature coefficient for K_La (theta factor)	1.024
	Minimum K_La	0 d^{-1}
	Maximum K_La	300 d^{-1}
	Diffuser type	Jet
	Alpha factor (jet)**	0.85
	Standard Oxygen Transfer Efficiency (SOTE) type	Correlation
	Diffuser submergence	9.1 m
	Specify diffuser setup	Enter number of diffusers
	Number of diffusers	12
	Tank floor area	100 m^2
	Area per diffuser***	0.038 m^2
	DO set point	**3.5**
	Controller form	Velocity

Data Type	Parameter	Value
	Controller type	PI
	Controller sampling time	5 minutes
	Proportional gain	10
	Integral time	1 minute
	Pumped flow	0 m^3/d
Consistency	HRT lower limit	0 d
	HRT upper limit	0.5 d
	MLSS lower limit	800 g/m^3
	MLSS upper limit	6 000 g/m^3

*Correction factor for DO saturation, takes into account salts, particulates and surface-active substances [210]
**Correction factor for jet aeration K_La value [210]
***Default value of 0.038 m^2 area per diffuser used due to lack of available data

The PI controller is tuned using rules of thumb [210]:

$K_C = 0.5/ K_P$
K_P = steady-state process gain
= change in controlled variable/ one-unit change in manipulated variable
$\tau_I = 1.5t$
t = time constant of first-order response that approximates the response of the controlled variable to a step in the manipulated variable

In the case of the dissolved oxygen control loop, the manipulated variable is the air flow rate and the controlled variable is the dissolved oxygen concentration in the selector or basin. For this scenario, K_C is estimated at 10 mg DO /L /m^3 air, and τ_I is estimated at 1 minute.

Aerated Basins

The Aerated Basins are modelled as two continuously-stirred tank reactor (CSTR) units, as detailed in Table 87. The aerated selectors and basins are considered to be deep tanks in GPS-X, since they are deeper than 8 metres.

Table 88: Aerated basins hydraulic model parameters

Data Type	*Parameter*	*Value*
Physical	Maximum volume	16 800 m^3
Operational	Aeration method	Diffused Air
	Specify oxygen transfer by	Using a DO controller
	Beta factor (for DO saturation)*	0.95
	Temperature coefficient for K_La (Theta factor)	1.024
	Minimum K_La	0 d^{-1}
	Maximum K_La	300 d^{-1}
	Diffuser type	Jet
	Alpha factor (jet)**	0.85
	Standard Oxygen Transfer Efficiency (SOTE) type	Correlation
	Diffuser submergence	9.1 m
	Specify diffuser setup	Enter number of diffusers
	Number of diffusers	90
	Tank floor area	1680 m^2
	Area per diffuser***	0.038 m^2
	DO set point	**2.0**
	Controller form	Velocity
	Controller type	PI
	Controller sampling time	5 minutes
	Proportional gain	10
	Integral time	1 minute
	Pumped flow	0 m^3/d
Consistency	HRT lower limit	0.05 d
	HRT upper limit	2 d
	MLSS lower limit	800 g/m^3
	MLSS upper limit	6 000 g/m^3

*Correction factor for DO saturation, takes into account salts, particulates and surface-active substances [210]

**Correction factor for fine bubble K_La value [210]

***Default value of 0.038 m^2 area per diffuser used due to lack of available data

Secondary Clarifiers

Both of the circular secondary clarifiers are considered sloping-bottomed units, with a slope of 4.1 degrees to the horizontal. The hydraulic details of these process units are presented in Table 89.

Table 89: Secondary Clarifiers hydraulic model parameters

Data Type	***Parameter***	***Value***
Physical	Clarifier type	Sloping bottom
	Number of layers	10
	Feed point from bottom*	4.3 m
	Surface	1018 m^2
	Water depth at sidewall	4.5 m
	Water depth at centre*	5.8 m
Operational	RAS Underflow rate	**7 000 L/min**
	RAS Underflow from layer	8
	WAS Pumped flow	**330 L/min**
	WAS Underflow from layer	10
	Sludge blanket threshold concentration**	2000 g TSS/m^3
	Critical sludge blanket level***	0.1 m
	Settling factor for non-volatiles****	1
Consistency	HRT lower limit	0.021 d
	HRT upper limit	0.5 d

*Does **not** include depression from base of clarifier to centre where sludge is extracted/ stored

** Concentration defines layer that will be considered 'sludge blanket' [210]

*** At this sludge blanket height, the dissolved oxygen in the underflow and pump streams will be zero [210]

**** Settling of particulate inert inorganic solids (X_{II}) compared to all other solids

5.1.1.2. Settling Model

Secondary Clarifiers

The secondary clarifiers are modelled using a point-settler model.

5.1.1.3. Biological Model: ASMPP

One major assumption in the ASM models is that the microbiological population is assumed to be healthy, diverse and constant in its behaviour; the model does not incorporate any adaptive behaviour.

This data is entered for each process unit operation under the Composite Variable Stoichiometry, Model Stoichiometry or Kinetic menu. The Petersen Matrix is modified using the Model Developer Excel spreadsheet.

Aerated Selectors & Basins

The kinetic parameters in Table 90 are identical for both the aerated selectors and aerated basins.

Table 90: Aerated selectors & basins biological model parameters

Data Type	***Parameter***	***Value***
Model	Model type	ASMPP*
Composite Variable Stoichiometry	XCOD / VSS (i_{CV})**	**1.63** g COD/g VSS
	BOD5 / BOD ultimate ratio†	**0.45**
	N content of active biomass‡	0.086 g N / g COD
	N content of endogenous / inert mass‡	0.06 g N / g COD
	P content of active biomass#	0.016 g P / g COD
	P content of endogenous / inert mass#	0.015 g P / g COD
Model Stoichiometry	Fraction of biomass leading to particulate products‡	0.08 g COD / g COD
	Heterotrophic yield (active biomass) ‡	0.666 g COD / g COD
	Autotrophic yield (active biomass) ‡	0.24 g COD / g N
Kinetic	Heterotrophic maximum specific growth rate‡	6.0 d^{-1}
	Readily biodegradable substrate half saturation…‡	20 g COD / m^3
	Oxygen half saturation coefficient‡	0.2 g O_2 / m^3
	Nitrate half saturation coefficient‡	0.5 g N / m^3
	Anoxic growth factor‡	0.8
	Heterotrophic decay rate‡	0.62 d^{-1}
	Ammonia half saturation coefficient for	0.05 g N / m3

Data Type	*Parameter*	*Value*
	heterotrop...^	
	Phosphorus half saturation coefficient for heterot..	0.01 g P / m^3
	Autotrophic maximum specific growth rate‡	0.8 d-1
	Ammonia half saturation coefficient for autotrophic...‡	1.0 g N / m3
	Autotrophic decay rate‡	0.2 d-1
	Oxygen half saturation coefficient for autotrophic...‡	0.4 g O2 / m3
	Phosphorus half saturation coefficient for autotro...	0.01 g P / m3
	Maximum specific hydrolysis rate‡	3.0 d^{-1}
	Slowly biodegradable substrate half saturation...‡	0.03 g COD / g COD
	Anoxic hydrolysis factor‡	0.4
	Ammonification rate‡	0.08 m^3 / g COD / d
	Temperature coefficient for muh**	1.072
	Temperature coefficient for ksh**	1.04
	Temperature coefficient for koh**	1.04
	Temperature coefficient for kno**	1.04
	Temperature coefficient for etag**	1.04
	Temperature coefficient for bh**	1.12
	Temperature coefficient for knh**	1.04
	Temperature coefficient for kph**	1.04
	Temperature coefficient for mua**	1.103
	Temperature coefficient for kna**	1.04
	Temperature coefficient for ba**	1
	Temperature coefficient for koa**	1.04
	Temperature coefficient for kpa**	1.04
	Temperature coefficient for kh**	1.116
	Temperature coefficient for kx**	1.116
	Temperature coefficient for etah**	1.04
	Temperature coefficient for ka**	1.072

*As defined by the modified Petersen matrix

**Theoretical values used
†Calculated from wastewater characterisation
‡ Values used for pulp and paper wastewater modelling by *Bolmstedt* [195]
#GPS-X ASM1 model default value
∧GPS-X ASM2d model default value

5.1.2. State variables, stoichiometric & kinetic parameters

5.1.2.1. State variables

Each of the twenty-six state variables in the ASM-PP model are entered into the model developer as model variables, with appropriate symbols, units, diffusion constants and an initial value in the activated sludge. The model variables are listed in Table 91 below.

Table 91: Model state variables

#	*Symbol*	*State Variable*	*Diffusion Coeffic.*	*Initial value in sludge*	*Units*
1	S_I	Soluble inert organics	1×10^{-5}	30	g COD/ m^3
2	S_S	Readily biodegradable (soluble) substrate	1×10^{-5}	5	g COD/ m^3
3	X_I	Particulate inert organics		1000	g COD/ m^3
4	X_S	Slowly biodegradable (stored, particulate) substrate		100	g COD/ m^3
5	X_{BH}	Active heterotrophic biomass		500	g COD/ m^3
6	X_{BA}	Active autotrophic biomass		100	g COD/ m^3
7	X_U	Particulate inerts from cell decay (fraction)		100	g COD/ m^3
8	S_O	Dissolved oxygen	2.5×10^{-5}	2	g O_2/ m^3
9	S_{NH}	Free and ionized ammonia	2.5×10^{-5}	2	g N/

#	Symbol	State Variable	Diffusion Coeffic.	Initial value in sludge	Units
					m^3
10	S_{NO}	Nitrate (and nitrite) N	2×10^{-5}	20	g N/ m^3
11	S_{ND}	Soluble biodegradable organic nitrogen (in influent and from hydrolysis of X_{ND})	1×10^{-5}	1	g N/ m^3
12	X_{ND}	Particulate biodegradable organic nitrogen (in influent and from biomass decay)		1	g N/ m^3
13	S_P	Soluble phosphorus (ortho-phosphates in influent and from phosphatification (hydrolysis of X_{PD}))	1×10^{-5}	1	g P/ m^3
14	X_{PD}	Particulate biodegradable organic phosphorus (in influent and from biomass decay)		1	g P/ m^3
15	S_{PD}	Soluble biodegradable organic phosphorus (in influent and from hydrolysis of X_{PD})	1×10^{-5}	1	g P/ m^3
16	X_{II}	Inert inorganic suspended solids		1000	g/m^3
17	S_{NN}	Dinitrogen	1.9×10^{-5}	0	g N/ m^3
18	S_{ALK}	Alkalinity	2.0×10^{-5}	7	mole / m^3

The fraction added to the original model must be entered under a substitute or proxy that is included in the CNPIP library. A list of the proxy used is presented in Table 92 below.

Table 92: State variable proxies used CNPIP library

#	Symbol	Proxy	State Variable
14	X_{PD}	X_{ZA}	Particulate biodegradable organic phosphorus (in influent and from biomass decay)
15	S_{PD}	S_{ZA}	Soluble biodegradable organic phosphorus (in influent and from hydrolysis of X_{PD})

5.1.2.2. Composite variables

The state variables added to the ASM model must be included in the calculation of composite variables. The necessary modifications to the composite variable calculation are presented in Table 93 below. These calculations correspond to the summations presented visually in Figure 86, Figure 27 and Figure 28 below.

According to the ASM-PP model, some of the nutrient fractions are defined as a constant fraction of the relevant COD fraction. For example, the nutrient fractions relating to the particulate inerts from cell decay, X_U, are constant (X_{NU}, X_{PU}). This is to say that X_{NU} is a constant fraction of X_U, and is unchanged directly by processes described by the Petersen matrix.

Table 93: Composite variable calculation ASMPP (modifications in red)

Parameter	*Calculation*
sbodu	ss
xbodu	xs+xbh+xba~~+xsto~~
bodu	sbodu+xbodu
sbod	fbod*sbodu
xbod	fbod*xbodu
bod	sbod+xbod
scod	sbodu+si
xcod	xbodu+xi+xu
cod	scod+xcod
xnu	**inxu*xu**
xnb	**inxbh*xbh+ inxba*xba**
stkn	snh+snd~~+insi*si+inss*ss~~
xtkn	tkn - stkn
tkn	stkn+xnd+inxbh*xbh+inxba*xba+**inxu***xi+inxu*xu~~+inxs*xs~~
tn	tkn+sno
xpu	**ipxu*xu**
xpb	**ipxbh*xbh+ ipxba*xba**
xtp	ipxbh*xbh+ipxba*xba+**ipxu***xi+ipxu*xu~~+ipxs*xs~~ **+xpd**
stp	sp ~~+ si*ipsi + ipss*ss~~**+spd**
tp	xtp + stp
vss	xcod/icv
x	vss + xiss

Parameter	***Calculation***
xiss	xii
ivt	vss/x

Where **xpd = xza, spd = sza**

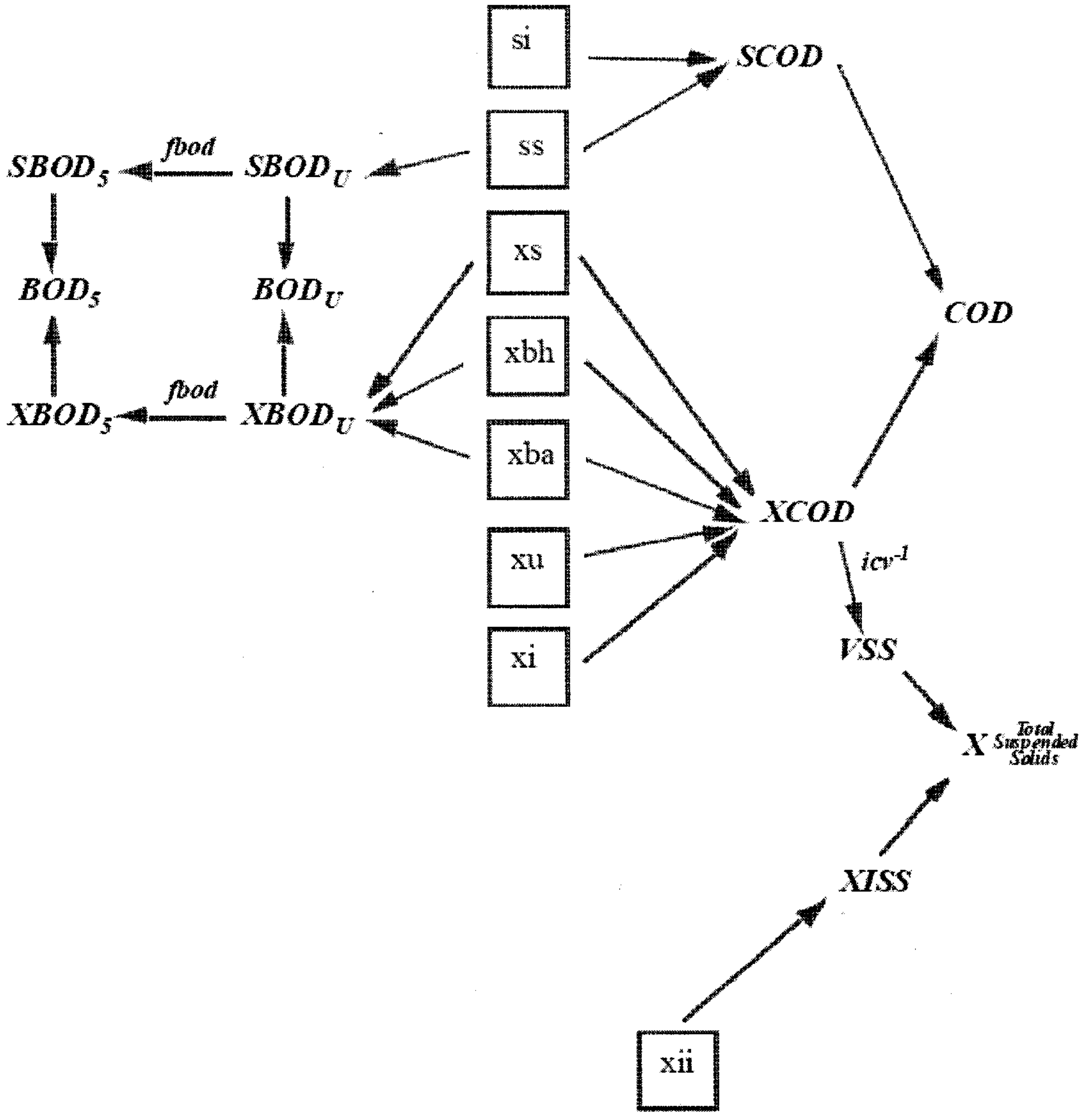

Figure 86: CNP Library state and composite variables: COD [210][7]

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[7] Note that a summation operator is implied at converging arrows, and indices sitting on an arrow indicate a multiplication operator (default of 1).

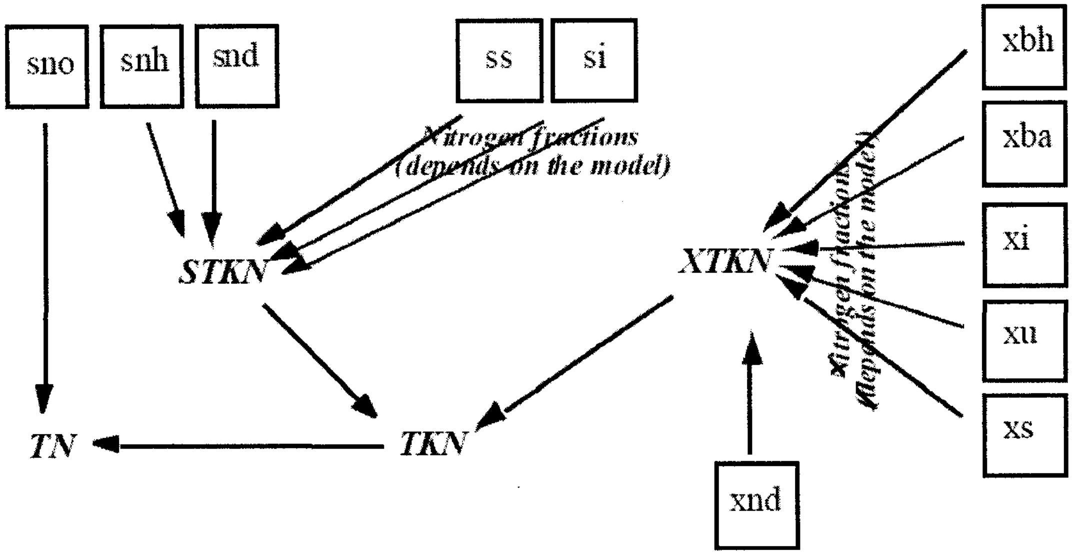

Figure 87: CNP Library state and composite variables: Nitrogen [210], modified

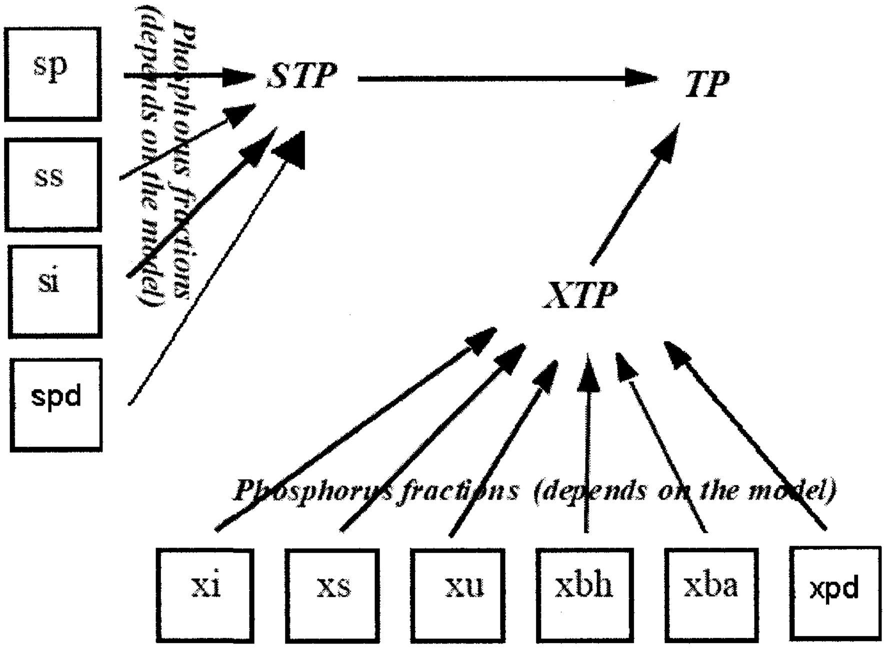

Figure 88: CNP Library state and composite variables: phosphorus [210], modified

5.1.3. Influent Advisor

Parameters that change value for each steady state are listed in Appendix 3.

5.1.3.1. COD

The 'States' version of the influent characterisation is used in GPS-X for simplicity, as it corresponds best with the experimental fractionation carried out. The measured COD fractions S_I, S_S, X_S, X_I and total COD are presented in Table 94 below, in terms of measured concentrations and their corresponding fraction of total COD in the influent stream, using the influent to the AST system as the 'influent'. It should be noted that the fractions X_U, X_U, X_{BH}, X_{BA} and S_O are assumed to be zero in the influent: these fractions are not measured.

Table 94: Wastewater characterisation COD fractions (AST Influent, example)

Fraction	Value	Units
	Steady State No. 1	
X_U	0	g COD/m3
X_{BH}	0	g COD/m3
X_{BA}	0	g COD/m3
S_O	0	g O_2/m3
S_I	109	g COD/m^3
S_S	1,237	g COD/m^3
X_S	185	g COD/m^3
X_I	824	g COD/m^3
COD total	2,355	g COD/m^3
S_I (fraction)	0.05	-
S_S (fraction)	0.53	-
X_S (fraction)	0.08	-
X_I (fraction)	0.35	-

5.1.3.2. Solids

The measured total suspended solids plus the average wastewater solids fractionation is used for all steady states, as presented in Table 95 below. The inert inorganic suspended solids fraction X_{II} is calculated as the difference between the TSS and the VSS in the influent: this is zero in all cases.

The PI system data recorded for the TSS at the inlet to the AST was reconciled with the laboratory records. Two data points in the PI system did not correspond to those recorded by the laboratory, by more than 100%, and a linear approximation of the lab data was used for these data points (steady states numbers 23 and 24).

The influent ratio of COD to VSS is calculated according to influent advisor by the ratio:

$$i_{CV}=\frac{XCOD}{VSS}=\frac{XBOD_U+X_U+X_I}{VSS}=\frac{X_S+X_{BH}+X_{BA}+X_U+X_I}{VSS}$$

This can be simplified in the influent due to the fact that X_{BH}, X_{BA} and X_U are all equal to zero in the influent:

$$i_{CV}=\frac{X_S+X_I}{VSS}$$

Due to the nature of pulp and paper wastewater, this ratio in the influent is significantly larger than the default value of 2.2 g COD/g VSS for municipal wastewater. The values in Table 95 are shown as examples; this ratio is calculated for each steady state.

As discussed in the literature review, the ratio of BOD_5 to ultimate BOD, f_{BOD}, is calculated from the wastewater characterisation exercise for the influent to the AST selectors. The result from the wastewater characterisation, 0.24, is notably different from the value calculated for each steady state via the on-line COD measurement and a COD:BOD_5 mass ratio determined by the mill (2.36). The latter value is supported by external laboratory data and is therefore the value used for each steady state. The value listed in Table 95 is different from the default value for municipal wastewater, 0.66 g BOD/g BOD.

As discussed in Appendix 2, the X_{II} fraction of inert inorganic material is equal to zero in the AST influent stream for all steady states. However, the solids fractionation work highlighted a difference between the VSS and TSS concentrations in the mixed liquor: 125 mg FSS/L on average. From the steady state data, the mixed liquor measurement for all steady states demonstrates a difference between the TSS and VSS measurements. For the purposes of modelling, it is necessary that the origin of this solids fraction is identified. Work by Ekama *et al.* highlights that 15% of the content of ordinary heterotrophic organisms is present as inert inorganic salts (mg ISS/mg VSS), or X_{II}, which precipitate during the VSS-TSS test procedure [261]. Given that the active biomass content of the VSS concentration has been measured at approximately 25% (mg active biomass/ mg VSS) for pulp and paper wastewater [262] this results in 4% mg ISS/mg VSS. It can therefore be assumed that the 5% of mixed liquor TSS concentration that is unaccounted for by VSS is present as X_{II} originating from these inert inorganic salts. This can be taken into account in the model by calculating the X_{II} fraction as a state variable, as a fraction fxii of the active biomass. The value of the fraction fxii is based on the following calculation:

$$f_{xii} = \frac{X_{II}}{VSS} * \frac{VSS}{Active\_biomass} = \frac{0.052}{0.25} = 0.208$$

Table 95: ASM1 wastewater characteristics

Fraction	Average	Units
	Steady State No. 1	
VSS	183	g VSS/m^3
X_{II}	0	g/m^3
TSS	183	g TSS/m^3
VSS (fraction)	100	-
X_{II} (fraction)	0	-
i_{cv}	**5.2**	g COD/g VSS
f_{BOD}	**0.598**	g BOD/g BOD
fxii	**0.208**	g COD/g COD

5.1.3.3. Nutrients

The average values of the measured nutrient fractionation are used for all steady states, as presented in Table 96 below. Measured averages are listed for the TN, TKN, S_{NH}, S_{NO}, TP and S_P fractions. The concentration of nitrogen gas in the influent is assumed to be zero (S_{NN}). Likewise, the fractions of particulate active biomass nitrogen (X_{NB}) and particulate nitrogen from cell decay inerts (X_{NU}) are assumed to be zero in the influent.

The calculations for TKN in the influent advisor are:

$$TKN = XTKN + STKN$$

$$XTKN = X_{ND} + X_{NU} + X_{NB}$$

$$STKN = S_{NH} + S_{ND}$$

The calculations for TP in the influent advisor are:

$$TP = XTP + STP$$

$$XTP = X_{PU} + X_{PD} + X_{PB}$$

$$STP = S_P + S_{PD}$$

The fractions of particulate active biomass phosphorus (X_{PB}) and particulate phosphorus from cell decay inerts (X_{PU}) are assumed to be zero in the influent. The fraction of particulate biodegradable organic phosphorus (X_{PD}) is assumed to account for the balance of the organic phosphorus measured in the AST influent, which is close to zero. Other fractions were calculated from wastewater characterisation data, the details are presented in Appendix 2.

Table 96: ASM1 wastewater characteristics, influent

Fraction	*Average*	*Units*	*Fraction*	*Average*	*Units*
TN	47.64 (5.67)†	g N/m^3	***TP***	11.03 (1.07)	g P/m^3
TKN	47.61 (5.64)†	g N/m^3	S_P	9.7 (0.26)†	g P/m^3
S_{NH}	41.9 (0.026)†	g N/m^3	X_{PD}	0.81	g P/m^3
S_{NO}	0.030	g N/m^3	X_{PU}	0	g P/m^3
S_{NN}	0	g N/m^3	X_{PB}	0	g P/m^3
S_{ND}	0.001	g N/m^3	***ipxbh*** ***ipxba***	0.016	g P/g COD
X_{ND}	5.61	g N/m^3	***ipxu***	0.015	g P/g COD
X_{NU}	0	g N/m^3	***ipxi***	0.0016	g P/g COD
X_{NB}	0	g N/m^3			
inxbh ***inxba***	0.086	g N/g COD			
inxu	0.06	g N/g COD			
inxi	0.03	g N/g COD			

†The simulation environment necessitates including the nutrient dosing in the influent characterisation, the original wastewater characterisation is included in parenthesis.

5.1.3.4. Variable definition & dimension

The definition and dimension of each variable modified must be entered in the model Fortran and Advanced Continuous Simulation Language (ASCL) 'macro code' as well as the model developer, in order to customise the GPS-X model [270]. The modifications made to each file are detailed in Table 97 below. Some modifications were made to the CNPIP library and some were made to the model layout file, as appropriate.

Table 97: Variable definition & dimension, code modifications

File	*Modification*	*Proxy*
gps-x502\cnpiplib\state.var layout.var	display xza !particulate phosphorus from cell decay inerts !gP/m3	xpd
gps-x502\cnpiplib\stateinf.con	constant xza&o = 0.0 !particulate phosphorus from cell decay inerts !gP/m3	xpd

5.1.4. ASM-PP General

5.1.4.1. Model layout

In order to reduce the computation time and complexity of the model layout corresponding to the physical layout of the mill wastewater treatment (parallel operation of the AST selectors, basins and secondary clarifiers), the model layout was simplified: the two parallel streams of process units were modelled as a single stream: one selector, one AST basin and one clarifier. The volume of the completely-mixed selector and AST basin were doubled, the surface area of the clarifier was doubled. This simplified layout accurately represents the reactor and clarifier kinetics, hydraulics and settling since the mill parallel streams operated identically in all steady states, particularly since the model does not consider wall effects or a heat and energy balance. Results from the two layouts are generally within the limits of measurement (for solids concentrations, for example) and well within the bounds of uncertainty calculated in the error analysis.

The roughly calibrated base case of steady state number two was used to demonstrate the difference between the more complex and the simplified layouts, where 'complex' refers to the two-selector, two-AST, two-clarifier model and 'simplified' refers to the one-selector, one-AST, one-clarifier model. Both layouts are equal in terms of temperatures, flow rates, concentrations and physical process unit volumes, and should therefore produce identical results.

The output values on the target output parameters are presented in Table 98.

Table 98: Target output parameters, steady state #2, ASMPP simplified vs. complex layouts

Parameter	*Units*	*Simplified, ASM-PP*	*Complex, ASM-PP*
Final Effluent TSS	mg TSS/L	16.6	16.6
Final Effluent VSS	mg VSS/L	15.5	15.4
WAS TSS	mg TSS/L	15,400	15,400
RAS TSS	mg TSS/L	4,770	4,710
Final Effluent BOD	mg BOD/L	5.73	5.73
Final Effluent COD	mg COD/L	129	129
AST MLSS	mg TSS/L	2,330	2,370
AST MLVSS	mg VSS/L	2,170	2,140
Final Effluent NH4	mg N/L	0.369	0.373
Final Effluent NO3	mg N/L	0.191	0.188
Final Effluent PO4	mg P/L	7.55	7.54
Final Effluent S_{NN}	mg N/L	33.70	33.60

The rate of each biological process occurring in the selector and AST is presented in Table 99. The process rates are very similar between the layouts in the selector. There is even less difference between the models as the absolute value of the process rates diminish. The slight difference in the growth and decay rates of autotrophs explains the slight difference between final effluent ammonia and nitrate concentrations listed in Table 98, both of which are within the measurement accuracy determined in the error analysis. Therefore the simplified layout will continue to be used for further modelling work.

Table 99: Biological process rates, steady state #2, ASMPP simplified vs. complex layouts

Process Rate	*Units*	*Simplified, ASM-PP*	*Complex, ASM-PP*
Selector			
Aerobic growth of heterotrophs	gCOD/m^3/d	7130	7120
Anoxic growth of heterotrophs	gCOD/m^3/d	416	415
Aerobic growth of autotrophs	gCOD/m^3/d	22	21.9
Decay of heterotrophs	gCOD/m^3/d	1580	1580
Decay of autotrophs	gCOD/m^3/d	0.957	0.944
Ammonification of soluble organic nitrogen	gN/m^3/d	200	200

Process Rate	***Units***	***Simplified, ASM-PP***	***Complex, ASM-PP***
Hydrolysis of entrapped organics	gCOD/m^3/d	4700	4700
Hydrolysis of entrapped organic nitrogen	gN/m^3/d	237	237
Phosphatification	gP/m^3/d	53.7	53.6
AST			
Aerobic growth of heterotrophs	gCOD/m^3/d	1070	1070
Anoxic growth of heterotrophs	gCOD/m^3/d	126	125
Aerobic growth of autotrophs	gCOD/m^3/d	5.12	5.11
Decay of heterotrophs	gCOD/m^3/d	1340	1340
Decay of autotrophs	gCOD/m^3/d	1.07	1.06
Ammonification of soluble organic nitrogen	gN/m^3/d	123	123
Hydrolysis of entrapped organics	gCOD/m^3/d	1410	1410
Hydrolysis of entrapped organic nitrogen	gN/m^3/d	123	123
Phosphatification	gP/m^3/d	29.8	29.8

5.1.4.2. Wastewater ratios

A number of wastewater ratios were determined from experimental data, details of which are presented in Appendix 2. The values of these ratios are reiterated here in Table 100 for clarity.

Table 100: Wastewater measured ratios, summary from Appendix 2

Location	***Parameter or Ratio***	***Units***	***Measured Range***	***ASM1, ASM2, ASM3 default values***	***Model uses:***
Influent	Organic nitrogen to total COD ratio	mg N/ mg COD	0.0016 – 0.0093	0.01 – 0.04	Zero nutrient concentration: insi, inss, inxs inxi = 0.03*
Influent	Organic phosphorus to total COD ratio	mg P/ mg COD	0.00025 - 0.00085	0 – 0.01	Zero nutrient concentration: ipsi, ipss, ipxs ipxi = 0.0016*
Influent	f_{CV} (particulate COD to VSS ratio)	mg XCOD/ mg VSS	1.93 – 2.64	2.2	Calculate for each steady state $f_{CV} = \frac{XCOD}{VSS} = \frac{X_I + X_S}{VSS}$
Influent	X_{II}	mg COD/L	0		Zero concentration
Influent	f_{BOD} (BOD_5: BODu)	mg BOD/ mg COD	PI: 0.18 – 0.28 PE: 0.21 – 0.23	0.66	Calculate for each steady state $f_{BOD} = \frac{BOD_5}{S_S + X_S}$
Mixed liquor	Organic nitrogen to COD ratio	mg N/ mg COD	0.049 – 0.058	0.086	inxbh = inxba = 0.086 inxu = 0.06 inxi = 0.03
Mixed liquor	Organic phosphorus to COD ratio	mg P/ mg COD	0.0064 - 0.0101	0.02	ipxbh = ipxba = 0.016 ipxu = 0.015 ipxi = 0.0016
Mixed liquor	f_{CV} (particulate COD to	mg XCOD/ mg VSS	1.34 – 1.85	1.48	Average value:

Location	***Parameter or Ratio***	***Units***	***Measured Range***	***ASM1, ASM2, ASM3 default values***	***Model uses:***
	VSS ratio)				1.63 mg XCOD/mg VSS
Mixed liquor	X_{II}	mg COD/L	X_{II} = 5%TSS		fxii = 0.208[†]

(PI) Primary Influent, (PE) Primary Effluent

†Calculated from: Average mixed liquor xii = 0.052*vss; active biomass = 0.25*vss[‡]; xii = 0.052/0.25*(active biomass)

‡ Approximately 25% of MLVSS is present as active biomass [260]
*inxi(primary effluent) = inxi(mixed liquor), ipxi(primary effluent) = ipxi(mixed liquor), all influent nutrients attributed to X_I fraction

5.1.4.3. *Oxygen Transfer*

In response to errors relating to the oxygen transfer by jet aerators based on the design data from the mill, a user-defined SOTE based on the default diffuser density was used in the model, as presented in Table 101 below. It was also necessary to increase the maximum K_La in the selectors to 10,000 1/d. This allowed the model to easily attain the target dissolved oxygen concentration in each of the selectors and AST basins and is considered reasonable for the purposes of this model. Future work may include modelling of oxygen transfer and this approach should be modified for other purposes.

Table 101: Modified oxygen transfer AST selector & basin

Data Type	*Parameter*	*Value*
Operational	Maximum oxygen mass transfer coefficient	10 000 1/d
	Diffuser type	User-defined
	Alpha factor (jet)**	0.6
	Standard Oxygen Transfer Efficiency (SOTE) type	Constant
	SOTE	0.3
	Specify diffuser setup	Enter diffuser density
	Diffuser density	0.1

5.1.4.4. *Nutrient dosing*

As noted in the methodology section, the simulator did not allow the dosing of nutrients separately to the influent object containing the organic substrate. For this purpose, the concentrations of nitrogen and phosphorus were recalculated as if the nutrients had been directly dosed into the influent.

5.1.4.5. *AST Selector & Basin*

The AST basin was 'sourced' to the selector. This allows the setting of kinetic parameters once in the selector; the software automatically updates the parameters in the other process unit.

5.1.4.6. *Secondary clarifier*

The secondary clarifier model was set to a point settler model after much research into the reactive clarifier model. It was found that a single set of clarifier parameters (RAS extraction layers, maximum Vesilind settling velocity, hindered settling parameter) did not exist to describe the range of data in this study. This is considered reasonable given the fact that the SVI and sludge blanket height both vary significantly during the period of data collection. It is thought that a mechanistic clarifier model for this plant would require correlation of the SVI with the hindered settling parameter and maximum Vesilind settling velocity or computation fluid dynamic modelling, which is beyond the scope of this study.

The inclusion of the point settler secondary clarifier necessitates all solids to be removed in a single stream from the base of the clarifier, contrary to the physical arrangement of the suction clarifiers at the mill. This solids stream is further split into the WAS stream and a concentrated RAS stream, the latter is diluted to the RAS solids concentration determined in the mass balance calculations. This arrangement in the model assumes that the concentrated RAS stream is identical in composition to the WAS stream, which is consistent with the assumptions made in the mass balance calculations.

The lack of a reactive clarifier model dictates that a nutrient transformations occurring in the secondary clarifier are not modelled. Mass balance calculations indicated small amounts of nitrification and denitrification were occurring in the secondary clarifier at the mill, and by not modelling these transformations, there is a risk that the RAS stream composition in the model is not fully descriptive of the actual RAS stream. This is a limitation of the model.

5.1.4.7. Solids

Inert Suspended Solids (X_{II})

The difference between the TSS and VSS concentrations in the modelled AST basins is dependent on the X_{II} fraction in the influent. Although the wastewater characterisation shows that the measured TSS and VSS concentrations in the AST inlet are equal, the measured VSS concentration in the AST outlet (mixed liquor) is typically 95% of the TSS concentration, the difference must be attributed to accumulated X_{II} in the model. As discussed in Appendix 2, the mixed liquor X_{II} fraction originates from the inorganic salt content of bacteria which is detected in the VSS-TSS test method. This is taken into account in the model by modifying the calculation of the X_{II} fraction as specified in Table 100.

5.1.5. ASM-PP Calibration Criteria, Literature values & Procedure

5.1.5.1. Calibration criteria

The criteria by which a scenario is deemed to be calibrated are dependent on the output parameters chosen for this purpose. A number of output parameters were chosen as representative of the solids, COD and nutrient balances that were carried out previously. These parameters are listed in Table 102 along with the calibration criteria in terms of relative error as a percentage of the value calculated in the mass balance exercise[8]. The basis of the selection of relative error value is the measurement accuracy analysis conducted previously, as outlined in Appendix 6. The final effluent characteristics are not modelled using the point settler clarifier model, and therefore can not be included in the calibration criteria.

Table 102: Target output parameters & calibration criteria

Parameter	*Units*	*Calibration Criteria: Relative Error (%)*
AST MLSS	mg TSS/L	3 %
AST MLVSS	mg VSS/L	3 %
WAS TSS	mg TSS/L	25 %
RAS TSS	mg TSS/L	7 %
AST Outlet NH4	mg N/L	4 %
AST Outlet NO3	mg N/L	3 %
AST Outlet PO4	mg P/L	9 %

5.1.5.2. Literature values

Kinetic and stoichiometric parameter values from other ASM-based studies of pulp and paper wastewater are presented in Table 103 and summarised in Table 104 with the relevant Arrhenius coefficients. These studies cover a broad range of pulp and paper processes as well as a range of wastewater treatment plant processes. The study results range from "good agreement with plant operating data" [196] to "a poor model response for the effluent COD and suspended solids concentrations" [263]. Some interesting characterisation and modelling work was conducted for the Hylte mill in Sweden, which has unusual pulp and paper and wastewater process configurations and is therefore not included in the comparison [134, 195]. The comparison is used during calibration of the model as a cross-check of

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[8] Relative error (%) = (Model value – Mass balance value) / Mass balance value x 100

the value of the kinetic and stoichiometric parameters investigated in the study model.

Table 103: Literature values: Kinetic & Stoichiometric Parameters

Parameter	***Symbol***	***Units***	***Sreckovic***	***Stanyer***	***PAPRO***	***Barañao & Hall***	***Horan & Chen****	***ASM1***	***Siegrist & Tschui***
		Model	Non-constrained	-	-	ASM1	ASM3	ASM1	ASM1
		Temperature	30ºC†	30ºC	25ºC	20ºC	30ºC	20ºC	12 - 20ºC
		Reference	[197]	[199]	[198]	[200]	[196]	[204]	[249]
Oxygen Saturation constant	K_{O2}	g O_2 /m^3				0.3		K_{OH} 0.2 K_{OA} 0.4	
Heterotrophic maximum growth rate	μ_H	1/d	39	5 - 16	0.52	17.5 (0.05) ‡	2.3 4.79	6.0	2.5 (0.07) ‡ 2.9 (0.07) ‡
Autotrophic maximum growth rate	μ_A	1/d	15					0.8	0.40
Heterotrophic decay rate	b_H	1/d	0.53	0.16 – 0.18	0.19	0.13 (0.04) ‡	0.41 0.51	0.62	0.5 (0.07) ‡ 0.58 (0.07) ‡
Autotrophic decay rate	b_A	1/d	0.29					0.05 – 0.15**	
Yield of heterotrophic biomass growth	Y_H	g COD/ g SS	0.58	0.44 – 0.62	0.51	0.76	0.66	0.67	0.57 0.64
Yield of autotrophic biomass growth	Y_A	g COD/ g N	0.3					0.24	
Half saturation constant for	K_{SH}	g COD /m^3	158		1			20.0	5

Parameter	Symbol	Units	Sreckovic	Stanyer	PAPRO	Barañao & Hall	Horan & Chen*	ASM1	Siegrist & Tschui
		Model	Non-constrained	-	-	ASM1	ASM3	ASM1	ASM1
		Temperature	30ºC†	30ºC	25ºC	20ºC	30ºC	20ºC	12 - 20ºC
		Reference	[197]	[199]	[198]	[200]	[196]	[204]	[249]
assimilation of carbon (heterotrophs)									
Half saturation constant for assimilation of nitrogen (autotrophs)	K_{NA}	g COD /m³	2.7					1.0	
Maximum specific hydrolysis rate	k_h	g COD /g cell COD.d	7.91		0.5	8.1		3.0	50 (0.03) ‡ 55 (0.03) ‡
Hydrolysis half saturation constant	K_X	g COD /g cell COD	0.5		0.02			0.03	10 (0) ‡ 10 (0) ‡
Specific ammonification rate	k_a	m³/g COD. d	0.07					0.08	

†30ºC with $\theta_T = 1.04$ for $\mu_T = \mu_{20^\circ C} {*} (\theta)^{T-20}$, which is approximately equivalent to a k_T value of 0.07 $^\circ C^{-1}$

‡ k_T in parentheses

*1993, 1994 model

**Discussed as range reported in literature

Table 104: Literature range & Arrhenius coefficients: Kinetic & Stoichiometric Parameters

STOICHIOMETRIC AND KINETIC PARAMETERS		**at 20℃**	**Arrhenius coefficient**	**Literature Range**	**Units**
Composite Variable Stoichiometry					
Organic Fractions					
icv	XCOD/VSS	1.48			gCOD/gVSS
f_{bod}	BOD5/BODultimate ratio	0.514 *			-
Nutrient Fractions					
inxb	N content of active biomass	0.086			g N / g COD
inxu	N content of endogenous/inert mass	0.06			g N / g COD
ipxb	P content of active biomass	0.021			gP/gCOD
ipxu	P content of endogenous/inert mass	0.02			gP/gCOD
Model Stoichiometry					
General Fractions					
fu	fraction of biomass leading to particulate products	0.08			gCOD/gCOD
Active Heterotrophic Biomass					
Y_H	heterotrophic yield	0.666		0.44 – 0.76	g COD / g COD
Active Autotrophic Biomass					
Y_A	autotrophic yield	0.24		0.24 – 0.3	g COD/ g N

STOICHIOMETRIC AND KINETIC PARAMETERS		**at 20℃**	**Arrhenius coefficient**	**Literatu re Range**	**Units**
Kinetic					
Active Heterotrophic Biomass					
μ_H	heterotrophic maximum specific growth rate	6.0	1.072	2.5 - 39	1/d
K_{SH}	readily biodegradable substrate half saturation coefficient	20.00	1.04	1 - 158	$gCOD/m^3$
K_{OH}	oxygen half saturation coefficient	0.2	1.04	0.2 - 0.3	gO_2/m^3
K_{NO}	nitrate half saturation coefficient	0.500	1.04		gN/m^3
η_g	anoxic growth factor	0.80	1.04		-
b_h	heterotrophic decay rate	0.62	1.12	0.13 – 0.62	1/d
K_{NH}	ammonia half saturation coefficient for heterotrophs growth	0.05	1.04		gN/m^3
K_{PH}	phosphorus half saturation coefficient for heterotrophs growth	0.01	1.04		gP/m^3
Active Autotrophic Biomass					
μ_A	autotrophic maximum specific growth rate	0.80	1.103	0.8 - 15	1/d
K_{NA}	ammonia half saturation coefficient for autotrophs growth	1.00	1.04	1 – 2.7	gN/m^3
b_a	autotrophic decay rate	0.04	1	0.2 – 0.29	1/d
K_{OA}	oxygen half saturation coefficient for autotrophs growth	0.4	1.04		gO_2/m^3

STOICHIOMETRIC AND KINETIC PARAMETERS		**at 20℃**	**Arrhenius coefficient**	**Literature Range**	**Units**
K_{PA}	phosphorus half saturation coefficient for autotrophs growth	0.01	1.04		gP/m^3
Hydrolysis					
k_h	maximum specific hydrolysis rate	3.00	1.116	3 – 8.1	1/d
K_x	slowly biodegradable substrate half saturation coefficient	0.03	1.116	0.02 – 0.5	gCOD/gCOD
η_h	anoxic hydrolysis factor	0.40	1.04		-
Ammonification					
k_a	ammonification rate	0.08	1.072	0.07 – 0.08	m^3/g COD/d

*Varies according to steady state case

5.1.5.3. Calibration procedure

The parameters deemed to be the most sensitive will be used in the calibration of the model, in the order outlined in Table 105 below. Kinetic and stoichiometric parameters such as the autotrophic maximum growth rate, the heterotrophic decay rate, the heterotrophic yield, the half saturation constant for autotrophic assimilation of nitrogen, or the specific ammonification rate, all demonstrate significant sensitivity with respect to AST outlet nutrient concentrations. The calibration process is an iterative one, and thus step 6 was repeated until the steady state case was calibrated. The influent phosphate and ammonia concentrations were verified to determine if BOD removal was limited due to a nutrient deficiency.

Table 105: Calibration process & parameters (general order)

Step	***Process***	***Fitting or calibration criteria***	***Target output variable***
1.	Plant configuration & model modification	Design parameters ASMPP model	-
2.	Specify steady-state data	Steady-state parameters: Temperature, influent etc	-
3.	Solids balance	Influent parameters: X_I & X_S	MLSS
4.	Organic load removal	4.1. ASMPP model 4.2. Heterotrophic decay rate 4.3. Heterotrophic yield	BOD Removal
5.	Nutrient transformations	5.1. Autotrophic growth rate 5.2. Ammonification rate 5.3. Anoxic growth correction factor 5.4. Phosphatification rate	AST Outlet NH_4, NO_3, PO_4

Many other parameters were investigated during a preliminary sensitivity analysis and were deemed to have very little effect on the BOD removal or nutrient transformations in the model. These parameters are listed in Table 106.

Table 106: Low-sensitivity model parameters

Parameter	*Symbol*	*Units*
Autotrophic decay rate	b_A	1/d
Yield of autotrophic biomass growth	Y_A	g COD/ g N
Half saturation constant for assimilation of carbon (heterotrophs)	K_{SH}	g COD /m^3
Phosphorus half saturation constant (heterotrophic)	K_{PH}	mg P/L
Phosphorus half saturation constant (autotrophic)	K_{PA}	mg P/L
Half saturation constant for assimilation of nitrogen (heterotrophs)	K_{NH}	g COD /m^3
Half saturation constant for assimilation of nitrogen (autotrophs)	K_{NA}	g COD /m^3
Maximum specific hydrolysis rate	k_h	g COD /g cell COD.d
Hydrolysis half saturation constant	K_X	g COD /g cell COD
Oxygen half saturation coefficient for growth (heterotrophs)	K_{OH}	mg O_2/L
Oxygen half saturation coefficient for growth (autotrophs)	K_{OA}	mg O_2/L

5.1.6. ASM-PP Calibration: Solids balance

The characterisation of the wastewater influent (primary effluent) highlighted a number of steady state cases for which the estimated particulate inert (X_I) or slowly biodegradable (X_S) COD fractions were less than zero. These 10 steady state cases were therefore excluded from further modelling work.

5.1.6.1. Influent solids calibration

The modelled solids balance of the remaining 22 steady state cases were calibrated by varying the particulate inert (X_I) and slowly biodegradable (X_S) COD fractions to fit to the measured total suspended solids concentrations in the mixed liquor. This exercise resulted in the calibrated influent fractions presented in Table 107.

Table 107: Steady state cases COD influent fractions, calibrated solids balance model

Characterisation											
Steady state Case No.	***On-line fCOD***	***BOD5: BODu AST****	***TSS***	***VSS***	i_{CV}	S_I	S_S	X_I	X_S	***Total COD (calc)***	$BOD_5^{\dagger}$
Units	*mg COD/L*	-	*mg TSS/L*	*mg VSS/L*	*g/g*	*mg COD/L*	*mg COD/L*	*mg COD/L*	*mg COD/L*	*mg COD/L*	*mg BOD/L*
2	1,622	0.452	154	154	6.18	97	1,021	450	500	2,068	687
3	1,603	0.479	158	158	5.96	100	1,005	525	414	2,045	679
4	1,707	0.455	163	163	6.15	110	1,066	475	525	2,177	723
5	1,712	0.499	186	186	5.40	105	1,076	625	378	2,183	725
6	1,717	0.488	162	162	6.21	73	1,111	625	381	2,190	728
7	1,624	0.527	169	169	5.63	64	1,056	700	251	2,070	688
10	1,649	0.464	170	170	5.69	71	1,066	525	441	2,103	699
11	1,540	0.466	128	128	7.04	43	1,019	520	382	1,964	653
12	1,525	0.471	123	123	7.28	52	999	520	373	1,945	646
13	1,531	0.477	186	186	4.82	76	979	515	382	1,953	649
14	1,500	0.445	119	119	7.36	85	949	400	479	1,912	635
15	1,609	0.407	173	173	5.44	86	1,024	290	653	2,052	682
16	1,555	0.473	187	187	4.88	79	993	510	401	1,983	659
17	1,582	0.447	197	197	4.71	77	1,013	440	487	2,017	670
18	1,579	0.482	208	208	4.44	75	1,014	550	375	2,014	669
19	1,616	0.482	237	237	4.00	70	1,044	570	377	2,061	685

Characterisation											
Steady state Case No.	**On-line fCOD**	**BOD5: BODu AST***	**TSS**	**VSS**	i_{CV}	S_I	S_S	X_I	X_S	**Total COD (calc)**	**BOD$_5$†**
Units	*mg COD/L*	-	*mg TSS/L*	*mg VSS/L*	*g/g*	*mg COD/L*	*mg COD/L*	*mg COD/L*	*mg COD/L*	*mg COD/L*	*mg BOD/L*
20	1,835	0.449	139	139	7.72	68	1,196	540	535	2,340	777
21	1,824	0.479	164	164	6.50	72	1,186	640	429	2,326	773
22	1,761	0.457	110	110	9.34	72	1,142	540	492	2,245	746
23	1,737	0.425	155	155	6.57	151	1,046	330	688	2,216	736
24	1,669	0.420	172	172	5.68	124	1,027	320	658	2,129	707
25	1,687	0.393	176	176	5.63	84	1,079	250	739	2,152	715

*Calculated: fbod=$BOD_5/(S_S+X_S)$ in influent

†BOD_5 calculated from the filtered COD:BOD_5 mass ratio determined by the mill (2.36)

The value of the influent X_{II}, S_{ND} and X_{ND} fractions are zero, X_{PD} is 0.81 mg P/L, S_{NO} is 0.03 mg N/L, for all steady state cases. These values arise from the average wastewater fractionation work.

5.1.7. ASM-PP Calibration: BOD removal

Once the solids balance had been established, the models were found to be very sensitive to three parameters: the heterotrophic maximum growth rate, μ_H, the autotrophic maximum growth rate, μ_A, and the anoxic growth factor, η_g. The heterotrophic maximum growth rate, μ_H, was set at a value of 18 d^{-1}, which gave good results for BOD removal ($\mu_A = 0.5$, $\eta_g = 0.08$) for the data sets where nitrate residuals were measured (where partial nitrification-denitrification is obviously occurring). This μ_H value is in agreement with that found in recent research of a similar pulp and paper wastewater treatment plant [262].

5.1.8. ASM-PP Nutrients Calibration: Uniform model

Once the heterotrophic maximum growth rate was determined, the autotrophic maximum growth rate, μ_A, and the anoxic growth factor, η_g, were calibrated for individual pseudo-steady state cases. The range of values investigated for each case was 0 to 1.0 d^{-1} for μ_A and 0 to 0.1 for η_g, which were used to calibrate the nitrate concentration at the AST outlet. The ammonification rate, ka, was used to further calibrate the ammonia concentration at the AST outlet.

A uniform model capable of describing the entire data set was extensively investigated but was not found. Two possible scenarios can be proposed to explain the residual nitrates and ammonia measured at the outlet of the AST: (A) partial nitrification-denitrification is occurring, and subsequently the rate of nitrification diminishes, or (B) partial nitrification-denitrification is occurring, and subsequently the rate of denitrification increases. The proposed models were calibrated according to scenario (A), it was not possible to evaluate scenario (B) with any great accuracy given the already low-to-zero autotrophic maximum growth rates, the range of anoxic growth correction factors that reasonably fit the measured data is quite large.

Two models that each describe a part of the nutrient residual data were investigated, the model results are compared to the measured nutrient residual data in Figure 89. Model 1 refers to the situation were partial nitrification-denitrification is occurring ($\mu_A = 0.5\ d^{-1}$, $\eta_g = 0.08$, $k_a = 0.08$, $k_p = 0.08$, $b_H = 0.62$) and Model 2 refers to the situation where nitrification is not occurring ($\mu_A = 0$, $\eta_g = 0$, $k_a = 0.025$, $k_p = 0.08$, $b_H = 0.50$). It is clear that two disparate process conditions, zero nitrification and partial nitrification-denitrification, can each be modelled by a uniform model, but in fact a uniform model does not describe the entire data set in this study. For this reason, the nutrient transformations kinetic parameters were adjusted for each individual pseudo-steady state, as described in section 5.1.9.

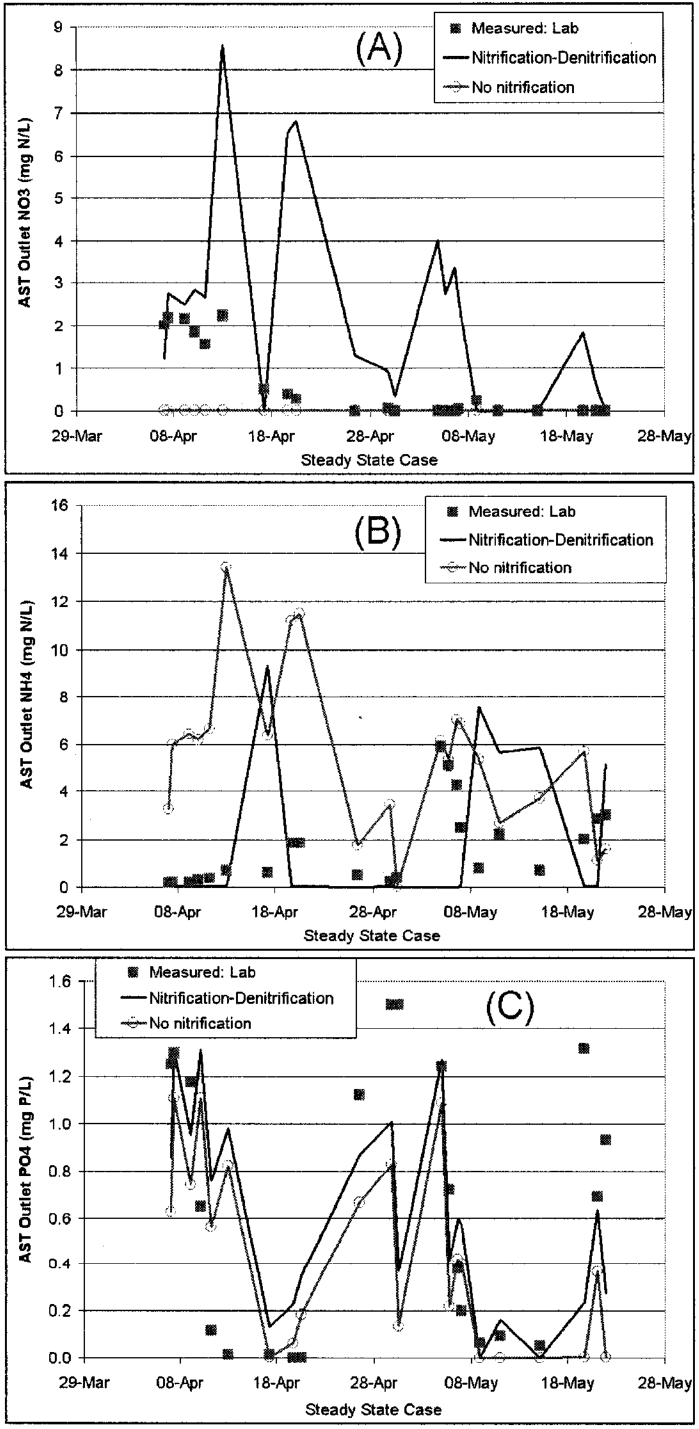

Figure 89: Uniform model approach, AST outlet nutrient residuals measured & modelled (a) Nitrate (b) Ammonia (c) Phosphate

5.1.9. ASM-PP Nutrients: Individually adjusted kinetic parameters

The proposed model was calibrated including adjustment of kinetic parameters for individual pseudo-steady state cases; which are presented in Table 108 in comparison with selected values from literature ranging from the ASM default parameters to studies on pulp and paper wastewater. Two of the parameters that were used to calibrate each case, μ_A and ka, were found to have values generally lower than those found in the literature, although ka was found to have a large range of values in this study. Many of the parameters listed in Table 108 are default parameters that were investigated but found not to be sensitive in this model. The calibrated values of μ_A, η_g, k_a and k_p for individual pseudo-steady state cases are presented in Table 109.

The half saturation constant for the assimilation of nitrogen for autotrophs, K_{NA}, was reduced to a value of 0.05 g COD/m3 for all model calibration work in order to allow the nitrification process to proceed at low ammonia concentrations. The effect of varying the half saturation constant in the Monod switching function can be seen in Figure 90 below.

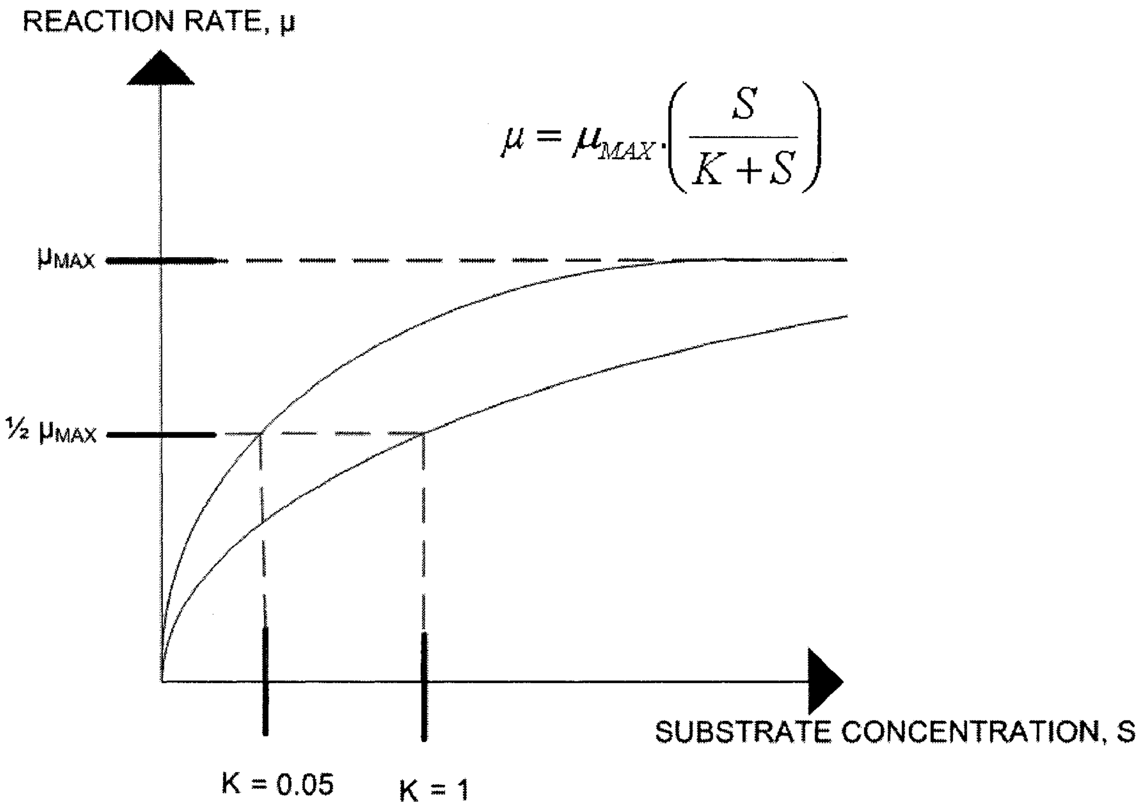

Figure 90: Monod switching function, variation of half saturation constant

Table 108: Kinetic & stoichiometric parameters: Calibrated model

Parameter	***Symbol***	***Units***	***Literature Values***	***Literature References***	***Model (Range)***
Individually adjusted kinetic parameters					
Autotrophic maximum growth rate	μ_A	1/d	0.8 15 0.4	[204] [197] [249]	**0.05 – 0.30**
Correction factor for anoxic growth of heterotrophs (denitrification)	η_g	-			**0 – 0.7**
Specific ammonification rate	k_a	m^3/g COD. d	0.08 0.07 0.003-0.004	[204] [197] [262]	**0.009 – 0.4**

Parameter	***Symbol***	***Units***	***Literature Values***	***Literature References***	***Model (Range)***
Specific phosphatification rate	k_p	m^3/g COD. d	0.03 – 0.8	[262]	**0.029 – 0.4**
Constant kinetic parameters					
Heterotrophic maximum growth rate	μ_H	1/d	6 39 2.3 – 4.79	[204] [197] [196]	18
Heterotrophic decay rate	b_H	1/d	0.62 0.5 – 0.58 0.13	[204] [249] [200]	0.50
Autotrophic decay rate	b_A	1/d	0.05 0.29	[204] [197]	0.04
Yield of heterotrophic biomass growth	Y_H	g COD/ g COD	0.67 0.44, 0.62 0.76	[204] [199] [200]	0.666
Yield of autotrophic biomass growth	Y_A	g COD/ g N	0.24 0.3	[204] [197]	0.24
Correction factor for anoxic hydrolysis	η_h	-			0.40
Half saturation constant for assimilation of carbon (heterotrophs)	K_{SH}	g COD /m^3	20 158 5	[204] [197] [249]	20
Phosphorus half saturation constant (heterotrophic)	K_{PH}	mg P/L			0.01
Phosphorus half saturation constant (autotrophic)	K_{PA}	mg P/L			0.01
Half saturation constant for assimilation of nitrogen (heterotrophs)	K_{NH}	g COD /m^3			0.05
Half saturation constant for assimilation of nitrogen (autotrophs)	K_{NA}	g COD /m^3	1 2.7	[204] [197]	0.05
Maximum specific hydrolysis rate	k_h	g COD /g cell	3 7.9	[204]	3

Parameter	***Symbol***	***Units***	***Literature Values***	***Literature References***	***Model (Range)***
		COD.d	8.1	[197] [200]	
Hydrolysis half saturation constant	K_X	g COD /g cell COD	0.03 0.5	[204] [197]	0.03
Oxygen half saturation constant (autotrophic)	K_{OH}	g O_2/m^3			0.20
Oxygen half saturation constant (heterotrophic)	K_{OA}	g O_2/m^3			0.40

Table 109: Steady state cases calibrated nutrient transformation process rates

Steady state Case No.	***Maximum autotrophic growth rate, μ_A***	***Anoxic correction factor, η_g***	***Ammonification rate, k_a***	***Phosphatification rate, k_p***
Units	***1/d***	**-**	***m^3/g COD. d***	***m^3/g COD. d***
2	0.18	0.04	0.10	0.40
3	0.17	0.08	0.13	0.40
4	0.16	0.07	0.09	0.40
5	0.16	0.08	0.06	0.03
6	0.20	0.09	0.40	0.04
7	0.14	0.17	0.07	0.06
10	0.30	0.18	0.20	0.30
11	0.11	0.30	0.04	0.18
12	0.11	0.45	0.05	0.09
13	0.08	0.70	0.05	0.40
14	0.12	0.50	0.07	0.40
15	0.05	0	0.03	0.40
16	0.08	0	0.02	0.17
17	0.05	0	0.02	0.40
18	0.05	0	0.01	0.07
19	0.05	0	0.01	0.05
20	0.05	0	0.01	0.08

Steady state Case No.	***Maximum autotrophic growth rate, μ_A***	***Anoxic correction factor, η_g***	***Ammonification rate, k_a***	***Phosphatification rate, k_p***
Units	***1/d***	***-***	***m^3/g COD. d***	***m^3/g COD. d***
21	0.05	0	0.02	0.08
22	0.05	0	0.01	0.08
23	0.05	0	0.01	0.40
24	0.05	0	0.08	0.40
25	0.05	0	0.05	0.40

It should be noted that the pseudo-steady state cases 20 and 22 (21:06 8 May and 3:52 15 May) have poor BOD removal due to phosphorus deficiency, with modelled BOD residuals of 77 mg BOD/L and 60 mg BOD/L. This indicates that either the calculated phosphoric addition rate from the mass balances is inadequate or that phosphorus previously stored by the biomass became available, in addition to the phosphorus calculated in the mass balances.

The nutrient residuals for nitrate, ammonia and phosphate found from the pseudo-steady states with individually adjusted kinetic parameters are compared to the measured values in Figure 91. The modelled nitrogen residuals are found to fit very well to the measured data, while the modelled phosphate residuals fit less well, which is understandable given the existence of three fitting parameters for the nitrogen transformation processes, μ_A, η_g and k_a, compared to one fitting parameter, k_p, for the phosphorus transformation processes. There is also more uncertainty associated with the phosphoric acid dosing rate calculated in the mass balances compared to the measured urea dosing rate due to the quality of measured data available.

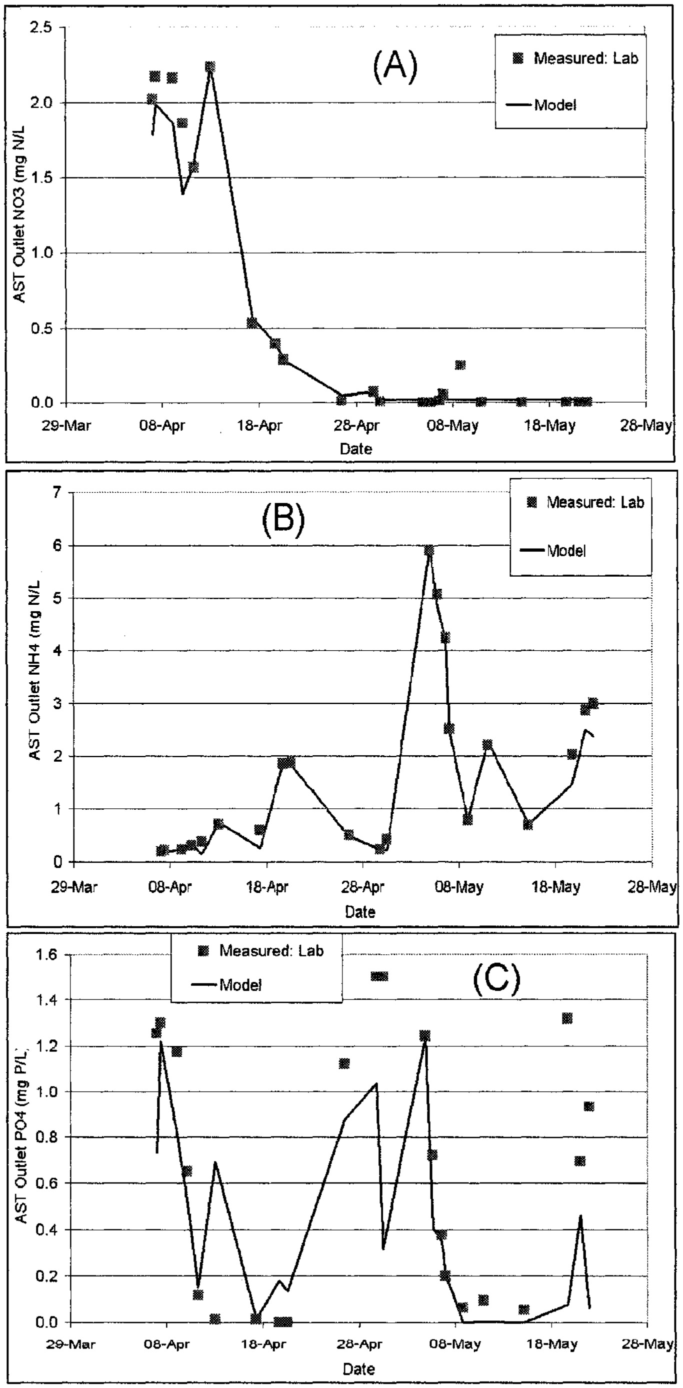

Figure 91: Individual scenario calibration approach, AST outlet nutrient residuals measured & modelled (a) Nitrate (b) Ammonia (c) Phosphate

APPENDIX 6
Error Analysis

6.1. Error Analysis

6.1.1. Measurement Accuracy: Laboratory

Experimental error is reported in three ways: (1) for individual observations as half of the smallest scale markings (precision); (2) the average and range for repeated measurements [271]; and (3) the repeatability of internal laboratory experiments.

6.1.1.1. Nutrients: Wastewater Characterisation

The precision for each of the automated external laboratory nutrient measurements is specified in Table 110 below.

Table 110: Nutrient test precision (wastewater characterisation)

Nutrient test	*Units*	*Instrument Precision*	*Precision*
Ortho-phosphate	*mg P/L*	0.001	0.0005
Total phosphorus	*mg P/L*	0.001	0.0005
Total Kjeldahl Nitrogen	*mg N/L*	0.01	0.005
Ammonia nitrogen	*mg N/L*	0.001	0.0005
Nitrate nitrogen	*mg N/L*	0.001	0.0005

6.1.1.2. Nutrients: Mill Laboratory

The precision for each of the mill laboratory measurement methods for the calculated of nutrient fractions is specified in Table 111 below.

Table 111: Nutrients test precision (mill laboratory)

Nutrient test	*Units*	*Method Precision*	*Method Bias*	*Precision*
Ortho-phosphate	*mg P/L*	4.0 - 9.1%	4.4 - 10%	9.1%
Ammonia	*mg N/L*	2.2 - 3.8%	NR	3.8%
Nitrate	*mg N/L*	3.0%	NR	3.0%

NR = Not reported

6.1.1.3. Solids

The precision for each of the mill laboratory measurements for the calculated of suspended solids is specified in Table 112 and Table 113 below. The propagation of uncertainty in the calculation of suspended solids is discussed further in section 6.1.3.

Table 112: Solids test precision (Characterisation)

Solids test	*Units*	*Instrument Precision*	*Precision*
Volume	mL	1	0.5
Mass	mg	0. 1	0.05

Table 113: Solids test precision (Standard Methods)

Solids test	*Units*	*Method Precision*	*Method Bias*	*Precision*
TSS	*mg/L*	33% at 15 mg/L 10% at 242 mg/L 0.76% at 1707 mg/L	2.8 mg/L	0.76% – 33%
VSS	*mg/L*	6.47% at 170 mg/L	NR	6.47%

6.1.1.4. COD

The precision of the test method is reported by HACH to be +/- 18 mg/L for the 0 to 1500 ppm COD range.

6.1.1.5. Continuous BOD$_{1\text{-}28}$

The precision of this test method is reported to be 5% for a BOD concentration of 50 to 100 mg/L and 3% for "more concentrated samples" [264]. The bias of this test method cannot be determined [264].

6.1.2. Measurement Accuracy: On-line

Measurement error for on-line instruments is reported in two ways: (1) precision; and (2) accuracy. The following is a discussion of measurement error for instruments used for the construction of mass balances, which were further used in the construction of the process model. Steady-state case number 2 is used as an example as it has non-zero values for all flows and concentrations.

6.1.2.1. Flow rates

A summary of the instrument accuracy of measured flow rate data used as the basis of mass balance calculations is presented in Table 114 below, along with the measurements used in steady state number two. This analysis assumes that the ABB magnetic flow meters are operating at greater than 10% of the full scale calibration in all cases. The difference between the theoretical volume of water in the Parshall Flume and test meter in the 2006 test (2.0%) is used as the accuracy for the final effluent flow rate. The propagation of uncertainty in the calculation of other flow rates is discussed further in section 6.1.3.

Table 114: Flow rate: mass balance results, instrument accuracy

Flow rate	***Inlet Primary Clarifier***	***Primary Sludge***	***WAS 1***	***WAS 2***	***RAS 1***	***RAS 2***	***Final Effluent***
Units	*L/min*	*L/min*	*L/min*	*L/min*	*L/min*	*L/min*	*L/min*
Steady state case #2	18,856	375	325	325	6,719	6,719	19,198
Instrument accuracy	1%	1%	1%	1%	1%	1%	2%
L/min	189	3.7	3.25	3.25	67	67	384

6.1.2.2. Phosphorus

A summary of the instrument accuracy of measured data used as the basis of phosphorus mass balance calculations is presented in Table 115 below. While the accuracy of the phosphoric acid dosing flow meter is quite high, it is suspected that this measurement contains a gross error, as discussed in section 0.

Table 115: Phosphorus: mass balance results, instrument accuracy

Measurement	***Phosphoric Acid*** *Addition (measured)*	***Phosphoric Acid*** *Concentration*
Units	*L/min*	*kg P/L*
Steady state case #2	0.14	0.394
Instrument accuracy	0.15%	Supplier*
L/min	0.000203	

*See propagation of uncertainty section 6.1.3

6.1.2.3. Solids

A summary of the instrument accuracy of measured data used as the basis of solids mass balance calculations is presented in Table 116 below.

Table 116: Total Suspended Solids: mass balance results, instrument accuracy

Flow rate	***AST Outlet*** *TSS*	***Final Effluent*** *TSS*
Units	*mg/L*	*mg/L*
Steady state case #2	2,355	22

Flow rate	***AST Outlet*** *TSS*	***Final Effluent*** *TSS*
Units	*mg/L*	*mg/L*
Instrument accuracy	0.76%	5%
mg/L	17.9	1.1

6.1.2.4. Carbon (COD)

A summary of the instrument accuracy of measured data used as the basis of COD mass balance calculations is presented in Table 117 below.

Table 117: COD: mass balance results, instrument accuracy

Flow rate	***AST Inlet*** *UV 254*	***Final Effluent*** *COD*
Units	*m^{-1}*	*mg/L*
Steady state case #2	867	132
Instrument accuracy	3% + 0.5 m^{-1}	18 mg/L at 0 to 1500 ppm COD
m^{-1}	26.5	-
mg/L	-	18

6.1.2.5. Nitrogen

A summary of the instrument accuracy of measured data used as the basis of nitrogen mass balance calculations is presented in Table 118 below.

Table 118: Nitrogen: mass balance results, instrument accuracy

Flow rate	***AST Effluent*** *Nitrate concentration*	***Final Effluent*** *Nitrate concentration*	***Final Effluent*** *Ammonia concentration*	***Urea*** *Addition (measured)*	***Urea*** *Concentration*
Units	*mg/L*	*mg N/L*	*mg/L*	*L/min*	*kg N/L*
Steady state case #2	2.0	2.8	0.0187	2.740	0.262
Instrument accuracy	3.0%	3.0%	3% ± 0.05 mg/L	0.15%	Supplier*
mg/L	0.06	0.08	(0.00056) 0.05	0.00411	-

*See propagation of uncertainty section 6.1.3

6.1.3. Propagation of Measurement Uncertainty

The propagation of uncertainty from the measured values to calculated values must be quantified in order to ascertain the uncertainty related to calculation results, such as mass balances. The propagation of uncertainty can be calculated according to the rules presented in Table 119 below [272].

Table 119: Propagation of uncertainty rules [272]

Calculation	*Uncertainty*
$A = B + C$ or $A = B - C$	$\Delta A = \Delta B + \Delta C$
$A = B \times C$ or $A = B / C$	$\frac{\Delta A}{\lvert A\rvert} = \frac{\Delta B}{\lvert B\rvert} + \frac{\Delta C}{\lvert C\rvert}$
$A = B^C$ where C is any number	$\frac{\Delta A}{\lvert A\rvert} = \lvert C\rvert \cdot \frac{\Delta B}{\lvert B\rvert}$
$A = \ln(x)$, e^x or any function with extremum	$\Delta A = \frac{A_{MAX} - A_{MIN}}{2}$

6.1.3.1. Flow rates

The volumetric flow balances were carried out over activated sludge selector, basin, primary and secondary clarifiers, according to the equations:

WAS $Q_{WAS,\,Total} = Q_{WAS1} + Q_{WAS2}$
RAS $Q_{RAS,\,Total} = Q_{RAS1} + Q_{RAS2}$
AST and Secondary Clarifier: $Q_{AST\text{-}inlet} = Q_{Effluent} + Q_{WAS}$
Primary Clarifier: $Q_{PC\text{-}inlet} = Q_{PC\text{-}outlet} + Q_{PC\text{-}sludge}$
Press Filtrate return: $Q_{AST\text{-}inlet} = Q_{PC\text{-}outlet} + Q_{Press\text{-}Filtrate}$

In the case of the AST inlet flow rate for Steady-state case number 2:

$$\Delta A = \Delta B + \Delta C$$

$$\Delta\, Q_{AST\text{-}inlet} = \Delta(Q_{Effluent}) + \Delta(Q_{WAS,T}) = 384 + 6.5 = 390 \text{ L/min}$$

Accuracy values were similarly calculated for the outlet from the primary clarifier and the press-filtrate flow rates, which are presented in Table 120 below, with the accuracy divided by total flow rate for each steady state presented as a percentage average over all steady states.

Table 120: Flow rate: mass balance results: calculated accuracy (L/min)

Steady State No.	***Inlet Primary Clarifier***	***Outlet Primary Clarifier***	***Primary Sludge***	***Press Filtrate***	***AST Inlet***	***WAS***	***RAS***	***Final Effluent***
Average %	1.0%	1.0%	1.0%	68.6%	2.0%	1.0%	1.0%	2.0%

Steady State No.	Inlet Primary Clarifier	Outlet Primary Clarifier	Primary Sludge	Press Filtrate	AST Inlet	WAS	RAS	Final Effluent
1	175	178	3.0	540	362	12.0	122	350
2	189	192	3.7	583	390	6.5	134	384
3	182	185	3.9	560	375	6.5	129	368
4	183	187	3.7	560	373	6.5	128	367
5	188	191	3.0	576	385	8.0	132	377
6	189	192	2.6	578	386	7.5	133	379
7	184	186	2.1	564	378	7.9	129	370
8	183	186	2.8	565	379	10.0	129	369
9	185	188	2.8	567	379	10.0	129	369
10	193	196	2.8	590	394	8.0	135	386
11	178	181	2.6	548	368	7.0	126	361
12	183	185	2.5	559	374	7.1	128	366
13	178	181	2.7	546	364	6.4	125	358
14	184	187	2.5	565	379	6.4	130	372
15	182	184	2.3	560	376	5.6	129	370
16	184	186	2.0	575	389	6.8	134	382
17	185	188	2.1	576	389	6.2	134	382
18	185	187	2.0	573	386	6.8	133	379
19	187	189	2.0	576	388	6.8	133	381
20	194	196	2.0	595	399	7.5	137	391
21	182	184	2.5	554	370	8.4	126	361
22	184	186	2.5	562	376	8.4	129	367
23	192	195	2.9	582	388	7.2	133	381
24	192	195	2.9	585	390	7.2	134	383
25	190	193	2.9	575	382	6.8	131	375
26	197	200	3.0	592	392	5.4	135	387
27	204	207	2.9	623	416	5.0	144	411
28	209	212	3.5	629	417	4.4	144	413
29	189	193	3.6	572	379	4.5	131	375
30	195	199	3.7	588	389	4.5	135	384

Steady State No.	Inlet Primary Clarifier	Outlet Primary Clarifier	Primary Sludge	Press Filtrate	AST Inlet	WAS	RAS	Final Effluent
31	195	199	3.8	594	395	4.2	137	391
32	201	205	3.8	599	395	3.2	137	392

6.1.3.2. Phosphorus

Due to the limited measured data available for the phosphorus mass balance, some ratios were used to relate measured data to non-measured variables for each steady state. These ratios are presented in Table 121 below. The reported instrument accuracy for laboratory measurements in section 6.1.1 are used to calculate the uncertainty associated with each of the ratios, according to the following methodology.

In the case of the final effluent ratio of average ortho-phosphate to average total phosphorus for Steady-state case number 2:

$$\frac{\Delta A}{|A|} = \frac{\Delta B}{|B|} + \frac{\Delta C}{|C|}$$

$$\frac{\Delta(PO_4)}{|PO_4|} = \Sigma\left(\frac{\Delta x_i}{x_i}\right) = \frac{0.0005}{1.69} + \frac{0.0005}{0.778} + \frac{0.0005}{1.76} + \frac{0.0005}{0.538} + \frac{0.0005}{0.0437} + \frac{0.0005}{0.0287}$$

$$= 0.0310 = 3.10\%$$

$$\frac{\Delta\ \text{ratio}}{|\text{ratio}|} = \frac{\Delta(\text{Ortho-P})}{|\text{Ortho-P}|} + \frac{\Delta(TP)}{|TP|} = 3.10\% + 0.668\% = 3.77\%$$

Accuracy values were similarly calculated for the other phosphorus ratios and concentrations used in the mass balances, which are presented in Table 121 below. The accuracy for the phosphoric acid concentration was evaluated from the certified specific gravity and phosphorus concentration from extremum of the deliveries made during the steady state detection period.

Table 121: Phosphorus: wastewater characterisation ratios used in mass balance calculations

Streams	***WAS***	***RAS***	***Final Effluent***	***Press filtrate: WAS***	***Phosphoric Acid***	***Outlet Primary Clarifier***
Ratio	*TP: TSS**	*TP: TSS**	*Ortho-P: TP**	*TP:TP**	*Concentration ***	*TP concentration ***
Units	*mg TP/ mg TSS*	*mg TP/ mg TSS*	*mg PO_4/mg TP*	*mg P/L*	*mg P/L*	*mg P/L*
Steady state case #2	0.0101	0.0113	0.821	0.0635	394,000	0.807
Uncertainty	8.36%	8.63%	3.77%	0.0074%	0.602%	0.053%
mg TP/mg TSS	0.000843	0.000885	-	-	-	-
mg P/mg P	-	-	0.031	4.67×10^{-6}	-	-
mg P/L	-	-	-	-	2,371	0.000566

* Average data used in ratio for each steady state

** Average data used for all steady states

The fact that the total phosphorus was measured on a limited number of occasions during the steady states detected results in the limited insight that can be derived from the data, and necessitates the use of average values.

Accuracy values were calculated for the phosphorus mass balance results, which are presented in Table 122 below, with the accuracy divided by total phosphorus load for each steady state presented as a percentage average over all steady states.

Table 122: Total Phosphorus: mass balance results: calculated accuracy (kg P/d)

Steady State No.	***Inlet Primary Clarifier***	***Outlet Primary Clarifier***	***Primary Sludge***	***Press Filtrate***	***PO4 Add (meas)***	***AST Inlet***	***WAS***	***RAS***	***Final Effluent***
Avg %	265%	269%	1.1%	33.9%	0.8%	30.6%	33.2%	16.5%	14.9%

Steady State No.	Inlet Primary Clarifier	Outlet Primary Clarifier	Primary Sludge	Press Filtrate	PO4 Add (meas)	AST Inlet	WAS	RAS	Final Effluent
1	103.9	103.9	0.004	7.48	1.3	95.1	91.9	167.3	3.2
2	65.5	65.5	0.005	6.85	0.6	58.1	50.8	178.4	7.3
3	65.3	65.3	0.005	6.58	0.6	58.2	51.1	172.5	7.0
4	63.5	63.5	0.005	5.40	0.6	57.5	51.1	171.8	6.3
5	72.2	72.1	0.004	5.80	0.6	65.7	61.3	174.3	4.4
6	67.3	67.3	0.003	5.25	0.6	61.4	59.9	181.8	1.4
7	66.8	66.8	0.003	5.21	0.6	61.0	60.8	172.1	0.2
8	77.7	77.7	0.003	6.28	0.6	70.8	70.6	160.6	0.3
9	74.5	74.5	0.003	5.41	0.6	68.4	68.1	155.3	0.3
10	62.8	62.8	0.003	4.85	0.6	57.3	56.8	165.2	0.4
11	54.9	54.9	0.003	5.26	1.5	48.1	47.7	147.2	0.4
12	54.7	54.7	0.003	4.45	1.4	48.8	48.5	149.1	0.3
13	52.9	52.9	0.003	4.30	1.2	47.4	44.2	147.7	3.2
14	53.8	53.8	0.003	4.36	1.4	48.0	40.7	140.7	7.3
15	49.3	49.3	0.003	4.54	1.3	43.5	36.2	142.1	7.2
16	62.9	62.9	0.002	6.96	0.8	55.1	47.6	160.3	7.5
17	55.6	55.6	0.003	6.43	0.8	48.4	44.6	163.2	3.8
18	58.4	58.4	0.002	6.47	0.8	51.2	49.7	165.6	1.5
19	59.1	59.1	0.002	6.03	0.8	52.3	51.3	171.3	1.0
20	66.8	66.8	0.002	5.77	0.9	60.2	59.8	186.6	0.4
21	69.6	69.6	0.003	4.77	0.8	64.0	63.8	166.2	0.2
22	64.9	64.9	0.003	4.78	1.0	59.1	58.8	155.8	0.2
23	60.2	60.2	0.004	3.68	1.4	55.2	47.1	149.8	8.1
24	62.9	62.9	0.004	4.24	1.2	57.4	47.2	149.9	10.2
25	58.0	58.0	0.004	3.17	1.2	53.6	43.8	144.0	9.8
26	46.3	46.3	0.004	1.95	1.1	43.3	34.2	143.9	9.0
27	43.5	43.4	0.004	3.93	1.0	38.5	31.1	149.1	7.4
28	33.7	33.7	0.004	2.09	0.8	30.8	26.1	143.3	4.7
29	31.5	31.5	0.004	2.41	0.7	28.4	25.9	126.0	2.5

Steady State No.	***Inlet Primary Clarifier***	***Outlet Primary Clarifier***	***Primary Sludge***	***Press Filtrate***	***PO4 Add (meas)***	***AST Inlet***	***WAS***	***RAS***	***Final Effluent***
30	29.2	29.2	0.005	1.88	0.7	26.6	25.2	126.5	1.4
31	27.6	27.6	0.005	2.92	0.6	24.1	23.4	127.4	0.6
32	20.7	20.7	0.005	0.74	0.8	19	19.2	134.6	0

6.1.3.3. Solids

Accuracy values were calculated for the solids ratios and concentrations used in the mass balances, which are presented in Table 123 below, according to the methodology described previously.

Table 123: Solids: wastewater characterisation ratios used in mass balance calculations

Streams	***WAS: RAS***	***Inlet Primary Clarifier***	***Outlet Primary Clarifier***
Ratio	*TSS: TSS**	*Concentration**	*Concentration**
Units	*mg/mg*	*mg TSS/L*	*mg TSS/L*
All steady state cases	3.25	1204	191.3
Uncertainty	17%	9.5%	2.0%
mg TSS/ mg TSS	0.55	-	-
mg TSS/L	-	115	3.75

*Average data used for all steady states

Accuracy values were calculated for the solids mass balance results, which are presented in Table 124 below, with the accuracy divided by total suspended solids load for each steady state presented as a percentage average over all steady states.

Table 124: Total suspended Solids: mass balance results: calculated accuracy (kg TSS/d)

Steady State No.	***Inlet Primary Clarifier***	***Outlet Primary Clarifier***	***Primary Sludge***	***AST Outlet***	***WAS***	***RAS***	***Final Effluent***
Average %	*10.5%*	*3.0%*	*13.0%*	*2.7%*	*23.9%*	*6.9%*	*7.0%*

Steady State No.	Inlet Primary Clarifier	Outlet Primary Clarifier	Primary Sludge	AST Outlet	WAS	RAS	Final Effluent
1	3,184	142	3,326	2,924	6,666	6,935	0
2	3,437	153	3,590	3,078	3,613	6,495	42
3	3,309	147	3,456	2,975	3,638	6,324	38
4	3,334	148	3,482	2,964	3,639	6,304	39
5	3,422	152	3,574	3,013	4,388	6,614	48
6	3,452	154	3,606	3,139	4,279	6,804	40
7	3,361	150	3,511	2,969	4,347	6,514	16
8	3,340	149	3,489	2,815	5,095	6,467	185
9	3,374	150	3,524	2,723	4,917	6,256	186
10	3,524	157	3,681	2,854	4,063	6,236	36
11	3,244	144	3,388	2,539	3,403	5,481	17
12	3,329	148	3,478	2,571	3,461	5,553	14
13	3,253	145	3,398	2,567	3,150	5,503	140
14	3,360	150	3,510	2,426	2,897	5,132	26
15	3,317	148	3,465	2,468	2,574	5,148	138
16	3,358	150	3,507	2,792	3,396	5,992	192
17	3,381	151	3,532	2,841	3,178	6,009	192
18	3,365	150	3,515	2,863	3,542	6,111	69
19	3,405	152	3,557	2,951	3,653	6,276	11
20	3,534	158	3,692	3,216	4,266	6,925	10
21	3,312	148	3,459	2,871	4,571	6,396	13
22	3,353	149	3,502	2,690	4,215	5,974	10
23	3,494	156	3,650	2,612	3,366	5,666	191
24	3,493	156	3,649	2,583	3,362	5,543	12
25	3,458	154	3,612	2,481	3,118	5,291	9
26	3,593	160	3,753	2,483	2,424	5,074	35
27	3,714	165	3,879	2,571	2,195	5,131	24
28	3,806	169	3,975	2,481	1,842	4,862	62
29	3,444	153	3,597	2,192	1,829	4,418	141
30	3,559	158	3,717	2,208	1,785	4,452	188

Steady State No.	**Inlet Primary Clarifier**	**Outlet Primary Clarifier**	**Primary Sludge**	**AST Outlet**	**WAS**	**RAS**	**Final Effluent**
31	3,562	158	3,720	2,222	1,656	4,415	167
32	3,663	163	3,826	2,341	1,347	4,447	102

6.1.3.4. COD

Accuracy values were calculated for the various ratios and concentrations used in the COD mass balances, which are presented in Table 125 and Table 126 below, according to the methodology described previously.

It is assumed that there is zero uncertainty associated with the stoichiometric ratios derived from chemical equations. It is assumed that there is some variation in the water level in the aerated selectors and aerated basins, due to wind disturbances for example: this is assumed to be no more than 0.01% of the total volume.

The calculation of the COD concentration in the inlet to the AST basin involves a linear regression determined by the mill to explain 69% of the variation in the signal from the UV instrument (Pearson's $R^2 = 0.69$). The standard error of the regression, S_Y, for this data set was determined to be 127 (or 9.8% of the average Y values), according to the calculation [273]:

$$S_Y = \left[\frac{\sum_{i=1}^{N} (Y_i - mX_i - c)^2}{N-2} \right]^{1/2}$$

Where N is the number of pairs of form (X,Y) analysed in the linear regression, and the linear regression is of the form Y= mX + c. In this case, N = 22.

The measured UV signal and the laboratory COD measurement do no share any sources of error. The accuracy of the correlation is 9.8% for the purposes of quantifying the incertitude of the calculated COD concentration.

Table 125: COD: wastewater characterisation ratios used in mass balance calculations

Measurement	***WAS (X_V)****	***AST Inlet***	***AST BASIN***	***AST BASIN***
Ratio	*TSS:VSS*	*COD concentration*	*SOUR Concentration*	*VSS Concentration*
Units	*mg VSS/mg TSS*	*mg COD/L*	*mg O_2/L*	*mg VSS/L*
Steady state case #2	0.94	1,722	8.7	2,192
Uncertainty	9.0%	12.8%	ND	6.47% at 170 mg/L
mg/mg	0.084	-	-	-
mg/L	-	221	-	142

*Average data used for all steady states
ND = not determined

Table 126: COD: theoretical ratios & design parameters used in mass balance calculations

Measurement	***WAS (f_{CV})***	***Nitrification***	***AST Basins & Selectors***	***Nitrification***
Ratio	*COD/VSS***	*Nitrate/ ammonia***	*Volume*	*Nitrate/ oxygen***
Units	*mg COD/mg VSS*	*mg NO_3 /mg NH_4^+*	*m^3*	*mg O_2/mg NO_3*
Steady state case #2	1.48	4.57	35,600	2.86
Accuracy	-	-	0.01%	-
m^3	-	-	3.56	-

**Theoretical data used for all steady states

Accuracy values were calculated for the COD mass balance results, which are presented in Table 127 below, with the accuracy divided by total COD load for each steady state presented as a percentage average over all steady states.

Table 127: COD: mass balance results: calculated accuracy (kg COD/d)

Steady State No.	***Input COD***	***Output COD***		
	AST Inlet	***COD Oxidised***	***WAS***	***Final Effluent***
Average %	14.8%	6.6%	32.8%	17.8%

Steady State No.	Input COD	Output COD		
	AST Inlet	COD Oxidised	WAS	Final Effluent
1	7,947	798	12,566	528
2	7,293	1076	6,941	571
3	6,930	1090	6,983	550
4	7,317	1206	6,983	555
5	7,591	1078	8,381	566
6	7,635	1077	8,189	546
7	7,086	950	8,307	525
8	7,143	769	9,647	527
9	7,180	666	9,310	530
10	7,503	914	7,767	555
11	6,557	929	6,517	498
12	6,599	957	6,630	512
13	6,455	1184	6,033	518
14	6,572	923	5,564	544
15	6,954	997	4,949	542
16	6,983	902	6,501	554
17	7,085	885	6,097	553
18	7,038	887	6,793	547
19	7,220	953	7,012	546
20	8,380	891	8,175	560
21	7,749	842	8,715	519
22	7,616	833	8,039	528
23	7,741	905	6,432	606
24	7,503	1035	6,444	590
25	7,414	977	5,983	549
26	8,144	1331	4,676	581
27	8,695	1244	4,247	621
28	8,001	1110	3,570	628
29	7,665	1021	3,531	574
30	7,613	966	3,443	591
31	7,685	929	3,202	603

Steady State No.	Input COD	Output COD		
	AST Inlet	COD Oxidised	WAS	Final Effluent
32	7,749	932	2,618	587

6.1.3.5. Nitrogen

Accuracy values were calculated for the various ratios and concentrations used in the nitrogen mass balances, which are presented in Table 128 below, according to the methodology described previously. The accuracy for the urea specific gravity was assumed to be the same as that of the phosphoric acid specific gravity (+/- 0.01), both of which were reported to two decimal places, due to a lack of information from the urea supplier.

Table 128: Nitrogen: wastewater characterisation ratios used in mass balance calculations

Measurement	Final effluent	AST Inlet	Urea	Activated sludge
Ratio	*TKN/ ammonia**	*TN Concentration*	*Concentration**	*Nitrogen/sludge***
Units	*mg TKN/ mg NH_4^+*	*mg N/L*	*mg N/L*	*mg N/mg VSS*
All steady state cases	4.36	5.67	262,000	0.1
Accuracy	1.8%	0.97%	0.88%	ND
mg/mg	0.080	-	-	-
mg/L	-	0.055	2,298	-

*Average data used for all steady states
**Theoretical data used for all steady states

The ratio of total Kjeldahl nitrogen (TKN) to ammonia nitrogen (NH_4) concentration in the final effluent is affected by a larger variation in the TKN concentration than in the ammonia nitrogen concentration. It is possible that the TKN and ammonia concentrations varied on a shorter time basis than the wastewater characterisation was carried out. The variation in the TKN and ammonia nitrogen in the final effluent compared to the ratio of these values is presented in Figure 92 below. It is suggested that future work include a more extensive wastewater characterisation regime.

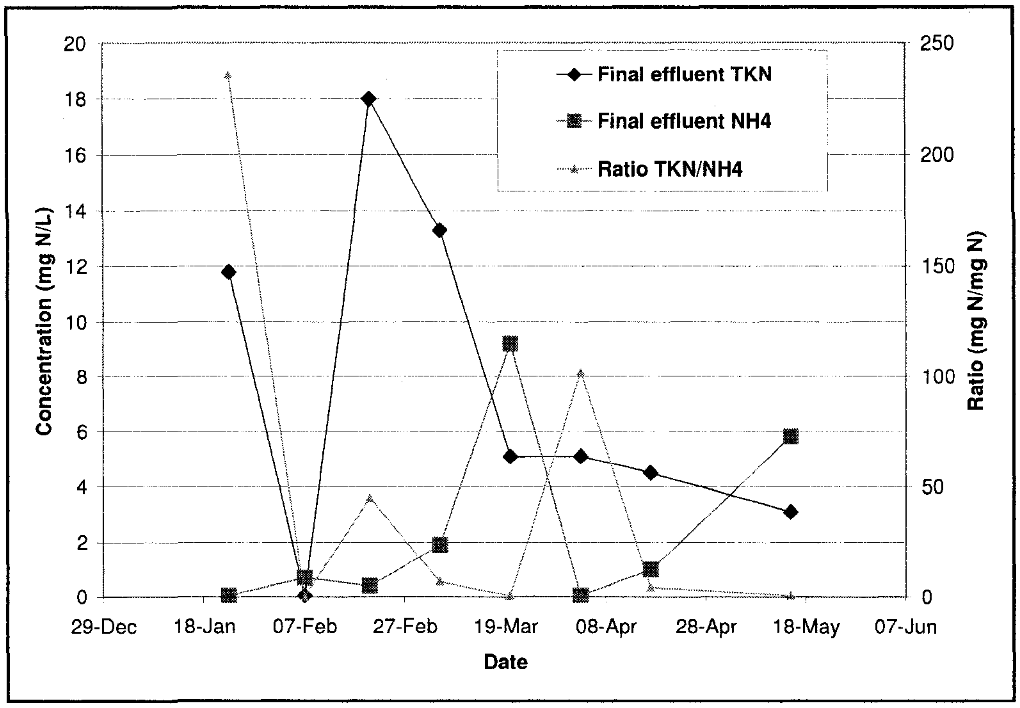

Figure 92: Final effluent ratio TKN/NH4

Accuracy values were calculated for the nitrogen mass balance results, which are presented in Table 129 below, with the accuracy divided by nitrogen load for each steady state presented as a percentage average over all steady states. A large source of uncertainty in the calculation of the TKN in the final effluent is the fact that the ammonia concentrations from which it is calculated are very small, often smaller than the limit of detection of the on-line instrument. This leads to a large relative uncertainty in the measured value.

Table 129: Nitrogen: mass balance results: calculated accuracy (kg N/d)

Steady State No.	**Input Nitrogen**		**Output Nitrogen**			
	AST Inlet	**Urea**	**NO3 Denitrified**	**WAS**	**NO3 Final Effluent**	**TKN Final Effluent**
Average %	*2.9%*	*1.03%*	*13.1%*	*10.0%*	*5.0%*	*200%*
1	4.43	10.7	0	246	0	0
2	4.76	10.6	6.75	143	3.88	6.17
3	4.57	10.7	6.96	143	4.00	5.90
4	4.55	11.4	7.43	143	4.50	5.93

Steady State No.	Input Nitrogen		Output Nitrogen			
	AST Inlet	Urea	NO3 Denitrified	WAS	NO3 Final Effluent	TKN Final Effluent
5	4.70	11.4	7.07	170	4.47	6.38
6	4.71	11.6	6.52	167	4.31	7.58
7	4.61	13.6	6.33	169	3.25	6.06
8	4.63	13.6	5.80	191	3.20	5.99
9	4.64	13.6	5.44	184	3.19	6.30
10	4.81	12.0	4.06	158	3.29	6.18
11	4.49	12.1	1.04	133	0.51	9.40
12	4.56	12.2	0.76	135	0.37	5.91
13	4.44	7.5	6.84	123	6.83	5.70
14	4.61	8.8	0.10	115	0	5.99
15	4.58	8.0	0.01	102	0	5.89
16	4.74	10.4	0	133	0	6.38
17	4.73	10.1	0	125	0	6.52
18	4.71	10.4	0.01	139	0	7.02
19	4.73	10.5	0.07	144	0	8.75
20	4.86	12.0	0.36	167	0	7.65
21	4.51	11.3	0	176	0	8.79
22	4.59	11.0	0	162	0	11.05
23	4.73	12.8	0	131	0	6.03
24	4.76	10.9	0	132	0	9.66
25	4.66	11.2	0	123	0	5.95
26	4.78	12.0	0.34	97	0	6.59
27	5.07	13.7	0.88	89	0.07	9.83
28	5.07	11.4	0.83	75	0.22	9.44
29	4.61	11.3	0.72	74	0.29	6.25
30	4.73	11.2	0.72	72	0.36	6.11
31	4.81	11.3	0.68	67	0.40	6.19
32	4.80	11.4	0	56	0	6.71

6.1.3.6. Influent Characterisation

Accuracy values were calculated for the various ratios and concentrations used in the influent characterisation, which are presented in Table 130, Table 131, Table 132 and Table 133 below, according to the methodology described previously. The ortho-phosphate balance is based on the results of the total phosphorus mass balance plus utilisation of the ratios in Table 131. It is assumed that all phosphorus in the phosphoric acid is available as ortho-phosphate, and all nitrogen in the urea is available as ammonia-nitrogen.

Table 130: Influent characterisation ratios: COD, VSS

Measurement	***AST Inlet***	***AST Inlet***	***Activated sludge***	***Final effluent***
Ratio	*Soluble COD/ total COD**	*Filtered COD/ total COD**	*Mixed liquor XCOD/ VSS**	*Soluble COD/ total COD**
Units	*mg COD/ mg COD*	*mg COD/ mg COD*	*mg XCOD/ mg VSS*	*mg COD/ mg COD*
All steady state cases	0.5406	0.7842	1.63	0.7340
Accuracy	12.5%	9.96%	11.0%	237%
mg /mg	0.0677	0.0781	0.179	1.768

*Average data used for all steady states

Table 131: Influent characterisation ratios: nutrients

Measurement	***AST Inlet***	***AST Inlet***	***Press Filtrate***
Ratio	*Ammonia nitrogen concentration**	*Ortho-phosphorus /Total Phosphorus**	*Ortho-phosphorus /Total Phosphorus**
Units	*mg N/L*	*mg PO4/mg TP*	*mg PO4/mg TP*
All steady state cases	0.026	0.2410	0.5166
Accuracy	2.52%	2.74%	0.02%
mg /L	0.000658	-	-
mg/mg	-	0.0005112	0.00008346

*Average data used for all steady states

Table 132: Influent characterisation theoretical data

Measurement	***Activated sludge***	***Activated sludge***	***Activated sludge***
Ratio	*Heterotrophic Yield***	*Heterotrophic decay rate***	*Endogenous residue factor***
Units	*mg COD/mg COD*	*1/d*	*mg VSS/mg VSS*
All steady state cases	0.666	0.24	0.2
Accuracy	ND	ND	ND

**Theoretical data used for all steady states

Accuracy values were calculated for the influent characterisation results for each steady state case, which are presented in Table 133 below, with the accuracy divided by concentration for each steady state presented as a percentage average over all steady states.

Table 133: Influent characterisation results: calculated accuracy (mg/L)

Steady State No.	***Nutrients***		***Carbonaceous fractions***			
	NH_4	PO_4	S_I	S_S	X_I	X_S
Average %	*2.99%*	*14.1%*	*253%*	*59.7%*	*131%*	*1240%*
1	1.14	1.3	273	735	273	735
2	1.09	0.8	243	639	243	639
3	1.14	0.9	252	642	252	642
4	1.22	0.8	275	691	275	691
5	1.18	0.9	261	678	261	678
6	1.19	0.8	187	606	187	606
7	1.42	0.8	164	560	164	560
8	1.41	1.0	175	570	175	570
9	1.40	0.9	181	578	181	578
10	1.21	0.8	182	583	182	583
11	1.31	0.7	114	489	114	489
12	1.30	0.7	137	508	137	508
13	0.82	0.7	194	567	194	567
14	0.92	0.7	214	579	214	579

Steady State No.	Nutrients		Carbonaceous fractions			
	NH_4	PO_4	S_I	S_S	X_I	X_S
15	0.85	0.7	216	608	216	608
16	1.06	0.8	202	580	202	580
17	1.04	0.7	196	581	196	581
18	1.07	0.7	191	575	191	575
19	1.08	0.7	180	574	180	574
20	1.20	0.8	176	622	176	622
21	1.21	0.9	184	628	184	628
22	1.16	0.8	183	612	183	612
23	1.31	0.7	373	796	373	796
24	1.11	0.8	307	713	307	713
25	1.17	0.7	214	624	214	624
26	1.23	0.6	263	706	263	706
27	1.32	0.5	271	718	271	718
28	1.10	0.4	288	697	288	697
29	1.20	0.4	299	731	299	731
30	1.16	0.4	307	724	307	724
31	1.15	0.3	310	724	310	724
32	1.17	0.2	260	679	260	679

6.1.4. Process Variation

The propagation of uncertainty from the process variation, reported as standard deviation, to calculated values must be quantified in order to ascertain the uncertainty related to calculation results, such as mass balances. The propagation of uncertainty can be calculated according to the rules presented in Table 134 below [271]. These rules are based on the premise that the variation of the process parameters can be described by a normal distribution. It is assumed that ratios used in calculations do not vary with the process but are constant: the following describes the variation in measured process parameters only.

Table 134: Propagation of uncertainty rules: process variation (normal distribution) [271]

Calculation	Process Uncertainty

Calculation	***Process Uncertainty***
A = q (x, y)	$\sigma^2_A = \left(\frac{\delta q}{\delta x}.\sigma_x\right)^2 + \left(\frac{\delta q}{\delta y}.\sigma_y\right)^2$
A = B + C or A = B – C	$\sigma^2_A = \sigma^2_B + \sigma^2_C$
A = B x C or A = B / C	$\frac{\sigma^2_A}{A^2} = \frac{\sigma^2_B}{B^2} + \frac{\sigma^2_C}{C^2}$
A = B x C where C is any constant number	$\sigma^2_A = (C.\ \sigma_B)^2$

6.1.4.1. Flow rates

Process variation values were calculated for flow rate mass balance results which are presented in Table 135 below, with the process variation divided by total flow rate for each steady state presented as a percentage average over all steady states.

Table 135: Flow rate: mass balance results: calculated process variation (L/min)

Steady State No.	***Inlet Primary Clarifier***	***Outlet Primary Clarifier***	***Primary Sludge***	***Press Filtrate***	***AST Inlet***	***WAS***	***RAS***	***Final Effluent***
Avg %	0.20%	0.21%	1.98%	5.23%	0.07%	0.09%	0.12%	0.08%
1	152	152	2.1	153	18	1.9	16	18
2	31	80	73.6	81	14	0.4	16	14
3	26	55	48.0	57	18	0.4	17	18
4	25	25	4.6	31	18	0.5	17	18
5	24	24	4.8	32	21	1.1	19	21
6	33	34	5.2	38	17	0.9	17	17
7	30	31	3.9	34	15	1.5	16	15
8	29	29	2.1	32	14	1.4	15	14
9	31	31	1.9	35	16	1.5	15	16
10	42	42	1.5	45	17	1.0	16	17
11	35	35	2.2	38	14	0.8	14	14
12	36	36	2.4	38	14	0.8	14	14
13	44	44	2.9	47	17	0.2	15	17
14	33	33	1.7	37	16	0.2	17	16
15	36	36	1.8	40	18	0.1	17	18
16	29	29	1.5	32	13	0.3	15	13

Steady State No.	*Inlet Primary Clarifier*	*Outlet Primary Clarifier*	*Primary Sludge*	*Press Filtrate*	*AST Inlet*	*WAS*	*RAS*	*Final Effluent*
17	34	35	8.2	37	13	2.9	15	13
18	29	29	1.1	32	12	0.1	14	12
19	25	25	1.6	27	10	0.2	15	10
20	62	62	1.6	63	12	0.5	13	12
21	21	21	1.5	23	8	0.9	13	8
22	26	26	1.5	28	9	0.7	14	9
23	25	25	1.6	27	10	0.2	14	10
24	21	21	1.6	24	12	0.4	15	12
25	24	24	1.6	28	14	0.3	16	14
26	25	25	1.9	29	13	0.1	15	13
27	32	32	3.3	35	15	0.1	14	15
28	45	45	5.4	48	16	0.8	16	16
29	39	39	4.9	42	14	0.1	17	14
30	25	26	5.5	29	14	0.1	17	14
31	35	35	5.3	38	13	0.1	17	13
32	72	72	2.1	74	15	0.2	17	15

6.1.4.2. Phosphorus

Process variation values were calculated for the phosphorus mass balance results, which are presented in Table 136 below, with the process variation divided by total phosphorus load for each steady state presented as a percentage average over all steady states.

Table 136: Phosphorus: mass balance results: calculated process variation (kg P/d)

Steady State No.	*Inlet Primary Clarifier*	*Outlet Primary Clarifier*	*Primary Sludge*	*Press Filtrate*	*PO4 Add (meas)*	*AST Inlet*	*WAS*	*RAS*	*Final Effluent*
Avg %	0.20%	0.20%	1.98%	5.23%	0.06%	0.90%	1.05%	0.33%	0.08%
1	0.177	0.177	0.002	2.139	0	1.777	1.777	1.717	0.022
2	0.037	0.093	0.086	1.220	0	0.709	0.709	1.904	0.035
3	0.030	0.064	0.056	0.866	0	0.771	0.770	2.047	0.045

Steady State No.	***Inlet Primary Clarifier***	***Outlet Primary Clarifier***	***Primary Sludge***	***Press Filtrate***	***PO4 Add (meas)***	***AST Inlet***	***WAS***	***RAS***	***Final Effluent***
4	0.029	0.029	0.005	0.466	0	0.794	0.793	2.029	0.042
5	0.028	0.028	0.006	0.461	0.002	1.202	1.202	2.149	0.032
6	0.039	0.039	0.006	0.576	0.001	1.504	1.504	2.828	0.009
7	0.035	0.036	0.005	0.499	0	1.353	1.353	1.777	0.001
8	0.033	0.034	0.002	0.419	0	1.253	1.253	1.539	0.001
9	0.036	0.036	0.002	0.435	0	1.245	1.245	1.490	0.002
10	0.048	0.048	0.002	0.606	0.001	1.790	1.790	3.198	0.003
11	0.041	0.041	0.003	0.489	0.356	0.738	0.738	1.444	0.002
12	0.041	0.041	0.003	0.495	0.098	0.768	0.768	1.442	0.002
13	0.051	0.051	0.003	0.617	0.006	0.565	0.564	1.575	0.020
14	0.038	0.038	0.002	0.447	0.002	0.537	0.536	1.571	0.043
15	0.042	0.042	0.002	0.499	0.004	3.029	3.028	7.495	0.047
16	0.033	0.033	0.002	0.420	0.002	0.566	0.565	1.514	0.035
17	0.039	0.041	0.010	0.510	0	2.110	2.110	1.690	0.017
18	0.034	0.034	0.001	0.444	0.912	5.299	5.299	10.985	0.006
19	0.029	0.029	0.002	0.388	0.759	0.565	0.565	1.620	0.004
20	0.072	0.072	0.002	0.954	0.003	0.688	0.688	1.565	0.001
21	0.025	0.025	0.002	0.325	0.003	0.903	0.903	1.439	0.001
22	0.030	0.030	0.002	0.363	0.003	0.755	0.755	1.370	0.001
23	0.029	0.029	0.002	0.334	0.002	0.481	0.480	1.281	0.027
24	0.024	0.024	0.002	0.299	0.018	0.560	0.558	1.411	0.042
25	0.028	0.028	0.002	0.342	0.004	0.550	0.548	1.503	0.049
26	0.030	0.030	0.002	0.353	0.003	3.104	3.104	8.271	0.041
27	0.037	0.037	0.004	0.428	0	0.368	0.366	1.459	0.037
28	0.052	0.053	0.006	0.567	0.005	0.985	0.985	3.213	0.024
29	0.045	0.045	0.006	0.463	0.002	1.680	1.680	5.265	0.013
30	0.029	0.030	0.006	0.315	0.010	0.715	0.715	2.463	0.007
31	0.040	0.041	0.006	0.409	0.003	2.471	2.471	8.558	0.003
32	0.084	0.084	0.002	0.872	0.003	2	1.737	7.902	0

6.1.4.3. Solids

Process variation values were calculated for the solids mass balance results, which are presented in Table 137 below, with the process variation divided by total suspended solids load for each steady state presented as a percentage average over all steady states.

Table 137: Solids: mass balance results: calculated process variation (kg TSS/d)

Steady State No.	***Inlet Primary Clarifier***	***Outlet Primary Clarifier***	***Primary Sludge***	***AST Outlet***	***WAS***	***RAS***	***Final Effluent***
Average %	0.20%	0.21%	0.24%	0.06%	1.05%	0.33%	20.4%
1	263	42	267	84	176	152	0
2	55	22	59	73	70	169	5.5
3	45	15	48	85	76	182	8.1
4	43	7	43	86	79	180	5.3
5	41	7	42	94	119	191	43
6	58	9	59	84	149	251	213
7	53	8	53	73	134	158	17
8	50	8	51	67	124	137	16
9	53	8	54	69	124	132	1.9
10	72	11	73	74	178	284	289
11	61	10	61	59	73	128	5.8
12	62	10	62	59	76	128	0.2
13	76	12	77	69	56	140	12
14	57	9	58	64	53	139	14
15	62	10	63	70	300	665	772
16	50	8	50	61	56	134	17
17	59	10	60	62	209	150	17
18	51	8	52	60	526	975	1148
19	43	7	43	59	56	144	15
20	107	17	108	61	68	139	6.0
21	37	6	37	51	90	128	39
22	45	7	45	51	75	122	6.6
23	44	7	44	48	48	114	2.5

Steady State No.	Inlet Primary Clarifier	Outlet Primary Clarifier	Primary Sludge	AST Outlet	WAS	RAS	Final Effluent
24	36	6	37	54	55	125	9.8
25	41	7	42	59	54	133	2.1
26	44	7	45	54	308	734	826
27	55	9	55	56	36	130	42
28	78	13	79	57	98	285	283
29	67	11	68	56	167	467	524
30	43	7	44	53	71	219	211
31	60	10	61	52	245	760	873
32	125	20	127	59	172	702	764

6.1.4.4. COD

Process variation values were calculated for the COD mass balance results, which are presented in Table 138 below, with the process variation divided by total COD load for each steady state presented as a percentage average over all steady states.

Table 138: COD: mass balance results: calculated process variation (kg COD/d)

Steady State No.	Input COD	Output COD		
	AST Inlet	COD Oxidised	WAS	Final Effluent
Average %	*0%*	*0.001%*	*0%*	*0.076%*
1	0	0	0	3.8
2	0	1	0	2.6
3	0	1	0	3.5
4	0	1	0	4.0
5	0	1	0	4.2
6	0	1	0	2.5
7	0	1	0	1.9
8	0	0	0	1.9
9	0	0	0	2.2
10	0	0	0	2.4
11	0	0	0	1.2
12	0	0	0	1.4

Steady State No.	Input COD	Output COD		
	AST Inlet	COD Oxidised	WAS	Final Effluent
13	0	1	0	2.5
14	0	0	0	2.7
15	0	0	0	3.0
16	0	0	0	2.0
17	0	0	0	1.9
18	0	0	0	1.8
19	0	0	0	1.4
20	0	0	0	1.5
21	0	0	0	1.1
22	0	0	0	1.3
23	0	0	0	2.8
24	0	0	0	2.8
25	0	0	0	2.3
26	0	0	0	2.7
27	0	0	0	3.3
28	0	0	0	3.6
29	0	0	0	3.4
30	0	0	0	3.3
31	0	0	0	3.3
32	0	0	0	3.1

6.1.4.5. Nitrogen

Process variation values were calculated for the nitrogen mass balance results, which are presented in Table 139 below, with the process variation divided by nitrogen load for each steady state presented as a percentage average over all steady states.

Table 139: Nitrogen: mass balance results: calculated process variation (kg N/d)

Steady State No.	*Input Nitrogen*		*Output Nitrogen*			
	AST Inlet	***Urea***	***NO3 Denitrified***	***WAS***	***NO3 Final Effluent***	***TKN Final Effluent***
Average %	*0.07%*	*0.61%*	*0.19%*	*0%*	*0.05%*	*0.07%*
1	0.15	2.0	0	0	0	0
2	0.11	4.8	0.08	0	0.06	0
3	0.14	4.5	0.11	0	0.08	0
4	0.15	6.6	0.12	0	0.09	0
5	0.17	7.8	0.12	0	0.10	0.01
6	0.14	6.4	0.09	0	0.08	0.02
7	0.12	6.4	0.09	0	0.05	0
8	0.12	6.1	0.07	0	0.05	0
9	0.13	6.7	0.07	0	0.05	0.01
10	0.14	5.0	0.06	0	0.06	0
11	0.11	5.3	0.01	0	0.01	0.04
12	0.11	3.7	0.01	0	0.01	0
13	0.14	7.4	0.13	0	0.13	0
14	0.13	7.7	0	0	0	0
15	0.15	7.5	0	0	0	0
16	0.11	7.1	0	0	0	0
17	0.11	7.0	0	0	0	0.01
18	0.10	6.9	0	0	0	0.01
19	0.09	7.6	0	0	0	0.02
20	0.09	7.1	0.01	0	0	0.01
21	0.06	8.3	0	0	0	0.02
22	0.08	6.8	0	0	0	0.04
23	0.08	7.9	0	0	0	0
24	0.10	6.1	0	0	0	0.03
25	0.11	7.8	0	0	0	0
26	0.11	4.4	0.01	0	0	0.01
27	0.13	7.9	0.02	0	0	0.04

Steady State No.	***Input Nitrogen***		***Output Nitrogen***			
	AST Inlet	***Urea***	***NO3 Denitrified***	***WAS***	***NO3 Final Effluent***	***TKN Final Effluent***
Average %	*0.07%*	*0.61%*	*0.19%*	*0%*	*0.05%*	*0.07%*
28	0.13	8.7	0.01	0	0	0.03
29	0.12	7.7	0.01	0	0	0
30	0.11	7.3	0.01	0	0.01	0
31	0.11	7.3	0.01	0	0.01	0
32	0.12	6.7	0	0	0	0.01

6.1.5. Measurement Precision: Repeatability

A summary of repeatability testing for mill laboratory tests is presented in Table 140 below. Each parameter was tested 10 times on a single sample by the same person. Variation in experimental repeatability is expressed as the standard deviation as a percentage of the average value.

Table 140: Repeatability test results: internal laboratory tests (n = 10 for all tests)

Test Parameter	***Sample location***	***Average***	***Range***	***Std Dev (% Avg)***
COD: Total	Primary Clarifier Inlet	3,222	3,012 – 3,560	5.9
	Primary Clarifier Outlet	2,320	2,236 – 2,456	3.0
	Aeration Basin Outlet	3,240	2,964 – 3,404	4.1
	Final Effluent	107	88 – 138	12.4
	RAS	10,466	9,688 – 11,368	5.8
	WAS	36,884	34,472 – 38,440	3.7
COD: Filtered (1.0µm)	Primary Clarifier Inlet	2,061	1,638 -2,214	7.8
	Primary Clarifier Outlet	1,549	1,442 – 1,882	8.1
	Aeration Basin Outlet	91	84 – 95	3.8
	Final Effluent	77	68 – 87	7.4
	RAS	132	123 – 146	5.2
	WAS	271	253 – 300	5.6
TSS	Primary Clarifier Inlet	1,243	1,213 – 1,292	1.8
	Primary Clarifier Outlet	173	168 – 181	2.2
	Aeration Basin Outlet	2,036	1,966 – 2,089	2.0
	Final Effluent	15	10 – 18	13.4
	RAS	4,482	4,344 – 4,566	1.3
	WAS	13,249	13,116 – 13,513	0.9
VSS	Primary Clarifier Inlet	1,242	1,196 – 1,313	3.2

Test Parameter	***Sample location***	***Average***	***Range***	***Std Dev (% Avg)***
	Primary Clarifier Outlet	173	166 – 181	2.4
	Aeration Basin Outlet	2,036	1,981 – 2,102	2.3
	Final Effluent	15	10 – 17	12.4
	RAS	4,259	4,095 – 4,337	1.8
	WAS	12,369	12,251 – 12,605	0.9
OUR	Aeration Basin Outlet	17.8	14.5 – 20.3	12.0
SOUR*	Aeration Basin Outlet	7.87	6.39 – 8.99	12.0
PO4	Aeration Basin Outlet	1.5	1.3 – 1.6	6.7
	Final Effluent	0.71	0.67 – 0.73	2.3
SSV-30	Aeration Basin Outlet	412	380 - 460	5.7
Sludge dryness	Sludge press	24.4	23.9 – 25.2	1.8
	Primary sludge	49,548	48,444 – 52,076	2.3
Polymer concentration	Polymer tank	0.3311	0.3165 - 0.3440	2.9

*VSS used in calculation was a single value taken from lab results for the day, not repeated: the compounded variation in repeatability is not calculated

6.1.6. Measurement Redundancy

Measurement redundancy is used in this context to describe a parameter that was evaluated using two or more analytical. In this study, the only parameters where this information is available is the ammonia nitrogen and the ortho-phosphate in the final effluent for those steady states where the on-line instrumentation was installed.

From Figure 93 below, it is clear that there is little correlation between the on-line ammonia concentration and the laboratory measurement. In this case, the on-line measurements were used in the mass balances due to the fact that the laboratory method was impossible to repeat more than once per day due to electrode saturation, and therefore there was less confidence in the laboratory method. The on-line instrument also conducted calibration of the instrument against known standard concentrations on a regular basis and there was more confidence in these results.

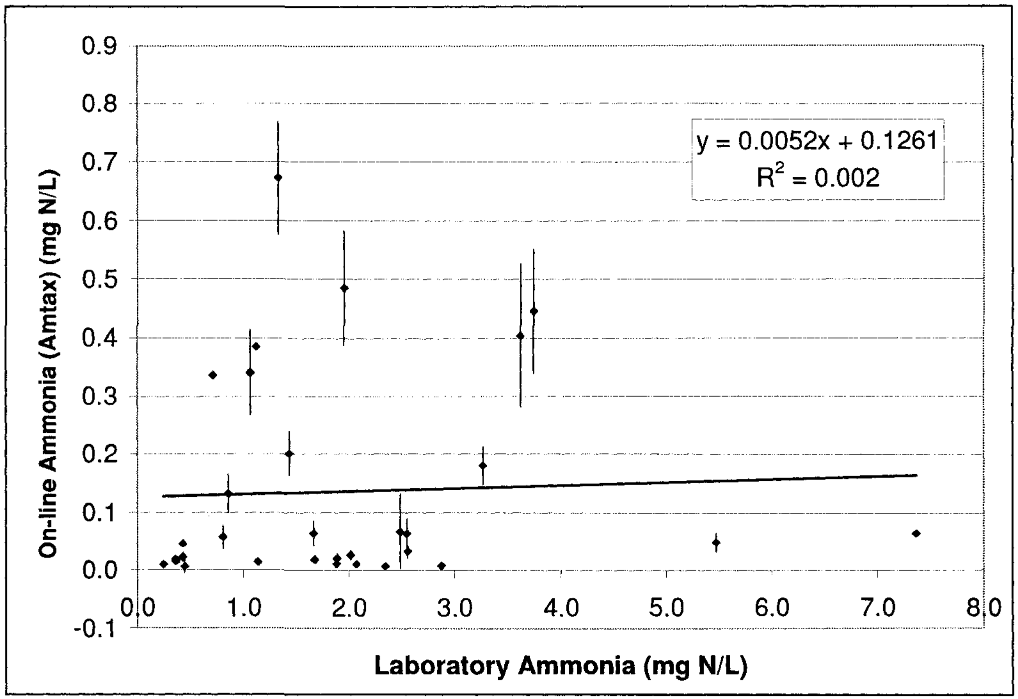

Figure 93: Measurement redundancy - final effluent ammonia (mg N/L)

In contrast, from Figure 94 below, it is clear that there is a statistically significant correlation between the ortho-phosphate measured in the laboratory and that measured on-line, for the steady state data used in the mass balances. Anecdotally, mill personnel have extended this correlation and use the correlation to verify the on-line results with the laboratory results.

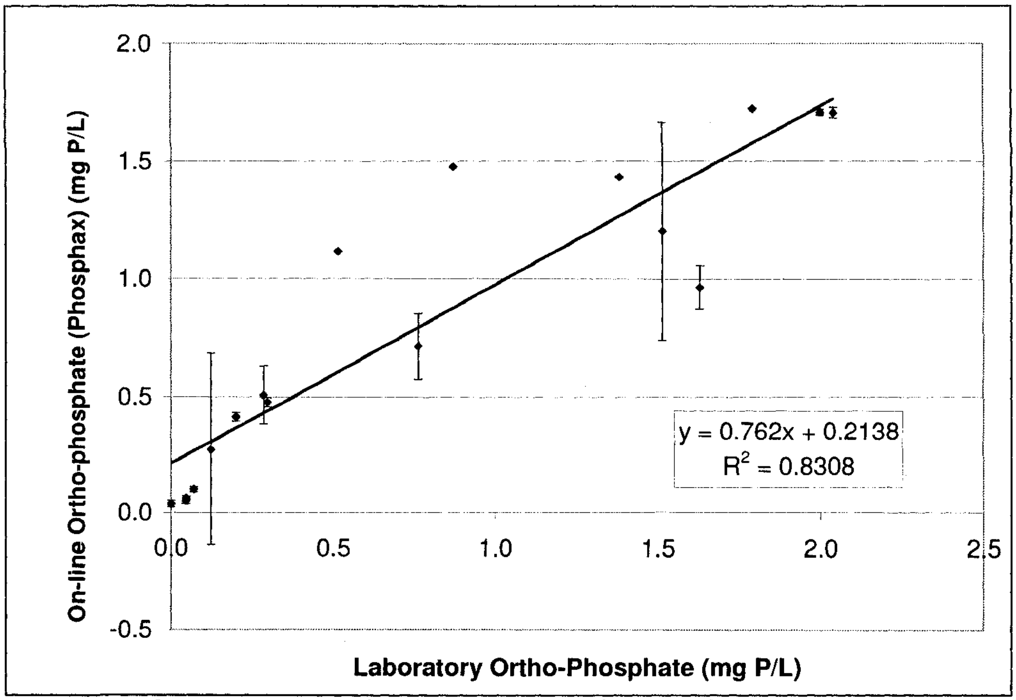

Figure 94: Measurement redundancy - final effluent ortho-phosphate (mg P/L)

6.1.7. Measurement Bias, Gross error (systematic error)

The bias of a measurement can only be assessed when the true value of a measurement is known, which was not the case for any of the experiments carried out in this study.

In two cases, it was determined that data from measured parameters was not reliable, namely the measured phosphoric acid dosing flow rate and the TSS measured at the outlet of the primary clarifier (two steady state case values for the latter). In both of these cases, a judgement was made on the confidence in each of the data sources, and the source thought to be more reliable was used. In both cases, the data that was thought to contain a systematic error was identified and not used in further calculations.

Possible sources of systematic error include the miscalibration or lack of calibration of flow meters and other on-line instruments. However, the instrumentation personnel at the site were vigilant and proactive with regards to instrument calibration, so this is not thought to be a major issue.

Another possible source of gross error in the flow rate calculations is the assumption that volume is a conserved quantity, which comes from the assumptions that water is incompressible, temperature is constant (therefore density is not changing) and zero evaporation occurs in the basins.

Apart from the cases discussed above, it is difficult to quantify systematic error in measurements used in this study.

APPENDIX 7
Sensitivity Analysis

7.1. *Sensitivity Analysis*

The sensitivity analysis was conducted on the pseudo-steady state case number two, as an example of process conditions including partial nitrification-denitrification in the AST selector and basin.

7.1.1. Base Case: Steady State #2

The target output parameters for the pseudo-steady state case number two are presented in this section. The calibrated model parameters are presented in the next section.

7.1.1.1. Output values

The output values and the relative error on the target output parameters for the base case are presented in Table 141. Bold values fall outside the set calibration criteria.

Table 141: Target output parameters: Base Case (Pre-Sensitivity Analysis)

Parameter	*Units*	*Calibrated Value*	*Relative error (%)*	*Calibration Criteria (Relative error)*
AST MLSS	mg TSS/L	2,410	2%	3 %
AST MLVSS	mg VSS/L	2,220	1%	3 %
WAS TSS	mg TSS/L	16,800	3%	25 %
RAS TSS	mg TSS/L	5,150	3%	7 %
AST Outlet NH4	mg N/L	0.172	**-10%**	4 %
AST Outlet NO3	mg N/L	1.780	**-12%**	3 %
AST Outlet PO4	mg P/L	0.73	**-41%**	9 %

7.1.2. Sensitivity Analysis Range

The following section presents the extent of the sensitivity analysis for the variation of single parameters. For each parameter identified, the sensitivity analysis was conducted from 50% to 150% of the default value (or base case value). This is considered to be a large enough range to identify the sensitivity of the parameter to change.

7.1.2.1. Activated sludge: aerated selectors & aerated basins

The stoichiometric and kinetic parameters varied for the analysis of the AST selectors and basins are listed in Table 106 below.

Table 142: AST Parameters, Calibrated Steady State #2 & Sensitivity Analysis Range

Parameter	***Symbol***	***Units***	***Calibrated value***	***Sensitivity Analysis Range***
Biomass nitrogen fraction	Inxb	mg N/mg COD	0.086	0.043 - 0.129
Cell decay products nitrogen fraction	Inxu	mg N/mg COD	0.06	0.03 - 0.09
Particulate inerts nitrogen fraction	Inxi	mg N/mg COD	0.03	0.015 - 0.045
Biomass phosphorus fraction	Ipxb	mg P/mg COD	0.016	0.008 - 0.024
Cell decay products phosphorus fraction	Ipxu	mg P/mg COD	0.015	0.0075 - 0.225
Particulate inerts phosphorus fraction	Ipxi	mg P/mg COD	0.0016	0.0008 - 0.0024
Heterotrophic maximum growth rate	μ_H	1/d	18	9 - 27
Autotrophic maximum growth rate	μ_A	1/d	**0.18**	0.09 - 0.27
Correction factor for anoxic growth of heterotrophs (denitrification)	η_g	-	**0.04**	0.02 - 0.06
Heterotrophic decay rate	b_H	1/d	0.5	0.25 - 0.75
Autotrophic decay rate	b_A	1/d	0.04	0.02 - 0.06
Yield of heterotrophic biomass growth	Y_H	g COD/ g SS	0.666	0.333 - 0.999
Yield of autotrophic biomass growth	Y_A	g COD/ g N	0.24	0.12 - 0.36
Half saturation constant for assimilation of carbon (heterotrophs)	K_{SH}	g COD /m^3	20	10 - 30
Phosphorus half saturation constant (heterotrophic)	K_{PH}	mg P/L	0.01	0.005 - 0.015

Parameter	***Symbol***	***Units***	***Calibrated value***	***Sensitivity Analysis Range***
Phosphorus half saturation constant (autotrophic)	K_{PA}	mg P/L	0.01	0.005 - 0.015
Half saturation constant for assimilation of nitrogen (heterotrophs)	K_{NH}	g COD $/m^3$	0.05	0.025 - 0.075
Half saturation constant for assimilation of nitrogen (autotrophs)	K_{NA}	g COD $/m^3$	1	0.5 - 1.5
Maximum specific hydrolysis rate	k_h	g COD /g cell COD.d	3	1.5 - 4.5
Hydrolysis half saturation constant	K_X	g COD /g cell COD	0.03	0.015 - 0.045
Specific ammonification rate	k_a	m^3/g COD. d	**0.1**	0.05 - 0.15
Specific phosphatification rate	k_p	m^3/g COD. d	**0.4**	0.2 - 0.6
Half saturation constant for oxygen (heterotrophs)	K_{OH}	g O_2 $/m^3$	0.2	0.1 - 0.3
Half saturation constant for oxygen (autotrophs)	K_{OA}	g O_2 $/m^3$	0.4	0.2 - 0.6

7.1.2.2. Physical parameters, influent parameters

The physical parameters and influent parameters varied for the analysis of the model are listed in Table 143 below. The sensitivity analysis range represents the accuracy of the instrument in the case of the measured parameters, or calculated uncertainty of the influent characteristics, as assessed in Appendix 6. The sensitivity analysis range for the carbonaceous fraction concentrations is from 50% to 150%, although the error calculated for each fraction is higher than this. The sensitivity analysis range for the fxii fraction represents the range of mixed liquor X_{II} concentration for all the steady state cases.

Table 143: Physical & influent parameters, Sensitivity Analysis Range

Parameter	***Units***	***Steady State Case Value***	***Sensitivity Analysis Range***
Temperature	ºC	31.6	30.8 – 32.4
Dissolved oxygen: selector	mg O_2/L	3.49	3.39 – 3.59
Dissolved oxygen: AST basin	mg O_2/L	0.99	0.89 – 1.09
Influent NH_4 concentration	mg N/L	36.2	35.1 – 37.3
Influent PO_4 concentration	mg P/L	8.34	6.7 – 9.9
Influent S_I concentration	mg COD/L	97	49 – 146
Influent S_S concentration	mg COD/L	1021	511 – 1532
Influent X_I concentration	mg COD/L	450	225 – 675
Influent X_S concentration	mg COD/L	500	250 – 750
fxii fraction	mg COD/mg COD	0.208	0.14 – 0.30

7.1.3. Sensitivity Analysis Results

The following section presents the results of the sensitivity analysis in terms of the variation in the output parameters: the mixed liquor suspended solids and the AST outlet nutrient concentrations. In the case where the model demonstrated significant departures from reality (near zero biomass growth, for example), the range of the sensitivity analysis was limited, as indicated in the tables below. Variation of a single parameter was the only variation considered, although it is known that certain parameters would vary together or inversely, such as the nutrient content of the biomass fractions and that of the cell decay products.

7.1.3.1. Activated sludge: aerated selectors & aerated basins

The stoichiometric and kinetic parameters varied for the analysis of the AST selectors and basins are listed in Table 144 below. Bold values fall outside of the 50 to 100% response range.

Table 144: Kinetic & Stoichiometric Parameters, Sensitivity Analysis Results

Parameter	***Symbol***	***Units***	***% of parameter***	***% of MLSS***	***% of final effluent NH4***	***% of final effluent NO3***	***% of final effluent PO4***
Biomass nitrogen fraction	inxb	mg N/mg COD	50% to 150%	100 – 97%	100 – **5%**	**409** – 0%	98 – 135%
Cell decay products nitrogen fraction	inxu	mg N/mg COD	50% to 150%	100%	100 – 109%	**247** – **16%**	99 – 101%
Particulate inerts nitrogen fraction	inxi	mg N/mg COD	50% to 150%	100%	100 – 99%	101 – 100%	100%
Biomass phosphorus fraction	ipxb	mg P/mg COD	50% to 150%	100 – 96%	97 – **3806%**	101 – **0%**	260 – 0%
Cell decay products phosphorus fraction	ipxu	mg P/mg COD	50% to 150%	100 – 99%	98 – **3130%**	100 – **0%**	216 – 0%
Particulate inerts phosphorus fraction	ipxi	mg P/mg COD	50% to 150%	100%	99 – 100%	100 – 101%	100%
Heterotrophic maximum growth rate	μ_H	1/d	50% to 150%	100 %	92 – 103%	103 – 99%	102 – 100%
Autotrophic maximum growth rate	μ_A	1/d	50% to 150%	100%	**2874** – **39%**	**0** – 104%	101 – 100%
Correction factor for anoxic growth of	η_g	-	50% to 150%	100%	101 – 102%	**169** – 60%	100%

Parameter	***Symbol***	***Units***	***% of parameter***	***% of MLSS***	***% of final effluent NH4***	***% of final effluent NO3***	***% of final effluent PO4***
heterotrophs (denitrification)							
Heterotrophic decay rate	b_H	1/d	50% to 150%	111 – 93%	**386** – 98%	0 – **199**%	0 – **165**%
Autotrophic decay rate	b_A	1/d	50% to 150%	100%	76 – 140%	101 – 98%	100%
Yield of heterotrophic biomass growth	Y_H	g COD/ g SS	50% to **114%**	66 – 109%	80 – **828**%	**812** – 0%	**472** – 0%
Yield of autotrophic biomass growth	Y_A	g COD/ g N	50% to 150%	100%	102 – 103%	101 – 97%	101 – 99%
Half saturation constant for assimilation of carbon (heterotrophs)	K_{SH}	g COD /m^3	50% to 150%	100%	105 – 102%	98 – 100%	99 – 100%
Phosphorus half saturation constant (heterotrophic)	K_{PH}	mg P/L	50% to 150%	100%	101 – 103%	100 – 99%	100%
Phosphorus half saturation constant (autotrophic)	K_{PA}	mg P/L	50% to 150%	100%	98 – 106%	100%	100%
Half saturation constant for assimilation of nitrogen (heterotrophs)	K_{NH}	g COD /m^3	50% to 150%	100%	105 – 100%	100%	100%
Half saturation constant for assimilation of nitrogen (autotrophs)	K_{NA}	g COD /m^3	50% to 150%	100%	**49** – **156**%	103 – 96%	100%
Maximum specific	k_h	g COD /g	50% to 150%	101 –	100 – 103%	84 – 103%	89 – 102%

Parameter	*Symbol*	*Units*	*% of parameter*	*% of MLSS*	*% of final effluent NH4*	*% of final effluent NO3*	*% of final effluent PO4*
hydrolysis rate		cell COD.d		100%			
Hydrolysis half saturation constant	K_X	g COD /g cell COD	50% to 150%	100%	102 – 104%	104 – 95%	103 – 97%
Specific ammonification rate	k_a	m^3/g COD. d	50% to 150%	100%	103 – 102%	76 – 108%	100%
Specific phosphatification rate	k_p	m^3/g COD. d	50% to 150%	100%	103 – 106%	100 – 99%	94 – 102%
Half saturation constant for oxygen (heterotrophs)	K_{OH}	g O_2 /m^3	50% to 150%	100%	105 – 103%	170 – 59%	100 – 99%
Half saturation constant for oxygen (autotrophs)	K_{OA}	g O_2 /m^3	50% to 150%	100%	57 – **218**%	103 – 92%	100%

7.1.3.2. *Physical parameters, influent parameters*

The nutrient fractions varied for the analysis of the model are listed in Table 145 below. Bold values fall outside of the expected response range.

Table 145: Physical & influent parameters, Sensitivity Analysis Results

Parameter	*Units*	*% of parameter*	*% of MLSS*	*% of AST outlet NH4*	*% of AST outlet NO3*	*% of AST outlet PO4*
Temperature	ºC	97% to 103%	102 - 98%	**124 - 83%**	**79 - 120%**	**83 - 117%**
Dissolved oxygen: selector	mg O_2/L	97% to 103%	100%	98 - 99%	101 - 101%	100%
Dissolved oxygen: AST basin	mg O_2/L	90% to 110%	100%	**115 - 89%**	**88 - 112%**	100%

Parameter	***Units***	***% of parameter***	***% of MLSS***	***% of AST outlet NH4***	***% of AST outlet NO3***	***% of AST outlet PO4***
Influent NH_4 concentration	mg N/L	97% to 103%	100%	99 - 101%	**74 - 129**%	100%
Influent PO_4 concentration	mg P/L	80% to 119%	100%	**122** - 98%	**125** - 101%	**25 - 175**%
Influent S_I concentration	mg COD/L	50% to 150%	100%	101 - 101%	100%	100%
Influent S_S concentration	mg COD/L	50% to 150%	83 - 109%	92 - **830**%	**485 - 0**%	**281 – 0**%
Influent X_I concentration	mg COD/L	50% to 150%	75 - 125%	102 - 100%	100%	100 - 101%
Influent X_S concentration	mg COD/L	50% to 150%	92 - 108%	96 - **1038**%	274 - 0%	**189 – 11**%
fxii fraction	mg COD/mg COD	67% to 144%	97 - 103%	99 - 99%	101 - 100%	100%

7.1.4. Discussion

The most sensitive kinetic and stoichiometric parameters were determined to be:

- Biomass and cell decay nutrient fractions;
- Autotrophic maximum growth rate;
- Correction factor for anoxic growth of heterotrophs;
- Heterotrophic decay rate;
- Heterotrophic yield;
- Half saturation constant for assimilation of nitrogen (autotrophs); and
- Half saturation constant for oxygen (autotrophs).

The most sensitive physical and influent parameters were determined to be:

- Temperature;
- Dissolved oxygen (AST basin);
- Influent nutrient concentrations; and
- Influent biodegradable COD concentrations (S_S and X_S).

There is no experimental evidence to support modification of kinetic and stoichiometric parameters, this should form part of future work for pulp and paper wastewater modelling.

APPENDIX 8
Equivalent modelling nomenclature

8.1. *Equivalent modelling nomenclature*

A number of different systems of nomenclature exist in the modelling literature, depending on different models developed by different universities or research groups and varying with the evolution of modelling in general. These were investigated and compared by Yves Comeau [274], a summary of which is presented in this appendix as Table 146.

8.1.1. Nomenclature summary

Table 146: Summary of equivalent modelling nomenclature [274]

Group	Units	Reference of model:	This study	Henze et al., 1987	Henze et al., 1999	Rieger et al., 2001	EnviroSim 2007	Hu et al., 2007	de Kreuk, 2006	Batstone et al., 2002
		Description	*ASMPP*	*ASM1*	*ASM2d*	*ASM3-P*	*Gen ASDM*	*UCTPHO+*	*PAO-Delft*	*ADM1*
Organic matter										
sCOD	mg COD/L	Readily biodegradable organic matter	S_S	S_S		S_S				
	mg COD/L	Fermentable organic matter			S_F		S_{BSC}	S_F		
	mg COD/L	Volatile fatty acids			S_A			S_A	S_{AC}	
	mg COD/L	Propionate					S_{BSP}			S_{pro}
	mg COD/L	Acetate					S_{BSA}			S_{ac}
	mg COD/L	Methanol					S_{BMETH}			
	mg COD/L	Dissolved hydrogen					S_{BH2}			S_{h2}
	mg COD/L	Dissolved methane					S_{CH4}			S_{ch4}

Group	Units	Reference of model:	This study	Henze et al., 1987	Henze et al., 1999	Rieger et al., 2001	EnviroSim 2007	Hu et al., 2007	de Kreuk, 2006	Batstone et al., 2002
		Description	**ASMP P**	**ASM 1**	**ASM2 d**	**ASM3-P**	**Gen ASDM**	**UCT PHO +**	**PAO-Delft**	**ADM1**
	mg COD/L	Soluble inert organic matter	S_I	S_I	S_I	S_I	S_{US}	S_I		S_I
	mg COD/L	Soluble inert endogenous organic matter								
O_2	mg O2/L	Dissolved oxygen	S_O	S_O	S_{O2}	S_{O2}	DO	S_{O2}		
xCOD	mg COD/L	Slowly biodegradable colloidal organic matter					X_{SC}			
	mg COD/L	Slowly biodegradable particulate (non colloidal) organic matter					X_{SP}			
	mg COD/L	Slowly biodegradable organic matter	X_S	X_S	X_S	X_S				
	mg COD/L	Influent XS instantaneously enmeshed onto						X_{ENM}		

Group	*Units*	*Reference of model:*	*This study*	*Henze et al., 1987*	*Henze et al., 1999*	*Rieger et al., 2001*	*EnviroSim 2007*	*Hu et al., 2007*	*de Kreuk, 2006*	*Batstone et al., 2002*
		Description	*ASMPP*	*ASM1*	*ASM2d*	*ASM3-P*	*Gen ASDM*	*UCTPHO+*	*PAO-Delft*	*ADM1*
		biomass								
	mg COD/L	XENM adsorbed or produced from biomass decay						X_{ADS}		
	mg COD/L	General storage compound				X_{STO}				
	mg COD/L	Stored PHA			X_{PHA}		S_{PHB}	X_{PHA}	X_{PHB}	
	mg COD/L	Stored glycogen							X_{GLY}	
	mg COD/L	Particulate inert endogenous organic matter	X_U	X_P			Z_E	X_E		
	mg COD/L	Particulate inert organic matter	X_I	X_I	X_I	X_I	X_I	X_I	X_I	X_I
Nitrogen (N)										
	mg N/L	Particulate biodegradable organic N	X_{ND}	X_{ND}			X_{ON}			
	mg N/L	Soluble biodegradable	S_{ND}	S_{ND}			N_{OS}			

Group	Units	Reference of model:	This study	Henze et al., 1987	Henze et al., 1999	Rieger et al., 2001	EnviroSim 2007	Hu et al., 2007	de Kreuk, 2006	Batstone et al., 2002
		Description	ASMPP	ASM1	ASM2d	ASM3-P	Gen ASDM	UCTPHO+	PAO-Delft	ADM1
		organic N								
	mg N/L	Particulate inert organic N					X_{IN}			
	mg N/L	Soluble inert organic N					N_{US}			
	mg N/L	Total ammonia	S_{NH}	S_{NH}	S_{NH4}	S_{NH4}	S_{NH3}	S_{NH4}	S_{NH4}	
	mg N/L	Total nitrite + nitrate	S_{NO}	S_{NO}	S_{NO3}	S_{NOX}		S_{NO3}		
	mg N/L	Total nitrite					S_{NO2}		S_{NO2}	
	mg N/L	Total nitrate					S_{NO3}		S_{NO3}	
	mg N/L	Nitrogen gas	S_{NN}		S_{N2}	S_{N2}	S_{N2}		S_{N2}	
Phosphorus (P)										
	mg P/L	Inorganic soluble phosphorus (o-PO4 test)	S_P		S_{PO4}			S_{PO4}	S_{PO4}	
	mg P/L	Total phosphate (soluble-P + metal-P)					cPO_4			
	mg P/L	P content of partic. biodegr. organic matter					X_{OP}			

Grou p	**Units**	***Reference of model:***	***This study***	***Henze et al., 1987***	***Henze et al., 1999***	***Rieger et al., 2001***	***EnviroSim 2007***	***Hu et al., 2007***	***de Kreuk, 2006***	***Batstone et al., 2002***
		Description	***ASMP P***	***ASM 1***	***ASM2 d***	***ASM3-P***	***Gen ASDM***	***UCT PHO +***	***PAO-Delft***	***ADM1***
	mg P/L	P content of particulate inert organic matter					X_{IP}			
	mg P/L	Stored polyphosphates			X_{PP}			X_{PP}	X_{PP}	
	mg P/L	Releasable stored polyphosphates					PP_{LO}			
	mg P/L	Non releasable stored polyphosphates					PP_{HI}			
	mg P/L	Particulate biodegradable organic P	X_{PD}							
	mg P/L	Soluble biodegradable organic P	S_{PD}							
Biomass										
	mg COD/L	Ordinary heterotrophic organisms	X_{BH}	$X_{B,H}$	X_{HET}	X_{H}	Z_{BH}	X_{H}	X_{HET}	
	mg	Methylotrophic					Z_{BMETH}			

Group	Units	Reference of model:	This study	Henze et al., 1987	Henze et al., 1999	Rieger et al., 2001	EnviroSim 2007	Hu et al., 2007	de Kreuk, 2006	Batstone et al., 2002
		Description	ASMP P	ASM 1	ASM2 d	ASM3-P	Gen ASDM	UCT PHO +	PAO-Delft	ADM1
	COD/L	organisms								
	mg COD/L	Nitrifying organisms (NH4 to NO3)	X_{BA}	$X_{B,A}$	X_{AUT}	X_A		X_{NIT}		
	mg COD/L	Ammonia oxidizing organisms					Z_{BA}		X_{NH}	
	mg COD/L	Nitrite oxidizing organisms					Z_{BN}		X_{NO}	
	mg COD/L	Anammox organisms					Z_{BAMO}			
	mg COD/L	Phosphorus accumulating organisms			X_{PAO}		Z_{BP}	X_{PAO}	X_{PAO}	
	mg COD/L	Propionic acetogens					Z_{BPA}			X_{pro}
	mg COD/L	Acetoclastic methanogens					Z_{BAM}			X_{ac}
	mg COD/L	Hydrogenotrophic methanogens					Z_{BHM}			X_{h2}
Inorganics										
	mg	Particulate inert	X_{II}							

Group	Units	Reference of model:	This study	Henze et al., 1987	Henze et al., 1999	Rieger et al., 2001	EnviroSim 2007	Hu et al., 2007	de Kreuk, 2006	Batstone et al., 2002
		Description	**ASMP P**	**ASM 1**	**ASM2 d**	**ASM3-P**	**Gen ASDM**	**UCT PHO +**	**PAO-Delft**	**ADM1**
	COD/L	inorganic matter								
	mg TSS/L	Inorganic (fixed) suspended solids					ISS			
	mg Ca/L	Soluble calcium					S_{CA}			
	mg Mg/L	Soluble magnesium					Mg			
	mg ME/L	Metals (Al - Fe)					C_{ME}			
	mg TSS/L	Metal hydroxides			X_{MEOH}					
	mg TSS/L	Metal phosphate compounds			X_{MEP}					
	mg TSS/L	Hydroxy dicalcium phosphate (CaHPO4(OH)2)					X_{HDP}			
	mg TSS/L	Hydroxyapatite (Ca5(PO4)3OH)					X_{HAP}			
	mg TSS/L	Struvite (magnesium ammonium					X_{STRU}			

Group	Units	Reference of model:	This study	Henze et al., 1987	Henze et al., 1999	Rieger et al., 2001	EnviroSim 2007	Hu et al., 2007	de Kreuk, 2006	Batstone et al., 2002
		Description	**ASMPP**	**ASM1**	**ASM2d**	**ASM3-P**	**Gen ASDM**	**UCTPHO+**	**PAO-Delft**	**ADM1**
		phosphate)								
	mg TSS/L	Polyphosphate bound cations					X_{PPCat}			
	mg CaCO3/L	Alkalinity	S_{ALK}	S_{ALK}	S_{ALK}	S_{ALK}				
	mmol C/L	Total inorganic carbon					S_{CO2t}			
	meq/L	Other cations					S_{CAT}			S_{cat}
	meq/L	Other anions					S_{AN}			S_{an}
Other										
Water	mg H2O/L	Water					S_{H2O}			
TSS	mg TSS/L	Total suspended solids			X_{TSS}	X_{SS}				

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