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POLYTECHNIQUE MONTRÉAL

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BALLASTED FLOCCULATION FOR THE REMOVAL OF TRACE PETROLEUM HYDROCARBONS FROM SURFACE WATER

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Thèse présentée en vue de l’obtention du diplôme de *Philosophiae Doctor*

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Cette thèse intitulée :

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Présentée par **Oluchi OKORO**

en vue de l’obtention du diplôme de *Philosophie Doctor*

a été dûment acceptée par le jury d’examen constitué de :

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DEDICATION

To my dad, Sunday Okoro

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RÉSUMÉ

Les déversements des produits pétroliers à proximité des eaux de surface représentent des enjeux vitaux. Une fuite ou un bris d'un oléoduc situé à proximité de ces eaux peut causer le déversement de divers composés toxiques et/ou cancérogènes tel que le benzène. Selon les études de cas récentes, ces composés arriveraient aux usines de traitement d'eau potable (UTEP) à des concentrations *traces*. Si les dispersants sont utilisés pour mitiger les effets des déversements, d'autres composés seront introduits dans les eaux de surface. Afin d'assurer la distribution d'une eau de bonne qualité, celle-ci subit un long processus de purification et de contrôle qualité. En effet, les UTEP rendent l'eau potable encore plus sécuritaire par l'implémentation des meilleures pratiques. La plupart des UTEP ont leurs prises d'eau brute dans les eaux de surface et elles utilisent un procédé physicochimique comme barrière principale contre une contamination par les hydrocarbures pétroliers. Ce projet a évalué l'efficacité de la floculation lestée (ou Actiflo®) pour l'abattement des concentrations *traces* d'hydrocarbures pétroliers.

En premier lieu, il était important d'étudier l'abattement de concentrations *traces* **dissoutes** d'hydrocarbures pétroliers, à savoir le benzène, le toluène, l'ethylbenzène, et les xylènes (BTEX). En raison de leurs teneurs importantes en BTEX, le diesel et l'essence ont été utilisés pour simuler un déversement dans les eaux de surface. Les solutions mères de la partie filtrée et dissoute de diesel et d'essence ont été ajoutées dans l'eau et agitées pendant 24 h. Les tests de floculation lestée ont été ensuite réalisés en utilisant l'alun et le sulfate ferrique comme coagulants. Pour chaque essai, un suivi des paramètres physicochimiques tels que la turbidité, le carbone organique dissous (COD), l'absorbance UV à 254 nm (UVA_{254}), la tension superficielle, et le potentiel zêta ainsi que la concentration de BTEX a été effectué. Selon les résultats obtenus, la floculation lestée seule ne permet pas de réduire la concentration de benzène en bas de 0,5 µg/L (la norme en eau potable au Québec). Par conséquent, l'ajout d'un adsorbant, le charbon actif en poudre (CAP), a été testé par des essais d'adsorption et de cinétiques pour l'abattement de benzène. La dose optimale de CAP (80 mg CAP/L) a été appliquée simultanément avec le coagulant pour simuler le pire scénario de traitement. Bien que la concentration de benzène soit réduite significativement, la présence de coagulant a diminué l'efficacité de CAP en raison de colmatage de ses pores.

Dans un second temps, il était important de comprendre l'impact de dispersant sur l'efficacité de la floculation lestée. Afin d'atteindre cet objectif, il a été primordial d'analyser la qualité de l'eau, l'enlèvement des gouttes stabilisées, et la réduction de la concentration d'hydrocarbures pétroliers mesurée en carbone organique total (COT) et de dispersant résiduel en dioctyl sulfosuccinate de sodium (DOSS). Dans les eaux de surface, une concentration de pétrole brut dispersé par un dispersant commercial, Finasol® OSR 52 (Total Fluides), a été traitée par la floculation lestée en utilisant l'alun et le sulfate ferrique. Le même procédé a été effectué pour l'eau contaminée par du pétrole brut seul. Les résultats ont démontré que le COT, mesuré à l'eau brute, était sensible à de telles faibles contaminations et que suite à un traitement à l'alun, l'eau décantée a atteint les critères de traitement (turbidité < 1 UTN) avec un potentiel zêta ≈ 0 mV. Néanmoins, l'ajout de dispersant a introduit des polluants organiques qui étaient difficiles à enlever par la floculation lestée.

En dernier lieu, des essais ont été effectués pour comprendre la contribution des caractéristiques et de la concentration de dispersant à la contamination des eaux de surface. Un dispersant formulé, composé de Tween 80 (20 %) et de dodecyl sulfate de sodium (SDS, 80 %), a été préparé afin de simuler la diminution en tension superficielle qu'un dispersant commercial, Finasol® OSR 52, pourrait engendrer. Une comparaison a été faite des impacts de l'ajout des deux types de dispersant sur la contamination et le traitement des eaux de surface. En présence de pétrole brut dans les eaux de surface, l'ajout d'une faible et d'une haute concentration de dispersant a été également étudiée pour surligner l'impact de micelles sur la contamination et l'efficacité du traitement. En se basant sur les résultats obtenus, les tensioactifs ne sont pas les seuls composés qui accentuent les effets de la contamination. Peu importe le type et la concentration, les dispersants ont introduit des tensioactifs qui n'étaient pas auparavant présents dans les eaux de surface et qui ne pouvaient pas être éliminés par la floculation lestée. En présence de pétrole brut et de micelles, un impact plus négatif sur la qualité de l'eau et sa capacité d'être traitée a été observé.

Cette étude a démontré l'efficacité de la floculation lestée pour l'enlèvement d'hydrocarbures *traces* dans les eaux de surface. La floculation lestée seule n'est pas suffisante pour diminuer la concentration de *traces* dissoutes de BTEX et de tensioactifs résiduel (provenant de dispersants). Les résultats seront utiles aux UTEP dans leurs efforts de mettre à jour leurs plans d'urgence, leurs filières de traitement, et leurs paramètres de suivi afin de pourvoir gérer un déversement dans les eaux de surface toute en assurant la qualité de l’eau.

ABSTRACT

Oil spills are likely to occur in regions where oil pipelines are present in close proximity to surface waterbodies. Based on recent case studies, such a spill will introduce toxic and carcinogenic compounds such as benzene that would arrive at drinking water treatment plants (DWTP) at *trace* concentrations. If oil-spill dispersants are applied as a remediation measure, other dispersant-related compounds with unknown impacts on drinking water quality will also be introduced. Many DWTP in Quebec utilize surface water for potable water generation and employ a physicochemical treatment technology (Actiflo® or Pulsators®), which will serve as the first barrier against petroleum hydrocarbon contamination. This study evaluated ballasted flocculation (or Actiflo®) for its efficiency to remove *trace* petroleum hydrocarbons from surface water.

First, the efficiency of ballasted flocculation for the removal of *trace* **dissolved** petroleum hydrocarbons (benzene, toluene, ethylbenzene, and xylenes (BTEX)) was investigated. Due to their relatively high BTEX content, diesel and gasoline were employed to simulate a spill in surface water. Stock solutions of the filtered and dissolved portions of diesel and gasoline were introduced in surface water and agitated for 24 hours. Laboratory ballasted flocculation tests were then carried out using alum and ferric sulfate as coagulants. For each test, water quality parameters – turbidity, dissolved organic carbon (DOC), UVA_{254}, surface tension, zeta potential – and BTEX concentrations were monitored. Results showed that ballasted flocculation <u>alone</u> was not effective to reduce benzene concentrations below 0.5 µg/L (Quebec threshold in drinking water). As a result, the addition of an adsorbent, powdered activated carbon (PAC), was evaluated for benzene reduction through adsorption isotherm and kinetics studies. The optimized PAC dose (80 mg PAC/L) was then utilized to simulate a worst-case treatment scenario, that is, ballasted flocculation involving simultaneous injection of PAC and coagulant. Results showed that although benzene concentration reduced appreciably, the presence of a coagulant limited PAC adsorption efficiency through possible pore blockage.

Second, dispersant application on an oil spill in surface water was studied in order to understand its impact on ballasted flocculation efficiency for potable water production. In addition to water quality, the removal of dispersant-stabilized oil droplets, petroleum hydrocarbons measured as

total organic carbon (TOC), and residual dispersant concentration measured as sodium dioctyl sulfosuccinate (DOSS) served as the basis of the analysis. Oil in surface water dispersed by a commercial oil-spill dispersant, Finasol® OSR 52 (Total Fluides), was evaluated and subsequently treated by ballasted flocculation with alum and ferric sulfate. The same was done for crude oil only-contaminated surface water. Results showed that for both types of contamination, TOC (measured in raw water) was a good indicator of contamination and ballasted flocculation with alum generated settled water that met treatment objectives. However, dispersant application introduced organic contaminants that were difficult to remove by ballasted flocculation.

Lastly, the influence of dispersant matrix characteristics and its concentration on surface water contamination and treatment was studied. A formulated dispersant, comprised of Tween 80 (20 %) and sodium dodecyl sulfate (SDS, 80 %), was prepared to mimic the reduction in interfacial tension that a commercial dispersant, Finasol® OSR 52, would cause. The application of both the formulated and commercial dispersants to surface water and the subsequent settled water quality following ballasted flocculation were compared. In the presence of crude oil, low and high concentrations of the formulated dispersant were applied to highlight the impact of surfactant micelles on crude oil contamination and treatability. Results showed that surfactants alone are not the only driving factors to contamination and regardless of the type and concentration, dispersants introduced surfactants that were otherwise not present in surface water and whose removal was unachievable by ballasted flocculation. When crude oil and micelles were present, a more negative synergistic effect on water quality and treatability was observed.

Overall, this study demonstrated the efficiency of ballasted flocculation for *trace* petroleum hydrocarbon removal from surface water. It has been shown that ballasted flocculation alone is not sufficient to reduce *trace* dissolved BTEX and residual surfactant concentrations (stemming from oil-spill dispersants). Findings in this study will be beneficial to DWTP in their efforts to evaluate and upgrade their treatment chain and prepare adequate oil-spill contingency plans.

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LIST OF SYMBOLS AND ABBREVIATIONS

API	American Petroleum Institute
ARE	Average Relative Error
AWWA	American Water Works Association
BaP	Benzo(a)pyrene
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CF-DAF	Coagulation Flocculation-Dissolved Air Flotation
CMC	Critical Micelle Concentration
CO	Crude Oil
DAF	Dissolved Air Flotation
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOSS	Sodium Docusate, bis(2-ethylhexyl) sodium sulfosuccinate, or sodium dioctyl sulfosuccinate
DWTP	Drinking Water Treatment Plant
FDA	Food and Drug Administration
GC-FID	Gas Chromatography-Flame Ionization Detection
GC-MS	Gas Chromatography-Mass Spectrometer
HLB	Hydrophilic-Lipophilic Balance
HSDM	Homogenous Surface Diffusion Model
LOD	Limit of Detection
Log K_{ow}	Octanol-Water Coefficient
LOQ	Limit of Quantification

MAC	Maximum Acceptable Concentration
OPA	Oil-Particle Aggregate
PAC	Powdered Activated Carbon
PAH	Polynuclear Aromatic Hydrocarbon
PHC	Petroleum Hydrocarbons
RW	Raw Water
RW + CO	Raw Water contaminated with Crude Oil
RW + CO + F	Raw Water contaminated with Crude Oil and Finasol OSR 52
RW + CO + M	Raw Water contaminated with Crude Oil and Surfactant Micelles
SBSE	Stir Bar Sorptive Extraction
SDS	Sodium Dodecyl Sulfate
TOC	Total Organic Carbon
TKN	Total Kjeldahl Nitrogen
TPH	Total Petroleum Hydrocarbon
UHPLC-MS/MS	Ultra-High Performance Liquid Chromatography Tandem Mass Spectrometry
U.S. EPA	United States Environmental Protection Agency
UV_{254}	Ultraviolet Absorbance at 254 nm

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CHAPTER 1 INTRODUCTION

In North America, over the past two decades, rail and pipeline transportation of crude oil and refined petroleum products such as gasoline and diesel have increased due to advancements in oil exploration and production (Canada Energy Regulator - CER, 2020; U.S. Energy Information Administration, 2020). In the region of Montreal, Québec, there are three major and active pipelines – Trans-Northern, St-Laurent, and Enbridge Line 9B – that cross four principal sources of potable water, which are Des Prairies River, Mille-Îles River, St. Lawrence River, and Outaouais River. The presence of these pipelines and rail tracks near surface water however poses a risk of contamination in the event of train derailment or pipeline damage. The Lac-Mégantic accident in 2013 resulted from train derailment and led to the loss of about 6000 m^3 of crude oil to the environment, of which 100 m^3 contaminated the Chaudière River, which serves three drinking water treatment plants (DWTP) in the surrounding region (Galvez-Cloutier, Guesdon, & Fonchain, 2014).

Contamination of surface water due to an oil spill introduces toxic aromatic compounds whose concentrations in drinking water sources are limited by strict thresholds. Of these compounds, benzene, toluene, ethylbenzene and xylenes (BTEX) are the most soluble, volatile and toxic, with benzene known to be carcinogenic (C. Yang et al., 2017). Benzo(a)pyrene, a polynuclear aromatic hydrocarbon (PAH), is another toxic and carcinogenic compound that can also be introduced in surface water from an oil spill (C. Yang et al., 2017). In the US, according to regulations set by the Environmental Protection Agency (EPA), benzene and benzo(a)pyrene concentrations in drinking water must be below 5 µg/L and 0.2 µg/L, respectively (United States Environmental Protection Agency (USEPA), 2011). In Québec, threshold concentrations in drinking water are set at 0.5 µg/L and 0.01 µg/L for benzene and benzo(a)pyrene, respectively (Gouvernement du Québec, 2020). Although not regulated in drinking water, $C_{10} – C_{50}$ is another parameter that is also measured to quantify petroleum hydrocarbon content in water. Case studies of recent oil-spill events show that *trace* concentrations of these contaminants, measured at the drinking water intakes, were still higher than the required threshold limits. For example, after the Lac-Mégantic accident, benzene and C_{10}-C_{50} concentrations in the Chaudière River were quantified as 17 µg/L and 12 mg/L (average), respectively (Barrette, Dorner, & Prévost, 2017; Galvez-Cloutier et al., 2014).

Depending on the type of remediation technique employed, additional contaminants that adversely impact aquatic life might be introduced into surface water. While booms and other mechanical remediation techniques can be applied to contain a spill in surface water, dispersants are also likely to be employed. In offshore waters, dispersant application is more common; however, several studies have pointed to the need to investigate the impact of dispersant use on inland freshwater, especially on drinking water intakes (Bhattacharyya, Klerks, & Nyman, 2003a; Flaherty, 1989; Green & Trett, 1989; Herndon, 2010; Owens & Michel, 1995; Owens, Taylor, Marty, & Little, 1993; Wrenn, Virkus, Mukherjee, & Venosa, 2009). These studies evaluated dispersant effectiveness and toxicity to aquatic plant and animal life in freshwater as well as offered recommendations for dispersant application in inland freshwater. However, the effects of dispersant use and the presence of dispersant-stabilized oil droplets on DWTP efficiency and potable water generation were not investigated.

Following an oil spill in surface water, the most pertinent question for a DWTP will be whether its first barrier, that is, the physicochemical treatment chain, can eliminate soluble contaminants such as BTEX, dispersant-stabilized oil droplets, and other dispersant-related contaminants. In Québec, either Actiflo® (ballasted flocculation) or Pulsators® (coagulation-flocculation with sludge blanket) is employed for conventional physicochemical treatment of surface water in many DWTP. To generate the required settled water quality, the Actiflo® technology involves the addition of microsand (ballasting agent) during the coagulation process to increase floc density and reduce the time required for flocculation and settling (E Guibelin, F Delsalle, & P Binot, 1994).

Coagulation-flocculation has been applied for the removal of petroleum hydrocarbons, including BTEX, from surface water (Tansel & Dimitric-Clark, 2002; Tansel & Vilar, 2005), produced water (Luthy, Selleck, & Galloway, 1978; Pourrezaei et al., 2011; Rosenblum, Sitterley, Thurman, Ferrer, & Linden, 2016; Zhai et al., 2017; Zhang, 2017), oil refinery wastewater (Moursy & El-Ela, 1982; Santo et al., 2012; Wang, Shui, Ren, & He, 2017), and other types of wastewater (Campo, Giustra, De Marchis, Freni, & Di Bella, 2017; Mancini et al., 2017; Ribera-

Pi et al., 2020; Shouli, Bewtra, & Biswas, 1992; Tansel & Eifert, 1999; Tansel & Sevimoglu, 2006; J. Y. Yang, Yan, Li, & Xu, 2016; You, Xu, Sun, Zhang, & Zhang, 2018; Jessica M Younker & Walsh, 2016). It has also been employed for the removal of emulsified oil droplets in oil-in-water (O-W) emulsions that contain surfactants, which are the active ingredients in dispersants (Al-Shamrani, James, & Xiao, 2002; Canizares, Martínez, Jiménez, Sáez, & Rodrigo, 2008; Jaji, 2012b; Shin & Kim, 2001; Tansel & Pascual, 2011; Jessica M. Younker & Walsh, 2014). These studies were however conducted for highly-concentrated oily waters. For the removal of *trace* concentrations of petroleum hydrocarbons, the majority of past coagulation-flocculation studies focused on PAH compounds, including benzo(a)pyrene (Nowacka & Włodarczyk-Makuła, 2014; Pham & Proulx, 1997; Rosińska & Dąbrowska, 2018; Shabeer et al., 2014; Smol & Włodarczyk-Makuła, 2017; Stackelberg et al., 2007; Vogelsang, Grung, Jantsch, Tollefsen, & Liltved, 2006).

Ballasted flocculation has also been investigated for the removal of petroleum hydrocarbons (Ribera-Pi et al., 2020; Vincent, 2017). The former study however includes no detail on hydrocarbon concentrations while the latter involves a relatively high benzene and DOC concentration (> 100 µg benzene/L and > 90 mg DOC/L). The use of ballasted flocculation for the removal of *trace* (dissolved and emulsified) petroleum hydrocarbons (< 20 µg benzene/L, $C_{10} – C_{50}$ = 9 – 15 mg/L), dispersant-stabilized oil droplets, and residual dispersant concentrations remains yet to be studied. Hence, this thesis aims to answer the following research questions:

a) How efficient are alum and ferric sulfate as coagulants during ballasted flocculation for the removal of *trace* dissolved petroleum hydrocarbons?

b) Is there a need to add an adsorbent to reduce *trace* dissolved hydrocarbon concentrations below drinking water regulations?

c) What is the impact of the addition of an adsorbent on contaminant removal and settled water quality?

d) Are there suitable indicators that can be easily measured at the DWTP for *trace* hydrocarbon contamination?

e) How efficient is ballasted flocculation for the removal of dispersant-stabilized oil droplets and residual dispersant concentrations?

f) How does the presence of a dispersant affect the efficiency of ballasted flocculation in terms of settled water quality?

g) How do the dispersant matrix characteristics and the presence of micelles impact the efficiency of ballasted flocculation?

This thesis is comprised of 8 chapters. Chapter 2 presents an overview of oil-spill contamination of inland waterbodies that serve as sources of drinking water. Issues related to the application of dispersants are discussed and an evaluation of existing research on the efficiency of the physicochemical treatment process (coagulation, flocculation and sedimentation) for petroleum hydrocarbon removal is presented. Chapter 3 enumerates the research objectives, hypotheses and methodology. Chapters 4 to 6 present published articles that respond to the aforementioned research questions. Chapter 4 investigates the efficiency of conventional drinking water treatment for the removal of *trace* dissolved petroleum hydrocarbons originating from gasoline and diesel spills in surface water. It answers questions (a) – (c). Chapter 5 explores the performance of ballasted flocculation for the removal of dispersant-stabilized oil droplets, dispersant-related contaminants, and petroleum hydrocarbons stemming from crude oil. It answers questions (d) – (f). Chapter 6 focuses on the impact of dispersant matrix characteristics and the presence of micelles on the performance of ballasted flocculation. It answers question (g). A general discussion of the research findings is presented in Chapter 7. Conclusions, recommendations and future research areas are described in Chapter 8.

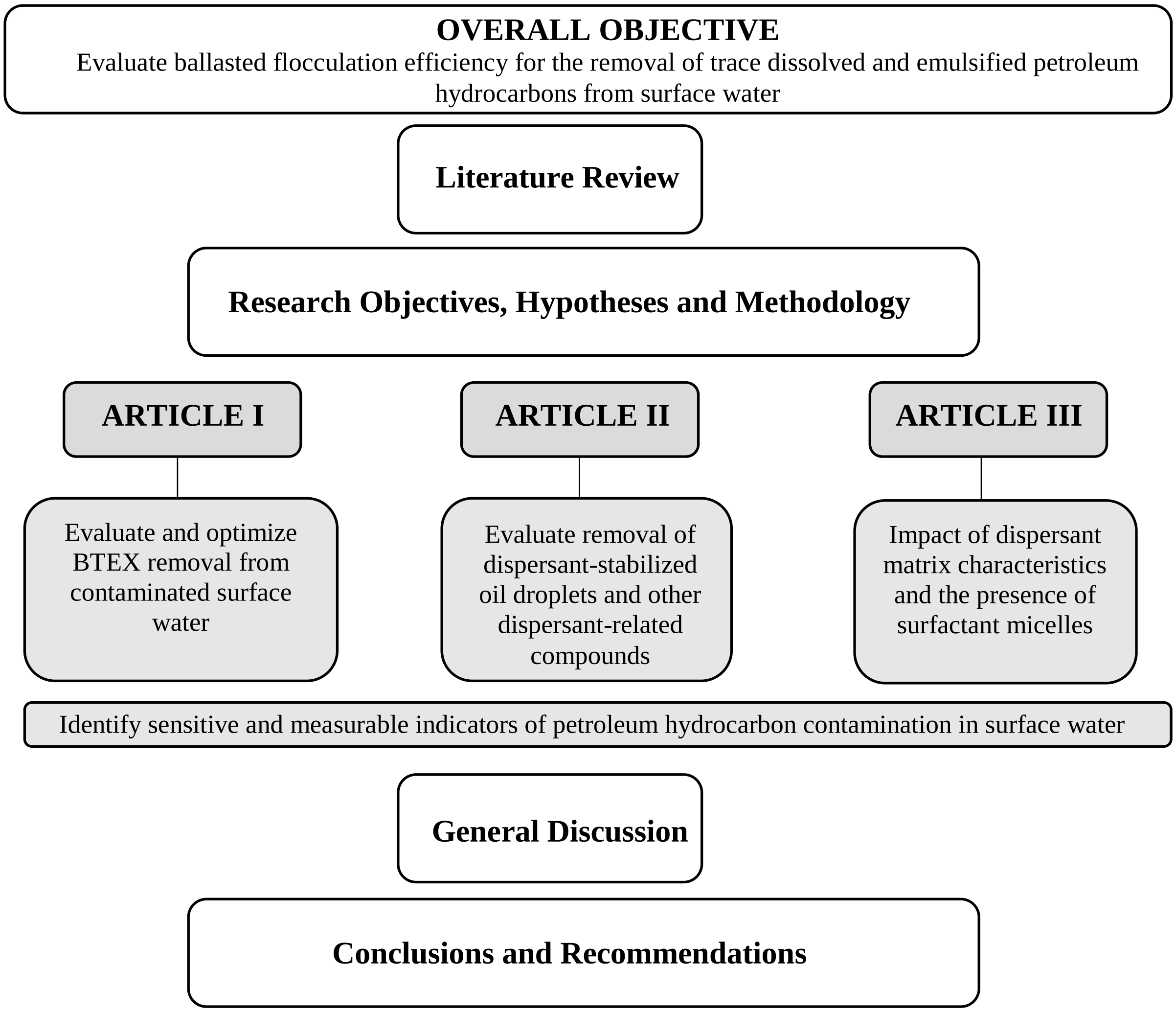


Figure 1.1: Organization of thesis.

CHAPTER 2 LITERATURE REVIEW

2.1 Crude oil and petroleum products: Overview

Crude oil is made up of a variety of compounds – mainly *hydrocarbons*, *metals* such as nickel and vanadium, and *other elements* such as sulfur and nitrogen. To separate useful petroleum fractions, fractional distillation is typically employed at a range of temperatures (Table 2.1).

Table 2.1: Petroleum products from the fractional distillation of crude oil (adapted from (M. F. Fingas, 2011, 2015)).

Fractional distillation products	Temperature range (ºC)
Gasoline	30 – 200
Naphtha	100 – 200
Jet fuel and Kerosene	150 – 250
Diesel fuel	160 – 400
Heavy fuel oils	315 – 540
Residue	> 600

2.1.1 Physical properties

Crude oil and its refined products can be characterized based on specific properties such as viscosity, density, solubility, specific gravity, pour point, flash point, and interfacial tension (Table 2.2). Oil viscosity is affected by temperature and asphaltene content. Viscous oils typically have high asphaltene content and low temperatures favor increased oil viscosity. Oil viscosity can be expressed either as dynamic or kinematic viscosity, although the former is commonly used. Dynamic viscosity, with units of centipoise (cP) or milliPascal second (mPa·s), describes a fluid's inherent resistance to flow while kinematic viscosity, with units of centiStokes (cSt or m^2/s), is the dynamic viscosity divided by the fluid density (M. F. Fingas, 2011).

Oil density is a measure of mass per unit volume of oil (units of g/mL or kg/m^3) and it determines oil floatability. Oils such as Bunker C that are denser than water (1.0 g/cm^3) will sink; however, most oils have densities that are below this value and will therefore float on water. Oil floatability can also be characterized by specific gravity and American Petroleum Institute (API) gravity. Specific gravity is a ratio of the densities of oil and water. Oils with specific gravity greater than 1 will sink and if less than 1, oils will float. API gravity is the inverse of oil density. It employs a 10^o reference value for water and can be calculated as API gravity = [141.5 ÷ (oil specific gravity at 15.5^{o}C)] – 131.5. Dense oils generally have a low API gravity while lighter oils have a higher API gravity. More specifically, lighter crude oils have an API gravity greater than 31.1^{o} while for heavier or denser oils such as bitumen or heavy crude, API gravity ranges from 5 - 15^{o}. Similar to viscosity, oil density, specific gravity, and API gravity are temperature dependent (M. F. Fingas, 2011).

Table 2.2: Physical properties of crude oil and refined petroleum products (retrieved from (M. F. Fingas, 2011, 2015; Lee et al., 2015)).

Property	Unit	Gasoline	Diesel	Light crude	Heavy crude	Intermediate fuel oil	Bunker C
Viscosity	mPa ·s @ 15^{o}C	0.5	2	5-50	50-50,000	1000-15,000	10,000-50,000
Density	g/mL @ 15^{o}C	0.72	0.84	0.78-0.88	0.88-1.00	0.94-0.99	0.96-1.04
API gravity		65	35	30-50	10-30	10-20	5-15
Pour point	^{o}C	NR	-35 to -10	-40 to 30	-40 to 30	-10 to 10	5-20
Solubility in water	ppm	200	40	10-50	5-30	10-30	1-5
Flash point	^{o}C	-35	45	-30 to 30	-30 to 60	80-100	>100
Interfacial tension	mN/m @ 15^{o}C	27	27	10-30	15-30	25-30	25-35

An oil’s pour point is the minimum temperature at which limited oil flow is observed for a specific time duration, typically 5 seconds. Generally, the lighter the oil, the lower its pour point. Solubility refers to the amount of oil that can dissolve in water. Although oil is known to be immiscible with water, a certain fraction is water-soluble, mainly the monoaromatics. Solubility is inversely related with another parameter, the octanol-water coefficient (log K_{ow}), which is a measure of the partitioning of a compound between an organic phase (octanol) and water. A compound that is barely soluble in water will have a high K_{ow}. The flash point of oil indicates its flammability and hazardous potential. It is the lowest temperature at which oil is ignitable in air and it depends on the percentage of volatile components present. Interfacial tension refers to the force between the oil-water interface and it can limit the extent of oil spreading on water (M. F. Fingas, 2011, 2015; Lee et al., 2015).

2.1.2 Chemical properties

The compounds that make up crude oil can be classified into four main groups – saturates, aromatics, resins, and asphaltenes. Trace concentrations of metals such as nickel and chromium are also found to be present (M. F. Fingas, 2011, 2015; Lee et al., 2015).

Saturates – This group comprises of cyclic, straight- or branched-chain compounds of carbon and hydrogen. Each carbon is bound to the maximum number of hydrogen atoms and there are no aromatic rings. These compounds are also called alkanes and the higher molecular weight alkanes ($> C_{18}$) are referred to as waxes. Alkanes are generally insoluble in water, biodegradable and of lesser toxicological risk. However, waxes, branched-chain and cyclic alkane forms resist biodegradation. Some refined products such as gasoline and diesel also contain a small percentage of alkenes (hydrocarbons with double bonds) (M. F. Fingas, 2011, 2015; Lee et al., 2015).

Aromatics – Compounds in this group have one or more benzene rings. Of interest are the monoaromatic (one benzene ring) and polyaromatic (two or more benzene rings) compounds. Monoaromatic compounds include benzene, toluene, ethylbenzene and o-, m-, p-xylenes (BTEX). These compounds are the most soluble and volatile. They are also toxic to humans and aquatic life. Polyaromatic hydrocarbons include naphthalene, anthracene, benzo(a)pyrene, and chrysene, amongst others. These compounds are less volatile and soluble. They are also toxic and more persistent in the environment (M. F. Fingas, 2011, 2015; Lee et al., 2015).

Resins – These compounds contain other elements such as nitrogen, sulfur and oxygen. They are soluble in polar and organic solvents, including water. Although their exact structure is not well-defined, resins are toxic and are known to resist biodegradation (M. F. Fingas, 2011, 2015; Lee et al., 2015).

Asphaltenes – Similar to resins, asphaltenes contain other atoms such as nitrogen and oxygen. They also do not have a well-defined structure. However, they have a higher molecular weight and lesser polarity. They are insoluble in water and affect the adhering and wetting properties of crude oil. Asphaltenes resist biodegradation (M. F. Fingas, 2011, 2015; Lee et al., 2015).

The composition of different oil types and refined products dictates their behavior and fate in the environment (Table 2.3). Bunker C is a heavy fuel oil residue from the distillation process and it can be used for combustion. Intermediate fuel oil is a mixture of residual and diesel fuel. Of equal importance, although not included on the table, are diluted bitumen (or dilbit) and Bakken light crude. Prior to processing, the latter is extracted from the Bakken shale formation that covers the regions of Saskatchewan, Manitoba and North Dakota. It contains a considerable amount of light volatile organics and was the crude implicated in the Lac Mégantic accident. Diluted bitumen or dilbit is a mixture of bitumen and a diluent at a typical ratio of 70:30 (Lee et al., 2015). Due to the highly viscous nature of bitumen, a diluent such as naphtha or condensates (extremely light oil from natural gas fields) is required to enable bitumen transport. It is expected that in the event of a spill, the lighter fractions will evaporate, leaving a highly viscous and poorly biodegradable bituminous fraction (Lee et al., 2015).

Table 2.3: Chemical properties of crude oil and refined petroleum products (retrieved from (Centre d'expertise en analyse environnementale du Québec (CEAEQ), 2015)).

Group	Form	Unit	Gasoline	Diesel	Light crude	Heavy crude	Intermediate fuel oil	Bunker C
Alkanes	Non-cyclic	%	45-55	35-45	40-85	20-60	10-25	10-20
	Cyclic		5	25-50	5-35	0-10	0-5	0-5
	Total		50-60	65-95	55-90	25-80	25-35	20-30
Olefins			5-10	0-10	-	-	-	-
Aromatics	BTEX		15-25	0.5-2	0.1-2.5	0.01-2	0.05-1	0-1
	PAH		-	0-5	10-35	15-40	30-50	30-50
	Total		25-40	5-25	10-35	15-40	40-60	30-50
Polar compounds	Resins		-	0-2	0-10	2-25	10-15	10-20
	Asphaltenes		-	-	0-10	0-20	5-10	5-20
	Total		-	0-2	1-15	5-40	15-25	10-30
Metals		ppm	-	-	30-250	100-500	100-1000	100-2000
Sulfur		%	0.02	0.1-0.5	0-2	0-5	0.5-2	2-4

2.2 Region of Montreal: Water intakes and risks

In the region of Montreal, three active underground oil pipelines – Trans-Northern, St-Laurent, and Enbridge Line 9B – cross four rivers that serve as sources of drinking water to about 28 DWTP (Figure 2.1) (Barrette, 2018). Denoted on the figure is a fourth pipeline, Énergie Est, whose construction was suspended in 2017. Enbridge Line 9B transports crude oil at 300,000 barrels per day while the suspended Énergie Est project was to transport 1.1 million barrels of crude oil per day. Trans-Northern and St-Laurent pipelines transport refined petroleum products at 172,900 barrels and 100,000 barrels per day, respectively (Table 2.4) (Barrette, 2018; Communauté Métropolitaine de Montréal (CMM), 2019). Trans-Northern and Enbridge Line 9B pipelines cross Outaouais River, Mille-Îles River, and Des Prairies River while the St-Laurent pipeline crosses the St. Lawrence River. In addition to contamination risks from trucks and trains carrying petroleum products, the presence of oil pipelines near surface water increases the vulnerability of drinking water intakes and poses a risk of contamination in the event of pipeline damage (Barrette, 2018; Brody, Bianca, & Krysa, 2012; Communauté Métropolitaine de Montréal (CMM), 2019).

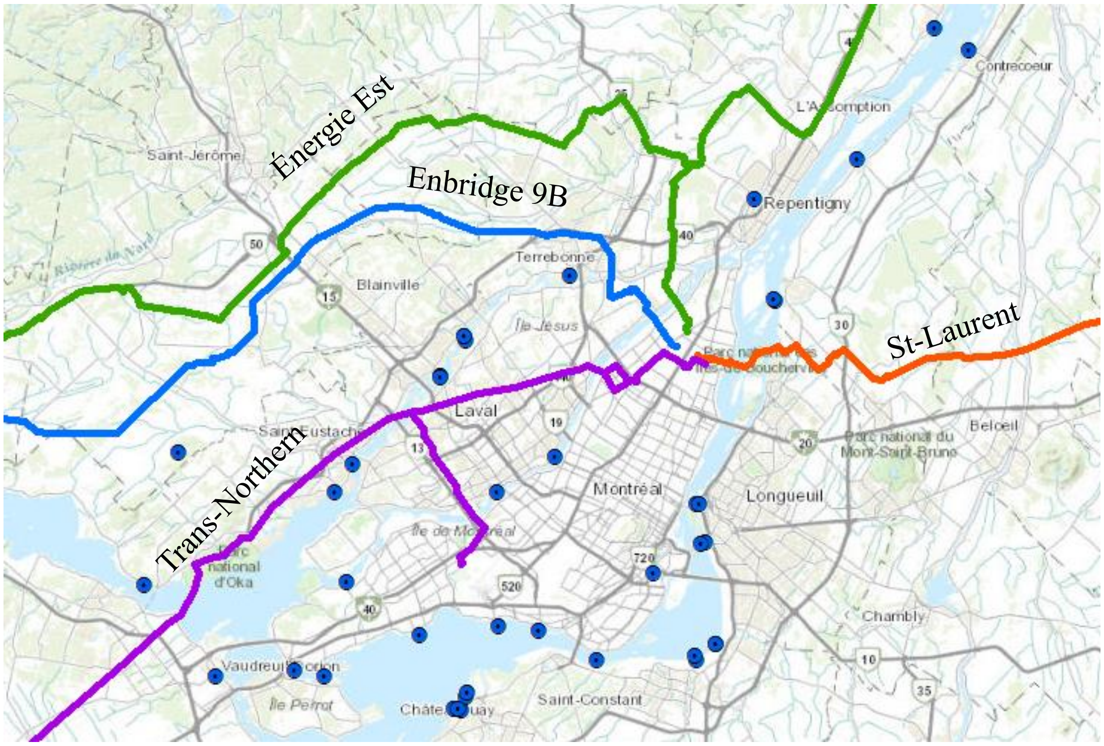


Figure 2.1: Oil pipelines (colored lines) and water intakes (blue circles) in the region of Montreal (retrieved from (Barrette, 2018)).

Table 2.4: Information on the pipelines in the region of Montreal (retrieved from (Barrette, 2018; Communauté Métropolitaine de Montréal (CMM), 2019)).

Pipeline	Product transported	Volume (barrels/day)	Vulnerable surface water
Trans-Northern	Refined petroleum products - kerosene	172,900	Outaouais River, Mille-Îles River, and Des Prairies River
St-Laurent	Refined petroleum products - gasoline	100,000	St-Lawrence River
Enbridge Line 9B	Bakken light crude/medium to heavy crude oil from Western Canada	300,000	Outaouais River, Mille-Îles River, and Des Prairies River
Énergie Est	Bakken light crude/diluted bitumen from Alberta	1,100,000	-

*1 barrel = 159 L

2.3 Oil spills in surface water: Case studies, contaminants and their fate in the environment

Over the years, public attention has focused on major oil spills in marine environments. However, oil spills of an appreciable magnitude do occur in freshwater environments due to pipeline breakage, train derailment or other sources of anthropogenic contamination (Table 2.5). In Canada, from 2008 to 2018, an average of 6 pipeline accidents was reported yearly. 41 out of 66 accidents during this timeline involved the release of a petroleum product. 13 accidents resulted in the release of crude oil or other refined products, with 6 pipeline failures involving volumes between 100 – 10,000 m^3 (Transportation Safety Board of Canada (TSB), 2018).

Table 2.5: Oil spill events and their reported environmental impacts.

Location	Date	Product	Measured/observed concentration at the time of spill	Reported impacts	Source
Lac Mégantic, Québec, CA	16 July, 2013	5930 m^3 light crude oil	B = 17 µg/L C_{10}-C_{50} = 8.8 - 15 mg/L	Soil and surface water contamination	(Barrette, 2018; Galvez-Cloutier et al., 2014)
Yellowstone River, Montana, US	17 January, 2015	121 m^3 light crude oil	B = 14 µg/L	Contamination of drinking water sources	(Barrette, 2018)

Table 2.5: Oil spill events and their reported environmental impacts (continued).

Location	Date	Product	Measured/observed concentration at the time of spill	Reported impacts	Source
Pine River, British Columbia, CA	1 August, 2000	985 m^3 light crude oil	0.2 µg/L alkylated PAH	Death of more 1 600 fish and contamination of drinking water sources	(Barrette, 2018; Government of British Columbia, 2016; Lee et al., 2015)
Red Deer River, Alberta, CA	7 June, 2012	465 m^3 light crude oil	B = 13 µg/L, TEX = 68 µg/L	Contamination of land, recreational waterbodies and drinking water sources	(Lee et al., 2015; Zhou, Dettman, & Bundred, 2015b)
North Saskatchewan River, Saskatchewan, CA	21 July, 2016	225 m^3 heavy crude oil	B = 0.88 µg/L, TEX = 10 µg/L, BaP = 0.011 µg/L C_{10}-C_{50} = 14 µg/L,	Contamination of drinking water sources	(Barrette, 2018; Inc., 2016)

B = benzene; TEX = toluene, ethylbenzene, xylenes; BaP = benzo(a)pyrene

Compared to marine environments, wave action, water volume and depth are not as pronounced in freshwater bodies, leading to a greater impact on the ecosystem in the event of an oil spill (Galvez-Cloutier et al., 2014; Green & Trett, 1989; Maloney et al., 2017; Owens & Michel, 1995; Owens et al., 1993). Regardless of the size of the waterbody, an oil spill negatively impacts water quality and aquatic life. Freshwater bodies are in close proximity to humans and typically serve as sources of drinking water or other recreational uses. An oil spill however introduces toxic substances that limit the accessibility and adequacy of these freshwater bodies for human use. These substances can be biotransformed, bioaccumulated or biomagnified in the cells or membranes of aquatic animals and their corresponding heterotrophs (Green & Trett, 1989; Lee et al., 2015).

Seabirds and fish experience oiling and tainting of their scales, respectively (M. F. Fingas, 2015; Green & Trett, 1989; Lee et al., 2015; Prince, 2015). These aquatic animals are also exposed to the more soluble and toxic oil components, which can lead to their mortality. The presence of oil also exerts physical (possible permanent destruction of plants due to limited sunlight penetration), biophysical (damage of cell membranes), and biochemical (enzymatic inhibition) effects on submerged aquatic plants (M. F. Fingas, 2015; Green & Trett, 1989; Lee et al., 2015). The volatile components that escape to the air pose a health risk to humans and in the event where the spilled oil is burned, particulate soot can endanger human respiratory system (Galvez-Cloutier et al., 2014).

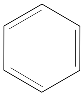
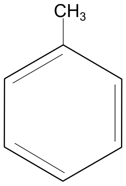
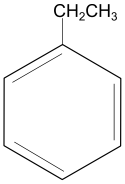
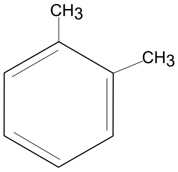
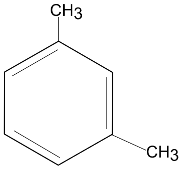
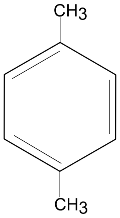
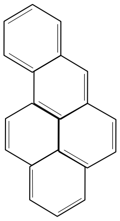
2.3.1 Contaminants of interest: BTEX and benzo(a)pyrene

An oil spill in surface water raises concerns about the presence of mono- and polyaromatic hydrocarbons in drinking water. More specifically, the presence of the compounds – benzene, toluene, ethylbenzene and xylenes (BTEX) and benzo(a)pyrene (BaP) – poses health risks to humans. Toluene, ethylbenzene and xylenes adversely affect the nervous and neurological systems, especially after prolonged exposure (Galvez-Cloutier et al., 2014). Benzene and benzo(a)pyrene are known to be carcinogenic and toxic (Agency for Toxic Substances and Disease Registry (ATSDR), U. S Department of Health and Human Services, & Public Health Service, 2007) and as a result, thresholds have been set to limit their concentrations and ensure low cancer risk due to drinking water exposure (Table 2.6). These thresholds are based on epidemiological studies and calculated lifetime cancer risks. The latter will reduce from 10^{-5} to 10^{-6} if a carcinogen concentration diminishes tenfold, where a lifetime is typically defined as a 70-year period of exposure (World Health Organization (WHO), 2004). Three points are noteworthy from Table 2.6: a) stricter regulations exist in Québec for benzene and benzo(a)pyrene, b) odor thresholds are higher than concentrations measured in surface water following an oil spill (Table 2.5) and c) one of the most toxic compound, benzene, is also the most soluble (1780 mg/L) (Table 2.7). This indicates that hydrocarbon contamination of source water can go unnoticed in the DWTP.

Table 2.6: Maximum acceptable concentrations (MAC) in drinking water (Agency for Toxic Substances and Disease Registry (ATSDR) et al., 2007; Gouvernement du Québec, 2020; Santé Canada, 2009, 2014, 2016; United States Environmental Protection Agency (USEPA), 2019).

Compound	Québec (µg/L)	Health Canada (µg/L)	U.S. EPA (µg/L)	WHO (µg/L)	Odor Threshold (µg/L)
Benzene	0.5	5	5	10	190-2000
Toluene	-	60	1000	700	960
Ethylbenzene	-	140	700	300	150
Xylene	-	90	10,000	500	20-1800
Benzo(a)pyrene	0.01	0.04	0.2	0.7	-

Table 2.7: Physicochemical properties of BTEX (El-Naas, Acio, & El Telib, 2014; Lawrence, 2006; United States Environmental Protection Agency (U.S. EPA), 2014).

	Benzene	Toluene	Ethylbenzene	o-xylene	m-xylene	p-xylene	BaP
Formula	C_6H_6	C_7H_8	C_8H_{10}	C_8H_{10}	C_8H_{10}	C_8H_{10}	$C_{20}H_{12}$
Structure							
Molecular weight (g/mol)	78.11	92.13	106.17	106.16	106.16	106.16	252.32
Boiling point (°C)	80	111	136	144	139	137	311
Vapor pressure (mm Hg)	95	28	4.5	6.6	8.3	3.2	5×10^{-7}
Density, 20 °C (g/L)	876	867	867	880	864	861	1351
Solubility in water, 25°C (mg/L)	1780	531	161	207	161	181	0.00162
Log K_{OW}	2.13	2.73	3.15	3.12	3.20	3.15	6.04

2.3.2 Fate of contaminants

Oil spilled in the environment undergoes weathering, which is a series of physical, biological and chemical processes that influence oil properties and its fate in the environment. These processes include spreading, dissolution, evaporation, photo oxidation, emulsification, sedimentation, biodegradation, and natural dispersion (Lee et al., 2015). The onset and rate of each process differ, leading to marked effects on the physicochemical properties of the spilled oil.

Spreading is a more common process for lighter oils and is influenced by wind, temperature and viscosity. Evaporation, dissolution and dispersion occur immediately after a spill and have a greater impact on surface water contamination (Brandvik, Myrhaug, Daling, Leirvik, & Fritt-Rasmussen, 2010; Lee et al., 2015). Evaporation involves the loss of lighter hydrocarbons and depending on the oil type, up to 50 % on average, of hydrocarbons can be lost (Green & Trett, 1989; Lee et al., 2015). This process therefore decreases the volume of spilled oil and increases oil viscosity and specific gravity. Dissolution and evaporation are competitive processes with respect to BTEX and other lighter hydrocarbons that also have a tendency to evaporate; however, evaporation is known to be more predominant than dissolution (Lee et al., 2015). Dissolution depends on temperature, salinity and solubility of the hydrocarbons, the latter of which is greater in the absence of alkyl substitutions (for aromatics) and in the presence of polar compounds (Green & Trett, 1989). In ice-covered surface waters, dissolution is more pronounced than evaporation.

The process of natural dispersion entrains oil droplets further down the water column, favoring biodegradation. Photo-oxidation, emulsification, sedimentation and biodegradation occur within days or weeks following an oil spill. Bacterial biodegradation of oil depends on several factors affecting the growth and proper functioning of the bacteria such as temperature, nutrients, oil composition, oil droplet size, and oxygen availability. Aerobic conditions are more favorable for oil biodegradation than anaerobic conditions. Biodegradation however increases oxygen demand. In the presence of oxygen and sunlight, photo-oxidation involves the transformation of aromatic compounds to more soluble and biodegradation-resistant by-products. Emulsification increases the volume of spilled oil and the type of emulsion formed (that is, water-in-oil *or* oil-in-water) depends on the mixing energy, oil type and volume of spill, and temperature. Sedimentation is possible, especially when oil is denser and sinks. Oil in sediments is however less bioavailable and thus more persistent due to the anaerobic environment and lack of nutrients (Lee et al., 2015).

BTEX compounds are highly soluble in water and this, combined with their volatility, adds to the complexity of their removal and abatement from the environment (Table 2.7). In the event of an oil spill in surface water, BTEX can evaporate, dissolve in the impacted surface water, or sorb to soil particles. BTEX concentrations in environmental sinks depend on the oil type, frequency and degree of contamination. As for benzo(a)pyrene, due to its molecular weight and log Kow, it is more likely to attach to sediments or soil particles.

2.4 Remediation technologies

Oil-spill recovery and cleanup involve the application of physical, chemical and biological response methods that aim to reduce the environmental impact of spilled oil. Physical methods comprise of the use of manual or mechanical means such as booms, sorbents, skimmers and in-situ burning to contain or limit the spread of the oil slick. Chemical methods necessitate the application of chemicals such as dispersants, herding agents, and solidifiers to either enable oil recovery or promote its degradation in the water column. Biological methods aim to enhance oil removal through microbial seeding and nutrient enrichment (M. F. Fingas, 2011; Green & Trett, 1989; Owens & Michel, 1995; Owens et al., 1993). Studies have been done that compare these remediation technologies based on their environmental impact in the presence and absence of oil (Owens & Michel, 1995; Owens et al., 1993). With respect to the region of Montreal and the location of its pipelines, the most vulnerable freshwater bodies are mainly large rivers. In the absence of oil, most response methods have been reported to show minimal adverse impact on large rivers (Table 2.8). However, in the presence of oil and depending on the oil type, sensitivity of large rivers to each response method varies.

Table 2.8: Sensitivity of large rivers to different remediation technologies in the presence and absence of different oil types (Adapted from (Owens & Michel, 1995)).

Response method	No oil	Gasoline products	Diesel-like oils	Medium oils	Heavy oils
Booms	L	A	A	A	A
Skimmers	L	-	A	A	A
Natural Recovery (or no cleanup)	-	A	A	B	C
Sorbents	L	-	B	B	B
In-situ burning	L	-	B	B	B
Emulsion treating agents	L	-	B	B	B
Solidifiers	L	-	B	B	-
Dispersants	L	D	C	C	-
Herding agents	L	D	D	D	-

“L = low: physical damage to the substrate and vegetation is minimal. Toxic impact is likely to be of limited areal extent and short duration. Restabilization or repopulation of the habitat is likely within six months. – = ineffective or inapplicable. A = may cause the least adverse habitat impact, B = may cause some adverse habitat impact, C = may cause significant adverse habitat impact, D = may cause the most adverse habitat impact”

In large rivers, skimmers, sorbents and solidifiers should not be applied to gasoline spills due to its fluidity, high volatility and flammability. The application of emulsion-treating and herding agents is also reported to be ineffective since gasoline does not emulsify (International Tanker Owners Pollution Federation Limited (ITOPF), 2011). In-situ burning following gasoline spills presents an environmental hazard that impacts air quality and safety of the surrounding habitants. For dispersant application, speculative C and D ratings are assigned to spills from diesel, gasoline, and medium oils mainly due to the lack of insight on the impact of dispersants on water intakes and drinking water quality (Herndon, 2010; Owens & Michel, 1995). Other reasons include herding observed for light refined products (such as gasoline and diesel) and possible increase in toxicity from dispersant application (International Tanker Owners Pollution Federation Limited (ITOPF), 2011; Owens & Michel, 1995). For heavy oils, chemical response methods are deemed ineffective due to the high viscosity of the product. No-cleanup or natural recovery is included as a viable option for gasoline and diesel spills in large rivers due to the high volatility of both products. However, this option is not advisable for heavy oils most likely due to the high asphaltene content and its persistence in the environment.

2.4.1 Dispersants and oil-in-water emulsions

Dispersion or the formation of oil-in-water emulsions is a phenomenon that can occur in the event of an oil spill (Section 2.3.2). These emulsions can however be unstable depending on the size of the oil droplets. As a result, dispersants are applied to enhance the formation of smaller and more stable oil droplets (National Research Council (NRC), 2005). Another possible yet undesirable phenomenon that could occur is the formation of water-in-oil emulsions, which are further stabilized by the presence of asphaltenes and resins in the oil (Bobra, Fingas, & Tennyson, 1992; M. F. Fingas, 2015). Contamination from dispersed and stabilized oil droplets is highly likely with respect to surface water and DWTP. Hence, more detail on this aspect is presented in the following subsections.

2.4.1.1 Role of dispersants

In the event of an oil spill, the application of dispersants favors not only oil droplet formation, but also droplet stability in the water column. This is accomplished by the reduction of interfacial tension in the oil-water interface, enabling the formation of small oil droplets and dispersant adsorption on the droplets to hinder their coalescence (M. F. Fingas, 2011; International Tanker Owners Pollution Federation Limited (ITOPF), 2011; John, Arnosti, Field, Kujawinski, & McCormick, 2016; Prince, 2015; Weiss & McClements, 2000). An effective diameter less than 70 µm has been suggested to ensure that droplet buoyancy is hindered (International Tanker Owners Pollution Federation Limited (ITOPF), 2011; Prince, 2015).

Surface tension (for an air-water *or* air-oil interface) or interfacial tension (for an oil-water interface) is defined as the minimum work or energy necessary to increase the area of the surface or interface by one unit (John et al., 2016; National Research Council (NRC), 2005) (Eq. 2.1).

$$W = \gamma \Delta A \qquad \text{Eq. 2.1}$$

where W: work required (mJ or mN·m), γ: surface or interfacial tension (J/m^2 or mN/m), and ΔA: change in interfacial area (m^2). For an air-water system, surface tension of pure water is 72 – 73 mN/m (Myers, 2006a). Three methods for the quantification of surface or interfacial tension employ several equations (Eqs. 2.2 – 2.4). The first two methods rely on the measured force of a plate or ring in contact with the liquid of interest while the last method calculates the surface or interfacial tension based on the shape of a liquid drop from a needle (Berry, Neeson, Dagastine, Chan, & Tabor, 2015; Ebnesajjad & Landrock, 2008; M. F. Fingas, 2011; Stauffer, 1965; Tadros, 2014).

$$\text{du Nuoy ring method: } F_T = w_r + 4\pi R\gamma_{ideal};\ \gamma = f.\gamma_{ideal} \qquad \text{Eq. 2.2}$$

$$\text{Wilhelmy plate method: } F_T = w_P + p\gamma_{ideal} + \rho g h A \qquad \text{Eq. 2.3}$$

$$\text{Pendant drop method: } \beta = \frac{\Delta\rho g R^2}{\gamma} \qquad \text{Eq. 2.4}$$

where F: total force, w_r: weight of the ring, w_P: weight of the plate, p: perimeter of the plate, R: radius of the ring, f: shape correction factor, γ: surface tension, h: height of the plate above or below the liquid, R: radius of the drop from the center, $\Delta\rho$: difference in density between the two phases, g: gravity, and β: shape parameter or bond number. Laplace pressure (ΔP) applies to the pendant drop due to its curvature and its relationship to surface or interfacial tension can be expressed as (Berry et al., 2015; Tadros, 2014):

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad \text{Eq. 2.5}$$

where ΔP: pressure difference and $R_1$and R_2: radii of curvature. When $R_1 = R_2 = R$ (perfect sphere), Eq. 2.5 becomes:

$$\Delta P = \frac{2\gamma}{R} \qquad \text{Eq. 2.6}$$

Thermodynamically, interfacial tension can be understood through the Gibbs energy equation (Myers, 2006a):

$$dG = -SdT + \gamma dA + VdP + \sum \mu_i dn_i \qquad \text{Eq. 2.7}$$

At equilibrium and constant T, P, and n (number of moles of component *i* in the system), Eq. 2.7 reduces to:

$$dG = \gamma dA \text{ and } \gamma = \left(\frac{dG}{dA}\right) \qquad \text{Eq. 2.8}$$

For the case of an oil spill and the subsequent formation of oil droplets in water, the Gibb's energy equation can be rewritten as (Tadros, 2014):

$$dG = -T\Delta S + \gamma \Delta A \qquad \text{Eq. 2.9}$$

Entropy and interfacial area change in such a system. Without dispersants, the process of oil droplet formation is not spontaneous, that is, $\Delta G > 0$. Hence, the system would tend to reverse to the original state of the spill where the oil plume remained on the water surface. The addition of dispersants, together with some turbulence or wave action, however enables the spontaneity of the oil droplet formation process (M. F. Fingas, 2011; Tadros, 2014).

2.4.1.2 Dispersant composition

Additives, solvents and surfactants are the three main components that make up oil spill dispersants (Poliakoff, 1969). Additives impact the dispersant's physicochemical properties such as pH, color, and stability. Solvents such as petroleum hydrocarbons, water and alcohols aid in reducing dispersant viscosity and providing conditions for surfactant accessibility and action on the oil. Surfactants, as the active agents in dispersants, are responsible for the reduction in interfacial tension (International Tanker Owners Pollution Federation Limited (ITOPF), 2011; John et al., 2016; Poliakoff, 1969; Wrenn et al., 2009).

Surfactants are “long-chain alkyl salts of strong acids” (Myers, 2006a). They are amphiphilic compounds that possess a hydrophobic tail and a hydrophilic head (Figure 2.2). Based on the charge of the head group, four main classes of surfactants exist – anionic, cationic, nonionic and amphoteric (Myers, 2006a; Wrenn et al., 2009). Anionic surfactants have a negative charge while cationic surfactants carry a positive charge on the hydrophilic head. A nonionic surfactant carries no charge on its head group while amphoteric surfactants possess both a positively and negatively head group. The hydrophobic tail could be composed of straight or branched chain alkyl groups, amongst others. To describe the strength of the hydrophilic and hydrophobic parts of surfactants, the hydrophile-lipophile balance (HLB) is used. It is a scale of 0 to 20 and oil-in-water emulsifiers are known to be in the range of 8 to 16 (M. F. Fingas, 2011; Lee et al., 2015; Poliakoff, 1969; Wrenn et al., 2009).

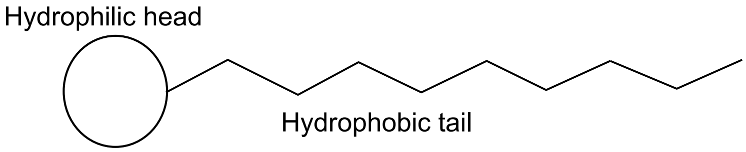


Figure 2.2: Schematic of a surfactant.

In an oil-water system, surfactants, due to their amphiphilic nature, enable interfacial interactions, that is, their hydrophilic head can interact with water while their hydrophobic tail can interact with oil. In this way, surfactants reduce the work done to increase the interfacial area as well as the free energy of the system (Myers, 2006a; Palmer & Hatley, 2018). The amount of surfactant adsorbed on the interface per unit area (Γ) can be calculated as (Myers, 2006a; Tadros, 2014):

$$\Gamma = \frac{n}{A} = \frac{-\frac{1}{RTf}d\gamma}{d\ln C} \qquad \text{Eq. 2.10}$$

where f accounts for the adsorbed units depending on the type of surfactant ($f = 1$ for nonionic surfactants and 2 for completely ionized ionic surfactants). $\frac{d\gamma}{d\ln C}$, and hence Γ, can be computed from the linear portion, right before the point of inflexion, of the graph of surface tension versus log(surfactant concentration). This equation is however valid for equilibrium conditions and dilute solutions in which surfactant concentrations are far below the critical micelle concentration (CMC) (Myers, 2006b). For a mixed surfactant system, “interfacial complexes” have been observed to form on the interface, thus increasing Γ and the stability of the emulsion (Myers, 2006a).

The exact composition of many dispersants is not disclosed to the public (Hemmer, Barron, & Greene, 2011). However, they are known to be comprised of a blend of nonionic and anionic surfactants such as Span 80, Tween 80, sodium dodecyl sulfate (SDS), sodium docusate or bis(2-ethylhexyl) sodium sulfosuccinate or sodium dioctyl sulfosuccinate (DOSS) (Figure 2.3, (International Tanker Owners Pollution Federation Limited (ITOPF), 2011; John et al., 2016; Wrenn et al., 2009)). SDS is the most well-studied and understood surfactant and it is made from the combination of sodium hydroxide and sulfuric acid ester. DOSS is commonly found in many oil-spill dispersants such as Corexit 9527 and Corexit 9500A (Kujawinski et al., 2011; Myers, 2006a). Both surfactants are anionic while Span and Tween surfactants are nonionic. In terms of solubility in water, Spans are insoluble; Tweens and SDS are soluble; and DOSS is slightly soluble (John et al., 2016).

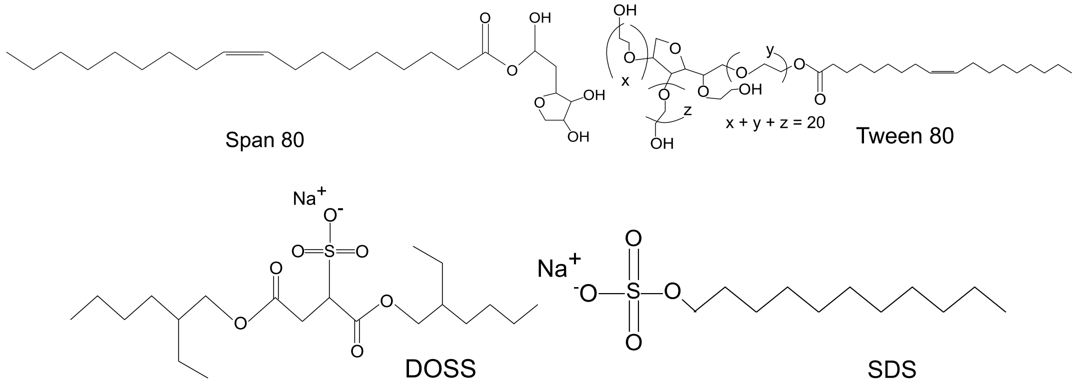


Figure 2.3: Structures of major surfactants in oil-spill dispersants (adapted from (John et al., 2016)).

Dispersants are applied based on the estimated amount of oil spilled. A typical volumetric ratio of 1 L of dispersant for 20 L of oil is common (M. F. Fingas, 2011; International Tanker Owners Pollution Federation Limited (ITOPF), 2011; Prince, 2015). Most of the recommended oil-spill dispersants on the U.S. EPA list have been tested for effectiveness mainly under seawater conditions. This test, also known as the swirling flask or baffled flask test, evaluates the ability of the dispersant to disperse a minimum of 45% of Prudhoe Bay or South Louisiana oil (Prince, 2015). For a dispersant to break an oil slick and form oil droplets, proper dispersant dose, appropriate surfactant orientation and action, adequate mixing energy, droplet dilution, and large size and depth of water body are required (National Research Council (NRC), 2005).

2.4.1.3 Micellization and Critical Micelle Concentration (CMC)

In an aqueous solvent such as water, surfactants will continue to adsorb on the air-water interface until the entire interface is occupied or saturated. Micelles, an agglomeration of surfactants, will then begin to form at a surfactant concentration called the critical micelle concentration (CMC) (Mysels, 1972). Below the CMC, surfactant monomers exist. Above the CMC, the formation of micelles is thermodynamically more advantageous for the system and surface or interfacial tension remains more or less constant (Figure 2.4).

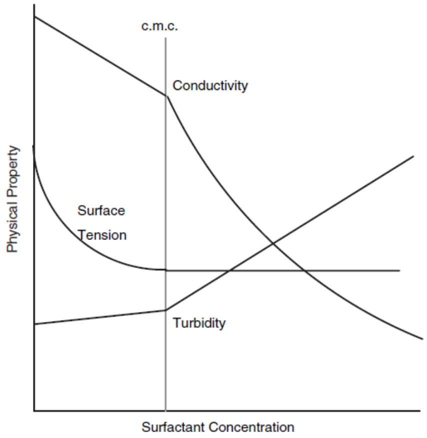


Figure 2.4: Effect of surfactant concentration and micelle formation on turbidity, surface tension and conductivity (retrieved from (Myers, 2006a)).

Generally, the CMC of a surfactant system is influenced by a number of factors, although deviations from the observed trends are possible (Table 2.9). CMC decreases as the length of the hydrophobic tail of the surfactant increases (Myers, 2006a; Sidim & Acar, 2013). CMC increases if an alkene group is present in the hydrophobic chain. This is most likely due to the unsaturated nature of alkenes and the arrangement of functional groups around the double bond (*cis* or *trans* forms). Compared to the *trans* form, CMC is higher for the *cis* since it necessitates a fixed configuration (Myers, 2006a). CMC also increases if the polarity of the hydrophobe is enhanced by the presence of atoms such as oxygen or nitrogen. CMC typically decreases when electrolytes are present in water. For ionic surfactants, interaction between electrolytes and micellar hydrophilic head groups promotes micelle formation since electrostatic repulsion in the system is reduced. For nonionic surfactants, their lack of charge limits interaction with electrolytes present in water, leading to a decrease in CMC (Corrin & Harkins, 1947; Jiang, Du, Cheng, Wang, & Zeng, 2003; Myers, 2006a).

Table 2.9: Factors affecting critical micelle concentration (CMC) (Adapted from (Corrin & Harkins, 1947; Jiang et al., 2003; Myers, 2006a; Sidim & Acar, 2013)).

Factor	Trend
Hydrophobic tail length	As carbon number ↑, CMC ↓
Alkene group	CMC↑
Polar atoms	CMC↑
Presence of electrolyte or salinity	CMC ↓

Some other factors, not listed on the table but worth mentioning, include the type of hydrophilic head (surfactants with larger-sized hydrophilic head groups such as sulfonates exhibit a lower CMC than those with smaller ones such as carboxylates) and the ionisability of the counter-ions on the hydrophilic head (ionic surfactants with head groups having counter-ions such as calcium and magnesium that bind strongly tend to have lower CMC than those having counter-ions such as sodium or potassium) (Myers, 2006a). When oil is present in water, the addition of surfactants at a concentration above the CMC will lead to the solubilization of oil within the micelles. Solubilization is a phenomenon that allows the incorporation of the oil molecules within the micelle in order to increase the solubility of a poorly miscible substance (Myers, 2006a).

2.4.1.4 Emulsion stability

Coalescence, flocculation, creaming, and Ostwald ripening are some emulsion destabilization processes that can occur. Coalescence is the formation of one large droplet from the combination of at least two droplets while flocculation is an agglomeration of droplets without the breakage of the film around each droplet. Creaming refers to the resurgence of an oil plume while Ostwald ripening increases droplet size due to the preference of more soluble compounds in the system for these droplets (M. Fingas, 2008; M. F. Fingas, 2011; Myers, 2006a).

Oil droplets in water will not resurface if they remain small in size and temperature, salinity and turbulence conditions are favorable (M. F. Fingas, 2011; Zhao et al., 2020). The Stokes equation (Eq. 2.11, (M. F. Fingas, 2011)) shows that compared to large oil droplets, smaller droplets will remain suspended and take longer to rise to the water surface.

$$\mathrm{s} = \frac{2\Delta\rho g r^2}{9\eta} \qquad \text{Eq. 2.11}$$

where η: viscosity of water for an oil-water system, r: radius of the droplet, g: acceleration due to gravity (9.81 m/s^2), and $\Delta\rho$: difference in the densities of water and the oil droplet.

Temperature and viscosity of water influence emulsion destabilization. Due to the relatively low viscosity of water, more collisions of oil droplets in water are possible (higher D, Eq. 2.12), leading to a greater likelihood for emulsion destabilization from coalescence. The same is true at higher water temperatures (M. F. Fingas, 2011).

$$\mathrm{D} = \frac{kT}{9\pi\eta r} \qquad \text{Eq. 2.12}$$

where D: diffusion rate, k: Boltzmann constant, T: absolute temperature, η: viscosity of water, and r: droplet radius. Other factors that affect emulsion stability include composition and quantity of surfactant applied, mode of application, and surfactant detachment from the interfacial film around oil droplets due to dilution (M. F. Fingas, 2011; Poliakoff, 1969).

2.4.2 Dispersant application in surface water: Issues

Toxicity and the **unconfirmed impact on drinking water intakes** are two main concerns associated with the application of dispersants in freshwater bodies. In the event of an oil spill, the application of dispersants has been reported to demonstrate synergistic toxicity to aquatic life in that the toxicity of the dispersant-oil mixture proves to be greater than that of the individual dispersant or crude oil (Bhattacharyya et al., 2003a; M. Fingas, 2008; M. F. Fingas, 2011; Green & Trett, 1989; Prince, 2015). Several explanations have been proposed: a) Since dispersants enable the formation, stability and availability of oil droplets in the depths of the waterbody, toxic petroleum compounds that might not have been within reach become more accessible to aquatic organisms (Green & Trett, 1989); b) Crude oil consists of relatively well-studied toxic compounds such as BTEX. The application of dispersants however introduces additional, potentially toxic contaminants whose identities are not disclosed to the public (Green & Trett, 1989; Prince, 2015); and c) Dispersant compounds, especially DOSS, are persistent and can promote bio-accumulation of petroleum hydrocarbons in aquatic organisms (Kujawinski et al., 2011; Prince, 2015).

Generally, most oil-spill incidents involving dispersant application are known to occur in marine environments. Spills such as the Deepwater Horizon spill have been extensively studied in order to understand oil and dispersant fate, toxicity effects, and dispersant effectiveness. The very few studies on dispersant use in freshwater have focused mainly on dispersant effectiveness (Belk, Elliott, & Flaherty; Nagy, Scott, & Hart, 1984; Wrenn et al., 2009) and toxicity effects or the impact on aquatic microbial population (Bhattacharyya et al., 2003a; M. Fingas, 2008; Green & Trett, 1989; B. F. Scott & Glooschenko, 1984; Brian F. Scott et al., 1984). While alluding to the possible risk of contamination from dispersants, several reports have however only emphasized the need to study the impact of dispersant application on drinking water sources (M. F. Fingas, 2011; Herndon, 2010; Owens & Michel, 1995; Vandermeulen & Ross, 1995).

The impact of dispersant application on water quality parameters of a lake pond was explored over a one-year period in one study (Brian F. Scott et al., 1984). Oil and dispersant concentrations were 75 – 100 ppm and 15 – 20 ppm, respectively. Water quality parameters that were monitored included dissolved organic carbon (DOC), dissolved oxygen (DO), nitrate ion, dissolved reactive phosphorus, Total Kjeldahl Nitrogen (TKN), ammonia, sulfate ion, magnesium and calcium ions, chloride ion, dissolved reactive silica, and alkalinity. The monitored parameters provided more insight on the microbial population and their nutrient availability and consumption. Data was however not presented to demonstrate the impact of the presence of crude oil and dispersant on DOC, a parameter that is commonly measured in DWTP. A further development of the previous work (B. F. Scott & Glooschenko, 1984) reported that in the control pond (no oil or dispersant), DOC concentration was about 4.5 ppm while in the oil-only pond, DOC was about 5 ppm. However, in the presence of oil and dispersant, a three-fold increase in DOC was observed (13 – 17 ppm) on day 0. The authors also mentioned that turbidity was high in the oil-dispersant pond, although no actual value was reported. In these studies, no treatment was applied on contaminated water.

Since freshwater bodies are in close proximity to humans and typically serve as sources of drinking water, toxic or potentially toxic compounds and activities that might lead to their introduction into surface water are generally discouraged. In the case of an oil spill and the subsequent application of dispersants, it is uncertain what impact micelles, dispersant-related compounds and dispersant-stabilized oil droplets would have on raw and settled water quality (that is, turbidity, total organic carbon (TOC), UV absorbance at 254 nm (UV_{254}), zeta potential, and surface tension). In addition, the capacity of the current infrastructure in DWTP to handle an oil spill in the presence and absence of dispersants and to generate potable water remains yet to be studied. Such a study will be beneficial to facilitate the development of contingency plans for oil spills in freshwater bodies.

2.5 Conventional drinking water treatment plants: Ballasted flocculation

Ballasted flocculation, under the trade name Actiflo®, combines all three conventional drinking water treatment processes – coagulation, flocculation and sedimentation. It differs from the conventional coagulation-flocculation process in that it requires the addition of microsand and a polymer to increase floc robustness and settling rate (C. Desjardins, Koudjonou, & Desjardins, 2002; E. Guibelin, F. Delsalle, & P. Binot, 1994; Ministère du Développement Durable de l'Environnement et des Parcs (MDDEP), 2009). As a result, retention time in the ballasted flocculation process (13 minutes) is much less than that of the conventional coagulation-flocculation process (30 – 240 minutes on average) (C. Desjardins et al., 2002; E. Guibelin et al., 1994). Lamellas are employed for clarification while sludge recycling to a hydro-cyclone is done to enable the separation and reuse of the microsand. The ballasted flocculation treatment process can be summarized as follows (Ministère du Développement Durable de l'Environnement et des Parcs (MDDEP), 2009): a) under constant mixing, raw water is spiked with coagulant in the coagulation tank; b) coagulated water enters the injection tank where microsand and polymer are injected under constant mixing conditions; c) mixing continues in the floc maturation tank for a given retention time and lastly, d) water enters the lamella-equipped settling tank where sludge settles, is recycled and treated water is directed for further treatment.

2.5.1 Processes involved in contaminant removal

The coagulation process itself requires the addition of chemicals (coagulants) in order to facilitate the destabilization of colloidal or suspended particles in water. Flocculation involves the formation of settleable agglomerates of these particles together with precipitates formed from coagulant addition. Destabilization is possible through the compression of the electrical double layer around particles (thus reducing their repulsion and enabling their aggregation), adsorption and charge neutralization, enmeshment in a growing hydroxide precipitate, and/or adsorption and inter-particle bridging (Crittenden, H., & Montgomery, 2012; R. Desjardins, 1997; Tansel & Sevimoglu, 2006). Charge neutralization occurs when hydrolyzed coagulants counteract charged contaminants in water. This mechanism is typically predominant when alum is dissolved in water at low concentrations to form soluble, monomeric aluminum species (Crittenden et al., 2012; Duan & Gregory, 2003). At high coagulant dosage (> 3 mg Al/L), enmeshment of contaminants in a growing hydroxide precipitate is predominant (Crittenden et al., 2012). Polymers, typically polyacrylamide, are applied and act as a bridge for the formation of denser and more settleable precipitates. In the case of an oil-in-water emulsion, an interplay of the aforementioned destabilization processes is expected to occur given the presence of dispersant-stabilized oil droplets (which would, in theory, function as colloids in water) (Campo et al., 2017; Canizares et al., 2008; Rubi, Fall, & Ortega, 2009).

Conventional coagulants that are typically employed in drinking water treatment include aluminum sulfate or alum, ferric sulfate and ferric chloride. These coagulants dissociate in water to form Al^{3+} and Fe^{3+} ions, which can be hydrolyzed to form monomeric or polymeric species and precipitates. Aluminum monomeric species include Al^{3+}, $Al(OH)_2{}^{+}$, $Al(OH)^{2+}$, $Al(OH)_3$ (precipitate form) and $Al(OH)^{4-}$ while those of ferric salts include Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_3$ (precipitate form) and $Fe(OH)^{4-}$ (Davis & Edwards, 2014; Duan & Gregory, 2003). DWTP typically tend to operate under conditions that favor the formation of precipitates (Figure 2.5).

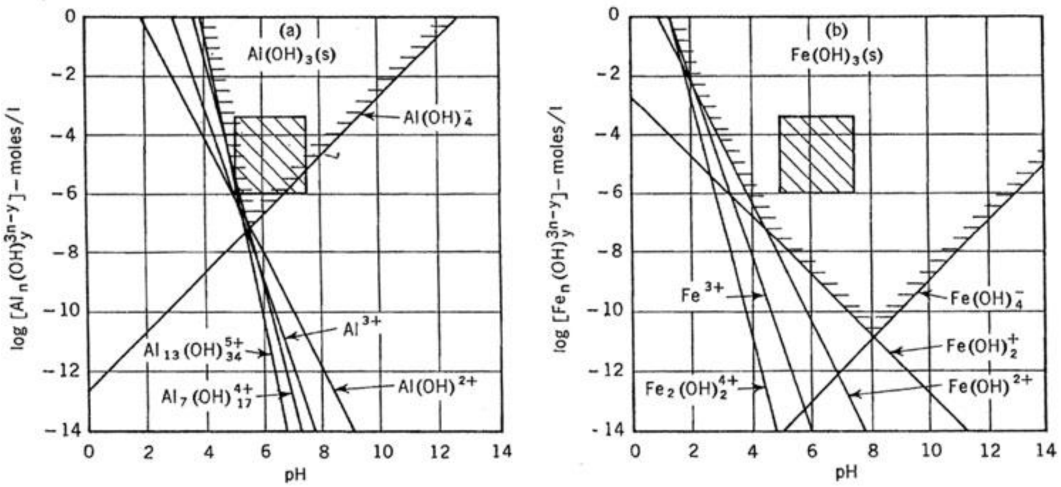


Figure 2.5: Solubility of aluminum- and ferric-hydrolyzed species and precipitates in equilibrium. The shaded square represents the region in which DWTP operate (retrieved from (Stumm & O'Melia, 1968)).

2.5.2 Factors affecting the efficiency of the treatment process

Efficiency of ballasted flocculation is influenced by coagulant type and dosage, water quality, and operational parameters such as pH, alkalinity and temperature. In terms of coagulant type, aluminum and ferric salts are advantageous due to their low cost and efficiency for surface water treatment (Davis & Edwards, 2014). In order to determine the optimum dosage, a jar test and an assessment of water quality parameters such as DOC, UV_{254} and turbidity are necessary. In terms of operational parameters, pH affects the hydrolysis and solubility of coagulants in water (Figure 2.5). pH of coagulation in many DWTP is typically maintained between 6 and 8, although the addition of aluminum and ferric salts tends to lower the pH of the solution. For alum, optimum pH ranges from 6 to 6.2 while for ferric salts, optimum pH is about 5.0 – 5.5 (Crittenden et al., 2012; Davis & Edwards, 2014).

The addition of coagulants to water consumes alkalinity, which leads to a decrease in the pH of water and affects precipitate formation (Davis & Edwards, 2014). For alum, 1 mg/L of $Al_2(SO_4)_3.14H_2O$ consumes 0.5 mg $CaCO_3$/L of alkalinity (R. Desjardins, 1997). Temperature also affects the rate of hydrolysis and solubility of coagulants in water. Typically, at lower temperatures, coagulants dissolve less rapidly and hydrolytic reactions are also quite slow (Duan

& Gregory, 2003). Natural organic matter (NOM) and other organics in water influence water quality and coagulant demand. For surface waters in the region of Montreal, DOC, which is indicative of NOM, varies between 3 and 8 mg C/L depending on the river.

With respect to the removal of petroleum hydrocarbons, the nature of the hydrocarbons will also play a role. Generally, the solubility of a hydrocarbon decreases as its carbon number increases. Hence, its affinity to adsorb on flocs also increases. BaP, for example, has a log K_{OW} value of 6.13 (Smol & Włodarczyk-Makuła, 2017; Stackelberg et al., 2007). Its high K_{OW} and low solubility might indicate why BaP is easily removed by coagulation-flocculation (Vogelsang et al., 2006). About 73% of BaP was successfully removed in Montreal Urban Community wastewater treatment plant through coagulation-flocculation (Pham & Proulx, 1997) using ferric chloride and an anionic polymer. An average of 46% was reported for the removal of 5-ring PAH compounds from coke wastewater and municipal landfill leachate (Smol & Włodarczyk-Makuła, 2017). It can thus be inferred that the more soluble, lighter-weight hydrocarbons might be more difficult to remove through ballasted flocculation.

2.5.3 Addition of powdered activated carbon (PAC) for petroleum hydrocarbon removal

Powdered activated carbon (PAC) is an adsorbent with high surface area and is employed in drinking water treatment for organics removal (Najm, Snoeyink, Lykins Jr., & Adams, 1991; Jessica M. Younker & Walsh, 2015). Its efficiency is influenced by several factors including the characteristics of the adsorbate, adsorbent, and contaminated water system (Rivas, 2017). Contamination of surface water with petroleum hydrocarbons leads to competitive adsorption on PAC surface (A. A. M. Daifullah & B. S. Girgis, 2003; El-Dib, Moursy, & Badawy, 1978; To, Mariñas, Snoeyink, & Ng, 2008). Both petroleum hydrocarbons and naturally occurring organic matter in surface water compete for adsorption sites on PAC, having impacts on petroleum hydrocarbon removal (Rivas, 2017). Depending on the degree of contamination, PAC dosage can range from 1 mg/L to as high as 1000 mg/L (Álvarez-Uriarte, Iriarte-Velasco, Chimeno-Alanís, & González-Velasco, 2010; Jessica M. Younker & Walsh, 2015; Jessica M Younker & Walsh, 2016). In DWTP, PAC can be dosed before coagulation (at the raw water intake) or in a pre-contact tank, at coagulant injection point, or in settled water prior to filtration (Najm et al., 1991). PAC dosage before coagulation offers better mixing conditions and longer contact times (Álvarez-Uriarte et al., 2010; El-Dib et al., 1978; Jaji, 2012a; Najm et al., 1991; Jessica M Younker & Walsh, 2016). However, competitive adsorption is likely to be more pronounced (Najm et al., 1991). Simultaneous PAC and coagulant injection takes advantage of the turbulent conditions present in the rapid mix to improve PAC contact with contaminants in water (Najm et al., 1991). The presence of coagulant has been reported to either have no effect (Altmann et al., 2015) or limit contaminant removal (Álvarez-Uriarte et al., 2010). The reason for the latter has been attributed to the incorporation of PAC in flocs (Altmann et al., 2015; Álvarez-Uriarte et al., 2010; Najm et al., 1991). When PAC is injected in settled water entering a filter unit, PAC adsorption capacity can be utilized to its maximum when its particles are trapped in filter media. However, PAC could also pass through the filter media and end up in the distribution network (Najm et al., 1991).

2.6 Ballasted flocculation for the removal of trace petroleum hydrocarbons from surface water

To the best of the author's knowledge, ballasted flocculation has been evaluated for its ability to remove petroleum hydrocarbons in only *two* studies – one in surface water and the other in wastewater. The efficiency of the Actiflo systems in Prince Albert DWTP was assessed for petroleum hydrocarbon removal following an oil spill (200,000 – 250,000 L of heavy crude) in the source water, the North Saskatchewan River (Vincent, 2017). Although the systems were praised for their effectiveness in hydrocarbon removal, given the sensitive nature of the information, there was no quantitative evidence of the concentration and type of measured hydrocarbons reported publicly in order to justify the effectiveness of the treatment process. A risk assessment (Inc., 2016) of the North Saskatchewan River after the incident evaluated the capacity of several DWTP, including that of Prince Albert, to generate potable water. The treatment process at the Prince Albert DWTP was clearly described to include powdered activated carbon (PAC) pre-contact basins and oxidation using potassium permanganate prior to the Actiflo systems. The assessment concluded that petroleum hydrocarbon removal in Prince Albert DWTP can be further augmented through higher PAC and coagulant dosage. It is however unclear whether the conclusion on the treatment efficiency of the Prince Albert DWTP, as presented in (Vincent, 2017), excludes the contribution of the PAC and advanced oxidation pre-treatment processes in the evaluation of the Actiflo system for petroleum hydrocarbon removal. It can however be inferred that, based on measured concentrations in the North Saskatchewan River (Table 2.5), trace hydrocarbon concentrations would have arrived at the DWTP.

Actiflo® was also tested as a pre-treatment for petrochemical wastewater (Ribera-Pi et al., 2020). Wastewater contained high concentrations of petroleum hydrocarbons (benzene = 139 µg/L, toluene = 233 µg/L, xylenes = 838 µg/L, naphthalene = 222 µg/L, and DOC ≈ 90 mg/L), which are not similar to those recorded from oil-spill case studies (Table 2.5). Removals ranged from 28 % (for benzene) to 80 % (for naphthalene) when 50 mg/L of ferric chloride was used. These findings might however not necessarily be transferable to the case of a trace petroleum contamination in surface water owing to the difference in water matrix.

Compared to the paucity of research on the application of ballasted flocculation for petroleum hydrocarbon removal, conventional coagulation-flocculation has been extensively studied for treating mainly highly-concentrated, petroleum-contaminated wastewaters (that is, real and synthetic produced water, refinery wastewater, and oil-in-water emulsions). Studies involving low concentrations of petroleum hydrocarbons exist mainly for polyaromatic hydrocarbons in the aforementioned wastewaters as well as surface water.

Surface water: Coagulation-flocculation with alum as coagulant was capable of significant reduction of BaP concentrations in some studies (Nowacka & Włodarczyk-Makuła, 2014; Rosińska & Dąbrowska, 2018). Up to 84 % BaP reduction from an initial concentration of 0.05 µg/L (Rosińska & Dąbrowska, 2018). Since a mix of PAH compounds was injected into surface water, BaP removal was not affected by the presence of other crude oil components such as monoaromatics and alkanes. Two other studies on the application of coagulation-flocculation for the treatment of petroleum-contaminated surface water involved higher oil concentrations and focused on the effect of the presence of oil on filter performance (Tansel & Vilar, 2005) and mechanism of oil droplet removal during the treatment process (Tansel & Dimitric-Clark, 2002). In both studies, the efficiency of the process for the removal of *trace* concentrations of specific oil components such as BTEX was however not evaluated.

Produced water/refinery wastewater: Coagulation-flocculation has been applied for the treatment of produced water from hydraulic fracturing operations and refinery wastewater (Pourrezaei et al., 2011; Wang et al., 2017; Zhai et al., 2017; Zhang, 2017). Coagulation has also been studied for its efficiency when combined with dissolved air flotation (DAF) for treating the same wastewater (Luthy et al., 1978; Moursy & El-Ela, 1982; Santo et al., 2012). For the reduction of total petroleum hydrocarbons (TPH) in produced water, coagulation alone was reported to be insufficient (< 90 %) and the addition of up to 1000 mg/L of powdered activated carbon (PAC) was necessary (Rosenblum et al., 2016). In all studies, the analysis of the removal of the regulated carcinogenic petroleum compounds such as BTEX was not performed.

Synthetic or other types of wastewater: The application of coagulation-flocculation for the removal of PAH compounds, high concentrations of TPH, oil and grease (O&G), and total organic carbon (TOC) in synthetic or other types of wastewater has been explored in several studies (Canizares et al., 2008; Mancini et al., 2017; Shabeer et al., 2014; Smol & Włodarczyk-Makuła, 2017; Tansel & Eifert, 1999; Tansel & Pascual, 2011; Tansel & Sevimoglu, 2006; Vogelsang et al., 2006; J. Y. Yang et al., 2016; You et al., 2018; Jessica M Younker & Walsh, 2016). Coagulation-flocculation was reported to be ineffective for the removal of soluble hydrocarbons (Campo et al., 2017; Pham & Proulx, 1997). In another study, 40 % benzene reduction was observed, from an initial concentration of 1000 µg/L, when ferric sulfate (80 mg/L) followed by 500 mg PAC/L was added (Shouli et al., 1992). When only ferric sulfate (80 mg/L) and a cationic polymer were used, an average benzene removal of 5 % was observed.

Oil-in-water emulsions: Studies on the application of coagulation-flocculation for the removal of emulsified oil droplets have mainly involved high oil concentrations, the use of synthetic produced water [that is, ultrapure water + crude oil + salt + nonionic surfactant (Triton-X or Span 20)], and the use of coagulation-flocculation-DAF (CF-DAF) treatment systems (Al-Shamrani et al., 2002; Jaji, 2012b; Jessica M. Younker & Walsh, 2014). It is also important to note that dispersants (mix of additives, solvents, and surfactants, typically anionic and nonionic) were not employed and a quantification of the residual dispersant or surfactant concentration was not performed. The studies did not also indicate whether surfactants were present above or below the CMC in order to account for the presence or absence of micelles.

To summarize, the existing literature demonstrates that:

a) Conventional coagulation-flocculation has been extensively studied for the removal of high concentrations of petroleum hydrocarbons from different types of wastewater.

- As part of their physicochemical treatment chain, many DWTP in North America and Europe are shifting from the use of conventional coagulation-flocculation systems to ballasted flocculation. As a result, it is necessary to evaluate the efficiency of ballasted flocculation for the removal of *trace* petroleum hydrocarbons from *surface* water.

b) More research is necessary on the application of ballasted flocculation for *trace* petroleum hydrocarbon (dissolved and emulsified) removal.

- The existing studies did not evaluate the removal of *trace* carcinogenic petroleum hydrocarbons from *surface* water. Trace concentration studies exist mainly for PAH compounds.

c) Literature lacks an analysis on the impact of dispersant use, at concentrations below and above CMC, on drinking water quality.

- Such a study would be helpful in the preparation of contingency plans in the event of an oil spill in surface water. It will also enable the identification of measurable indicators at DWTP for hydrocarbon contamination and treatment efficiency.

d) The efficiency of ballasted flocculation for diminishing residual dispersant concentration and dispersant-stabilized oil droplets in surface water needs to be evaluated.

- Oil-in-water emulsion studies focused on CF-DAF systems and employed a single surfactant (nonionic) during emulsification. The efficiency of the treatment for surfactant removal was also not evaluated.

CHAPTER 3 RESEARCH OBJECTIVES, HYPOTHESES AND METHODOLOGY

3.1 Knowledge Gaps

In light of the literature review on the application and efficiency of ballasted flocculation for the elimination of petroleum hydrocarbons from surface water, it is evident that there is a need to:

a) Study the efficiency of the removal of *trace* dissolved petroleum hydrocarbons (specifically BTEX) from surface water.

b) Evaluate the efficiency of ballasted flocculation for the removal of *trace* dispersant-related compounds and dispersant-stabilized oil droplets from surface water.

c) Analyze the impact of the presence of micelles and the influence of the dispersant matrix characteristics on surface water quality and treatability.

d) Identify suitable indicators of petroleum hydrocarbon contamination for the benefit of water treatment plant operators.

3.2 Research Objectives and Hypotheses

This research study aims to evaluate the effectiveness of ballasted flocculation for the removal of *trace* dissolved and emulsified petroleum compounds, dispersant-stabilized oil droplets and other dispersant-related compounds from surface water. More specifically, the research objectives include:

a) An evaluation of the performance of ballasted flocculation for the removal of *trace* dissolved petroleum hydrocarbons (BTEX) from surface water.

- Determine whether the addition of an adsorbent is necessary. If yes, what would be the concentration, contact time, and overall attainable removal?
- Evaluate the efficiency of conventional coagulants, alum and ferric sulfate, for *trace* dissolved petroleum hydrocarbon removal and the effect of the presence of coagulant on the adsorptive properties of the adsorbent.

b) An assessment of the impact of dispersant application on the efficiency of ballasted flocculation.

- Evaluate water quality and coagulant efficiency subsequent to ballasted flocculation of crude oil-contaminated surface water in the presence and absence of dispersant.
- Determine the capacity of ballasted flocculation for the elimination of dispersant-stabilized oil droplets and dispersant-related compounds in surface water.

c) Study the impact of the presence of micelles and the influence of the dispersant matrix characteristics on ballasted flocculation efficiency.

- Evaluate the contribution of surfactants (in the dispersant matrix) to surface water contamination and treatability.
- Investigate the impact of the presence of surfactant micelles on surface water contamination and treatability.

d) Identify measurable indicators of *trace* petroleum hydrocarbon contamination (dissolved and emulsified) in surface water.

- Evaluate commonly measured water quality parameters such as turbidity, dissolved organic carbon (DOC), UVA_{254}, and zeta potential in raw and settled water.
- Evaluate additional parameters such as total organic carbon (TOC) and surface tension in raw and settled water.

The hypotheses that were tested during this research work are enumerated:

Hyp. 1: The addition of an adsorbent is necessary to reduce *trace* dissolved petroleum hydrocarbon concentrations (below 0.5 µg/L) in surface water, as ballasted flocculation alone is not effective.

Novelty: Here, dissolved petroleum hydrocarbons refer to dissolved BTEX, specifically benzene. Since case studies show that only *trace* concentrations (< 20 µg/L of benzene) arrive at DWTP, a study on the removal of *trace* BTEX stemming from a simulated petroleum spill in surface water would shed more light on the treatment potential of the ballasted flocculation process. Such a study has however not yet been done.

The hypothesis will be refuted if benzene concentration in settled water is below 0.5 µg/L.

Hyp. 2: Ballasted flocculation efficiency is not limited by the presence of crude oil and dispersant concentrations.

Novelty: Crude oil contamination of surface water, combined with dispersant remediation, has not been evaluated for its impact on ballasted flocculation efficiency. Such a study will shed more light on the robustness of the treatment process to handle *trace* petroleum and dispersant concentrations while generating the required settled water quality.

The hypothesis will be refuted if the monitored water quality parameters for settled water, subsequent to ballasted flocculation of dispersant-crude oil-contaminated surface water, are not within the range of that observed following ballasted flocculation of uncontaminated surface water.

Hyp. 3: The application of low dispersant concentrations to crude oil spills in surface water introduces dispersant-related compounds, specifically surfactants, that are not identifiable by the monitored water quality parameters and not removed by ballasted flocculation.

Novelty: Ballasted flocculation has not been studied for its ability to remove dispersant-related compounds, specifically surfactants, stemming from the application of low dispersant concentrations to crude oil spills in surface water. Such a study will be necessary in order to conclude whether no-cleanup (that is, no dispersant application) is a better option with respect to drinking water quality.

The hypothesis will be refuted if residual surfactant (DOSS) concentration can be reduced below the U.S. EPA requirement for protection of aquatic life (40 µg/L).

Hyp. 4: When oil-spill dispersants are present in surface water, surfactants alone are not the major driving factors to contamination.

Novelty: Oil-spill dispersants are known to be made up of three classes of compounds – additives, surfactants, and solvents. Since surfactants are the active ingredients and are indispensable to the effective functioning of oil-spill dispersants, it is necessary to understand their contribution to surface water contamination and the subsequent treatability by ballasted flocculation. Such a study will also shed more light on the influence of the dispersant matrix characteristics.

The hypothesis will be refuted if compared to a commercial dispersant, a surfactant-only dispersant system does not show a delayed effect on surface water contamination and treatability through the monitored water quality parameters.

Hyp. 5: In the presence of crude oil, surfactant micelles account for majority of the observed organic carbon contamination of the source water.

Novelty: Such a study that quantifies the effect of the presence of surfactant micelles on crude oil contamination in surface water has not been done.

The hypothesis will be refuted if the percent organic carbon contribution from the applied surfactant concentration does not exceed that of crude oil droplets.

Hyp. 6: Among the commonly monitored water quality parameters, TOC is the best indicator of *trace* petroleum and dispersant contamination in raw surface water.

Novelty: The sensitivity of the monitored water quality parameters has not been investigated for *trace* petroleum and dispersant contamination in surface water. Such an analysis will enable DWTP to access the suitability of their water quality parameters as indicators of petroleum hydrocarbon contamination.

The hypothesis will be refuted if TOC, upon crude oil and dispersant contamination, does not show the most deviation from (i) the measured values in uncontaminated raw water at the time of the tests; and (ii) the observed variations in raw water based on source water monitoring data.

3.3 Research Methodology

In order to validate or refute the proposed hypotheses, the following steps were conducted:

a) Preparation of stock solution containing only dissolved petroleum hydrocarbons (Hyp. 1)

b) Preparation of contaminated surface water containing *trace* dissolved petroleum hydrocarbons (< 20 µg/L benzene) (Hyp. 1)

c) Design of batch adsorption and kinetics tests (Hyp. 1)

d) Design of ballasted flocculation tests (Hyp. 1 – 6)

e) Preparation of dispersant-crude oil- and crude oil-contaminated surface water (Hyp. 2 – 3)

f) Preparation of dispersant-contaminated surface water (Hyp. 4)

g) Preparation of surfactant-crude oil-contaminated surface water (Hyp. 5)

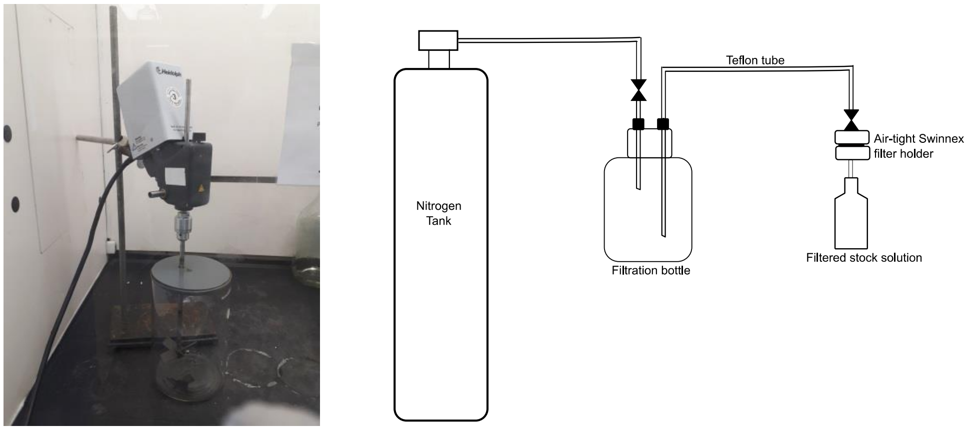
h) Analysis of relevant water quality parameters, including particle size and residual concentrations of dispersant-related compounds (Hyp. 1 – 6)

3.3.1 Trace dissolved petroleum hydrocarbons – contamination of surface water (Hyp. 1)

To simulate contamination by *trace* dissolved petroleum hydrocarbons (BTEX) in surface water, the type of petroleum products had to first be selected. Diesel and gasoline were chosen due to their relatively higher BTEX content compared to crude oil (Table 2.2). Filtered stock solutions of each petroleum product were prepared to obtain only the dissolved portion. Then, a given volume was spiked into surface water for the tests.

3.3.1.1 Preparation of filtered stock solution and contaminated surface water

Stock solution of each petroleum product was prepared by adding 25 mL of the product to 975 mL of ultrapure water in a 2-L circular beaker, which had to be custom-made (without a spout) and equipped with a Teflon-based lid to minimize volatilization. The work volume in the beaker was set to 1 L to allow a maximum theoretical equilibrium volatilization of 20 – 25 % BTEX based on Henry’s law constants. The lid was pierced at an off-center position for the impeller shaft of the overhead agitator (Heidolph RZR 1, 280 – 2200 rpm) (Figure 3.1a). An off-center mixing design, equipped with a pitch blade turbine (four blades, diameter = 7.5 cm), was chosen for optimized mixing of both liquid phases (Kevin J. Myers, Mark F. Reeder, & Julian B. Fasano, 2002). An offset distance of 20 mm was set based on one-third of the beaker radius, ensuring sufficient distance between the impeller blades and the beaker wall. The mixture was mechanically agitated at 1050 rpm for two minutes and then filtered through a 0.3 µm glass fiber filter (Advantec, GF-75) to obtain the dissolved fraction of petroleum hydrocarbons. Filtration was carried out using a nitrogen-based, air-tight setup to minimize volatilization and improve repeatability of the preparation (Figure 3.1b). Filtered stock solution samples were collected in sample vials that were filled to the brim with no headspace. Characterization of the filtered stock solution was performed to determine its BTEX and DOC concentrations.



(a) (b)

Figure 3.1: (a) Setup for mechanical agitation of stock solution; and (b) filtration setup to obtain dissolved petroleum hydrocarbons.

Surface water from the Des Prairies River (Quebec, Canada) was utilized for all tests in this thesis. After sampling, water quality was analyzed for pH, turbidity, DOC, UVA_{254}, zeta potential, surface tension and alkalinity. A volume of 150 mL of filtered diesel stock solution or 4 mL of filtered gasoline stock solution was spiked into 2.74 L of surface water in order to obtain a final BTEX concentration of less than 60 µg/L and benzene concentration below 10 µg/L. The mixture was agitated for 24 hours, without headspace, using a magnetic stir bar (United States Environmental Protection Agency (USEPA), 2016) in a capped amber bottle. Contaminated surface water was then transferred into the jar-test beaker for ballasted flocculation tests (Section 3.3.4) and initial samples were withdrawn and analyzed for BTEX, turbidity, DOC, UVA_{254}, zeta potential and surface tension.

3.3.1.2 Batch adsorption and kinetics tests

Powdered activated carbon (PAC) served as an ideal adsorbent for benzene reduction due to its high surface area and affinity for dissolved organics (A. A. M. Daifullah & B. S. Girgis, 2003; El-Dib et al., 1978). PAC is also readily available in many DWTP. Adsorption isotherm and kinetics tests were necessary to determine the appropriate PAC concentration and contact time.

For both tests, surface water was filtered using a pre-rinsed 0.45 µm membrane filter (PALL Corporation) to avoid interference from the water matrix. To simulate contamination, a volume of filtered stock solution of either diesel or gasoline was spiked into 250 mL amber bottles using an airtight Luerlock syringe (SGE). Then, to initiate adsorption or kinetics experiments, a calculated volume of pre-wetted PAC (Aquasorb CB1-MW-F (Jacobi, Sweden)) slurry was added to the bottles, which were completely filled with filtered surface water leaving no available headspace.

For adsorption isotherms, PAC concentrations of 1, 2, 5, 10, 30, 50, 70 and 100 mg/L were tested. The appropriate dose was determined as the concentration that reduces benzene concentration below Quebec regulations (0.5 µg/L). At this dose, kinetics tests were done at contact times of 1, 3, 5, 10, 15, 30, 60 min, 3 h and 24 h. A shaker was employed to agitate samples at 31 rpm, after which filtration using an airtight Luerlock syringe (SGE) and 0.3 µm glass fiber filters (Advantec, GF-75) was performed. Samples in both adsorption isotherm and kinetics tests were analyzed for residual BTEX and DOC concentrations. A duplicate bottle as well as a control bottle without PAC was included in all experiments to determine the experimental error and the initial BTEX concentration that considered losses due to adsorption on the bottle's material.

After determining the optimum PAC concentration and contact time, it was necessary to evaluate dissolved benzene removal for a combined PAC and ballasted flocculation scenario. This treatment was considered as a worst-case scenario where the DWTP has no pre-contact tank and hence, would inject PAC and coagulant simultaneously.

3.3.2 Emulsified petroleum hydrocarbons: contamination of surface water in the presence and absence of low dispersant concentrations (Hyp. 2 – 3)

In order to assess the impact of dispersant application, two crude oil contamination scenarios were studied in the presence and absence of dispersant. Dispersant was requested from manufacturers on the National Contingency Plan Product Schedule (U.S. EPA). Total Fluides (France) was the only manufacturer that was willing to provide a dispersant sample for tests. The dispersant, Finasol® OSR 52, has a density of 1100 g/L and contains more than 30 % nonionic surfactants and 15 – 30 % anionic surfactants (Total Fluides, 2015). Residual dispersant was measured by quantifying an anionic surfactant, sodium dioctyl sulfosuccinate (DOSS), which is present in Finasol® OSR 52 at 20 – 25 wt%. DOC and the critical micelle concentration (CMC), which is the concentration at and above which micelles form, were measured in ultrapure and raw surface water. Crude oil was retrieved following the spill at Prince Albert (Saskatchewan, Canada). Its composition was 70 – 80 % bitumen and 20 – 30 % condensate (dilbit) (Government of Canada, 2013).

After raw water sampling, the following parameters were analyzed: pH, turbidity, DOC, TOC, UVA_{254}, zeta potential, surface tension, alkalinity, particle size, and residual dispersant measured as DOSS. In the presence of dispersant, the standard protocol for the preparation of an oil-in-water emulsion was followed in order to generate dispersant-stabilized oil droplets in water (Katepalli & Bose, 2014). First, 2.5 L of raw surface water was added to a 4 L beaker and using an overhead agitator (Heidolph RZR 1), stirring began at 664 rpm. Then, Finasol® OSR 52 was added at a dispersant-to-oil ratio of 1 to 20 (1:20) and agitated for 1 min. Lastly, crude oil was introduced and agitation continued until the third minute. For crude oil-only tests, the same protocol was followed without dispersant addition. Crude oil was therefore added and the mixture was agitated for 3 min. After contaminated surface water was transferred to the jar-test beaker for ballasted flocculation tests (Section 3.3.4), initial samples were withdrawn and analyzed for oil droplet size, residual dispersant reported as DOSS, turbidity, TOC, UVA_{254}, zeta potential, and surface tension.

For efficient mixing, the impeller shaft was fixed off the center of the beaker and the attached pitch blade (four blades with a diameter of 7.5 cm) was positioned at one-third of the water height in the beaker (Kevin J Myers, Mark F Reeder, & Julian B Fasano, 2002). The 1:20 dispersant-to-oil ratio is typically employed in the event of a spill in marine environments (International Tanker Owners Pollution Federation Limited (ITOPF), 2011). Due to its viscosity, Finasol® OSR 52 was first diluted using ultrapure water at a ratio of 1 to 10 prior to use. In 2.5 L of raw water, dispersant and crude oil concentrations were 5.2 mg/L and 109 ± 13 mg/L, respectively. Relative to raw water, oil and dispersant concentrations were 0.010 % (w/w) and 0.00052 % (w/w), respectively.

3.3.3 Preparation of dispersant-contaminated surface water (Hyp. 4) and micelle-crude oil-contaminated surface water (Hyp. 5)

A formulated and commercial dispersant were used to study the influence of dispersant matrix characteristics and the contribution of surfactants to surface water contamination and treatability (**Hyp. 4**). The commercial oil-spill dispersant that was utilized was Finasol OSR® 52 while the formulated dispersant was a mix of a nonionic (Tween 80) (Fisher Scientific) and an anionic surfactant (sodium dodecyl sulfate, SDS) (Sigma-Aldrich). These surfactants were chosen based on the surfactant types present in Finasol® OSR 52 and their solubility in water. It was necessary to determine an appropriate ratio of these surfactants that would enable the formulated dispersant to reduce surface tension at the same degree as Finasol® OSR 52. First, individual solutions of both surfactants were prepared in ultrapure water at a concentration of 5 % (w/v). A mix of surfactants was then prepared at the following ratios (Tween80:SDS): 50:50, 40:60, and 20:80. Surface tension at each mix ratio was measured in ultrapure water at different concentrations (0 – 2.4 %) and compared with that of Finasol® OSR 52. The mix ratio with the closest decline in surface tension to that of Finasol® OSR 52 was chosen as the formulated dispersant. Its surface tension was also measured in raw surface water for comparison.

After raw water sampling, the following parameters were analyzed: pH, turbidity, DOC, TOC, UVA_{254}, zeta potential, surface tension, alkalinity, particle size, and residual dispersant measured as DOSS and SDS. Raw surface water contaminated with the formulated dispersant *or* the commercial dispersant was then prepared at increasing dispersant concentrations – 2 mg/L, 20 mg/L, 200 mg/L, 2000 mg/L, 4000 mg/L, and 8000 mg/L. First, 2.5 L of raw surface water was added to a 4 L beaker and using an overhead agitator (Heidolph RZR 1), stirring began at 664 rpm. Then, the formulated or commercial dispersant was added and agitated for 3 min. The resulting dispersant-contaminated surface water was then transferred to the jar-test beaker for ballasted flocculation and samples were withdrawn and analyzed for turbidity, TOC, UVA_{254}, zeta potential, surface tension, and residual dispersant as SDS or DOSS. A 10-month water quality monitoring of the Des Prairies River was also performed to evaluate the significance of measured changes. Ballasted flocculation was discontinued at the dispersant concentration that yielded settled water turbidity greater than 1 NTU (typical DWTP objective for settled water).

The formulated dispersant system was applied at two different concentrations in order to expound on the impact of surfactant micelles on crude oil-contaminated water quality and treatability (**Hyp. 5**). Low surfactant concentration, introducing only surfactant monomers, was applied at a dispersant-to-oil ratio of 1:20 (5.2 mg/L) while a high concentration was applied at 1.4 times the critical micelle concentration (1.4xCMC = 10 400 mg/L) to ensure the presence of surfactant micelles. An average crude oil concentration of 236 ± 27 mg was employed. The formulated dispersant was diluted ten times using ultrapure water to enable its extraction and injection in raw water. In both scenarios, contamination was as follows: 2.5 L of raw surface water in a 4 L beaker was stirred at 664 rpm. At t=0, the formulated dispersant was added at either 1:20 or 1.4xCMC. At t=1 min, crude oil was added and stirring was stopped at the third minute. Contaminated raw water was then transferred to the jar test beaker for ballasted flocculation tests. Samples were taken for turbidity, TOC, UVA_{254}, zeta potential, surface tension, and residual dispersant measured as SDS.

3.3.4 Design of jar tests (Hyp. 1 – 6)

For jar tests to validate Hyp. 1, ballasted flocculation was simulated in a single modified acrylic B-Ker™ jar (Phipps&Bird), whose bottom sampling port and hole had been removed and sealed. An acrylic-based lid was built to ensure air-tightness and minimize loss of volatile compounds while mixing was realized with an overhead stirrer (Caframo) (Figure 3.2). The lid was equipped with two orifices – one for microsand addition and the other for coagulant injection and sampling.

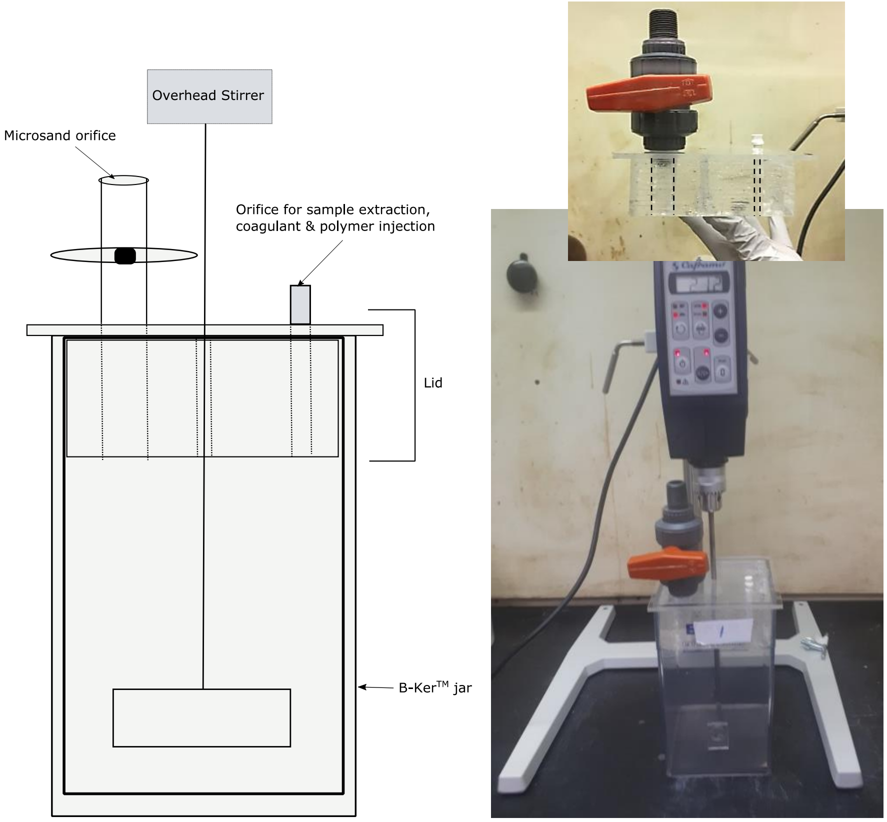


Figure 3.2: Experimental setup for jar tests including a modified B-Ker™ jar to treat 2 L of contaminated raw water. Beaker lid touched water surface (no headspace).

For jar tests involving dispersants (Hyps. 2 – 5), the common jar-test square beaker (B-Kr^2) could not be employed due to its adsorption affinity for petroleum hydrocarbons. As a result, a custom-made, round borosilicate glass beaker, whose design was based on specifications in (American Water Works Association (AWWA), 2004), was utilized for all tests. The beaker was equipped with baffles for adequate mixing, a lid to reduce volatilization, and an overhead agitator (BDC) that was connected to a flat blade impeller (Figure 3.3). Headspace was minimal.

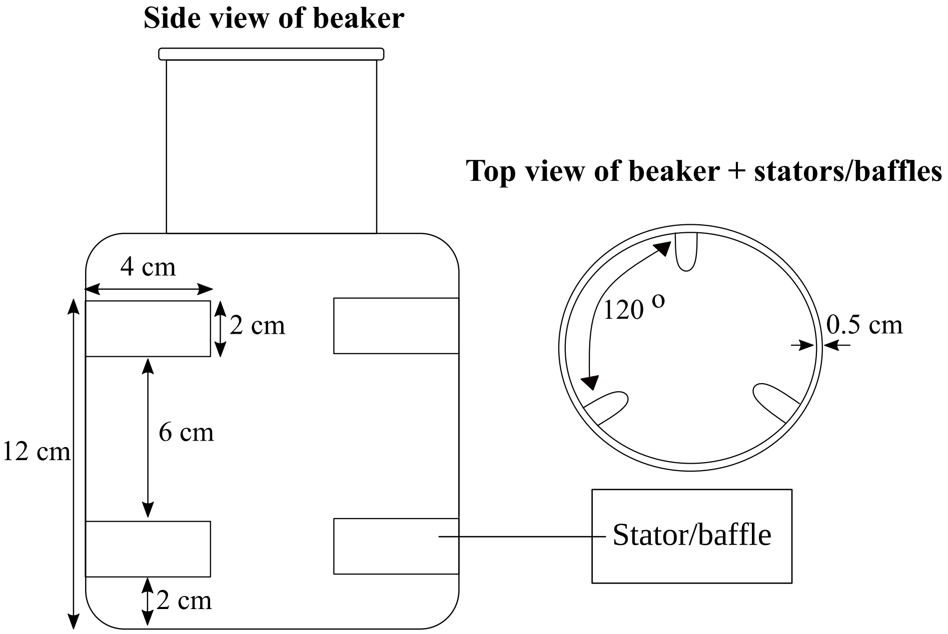


Figure 3.3: Modified beaker design (Hypotheses 2 – 5) to treat 2 L of contaminated raw water.

For all jar tests involving petroleum products (Hyps. 1 – 3, 5), a series of three ballasted flocculation tests were conducted for each simulated contamination. The first was a control test whose purpose was to evaluate the impact of agitation on contaminant volatilization as well as to account for volatilization and contaminant adsorption on the beaker. A 'mock' ballasted flocculation procedure was followed for all control tests. This means that instead of injecting coagulant at time=0 and polymer at the 2nd and 4th minutes, ultrapure water was injected at the same volume as that of the coagulant and polymer, respectively. In addition, instead of the addition of microsand, the orifice was opened for a few seconds and then closed. Measured contaminant concentration at the end of each control test was considered as the initial concentration (C_0) in order to calculate percent removals.

Ballasted flocculation tests were then conducted with alum (*ALS*, Kemira: 4.3 % Al by wt) and ferric sulfate (*PIX 312*, Kemira: 12.3 % Fe by wt), respectively. Alum doses were optimised based on DOC reduction in uncontaminated raw water and an equivalent ferric sulfate dose was then calculated and tested for comparison. The optimal dosages were determined for the source water in the absence of contamination in order to study the expected disturbance to treatment caused by contaminated waters reaching a treatment process operated under optimal conditions.

Hydrex 3613 (Veolia), a cationic polyacrylamide, was employed as polymer at a dose of 0.22 mg/L in all tests. Microsand was used in all tests at a dose of 4 g/L.

After contaminated surface water was transferred into the jar-test beaker and covered with the lid, stirring using a flat blade impeller began at 212 rpm and coagulant was injected at time=0. After two minutes of agitation, 8 g of microsand was added and 50 % of the polymer dose was injected. The remaining polymer dose was injected after two additional minutes of agitation and mixing was maintained at 212 rpm for floc maturation until the 10th minute. Finally, water samples were collected after 3 minutes of settling (Figure 3.4).

Ballasted flocculation tests with alum and ferric sulfate were also conducted for raw water containing no petroleum hydrocarbons. Results were then compared with those from tests ran on contaminated surface water to assess the impact of contamination on raw and settled water quality.

For jar tests involving only dispersants (Hyp. 4), ballasted flocculation tests were only done with alum as coagulant.

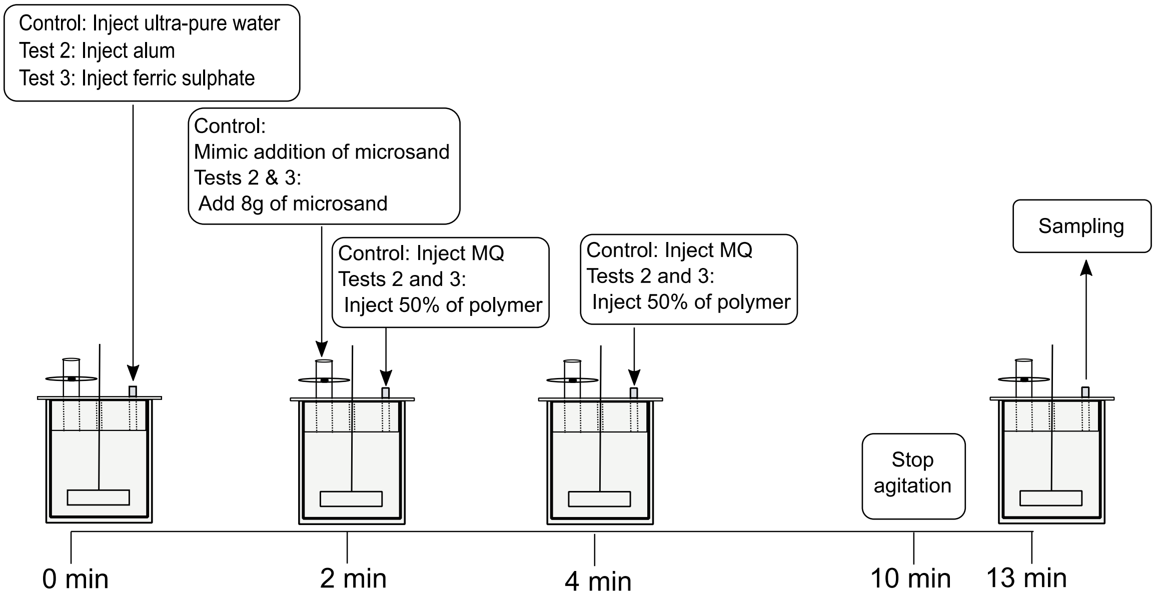


Figure 3.4: General procedure for ballasted flocculation tests.

3.3.5 Analytical methods

Different parameters were measured to quantify the removal and impact of *trace* petroleum hydrocarbons and dispersants on water quality (Table 3.1). Tests were analyzed for: a) BTEX, turbidity, DOC, UVA_{254}, surface tension, and zeta potential (***Hyp. 1***); b) oil droplet size, residual dispersant measured as DOSS, turbidity, TOC, UVA_{254}, surface tension, and zeta potential (***Hyp. 2 – 3***); c) residual dispersant measured as DOSS or SDS, turbidity, TOC, UVA_{254}, surface tension, and zeta potential (***Hyp. 4***); d) residual dispersant measured as SDS, turbidity, TOC, UVA_{254}, surface tension, and zeta potential (***Hyp. 5***). Analysis of benzo(a)pyrene was not possible since its concentration was too low in the utilized crude oil (***Hyp. 2 – 3, 5***).

Table 3.1: Monitored parameters and their corresponding analytical methods.

Parameter	Unit	Description
Alkalinity and pH	mg $CaCO_3$/L	Accumet AB15 pH meter, SM 2320 B (American Public Health Association (APHA), American Water Works Association (AWWA), & Water Environment Federation (WEF), 2012)
Turbidity	NTU	Turbidimeter, Hach 2100 N SM 2130 B (American Public Health Association (APHA) et al., 2012)
Dissolved Organic Carbon (DOC)	mg C/L	Sievers Innovox TOC Laboratory Analyzer (Suez) SM 5310 B (American Public Health Association (APHA) et al., 2012)
Total Organic Carbon (TOC)	mg C/L	Sievers Innovox TOC Laboratory Analyzer (Suez) SM 5310 B (American Public Health Association (APHA) et al., 2012)
UVA_{254}	cm^{-1}	Filtration using pre-rinsed 0.45 µm filter (PALL Corporation) (American Public Health Association (APHA) et al., 2012)
Surface Tension	mN/m	Pendant drop method using OCA20 (Dataphysics) (Berry et al., 2015; Stauffer, 1965)
Zeta Potential	mV	Zetasizer Nano (Malvern Instruments) (Duan, Wang, Guo, & Gregory, 2014)
Particle or Oil Droplet Size	µm	Mastersizer 3000^{TM} (Malvern Instruments) (Malvern Instruments Ltd., 2011)
C_{10} – C_{50}	mg/L	GC-FID ((CEAEQ), 2016)
BTEX	µg/L	SBSE-GC-MS (Pastor-Belda, Viñas, Campillo, & Hernández-Córdoba, 2019; Tienpont, David, Bicchi, & Sandra, 2000) ITEX-GC-MS (Jochmann, Yuan, Schilling, & Schmidt, 2008; Kędziora-Koch & Wasiak, 2018; Laaks, Jochmann, Schilling, & Schmidt, 2015)
Residual Dispersant as DOSS or SDS	µg/L	UHPLC-MS/MS (Mathew et al., 2012)

Table 3.2: Experimental approach to refute hypotheses and the corresponding peer-reviewed articles.

	Hypothesis	Experimental Approach	Expected Results	Article
1	The addition of an adsorbent is necessary to reduce *trace* dissolved petroleum hydrocarbon concentrations (below 0.5 µg/L) in surface water, as ballasted flocculation alone is not effective	Preparation of filtered stock solution and contaminated surface water Ballasted flocculation jar tests Batch adsorption and kinetics tests	Efficiency of ballasted flocculation for the removal of trace dissolved petroleum hydrocarbons Influence of the presence of coagulant on PAC adsorption efficiency for trace petroleum hydrocarbon removal	1
2	Ballasted flocculation efficiency is not limited by the presence of crude oil and dispersant concentrations	Preparation of dispersant-crude oil-contaminated surface water Preparation of crude oil-contaminated surface water Ballasted flocculation jar tests of contaminated and uncontaminated raw water	Comparison of settled water quality subsequent to ballasted flocculation of contaminated and uncontaminated raw water Efficiency of ballasted flocculation for the removal of crude oil droplets in the presence and absence of dispersants	2
3	The application of low dispersant concentrations to crude oil spills in surface water introduces dispersant-related compounds, specifically surfactants, that are not identifiable by the monitored water quality parameters and not removed by ballasted flocculation	Preparation of dispersant-crude oil-contaminated surface water Preparation of crude oil-contaminated surface water Ballasted flocculation jar tests	Efficiency of ballasted flocculation for the removal of dispersant-related compounds	2

Table 3.2: Experimental approach to refute hypotheses and the corresponding peer-reviewed articles (continued).

	Hypothesis	Experimental Approach	Expected Results	Article
4	When oil-spill dispersants are present in surface water, surfactants alone are not the major driving factors to contamination	Preparation of dispersant-contaminated surface water using a commercial and a formulated dispersant Ballasted flocculation jar tests	Identification and comparison of the concentration at which contamination is detected Impact of the dispersant matrix characteristics	3
5	In the presence of crude oil, surfactant micelles account for majority of the observed organic carbon contamination of the source water	Preparation of dispersant-crude oil-contaminated surface water using the formulated dispersant at a concentration below CMC (presence of surfactant monomers) Preparation of dispersant-crude oil-contaminated surface water using the formulated dispersant at a concentration above CMC (presence of surfactant micelles) Ballasted flocculation jar tests	Quantification of the TOC contribution of all components of the contaminated water system	3
6	Among the commonly monitored water quality parameters, TOC is the best indicator of *trace* petroleum and dispersant contamination in raw surface water	Preparation of dispersant-crude oil-contaminated surface water Preparation of crude oil-contaminated surface water Ballasted flocculation jar tests of contaminated and uncontaminated raw water	Comparison of water quality parameters – turbidity, UVA_{254}, TOC, zeta potential, and surface tension	1, 2 & 3

CHAPTER 4 ARTICLE I: SIMULTANEOUS POWDERED ACTIVATED CARBON AND COAGULANT INJECTION DURING BALLASTED FLOCCULATION FOR TRACE BENZENE REMOVAL FROM DIESEL AND GASOLINE-CONTAMINATED SURFACE WATERS

The objective of this study was to evaluate ballasted flocculation efficiency for *trace* benzene removal from surface water. Results showed that ballasted flocculation alone is insufficient for *trace* benzene reduction and the use of powdered activated carbon (PAC) up to 80 mg/L is necessary. Analysis of a worst-case treatment scenario, that is, simultaneous PAC and coagulant injection, showed that PAC adsorption efficiency was limited by the presence of coagulant. This study also demonstrated the robustness of ballasted flocculation in handling high PAC dosages. This chapter was published as a research paper in the *Journal of Water Process Engineering* in 2021.

SIMULTANEOUS POWDERED ACTIVATED CARBON AND COAGULANT INJECTION DURING BALLASTED FLOCCULATION FOR TRACE BENZENE REMOVAL FROM DIESEL AND GASOLINE-CONTAMINATED SURFACE WATERS

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ABSTRACT

Subsequent to an oil spill, conventional physicochemical treatment processes such as ballasted flocculation would serve as the principal barrier in drinking water treatment plants (DWTP) against contamination from toxic soluble contaminants such as benzene. Benzene is a well-known carcinogenic compound and its maximum threshold concentrations in drinking water are regulated at 5 µg/L and 0.5 µg/L in the United States and in Quebec, Canada, respectively. Our study focused on ballasted flocculation in order to determine its removal efficiency for traces of dissolved petroleum hydrocarbons originating from diesel and gasoline contamination. Results show that ballasted flocculation alone, using alum or ferric sulfate as coagulant, is not efficient for benzene reduction below regulations. Addition of an adsorbent such as powdered activated carbon (PAC) is necessary. From PAC adsorption isotherms and kinetics, we found an optimal dose of 80 mg PAC/L and contact times of 15 and 30 minutes for diesel- and gasoline-contaminated waters, respectively. The simultaneous addition of PAC and coagulant during ballasted flocculation showed that although benzene concentration declined substantially, alum treatment could not decrease concentrations below the Canadian threshold (0.5 µg/L) while the US regulation value was met. Analysis of PAC-ballasted flocculation tests demonstrated the likelihood of PAC pore blockage in the presence of coagulants. Although PAC doses as high as 80 mg PAC/L were introduced during ballasted flocculation, settled water quality was not negatively impacted. Findings from this study will help DWTP in their effort to prepare emergency response plans for the event of an oil spill.

KEYWORDS

Benzene, Ballasted flocculation, Powdered activated carbon (PAC), Drinking water production, Oil spill

4.1 Introduction

Crude and refined oil transportation via rail and pipelines is prevalent in many oil-producing countries such as Canada. Due to accidents and rupture in pipelines, the occurrence of oil spills within the vicinity of surface water bodies poses a constant risk to drinking water intakes. In

Canada, oil spill from pipelines alone amounted to 1084 barrels per year for the years 2011-2014 (CER, 2019). One of the most important oil spills occurred in 2013 in Lac-Mégantic following a train derailment, which released about 6000 m^3 of crude oil into the environment. Three drinking water intakes located downstream were shut down for several months following the incident. Oil spills introduce toxic aromatic compounds, of which benzene, toluene, ethylbenzene and xylenes, also known as BTEX, are the most soluble, volatile and toxic (C. Yang et al., 2017). Compared to toluene, ethylbenzene and xylene, the proven carcinogenity of benzene (Agency for Toxic Substances and Disease Registry (ATSDR) et al., 2007) led to the imposition of strict threshold concentrations of this contaminant in drinking water. The U.S. EPA enforced a maximum benzene concentration of 5 µg/L (United States Environmental Protection Agency (USEPA), 2011); however, in Quebec, Canada, a more stringent concentration of 0.5 µg/L is imposed (Gouvernement du Québec, 2011).

Following an oil spill, weathering processes such as evaporation and remediation techniques such as the application of dispersants will reduce BTEX concentrations in surface water (Lee et al., 2015; C. Yang et al., 2017). Nevertheless, trace, dissolved BTEX concentrations are expected to remain in water. These concentrations are typically below the odor threshold of each corresponding compound. For example, the odor threshold of benzene has been reported to be between 190 µg/L (Young, Horth, Crane, Ogden, & Arnott, 1996) and 2000 µg/L (Agency for Toxic Substances and Disease Registry (ATSDR) et al., 2007). Case studies show that after an oil spill, benzene concentrations quantified in drinking water treatment plants (DWTP) intakes range from 1-17 µg/L (Galvez-Cloutier et al., 2014; Inc., 2016; Lee et al., 2015; Zhou, Dettman, & Bundred, 2015a).

Since benzene concentrations are present only in traces (< 20 µg/L), it is worth ensuring that DWTP, with their current infrastructure, can remove trace, dissolved concentrations of BTEX. Most DWTP in Quebec draw their source water from surface water bodies and employ either one of these two types of conventional physicochemical treatment processes: Actiflo® (ballasted flocculation) or Pulsators® (coagulation-flocculation with sludge blanket). The Actiflo® is designed to attain an average surface loading of 40 $m^3/h/m^2$ in the clarifier. This is equivalent to

10 minutes of operation and 3 minutes of settling (that is, 2 minutes in the coagulation tank, 2 minutes in the flocculation tank, 6 minutes in the maturation tank, and 3 minutes in the settling tank) (C. Desjardins et al., 2002). Due to the addition of microsand, the Actiflo® technology requires less flocculation/settling time to achieve the required settled water quality (E Guibelin et al., 1994). These conventional physicochemical treatment processes would serve as principal barriers for the removal of the aforementioned contaminants in the event of an oil spill. Little is known on the performance of coagulation-flocculation for trace hydrocarbon removal, as most studies assessed the removal of higher concentrations of petroleum hydrocarbons, in the mg/L range, and are mainly focused on industrial wastewaters (Moursy & El-Ela, 1982; Rosenblum et al., 2016; Santo et al., 2012; Tansel & Eifert, 1999). To the best of our knowledge, no study has assessed the performance efficiency of ballasted flocculation for the removal of trace, dissolved hydrocarbons, specifically benzene, from surface waters.

Although the coagulation-flocculation process in itself is known to remove colloidal particles or in the case of oil-contaminated water, dispersed or emulsified oil droplets (Canizares et al., 2008; Jessica M Younker & Walsh, 2016), its efficiency for the removal of dissolved aromatic compounds like BTEX might necessitate the addition of a suitable adsorbent like powdered activated carbon (PAC). This might especially be the case if elevated levels of regulated organic contaminants like benzene are present in surface water. Due to its high surface area and affinity for organics, PAC has been applied for the removal of dissolved petroleum hydrocarbons (A. Daifullah & B. Girgis, 2003; El-Dib et al., 1978). The combination of PAC and coagulation-flocculation raises the question of the best point of application for optimum contaminant removal. PAC addition in conventional treatment plants may take place at the water intake point, close to coagulant injection or in settled water (Najm et al., 1991). Its point of application was shown to have little impact on micropollutant or dissolved organic carbon (DOC) removal (Altmann et al., 2015). Nevertheless, when possible, PAC should be applied before coagulation mainly to ensure greater contact time and sufficient mixing (Altmann et al., 2015). The best location to inject PAC for optimal BTEX removal in a combined PAC-ballasted flocculation process remains to be determined.

The objective of this study was first to evaluate the performance of ballasted flocculation for the removal of trace BTEX concentrations (< 60 µg/L, with benzene < 12 µg/L) originating from gasoline and diesel spills. Second, the process efficiency based on coagulant type – alum vs. ferric sulfate – was assessed. Third, the optimal PAC dose and contact time were determined based on PAC adsorption isotherm and kinetics tests conducted in gasoline- and diesel-contaminated surface waters. Finally, the effect of the simultaneous addition of PAC and coagulant during ballasted flocculation tests for trace BTEX removal from gasoline- and diesel-contaminated surface waters was evaluated.

4.2 Materials and Methods

4.2.1 Stock solution preparation

Gasoline (Grade 87) and regular diesel were retrieved from a gas station in Montreal in 2018. A volume of 25 mL of either petroleum product was added to 975 mL of ultrapure water in a 2-L round beaker, which was equipped with a Teflon-based lid to minimize volatilization. The lid was pierced at an off-center position for the impeller shaft of the overhead agitator (Heidolph RZR 1). An off-center mixing design, equipped with a pitch blade turbine (four blades, diameter = 7.5 cm), was used to mix both liquid phases (Kevin J Myers et al., 2002). An offset distance of 20 mm was set based on one-third of the beaker radius.

The mixture was agitated for two minutes at 1050 rpm and the resulting emulsion was filtered through a 0.3 µm glass fiber filter (Advantec, GF-75) to obtain the dissolved fraction of petroleum hydrocarbons. An airtight setup for mixing and filtration was used to minimize volatilization and improve the repeatability of the preparation (Figure 4.1). The resulting dissolved concentrations ranged from 0.36 ± 0.30 mg/L of benzene in the diesel stock solution and 11 ± 3.0 mg/L of benzene in the gasoline stock solution (Table 4.1). Due to the differing characteristics of both petroleum products, the final DOC concentration of the filtered gasoline solution was significantly higher than that of the filtered diesel solution.

Table 4.1: Characteristics of filtered gasoline and diesel stock solutions (± standard deviation).

Type of solution	Benzene (mg/L)	Toluene (mg/L)	Ethylbenzene (mg/L)	m,p-xylene (mg/L)	o-xylene (mg/L)	BTEX (mg/L)	DOC (mg C/L)
Filtered gasoline solution	11 ± 3.0	23 ± 4.0	1.7 ± 0.19	3.4 ± 0.30	3.5 ± 0.27	43 ± 7.8	1469 ± 52
Filtered diesel solution	0.36 ± 0.30	0.62 ± 0.055	0.14 ± 0.0027	0.24 ± 0.013	0.27 ± 0.018	1.6 ± 0.39	< 10

*DOC = dissolved organic carbon measured in the 0.3 µm filtered water

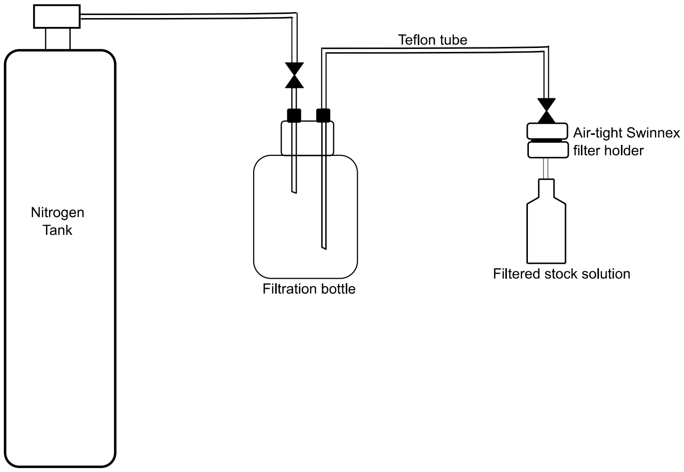

Figure 4.1: Filtration set-up for stock solution.

4.2.2 Surface water characteristics and preparation of contaminated surface water

Surface water from the Des Prairies River (Quebec, Canada) was used for all experiments. The raw water had the following characteristics: pH of 7.9 ± 0.2, turbidity of 3.4 ± 0.9 NTU, dissolved organic carbon (DOC) concentration of 5.3 ± 0.1 mg C/L, UV absorbance at 254 nm of 0.162 cm^{-1}, zeta potential of -17 ± 2 mV, surface tension of 66 ± 6 mN/m, and alkalinity of 42 ± 1 mg $CaCO_3$/L. To prepare contaminated surface water for ballasted flocculation tests, 150 mL of filtered diesel stock solution or 4 mL of filtered gasoline stock solution was added to 2.74 L of surface water to obtain a final concentration of less than 60 µg/L of BTEX. The mixture was agitated without headspace using a magnetic stir bar for 24 hours in a capped amber bottle to ensure complete mixing.

4.2.3 Batch PAC adsorption isotherms and kinetics

Powdered activated carbon, Aquasorb CB1-MW-F (Jacobi, Sweden), was employed for adsorption isotherm and kinetics tests. A summary of the carbon's characteristics is presented in Table 4.2. A PAC slurry of 2 g PAC/L was prepared in ultrapure water at least 12 h prior to experiments to pre-wet the carbon. Surface water was filtered on a pre-rinsed 0.45 µm membrane filter (PALL Corporation) and transferred into 250 mL amber bottles equipped with septum-based caps for injection and sampling. To simulate contamination, 15 mL of filtered diesel stock solution or 400 µL of filtered gasoline stock solution was spiked into the bottles. Different spiking volumes were used for diesel and gasoline in order to yield similar final benzene contaminations. To initiate adsorption experiments, a calculated PAC slurry volume was added to the bottles, which were then completely filled with filtered surface water leaving no available headspace.

Table 4.2: Characteristics of PAC (Aquasorb CB1-MW-F).

	Value	Units
Material	Wood/Bitumine	-
Iodine number	950	mg/g
BET surface area	869	m^2/g
Pore volume	0.42	cm^3/g
D_{50}	19	µm

For adsorption isotherms, PAC concentrations of 1, 2, 5, 10, 30, 50, 70 and 100 mg/L were injected. The bottles were sampled after 24 h, as equilibrium was already reached by 24 h based on kinetics tests. Kinetics tests were carried out using a selected optimal PAC dose and samples were collected after a contact time of 1, 3, 5, 10, 15, 30, 60 min, 3 h and 24 h. Note that for both adsorption and kinetics tests, agitation was stopped prior to sampling. Collected samples were immediately filtered using an airtight Luerlock syringe (SGE) and 0.3 µm glass fiber filters (Advantec, GF-75). BTEX and DOC analyses were performed for both adsorption and kinetics tests. In order to determine the experimental error and the initial BTEX concentration that considers losses due to adsorption on the bottle's material, a duplicate bottle as well as a control bottle without PAC was included in all experiments.

4.2.4 Jar test procedure

Ballasted flocculation was simulated in a single modified B-Ker™ jar (Phipps&Bird), whose bottom sampling port and hole had been removed and sealed. A lid was built to ensure air-tightness and minimize loss of volatile compounds while mixing was realized with an overhead stirrer (Caframo) (Figure 4.2a). The lid was equipped with two orifices – one for microsand addition and the other for coagulant injection and sampling.

a)

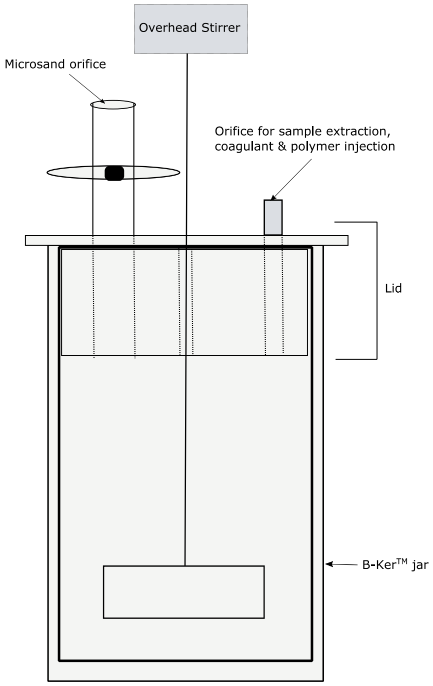

Figure 4.2a: Laboratory jar test setup with closed lid.

b)

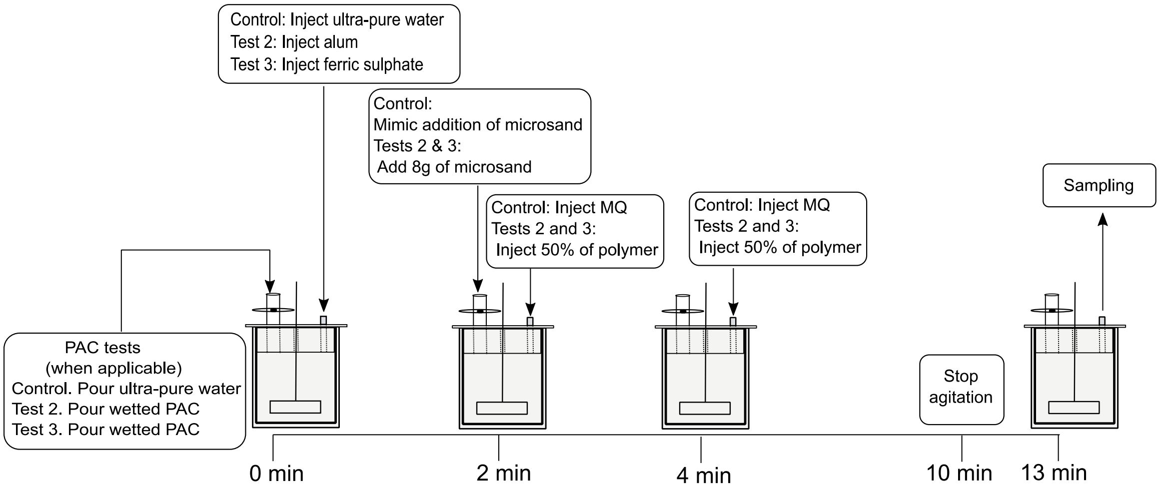

Figure 4.2b: Procedure for ballasted flocculation tests.

A series of three ballasted flocculation tests were conducted for each simulated contamination. The first was a control test whose purpose was to evaluate the impact of agitation on BTEX volatilization. Measured BTEX concentration at the end of each control test was considered as the initial concentration (C_0) in order to calculate BTEX removals by coagulation. Ballasted flocculation tests were then conducted with alum (*ALS*, Kemira: 4.3 % Al by wt) and ferric sulfate (*PIX 312*, Kemira: 12.3 % Fe by wt), respectively, to assess trace hydrocarbon removal by coagulation. An alum dose of 56 mg dry alum/L (= 4.9 mg Al/L = 0.54 mEq/L) was selected based on DOC removal in uncontaminated raw water. An equivalent ferric sulfate dose of 85 mg liquid/L (= 10 mg Fe/L = 0.54 mEq/L) was chosen for comparison. The polymer Hydrex 3613 (Veolia), a cationic polyacrylamide, was employed at a dose of 0.22 mg/L.

After contaminated surface water was transferred into the modified B-Ker™ jar and covered with the lid, stirring using a flat blade impeller began at 212 rpm and coagulant was injected at time=0 through the septum-based orifice for coagulant injection (Figure 4.2b). After two minutes of agitation, 8 g of microsand was added and 50 % of the polymer dose was injected. The remaining polymer dose was injected after two additional minutes of agitation and mixing was maintained at 212 rpm for floc maturation until the 10th minute. Finally, water samples were collected after 3 minutes of settling.

Ballasted flocculation tests with alum and ferric sulfate were also conducted using raw water containing no dissolved petroleum hydrocarbons. Results were compared with those from tests ran on contaminated surface water to assess the impact of contamination on raw and treated water quality.

Note that for all *control* tests, a 'mock' ballasted flocculation procedure was followed. This means that instead of injecting coagulant at time=0 and polymer at the 2nd and 4th minutes, ultrapure water was injected at the same volume as that of the coagulant and polymer, respectively. Also, instead of the addition of microsand, the orifice was opened for a few seconds and then closed. For *control* tests with PAC, mock PAC addition was performed by pouring a given volume of ultrapure water through the orifice for sand addition (Figure 4.2b).

4.2.5 Analytical methods

For BTEX analysis, certified reference standards of benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene (2000 mg/L in methanol) and internal standards, benzene-d_6 and 4-bromofluorobenzene (2000 mg/L in methanol) were purchased from Sigma Aldrich (St. Louis, MO) and were used in the preparation of a seven-point calibration curve for each sequence of analysis. The stir bar sorptive extraction (SBSE) method was used for the pre-concentration of BTEX compounds from 50 mL water samples using a polydimethylsiloxane (PDMS)-coated stir bar provided by Gerstel (Baltimore, MD). The PDMS-coated stir bars, also called Twisters®, were held in place within the vial cap with the help of a magnet in order to adsorb volatile BTEX compounds present in the vial headspace. 10 mL of sample was diluted in 40 mL of Milli-Q water present in the vials, which were then placed on a magnetic stirrer for extraction. Samples were extracted at room temperature for one hour by agitation at a speed of 1750 rpm using a regular magnetic stir bar. Twisters® were then placed in glass thermal desorption tubes for desorption and cryo-concentration in a thermal desorption unit-cooled injection system (TDU-CIS) provided by Gerstel (Baltimore, MD). A combined gas chromatograph-mass spectrometer (GC-MS) from Varian (Pablo Alto, CA), equipped with a PAL auto sampler (Zwingen, Switzerland), was used to perform analysis. Injection into the GC was done in splitless mode and separation of BTEX was achieved with a SLB-5ms column from

Sigma Aldrich (St. Louis, MO). Ionization of BTEX was done by electron impact before detection by MS in single ion monitoring mode. The average limit of detection (LOD) and quantification (LOQ) obtained for benzene measurement using this method are 0.021 and 0.069 µg/L, respectively. All validation parameters of the analytical method including LOD and LOQ of the other BTEX compounds can be found in the Supplementary Information (Appendix A). All parameters and analytical methods employed in this study are summarized in Table 4.3.

Table 4.3: Parameters and analytical methods employed.

Parameters	Units	Methods
Alkalinity	mg $CaCO_3$/L	Accumet AB15 pH meter, SM 2320 B (American Public Health Association (APHA) et al., 2012)
Turbidity	NTU	Turbidimeter, Hach 2100 N SM 2130 B (American Public Health Association (APHA) et al., 2012)
Dissolved Organic Carbon (DOC)	mg C/L	Sievers Innovox TOC Laboratory Analyzer (Suez) SM 5310 B (American Public Health Association (APHA) et al., 2012) Filtration using 0.3 µm filter (in metal Swinnex filter holder) pre-rinsed with sample
UVA_{254}	cm^{-1}	Filtration using 0.3 µm filter (in metal Swinnex filter holder) pre-rinsed with sample (American Public Health Association (APHA) et al., 2012)

Table 4.3: Parameters and analytical methods employed (continued).

Parameters	Units	Methods
Zeta potential	mV	Zetasizer Nano (Malvern) (Duan et al., 2014)
Surface tension	mN/m	Pendant drop method using OCA20 (Dataphysics) (Berry et al., 2015; Stauffer, 1965)
BTEX	µg/L	SBSE-GC-MS (Pastor-Belda et al., 2019; Tienpont et al., 2000)

4.3 Results and Discussion

4.3.1 Efficiency of ballasted flocculation for BTEX removal

Results from ballasted flocculation tests of diesel- and gasoline-contaminated surface waters show that benzene concentrations could not be reduced below the Quebec regulatory limit of 0.5 µg/L (Figure 4.3).

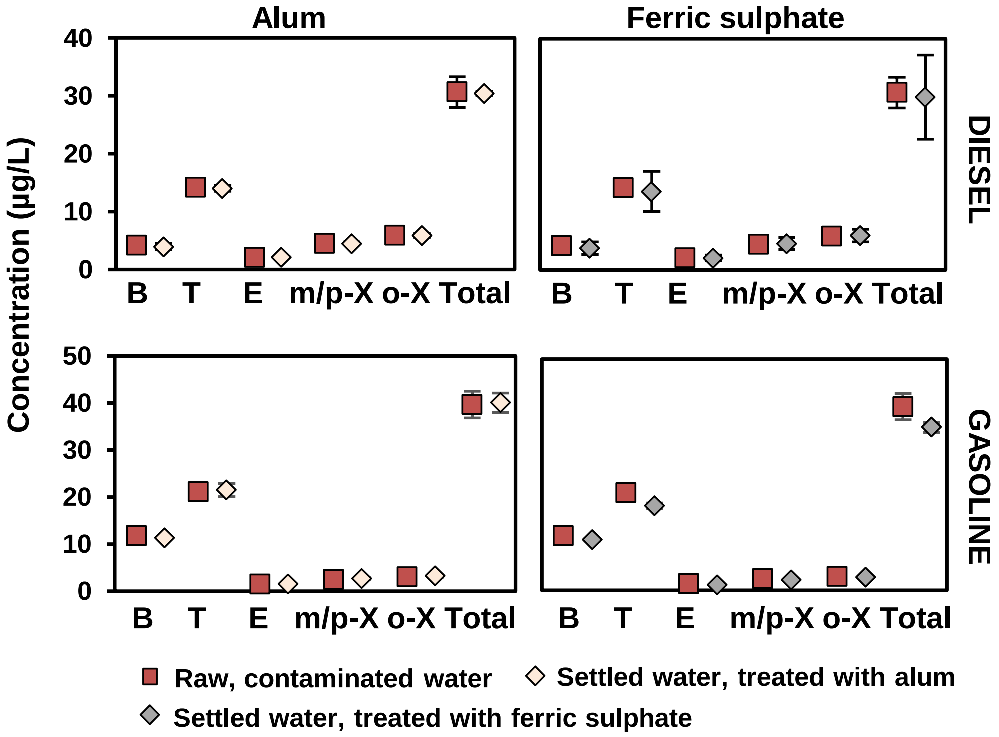

Figure 4.3: Efficiency of ballasted flocculation for the removal of dissolved petroleum hydrocarbons (BTEX) from diesel- and gasoline-contaminated surface waters. Alum and ferric sulfate were employed as coagulants, respectively. Benzene concentration could not be reduced below the maximum acceptable concentration (MAC) for benzene in drinking water in the US (5 µg/L). Error bars indicate minimum and maximum values.

Coagulation is known to be effective for the removal of colloidal and hydrophobic particles through charge neutralization, enmeshment in a growing precipitate or inter-particle bridging

(Davis & Edwards, 2014). Benzene, as a non-polar organic compound, possesses no charged functional groups to increase its affinity for the surface of flocs (Pourrezaei et al., 2011). The absence of such functional groups limits contaminant removal through mechanisms like charge neutralization. Nonetheless, weak Van der Waals interactions can occur between benzene and enmeshed organic contaminants in flocs or the cationic polyacrylamide polymer that serves as a bridge for flocs (Randtke, 1988). These interactions are however not effective to reduce benzene concentrations below the required threshold, as observed in this study. Furthermore, the added presence of microsand during flocculation did not lead to an appreciable reduction in the concentration of dissolved petroleum hydrocarbons through sorption onto sand grains. Inorganic microsand that was employed during the tests serves as ballast media to enable the formation of denser flocs and to reduce settling time. It lacks the appropriate surface functional groups that would increase the affinity of BTEX for its surface. Although not presented in detail in this study, trace BTEX adsorption on microsand alone was assessed and no reduction in BTEX concentration was observed. It was thus concluded that ballasted flocculation alone is not effective for the removal of trace, dissolved BTEX in surface water contaminated with diesel or gasoline. A similar finding was reported for a higher concentration of dissolved hydrocarbons (Ribera-Pi et al., 2020). It is therefore necessary to add an adsorbent, powdered activated carbon (PAC), to reduce benzene concentration below regulations.

4.3.2 Adsorption tests with Powdered Activated Carbon (PAC)

4.3.2.1 Adsorption isotherm tests

Results of adsorption isotherm tests for diesel- and gasoline-contaminated waters show that for the chosen PAC (Aquasorb CB1-MW-F) and a contact time of 24 hours, a PAC dose of 15-20 mg PAC/L was needed to reduce benzene concentration below U.S. EPA's maximum acceptable concentration (MAC) of 5 µg/L. However, a PAC dose greater than 70 mg/L was necessary to decrease benzene concentration below 0.5 µg/L, as required by Quebec MAC regulation (Figure 4.4). As a result, 80 mg PAC/L was chosen as the optimal dose to be applied in the kinetics test.

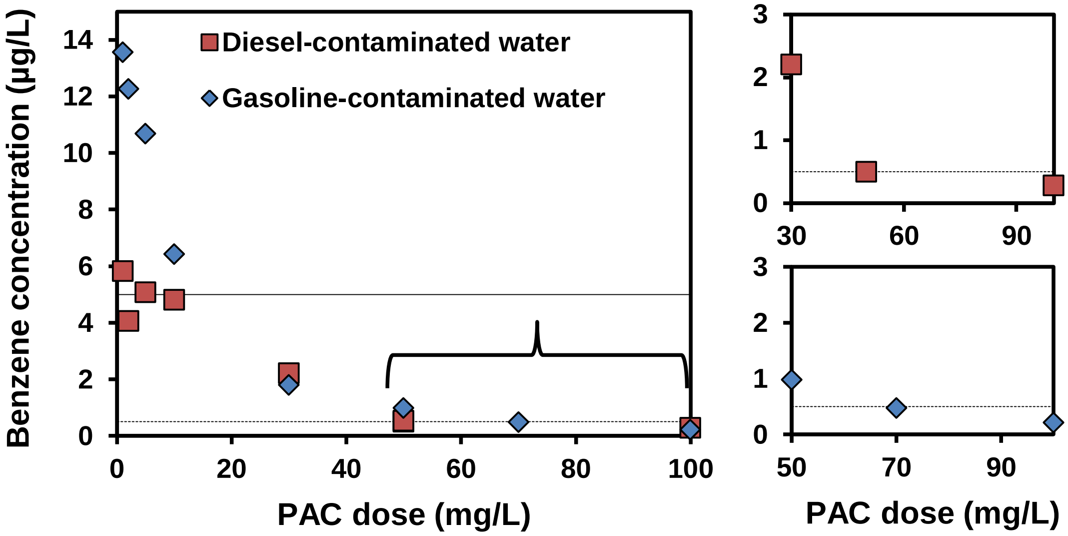

Figure 4.4: Benzene concentration (µg/L) as a function of PAC dose (mg/L) for diesel- and gasoline-contaminated surface waters. The dashed line (---) represents the Quebec MAC for benzene in drinking water (0.5 µg/L) while the bold line (—) represents the U.S. EPA MAC for benzene in drinking water (5 µg/L). Initial benzene concentrations in diesel- and gasoline-contaminated waters were 4.7 µg/L and 14 µg/L, respectively. Contact time was 24 h.

We analyzed adsorption data using the Langmuir and Freundlich isotherms for (i) BTEX as a sum parameter and (ii) benzene, an individual molecule in the sum parameter, since it is a regulated substance. For the Langmuir model, the linearized form is described in Equation 4.1.

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}b}\frac{1}{c_e} \qquad \text{Eq. 4.1}$$

where q_{max} is the maximum equilibrium contaminant concentration for monolayer coverage (µg/mg) and b is associated with the adsorption energy (L/µg) (Snoeyink & Summers, 1999). The Freundlich model is presented in its linearized form in Equation 4.2.

$$\log q_e = \log K + \frac{1}{n} logC_e \qquad \text{Eq. 4.2}$$

where q_e is the equilibrium contaminant concentration on the adsorbent surface (µg/mg) and K ((µg/mg)(Lµg$^{1/n}$)) and $1/n$ (unitless) are constants in the Freundlich isotherm related to the adsorbent capacity and bond strength, respectively (Snoeyink & Summers, 1999).

For benzene adsorption data, the Freundlich isotherm generated a better fit for gasoline-contaminated water (average relative error (ARE) = 8 %). However, the Freundlich isotherm could not properly model benzene data from diesel-contaminated water due to observed variabilities in the measured equilibrium benzene concentration. For the adsorption of the sum parameter, BTEX, the Freundlich isotherm fits were superior in both diesel- and gasoline-contaminated waters (ARE = 18 % and 10 %, respectively) (Table 4.4). From the 1/n values, it can be concluded that trace concentrations of benzene and BTEX in surface water show appreciable adsorption affinities for PAC (1/n = 0.44 – 0.93). Nevertheless, the source of either compound seems to influence PAC adsorption capacity (based on K values). For instance, compared to BTEX in diesel-contaminated water, PAC showed higher adsorption capacity for BTEX originating from gasoline-contaminated surface water. This observation might be due to the dissimilarities in the chemical composition of both petroleum products (Davis & Edwards, 2014). The corresponding graphs of the adsorption isotherms and their fits on the experimental data are available in the Supplementary Information (Appendix A).

Table 4.4: Langmuir and Freundlich isotherm parameters for benzene and BTEX adsorption on PAC.

Benzene								
	Langmuir				Freundlich			
Source of contamination	q_{max}	b	R^2	ARE[a] (%)	K	1/n	R^2	ARE[a] (%)
Diesel[b]	-0.053	-1.5	0.33	8.0	0.13	0.93	0.74	-676
Gasoline[b]	0.62	1.2	0.94	17	0.28	0.44	0.97	8.0

Table 4.4: Langmuir and Freundlich isotherm parameters for benzene and BTEX adsorption on PAC (continued).

BTEX								
	Langmuir				Freundlich			
Source of contamination	q_{max}	b	R^2	ARE[a] (%)	K	1/n	R^2	ARE[a] (%)
Diesel[b]	3.3	0.22	0.96	24	0.57	0.57	0.92	18
Gasoline	2.5	0.81	0.89	33	0.89	0.49	0.98	10

[a] $ARE = \frac{100}{n} \times \sum_{i=1}^{n} \frac{|\Delta q_i|}{q_i}$. Average Relative Error (ARE) was used to determine the quality of the non-linear fits from Langmuir and Freundlich isotherms on raw data.

[b] Adsorption data for the 1 mg PAC/L dose was removed as an outlier in the calculation of Langmuir and Freundlich fits.

4.3.2.2 Kinetics tests

Benzene kinetics were rapid in the first few minutes of contact with 80 mg PAC/L. Up to 98 % (± 3 %) and 96 % (± 5 %) benzene removals were attained within 10 minutes for diesel- and gasoline-contaminated waters, respectively. Equilibrium was already reached by the 24 h maximum time of contact. Benzene concentrations in diesel- and gasoline-contaminated surface waters were reduced below 0.5 µg/L (Quebec MAC) at 15 and 30 minutes of contact time, respectively (see Supplementary Information, Table A2). At 15 minutes, benzene concentrations were 0.3 µg/L and 0.5 µg/L for diesel- and gasoline-contaminated surface waters, respectively. However, to ensure that the benzene concentration, for contamination with gasoline, was below the required Quebec threshold (0.5 µg/L), the next measured contact time was chosen (30 minutes). At this contact time, measured benzene concentration in gasoline-contaminated water was 0.3 µg/L. External film and pore or surface diffusion processes are known to affect adsorption kinetics of a porous adsorbent like PAC (Crittenden et al., 2012). Using the batch kinetics data and the Freundlich isotherm results, the homogenous surface diffusion model (HSDM) can be applied to describe adsorbate surface diffusion by determining the surface diffusion coefficient (D_s). Kinetics data was fit to Equation 4.3 based on the methodology described by Crittenden et al. (Crittenden et al., 2012).

$$\frac{C-C_e}{C_0-C_e} = A_0 + A_1 ln(\bar{t}) + A_2 ln(\bar{t})^2 + A_3 ln(\bar{t})^3 \qquad \text{Eq. 4.3}$$

where C is the experimentally measured concentration at a given time t, C_e is the equilibrium concentration calculated from $\frac{C_0-C_e}{D_0} = K{C_e}^{1/n}$, C_0 is the initial concentration of the adsorbate, $A_{i=0\text{-}3}$ are constants that depend on the $\frac{C_e}{C_0}$ and the $\frac{1}{n}$ from the Freundlich isotherm model, and $\bar{t} = \frac{tD_s}{r^2}$ is the dimensionless time (t represents the measured time for kinetics batch tests, D_s is the surface diffusion coefficient and r is the mean PAC radius). HSDM was able to fit kinetics data for BTEX as a sum parameter in diesel- and gasoline-contaminated waters ($D_s = 4.8 \cdot 10^{-11}$ cm^2/s and $1.6 \cdot 10^{-11}$ cm^2/s, respectively) (Figures 4.5b and 4.5d). For benzene kinetics data in gasoline-contaminated water (Figure 4.5c), HSDM underestimated contaminant removal over time. Benzene adsorption kinetics based on the HSDM model simulation was also much slower than that observed during experiments. The variabilities observed in the benzene adsorption isotherm for diesel-contaminated water (Section 4.3.2.1) affected the Freundlich isotherm parameters and thus the HSDM fit (Figure 4.5a).

Reaction kinetics models were also applied to fit data and the pseudo-second order reaction kinetics model, in its linearized form in Equation 4.4, generated the best fit.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{Eq. 4.4}$$

where k_2 (mg/µg/min) is the rate constant for pseudo-second order kinetics and q_e is the adsorption capacity at equilibrium (mg/µg). Rate constants for a single solute (benzene) were similar in diesel- and gasoline-contaminated waters; that is, 18 mg/µg/min and 17 mg/µg/min, respectively. For the sum parameter, BTEX, a lower rate constant was observed in diesel-contaminated water (4 mg/μg/min) compared to that of gasoline-contaminated water (10 mg/μg/min).

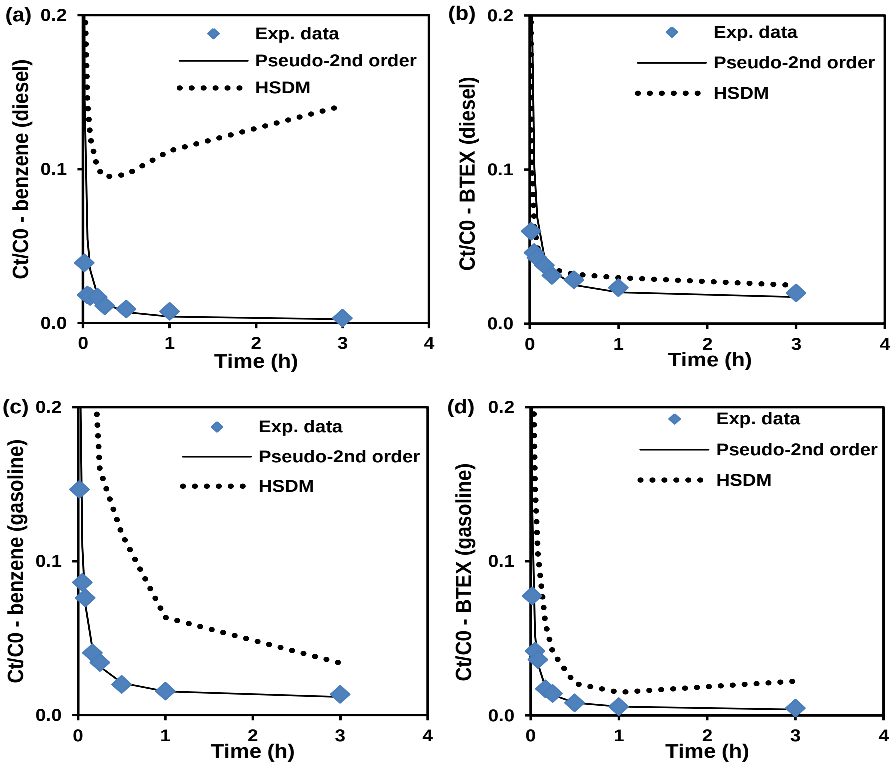

Figure 4.5: Experimental kinetics data and model fits (pseudo-second order models and HSDM) for benzene and BTEX in diesel (a and b) and gasoline (c and d) contaminated waters. 80 mg PAC/L was applied. Diffusion coefficients were (a) $1.9{\cdot}10^{-11}$ cm^2/s, (b) $4.8{\cdot}10^{-11}$ cm^2/s , (c) $1.0{\cdot}10^{-11}$ cm^2/s, and (d) $1.6{\cdot}10^{-11}$ cm^2/s.

It is important to note that the conclusions on the optimal contact time, in this case being 15 and 30 minutes for diesel- and gasoline-contaminated waters respectively, is applicable to a scenario where the DWTP has an existing PAC pre-contact tank prior to the injection of coagulant. For DWTP with no existing PAC pre-contact tank, it is likely that in the event of an oil spill, PAC will be added at the same time as coagulant in order to reduce benzene concentrations. This scenario may lead to a lower performance of PAC due to shorter contact times and the incorporation of PAC within the flocs. To test this hypothesis, ballasted flocculation tests with simultaneous PAC and coagulant addition were carried out.

4.3.3 Efficiency of ballasted flocculation: simultaneous addition of PAC and coagulant

4.3.3.1 Performance of alum vs ferric sulfate in diesel- and gasoline-contaminated waters

When 80 mg PAC/L and alum were dosed simultaneously, benzene concentrations declined appreciably in both diesel- and gasoline-contaminated waters (Table 4.5). Initial benzene concentrations were 2.2 µg/L ± 0.1 µg/L (standard deviation) and 7.7 µg/L ± 0.6 µg/L in diesel- and gasoline-contaminated waters, respectively. Final benzene concentrations were 0.6 µg/L ± 0.04 µg/L (diesel) and 1.3 µg/L ± 0.1 µg/L (gasoline) after only 10 min. These final concentrations still exceeded the Quebec MAC (0.5 µg/L). In contrast, with the same PAC dose and ferric sulfate as coagulant, benzene concentration decreased to 0.5 µg/L ± 0.03 µg/L in diesel-contaminated water and 0.6 ± 0.1 µg/L in gasoline-contaminated water after the same contact time of 10 min (initial benzene concentration of 2.2 µg/L and 7.7 µg/L in diesel- and gasoline-contaminated waters, respectively).

Ferric sulfate seemed to outperform alum in reducing benzene concentration in both diesel- and gasoline-contaminated surface waters. The applied doses of alum and ferric sulfate are based on the same milli-equivalent of the metal coagulant per liter in order to enable a comparison of the performance of the coagulants. Better performance observed for ferric sulfate stems most likely from the amount of precipitate formed and precipitate morphology, as discussed in the next sub-section. Other parameters that reflect water quality such as turbidity, DOC, UVA_{254}, surface tension, and zeta potential would also play a role in the efficiency of the flocculation-PAC adsorption process. In principle, any change in water quality through the addition of BTEX, for example, would affect raw water quality and consequently, the efficiency of the flocculation-adsorption process for potable water production. Although results are not presented in this article, the addition of trace dissolved BTEX concentrations from diesel and gasoline in the current study only marginally impacted the aforementioned parameters.

Table 4.5: Performance of ballasted flocculation for benzene removal during simultaneous PAC and coagulant addition (values ± standard deviation from duplicates).

Pollutant	Coagulant		PAC	Benzene		
Type	Type	Dose (mg/L) (Al or Fe)	Dose (mg/L)	Initial conc. (µg/L)	Final conc. (µg/L)	Removal (%)
Diesel	Alum	4.9	80	2.2 ± 0.1	0.6 ± 0.04	74 ± 3
	Ferric sulfate	10	80	2.2 ± 0.1	0.5 ± 0.03	80 ± 2
Gasoline	Alum	4.9	80	7.7 ± 0.6	1.3 ± 0.1	83 ± 3
	Ferric sulfate	10	80	7.7 ± 0.6	0.6 ± 0.1	92 ± 5

4.3.3.2 Effect of the presence of coagulant on PAC efficiency

The presence of coagulant has been reported to negatively affect adsorption efficiency of PAC (El-Dib et al., 1978; Najm et al., 1991). Results of three tests were compared in order to conclude on the effect of the presence of coagulant (alum or ferric sulfate) on the adsorption efficiency of PAC for the removal of trace, dissolved petroleum hydrocarbons. The three tests were: (i) the PAC adsorption capacity for benzene after 10 minutes of contact time for 80 mg PAC/L (no coagulant addition) (10 minutes was chosen based on the Actiflo® design) (Section 4.3.2.2), (ii) ballasted flocculation tests with the simultaneous addition of PAC and alum (Section 4.3.3.1), and (iii) ballasted flocculation tests with the simultaneous addition of PAC and ferric sulfate (Section 4.3.3.1). For the ballasted flocculation tests, 80 mg PAC/L was dosed and the contact time between PAC addition and sampling was 10 minutes (agitation time).

The presence of alum or ferric sulfate reduced PAC adsorption efficiency by 13-24 % and 4-18 %, respectively. Compared to tests with PAC and ferric sulfate, the simultaneous addition of PAC and alum decreased the PAC adsorption efficiency for benzene in both diesel- and gasoline-contaminated surface waters. Alum flocs have been shown to be gelatinous (Ebeling, Sibrell, Ogden, & Summerfelt, 2003) and can stick to PAC adsorption sites, thus hindering benzene adsorption. Ferric sulfate flocs are known to be ramified or chain-like in structure and possess more surface area (He, Leppard, Paige, & Snodgrass, 1996). Stoichiometric equations for the formation of metal hydroxide precipitates show that the addition of the same milli-equivalent concentrations of alum and ferric sulfate results in the generation of more flocs upon the addition of ferric sulfate (Crittenden et al., 2012). This, together with the ferric floc morphology, might have favored the entrapment and interaction between PAC particles and benzene and led to higher removals, as observed in the current study (Figure 4.6). Benzene removal was observed to be higher in gasoline-contaminated water since gasoline is a relatively cleaner fuel than diesel (M. F. Fingas, 2011). For diesel- and gasoline-contaminated waters, benzene removal proved to be superior in PAC adsorption tests without coagulant (10-minute kinetics test). Therefore, it can be concluded that for improved contaminant removal, PAC should be added prior to coagulant injection. Furthermore, from an operational perspective, it would also be desirable to remove as much volatile organic compounds prior to the rapid mixing step in order to minimize degassing within the DWTP.

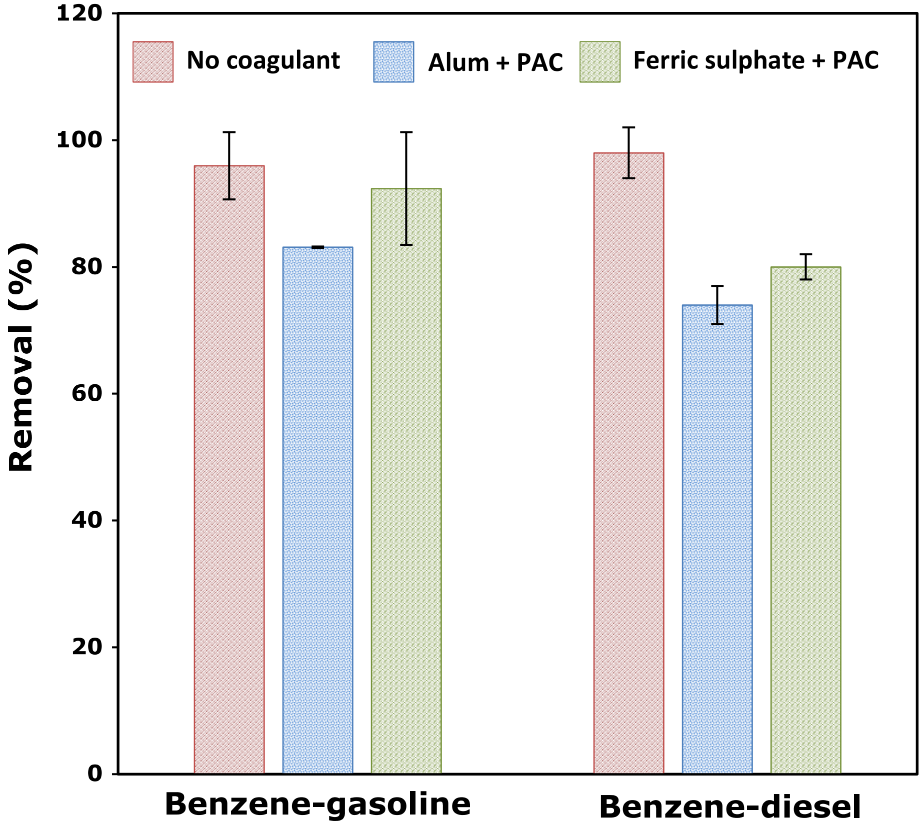

Figure 4.6: Benzene removal (%) in diesel- and gasoline-contaminated waters after 10 minutes contact time with 80 mg PAC/L (without coagulant) (red), subsequent to ballasted flocculation with simultaneous PAC (80 mg/L) and alum addition (blue), as well as subsequent to ballasted flocculation with simultaneous PAC (80 mg/L) and ferric sulfate addition (green). Error bars indicate minimum and maximum values. Benzene losses (not shown) during ballasted flocculation tests due to volatilization were 2-3 %, based on control tests.

4.3.3.3 Water quality after simultaneous PAC and coagulant addition

The high PAC concentration (80 mg/L) used for ballasted flocculation tests in the current study might affect the quality of settled or treated water, especially in terms of turbidity caused by PAC and PAC fines. Consequently, turbidity and DOC concentrations were compared for untreated and settled water from ballasted flocculation tests of (a) uncontaminated surface water, (b) diesel-contaminated surface water with and without the addition of PAC, and (c) gasoline-contaminated surface water with and without the addition of PAC. Turbidity results show that when alum is employed as coagulant, ballasted flocculation can handle up to 80 mg/L of PAC without significantly affecting the quality of settled water (Figure 4.7). It is important to note that this conclusion may not be applicable to other conventional settlers. In addition, the alum dose did not need to be increased due to the high PAC dosage applied. When ferric sulfate was employed as coagulant, turbidity increased in the presence of PAC. As for DOC, the addition of 80 mg/L PAC improved DOC removal for both alum and ferric sulfate-settled waters (Figure 4.7).

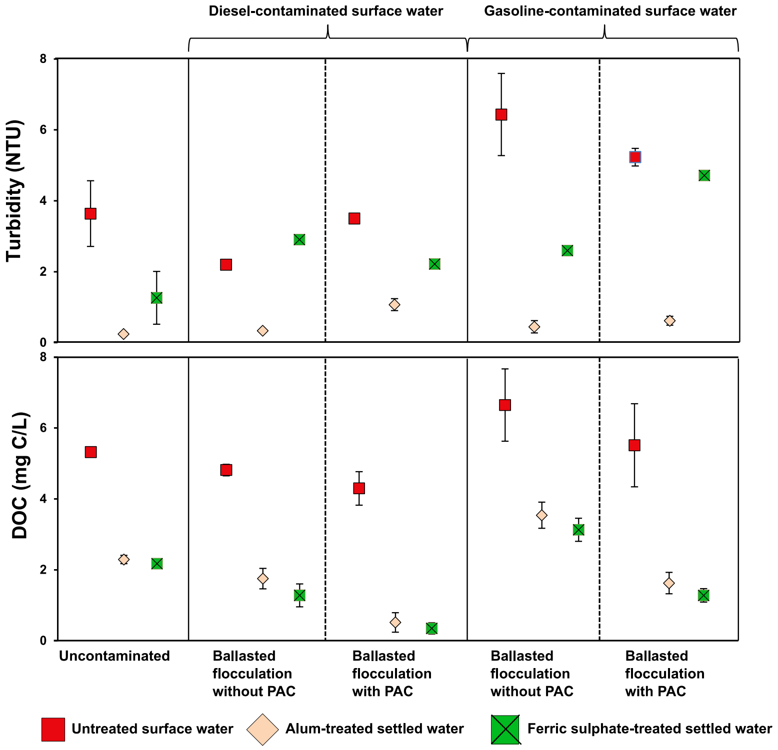

Figure 4.7: Physicochemical parameters (turbidity and dissolved organic carbon (DOC)) before and after ballasted flocculation tests for uncontaminated surface water, diesel- and gasoline-contaminated water (with and without PAC). Each block contains values for untreated surface water (square), alum-treated settled water (diamond) and ferric sulfate-treated settled water (square with cross). Error bars indicate minimum and maximum values.

4.4 Conclusion

This research highlights the vulnerability of conventional drinking water treatment processes to hydrocarbon spills in source waters. We showed that coagulation (and the added presence of microsand) is essentially inefficient for the removal of trace BTEX concentrations arriving at DWTP; thus, the addition of a high PAC dose is required. PAC adsorption isotherm tests showed that only 15-20 mg PAC/L was sufficient to decrease benzene concentration below 5 µg/L (U.S. EPA) from an initial concentration of 14 µg/L. At the same initial benzene concentration, 80 mg PAC/L was necessary in order to be below 0.5 µg/L (Quebec regulation). The study of a worst-case scenario involving the simultaneous addition of PAC and coagulant (alum or ferric sulfate) during ballasted flocculation demonstrated the necessity of PAC addition prior to coagulation for improved removal of dissolved petroleum hydrocarbons. As an emergency response, DWTP should install a PAC injection point prior to rapid mixing or better still, add a PAC pre-contact tank before coagulant addition, if possible. In the event of an oil spill, water utilities should make use of the maximum PAC dosage that can be added in their facility. To avoid process failure, the maximum dosage should be assessed upon the elaboration of emergency response plans. Finally, since the application of dispersants might be the most probable remediation technique to be employed in the event of an oil spill, future research should investigate the ability of conventional treatment processes to remove dispersant-stabilised oil droplets.

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CHAPTER 5 ARTICLE II: PERFORMANCE OF CONVENTIONAL DRINKING WATER TREATMENT FOLLOWING DISPERSANT REMEDIATION OF AN OIL SPILL IN SURFACE WATER

The objective of this study was two-fold – first, to evaluate the impact of dispersant application on surface water quality and ballasted flocculation efficiency for the removal of dispersant-stabilized crude oil droplets and dispersant-related compounds and second, to identify a suitable indicator of crude oil and dispersant contamination in surface water. Results showed that although ballasted flocculation with an optimized alum dose could generate settled water that met treatment objectives, it was unable to reduce concentrations of dispersant-related compounds. Total Organic Carbon (TOC) served as the most sensitive indicator to crude oil and dispersant contamination in surface water. This chapter was submitted as a research paper to the journal, *Science of the Total Environment*, in 2021.

PERFORMANCE OF CONVENTIONAL DRINKING WATER TREATMENT FOLLOWING DISPERSANT REMEDIATION OF AN OIL SPILL IN SURFACE WATER

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ABSTRACT

Physical remediation such as the use of booms has been applied for most oil-spill cleanup activities in surface water. The application of dispersants has been controversial primarily due to the unknown impacts on drinking water sources. This study investigated changes in surface water quality following dispersant application to crude oil spills and the subsequent impact on the efficiency of ballasted flocculation, a physicochemical treatment process applied in many drinking water treatment plants (DWTP). Contamination of surface water was performed in the presence of crude oil concentrations (109 ± 13 mg/L) with and without dispersants. Water quality parameters such as turbidity and UVA_{254} were monitored and ballasted flocculation efficiency was assessed based on water quality as well as the removal of oil droplets, residual dispersant, and petroleum hydrocarbons as total organic carbon (TOC). Results showed that the measured water quality parameters except TOC are unsuitable indicators of petroleum hydrocarbon contamination in surface water. However, TOC lacked sensitivity when used in settled water to detect hydrocarbon contaminants. Although ballasted flocculation efficiency was not limited by the presence of crude oil and low dispersant concentrations when an optimized alum dose was applied (41 mg dry alum/L), the process was unable to remove other dispersant-related compounds that are not identifiable by the monitored water quality parameters. Measured concentrations of these compounds in settled waters were above the U.S. EPA's aquatic life benchmark (40 µg/L). Findings would be beneficial to DWTP in their efforts to upgrade their treatment processes and prepare oil-spill contingency plans.

KEYWORDS

Ballasted flocculation, Indicators, Potable water, Water quality, Treatment efficiency

5.1 Introduction

In the past 20 years, several crude oil spills have occurred in North American surface water bodies, leading to adverse effects on aquatic life and drinking water sources (Galvez-Cloutier et al., 2014; Lee et al., 2015; Zhou et al., 2015a). Following these spills, several remediation techniques have been employed to recover spilled oil and protect affected environments. For example, pipeline breakage introduced 952 m^3 of sour crude oil into Pine River, British Columbia, Canada, of which only 5 m^3 and 21.4 m^3 were recovered by the application of adsorbents and soil excavation, respectively (Lee et al., 2015). Train derailment also caused the loss of 713 m^3 of heavy fuel oil and contamination of Wabamun Lake, Alberta, Canada through the introduction of 149 m^3 of crude oil into the lake. Booms and vacuuming were employed to recover an estimated 95 % of the spilled oil (Birtwell, 2008; Short, 2008). In Talmadge Creek and Kalamazoo River, Michigan, USA, skimming and aeration techniques were applied to recover floating and submerged volumes of the 3200 m^3 of spilled diluted bitumen (Fitzpatrick et al., 2015). The application of these physical cleanup technologies has shown little to no adverse effect on aquatic habitats and the treatment processes employed in drinking water treatment plants (DWTP) (Owens & Michel, 1995). They differ, however, from chemical remediation solutions such as dispersants.

Dispersants, as the name implies, work to disperse spilled oil in a water column by reducing the interfacial tension of oil and enabling the formation of small, stable droplets (M. F. Fingas, 2011; International Tanker Owners Pollution Federation Limited (ITOPF), 2011; National Research Council (NRC), 2005). Typically applied on crude oil spills in oceans, dispersants are composed of additives, solvents, and surfactants (Poliakoff, 1969). Additives impact the dispersant’s physicochemical properties such as pH, color, and stability. Solvents such as petroleum hydrocarbons, water, and alcohols are used to reduce the viscosity of dispersants and provide conditions for surfactant accessibility and action on the oil. Surfactants are the major active agents in dispersants and are responsible for the reduction in interfacial tension (International Tanker Owners Pollution Federation Limited (ITOPF), 2011; John et al., 2016; Poliakoff, 1969; Wrenn et al., 2009). Surfactants possess a hydrophilic head and a hydrophobic tail, making them influential in oil-water interactions (Myers, 2006b; Wrenn et al., 2009). Depending on the nature of the head group, surfactants can be nonionic, anionic, cationic, or zwitterionic. Although the exact composition of most oil-spill dispersants is proprietary, they are known to be composed of nonionic and anionic surfactants (Hemmer et al., 2011; International Tanker Owners Pollution Federation Limited (ITOPF), 2011). Major oil-spill dispersants such as Finasol® OSR 52, Corexit 9527 and Corexit 9500A contain an anionic surfactant, sodium dioctyl sulfosuccinate (DOSS), which is known to be persistent in the environment and promotes bioaccumulation of petroleum hydrocarbons in aquatic organisms (Kujawinski et al., 2011; Prince, 2015).

With respect to crude oil spills in surface water, dispersant application has been a debatable issue primarily due to toxicity effects and the unknown impacts on drinking water sources. Toxicity effects have been extensively explored in literature and it has been reported that the presence of a mixture of dispersant and crude oil is more toxic to aquatic life than the presence of the dispersant or crude oil alone (Bhattacharyya, Klerks, & Nyman, 2003b; M. Fingas, 2008; M. F. Fingas, 2011; Green & Trett, 1989; Prince, 2015). In the human system, accidental ingestion of dispersant-containing solutions can lead to lung damage and central nervous system depression (Total Fluides, 2015). Effects on water quality and the efficiency of treatment processes in DWTP are also of concern in terms of the introduction of oil droplets, petroleum hydrocarbons, and other known and unknown dispersant-related compounds. Existing literature lacks studies on these issues and several reports only allude to the need to study the impact of dispersant applications on drinking water sources (M. F. Fingas, 2011; Owens & Michel, 1994; SL Ross Environmental Research (SLRoss), 2010; Vandermeulen & Ross, 1995). One study examined the impact of dispersant application (15 – 20 mg/L) to a simulated oil spill (75 – 100 mg/L) in a lake pond. Although several water quality parameters were analyzed, no treatment was applied and evaluated on the contaminated lake water (B. F. Scott & Glooschenko, 1984; Brian F. Scott et al., 1984). There has not been a study done to assess the treatability of such contaminated surface water in the context of drinking water production.

Petroleum hydrocarbons from crude oil spills and additional organic compounds such as surfactants are expected to be introduced in the event of dispersant application. Some drinking water treatment facilities have their raw water intakes in surface water and in the event of a crude oil spill and the subsequent application of dispersants, drinking water treatment facilities might need to treat such contaminated water (at least for a time before the raw water intake is shut off and alternate water sources are utilized). As physicochemical treatment processes such as coagulation and sedimentation generally serve as the first barrier to particulate and dissolved organic carbon (DOC) removal in most DWTP, their ability to remove oil-related contaminants and surfactants is of paramount importance to ensure the adequate operation of subsequent treatment processes (Montgomery Watson Harza (MWH), 2005). In Quebec (Canada), these processes are commonly available in a combined technology, Actiflo® or ballasted flocculation, which involves the addition of microsand for rapid settling (up to 85 m/h). No study has thus far investigated the impact of oil-spill dispersants on the efficiency of ballasted flocculation following dispersant application to a crude oil spill in surface water. More specifically, the efficiency of ballasted flocculation for the removal of dispersant-stabilized oil droplets, dispersant-related compounds, and other petroleum hydrocarbons in dispersant-oil-contaminated surface water remains yet to be studied.

The objective of this study was therefore to conduct a comparative analysis and demonstrate the impact of the presence of crude oil and oil-spill dispersant concentrations on ballasted flocculation efficiency. Contamination of surface water with crude oil was simulated and treated in the presence and absence of dispersant. Besides the analysis of water quality parameters such as turbidity and zeta potential, efficiency was evaluated based on the removal of dispersant-stabilized oil droplets, residual dispersant measured as DOSS, and petroleum hydrocarbons quantified as total organic carbon (TOC). Findings in this study will be beneficial to DWTP in their efforts to evaluate and upgrade their treatment chain and to prepare contingency plans in the event of oil spills in surface water.

5.2 Materials and Methods

5.2.1 Characterization of dispersant and surface water

Des Prairies River (Quebec, Canada) served as source water for all tests. Raw surface water had a pH of 7.3, turbidity of 4.3 ± 0.1 NTU, dissolved organic carbon (DOC) concentration of 6.94 ± 0.03 mg C/L, TOC concentration of 7.54 ± 0.01 mg C/L, UV absorbance at 254 nm (UVA_{254}) of 0.254 ± 0.006 cm^{-1}, zeta potential of -20 ± 2 mV, surface tension of 75 ± 1 mN/m, conductivity of 89 ± 6 µS, and alkalinity of 23 ± 1 mg $CaCO_3$/L. DOSS (Figure 5.1) was not detected in raw surface water.

Dispersant was requested from manufacturers on the National Contingency Plan Product Schedule (U.S. EPA). Total Fluides (France) was the only manufacturer that was willing to provide a dispersant sample for tests. The dispersant, Finasol® OSR 52, is an alkaline and combustible liquid. It has a density of 1100 g/L and contains more than 30 % nonionic surfactants and 15 – 30 % anionic surfactants (Total Fluides, 2015). DOC and DOSS concentrations in Finasol® OSR 52 were quantified as 474 ± 16 g C/L and 207 ± 6 g/L, respectively. Finasol® OSR 52 had a measured critical micelle concentration (CMC) of 9130 mg/L and 4400 mg/L in ultrapure and raw surface water, respectively. At this concentration, micelles (that is, clusters of surfactant monomers) begin to form and further dispersant addition leads to no additional decline in surface tension.

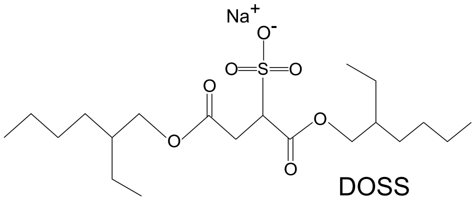

Figure 5.1: Molecular structure of sodium dioctyl sulfosuccinate (DOSS) or sodium docusate.

5.2.2 Preparation of contaminated surface water

Crude oil was retrieved following the spill at Prince Albert (Saskatchewan, Canada). Its composition was 70 – 80 % bitumen and 20 – 30 % condensate (dilbit) (Government of Canada, 2013). Two scenarios were studied – surface water contaminated with crude oil and Finasol® OSR 52 and surface water contaminated with only crude oil concentrations.

For contamination with crude oil and Finasol® OSR 52, the standard protocol for the preparation of an oil-in-water emulsion was followed in order to generate dispersant-stabilized oil droplets in water (Katepalli & Bose, 2014). First, 2.5 L of raw surface water was added to a 4 L beaker and using an overhead agitator (Heidolph RZR 1), stirring began at 664 rpm. Then, Finasol® OSR 52 was added at a dispersant-to-oil ratio of 1 to 20 (1:20) and agitated for 1 min. Lastly, the oil mass was introduced and agitation continued until the third minute. For contamination with only crude oil, the same protocol was followed without dispersant addition. Crude oil was therefore added and the mixture was agitated for 3 min.

For efficient mixing, the impeller shaft was fixed off the center of the beaker and the attached pitch blade (four blades with a diameter of 7.5 cm) was positioned at one-third of the water height in the beaker (Kevin J Myers et al., 2002). The dispersant-to-oil ratio was not varied in this study. The applied ratio, 1:20, is typically employed in the event of a spill in marine environments (International Tanker Owners Pollution Federation Limited (ITOPF), 2011). Due to its viscosity, Finasol® OSR 52 was first diluted using ultrapure water at a ratio of 1 to 10 prior to use. Applied dispersant concentration was 5.2 mg/L (13 mg in 2.5 L of raw water) while crude oil concentration was measured as 109 ± 13 mg/L (273 ± 32 mg in 2.5 L of raw water). Relative to raw water, oil and dispersant concentrations were 0.010 % (w/w) and 0.00052 % (w/w), respectively. Crude oil and dispersant concentrations were defined based on measured $C_{10} – C_{50}$ concentrations (5.4 mg/L), which were tailored to be within the range observed in oil-spill case studies in surface water (9 – 15 mg/L) (Galvez-Cloutier et al., 2014). Note that $C_{10} – C_{50}$ is a parameter that is used to quantify the presence of petroleum hydrocarbons and in uncontaminated source water, $C_{10} – C_{50}$ concentration was below the detection limit.

5.2.3 Ballasted flocculation protocol

The common jar-test square beaker (B-Kr^2) could not be employed due to its adsorption affinity for petroleum hydrocarbons. As a result, a custom-made, round borosilicate glass beaker, whose design was based on specifications in (American Water Works Association (AWWA), 2004), was utilized for all tests (Figure B1 in Supplementary Information). The beaker was equipped with baffles for adequate mixing, a lid to reduce volatilization, and an overhead agitator (BDC) that was connected to a flat blade impeller.

For all ballasted flocculation tests, alum (*ALS*, Kemira: 4.3 % Al by wt) and ferric sulfate (*PIX 312*, Kemira: 12.3 % Fe by wt) were employed as coagulants. Both coagulants are frequently used to treat Canadian surface waters. An optimized alum dose of 41 mg dry alum/L (= 3.6 mg Al/L = 0.40 mEq/L = 1.3×10^{-4} mol/L) and a calculated equivalent dose of ferric sulfate (62 mg liquid/L = 7.4 mg Fe/L = 0.40 mEq/L = 1.3×10^{-4} mol/L) were applied. Most DWTP fed by the same source water use alum as coagulant. Consequently, dose optimization trials for alum were conducted as pre-tests prior to the main tests presented in this study and were performed to determine the required dose for optimal turbidity and organic matter removal in uncontaminated raw water. The optimized alum dose was determined for the source water in the absence of contamination in order to study the expected disturbance to treatment caused by contaminated waters reaching a treatment process operated under optimal conditions. The resulting coagulation pH (pH = 6.0) and water temperature (21°C) were also assessed to validate that the selected dose favored floc formation and minimised residual aluminum concentrations in treated water. Interestingly, the selected optimized alum dose in lab-scale experiments corresponded to that which was applied on the same day of raw water sampling at the DWTP (41 mg dry alum/L). Ferric sulfate dose was not optimized; rather, for the sake of comparison of alum and ferric sulfate, the equivalent dose of the latter was calculated relative to the alum dose. A cationic polyacrylamide, Hydrex 3613 (Veolia), was used as polymer at a dose of 0.22 mg/L.

Contaminated raw water samples were prepared and treated immediately through ballasted flocculation to limit any impact of oil weathering and to simulate water quality and treatment efficiency on the day of oil contamination. Once 2 L of contaminated raw surface water was transferred to the beaker, the impeller and beaker lid were put in place and ballasted flocculation proceeded as follows: stirring at 212 rpm began and coagulant was injected at time = 0. Two minutes later, microsand at a dose of 4 g/L was added followed by 50 % of the polymer dose. At the fourth minute, the remaining 50 % polymer dose was injected. Stirring continued for an additional six minutes after which agitation was stopped (10th minute). Treated water was allowed to settle for 3 minutes, after which samples were withdrawn (Figure 5.2) (C. Desjardins et al., 2002).

Ballasted flocculation tests of raw surface water (containing no crude oil or dispersant) were performed using alum and ferric sulfate as coagulants. Raw and settled waters were sampled and analyzed for pH, particle size, DOSS, turbidity, DOC, UVA_{254}, zeta potential, and surface tension. When alum was employed at an optimized dose of 41 mg dry alum/L, pH in settled water was 6.0. When ferric sulfate was employed at an equivalent dose of 62 mg liquid/L, pH in settled water was 5.9.

For contaminated surface water, three ballasted flocculation tests were conducted per scenario. These tests included a control test, ballasted flocculation test with alum as coagulant, and ballasted flocculation test with ferric sulfate as coagulant. All three tests followed the previously described protocol except that for the control test, ultrapure water was injected at the same volume as that of alum and polymer and to simulate microsand addition, the beaker lid was left open for a few seconds. Samples collected at the end of the control test served as the initial concentration (C_o) for percent removal calculations. Raw and settled waters were collected and analyzed for oil droplet size, DOSS, turbidity, TOC, UVA_{254}, zeta potential, and surface tension.

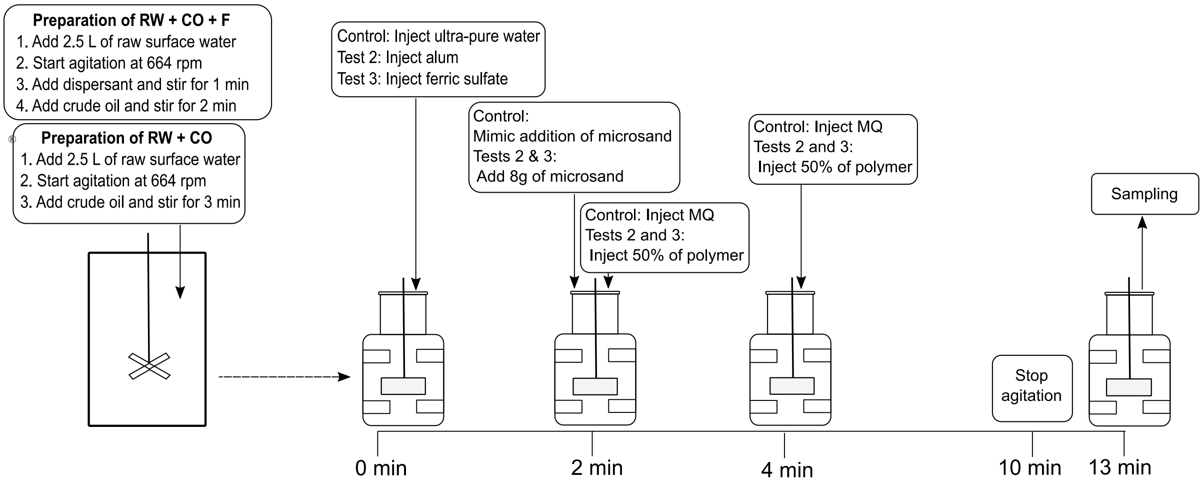

Figure 5.2: Graphical representation of the protocol for surface water contamination and subsequent treatment via ballasted flocculation. RW: uncontaminated raw water; CO: crude oil; and F: Finasol® OSR 52.

5.2.4 Analytical methods employed

5.2.4.1 Chemicals and reagents

Sodium docusate (DOSS, purity ≥ 99.0 %) and sodium bis (2-ethylhexyl-d17) sulfosuccinate (SBS-d_{34}, purity ≥ 99.0 %) were purchased from Sigma–Aldrich (St. Louis, MO, USA). All solvents used were of high-performance liquid chromatography (HPLC) grade and were purchased from Fisher Scientific (Whitby, ON, Canada). Water used was also of ultrapure grade (resistivity at 25°C was set on 18.2 MΩ/cm) and was obtained from a Milli-Q water purification system (Millipore Sigma, Bedford, MA, USA). Individual stock solutions of DOSS were prepared in methanol (MeOH) at a concentration of 1000 mg/L and kept at -20°C for a maximum of 3 months. Working solutions were prepared daily by dilution of the 1000 mg/L stock solution at a concentration of 10 mg/L in H_2O. Formic acid (HCOOH, purity ≥ 95.0 %) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Chromatographic mobile phases were prepared daily.

5.2.4.2 Surfactant analysis by LC-MS/MS

Quantitative analysis of surfactants was performed with an ultra-high performance liquid chromatography (UHPLC) and tandem mass spectrometry (MS/MS). A Thermo Scientific Accela 1250 pump (Thermo Fisher Scientific, Waltham, MA, USA), controlled by Chromeleon 7.2 software, was used for separation on the analytical column. A Hypersil GOLD$^{\text{TM}}$ C18 column (50 mm × 2.1 mm, 1.9 µm particles), preceded by a guard column (5 mm × 2.1 mm, 0.2 µm porosity) (Thermo Fisher Scientific, Waltham, MA, USA), was used for chromatographic separation of target compounds at 45°C. The delivery system, a Thermo Scientific Accela Open Autosampler (Thermo Fisher Scientific, Waltham, MA, USA), was used for injection and samples were kept at 4°C in a fresh compartment before injection. The gradient condition comprised of a mobile phase A (made of water and 0.1 % HCOOH) and mobile phase B (made of acetonitrile and 0.1 % HCOOH). A gradient was used starting from 10 % B. Then, acetonitrile was increased to 100 % from 0 – 5 min and was held constant at 100 % for 2.40 min. Finally, the mobile phase B was brought back to 5 % and maintained for 2.50 min for column conditioning before the next injection. A flow rate of 550 µL/min and an injection volume of 50 µL were employed.

Ionization of target compounds was achieved with a heated electrospray ionization (HESI) Ion Max ion source operated in negative mode. The parameters were set as follows: the ionization spray voltage was set at +3,650 V; temperature of the ion transfer tube was set at 350°C; temperature of the vaporizer was set at 400°C; and sheath gas and auxiliary gas flow were set at 50 and 25 arbitrary units, respectively. The TSQ Quantiva triple quadrupole mass spectrometer, manufactured by Thermo Fisher Scientific (Waltham, MA, USA), was operated in selected reaction monitoring (SRM) mode for quantification and detection. The respective relative intensity ratios per compound were used in SRM mode for detection and quantification. The mass spectrometer parameters were set as follows: Q1 and Q3 quadrupole resolutions were set, respectively, at 0.7 FWHM; dwell time was set at 0.020 s; and the collision gas (Ar) pressure was set at 1.5 mTorr. The different SRM transitions and their optimized parameters for the quantification and confirmation of target analytes are presented in the Supplementary Information (Table B1).

Glass fiber (GF), polyvinylidene fluoride (PVDF) and cellulose filters were selected and used to filter spiked water, which was then analyzed in triplicate using UHPLC-HRMS to evaluate surfactant recovery rates for each filter. Ultrapure water was utilized in the method development, optimization and validation for surfactant analysis in order to generate reference values for surfactant recovery rates. Overall, GF filter showed the best recovery rate for DOSS (average of 61 ± 2 %). Hence, GF filter was selected for sample filtration prior to analysis. Method validation was done by determining the method limit of detection (LOD) and limit of quantification (LOQ), linearity, precision and accuracy. LOD and LOQ were determined as 3.3 and 10 times the standard deviation of the y-intercept divided by the slope of the calibration curve. A seven-point calibration curve was obtained by spiking ultrapure water samples. Quantification of surfactants was done by using a seven-point, matrix-matched internal calibration curve. Thus, the instrument response was determined as the ratio of the area of the target compound to that of the internal standard. All validation parameters are presented in the Supplementary Information (Table B2).

5.2.4.3 Analysis of oil droplet size and other parameters

Oil droplet size (> 10 nm) was analyzed using the Mastersizer 3000 (Malvern Instruments, UK). The technique is based on laser diffraction and is equipped with a Hydro EV wet dispersion unit for circulation of the liquid sample to the analytical cell. Essentially, red and blue laser light are passed through the sample and the intensity of the diffracted or scattered light, measured at different angles, is utilized to compute particle size distributions (Andrews, Nover, & Schladow, 2010). The Mie theory was applied in particle size quantification and the volumetric diameter of an equivalent sphere (D_{v50}) was reported. The D_{v50} was reported as the average value of 10 measurements. Only volume-based diameters (D_{v50}) are presented in this study. D_{v10} and D_{v90} values are presented in the Supplementary Information (Tables B5 and B6). The methods utilized for the analysis of other parameters in this study are summarized in Table 5.1.

Table 5.1: Analytical parameters and methods.

Parameters	Units	Methods
Particle size	µm	Mastersizer 3000 (Malvern) (American Public Health Association (APHA) et al., 2012) Refractive index: 1.5 – 1.533 Obscuration range: 0.1 – 20 %
$C_{10} – C_{50}$	mg/L	GC-FID ((CEAEQ), 2016) Samples were analyzed externally with no prior sample preparation
DOSS	mg/L	Ultra-high performance liquid chromatography (UHPLC) and tandem mass spectrometry (MS/MS) (Mathew et al., 2012)
Alkalinity	mg $CaCO_3$/L	Accumet AB15 pH meter, SM 2320 B (American Public Health Association (APHA) et al., 2012)
Turbidity	NTU	Turbidimeter, Hach 2100 N SM 2130 B (American Public Health Association (APHA) et al., 2012)
UVA_{254}	cm^{-1}	Filtration using 0.45 µm filter, pre-rinsed with ultrapure water (American Public Health Association (APHA) et al., 2012)
Zeta potential	mV	Zetasizer Nano (Malvern) (Duan et al., 2014)
Surface tension	mN/m	Pendant drop method using OCA20 (Dataphysics) (Berry et al., 2015; Stauffer, 1965)
Total Organic Carbon (TOC)	mg C/L	Sievers Innovox TOC Laboratory Analyzer (Suez) SM 5310 B (American Public Health Association (APHA) et al., 2012)
Dissolved Organic Carbon (DOC)	mg C/L	Sievers M5310C Online TOC Analyzer (Suez) (American Public Health Association (APHA) et al., 2012) Filtration using 0.45 µm filter, pre-rinsed with ultrapure water

5.3 Results and Discussion

5.3.1 Water quality in raw and settled waters

Five water quality parameters – turbidity, surface tension, UVA_{254}, zeta potential, and TOC – were analyzed in raw (uncontaminated and contaminated) surface water and their corresponding settled waters. Residual dispersant concentrations as DOSS were also reported. The sensitivity of each measured parameter to petroleum hydrocarbon contamination, before and after ballasted flocculation, is explored as well as the impact of contamination on the treatment efficiency.

5.3.1.1 Turbidity

For uncontaminated surface water, initial turbidity was measured at 4.3 ± 0.1 NTU. Ballasted flocculation with alum and ferric sulfate generated similar settled water turbidity, that is, 0.75 ± 0.05 NTU (DOC = 2.3 mg C/L) and 0.82 ± 0.07 NTU (DOC = 2.2 mg C/L), respectively. Treatment objectives, based on settled water turbidity (< 1 NTU) and DOC concentration (≈ 2 mg C/L), were met with the applied alum and ferric sulfate doses. Therefore, the effectiveness of these doses to attain the same level of treatment for contaminated surface water was subsequently examined.

Addition of crude oil concentration to raw surface water at a concentration of 109 ± 13 mg/L led to a slight increase in raw water turbidity to 5.7 ± 0.1 NTU compared to that of uncontaminated raw water (Figure 5.3a). Ballasted flocculation with alum generated settled water with turbidity of 0.42 ± 0.03 NTU, lower than observed for alum-treated uncontaminated surface water. In the absence of dispersants, crude oil droplets tend to coalesce. They can attach to particles in water, which can increase oil droplet density and favor its removal (as well as that of particles in the system) through enmeshment in precipitates (Fitzpatrick et al., 2015). In contrast, settled water from ballasted flocculation with ferric sulfate did not meet treatment objectives generally used in drinking water production to ensure adequate coagulation. In fact, settled water turbidity was measured at 9.2 ± 3.2 NTU. It should be recalled that for comparison of treatment efficiency, the applied ferric sulfate dose in this study was calculated based on the optimized alum dose. In addition, even for ferric sulfate-treated settled water without prior contamination, pH was not at the optimal range of 5.0 – 5.5 [26].

In the presence of dispersant and crude oil, raw water turbidity increased to 7.2 ± 0.1 NTU as opposed to the measured value in crude oil-contaminated surface water. Ballasted flocculation with alum showed an increase in settled water turbidity to 0.92 ± 0.01 NTU compared to 0.42 ± 0.03 NTU in alum-treated settled water (crude oil-only test). Influence of the dispersant matrix characteristics might have played a role in the observed increase in settled water turbidity, which still met the defined treatment objective (turbidity < 1 NTU). Coagulant demand exerted by the dispersant limited the amount available and necessary for effective turbidity removal (hence, higher settled water turbidity). When ferric sulfate was applied, settled water turbidity (5.8 ± 0.2 NTU) was inferior than observed in the absence of dispersant (crude oil-only test: 9.2 ± 3.2 NTU). Nonetheless, treatment was still poor and could not attain settled water quality observed for ferric sulfate treatment of uncontaminated surface water. Crude oil in the presence and absence of dispersants therefore limited ballasted flocculation efficiency when ferric sulfate was employed as coagulant. This was not only due to sub-optimal coagulation conditions, but also due to the probable increase in solubility of iron (III) from complex formation with crude oil (Pourrezaei et al., 2011).

Turbidity in the Des Prairies River fluctuates according to the season and can range from 5 to 58 NTU (Amini et al., 2018). Observed variations in contaminated raw water suggest that the sensitivity of turbidity is insufficient to detect a diluted petroleum hydrocarbon contamination upstream of this drinking water plant intake. This is concurrent with observations made subsequent to a diesel and gasoline contamination of the same source water (Okoro et al., 2021). When an optimized coagulant dose (alum) was employed, ballasted flocculation generated settled water with an acceptable turbidity and thus, did not point to hydrocarbon contamination. This shows the limitation of the turbidity parameter to signal oil contamination in surface water.

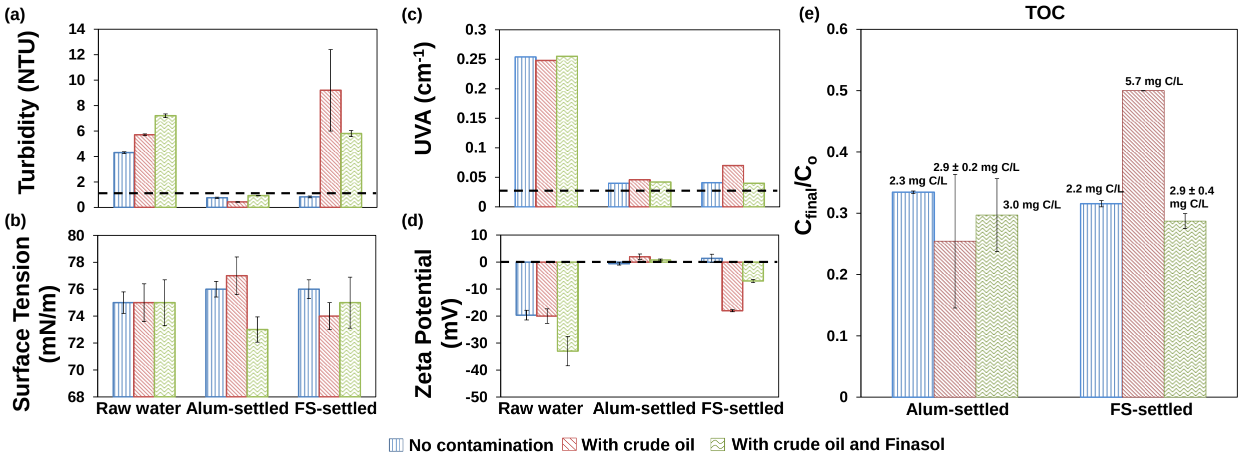

Figure 5.3: (a) Turbidity, (b) Surface tension, (c) UVA$_{254}$, and (d) Zeta potential in uncontaminated and contaminated raw waters and subsequent settled water quality from ballasted flocculation tests using alum and ferric sulfate (FS) as coagulants. Error bars indicate minimum and maximum values while dashed lines represent the typical criteria for settled water quality: turbidity less than 1 NTU, UVA$_{254}$ between 0.03 – 0.035 cm^{-1}, and zeta potential close to 0 mV. (e) Normalized TOC concentrations in alum- and ferric sulfate-treated settled waters following ballasted flocculation of uncontaminated and contaminated raw water. Error bars indicate minimum and maximum values. Values above error bars indicate the final TOC in settled water.

5.3.1.2 Surface tension

Uncontaminated surface water, at a surface tension of 75 ± 1 mN/m, exhibited no change upon ballasted flocculation with alum or ferric sulfate (76 ± 1 mN/m). The addition of crude oil or both crude oil and dispersant also led to no change in surface tension of contaminated raw water and its treated alum and ferric sulfate equivalents (Figure 5.3b). Findings are also similar to results in (Okoro et al., 2021) for petroleum hydrocarbon contamination in surface water. Surface tension is not monitored in DWTP in Quebec, but was analyzed in this study due to the addition of a dispersant in raw water. Since dispersants affect surface tension, it was hypothesized that this parameter might be a good indicator of contamination at the raw water intake upon dispersant application. However, dispersant concentration was too low and did not initiate a reduction of this parameter.

5.3.1.3 UVA_{254} and zeta potential

Uncontaminated surface water had an initial UVA_{254} and zeta potential of 0.254 cm^{-1} and -20 ± 2 mV, respectively. Upon ballasted flocculation with alum and ferric sulfate, UVA_{254} reduced to 0.040 cm^{-1} and 0.041 cm^{-1}, respectively, whereas zeta potential was measured at -0.59 ± 0.52 mV and 1.4 ± 2.0 mV, respectively. Treatment objectives, based on UVA_{254} between 0.035 and 0.040 cm^{-1} and zeta potential close to 0 mV (American Water Works Association (AWWA), 1999; Davis & Edwards, 2014), were attained using the applied alum and ferric sulfate doses. pH of settled water was 6.0 (alum-treated) and 5.9 (ferric sulfate-treated). At this pH and considering the applied molar concentration of both coagulants, coagulation conditions were within the required operating regions for the formation of amorphous precipitates (Davis & Edwards, 2014; Montgomery Watson Harza (MWH), 2005).

Addition of crude oil concentration to raw surface water led to no appreciable change in initial UVA_{254} and zeta potential (Figs. 3c and 3d). Both parameters were measured at 0.248 cm^{-1} and -17 ± 3 mV, respectively. Ballasted flocculation of crude oil-contaminated surface water led to UVA_{254} values of 0.046 cm^{-1} and 0.070 cm^{-1} for alum and ferric sulfate-treated settled waters, respectively, whereas zeta potential was measured at 2 ± 1 mV and -18 mV, respectively. For alum treatment, settled water UVA_{254} and zeta potential almost met common treatment objectives ($UVA_{254} = 0.035 – 0.040\ cm^{-1}$) for DOC removal. The opposite was true for ferric sulfate treatment.

In the presence of dispersant and crude oil, negligible change in UVA_{254} was observed (0.255 cm^{-1}) and the same was true for crude oil-contaminated raw water (Figure 5.3c). Contrary to the crude oil-only scenario, the addition of dispersant did induce a decline in zeta potential to -33 ± 5 mV, pointing to the possible impact of the complexity of the dispersant matrix (Total Fluides, 2015). Such a decrease means that particles exhibit greater repulsion and would require higher coagulant dose to achieve the required settled water quality (Sharp, Jarvis, Parsons, & Jefferson, 2006). Since the applied coagulant dose in this study remained the same, a reduction in ballasted flocculation efficiency is expected, leading to the observed higher settled water turbidity (Section 5.3.1.1) (Sharp et al., 2006). Ballasted flocculation with alum generated settled water with UVA_{254} and zeta potential of 0.042 cm^{-1} and 1 mV, both of which were within the same range as observed for alum treatment of crude oil-contaminated surface water. When ferric sulfate was applied, settled water UVA_{254} and zeta potential were measured at 0.040 cm^{-1} and -7 ± 1 mV, both of which were better than observed for ferric sulfate treatment of crude oil-contaminated surface water.

Similar to turbidity and surface tension parameters, the lack of sensitivity of UVA_{254} and zeta potential to petroleum hydrocarbon contamination in surface water has also been previously reported (Okoro et al., 2021). Although UVA_{254} and zeta potential were not suitable to assess raw water contamination, both parameters are of use to determine if process efficiency is impaired due to crude oil contamination. When an optimized alum dose was applied, ballasted flocculation efficiency was not limited by the presence of crude oil and dispersant. The similarity of settled water UVA_{254} and zeta potential to that of alum-treated settled water (without contamination) shows that both parameters are unsuitable indicators of petroleum hydrocarbon contamination. The negative zeta potential in ferric sulfate-treated settled water indicates sub-optimal coagulation at the applied dose.

5.3.1.4 TOC

Uncontaminated surface water had an initial TOC of 7.5 mg C/L. Measured DOC concentrations in alum and ferric sulfate-treated settled waters were 2.3 mg C/L and 2.2 mg C/L, respectively. Here, DOC was privileged over TOC measurements to assess coagulation performance for natural organic matter (NOM) removal. As the treatment objectives were expressed in terms of DOC, the same parameter was assessed in settled water.

Addition of crude oil concentration to raw surface water increased TOC to 11 mg C/L. Ballasted flocculation of crude oil-contaminated surface water reduced TOC to 2.9 mg C/L and 5.7 mg C/L for alum and ferric sulfate treatments, respectively (Figure 5.3e). In the presence of dispersant and crude oil, TOC was quantified as 10 ± 1 mg C/L. This value was not significantly different from what was observed in the absence of dispersant. Ballasted flocculation of the dispersant-oil-contaminated surface water reduced TOC to 3.0 mg C/L and 2.9 ± 0.4 mg C/L for alum and ferric sulfate treatments, respectively. When alum was applied, TOC was similar to that observed in alum-treated settled water (crude oil-only tests). When ferric sulfate was applied, TOC was lower than observed in ferric sulfate-treated settled water in the absence of dispersant (Figure 5.3e). In addition, the impact of coagulant type on ballasted flocculation performance proved to be negligible in terms of TOC removal when dispersant was present.

TOC may serve as an indirect indicator of changes in the physicochemical properties of source water caused by an oil spill. This is done to enable drinking water facilities to inquire on the source of this water quality modification and make timely decisions such as when to shut off or reopen the raw water intake. TOC concentrations in the Des Prairies River are fairly stable and generally vary seasonally from 7 to 9 mg C/L. Therefore, a 3 mg C/L difference in source water TOC, due to petroleum hydrocarbon contamination, should alert the DWTP operator of the likelihood of contamination. Comparing alum-treated settled waters of uncontaminated and contaminated waters shows no variation in residual TOC. This signifies that monitoring TOC at the raw water intake, as opposed to post-ballasted flocculation, would serve as a better indicator of hydrocarbon contamination. This observation is, however, limited to watersheds with fairly stable TOC concentrations. More research is needed to assess if TOC monitoring in source water would consist of a good indicator of hydrocarbon contamination in watersheds prone to TOC fluctuations greater than 5 mg C.

5.3.1.5 Residual dispersant

Residual dispersant was quantified by measuring sodium docusate (DOSS) concentration. DOSS was not detected in uncontaminated raw water. The addition of dispersant and crude oil to raw surface water led to an initial DOSS concentration of 722 ± 7 µg/L. Only two percent of this concentration was lost due to adsorption on jar test beaker even though DOSS has a strong affinity for surfaces, glass or plastic (Mathew et al., 2012). Ballasted flocculation of the dispersant-oil-contaminated surface water led to a decrease in docusate concentration to 319 ± 1 µg/L and 376 ± 1 µg/L for alum and ferric sulfate treatments, respectively. Although these concentrations exceed the required U.S. EPA threshold of 40 µg/L for aquatic life (Mathew et al., 2012), they are below the maximum acceptable concentrations set by the U.S. Food and

Drug Administration (FDA) (10 – 25 mg/L) (U.S. National Library of Medicine). DOSS is often employed as food additive and medication for stool softening and depending on the intended use, the U.S. FDA has set maximum concentrations.

Dispersant use introduced organic contaminants that were difficult to eliminate by ballasted flocculation, even though settled water quality (alum treatment) was within the required treatment objectives. Although not discussed in detail in this study, dispersant characterization confirmed the presence of benzene (16 µg/L), toluene, ethylbenzene, and xylenes (BTEX = 282 µg/L), whose removal in surface water by ballasted flocculation has been reported to be insignificant (Okoro et al., 2021). Observed limitation in ballasted flocculation efficiency might have been due to the impact of dispersant matrix characteristics.

5.3.2 Removal of crude oil droplets

To assess the impact of dispersant application on ballasted flocculation efficiency for crude oil droplet removal, settled water quality of jar test experiments, conducted on both uncontaminated and contaminated surface waters, was compared.

5.3.2.1 Uncontaminated raw and settled waters

Particle sizes in uncontaminated raw and settled waters were measured prior to contamination with crude oil. Small-sized particles, with D_{v50} of 8.8 µm, were present in raw untreated water. These particles stem most likely from the presence of silt and organic particles. Ballasted flocculation with alum and ferric sulfate generated settled waters with relatively similar turbidity (0.75 ± 0.1 NTU and 0.82 ± 0.1 NTU) but differed in terms of D_{v50} values (513 µm and 22 µm, respectively) (Figure 5.4). Coagulation conditions were optimal for alum treatment, where settled water pH was 6.0. Particle size was however observed to be much larger in alum-treated settled water probably due to the presence of hydrated alum flocs with low densities (Vadasarukkai, 2016). For ferric sulfate treatment, the smaller size could be explained by the inertness and compactness of ferric flocs compared to alum flocs (Montgomery Watson Harza (MWH), 2005).

5.3.2.2 Crude oil-contaminated raw and settled waters

Prior to treatment, the addition of crude oil concentration to raw surface water generated droplets with a larger mean size (D_{v50} = 186 µm). Its particle size distribution showed two peaks, where the peak of smaller particles represents particles in raw untreated water whereas peak of larger particles accounted for that of crude oil droplets (Figure 5.4). Subsequent to ballasted flocculation with alum and ferric sulfate, residual flocs measured in settled waters had D_{v50} values of 4.6 µm and 23 µm, respectively, with corresponding residual turbidity values of 0.42 NTU and 9.2 ± 3.2 NTU, respectively. Upon crude oil contamination in raw surface water, increase in residual turbidity in ferric sulfate-treated settled water points to poor floc aggregation while when alum was employed as coagulant, no hindrance in ballasted flocculation efficiency was observed.

Oil droplets are negatively charged and their removal during ballasted flocculation can occur through adsorption and enmeshment in positively charged aluminum or ferric hydroxide precipitates (Canizares et al., 2008; Duan & Gregory, 2003). Hydroxide precipitates were the major species, as coagulation pH was at its optimum for precipitate formation (Davis & Edwards, 2014). Both adsorption and enmeshment in precipitates were considered as the principal contaminant removal pathway during ballasted flocculation using alum. However, as previously mentioned, for ferric sulfate treatment, increased solubility of iron (III), due to the formation of complexes with oil compounds, and suboptimal coagulation pH might have contributed to poor flocculation and the overall decrease in efficiency of the treatment process (Pourrezaei et al., 2011).

5.3.2.3 Dispersant- and crude oil-contaminated raw and settled waters

Upon dispersant addition, dispersant-stabilized oil droplets (D_{v50} = 289 µm) were formed and were larger than those formed in raw crude oil-contaminated water (Figure 5.4). The observed increase in size stems most likely from dispersant-enhanced interactions between crude oil droplets and charged suspended particles in raw water. Red solid lines for RW disappear and become one peak in RW + CO + F (Figure 5.4). Dispersant-stabilized droplets represented a much larger percentage of the total volume of droplets (16 % in the presence of dispersant *vs* 7 %

in the absence of dispersant), which might explain the observed turbidity increase to 7.2 ± 0.1 NTU (with dispersant) as opposed to 5.7 ± 0.1 NTU (without dispersant). Smaller droplet sizes are possible at sufficiently higher dispersant concentrations, typically above the critical micelle concentration (CMC), in order to ensure the presence of micelles (agglomerated surfactant monomers) (Green & Trett, 1989). The tested dispersant concentration was however much below the CMC.

Residual flocs in settled water treated with alum possessed a D_{v50} value of 3.0 µm, which was smaller than found in alum-treated crude oil-contaminated water (Figure 5.4). Turbidity of settled water however doubled to 0.92 ± 0.01 NTU, most likely due to the influence of the dispersant matrix. As observed for alum-treated settled water (crude oil-only tests), ballasted flocculation with alum was effective, leaving only microflocs in settled water, and the presence of crude oil and dispersant did not seem to hinder the efficiency of the treatment process (turbidity was still less than 1 NTU). As for ferric sulfate, treatment was affected by the presence of both crude oil and dispersant. Ballasted flocculation with ferric sulfate generated relatively larger residual flocs in settled water (D_{v50} = 28 µm), which were comparable to that observed in the absence of dispersant (23 µm, ferric sulfate-treated settled water). Settled water turbidity was however slightly lower in the presence of dispersant (5.8 ± 0.2 NTU), but still largely exceeded the treatment objective of less than 1 NTU.

Generally, in the presence of dispersants, oil droplet removal can occur in two possible ways considering that surfactants in dispersants serve as bridges between the oil and water interface and enable the entrainment of oil droplets down the water column (M. F. Fingas, 2011; Prince, 2015; Weiss & McClements, 2000). First, the low concentration of dispersant means the hydrophobic tail of DOSS monomers can adsorb on oil droplets via Van der Waals interactions. At the same time, the negatively charged hydrophilic head can interact with water molecules or be neutralized on the surface of the positively charged aluminum or ferric hydroxide precipitates (Myers, 2006b; Palmer & Hatley, 2018; Shin & Kim, 2001). Oil droplets can therefore be removed from the solution. Second, due to the dilute state of the system, surfactants can be lost through detachment from the interfacial film, leading to destabilization of the emulsion, droplet aggregation, increased size, and consequently, its removal from the solution (Gerrity et al., 2018).

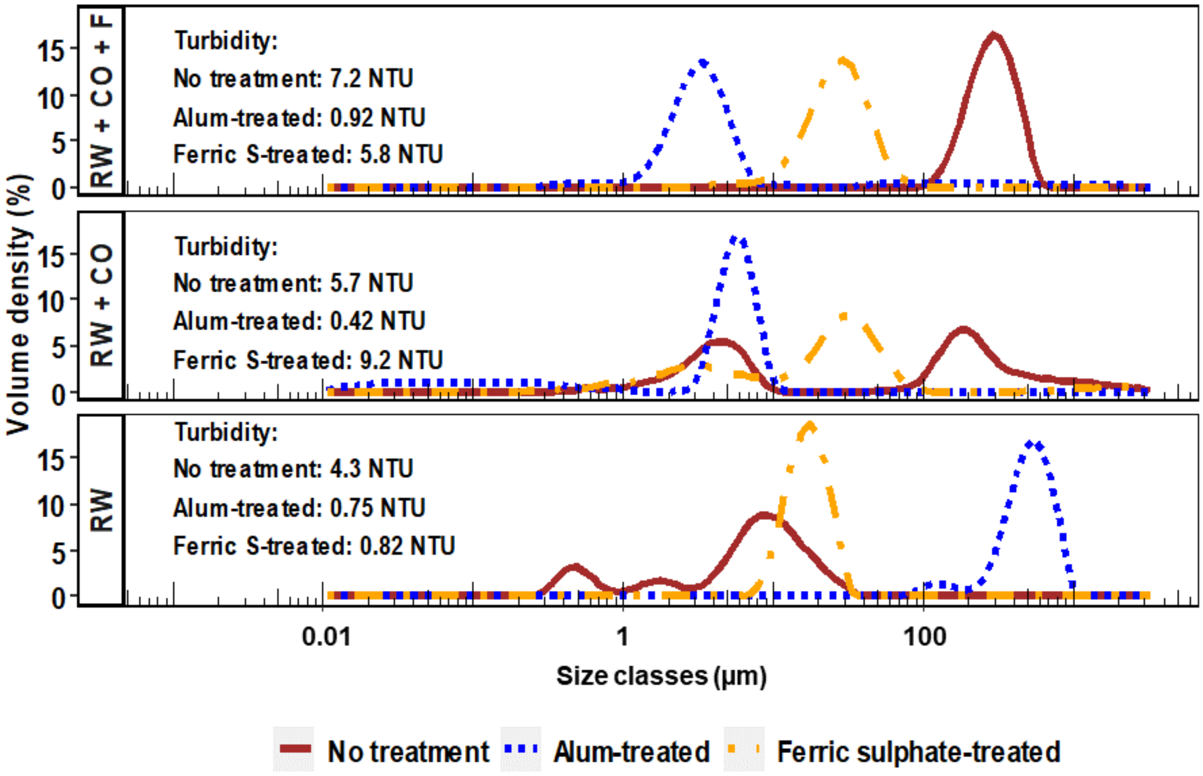

Figure 5.4: Volume-based particle size distributions for uncontaminated raw water (RW), raw water contaminated with crude oil (RW + CO), and raw water contaminated with crude oil and Finasol® OSR 52 (RW + CO + F) that underwent no treatment (control, red *solid lines*), ballasted flocculation with alum (blue *dotted lines*), and ballasted flocculation with ferric sulfate (orange *dot-dash lines*). Turbidity values are inserted for analysis of observed size distributions.

5.4 Implications

From a drinking water perspective, two important questions might be raised in the event of a crude oil spill in surface water and the subsequent application of oil-spill dispersants: a) Can petroleum hydrocarbon contamination be detected by the monitored parameters in DWTP? b) Can the treatment chain eliminate the hydrocarbon concentrations, oil droplets, and other dispersant-related contaminants that arrive at the DWTP? Many DWTP employ ballasted flocculation as the first treatment process towards drinking water production. These plants monitor turbidity, UVA_{254} and zeta potential in raw and settled waters in order to evaluate the efficiency of the treatment process. Findings from this study have shown that with and without dispersants, these parameters, as well as surface tension, are unsuitable as indicators of oil-spill concentrations in surface water. TOC was observed to be a good indicator only when measured upstream of the ballasted flocculation treatment process. If measured downstream, TOC is unable to demonstrate petroleum hydrocarbon contamination. It might therefore be advisable for DWTP in spill-prone areas to install TOC analyzers (or online hydrocarbon detectors) at their water intake to monitor changes in carbon concentration in source water.

Although alum treatment could respond to the required settled water quality, application of low dispersant concentrations and crude oil to surface water led to the introduction of additional hydrocarbons that were difficult to eliminate by ballasted flocculation alone. Adsorption-based filtration processes would be necessary to remove these compounds. Many DWTP in Quebec are equipped with rapid filtration units (sand-anthracite or sand-granular activated carbon). Particles entering these units must be less than 80 µm to avoid media blockage (Montgomery Watson Harza (MWH), 2005). Although the observed size of crude oil droplets after contamination exceeded this threshold, ballasted flocculation with alum and ferric sulfate generated smaller microflocs (3 – 30 µm) that would easily be trapped and eliminated in the pores of the filter media. However, since findings in this study are based on residual flocs in settled water, it might be expected that larger flocs would be present if settling is excluded prior to filtration (for example, direct filtration process). Such systems would most likely experience media blockage upon crude oil contamination.

5.5 Conclusion

This study investigated the impact of low dispersant and crude oil contamination on surface water quality and the efficiency of ballasted flocculation for potable water production. Raw water quality was negatively impacted upon contamination mainly due to the presence of dispersant-related compounds measured as DOSS and petroleum hydrocarbons measured as

TOC. Ferric sulfate at an equivalent dose (as mEq/L) was more sensitive to crude oil and dispersant contamination. Poor flocculation, probable increase in solubility of iron (III) in the presence of crude oil, and sub-optimal coagulation conditions contributed to the observed compromised water quality when ferric sulfate was applied at an equivalent dose to alum. Using a dose optimized for turbidity and DOC removal in uncontaminated raw water, alum treatment of contaminated surface water still generated settled water that met the required treatment objectives. Nonetheless, when dispersant was applied in raw water, DOSS concentrations measured in settled waters proved to be superior to the U.S. EPA guideline for protection of aquatic life (40 µg/L), but below U.S. FDA thresholds (10 – 25 mg/L). Findings in this study will be beneficial to DWTP in their efforts to evaluate and upgrade their treatment chain and to prepare contingency plans in the event of oil spills in surface water. Further research is necessary on the impact of dispersant matrix characteristics and surfactant micelles on ballasted flocculation efficiency.

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CHAPTER 6 ARTICLE III: CONTRIBUTION OF SURFACTANTS AND MICELLES TO CONTAMINATION AND TREATABILITY OF CRUDE OIL-CONTAMINATED SURFACE WATER

This study evaluated the impact of dispersant matrix characteristics and the presence of micelles and crude oil on surface water contamination and treatability. Results showed that surfactants alone are not the major driving factors to surface water contamination in the absence of crude oil. Contamination is however worsened by the presence of micelles and crude oil in surface water. This chapter was submitted as a research paper to the *Journal of Environmental Chemical Engineering* in 2021.

CONTRIBUTION OF SURFACTANTS AND MICELLES TO CONTAMINATION AND TREATABILITY OF CRUDE OIL-CONTAMINATED SURFACE WATER

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ABSTRACT

Subsequent to an oil spill in surface water, impacts of dispersant application on water treatability and residual contamination in distributed potable water remain largely unknown. The desired outcome of dispersant application is attributable to both nonionic and anionic surfactants which reduce interfacial tension. This study evaluated the contribution of surfactants and their agglomerates, micelles, to contamination and treatability of drinking water. Both a commercial oil-spill dispersant and a formulated dispersant solution were applied in surface water, with and without traces of crude oil, and treated by ballasted flocculation. In crude oil-contaminated surface water, the formulated dispersant was applied at two concentrations to generate surfactant monomers and surfactant micelles. Water quality degradation in the absence of crude oil was attributable to surfactants but more importantly to other organic contaminants present in the dispersant matrix. Ballasted flocculation could only handle low dispersant concentrations judging from the generated settled water quality. In the presence of crude oil, dispersant application hindered water quality and treatability due to the introduction of surfactants that were absent in surface water and whose removal was unachievable with an optimized coagulant dose for natural organic matter removal determined prior to contamination. This phenomenon was of greater significance in the presence of micelles. These findings are of relevance to regulators, petrochemical and water industry professionals in their efforts to best design contingency plans for oil-spill remediation of surface water used as drinking water supply.

KEYWORDS

Surfactants, Oil spill, Ballasted flocculation, Micelles, Water quality, Total organic carbon

6.1 Introduction

In marine environments such as oceans, dispersants are often applied to mitigate impacts of oil spills. In surface water such as rivers, the application of dispersants remains controversial due to possible effects on water quality and treatability (Green & Trett, 1989; Prince, 2015). Although the chemical composition of dispersants can be generally grouped into three classes – solvents, additives and surfactants, the actual breakdown of all compounds that make up a commercial oil-spill dispersant is usually undisclosed to the public (Hemmer et al., 2011). As a result, contamination cannot be attributed to a specific compound or class of compounds in the dispersant matrix. It would be necessary to explore a formulated dispersant system containing only one of the three classes of compounds in order to shed more light on its contribution to contamination.

As the main agents responsible for dispersion, surfactants reduce oil-water interfacial tension and allow the formation of small oil droplets (< 70 µm) from a mass of spilled oil on the surface of a waterbody (John et al., 2016). This is more evident when micelles are present at and above the critical micelle concentration (CMC). Micelles are an agglomeration of surfactant monomers that surround oil droplets in such a way that the hydrophobic portion of the surfactant monomers interacts with the oil droplet while the hydrophilic portion interacts with water molecules (Green & Trett, 1989; Myers, 2006a). Below the CMC, only surfactant monomers exist. Surfactants exist in anionic, cationic, nonionic, zwitterionic and amphoteric forms. In many oil-spill dispersants such as Finasol® OSR 52, a mix of anionic and nonionic surfactants is present. Surfactants have been reported to persist in the environment, causing petroleum hydrocarbon accumulation in aquatic life (Green & Trett, 1989; Hemmer et al., 2011). A formulated dispersant system, comprised of a mix of anionic and nonionic surfactants and tailored to generate the same reduction in interfacial tension as oil-spill dispersants, would mimic the behavior of oil-spill dispersants in surface water while excluding the influence of solvents and additives. The application of such a formulated dispersant system to a simulated crude oil spill would hone in on the contribution of surfactant monomers and micelles to surface water contamination and its treatability in drinking water treatment plants (DWTP).

In Canada, many DWTP are supplied by surface waterbodies and the application of a dispersant, in the event of an oil spill, would impair the removal of oil- and dispersant-related contaminants by DWTP processes. Many Canadian DWTP are equipped with either Actiflo® or Pulsators® technology, which consists of the first treatment barrier for dispersants and petroleum hydrocarbons removal. Actiflo® or ballasted flocculation entails 2-min coagulation, 2-min flocculation in the presence of microsand, 6-min maturation, and 3-min settling (C. Desjardins et al., 2002). The addition of coagulant acts to destabilize colloids and other charged particles present in raw water while flocculation enables the aggregation of the destabilized particles to form larger settleable flocs. Dispersants can be termed *anti-flocculants* since they aim to hinder the re-aggregation of dispersed and stabilized oil droplets (Prince, 2015). Hence, their presence in raw water, especially at high concentrations, is expected to reduce ballasted flocculation efficiency by limiting flocculation and settleability.

Some studies have evaluated coagulation-flocculation efficiency for surfactant removal (Hanif, Adnassssn, Latif, Zakaria, & Othman, 2012; Khan et al., 2019; Torres, Belloc, Vaca, Iturbe, & Bandala, 2009). Although residual surfactant concentrations were observed in settled waters, the presence of these surfactants was, however, not due to dispersant application following a simulated oil spill. One study explored contamination (not treatability) following dispersant application to an oil spill in a lake pond (B. F. Scott & Glooschenko, 1984; Brian F. Scott et al., 1984). To the best of the authors' knowledge, no study has investigated the influence of dispersant matrix characteristics on surface water contamination and ballasted flocculation efficiency and the contribution of surfactant micelles to crude oil contamination and treatability of surface water.

The objective of this study was first to evaluate the influence of dispersant matrix characteristics on contamination and ballasted flocculation efficiency upon dispersant application in surface water. This was done by analyzing raw and settled water quality after contamination with a commercial oil-spill dispersant and a formulated dispersant system containing only surfactants. Upon crude oil contamination, the impact of the presence of surfactant micelles on water quality and ballasted flocculation efficiency was studied by comparing low and high surfactant concentration scenarios. Water quality was evaluated based on parameters such as turbidity, zeta potential, total organic carbon (TOC), surface tension, residual surfactant concentration, and UVA_{254}.

6.2 Materials and Methods

6.2.1 Composition of the formulated dispersant system

A nonionic surfactant, Tween 80 (Fisher Scientific), and an anionic surfactant, sodium dodecyl sulfate (SDS) (Sigma-Aldrich), were utilized for all tests involving the formulated dispersant system. These surfactants were chosen based on their solubility in water and the surfactant composition described for a commercial oil-spill dispersant, Finasol® OSR 52. To simulate the reduction in interfacial tension that an oil-spill dispersant would generate, a formulated dispersant was designed as follows: Individual solutions of both surfactants were prepared in ultrapure water at a concentration of 5 % (w/v). A mix of surfactants was then prepared at the following ratios (Tween80:SDS): 50:50, 40:60, and 20:80. Surface tension at each mix ratio was measured in ultrapure water at different concentrations [0 – 2.4 % (v/v)] and compared with that of

Finasol® OSR 52. The mix ratio with the closest decline in surface tension to that of Finasol® OSR 52 was chosen as the formulated dispersant for the rest of the study. Its surface tension was then measured in raw surface water for comparison.

6.2.2 Raw surface water quality and its contamination

Raw surface water was sourced from Des Prairies River (Quebec, Canada), with pH of 7.3, dissolved organic carbon (DOC) concentration of 6.9 mg C/L, turbidity of 4.3 ± 0.1 NTU, UV absorbance at 254 nm (UVA_{254}) of 0.254 cm^{-1}, TOC concentration of 7.5 mg C/L, zeta potential of -20 ± 2 mV, alkalinity of 23 ± 1 mg $CaCO_3$/L, surface tension of 75 ± 1 mN/m, and conductivity of 89 ± 6 µS. The concentrations of SDS (in the formulated dispersant) and sodium dioctyl sulfosuccinate or sodium docusate (DOSS, in Finasol® OSR 52) were monitored in this study and served as the basis for the quantification of residual surfactant (Figure 6.1). Both were undetected in uncontaminated raw water. A 10-month water quality monitoring of the Des Prairies River was also performed to evaluate the significance of measured changes in water quality upon surfactant contamination.

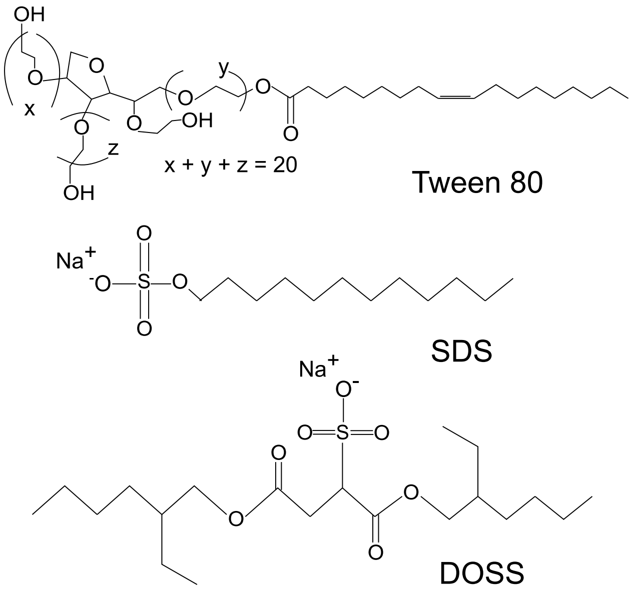

Figure 6.1: Chemical structure of analyzed surfactants.

After determining the adequate mix ratio of surfactants in the formulated dispersant, two contamination scenarios were studied in surface water contaminated with crude oil (retrieved from Prince Albert, Saskatchewan, Canada): a) in the presence of surfactant monomers (below CMC), and b) in the presence of micelles (above CMC). For the test with surfactant monomers, raw surface water was contaminated with crude oil concentrations and the formulated dispersant at a volume-based dispersant-to-oil ratio of 1:20 (International Tanker Owners Pollution Federation Limited (ITOPF), 2011). The amount of crude oil averaged at 94 ± 11 mg/L while the formulated dispersant was at a concentration of 5.2 mg/L. The formulated dispersant was diluted ten times with ultrapure water to enable its extraction and injection in raw water. For the test with micelles, a surfactant concentration at 1.4 times the CMC in raw surface water (1.4xCMC = 10 400 mg/L) was applied in the presence of crude oil concentrations. For both scenarios, contamination was as follows: 2.5 L of raw surface water in a 4 L beaker was stirred at 664 rpm. At t=0, the formulated dispersant was added at either concentration – 1:20 or 1.4xCMC. At t=1 min, crude oil was added and stirring was stopped at the third minute. Contaminated raw water was then transferred to the jar test beaker for ballasted flocculation tests. Samples were taken for oil droplet size, turbidity, TOC, UVA_{254}, zeta potential, surface tension, and SDS concentration.

To evaluate the influence of the dispersant matrix characteristics, another test was done in the absence of crude oil. Concentrations of the formulated and commercial dispersants were varied at 2 mg/L, 20 mg/L, 200 mg/L, 2000 mg/L, 4000 mg/L and 8000 mg/L and spiked in raw surface water. The same protocol for water preparation, as previously described, was followed without the addition of crude oil. The resulting dispersant-contaminated surface water was then treated by ballasted flocculation and analyzed for turbidity, TOC, UVA_{254}, zeta potential, surface tension, and residual dispersant as SDS or DOSS. Ballasted flocculation was discontinued at the dispersant concentration that yielded settled water turbidity greater than 1 NTU, which is considered as a poor performance when assessed in jar-test experiments.

6.2.3 Ballasted flocculation tests

To minimize stripping, ballasted flocculation was simulated in a closed setup based on the design by American Water Works Association (AWWA) (American Water Works Association (AWWA), 2004). The jar-test beaker was circular and baffled for better mixing (Figure C1 in Supplementary Information). Agitation was possible through an overhead agitator (BDC) and a flat blade impeller. Alum (*ALS*, Kemira: 4.3 % Al by wt) was employed as coagulant for all tests. The applied dose (41 mg dry alum/L = 3.6 mg Al/L) was optimized based on laboratory pre-tests for turbidity and organic matter removal in uncontaminated raw water. A cationic polyacrylamide polymer (0.22 mg/L of Hydrex 3613, Veolia) was used in all tested conditions.

For all tests, ballasted flocculation involved the following steps: 2 L of contaminated surface water in the jar-test beaker was stirred at 212 rpm. At t=0, coagulant injection took place and at t=2 min, microsand at 4 g/L and 50 % of the polymer dose were added. At t=4 min, 50 % of the polymer dose that was left was added. At t=10 min, agitation was stopped and sampling took place at t=13 min (Figure 6.2).

For tests in crude oil-contaminated surface water, two tests were conducted: ballasted flocculation with no coagulant, polymer or microsand (control test) and ballasted flocculation with alum. The latter followed the previously described ballasted flocculation protocol while the control test mimicked the same protocol excluding coagulant and polymer addition. Ultrapure water was injected instead while the beaker lid was also opened to simulate microsand addition. Concentrations measured at the end of the control test served as the initial concentration for evaluating changes in measured water quality parameters.

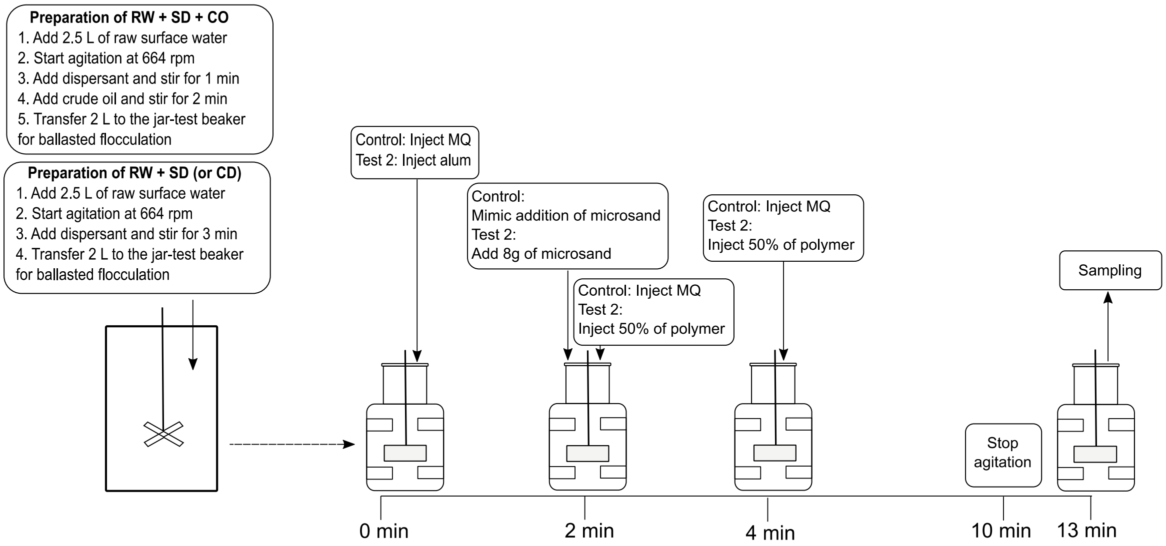

Figure 6.2: Protocol for ballasted flocculation tests. RW: raw water, SD: formulated dispersant, CO: crude oil, CD: commercial dispersant, and MQ: Milli-Q or ultrapure water.

6.2.4 Analytical methods

6.2.4.1 Chemicals and reagents

Docusate sodium (DOSS, purity ≥ 99.0 %), sodium dodecyl sulfate (SDS, purity ≥ 99.0 %) and sodium bis(2-ethylhexyl-d17) sulfosuccinate (SBS-d_{34}, purity ≥ 99.0 %) were purchased from Sigma–Aldrich (St. Louis, MO). Solvents and water employed for analysis were of high-performance liquid chromatography (HPLC) and ultrapure grade, respectively, and were purchased from Fisher Scientific (Whitby, ON, Canada). Working solutions were prepared daily by dilution of the 1000 mg/L stock solution at a concentration of 10 mg/L in water.

6.2.4.2 Analysis of monitored parameters

An Accumet AB15 pH meter was employed for pH and alkalinity measurements. Turbidity was analyzed using a turbidimeter (Hach 2100N) (American Public Health Association (APHA) et al., 2012). For UVA_{254} and DOC analysis, samples were filtered using a pre-rinsed 0.45 µm membrane filter (PALL Corporation) prior to analysis (American Public Health Association (APHA) et al., 2012). TOC analysis was performed using a Sievers Innovox TOC Laboratory

Analyzer (Suez) (American Public Health Association (APHA) et al., 2012). Zetasizer Nano (Malvern Instruments, UK) was employed for zeta potential analysis (Duan et al., 2014). OCA20 (Dataphysics), based on the analysis of a pendant drop, was employed and for surface tension measurements (Berry et al., 2015; Stauffer, 1965). For micelle-stabilized oil droplet size, Mastersizer 3000 (Malvern Instruments, UK) was utilized to compute volume-based diameter, D_{v50}, from an averaged 10 measurements per sample (American Public Health Association (APHA) et al., 2012). Surfactants were analyzed with an ultra-high performance liquid chromatography (UHPLC) with tandem mass spectrometry (MS/MS). A summary of the parameters in the analytical procedure is presented in Table 6.1. Optimized parameters for the quantification and confirmation of surfactants are presented in Supplementary Information (Tables C1 and C2).

Table 6.1: Summary of parameters used for surfactant analysis via UHPLC-MS/MS.

UHPLC	Thermo Scientific Accela 1250 pump
Column	C18 (50 mm × 2.1 mm, 1.9 µm particles)
Guard column	5 mm × 2.1 mm, 0.2 µm porosity
Mobile phase A	Water and 0.1% HCOOH
Mobile phase B	Acetonitrile and 0.1% HCOOH
Gradient	10%B (0 min); 100% from 0-5 min; 100% (2.40 min); 5% (2.50 min)
Flow	550 µL/min
Volume injection	50 µL
Column temperature	45 °C

Table 6.1: Summary of parameters used for surfactant analysis via UHPLC-MS/MS (continued).

UHPLC	Thermo Scientific Accela 1250 pump
Collision gas (pressure)	Ar (1.5 mTorr)
MS/MS	TSQ Quantiva triple quadrupole
Ionization	Heated electrospray
Mode	Negative mode
Spray voltage	-3,650V
Temperature transfer tube	350 °C
Temperature of vaporizer	400 °C
Sheath gas	50
Auxiliary gas	25
Dwell time	0.020 s

6.3 Results and Discussion

6.3.1 Selected surfactant ratio for the formulated dispersant system

The formulated dispersant was comprised of Tween 80 and SDS at a ratio of *20:80*. This composition yielded the closest surface tension to that of Finasol OSR® 52 (Figure 6.3). Increasing the volume of the anionic surfactant, SDS, led to a decrease in the surface tension of ultrapure water, as the charged hydrophilic head in SDS could form hydrogen bonds in water and enable the reduction in surface tension (Myers, 2006a). DOC and SDS concentrations in the formulated dispersant were quantified as 55 ± 7 g C/L and 48 g/L, respectively. Compared to

Finasol OSR® 52, the CMC of the formulated dispersant in ultrapure water was lower (Table 6.2). The opposite was true in raw surface water. Surfactant action in the formulated dispersant might have been hindered by the presence of particulate matter in raw water, increasing the concentration necessary for micelle formation. The observed lower CMC for Finasol OSR® 52 in raw surface water was favored by higher salinity and the presence of polar additives in the commercial dispersant, both of which have been shown to reduce repulsion among the hydrophilic heads of surfactant micelles and enable their formation at a lower concentration (Corrin & Harkins, 1947; Jiang et al., 2003; Sidim & Acar, 2013).

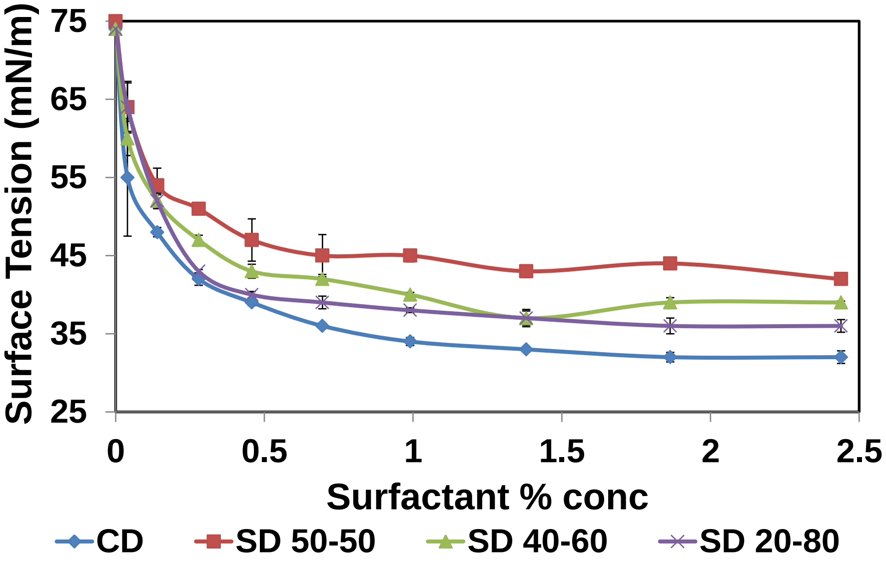

Figure 6.3: Surface tension (mN/m) in ultrapure water as a function of surfactant concentration (% v/v) for different ratios of the formulated dispersant (SD, Tween 80:SDS) and the commercial oil-spill dispersant, Finasol OSR® 52 (CD). Surfactant concentrations varied from 0 – 2.4 % (v/v).

Table 6.2: Surface tension at the critical micelle concentrations (CMC) for a commercial oil-spill dispersant, Finasol OSR® 52, and the formulated dispersant, Tween 80:SDS, at a ratio of 20:80.

Water type	Dispersant	CMC (v/v)	CMC (mg/L)	Surface tension (mN/m)
Ultrapure water	Finasol OSR® 52	0.83 %	9130	35
	Tween 80:SDS (20:80)	0.52 %	5138	40
Surface water	Finasol OSR® 52	0.40 %	4400	36
	Tween 80:SDS (20:80)	0.74 %	7311	38

6.3.2 Influence of the dispersant matrix characteristics on contamination and treatability of surface water

To assess the influence of the dispersant matrix characteristics on surface water contamination and treatability, two scenarios were studied using the formulated and commercial dispersants. Raw surface water contaminated with the formulated dispersant, Tween 80:SDS (20:80), was prepared at increasing dispersant concentrations and subsequently underwent ballasted flocculation with alum. The same was done with the commercial oil-spill dispersant, Finasol OSR® 52. The resulting raw and settled waters in both scenarios as well as the concentration at which contamination was detectable were compared. Water quality parameters such as turbidity, UVA_{254}, zeta potential, TOC, surface tension, and surfactant concentration measured as SDS or DOSS served as the basis for the analysis. During all these tests, the coagulant dose was not readjusted in order to detect the interference of a sudden arrival of contaminated water into an otherwise optimized ballasted flocculation process.

6.3.2.1 Raw water quality

At the time of the test, raw surface water had a turbidity of 4.3 ± 0.1 NTU, UV absorbance at 254 nm (UVA_{254}) of 0.254 cm^{-1}, TOC of 7.5 mg C/L, zeta potential of -20 ± 2 mV, and surface tension of 75 ± 1 mN/m. From the 10-month raw water monitoring, average turbidity was 6.1 ± 2.3 NTU; UVA_{254} was 0.244 ± 0.047 cm^{-1}; TOC in raw water generally varies between 7 to 9 mg C/L for this specific source water; zeta potential was -16 ± 2 mV; and surface tension was 75 ± 7 mN/m.

Upon addition of the commercial dispersant, contamination did not lead to an appreciable change in turbidity, zeta potential, UVA_{254}, and surface tension parameters at dispersant concentrations of 2 mg/L and 20 mg/L (Figure 6.4). Measured values were within the range observed for uncontaminated raw water and data from the 10-month raw water monitoring. However, at 20 mg/L, TOC was 13 mg C/L and was the most sensitive indicator of contamination. At 200 mg/L, significant changes due to contamination were observed in all measured parameters. Raw water became visibly turbid (25 NTU); UVA_{254} almost doubled (0.435 cm^{-1}); and TOC largely surpassed the usual range measured in raw water (89 ± 4 mg C/L). Surface tension was lower (60 ± 1 mN/m) since the addition of more dispersant acts to reduce the surface tension of water. A more negative zeta potential was observed (-30 ± 2 mV) due to an increase in the stability and repulsion of negatively-charged colloidal particles in surface water. Surfactant concentration (reported as DOSS) ranged from 0.20 mg/L to 30 ± 4 mg/L for dispersant concentrations of 2 – 200 mg/L.

Upon addition of the formulated dispersant, no change in water quality parameters, except TOC, was observed at dispersant concentrations of 2 mg/L, 20 mg/L, and 200 mg/L (Figure 6.4). Surfactant concentrations (reported as SDS) ranged from 0.03 mg/L to 5.2 ± 0.3 mg/L for dispersant concentrations of 2 – 200 mg/L. TOC at dispersant concentrations of 2 mg/L, 20 mg/L and 200 mg/L were 6.9 ± 0.8 mg C/L, 7.6 ± 0.1 mg C/L, and 12 ± 1 mg C/L, respectively. Variation in TOC was linear and corresponded to theoretical calculations at each dispersant concentration (see Tables C4 and C5 in Supplementary Information). At 200 mg/L, TOC was not as elevated as observed for the same concentration of the commercial dispersant. Although not presented graphically, when 2000 mg/L of the formulated dispersant was added to raw water, contamination became evident only in the measured TOC and surface tension parameters. Turbidity was 4.7 ± 0.1 NTU; TOC was 99 ± 4 mg C/L; surface tension was 67 mN/m; zeta potential was -19 ± 4 mV; and UVA_{254} was 0.261 cm^{-1}. Measured TOC at this dispersant concentration was similar to the one observed for the commercial dispersant at 200 mg/L.

For both dispersants, contamination was detectable by monitoring TOC. Changes in TOC due to contamination became evident at and above dispersant concentration of 20 mg/L for the commercial dispersant (TOC: 13 mg C/L). However, for the formulated dispersant, contamination became visible at and above dispersant concentration of 200 mg/L (TOC: 12 ± 1 mg C/L). This corresponded to theoretical calculations that show a progressive TOC contribution from the formulated dispersant – 0.05 mg C/L at 2 mg/L, 0.52 mg C/L at 20 mg/L, and 5.2 mg C/L at 200 mg/L. TOC was already 4 mg C/L above the maximum TOC observed in raw water and would be detectable by an online TOC meter at the raw water intake. Compared to the formulated dispersant, the commercial dispersant, Finasol OSR® 52, contains organic additives and solvents, which strongly impact the measured TOC. Finasol OSR® 52 was also characterized for BTEX (benzene, toluene, ethylbenzene, and xylenes) and petroleum hydrocarbons. It contains 282 µg/L and 54 ± 18 g/L, respectively. Therefore, contamination was more visible from a relatively lower dispersant concentration (≥ 20 mg/L). When only surfactants were present (formulated dispersant), a gradual increase in TOC was observed and contamination only became evident at higher dispersant concentrations (≥ 200 mg/L). This demonstrates that the dispersant matrix played a major role in contamination observed through monitored water quality parameters and as such, surfactants are not the only driving factors to contamination.

6.3.2.2 Settled water quality

Subsequent to raw water contamination with the commercial dispersant at 2 mg/L and 20 mg/L, ballasted flocculation yielded acceptable settled water turbidity (less than 1 NTU) (Figure 6.4). However, at 200 mg/L, settled water turbidity was similar to its contaminated raw water equivalent (25 NTU). This signified that no treatment was attained. No further tests were conducted if the measured settled water turbidity exceeded 1 NTU. For the formulated dispersant, contamination with 2, 20, and 200 mg/L and subsequent ballasted flocculation at each concentration yielded settled water that met treatment objectives (less than 1 NTU).

The impact of the initial organic concentration due to dispersant addition on the treatability of surface water can be better assessed by monitoring TOC (Figure 6.4). It is evident that at low dispersant concentrations, contamination of surface water with the commercial dispersant, compared to the formulated dispersant, generated poorly-treated settled water in terms of organic removal. The presence of additional organic compounds in the commercial dispersant contributed to the observed increase in the organic load in surface water. Since coagulant dose remained the same, poor treatability of the contaminated surface water was immediately visible in settled waters through the measured TOC parameter.

It should be noted that for both dispersants and at all measured concentrations, no removal of the measured anionic surfactants (DOSS or SDS) was observed (Table C3 in Supplementary Information). Both surfactants are, by nature, anionic and can form hydrogen bonds with water molecules at the interface (Livingstone, Nagata, Bonn, & Backus, 2015). This might explain their persistence and resistance to removal from surface water by physicochemical treatment, as observed in the current study. The applied coagulant dose was also optimized mainly for dissolved natural organic carbon and turbidity reduction; hence, ballasted flocculation at such a dose did not allow for significant surfactant removal. Poor surfactant removal in treated waters following coagulation-flocculation has also been reported in literature (Hanif et al., 2012).

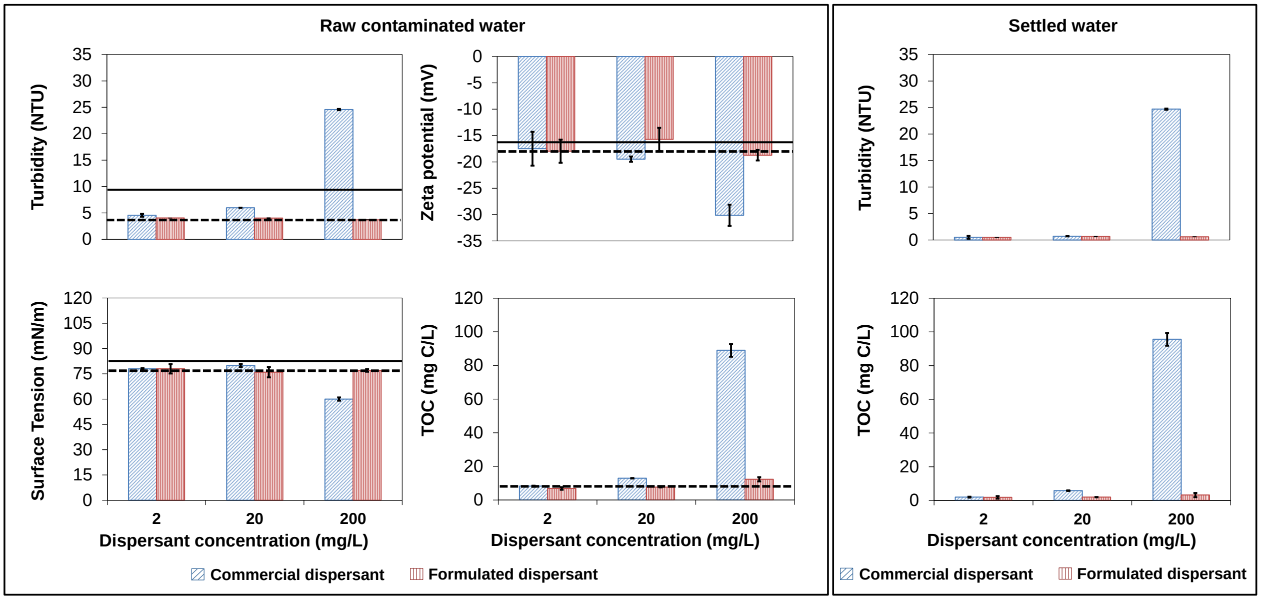

Figure 6.4: Raw water quality (turbidity, surface tension, zeta potential and TOC) after contamination with commercial dispersant and the formulated dispersant and the corresponding settled water quality (turbidity and TOC) following ballasted flocculation with alum as coagulant. Dashed line represents the maximum measured value for a given parameter in raw water at the time of the test while solid line represents the maximum measured value for a given parameter in raw water based on the 10-month monitoring data.

6.3.3 Influence of the presence of surfactant micelles on crude oil contamination in surface water

The formulated dispersant system was applied at two different concentrations in order to expound on the impact of surfactant micelles on crude oil-contaminated water quality and treatability. Low surfactant concentration, introducing only surfactant monomers, was applied at a dispersant-to-oil ratio of 1:20 (5.2 mg/L) while a high concentration was applied at 1.4 times the critical micelle concentration (10 400 mg/L) to ensure the presence of surfactant micelles.

6.3.3.1 Surfactant concentration below CMC

When 5.2 mg/L of the formulated dispersant was applied to crude oil-contaminated surface water, turbidity, zeta potential, surface tension, and TOC were measured at 5.8 ± 0.1 NTU, -25 ± 4 mV, 73 ± 3 mN/m, and 12 mg C/L, respectively. Studying such a formulated dispersant system enables the analysis of the contribution surfactants to measured TOC in raw water. This calculation was done based on the molecular formula of surfactants in the dispersant and the applied concentration. At a concentration of 5.2 mg/L, the formulated dispersant contributed to only 1% of the measured TOC concentration. Raw surface water contributed 63 % of the TOC load while crude oil accounted for the remaining 36 %.

Ballasted flocculation of surfactant-crude oil-contaminated surface water using alum as coagulant generated settled water that met treatment objectives. Turbidity, zeta potential, surface tension, and TOC were measured as 0.7 NTU, 3 mV, 75 mN/m, and 1.9 ± 0.7 mg C/L, respectively. In the current study, treatment was not limited by the presence of a low concentration of surfactants. However, residual surfactant concentration measured as SDS was present in settled water (35 ± 6 µg/L).

6.3.3.2 Surfactant concentration above CMC

When 10 400 mg/L of the formulated dispersant was applied to crude oil-contaminated surface water, changes in raw water quality were surprisingly not as considerable as expected. Turbidity, zeta potential and UVA_{254} were measured as 5.1 ± 0.2 NTU, -22 ± 3 mV, and 0.283 ± 0.008 cm^{-1}, respectively. It should be recalled that oil-to-water concentration was low [0.03 % (w/w)]. Small-sized and hence more stable crude oil droplets were observed (D_{v50}: 3 µm). When only crude oil was present, droplet size was measured as 286 µm. Although volume density of oil droplets was observed to be greater in the presence of micelles (Figure 6.5), it did not lead to a significant increase in turbidity. However, the impact of the presence of micelles was more evident through the high organic charge (TOC) and surface tension (1440 ± 660 mg C/L and 51 ± 1 mN/m, respectively). In the presence of micelles, the formulated dispersant contributed to

19 % of the measured TOC while 0.50 % stemmed from raw surface water. The remaining 80.5 % of the measured TOC was attributed to the micelle-stabilized crude oil droplets.

This analysis shows that the presence of surfactant micelles intensifies the impact of a crude oil spill in surface water by increasing the availability and stability of petroleum hydrocarbons in surface water. The resulting surfactant concentration as SDS in raw water spiked from being undetected in uncontaminated raw surface water to 317 ± 4 mg/L in the presence of micelles. Treatability was strongly affected by such a high organic charge due to the presence of surfactants and micelle-stabilized crude oil droplets. A drinking water facility operating at 41 mg dry alum/L would not be able to handle this organic charge and would need to dramatically increase its dose. As expected, no treatment was observed for ballasted flocculation with alum.

In the event of a crude oil spill in surface water, it has been shown that there is an adverse effect on water quality and treatability upon dispersant application regardless of the applied concentration. For a formulated dispersant containing only surfactants, its application adds to the contamination of an already contaminated waterbody. At low concentrations, surfactants were still present in raw and settled waters while at high concentrations, surfactant micelles led to the stabilization of crude oil droplets in the water column, increased the organic load, and negatively impacted water treatability. Therefore, contamination and treatability are worsened by the addition of dispersant to a crude oil spill in surface water.

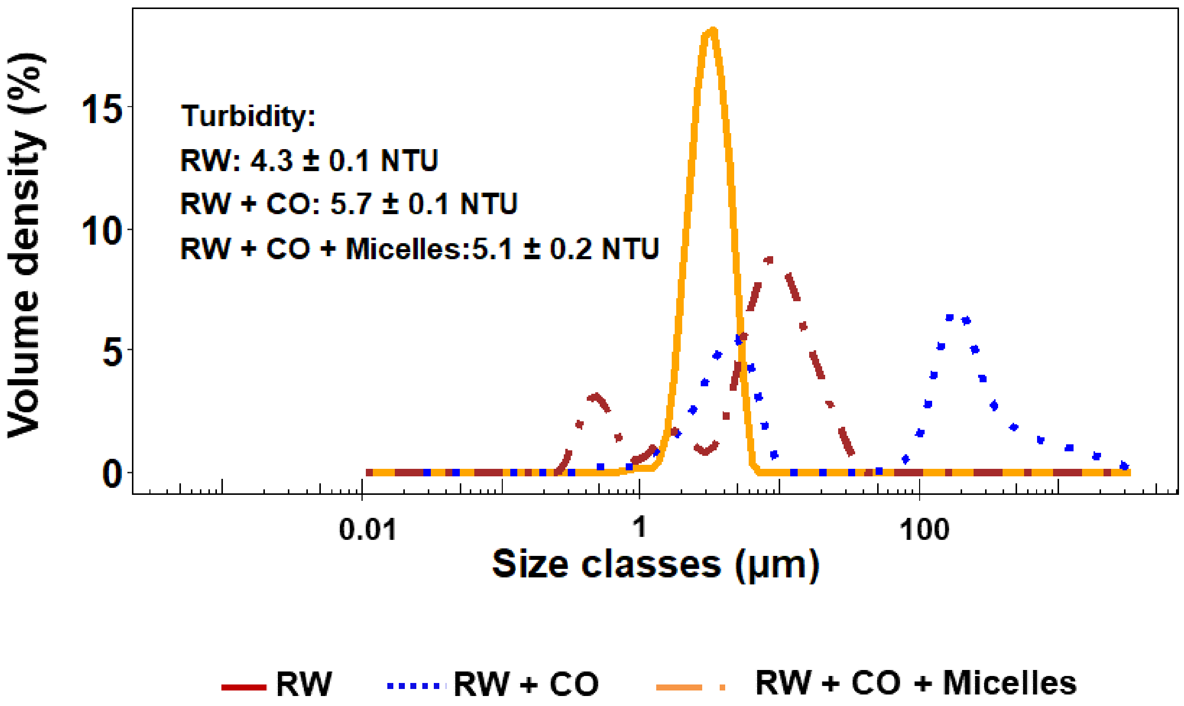

Figure 6.5: Volume-based particle size distribution for uncontaminated raw water (RW, red *dot-dash* line), raw water contaminated with crude oil (RW + CO, blue *dotted* line), and raw water contaminated with crude oil and surfactant micelles (RW + CO + M, orange *solid* line). D_{v50} in RW was 8.8 µm; in RW + CO, 186 µm; and in RW + CO + M, 3.0 µm. Two peaks for RW + CO account for large-sized crude oil droplets and small-sized particles in RW.

6.4 Conclusion

This study has shown that surfactants in dispersants, used as a remediation strategy subsequent to an oil spill, contribute to the contamination of surface water and disrupt process performance used for drinking water production. Moreover, the presence of other organic compounds such as solvents and polar additives in commercial oil-spill dispersants also negatively impacts surface water treatability. The addition of low concentrations of dispersant (< 20 mg/L) was thus sufficient to generate poor settled water quality (turbidity > 10 NTU). Regardless of the dispersant type and the applied concentration, no surfactant removal was observed during ballasted flocculation due to the nature and behavior of these organic compounds in water. Results demonstrate that conventional physicochemical treatment processes alone are thereby unsuitable for surfactant removal. In the presence of crude oil, the contribution of surfactants to surface water contamination was more significant when micelles were formed. A higher concentration of persistent hydrophilic surfactants was introduced and smaller, more stabilized, and neutrally buoyant oil droplets were formed, leading to a higher organic load in surface water. After contamination with the dispersant/oil mixture, the surface water could not be treated by ballasted flocculation using the optimized coagulant dose for turbidity and natural organic matter removal in the absence of contamination. From a drinking water perspective, dispersant application in surface water showed a negative synergistic effect on water quality and treatability due to the introduction of surfactants that were otherwise not present in surface water and whose removal was unachievable by ballasted flocculation. Findings in this study elucidate the impact of surfactants on water quality and treatability in a drinking water facility. Such scientific knowledge will be beneficial to regulators and decision-makers in the petrochemical and drinking water industry in their efforts to establish oil-spill contingency plans that allow spill remediation while ensuring the protection of public health.

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CHAPTER 7 GENERAL DISCUSSION

This chapter synthesizes the main findings in this study and discusses the implications in the context of the Montreal metropolitan region. The event of an oil spill in surface water will pose a risk of contamination to DWTP and the capacity of these facilities to generate potable water will also be questioned. The main objective of this study was therefore to evaluate the effectiveness of the first barrier, physicochemical treatment (specifically ballasted flocculation), for the removal of *trace* **dissolved** and **emulsified** petroleum hydrocarbons from surface water. Ballasted flocculation efficiency for *trace* **dissolved** BTEX removal was first studied and optimized to attain environmental thresholds in drinking water. For *trace* **emulsified** petroleum hydrocarbon contamination, ballasted flocculation efficiency was investigated for crude oil-contaminated surface water in the presence and absence of oil-spill dispersants. Focus was on the removal of dispersant-stabilized oil droplets and other dispersant-related compounds from surface water. Lastly, the impact of dispersant matrix characteristics and the presence of surfactant micelles on contamination and surface water treatability were evaluated. In all studies, water quality parameters were monitored in order to identify the most sensitive and measurable indicator of *trace* petroleum hydrocarbon contamination in surface water.

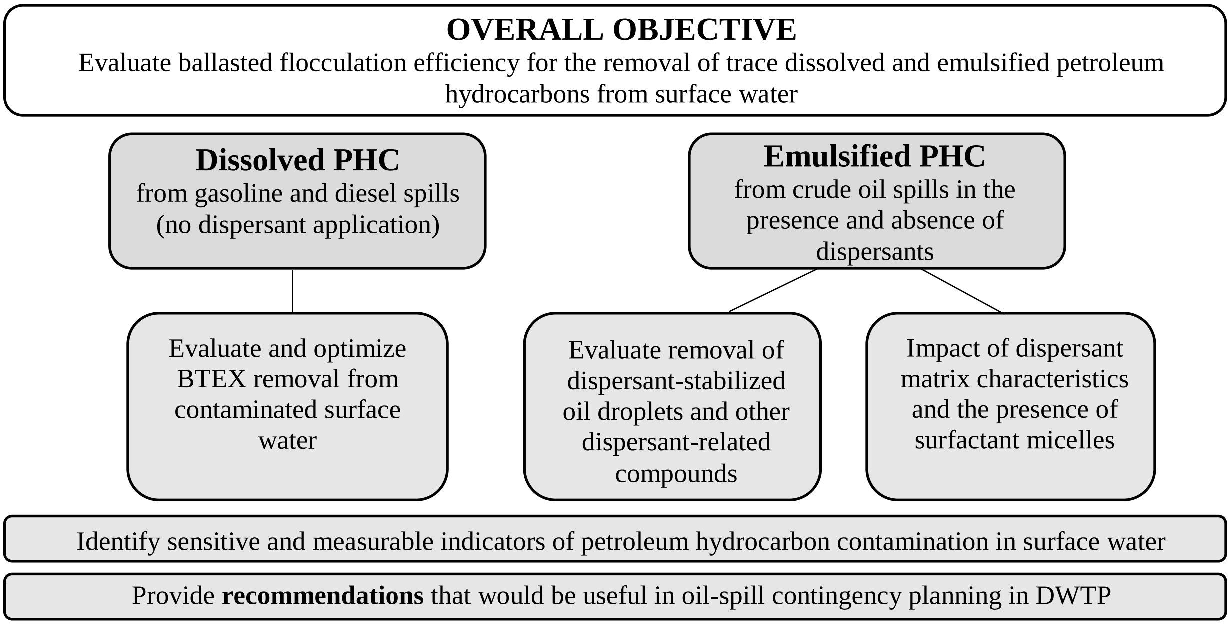


Figure 7.1: Structure of research work.

7.1 Vulnerable DWTP in the region of Montreal

The metropolitan region of Montreal comprises 82 municipalities, about 4 million people, and 28 vulnerable DWTP whose intakes are situated in surrounding surface waterbodies that are subject to potential spills from pipelines (Section 2.2) (Communauté Métropolitaine de Montréal (CMM), 2016). Hydrodynamics of these waterbodies is described as follows: River Outaouais flows into the Lake of Two Mountains (Lac des Deux Montagnes), which then distributes its flow into the Lake St. Louis, Mille-Îles River, and Des Prairies River, which are tributaries into the St. Lawrence River. The interconnectedness of these waterbodies shows that a pipeline rupture near the Outaouais River, for example, would present varying degrees of contamination to DWTP in the Montreal metropolitan region (Section 2.2). The susceptibility of these DWTP to contamination following an oil spill has been studied and the most at-risk facilities were identified as those that draw water from Mille-Îles and Des Prairies Rivers (Barrette, 2018). DWTP with intakes in these rivers include Chomedey (Des Prairies), Pont-Viau (Des Prairies), Pierrefonds (Des Prairies), and Sainte-Rose (Mille-Îles). Of interest are also drinking water facilities such as Atwater and Des Baillets that serve the Montreal municipality and have their intakes situated in the St. Lawrence River.

The distance between pipelines in the region and the raw water intakes of these DWTP ranges from 3 km to 72 km. Only Atwater and Des Baillets intakes are equipped with hydrocarbon detectors. The treatment processes employed in all the aforementioned DWTP include PAC pre-contact tank (Chomedey only), physicochemical treatment, filtration, biological granular activated carbon filtration (Sainte-Rose and Pont-Viau), ozonation (except Atwater), and chlorination. An average volume of potable water, ranging from 46 000 m^3 (Sainte-Rose) to 1.8 million m^3 (Atwater and Des Baillets), is produced daily (Barrette, 2018).

7.2 Capacity of the first barrier in DWTP for dissolved petroleum hydrocarbon removal

In many DWTP such as Chomedey, ballasted flocculation or Actiflo® is utilized for physicochemical treatment of surface water and would serve as the first barrier against *trace* petroleum hydrocarbon contamination. Its efficiency for the removal of *trace* dissolved petroleum hydrocarbons (PHC), specifically BTEX, was evaluated following gasoline and diesel contamination of surface water (Article I). Settled water quality was analyzed based on the required treatment objectives as well as the attainment of the regulatory threshold for the studied contaminant (benzene). In this part of the study, no oil-spill dispersant was applied and *trace* concentrations (< 20 µg benzene/L) were involved.

Ballasted flocculation was observed to be inefficient for reducing *trace* BTEX concentrations in contaminated surface water. The contribution of microsand and flocs to BTEX removal was negligible. Hence, the addition of an organic adsorbent such as PAC was necessary to reduce benzene concentration below the required threshold in drinking water. Three questions arose based on this finding: a) What is the appropriate dose that should be applied for *trace* dissolved PHC removal? b) What is the maximum dose that the settler technology is able to handle? and c) Where is the best point of application? Adsorption tests showed that in order to attain U.S. EPA's regulation of less than 5 µg benzene/L, only 15 – 20 mg PAC/L was necessary. However, 80 mg PAC/L was necessary to attain Québec's regulatory limit (0.5 µg benzene/L). This PAC concentration exceeds that which is typically applied in DWTP with PAC pre-contact tanks (15 – 20 mg PAC/L).

Except Chomedey, DWTP listed in Section 7.1 do not employ PAC pre-contact in their treatment chain and as a result, they would need to evaluate the robustness of their physicochemical treatment process to handle a higher PAC dosage and determine the most suitable point of application for emergency conditions. Simultaneous PAC and coagulant injection has been shown to negatively impact PAC adsorption efficiency due to shorter contact time and possible pore blockage by coagulant (Article I). It is therefore advisable to inject PAC prior to coagulant addition, preferably through a pre-contact tank, in order to maximize contaminant removal. PAC injection in settled water is another possibility which has been investigated in Germany for trace organic micropollutant removal (Altmann et al., 2015); however, more research is required on the impact of such high PAC dosage on filter systems in terms of run time, head loss, and filtered water quality. It is doubtful that a standard dual media filter would be able to handle

20 mg PAC/L on a sustained basis without undergoing turbidity breakthrough in the filtered effluent.

For DWTP with PAC pre-contact tanks (Chomedey, for example), operators would only need to increase PAC dose and apply the optimal contact time (15 – 30 min) in the event of diesel or gasoline spill in surface water. In the US, DWTP that are equipped with PAC pre-contact tanks can apply 15 – 20 mg PAC/L, but the contact time would need to be optimised. In the absence of a pre-contact tank, if the DWTP utilizes ballasted flocculation, it is not certain if the application of the same PAC dose would generate settled water with benzene concentration below 5 µg benzene/L, especially upon simultaneous PAC and coagulant application. Nonetheless, it might not be necessary to apply up to 80 mg PAC/L, as benzene concentrations in settled water in this study, subsequent to simultaneous PAC (80 mg PAC/L) and coagulant injection, were 10 times lower than the required U.S. threshold.

Simultaneous PAC (80 mg PAC/L) and alum dosage during ballasted flocculation generated settled water that met treatment objectives (turbidity < 1 NTU and DOC < 2 mg C/L). This cannot be said to be attainable with conventional settlers. Therefore, ballasted flocculation provided a more robust treatment technology to deal with the aftermath of trace contaminations of an oil spill arriving at the DWTP.

7.3 Capacity of the first barrier in DWTP for emulsified petroleum hydrocarbon removal

Ballasted flocculation was further evaluated for its efficiency to treat crude oil-contaminated surface water in the presence and absence of dispersants (Articles II and III). More specifically, settled water quality was analyzed based on the removal of oil droplets, residual petroleum hydrocarbons reported as TOC, and other dispersant-related compounds reported as surfactant concentrations. It is important to note that the scope of this research work does not cover dispersant effectiveness in freshwater nor policies regarding dispersant application in fresh water. However, the focus is on the impact of the presence of dispersant on contamination and treatability of surface water.

7.3.1 Settled water quality

Ballasted flocculation with alum generated acceptable settled water quality in the presence and absence of low dispersant concentrations (Article II). However, dispersant application introduced organic compounds such as surfactants that were otherwise not present in surface water and were unable to be removed by ballasted flocculation. Although residual dispersant concentration reported as DOSS was greater than the U.S. EPA threshold of 40 µg DOSS/L for protection of aquatic life, it was below the maximum acceptable concentrations set by the U.S. Food and Drug Administration (FDA) (10 – 25 mg/L) (Article II). Competitive influence of crude oil and the dispersant matrix characteristics might have affected process efficiency for surfactant removal. Further study of a commercial dispersant and a formulated dispersant containing only surfactants and applied to surface water in the absence of crude oil demonstrated that regardless of the dispersant type and concentration, ballasted flocculation alone was not sufficient to reduce surfactant concentrations introduced by oil-spill dispersants (Article III). The presence of other organic compounds such as BTEX, solvents and polar additives in commercial oil-spill dispersants also impact surface water treatability, as only low concentrations of such dispersants (≥ 20 mg/L) was sufficient to generate poor settled water quality (turbidity > 10 NTU) (Article III). Therefore, dispersant remediation of crude oil spills in surface water requires careful consideration of the dispersant concentration to be applied.

Although not presented in the articles, petroleum hydrocarbons measured as $C_{10} – C_{50}$ was analyzed in uncontaminated and contaminated raw waters and their settled water equivalents. $C_{10} – C_{50}$ concentration in uncontaminated raw water was less than 100 µg/L (detection limit), pointing to the absence of petroleum hydrocarbons. Subsequent to ballasted flocculation of crude oil-contaminated surface water in the presence and absence of dispersants, residual $C_{10} – C_{50}$ concentrations ranging from 500 to 640 µg/L were measured in settled water. In order to improve settled water quality and enable the removal of these hydrocarbons as well as residual dispersant-related compounds, adsorption-based processes through filtration (post-ballasted flocculation) or PAC application (as discussed in Section 7.2) would be necessary. For the latter, more research would be necessary to determine the optimal PAC dose and to evaluate the impact of the presence of low dispersant and crude oil concentrations on PAC adsorption efficiency.

7.3.2 Removal of crude oil droplets

In the event of an oil spill in surface water, crude oil droplets can be formed through natural dispersion and chemically-enhanced dispersion through dispersant use (Articles II and III). The stability of these droplets and their tendency to resurface are dependent on size, temperature, salinity, and turbulence (M. F. Fingas, 2011; Zhao et al., 2020). Based on the observed droplet sizes (Articles II and III), the rise velocity in a spill scenario without dispersants and with dispersants (micelles) were calculated as 2.1 x 10^{-3} m/s and 5.4 x 10^{-7} m/s, respectively (assuming an oil density of 0.89 g/mL). These correspond to droplet sizes of 186 µm and 3 µm, respectively. After 1 h, both droplets will have risen 7.6 m and 0.0019 m, respectively, while after 24 h, both will have risen 181 m and 0.047 m, respectively. Assuming favorable hydrodynamic conditions that enhance droplet stability in surface water, the presence of micelles would therefore increase the chances of small crude oil droplets accessing raw water intakes (National Research Council (NRC), 2005).

In the presence and absence of low dispersant concentrations (no micelles), crude oil droplets were observed to be effectively removed upon ballasted flocculation with alum. Their presence in raw water did not hinder ballasted flocculation efficiency. Droplets acted as negatively-charged colloids and were removed through adsorption and enmeshment in positively charged aluminum hydroxide precipitates (Article II). Considering the type of filtration subsequent to ballasted flocculation, the presence of crude oil droplets would pose a risk of pore blockage in filter media. Residual floc sizes in settled water were observed to be below the required threshold of 80 µm (to avoid media blockage). However, larger sizes are to be expected when direct filtration units are utilized such as in Des Baillets DWTP (Montreal, Canada).

The interaction between oil droplets and particles in raw surface water was not covered in this study. In the presence of crude oil, particles in raw surface water cause the formation of oil-particle aggregates (OPA) and constitute a three-element system (oil, particle, and water).

These particles can either stabilize oil droplets and hinder coalescence or increase droplet density and promote settleability (Fitzpatrick et al., 2015). The nature of the particles – their hydrophobicity, size and surface area – as well as the presence of dispersants has been shown to influence OPA formation (Fitzpatrick et al., 2015) and implicitly affect treatability of contaminated surface water. More research is necessary to explore the impact of the presence of different particle types on oil droplet formation and removal through ballasted flocculation.

7.4 Sensitivity of indicators

In raw and settled waters, none of the water quality parameters that are typically monitored in DWTP – turbidity, UVA_{254}, DOC, and zeta potential – as well as surface tension served as good indicators of *trace* dissolved PHC contamination. Diesel and gasoline contamination of surface water introduced *trace* BTEX concentrations of 260 ± 21 µg/L and 63 ± 11 µg/L, respectively. Corresponding DOC concentrations reported minimal increases of 0.2 mg C/L and 1.5 mg C/L, respectively. These concentrations fall within the normal DOC range reported for the studied surface water. This signifies that contamination would go unnoticed if operators rely only on changes in these parameters to detect an aberrance in source water.

When crude oil was involved in the presence and absence of dispersants, TOC measured in raw water was observed to be the most sensitive indicator of *trace* emulsified PHC contamination. Measured concentrations exceeded the maximum observed TOC in the studied surface water by 2 – 3 mg C/L. It is therefore advisable for DWTP in spill-prone areas to install TOC analyzers at their water intake to monitor changes in organic carbon concentration in source water. In the absence of contamination, this online indicator could be used to optimize coagulation, one of the key drinking water treatment processes.

The installation of online hydrocarbon detectors would also be beneficial. Their ability to indicate contamination has been shown to be dependent on several factors, including temperature and the type of petroleum product (Nguyen, 2018). However, only two out of the seven DWTP listed in Section 7.1 are equipped with such a device.

7.5 Coagulant choice and dose

Alum and ferric sulfate were the two coagulants that were utilized in this research project. Alum was always employed at a dose optimized for turbidity and natural organic matter removal in uncontaminated raw water while ferric sulfate was employed at a calculated equivalent dose to that of alum. For *trace* dissolved PHC removal, ballasted flocculation alone, with either alum or ferric sulfate, was ineffective (Article I). In the presence of low dispersant (< 20 mg/L) and crude oil concentrations in surface water, ballasted flocculation with alum (not ferric sulfate) generated acceptable settled water quality (turbidity < 1 NTU and TOC ≈ 2 – 3 mg C/L) (Article II). The application of a higher ferric sulfate dose was evaluated without pH and alkalinity control and as expected, treatment efficiency was not improved. Regardless of the type of coagulant, higher dispersant concentrations that induced the formation of micelles and stabilization of crude oil droplets rendered the contaminated surface water untreatable by ballasted flocculation (Article III).

In the presence of crude oil and micelles, the injection of higher coagulant doses was not explored. Alum dose relative to the organic loading in uncontaminated raw water was quantified as 0.48 mg Al/mg C. In the presence of monomers and micelles, this ratio became 0.47 mg Al/mg C (similar to what was observed for uncontaminated raw water) and 0.013 mg Al/mg C, respectively. The presence of monomers increased the organic charge in surface water by 4 mg C/L, but did not render the water untreatable. However, when micelles were present, the applied coagulant dose was ineffective for such highly-charged surface water. More research involving the use of higher coagulant doses during ballasted flocculation treatment (in conjunction with pH and alkalinity control) of micelle-stabilized oil droplets in surface water would shed light on the behavior and removal mechanism of these droplets.

Generally, different factors influence coagulant efficiency for *trace* PHC removal from surface water. These factors include the type of petroleum product, the nature of targeted contaminants, coagulant dose, and surface water quality, among others. It is therefore difficult to recommend one coagulant for all contamination scenarios.

7.6 Emergency response plans

The findings in this research project have implications with respect to emergency response plans prepared by a) DWTP for potable water protection; and b) regulated parties in the petrochemical industry for environmental protection. In the US and Canada, petroleum suppliers are required to prepare emergency response plans that detail containment and cleanup strategies in the event of a spill. Enbridge, for example, with pipeline transporting crude oil from western Canada and the US to a refinery on the east of Montreal, has developed and disclosed its emergency response plan (Enbridge Pipelines Inc., 2016). This plan includes no mention of the use of dispersants for oil-spill remediation in surface water. Rather, physical remediation such as the use of booms and adsorbents are listed. Many DWTP, especially those in spill-prone areas, have also prepared emergency response plans in order to be able to mitigate the impacts of such unexpected events on potable water production. No requests were made to the DWTP listed in Section 7.1 for their emergency response plans. However, the emergency response plan of Dawson Creek DWTP in British Columbia can be easily retrieved online (Creek, 2007). In the event of petroleum hydrocarbon contamination signaled by the installed hydrocarbon detector and prior notification of upstream contamination, the facility plans to shut off pumps at the raw water intake and monitor water quality parameters, among other measures. The latter highlights the importance of the findings in Section 7.4. The facility also monitors TOC in raw and settled waters and employs an adsorption-based process in its treatment chain. Overall, findings in this research work will enable DWTP to evaluate, revise, and upgrade their emergency oil-spill response plans and treatment chain, as needed. Findings will also fill the knowledge gap related to dispersant use in surface water employed as drinking water sources and thus enable regulators to take accurate decisions for the protection of the environment and public health.

CHAPTER 8 CONCLUSION AND RECOMMANDATIONS

This research project evaluated ballasted flocculation efficiency for the removal of *trace* petroleum hydrocarbons (dissolved and emulsified) from surface water. More specifically, the removal of *trace* BTEX, crude oil droplets, and residual dispersant concentrations was investigated. The six hypotheses that were tested in this project were validated or rejected based on experimental findings, which are summarized below:

Hyp. 1: The addition of an adsorbent is necessary to reduce *trace* dissolved petroleum hydrocarbon concentrations (below 0.5 µg/L) in surface water, as ballasted flocculation alone is not effective.

This study showed that ballasted flocculation alone was not effective to reduce trace dissolved benzene concentrations in diesel and gasoline-contaminated surface waters.

- The chosen adsorbent was powdered activated carbon. Adsorption isotherm and kinetics tests reported efficient benzene reduction below 0.5 µg/L (Quebec regulation) at a dose of 80 mg PAC/L and contact times of 15 min and 30 min for diesel and gasoline contaminations, respectively.
- To meet U.S. EPA requirement of 5 µg benzene/L, only 15 – 20 mg/L was necessary.
- At a PAC dose of 80 mg/L, simultaneous PAC and coagulant (alum or ferric sulfate) injection during ballasted flocculation tests led to appreciable reductions in benzene concentration. However, PAC adsorption efficiency was limited by the presence of coagulant due to possible pore blockage.
- Ballasted flocculation with 80 mg PAC/L and an optimized alum dose generated settled water that met treatment objectives (turbidity < 1 NTU and DOC < 2 mg C/L), pointing to the robustness of the treatment to handle such a high PAC dosage.

Hyp. 2: Ballasted flocculation efficiency is not limited by the presence of crude oil and dispersant concentrations.

This study showed that monitored water quality parameters for settled water, subsequent to ballasted flocculation of dispersant-crude oil-contaminated surface water, were within the range of that observed following ballasted flocculation of uncontaminated surface water.

- In this study, this hypothesis was validated for ballasted flocculation that was conducted with an optimized alum dose. This dose was determined based on natural organic matter removal in uncontaminated surface water. However, with an equivalent ferric sulfate dose, settled water was compromised due to suboptimal coagulation conditions and possible increase in solubility of iron (III) in the presence of crude oil.
- Ballasted flocculation with alum and ferric sulfate generated microflocs (3 – 30 µm) in settled water. Since filtration is typically the next treatment process after physicochemical treatment, blockage of filter media is not expected to occur, as the generated microflocs are below the required threshold of 80 µm. However, larger flocs are to be expected if settling is excluded prior to filtration (that is, in direct filtration units). Such systems would most likely experience media blockage upon crude oil and dispersant contamination.

Hyp. 3: The application of low dispersant concentrations to crude oil spills in surface water introduces dispersant-related compounds, specifically surfactants, that are not identifiable by the monitored water quality parameters and not removed by ballasted flocculation.

This study showed that residual dispersant reported as DOSS could not be reduced below the U.S. EPA requirement for protection of aquatic life (40 µg/L).

- Although alum-treated settled water met the required treatment objectives in terms of the monitored water quality parameters, surfactants were still present at concentrations above 40 µg/L but below the limits set by the U.S. FDA (10 – 25 mg/L).
- It was speculated that the dispersant matrix characteristics and the presence of crude oil hindered ballasted flocculation efficiency for surfactant removal. Further analysis of a formulated dispersant containing only surfactants confirmed that ballasted flocculation,

operating with a coagulant dose optimized for turbidity and natural organic matter removal in uncontaminated surface water, was unable to remove these compounds.

- For their removal, the application of adsorption-based processes such as PAC or carbon filtration units should be evaluated.

Hyp. 4: When oil-spill dispersants are present in surface water, surfactants alone are not the major driving factors to contamination.

This study showed that compared to a commercial dispersant, a formulated dispersant containing only surfactants showed a delayed effect on surface water contamination and treatability through the monitored water quality parameters.

- In the absence of crude oil, contamination of surface water with a commercial dispersant up to a concentration of 20 mg/L was treatable by ballasted flocculation, operating with a coagulant dose optimized for turbidity and natural organic matter removal in uncontaminated surface water. Higher dispersant concentrations yielded compromised settled water quality (turbidity > 20 NTU and TOC ≈ 90 mg C/L).
- Contamination of surface water with a formulated dispersant up to a concentration of 2000 mg/L was treatable by ballasted flocculation, operating with a coagulant dose optimized for turbidity and natural organic matter removal in uncontaminated surface water. Higher dispersant concentrations yielded compromised settled water quality (turbidity > 1 NTU and TOC ≈ 100 mg C/L).
- Upon dispersant application, other dispersant-related compounds, classified as solvents and additives and present in commercial oil-spill dispersants, were introduced into surface water and impacted its treatability by ballasted flocculation.

Hyp. 5: In the presence of crude oil, surfactant micelles account for majority of the observed organic carbon contamination of the source water.

This study showed that percent organic carbon contribution from the applied surfactant concentration (19 %) was inferior to that of the stabilized crude oil droplets (80.5 %).

- TOC measured in the presence of surfactant micelles and crude oil pointed to the impact of the presence of high dispersant concentrations on crude oil-contaminated surface water.
- When only monomers were present (formulated dispersant concentration below CMC), surfactants accounted for only 1 % of the measured TOC in crude oil-contaminated surface water while crude oil accounted for 36 %.
- When micelles were present (formulated dispersant concentration above CMC), surfactants accounted for 19 % of the measured TOC in crude oil-contaminated surface water while crude oil accounted for 80.5 %.
- Ballasted flocculation, operating with a coagulant dose optimized for natural organic matter removal in uncontaminated surface water, was unable to treat such highly-concentrated surface water.
- Micelles increased the availability of crude oil in surface water through the formation of small, stable oil droplets. Therefore, dispersant remediation of crude oil spills in surface water requires careful consideration of the dispersant concentration to be applied.

Hyp. 6: Among the commonly monitored water quality parameters, TOC is the best indicator of *trace* petroleum and dispersant contamination in raw surface water.

TOC, upon crude oil and dispersant contamination, showed the most deviation from (i) the measured values in uncontaminated raw water at the time of the tests; and (ii) the observed variations in raw water based on source water monitoring data.

- For both *trace* dissolved and emulsified hydrocarbon contamination of surface water, marginal changes in turbidity, UVA_{254}, surface tension, and zeta potential were observed.
- For *trace* emulsified hydrocarbon contamination of surface water, measured TOC concentrations exceeded the maximum observed TOC in the studied surface water by 2 – 3 mg C/L.

- This observation is mainly for surface water with fairly stable TOC and more research will be necessary to observe the sensitivity of TOC for surface water with more variable TOC.
- Installation of online TOC analyzers at raw water intakes of DWTP in spill-prone areas is advised.

Additional areas of study based on findings from the current work include:

- Evaluating PAC injection in settled water and the effect on filter systems in terms of run time, head loss, and filtered water quality.
- Determining the impact of the presence of low dispersant and crude oil concentrations on PAC adsorption efficiency.
- Assessing the impact of the presence of different particle types on oil droplet formation and removal in the presence and absence of dispersants.

REFERENCES

(CEAEQ), C. d. e. e. a. e. d. Q. (2016). *Analytical Method – Determination of Petroleum Hydrocarbons (C10 to C50): Determination of Petroleum Hydrocarbons (C10 to C50): Gas Chromatography-Flame Ionization Detection Technique* (MA. 400 – HYD 1.1, Rév. 3). Retrieved from http://www.ceaeq.gouv.qc.ca/methodes/pdf/MA400HYD11.pdf

Agency for Toxic Substances and Disease Registry (ATSDR), U. S Department of Health and Human Services, & Public Health Service. (2007). A toxicological profile for benzene. 438. Retrieved from https://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=40&tid=14

Al-Shamrani, A. A., James, A., & Xiao, H. (2002). Destabilisation of oil–water emulsions and separation by dissolved air flotation. *Water Research, 36*(6), 1503-1512. doi:10.1016/S0043-1354(01)00347-5

Altmann, J., Zietzschmann, F., Geiling, E.-L., Ruhl, A. S., Sperlich, A., & Jekel, M. (2015). Impacts of coagulation on the adsorption of organic micropollutants onto powdered activated carbon in treated domestic wastewater. *Chemosphere, 125*, 198-204. doi:10.1016/j.chemosphere.2014.12.061

Álvarez-Uriarte, J. I., Iriarte-Velasco, U., Chimeno-Alanís, N., & González-Velasco, J. R. (2010). The effect of mixed oxidants and powdered activated carbon on the removal of natural organic matter. *Journal of hazardous materials, 181*(1-3), 426-431.

American Public Health Association (APHA), American Water Works Association (AWWA), & Water Environment Federation (WEF). (2012). *Standard methods for the examination of water and wastewater* (Vol. 5). Washington, D.C.: American Public Health Association.

American Water Works Association (AWWA). (1999). *Water quality and treatment. A handbook of community water supplies (Fifth Edition)*. New York, NY, USA: McGraw-Hill, Inc.

American Water Works Association (AWWA). (2004). *M37-Manual of water supply practices. Operational control of coagulation and filtration processes (Second Edition)*. Denver, Colorado, USA.

Amini, N., Papineau, I., Storck, V., Bérubé, P. R., Mohseni, M., & Barbeau, B. (2018). Long-term performance of biological ion exchange for the removal of natural organic matter and ammonia from surface waters. *Water Research, 146*, 1-9. doi:10.1016/j.watres.2018.07.057

Andrews, S., Nover, D., & Schladow, S. G. (2010). Using laser diffraction data to obtain accurate particle size distributions: the role of particle composition. *Limnology and Oceanography: Methods, 8*(10), 507-526.

Barrette, S. (2018). *Vulnérabilité des usines de traitement d'eau potable de la région métropolitaine de Montréal aux déversements accidentels d'oléoducs.* (M.Sc.A). Polytechnique Montréal, Montréal, QC, Canada.

Barrette, S., Dorner, S., & Prévost, M. (2017, Nov 12-16). *Vulnerability of the water treatment plants in the greater Montreal to pipeline spills.* Paper presented at the American Water Works Association-Water Quality Technology Conference (WQTC), Portland, OR, USA.

Belk, J. L., Elliott, D. J., & Flaherty, L. M. (1989). *The comparative effectiveness of dispersants in fresh and low salinity waters*.

Berry, J. D., Neeson, M. J., Dagastine, R. R., Chan, D. Y. C., & Tabor, R. F. (2015). Measurement of surface and interfacial tension using pendant drop tensiometry. *Journal of Colloid and Interface Science, 454*, 226-237. doi:10.1016/j.jcis.2015.05.012

Bhattacharyya, S., Klerks, P. L., & Nyman, J. A. (2003a). Toxicity to freshwater organisms from oils and oil spill chemical treatments in laboratory microcosms. *Environmental Pollution, 122*, 205-215.

Bhattacharyya, S., Klerks, P. L., & Nyman, J. A. (2003b). Toxicity to freshwater organisms from oils and oil spill chemical treatments in laboratory microcosms. *Environmental Pollution, 122*(2), 205-215. doi:10.1016/s0269-7491(02)00294-4

Birtwell, I. K. (2008). Comments on the effects of oil spillage on fish and their habitat–Lake Wabamun, Alberta. *Final Report submitted to Public Prosecution Service of Canada, Alberta Regional Office. Fisheries and Oceans Canada, Ottawa, Ontario, Canada*.

Bobra, M., Fingas, M., & Tennyson, E. (1992). When oil spills emulsify. *Chemtech, 22*(4), 236-241.

Brandvik, P. J., Myrhaug, J. L., Daling, P. S., Leirvik, F., & Fritt-Rasmussen, J. (2010). *Meso-scale weathering of oil as a function of ice conditions, oil properties, dispersibility and in situ burnability of weathered oil as a function of time* (n^0 : 19). Retrieved from https://www.sintef.no/globalassets/project/jip_oil_in_ice/dokumenter/publications/jip-rep-no-19-common-meso-scale-final.pdf

Brody, T. M., Bianca, P. D., & Krysa, J. (2012). Analysis of inland crude oil spill threats, vulnerabilities, and emergency response in the Midwest United States. *Risk Analysis, 32*(10), 1741-1749. doi:10.1111/j.1539-6924.2012.01813.x

Campo, R., Giustra, M. G., De Marchis, M., Freni, G., & Di Bella, G. (2017). Characterization and treatment proposals of shipboard slop wastewater contaminated by hydrocarbons. *Water, 9*(8), 581. doi:10.3390/w9080581

Canada Energy Regulator - CER. (2020). Commodity Statistics. Retrieved from https://apps.cer-rec.gc.ca/CommodityStatistics/Statistics.aspx?language=english

Canizares, P., Martínez, F., Jiménez, C., Sáez, C., & Rodrigo, M. A. (2008). Coagulation and electrocoagulation of oil-in-water emulsions. *Journal of hazardous materials, 151*(1), 44-51.

Centre d'expertise en analyse environnementale du Québec (CEAEQ). (2015). *Hydrocarbures pétroliers : caractéristiques, devenir et criminalistique environnementale. Études GENV22 et GENV23 Évaluation environnementale stratégique globale sur les* *hydrocarbures*. Retrieved from Montréal, Canada: https://mern.gouv.qc.ca/energie/filiere-hydrocarbures/etudes/GENV22-23.pdf

CER, C. E. R.-. (2019). Frequently Asked Questions (FAQs) Concerning Federally-Regulated Petroleum Pipelines in Canada. Retrieved from https://www.nrcan.gc.ca/our-natural-resources/energy-sources-distribution/clean-fossil-fuels/pipelines/faqs-federally-regulated-petroleum-pipelines-canada/5893#h-3-2

Communauté Métropolitaine de Montréal (CMM). (2016). *Plan d'action métropolitain de mise en valeur du territoire et des activités agricoles*. Retrieved from https://cmm.qc.ca/wp-content/uploads/2019/03/20160225_PAMAA_2016-2020.pdf

Communauté Métropolitaine de Montréal (CMM). (2019). *Rapport du groupe de travaila métropolitain sur les mesures additionnelles pour assurer l'alimentation en eau potable en cas de déversement de produits pétroliers*.

Corrin, M. L., & Harkins, W. D. (1947). The effect of salts on the critical concentration for the formation of micelles in colloidal electrolytes1. *Journal of the American Chemical Society, 69*(3), 683-688.

Creek, C. o. D. (2007). *City of Dawson Creek Potable Water Systems Emergency Response Plan*. Retrieved from https://www.dawsoncreek.ca/wordpress/wp-content/uploads/2011/10/PotableWaterSystememergencyresponseplan-rev01_000.pdf

Crittenden, J. C., H., B. J., & Montgomery, W. H. (2012). *MWH's water treatment : Principles and design*. Hoboken, N.J.: John Wiley & Sons.

Daifullah, A., & Girgis, B. (2003). Impact of surface characteristics of activated carbon on adsorption of BTEX. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 214*(1-3), 181-193.

Daifullah, A. A. M., & Girgis, B. S. (2003). Impact of surface characteristics of activated carbon on adsorption of BTEX. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 214*(1), 181-193. doi:10.1016/S0927-7757(02)00392-8

Davis, C. C., & Edwards, M. (2014). Coagulation with hydrolyzing metal salts: Mechanisms and water quality impacts. *Critical Reviews in Environmental Science and Technology, 44*(4), 303-347. doi:10.1080/10643389.2012.718947

Desjardins, C., Koudjonou, B., & Desjardins, R. (2002). Laboratory study of ballasted flocculation. *Water Research, 36*(3), 744-754.

Desjardins, R. (1997). *Le traitement des eaux, 2e édition revue et enrichie*. Québec, Canada: Édition de l'École Polytechnique de Montréal.

Duan, J., & Gregory, J. (2003). Coagulation by hydrolysing metal salts. *Advances in Colloid and Interface Science, 100-102*, 475-502. doi:10.1016/s0001-8686(02)00067-2

Duan, J., Wang, J., Guo, T., & Gregory, J. (2014). Zeta potentials and sizes of aluminum salt precipitates – Effect of anions and organics and implications for coagulation mechanisms. *Journal of Water Process Engineering, 4*, 224-232. doi:10.1016/j.jwpe.2014.10.008

Ebeling, J. M., Sibrell, P. L., Ogden, S. R., & Summerfelt, S. T. (2003). Evaluation of chemical coagulation-flocculation aids for the removal of suspended solids and phosphorus from intensive recirculating aquaculture effluent discharge. *Aquacultural Engineering, 29*(1-2), 23-42. doi:10.1016/S0144-8609(03)00029-3

Ebnesajjad, S., & Landrock, A. H. (2008). *Adhesives Technology Handbook*: William Andrew.

El-Dib, M. A., Moursy, A. S., & Badawy, M. I. (1978). Role of adsorbents in the removal of soluble aromatic hydrocarbons from drinking waters. *Water Research, 12*(12), 1131-1137. doi:10.1016/0043-1354(78)90061-1

El-Naas, M. H., Acio, J. A., & El Telib, A. E. (2014). Aerobic biodegradation of BTEX: Progresses and prospects. *Journal of Environmental Chemical Engineering, 2*(2), 1104-1122. Retrieved from http://dx.doi.org/10.1016/j.jece.2014.04.009

Enbridge Pipelines Inc. (2016). *Plan d'urgence intégré, Région de l'Est, zone d'intervention* (Version: Core 2.5 | Annexe 1.3. 2015/2016 Est-ICP ##). Retrieved from http://www.enbridge.com/~/media/Rebrand/Documents/Public%20Awareness/ERAP%20ICP/EasternRegion%20ICPC25AV13FrenchRedactedcompressed.pdf?la=en

Fingas, M. (2008). *A Review of literature related to oil spill dispersants especially relevant to Alaska 2002-2008. For Prince William Sound Regional Citizens' Advisory Council (PWSRCAC)* (PWSRCAC Contract Number - 955.08.03). Retrieved from Edmonton, AL, Canada: https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.407.6877&rep=rep1&type=pdf

Fingas, M. F. (2011). *Oil spill science and technology : prevention, response, and clean up*.

Fingas, M. F. (2015). *Handbook of oil spill science and technology*: Wiley.

Fitzpatrick, F. A., Boufadel, M. C., Johnson, R., Lee, K., Graan, T. P., Bejarano, A. C., . . . Hayter, E. (2015). *Oil-Particle Interactions and Submergence from Crude Oil Spills in Marine and Freshwater Environments: Review of the Science and Future Science Needs*: US Department of the Interior, US Geological Survey.

Flaherty, L. M. (1989). *Oil dispersants: New ecological approaches* (Vol. 1018). West Conshohocken, PA, USA: ASTM International.

Galvez-Cloutier, R., Guesdon, G., & Fonchain, A. (2014). Lac-Mégantic : analyse de l'urgence environnementale, bilan et évaluation des impacts. *Revue canadienne de génie civil, 41*(6), 531-539. doi:10.1139/cjce-2014-0011

Gerrity, D., Arnold, M., Dickenson, E., Moser, D., Sackett, J. D., & Wert, E. C. (2018). Microbial community characterization of ozone-biofiltration systems in drinking water and potable reuse applications. *Water Research, 135*, 207-219. doi:10.1016/j.watres.2018.02.023

Gouvernement du Québec. (2011). *Règlement sur la qualité de l'eau potable. Loi sur la qualité de l'environnement*. (Chapitre Q-2, r. 40). Québec, Canada: Éditeur officiel du Québec

Gouvernement du Québec. (2020). *Règlement sur la qualité de l'eau potable. Loi sur la qualité de l'environnement*. (Chapitre Q-2, r. 40). Québec, Canada: Éditeur officiel du Québec Retrieved from http://legisquebec.gouv.qc.ca/fr/ShowDoc/cr/Q-2,%20r.%2040

Government of British Columbia. (2016). Past Spill Events. Retrieved from https://www2.gov.bc.ca/gov/content/environment/air-land-water/spills-environmental-emergencies/spill-incidents/past-spill-incidents

Government of Canada. (2013). *Properties, composition and marine spill behaviour, fate and transport of two diluted bitumen products from the canadian oil sands: Federal government technical report*. Ottawa, ON, CANADA Retrieved from http://publications.gc.ca/site/eng/457066/publication.html

Green, J., & Trett, M. W. (1989). *The fate and effects of oil in freshwater*. London, UK: Elsevier Applied Science.

Guibelin, E., Delsalle, F., & Binot, P. (1994). Actiflo process: A highly compact and efficient process to prevent water pollution by stormwater flows. *Water Science and Technology, 30*(1 pt 1), 87-96.

Guibelin, E., Delsalle, F., & Binot, P. (1994). The Actiflo® process: A highly compact and efficient process to prevent water pollution by stormwater flows. *Water Science and Technology, 30*(1), 87-96.

Hanif, N. M., Adnassssn, S. N., Latif, M., Zakaria, A. M., & Othman, M. R. (2012). The composition of surfactants in river water and its influence to the amount of surfactants in drinking water. *World Applied Sciences Journal, 17*(8), 970-975.

He, Q. H., Leppard, G. G., Paige, C. R., & Snodgrass, W. J. (1996). Transmission electron microscopy of a phosphate effect on the colloid structure of iron hydroxide. *Water Research, 30*(6), 1345-1352. doi:10.1016/0043-1354(95)00305-3

Hemmer, M. J., Barron, M. G., & Greene, R. M. (2011). Comparative toxicity of eight oil dispersants, Louisiana sweet crude oil (LSC), and chemically dispersed LSC to two aquatic test species. *Environmental Toxicology and Chemistry, 30*(10), 2244-2252. doi:10.1002/etc.619

Herndon, V. A. (2010). Literature Review of Chemical Oil Spill Dispersants and Herders in Fresh and Brackish Waters.

Inc., H. E. (2016). *North Saskatchewan river water source risk assessment*.

International Tanker Owners Pollution Federation Limited (ITOPF). (2011). *Use of dispersants to treat oil spills*. Technical Information Paper. Canterbury, UK.

Jaji, K. T. (2012a). *Treatment of oilfield produced water with dissolved air flotation.* (M.Sc). Dalhousie University, Retrieved from https://dalspace.library.dal.ca/handle/10222/15347

Jaji, K. T. (2012b). Treatment of oilfield produced water with dissolved air flotation.

Jiang, B. y., Du, J., Cheng, S. q., Wang, Q., & Zeng, X. c. (2003). Effects of amine additives on critical micelle concentration of ionic surfactants. *Journal of Dispersion Science and Technology, 24*(6), 755-760. doi:10.1081/Dis-120025542

Jochmann, M. A., Yuan, X., Schilling, B., & Schmidt, T. C. (2008). In-tube extraction for enrichment of volatile organic hydrocarbons from aqueous samples. *Journal of Chromatography A, 1179*(2), 96-105.

John, V., Arnosti, C., Field, J., Kujawinski, E., & McCormick, A. (2016). The role of dispersants in oil spill remediation: Fundamental concepts, rationale for use, fate, and transport issues. *Oceanography, 29*(3), 108-117. doi:10.5670/oceanog.2016.75

Katepalli, H., & Bose, A. (2014). Response of surfactant stabilized oil-in-water emulsions to the addition of particles in an aqueous suspension. *Langmuir, 30*(43), 12736-12742.

Kędziora-Koch, K., & Wasiak, W. (2018). Needle-based extraction techniques with protected sorbent as powerful sample preparation tools to gas chromatographic analysis: trends in application. *Journal of Chromatography A, 1565*, 1-18.

Khan, R., Inam, M. A., Khan, S., Jiménez, A. N., Park, D. R., & Yeom, I. T. (2019). The influence of ionic and nonionic surfactants on the colloidal stability and removal of CuO nanoparticles from water by chemical coagulation. *International journal of environmental research and public health, 16*(7), 1260.

Kujawinski, E. B., Kido Soule, M. C., Valentine, D. L., Boysen, A. K., Longnecker, K., & Redmond, M. C. (2011). Fate of dispersants associated with the deepwater horizon oil spill. *Environmental Science & Technology, 45*(4), 1298-1306. doi:10.1021/es103838p

Laaks, J., Jochmann, M. A., Schilling, B., & Schmidt, T. C. (2015). Optimization strategies of in-tube extraction (ITEX) methods. *Analytical and bioanalytical chemistry, 407*(22), 6827-6838.

Lawrence, S. J. (2006). *Description, Properties, and Degradation of Selected Volatile Organic Compounds Detected in Ground Water--A Review of Selected Literature* (2331-1258).

Lee, K., Boufadel, M., Foght, J., Hodson, P., Swanson, S., & Venosa, A. (2015). *Expert panel report on the behaviour and environmental impacts of crude oil released into aqueous environments* (EPR 15-1). Retrieved from Ottawa, ON, Canada: http://www.rsc.ca/en/expert-panels/rsc-reports/behaviour-and-environmental-impacts-crude-oil-released-into-aqueous

Livingstone, R. A., Nagata, Y., Bonn, M., & Backus, E. H. G. (2015). Two Types of Water at the Water–Surfactant Interface Revealed by Time-Resolved Vibrational Spectroscopy. *Journal of the American Chemical Society, 137*(47), 14912-14919. doi:10.1021/jacs.5b07845

Luthy, R. G., Selleck, R. E., & Galloway, T. R. (1978). Removal of emulsified oil with organic coagulants and dissolved air flotation. *J. Water Pollut. Control Fed.; (United States)*. Retrieved from https://www.osti.gov/servlets/purl/5030851

Maloney, K. O., Baruch-Mordo, S., Patterson, L. A., Nicot, J.-P., Entrekin, S. A., Fargione, J. E., . . . Trainor, A. M. (2017). Unconventional oil and gas spills: Materials, volumes, and risks to surface waters in four states of the US. *Science of the Total Environment, 581*, 369-377. doi:10.1016/j.scitotenv.2016.12.142

Malvern Instruments Ltd. (2011). *Mastersizer 3000. User manual*.

Mancini, G., Panzica, M., Fino, D., Cappello, S., Yakimov, M. M., & Luciano, A. (2017). Feasibility of treating emulsified oily and salty wastewaters through coagulation and bio-regenerated GAC filtration. *Journal of Environmental Management, 203*, 817-824. doi:10.1016/j.jenvman.2016.07.014

Mathew, J., Schroeder, D. L., Zintek, L. B., Schupp, C. R., Kosempa, M. G., Zachary, A. M., . . . Wesolowski, D. J. (2012). Dioctyl sulfosuccinate analysis in near-shore Gulf of Mexico water by direct-injection liquid chromatography–tandem mass spectrometry. *Journal of Chromatography A, 1231*, 46-51.

Ministère du Développement Durable de l'Environnement et des Parcs (MDDEP). (2009). *Actiflo® + Dusenflo®. John meunier inc. Fiche d'évaluation technique du comité sur les technologies de traitement en eau potable*. Retrieved from Canada: http://www.mddep.gouv.qc.ca/eau/potable/guide/actiflo.pdf

Montgomery Watson Harza (MWH). (2005). *Water treatment: principles and design (Second Edition)*. Hoboken, New Jersey, USA: John Wiley and Sons, Inc.

Moursy, A. S., & El-Ela, S. E. A. (1982). Treatment of oily refinery wastes using a dissolved air flotation process. *Environment International*, *7*(4), 267-270.

Myers, D. (2006a). *Surfactant science and technology. 3rd edition*: Wiley Online Library.

Myers, D. (2006b). *Surfactant science and technology. 3rd edition*: Wiley Online Library.

Myers, K. J., Reeder, M. F., & Fasano, J. B. (2002). Optimize mixing by using the proper baffles. *Chemical Engineering Progress, 98*(2), 42-47. Retrieved from https://www.tib.eu/en/search/id/ceaba%3ACEAB20020301087/Optimize-mixing-by-using-the-proper-baffles/

Myers, K. J., Reeder, M. F., & Fasano, J. B. (2002). Optimize mixing by using the proper baffles. *Chem. Eng. Prog, 91*, 42-47.

Mysels, P. M. a. K. J. (1972). Critical micelle concentrations of aqueous surfactant systems. Prepared under contract for the Office of Standard Reference Data, National Bureau of Standards of NSRDS-NBS 36, Washington, DC 20234, 1971 v + 227 pp. 20.5 × 27 cm. Price $3.75. *Journal of Pharmaceutical Sciences, 61*(2), 319-319. doi:10.1002/jps.2600610254

Nagy, E., Scott, B. F., & Hart, J. (1984). The fate of oil and oil—dispersant mixtures in freshwater ponds. *Science of the Total Environment, 35*(2), 115-133. doi:10.1016/0048-9697(84)90058-5

Najm, I. N., Snoeyink, V. L., Lykins Jr., B. W., & Adams, J. Q. (1991). Using powdered activated carbon: A critical review. *Journal American Water Works Association, 83*(1), 65-76.

National Research Council (NRC). (2005). *Oil spill dispersants: Efficacy and effects*. Washington, DC, USA: National Academies Press.

Nguyen, T. K. M. (2018). *Évaluation de sondes en continu pour la détection rapide d'hydrocarbures dans l'eau brute.* (M.Sc.A). Polytechnique Montréal, Montréal, QC, Canada. Retrieved from https://publications.polymtl.ca/3316/

Nowacka, A., & Włodarczyk-Makuła, M. (2014). The coagulant type influence on removal efficiency of 5-and 6-ring PAHs during water coagulation process. *Civil and Environmental Engineering Reports, 13*(2), 63-73. doi:10.2478/ceer-2014-0015

Okoro, O., Lompe, K., Papineau, I., Solliec, M., Fradette, L., & Barbeau, B. (2021). Simultaneous powdered activated carbon and coagulant injection during ballasted flocculation for trace benzene removal from diesel and gasoline-contaminated surface waters. *Journal of Water Process Engineering, 40*, 101846. doi:10.1016/j.jwpe.2020.101846

Owens, E. H., & Michel, J. M. (1994). *Options for minimizing environmental impacts of freshwater spill response*: American Petroleum Institute, Health and Environmental Sciences Department.

Owens, E. H., & Michel, J. M. (1995). *Options for Minimizing Environmental Impacts of Freshwater Spill Response*: American Petroleum Institute, Health and Environmental Sciences Department.

Owens, E. H., Taylor, E., Marty, R., & Little, D. I. (1993, 1993). *An inland oil spill response manual to minimize adverse environmental impacts*.

Palmer, M., & Hatley, H. (2018). The role of surfactants in wastewater treatment: impact, removal and future techniques: A critical review. *Water Research, 147*, 60-72. doi:10.1016/j.watres.2018.09.039

Pastor-Belda, M., Viñas, P., Campillo, N., & Hernández-Córdoba, M. (2019). Headspace sorptive extraction coupled to gas chromatography–mass spectrometry for the determination of benzene, toluene, ethylbenzene and xylenes in finger paints. *Microchemical Journal, 145*, 406-411. doi:10.1016/j.microc.2018.10.062

Pham, T. T., & Proulx, S. (1997). PCBs and PAHs in the Montreal Urban Community (Quebec, Canada) wastewater treatment plant and in the effluent plume in the St Lawrence River. *Water Research, 31*(8), 1887-1896. doi:10.1016/S0043-1354(97)00025-0

Poliakoff, M. Z. (1969). *Oil dispersing chemicals: a study of the composition, properties, and use of chemicals for dispersing oil spills*: US Federal Water Pollution Control Administration.

Pourrezaei, P., Drzewicz, P., Wang, Y., Gamal El-Din, M., Perez-Estrada, L. A., Martin, J. W., . . . Giesy, J. P. (2011). The impact of metallic coagulants on the removal of organic compounds from oil sands process-affected water. *Environmental Science and Technology, 45*(19), 8452-8459. doi:10.1021/es201498v

Prince, R. C. (2015). Oil spill dispersants: Boon or bane? *Environmental Science & Technology, 49*(11), 6376-6384. doi:10.1021/acs.est.5b00961

Randtke, S. J. (1988). Organic contaminant removal by coagulation and related process combinations. *Journal-American Water Works Association, 80*(5), 40-56. doi:10.1002/j.1551-8833.1988.tb03037.x

Ribera-Pi, J., Badia-Fabregat, M., Arias, D., Gómez, V., Taberna, E., Sanz, J., . . . Jubany, I. (2020). Coagulation-flocculation and moving bed biofilm reactor as pre-treatment for water recycling in the petrochemical industry. *Science of the Total Environment, 715*, 136800. doi:10.1002/j.1551-8833.1988.tb03037.x

Rivas, M. (2017). *Performance assessment of powdered activated carbon for the removal of benzene from surfacewaters.* (M.Sc. M.Sc.). Technical University of Munich,

Rosenblum, J. S., Sitterley, K. A., Thurman, E. M., Ferrer, I., & Linden, K. G. (2016). Hydraulic fracturing wastewater treatment by coagulation-adsorption for removal of organic compounds and turbidity. *Journal of environmental chemical engineering, 4*(2), 1978-1984.

Rosińska, A., & Dąbrowska, L. (2018). Selection of coagulants for the removal of chosen PAH from drinking water. *Water, 10*(7), 886.

Rubi, H., Fall, C., & Ortega, R. E. (2009). Pollutant removal from oily wastewater discharged from car washes through sedimentation–coagulation. *Water Science and Technology, 59*(12), 2359-2369. doi:http://dx.doi.org/10.2166/wst.2009.307

Santé Canada. (2009). *Recommandations pour la qualité de l'eau potable au Canada. Document technique - Benzène*. Retrieved from Ottawa, ON, Canada: https://www.canada.ca/fr/sante-canada/services/publications/vie-saine/recommandations-pour-qualite-eau-potable-canada-document-technique-benzene.html

Santé Canada. (2014). *Recommandations pour la qualité de l'eau potable au Canada. Document technique - Le toluène, l'éthylbenzène et les xylènes*. Retrieved from Ottawa, ON, Canada: www.santecanada.gc.ca

Santé Canada. (2016). *Recommandations pour la qualité de l'eau potable au Canada. Document technique - Le benzo[a]pyrène*. Retrieved from https://www.canada.ca/fr/sante-canada/services/publications/vie-saine/recommandations-pour-qualite-eau-potable-canada-document-technique-benzo-pyrene.html

Santo, C. E., Vilar, V. J., Botelho, C. M., Bhatnagar, A., Kumar, E., & Boaventura, R. A. (2012). Optimization of coagulation–flocculation and flotation parameters for the treatment of a petroleum refinery effluent from a Portuguese plant. *Chemical Engineering Journal, 183*, 117-123.

Scott, B. F., & Glooschenko, V. (1984). Impact of oil and oil-dispersant mixtures on flora and water chemistry parameters in freshwater ponds. *Science of the Total Environment, 35*(2), 169-190. doi:10.1016/0048-9697(84)90061-5

Scott, B. F., Nagy, E., Dutka, B. J., Sherry, J. P., Taylor, W. D., Glooschenko, V., . . . Hart, J. (1984). The fate and impact of oil and oil—dispersant mixtures in freshwater pond ecosystems: Introduction. *Science of the Total Environment, 35*(2), 105-113. doi:10.1016/0048-9697(84)90057-3

Shabeer, T. P. A., Saha, A., Gajbhiye, V. T., Gupta, S., Manjaiah, K. M., & Varghese, E. (2014). Removal of poly aromatic hydrocarbons (PAHs) from water: Effect of nano and modified nano-clays as a flocculation aid and adsorbent in coagulation-flocculation process. *Polycyclic Aromatic Compounds*, *34*(4), 452-467. doi:10.1080/10406638.2014.895949

Sharp, E. L., Jarvis, P., Parsons, S. A., & Jefferson, B. (2006). The impact of zeta potential on the physical properties of ferric− NOM flocs. *Environmental Science & Technology, 40*(12), 3934-3940. doi:10.1021/es051919r

Shin, S. H., & Kim, D. S. (2001). Studies on the interfacial characterization of O/W emulsion for the optimization of its treatment. *Environmental Science & Technology*, *35*(14), 3040-3047. doi:10.1021/es001592o

Short, J. W. (2008). An evaluation of oil fate, persistence, and toxic potential to fish following the August 2005 Canadian national derailment sill into Lake Wabamun, Alberta. *Report submitted to Public Prosecution Service of Canada, Alberta Regional Office. National Oceanographic and Atmospheric Administration.*

Shouli, A. S., Bewtra, J. K., & Biswas, N. (1992). Effectiveness of coagulation and flocculation processes in removal of selected volatile organic contaminants from wastewaters. *International Journal of Environmental Studies, 40*(1), 27-40. doi:10.1080/00207239208710711

Sidim, T., & Acar, G. (2013). Alcohols effect on critic micelle concentration of polysorbate 20 and cetyl trimethyl ammonium bromine mixed solutions. *Journal of surfactants and detergents, 16*(4), 601-607.

SL Ross Environmental Research (SLRoss). (2010). *Literature review of chemical oil spill dispersants and herders in fresh and brackish waters. For U.S. Department of the Interior Minerals Management Service*. Retrieved from Ottawa, ON, Canada: https://www.bsee.gov/sites/bsee.gov/files/osrr-oil-spill-response-research/635ab.pdf

Smol, M., & Włodarczyk-Makuła, M. (2017). The effectiveness in the removal of PAHs from aqueous solutions in physical and chemical processes: a review. *Polycyclic Aromatic Compounds, 37*(4), 292-313. doi:10.1080/10406638.2015.1105828

Snoeyink, V. L., & Summers, R. S. (1999). Chapter 13: Adsorption of organic compounds. In *Water quality and treatment: A handbook of community water supplies* (Fifth Edition ed., pp. 13.11-13.83): American Water Work Association.

Stackelberg, P. E., Gibs, J., Furlong, E. T., Meyer, M. T., Zaugg, S. D., & Lippincott, R. L. (2007). Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. *Science of the Total Environment, 377*(2-3), 255-272. doi:10.1016/j.scitotenv.2007.01.095

Stauffer, C. E. (1965). The measurement of surface tension by the pendant drop technique. *The Journal of Physical Chemistry*, *69*(6), 1933-1938. doi:10.1021/j100890a024

Stumm, W., & O'Melia, C. R. (1968). Stoichiometry of coagulation. *Journal-American Water Works Association*, *60*(5), 514-539. doi:10.1002/j.1551-8833.1968.tb03579.x

Tadros, T. F. (2014). *Formulation of Disperse Systems: Science and Technology*: John Wiley & Sons.

Tansel, B., & Dimitric-Clark, V. (2002). Microscopic Characterization Of Oil Droplets Removed By Flocs After Coagulation Of Oil-Water Emulsions. *Journal of Environmental Science and Health, Part A, 37*(2), 127-138. doi:10.1081/ESE-120002577

Tansel, B., & Eifert, J. L. (1999). Removal of emulsified PHCs from brackish water by coagulation. *Journal of Environmental Engineering, 125*(12), 1173-1176.

Tansel, B., & Pascual, B. (2011). Removal of emulsified fuel oils from brackish and pond water by dissolved air flotation with and without polyelectrolyte use: Pilot-scale investigation for estuarine and near shore applications. *Chemosphere, 85*(7), 1182-1186. doi:10.1016/j.chemosphere.2011.07.006

Tansel, B., & Sevimoglu, O. (2006). Coalescence and size distribution characteristics of oil droplets attached on flocs after coagulation. *Water, Air, and Soil Pollution, 169*(1-4), 293-302. doi:10.1007/s11270-006-3110-3

Tansel, B., & Vilar, F. (2005). Enhancement of media filter performance with coagulant use for treatment of diesel oil contaminated surface water. *Desalination, 173*(1), 69-76. doi:10.1016/j.desal.2004.08.028

Tienpont, B., David, F., Bicchi, C., & Sandra, P. (2000). High capacity headspace sorptive extraction. *Journal of Microcolumn Separations, 12*(11), 577-584.

To, P. C., Mariñas, B. J., Snoeyink, V. L., & Ng, W. J. (2008). Effect of strongly competing background compounds on the kinetics of trace organic contaminant desorption from activated carbon. *Environmental science & technology, 42*(7), 2606-2611.

Torres, L. G., Belloc, C., Vaca, M., Iturbe, R., & Bandala, E. R. (2009). Coagulation-flocculation process applied to wastewaters generated in hydrocarbon-contaminated soil washing: Interactions among coagulant and flocculant concentrations and pH value. *Journal of Environmental Science and Health, Part A, 44*(13), 1449-1456.

Total Fluides. (2015). *Safety Data Sheet. According to regulation (EC) No. 1907/2006*.

Transportation Safety Board of Canada (TSB). (2018). Statistical summary: Pipeline transportation occurrences in 2018. In. Gatineau, QC, CANADA.

U.S. Energy Information Administration. (2020). U.S. Field Production of Crude Oil. Retrieved from https://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=pet&s=mcrfpus2&f=a

U.S. National Library of Medicine. Toxicology data network. Retrieved from https://toxnet.nlm.nih.gov/

United States Environmental Protection Agency (U.S. EPA). (2014). *Toxicological Review of Benzo[a]pyrene (External Review Draft), EPA/635/R-14/312*. (EPA/635/R-14/312). Washington, DC Retrieved from https://cfpub.epa.gov/ncea/iris/iris_documents/documents/toxreviews/0136tr.pdf

United States Environmental Protection Agency (USEPA). (2011). *2011 Edition of the drinking water standards and health advisories*. Retrieved from Washington, DC, USA: http://water.epa.gov/action/advisories/drinking/upload/dwstandards2011.pdf

United States Environmental Protection Agency (USEPA). (2016). *Testing large-volume water treatment and crude-oil decontamination using the EPA water security test bed* (EPA/600/R-161/126). Retrieved from Cincinnati, OH, USA: https://www.epa.gov/homeland-security-research

United States Environmental Protection Agency (USEPA). (2019). National primary drinking water regulations. Retrieved from https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations

Vadasarukkai, Y. S. (2016). Investigation of the Mixing Energy Consumption Affecting Coagulation and Floc Aggregation.

Vandermeulen, J. H., & Ross, C. W. (1995). Oil spill response in freshwater: Assessment of the impact of cleanup as a management tool. *Journal of Environmental Management, 44*(4), 297-308. doi:10.1016/S0301-4797(95)90338-0

Vincent, S., Elliott, W., and Meunier, M.,. (2017). Trusted Drinking Water Treatment Supporting Prince Albert's oil spill response. *Western Canada Water, 69(2),* 38-39. Retrieved from https://cdn.ymaws.com/www.wcwwa.ca/resource/resmgr/magazine/wcw_summer2017.pdf

Vogelsang, C., Grung, M., Jantsch, T. G., Tollefsen, K. E., & Liltved, H. (2006). Occurrence and removal of selected organic micropollutants at mechanical, chemical and advanced wastewater treatment plants in Norway. *Water Research, 40*(19), 3559-3570. doi:10.1016/j.watres.2006.07.022

Wang, B., Shui, Y., Ren, H., & He, M. (2017). Research of combined adsorption-coagulation process in treating petroleum refinery effluent. *Environmental Technology, 38*(4), 456-466. doi:10.1080/09593330.2016.1197319

Weiss, J., & McClements, D. J. (2000). Mass transport phenomena in oil-in-water emulsions containing surfactant micelles: Solubilization. *Langmuir, 16*(14), 5879-5883. doi:10.1021/la9914763

World Health Organization (WHO). (2004). *Guidelines for drinking water-quality. Third Edition (Volume 1). Recommendations*. Retrieved from Geneva, Switzerland: http://www.who.int/water_sanitation_health/dwq/GDWQ2004web.pdf

Wrenn, B. A., Virkus, A., Mukherjee, B., & Venosa, A. D. (2009). Dispersibility of crude oil in fresh water. *Environmental Pollution, 157*(6), 1807-1814. doi:10.1016/j.envpol.2009.01.025

Yang, C., Brown, C. E., Hollebone, B., Yang, Z., Lambert, P., Fieldhouse, B., . . . Wang, Z. (2017). Chemical fingerprints of crude oils and petroleum products. In *Oil Spill Science and Technology* (pp. 209-304): Elsevier.

Yang, J. Y., Yan, L., Li, S. P., & Xu, X. R. (2016). Treatment of aging oily wastewater by demulsification/flocculation. *Journal of Environmental Science and Health, Part A, 51*(10), 798-804. doi:10.1080/10934529.2016.1181436

You, Z., Xu, H., Sun, Y., Zhang, S., & Zhang, L. (2018). Effective treatment of emulsified oil wastewater by the coagulation–flotation process. *RSC Advances, 8*(71), 40639-40646. doi:10.1039/c8ra06565a

Young, W. F., Horth, H., Crane, R., Ogden, T., & Arnott, M. (1996). Taste and odour threshold concentrations of potential potable water contaminants. *Water Research, 30*(2), 331-340.

Younker, J. M., & Walsh, M. E. (2014). Impact of salinity on coagulation and dissolved air flotation treatment for oil and gas produced water. *Water Quality Research Journal of Canada, 49*(2), 135-143. doi:10.2166/wqrjc.2013.118

Younker, J. M., & Walsh, M. E. (2015). Impact of salinity and dispersed oil on adsorption of dissolved aromatic hydrocarbons by activated carbon and organoclay. *Journal of hazardous materials, 299*, 562-569.

Younker, J. M., & Walsh, M. E. (2016). Effect of adsorbent addition on floc formation and clarification. *Water research, 98*, 1-8.

Zhai, J., Huang, Z., Rahaman, M. H., Li, Y., Mei, L., Ma, H., . . . Wang, K. (2017). Comparison of coagulation pretreatment of produced water from natural gas well by polyaluminium chloride and polyferric sulphate coagulants. *Environmental Technology, 38*(10), 1200-1210. doi:10.1080/09593330.2016.1217937

Zhang, Z. (2017). Treatment of oilfield wastewater by combined process of micro-electrolysis, Fenton oxidation and coagulation. *Water Science and Technology, 76*(12), 3278-3288. doi:10.2166/wst.2017.486

Zhao, X., Ya, Z., Wang, Z., Sun, B., Fu, H., & Bénédicte, M.-C. J. (2020). Study on the effects of waves and dispersant on the submergence of spilled oil. *Water Resources, 47*(1), 95-102. doi:10.1134/S0097807820010157

Zhou, J., Dettman, H., & Bundred, M. (2015a). *A comparative analysis of environmental behavior of diluted bitumen and conventional crudes.* Paper presented at the 38th AMOP Technical Seminar on Environmental Contamination and Response, June 2, 2015 - June 4, 2015, Vancouver, BC, Canada.

Zhou, J., Dettman, H., & Bundred, M. (2015b, Jun 2-4). *A comparative analysis of environmental behavior of diluted bitumen and conventional crudes.* Paper presented at the 38th AMOP Technical Seminar on Environmental Contamination and Response, Vancouver, BC, Canada.

APPENDIX A SUPPLEMENTARY INFORMATION FOR ARTICLE I

Table A1: Constants for HSDM model based on the method described by Crittenden et al. Model equation is described as $\frac{C-C_e}{C_0-C_e} = A_0 + A_1 ln(\bar{t}) + A_2 ln(\bar{t})^2 + A_3 ln(\bar{t})^3$. $1/n$ is determined from the Freundlich isotherm fit. C_e is the equilibrium concentration calculated from $\frac{C_0-C_e}{D_0} = KC_e{}^{1/n}$.

	Benzene – gasoline contaminated water	**Benzene – diesel contaminated water**	**BTEX – gasoline contaminated water**	**BTEX – diesel contaminated water**
	$1/n = 0.4\ and\ C_e/C_0 = 0.01$	$1/n = 0.9\ and\ C_e/C_0 = 0.1$	$1/n = 0.5\ and\ C_e/C_0 = 0.01$	$1/n = 0.6\ and\ C_e/C_0 = 0.01$
A_0	0.294919	0.032362	0.0957667	-0.0232271
A_1	0.217595	0.044662	0.0599179	-0.0277669
A_2	0.0453972	0.0161704	0.00787512	-0.0112094
A_3	0.00163889	0.00014277	-0.000691859	-0.00170026
Lower $\bar{t}$	0.000165	0.000152	0.000117	0.000159
Upper $\bar{t}$	0.074500	0.233000	0.0636	0.0742

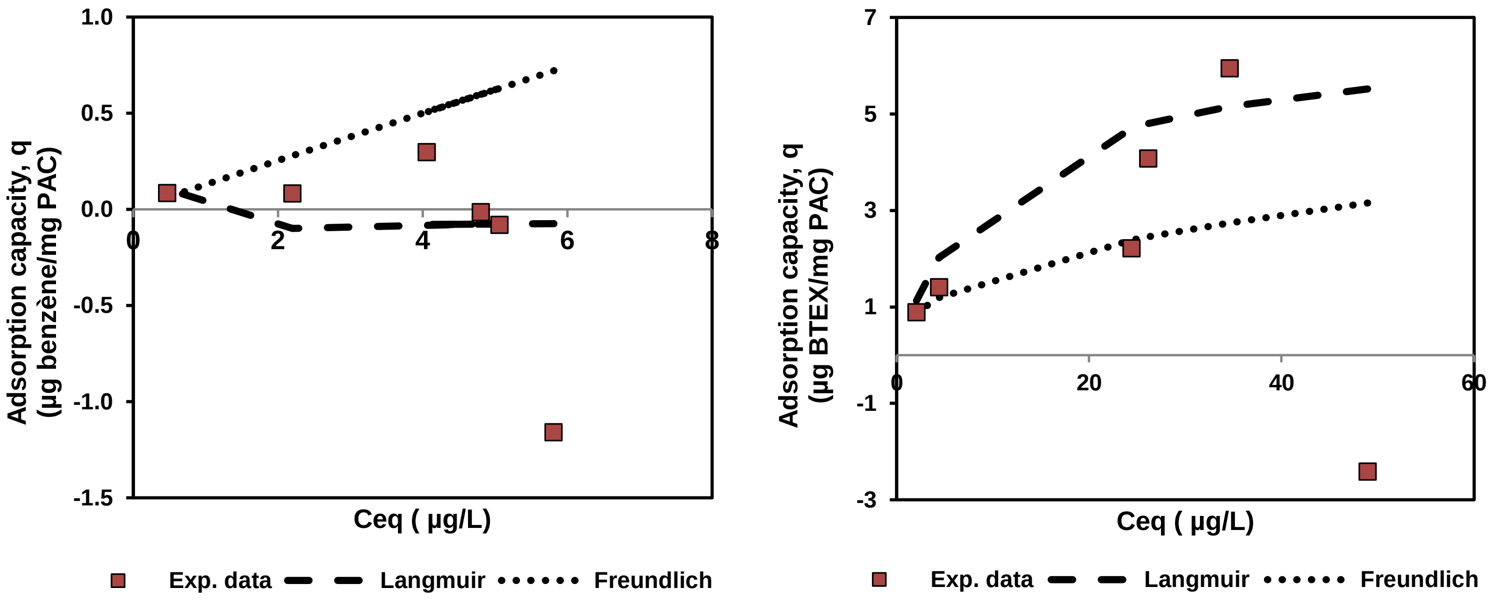


Figure A1: Adsorption capacity of benzene (left) and BTEX (right) as a function of equilibrium concentration for diesel-contaminated water, including Langmuir and Freundlich fits. Initial benzene, BTEX and dissolved organic carbon (DOC) concentrations were 4.7 µg/L, 47 µg/L and 6.1 mg C/L, respectively. Adsorption data for the 1 mg PAC/L dose was removed as an outlier in the calculation of Langmuir and Freundlich fits.

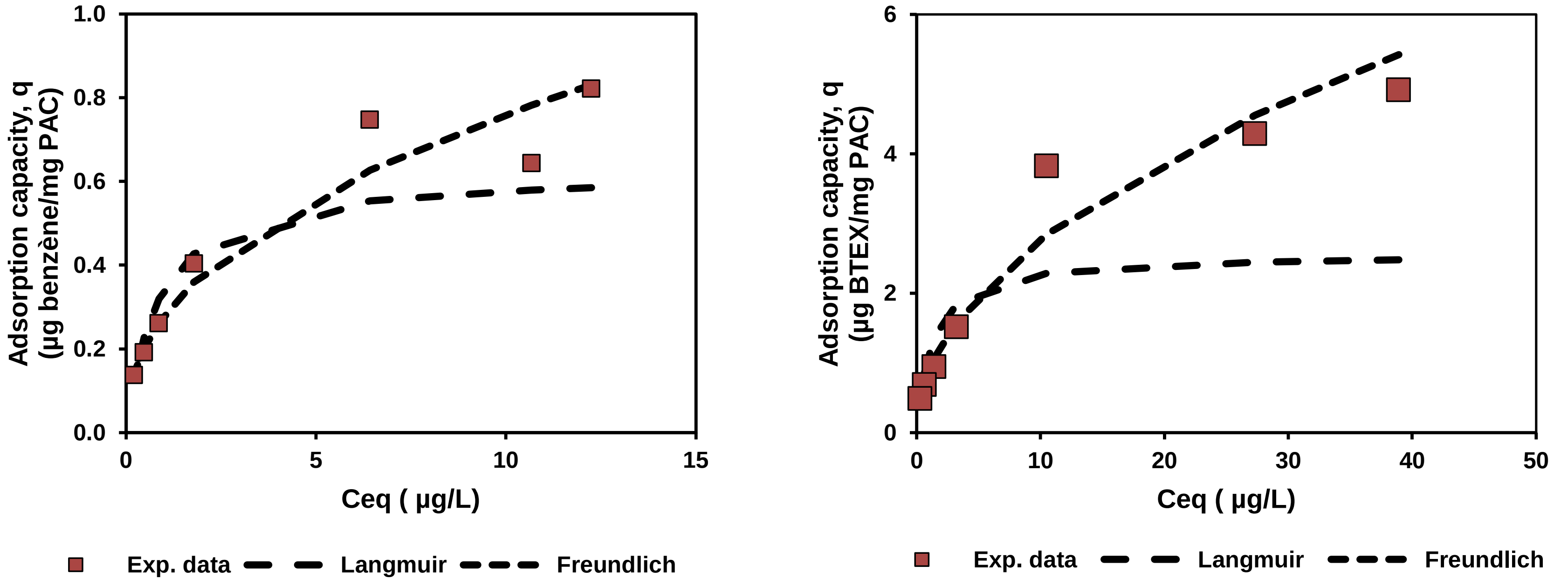


Figure A2: Adsorption capacity of benzene (left) and BTEX (right) as a function of equilibrium concentration for gasoline-contaminated water, including Langmuir and Freundlich fits. Initial benzene, BTEX and DOC concentrations were 14 µg/L, 49 µg/L and 9.1 mg C/L, respectively. Adsorption data for the 1 mg PAC/L dose was removed as an outlier in the calculation of Langmuir and Freundlich fits.

Table A2: Residual benzene concentrations (µg/L) as a function of time (kinetics tests) for diesel and gasoline contaminated waters.

Diesel-contaminated water	
Time	Residual benzene (µg/L)
1 min	1.0
3 min	0.49
5 min	0.46
10 min	0.45
15 min	**0.30**
30 min	0.24
1 hr	0.20
3 hr	0.08
24 hr	0.04
Control	27

Gasoline-contaminated water	
Time	Residual benzene (µg/L)
1 min	2.1
3 min	1.2
5 min	1.1
10 min	0.58
15 min	0.49
30 min	**0.28**
1 hr	0.22
3 hr	0.19
24 hr	0.15
Control	14

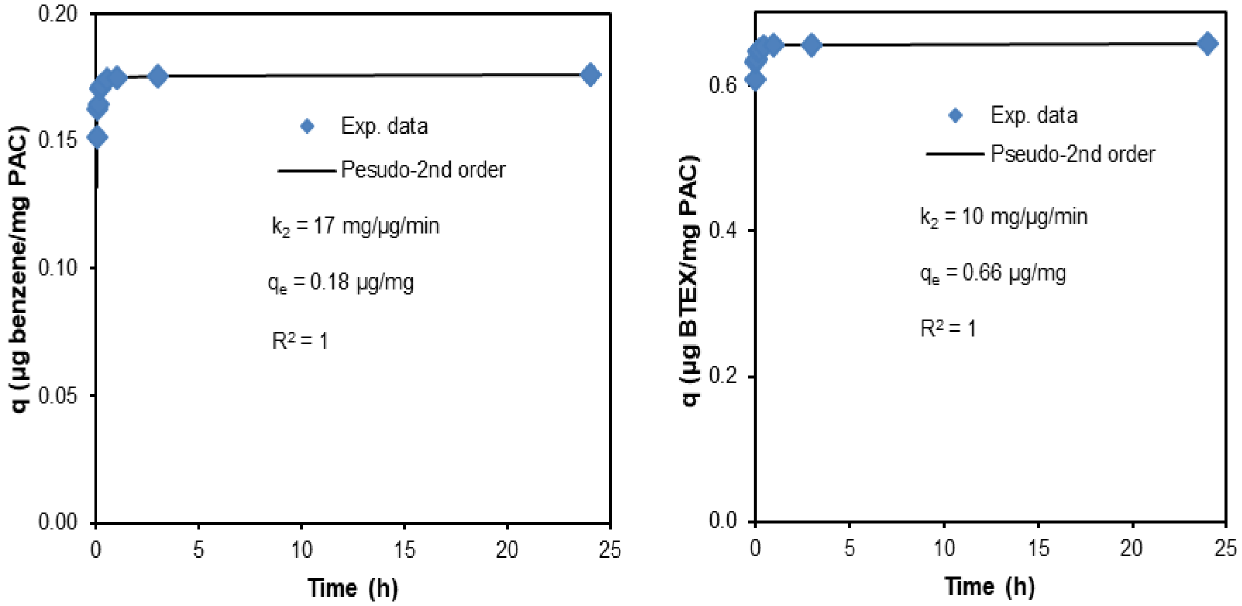


Figure A3: Adsorption capacity of benzene (left) and BTEX (right) as a function of time for gasoline-contaminated water. Initial benzene and BTEX concentrations were 14 µg/L and 53 µg/L, respectively.

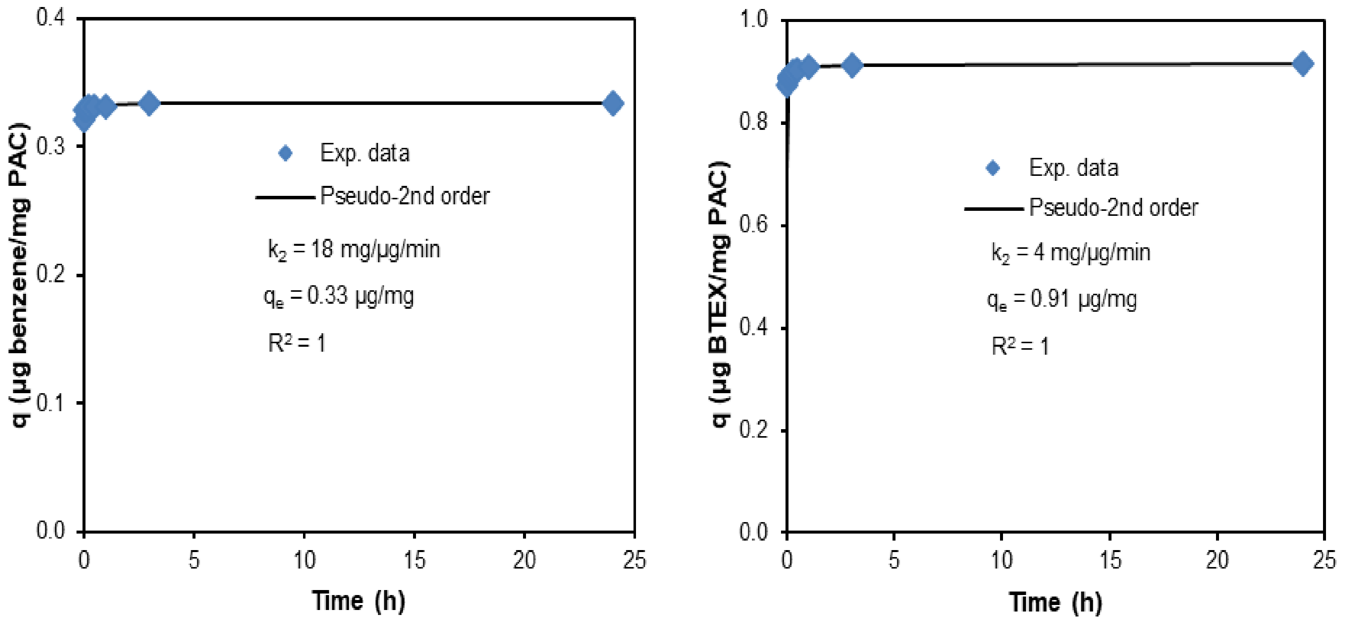


Figure A4: Adsorption capacity of benzene (left) and BTEX (right) as a function of time for diesel-contaminated water. Initial benzene and BTEX concentrations were 27 µg/L and 74 µg/L, respectively.

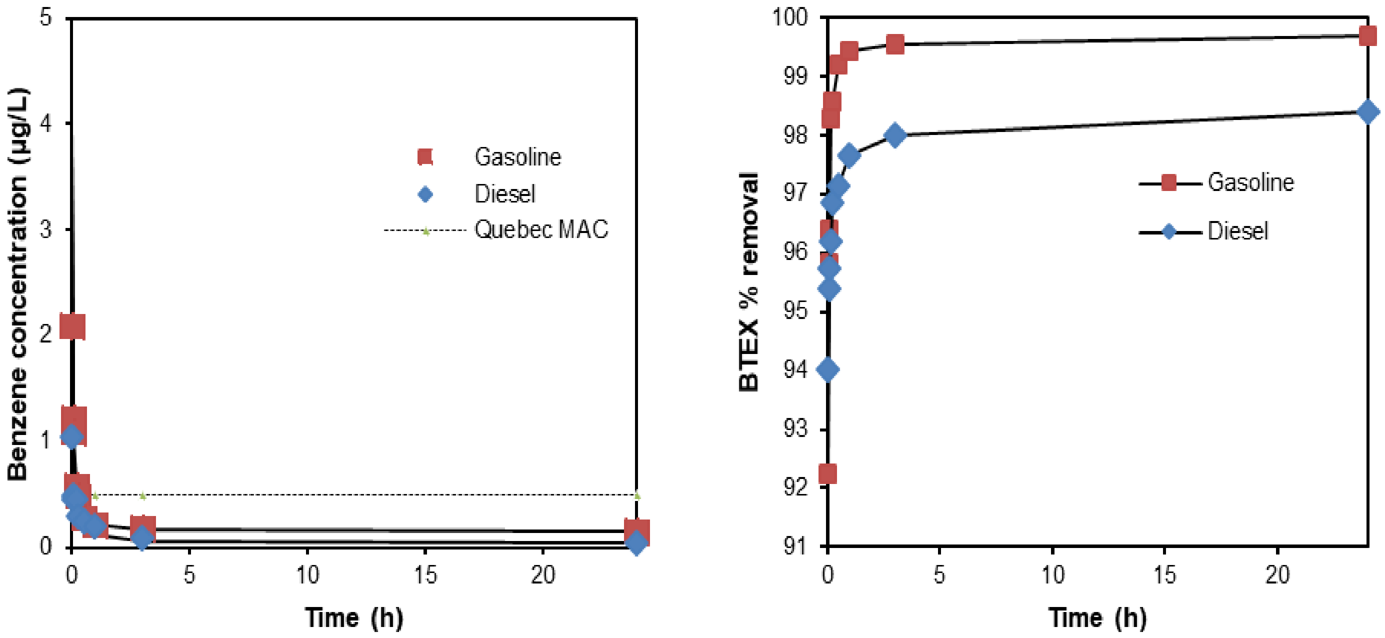


Figure A5: Left - Benzene concentration as a function of time for diesel (diamond) and gasoline (square) contaminated waters. Right - BTEX % removal as a function of time for diesel (diamond) and gasoline (square) contaminated waters. 80 mg PAC/L was applied. Initial benzene concentrations in diesel and gasoline-contaminated waters were 27 µg/L and 14 µg/L, respectively. Initial BTEX concentrations in diesel and gasoline-contaminated waters were 74 µg/L and 53 µg/L, respectively.

Table A3: Method validation parameters of BTEX compounds in surface water measured by SBSE-GC-MS in SIM mode including coefficient correlation (R^2), LOD and LOQ. The LOD and LOQ were determined as 3 and 10 times, respectively, the standard deviation of the y-intercept divided by the slope of the calibration curve in surface water sample. The linearity of the method was determined by analysing spiked surface water samples in the range of 0.01 to 5 µg/L.

Compounds	LOD (µg/L)	LOQ (µg/L)	R^2
Benzene	0.021	0.069	99.9
Toluene	0.094	0.315	99.5
Ethylbenzene	0.045	0.151	99.9
m,p-Xylene	0.068	0.228	99.7
o-xylene	0.042	0.139	99.9

APPENDIX B SUPPLEMENTARY INFORMATION FOR ARTICLE II

Table B1: Liquid chromatography and triple quadrupole parameters including retention times (Rt), precursor ion, quantification ion and confirmation ion with associated collision energies.

Compounds	Rt (min)	Precursor ion (*m/z*)	Quantification ion (*m/z*)[a]	Confirmation ion (*m/z*)[a]	RF Lens (eV)
Docusate sodium (DOSS)	4.10	421.3 $[M-H]^-$	81.1 (26)	227.1 (22)	102
Sodium dodecyl sulfate (SDS)	3.50	265.1 $[M-H]^-$	97.1 (28)	80.0 (55)	96
Sodium bis(2-ethylhexyl-d_{17}*) sulfosuccinate (SBS-*d_{34}*)*	4.07	455.4 $[M-H]^-$	81.0 (29)	244.4 (24)	80

Compound name in italic is the internal standard used for quantitation purposes.
[a] Collision energies are given in brackets (eV)

Table B2: Method validation parameters.

Compounds	LOD (µg/L)[a]	LOQ (µg/L)[a]	R^2	Precision 50 µg/L (%)[b]	Precision 500 µg/L (%)[b]	Accuracy 50 µg/L (%)	Accuracy 500 µg/L (%)
Docusate sodium (DOSS)	11	37	0.999	-1	2	5	9
Sodium dodecyl sulfate (SDS)	11	41	0.999	-5	6	6	11

[a] Limit of detection (LOD) and limit of quantification were calculated

[b] Precision was calculated at 50 and 500 (µg/L) and was expressed as s residual standard deviation (%)

Table B3: Water quality results for ballasted flocculation of raw surface water (RW), surface water contaminated with crude oil (RW+CO), and surface water contaminated with crude oil and Finasol® OSR 52 (RW+CO+Fin) using alum and ferric sulfate as coagulants.

	Turbidity (NTU)			UVA254 (cm^{-1})		
	RW	RW+CO	RW+CO+Finasol	RW	RW+CO	RW+CO+Finasol
Control	4.3	5.7	7.2	0.254	0.248	0.255
Alum	0.75	0.42	0.92	0.040	0.046	0.042
FS	0.82	9.2	5.8	0.041	0.070	0.040
Standard deviation	Turbidity (NTU)			UVA254 (cm^{-1})		
	RW	RW+CO	RW+CO+Finasol	RW	RW+CO	RW+CO+Finasol
Control	0.072	0.07	0.14			
Alum	0.054	0.03	0.010			
FS	0.074	3.20	0.24			

Table B3 (continued): Water quality results for ballasted flocculation of raw surface water (RW), surface water contaminated with crude oil (RW+CO), and surface water contaminated with crude oil and Finasol® OSR 52 (RW+CO+Fin) using alum and ferric sulfate as coagulants.

	Zeta Potential (mV)			Surface Tension (mN/m)		
	RW	RW+CO	RW+CO+Finasol	RW	RW+CO	RW+CO+Finasol
Control	-20	-17	-33	75	75	75
Alum	-0.59	2	1	76	77	73
FS	1.4	-18	-7	76	74	75
Standard deviation	Zeta Potential (mV)			Surface Tension (mN/m)		
	RW	RW+CO	RW+CO+Finasol	RW	RW+CO	RW+CO+Finasol
Control	1.8	3	5.4	0.80	1.4	1.7
Alum	0.52	0.98	0.34	0.58	1.4	0.9
FS	2	0.40	1	0.70	1.0	1.9

Table B4: Water quality data before and after ballasted flocculation of raw surface water contaminated with increasing concentrations of Finasol® OSR 52 (RW + Finasol). Alum was employed as coagulant at a dose of 41 mg dry alum/L.

	Turbidity (NTU)		TOC (mg C/L)		Surface tension (mN/m)	
Dispersant concentration (mg/L)	RW + Finasol	Settled	RW + Finasol	Settled	RW + Finasol	Settled
2	4.6	0.51	8.3	1.9	78	77
20	6.0	0.70	13	5.9	80	77
200	25	25	89	96	60	70
Standard deviation	Turbidity (NTU)		TOC (mg C/L)		Surface tension (mN/m)	
Dispersant concentration (mg/L)	RW + Finasol	Settled	RW + Finasol	Settled	RW + Finasol	Settled
2	0.27	0.01	0.28	0.01	0.37	2.1
20	0.02	0.1	0.2	0.0	0.91	1.5
200	0.12	0.0	3.8	10.0	0.96	2.4

Table B4 (continued): Water quality data before and after ballasted flocculation of raw surface water contaminated with increasing concentrations of Finasol® OSR 52 (RW + Finasol). Alum was employed as coagulant at a dose of 41 mg dry alum/L.

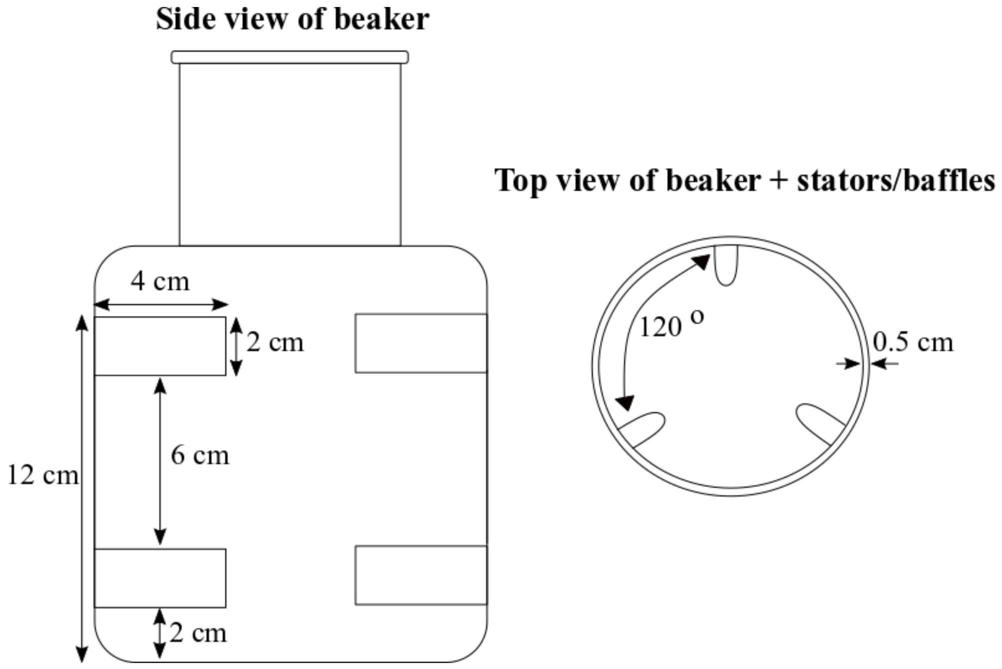
	UVA (cm^-1)		Zeta potential (mV)		DOSS concentration (mg/L)	
Dispersant concentration (mg/L)	RW + Finasol	Settled	RW + Finasol	Settled	RW + Finasol	Settled
2	0.255	0.048	-18	0.67	0.21	0.22
20	0.248	0.040	-19	2.7	2.6	1.9
200	0.435	0.273	-30	-27	30	27
Standard deviation	UVA (cm^-1)		Zeta potential (mV)		DOSS concentration (mg/L)	
Dispersant concentration (mg/L)	RW + Finasol	Settled	RW + Finasol	Settled	RW + Finasol	Settled
2			3	0.97	0.00075	0.0068
20			1	0.5	0.072	0.064
200			2	1	2.9	2.3

Table B5: D_{v10} , D_{v50}, and D_{v90} values for raw surface water, alum-treated settled water, and ferric sulfate-treated settled water. Ballasted flocculation tests were performed for both contaminated (RW + CO) and uncontaminated (RW) surface water.

	µm					
	Raw water		Alum-treated water		Ferric sulfate-treated water	
	RW	RW + CO	RW	RW + CO	RW	RW + CO
D_{v10}	0.72	20.2	288	1.7	14	3.3
D_{v50}	8.8	186	513	4.6	22	23
D_{v90}	16	500	766	7.55	32.3	369

Table B6: D_{v10} , D_{v50}, and D_{v90} values for raw surface water, alum-treated settled water, and ferric sulfate-treated settled water after ballasted flocculation of RW + CO and RW + CO + Finasol.

	µm					
	Raw water		Alum-treated water		Ferric sulfate-treated water	
	RW + CO	RW + CO + Finasol	RW + CO	RW + CO + Finasol	RW + CO	RW + CO + Finasol
D_{v10}	20	180	1.7	1.6	3.4	15
D_{v50}	186	289	4.6	3.0	23	28
D_{v90}	500	442	7.6	5	369	45


Side view of beaker

Top view of beaker + stators/baffles

Figure B1: Design of a custom-made, round glass beaker for ballasted flocculation tests [adapted from (American Water Works Association (AWWA), 2004)].

APPENDIX C SUPPLEMENTARY INFORMATION FOR ARTICLE III

Table C1: Liquid chromatography and triple quadrupole parameters including retention times (Rt), precursor ion, quantification ion and confirmation ion with associated collision energies.

Compounds	Rt (min)	Precursor ion (*m/z*)	Quantification ion (*m/z*)[a]	Confirmation ion (*m/z*)[a]	RF Lens (eV)
Docusate sodium (DOSS)	4.10	421.3 $[M-H]^-$	81.1 (26)	227.1 (22)	102
Sodium dodecyl sulfate (SDS)	3.50	265.1 $[M-H]^-$	97.1 (28)	80.0 (55)	96
Sodium bis(2-ethylhexyl-d_{17}) sulfosuccinate (SBS-d_{34})	4.07	455.4 $[M-H]^-$	81.0 (29)	244.4 (24)	80

Compound name in italic is the internal standard used for quantitation purposes.

[a] Collision energies are given in brackets (eV)

Table C2: Method validation parameters for surfactant analysis.

Compounds	LOD (µg/L)[a]	LOQ (µg/L)[a]	R^2	Precision 50 µg/L (%)[b]	Precision 500 µg/L (%)[b]	Accuracy 50 µg/L (%)	Accuracy 500 µg/L (%)
Docusate sodium (DOSS)	11	37	0.999	-1	2	5	9
Sodium dodecyl sulfate (SDS)	11	41	0.999	-5	6	6	11

[a] Limit of detection (LOD) and limit of quantification were calculated

[b] Precision was calculated at 50 and 500 (µg/L) and was expressed as s residual standard deviation (%)

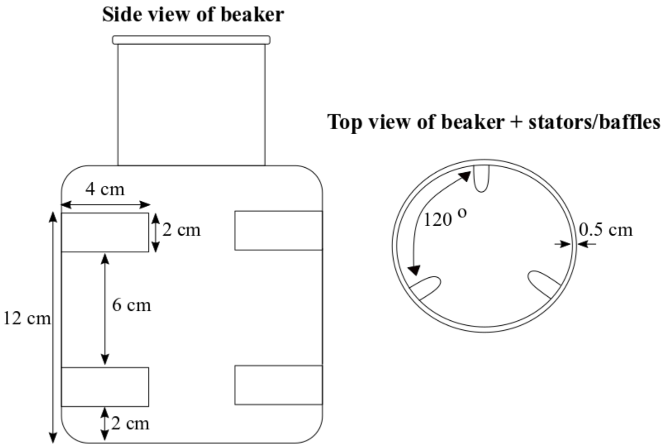


Figure C1: Design of jar-test beaker for ballasted flocculation tests.

Table C3: Surfactant concentrations in raw waters contaminated with commercial (Finasol OSR® 52) and formulated dispersants (Tween 80:SDS (20:80)) and in their corresponding settled waters after ballasted flocculation with alum.

Dispersant concentration (mg/L)	Surfactant concentration (mg/L)			
	Commercial dispersant		Formulated dispersant	
	Raw	Settled	Raw	Settled
2	0.21	0.22 ± 0.01	ND	0.058
20	2.6 ± 0.1	1.9 ± 0.1	0.43 ± 0.03	0.65 ± 0.03
200	30 ± 3	27 ± 2	5.2 ± 0.3	4.1 ± 0.4

*ND = not detected

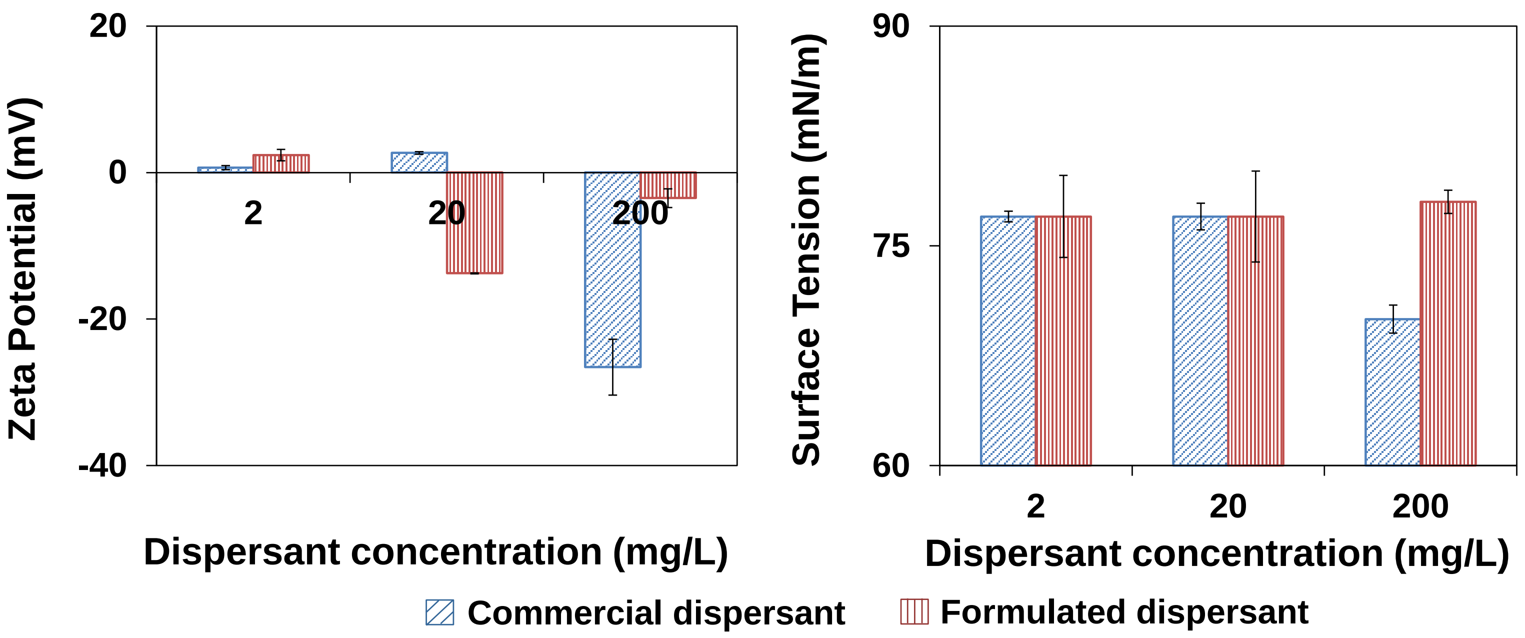


Figure C2: Zeta potential and surface tension values in settled waters following ballasted flocculation treatment of raw dispersant-contaminated surface waters. Two types of dispersants were tested: a commercial dispersant, Finasol OSR® 52, and a formulated dispersant, Tween 80:SDS (20:80).

Table C4: Total Organic Carbon contribution in the formulated dispersant (FD).

	Ratio	Formula	Molecular weight (g/mol)	Concentration (%)	Organic carbon contribution (g/mol)	Organic carbon in FD
SDS	0.8	$C_{12}H_{25}SO_4Na$	288	5	144	0.026
Tween 80	0.2	$C_{64}H_{124}O_{26}$	1310	5	769	

$$\textbf{Organic carbon in FD} = \left[\frac{144\frac{g}{mol}}{288\frac{g}{mol}} \times \frac{5}{100} \times 0.8\right] + \left[\frac{769\frac{g}{mol}}{1310\frac{g}{mol}} \times \frac{5}{100} \times 0.2\right]$$

$$\textbf{TOC – FD (mg C/L)} = Organic\ carbon\ in\ FD\ \times FD\ (\frac{mg}{L})$$

Table C5: Theoretical organic carbon in raw water contaminated with formulated dispersant (RW + FD) at different concentrations.

SD (mg/L)	TOC – FD (mg C/L)	TOC actual - RW	TOC - RW + FD (mg C/L)
2	0.052	7.5	7.55
20	0.52		8.02
200	5.2		12.7

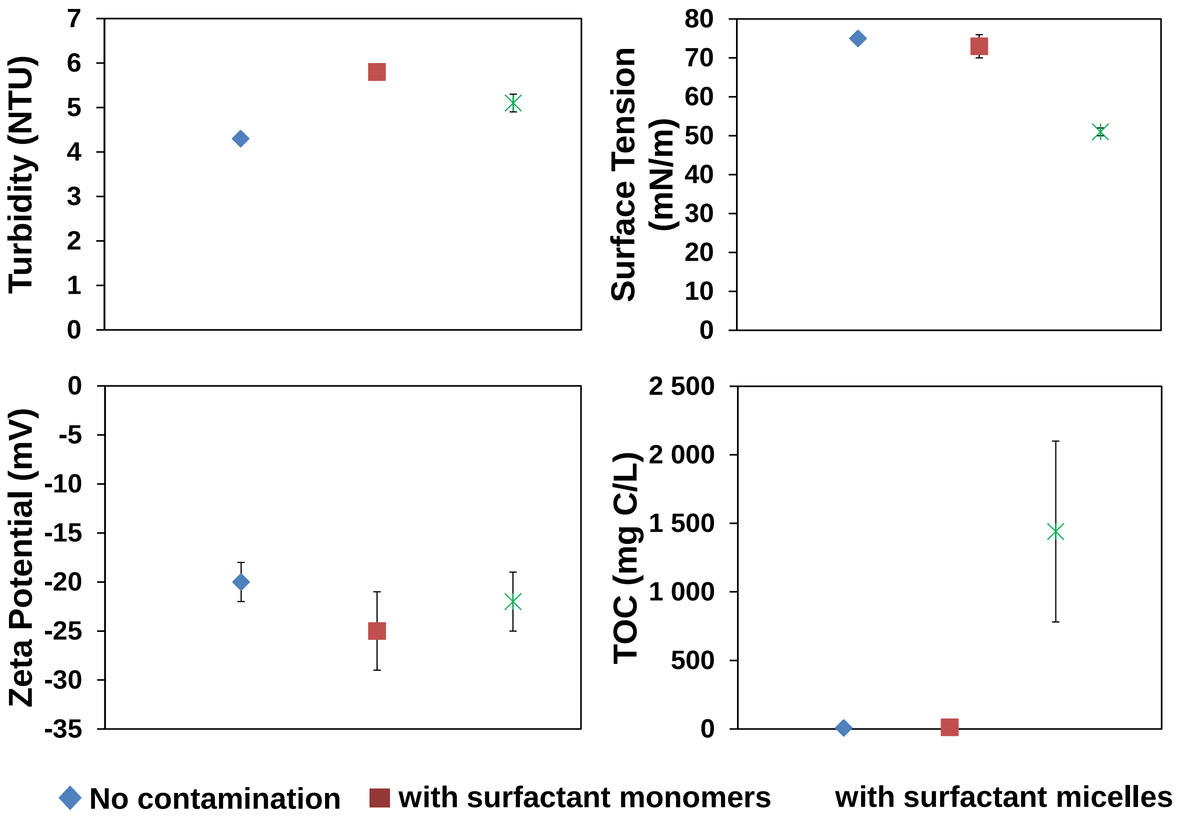


Figure C3: Water quality parameters for raw water (no contamination), raw water contaminated with crude oil and surfactant monomers (with surfactant monomers), and raw water contaminated with crude oil and surfactant micelles (with surfactant micelles). The formulated dispersant, Tween 80:SDS (20:80), was applied at a low concentration (5.2 mg/L) to generate surfactant monomers and at a high concentration (10400 mg/L) to generate surfactant micelles.