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IMPACTS OF BUILDING SAMPLING PROTOCOL, SERVICE LINE CHARACTERISTICS, AND SUPPLY WATER QUALITY ON DISSOLVED AND PARTICULATE LEAD AND COPPER IN DRINKING WATER

EVELYNE DORÉ
DÉPARTEMENT DES GÉNIES CIVIL, GÉOLOGIQUE ET DES MINES
ÉCOLE POLYTECHNIQUE DE MONTRÉAL

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présentée par : DORÉ Evelyne

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

M. COMEAU Yves, Ph. D., président

Mme PRÉVOST Michèle, Ph. D., membre et directrice de recherche

M. TOBIASON John E., Ph. D., membre

M. LYTLE Darren A., Ph. D., membre

DEDICATION

To my mom and dad, who taught us that there are no limits to what we can achieve

My friends, love is better than anger. Hope is better than fear. Optimism is better than despair.
So let us be loving, hopeful and optimistic. And we'll change the world.
- Jack Layton

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RÉSUMÉ

Lorsque l'eau traitée circule dans un réseau de distribution, sa qualité peut se dégrader lorsqu'elle entre en contact avec des éléments de plomberie pouvant contenir du plomb, tels que des entrées de service en plomb ou encore du laiton ou des soudures au plomb. À la suite des scandales de Flint (Michigan, États-Unis) et de Washington, D.C., (États-Unis), la présence de plomb dans l'eau potable a capté l'attention du public ainsi que des chercheurs. Les inquiétudes associées à la présence de plomb dans l'eau potable sont dues au fait que ce contaminant est classé comme cancérigène et qu'il est une neurotoxine. Par ailleurs, les sources de cuivre dans les réseaux de distribution sont nombreuses. Les craintes associées à la présence de cuivre dans l'eau potable sont tout d'abord d'ordre esthétique puisqu'il tache la plomberie et les vêtements à des concentrations plus basses que celles auxquelles des effets sur la santé sont recensés.

L'objectif principal de ce projet était de déterminer la présence de plomb et de cuivre, causée par la corrosion galvanique dans les réseaux de distribution d'eau potable. Ce projet de recherche se concentre sur la présence de plomb et de cuivre dans les réseaux de distribution des écoles et des grands bâtiments ainsi que dans les entrées de service en plomb à l'échelle pilote. De manière plus détaillée, ce projet visait à : (1) quantifier l'exposition au plomb et au cuivre, par la consommation d'eau potable dans les grands bâtiments et les écoles; (2) quantifier l'efficacité de mesures de mitigations telles que l'ajout d'inhibiteur de corrosion et le rinçage avant la consommation d'eau; (3) déterminer l'impact que le type de robinet a sur les concentrations de plomb et de cuivre mesurées dans les écoles et les grands bâtiments; (4) évaluer les effets à long terme des remplacements partiels d'entrée de service en plomb sous différentes qualités d'eau, ainsi que de quantifier l'importance de la corrosion galvanique; (5) mesurer l'effet de l'ajout de chlore ainsi que du changement de dose d'orthophosphates sur les concentrations de plomb dans les entrées de service en plomb avec et sans remplacement partiel; (6) déterminer l'impact des temps de stagnation avec l'échantillonnage ainsi que les impacts de l'augmentation des vitesses d'écoulement sur les concentrations de plomb et de cuivre; (7) déterminer les conditions pour lesquelles un remplacement partiel d'entrée de service en plomb permet de diminuer les concentrations mesurées au robinet et (8) d'étudier les dépôts de corrosion présents à l'intérieur des entrées de service en plomb avec et sans remplacement partiel.

L’eau potable d’écoles et de grands bâtiments, recevant différentes qualités d'eau, avec et sans l’ajout d’inhibiteur de corrosion, a été échantillonnée. L’eau plus agressive a engendré les concentrations de plomb les plus élevées au robinet. L’ajout d’un inhibiteur de corrosion a permis de diminuer les concentrations élevées de plomb. Les résultats démontrent l’importante variation dans les concentrations de plomb et de cuivre entre les divers points d’échantillonnage à l’intérieur d’un même bâtiment. De plus, les concentrations de plomb et de cuivre mesurées variaient en fonction du temps de stagnation préalable à la prise de l’échantillon. Les concentrations de plomb et de cuivre les plus élevées ont été mesurées après une stagnation d’une nuit et les valeurs ont diminué après avoir laissé l’eau couler le point de consommation d’eau. Par contre, les résultats obtenus démontrent que les concentrations de plomb et de cuivre augmentent suite à une courte stagnation et peuvent atteindre des valeurs représentant la moitié de celles mesurées après une stagnation d’une nuit. De plus, nos résultats montrent l’importance de laisser couler l’eau, minimalement les premiers 250 mL, avant de la consommer.

Les travaux ont été réalisés à l’échelle pilote en utilisant des conduites de plomb excavées du réseau de distribution de la Ville de Montréal. L'étude pilote des concentrations de plomb et de cuivre provenant d’entrées de service en plomb avec et sans remplacement partiel a démontré que des concentrations de plomb élevées sont toujours mesurées 155 semaines après la simulation du remplacement partiel. Par ailleurs, nous avons observé que les conduites de cuivre se sont passivées suite à la simulation des remplacements partiels. Ainsi, à long terme, les concentrations de cuivre ont diminué lors des échantillonnages de suivis, prélevés après stagnation de 16 heures. Nous avons aussi démontré que le rinçage à haut débit permet de diminuer les concentrations de plomb total et particulaire provenant des conduites avec et sans remplacement partiel. Ceci implique que la présence de plomb particulaire peut être diminuée par des rinçages à haut débit.

Suite à l’ajout de l’effet de la corrosion galvanique par la simulation des remplacements partiels, différents inhibiteurs de corrosion ont permis de diminuer les concentrations de plomb, en fonction de la configuration de l’entrée de service. L’ajout d’orthophosphates est le traitement qui diminue le plus les concentrations de plomb provenant des entrées de service sans remplacement partiel. L’ajustement du ratio massique chlorures/sulfates est quant à lui le traitement qui permet de mieux contrôler les concentrations de plomb en provenance des entrées de service avec remplacement partiel. L’étude des dépôts de corrosion présents à l’intérieur des conduites a permis de confirmer la présence de corrosion galvanique dans les entrées de service en plomb avec remplacement partiel, sauf pour les conduites traitées par un ajout de sulfates. L'occurrence de la corrosion galvanique a été confirmée par un changement des formes de plomb dominantes. Ainsi lorsque les dépôts étaient formés de composés de plomb présents préférentiellement à faible pH, l'occurrence de corrosion galvanique a été confirmée. De plus, il a été confirmé que la conduite de plomb joue le rôle de l'anode dans le couple galvanique, en raison de la baisse de pH observée à sa surface. Il a aussi été déterminé quelle longueur d'entrée de service en plomb doit être enlevée afin de contrebalancer l'effet de l'ajout de la corrosion galvanique suite au remplacement partiel de l'entrée de service en plomb.

En somme, ce projet de recherche a permis de mettre en évidence les facteurs qui augmentent les concentrations de plomb et de cuivre mesurées au robinet et l'occurrence de la corrosion galvanique dans les écoles et les grands bâtiments, ainsi que dans les entrées de service en plomb. Les caractéristiques de l'eau potable sont des paramètres clé dans le contrôle de la corrosion du plomb et du cuivre. Aussi, nous avons identifié l'importance du protocole d'échantillonnage ainsi que la durée de la stagnation avant la collecte d'un prélèvement. De plus, nous avons démontré l'importance d'avoir des échantillonnages spécifiques pour le plomb et le cuivre en raison des différents mécanismes de dissolution. Finalement, comme mesure de mitigation, nous avons évalué l'efficacité de laisser couler l'eau avant de la consommer dans les écoles et les grands bâtiments, mais aussi dans les entrées de service en plomb.

ABSTRACT

When water enters the drinking water distribution system, its quality can be degraded as it comes into contact with lead bearing plumbing elements such as lead service lines (LSL) or brass and leaded-solder in large buildings. Following the events of Flint (Michigan, United States) and of Washington, D.C. (United States), lead in drinking water gained attention from the public, but also from researchers. Concerns associated with lead in drinking water are due to the facts that this contaminant is a neurotoxin and it has been classified as being carcinogenic. There are also widespread sources of copper in drinking water distribution system. Concerns associated with copper are first aesthetic as it can stain the laundry and plumbing fixture at lower concentrations than it can cause health effects such as nausea, vomiting and diarrhea.

The main objective of this project was to determine the presence of lead and copper in drinking water, caused by galvanic corrosion. Focus was on schools and large buildings as well as on the study of full and partial LSL at pilot scale. On a more detailed level, this project sought to: (1) quantify the exposure to lead and copper in schools and large buildings; (2) assess the effectiveness of mitigation strategies such as the addition of corrosion control and flushing prior to consumption; (3) determine the impact of the type of tap on lead and copper release in schools and large buildings; (4) evaluate the long-term effects of partial LSL replacements under different water qualities on lead and copper concentrations and the importance of galvanic corrosion; (5) measure the effect of the onset of chlorination and change in orthophosphate dosage in full and partial LSL; (6) assess the impact of stagnation time prior to sampling and the increase in flow velocity on lead and copper; (7) determine the conditions under which partial LSL replacements would result in a reduction in Pb at the tap; (8) investigate the scales formed in full and partial LSL.

Schools and large buildings were sampled in different water qualities, with and without the presence of corrosion control. The most aggressive water, characterized using an aggressivity index, resulted in the highest lead concentrations at the tap, which were decreased for similar water qualities with the addition of a corrosion control treatment (pH increase). Results highlighted the wide variation in lead and copper concentrations between taps within the same building, but also when sampling after different stagnation time or flushing duration. Highest concentrations of lead and copper were measured following overnight stagnation and decreased as water was flushed. However, we demonstrated that concentrations increase after only 30 minutes of stagnation and

can reach values representing half of the concentrations measured after overnight stagnation. Our results highlighted the importance of flushing the taps prior to consumption as well as to sample every tap used for drinking water.

The long-term study (155 weeks) of Pb and Cu concentrations following partial LSL replacement simulations in a pilot setup made of harvested LSL from the City of Montreal showed sustained elevated lead release from partial LSL. No decrease in Pb concentrations were observed after partial LSL replacement simulations in the long-term. However, passivation of the newly added copper pipe occurred, and concentrations measured after 16 hours of stagnation decreased during the study. It was also demonstrated that high velocity flushing of full and partial LSL results in a decrease in total and particulate Pb concentrations in subsequent sampling after 16 hours of stagnation. This implies that particulate Pb can be mobilized and removed from the LSL using appropriate flushing.

Due to the addition of galvanic corrosion in partial LSL, different corrosion control treatments resulted in the decrease of lead concentrations, depending on the configuration of the LSL. The addition of orthoP decreased the most concentrations from full LSL, whereas the decrease in chloride to sulfate mass ratio (addition of sulfate) resulted in the best control of the Pb concentrations from partial LSL. The investigation of scale corrosion products in the full and partial LSL confirmed the presence of galvanic corrosion in the partial LSL, except for the pipes tested with the addition of sulfate. The presence of galvanic corrosion was confirmed by the switch from corrosion solids preferentially formed at low pH value on the lead pipe, confirming it acts as the anode in the galvanic couple. The length of Pb pipe which should be removed, to offset the additional release of Pb from galvanic corrosion, was also calculated for different water qualities, based on the results obtained from the pilot study.

Overall, this research project evidenced factors exacerbating the occurrence of galvanic corrosion in schools and large buildings as well as in partial LSLs. Water quality was presented as one of the key controls for lead and copper concentrations, with more corrosive water releasing higher concentrations of Pb and Cu. Also, the importance of the sampling protocol and the duration of stagnation prior to sampling was demonstrated, as well as the importance to target sampling for lead and for copper. Finally, the effectiveness of flushing the water prior to consumption was presented in schools as well as in full and partial LSL, as a temporary effective mitigation strategy to decrease exposure to lead.

TABLE OF CONTENTS

DEDICATION III

ACKNOWLEDGEMENTS IV

RÉSUMÉ VII

ABSTRACT X

TABLE OF CONTENTS XIII

LIST OF TABLES XX

LIST OF FIGURES XXIII

LIST OF SYMBOLS AND ABBREVIATIONS XXXI

LIST OF APPENDICES XXXV

CHAPTER 1 INTRODUCTION – LEAD AND COPPER CORROSION IN DRINKING WATER……… 1

1.1 Background 1

1.2 Structure of the dissertation 3

CHAPTER 2 LITERATURE REVIEW 5

2.1 Health impacts of lead and copper 5

2.1.1 Lead 5

2.1.2 Copper 5

2.2 Recommendations/Regulations on lead and copper in drinking water 6

2.2.1 Canada 6

2.2.2 United States 7

2.2.3 European Union 7

2.3 Sources of lead and copper in large buildings 7

2.4 Full and partial lead service lines 9

2.5 Galvanic corrosion 10

2.5.1 Galvanic corrosion in leaded brass 12

2.5.2 Galvanic corrosion in leaded solders 12

2.6 Factors affecting lead and copper concentrations in drinking water 13

2.6.1 Temperature 13

2.6.2 pH and alkalinity 13

2.6.3 Chlorine residual 14

2.6.4 Chloride to sulfate mass ratio (CSMR) 15

2.6.5 Phosphate addition 16

2.7 Scales formed in full and partial lead service lines 18

2.7.1 Lead scales 19

CHAPTER 3 RESEARCH OBJECTIVES, HYPOTHESIS AND METHODOLOGY 21

3.1 Critical review of previous research findings 21

3.2 Objectives 22

3.3 Methodology 30

3.3.1 Sampling sites 30

3.3.2 Pb and Cu measurements in water 36

3.3.3 Surface area normalized mass release (SANMR) determination in full and partial lead service lines 37

3.3.4 Scale analysis in full and partially replaced lead service lines 37

CHAPTER 4 ARTICLE 1 – SAMPLING IN SCHOOLS AND LARGE INSTITUTIONAL BUILDINGS: IMPLICATIONS FOR REGULATIONS, EXPOSURE AND MANAGEMENT OF LEAD AND COPPER 42

4.1 Introduction 43

4.2 Materials and methods 46

4.2.1 Building selection and sampling campaign....46

4.2.2 Sampling protocol....48

4.2.3 Analytical methods....48

4.2.4 Statistical analysis and IEUBK modeling....49

4.3 Results and discussion....49

4.3.1 Lead and copper concentrations per type of sampling protocol....49

4.3.2 Water quality and type of faucet....53

4.3.3 Impact of flushing....55

4.3.4 Particulate lead and copper....60

4.3.5 Particulate simulation sampling....62

4.3.6 Contributors to lead and copper concentrations....63

4.3.7 Blood lead levels modelling and copper intake....64

4.3.8 Possible remedial actions....66

4.3.9 Selecting a sampling protocol....68

4.4 Conclusions....70

CHAPTER 5 ARTICLE 2 – STUDY OF THE LONG-TERM IMPACTS OF TREATMENTS ON LEAD RELEASE FROM FULL AND PARTIALLY REPLACED HARVESTED LEAD SERVICE LINES....72

5.1 Introduction....73

5.2 Materials and methods....76

5.2.1 Pilot setup and operation....76

5.2.2 Sampling....78

5.2.3 Water quality monitoring....78

5.2.4 Statistical analysis....79

5.2.5 Surface area-normalized mass release (SANMR) calculations....79

5.2.6 Field monitoring of LSL households 81

5.3 Results and discussion..81

5.3.1 Changes in total Pb concentrations over time 81

5.3.2 Impact of treatments on Pb concentrations after stagnation and under flow conditions 83

5.3.3 Impact of pipe configuration..87

5.3.4 Surface area-normalized mass release (SANMR)..87

5.3.5 Comparison of Pb release between pilot and field investigations.............................90

5.3.6 Managerial implication of partial LSL replacement 94

5.3.7 Options for utilities to decrease Pb concentrations 97

5.4 Conclusion...99

CHAPTER 6 ARTICLE 3 – LEAD AND COPPER RELEASE FROM FULL AND PARTIALLY REPLACED HARVESTED LEAD SERVICE LINES: IMPACT OF STAGNATION TIME PRIOR TO SAMPLING AND WATER QUALITY 101

6.1 Introduction 102

6.2 Materials and methods 105

6.2.1 Pilot setup...105

6.2.2 Sampling for lead and copper...105

6.2.3 Determination of lead and copper release rates 106

6.2.4 Scale analysis 107

6.2.5 Statistical analysis 107

6.3 Results and discussion...107

6.3.1 Copper concentrations after PLSLR simulation...107

6.3.2 Effect of stagnation time on copper concentrations 110

6.3.3 Effect of stagnation time on lead concentrations 116

6.3.4 Impact of high velocity flushing 127

6.3.5 Implications for exposure to lead and copper 129

6.3.6 Implications for lead and copper sampling 129

6.3.7 Conclusion 133

CHAPTER 7 ONSET OF CHLORINATION, CHANGES IN ORTHOP DOSAGE IN FULL AND PARTIAL LEAD SERVICE LINES 134

7.1 Addition of chlorination 134

7.1.1 Lower CSMR and addition of chlorine 135

7.1.2 Increased pH and addition of chlorine 136

7.2 Changes in orthoP dosage 138

CHAPTER 8 CHANGES IN CORROSION SCALES IN FULL AND PARTIALLY REPLACED LEAD SERVICE LINES: IMPACT OF WATER QUALITY 141

8.1 General observations on scale formation 141

8.2 Do scales in 100%Pb pipes change with water quality? 143

8.2.1 Control condition and smaller diameter pipes 143

8.2.2 Sulfate addition with and without chlorine residual 145

8.2.3 Increase to pH 8.3 147

8.2.4 orthoP 149

8.3 Are the scales present in the non-galvanic section of the Pb pipe affected by the presence of a downflow galvanic connection? 152

8.3.1 Control condition and smaller diameter pipes 152

8.3.2 Sulfate addition 155

8.3.3 Increase in pH 155

8.3.4 orthoP 155

8.4 Which minerals are present in the galvanic zone of the partial LSL? How do copper minerals differ between the galvanic and non-galvanic zones? 159

8.4.1 Control condition and smaller diameter pipes 159

8.4.2 Sulfate addition 161

8.4.3 Increase to pH 8.3 162

8.4.4 orthoP 163

8.5 Can minerals confirm the presence of galvanic corrosion and indicate anodic/cathodic sites? 164

8.6 Concluding remarks 165

CHAPTER 9 GENERAL DISCUSSION 166

9.1 What are Pb and Cu sources in distribution systems? 169

9.1.1 Schools and large buildings 169

9.1.2 Lead service lines 171

9.2 What are the impacts of pH, chloride to sulfate mass ratio and orthophosphate on Pb and Cu? 174

9.2.1 pH 174

9.2.2 Decrease of the CSMR 175

9.2.3 Addition of orthoP 175

9.3 Presence of particulate Pb 176

9.4 Is flushing an effective mitigation strategy to decrease Pb and Cu? 178

9.4.1 Schools and large buildings 178

9.4.2 Full and partial LSLs 179

9.5 What are the regulatory implications of the findings and how to sample for Pb and Cu? 179

9.5.1 Schools and large buildings 179

  9.5.2 Lead service line 180

CHAPTER 10 CONCLUSION AND RECOMMENDATIONS 181

BIBLIOGRAPHY 185

APPENDICES 199

LIST OF TABLES

Table 3.1 Experimental approach to validate (or invalidate) the research hypothesis and corresponding chapters of the thesis. 27

Table 3.2 General water quality of the water entering the pilot setup, prior to addition of treatments... 32

Table 3.3 Timeline the changes applied to the water quality and operation of the pilot setup. 35

Table 3.4 Description of pipes available for scale analysis. 38

Table 4.1 Information regarding buildings sampled, water quality and number of samples collected per building. 47

Table 4.2 Percentage of samples with total Pb concentrations greater than 10 µg Pb/L and greater than 5 µg Pb/L (in brackets), all types of samples considered at each type of tap and building…..56

Table 4.3 Median, 90th percentile and maximum total Pb and Cu concentrations for a given type of tap and group of building for all the samples, in µg/L. 59

Table 5.1 Corrosion control treatment, pipe configuration, and internal diameters tested in the pilot setup as well as median and 90th percentile total Pb concentrations after 16HS and flowing condition. 77

Table 5.2 Apparent SANMR (total, dissolved and particulate Pb), expressed in µg/m^2 under the control condition for various experimental conditions tested compared to 6HS samples from the distribution system of the City of Montreal (Deshommes et al. 2016, 2017). 92

Table 5.3 Length of LSL (in m) at which total Pb mass from non-galvanic corrosion equals Pb mass from galvanic corrosion. 97

Table 6.1 Total, dissolved, and particulate copper release rate (µg Cu/h) for the partial LSLs with the Cu pipe upstream (Cu-Pb) and downstream (Pb-Cu) for the different treatments tested on the pilot setup. The release rate is presented for the first 16 hours of stagnation and from 24 to 336 hours (2 weeks) of stagnation. 115

Table 6.2 Total, dissolved, and particulate lead release rate (µg/h) for the full LSL (100%Pb) and partial LSLs (Cu-Pb and Pb-Cu) for the different treatment tested on the pilot setup. The release rate is presented for the first 16 hours of stagnation, and from 24 to 336 hours (2 weeks) of stagnation. 122

Table 6.3 Median total Cu concentrations represented as X fold of the median concentration after 30 minute stagnation (30MS) and after 6 hour stagnation (6HS). 131

Table 6.4 Median total Pb concentrations represented as X fold of the median concentration after 30 minute stagnation (30MS) and after 6 hour stagnation (6HS). 132

Table 8.1 Lead corrosion solids identified in 100%Pb pipe for the control and smaller diameter conditions, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected. 144

Table 8.2 Lead corrosion solids identified in 100%Pb pipe for the sulfate addition and the increase in pH conditions, with and without chlorination, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected...146

Table 8.3 Lead corrosion solids identified in 100%Pb pipe for addition o orthoP, before and after the increase in dosage to 1.5 mg P/L, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected. 150

Table 8.4 Lead corrosion solids identified in Cu-Pb pipes for the control condition, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected. 153

Table 8.5 Lead corrosion solids identified in Cu-Pb pipes for the smaller diameter pipes, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected. 154

Table 8.6 Lead corrosion solids identified in Cu-Pb pipes treated with sulfate addition, before and after chlorination, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected. 156

Table 8.7 Lead corrosion solids identified in Cu-Pb pipes treated with an increase in pH to 8.3, before and after addition of chlorination ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected.

0-S indicates the pipe disconnected 30 weeks after PLSLR (short-term) and 0-L the pipe disconnected after 156 weeks, both treated with pH 8.3. 157

Table 8.8 Lead corrosion solids identified in Cu-Pb pipes treated with orthoP, before and after increase in dosage, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected. 1-S indicates the pipe disconnected 30 weeks after PLSLR (short-term) and 1-L the pipe disconnected after 156 weeks, both treated with 1 mg P/L. 158

Table 8.9 Evidence of galvanic corrosion of the Pb pipe...164

Table A.1 Overview of Canadian, American and European guidance and regulations on sampling lead and copper in schools are large buildings..200

Table A.2 Overview of studies on lead and copper in drinking water in large buildings, schools and daycares...204

Table A.3 Percentage of the samples with a total Pb concentration greater than 1 µg Pb/L, all types of samples considered at each types of tap and buildings. 214

Table A.4 Multivariate Adaptative Regression (MARSpline) results presenting significant variables for total lead and copper concentrations. 215

Table A.5 Number of samples required to estimate the true geometric mean total Pb concentrations for each school sampled. 217

LIST OF FIGURES

Figure 2.1 Schematic representation of reactions occurring in a galvanic couple comprised of lead and copper, adapted from Triantafyllidou and Edwards (2010). 11

Figure 3.1 Photograph of the pilot setup. 31

Figure 3.2 Schematic of the pilot setup installed in the CREDEAU Laboratory at Polytechnique Montréal. 33

Figure 3.3 An example of a lead service line connected to a copper pipe using (A) a red brass compression fitting and (B) a soldered fitting. 34

Figure 3.4 Example of a full LSL being prepared for scale analysis. 38

Figure 3.5 Cross-sectional representation of the different layers which can be present in the pipes. 39

Figure 3.6 Schematic representation of the corrosion zones present in a partial lead service line in the presence of galvanic corrosion. 39

Figure 3.7 Samples mounted on a zero-background plate for XRD analysis: A) Sample placed in the well of the plate, B) Sample mounted using amyl acetate. 40

Figure 4.1 Total, particulate and dissolved lead (A) and copper (C) concentrations (in black, light grey and darker grey), and fraction of particulate Pb (B) and Cu (D), for 1st draw samples collected following overnight stagnation (1S>8h, 250 mL) and 2nd draw (2S>8h, 250 mL), 30 seconds (30sF, 250 mL) and 5 minutes (5minF, 250 mL) of flushing and 30 minutes of stagnation (30minS, 250 mL) (n=130).Whiskers represent min-max values, boxes 10th-90th percentiles, and the square represents median concentrations. 50

Figure 4.2 Total Pb and Cu concentrations (µg/L) for all taps sampled in schools without corrosion control, low alkalinity (A for Pb and B for Cu), with corrosion control (C for Pb and D for Cu) and large buildings (E for Pb and F for Cu). Whiskers represent the min-max values and the line the median concentrations for the 5 samples collected at each tap, after stagnation (1S>8h, 2S>8h, 30minS) and flushing (30sF, 5minF). Vertical dotted lines separate the buildings sampled (B1 to B11)...52

Figure 4.3 Total, particulate and dissolved lead and copper (in black, light grey and dark grey) for (A, B) fountains (n=385), (C, D) kitchen (n=140) and (E, F) bathroom (n=125) taps as a function of specific groups of buildings (all samples combined). 54

Figure 4.4 Particulate lead and copper concentration (A, C) and fraction (B, D) presented as cumulative frequency for each type of building sampled. For A and C, the dark square represents the median, boxes represent the 10-90th percentiles, and whiskers the non-outlier range (n=130). 61

Figure 4.5 Mean total and particulate lead concentrations (in dark and light grey) for kitchen taps sampled in elementary schools receiving low pH and low alkalinity water (N=7 taps in 5 schools). Black dots represent the mean Pb particulate fraction as a percentage. 63

Figure 4.6 Geometric mean BLL (grey boxes) for children of age 5-7 years for each group of buildings, modeled using 90th percentiles total Pb concentrations observed in school tap water (black dots). 65

Figure 5.1 The apparent surface area-normalized mass release (SANMR), galvanic and non-galvanic zones present in lead (Pb) pipes connected to copper (Cu) pipes using a compression fitting (A). A partial lead service line (PLSL) from the pilot setup with a gap between the Cu and Pb pipe junction (B) and a PLSL where the Pb pipe is in direct contact with the Cu pipe (C)..80

Figure 5.2 Total lead (Pb) concentration after 16 hours of stagnation presented as a function of time (in weeks) following partial lead service line replacement (PLSLR) simulation. Smaller diam.: smaller diameter pipe; orthoP: orthophosphate treatment. N=46 for Cu-Pb and Pb-Cu pipe configurations, N=60 for 100% Pb pipe configuration. 82

Figure 5.3 Total (A-B), dissolved (C-D) and particulate (E-F) lead (Pb) concentrations measured after a 16 hour stagnation period (left) or under flowing conditions (right) under different corrosion control treatments. The 100% Pb pipe configuration is represented in grey, the Cu-Pb configuration in white and the Pb-Cu configuration with black dots. The line within each box represents the median concentration. The bottom and top of each box represents the 10th-90th percentiles, respectively. The whiskers represent the minimum and maximum values. 84

Figure 5.4 Example of a Pb-Cu pipe under the control condition showing external corrosion of the Pb and Cu pipes. 88

Figure 5.5 Apparent surface area-normalized masse release (SANMR) of total Pb for (A) 100% Pb pipes, (B) Cu-Pb pipes and (C) Pb-Cu pipes is presented in dark grey. For PLSL (B and C), non-galvanic SANMR is presented in white and galvanic SANMR in light grey. The latter is calculated considering a 2 cm galvanic zone on the Pb and Cu pipes flanking the fitting, as well as the interior surface of the brass fitting. The galvanic SANMR was computed using median non-galvanic SANMR. 89

Figure 5.6 Mass of Pb released due to non-galvanic corrosion (grey), galvanic corrosion based on median non-galvanic SANMR (orange and dotted) and the sum of both (black) in the Cu-Pb pipe configuration under the (A) control, (B) smaller diameter, (C) sulfate treatment, (D) orthoP treatment and (E) pH 8.3 conditions. 96

Figure 5.7 Framework for the management of full lead service Lines (FLSLs) and partial lead service lines (PLSLs) in a distribution system. POU: point-of-use, SANMR: surface area-normalized mass release, PLSLRs: partial lead service line replacements, CCT: corrosion control treatment. 98

Figure 6.1 Total copper concentrations (µg Cu/L) after 16 hour stagnation inside the Cu pipe section for partial LSLs with the Cu pipe: (A) upstream (Cu-Pb) and (B) downstream (Pb-Cu) of an aged Pb pipe as a function of the number of weeks after the simulation of a PLSLR. Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent the 10th and 90th percentile concentrations. 108

Figure 6.2 Copper concentrations (µg Cu/L) in the copper pipe section as a function of stagnation time for partial LSLs in which the copper pipes are upstream of the Pb pipes (Cu-Pb). Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent 10th-90th percentile concentrations...112

Figure 6.3 Copper concentrations (µg Cu/L) in the copper pipe as a function of stagnation time for partial LSLs in which the copper pipes are downstream of the Pb pipes (Pb-Cu). Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent 10th-90th percentile concentrations. 113

Figure 6.4 Lead concentrations (µg Pb/L) in the lead pipe section as a function of stagnation time for full LSL (100%Pb). Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent 10th-90th percentile concentrations. 118

Figure 6.5 Particulate Pb fraction after different stagnation times for (A) 100%Pb, (B) Cu-Pb, and (C) Pb-Cu. Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent 10th-90th percentile concentrations. 120

Figure 6.6 Lead concentrations (µg Pb/L) in the lead pipe section as a function of stagnation time for partial LSLs in which the copper pipes are upstream of the Pb pipes (Cu-Pb). Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent 10th-90th percentile concentrations. 124

Figure 6.7 Lead concentrations (µg Pb/L) in the lead pipe section as a function of stagnation time for partial LSLs in which the copper pipes are downstream of the Pb pipes (Pb-Cu). Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent 10th-90th percentile concentrations. 125

Figure 6.8 Total (grey) and particulate Pb (white) concentrations (µg Pb/L) for the smaller diameter pipes sampled at (A) 5 LPM and (B) 15 LPM as well as concentrations after 16 hour of stagnation, (C) before increasing the flow rate, and (D) after increasing the flow rate (Q). Square: median concentrations, box: 10-90th percentiles, whiskers: min-maximum concentrations..128

Figure 7.1 Total Pb concentrations as a function of the number of weeks following the simulation of partial LSL replacements for the pipes treated with the addition of sulfate, before and after the onset of chlorination. Squares (Cu-Pb), triangle (100%Pb) and circles (Pb-Cu) represent median concentrations and whiskers represent minimum-maximum values. Pb pipes of full LSLs are 5 times longer than partial LSLs (3 and 0.6 m). N=46 and 11 for PLSL, N=60 and 22 for FLSL, before and after chlorination. 135

Figure 7.2 Dissolved Pb concentrations as a function of the number of weeks following the simulation of partial LSL replacements for the pipes treated with the addition of sulfate, before and after the onset of chlorination. Squares (Cu-Pb), triangle (100%Pb) and circles (Pb-Cu) represent median concentrations and whiskers represent minimum-maximum values. Pb pipes of full LSLs are 5 times longer than partial LSLs (3 and 0.6 m). N=46 and 11 for PLSL, N=60 and 22 for FLSL, before and after chlorination. 136

Figure 7.3 Total Pb concentrations as a function of the number of weeks following the simulation of partial LSL replacements for the pipes treated with the increase in pH to 8.3, before and after the onset of chlorination. Squares (Cu-Pb), triangle (100%Pb) and circles (Pb-Cu) represent median concentrations and whiskers represent minimum-maximum values. Pb pipes of full LSLs are 5 times longer than partial LSLs (3 and 0.6 m). N=46 and 11 for PLSL, N=60 and 22 for FLSL, before and after chlorination. 137

Figure 7.4 Dissolved Pb concentrations as a function of the number of weeks following the simulation of partial LSL replacements for the pipes treated with the increase in pH to 8.3, before and after the onset of chlorination. Squares (Cu-Pb), triangle (100%Pb) and circles (Pb-Cu) represent median concentrations and whiskers represent minimum-maximum values. Pb pipes of full LSLs are 5 times longer than partial LSLs (3 and 0.6 m). N=46 and 11 for PLSL, N=60 and 22 for FLSL, before and after chlorination. 138

Figure 7.5 Total Pb concentrations as a function of the number of weeks following the simulation of partial LSL replacements for the pipes treated with 1 mg P/L with pH adjustment, without pH adjustment and with an increase in orthoP dosage to 1.5 mg P/L. Squares (Cu-Pb), triangle

(100%Pb) and circles (Pb-Cu) represent median concentrations and whiskers represent minimum-maximum values. Pb pipes of full LSLs are 5 times longer than partial LSLs (3 and 0.6 m). N=46, 7 and 4 for PLSL, N=60, 12 and 8 for FLSL, before changes in treatment, after decrease in pH and after increase in orthoP. 139

Figure 7.6 Dissolved Pb concentrations as a function of the number of weeks following the simulation of partial LSL replacements for the pipes treated with 1 mg P/L with pH adjustment, without pH adjustment and with an increase in orthoP dosage to 1.5 mg P/L. Squares (Cu-Pb), triangle (100%Pb) and circles (Pb-Cu) represent median concentrations and whiskers represent minimum-maximum values. Pb pipes of full LSLs are 5 times longer than partial LSLs (3 and 0.6 m). N=46, 7 and 4 for PLSL, N=60, 12 and 8 for FLSL, before changes in treatment, after decrease in pH and after increase in orthoP..140

Figure 8.1 Example of surface layers with islands of red deposits (pipe treated with orthoP)....142

Figure 8.2 Photographs of the interior of a 100%Pb pipe from the control condition.................143

Figure 8.3 Interior deposits of a smaller diameter pipe..143

Figure 8.4 Total, dissolved and particulate Pb concentrations after 16 hour stagnation in FLSL for both pipes of the control condition. Line: mean concentration, boxes: mean ± SE, whiskers: minimum-maximum concentrations. N=31. 145

Figure 8.5 Full LSL treated with the addition of sulfate (A) and the combination of sulfate and chlorine (B). 147

Figure 8.6 Full LSLs treated with an increase in pH (A and B) and an increase in pH combined with chlorine (C and D). Picture on the right were taken with a stereomicroscope to enhance the details of the scale. 148

Figure 8.7 Total, dissolved and particulate Pb concentrations after 16 hour stagnation in FLSL for both pipes of the increased pH condition with and without 1 mg Cl_2/L. Line: mean concentration, boxes: mean ± SE, whiskers: minimum-maximum concentrations. 149

Figure 8.8 Full LSL fed with water dosed at 1 mg P/L (A and B) and 1.5 mg P/L (C and D). Pictures on the right were taken using a stereomicroscope..151

Figure 8.9 Total, dissolved and particulate Pb concentrations after 16 hour stagnation in FLSL for pipes with the addition of orthoP before and after changes in dosage (1 vs 1.5 mg P/L). Line: mean concentration, boxes: mean ± SE, whiskers: minimum-maximum concentrations....151

Figure 8.10 Partial LSL of the control condition (A) without visual changes in scale composition at the galvanic zone and (B) with visual changes and for two duplicate pipes of the smaller diameter (C and D)..160

Figure 8.11 Interior of partial LSL treated with sulfate (A) and the combination of sulfate and chlorine (B). 161

Figure 8.12 Partial LSL treated with an increased pH to 8.3 (A) and the combination of increased pH and chlorine (B)..162

Figure 8.13 Interior of an orthoP treated partial LSL (A) shortly after PLSLR simulation, (B) before changes in water quality and (C) after an increased in orthoP (1 vs 1.5 mg P/L)...............163

Figure 9.1 Summary of the research conducted..166

Figure 9.2 Factors influencing Pb release in a lead service line. 168

Figure A.1 Total lead concentration per type of tap and building sampled. Schools without corrosion control and with low alkalinity (A n=5, B n=20, C n=12), Schools with corrosion control and with low alkalinity (A n=3, B n=19, C n=7), Large buildings (A n=17, B n=38, C n=9). Whiskers represent minimum and maximum values, boxes the 10th and 90th percentile, white squares the median concentration...212

Figure A.2 Total copper concentration per type of and building. Schools without corrosion control and with low alkalinity (A n=5, B n=20, C n=12), Schools with corrosion control and with low alkalinity (A n=3, B n=19, C n=7), Large buildings (A n=17, B n=38, C n=9). Whiskers represent minimum and maximum values, boxes the 10th and 90th percentile, white squares the median concentration. 213

Figure B.1 Schematic of the pilot setup built using aged LSLs from the distribution system of Montreal and new copper pipes connected to the Pb pipes using red brass compression fittings..219

Figure B.2 Total (A-B), dissolved (C-D) and particulate (E-F) lead (Pb) concentrations measured after a 16 hour stagnation period (left) or under flowing conditions (right) normalized for the length of the pipe for the control, smaller diameter, sulfate treatment, orthoP treatment, and pH 8.3 conditions. The 100% Pb pipe configuration is represented in grey, Cu-Pb configuration in white and Pb-Cu configuration with black dots. The line within each box represents the median concentration. The bottom and top of each box represents the 10^{th}-90^{th} percentiles, respectively. The whiskers represent the minimum and maximum values.......220

Figure C.1 Total (left) and dissolved (right) Cu concentration (µg/L) in the copper pipe depending on stagnation time for the control condition (A and B) and the orthoP condition (C and D) in Cu-Pb pipe configurations (Cu pipes upstream of Pb pipes). Each colour/type of line represents consecutive sampling events. The full line (orange) is the 1^{st} event, the long dashes (teal) the 2^{nd} event and the short dashes (purple) the 3^{rd} event. The triangles and the circles each represent one pipe. 223

Figure C.2 Total (left) and dissolved (right) Pb concentration (µg/L) in the lead pipe depending on stagnation time for the control condition (A and B) and the orthoP condition (C and D), for the full LSLs (100%Pb). The squares, triangles, and circles each represent one pipe, as well as each colour/type of line...224

Figure C.3 Total (left) and dissolved (right) Pb concentration (µg/L) in the lead pipe depending on stagnation time for the control condition (A and B) and the pipes dosed with orthoP (C and D), for the partial LSLs in which the Cu pipe is upstream of the Pb pipe (Cu-Pb). The triangles and the circles each represent one pipe, as well as each colour. 225

LIST OF SYMBOLS AND ABBREVIATIONS

100%Pb	Full lead service line
16HS	16 hour of stagnation
1S>8h	First draw sample after overnight stagnation
2S>8h	Second draw sample after overnight stagnation
30minS	30 minute stagnation
30sF	30 second flush
3Ts	Training, testing and telling
5minF	5 minute flush
6HS	6 hour of stagnation
A	Alkalinity
AAP	American Academy of Pediatrics
AI	Aggressivity index
AL	Action level
Al	Aluminium
AMSARC	Advanced Materials and Solids Analysis Research Core
ANOVA	Analysis of variance
AO	Aesthetic objective
AWWA	American Water Works Association
BLL	Blood lead level
°C	Degree Celsius
CA	California
Ca	Calcium
$CaCO_3$	Calcite
CC	Corrosion control
CCT	Corrosion control treatment
Cl_2	Chlorine
cm	Centimeter
CSMR	Chloride to sulfate mass ratio
Cu	Copper
$Cu_2Cl(OH)_2$	Clinoatacamite
$CuCO_3Cu(OH)_2$	Malachite

Cu_2O	Cuprite
CuO	Tenorite
$Cu(OH,Cl)_2\ 2H_2O$	Calumetite
$CuOH_2$	Cupric hydroxide
Cu-Pb	Partial lead service line with copper upstream of lead
$Cu_4(SO_4)(OH_6)H_2O$	Posnkjakite
CWN	Canadian Water Network
Diss.	Dissolved
DO	Dissolved oxygen
EPA	Environmental Protection Agency
EU	European Union
Fe	Iron
FLSL	Full lead service line
GM	Geometric mean
H	Hardness
HC	Health Canada
HCl	Hydrochloric acid
HNO_3	Nitric acid
ICP-MS	Inductively coupled mass spectrometry
I.D.	Internal diameter
IEUBK	Integrated Exposure uptake biokinetic
L	Liter
LCR	Lead and copper rule
LPM	Liters per minute
LSL	Lead service line
m	Meter
MAC	Maximum acceptable concentration
MARSpline	Multivariate Adaptive Regression Splines
mL	Milliliter
NA	Not available
NOM	Natural organic matter
NS	Not specified
NSERC	Natural Sciences and Engineering Research Council of Canada

OH	Ohio
OK	Oklahoma
ON	Ontario
ORP	Oxidation reduction potential
orthoP	orthophosphate
P	Phosphate
PACl	Polyaluminium chloride
Part.	Particulate
Pb	Lead
$PbCO_3$	Cerussite
$Pb_3(CO_3)_2(OH)_2$	Hydrocerussite
$Pb_{10}(CO_3)_6(OH)_6O$	Plumbonacrite
Pb-Cu	Partial lead serice line with lead upstream of copper
PbO	Litharge
PbO_2	Plattnerite
Pb_3O_4	Minium
Pb(OH)Cl	Laurionite
$Pb_3(PO_4)_2$	Tertiary lead phosphate
$Pb_5(PO_4)_3(OH)$	Hydroxypyromorphite
$Pb_5(PO_4)_3\text{-}Cl$	Chloropyromorphite
$PbSO_4$	Anglesite
$Pb_4(SO_4)(CO_3)_2(OH)_2$	Susannite / Leadhillite
PHG	Public health goal
PLSL	Partial lead service line
PLSLR	Partial lead service line replacement
PSS1	Particulate stimulation sampling, first liter
PSS2	Particulate stimulation sampling, second liter
PSS3	Particulate stimulation sampling, third liter
PVDF	Polyvinylidene Fluoride
PXRD	Powder x-ray diffraction
QC	Québec
RDT	Random daytime
SANMR	Surface area-normalized mass release

SI	Supplementary Information
Sn	Tin
SO_4	Sulfate
TOC	Total organic carbon
UK	United-Kingdom
USA	United States of America
USEPA	United States Environmental Protection Agency
USPSC	United States Consumer Product Safety Commission
WHO	World Health Organization
Zn	Zinc
µg	microgram

LIST OF APPENDICES

Appendix A Supplementary information, article 1: schools and large institutional buildings: Implications for regulation, exposure and management of lead and copper........................199

Appendix B Supplementary information, article 2: Study of the long-term impacts of treatments on lead release from full and partially replaced harvested lead service lines.....218

Appendix C Supplementary information, article 3: Lead and copper release from full and partially replaced harvested lead service lines: Impact of stagnation time prior to sampling and water quality 221

CHAPTER 1 INTRODUCTION – LEAD AND COPPER CORROSION IN DRINKING WATER

1.1 Background

The presence of lead in drinking water has received unprecedented attention from the public since the scandal of Flint (Michigan, United States) was revealed in 2015 (Hanna-Attisha et al., 2016). Aside from being a probable carcinogen to humans (Health Canada, 2017; Silbergeld et al., 2000), lead is a neurotoxin linked to intellectual deficits in children (Jusko et al., 2008; Lanphear et al., 2005) and recently to cardiovascular disease mortality (Lanphear et al., 2018; Lustberg & Silbergeld, 2002; Schober et al., 2006). As environmental sources of lead have been reduced, drinking water has become one of the primary sources of exposure (Health Canada, 2017). Concerns associated with copper in drinking water are first aesthetic due to the blue water phenomenon (Edwards et al., 2000) as it can stain laundry and plumbing fixtures at concentrations below which there are health concerns (Health Canada, 2018). Despite being an essential element for humans, copper can also cause short and long-term health effects such as nausea, vomiting and diarrhea (WHO, 2004).

As water comes in contact with leaded plumbing components such as service lines, fixtures and solders, it becomes contaminated. Until 1975, lead service lines (LSL) were commonly installed in Canada and the use of solder containing lead was stopped in 1986 (Health Canada, 2017). At the time, “lead-free” was defined as containing less than 0.2% of Pb in solders and flux and 8% in pipes and pipe fittings. Since 2015 in the United States and 2014 in most Canadian provinces, no more than 0.25% of Pb must be found across the wetted surface of pipes, pipe fittings and fixtures (Health Canada, 2017; U. S. Government, 2011). Although these new standards will limit the use of leaded materials, utilities and building owners must manage a legacy of leaded materials. Recommended and regulated sampling protocols and action levels/maximum acceptable concentrations for lead and copper in drinking water in houses and in schools vary significantly in Canada, the United States and the European Union.

Amongst the different types of corrosion possible in plumbing components, uniform and galvanic corrosion are contributors to lead concentrations in tap water. Galvanic corrosion arises when two different metals of different nobility are in contact (Oldfield, 1988). As there is a difference in potential between the two metals, a current flow is established, and each metal becomes either the anode or the cathode (Larson, 1975). The less noble metal, the anode, is oxidized and a decrease in pH can be observed compared to the conditions of the bulk water (Ma et al., 2017). The more noble metal, the cathode, becomes protected and oxidants are reduced at its surface and pH is increased (Larson, 1975; Oldfield, 1988). In presence of galvanic corrosion, the release of lead in water is increased (Dudi & Edwards, 2005; Edwards & Triantafyllidou, 2007; Schock & Lytle, 2011). Instances where the lead pipe was galvanically protected in a partial LSL have also been documented (Arnold & Edwards, 2012; DeSantis et al., 2018).

Alkalinity, pH, hardness, temperature, disinfectant residual, chloride to sulfate mass ratio (CSMR), dissolved oxygen and natural organic matter (NOM) are some of the factors affecting lead and copper solubility (Schock & Lytle, 2011). The presence of corrosion control treatments, such as orthophosphate or an increase in pH will also affect the extent of Pb and Cu leaching in water (Cardew, 2009; Cartier et al., 2013; Schock et al., 1995). Empirical galvanic series define that copper is more noble than brass and that lead is the less noble of the 3 metals (Matsukawa et al., 2010). When galvanic couples are formed between lead, brass and/or copper, lead is preferentially corroded and a drop in pH can be observed at its surface. Changes in local water quality are reflected in modifications in the scale composition (DeSantis et al., 2018).

Recent studies highlighted the impact of drinking water at schools on the blood lead levels (BLL) of children (Deshommes et al., 2016a; Sathyanarayana et al., 2006; Triantafyllidou et al., 2014). Multiple North American studies have demonstrated high and varying lead concentrations in tap water in large buildings and some also reported elevated copper levels. In a meta-analysis of Canadian schools and large buildings, Deshommes et al. (2016a) demonstrated that Pb levels vary depending on the sampling protocol, with highest concentrations measured in the first draw after extended stagnation and reaching a maximum concentration of 13,200 µg Pb/L in one specific case. Lower concentrations were measured after 30 minutes of stagnation, as it was the case in a school investigated in New Jersey when concentrations were measured after 10 minutes of flushing followed by a random stagnation time (Murphy, 1993). Studies also report that flushing the tap prior to drinking water reduced the Pb and Cu concentrations (Barn et al., 2014; Boyd et al., 2008b; Triantafyllidou et al., 2014). However, there is no published study on the impact of water quality, type of taps where samples are collected and sampling protocol on Pb and Cu concentrations in schools and large buildings.

The number of LSLs in the United States is estimated to range between 5.5 and 7.1 million, providing water to 15 to 22 million Americans (Cornwell et al., 2016). In Canadian and American cities with population ranging between 24,000 and 3,000,000 inhabitants, up to 69,000 LSLS are still present (Deshommes et al., 2018a). According to the same study, utilities stopped installing LSLs between 1930 and 1975. In most instances, due to share ownership of the service line between the utility and the homeowner, only the public section of the LSL can be removed when municipalities are conducting replacement. It results in partial LSL replacements (PLSLR) in which the private section of the LSL remains as is. Regulatory agencies are also making full LSL replacement mandatory. As an example, the Michigan Department of Environmental Quality requires full LSL replacement, at the expense of the utilities, within the next 20 years (Department of Environmental Quality of State of Michigan, 2018). Field studies conducted in North American cities using different water qualities, report that Pb concentrations increase shortly after PLSLR and then decrease to levels comparable to before the replacement or to lower levels (Deshommes et al., 2016a; Deshommes et al., 2017; Muylwyk et al., 2011; Swertfeger et al., 2006). Short and long-term pilot studies have shown the importance of corrosion inhibitors, flow rate, type of couplings, stagnation time prior to sampling and water quality on the release of particulate Pb in partial LSLs (Cartier et al., 2012a; Cartier et al., 2013; Kogo et al., 2017; St. Clair et al., 2016; Triantafyllidou & Edwards, 2011; Wang et al., 2012; Wang et al., 2013; Zhou et al., 2015).

1.2 Structure of the dissertation

This thesis is divided in 10 chapters. A review of the state of the literature on the presence of lead and copper in drinking water distribution system is presented in Chapter 2. It is followed (Chapter 3) by the presentation of the research objectives as well as a short overview of the methodology used. Chapter 4 through Chapter 6 present research results in the form of 3 submitted or published scientific publications. The first article (Chapter 4, published in *Water Research*) investigates the sources of lead and copper in schools and large institutional buildings as well as the impact of water quality, type of taps and sampling protocols on concentrations measured. The focus of the dissertation then moves on to the presence of lead and copper in service lines, at pilot scale. The second article (Chapter 5, submitted to *Water Research*) reports the long-term trends in lead release following simulation of partial LSL replacements and proposes a framework for the management of full and partial LSL. The third article (Chapter 6 , submitted to *Water Research*), presents the trend in copper concentrations following partial LSL replacements and investigates the use of different stagnation times prior to sampling for lead and copper. The changes in lead leaching associated with changing flow velocity are also investigated. Chapter 7 presents the impact of the onset of chlorination on lead release in full and partial LSLs, as well as the increase in orthophosphate dosage. The next chapter (Chapter 8) reports the changes in scale composition and relative abundance between full and partial LSLs, under different water qualities. Chapter 7 and Chapter 8 will be submitted for publication at a later date. Finally, a general discussion on galvanic corrosion and the release of lead and copper is presented in Chapter 9 and is followed by conclusions and recommendations (Chapter 10).

CHAPTER 2 LITERATURE REVIEW

2.1 Health impacts of lead and copper

2.1.1 Lead

Changes in water quality in Flint (Michigan, United States) and Washington, D.C. (United States) resulted in increases in blood lead levels (BLL) of children as water lead levels rose (Brown et al., 2011; Hanna-Attisha et al., 2016). Triantafyllidou and Edwards (2012) listed 14 studies, published between 1977 and 2009, clearly linking drinking water to increased BLLs. With decreasing environmental exposure to lead, drinking water is now a major source of exposure (Health Canada, 2017). Elevated BLLs are of concerns as there are no levels of exposure that are considered to be safe (Bellinger et al., 1992; Needleman, 2004; WHO, 2011) and exposure to low levels of Pb in water result in a significant increase in BLLs (Ngueta et al., 2016). Indeed, intellectual deficits arise at low levels of exposure to lead (Bellinger, 2008; Canfield et al., 2003; Health Canada, 2013; Lanphear et al., 2005) and children have a higher uptake of lead than adults, 40-50% vs 3-10% respectively (Manton et al., 2000; Mushak, 1998; Ziegler et al., 1978). Exposure to lead has also been linked to cardiovascular disease mortality in the United States (Lanphear et al., 2018; Lustberg & Silbergeld, 2002; Schober et al., 2006).

2.1.2 Copper

Despite being an essential element for humans, ingesting concentrations of copper greater than 3,000 µg Cu/L was shown to cause nausea, abdominal pain or vomiting in healthy adults (Pizarro et al., 1999; WHO, 2004). Infants (<1 year old) are the most at risk of copper toxicity as their body has not yet developed homeostatic mechanisms required to clear copper and prevent its intestinal entry (Georgopoulos 2001; Müller-Höcker et al., 1988). However, health impacts arise at concentrations greater than those at which there are aesthetic impacts, which include staining the laundry and plumbing fixtures (Edwards et al., 2000). Interestingly, Swedish researchers showed that daily copper requirements could be met only from drinking tap water (Pettersson & Rasmussen, 1999). Overall, health issues that are associated with exposure to copper appear to be of less concern than those associated with lead exposure.

2.2 Recommendations/Regulations on lead and copper in drinking water

Sampling protocols for lead and copper, as wells as maximum acceptable concentrations (MAC) and action levels (AL) are different in Canada, the United States and the European Union. Also, the Canadian government can only provide recommendations for sampling and acceptable concentrations, as drinking water standards are regulated by provinces and territories. Also, some regulatory agencies provide specific requirements for lead and copper sampling in schools and daycares, while others only provide protocols for general sampling in the distribution system.

The same sampling protocol is applied for lead and copper in many jurisdictions, raising concerns about the effectiveness of such an approach as dissolution dynamics as well as effects of temperature are different for both metals (Lytle & Schock, 2000; Masters et al., 2016). The appropriate estimation of particulate Pb is also a concern associated with lead sampling and the handling of samples (Deshommes et al., 2016a; Triantafyllidou et al., 2014; Triantafyllidou et al., 2007).

2.2.1 Canada

In 2017, Health Canada issued new proposed recommendations concerning lead sampling in houses, suggesting sampling after 30 minutes of stagnation or random day time (RDT) rather than after at least 6 hours of stagnation as in the previous recommendations. Also, the proposed MAC is decreased from 10 µg Pb/L to 5 µg Pb/L (Health Canada, 2009, 2014, 2017). Maximum copper concentration allowed in drinking water are based on aesthetic objectives as it can stain the laundry and plumbing fixtures. As such, aesthetic objectives (AO) are recommended for copper as well as MAC based on health effects. Health Canada recommends an AO of 1,000 µg Cu/L as well as a newly proposed MAC of 2,000 µg Cu/L (Health Canada, 2018).

Multiple Canadian provinces, such as Alberta, Québec and Manitoba require that samples for lead, in houses and in schools, be collected after flushing the taps and their MAC are in line with current adopted Canadian Guidelines (Table A.1). Whereas Ontario requires sampling targeted to schools and daycares which includes collecting samples after at least 6 hour stagnation, as well as after 30 minutes of stagnation at every outlet used by children (Government of Ontario, 2017, 2018).

2.2.2 United States

As in Canada, in the United States, the Environmental Protection Agency (USEPA) recommends action levels and sampling protocols and each state sets its own regulation. In houses, under the Lead and Copper Rule (LCR), 1L samples must be collected after 6 hours of stagnation, with an action level set at a 90th percentile concentration, calculated for the distribution system, of 15 µg Pb/L (USEPA 1991). When serviced by a public water system, schools fall under the Lead Contamination Control Act (USEPA 1989). However, the number of states regulating sampling for lead in schools is growing (Government of California, 2018; New York State, 2018; State of Illinois, 2017).

2.2.3 European Union

In the European Union, random day time sampling is recommended for lead and copper while giving each country the choice to decide if fixed stagnation should be employed instead. European drinking water standards of 2,000 µg Cu/L and 10 µg Pb/L are in line with the current recommendations of the World Health Organization (WHO) (European Commission, 2015; WHO, 2017).

2.3 Sources of lead and copper in large buildings

In schools, the main sources of lead are most often leaded plumbing materials, including brass and solder. Brass is one of the most commonly used material when manufacturing plumbing components such as faucets (Churchill et al., 2000). In 1986, the United States Safe Drinking Water Act required the use of “lead-free” components in public water systems. At the time, “lead-free” was defined as containing less than 0.2% of Pb in solders and flux and 8% in pipes and pipe fittings. Since 2015 in the US and 2014 in most Canadian provinces, no more than 0.25% of Pb must be found across the wetted surface of pipes, pipe fittings and fixtures (Health Canada, 2017; U. S. Government, 2011). Although these new standards will limit the use of leaded materials, schools must manage a legacy of leaded materials, limitations of current low lead certification processes (Raetz et al., 2011) and the continued risk of non-compliant material such as shown by the recent Hong Kong Commission on excess lead in drinking water (The Commission of Inquiry and Hong Kong Government 2016).

In large buildings, sources of lead can leach significant levels of particulate lead as studies have shown that it represents an important fraction of total lead (Deshommes et al., 2012a; Triantafyllidou et al., 2007). The quality of the plumbing materials and the brass can also vary in large buildings (Cartier et al., 2012c; Deshommes et al., 2012a; McIlwain et al., 2015). The presence of galvanic corrosion between plumbing components made of different metals is one important sources of Pb. Galvanic corrosion and the presence of solders can account for 48% of high particulate Pb release (Cartier et al., 2012c; Deshommes et al., 2012a).

Multiple studies conducted in large buildings, including schools, have identified the taps and its connecting plumbing as important sources of lead and copper and are summarized in Table A.2. Detailed investigations of a specific building allow for a better understanding of the sources of lead. Within a type of building, the type of fixture influences the concentrations of Pb observed. In Philadelphia, the percentage of taps with Pb concentrations > 20 µg Pb/L ranged from 7.1% to 62.5% depending on the type of taps (Bryant, 2004). Dissolved and particulate Pb concentrations were lower at fountains (35 and 24 µg Pb/L respectively) than at faucets (214 and 82 µg Pb/L) in a penitentiary complex (Deshommes et al., 2012a). The presence of a cooling chamber also affects the Pb concentrations, as well as the presence of leaded components such as brass, fixtures and solders (Cartier et al., 2012c; Deshommes et al., 2012a; McIlwain et al., 2015). Water usage or the frequency of use of the taps can also influence the Pb concentrations at the tap. In Halifax (Canada), within the same university building, fountains with a low water use released more Pb than similar fountains with a higher water use (McIlwain et al., 2015).

Sequential sampling can be used to determine the source of lead in a large building. In a penitentiary complex, it was found that 74% of Pb measured in the first 1.5 L can be accounted for by the contribution of the first 250 mL collected (Cartier et al., 2012c). This first draw volume identifies the tap and its connecting plumbing as the sources of lead. Profiling can also identify the presence of a leaded cooling tank at a fountain (McIlwain et al., 2015). Correlating high Pb concentrations with other metals, such as Zn and Sn, can also identify brass fixtures containing Pb as one of the sources of particulate Pb (Deshommes et al., 2012a).

2.4 Full and partial lead service lines

In North American cities, utilities stopped installing lead service lines (LSL) between 1930 and 1975 (Deshommes et al., 2018a). It is estimated that between 5.5 and 7.1 million LSL are still in use in the United States, deserving between 15 and 22 million Americans (Cornwell et al., 2016). A recent survey of 21 Canadian and American utilities revealed that in one of the utilities studied, up to 69,000 LSLs are still in place (Deshommes et al., 2018a). To decrease exposure of customers to Pb in drinking water, as LSL are an important source of Pb (50-75%) (Sandvig et al., 2008), utilities conduct LSL replacements. Since the ownership of the service line is shared between the utility and the homeowner, typically, only the public portion of the LSL is replaced when the utility conducts replacements, resulting in a partial LSL replacement (PLSLR). In order to maintain an electrical connection within the service, in cold climates, brass connectors are often installed (St. Clair & Edward, 2014). This type of connector has been linked to increases in Pb concentrations following PLSLR (Cartier et al., 2013; Wang et al., 2013). Some regulating agencies, such as the Department of Environmental Quality of the State of Michigan (USA) requires that full LSL replacement, at the expense of the utilities, be completed within the next 20 years (Department of Environmental Quality of State of Michigan, 2018). The cities of Madison and Milwaukee have made full LSL replacement compulsory in order to remove lead sources from their distribution system (Sandvig et al., 2008; Schock et al., 2014; Slabaugh, 2017). A new source of copper is added upstream of the consumer’s tap when conducting partial and full LSL replacements, as this type of piping is often installed to replace lead pipe.

Field studies of lead service lines and the impacts of PLSLR are available for some North American distribution systems but mostly focus on the transient increase in Pb concentrations at the consumers’ tap (Brown & Cornwell, 2015; Camara et al., 2013; Lewis et al., 2017; Trueman et al., 2016). In these short term (less than 6 months) studies, it is demonstrated that Pb concentration decrease to levels similar, or lower, to those measured before PLSLRs. However, long-term studies are available for a few distribution systems, such as Cincinnati (OH, USA), Guelph (ON, Canada), and Montreal (QC, Canada), in which an initial increase in Pb levels, followed by a decrease, was observed after PLSLR (Deshommes et al., 2016b; Deshommes et al., 2017; Deshommes et al., 2018b; Muylwyk et al., 2011; Swertfeger et al., 2006).

Short and long-term pilot studies, using new or harvested LSLs, have shown that these PLSLRs can lead to spikes of elevated particulate Pb concentrations depending on water qualities, corrosion inhibitors, flow rate, type of coupling and stagnation time prior to sampling (Arnold & Edwards, 2012; Cartier et al., 2012a; Cartier et al., 2013; St. Clair et al., 2016; Triantafyllidou & Edwards, 2011; Wang et al., 2012; Wang et al., 2013; Zhou et al., 2015).

2.5 Galvanic corrosion

Oliphant (1983) and Gregory (1990) were the first to highlight the importance of galvanic corrosion in the leaching of lead of a leaded solder connected to copper. The connection of dissimilar metals (Pb, Cu and brass) adds a new type of corrosion in the service line: galvanic corrosion (DeSantis et al., 2018; Oldfield, 1988). The nobility, therefore the electrochemical potential, of the metals determines which will act as the anode and which will be the cathode in the galvanic couple. As the anode is preferentially oxidized there is a decrease in pH in the water surrounding as OH^- ions are removed from the water when soluble complexes or insoluble precipitates (Dudi, 2004). In the galvanic couple consisting of lead and copper, free lead (Pb^{2+}) is released in the water as a Lewis acid. At the cathode, which is protected, there is an increase in pH and a reduction in the oxidant. Accelerated Pb corrosion at the galvanic connection has been corroborated by field observations (DeSantis et al., 2009) as well as by laboratory experiments using micro-electrodes (Ma et al., 2018; 2017). After stagnation, a drop in pH was observed at the anodic surface using microelectrodes on brass-leaded soldered joints, a pH difference of 2.1 between the anodic and cathodic sites was observed (Ma et al., 2017), confirming local changes in water chemistry compared to the bulk water.

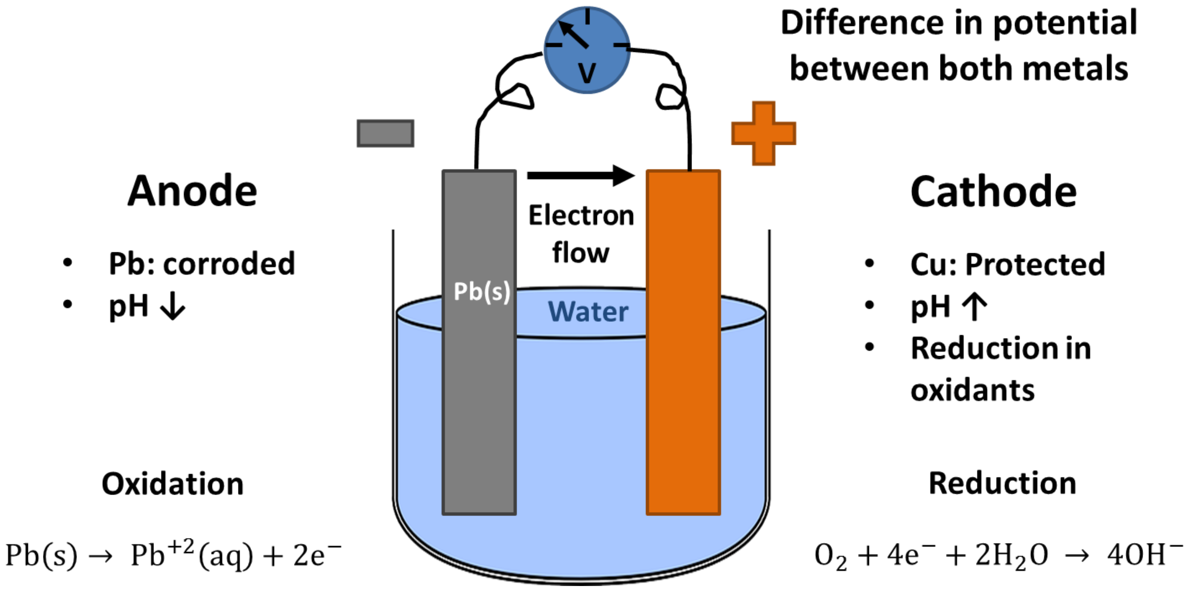

Figure 2.1 Schematic representation of reactions occurring in a galvanic couple comprised of lead and copper, adapted from Triantafyllidou and Edwards (2010).

In tap water, lead is preferentially corroded, then brass and then copper, as the nobility of the metal increases (Matsukawa et al., 2010). This has been confirmed by multiple studies (Cartier et al., 2013; Edwards & Triantafyllidou, 2007; Oliphant, 1983; Wang et al., 2012; Wang et al., 2013). However, instances where the Pb acted as the cathode, and was therefore protected have also been reported (Arnold & Edwards, 2012; DeSantis et al., 2018; Triantafyllidou & Edwards, 2007). Measuring the current between the anode and the cathode in a galvanic couple can be an indicator of the importance of galvanic corrosion (ASTM International, 2009). Such negative currents were observed by Nguyen et al. (2010) between lead-tin solder, lead and tin wires connected to copper pipes and a relationship between the intensity of the current and the lead release in the water was established.

The addition of galvanic corrosion results in non-uniform corrosion in a short section of the service line (Reiber & Dufresne, 2006), which is reflected in the composition of the scales at the galvanic junction as there is a change in water quality (DeSantis et al., 2018; Schock & Lytle, 2011). The decrease in pH at the anode can inhibit the formation of passivating films on the lead anode and could exacerbate the self-perpetuation of the attack on the anode (Nguyen et al., 2010).

In the absence of connection to another metal, corrosion of lead can be summarized as the oxidation of lead (anodic reaction) and oxygen reduction to water (cathodic reaction) (Dudi, 2004; Vasquez et al., 2006). This reaction results in a small pH increase, or no noticeable change, as the OH^- produced at the cathodic site is neutralized by the acid produced at the anodic site (Edwards & Triantafyllidou, 2007). However, in drinking water distribution systems, lead is often in contact with other metals of different nobilities, such as in partial lead service lines, leaded solders, brass or other leaded plumbing components. In these situations, the corrosion rate of lead, when present, is accelerated as the anodic and cathodic reactions each take place at the surface of the Pb or the Cu pipe (Edwards & Triantafyllidou, 2007).

2.5.1 Galvanic corrosion in leaded brass

Using a brass coupon, made out of the most commonly found brass in faucets (C83600), which contains 5% of Pb by weight, Edwards and Triantafyllidou (2007) showed that a galvanic connection exacerbated lead leaching by 52% in high CSMR water during the first few weeks of testing. However, after 5 weeks of experiments, the authors noticed a decrease in lead leaching in brass galvanically connected to copper, as well as little pH differences between the surface of the brass and the surface of the copper. In the galvanic series, brass is close to copper (Matsukawa et al., 2010) and under specific conditions, brass can be protected by galvanic corrosion as is becomes cathodic to copper (Dudi, 2004; Triantafyllidou, 2006). Similar reversal of the galvanic couple have also been observed between Pb and Cu in distribution systems in which Pb(IV) is present (Arnold & Edwards, 2012; DeSantis et al., 2018).

2.5.2 Galvanic corrosion in leaded solders

Using a 50:50 lead-tin solder, Edwards and Triantafyllidou (2007) demonstrated that the galvanic connection to a copper pipe increased the Pb concentrations in water by 6 to 16-fold, for low and high CSMR respectively. Measurements of the pH at the surface of the solder was lower than pH values measured at the surface of the copper pipe, which confirms the presence of galvanic corrosion. During the first week of experiment, in the high chloride to sulfate mass ratio (CSMR) water tested by Edwards and Triantafyllidou (2007), Pb concentrations reached 14,400 µg Pb/L in the presence of galvanic corrosion, vs 220 µg Pb/L when the solder was not galvanically connected.

2.6 Factors affecting lead and copper concentrations in drinking water

High copper concentrations are associated with new unpassivated pipes (Schock & Lytle, 2011; Schock et al., 1995; Turek et al., 2011), therefore elevated copper concentrations are associated with new buildings or plumbing components. However, elevated Pb concentrations are associated with old plumbing materials, installed when regulation on the presence of lead in plumbing material was less stringent as it is nowadays (Lytle & Schock, 2000; Schock & Gardels, 1983; Schock & Lytle, 2011). This is one of the examples of different conditions linked to the highest risks of elevated lead or copper at the tap.

2.6.1 Temperature

In theory, as temperature increases, the thermodynamic driving force for corrosion rate increases (Schock & Lytle, 2011). Masters et al. (2016) demonstrated the solubility of different lead corrosion products at 4°C and 20°C in the presence and absence of natural organic matter (NOM). They proved that the impact of temperature depends on the corrosion products in place and that there is a 35-fold increase in lead concentrations from the dissolution of lead oxide in the presence of NOM. However, the cuprosolvency is highest at low temperature (Rushing & Edwards, 2004). This was evidenced by elevated copper concentrations measured in winter times rather than summertime in Providence (Rhode Island, USA) (Masters et al., 2016). Differences in the effect of temperature on solubility of lead and copper can have regulatory implications as when should sampling be carried out to have water temperatures that are more prone to elevated levels.

2.6.2 pH and alkalinity

Depending on alkalinity and pH of the water, different corrosion products, with different solubilities, will form inside the lead and copper pipe (Schock & Lytle, 2011), as controlling the pH also manages the deposition of calcium carbonate (Crittenden et al., 2012), a key constituent of lead and copper corrosion products. The water qualities at which lead and copper corrosion is worsened are different.

Highest copper solubility occurs at alkalinity below 25 mg $CaCO_3$/L and above 75 mg $CaCO_3$/L (Schock et al., 1995). However, lead is more vulnerable to corrosion in low alkalinity water

(Schock & Lytle, 2011). Low alkalinity water can be naturally occurring as it is the case in Eastern Canada and New England (USA), due to the specific geology of the area (Payne, 2013).

In water with pH values lower than 7.5, the formation of cerussite ($PbCO_3$) is favoured over other less soluble Pb(II) corrosion products, such as hydrocerussite ($Pb_3(CO_3)_2(OH)_2$). A high alkalinity can offset the impact of having low pH water on Pb release (Boffardi, 1995; Edwards et al., 1999; Schock, 1990; Sheiham & Jackson, 1981). With increases in pH, there is a decrease in the solubility of the Pb scales as above pH values of 8.0-8.5, the formation of hydrocerussite is favoured (Kim et al., 2011; Schock & Gardels, 1983).

2.6.3 Chlorine residual

The oxidation reduction potential (ORP) of the water present in the distribution system is influenced by the secondary disinfectants (Schock & Lytle, 2011). The pH of the water is also influenced by the addition of chlorine; gaseous chlorine can lower the pH of the water whereas the sodium hypochlorite increases the pH. Changes in pH are also controlled by the alkalinity and carbonate content of the water; water with limited buffering capacity will experience more important changes in pH values (Schock & Lytle, 2011). The corrosion of lead can be summarized as being an electrochemical process in which lead is oxidized, and electrons released react with different possible oxidizing agents present in the distribution system (Lin et al., 1997). Using the Nernst equation and thermodynamics considerations, Lin et al. (1997) state that dissolved oxygen and different chlorine species are the oxidants controlling the oxidation of lead, with free chlorine being the most corrosive.

The type of scale formed in the lead and copper piping depends on different water qualities, such as the oxidation reduction potential (ORP). When a sufficient ORP is achieved in water, stable and insoluble Pb(IV) oxides form a protective layer in the lead pipes (Triantafyllidou et al., 2015). The ORP of free chlorine and chloramines is an important factor controlling lead release in water, with free chlorine having a higher ORP and being a stronger oxidant than chloramines (Vasquez et al., 2006). The addition of chlorine is beneficial as it increases the ORP (Vasquez et al., 2006) of the water and drives scale equilibrium towards less soluble corrosion solids. This difference explains the important release of lead when Washington D.C. (USA) following the change from free chlorine to chloramines as a disinfectant residual (Renner, 2004). Studies also report a higher corrosion rate in the presence of free chlorine than chloramine, for example when measuring pipe weight loss (Lin et al., 1997; Treweek et al., 1985).

Under uniform corrosion, the levels of oxidizing agents in water, such as chlorine, is an important factor controlling corrosion rates and leaching of copper (Schock & Lytle, 2011; Schock et al., 1995; Werner et al., 1994). During stagnation, copper concentrations in water increase in the presence of oxidant and decrease in the absence of oxidant (Schock et al., 1995; Werner et al., 1994).

In hard and soft well water, the addition of chlorine decreased the lead corrosivity and the resulting concentrations in water (Cantor et al., 2003). However, in this specific experiment, an increase in copper concentrations was observed as copper corrosion is driven by the presence of oxidants, such as dissolved oxygen or chlorine (Schock & Lytle, 2011).

2.6.4 Chloride to sulfate mass ratio (CSMR)

Chloride can protect leaded materials in the absence of copper, but stimulates the attack on lead, by the formation of a soluble lead complex, when it is galvanically connected to copper (Edwards & Triantafyllidou, 2007; Nguyen et al., 2011a; Oliphant, 1983). Whereas sulfates inhibit lead corrosion in presence and in absence of galvanic corrosion (Oliphant, 1983) by the formation of a protective coating (Nguyen et al., 2011a; Sato, 1996). Scanning electron microscopy revealed the presence of flat platelets in the presence of sulfate, rather than corrosion products that look more like needle crystals, which better protect the lead pipe. If chloride is present in elevated concentrations in drinking water, an increase in lead solubility would be observed as it would react with lead to form a soluble complex. However, when sulfate reacts with lead, it forms an insoluble precipitate which results in a reduction of the solubility of lead (DeSantis et al., 2009; Nguyen et al., 2010). It has been proposed that salts, such as $PbSO_4$ or others, could be present as passivating films (Guo, 1992; Sato, 1996). The concentration of sulfate in water must be sufficient to offset the negative impacts of chloride in the presence of galvanic corrosion (Edwards & Triantafyllidou, 2007).

In the presence of galvanic corrosion, in order to balance the electroneutrality following the release of Pb^{2+}, the migration of anions, including chloride and sulfate must be considered (Nguyen et al., 2010). When current density > $2 \mu A/cm^2$, there is anion transport towards the anode, which in most cases is the Pb element of the galvanic couple. This results in an accumulation of anion, either Cl^- or SO_4^{2-} at the surface of the anode (Horng, 1993).

The concept of chloride to sulfate mass ratio (CSMR) was developed by Gregory (1985). A CSMR below 0.5, for which there is a high chloride concentration relative to sulfate, increases the galvanic corrosion of leaded solder connected to a copper pipe (Edwards & Triantafyllidou, 2007; Gregory, 1985).

In a utility survey, when the relative concentration of chloride to sulfate increased, which can be referred to as increasing the CSMR, resulted in higher 90th percentile Pb concentrations at the utility level (Dodrill & Edwards, 1995). More specifically, these authors noted that utilities with CSMRs below 0.58 respected the action level of 15 µg Pb/L, but only 36% of utilities with CSMRs > 0.58 presented a 90th percentile concentration below the action level. This study highlights the importance of the CSMR in controlling Pb concentrations in water. When the county of Stafford, VA (USA) change the coagulant type from alum to ferric chloride in one of its treatment plants, it decreased the concentration of sulfate and triggered a change in the CSMR from 0.29-0.38 to 4.75 (Edwards & Triantafyllidou, 2007). Prior to changes, the 90th percentile Pb concentrations were below 2 µg Pb/L and increased to 40 µg Pb/L following changes in coagulant.

The passivation of the galvanic attack in high sulfate waters, as observed by Gregory (1985) and Oliphant (1983), was confirmed in laboratory and pilot studies investigated the impact of changing the CSMR on the Pb release from galvanically connected Pb solders and pipes. In 50:50 lead-tin solder galvanically connected to a copper pipe, the increase in Pb concentrations caused by galvanic corrosion was attenuated in the high sulfate water (low CSMR) when compared to the low sulfate waters (high CSMR) (Edwards & Triantafyllidou, 2007). In simulated PLSLR, using harvested LSLs, adding sulfate to decrease the CSMR resulted in a decreased in Pb release from partial LSLs, but had no effect on full LSLs (Cartier et al., 2013), in agreement with Oliphant (1993). At bench scale, a change in the coagulant from Alum to PACl increased the CSMR and caused an increase in Pb concentrations from harvested LSLs (Knowles et al., 2015).

2.6.5 Phosphate addition

Phosphates are added in drinking water distribution systems in order to form relatively insoluble lead phosphate complexes such as hydroxypyromorphite ($Pb_5(PO_6)_3OH$) or tertiary lead orthophosphate ($Pb_3(PO_4)_2$) (Nadagouda et al., 2011; Schock & Lytle, 2011). The addition of orthophosphate to water increases the alkalinity of the water, which impacts the corrosion rate of lead (Nadagouda et al., 2009). When free lead ions (Pb^{2+}) are in solution, they can react with carbonate or orthophosphate to precipitate into passivating solids (Schock & Gardels, 1983). The reactions occurring can be summarized as follow (Nadagouda et al., 2009):

$$\mathrm{PbO_2(s) + 4H^+ \rightarrow PbO^{2+} + 2H_2O} \text{ (2.1)}$$

$$\mathrm{PbO^{2+} + 2H^+ + 2e^- \leftrightarrow PbO(s) + H_2O} \text{ (2.2)}$$

Or

$$\mathrm{PbO_2(s) + 2H^+ + 2e^- \leftrightarrow PbO(s) + H_2O} \text{ (2.3)}$$

$$\mathrm{PbO(s) + 2H^+ \leftrightarrow Pb^{2+} + H_2O} \text{ (2.4)}$$

$$\mathrm{3Pb^{2+} + 2H_2O + 2CO_3^{2-} \leftrightarrow Pb_3(CO_3)_2(OH)_2(s) + 2H^+} \text{ (2.5)}$$

$$\mathrm{5Pb^{2+} + 3PO_4^{3-} + H_2O \leftrightarrow Pb_5(PO_4)_3(OH)(s)} \text{ (2.6)}$$

$$\mathrm{9Pb^{2+} + 6PO_4^{3-} \leftrightarrow Pb_9(PO_4)_6(s)} \text{ (2.7)}$$

Precipitation of phosphorus was observed at pH of 7.5 and 8.5 in a recirculating system made out of new lead pipes (Nadagouda et al., 2009). The same authors observed a change in the structure formed in the presence of orthophosphate; at pH 6.5 nanometers thick tubes including phosphate deposits of several microns in length were observed, whereas an increase in pH to 8 and above yielded the formation of spheres and a more uniform layer of phosphate and cerussite deposits.

Decreases in Pb concentrations, with the addition of phosphates, have been observed in field and pilot studies (Cardew, 2009; Cartier et al., 2013; Edwards & McNeill, 2002; Trueman et al., 2018). Different types of phosphate are in use in drinking water distribution systems, yielding different outcomes in terms of lead decrease, including orthophosphate, zinc-orthophosphate, polyphosphate and hexametaphosphate (Edwards & McNeill, 2002; McNeill & Edwards, 2002).

Orthophosphates (orthoP) have been reported to decrease plumbosolvency, in pilot systems and in distribution systems, but to fail to control elevated particulate lead concentrations (Cardew, 2009; Cartier et al., 2013; Edwards & McNeill, 2002; Noel et al., 2014; Trueman et al., 2018; Xie & Giammar, 2011). Total Pb decrease following the addition of orthoP resulted in decreases of 90% in a study of multiple distribution systems in random day time (RDT) samples and of 68% in full

LSL in a pilot setup after 16 hours of stagnation (Cardew, 2009; Cartier et al., 2013). Laboratory experiments demonstrated that the rate of the dissolution of hydrocerussite, a common Pb(II) corrosion products in lead service line, is decreased in presence of orthoP (Noel et al., 2014). The insoluble lead phosphate hydroxypyromorphite ($Pb_5(PO_4)_3OH$) was present in distribution systems treated with orthoP (Trueman et al., 2018).

In a study conducted in North West of England, Cardew (2009) demonstrated that Pb concentrations above the 90th percentile were caused by spikes in the particulate Pb fraction. Which was also observed by Trueman et al. (2018) in a field study. In a pilot study simulating partial LSL replacement on harvested pipes, orthoP increased total Pb concentrations by 13-fold as particulate concentration increased (Cartier et al., 2013). But different observations were made by Kogo et al. (2017) in a recirculating system comprised of lead and copper pipes galvanically connected together. When a leaded solder was galvanically connected to a copper pipe, the presence of orthophosphate in water was ineffective at decreasing the voltage of the galvanic corrosion (Gregory & Gardiner, 1985). Interestingly, Cardew (2009) demonstrated different response time to the onset of treatment for dissolved and particulate Pb, the later decreasing after a longer period.

The addition of orthoP is not only beneficial for LSL. Adding orthoP (0.8 mg P/L) decreased Pb concentrations from faucets by 41%, but caused an increase the proportion of particulate Pb (31% to 54%) (Cartier et al., 2012c).

Decreases in copper concentrations are also observed when orthoP are in use in a distribution system. Cuprosolvency is decreased by the formation of the $Cu_3(PO_4)_2$ which is less soluble than cupric hydroxide ($Cu(OH)_2$).

2.7 Scales formed in full and partial lead service lines

The layer of corrosion products in direct contact with the water determines the concentrations of lead and copper measured in solution (Schock & Lytle, 2011). For example, the dissolution of cerussite ($PbCO_3$), when in contact with water for 6 hours is 227-fold higher than the dissolution of hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) at 20°C (Masters et al., 2016).

2.7.1 Lead scales

Pb passivation in the LSL occurs through time and generally, Pb(II) and Pb(IV) oxides and carbonates are formed depending on the water quality: cerussite ($PbCO_3$), hydrocerrusite ($Pb_3(CO_3)_2(OH)_2$), plumbonacrite ($Pb_{10}(CO_3)_6(OH)_6O$), litharge (PbO) and plattnerite (PbO_2) (Kim & Herrera, 2010; Schock & Lytle, 2011). The following sequence of minerals can be formed in LSLs, at pH ranging between 6,5 and 8: hydrocerussite, cerussite, plattnerite and finally scrutinyite (Lytle & Schock, 2005). Intermediate Pb(III) products have also been observed, but there are gaps in knowledge when it comes to Pb(II) conversion to Pb(IV) (Kim & Herrera, 2010). Pb(IV) oxides can also reverse to Pb(II) oxides depending on the changes in water quality or as oxidants like chlorine are depleted (Lytle & Schock, 2005). Pb(II) carbonates, oxides and phosphate scales are fairly common amongst LSLs in North American distribution systems (DeSantis et al., 2009; Hozalski et al., 2005; Schock & Lytle, 2011; Wang et al., 2012).

Lower solubility Pb(IV) scales have also been reported and their formation can be an effective mitigation strategy in decreasing Pb concentrations in tap water (Lytle & Schock, 2005; Schock et al., 2005b; Triantafyllidou et al., 2015). Based on solubility modelling, Pb(IV) oxide PbO_2 is orders of magnitude less soluble than Pb(II) but is only stable at high ORP (Schock et al., 2001). Formation of Pb(IV), which has a higher electrochemical potential than copper and is therefore more noble, protects the Pb pipe in and reverses the galvanic couple (Arnold & Edwards, 2012). Pb(IV) scales may form when free chlorine is present in the water as it can oxidize Pb(II) into Pb(IV) (Xie & Giammar, 2011).

2.7.1.1 Orthophosphate

The addition of phosphate has been reported to form low solubility lead phosphates such as hydroxypyromorphite ($Pb_5(PO_4)_3OH$), chloropyromorphite ($Pb_5(PO_4)_3$-Cl) and tertiary lead phosphate ($Pb_3(PO_4)_2$) in lead pipes (Davidson et al., 2004; Hopwood et al., 2002; Noel et al., 2014; Schock et al., 2005a; Trueman et al., 2018; Wang et al., 2013). However, no Pb(II)-orthophosphate solids were observed in a system using blended phosphates, whereas Al and Ca reacted with P and was deposited in the scales (Wasserstrom et al., 2017). Therefore, one should be careful about generalizations made with phosphate addition to drinking water as its form is important, which will also be reflected in its effectiveness as a corrosion control treatment (CCT) (Edwards & McNeill, 2002).

2.7.1.2 Sulfate addition

In water containing 210-218 mg SO_4/L, at a pH of 8.0, Lytle and Schock (2005) observed the formation of hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) on the coupon. Shortly after the beginning of the experiment, cerussite ($PbCO_3$) became the dominant corrosion product, with increasing amounts of both polymorphs of PbO_2 over time. Interestingly, despite the elevated sulfate concentration, none was detected as part of a Pb corrosion solids.

2.7.1.3 pH increase

The rate of aging of the Pb scale is pH dependent as the rate of formation of the Pb(IV) oxide PbO_2 increases with increases in pH (Lytle & Schock, 2005). As pH increases, between values of 6 and 8, the predicted and observed solubility of hydrocerussite decreases and was observed to be 2 orders of magnitude different (Kim et al., 2011; Nadagouda et al., 2011; Noel et al., 2014). The pH, between 7 and 10, also influences the rate at which the Pb is leached from the scale (Kim et al., 2011). At pH values of 10, hydrocerussite was mostly present, whereas at pH 6 only cerussite was present inlab experiments, which Kim et al. (2011) hypothesized could be due to a shift in the most dominant phase in the samples, as hydrocerussite is transformed into cerussite at pH values below 8 (Dando & Glasson, 1989).

CHAPTER 3 RESEARCH OBJECTIVES, HYPOTHESIS AND METHODOLOGY

3.1 Critical review of previous research findings

Multiple research articles have been published on the factors affecting the extent of lead and copper corrosion in drinking water. When considering this information, main observations can be summarized and remaining data gaps and areas where more research appears justified identified, including:

- Schools/large buildings
    - Few studies evaluated Pb and Cu concentrations using different sampling protocols.
    - Fixed stagnation protocols do not allow the determination of the possible sources of lead and copper or exposure.
    - Few studies have looked at the impacts of water qualities and type of faucets on Pb and Cu concentrations: using the same sampling protocol in multiple buildings.
    - There is a need to show the variability of Pb and Cu concentrations within each building: is it possible to only sample one tap and obtain a realistic view of the situation?
- Lead service lines
    - Most studies rely on new materials/piping: does not represent current state of distribution systems where legacy scales are present prior to doing partial lead service lines
    - Multiple coupon and pilot studies on the impact of galvanic corrosion do not take into account flow and stagnation in pipes.
    - Several bench scale studies use wire to add a galvanic current, instead of using fittings which are used in real field conditions. The simplified approach is adequate to investigate the impact of a galvanic current, but may not reflect real life conditions.

- There are multiple short-term studies on the impact of PLSLR, but few long-term studies.
- Few studies have looked at scale formed under different water qualities, and how galvanic corrosion impacts scale formation.

3.2 Objectives

The main objective of this project was to determine the presence of particulate lead and copper, caused by galvanic corrosion, in drinking water distribution systems. Lead and copper can be found in the plumbing components in schools and large institutional buildings as well as in service lines.

More specifically, this research project seeks to:

1. Quantify the exposure to lead and copper in drinking water distribution systems of schools and large buildings prone to galvanic corrosion;
2. Assess the effectiveness of mitigation strategies, such as addition of corrosion control and flushing the water prior to consumption, to decrease exposure to lead and copper in schools and large buildings;
3. Determine how the type of tap and water quality influence lead and copper concentrations in schools and large buildings;
4. Evaluate the long-term effects of partial lead service lines replacements, under different water qualities, on lead and copper concentrations and the importance of galvanic corrosion;
5. Measure the effect of the onset of chlorination and of changes of orthophosphate dosage on lead and copper release from full and partial lead service lines;
6. Assess the impact of stagnation time prior to sampling and flow velocity on lead and copper concentrations;
7. Determine conditions under which partial lead service line replacements result in a reduction of lead concentrations at the tap, despite the addition of galvanic corrosion;
8. Investigate the type of scale deposits being formed in full and partial lead service lines under different water qualities/corrosion control treatments.

Achieving these objectives will allow us to answer fundamental questions concerning the quantification of exposure and the management of lead and copper from various sources in drinking water:

- What are the conditions under which lead and copper sampling should be prioritized in schools and large buildings?
- How should lead and copper sampling be carried out in schools and large buildings?
- Are corrosion control treatments as effective in reducing lead concentrations in full lead service lines as in partial lead service lines?
- How does the water quality affect the scale formation inside full and partial lead service lines?
- When does the addition of galvanic corrosion, caused by partial lead service line replacements, increase the lead concentrations at the consumers' tap?
- Is it possible to use the same stagnation time prior to sampling to detect elevated lead and copper concentrations?

The objectives of the project are derived from the following hypotheses:

1. Concentrations of lead and copper vary significantly across drinking water outlets in a large building. For each outlet, concentrations also vary depending on stagnation time prior to sampling and an appropriate sample protocol can quantify this variability.

   <u>Originality:</u> The sampling protocol developed for this research project can identify lead and copper sources in a large building and allows to capture the variability in concentrations in profile sampling.

   The hypothesis will be discarded if total/dissolved/particulate lead and copper concentrations are similar between outlets in one building. As well, if no changes in concentrations are observed between samples collected after extended and long stagnation or short and long periods of flushing.

2. In schools and large buildings, flushing the water prior to consumption can be an effective temporary mitigation strategy. However, this mitigation strategy is short-lived as after

stagnation of 30 minutes, lead levels can increase back to concentrations measured after overnight stagnation.

<u>Originality:</u> Lead and copper concentrations measured after overnight stagnation will be compared to concentrations obtained after 30 minutes of stagnation, for different water qualities and types of outlets (fountains, kitchen taps and bathroom taps). This comparison will allow to evaluate the effectiveness of flushing as a mitigation strategy.

The hypothesis will be refused if, generally, lead and copper levels do not increase significantly after 30 minutes of stagnation compared to overnight stagnation.

3. Water quality and pH adjustment in a drinking water distribution system can effectively decrease lead concentrations at the tap in large buildings.

   <u>Originality:</u> Lead release from a wide range of faucets and connecting piping will be measured in schools and large buildings receiving different water qualities.

   The hypothesis will be proven wrong if the change in pH does not result in a generalized decrease in lead concentrations. This would mean that adjusting pH is not an effective mitigation strategy for lead control in these buildings.

4. The type of outlets from which a sample is collected in schools and large buildings influences lead and copper concentrations.

   <u>Originality:</u> As flow rates, water usage patterns and plumbing materials, vary depending on the type of outlet installed in a school or a large building, concentrations of lead and copper should be different between drinking water fountains, kitchen taps and bathroom taps. No other studies have measured the combined impact of the type of outlet, water quality and sampling protocol on lead and copper concentrations.

   The hypothesis will be rejected if lead and copper concentrations are similar amongst types of outlets in each building.

5. In the long-term (>1 year), PLSLR decrease Pb concentrations. As new copper pipes passivate, copper concentrations decrease following their installation.

   <u>Originality:</u> No other long-term (>1 year) study has been conducted at pilot scale using harvested lead service lines fed with water from the same distribution system. The red-brass

compression fittings installed in the pilot setup are the same type as the one used by the utility. The pilot setup also allows for a comparison of PLSLR conducted by the utility (Cu upstream of Pb) or by the homeowner (Pb upstream of Cu).

The hypothesis will be proven wrong, if in the long-term, PLSLR does not result in a decrease in lead concentrations compared to harvested full LSLs installed in the pilot. If this is the case, it implies that galvanic corrosion is an important contributor to lead sources after PLSLR and that the impact does not diminish thought time.

6. During a long-term study following PLSLR simulations, corrosion control treatments decrease lead release from galvanic corrosion.

   <u>Originality:</u> *No other study, using harvested LSL installed in a flow through pilot, has investigated the combined effect of PLSLR and changes in water quality (addition of sulfate to decrease the CSMR, dosing orthoP and increasing the pH). Comparing results before and after PLSLR simulation, and data from full LSLs allows to quantify the contribution from galvanic corrosion to total Pb release from partial LSL.*

   The hypothesis will be rejected if the addition of corrosion control treatment, after PLSLR, cannot decrease lead release from partial lead service lines compared to full lead service lines.

7. The addition of chlorine and increasing the orthoP dosage to the water intake of full and partial LSL in the pilot decreases Pb dissolution, resulting in lower lead concentrations in water samples.

   <u>Originality:</u> *The combined effect of chlorine and the decrease in CSMR on lead release from Pb pipes not influenced by galvanic corrosion, has not been studied in a pilot setup made out of harvested LSL, as well as on lead release from partial LSL influenced by galvanic corrosion. Also, few other studies have quantified the impact of increasing the orthoP dosage on full and partial LSL at pilot scale.*

   The hypothesis will be rejected if the onset of chlorination and the increase in orthoP dosage does not change lead concentrations measured.

8. Lead and copper concentrations increase in full and partial LSL during stagnation until concentrations reach a plateau. The rate of increase of Pb is different depending on the pipe

configuration. As well, the water quality also influences the rate at which Pb and Cu increase during stagnation.

<u>Originality</u>*: Previous work indicates an increase in Pb and Cu concentrations as stagnation time increases. The quantification of changes in total, dissolved and particulate Pb and Cu, in different water qualities and pipe configuration is novel. This work also allows to determine if sampling for lead and copper can be carried out using the same sampling protocol or if different stagnation times prior to sampling should be used for each metal based on the kinetics of dissolution and precipitation.*

The hypothesis will be rejected if no significant change in Pb and Cu is observed after different stagnation times.

9. Changes in water quality and connecting the Pb pipe to a red-brass fitting and a copper pipe result in modifications in the quantity, stability and type of scale present in the service line.

   <u>Originality:</u> *No other study has investigated how changes in water quality (addition of sulfate, orthoP dosing and increase in pH) affect scale formation in full and partial harvested LSL. Furthermore, modification of scale deposits with onset of chlorination is also conducted.*

   The hypothesis will be refused if there are no changes in scale composition between the galvanic and the non-galvanic zones in partial LSL and if changes in water quality are not reflected in the composition of the scale.

Table 3.1 presents a summary of the experimental approach for each hypothesis along with expected results and the corresponding chapter of the thesis.

Table 3.1 Experimental approach to validate (or invalidate) the research hypothesis and corresponding chapters of the thesis.

	Hypothesis	**Scale**	**Experimental approach**	**Expected results**	**Chapter**
1	Concentrations of lead and copper vary significantly across drinking water outlets in a large building. For each outlet, concentrations also vary depending on stagnation time prior to sampling and an appropriate sample protocol can quantify this variability	Field, Schools and large buildings sampling	Sampling after overnight stagnation (1st and 2nd draw), after 30 seconds and 5 minutes of flushing and after 30 minutes stagnation. In each building, sample 6-10 taps to capture variability	Highest Pb and Cu concentrations at each tap Taps with highest concentrations in each building	4
2	In schools and large buildings, flushing the water prior to consumption can be an effective temporary mitigation strategy. However, this mitigation strategy is short-lived as after stagnation of 30 minutes, lead levels can increase back to concentrations measured after overnight stagnation	Field, Schools and large buildings sampling	Sampling after overnight stagnation (1st and 2nd draw), after 30 seconds and 5 minutes of flushing and after 30 minutes stagnation.	The percentage of the overnight stagnation samples represents the 30 minutes stagnation samples Exceedances of MAC/AE for each type of samples	4
3	The addition of corrosion control treatment in a drinking water distribution system can effectively decrease lead and copper concentrations measured in a large building	Field, Schools and large buildings sampling	Measuring Pb and Cu concentrations in schools/large buildings using different water qualities and with pH increase as a corrosion control treatment	Differences between Pb/Cu concentrations depending on the water quality/aggressivity	4

Table 3.1 Experimental approach to validate (or invalidate) the research hypothesis and corresponding chapters of the thesis (continued).

	Hypothesis	**Scale**	**Experimental approach**	**Expected results**	**Chapter**
4	The type of outlets from which a sample is collected in schools and large buildings influences lead and copper concentrations	Field. Schools and large buildings sampling	In each building, sample 6-10 taps to capture variability. Sample drinking water fountains, kitchen taps and bathroom taps in each building (when feasible) Measure flow rate at each tap	Impact of flow rate on Pb/Cu concentrations Type of taps with exceedances in Pb/Cu concentrations	4
5	In the long-term (>1 year), PLSLR decrease Pb concentrations. As new copper pipes passivate, copper concentrations decrease following their installation	Pilot setup, long-term monitoring	Long-term (155 weeks) study of Pb and Cu concentrations in full and partial LSL Calculation of the contribution galvanic and non-galvanic zones in the Pb pipe to total Pb.	Demonstration of the sustained Pb released from partial LSL Determine the length of Pb pipe to remove in PLSLR to offset the addition of galvanic corrosion	5
6	During a long-term study following PLSLR simulations, corrosion control treatments decrease lead release from galvanic corrosion	Pilot setup, long-term monitoring	Measurements of Pb and Cu for 155 weeks depending on different water qualities: Control, decreased CSMR (0.9 to 0.3), addition of orthoP (1 mg P/L) and pH increase (pH 8.3)	Quantify which corrosion control treatment/water quality yields the lowest Pb concentrations in full and partial LSLs	5

Table 3.1 Experimental approach to validate (or invalidate) the research hypothesis and corresponding chapters of the thesis (continued).

	Hypothesis	**Scale**	**Experimental approach**	**Expected results**	**Chapter**
7	The addition of chlorine and increasing the orthoP dosage to the water intake of full and partial LSL in the pilot decreases Pb dissolution, resulting in lower lead concentrations in water samples.	Pilot setup, onset of chlorination and increase in orthoP	Short-term monitoring of Pb and Cu concentrations after dosing 1 mg Cl_2/L to the pipes treated with a decrease in CSMR and an increase in pH Increase the orthoP dosage from 1 to 1.5 mg P/L	Effect of dosing chlorine on galvanic corrosion Quantify the change in Pb concentrations with an increase in orthoP	7
8	Lead and copper concentrations increase in full and partial LSL during stagnation until concentrations reach a plateau. The rate of increase of Pb is different depending on the pipe configuration. As well, the water quality also influences the rate at which Pb and Cu increase during stagnation	Pilot setup, sampling after different stagnation times.	Measure total, dissolved and particulate Pb and Cu after different stagnation times: 0.5, 6, 16, 4, 48, 72 and 336 hours as well as under flowing conditions	Impact of stagnation time on the particulate (fraction and concentration) release.	6
9	Changes in water quality and connecting the Pb pipe to a red-brass fitting and a copper pipe result in modifications in the quantity, stability and type of scale present in the service line	Pilot setup, scale analysis	PXRD analysis of full and partial LSLs	Identify minerals present in the galvanic and non-galvanic zones in partial and in different layers Associate changes in dominant minerals to changes in water qualities	8

3.3 Methodology

The experimental approach was divided into five main components:

1. Evaluating the importance of the sampling protocol, type of tap and water quality on the sources of lead and copper in schools and large institutional buildings (Obj. 1-3);
2. Measure the long-term impacts of partial lead service line replacements, at pilot scale, on the release of total, dissolved and particulate lead and copper, for different water qualities and determine the contribution of galvanic corrosion to lead release in partial LSL (Obj. 4 and 7);
3. Quantify the impacts of changing chlorine concentration and orthophosphate dosage on the release of particulate lead and copper, in full and partial lead service lines (Obj. 5);
4. Determine the impact of stagnation time and flow velocity prior to sampling on total, dissolved and particulate lead and copper concentrations, for multiple water qualities, on full and partial lead service lines, at pilot scale (Obj. 6);
5. Assess changes in scale composition in full and partial lead service lines caused by modifications to the water quality or the onset of galvanic corrosion (Obj. 8).

To avoid repetition with the upcoming chapters, a summary of the methods is presented hereafter. Details on the methods used for the schools and large building sampling is presented in more details in Chapter 4 and more information is provided on the pilot sampling in Chapter 5 and in Chapter 6.

3.3.1 Sampling sites

Sampling campaigns were conducted in the field for the study of schools and large building and at pilot scale for the measurements of Pb and Cu from full and partially replaced lead service lines.

3.3.1.1 Schools and large buildings

A sample of schools and large buildings located in Canada and receiving water treated by utilities using surface water were sampled in May and June 2012. Three groups of buildings were distinguished during this study, and are presented in more details in Chapter 4: (1) schools without corrosion control added by the utility and low alkalinity water (<40 mg $CaCO_3$/L), (2) schools with pH control (pH>8.5), added at the drinking water treatment plant, and low alkalinity water and (3) large building complexes with high alkalinity (>70 mg $CaCO_3$/L), moderate pH (pH 7.5-8.0) without corrosion control. Drinking water fountains, kitchen taps and bathroom taps were sampled, for a total of 130 sampling points in 11 different buildings. Sampling points were spread within each building to capture the variability in the metal release amongst sampling points.

3.3.1.2 Pilot setup

3.3.1.2.1 Description of the pilot setup

The pilot setup was made of harvested LSLs, from the distribution system of Montreal, and details are presented in Chapter 5 and in Cartier et al. (2013). The LSLs were excavated using the method described by Kim et al. (2011) to minimize disturbing the scale deposits inside the pipes. The pipes were collected in 2 different areas of Montreal's drinking water distribution system. The setup was installed in the CREDEAU laboratory at Polytechnique Montréal (Figure 3.1).

Figure 3.1 Photograph of the pilot setup.

The pilot setup was operated using water from the City of Montreal, to which no corrosion control treatment is added and in which no chlorine residual was present. Water was stored in a 40 m^3 concrete tank which was filled overnight when the pilot was not in operation. Different water qualities were studied: (1) control condition (CSMR 0.9, pH 7.7), (2) high sulfate by the addition of Na_2SO_4 (CSMR 0.3 and pH 7.7), (3) orthophosphate (orthoP) dosed at 1 mg P/L with H_3PO_4 and NaOH for pH re-stabilization (CSMR 0.9, pH 7.7), (4) higher pH at 8.3 by dosing NaOH (CSMR 0.9). General water quality parameters are summarized in Table 3.2.

Table 3.2 General water quality of the water entering the pilot setup, prior to addition of treatments.

Parameter	Units	Mean value
pH	-	7.9
Alkalinity	mg $CaCO_3$/L	88
Total organic carbon	mg/L	2.7
Free chlorine	mg Cl_2/L	0.05
Chloride	mg/L	23.2
Sulfate	mg/L	24.5

A schematic of the pilot setup is presented in Figure 3.2. It can be noted that under normal operating conditions, water first flowed in the Cu-Pb pipes, then in the 100%Pb pipe and finally in the Pb-Cu section. Prior to sampling, the flow pattern was modified to bring fresh water in each section, as detailed in Chapter 5. General water quality (pH, alkalinity, dissolved oxygen, conductivity, chloride, sulfate and chlorine concentrations) was monitored weekly and details on the specific methods are presented in Chapter 5.

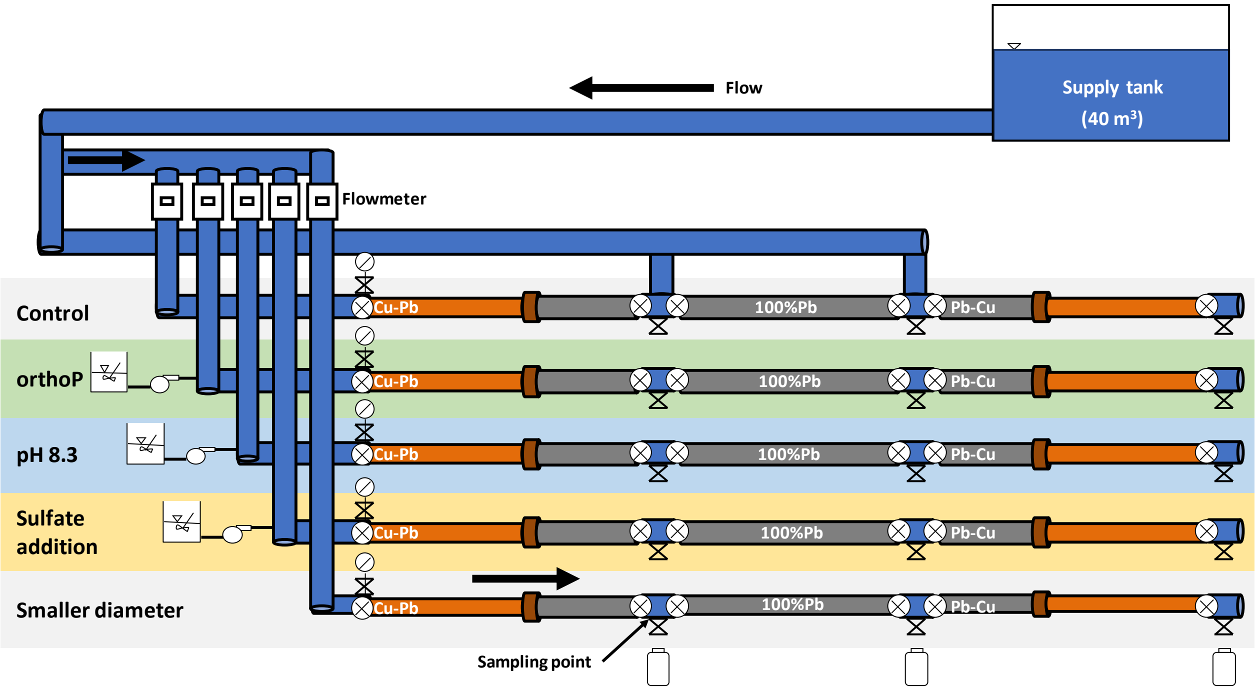

Figure 3.2 Schematic of the pilot setup installed in the CREDEAU Laboratory at Polytechnique Montréal.

First, the harvested LSLs were installed in the pilot and conditioned during 8 months under normal operating conditions. Then, during a 4 months period, baseline sampling was carried out to ensure adequate conditioning of the pipes. Following this first year of characterization, different treatment conditions were introduced in the pilot, for a duration of 4 months. Results from these periods are presented in Cartier et al. (2013).

For each water quality full LSLs (FLSLs) and partial LSLs (PLSLs) were tested on the setup. PLSLRs were simulated in the lab, as described in Chapter 5 and in Cartier et al. (2013). Red brass compression fittings (Ford, Wabash, Indiana, USA) were used to connect the copper pipes (180 cm, I.D. 22 mm) to the lead pipes (60 cm, I.D. 16 mm), resulting in the Cu-Pb configuration (Figure 3.3A). Additionally, Pb pipes with a smaller diameter (13 mm) were connected to Cu pipes (I.D. 16 mm) using a soldered fitting (Figure 3.3B). When the partial LSL replacements were simulated in the laboratory, the Pb pipes were already cut to the appropriate length. Therefore, the experiments only reflect the addition of a brass connector and a copper pipe to a lead pipe, and not the effect of cutting the Pb pipes on the lead release. FLSLs installed in the pilot each measured 3 m.

Figure 3.3 An example of a lead service line connected to a copper pipe using (A) a red brass compression fitting and (B) a soldered fitting.

The pilot was operated for 8 hours per day, 5 days per week at a flow rate of 5 LPM (0.4-0.7 m/s, Re 7525-8802) and a pressure of 30 psi. No stagnation >72 hours were allowed, except during stagnation trials.

3.3.1.2.2 Experimental sequence

The sequence of changes in water quality and operating conditions are summarized in

Table 3.3 Short-term results following PLSLR in the pilot are presented in Cartier et al. (2013) whereas this research project investigates changes in Pb and Cu in the long-term as well as changes in water quality.

During the long-term study of the impact of PLSLR in Pb concentrations, the effect of changes in stagnation time prior to sampling was also investigated. The methodology used for this section of the work is presented in more details in Chapter 6.

Shortly after (39 weeks) PLSLR simulation, one pipe per PLSL configuration was disconnected from the pilot to observe changes in scale composition from the newly added galvanic connection. Before inducing changes in water quality (chlorination and orthoP dosage), one pipe per PLSL and FLSL configurations was also disconnected, in this case, to investigate the long-term impacts of the corrosion treatments added to the water as well as the galvanic connection. Details on scale analysis are presented in subsequent sections.

Table 3.3 Timeline the changes applied to the water quality and operation of the pilot setup.

# of weeks after PLSLR simulations	Changes in operation/water quality	Objectives
20 – 155	Sampling was carried out under different conditions to assess the impact of stagnation on Pb and Cu release	Long-term study of the impacts of PLSLR
39	Disconnection of one PLSL per water quality	Study the short-term effects of PLSLR on scale deposits
155	Disconnection of one PLSL and one FLSL per water quality	Study the long-term effects of PLSLR on scale deposits
156	Addition of chlorine (1 mg/L) to rigs treated with a decreased CSMR and an increase in pH	Quantify the impacts of the onset of chlorination on Pb and Cu release
	In the water feeding the pipes treated with orthoP, the pH stabilization to its initial value was stopped	Assess the impact of a decrease in pH in pipes treated with orthoP
160 - 167	The section of the pilot with a smaller diameter was operated at a high flow rate (15 LPM) for one hour twice a day (after start up in the morning and before shut down in the evening)	Evaluate the impact of changes in flow rate
164	Increase in orthoP dosage from 1 to 1.5 mg P/L	Quantify the Pb and Cu release after an increase in orthoP
168	End of Pb and Cu monitoring	

To better simulate sections of the distribution systems in which a chlorine residual is observed, 1 mg Cl_2/L was added to rigs treated with a lower CSMR and an increase in pH. A concentrated sodium hypochlorite solution generated at the Charles J. DesBaillets drinking water treatment plants of the City of Montreal was used. Prior to dosing chlorine in the pilot setup, chlorine demand trials were carried out and revealed that the water entering the pilot had no chlorine demand. Chlorine residual was measured daily to make sure that the proper residual was dosed.

Initially, the pH of the water entering pipes treated with 1 mg P/L was adjusted back to its initial value using NaOH. On week 156, pH restabilization was stopped and a drop in pH of 0.3 units was observed. Shortly after, concentration of orthoP was increased to 1.5 mg P/L and remained until the end of the experiment.

Increase in flow rate was carried in the smaller diameter pipes. After starting the pilot and before closing it for the evening, the flow rate was increased to 15 LPM (1.3-2.0 m/s, Re 24,455-25,149), which is three times higher than normal operating conditions. The aim of the increase in flow velocity was to determine if Pb concentrations were lowered after high velocity flushing.

3.3.2 Pb and Cu measurements in water

Metal determinations (Cu, Pb, Zn, Fe) were carried out using inductively coupled plasma mass spectrometry (ICP-MS). Dissolved metal determination was done by filtering an aliquot using a syringe mounted 0.45 µm filter and acidified using 0.5% HNO_3. Filters were first rinsed with 20 mL of sample to be filtered in order to minimize adsorption of dissolved metals as well as leaching of Zn (Cartier et al., 2011).

The remaining sample was acidified in the bottle to ensure complete metal recovery. Samples from the schools and large buildings were acidified at 2% while sampled from the pilot were acidified at 0.5%, using HNO_3 in both cases. To obtain the appropriate matrix, 0.5% HCl was also added to the sampled from the pilot setup. Further details are presented in Chapter 4 and Chapter 5 and in Cartier et al. (2013).

3.3.2.1 Schools and large buildings

The sampling protocol used in schools and large buildings in this project is a combination of regulated and recommended sampling by Health Canada, the US EPA and specificities of sampling protocols in Canadian provinces (Government of Ontario, 2010; Government of Québec, 2017; Health Canada, 2009; USEPA 2006b). The sampling protocol used in this part of the research project is presented in detail in Chapter 4.

3.3.2.2 Pilot setup

In order to be able to compare long and short-term trends in Pb and Cu release, the same sampling protocol as applied in Cartier et al. (2013). Details are presented in Chapter 5.

Furthermore, the impact of stagnation time prior to sampling was assessed after 0.5, 6, 16, 24, 48. 72 and 336 hours of stagnation. Sampling was also carried under flowing conditions. Details are presented in Chapter 6.

3.3.3 Surface area normalized mass release (SANMR) determination in full and partial lead service lines

As detailed in Chapter 5, the surface area normalized mass release (SANMR) was calculated after 16HS for full and partial LSLs for Pb_{total}, $Pb_{diss.}$ and $Pb_{part.}$ adapting the approach presented by McFadden et al. (2011). The SANMR is expressed as µg of Pb per m^2 of pipe in contact with water. We assumed that the SANMR was constant in full LSLs as uniform corrosion should be the main mechanism of Pb release in water. However, for partial LSLs, two different corrosion zones were defined based on visual observations of changes in scale composition: (1) non-galvanic and (2) galvanic. Detailed calculations are presented in Chapter 5.

From the galvanic and non-galvanic SANMR in partial LSLs, it is possible to calculate the length of Pb pipe which has to be removed to offset the addition of galvanic corrosion, which increases Pb release.

3.3.4 Scale analysis in full and partially replaced lead service lines

3.3.4.1 Sample preparation and collection

Thirty-nine weeks after the simulation of the PLSLR, for each water quality and for the smaller diameter pipes, one rigs was removed from the pilot to study the short-term impacts of PLSLR on the scale formation. Pipes were shipped to the USEPA's (Environmental Protection Agency) Advanced Materials and Solids Analysis Research Core (AMSARC) laboratory in Cincinnati, Ohio (USA). The interior of the pipes was kept moist for shipping and the ends were caped using rubber stoppers (Schock et al., 2014; Wasserstrom et al., 2017).

To investigate the changes in the long-term, one FLSL and one PLSL for each water quality was then disconnected 155 weeks after the PLSLR. The end of these pipes was also capped, and the interior kept moist until sample collection at Polytechnique Montreal, as summarized in Table 3.4. Only the Cu-Pb and 100%Pb configurations were analyzed at Polytechnique.

Table 3.4 Description of pipes available for scale analysis.

# of weeks after PLSLR simulation	**Pipe disconnected**	**Number of pipes**	**Conditions tested**	**Where analysis was conducted**
39	Cu-Pb	5	Initial water quality, short-term impacts of PLSLR	USEPA
	Pb-Cu	5		
155	Cu-Pb	5	Initial water quality, long-term impacts of PLSLR	Polytechnique
	Pb-Cu	5		
	100%Pb	5		
End of study	Cu-Pb	5	Long-term impacts of PLSLR on the control and smaller diameter conditions. Impact of chlorine on pipes with decreased CSMR and pH increase. Impact of increased orthoP.	
	Pb-Cu	5		
	100%Pb	10		

The exterior of the pipes was carefully washed to remove excess debris. Using a band saw, pipes were sectioned in approximately 30 cm pieces, to ease their manipulation. Pipes were then cut longitudinally, using a band saw (Figure 3.4), to expose the interior (Schock et al., 2008; Wasserstrom et al., 2017). Prior to cutting, tape was wrapped around the compression fitting of the PLSL to keep the pipes from moving.

Figure 3.4 Example of a full LSL being prepared for scale analysis.

Scales were harvested from inside the Cu and Pb pipes, as well as from the compression fitting as described elsewhere (DeSantis et al., 2018; Schock et al., 2014; 2008). Scale layers and galvanic/non-galvanic zones were differentiated based on colour and texture. Figure 3.5 presents the different layers of scale which can be present in FLSL and in PLSL. The outermost layer, which is in contact with the water flowing in the pipe is labelled L1. The number of layers varied from pipe, usually ranging between 2 and 4.

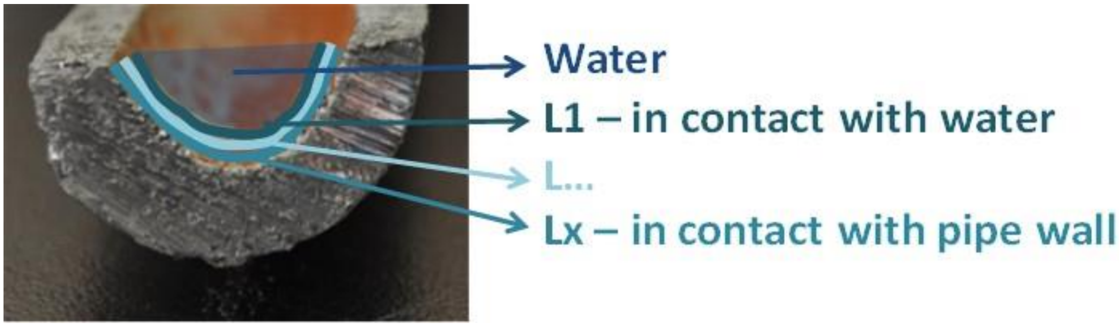

Figure 3.5 Cross-sectional representation of the different layers which can be present in the pipes.

A schematic of the different corrosion zones expected in PLSL is presented in Figure 3.6.

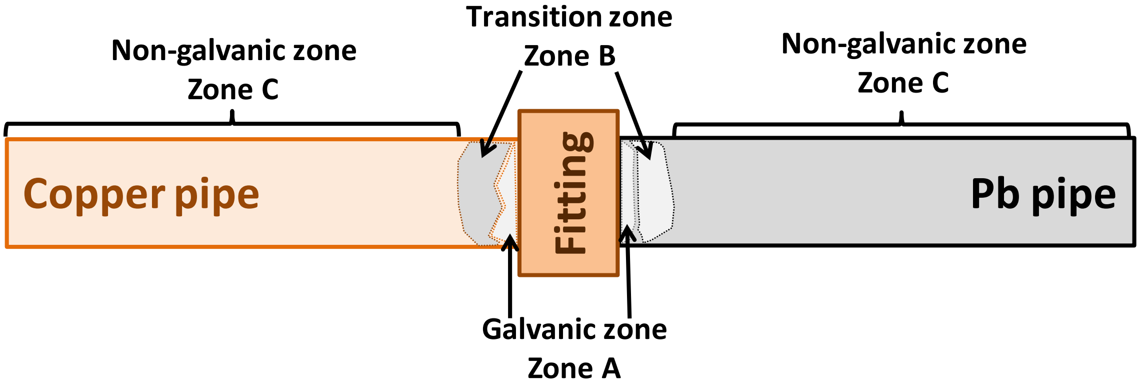

Figure 3.6 Schematic representation of the corrosion zones present in a partial lead service line in the presence of galvanic corrosion.

Before sampling the scale, any shavings left from cutting the pipes were carefully removed using small pliers and toothpicks. Photographs showing the interior of the pipes were taken. Samples were collected in an adapted glove-box to avoid dispersion of lead dust in the laboratory. To better view the differences amongst the scale layers and zones, a stereomicroscope (Zeiss Stemi 305) with a camera (Axiocam) mounted on it was used. Multiple pictures were taken throughout the scale collection to document observations. Due to the curve in the pipes, the software Zerene Stacker was employed to combine multiple pictures with different focus point, resulting in a focused photograph. Scales were collected using small paintbrushes, pliers and scalpel. Using an agate mortar and pestle, samples were finely grounded, until it could pass through a 200-mesh (≤75 μm).

3.3.4.2 Sample analysis

The main crystalline forms present in the samples were analysed using powder X-ray diffraction (PXRD) as described in DeSantis et al. (2018) at the US EPA's AMSARC laboratory. As in DeSantis et al. (2018), samples were loaded in quartz or silicates zero background sample holders (Figure 3.7). When only small amounts of samples could be collected, as in the galvanic zones, a slurry was made with amyl acetate to pipette the samples on a zero-background plate. The amyl acetate was then allowed to evaporate prior to analysis (DeSantis et al., 2018). Amyl acetate was used as it is less likely to dissolve compounds such as sulfate minerals then other alcohols would (Schock et al., 2001). Some of the samples mostly from the galvanic zones or the L1 layer were not sufficient to be analyzed. Scans were performed on a PANalytical X-pert Pro diffractometer and an X'celerator RTMS detector using specifications described in DeSantis et al. (2018). Crystalline forms were identified using JADE software (versions 7-9, Materials Data Inc.) and the ICDD PDF-2 database.

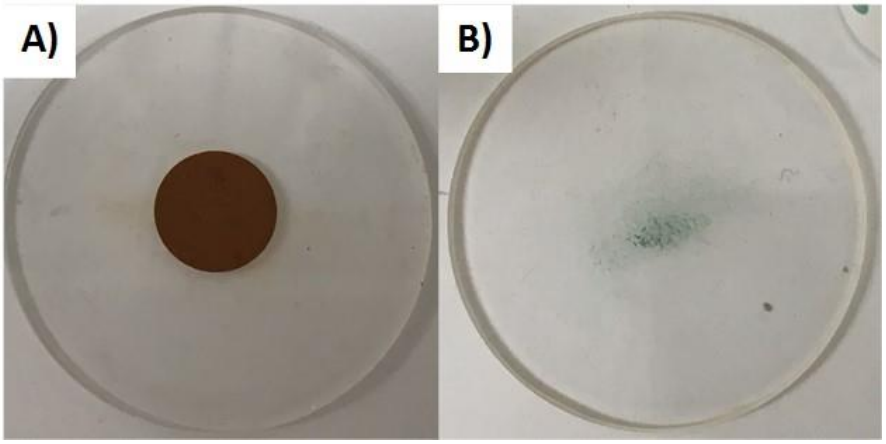

Figure 3.7 Samples mounted on a zero-background plate for XRD analysis: A) Sample placed in the well of the plate, B) Sample mounted using amyl acetate.

Relative abundance of each mineral was estimated based on the relative intensity of the peaks in the XRD patterns. Abundance was classified as major (‘++++’), moderate (‘+++’), minor (‘++), traces (‘+’) or detected (‘D’). If minerals from the environment, such as sand from the exterior wall of the pipe, cuttings from the Pb pipe or the zero-background plate, were detected, they are omitted in the results. The possible presence of amorphous materials is determined by the intensity of the background and by the presence of a rise in the intensity in some locations (DeSantis et al., 2018; DeSantis et al., 2009; Wasserstrom et al., 2017).

CHAPTER 4 ARTICLE 1 – SAMPLING IN SCHOOLS AND LARGE INSTITUTIONAL BUILDINGS: IMPLICATIONS FOR REGULATIONS, EXPOSURE AND MANAGEMENT OF LEAD AND COPPER

In schools and large buildings, a better control of lead and copper concentrations at the drinking water outlet requires a deeper understanding of the sources of contamination in the building as well as the mechanisms at play when water is flushed or stagnates. This chapter seeks to understand the importance of the water quality and the type of outlet in the occurrence of elevated lead and copper concentrations. The effectiveness of flushing the taps is assessed. An evaluation of the impact of drinking water in large building on the BLL of children is also presented. It also compares various recommended sampling protocols and Canada and the United States. Recommendations for sampling lead and copper as well as to decrease their concentrations in water are presented. This paper was published in *Water Research*. Supplementary information is presented in Appendix A.

SAMPLING IN SCHOOLS AND LARGE INSTITUTIONAL BUILDINGS: IMPLICATIONS FOR REGULATIONS, EXPOSURE AND MANAGEMENT OF LEAD AND COPPER

Evelyne Doré[1], Elise Deshommes[1], Robert C. Andrews[2], Shokoufeh Nour[1], Michèle Prévost[1]*

[1]Department of Civil, Mining and Geological Engineering, Polytechnique Montréal, Montréal, QC, Canada

[2]Department of Civil Engineering, University of Toronto, Toronto, ON, Canada

[*]Corresponding author: Tel: 514-340-4711 #3711; Fax: 514-340-5918; email: evelyne.dore@polymtl.ca

ABSTRACT

Legacy lead and copper components are ubiquitous in plumbing of large buildings including schools that serve children most vulnerable to lead exposure. Lead and copper samples must be collected after varying stagnation times and interpreted in reference to different thresholds. A total of 130 outlets (fountains, bathroom and kitchen taps) were sampled for dissolved and particulate lead as well as copper. Sampling was conducted at 8 schools and 3 institutional (non-residential) buildings served by municipal water of varying corrosivity, with and without corrosion control (CC), and without a lead service line. Samples included first draw following overnight stagnation (>8h), partial (30 seconds) and fully (5 minutes) flushed, and first draw after 30 minutes of stagnation. Total lead concentrations in first draw samples after overnight stagnation varied widely from 0.07 to 19.9 µg Pb/L (median: 1.7 µg Pb/L) for large buildings served with non-corrosive water. Higher concentrations were observed in schools with corrosive water without CC (0.9-201 µg Pb/L, median: 14.3 µg Pb/L), while levels in schools with CC ranged from 0.2 to 45.1 µg Pb/L (median: 2.1 µg Pb/L). Partial flushing (30 s) and full flushing (5 min) reduced concentrations by 88% and 92% respectively for corrosive waters without CC. Lead concentrations were <10 µg Pb/L in all samples following 5 minutes of flushing. However, after only 30 minutes of stagnation, first draw concentrations increased back to >45% than values in 1st draw samples collected after overnight stagnation. Concentrations of particulate Pb varied widely (≥0.02-846 µg Pb/L) and was found to be the cause of very high total Pb concentrations in the 2% of samples exceeding 50 µg Pb/L . Pb levels across outlets within the same building varied widely (up to 1000X) especially in corrosive water (0.85-851 µg Pb/L after 30MS) confirming the need to sample at each outlet to identify high risk taps. Based on the much higher concentrations observed in first draw samples, even after a short stagnation, the first 250mL should be discarded unless no sources of lead are present. Results question the cost-benefit of daily or weekly flushing as a remediation strategy. As such, current regulatory requirements may fail to protect children as they may not identify problematic taps and effective mitigation measures.

KEYWORDS: Lead, Copper, Drinking water, Sampling, Large building, School

4.1 Introduction

The exposure of young children to lead from drinking tap water at schools is a serious concern to parents, utilities, school boards and health agencies as intellectual deficits have been reported even at low levels of exposure since it is a neurotoxic (Health Canada, 2013). Sampling protocols and action levels for lead and copper at the tap vary significantly across Canada, the United States and the European Union (Table A.1, in Supplementary information, SI). In Canada and the United

States, the federal government provides recommendations for sampling. Canadian provinces and territories are the regulatory agencies. In the United States, most schools fall under the Lead Contamination Control Act as they are serviced by public water systems (Triantafyllidou & Edwards, 2012). A growing proportion of the states have recently regulated mandatory sampling for lead in schools and child care facilities (Government of California, 2018; New York State, 2018; State of Illinois, 2017). Lead in drinking water in schools is regulated in many provinces and states while this is not the case for copper. Concerns have been raised over the fact that current sampling protocols may not accurately measure total lead concentrations to which a child can be exposed, as they are unable to fully account for particulate lead (Deshommes et al., 2016a; Triantafyllidou et al., 2014) which can represent an important fraction of the total lead in large buildings (Deshommes et al., 2012a; Triantafyllidou et al., 2007). Portable anodic stripping voltammetry, which has been approved by USEPA (Palintest Ltd, 1999; USEPA 2016), has been successfully used to detect lead service lines (LSLs) in houses (Cartier et al., 2012b; Deshommes et al., 2016b). In large buildings, on-site measurements could also be considered as an alternative to reference ICP-MS analyses to detect taps with high lead levels.

Materials for piping, the use of solder as well as the quality of brass varies widely in large buildings (Cartier et al., 2012c; Deshommes et al., 2012a; McIlwain et al., 2015) and these materials can release Pb and Cu in drinking water. Although new standards have lowered the lead content to 0.25% in brass (Health Canada, 2017; U. S. Government, 2011), schools must manage legacy plumbing. Current low lead certification processes have been questioned as certified materials may release more lead than authorized (Elfland et al., 2010; Triantafyllidou & Edwards, 2007).

Water quality, stagnation time and galvanic corrosion directly impact the extent of lead and copper release in large buildings (Boyd et al., 2008a; Cartier et al., 2012c). The solubility of lead and copper is influenced by pH, alkalinity, hardness, temperature, disinfectant residual (oxidation-reduction potential), chloride to sulfate mass ratio (CSMR), dissolved oxygen, natural organic matter (NOM) as well as the addition of phosphates (Schock & Lytle, 2011). Problematic taps, when considering lead and copper, are likely to vary, as critical water quality conditions for dissolved and particulate metals differ (Cartier et al., 2012c; Schock & Lytle, 2011). Alkalinities below 25 mg $CaCO_3$/L and above 75 mg $CaCO_3$/L are associated with the highest copper solubility (Schock et al., 1995).

High and varying lead concentrations have been reported in the literature for large buildings in Canada and the United States since the 1990s (Table A.2). These results should be considered in light of the specific sampling protocols and preservation techniques that were used. A meta-analysis of Canadian schools and large buildings demonstrated the importance of the sampling protocol and stagnation time prior to sampling (Deshommes et al., 2016a). First draw (>8h) 90th percentile lead concentrations reached 11 µg Pb/L (n=31,679 taps) with a maximum concentration of 13,200 µg Pb/L; 90th percentile concentrations measured after 30 minutes of stagnation were lower (4.7 µg Pb/L) but still >400 µg Pb/L in specific worst-case schools investigated. Flushing for 30 seconds prior to sampling reduced the fraction of samples >20 µg Pb/L to 3% in Seattle Public Schools (n=71) (Boyd et al., 2008b; Triantafyllidou et al., 2014). Similarly, this fraction decreased from 6% (1st draw) to 1% (30 s flush) in Los Angeles' schools (n=629) (Sathyanarayana et al., 2006; Triantafyllidou et al., 2014). Finally, concentrations decreased from 71.1 to 5.0 µg Pb/L following flushing in 3 elementary schools in British-Columbia (Barn et al., 2014).

Solder and brass fixtures have been associated with high particulate lead release, accounting for up to 48% of total Pb concentrations (Cartier et al., 2012c; Deshommes et al., 2012a). Correlating high Pb concentrations with other metals, such as Zn and Sn, can confirm brass fixtures as one of the sources of particulate Pb. Frequency of use of the taps also influences Pb concentration with low use fountains releasing more Pb than similar fountains with a higher water use (McIlwain et al., 2015).

The relative contribution of exposure through drinking tap water in schools to blood lead level (BLLs) of young children remains a challenge considering the need to reconstruct plausible exposure and determining the daily water intake. Biokinetic modeling has been used to investigate the potential impact of lead in tap water consumed in schools on the BLL of children (Barn et al., 2014; Deshommes et al., 2016a; Sathyanarayana et al., 2006; Triantafyllidou et al., 2014). Most studies concur that specific large buildings and taps can contribute to BLL exceedances and underline the importance of identifying these buildings and taps to protect vulnerable populations (Barn et al., 2014; Deshommes et al., 2016a; Triantafyllidou et al., 2014). Differences in conclusions reflect: (1) the sampling protocols used, (2) the proportion of the water consumed at school, (3) the Pb concentration of water at home, (4) the proportion of flushed water values incorporated in the daily intake, and (5) the selection of the statistical reference water lead value to establish baseline and exposure scenarios.

The objectives of this study were to: (1) apply a combination of sampling protocols to quantify the source and occurrence of dissolved and particulate lead and copper, (2) investigate the importance of water quality and type of outlets on lead release, (3) document the extent and duration of the benefits associated with flushing (4) establish realistic exposure scenarios by combining results from several sampling protocols, and (5) discuss the efficacy and feasibility of management options to decrease exposure to lead and copper.

4.2 Materials and methods

4.2.1 Building selection and sampling campaign

In May and June 2012, drinking water was sampled in schools and large buildings located in two Canadian provinces. Buildings sampled were served by municipal distribution systems fed by surface water sources. Three types of buildings were sampled: (1) schools without corrosion control (CC) and low alkalinity water (<40 mg $CaCO_3$/L), (2) schools with pH control (pH >8.5) and low alkalinity, and (3) large building complexes with high alkalinity (>70 mg $CaCO_3$/L) moderate pH (pH 7.5-8.0) without CC. In this context, schools were defined as small buildings with 80 to 850 students, large building complexes as multi-storey buildings with an average capacity ranging from 7,000 to 60,000 people. Large buildings B9 and B11 are university complexes, building B10 is a pediatric hospital. There were no LSLs installed in the buildings sampled.

In total, 130 taps were sampled, including fountains, kitchen and bathroom faucets. Table 4.1 shows the number of samples collected, pH, alkalinity and mean temperature, the type of faucets and the year of construction of the building. The aggressivity index (AI) was computed, recognizing that it may not be the best predictor of lead release. AI = pH + log(AH), A being the alkalinity and H the hardness, both expressed as concentration of calcium or as mg/L equivalent $CaCO_3$ (AWWA 1977).

Table 4.1 Information regarding buildings sampled, water quality and number of samples collected per building.

Group of schools	**Building ID**	**Population**	**Construction year (addition of wings)**	**Number of samples collected**	**pH**	**Alkalinity (mg $CaCO_3$/L)**	**AI**	**Free Cl_2 (mg Cl_2/L mean after 10 min of flushing)**	**Temperature (°C, mean after 30 s of flushing)**	**Corrosion control used**
Schools without corrosion control, low alkalinity	B1	80	1924 (1956)	6	7.7	8.5	9.7	0.57	17°C	None
	B2	85	1937 (1956)	6	7.6	NA	NA	0.073	17°C	
	B3	250	1938 (1958, 1977)	9	7.2	NA	NA	0.36	20°C	
	B4	220	1941	6	7.8	NA	NA	0.61	20°C	
	B5	660	1959 (1966, 1971)	10	6.6-7.5	15	9.9	0.44	20°C	
Schools with pH control, low alkalinity	B6	300	1924	10	8.8	36	12.1	0.35	25°C	Remineralisation CO_2 + pH increase (lime)
	B7	430	1957	9	9.2	35	12.6	2.13	22°C	pH increase
	B8	850	1968	10				1.64	23°C	
Large buildings without corrosion control, high alkalinity	B9	7,500	1958 (1975, 1989, 2003)	9	7.6 (6.5-8.0)	86 (77-93)	11.6	NA	17°C	None
	B10	490*	1950	15				0.63	26°C	
	B11	58,290	1907, 1919, 1950, 1960	40	7.5-8.0	85	11.7	0.03	20°C	

*490 beds, pediatric hospital

NA: Not available

4.2.2 Sampling protocol

The sampling protocol included the sequential collection of 5 samples at selected tap. Leaving the aerator in place, a first draw of 250 mL (1S>8h) and second draw sample of 1.75 L (2S>8h) were collected following at least 8h of stagnation. Immediately there after, the water was left running and two additional 250 mL samples were collected; one after 30 seconds of flushing (30sF) and the other after 5 minutes (5minF). Flushing was timed after the second draw (2S>8h) was taken. Therefore, the 30sF sample corresponded more precisely to a sample collected between 30 seconds and 1 minute of flushing. Finally, a stagnation of 30 minutes was performed, and a 250 mL sample was collected (30minS). Following completion of sampling, aerators were removed from kitchen and bathroom faucets such that particles could be collected, where possible.

Water temperature was measured after both 30 seconds and 5 minutes of flushing. All samples were drawn at maximum flow rate (0.8-7.7 LPM for fountains, 0.8-18 LPM for kitchen faucets and 1.6-13 LPM for bathroom faucets) and collected using wide-mouth bottles. Sampling points were allocated across the building. General water quality parameters, including pH, total and free chlorine (Cl_2) and heterotrophic plate count, were evaluated at the closest point to the main water entry and at the point the furthest away, after overnight stagnation and 10 minutes of flushing.

Additional testing was performed at the schools the most at risk of elevated Pb based on their low pH and alkalinity as well as on the absence of corrosion control treatment. During the second day, kitchen faucets (n=7) were sampled according to the procedure described by Deshommes et al. (2010) to stimulate particulate detachment: following overnight stagnation a 1L sample (PSS1) was collected by opening and closing the tap 5 times (reaching maximum flow rate), a second 1L sample (PSS2) was collected using maximum flow rate and a third 1 L sample (PSS3) was collected using the same procedure as for PSS1.

4.2.3 Analytical methods

Water samples were analyzed for total and dissolved lead, copper, zinc, tin, and iron. A 40 mL aliquot was immediately filtered (0.45 µm). For digestion of colloids and particles, samples were acidified within 36 hours, using 2% ultra pure HNO_3 for total metals, and 0.5% ultra pure HNO_3 for dissolved metal samples as modified from Triantafyllidou et al. (2007). Analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS) based on the EPA 200.8 protocol.

Detection limits were 0.02 µg Pb/L, 0.06 µg Cu/L, 0.2 µg Zn/L, 1 µg Sn/L, 0.9 µg Fe/L. On site, temperature and pH were measured using a Hach SensIon-1 portable pH meter, total and residual chlorine using a Hach Pocket Colorimeter^{TM} II.

4.2.4 Statistical analysis and IEUBK modeling

Non-parametric statistical analyses, including MARSpline analyses and Kruskal Wallis ANOVA tests, were performed in Statistica Version 13 (StatSoft, OK, USA). Differences were considered significant if $p < 0.05$, unless stated otherwise. The USEPA IEUBK (version win1_1 Build11) model was used to predict the BLLs for children 5-7 years old as described by Deshommes et al. (2016a) when considering Canadian inputs for lead sources other than water. Tap water intake at school was attributed to be 50% of the daily water intake.

4.3 Results and discussion

4.3.1 Lead and copper concentrations per type of sampling protocol

The overall distribution of total, dissolved and particulate lead as well as copper concentrations and the percentage of particulate content are presented in Figure 4.1. The highest Pb and Cu concentrations were observed in the first 250 mL sampled following overnight stagnation (1S>8h). Subsequently, as water was flushed, concentrations decreased. Lead concentrations after extended stagnation (>8h) and short stagnation (30min) periods are statistically different, whereas they are similar for copper (Kruskal-Wallis ANOVA test).

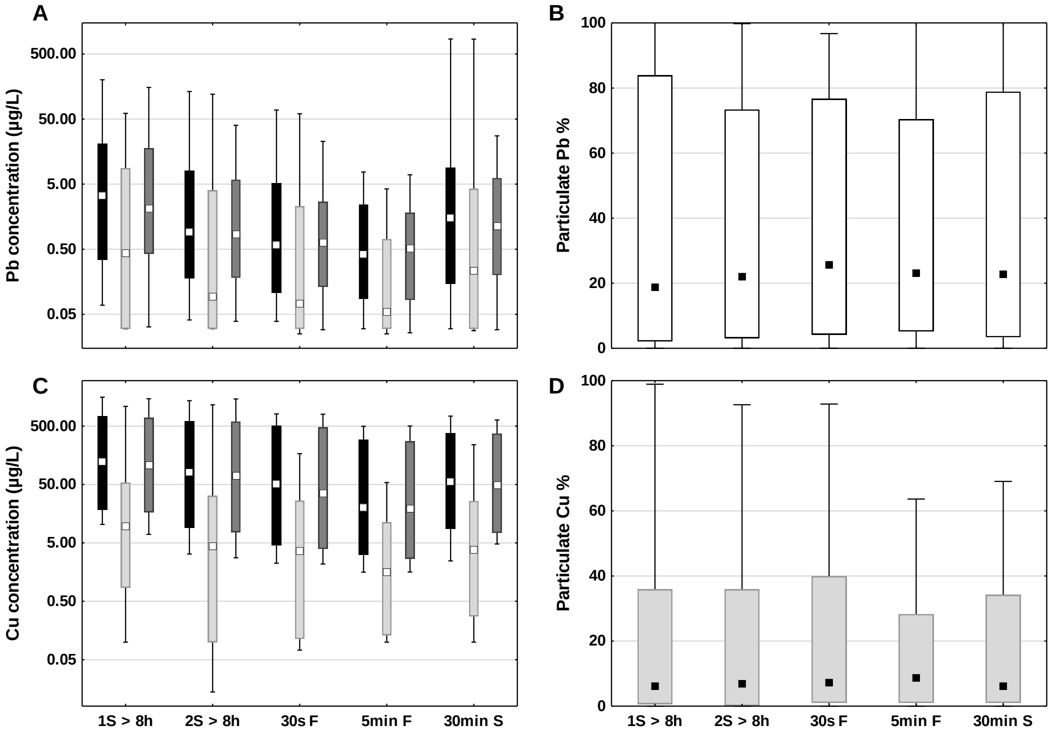

Figure 4.1 Total, particulate and dissolved lead (A) and copper (C) concentrations (in black, light grey and darker grey), and fraction of particulate Pb (B) and Cu (D), for 1st draw samples collected following overnight stagnation (1S>8h, 250 mL) and 2nd draw (2S>8h, 250 mL), 30 seconds (30sF, 250 mL) and 5 minutes (5minF, 250 mL) of flushing and 30 minutes of stagnation (30minS, 250 mL) (n=130).Whiskers represent min-max values, boxes 10th-90th percentiles, and the square represents median concentrations.

Among the various samples, 90th percentile concentrations were highest in the first (21 µg Pb/L) and second (8.1 µg Pb/L) draws following an extended (>8h) stagnation. Levels decreased to 5.2 and 2.4 µg Pb/L after flushing for 30 seconds and 5 minutes and increased to 8.9 µg Pb/L after 30 minutes of stagnation. The median and 90th percentile concentrations following 30 minutes of stagnation represented 45.2% and 42.8% of those following extended stagnation. The highest lead concentration was observed after 30 minutes of stagnation (850 µg Pb/L) of which 99.4% was $Pb_{particulate}$. These results follow expected trends of a decrease of Pb_{total} as water is flushed from the tap (Barn et al., 2014; Boyd et al., 2008b; Cartier et al., 2012c; McIlwain et al., 2015;

Triantafyllidou et al., 2014). Figure 4.1 also shows large variability for a given type of sample, typically exceeding one order of magnitude.

Wide variability between taps was observed in schools which received aggressive water in a community in British-Columbia (Canada), as shown by first draw Pb_{total} concentrations ranging from 5.9-306 µg Pb/L (Barn et al., 2014). Larger datasets from across Canada indicate an even greater variation of over 4 orders of magnitude (Deshommes et al., 2016a). In the current study, short 30 seconds flush decreased lead and copper concentrations by 81% and 59% respectively from first draw samples, while elevated concentrations continued to occur. First draw 90th percentile concentrations of 738 µg Cu/L decreased to 502 µg Cu/L after a 30 seconds flush and to 381 µg Cu/L after 30 minutes of stagnation. Approximately 78% of our first draw samples exceed the California Public Health Goal (PHG) of 300 µg Cu/L.

Figure 4.2 shows the variability of Pb and Cu concentrations at each of the tap of the 11 buildings sampled (B1-B11). Firstly, lead and copper concentrations at a given tap can vary up to 415-fold for lead up to 39-fold for Cu depending on the sampling protocol used and the presence of particulate metals. Furthermore, within a given school, the median concentrations measured at the different outlets can vary by 114-fold for Pb and 202-fold for Cu, regardless of the groups of buildings considered. Lower corrosivity clearly decreases all Pb and Cu concentrations observed, but elevated Pb taps remain as shown in building B8. These results reinforce the need to sample at every outlet used for drinking water, with the objective of identifying taps at risk of elevated concentration of lead and/or copper.

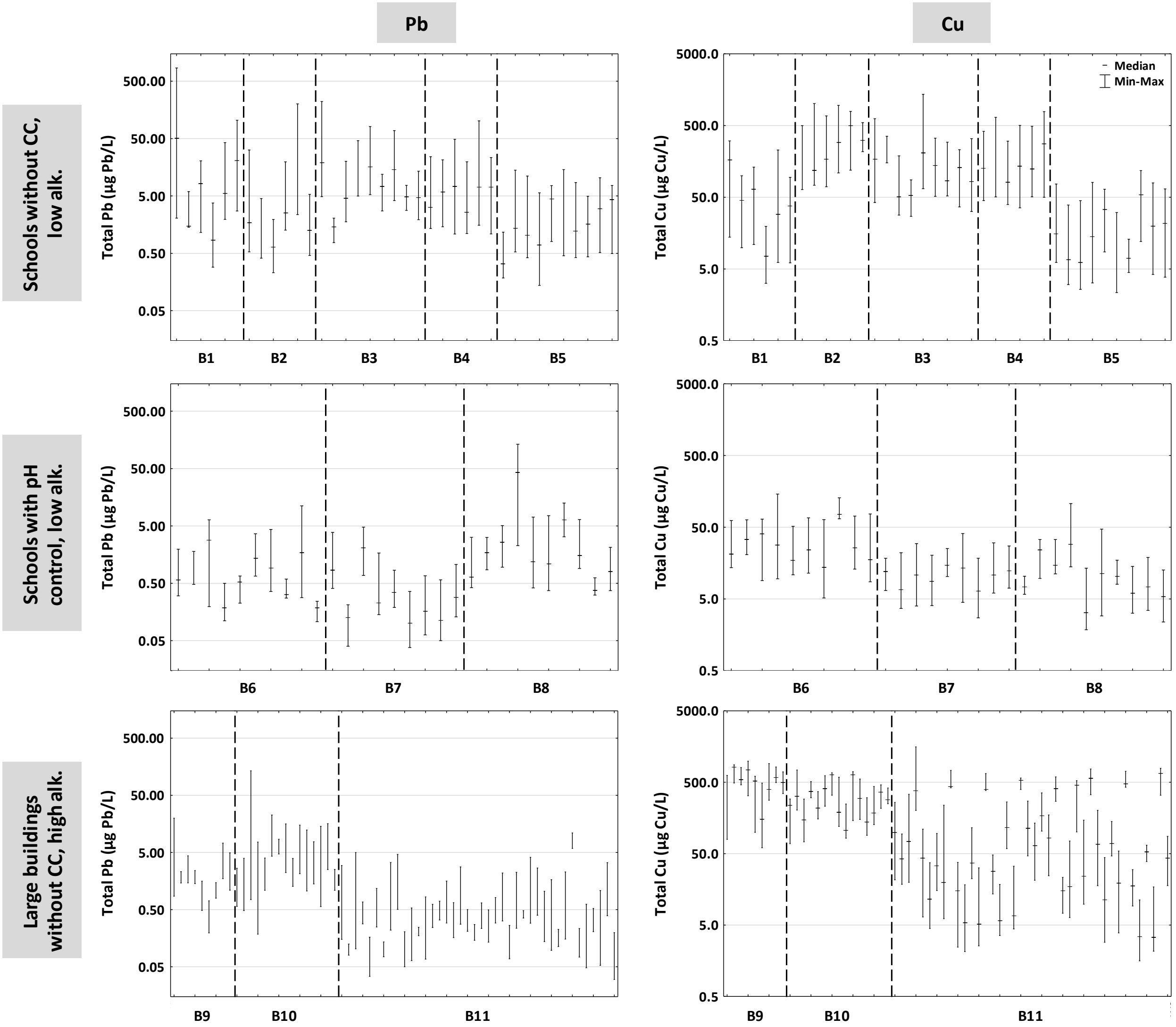

Figure 4.2 Total Pb and Cu concentrations (µg/L) for all taps sampled in schools without corrosion control, low alkalinity (A for Pb and B for Cu), with corrosion control (C for Pb and D for Cu) and large buildings (E for Pb and F for Cu). Whiskers represent the min-max values and the line the median concentrations for the 5 samples collected at each tap, after stagnation (1S>8h, 2S>8h, 30minS) and flushing (30sF, 5minF). Vertical dotted lines separate the buildings sampled (B1 to B11).

4.3.2 Water quality and type of faucet

Overall, results show that the first 250 mL collected following 8h stagnation contains significantly higher Pb levels, suggesting that the faucet and its connecting piping are dominant lead contributors in the buildings sampled. The internal volumes of faucet can vary between 24 and 106 mL (Cartier et al., 2012c) and tank volume of fountain have been estimated to be <750 mL (McIlwain et al., 2015).

Lead levels measured were the highest in schools which received low pH and low alkalinity water per type of tap (Figure 4.3) with median and 90th percentile respectively, of 3.0 and 21.1 µg Pb/L for fountains, 4.7 and 47.4 µg Pb/L for kitchen taps and 3.0 and 175 µg Pb/L for bathroom taps. This group of buildings is statistically different from the other two ($p < 0.05$). Similar to Murphy (1993), corrosive water (low AI) was associated with the highest lead release. After overnight stagnation, median first draw concentrations measured in fountains (13.8 µg Pb/L, Figure A.1B) were similar to values reported by the same author (15 µg Pb/L) for similar water corrosivity. When considering the schools investigated, first draw (1S>8h) median lead concentration in locations serviced by water with high alkalinity and with pH adjustment were 78 times lower (1.7 – 133 µg Pb/L). Therefore, CC treatment can effectively be used to decrease lead concentrations in buildings.

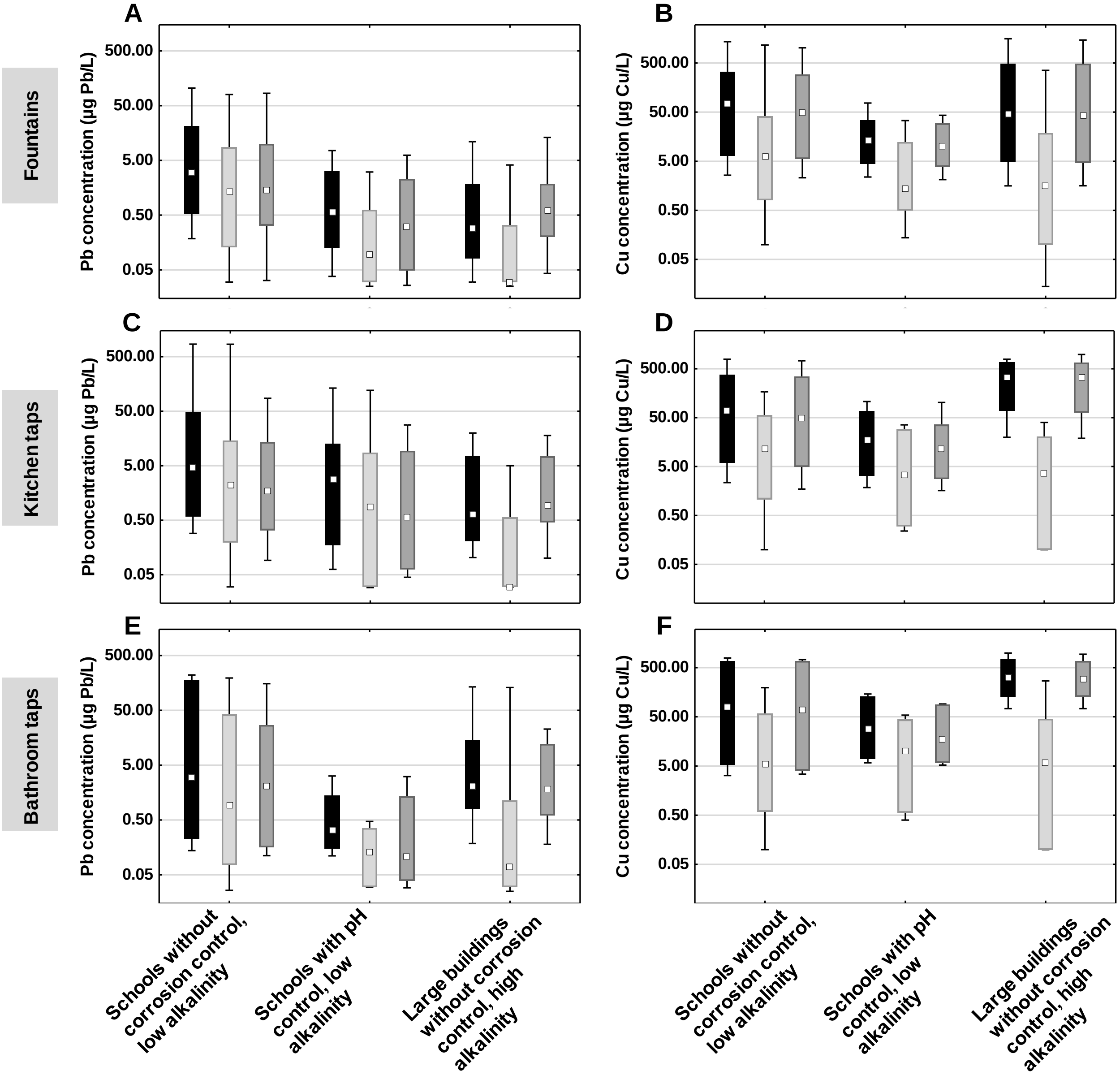

Figure 4.3 Total, particulate and dissolved lead and copper (in black, light grey and dark grey) for (A, B) fountains (n=385), (C, D) kitchen (n=140) and (E, F) bathroom (n=125) taps as a function of specific groups of buildings (all samples combined).

Median and 90th percentile copper concentrations were generally higher in the large building group (141 and 619 µg Cu/L) when compared to schools with (13.7 and 63.5 µg Cu/L) and without (73.5 and 415 µg Cu/L) CC (Figure 4.3 and Figure A.2). In contrast to total Pb concentrations which were generally the highest in schools without CC, copper levels overlap between the various water qualities investigated and between the different types of samples (Figure A.2). This suggests that the sources of copper are more widespread (confirmed by the frequent presence of copper piping) or different within the buildings water system than the sources of lead. This is also consistent with the fact that it takes a longer flushing time to decrease copper concentrations when compared to lead (Barn et al., 2014). As expected, and previously reported by Murphy (1993), AI is not a useful predictor of copper concentrations since the factors influencing lead and copper corrosion differ. Copper corrosion increases at alkalinities below 25 mg $CaCO_3$/L and above 75 mg $CaCO_3$/L (Schock et al., 1995), which cannot be determined by the AI.

4.3.3 Impact of flushing

The percentage of samples >10 µg Pb/L decreases with flushing (Table 4.2) in agreement with previous studies (Cartier et al., 2012c; Deshommes et al., 2016a; McIlwain et al., 2015; Triantafyllidou et al., 2014). First draw samples in schools without CC most frequently (65%) exceeded 10 µg Pb/L regardless of the type of tap. The percentage exceedance decreased to 22% in the second 1.75L draw after 8h stagnation; a short 30s flush resulted in a further reduction to 14%, as observed in Bryant (2004). In schools supplied by water with pH control, only kitchen taps exceeded 10 µg Pb/L in first draw samples (43%), while fountains and bathroom taps remained <10 µg Pb/L, even following overnight stagnation.

Table 4.2 Percentage of samples with total Pb concentrations greater than 10 µg Pb/L and greater than 5 µg Pb/L (in brackets), all types of samples considered at each type of tap and building.

	Mean pH	**Mean alkalinity (mg $CaCO_3$/L)**	**AI**	**Type of taps**	**1S>8h (1st 250 mL)**		**2S>8h (1.75 L)**		**30sF (250 mL)**		**5minF (250 mL)**		**30minS (250 mL)**	
Schools, without corrosion control, low alk. n=37	7.0	15	9.8	**Bathroom n=5**	65% (78%)	60% (80%)	22% (51%)	40% (60%)	14% (22%)	20% (40%)	0% (5%)	0% (0%)	22% (51%)	40% (40%)
				Fountain n=20		65% (75%)		20% (35%)		10% (15%)		0% (10%)		10% (43%)
				Kitchen n=12		67% (83%)		17% (75%)		17% (25%)		0% (0%)		33% (67%)
Schools, with pH control, low alk. n=29	9.1	35	12.4	**Bathroom n=3**	10% (28%)	0% (0%)	3% (7%)	0% (0%)	0% (3%)	0% (0%)	0% (0%)	0% (0%)	3% (7%)	0% (0%)
				Fountain n =19		0% (16%)		0% (0%)		0% (0%)		0% (0%)		0% (0%)
				Kitchen n=7		43% (71%)		14% (29%)		0% (14%)		0% (0%)		14% (29%)
Large buildings without corrosion control, high alk. n=64	7.7	86	11.7	**Bathroom n=17**	11% (19%)	35% (53%)	2% (9%)	6% (18%)	5% (6%)	12% (12%)	0% (2%)	0% (0%)	5% (13%)	18% (35%)
				Fountain n=38		0% (3%)		0% (3%)		3% (3%)		0% (3%)		0% (3%)
				Kitchen n=9		11% (22%)		0% (22%)		0% (11%)		0% (0%)		0% (11%)

Periodical flushing at taps used for consumption has been proposed as a remediation method (Government of Ontario, 2010; Health Canada, 2009; USEPA 2006a). Prior investigations document the efficacy of a short flush (30 seconds) in decreasing lead concentrations in schools. When sampling fountains in Seattle, 33% of first draw samples exceeded 10 µg Pb/L down to 7% after a 30 second flush (Boyd et al., 2008b). The effectiveness of flushing varied within each school in British-Columbia (Canada) and reduced more lead than copper (Barn et al., 2014). Flushing taps for 10 minutes in the morning did not result in lead and copper reductions throughout the day in schools in New Jersey (Murphy, 1993), questioning the benefits from flushing. Considered together, these results show the benefits of avoiding the very first draw (after both a short or extended stagnation) and of flushing to reduce the proportion of samples with elevated lead. However, this mitigation method is not effective in reducing lead levels in all taps since a significant proportion of them still exceed 10 µg Pb/L.

Considering the health based standard of 5 µg Pb/L recently proposed by Health Canada (2017) schools with adequate CC in this study had Pb levels that were lower in most samples, except the first 250 mL after 8h stagnation (Table 4.2). Finally, considering the American Academy of Pediatrics (AAP) proposed level of 1 µg Pb/L, only the fully flushed (5 minutes) samples in schools with pH adjustment would meet this low threshold at most taps (93%) (Table A.3).

Similar to lead, copper concentrations also decrease when taps are flushed. The maximum concentration measured after 5 minutes of flushing in this study (784 µg Cu/L) is 10-fold lower than that reported by Barn et al. (2014) for elementary (10,700 µg Cu/L) and secondary schools (7,000 µg Cu/L) following a 10 minute flush. This reinforces the fact that the impact of flushing can vary depending on the building and water quality, as also reported by Murphy (1993) for a 10 minute flush. In schools without CC, the median concentration in first draw samples collected from fountains following a 30 minute stagnation (81.7 µg Cu/L) was 35.6% of that observed after extended overnight stagnation (229 µg Cu/L).

When considering all samples collected, 90th percentile concentrations at fountains (331 µg Cu/L) exceed the Californian PHG (300 µg Cu/L) for schools without CC and having low alkalinity, as well as large buildings without CC and high alkalinity (482 µg Cu/L) (Table 4.3). Flushing the first 250 mL decreased the 90th percentile concentrations to 215 µg Cu/L in the schools without CC and low alkalinity. However, in the large buildings, flushing the stagnated water did not reduce the 90th percentile copper concentrations below 300 µg Cu/L. For schools with pH control and low alkalinity, all concentrations were <300 µg Cu/L (maximum: 146 µg Cu/L).

Table 4.3 Median, 90th percentile and maximum total Pb and Cu concentrations for a given type of tap and group of building for all the samples, in µg/L.

		Total Pb (µg Pb/L)			**Total Cu (µg Cu/L)**		
		Schools without CC, low alk.	**Schools with pH control, low alk.**	**Large buildings without corrosion control, high alk.**	**Schools without CC, low alk.**	**Schools with pH control, low alk.**	**Large buildings without corrosion control, high alk.**
Fountains	**Median**	3.0	0.56	0.30	73.4	13.2	46.0
	w/o 1st draw (250mL)	2.3	0.47	0.27	53.8	10.9	38.2
	w/o 1st 2L	2.1	0.41	0.25	48.9	9.2	35.8
	w/o 1st draw & 30minS (250mL)	2.0	0.41	0.24	50.9	10.3	31.9
	w/o 1st 2L and 30minS (250 mL)	1.7	0.37	0.22	39.1	7.4	22.9
	90th percentile	21.1	3.2	1.9	331	33.7	482
	w/o 1st draw (250mL)	10.1	2.0	1.2	215	24.6	453
	w/o 1st 2L	8.3	2.1	1.4	189	21.2	440
	w/o 1st draw & 30minS (250mL)	9.4	1.3	0.82	201	27.9	460
	w/o 1st 2L and 30minS (250 mL)	5.6	1.1	0.70	128	20.7	440
	Max	105	7.6	11.0	1364	76.6	1566
	w/o 1st draw (250mL)	80.9	4.8	11.0	1364	63.5	1233
	w/o 1st 2L	46.0	4.8	11.0	301	33.5	662
	w/o 1st draw & 30minS (250mL)	80.9	4.6	11.0	1364	63.5	1233
	w/o 1st 2L and 30minS (250 mL)	33.5	2.1	11.0	206	33.5	662
Kitchen taps	**Median**	4.7	2.8	0.65	68.4	17.1	337
	w/o 1st draw (250mL)	3.9	1.5	0.47	65.0	12.6	329
	w/o 1st 2L	1.7	1.4	0.59	50.4	11.5	290
	w/o 1st draw & 30minS (250mL)	1.7	1.4	0.40	64.4	12.2	330
	w/o 1st 2L and 30minS (250 mL)	1.1	0.66	0.40	49.1	10.2	300
	90th percentile	47.4	12.5	7.6	376	67.6	672
	w/o 1st draw (250mL)	46.2	7.6	7.5	306	65.0	632
	w/o 1st 2L	46.2	6.5	4.7	216	29.1	595
	w/o 1st draw & 30minS (250mL)	11.9	7.2	7.5	306	40.7	655
	w/o 1st 2L and 30minS (250 mL)	8.3	4.8	4.7	203	25.9	632
	Max	851	133	19.9	782	107	784
	w/o 1st draw (250mL)	851	133	8.5	494	93.4	784
	w/o 1st 2L	851	43.4	7.7	310	65.0	672
	w/o 1st draw & 30minS (250mL)	72.5	133	8.5	494	93.4	784
	w/o 1st 2L and 30minS (250 mL)	69.0	7.2	7.5	281	40.5	672
Bathroom taps	**Median**	3.0	0.33	2.1	80.7	28.1	316
	w/o 1st draw (250mL)	2.0	0.31	1.8	70.4	21.2	277
	w/o 1st 2L	1.3	0.32	1.8	70.1	14.3	271
	w/o 1st draw & 30minS (250mL)	1.6	0.31	1.6	70.1	14.3	247
	w/o 1st 2L and 30minS (250 mL)	0.64	0.31	1.4	56.1	11.9	223
	90th percentile	176	1.4	14.3	682	129	741
	w/o 1st draw (250mL)	34.4	0.65	8.0	563	109	697
	w/o 1st 2L	43.1	1.4	7.4	235	75.9	586
	w/o 1st draw & 30minS (250mL)	19.1	0.65	4.5	623	145.5	697
	w/o 1st 2L and 30minS (250 mL)	10.4	0.52	4.3	320	75.9	529
	Max	221	3.2	134	787	146	989
	w/o 1st draw (250mL)	221	1.4	134	787	146	878
	w/o 1st 2L	221	1.4	134	502	75.9	134
	w/o 1st draw & 30minS (250mL)	25.7	0.65	22.6	787	145.5	878
	w/o 1st 2L and 30minS (250 mL)	15.3	0.52	22.6	502	75.9	808

4.3.4 Particulate lead and copper

Figure 4.4 shows the distributions of the concentrations and fractions of particulate lead (Figure 4.4 A and B) and copper (Figure 4.4 C and D). Schools without CC present the highest particulate lead and copper concentrations, with 90th percentile concentrations of 14 µg Pb/L and 54 µg Cu/L. These values are considerably lower than prior reports for a large penitentiary complex serviced with corrosive water and with low water usage (90th percentiles of 98 µg Pb/L and 2,720 µg Cu/L for drinking fountains) (Cartier et al., 2012c). The Pb_{part} and Cu_{part} fractions were the lowest for large buildings with 56% and 17.9%, respectively, of non-detectable particulate corresponding to low Pb_{part} concentrations (median 0.03 µg Pb/L – 10.7%). Higher median Pb_{part} were present at taps with low alkalinity water with (0.17 µg Pb/L – 26.5%) and without (1.55 µg/L – 37%) CC. These results illustrate that high particulate fractions are not necessarily associated with elevated lead levels.

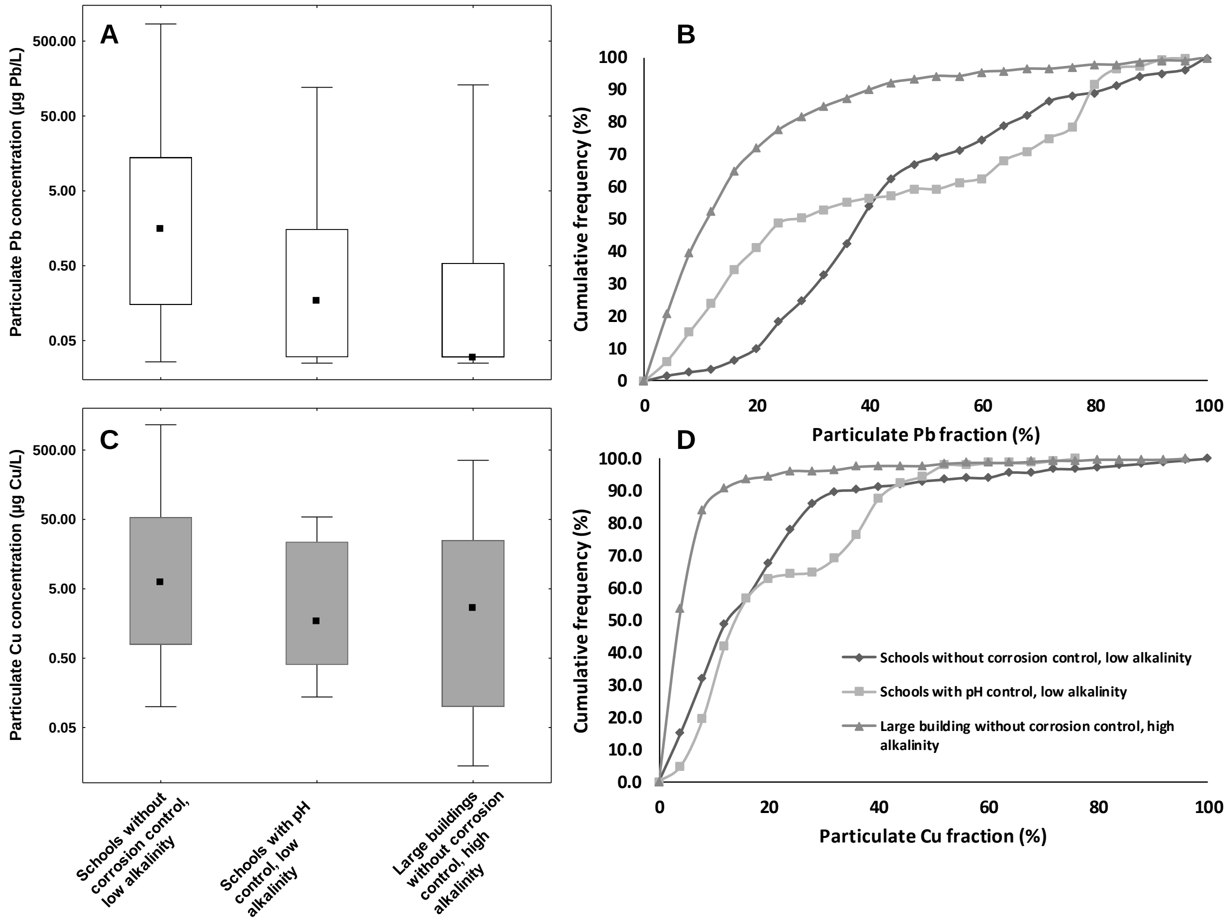

Figure 4.4 Particulate lead and copper concentration (A, C) and fraction (B, D) presented as cumulative frequency for each type of building sampled. For A and C, the dark square represents the median, boxes represent the 10-90th percentiles, and whiskers the non-outlier range (n=130).

For the 13/650 samples that exceeded 50 µg Pb_{total}/L, the particulate fraction ranged from 15.2% to ≥99.9%. Interestingly, 11 of the 13 high concentrations samples were detected in schools supplied with low alkalinity water without CC. The particulate fraction exceeded 87% in most of (8/13) of the elevated samples, while 4 samples contained mainly Pb_{diss} (15-24% Pb_{part}). Higher particulate median concentrations and fractions were present at the taps without CC (6.3 µg Pb/L – 12.2%) in comparison to those with low alkalinity water with pH control (1.7 µg/L – 13.8%) and large buildings with high alkalinity (2.6 µg/L – 3.6%). For the 5/650 samples that exceeded 1,000 µg Cu_{total}/L, the particulate fraction ranged from 0.1% to ≥99.9%. These were all detected in fountains following a period of extended stagnation. Furthermore, the two samples for which Cu_{part}

was elevated (≥ 84.9%) also showed high particulate Pb and Zn, indicating galvanic corrosion of leaded brass as a probable source of both the particulate Pb concentrations and fractions.

In this study, particulate Pb concentrations and fractions were considerably lower than reported previously for a penitentiary complex (50 µg Pb/L vs 2.1 µg Pb/L and 48% vs 14%), where it was found to be twice the concentration of Pb_{diss} (Deshommes et al., 2012a). Such a relationship cannot be observed at the points sampled. In this study, only one sample collected at a kitchen faucet after 30 minutes of stagnation exceeded the acute single dose equivalent concentration of 580 µg/L (USCPSC, 2005).

4.3.5 Particulate simulation sampling

When considering schools with low pH water and alkalinity, 7 taps were re-sampled on the second day of sampling, using a protocol designed to stimulate particulate release from the taps (Figure 4.5). On the first day of sampling, the taps were flushed for 5 minutes. The following day, when sampling for the PSSs, concentrations >10 µg Pb/L were observed in the first 2 liters sampled at high flow rate. Total lead concentrations were highest in the second sample collected. When combining samples 1S>8h and 2S>8h (first 2L from day 1), a weighted average of 15.2 µg Pb/L was obtained with most of the Pb being contributed by the 1st sample (250 mL). The weighted average is comparable to the mean concentration obtained when PSS1 and PSS2 are combined (16.2 µg Pb/L). Disturbances in the sampling flow rate did not increase the lead release and mean lead concentrations in the 3rd liter (PSS3) were lower than in PSS1 and PSS2, again showing the benefits of avoiding the first draw volume. Disturbances in flow rate during sampling have been shown to increase the detachment of small colloids (<0.45 µm) from scales formed inside LSLs of single-family homes, whereas lead particles from solders and brass fixtures were released in first draw samples (Deshommes et al., 2010). The difference observed in this study could therefore be explained by the nature and source of the particles re-suspended in water with hydraulic disturbances and the premise plumbing.

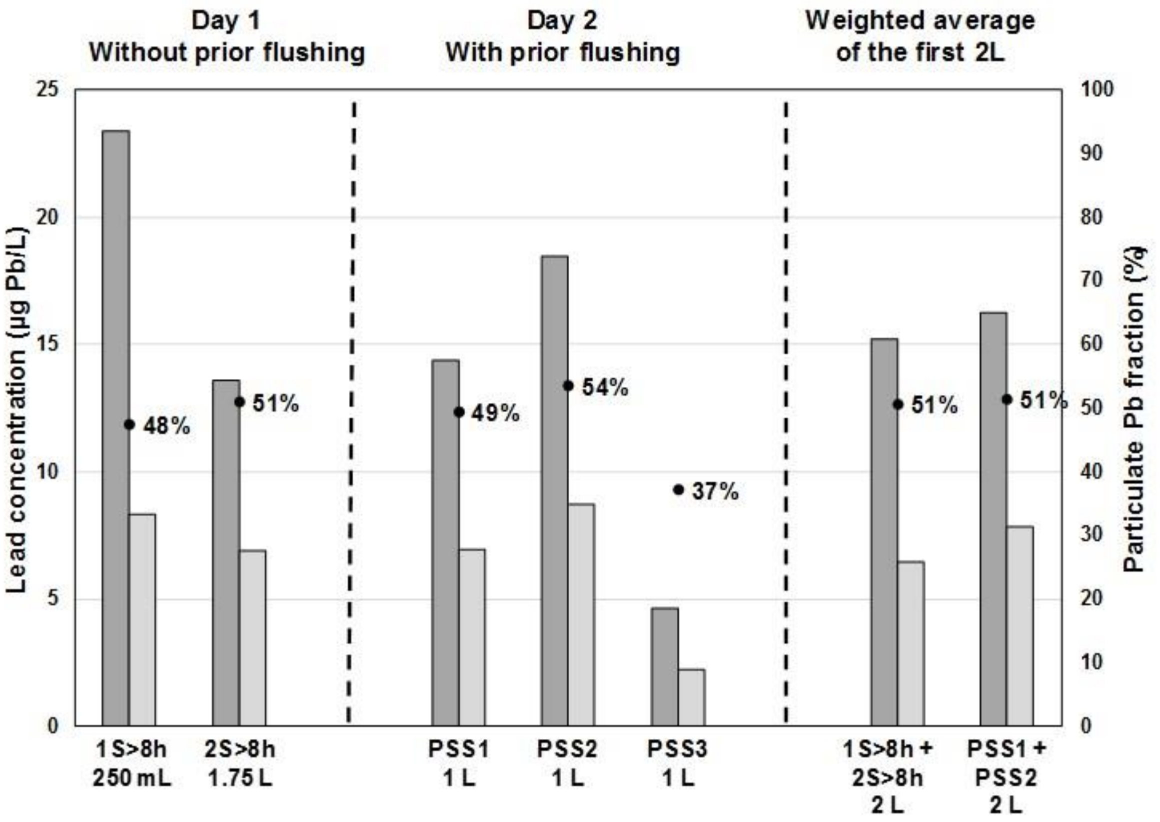

Figure 4.5 Mean total and particulate lead concentrations (in dark and light grey) for kitchen taps sampled in elementary schools receiving low pH and low alkalinity water (N=7 taps in 5 schools). Black dots represent the mean Pb particulate fraction as a percentage.

4.3.6 Contributors to lead and copper concentrations

MARSpline regressions were conducted to identify the factors which impact lead and copper concentrations when considering metal analyzed (total and particulate Pb, Fe, Sn, Zn and Cu), sampling point, group of building/water quality, school and type of taps, and flow rate (Table A.4). Following overnight stagnation, the building and specific point of sampling were the dominant factors predicting Pb_{total}, followed to a lesser degree by other total metals (Sn>Zn-Fe>Cu). If only concentrations exceeding 5 or 10 µg Pb/L are considered, the relative contribution of Sn_{total}, indicative of the contribution of leaded solder, increases. Following a 30 second flush, multiple metals become important (Fe>>Zn-Sn>Cu) revealing multiple sources of lead. The strong contribution of iron potentially reflects the impact of water quality defining the combined level of iron release from the iron water mains in the building, as well as lead release from both solders and leaded brass. Following extended flushing, the dominant contribution of Sn was no longer present, with Cu and Zn becoming the most important factors along with the specific sampling point and building. As such as, the 5 minute flushed sample cannot be used to detect the contribution of leaded solders. When considering a shorter (30 min) stagnation, tin becomes the dominant factor over building, reflecting the contribution of solders at the tap and its connecting plumbing. Unlike the 8h stagnation particulate samples, only tin and not copper were associated with elevated Pb_{part} after a shorter stagnation. This suggests that a 30 minute stagnation can be used to detect the contribution of lead from distal solders.

Pb_{part} is best predicted when considering different factors than those for Pb_{total} including Cu_{part}, sampling point and Sn_{part}; leaded brass and solder both generated lead particles. Factors associated with Pb_{part} following short (30 min) and overnight stagnation suggest that different mechanisms are at play in the release of Pb_{part}. Following overnight stagnation, all particulate metal concentrations are considered to be factors associated with Pb_{part} (Cu>Sn>>Fe>Zn) as well as the sampling point, the group of buildings, the buildings, and taps.

In large buildings, the main sources of copper are copper piping and brass fixtures. Following overnight stagnation and 30 minute stagnation, the building, sampling point, and zinc concentrations are dominant factors explaining in copper concentrations. As such, the sources of copper in the buildings are leaded brass components. For flushed samples (30sF), the group of buildings represents the main factor for predicting copper concentrations. Sampling point, Pb and Zn concentrations remain important predictors. For fully flushed samples (5minF), the sampling point, building, and water quality are important predictors, as well as the other metals measured (Pb>Fe>Zn>Sn), indicating that the sources of copper are different and could come from solder.

4.3.7 Blood lead levels modelling and copper intake

Drinking water consumption scenarios typically assume that children consume 50% of their daily intake at home and 50% at schools (Triantafyllidou et al., 2014), with a house lead concentration of 2 µg Pb/L (Deshommes et al., 2016a). As the statistical analysis confirmed the overwhelming importance of the sampling point and building, we elected to use mean values from all 90th percentile concentrations, including first and second draw after extended stagnation, partially and fully flushed samples and samples after a short 30 min stagnation. A measurable impact of water consumption while at school on the GM BLLs is seen in schools without CC and low alkalinity

(Figure 4.6). For this case, avoiding the first draw 250 mL results in a 21.7% decrease of the GM BLL (to 2.16 µg/dL without 1S>8h) and of 38.7% (to 1.69 µg/dL without both 8h and 30minS). Avoiding all first 250 mL draw is not as beneficial when pH adjustment is practiced (7.8% GM BLL) or for high alkalinity waters (10.5%). Modelled BLLs are comparable to those reported by Deshommes et al. (2016a) who showed that lead at the tap could cause elevated BLL in some children and, in some cases, a rare but concerning risk of acute exposure. Our detailed sampling results confirm the need to use a sampling protocol capable of identifying outlets with elevated lead.

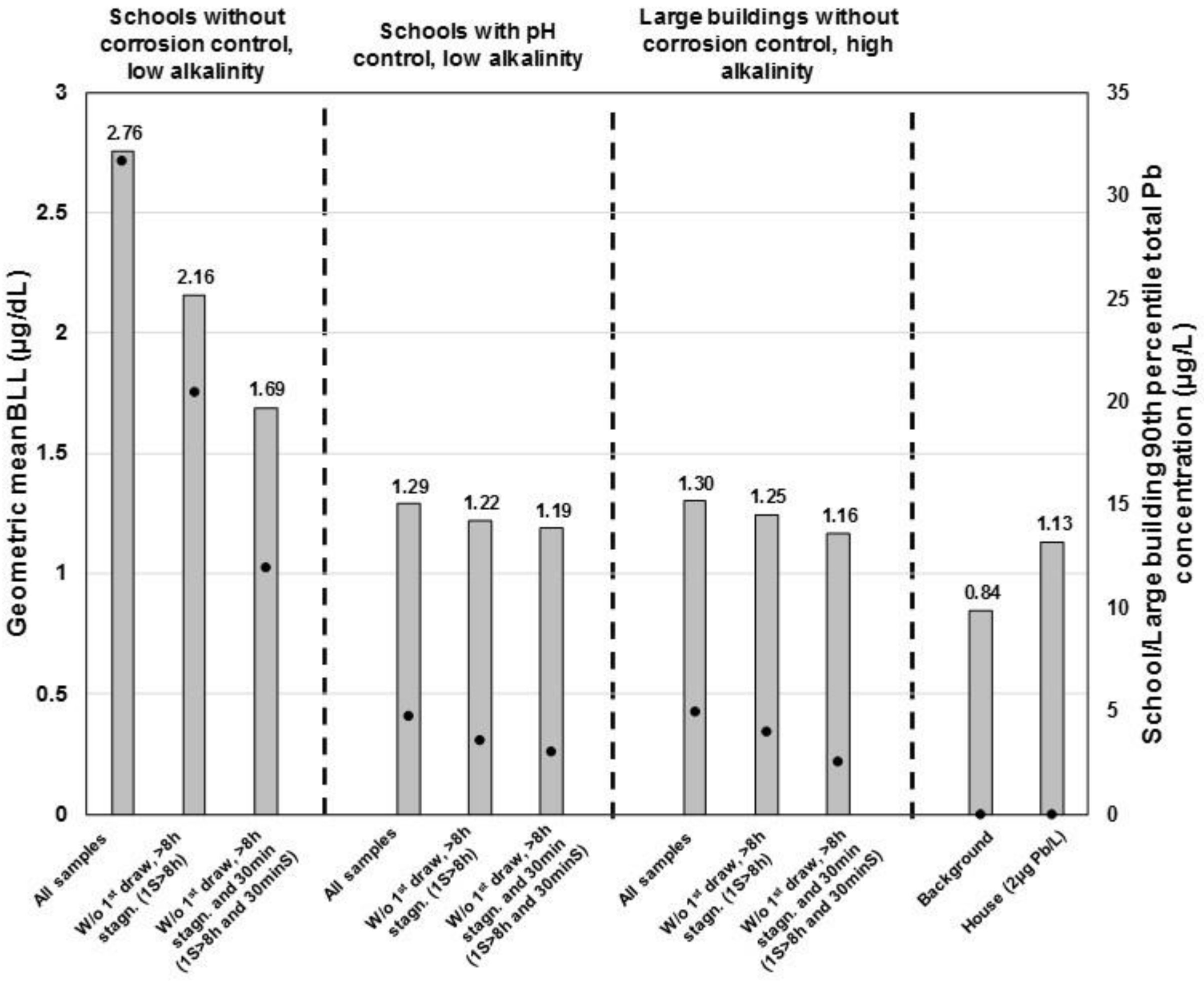

Figure 4.6 Geometric mean BLL (grey boxes) for children of age 5-7 years for each group of buildings, modeled using 90th percentiles total Pb concentrations observed in school tap water (black dots).

The impact of Cu from drinking water from large buildings can be assessed by considering the fraction of the daily intake versus the recommended daily allowance and the tolerable upper intake level recommended for children aged between 4 and 8 years old. Health Canada, WHO and the State of California refer a daily allowance of 340 µg/d and a tolerable upper intake level of 3,000 µg/d (California EPA, 2008). The median exposure for all buildings sampled represented 37.7% of the recommended daily allowance and reached 83.1% in the case of large buildings group. Using the 90th percentile values, the daily intake of copper from drinking water exceeded the total daily recommended allowance in all but one group of schools with corrosion control, but did not exceed the tolerable upper level intake. Most observed copper levels represent a significant fraction of the recommended total daily allowance that should be avoided in the case of formula fed infants (California EPA, 2008).

4.3.8 Possible remedial actions

Various actions can be considered to lower lead exposure at the tap in schools and large buildings and to guide sampling.

4.3.8.1 Replacement of leaded components

As observed in Boyd et al. (2008b), the removal of lead containing components in fountains and faucets, as well as their connecting piping resulted in the removal of the distal volume in which the highest lead concentrations were systematically measured. Despite replacing these taps and their connecting piping, the remaining sources such as leaded solders and brass and, in rarer cases, lead pipes and service lines, may still be present in schools. Lead concentrations measured after 5 min of flushing in this study indicate that some non-distal sources of lead were present in the buildings. Whilst the removal of all sources of lead in large building would be desirable, our results suggest that removing the sources of lead at the tap and its connecting immediate piping may suffice to considerably decrease Pb exposure. A system wide investigation of all sources of lead in the internal plumbing of large buildings may appear the best approach to identify sources of lead to be removed. However, as older buildings contain a variety of materials for piping, solders, brass fittings and faucets, it would be difficult or even impossible to conduct a thorough assessment of all Pb sources by inspection, as many of these elements are not readily accessible. Water sampling can be used as a proxy to identify Pb sources; it is widely accepted for the detection of LSLs (Cartier et al., 2012b; Deshommes et al., 2016b).

4.3.8.2 Corrosion control

pH adjustment of low alkalinity water can be efficient to lower lead levels when considering various types of faucets and fountains, compensating in part for the presence of leaded materials at the tap. Various onsite CC treatments have been shown to be effective for the control of lead release from taps and their connecting piping (Cartier et al., 2012c). Our results confirm that system wide corrosion control contributes to lowering lead in large buildings. In the absence of system wide corrosion control, on site corrosion control could be considered. However, on site treatment may have regulatory implications and requires human and financial resources that may not be available or feasible in many schools.

4.3.8.3 Flushing

Extended flushing of taps in the morning is ineffective for lowering lead and copper concentrations throughout the day, as Pb concentrations can again exceed 10 µg Pb/L after only 30 minutes of stagnation and 90th percentile Cu concentrations exceed the California PHG. It is not realistic to recommend a 5 minute flush prior to each use. The waiting time would be unacceptable to the user and the wasted water would be considerable. To fully flush premise plumbing, a volume equivalent to both the service line and internal plumbing or more is needed. In this study, the service line volumes were considerable, ranging from 50 L to 180 L. Furthermore, the lower flows at fountains and the need to manually maintain the flow make it even more unpractical. Alternatively, flushing for 20 s or less was sufficient to flush out the first 250 mL (at maximum flow rate) in our study. Such a procedure would be more feasible to implement and did decrease potential exposure significantly in buildings with corrosive water.

4.3.8.4 Designating drinking points

Within buildings, lead-free supply locations should be designated for drinking water and food preparation and regularly sampled to ensure acceptable water quality. If the presence of leaded components is suspected building wide, a POU device installed prior to the tap or fountain should be considered to help ensure low lead and copper concentrations as previously reported by Deshommes et al. (2012a).

4.3.9 Selecting a sampling protocol

The optimal sampling protocols depends on the sampling specific objectives.

Assessing typical exposure: The best approach to measure typical metal concentrations at drinking water points in households is proportional sampling (van den Hoven & Slaats, 2006). Such sampling is resource intensive, costly, invasive and only feasible for research purposes. A combination of the various protocols examined including long and short stagnation and flushed samples can serve to estimate a realistic range of concentrations to which children can be exposed. Random day time (RDT) and 30minS can provide results more indicative of typical exposure than 1st draw samples collected after overnight stagnation in households (Deshommes et al., 2016b; van den Hoven & Slaats, 2006). However, a much larger number of RDT samples would need to be collected to estimate typical exposure in this study (Table A.5).

Assessing acute exposure: The assessment of acute exposure at a tap poses a challenge, as extreme lead concentrations are typically caused by sporadic release of Pb_{part}. In this study, we did not observe an impact of the type of sampling protocol on the likelihood of elevated particulate lead, as even the PSS protocol did not produce more Pb_{part} release. However, very high lead concentrations in this study mostly only exceeded 100 µg Pb/L in 4/130 taps after >8h of stagnation. For these taps, 30minS samples all exceeded 10 µg Pb/L. However, some elevated values (>100 µg Pb/L) were also measured after 30 minute stagnation (3/130), suggesting 'worst case' taps as previously reported by Deshommes et al. (2016a). Using extended stagnation and profiling sampling are most likely to provide worst case exposure.

***Identifying sources of lead*:** The collection of consecutive samples following overnight stagnation (profiling) can be used to identify sources of lead and copper in large buildings (Cartier et al., 2012c; McIlwain et al., 2015). First draw samples collected after stagnation can confirm distal contamination from the tap and its connecting plumbing. Subsequent samples collected as water is flowing can help identify other sources of lead in the remaining premise plumbing. The concentrations in semi and fully flushed samples can also be used to identify buildings with more systemic presence of lead components in premise plumbing. In our study, 2.3% of flushed samples exceeded 5 µg Pb/L and 15.4% were >2 µg Pb/L. When contamination is found in flushed samples, then sequential sampling can be considered for detailed investigative work or research. It is however very costly, time consuming and more disruptive (Health Canada 2009).

Estimating the effectiveness of treatment and remediation measures RDT sampling, representative of a typical inter-use stagnation is recommended in the EU (European Commission, 2015; Hoekstra et al., 2009). The same reference stagnation time should be used to be able to compare the results before and after the remediation measures at a given site.

Identifying critical taps (>10 µg Pb/L) Recent investigations, including this study, reveal that (1) outlets with a high potential for lead release can be found in all buildings, even when other taps show low lead release, and (2) these high risk outlets can be a significant source of lead for children. Therefore, identifying outlets of concern that are used for drinking water consumption and meal preparation should be a priority. Identifying high lead outlets is possible using a fixed stagnation protocol, either 30 minutes or overnight. In this study, 30 minute stagnation samples increased back to about 50% of the concentration of samples collected following overnight stagnation. When lead levels after a 30 minute stagnation exceed 5 µg Pb/L, more detailed investigation including sequential sampling should be conducted to confirm if the problem is distal or systemic. If this is not the case, then full profiling and material investigations should be conducted. This study's results and the meta-analysis conducted by Deshommes et al. (2016a) suggest that lead concentrations are highest at the distal point directly at the outlet and its connecting plumbing.

Recommended sampling approach to minimize lead exposure in school outlets We recommend a two-tier sampling approach consisting of: (1) sampling after ≥6 hours of stagnation and (2) investigative sampling combining a first draw (250 mL) and second draw (1 minute flush) samples after fixed stagnation at all taps exceeding 10 µg Pb/L. All outlets used for drinking water and cooking in a building should be tested. With this approach, the elevated lead outlets can be quickly identified and the significant sources of lead identified. Elevated lead outlets or taps have been shown to the most significant in terms of exposure in the meta analysis conducted by Deshommes et al. (2016a) as well as by the BLL analysis this study.

Sampling after extended stagnation is difficult to implement in private households as it is invasive; it is easier to implement in a school, as it is possible to sample prior to the beginning of a school day. Although we sampled after at least 8h of stagnation in this study, we recommend a minimum stagnation time of 6 hours for the following reasons: (1) although lead levels may increase after 6 hours, they will be sufficient to allow the detection of high risk outlets; (2) the presence of extended child care services and evening use of facilities may limit the possibility to sample after more than 6 hour stagnation. Considering the necessity to flush ≥5 minutes and the challenge of ensuring a controlled stagnation of 30 minutes, the 30minS would be more difficult to implement in large buildings. Sampling after 1 minute of flushing would allow the detection of leaded materials in the plumbing.

Considering the limited resources available to many school boards and schools, we believe that the use of a portable anodic stripping voltammetry analyzers is an attractive option to rapidly identify elevated lead taps in schools preventing further exposure of children. These devices are low-cost and can be used with minimal training by local staff including janitors. Furthermore, as samples collected following overnight stagnation typically corresponded to a high estimate of potential concentration at the tap, such samples can be measured on-site using portable devices despite their high detection limit (2 µg Pb/L). However, on-site portable anodic stripping voltammetry could only detect a fraction of all particulate lead present in samples containing high proportions of particulate lead after partial lead service line replacements (Cartier et al., 2012a). However, even with this partial detection (24 ± 9% for total Pb), the 68 samples which exceeded 10 µg Pb/L in this study would have been detected. Even if no particulate lead was detected by voltammetry, we estimate that still 88% of the taps exceeding 10 µg Pb/L would have been identified. In the case of cold water samples (<15°C), samples should be allowed to reach room temperature prior to analysis. Nonetheless, additional validation of the use if these devices appears desirable to ensure their proper use.

Finally, schools more likely to contain legacy solder and leaded brass should be prioritized for intervention, especially those receiving corrosive water as the proportion of outlets with elevated lead and the levels of lead measured will be more significant.

4.4 Conclusions

- Flushing taps in large buildings provides short term benefits that are lost following a short stagnation (30 minute) as lead and copper concentrations increase to values about half of those measured following extended stagnation.
- Flushing represented a less effective mean to decrease copper when compared to lead concentrations at the tap. Furthermore, copper concentrations were not as well controlled using pH adjustment as for lead.

- A simple aggressivity index may be useful screening index to identify buildings at risk for elevated lead concentrations but should not be used to predict lead and copper concentrations.
- All types of consumption points are at risk in buildings supplied by corrosive water.
- Buildings susceptible to having leaded components in their plumbing (faucets, valves, LSLs, etc.) and/or serviced with water of low alkalinity and pH should be prioritized.
- The first 250 mL of water stagnating in taps should not be consumed; water should be flushed prior to consumption even following short stagnation. In most fountains, it takes 2-20 seconds to flush this volume of water.
- A first draw collected after overnight stagnation allows for quick and easy identification of the distal sources of lead which have been shown to be dominant in large buildings. The probability for exposure to high lead levels being increased if follow-up samples collected after shorter stagnation present significant concentrations. All outlets used for drinking water consumption should be tested for lead.

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CHAPTER 5 ARTICLE 2 – STUDY OF THE LONG-TERM IMPACTS OF TREATMENTS ON LEAD RELEASE FROM FULL AND PARTIALLY REPLACED HARVESTED LEAD SERVICE LINES

To decrease the customers’ exposure to lead, utilities replace the public section of the lead pipe by copper, resulting in partial lead service line (LSL) replacements, due to shared ownership of the service line. This chapter seeks to understand the importance of the water quality as well as on the configuration of the service line (full LSL vs partial LSL) in determining the lead concentrations released after 16 hours of stagnation and under flowing conditions. The effectiveness of different corrosion control treatments is assessed. We also determined the length of LSL which utilities should remove in order to offset the additional lead release from the newly added galvanic connection. Furthermore, this study also presents a comparison of pilot and field results, showing important difference in results depending on the scale of the experimentation. This paper was submitted in *Water Research*. Supplementary information is presented in Appendix B.

STUDY OF THE LONG-TERM IMPACTS OF TREATMENTS ON LEAD RELEASE FROM FULL AND PARTIALLY REPLACED HARVESTED LEAD SERVICE LINES

Evelyne Doré[1], Elise Deshommes[1], Laurent Laroche[2], Shokoufeh Nour[1], Michèle Prévost[1]

[1]Department of Civil, Mining and Geological Engineering, Polytechnique Montréal, Montréal, QC, Canada

[2]Ville de Montréal, Technical Expertise Division, Montréal, Canada

[*]Corresponding author: Tel: 514-340-4711 #3711; Fax: 514-340-5918; email: evelyne.dore@polymtl.ca

ABSTRACT

Long-term (155 weeks) Pb concentrations, following partial lead service lines replacements (PLSLR), were measured in a flow through pilot made of harvested lead service lines (LSL) from the distribution system of the City of Montreal. The present study also investigates how release of Pb from full and partial LSLs is influenced by: pipe diameter, decrease in chloride-to-sulfate mass ratio (CSMR) from 0.9 to 0.3, addition of orthophosphate (1 mg P/L), and increase in pH to (8.3). Pb concentrations were measured after 16 hours of stagnation and under flow conditions. In this study, Pb concentrations did not decrease, in the long term, after partial LSL replacement. Moreover, the most effective corrosion control treatment in full LSLs was the addition of orthoP. In contrast, the decrease of the CSMR best reduced lead release from partial LSLs. The impact of pipe configuration therefore influenced the effectiveness of corrosion control treatments. It is noteworthy that the increase in Pb concentrations following PLSLR were attributed to particulate Pb release from the galvanic section of the pipe. The occurrence of galvanic corrosion, caused by the connection between Pb and copper pipes, adds a new source of Pb in the partial LSL. This new source of has to be offset by the removal of a long enough section of LSL during PLSLR.

*KEYWORDS**:** Lead service line, Partial lead service line replacement, Corrosion control, Orthophosphate, CSMR, Drinking water*

5.1 Introduction

Over 5.5 million lead service lines (LSL) are responsible for providing water to 15 to 22 million Americans (Cornwell et al., 2016) and being a major contributor (50–75%) to sources of Pb in tap water (Cartier et al., 2011; Levallois et al., 2013; Sandvig et al., 2008). The replacement of LSLs is a mitigation strategy used by utilities to decrease Pb concentrations at the tap. Due to shared ownership of service lines, utilities replace the public portion of LSLs, leaving the private section unmodified. This action is termed a partial LSL replacement (PLSLR). To date, only a few American cities, such as Madison and Milwaukee, have prohibited PLSLRs (Schock et al., 2014; Slabaugh, 2017).

Field studies on LSLs and the impact of PLSLR on Pb concentrations are limited and are mostly short-term studies, spanning less than 6 months (Brown & Cornwell, 2015; Camara et al., 2013; Lewis et al., 2017; Trueman et al., 2016). The few long-term North American studies available in the literature report an initial increase, followed by a subsequent decrease in Pb levels after PLSLR (Deshommes et al., 2016b; Deshommes et al., 2017; Muylwyk et al., 2011; Swertfeger et al., 2006).

A similar trend was observed in Scottish households where the LSLs contained a section of copper (Cu) (Britton & Richards, 1981).

Short and long-term pilot studies using new or harvested LSLs have shown that PLSLRs can lead to spikes in particulate Pb ($Pb_{part.}$). The level of $Pb_{part.}$ detected is influenced by the presence of corrosion inhibitors, flow rate, type of coupling and stagnation time prior to sampling (Arnold & Edwards, 2012; Cartier et al., 2012a; Cartier et al., 2013; St. Clair et al., 2016; Triantafyllidou & Edwards, 2011; Wang et al., 2012; Wang et al., 2013; Zhou et al., 2015).

Corrosion control treatments (CCT) often used as a means to reduce lead levels from full (FLSLs) and partial LSLs (PLSLs), include the addition of phosphates (Cartier et al., 2013; Edwards & McNeill, 2002; Kogo et al., 2017; McNeill & Edwards, 2004; Trueman et al., 2018; Wasserstrom et al., 2017; Xie & Giammar, 2011), pH adjustment (Cartier et al., 2013; Kim et al., 2011; Xie & Giammar, 2011), changing the chloride-to-sulfate mass ratio (CSMR) (Cartier et al., 2013; Edwards & Triantafyllidou, 2007; Knowles et al., 2015; Nguyen et al., 2010; Nguyen et al., 2011c; Triantafyllidou & Edwards, 2011; Wang et al., 2013) and dosing sodium silicates (Kogo et al., 2017; Zhou et al., 2015). The results of these treatments can vary depending on water quality and the pipe configuration, as scales that forms inside PLSLs are different from that in FLSLs.

Overall, the application of orthoP has been highly successful in reducing >90% of total Pb (Pb_{total}) (Cardew, 2009) and Pb solubility (Trueman et al., 2018; Wasserstrom et al., 2017). However, Cardew (2009) states that orthoP may not be a good CCT for the reduction of particulate Pb ($Pb_{part.}$), as $Pb_{part.}$ spikes were found to persist post-treatment. $Pb_{part.}$ is the main concern associated with galvanic corrosion after PLSLR (Triantafyllidou & Edwards, 2011). Pilot-scale studies using harvested FLSLs found that the addition of orthoP resulted in a 68% decrease in Pb_{total} concentrations following 16 hours of stagnation (Cartier et al., 2013), and caused a 70% decrease in dissolved Pb ($Pb_{diss.}$) (Edwards & McNeill, 2002). In new, conditioned Pb pipes, orthoP maintained $Pb_{diss.}$ below 15 µg/L following 8 hours of stagnation (Xie & Giammar, 2011). However, in PLSL at pilot scale, orthoP caused a 13-fold increase in Pb_{total} concentrations (Cartier et al., 2013), attributable to $Pb_{part.}$ release. In field studies, $Pb_{part.}$ release has been observed to be erratic and unpredictable, as it depends on scale detachment (Cardew, 2009). OrthoP decreased Pb concentrations in new Pb pipes galvanically connected to Cu pipes, (McNeill & Edwards, 2004). Similarly, orthoP decreased Pb concentrations (5.3-fold for high CSMR and low conductivity water) in harvested LSLs independently of the presence of galvanic connections to Cu pipes in a recirculating system (Kogo et al., 2017).

In the presence of galvanic corrosion, a CSMR lower than 0.77 can protect the Pb anode of the galvanic couple (Nguyen et al., 2011b), in agreement with the threshold of 0.6 presented in Edwards and Triantafyllidou (2007). However, an increase in the CSMR associated with the presence of galvanic corrosion also reportedly exacerbated Pb release in pilot scale experiments (Edwards & Triantafyllidou, 2007; Nguyen et al., 2010; Triantafyllidou & Edwards, 2011). On the other hand, the addition of sulfate better controlled Pb concentrations in simulated PLSLRs, but did not significantly change Pb concentrations released from FLSLs (Cartier et al., 2013). At bench scale, changing coagulants (Alum *vs* PACl) decreased the CSMR and increased Pb concentrations in harvested LSLs galvanically connected to Cu pipes (Knowles et al., 2015).

The solubility of Pb decreases as pH increases, resulting in lower Pb concentrations in water (Kim et al., 2011; Schock & Gardels, 1983). The interplay between pH and alkalinity, as well as the drop in pH observed at the junction of Pb-Cu pipes is an important determinant of lead release into water (DeSantis et al., 2018). Increasing the pH from 7.1 to 7.8 in a pipe loop experiment using harvested LSLs resulted in a decrease of the total Pb concentration (Kim et al., 2011). However, increasing the pH of FLSLs from 7.7 to 8.3 did not significantly decrease Pb concentrations (Cartier et al., 2013).

Pilot studies using plastic couplings to connect Pb and Cu pipes induced galvanic corrosion by connecting them using a wire, which allows measurement of the galvanic current between the pipes (Arnold & Edwards, 2012; Knowles et al., 2015; Kogo et al., 2017; Triantafyllidou & Edwards, 2011; Wang et al., 2013; Zhou et al., 2015). In this experimental model, the type of connector utilized caused significant differences in the galvanic corrosion of the exposed surface. Notably, lower Pb concentrations have been measured using this technique than with a brass coupling (Wang et al., 2013).

Numerous pilot studies have been completed using recirculating pipe loops which are not representative of reality as Pb can accumulate in the recirculating water. Pilot studies using external wires to induce a galvanic current between the Cu and the Pb pipes may not be representative of real conditions at the galvanic connection.

The objectives of this study were to: (1) Evaluate the long-term effectiveness of CCTs on harvested FLSLs and PLSLs (follow-up of Cartier et al. (2013)) under flow conditions and after 16 hours of stagnation; (2) Verify the impact of pipe configurations on Pb release; (3) Determine the minimum Pb pipe length that needs to be removed during a PLSLR in order to offset the additional release of Pb caused by galvanic corrosion. To the best of our knowledge, this investigation provides the first controlled comparison of Pb release from partial LSLs at pilot scale and in households prior to and after PLSLR.

5.2 Materials and methods

5.2.1 Pilot setup and operation

The pilot setup used for this study is described in Cartier et al. (2013). It consists of aged Pb pipes harvested from the City of Montreal and installed in a large building fed with dechlorinated water from the same distribution system (Figure B.1). This study presents the long-term (155 weeks) Pb release after PLSLR simulation whereas Cartier et al. (2013) presented the short-term (11 weeks) results. Three pipe configurations were tested: (1) a 3 m long aged LSL (100%Pb), (2) a 1.8 m copper pipe (Type M) connected upstream of an aged LSL of 0.6 m using a red brass compression fitting (Ford, Wabash, Indiana, USA), simulating a Cu-Pb configuration and (3) a 0.6 m aged LSL connected to a 1.8 m copper pipe with a red brass compression fitting (Pb-Cu configuration). Four water conditions were tested: (1) control (CSMR 0.9, no added phosphate, pH 7.7), (2) high sulfate, by addition of Na_2SO_4 (CSMR 0.3 and pH 7.7), (3) orthophosphate (orthoP) dosed at 1 mg P/L with H_3PO_4 and NaOH for pH re-stabilization (CSMR 0.9, pH 7.7), (4) pH of 8.3 adjusted using NaOH (CSMR 0.9) (Table 5.1). The internal diameter (I.D.) of the lead pipes were 16 mm. The fifth condition tested consisted of lead pipes of a smaller internal diameter of 13 mm carrying control water. In the last conditions, partial LSLs (PLSL) were connected to the copper pipe using a soldered red brass fitting. For the PLSL configurations, the internal volume of the lead pipes was 120 mL (I.D.=16 mm) or 80 mL (I.D.=13 mm) and for the full LSL configuration, it was 600 mL (I.D.=16 mm) or 400 mL (I.D.=13 mm). Initially, all pipe configurations and treatments were tested in triplicates (N=45).

Table 5.1 Corrosion control treatment, pipe configuration, and internal diameters tested in the pilot setup as well as median and 90th percentile total Pb concentrations after 16HS and flowing condition.

Water treatment	**Pipe configuration**	**Internal diameter of Pb pipe (mm)**	**Pb pipe length (m)**	**Number of rigs**	**16HS**			**Flowing**		
					N	**Median Pb_{total} (µg/L)**	**90th percentile Pb_{total} (µg/L)**	**N**	**Median Pb_{total} (µg/L)**	**90th percentile Pb_{total} (µg/L)**
Control	**100% Pb**	16	3	3	60	79.5	180	27	1.7	7.8
	Cu-Pb	16	0.6	3*	46	45.7	187	18	0.69	2.9
	Pb-Cu	16	0.6	3*	46	81.3	425	18	1.3	9.9
Smaller diameter	**100% Pb**	13	3	3	57	135	625	27	1.9	4.6
	Cu-Pb	13	0.6	3*	44	238	869	18	1.0	184
	Pb-Cu	13	0.6	3*	44	59.2	339	18	0.46	2.0
Sulfate addition	**100% Pb**	16	3	3	60	76.7	99.2	27	1.5	4.7
	Cu-Pb	16	0.6	3*	46	25.1	66.3	18	0.90	2.4
	Pb-Cu	16	0.6	3*	46	25.0	61.7	18	0.91	2.0
orthoP	**100% Pb**	16	3	3	60	20.8	62.8	27	0.43	1.0
	Cu-Pb	16	0.6	3*	46	38.4	859	18	0.30	0.63
	Pb-Cu	16	0.6	3*	46	39.7	1332	18	0.52	1.7
pH 8.3	**100% Pb**	16	3	3	60	84.1	162	27	1.5	2.9
	Cu-Pb	16	0.6	3*	46	54.0	193	18	0.68	2.1
	Pb-Cu	16	0.6	3*	44	185	14.1	18	0.65	2.5

*****39 weeks after PLSLR simulation, 1 rig per partial configuration per treatment was disconnected for scale analysis studies.

16HS: 16 hours of stagnation; 100% Pb = Full lead service lines; Cu-Pb = Partial lead service line (PLSL) with copper pipes upstream of Pb pipes; Pb-Cu = PLSLs with Pb pipes upstream if Cu pipes; orthoP = orthophosphate

Normal operating conditions consisted of water flowing at 5 LPM (litres per minute), 30 psi for 8 h per day, 5 days per week, without stagnation exceeding 72 h, except during stagnation and high velocity flushing trials. A flow rate of 5 LPM was selected as it is the representative flow rate of a kitchen faucet (Kogo et al., 2017; Welter, 2016).

5.2.2 Sampling

Prior to each sampling event, sampling valves were flushed to remove particles that may have accumulated under normal operating conditions. The flow pattern was modified to bring fresh water into the pipes to avoid contribution from upstream pipes, as described in Cartier et al. (2013). Samples were collected under the same flow rate as the operational rate (5 LPM), except for the section with a smaller diameter (15 LPM). 2 L samples were collected to ensure complete recovery of the water stagnating in the lead pipes (Cartier et al., 2013). Dissolved lead concentrations were measured by filtering a 40 mL aliquot using a 0.45 µm PVDF filter (SETI International Scientific, Canada).

Metal concentrations were monitored after a 16 h stagnation (16HS) period and a 6HS period. Water pressure remained constant (30 psi) inside the rigs during stagnation. Flowing sampling was conducted under pressurized conditions. Samples were collected every 30 minutes (3 samples) after a one-hour flush.

5.2.3 Water quality monitoring

Samples for total and dissolved metal measurements were acidified with 0.5% HNO_3. Prior to analysis, 0.5% HCl was also added to obtain the appropriate matrix. Metal concentrations (Cu, Pb, Zn, Fe) were measured in an ISO179025 certified laboratory with an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS; Agilent Technologies, Santa Clara, CA). Detection limits were: 0.11 µg Cu/L, 0.02 µg Pb/L, 0.17 µg Zn/L and 4.32 µg Fe/L. Weekly water quality monitoring included the measurement of pH (electrode, Accumet 13-620-183A, UK), alkalinity (SM 2320), total and residual chlorine (SM 4500-Cl, with Cary 100 Variant Spectrophotometer, Agilent), dissolved oxygen (Hach LDO electrode, Hach HQ40d meter), total organic carbon (TOC) (Sievers 5310C) and turbidity (Hach turbidimeter Model 2100AN, Standard methods 2130B). Chloride, sulfate (ionic chromatography) and phosphate (Flow injection Quikchem 8500) concentrations were monitored monthly. All measurements were carried out on both flowing and stagnant samples (16HS).

5.2.4 Statistical analysis

Non-parametric statistical analysis, including the Kruskal Wallis ANOVA test, were performed using Statistica (StatSoft, Version 13.3). Differences were considered significant if $p<0.05$, unless stated otherwise.

5.2.5 Surface area-normalized mass release (SANMR) calculations

For each pipe, the surface area-normalized mass release (SANMR) measured after 16HS was calculated using Pb_{total}, $Pb_{diss.}$ and $Pb_{part.}$, adapted from McFadden et al. (2011). The Pb piping and galvanic corrosion are presumed to be the major contributors of Pb in samples. The incoming concentration of Pb_{total} from the dilution water was <0.4 µg/L. SANMR is expressed as µg of Pb per m^2 of Pb pipe exposed to water. For FLSLs, the SANMR is considered to be the same throughout the pipe. It is calculated by dividing the mass of Pb measured in each sample by the internal surface area of the Pb pipe. For PLSLs, the SANMR includes the release from the galvanic connection at the junction of the Pb and Cu pipes, the brass fitting and the Pb section free of galvanic corrosion. It is calculated using the following equation:

$$\text{Apparent SANMR} = \text{Background SANMR} + \text{Galvanic SANMR} \quad (5.1)$$

Where,

- the apparent SANMR is computed from the measured mass of Pb per internal surface area of the Pb pipe (µg/m^2);
- the background SANMR is computed from the mass of Pb per internal surface area of the Pb pipe (µg/m^2) released from each pipe before the simulated PLSLR;
- the galvanic SANMR is computed as the difference between mass of the apparent and background SANMRs over the internal surface containing galvanic corrosion.

The galvanic zone is comprised of the brass fitting and the flanking 2 cm regions of Cu and Pb immediately next to the fitting (both on the inside and the outside of the pipes), thereby encompassing all the surfaces that are in contact with water at the galvanic junction (Figure 5.1).

Our visual observations and a previous report suggest that scale formed beyond the 2 cm of pipe included in the galvanic junction are markedly different (DeSantis et al., 2018). The non-galvanic (background) SANMR value used in the aforementioned calculation is based on the median Pb concentrations after 16HS measured before PLSLR simulation for each pipe. Apparent SANMR was also calculated for samplings after 6HS.

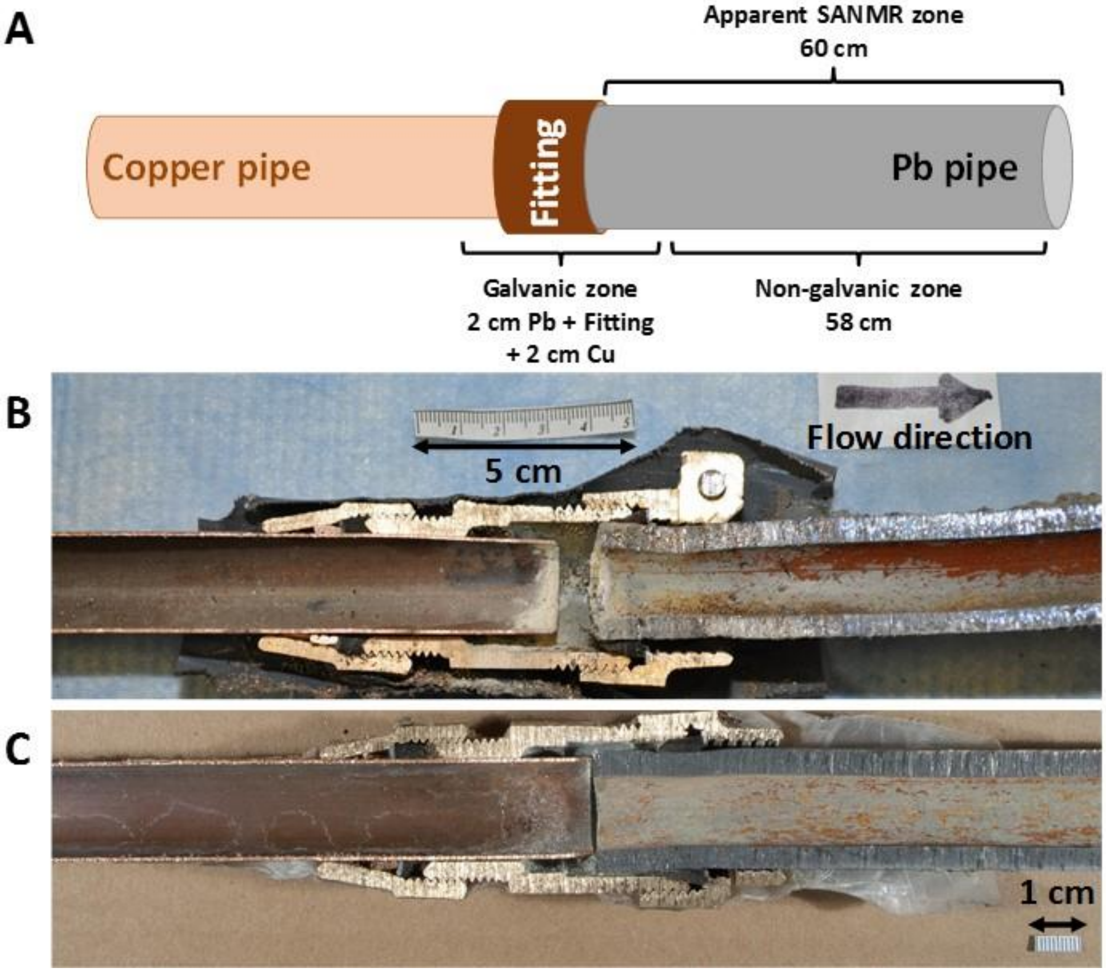

Figure 5.1 The apparent surface area-normalized mass release (SANMR), galvanic and non-galvanic zones present in lead (Pb) pipes connected to copper (Cu) pipes using a compression fitting (A). A partial lead service line (PLSL) from the pilot setup with a gap between the Cu and Pb pipe junction (B) and a PLSL where the Pb pipe is in direct contact with the Cu pipe (C).

5.2.6 Field monitoring of LSL households

Apparent SANMR for houses with FLSLs and PLSLs was computed using the estimated mass of Pb pipes contributing to the Pb concentration in sequential samples collected after 6HS (Deshommes et al., 2016b; 2017). A total of 25 houses were used for this calculation, with 1 to 13 sampling profiles per house: 9 FLSLs (51 profiles), 11 recent Cu-Pb configurations (51 profiles), 3 aged Cu-Pb configurations (33 profiles), 1 recent Pb-Cu configuration (1 profile) and 4 aged Pb-Cu configurations (24 profiles).

5.3 Results and discussion

5.3.1 Changes in total Pb concentrations over time

Mirroring the previous, 11 week study (Cartier et al. 2013), we report that the total lead (Pb_{total}) levels did not decrease during the 155 weeks following partial lead service line replacement (PLSLR) simulation (Figure 5.2). Pb_{total} varied over time, with peak concentrations attributed to the presence of particulate Pb ($Pb_{part.}$) (median $Pb_{part.}$ fraction in Cu-Pb and Pb-Cu configurations was 67% for all treatments). Pb levels were best stabilized when sulfate was added to water in both the full lead service line (FLSL) (10^{th}-90^{th} percentile: 55.7-99.2 µg Pb_{total}/L) and partial lead service line (PLSL) (10^{th}-90^{th} percentile: Cu-Pb: 16.0-66.3 µg Pb_{total}/L) configurations (Table 5.1 and Figure 5.2C). Similar to Cartier et al. (2013), orthophosphate (orthoP) treatment caused the highest and most variable Pb concentrations, in PLSLs spanning up to 3 orders of magnitude (Table 5.1).

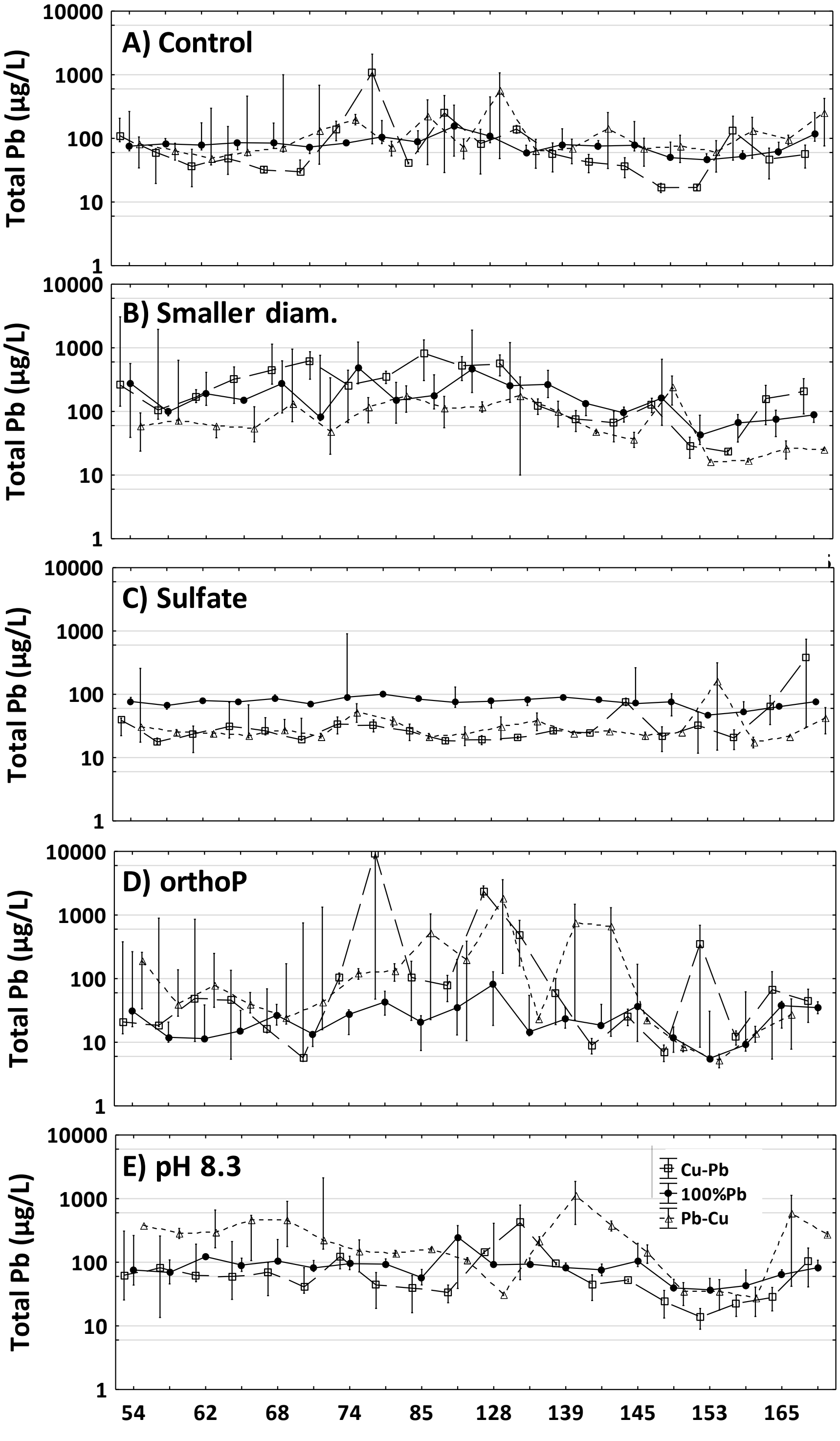

Figure 5.2 Total lead (Pb) concentration after 16 hours of stagnation presented as a function of time (in weeks) following partial lead service line replacement (PLSLR) simulation. Smaller diam.: smaller diameter pipe; orthoP: orthophosphate treatment. N=46 for Cu-Pb and Pb-Cu pipe configurations, N=60 for 100% Pb pipe configuration.

5.3.2 Impact of treatments on Pb concentrations after stagnation and under flow conditions

The effectiveness of corrosion control treatments (CCTs) in reducing Pb concentrations varies depending on the pipe configuration and type of sampling (16 hours of stagnation *vs* flowing samples). As expected, the median Pb_{total}, dissolved Pb ($Pb_{diss.}$) and $Pb_{part.}$ concentrations were lower under flow conditions than after 16HS, and the 100% Pb pipes released the lowest Pb concentrations (Table 5.1 and Figure 5.3).

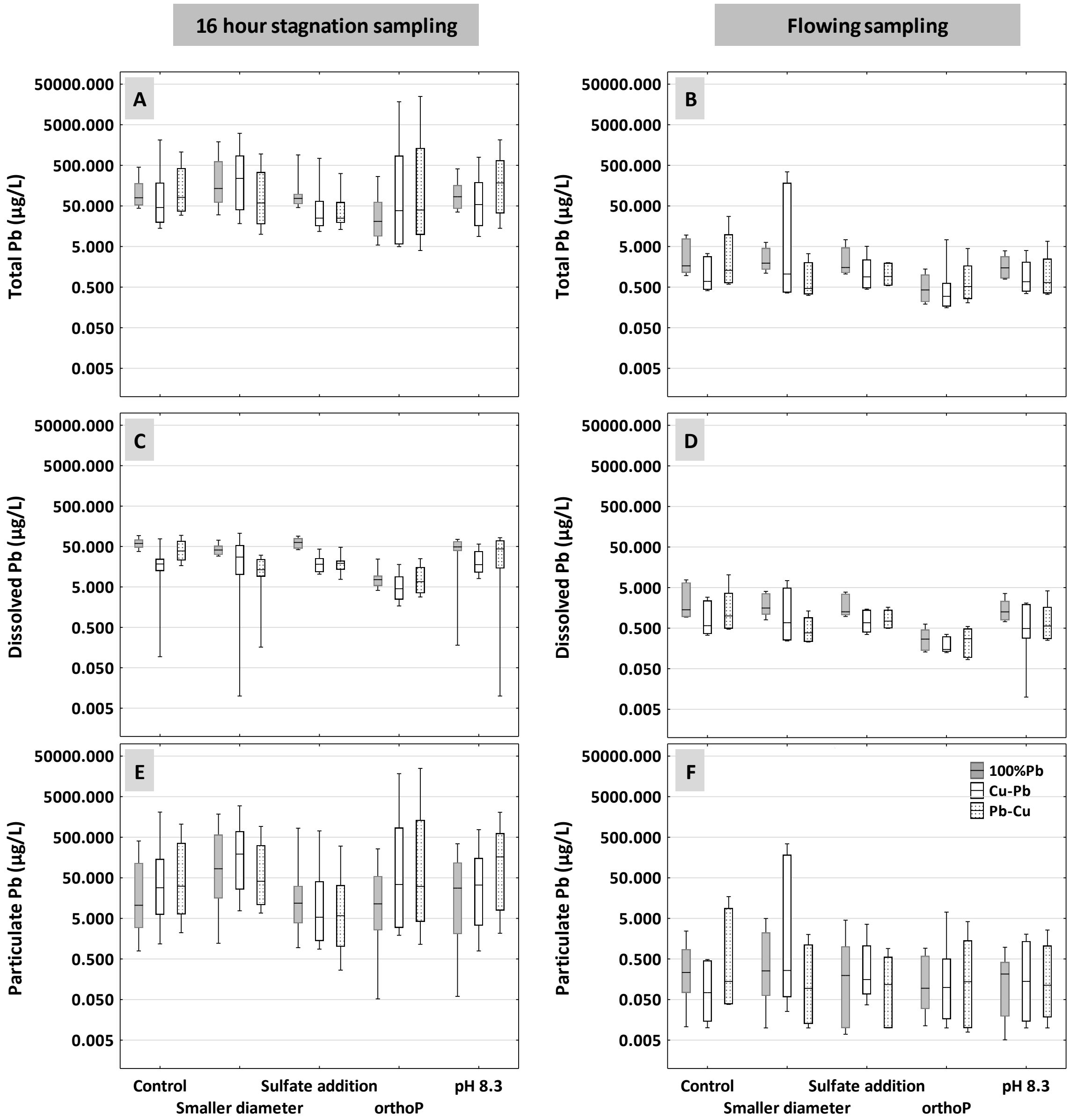

Figure 5.3 Total (A-B), dissolved (C-D) and particulate (E-F) lead (Pb) concentrations measured after a 16 hour stagnation period (left) or under flowing conditions (right) under different corrosion control treatments. The 100% Pb pipe configuration is represented in grey, the Cu-Pb configuration in white and the Pb-Cu configuration with black dots. The line within each box represents the median concentration. The bottom and top of each box represents the 10th-90th percentiles, respectively. The whiskers represent the minimum and maximum values.

5.3.2.1 Full Lead Service Lines (FLSLs)

After 16HS, Pb_{total} between the control, sulfate treatment and pH 8.3 samples was statistically similar (median of 79.5 *vs* 76.7 *vs* 84.1 µg Pb_{total}/L, respectively; Figure 5.2 and Figure 5.3). Pb_{total} was best reduced by orthoP treatment, both after stagnation (3.8-fold, median of 20.8 *vs* 79.5 µg Pb_{total}/L) and under flowing conditions (3.9-fold, 1.7 *vs* 0.43 µg Pb_{total}/L) (Table 5.1 and Figure 5.3). This observed 73% decrease is consistent with short-term post-PLSLR studies reporting a 68% (Cartier et al., 2013) or 70% (Edwards & McNeill, 2002) decrease in Pb concentrations under similar conditions or in a dump-and-fill experiment, respectively. We also found that $Pb_{diss.}$ is reduced by orthoP treatment, in agreement with (Xie & Giammar, 2011). In contrast, orthoP failed to decrease $Pb_{part.}$ (11.4 *vs* 10.5 µg $Pb_{part.}$/L control *vs* orthoP, respectively), thereby contradicting a previous dump-and-fill study using new Pb pipes (McNeill & Edwards, 2004), but in agreement with the findings of Xie and Giammar (2011). The increase in the particulate Pb fraction is comparable to faucets and brass materials treated with orthoP (0.8 mg P/L), with reported increases from 31% to 54% (Cartier et al., 2012c). When orthoP is the CCT, Pb-phosphate compounds, such as hydroxypyromorphite (Trueman et al., 2018), are expected to be formed. When these forms are present, they may to contribute less to exposure because of the very low bioavailability as compared to other forms present (Deshommes et al., 2012b; Xie & Giammar, 2011).

After 16Hs, there were no significant differences in $Pb_{part.}$ concentrations, except for the smaller diameter condition. Indeed, highest $Pb_{part.}$ was recorded under this condition (8-fold higher *vs* control). The increase in $Pb_{part.}$ under this condition could be attributed to increased flow velocity relative to the control. In terms of $Pb_{part.}$ fraction, smaller diameter pipes (67.1%) and orthoP treatment (59.8%) also exhibited the highest values among all conditions tested. All other conditions were comparable in terms of particulate Pb fraction. It is also noteworthy that the addition of sulfate decreased both the 90th percentile $Pb_{part.}$ (31.7 *vs* 115.8 µg $Pb_{part.}$/L sulfate *vs* control; Figure 5.3E) and $Pb_{part.}$ fraction (41.0 *vs* 66.1%). The median Pb_{total} was 48-69 fold lower under flow conditions compared to 16HS (Table 5.1). Corroborating a previous study, we report that an increase in water pH did not cause changes to Pb levels under flowing or stagnation conditions (Kim et al., 2011).

5.3.2.2 Partial Lead Service Lines (PLSLs)

In contrast to the short-term study results (Cartier et al., 2013), we observed that pipe configuration affected Pb release over the long-term (155 weeks). Nevertheless, the high level of Pb detected post-PLSLR at 11 weeks (Cartier et al., 2013) persisted through to 155 weeks.

Sulfate treatment, which decreases the CSMR from 0.9 to 0.3. yielded the lowest Pb_{total} concentrations for both partial configurations (Cu-Pb and Pb-Cu) after 16HS. The addition of sulfate reduced Pb_{total} by 1.8-fold (Cu-Pb) and 3.2-fold (Pb-Cu) relative to the control condition. Comparably to FLSLs, we observed that orthoP decreased median $Pb_{diss.}$ concentrations by 4.1-fold in Cu-Pb rigs (18.5 vs 4.5 µg $Pb_{diss.}$/L) and by 5.8-fold in Pb-Cu rigs (38.8 vs 6.7 µg $Pb_{diss.}$/L, Figure 5.1 1) after 16HS. The same trend was observed for samples collected under flowing conditions (Table 5.1). Pb_{total} concentrations in PLSLs were higher relative to 100% Pb pipes after stagnation for the pipes treated with the addition of orthoP. This is caused by spikes of both the concentration and fraction of $Pb_{part.}$ which are not controlled by the addition of orthoP. The $Pb_{part.}$ fractions for the control and orthoP treatments were 61% and 85% in the Cu-Pb configuration, and 49% and 80% in the Pb-Cu configuration, respectively. This increase in $Pb_{part.}$ is in line with a reported increase observed in a recirculating pipe-loop comprising Pb-Cu galvanic couples and fed by chlorinated water treated with 2 mg P/L of orthoP (Arnold & Edwards, 2012). However, orthoP was also shown to decrease Pb_{total} and $Pb_{diss.}$ more effectively than $Pb_{part.}$ in harvested PLSLs (partial and PVC-Pb) (Kogo et al., 2017).

Lowering the CSMR was effective in controlling the $Pb_{part.}$ concentration and fraction after 16HS and under flowing conditions (Table 5.1 and Figure 5.3). This is in accordance with prior bench-scale studies (Nguyen et al., 2010). When compared to the control condition, $Pb_{part.}$ concentrations were 5.4-fold lower for both the Cu-Pb (28.5 *vs* 5.3 µg $Pb_{part.}$/L) and Pb-Cu (31.1 *vs* 5.8 µg $Pb_{part.}$/L) configurations under low CSMR. Increasing the CSMR (0.1 to 1.0), using 50:50 Pb-tin coupons galvanically connected to copper, has been shown to dramatically increase Pb concentrations (Nguyen et al., 2011c), indicating that the CSMR should be a concern to utilities with PLSLRs. Increasing sulfate concentrations has been shown to reduce galvanic currents in copper pipes containing solder joints, thereby reducing the Pb release arising from galvanic corrosion (Nguyen et al., 2010).

Under the conditions tested in the present study, the optimal CCT for FLSLs and PLSLs are different. Utilities should, therefore, identify the CCT which would be effective for all lead service line configurations. In general, the most beneficial CCT for FLSLs was orthoP treatment, while decreasing the CSMR yielded the best results within PLSLs.

5.3.3 Impact of pipe configuration

After 16HS, the 100% Pb pipes released less Pb_{total}, $Pb_{diss.}$, and $Pb_{part.}$, when adjusting for pipe length, compared to both partial configurations under all tested conditions (Figure B.2). Under the control condition, the median Pb_{total} concentration, linearized for pipe length, in 100% Pb pipes was 2.9-fold lower than in Cu-Pb pipes and 5.1-fold lower than in Pb-Cu pipes. Cartier et al. (2013) previously observed that Pb release was higher in PLSLs shortly after PLSLR. Similar observations have been reported in PLSLR field studies (Trueman et al., 2016) and lab experiments (St. Clair et al., 2016; Triantafyllidou & Edwards, 2011; Wang et al., 2012) using diverse water conditions. In contrast to our findings, one field study completed in the same distribution system reported that Pb concentrations were lower in houses with PLSLs than FLSLS when a PLSLR was completed less than 2 years ago (90th percentile after 15 minutes of stagnation: 11-18 µg/L for PLSLs *vs* 11-25 µg/L for FLSLs) (Deshommes et al., 2016b). These lower levels persisted in older (PLSLR completed ≥2 years ago), partial replacements (Deshommes et al., 2017).

The $Pb_{part.}$ fraction measured in both partial configurations, for each treatment, were statistically similar after 16HS. The control condition, orthoP treatment and high pH released statistically lower $Pb_{part.}$ fractions in the FLSL than in the partial configurations after 16HS. Under flowing conditions, the $Pb_{part.}$ fraction was similar for all conditions and treatments, confirming that the effects of galvanic corrosion are mostly observed after stagnation. Furthermore, the $Pb_{part.}$ fraction decreases drastically under flowing condition as compared to 16HS (example: 37% *vs* 85% for the Cu-Pb configuration treated with orthoP). Under flow conditions, Pb_{total}, $Pb_{diss.}$ and $Pb_{part.}$ concentrations per metre of pipe were statistically similar for both partial configurations. unlike the 16HS samples.

5.3.4 Surface area-normalized mass release (SANMR)

While the SANMR within 100% Pb pipes is assumed to be homogenous throughout its length, this is a simplified model of reality as the scale layers within a pipe are usually non-uniform (DeSantis et al., 2018; Wasserstrom et al., 2017). We defined the galvanic zone based on visually apparent changes to the scales (Figure 5.1: 2 cm on the Pb and Cu pipes flanking the fitting), which corresponded to a projected surface area of 107 cm^2 for pipes with an internal diameter (I.D.) of 16 mm and 86 cm^2 for pipes with an I.D. of 13 mm. Figure 5.1 and Figure 5.4 show that corrosion deposits can be abundant on the inside, as well as the outside of the Cu and Pb pipes. Indeed, large amounts of deposits were found in most fittings.

Figure 5.4 Example of a Pb-Cu pipe under the control condition showing external corrosion of the Pb and Cu pipes.

The trends in apparent SANMR are the same as the trends observed in the Pb concentrations for the various treatments. For example, the lowest apparent SANMR was associated with orthoP treatment (median 276 $\mu g/m^2$ *vs* 991 $\mu g/m^2$ for the control) after 16HS in 100% Pb pipes (Figure 5.5A).

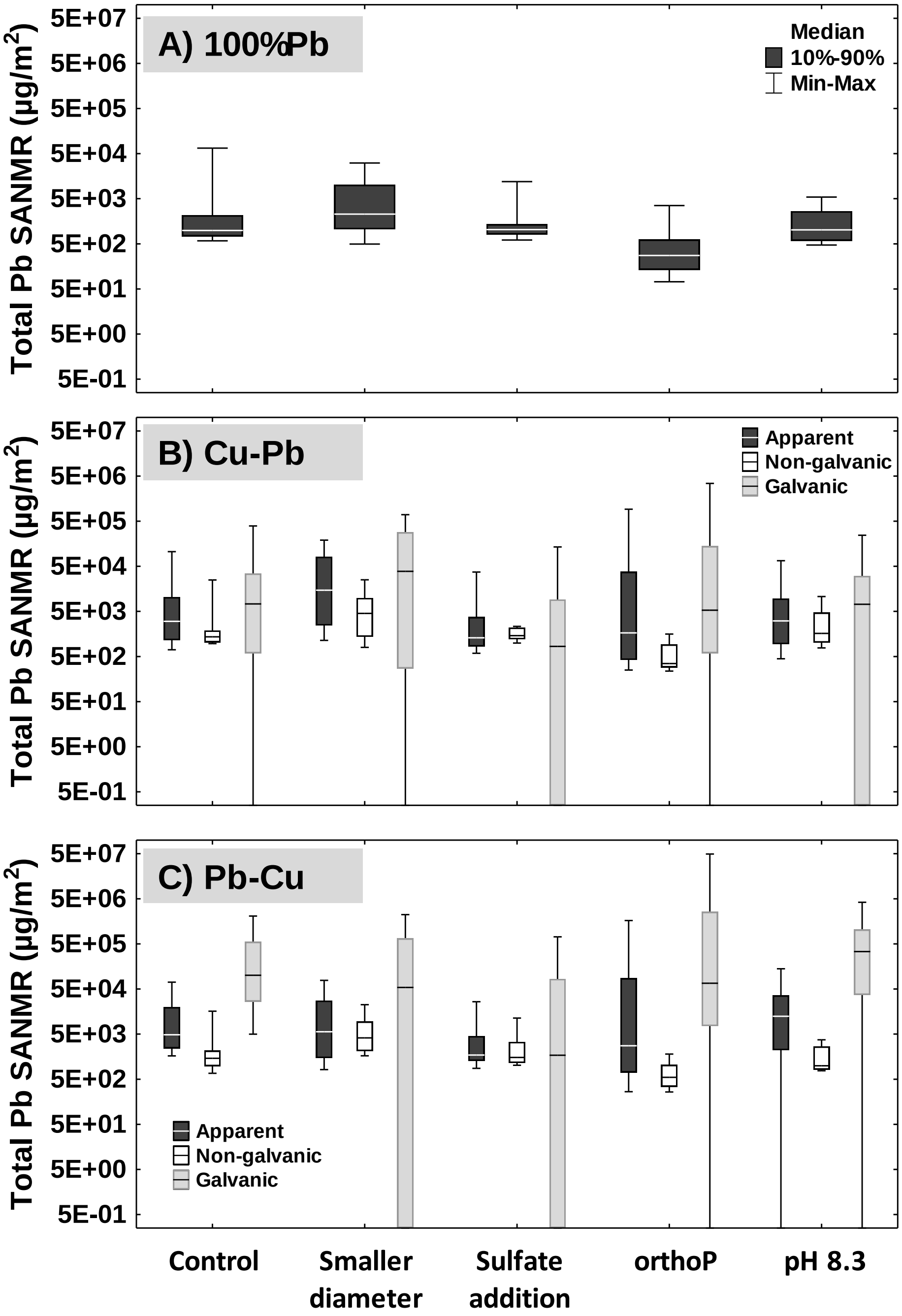

Figure 5.5 Apparent surface area-normalized masse release (SANMR) of total Pb for (A) 100% Pb pipes, (B) Cu-Pb pipes and (C) Pb-Cu pipes is presented in dark grey. For PLSL (B and C), non-galvanic SANMR is presented in white and galvanic SANMR in light grey. The latter is calculated considering a 2 cm galvanic zone on the Pb and Cu pipes flanking the fitting, as well as the interior surface of the brass fitting. The galvanic SANMR was computed using median non-galvanic SANMR.

For the partial configurations (Figure 5.5B and 5C), the calculation of the galvanic and the non-galvanic SANMR better represents the mechanisms at play when adding CCTs. The contribution of the galvanic SANMR was significant and highly variable between the partial pipe configurations for all water conditions tested. The 10th and 90th percentile Pb releases (calculated based on median non-galvanic rates) varied greatly in the control condition between the Cu-Pb (589 and 34,608 µg/m^2) and the Pb-Cu (2,485 and 52,690 µg/m^2) configurations. The mass of Pb from the galvanic zone contributed to 73% (median) of the Pb$_{total.}$ mass in PLSLs treated with orthoP.

In general, the median galvanic SANMRs were greater for the Cu-Pb (sulfate addition: 839 µg/m^2) configuration than for the Pb-Cu (sulfate addition: 161 µg/m^2) configuration. The non-galvanic SANMR, accounting for the Pb originating from the background zones of the Pb pipes, was considerably lower and less variable than the galvanic SANMR (15.3-fold for the Cu-Pb configuration treated with orthoP). Interestingly, PLSLs treated with sulfate show the lowest galvanic SANMR (7,349 and 9,499 µg/m^2 for the control *vs* 839 and 160 µg/m^{2}for the sulfate treated Cu-Pb and Pb-Cu configurations, respectively). This can be attributed to better control of Pb$_{part.}$ with the addition of sulfate, which is reflected in lower levels of Pb$_{diss.}$ and Pb$_{part.,}$ although significant particulate release remains (Figure 5.3).

The high galvanic SANMR value highlights the acute Pb concentrations that can potentially be present in the small volume of water at the junction of the Pb and Cu pipes (62 mL for 1.6 cm I.D and 41 mL for 1.3 cm I.D.). The median Pb concentrations at this junction was found to reach 1,271 (Cu-Pb) and 1,643 µg/L (Pb-Cu), in a small volume of water. While this high Pb level is likely to be diluted during water usage at the faucet or sampling, a volume of 250 mL would still carry a median of 314 (Cu-Pb) or 405 µg/L (Pb-Cu). It is noteworthy that an ingested dose of 175 µg of Pb is defined as an acute health risk for lead-contaminated toys (USCPSC, 2005). With the exception of sulfate treated water, a dose exceeding 175 µg would indeed be delivered in the volume of water in contact with the galvanic zone (1,208 and 1,563 µg Pb for the Cu-Pb and Pb-Cu configurations for the control condition) after 16HS, calculated using median galvanic SANMR values.

5.3.5 Comparison of Pb release between pilot and field investigations

In parallel to the present pilot study, a comprehensive field study was conducted in 112 households with FLSLs or PLSLs. This previous report included a detailed, longitudinal study before and after partial and complete LSL replacement at 25 sites (Deshommes et al., 2016b; Deshommes et al., 2017). Field and pilot study results can be compared by computing Pb released after 6HS under the control condition and expressing them as a SANMR value. Given that the current pilot study was operated for 155 weeks, we only considered the PLSLRs that were less than 2 years old from the previously published field study for the following comparison. Median Pb release from 100% Pb pipes after 6HS were 2.7-fold higher in the pilot pipes than in the field sites (Table 5.2). The following trend in SANMR values was observed in both pilot and field studies: Pb-Cu > Cu-Pb > 100%Pb. This comparison also shows that differences between pipe configurations are amplified at the pilot scale. After PLSLRs, field SANMRs for 100% Pb pipes increased by 1.2-fold *vs* Cu-Pb pipes and 3.9-fold *vs* Pb-Cu pipes, while the pilot study revealed increases of 2.7-fold and 11.8-fold, respectively. The variability of Pb release at the pilot-scale is due to the high $Pb_{part.}$ fraction. This is exemplified by the high contribution of the particulate SANMR to the total Pb SANMR estimates in the pilot, as opposed to the field observations (Table 5.2; 31-62% *vs* 4.4-11.6%).

Table 5.2 Apparent SANMR (total, dissolved and particulate Pb), expressed in μg/m^2 under the control condition for various experimental conditions tested compared to 6HS samples from the distribution system of the City of Montreal (Deshommes et al. 2016, 2017).

Pipe configuration	Pilot or field study	N	Median	10th percentile	90th percentile
SANMR of total Pb (μg/m^2)					
100%Pb	***Pilot***	*9*	*616.7*	*401.9*	*1,268*
	Field	51*	225.4	74.6	599.7
Cu-Pb	***Pilot***	*6*	*1657*	*596.7*	*7,112*
	Field, Recent*	51*	266.8	139.8	525.2
	Field, Aged**	33*	129.8	86.7	1,109
Pb-Cu	***Pilot***	*6*	*7262*	*906.5*	*545,769*
	Field, Recent	1*	882.9	-	-
	Field, Aged	24*	301.4	203.3	453.3
SANMR of dissolved Pb (μg/m^2)					
100%Pb	***Pilot***	*9*	480.8	244.6	753.9
	Field	49*	203.5	54.7	556.6
Cu-Pb	***Pilot***	*6*	636.7	515.7	1,197.0
	Field, Recent	50*	228.3	118.9	524.0
	Field, Aged	32	111.1	76.0	693.2
Pb-Cu	***Pilot***	*6*	2737.4	847.5	5,990.2
	Field, Recent	1	844.4	-	-
	Field, Aged	22	260.1	176.7	426.3
SANMR of particulate Pb (μg/m^2)					
100%Pb	***Pilot***	*9*	190.2	64.1	695.8
	Field	49*	18.7	3.4	72.7
Cu-Pb	***Pilot***	*6*	862.4	24.9	6,435
	Field, Recent	50*	30.9	11.7	130.3
	Field, Aged	32	13.1	5.8	266.8
Pb-Cu	***Pilot***	*6*	4525	59.0	539,779
	Field, Recent	1	38.5	-	-
	Field, Aged	22	29.8	10.0	97.1

SANMR values for field samples were obtained after 6 hours of stagnation, *Recent PLSLR are defined as those that are < 2 years old. **Aged PLSLRs are defined as those > 2 years old

The observed differences between pilot and field studies, especially for $Pb_{part.}$ levels, can be explained by the following statements:

- The method to estimate the Pb release varies between the pilot and field studies. In field investigations, the Pb mass in water is estimated from a concentration profile generated by sequential samplings at the tap. As a result, these measurements may also include Pb contributions from sources such as brass or scale present within the premise plumbing. Inaccurate estimations of the premises piping or the LSL and the presence of faucet aerators that can trap $Pb_{part.}$ may also influence Pb estimations from in LSLs. In contrast, directly sampling the LSLs at the pilot-scale only captures the contribution of the LSL and the galvanic connection and, in turn, may not provide an accurate depiction of an actual plumbing system. When collecting a 2L sample, we ensured that the complete volume of water stagnating within the LSL is collected, thereby allowing a better estimation of the SANMR. This is an advantage compared to residential sampling, where there are contributions from multiple sources of lead (brass, scales, etc.) within the premises plumbing.

- Water usage patterns differ considerably between pilot experiments and households (DeSantis et al., 2018), although water usages can also vary drastically between households (Del Toral et al., 2013). The pilot was continuously operated at a steady flow rate during the day for 8h, and then, submitted to an extended stagnation every night and over the weekends.

- Small differences in water quality may cause significant changes to the leaching of Pb into water. The pilot setup was fed with dechlorinated water from a distribution system containing moderate levels of total iron. The iron concentrations ranged from below detection limit to 141.4 µg Fe/L which is below the levels measured in the system's dead-ends (Dias et al., 2017). The maintenance of a chlorine residual impacts scale formation and composition, while iron has been shown to be associated with elevated $Pb_{part.}$ (Trueman & Gagnon, 2016).

- Most importantly, temperature fluctuations in the pilot study were more pronounced than what is experienced within buried pipes in the field. During overnight stagnation, the water temperature in the pilot pipes adjusted to room temperature. Moreover, mechanical expansion and contraction of the pipes throughout the day might have disrupted scales and caused more intense particle detachment. The detachment of scale deposits due to mechanical disturbances have been shown to increase Pb concentrations in LSLs (Del Toral et al., 2013; Lewis et al., 2017).

- The fate of Pb_{part} in a pilot pipe loop may differ between households. Pb_{part} released from an LSL or a galvanic connection may not reach the kitchen sampling faucet in households, as previously demonstrated (Deshommes et al., 2017). Indeed, complex premises plumbing may trap and redistribute Pb particles to the multiple points-of-use in a household. In our pilot study, we consider that most of particles are captured by sampling.
- Despite using the same fittings as the utility, their installation in the pilot study could have been different depending on how tightly they were assembled. Furthermore, the pilot pipes are not buried in the ground. As such, they experience different vibrations and movements compared to household pipes (Deshommes et al., 2017).

Our findings show the importance of using both a pressurized pilot system constructed with harvested LSLs, and field samplings to identify Pb release trends following changes to water quality and CCTs. Our data also reveals the limitations of using a pilot study to predict Pb levels at the consumer's tap. Some of these limitations could be overcome by implementing more realistic water usage patterns at the pilot-scale and by better assessing $Pb_{part.}$ release in households (Deshommes et al., 2017).

5.3.6 Managerial implication of partial LSL replacement

The main concern for utilities is whether PLSLR would increase lead concentrations at the consumer's tap. The present study contributes new knowledge to help determine whether PLSLR will be beneficial in a distribution system given its pre-existing water quality. It is clear that removing part of an LSL in order to reduce Pb levels may not compensate for the added Pb released at a new galvanic connection. Figure 5.6 shows the interplay between the non-galvanic release as a function of remaining length of Pb pipe, and the constant contribution of the galvanic connection. Using data acquired from the partial configurations, it is possible to determine the equivalence point at which the addition of a galvanic connection will not increase the mass of Pb released from the service line. Table 5.3 provides the approximate length of Pb pipe that need to be removed to balance Pb release from a new galvanic connection using both the median and 90th percentile SANMR values. 90th percentile values could be considered as the periods of peak Pb release from a group of LSLs operated in the same configuration. These equivalence points vary significantly depending on the CCT. When sulfate is added to decrease CSMR, a PLSLR of less than 0.8 m (using the 90th percentile SANMR) offsets the additional Pb released from galvanic corrosion. In contrast, orthoP treatment requires the greatest length of LSL to be removed in order to offset the Pb released by galvanic corrosion: 2.4 m (using the median SANMR) and 49.3 m (using the 90th percentile) (Table 5.3). This may be because (1) orthoP resulted in the highest galvanic SANMR, which was primarily explained by $Pb_{part.}$ release or (2) orthoP is highly effective in removing $Pb_{diss.}$ prior to PLSLR. Following the PLSLR, depending on the CCT implemented by the utility, the maximum length of Pb remaining to observe benefits will vary depending on the contribution from the galvanic lead release.

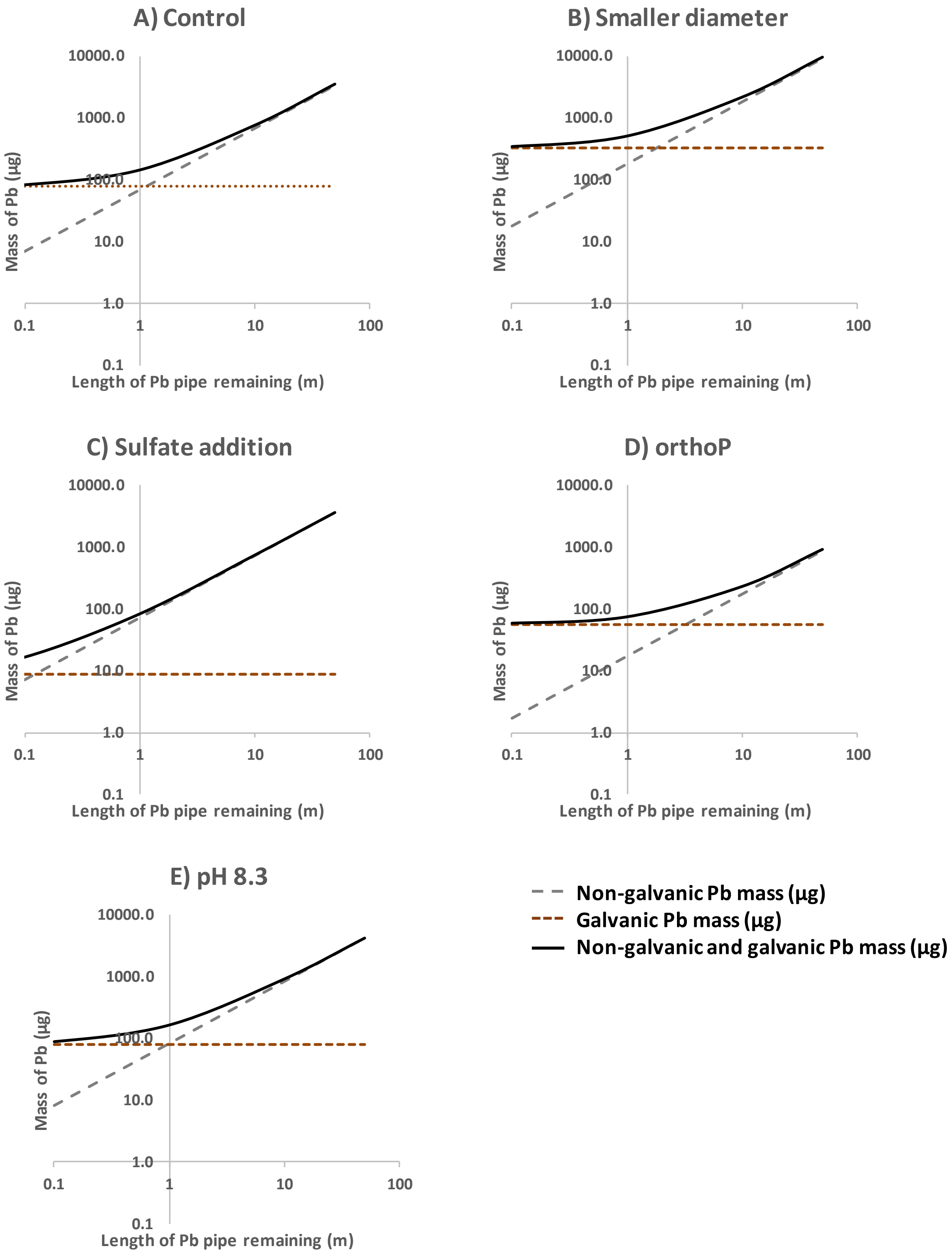

Figure 5.6 Mass of Pb released due to non-galvanic corrosion (grey), galvanic corrosion based on median non-galvanic SANMR (orange and dotted) and the sum of both (black) in the Cu-Pb pipe configuration under the (A) control, (B) smaller diameter, (C) sulfate treatment, (D) orthoP treatment and (E) pH 8.3 conditions.

Table 5.3 Length of LSL (in m) at which total Pb mass from non-galvanic corrosion equals Pb mass from galvanic corrosion.

Treatment	Pipe-configuration	Length (m) computed with median non-galvanic SANMR	Length (m) computed with 90th percentile non-galvanic SANMR
Control	**Cu-Pb**	1.1	3.8
	Pb-Cu	1.4	5.1
Smaller diameter	**Cu-Pb**	1.8	5.3
	Pb-Cu	0.3	1.0
Sulfate addition	**Cu-Pb**	0.1	0.8
	Pb-Cu	0.02	0.4
orthoP	**Cu-Pb**	3.2	31.9
	Pb-Cu	2.4	49.3
pH 8.3	**Cu-Pb**	0.9	1.2
	Pb-Cu	6.8	7.6

One of the key questions for utilities is whether they should conduct PLSLR when the owner cannot be required to replace the private section of the LSL. In the case of the utility studied, an average length of 7.5 m of Pb pipe is removed by the city during PLSLRs. According to the 90th percentile SANMR for the Pb-Cu configuration, a minimum length of 3.8 m would need to be removed to offset the adverse effects from galvanic contribution.

5.3.7 Options for utilities to decrease Pb concentrations

A decision framework to assist utilities in addressing managerial implications of new and legacy PLSL, including remedial actions is presented in Figure 5.7. In order to draft a management plan for LSLs, utilities must complete an inventory of FLSLs and PLSLs on their territory. This can be accomplished by obtaining households' years of construction and the historical use of Pb for service lines within the distribution system (Deshommes et al., 2016b). A field study should be conducted to estimate Pb release from FLSLs and PLSLs in sentinel homes, including new and legacy PLSLRs. The resulting data will provide an estimate of galvanic and non-galvanic SANMR, determining the length of Pb pipe to be removed to offset the addition of galvanic corrosion.

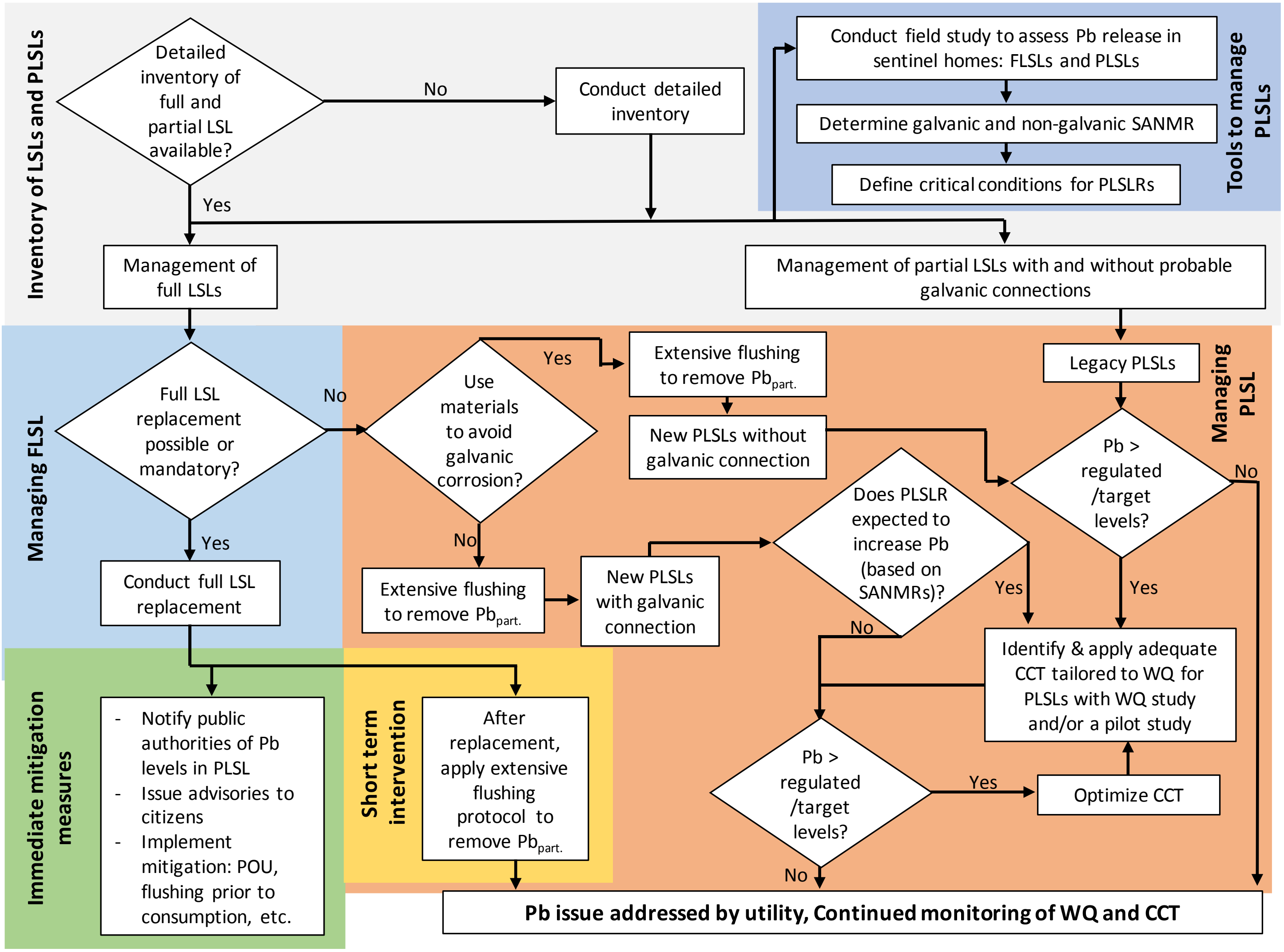

Figure 5.7 Framework for the management of full lead service Lines (FLSLs) and partial lead service lines (PLSLs) in a distribution system. POU: point-of-use, SANMR: surface area-normalized mass release, PLSLRs: partial lead service line replacements, CCT: corrosion control treatment.

Full LSL replacement should be the preferred approach. If this is not possible, utilities should aim to decrease galvanic corrosion by selecting materials such as PVC pipes or dielectric couplings (Deshommes et al., 2017; Wang et al., 2013). After any intervention, whether full or partial replacement, extensive flushing should be mandatory as acute exposure can result from pipe disturbances (Del Toral et al., 2013; Deshommes et al., 2017; Lewis et al., 2017). For new and legacy PLSLs, SANMRs can be used to estimate the likelihood of an increase in Pb concentrations. If partial replacements are likely to increase Pb concentrations, a CCT optimization process should be initiated to adjust the CCT in order to meet regulated/targeted Pb levels.

It is important to note that the findings of this study reflect the water quality and scale structure specific to Montreal's water distribution system and cannot be directly translated to any other system.

Although our results show that some CCTs can be effective at decreasing Pb concentrations in both FLSLs and PLSLs, other treatments are only adequate for one of the two pipe configurations. As a consequence, the best long-term solution is undoubtedly the complete removal of the LSL. When full LSL replacement is possible, temporary mitigation measures should be implemented to decrease exposure to Pb until all replacements are complete. Once a full replacement has been completed, extensive flushing protocols should be implemented to remove $Pb_{part.}$ (AWWA 2017; Deshommes et al., 2016b; Deshommes et al., 2017).

5.4 Conclusion

- Trends of higher Pb concentrations released from PLSLs than from FLSLs are sustained through time (155 weeks), as partial configurations released systematically higher Pb concentrations than the full lead service lines.
- The addition of orthoP was not effective to control $Pb_{part.}$ release from galvanic corrosion in PLSLs, but decreased $Pb_{diss.}$ in FLSLs. Under the water conditions tested, orthoP is a sub-optimal choice to control Pb release from both PLSLs and FLSLs.
- Decreasing CSMR by sulfate addition was the most effective treatment to decrease Pb concentrations from PLSLs due to its impact on $Pb_{part.}$, but it was not a viable solution to decrease Pb in FLSLs.

- SANMR values are useful to determine when a partial replacement is unlikely to increase the mass of Pb released and to determine the minimum length of lead pipe that should be removed to compensate for the addition of a galvanic junction.
- Pilot studies can be used as a proxy to determine the relative effectiveness of CCTs on Pb release in FLSLs and PLSLs, but they cannot predict true Pb levels at the tap.
- CCT efficacity depends on the configuration of the LSL. Utilities should take into account the number of FLSLs and PLSLs before selecting their corrosion control strategy (CCT and/or FLSL). Treatment solutions should be carefully selected to ensure risk reduction for both FLSLs and PLSLs.

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CHAPTER 6 ARTICLE 3 – LEAD AND COPPER RELEASE FROM FULL AND PARTIALLY REPLACED HARVESTED LEAD SERVICE LINES: IMPACT OF STAGNATION TIME PRIOR TO SAMPLING AND WATER QUALITY

When conducting partial lead service line (LSL) replacements, utilities aim at reducing customers' exposure to lead by replacing the lead pipe by a copper pipe. Studies have shown that this configuration in the LSL results in galvanic corrosion which increases Pb concentrations at the tap. Concerns with galvanic corrosion are from the increase in particulate Pb leaching. We provide a systematic evaluation to understand the role of the duration of stagnation (30 minutes to 2 weeks) on the production and the subsequent release of total and particulate lead as well as copper. We also present long-term (155 weeks) data on the impact of water quality adjustment on the passivation of copper pipes and on the release of soluble and particulate copper following partial LSL replacements. Our results show the importance of the pipe configuration (copper upstream or downstream of lead) as well as the water quality on copper leaching. Our results are interesting as it demonstrates how complex galvanic corrosion can be, as illustrated by the differences in lead and copper releases between the configurations studied. We observed that stagnation times greater than 16 hours do not increase the particulate Pb fraction. Therefore, increasing the stagnation time does not worsen the particulate Pb fraction. Finally, we provide insight on the impact of high velocity flushing in the accumulation and release of total and particulate Pb in full and partial LSL.This paper was submitted in *Water Research*. Supplementary information is presented in Appendix C.

LEAD AND COPPER RELEASE FROM FULL AND PARTIALLY REPLACED HARVESTED LEAD SERVICE LINES: IMPACT OF STAGNATION TIME PRIOR TO SAMPLING AND WATER QUALITY

Evelyne Doré[1], Elise Deshommes[1], Shokoufeh Nour[1], Michèle Prévost[1]

[1]Department of Civil, Mining and Geological Engineering, Polytechnique Montréal, Montréal, QC, Canada

[2]Ville de Montréal, Technical Expertise Division, Montréal, Canada

[*]Corresponding author: Tel: 514-340-4711 #3711; Fax: 514-340-5918; email: evelyne.dore@polymtl.ca

ABSTRACT

Partial lead service line replacement (PLSLR) results in the addition of a new galvanic connection and can increase lead concentrations at the tap. Focus has been given to minimizing lead release after PLSLR, but little information is available on the impact of lead remedial actions on copper concentrations, especially before passivation occurs. The impact of water quality (decreased chloride-to-sulfate mass ratio from 0.9 to 0.3; addition of orthoP; pH increase to 8.3) on lead and copper concentrations was investigated after stagnation (30 minutes to 336 hours) in a pipe rig comparing full lead service line (LSL), and two configurations of partial LSLs (Cu-Pb and Pb-Cu). Results show different trends for lead and copper: maximum lead concentrations were reached in 16 hours while copper concentrations continued to increase over 336 hours. Lead release rates were also the highest in the first 16 hours of stagnation and were strongly impacted by water quality and the configuration of PLSLR (Cu-Pb vs Pb-Cu). Increasing the sampling flow rate from 5 to 15 LPM drastically increased the particulate lead release (78-fold) in Pb-Cu configurations; this effect was however not observed in 100% Pb or Cu-Pb configurations. High velocity flushing prior to 16 hour stagnation decreased total Pb release by a factor of 12-fold for Cu-Pb, 1.6-fold for Pb-Cu and 2.0-fold for 100% Pb. Results support the definition of sampling protocols targeted for the detection of lead and copper sources and the proscription of flushing prior to sampling.

KEYWORDS: *Lead, copper, drinking water, partial lead service line replacement, sampling*

6.1 Introduction

Lead is a neurotoxin especially for young children, and low-level exposure has been linked with increased cardiovascular disease mortality in the United States (Lanphear et al., 2005; 2018). Exposure to elevated copper (4 mg/L) can cause nausea, vomiting and diarrhea while the long-term effects are not well documented (Health Canada, 2018; WHO, 2004).

Copper corrosion is mostly influenced by pH, alkalinity, dissolved inorganic carbon (DIC), redox potential (ORP), plumbing age and stagnation time prior to sampling (Edwards et al., 1994a; Lagos et al., 2001; Schock & Lytle, 2011; Schock & Sandvig, 2009). Increasing the pH of water reduces the solubility of copper from coupons and pipes, and therefore the concentration in water, although less benefits are observed above pH 7.2 (Edwards et al., 1994b; Pehkonen et al., 2002). The dissolution rate of copper is also affected by the type of copper corrosion products present in the pipes (Lagos et al., 2001). Indeed, the effect of chloride and sulfate on corrosion rate of copper is highly influenced by the scale materials present inside the pipes; chloride increasing corrosion at first, but then decreasing it as a protective layer formed, whereas the reverse phenomenon has been documented for sulfate (Edwards et al., 1994a). Adding Zn-orthoP and orthoP to simulated PLSLR rigs decreased copper concentrations in samples collected after 30 minutes and 6 hours of stagnation; no copper precipitation was observed when extending the stagnation up to 65 hours, whereas precipitation occurred in untreated pipes (Kogo et al., 2017). The addition of orthoP initially decreases copper scale solubility. However, it also inhibits the deposition of cuprite and malachite, which naturally form over decades, and results in lower solubility deposits (Schock & Sandvig, 2009). Finally, copper rarely gets corroded as a result of galvanic corrosion as it is more noble than other metals used in plumbing components (Edwards et al., 1994a), except when reversal of the Pb:Cu galvanic couple occurs (Arnold & Edwards, 2012).

Copper pipe experiments show an initial increase in copper concentrations with stagnation time along with a decrease in oxygen levels, and followed by a decrease in copper concentrations (Werner et al., 1994). As stagnation time increases, most studies concur that an increase in dissolved copper concentrations is observed as materials dissolved, and is followed by a decrease in concentrations as the copper scale is building up and there is precipitation (Hidmi & Edwards, 1999; Merkel et al., 2002). The duration of the increase in copper concentrations before reaching a plateau varies in the literature (6-92 hours), depending on experimental conditions and water quality parameters (Hidmi & Edwards, 1999; Lytle & Schock, 2000; Merkel et al., 2002). However, in cases where an oxidant residual was still present at the end of the stagnation period, such a decrease was not observed (Lytle & Schock, 2000).

Regarding lead pipe rig experiments, Schock et al. (1996) showed that lead concentrations aimed towards equilibrium following approximately overnight stagnation, despite a variable rate of increase within the first hours of stagnation, and which is in agreement with mass-transfer stagnation curve models (Kuch & Wagner, 1983; Schock, 1990). In pure lead coupons, an increase of 100 µg/L was observed at pH 7.0 between 24 and 72 hours of stagnation. However, such a difference was not observed at pH 8.5 (Lytle & Schock, 2000). In a pilot setup made of harvested LSLs with simulated PLSLR, increasing the stagnation time from 30 minutes to 16 hours prior to sampling resulted in an increase in dissolved lead concentrations (Cartier et al., 2013). Similar observations were made by Kogo et al. (2017) after stagnation times of 30 minutes, 6 hours and 65 hours in simulated PLSLR (untreated water, orthoP, Zn-orthoP and sodium silicate dosing). In Wang et al. (2013) study, lead pipes connected to copper pipes using plastic or brass connectors were left stagnating in water for 6 and 65 hours, with CSMR conditions of 0.7 and 7. Higher concentrations were measured after 65 hours and more so in the 0.7 CSMR water. Flushing water from the pipes decreases metal concentrations, as observed in LSLs after 1 and 5 minutes of flushing (Cartier et al., 2011). Then, diffusion modelling can be used to describe lead and copper release depending on varying stagnation time, however, when a higher fraction of particulate is present in the samples considerable scatter is shown in the model (Lytle & Schock, 2000).

Water quality and scale composition influence the shape of the stagnation pattern for both lead and copper release as a function on varying stagnation time (Lytle & Schock, 2000). Hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) oxidation rate changes with chlorine residual, a lag phase being observed at the beginning of stagnation and followed by a rapid oxidation (Liu et al., 2008). The oxidation rate of hydrocerussite, commonly found in LSLs (DeSantis et al., 2018), is a determining factor for the concentration of lead in water. In dissolution experiments using minium (Pb_3O_4) in the presence of free chlorine, Guo et al. (2016) observed an immediate lead dissolution, which is in agreement with previous experiments.

The objectives of this study were: (1) to analyze the impact of stagnation time on total, dissolved and particulate lead and copper concentrations in full and partial LSLs at pilot scale and (2) to determine how changing the water quality affects the release of lead and copper using different stagnation times for sampling.

6.2 Materials and methods

6.2.1 Pilot setup

Excavated LSLs from the Montreal distribution system were installed in a flow through pilot fed by dechlorinated water from the same distribution system, as detailed in Cartier et al. (2013) and in (Doré et al., 2018b). Under normal conditions, the setup was operated 8 hours per day, 5 days per week without stagnation exceeding 72 hours at a flow rate of 5 LPM per pipe (30 psi). The pilot was run with harvested LSLs over one year, and after that, PLSLR were simulated for a fraction (2/3) of the LSLs in the pilot by connecting the LSLs to a new copper pipe using a red-brass compression fitting (Cartier et al., 2013), resulting in three different pipe configurations.

The pipe configurations tested included: (1) a 100%Pb LSL of 3 m with no compression fitting, (2) a partial LSL with a 1.8 m new copper pipe (Type M) connected upstream of a 0.6 m aged LSL using a compression fitting (Cu-Pb configuration), (3) a partial LSL with an aged LSL (0.6 m) connected downstream of a new copper pipe (1.8 m) using a compression fitting (Pb-Cu configuration). The three configurations installed represent respectively an LSL without replacement (100%Pb), a PLSLR completed by the utility (Cu-Pb) or by the homeowner (Pb-Cu).

As described in Cartier et al. (2013) and in Doré et al. (2018b), different water qualities were tested in the pilot for LSLs with an internal diameter (I.D.) of 16 mm, including: (1) control condition (CSMR 0.9, pH 7.7, alk. 88 mg $CaCO_3$/L), (2) addition of sulfate as Na_2SO_4 (CSMR 0.3), (3) orthophosphate addition at 1 mg P/L with pH re-stabilisation to 7.7, and (4) increase in pH to 8.3 by dosing NaOH. A fifth condition consisted of smaller I.D. LSLs (13 mm) under control conditions and for which soldered red brass fittings were used for the PLSLR configurations.

6.2.2 Sampling for lead and copper

Lead and copper concentrations from the three pipe configurations tested in the pilot were monitored by repeated sampling after 16 hours of stagnation (16HS) over 155 weeks after PLSLR simulation to investigate the impact of PLSLR over long-term. A hundred weeks after PLSLR, additional sampling was performed over 7 to 11 weeks after varying stagnation times, including 6, 24, 48 and 72 hours as well as two weeks stagnation, and repeated three times. Finally, samples were collected twice after 30 minute stagnation, and 9 times under flowing conditions (0 minute stagnation). Batches of sampling were separated by a period of 4-6 weeks, during which the pilot was operated under normal conditions to allow the pipes to recover from the changes in operation.

Before any sampling event, water flow was modified to ensure that fresh water was brought to the pilot, to refrain contamination from upstream pipes (Cartier et al., 2013; Doré et al., 2018b). Then, water was allowed to sit for the pre-determined stagnation time. Pressure was maintained within each pipe rig throughout the duration of the stagnation. Sampling was carried out under the same flow rate as under operation, except for the smaller diameter pipes for which a flow rate of 15 LPM was elected. Sampling performed under flowing conditions is detailed elsewhere (Doré et al., 2018b). In all cases, to ensure that all water in contact with the lead and copper pipes was sampled, 2 L samples were collected.

Finally, for a period of 7 weeks, the smaller diameter pipes were operated under high flow rate (15 LPM) for a period of 1 hour, followed by 6 hours under normal flow rate (5 LPM) and by second period of high flow rate (1 hour). Grab samples were collected during periods of high and low flow rates.

Dissolved metals were measured after filtering a 40 mL aliquot on a 0.45 µm PVDF filter. Samples for total and dissolved metals were acidified with 0.5% HNO_3 directly in the sampling bottle for at least 24 hours at room temperature, and then, 0.5% HCl was added to obtain the appropriate matrix. Metal concentrations were measured in an ISO179025 certified laboratory using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). Detection limits were of 0.11 µg Cu/L and 0.02 µg Pb/L. Other water quality monitoring (pH, Cl_2, dissolved oxygen, TOC, turbidity, chloride, sulfate and phosphate) is described in Cartier et al. (2013) and in (Doré et al., 2018b).

6.2.3 Determination of lead and copper release rates

For each pipe configuration and water quality tested in the pilot setup, a release rate (µg/h) was estimated from the data obtained from the stagnation trials. A first release rate was calculated by fitting a linear equation for the data obtained under conditions of flowing and stagnation of 0.5, 6 and 16 hours. Then, a second linear equation was fitted to obtain the release rate for stagnation times ranging between 24 hours and 2 weeks.

6.2.4 Scale analysis

Scales present inside the full and partial LSLs were sampled depending on corrosion zones in partial LSLs and were then analyzed by powder XRD to identify major crystalline minerals present, as detailed in DeSantis et al. (2018) and Schock et al. (2008).

6.2.5 Statistical analysis

Statistica (StatSoft, Version 13.3) was used to carry out non-parametrical statistical analysis (Kruskal-Wallis ANOVA). Differences were considered significant if $p < 0.05$, unless stated otherwise.

6.3 Results and discussion

One of the key concerns raised with partial LSL replacements (PLSLRs) is the enhanced release of particulate lead ($Pb_{part.}$) and its contribution to exposure, including acute exposure, at the tap (Deshommes et al., 2010). A similar concern could be raised for particulate copper. Trends for the release of all forms of Pb and Cu can be examined after both short (0.5-16 hours) stagnation that can occur during normal water usage in residential buildings and after prolonged stagnations (24-336 hours) that are representative of extended inoccupancy periods.

6.3.1 Copper concentrations after PLSLR simulation

Following PLSLR simulation and after 16 hour stagnation, copper concentrations decreased from week 20 to 155 for both PLSLR configurations and for all water qualities (Figure 6.1). The formation of a passivating film is expected after the installation of Cu pipes in a distribution system with highest solubility associated with new un-passivated pipes (Edwards et al., 2002; Lagos et al., 2001; Schock et al., 1995; Turek et al., 2011). Copper concentrations in water are determined by the scales, and their solubility, formed at the interface between the pipe and the water (Schock & Lytle, 2011). For example, the solubility of cupric solids can be 10-1,000X greater than cuprous oxide or hydroxide (Lytle & Schock, 2000), which can impact the concentrations of copper in water. A brief investigation of the scale composition, present in this pilot, by powder XRD revealed that the dominant mineral present in all pipes was cuprite (CuO_2) with some presence of Cu(II) such as tenorite (CuO), malachite ($Cu_2CO_3(OH)_2$) and traces of posnjakite ($Cu_4(SO_4)(OH)_6 \cdot H_2O$).

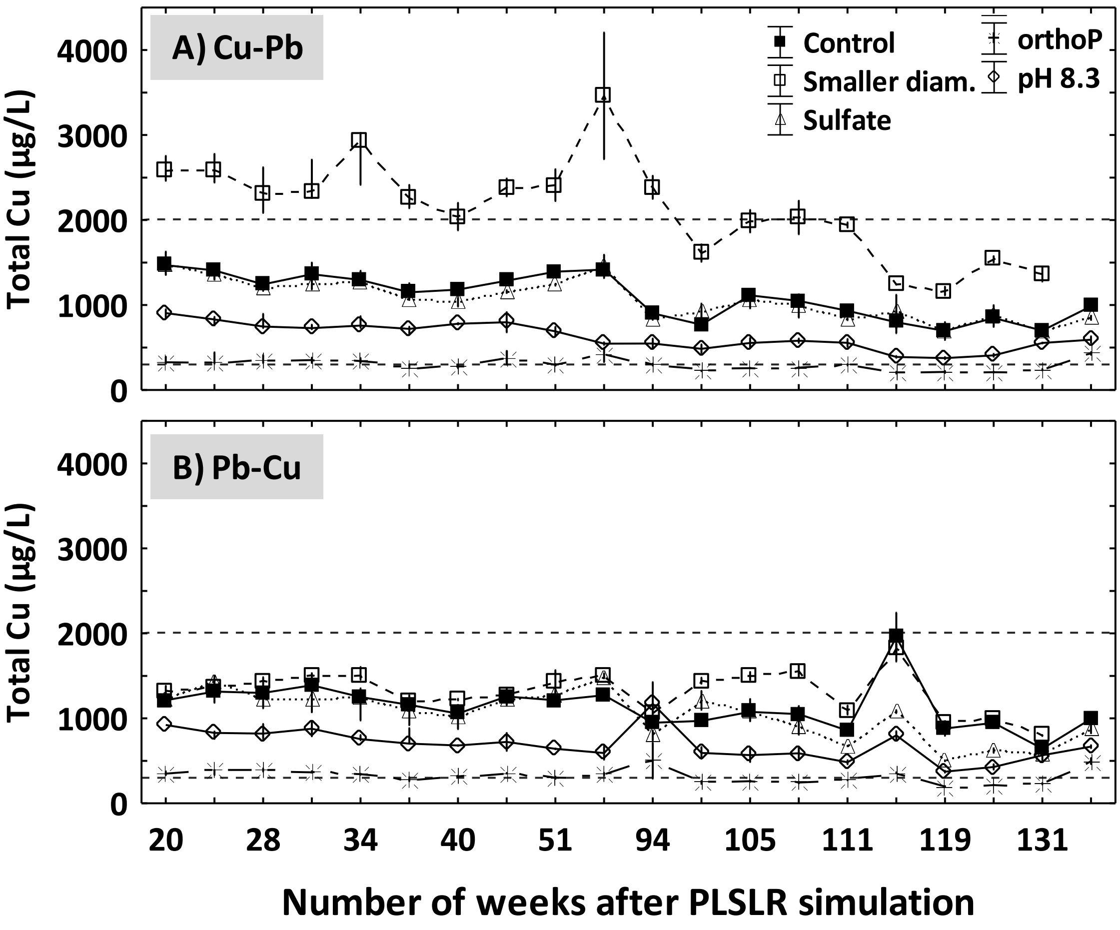

Figure 6.1 Total copper concentrations (µg Cu/L) after 16 hour stagnation inside the Cu pipe section for partial LSLs with the Cu pipe: (A) upstream (Cu-Pb) and (B) downstream (Pb-Cu) of an aged Pb pipe as a function of the number of weeks after the simulation of a PLSLR. Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent the 10th and 90th percentile concentrations.

Median concentrations were clearly highest for the smaller diameter (16 mm) pipes and trended downward after week 104, globally decreasing by 1.6-fold (Cu-Pb) and 1.7-fold (Pb-Cu). To account for the lower dilution in the smaller diameter, median masses of copper released from the Cu-Pb configuration over the whole period were compared to the control condition and found to be similar (815.8±213.5 µg Cu for the 16 mm vs 798.7±178.3 µg Cu for the 22 mm). Interestingly, median masses of copper were significantly lower in the small diameter pipe in the Pb-Cu configuration (487.9±87.5 µg Cu for the 16 mm vs 803.7±180.8 µg Cu for the 22 mm, $p < 0.001$).

With the exception of the smaller diameter pipe in the Cu-Pb configuration in the first 104 weeks, 90th percentile Cu concentrations remained well below 2,000 µg Cu/L after 16HS, which is the new health-based maximum acceptable concentration (MAC) recommended by Health Canada (2018) and WHO (2017). However, not even the addition of orthoP reduced copper concentrations below the California PHG of 300 µg Cu/L, as 90th percentile values reached 415.1 µg Cu/L and 394.1 µg Cu/L for the Cu-Pb and Pb-Cu configuration respectively.

The modest increase of pH from 7.8 to 8.3 decreased median Cu concentrations by 42-44% in both PLSLR configurations, in agreement with the low solubility of CuO (Schock et al., 1995), the dominant mineral detected. A similar decrease in copper concentrations, associated to an increase in pH (pH 7.15 to 7.8, alk. 200 mg $CaCO_3$/L), was observed at bench scale in new copper pipes (Edwards et al., 2011) and in copper coupons in contact with synthetic water (Pehkonen et al., 2002). The addition of sulfate to decrease the CSMR from 0.9 to 0.3 did not influence Cu release in agreement with findings from Shock et al. (1995) stating that sulfate complexes are not likely to be significant for cuprosolvency. However, in copper pipes connected to Pb pipes at bench scale, Kogo et al. (2017) related an increase in CSMR to an increase in copper concentrations after 30 minutes and 6 hours of stagnation.

Copper concentrations in presence of orthoP remained quasi constant throughout the duration of the experiment with 90th percentile concentrations of 441.4 and 394.1 µg Cu/L 104 weeks before the PLSLR simulation for the Cu-Pb and Pb-Cu configurations respectively, and of 415.1 and 463.4 µg Cu/L after 104 weeks. The addition of orthoP was the most effective treatment to reduce copper concentrations in both PLSLR configurations after 16HS, with median concentrations 3.9-fold (Cu-Pb) and 3.6-fold (Pb-Cu) lower than concentrations for the control condition.

The addition of orthoP has been shown to cause a rapid decrease of Cu concentrations in similar water quality in coupon (Pehkonen et al., 2002), pilot (Edwards et al., 2002), and full scale (Schock & Sandvig, 2009) testing. Dosing 1 mg P/L of orthoP showed a similar decrease in copper concentrations in a pipe rig, it however required a dose of 2 mg P/L to decrease concentrations below 1,300 µg Cu/L (Edwards et al., 2011). Utilities which added orthoP for the control of lead concentrations also witnessed an initial decrease in copper levels shortly after the onset of the added corrosion control treatment (Schock & Sandvig, 2009).

6.3.2 Effect of stagnation time on copper concentrations

Copper concentrations measured in the 2 L samples were adjusted to reflect the concentration of water stagnating in the copper pipe section (362-684 mL). As triplicate stagnation trials were conducted over a period of 40 weeks, the sampling period was sufficiently long to provide time for scales to age. Aging of the copper pipes in the pilot is expected to promote the formation of cuprite (CuO_2) and then malachite ($Cu_2CO_3(OH)_2$) and tenorite (CuO) (Ives & Rawson, 1962; Schock & Lytle, 2011).

Figure C.1 shows the variability of the copper concentrations between sampling events for duplicate pipes as a function of stagnation time. Indeed, copper concentrations released for the control condition and the orthoP in the Cu-Pb configuration follow similar trends for a given sampling event (flowing to 72 hours). However, different long-term trends of copper concentrations are observed after extended 336 hours of stagnation for the same pipe during one sampling event, between duplicate pipes, between events and between water qualities. The application of orthoP stabilizes the concentrations of dissolved copper ($Cu_{diss.}$) as these concentrations are clearly more stable throughout the sampling period, even after long stagnation times, as compared to the control condition (Figure C.1, B and D).

For nearly all water qualities tested, concentrations of total, dissolved and particulate copper (Cu_{total}, $Cu_{diss.}$ and $Cu_{part.}$) increase sharply within the first 16 hours of stagnation (Figure 6.2 for Cu-Pb, Figure 6.3 for Pb-Cu). A similar increase was also observed for total copper over 20-25 hours by Lytle and Schock (2000) in a pipe loop fed by hard softened and untreated groundwaters, while the maximum was observed after only 10 hours for a new pipe-rig with similar water quality (alk. 89 mg $CaCO_3$/L, pH 7.3) (Merkel et al., 2002). After the sharp initial increase, copper concentrations tend to fluctuate for all water qualities, with a few pipes showing peak concentrations after 336 hours. As the duration of stagnation increases, dissolution and precipitation of copper can both occur. No trend of decreasing concentrations with extended stagnation, following a 'Werner' characteristic curve, was systematically observed. This is in contrast to sharp decreases (>90%) reported by Lytle and Schock (2000) after 72-92 hours (DO <0.4 mg O_2/L), or after 60-72 hours (Merkel et al., 2002; Merkel & Pehkonen, 2006). Dissolved oxygen concentrations in the pilot after stagnation ranged from 3.0-11.7 mg O_2/L reflecting the oversaturation in the distributed water. In the presence of orthoP, Edwards et al. (2002) observed an increase in copper concentrations by 2-fold from 8 to 72 hours in a pipe rigs, which is consistent with the 1.4-fold increase between 6 and 72 hours for both partial configurations orthoP treated pipes in this study.

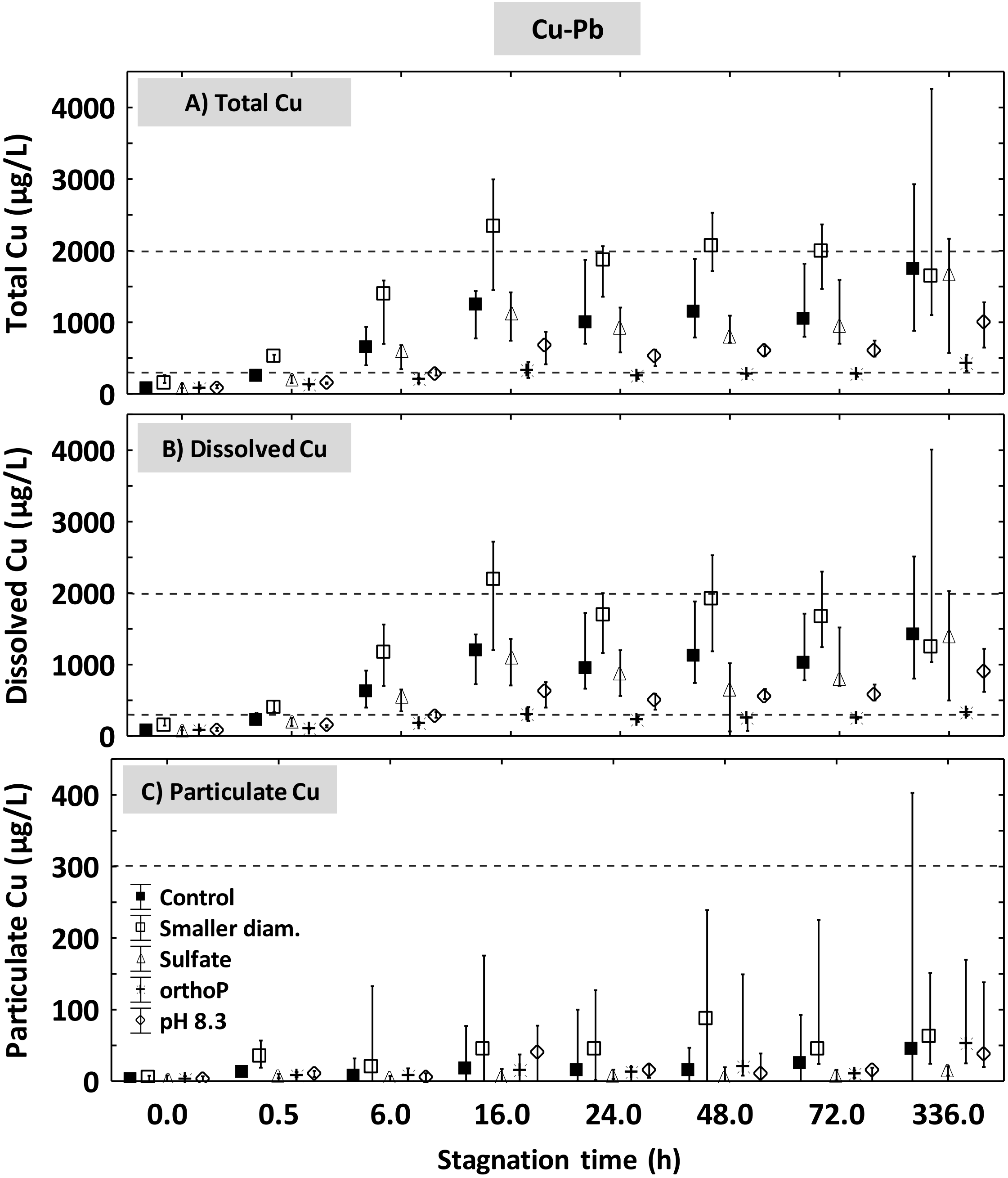

Figure 6.2 Copper concentrations (µg Cu/L) in the copper pipe section as a function of stagnation time for partial LSLs in which the copper pipes are upstream of the Pb pipes (Cu-Pb). Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent 10th-90th percentile concentrations.

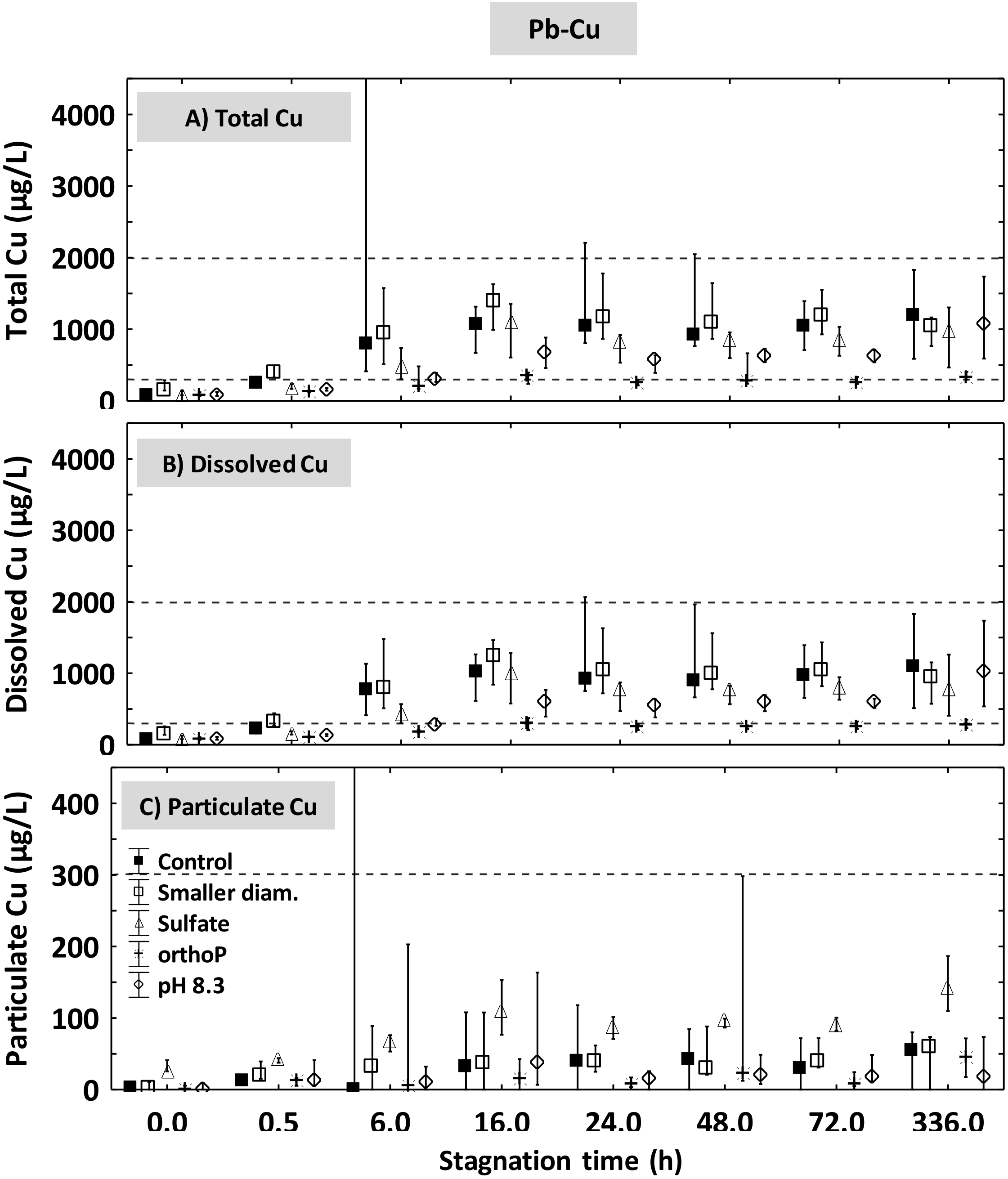

Figure 6.3 Copper concentrations (µg Cu/L) in the copper pipe as a function of stagnation time for partial LSLs in which the copper pipes are downstream of the Pb pipes (Pb-Cu). Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent 10th-90th percentile concentrations.

The impact of the induced water quality changes can also be assessed by comparing the release rates of Cu_{total}, $Cu_{diss.}$, and $Cu_{part.}$ (µg Cu/h) presented in Table 6.1. Overall, the rate of increase in $Cu_{diss.}$ can be well predicted for the first 16 hours of stagnation (R^2 range: 0.54-0.95) for all but the control Pb-Cu pipes. Resulting rates of release vary widely from 8.3 to 40.3 µg Cu_{total}/h depending on water quality. The rate of increase of Cu_{total} concentrations in the pipe (µg Cu/h) is comparable for the control and small diameter pipes for the Cu-Pb, but not for the Pb-Cu, reflecting the larger mass released in the Cu-Pb configuration (Figure 1). The release of $Cu_{diss.}$ is the main contributor to Cu_{total} in the Cu-Pb configuration (74-89%), and to a lesser degree for the Pb-Cu configuration (65-94%). The contributions from $Cu_{part.}$ could only be predicted as a function of stagnation time for the Cu-Pb configuration showing modest values ranging from 1.19-10.3 µg Cu_{part}/h.

Table 6.1 Total, dissolved, and particulate copper release rate (µg Cu/h) for the partial LSLs with the Cu pipe upstream (Cu-Pb) and downstream (Pb-Cu) for the different treatments tested on the pilot setup. The release rate is presented for the first 16 hours of stagnation and from 24 to 336 hours (2 weeks) of stagnation.

Pipe configuration	Treatment	Cu form	0 to 16HS		24 to 336HS	
			Rate	R^2	Rate	R^2
Cu-Pb	**Control**	$\mathrm{Cu_{total}}$	32.2	0.83	1.3	0.21
		$\mathrm{Cu_{diss.}}$	28.8	0.79	0.9	0.14
		$\mathrm{Cu_{part.}}$	4.0	0.53	0.4	0.22
	Smaller diameter	$\mathrm{Cu_{total}}$	39.2	0.83	0.2	0.01
		$\mathrm{Cu_{diss.}}$	28.9	0.81	0.2	<0.01
		$\mathrm{Cu_{part.}}$	10.3	0.56	0.03	<0.01
	Sulfate addition	$\mathrm{Cu_{total}}$	29.5	0.84	1.2	0.24
		$\mathrm{Cu_{diss.}}$	25.9	0.85	1.1	0.20
		$\mathrm{Cu_{part.}}$	4.2	0.53	0.05	<0.01
	orthoP	$\mathrm{Cu_{total}}$	8.3	0.90	0.4	0.72
		$\mathrm{Cu_{diss.}}$	6.9	0.90	0.2	0.47
		$\mathrm{Cu_{part.}}$	1.4	0.60	0.2	0.23
	pH 8.3	$\mathrm{Cu_{total}}$	19.7	0.97	1.0	0.72
		$\mathrm{Cu_{diss.}}$	16.3	0.93	0.8	0.66
		$\mathrm{Cu_{part.}}$	3.4	0.50	0.2	0.42
Pb-Cu	**Control**	$\mathrm{Cu_{total}}$	40.3	0.08	-0.1	<0.01
		$\mathrm{Cu_{diss.}}$	31.5	0.66	-0.1	<0.01
		$\mathrm{Cu_{part.}}$	8.8	<0.01	-0.003	<0.01
	Smaller diameter	$\mathrm{Cu_{total}}$	19.5	0.58	-0.2	0.09
		$\mathrm{Cu_{diss.}}$	18.3	0.61	-0.2	0.09
		$\mathrm{Cu_{part.}}$	1.2	0.14	0.02	<0.01
	Sulfate addition	$\mathrm{Cu_{total}}$	26.1	0.83	0.2	0.04
		$\mathrm{Cu_{diss.}}$	24.6	0.90	0.1	0.01
		$\mathrm{Cu_{part.}}$	1.8	0.13	0.1	0.08
	orthoP	$\mathrm{Cu_{total}}$	10.8	0.54	0.1	0.07
		$\mathrm{Cu_{diss.}}$	7.3	0.90	0.07	0.15
		$\mathrm{Cu_{part.}}$	3.6	0.13	0.05	<0.01
	pH 8.3	$\mathrm{Cu_{total}}$	27.5	0.73	1.3	0.59
		$\mathrm{Cu_{diss.}}$	17.9	0.95	1.3	0.55
		$\mathrm{Cu_{part.}}$	9.6	0.24	0.03	0.05

For long term stagnation ranging from 16 hours to 2 weeks, release rates could not be quantified because of the high variability in Cu concentrations, except for the pH 8.3 (Cu-Pb and Pb-Cu) and the addition of orthoP (Cu-Pb) ($R^2 \geq 0.58$). For those conditions, estimated rates show that copper release represent less than 6.1% of the rates observed during the first 16 hours. However, Cu_{diss} remained most dominant over time during extended stagnation (48-83%).

Overall, orthoP and increased pH (8.3) treatment were most effective to decrease all forms of copper after both short and extended stagnation which could be expected based on preferred scale minerals formed. Indeed, solids such as $Cu_3(PO_4)_2$ form in the presence of orthoP, which have a lower solubility than $Cu(OH)_2$, explaining the lower copper concentrations measured (Edwards et al., 2002). Increasing pH from 7.8 to 8.3 will also lower the solubility of Cu(II) and malachite at low DIC such as in the test water (Schock & Lytle, 2011).

As the pilot included brass fittings, it is possible that the red-brass compression fittings present in the pilot contributed to copper levels in the water. Furthermore, copper release could be reduced if the copper pipe is galvanically protected when acting as the cathode in the galvanic couple (Pb-Cu and Cu-brass) (DeSantis et al., 2018). However, a reversal of the galvanic couple is possible under specific water quality promoting the formation of low solubility Pb(IV) solids (Arnold & Edwards, 2012; DeSantis et al., 2018).

6.3.3 Effect of stagnation time on lead concentrations

As stagnation increases, lead concentrations are expected to rise first rapidly and then taper off to reach a quasi-equilibrium after about 15 hours, in agreement with mass-transfer stagnation curve models derived from lead pipe-rigs (pH 6.8 alk. 10 mg $CaCO_3$/L and pH 7.2 alk. 213 mg $CaCO_3$/L) (Kuch & Wagner, 1983; Schock, 1990). Lead concentrations in water after stagnation are determined by the composition of the scale, Pb(IV) solids being less soluble than Pb(II) products (Schock & Lytle, 2011; Triantafyllidou et al., 2015) and depend on the contribution of $Pb_{part.}$ (Cartier et al., 2013; Deshommes et al., 2010). Preliminary analysis of the scales in the pipe rig revealed the dominance of the Pb(II) compounds, cerussite ($PbCO_3$) and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), which are both very soluble.

Figure C.2 and Figure C.3 show detailed results per replicate pipe for 100% Pb and Cu-Pb configurations for control and orthoP conditions over the repeat stagnation trials extending over

40 weeks. Unlike observations on the variability of copper release over time, lead release, for a given pipe, was found to be stable. However, significant variability was noted between replicate pipe concentrations either in the full LSL or PLSLR configurations. The variability between replicate pipes most probably reflect heterogeneity of scales of the harvested lead pipes from the distribution system of the city, in contrast to the uniform initial surfaces of newly installed copper piping.

6.3.3.1 100%Pb configuration

For all conditions tested, total, dissolved and particulate lead (Pb_{total}, $Pb_{diss.}$ and $Pb_{part.}$) released from 100%Pb pipes (Figure 6.4) follow the same trend of increasing concentrations as a function of stagnation time. A sharper increase is observed at short stagnation times (< 16h). Rapid increase in concentrations is expected to be followed by a plateau after 16HS as predicted by solubility modelling (Kuch & Wagner, 1983), and as verified for different water qualities and corrosion treatment (Edwards & McNeill, 2002).

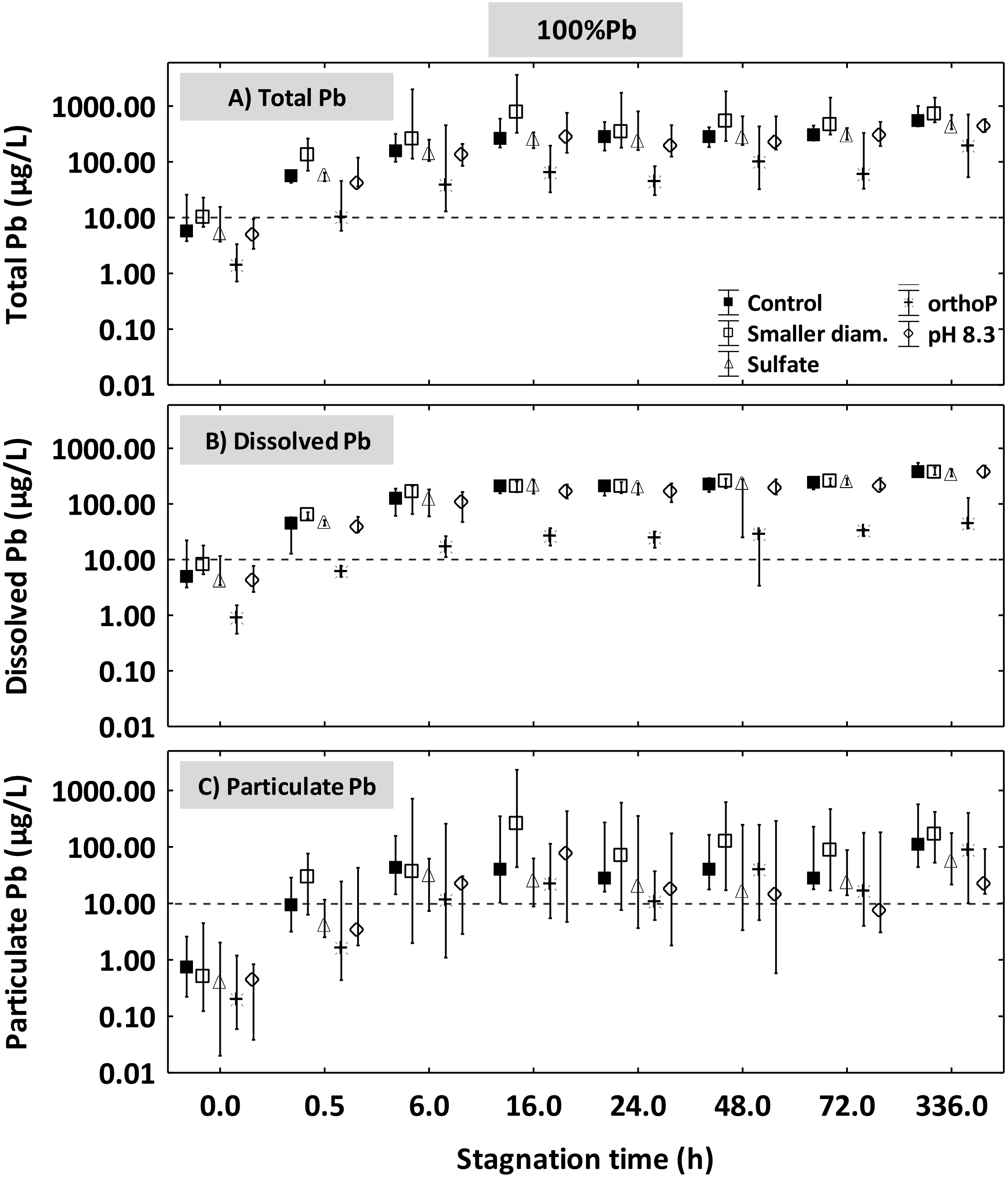

Figure 6.4 Lead concentrations (µg Pb/L) in the lead pipe section as a function of stagnation time for full LSL (100%Pb). Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent 10th-90th percentile concentrations.

For stagnation times up to 16 hours, median lead concentrations were the lowest for the orthoP condition as compared to the smaller diameter pipes, showing differences ranging from 6.4-9.8X for Pb_{total}, 8.2-14.4X for Pb_{diss}, and 2.7-7.3X for Pb_{part}. The maximum Pb concentrations were generally measured after 16HS for all conditions tested and reached a median of 777.6 µg Pb_{total}/L in the small diameter (13 mm) Pb pipe. Despite an apparent increase in Pb concentrations, flowing and 30 minute stagnation samples results were not significantly different ($p < 0.05$). However, 30 minute stagnation concentrations were significantly lower ($p < 0.1$) than those after 16 hours for all conditions but the orthoP, for which a significant increase was only observed after 2 weeks. Lytle and Schock (2000) reported also small differences after 24 and 72 hours of stagnation using lead coupons exposed to pH 8.5 water.

The trends in the particulate lead fraction as stagnation increases can be observed on Figure 6.5A showing wide variations of fractions at any given time for a pipe, corresponding to the sporadic release of particles captured by the 0.45 µm filters. Nevertheless, a clear trend of smaller yet variable particulate fractions was measured in flowing samples (13.2-36.6%) and, to a lesser extent in 30 minute stagnation samples (14.4-84.4%), for all conditions tested. A clear trend of increased particulate fraction after 6 hours of stagnation was only observed for the orthoP and small diameter conditions, as particulate fractions increased from a median of 30.2% and 33.5% after 0-30 minutes to 56.6% and 54.2% after 6 hours respectively. Our findings are consistent with elevated fractions of 58-78% (2 hour stagnation) and up to 46% (flowing) reported for 1 mg/L-P orthoP at pH 7.5 in newly aged lead pipes (Xie & Giammar, 2011). For other conditions (pH 8.3, sulfate and control), fractions remained steady in flowing samples and throughout stagnation, ranging from 12.5-16.9%. In the orthoP condition, it must be noted that the high particulate fraction corresponds to a concentration of Pb_{part} lower than with other conditions (Figure 6.4C).

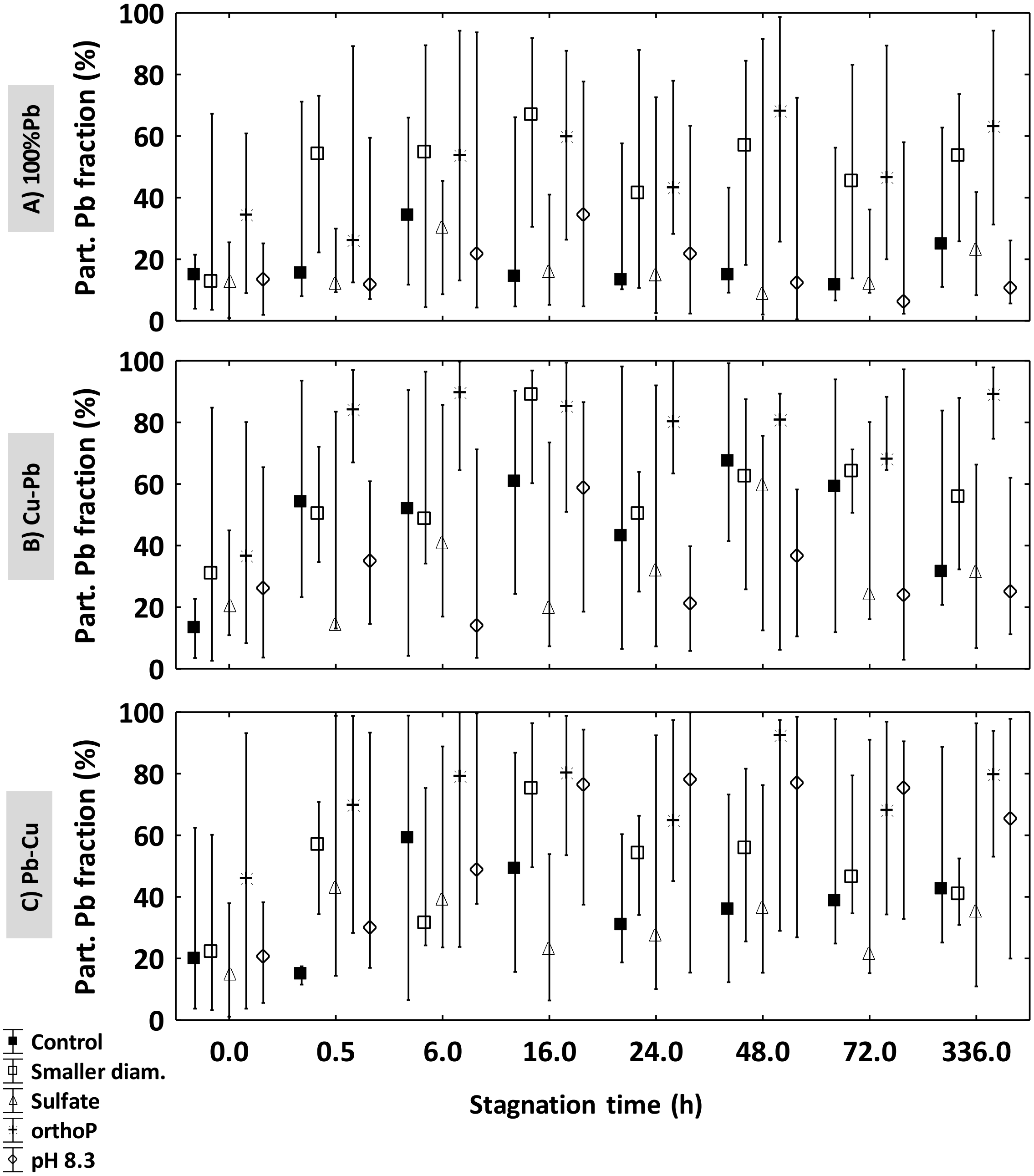

Figure 6.5 Particulate Pb fraction after different stagnation times for (A) 100%Pb, (B) Cu-Pb, and (C) Pb-Cu. Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent 10th-90th percentile concentrations.

Depending on water quality, Pb_{total} release rates vary widely (7.6 to 37.0 µg Pb_{total}/h) within the first 16 hours of stagnation, with the worst release in the small diameter pipe (Table 6.2). As for copper, the lowest lead release rates are observed after the addition of orthoP, with dissolved lead release rates 2-fold lower than for the control condition (0-16HS). Dissolved lead concentrations from 100%Pb pipes can be well predicted (R^2>0.80) and accounted for 13-61% of the Pb_{total} release rate (Table 6.2). The release of particulate lead could not be predicted because of its high intrinsic variability (Figure 6.5C), most probably caused by the sporadic detachment of Pb_{part} from the scales as observed in Figure 6.4C. When considering stagnation extending from 24-336 hours, much smaller $Pb_{diss.}$ release rates were observed, representing less than 6.2% of the rates observed during the first 16 hours (R^2 = 0.46-0.82). The release of Pb_{total} during extended stagnation are poorly predicted (R^2 ≤0.54), again because of the random nature of $Pb_{part.}$ detachment. As with copper concentrations for extended stagnation, total lead release rates are harder to predict with the co-occurrence of dissolution and precipitation mechanisms in the pipes.

Table 6.2 Total, dissolved, and particulate lead release rate (µg/h) for the full LSL (100%Pb) and partial LSLs (Cu-Pb and Pb-Cu) for the different treatment tested on the pilot setup. The release rate is presented for the first 16 hours of stagnation, and from 24 to 336 hours (2 weeks) of stagnation.

Pipe configuration	**Treatment**	**Pb form**	**0 to 16HS**		**24 to 336HS**	
			Rate	**R^2**	**Rate**	**R^2**
100%Pb	**Control**	Pb_{total}	15.9	0.47	0.6	0.54
		$Pb_{diss.}$	7.0	0.86	0.4	0.69
	Smaller diameter	Pb_{total}	37.0	0.32	0.4	0.08
		$Pb_{diss.}$	4.8	0.80	0.2	0.82
	Sulfate addition	Pb_{total}	11.1	0.58	0.4	0.26
		$Pb_{diss.}$	6.8	0.84	0.3	0.67
	orthoP	Pb_{total}	7.6	0.40	0.3	0.17
		$Pb_{diss.}$	1.0	0.87	0.07	0.46
	pH 8.3	Pb_{total}	15.7	0.52	0.4	0.33
		$Pb_{diss.}$	6.5	0.87	0.4	0.81
Cu-Pb	**Control**	Pb_{total}	6.8	0.41	-1.5	0.03
		$Pb_{diss.}$	2.0	0.81	0.2	0.90
	Smaller diameter	Pb_{total}	33.7	0.38	1.0	0.18
		$Pb_{diss.}$	5.2	0.51	0.1	0.08
	Sulfate addition	Pb_{total}	6.6	0.50	0.2	0.04
		$Pb_{diss.}$	2.0	0.79	0.02	0.8
	orthoP	Pb_{total}	100.4	0.27	-2.6	0.02
		$Pb_{diss.}$	0.5	0.66	-0.04	0.02
	pH 8.3	Pb_{total}	9.0	0.59	0.1	<0.01
		$Pb_{diss.}$	2.0	0.82	0.2	0.76
Pb-Cu	**Control**	Pb_{total}	58.5	0.016	0.2	0.0002
		$Pb_{diss.}$	5.00	0.45	0.2	0.19
	Smaller diameter	Pb_{total}	17.9	0.40	0.1	0.09
		$Pb_{diss.}$	1.3	0.52	0.1	0.81
	Sulfate addition	Pb_{total}	-0.3	<0.01	1.4	0.09
		$Pb_{diss.}$	2.2	0.66	0.1	0.44
	orthoP	Pb_{total}	182.2	<0.01	-0.102	<0.01
		$Pb_{diss.}$	1.1	0.42	0.0095	0.04
	pH 8.3	Pb_{total}	36.7	0.087	-24.1	0.04
		$Pb_{diss.}$	3.1	0.76	0.1	0.31

Stagnation curves were produced by Cartier et al. (2013) shortly after the simulated PLSLR (less than 4 months) reporting marked increases in both dissolved/colloidal lead after extending the stagnation from 30 minutes to 16 hours. A growing proportion of $Pb_{part.}$ was observed after 16HS. For 100% lead pipes, $Pb_{part.}$ release increased by 7-27X between 30 minute and 16 hour stagnation sampling, while in PLSLR, the increase of $Pb_{part.}$ ranged from 3-25X excluding the condition at pH 8.3.

6.3.3.2 Cu-Pb and Pb-Cu configurations

The role of $Pb_{part.}$ in increasing Pb concentrations at the tap after extended stagnation is a key question, especially in the case of partial LSL replacements. It has been suggested that extending stagnation will increase the relative contribution of particulate lead in the total lead released during stagnation (Cartier et al., 2013). In simulated PLSLRs, the addition of the galvanic connection between the Pb and the Cu pipes as well as the brass fittings adds new sources for metal release as compared to 100%Pb configurations. Overall, more variability in total lead concentrations can be observed in the partial LSLs (Figure 6.6 and Figure 6.7) than in the full LSLs (Figure 6.4). This variability can be explained by the sporadic spikes of particulate lead concentrations in the samples, which is reflected in the higher fraction of particulate Pb (Figure 6.5B and Figure 6.6C for Cu-Pb and Pb-Cu respectively). A clear trend of smaller yet variable particulate fractions is found in flowing samples for all conditions (13.2-36.6%) except for orthoP (36.6-45.8%). Extremely high median particulate fractions were observed after any stagnation (30 minutes to 2 weeks) for the orthoP (68-92.3%) and small diameter (31.7-89.0%) conditions. For other conditions (pH 8.3 and control), particulate fractions also increased after stagnation, it was however less so for the sulfate condition (21.6-43.4%). In the case of the orthoP condition, it can be noted that the high particulate fraction corresponds to elevated concentrations of Pb_{part}, unlike observations with 100%Pb pipes.

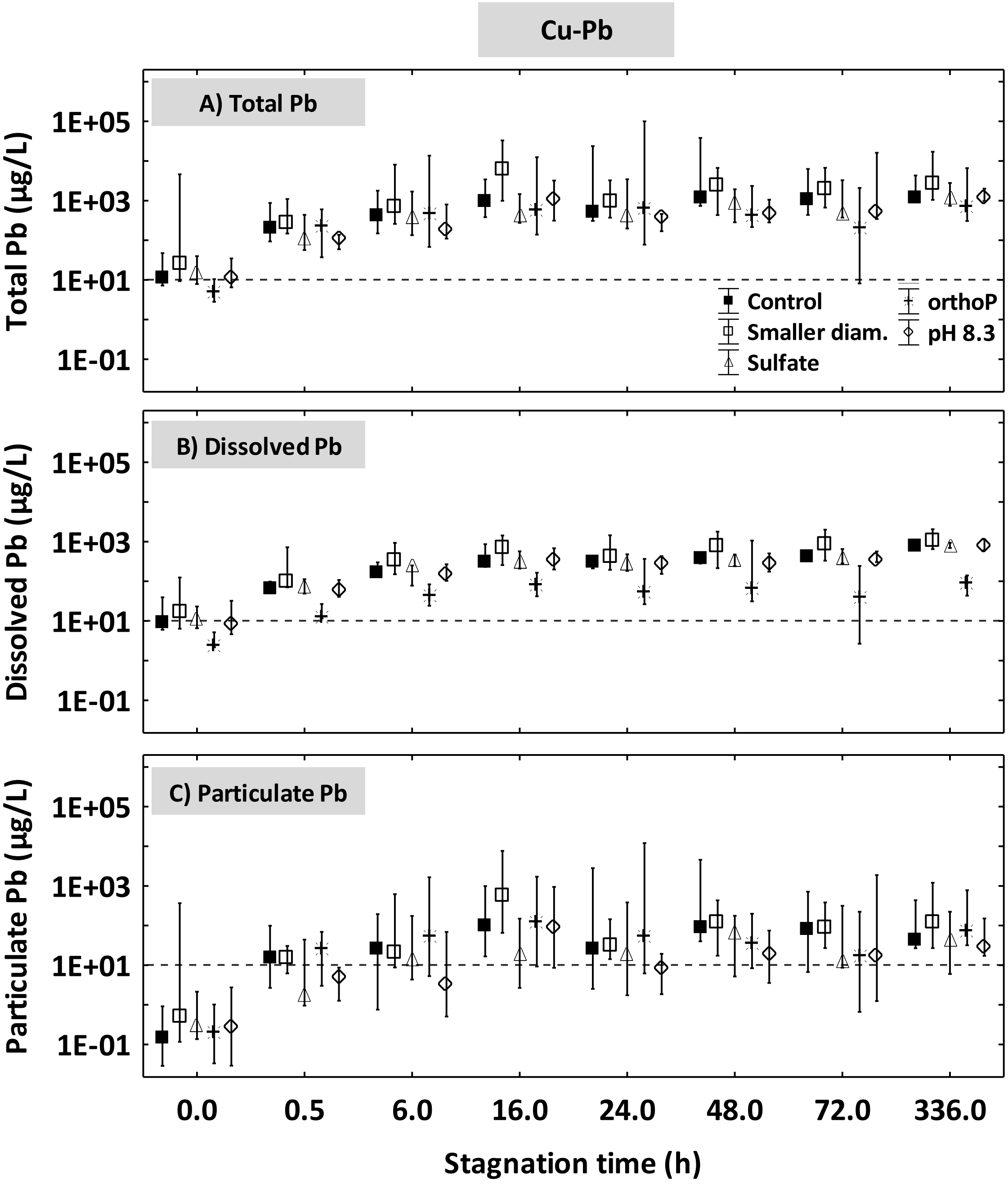

Figure 6.6 Lead concentrations (µg Pb/L) in the lead pipe section as a function of stagnation time for partial LSLs in which the copper pipes are upstream of the Pb pipes (Cu-Pb). Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent 10th-90th percentile concentrations.

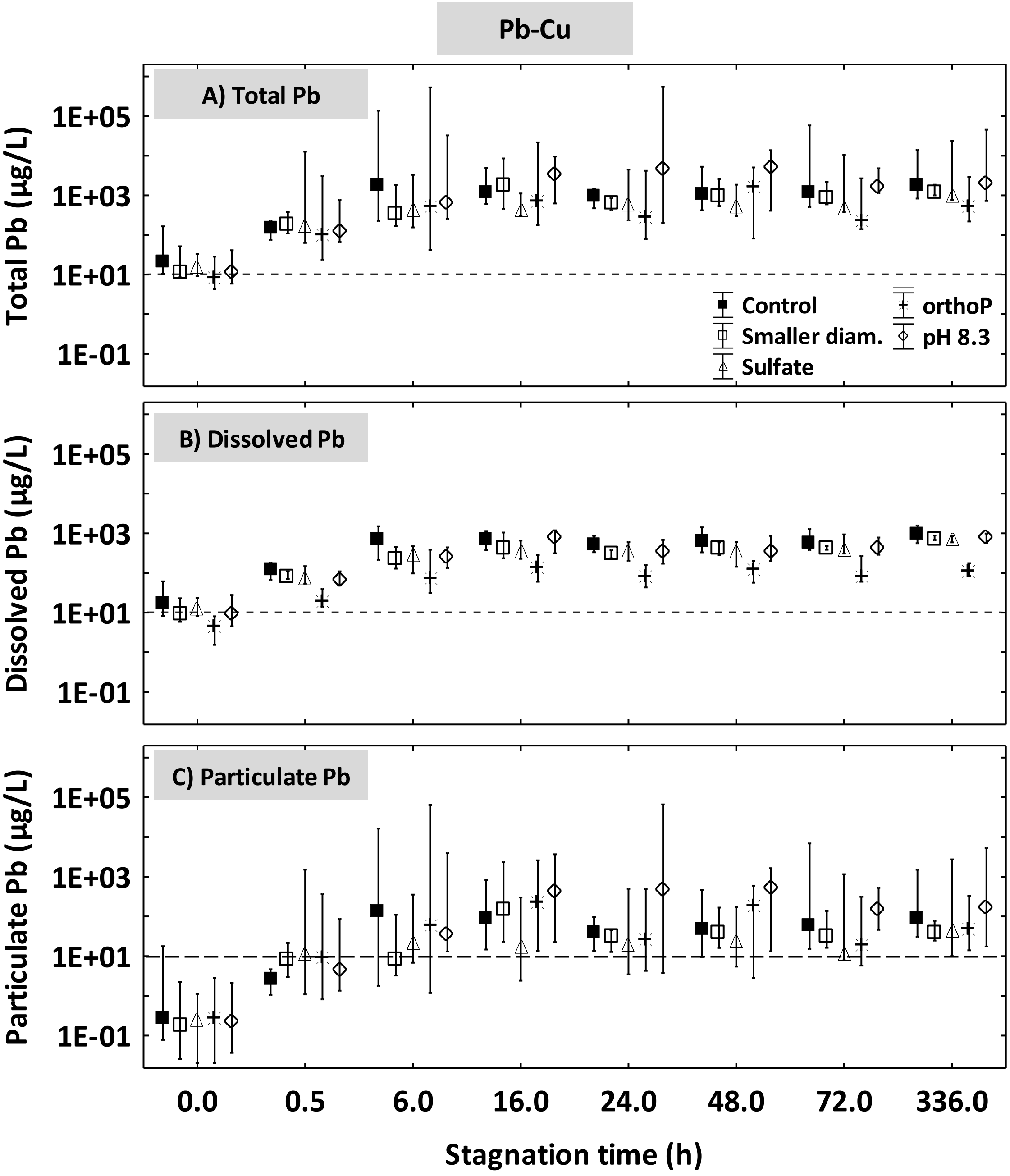

Figure 6.7 Lead concentrations (µg Pb/L) in the lead pipe section as a function of stagnation time for partial LSLs in which the copper pipes are downstream of the Pb pipes (Pb-Cu). Median concentrations for different water qualities are presented: control condition (black square), sulfate addition (white triangle), orthoP dosing (star), and increase in pH to 8.3 (white diamond). The smaller diameter condition is represented by white squares. The whiskers represent 10th-90th percentile concentrations.

As with copper in partial LSLs and lead in full LSLs, Pb_{total} concentrations increased and then tapered off to fluctuate after 16 hour stagnation (Figure 6.6 and Figure 6.7). Despite an apparent increase in concentrations, flowing and 30 minute stagnation samples were not significantly different ($p < 0.05$). Overall, only flowing samples were significantly lower ($p < 0.1$) than those measured after 16 hours for all conditions, and all Pb_{total} concentrations were highly variable after more than 6-16 hours of stagnation and not significantly distinct. During extended stagnation, precipitation and dissolution of different forms of lead can occur as the water quality in the pipe change with the depletion of dissolved oxygen and oxidants (Lytle & Schock, 2000). Similar fluctuations after 6 hour stagnation were observed in simulated PLSLR under control, orthoP and silicate addition conditions (Kogo et al., 2017). The addition of orthoP decreased Pb_{total} the most in both PLSLR configurations, mainly through its action on Pb_{diss} (Figure 6.6 and Figure 6.7). These findings are in agreement with the short-term trends (4 months) after partial replacement showing a 3-25X Pb_{part} increase between stagnation times of 30 minutes and 16 hours (Cartier et al. (2013). After an extended period of operation of 155 weeks, Pb_{part} concentrations increased by a factor of 2.8-25X, except for the sulfate addition (1.0X) and the pH 8.3 (73X) conditions in the Pb-Cu configuration.

The Pb_{total} release rate is higher during the first 16 hours of stagnation and then tappers off with increased stagnation times (Table 6.2). The additional sources of lead in the partial LSLs could explain the lower R^2 for certain water qualities.

Depending on water quality, Pb_{total} release rates from PLSLRs vary widely (-0.3 to 100.4 µg Pb_{total}/h) within the first 16 hours of stagnation, with the orthoP condition systematically the highest (Table 6.2). Dissolved lead concentrations from partial LSLs can be well predicted (R^2 0.41-0.82) unlike Pb_{total} or Pb_{part} concentrations because of the high intrinsic variability of Pb_{part} (Figure 6.6C and Figure 6.7C). When corrected for the length of lead pipe in contact with water, the dissolved lead release in the partials with only 60 cm of LSL were 43-150% higher than for 100%Pb pipes of 300 cm. In stark contrast with observations for the 100%Pb pipes, Pb release rates for partial LSLs were dominated by particulate lead release. Dissolved lead rates during the first 16 hours for the Cu-Pb configuration represent indeed a minor proportion (15.4-30.3%) of the Pb_{total} release rates, accounting for less than 1% for the orthoP condition (Table 6.2). The intensified release of both forms of Pb after partial replacement can be attributed mainly to galvanic corrosion as reported by Doré et al. (2018b) who differentiated lead release from the galvanic connection from non-galvanic surfaces. Nevertheless, the brass fittings could have contributed to Pb concentrations after extended stagnation (65-72 h) (Lytle & Schock, 2000; Triantafyllidou & Edwards, 2007; Wang et al., 2013).

6.3.4 Impact of high velocity flushing

Adjusting the operational flow of the pilot from 5 to 15 LPM resulted in drastic increases in median total (5.2-fold) and particulate Pb (78-fold) for the Cu-Pb small diameter configuration (Figure 6.8 A and B). Tripling the flow rate had however a less important impact for the 100%Pb (1.2-fold) and the Pb-Cu (0.9-fold) configurations. To simulate the impact of higher water usage or preventive high velocity flushing such as performed after PLSLR on the accumulation of particulate lead, additional testing was conducted at the end of the pilot operation period. High velocity flushing at 15 LPM was conducted twice a day for 7 weeks. Lead release after 16 hours of stagnation, before and after the high velocity flushing trials are compared in Figure 6.8C and Figure 6.8D for 16 hour stagnation samples. After stagnation (16HS), median total Pb concentrations decreased by 1.6-fold (Pb-Cu) to 12-fold (Cu-Pb) while median particulate Pb decreased by up to 24-fold. High velocity flushing therefore appears to be an effective tool to reduce the accumulated particulate lead in a service line. Therefore, flushing decreased the mobilized particulate lead levels under flowing conditions, but even more so after extended stagnation (from 192 to 7.9 µg Pb_{part}/L). However, these observations also show that systematic flushing prior to stagnation leads to an underestimation of lead at the tap and supports the proscription of flushing in regulatory protocols.

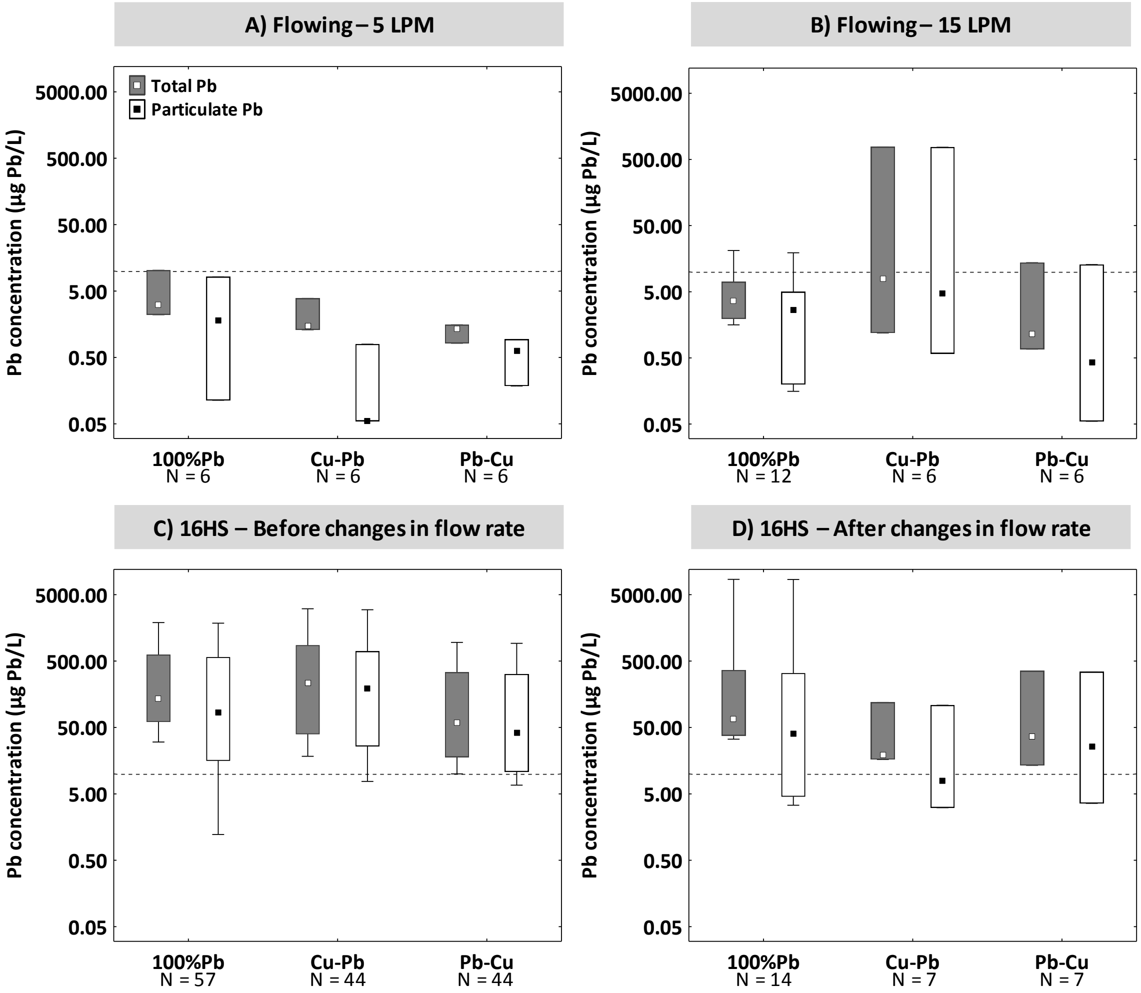

Figure 6.8 Total (grey) and particulate Pb (white) concentrations (µg Pb/L) for the smaller diameter pipes sampled at (A) 5 LPM and (B) 15 LPM as well as concentrations after 16 hour of stagnation, (C) before increasing the flow rate, and (D) after increasing the flow rate (Q). Square: median concentrations, box: 10-90th percentiles, whiskers: min-maximum concentrations.

6.3.5 Implications for exposure to lead and copper

Copper concentrations were always below the 300 µg Cu/L California PHG for flowing samples. However, after only 30 minutes of stagnation, all samples exceeded this threshold for the smaller diameter pipes and frequent exceedances of the proposed health based level of 2,000 µg Cu/L were observed after 16HS. For the Cu-Pb configuration 13/58 samples (all stagnation times) exceeded 2,000 µg Cu/L. It is important to note that these elevated copper concentrations were measured in relatively short pipes (1.8 m) even after 155 weeks of operation. It raises the potential of large volumes of copper with elevated concentrations reaching the tap when copper piping is used for premise plumbing. Avoiding these elevated concentrations would require prolonged flushing before concentrations are lowered as observed in large buildings (Doré et al., 2018a). For the pipes treated with the addition of orthoP, maximum concentrations never exceeded 1,000 µg Cu/L and only 8/58 (Cu-Pb) and 11/58 (Pb-Cu) samples exceeded 300 µg Cu/L.

Exceedances of maximum recommended levels of 5 and 10 µg/L Pb are more ubiquitous amongst stagnation times for all water qualities tested. Similar to trends reported in schools and large buildings (Doré et al., 2018a), lead concentrations in LSLs exceeded recommended levels in few flushed samples (small diameter pipes) and in nearly all samples collected after only 30 minutes of stagnation. The PLSLR observations in this study represent worst case scenarios in terms of exposure to elevated Pb concentrations, because they include very high contributions from the galvanic connection in the partial LSLs (Doré et al., 2018b). However, in pipe concentrations measured in this study could be present in longer LSLs typically present in distribution systems (Deshommes et al., 2017). After 6 hours of stagnation, which is realistic in a household after overnight or after workday, the masses of Pb release from the lead pipe volumes (80-603 mL) exceeded 175 µg Pb in 26% of samples, with at least one high occurrence for each condition tested. If consumed at the tap, it would correspond to an acute exposure threshold (USCPSC, 2005).

6.3.6 Implications for lead and copper sampling

The various stagnation times and targeted levels currently being used for lead and copper sampling determine the concentrations that are detected at the tap. If sampling results are compared to a set standard, the selection of the stagnation duration before collecting the sample is critical. Major differences exist in the various guidelines and standards regarding sampling protocols used for the detection of lead and copper, especially the duration of stagnation, preflush prior stagnation, and the selection of the sampling volume (Appendix B). Stagnation time used prior to sampling can therefore have repercussions on the concentrations measured (Cartier et al., 2011). The stagnation time used prior to sampling will impact the percentage of houses with exceedances in lead or copper concentrations in a distribution system, as reported in schools and large buildings (Doré et al., 2018a). A very short stagnation period will lead to an under evaluation of the exceedances and of the exposure to potential elevated lead levels at the tap, and even more so for copper. Sampling targeted towards the detection of lead sources is also likely to miss the sources of copper as its leaching rate is slower than lead, depending on the scales present inside the pipes. Different stagnation times should be considered depending on the objectives of sampling.

If the intention is to measure peak concentrations to which the consumer may be exposed, metal concentrations after typical and prolonged stagnation should be targeted. In the case of lead, even the lower 10th percentile concentrations exceeded regulated levels (10 µg Pb/L) within the first 30 minutes of stagnation, except for the 100%Pb pipe treated with orthoP. However, after the same stagnation time, maximum copper concentrations did not exceed the aesthetic objective of 1,000 µg Cu/L and few water qualities/pipe configuration exceeded the PHG of California (300 µg Cu/L). Therefore, a 30 minute stagnation prior to sampling would not detect households at risk of elevated copper concentrations. For copper, only 90th percentiles of the smaller diameter pipes and the control condition (Cu-Pb) exceeded 1,000 µg Cu/L after 6 hour stagnation.

For most water qualities and pipe configurations, lead and copper median concentrations increased between 6 and 16 hours of stagnation (Table 6.3 and Table 6.4). However, between stagnation times of 16 and 24 hours, in multiple instances, a slight decrease in median concentrations was observed, probably due to onset of deposition. In some water qualities, and depending on the type of scale deposits present, a longer stagnation time has been shown to underestimate the maximum concentration of copper (Lytle & Schock, 2000). This difference between how lead and copper concentrations vary during extended stagnation can therefore have monitoring implications (Schock & Lemieux, 2010). Comparing 6 hour stagnation samples and 16 hour stagnation samples, Lytle and Schock (2000) found a 35% difference in lead increases and a 270% in the case of copper, depending on the age of the copper pipes. Finally, temperature has been shown to have a reverse impact on copper and lead concentrations, with cold water representing a higher risk of elevated copper release, unlike lead (Masters et al., 2016).

Table 6.3 Median total Cu concentrations represented as X fold of the median concentration after 30 minute stagnation (30MS) and after 6 hour stagnation (6HS).

Pipe configuration	**Treatment**	**VS 30MS**						
		Flowing	**6HS**	**16HS**	**24HS**	**48HS**	**72HS**	**336HS**
Cu-Pb	**Control**	0.3	2.6	4.6	4.1	4.6	4.3	7.0
	Smaller diameter	0.3	2.7	4.4	3.6	3.9	3.9	3.2
	Sulfate addition	0.4	2.9	5.4	4.3	3.9	4.6	8.0
	orthoP	0.6	1.6	2.5	2.0	2.4	2.2	3.4
	pH 8.3	0.5	1.8	4.2	3.4	3.8	3.7	6.4
Pb-Cu	**Control**	0.3	3.1	4.5	4.1	3.5	4.2	4.8
	Smaller diameter	0.4	2.4	3.3	2.9	2.7	3.0	2.6
	Sulfate addition	0.5	2.7	6.1	4.5	4.6	4.7	5.4
	orthoP	0.6	1.6	2.7	2.1	2.3	2.1	2.7
	pH 8.3	0.5	1.9	4.4	3.3	4.0	4.1	6.9
Pipe configuration	**Treatment**	**VS 6HS**						
		Flowing	**30MS**	**16HS**	**24HS**	**48HS**	**72HS**	**336HS**
Cu-Pb	**Control**	0.1	0.4	1.8	1.6	1.8	1.6	2.7
	Smaller diameter	0.1	0.4	1.6	1.3	1.4	1.4	1.2
	Sulfate addition	0.1	0.3	1.9	1.5	1.3	1.6	2.7
	orthoP	0.4	0.6	1.5	1.2	1.4	1.4	2.1
	pH 8.3	0.3	0.6	2.3	1.8	2.1	2.0	3.5
Pb-Cu	**Control**	0.1	0.3	1.4	1.3	1.1	1.3	1.5
	Smaller diameter	0.2	0.4	1.4	1.2	1.2	1.3	1.1
	Sulfate addition	0.2	0.4	2.3	1.7	1.7	1.8	2.0
	orthoP	0.4	0.6	1.7	1.3	1.5	1.4	1.7
	pH 8.3	0.3	0.5	2.3	1.7	2.1	2.1	3.6

Table 6.4 Median total Pb concentrations represented as X fold of the median concentration after 30 minute stagnation (30MS) and after 6 hour stagnation (6HS).

Pipe configuration	**Treatment**	**VS 30MS**						
		Flowing	**6HS**	**16HS**	**24HS**	**48HS**	**72HS**	**336HS**
100%Pb	**Control**	0.1	2.9	5.0	5.2	5.3	5.6	9.9
	Smaller diameter	0.07	1.8	4.9	2.4	4.0	3.4	5.4
	Sulfate addition	0.09	2.5	4.5	4.2	4.9	5.1	7.7
	orthoP	0.1	4.0	7.0	4.5	9.8	5.9	19.8
	pH 8.3	0.1	3.2	6.7	4.7	5.4	7.1	10.3
Cu-Pb	**Control**	0.06	2.0	3.7	2.4	5.7	5.4	5.6
	Smaller diameter	0.09	2.5	20.6	3.3	8.0	6.7	9.5
	Sulfate addition	0.1	3.5	3.9	3.8	8.4	4.5	10.7
	orthoP	0.02	2.2	2.9	3.1	1.9	0.9	3.1
	pH 8.3	0.1	1.6	7.8	3.3	4.2	4.5	10.2
Pb-Cu	**Control**	0.2	12.6	9.3	6.5	7.0	7.9	11.9
	Smaller diameter	0.06	1.9	8.0	3.6	5.0	4.5	6.3
	Sulfate addition	0.09	2.6	2.5	3.4	3.1	2.8	6.1
	orthoP	0.09	5.6	6.8	2.9	16.8	2.4	5.5
	pH 8.3	0.08	5.1	24.1	34.8	40.2	12.8	16.5
Pipe configuration	**Treatment**	**VS 6HS**						
		Flowing	**30MS**	**16HS**	**24HS**	**48HS**	**72HS**	**336HS**
100%Pb	**Control**	0.04	0.3	1.7	1.8	1.8	1.9	3.4
	Smaller diameter	0.04	0.6	2.7	1.3	2.2	1.9	3.0
	Sulfate addition	0.04	0.4	1.8	1.7	2.0	2.1	3.1
	orthoP	0.04	0.3	1.8	1.1	2.5	1.5	5.0
	pH 8.3	0.04	0.3	2.1	1.5	1.7	2.2	3.2
Cu-Pb	**Control**	0.03	0.5	1.8	1.2	2.8	2.7	2.8
	Smaller diameter	0.04	0.4	8.4	1.3	3.3	2.7	3.9
	Sulfate addition	0.04	0.3	1.1	1.1	2.4	1.3	3.1
	orthoP	0.01	0.5	1.3	1.4	0.9	0.4	1.4
	pH 8.3	0.06	0.6	5.0	2.1	2.7	2.9	6.5
Pb-Cu	**Control**	0.01	0.08	0.7	0.5	0.6	0.6	1.0
	Smaller diameter	0.03	0.5	4.3	1.9	2.7	2.4	3.4
	Sulfate addition	0.04	0.4	2.0	1.3	1.2	1.1	2.3
	orthoP	0.02	0.2	1.2	0.5	3.0	0.4	1.0
	pH 8.3	0.02	0.2	4.8	6.9	7.9	2.5	3.3

To assess typical exposure, stagnation times representative of the time between usages in a household should be used, such as the 30 minute stagnation or random day time sampling system wide (van den Hoven & Slaats, 2006). Composite sampling is the best approach to measure exposure but is only feasible for research purposes (van den Hoven & Slaats, 2006).

6.3.7 Conclusion

- Dissolved lead and copper concentrations can be well predicted for the first 16 hours of stagnation, in full and partial LSLs, under different water qualities.
- The addition of orthoP decreased copper concentrations in partial LSLs, independently of the duration of stagnation prior to sampling. In full LSLs, it was also the most effective treatment in reducing total lead concentrations.
- The increase rates of dissolved lead and copper during stagnation can be better predicted than those for particulate lead and copper.
- Increasing the sampling flow rate from 5 to 15 LPM drastically increased particulate lead release in Cu-Pb configurations (78-fold), while having almost no impact for the 100% Pb pipe or Cu-Pb configurations.
- High velocity flushing prior to 16 hour stagnation decreased total Pb release by 12-fold for Cu-Pb, 1.6-fold for Pb-Cu, and 2.0-fold for 100% Pb, showing that flushing prior to stagnation should be proscribed.
- Stagnation time prior to sampling should reflect the differences in kinetic dissolution of lead and copper. Sampling should be targeted for the detection of either Pb or Cu, as measuring both metals in the same sample is sub-optimal in light of the results obtained.

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CHAPTER 7 ONSET OF CHLORINATION, CHANGES IN ORTHOP DOSAGE IN FULL AND PARTIAL LEAD SERVICE LINES

This chapter presents short-term changes in Pb concentrations following modifications made to the water quality in the pilot. The purpose of these adjustments was to investigate the short-term effect of simple water quality adjustments that utilities could consider such as increasing pH and chlorine residuals. Water quality changes included the addition of chlorination to rigs treated with the addition of sulfate and the increase in pH as well as the increase in orthoP dosage. Adding chlorine changes the oxidation-reduction potential of water and is expected to affect Pb release from PLSL and FLSL. Increasing the orthoP dosage should also result in a reduction of Pb concentrations.

7.1 Addition of chlorination

About 156 weeks after the PLSLR simulation, sodium hypochlorite was added at a dose of 1 mg Cl_2/L to the water feeding the rigs treated with the addition of sulfate and pH adjusted up to 8.3. The combination of the initial treatment and the onset of chlorination was monitored for a period of 12 weeks. Prior to changes in water quality, one PLSL and one FLSL rig of each water quality was disconnected from the pilot for scale analysis. Therefore, changes in treatment were applied to 1 PLSL and to 2 FLSL. Laboratory tests revealed that the water entering the pilot, with the additional treatments, had no chlorine demand. Therefore, the concentration of chlorine which was dosed in the pilot and the chlorine residual were the same.

The addition of chlorine in the water increases the oxidation-reduction potential (ORP) of the water and should therefore change Pb(II) scales into less soluble Pb(IV) scales, which explains why a decrease in concentrations is expected when chlorine is added in a distribution system (Triantafyllidou et al., 2015). In a study of groundwater newly chlorinated, lead and copper exhibited opposite trend with the addition of chlorine: Pb concentrations decreased and copper concentration increased in the presence of the oxidant (Cantor et al., 2003). Different reactions to changes in water quality demonstrate how different conditions exacerbate either Pb or Cu corrosion.

7.1.1 Lower CSMR and addition of chlorine

The addition of sulfate (lower CSMR) was the treatment which decreased the most Pb release from the partial LSLs, as presented in Chapter 5. Before and after the addition of chlorine, Pb_{total} was variable with peaks in concentrations attributed to the release of $Pb_{part.}$. The addition of chlorine statistically decreased (Kruskal Wallis ANOVA) total Pb concentrations for the full LSL (1.2-fold decrease), whereas concentrations remained similar for both partial pipe configurations (median of 25.1 µg Pb/L before changes, both PLSLs configurations) (Figure 7.1). Pb_{total} from the PLSLs are 3.1-fold lower than for the FLSL (100% lead). If the effects of galvanic corrosion were not present, concentrations should have been 5-fold lower since it is the difference in length between the Pb pipes of both configuration (0.6 and 3 m). $Pb_{diss.}$ only remained statistically similar, before and after the onset of chlorination for the Cu-Pb rigs (Figure 7.2). A small decrease in $Pb_{diss.}$ was observed for the Pb-Cu (1.5-fold) and for the 100%Pb (1.2-fold). Particulate Pb concentrations remained similar before and after changes in treatment and were variable after 16HS.

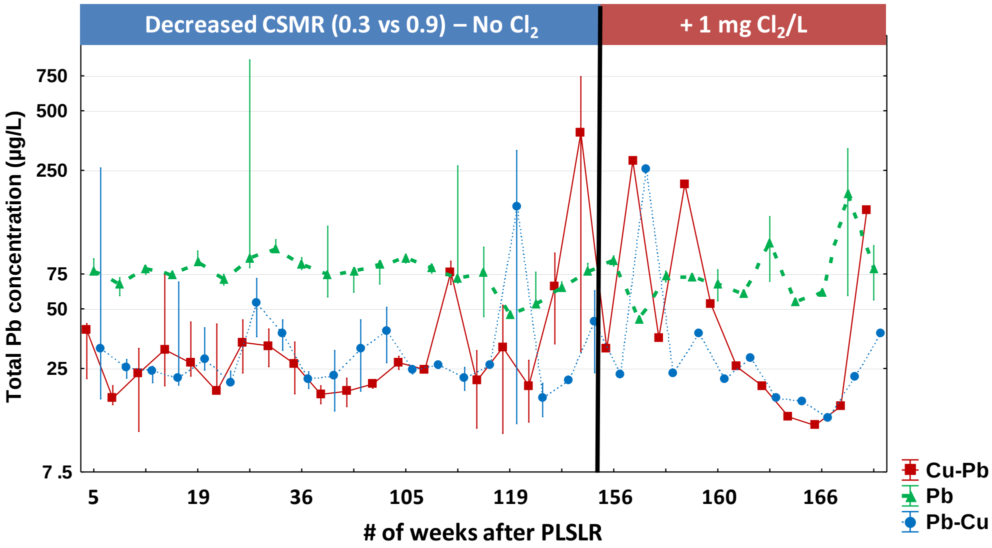


Figure 7.1 Total Pb concentrations as a function of the number of weeks following the simulation of partial LSL replacements for the pipes treated with the addition of sulfate, before and after the onset of chlorination. Squares (Cu-Pb), triangle (100%Pb) and circles (Pb-Cu) represent median concentrations and whiskers represent minimum-maximum values. Pb pipes of full LSLs are 5 times longer than partial LSLs (3 and 0.6 m). N=46 and 11 for PLSL, N=60 and 22 for FLSL, before and after chlorination.

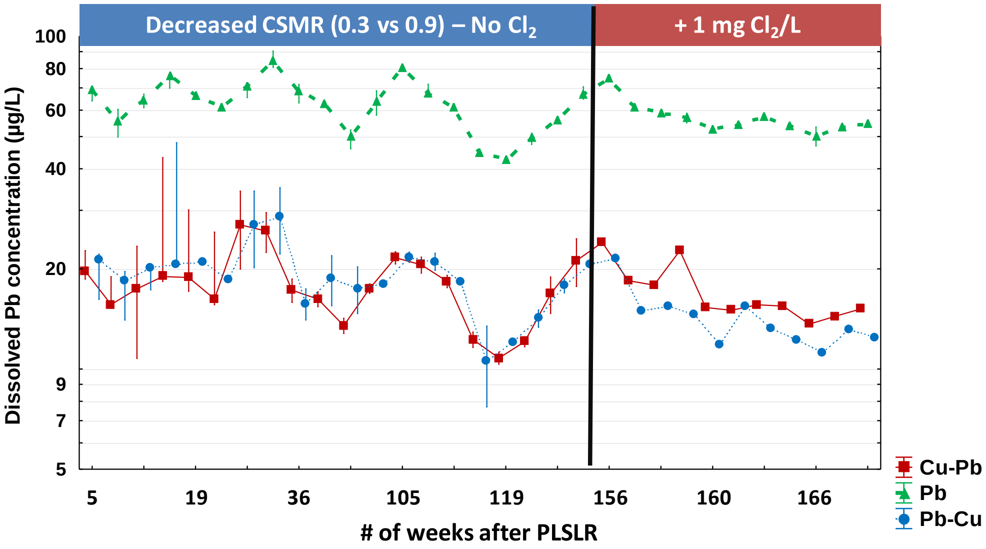


Figure 7.2 Dissolved Pb concentrations as a function of the number of weeks following the simulation of partial LSL replacements for the pipes treated with the addition of sulfate, before and after the onset of chlorination. Squares (Cu-Pb), triangle (100%Pb) and circles (Pb-Cu) represent median concentrations and whiskers represent minimum-maximum values. Pb pipes of full LSLs are 5 times longer than partial LSLs (3 and 0.6 m). N=46 and 11 for PLSL, N=60 and 22 for FLSL, before and after chlorination.

7.1.2 Increased pH and addition of chlorine

The addition of chlorine to the water with an adjusted pH of 8.3 statistically decreased the median Pb_{total} after 16HS for the 100%Pb configuration (1.4-fold) and for the Pb-Cu (3.4-fold) (Figure 7.3). The Cu-Pb configuration remained statistically similar to values before the onset of chlorination. However, $Pb_{diss.}$ decreased for both PLSL configurations and remained similar for the FLSL (Figure 7.4). Similar to the decrease in CSMR, Pb concentrations were variable throughout the experiment.

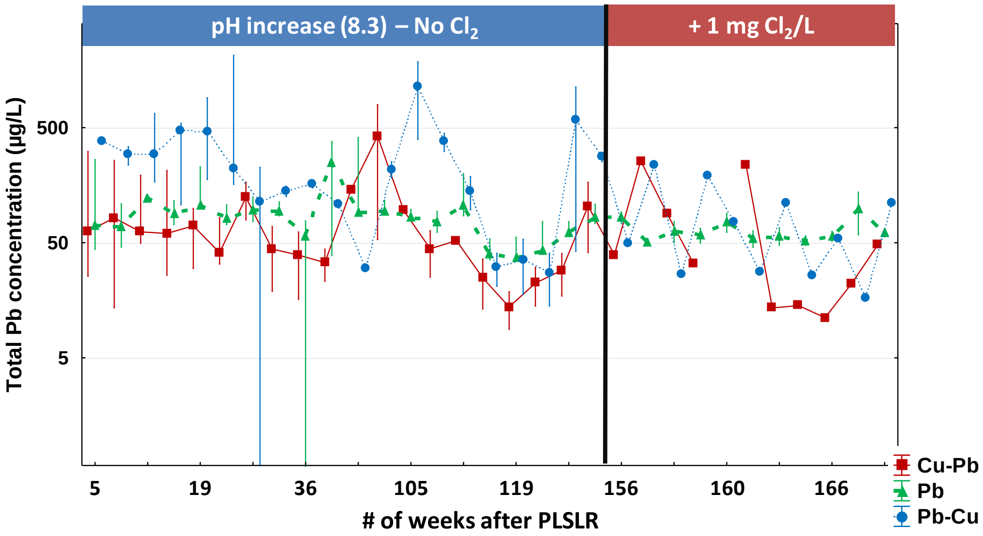


Figure 7.3 Total Pb concentrations as a function of the number of weeks following the simulation of partial LSL replacements for the pipes treated with the increase in pH to 8.3, before and after the onset of chlorination. Squares (Cu-Pb), triangle (100%Pb) and circles (Pb-Cu) represent median concentrations and whiskers represent minimum-maximum values. Pb pipes of full LSLs are 5 times longer than partial LSLs (3 and 0.6 m). N=46 and 11 for PLSL, N=60 and 22 for FLSL, before and after chlorination.

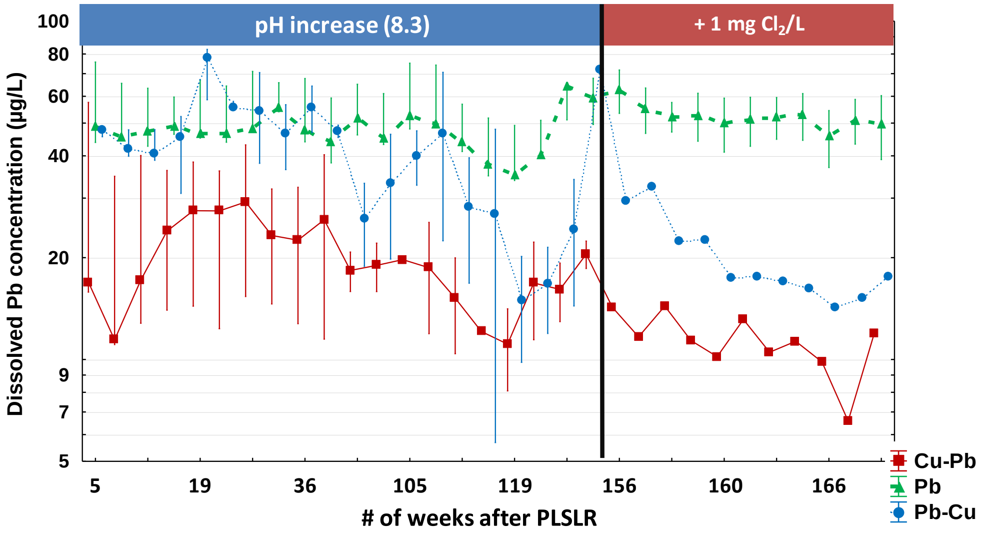


Figure 7.4 Dissolved Pb concentrations as a function of the number of weeks following the simulation of partial LSL replacements for the pipes treated with the increase in pH to 8.3, before and after the onset of chlorination. Squares (Cu-Pb), triangle (100%Pb) and circles (Pb-Cu) represent median concentrations and whiskers represent minimum-maximum values. Pb pipes of full LSLs are 5 times longer than partial LSLs (3 and 0.6 m). N=46 and 11 for PLSL, N=60 and 22 for FLSL, before and after chlorination.

Changes in Pb concentrations with the addition of chlorine are similar to the observations reported by Cantor et al. (2003), where the addition of the oxidant decreased Pb concentrations. When adding chlorine to the water, the ORP also increases which in returns should favour the formation of lower solubility Pb(IV) scale (Masters et al., 2016; Schock & Lytle, 2011; Schock et al., 1996). Reiber and Dufresne (2006) demonstrated that in the presence of a galvanic connection, the addition of chlorine increases the galvanic effect. However, they did not observe significant changes on Pb concentrations in water, similar to results obtained in the current study.

7.2 Changes in orthoP dosage

Pipes treated with the addition of orthoP remained variable with changes of the set pH and in dosage (Figure 7.5). There were no statistical differences when comparing median Pb_{total} concentrations before and after changes were made to the water quality (Kruskal Wallis ANOVA). After stopping the addition of NaOH for pH stabilization to ambient pH after adding orthophosphoric acid, $Pb_{diss.}$ decreased for the Cu-Pb pipes (2.1-fold) and increased for the 100%Pb (1.4-fold) and Pb-Cu pipes (1.9-fold) (Figure 7.6). When increasing the orthoP dosage, Cardew (2009) observed decreases in Pb concentrations in distribution systems in which full and partial LSLs were present. When doubling the orthoP concentrations, Trueman et al. (2018) demonstrated a decrease of 62% when comparing data from the month of December before and after changes as well as a reduction of 68-71% when comparing data obtained in the spring. However, in both studies, despite higher orthoP concentrations, peaks of elevated Pb concentrations remained and were caused by the presence of particulate Pb.

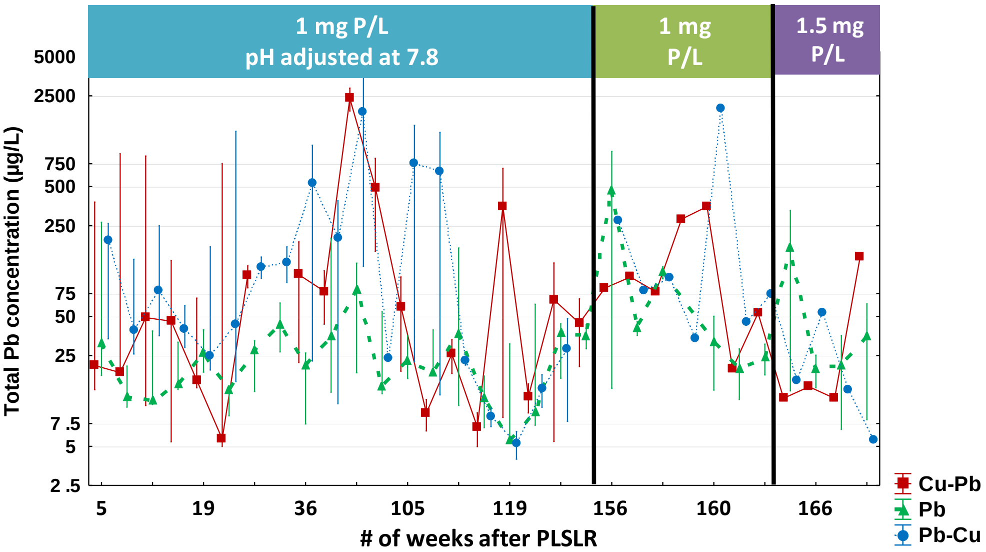


Figure 7.5 Total Pb concentrations as a function of the number of weeks following the simulation of partial LSL replacements for the pipes treated with 1 mg P/L with pH adjustment, without pH adjustment and with an increase in orthoP dosage to 1.5 mg P/L. Squares (Cu-Pb), triangle (100%Pb) and circles (Pb-Cu) represent median concentrations and whiskers represent minimum-maximum values. Pb pipes of full LSLs are 5 times longer than partial LSLs (3 and 0.6 m). N=46, 7 and 4 for PLSL, N=60, 12 and 8 for FLSL, before changes in treatment, after decrease in pH and after increase in orthoP.

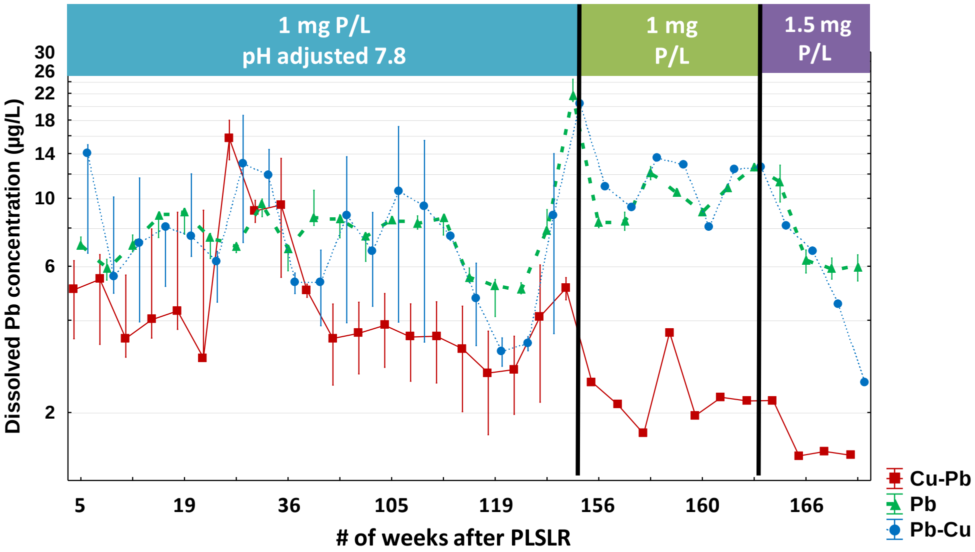


Figure 7.6 Dissolved Pb concentrations as a function of the number of weeks following the simulation of partial LSL replacements for the pipes treated with 1 mg P/L with pH adjustment, without pH adjustment and with an increase in orthoP dosage to 1.5 mg P/L. Squares (Cu-Pb), triangle (100%Pb) and circles (Pb-Cu) represent median concentrations and whiskers represent minimum-maximum values. Pb pipes of full LSLs are 5 times longer than partial LSLs (3 and 0.6 m). N=46, 7 and 4 for PLSL, N=60, 12 and 8 for FLSL, before changes in treatment, after decrease in pH and after increase in orthoP.

CHAPTER 8 CHANGES IN CORROSION SCALES IN FULL AND PARTIALLY REPLACED LEAD SERVICE LINES: IMPACT OF WATER QUALITY

This chapter presents the effects of performing partial lead service line replacements (PLSLR) on the mineralogy of the scales. Also, the impact of changing water qualities on existing legacy scales are also investigated. The section of this chapter on scale analysis is to be processed for improvements and comments by our collaborators (M.R. Schock and M.K. DeSantis) at the USEPA. It is now presented in a chapter form to facilitate the upcoming completion of the proposed work. I elected to use this chapter as I use some of the information on scales to discuss the articles 2 and 3.

The objectives of this chapter are the following:

1. Investigate the impact of corrosion control treatment such as decreasing the CSMR, dosing orthoP and pH increase on the scale formation;
2. Determine the extent of galvanic corrosion depending on the water quality;
3. Relate the Pb concentrations in water to the scales present;
4. Determine how scales formed in PLSLs vary following the PLSLR simulations (short vs long-term).

Results are presented to answer key questions of relevance to understanding the impact of water quality on lead release in 100% legacy pipes and PLSLR pipes.

8.1 General observations on scale formation

The layer L1 was often more patchy than other layers, and more so on the Pb pipe than on the Cu pipe (Figure 8.1). This can be in part due to the sloughing off of materials during sample preparation. Similar observations were made by Kim and Herrera (2010) in harvested Pb pipes from the City of London (Ontario, Canada), it was noted that the easily separated L1 layer could also be disturbed with physical disturbances of the scale material, such as an increase in flow rate. This would result in flaky particulate Pb in the water (Schock et al., 2014). Uneven L1 layers were also reported in distribution systems with Pb(IV) scale present, but there was a dominance in some materials (Triantafyllidou et al., 2015).

Also, the number of layers varied from pipe to pipe as well as the thickness and the area covered. It can be noted that the amount of scale present in the samples from the pilot setup is less abundant, when comparing photographs, than reported elsewhere (DeSantis et al., 2018; Wasserstrom et al., 2017).

Most samples from the uppermost layer, L1, present some extent of poorly crystalline or amorphous materials, which could not be identified using PXRD, as reported in other studies (Kim & Herrera, 2010; Nadagouda et al., 2011). In many samples, the raised background is an indication that amorphous materials could be present (Schock et al., 2014). In some of the samples containing copper minerals, significant scatter was observed in the pattern, which sometimes hindered appropriate mineral identification. Lastly, some peaks in the PXRD patterns could not be attributed to any minerals in the databases and remained unidentified.

Figure 8.1 Example of surface layers with islands of red deposits (pipe treated with orthoP).

Pipes that were considered to be duplicates on the pilot setup, as they were installed next to each other and received the same water for the same duration, sometimes showed differences in the scale composition and abundance. These differences can be attributed to the fact that initially, not all the harvested LSLs were from the same area of the distribution system and the water quality might have been different. Dias et al. (2017) documented significant changes in water quality within the distribution system from where the pipes were harvested. Furthermore, despite receiving the same water quality, two neighbouring houses can leach different levels of lead in the water depending on water usage pattern per example (Del Toral et al., 2013).

8.2 Do scales in 100%Pb pipes change with water quality?

8.2.1 Control condition and smaller diameter pipes

Different shades of orange material, unevenly distributed, were observed on the L1 layer of the pipes of the control condition and the smaller diameter (Figure 8.2 and Figure 8.3). This material could easily be brushed off. The innermost layer better adhered to the pipe wall, and was of a lighter colour.

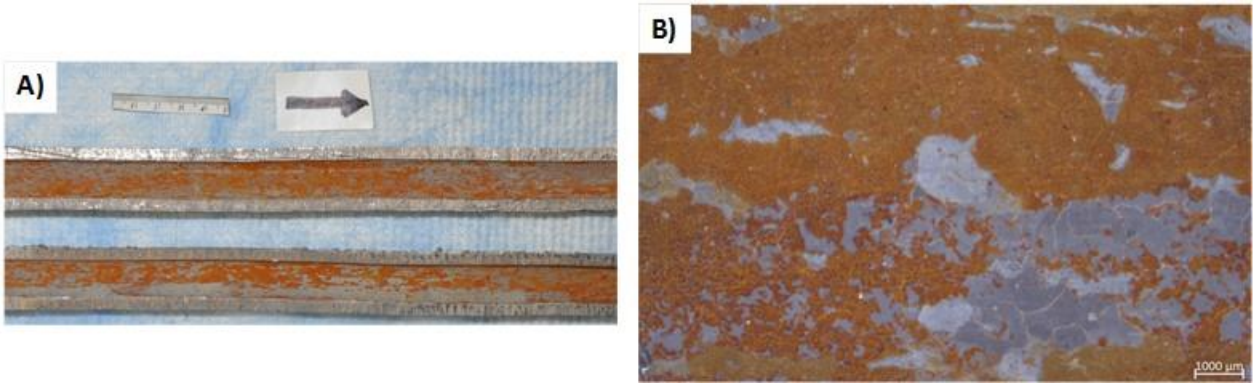


Figure 8.2 Photographs of the interior of a 100%Pb pipe from the control condition.

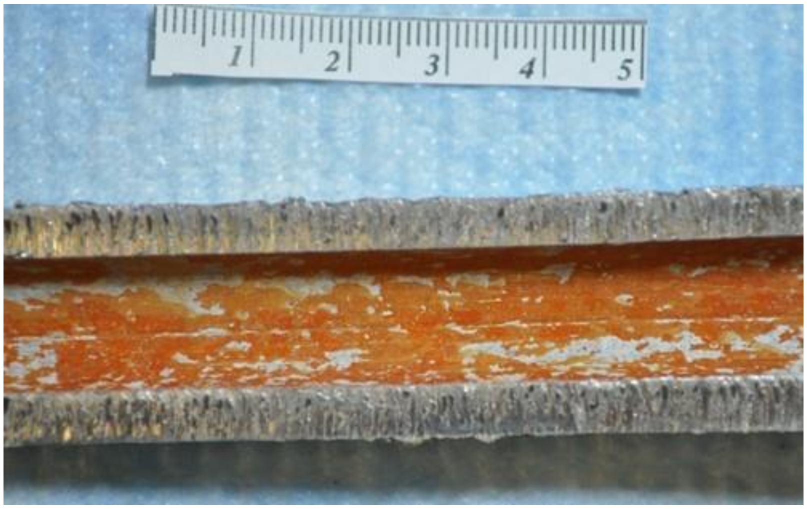


Figure 8.3 Interior deposits of a smaller diameter pipe.

For the control condition and the smaller diameter pipes, in the full LSLs (100%Pb), the dominant mineral was hydrocerussite in both L1 and L2, with traces of cerussite identified in only one of the samples (Table 8.1). Kim and Herrera (2010) also observed hydrocerussite as the dominant crystalline form in LSLs harvested from the distribution system of London (Ontario, Canada). Calcite was more abundant on the outermost layer than on the layer in direct contact with the pipe wall, ranging from a moderate presence to traces, depending on the triplicates. Plumbonacrite was observed in all samples of this water quality in innermost layer, but only accounted for traces. This Pb carbonate has a solubility orders of magnitude lower than cerussite and hydrocerussite (Masters et al., 2016).

As presented in Table 8.1, for each pipe triplicate, the minerals present are similar, in terms of phase present and relative abundance. This is in line with similar Pb concentrations presented in Figure 8.4 for duplicate pipe of the control condition.

Table 8.1 Lead corrosion solids identified in 100%Pb pipe for the control and smaller diameter conditions, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected.

Minerals		**Rep.**	**Control**		**Smaller diameter**	
			L1	**L2**	**L1**	**L2**
Litharge	PbO	**1**	++	+	+	+
		2	+	+	+	+
		3	++	+	+	+
Cerussite	$PbCO_3$	**1**				
		2				
		3	+			
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	**1**	++++	++++	++++	++++
		2	++++	++++	++++	++++
		3	++++	++++	++++	++++
Plumbonacrite	$Pb_5O(OH)_2(CO_3)_3$	**1**		+		+
		2		+		+
		3		+		+
Calcite	$CaCO_3$	**1**	+	+	+	+
		2	++		+	+
		3	+++	+	++	+

The presence of Pb(IV) oxides (PbO_2) was observed in other studies (Kim & Herrera, 2010; Triantafyllidou et al., 2015). This mineral was not observed in these pipes, probably because the ORP was not high enough to sustain the formation and persistence of Pb(IV). Minerals present in the innermost layer are likely to be legacy materials which formed when the Pb pipes were installed in the distribution system. They are likely to have been influenced by the water from the pilot but might not have completely changed.

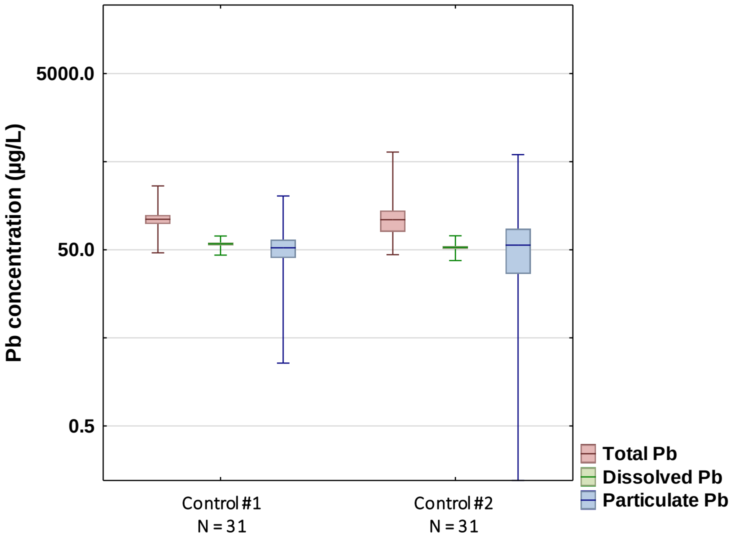


Figure 8.4 Total, dissolved and particulate Pb concentrations after 16 hour stagnation in FLSL for both pipes of the control condition. Line: mean concentration, boxes: mean ± SE, whiskers: minimum-maximum concentrations. N=31.

8.2.2 Sulfate addition with and without chlorine residual

More layers could be differentiated in this water quality than in the control condition. Also, the layer L2, was much thicker and whiter than any layers present in the control condition and had a chalky texture (Figure 8.5).

As it was the case with untreated pipes (control and smaller diameter conditions), the condition where sulfate is added to the water resulted in scale deposits dominated by the presence of Pb(II) carbonates such as cerussite and hydrocerussite (Table 8.2). However, it is noteworthy that in the presence of sulfate, the high solubility Pb(II) carbonate cerussite (Masters et al., 2016) is present while it was not detected in the control condition. In the range of pH measured in the pilot setup, the hydrocerussite is formed, followed by cerussite. Minerals containing sulfate were not detected by PXRD, which was also the case for Pb pipes treated with 210-218 mg SO_4 (Lytle & Schock, 2005). The presence of litharge was more dominant in the innermost layer, as only traces were observed on the outermost layer. Traces of plumbonacrite were only detected in L2 and L3, whereas it was not seen on the outermost layer L1.

The addition of 1 mg Cl_2/L did not result in the presence of Pb(IV) minerals as it has been reported in the literature as it increases the ORP and therefore favours the formation of Pb(IV) (Schock & Lytle, 2011). Pb concentrations remained similar before and after the onset of chlorination, which hints to the fact that scale composition did not undergo drastic modifications.

Table 8.2 Lead corrosion solids identified in 100%Pb pipe for the sulfate addition and the increase in pH conditions, with and without chlorination, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected.

Minerals		**Cl_2 (mg/L)**	**Sulfate addition**				**pH 8.3**	
			L1	**L2**	**L3**	**L4/L5**	**L1**	**L2**
Litharge	PbO	**0**	+	+	+++	▨	++	++
		1	+	+	+++	▨	++	▨
		1	+	+		+++	+++	++
Cerussite	$PbCO_3$	**0**	++++	++	+	▨	+++	
		1	+++	++	+	▨		▨
		1	++++	++++	++	+++	+++	
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	**0**	+++	++++	++	▨	++++	++++
		1	++++	++++	+++	▨	++++	▨
		1	+++	+++	++++	+++	++++	++++
Plumbonacrite	$Pb_5O(OH)_2(CO_3)_3$	**0**		+	+	▨		+
		1		+	+	▨	++	▨
		1		+	+	++		+
Calcite	$CaCO_3$	**0**	+			▨	+	
		1	++			▨	+	▨
		1	+	+			+	

Figure 8.5 Full LSL treated with the addition of sulfate (A) and the combination of sulfate and chlorine (B).

8.2.3 Increase to pH 8.3

Hydrocerussite is the dominant phase for the control condition and for the rigs with the increased pH to a value of 8.3 for the 100%Pb pipes (Table 8.2). The shift in pH from 7.8 (control condition) to 8.3 changed the scale composition as the presence of cerussite was only minor in the control condition. At pH greater than 8, cerussite is transformed into hydrocerussite (Dando & Glasson, 1989; Xie & Giammar, 2011). This was not clearly observed in this pilot, as in both the control condition and the pH 8.3 pipes, hydrocerussite was the dominant Pb(II) carbonate.

Similar to the pipes treated with a decrease CSMR and the addition of chlorine, no Pb(IV) phases were present. However, it is worth mentioning the impressive change in the distribution of the L1 layer when chlorine is added (Figure 8.6), as this layer was almost completely removed.

Similarity in the scale deposits between duplicate pipes treated with the addition of chlorine is reflected in similar Pb concentrations (Figure 8.7) which was also observed for the control conditions. Furthermore, before the onset of chlorination, all pipes presented similar mean Pb concentrations, but differences in maximum concentrations were observed.

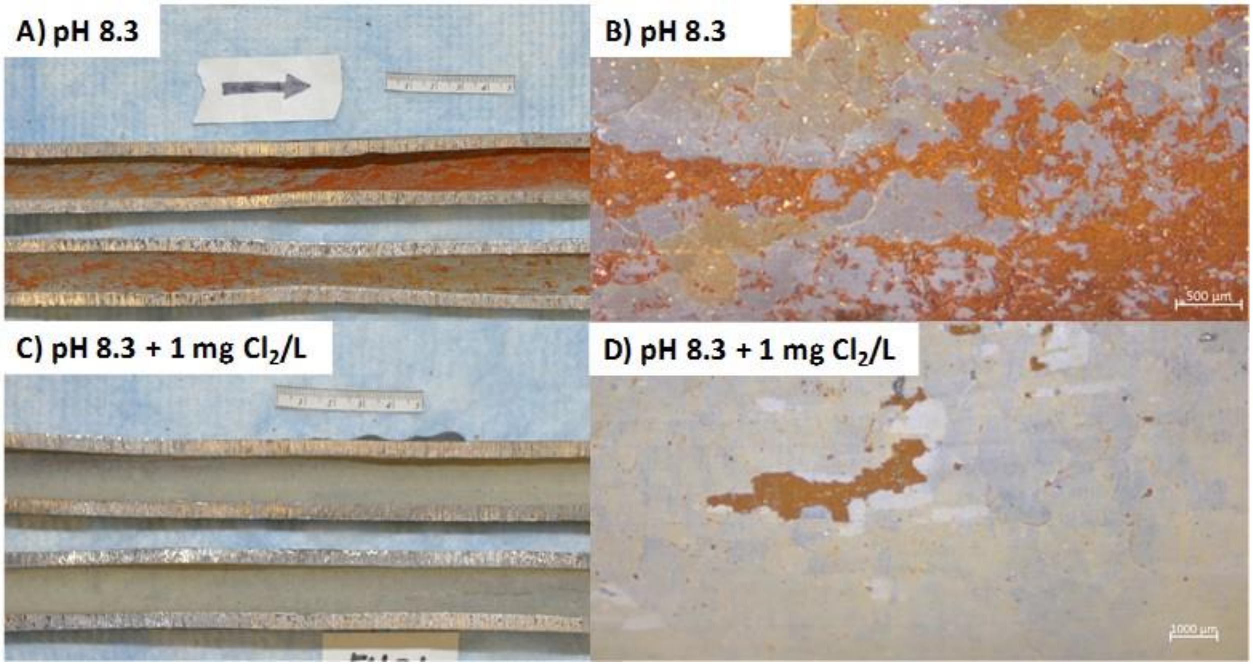


Figure 8.6 Full LSLs treated with an increase in pH (A and B) and an increase in pH combined with chlorine (C and D). Picture on the right were taken with a stereomicroscope to enhance the details of the scale.

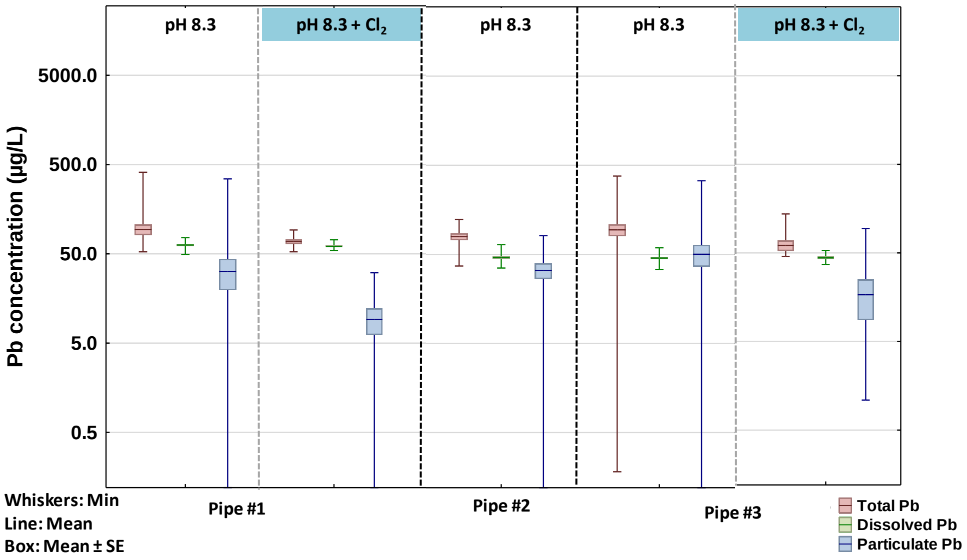


Figure 8.7 Total, dissolved and particulate Pb concentrations after 16 hour stagnation in FLSL for both pipes of the increased pH condition with and without 1 mg Cl_2/L. Line: mean concentration, boxes: mean ± SE, whiskers: minimum-maximum concentrations.

8.2.4 orthoP

As for the control condition, for the 100%Pb pipes, the outermost layer of the pipes treated with orthoP showed an uneven distribution throughout the pipe surface (Figure 8.8). Furthermore, the scales from both the control condition and the orthoP treated pipes were dominantly hydrocerussite with traces of litharge (L1 and L2) (Table 8.3). Calcite was also present and mostly in the outer layer. However, both before and after changes were made in dosage of the orthoP, hydroxypyromorphite and lead phosphates were present in the L2 layer. This is interesting as the Pb(II)-phosphates were incorporated in the innermost layer and not in the layer in direct contact with water. This supposes that the L1 layer was porous and allowed migration of phosphate compounds within the scale layer. Pb-phosphate were present throughout the layers in Pb pipes treated with orthoP and not only in the outermost layer (Davidson et al., 2004). Changes in dosage of orthoP did not affect the scale composition of the 100%Pb pipes aside from traces of lead phosphate observed on the L1 layer with the increased dose. Despite having similar corrosion products identified using PXRD, differences in concentrations are observed between triplicate pipes (Figure 8.9). The differences in concentrations are caused by peaks in particulate Pb release, as dissolved Pb concentrations are similar for each pipe.

The minerals observed are in agreement with field observations from utilities using blended-phosphate as a CCT for lead (Trueman et al., 2018; Wasserstrom et al., 2017). Our observations are different to those of Wang et al. (2013) as hyroxypyromorphite was not the dominant phase in our case in the orthoP treated pipes. However, Wasserstrom et al. (2017) and Wang et al. (2013) observed the presence of Pb(IV) oxides (plattnerite and scrutinyite), which was not observed in the pilot. This might be explained by the fact that the pilot used dechlorinated water, which has a lower ORP than chlorinated waters. The formation of Pb(IV) requires a sustained high ORP in the water.

Table 8.3 Lead corrosion solids identified in 100%Pb pipe for addition o orthoP, before and after the increase in dosage to 1.5 mg P/L, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected.

Minerals		**orthoP dose (mg P/L)**	**orthoP**	
			L1	**L2**
Litharge	PbO	**1**	+	+++
		1.5	+	++
			+	++
Cerussite	$PbCO_3$	**1**	+	+
		1.5	++	
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	**1**	++++	++++
		1.5	++++	++++
			++++	++++
Hydroxypyromorphite	$Pb_5(OH)(PO_4)_3$	**1**		+
		1.5		
Lead phosphate	$Pb_9(PO_4)_6$	**1**		+
		1.5		+
			+	+
Calcite	$CaCO_3$	**1**	++++	
		1.5	+	
			++++	+

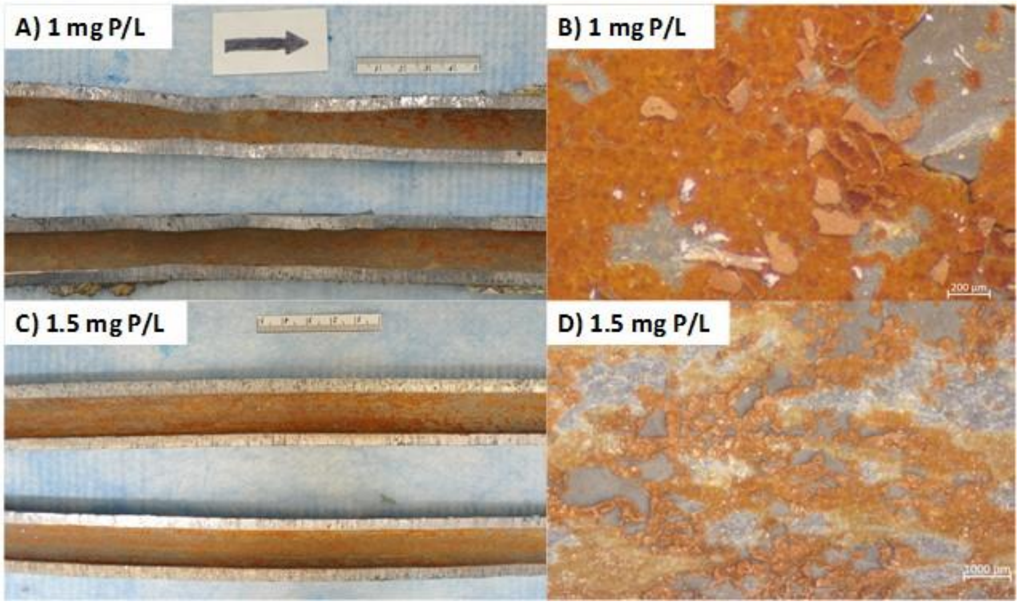
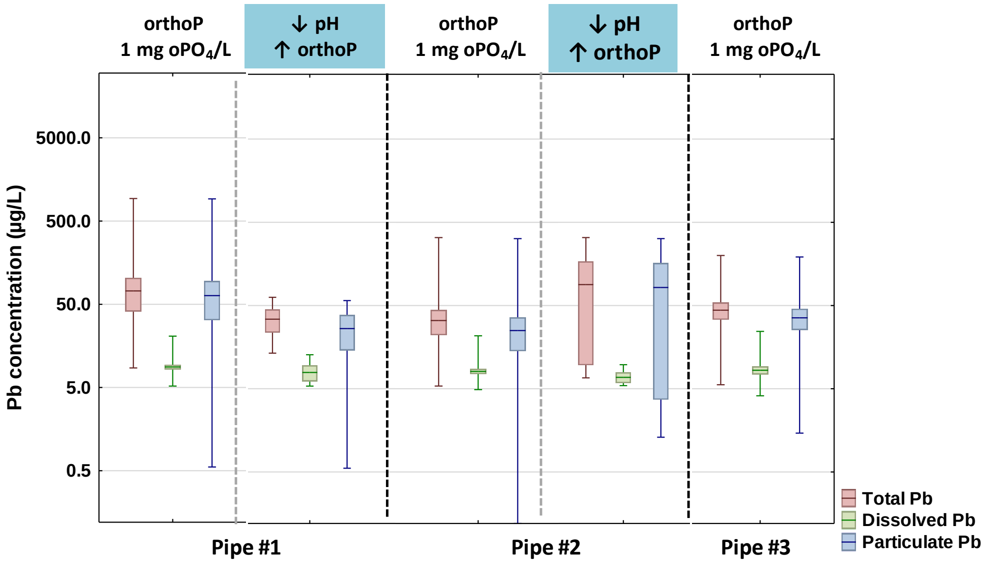


Figure 8.8 Full LSL fed with water dosed at 1 mg P/L (A and B) and 1.5 mg P/L (C and D). Pictures on the right were taken using a stereomicroscope.



Whiskers: Min-Max
Line: Mean
Box: Mean ± SE

Figure 8.9 Total, dissolved and particulate Pb concentrations after 16 hour stagnation in FLSL for pipes with the addition of orthoP before and after changes in dosage (1 vs 1.5 mg P/L). Line: mean concentration, boxes: mean ± SE, whiskers: minimum-maximum concentrations.

8.3 Are the scales present in the non-galvanic section of the Pb pipe affected by the presence of a downflow galvanic connection?

Before being connected to the copper pipe with red-brass compression fittings, the Pb pipes of the partial LSL were full LSL. If the non-galvanic zone is not influenced by the presence of the brass connector and the copper pipe, minerals present in the non-galvanic zone should resemble those present in the full LSL and explained previously.

8.3.1 Control condition and smaller diameter pipes

Pb(II) oxides and carbonates present in the background zone of the Cu-Pb pipes are the same as the ones present in the full LSL, but are different than the minerals present in the galvanic zone (Table 8.4). This confirms that under the control condition, the background zones should have similar Pb release then the full LSLs. The pipe connected shortly after the PLSLR simulation also has similar minerals in the background zone then the pipes disconnected at the end of the study.

For the smaller diameter condition (Table 8.5), the only difference between the non-galvanic zone and the full LSL is the presence of susannite/leadhillite ($Pb_4(SO_4)(CO_3)_2(OH)_2$).

Table 8.4 Lead corrosion solids identified in Cu-Pb pipes for the control condition, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected.

	Mineralogy		**Week removed**	**Copper pipe**			**Fitting**	**Lead pipe**		
	Name	Formula		Non-galvanic zone (Zone C)		Galvanic zone (Zone A)		Galvanic zone (Zone A)	Non-galvanic zone (Zone C)	
				L1	L2				L1	L2
Lead minerals	Litharge	PbO	39		▨		▨	+	+	▨
			End			▨		+	++	+
			End				+		++	++
	Cerussite	$PbCO_3$	39	+	▨	++++	▨	++++		▨
			End			▨	++++	+++		
			End	+	+		+++		+	
	Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	39	+	▨	+++	▨	+++	++++	▨
			End	++		▨	+++	+++	++++	++++
			End				+++	++++	+++	++++
	Plumbonacrite	$Pb_5O(OH)_2(CO_3)_3$	39		▨		▨			▨
			End			▨	+			+
			End				+	+		+
	Anglesite	$PbSO_4$	39		▨		▨	+		▨
			End			▨		+		
			End							
	Susannite/Leadhillite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	39		▨		▨			▨
			End			▨	+	+		
			End				+	+		
	Laurionite	$Pb(OH)Cl$	39		▨	+	▨	+++		▨
			End			▨		++		
			End	+			++			
Copper minerals	Tenorite	CuO	39		▨		▨			▨
			End	++	+	▨				
			End	+	+	+				
	Cuprite	Cu_2O	39	++++	▨		▨			▨
			End	++++	++++	▨				
			End	+++	++++	+				
	Clinoatacamite	$Cu_2Cl(OH)_3$	39		▨		▨			▨
			End			▨				
			End	+						
	Malachite	$CuCO_3Cu(OH)_2$	39		▨		▨			▨
			End	+		▨				
			End			+++				
	Calcite	$CaCO_3$	39	++++	▨	+	▨			▨
			End	++		▨		+	+++	+
			End	++++					+++	

Table 8.5 Lead corrosion solids identified in Cu-Pb pipes for the smaller diameter pipes, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected.

Mineralogy			**Rep.**	**Copper pipe**						**Fitting**	**Lead pipe**			
	Name	Formula		Non-galvanic zone (Zone C)			Transition zone (Zone b)	Galvanic zone (Zone A)			Galvanic zone (Zone A)		Non-galvanic zone (Zone C)	
				L1	L2	Dark		L1	Exterior		L1	Exterior	L1	L2
Lead minerals	Litharge	PbO	39		▨	▨			▨	▨		▨		▨
			End					▨	▨	+	+	▨	++	+
			End								++		+	+
	Cerussite	$PbCO_3$	39	++++	▨	▨	++	++++	▨	▨	++++	▨		▨
			End	++				▨	▨	++++	++++	▨		
			End	++	+	+	+++	++++	++++	++++		++++		
	Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	39	+	▨	▨	++	++	▨	▨	++	▨	++++	▨
			End	+++				▨	▨	++++	+++	▨	++++	++++
			End	+	+	+	++	++	++	+++	++++	+++	++++	++++
	Plumbonacrite	$Pb_5O(OH)_2(CO_3)_3$	39		▨	▨			▨	▨		▨		▨
			End					▨	▨	+	++	▨		
			End								++			+
	Anglesite	$PbSO_4$	39		▨	▨		+	▨	▨	+	▨		▨
			End					▨	▨			▨		
			End											
	Susannite/ Leadhilite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	39	++	▨	▨	++	++	▨	▨	+++	▨	++	▨
			End					▨	▨	++		▨		
			End				+	+	+	++		+++		
	Laurionite	$Pb(OH)Cl$	39		▨	▨			▨	▨	++	▨		▨
			End					▨	▨	+		▨		
			End					+		+		++		
Copper minerals	Tenorite	CuO	39		▨	▨			▨	▨		▨		▨
			End			+		▨	▨			▨		
			End			++								
	Cuprite	Cu_2O	39	+	▨	▨	+		▨	▨		▨		▨
			End	++	++++	++		▨	▨			▨		
			End		++++	++++								
	Calumetite	$Cu(OH,Cl)_2\ 2H_2O$	39		▨	▨			▨	▨		▨		▨
			End					▨	▨			▨		
			End	+										
	Posnjakite	$Cu_4SO_4(OH)_6H_2O$	39		▨	▨			▨	▨		▨		▨
			End	+				▨	▨			▨		
			End	+										
	Calcite	$CaCO_3$	39	+++	▨	▨	++++	++	▨	▨		▨	+	▨
			End		▨	▨			▨	▨		▨		▨

8.3.2 Sulfate addition

With and without the combination of 1 mg Cl_2/L and addition of sulfate, corrosion products observed in the background zone (Table 8.6) are similar to those of the full LSL. The only difference is traces of plumbonacrite found on one L1 layer when 1 mg Cl_2/L is added. However, as the outermost layer does not completely cover the surface of the Pb pipe, it is possible that some material from L2 was picked up during sampling.

8.3.3 Increase in pH

Full LSL and the galvanic zone of the Pb pipe of the partial LSL treated with an increase in pH, with and without 1 mg Cl_2/L have similar corrosion products present Table 8.7. The only difference is the absence of cerussite on the L1 layer before the addition of chlorine in the partial LSL whereas cerussite was present in the full LSL. As cerussite has a much higher solubility than hydrocerussite (Masters et al., 2016), this could have repercussion in Pb concentrations in the water.

8.3.4 orthoP

It is worth mentioning that less scale material was present in the non-galvanic zone of the partial LSL than on the full LSL treated with orthoP. It results in less layers being differentiated or data missing for some layers as there was not enough material to conduct the analysis. No calcite was observed on the non-galvanic zone of the partial LSL, as it was a major phase in the outer layer of the full LSL (Table 8.8). Lead phosphate and hydroxypyromorphite were again detected throughout the layers of the orthoP treated pipes.

Table 8.6 Lead corrosion solids identified in Cu-Pb pipes treated with sulfate addition, before and after chlorination, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected.

	Mineralogy		**Cl_2 (mg/L)**	**Copper pipe**				**Fitting**	**Lead pipe**							
	Name	Formula		Non-galvanic zone (Zone C)			Galvanic zone (Zone A)		Galvanic zone (Zone A)		Transition (Zone B)			Non-galvanic zone (Zone C)		
				L1	L2	L3			L1	L2	L1	L2	L3	L1	L2	L3
Lead minerals	Litharge	PbO	0				+						++	+		++
			1			▨			+	+++	▨	▨	▨	+	+	++++
	Cerussite	$PbCO_3$	0				++++	▨	++++	++++	++++	++++	+++	++++	+++	+++
			1			▨	++++	++++	++++	++	▨	▨	▨	++++	+++	++
	Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	0	+			+++	▨	+++	+++	+++	+++	+++	+++	++++	+++
			1			▨	+++	++++	++++	++	▨	▨	▨	++++	++++	+++
	Plumbonacrite	$Pb_5O(OH)_2(CO_3)_3$	0				+		+	+	+	+	+		+	+
			1			▨								+		+
	Anglesite	$PbSO_4$	0					▨								
			1				+	+			▨	▨	▨			
	Susannite/Leadhilite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	0					▨								
			1				+++	++	++		▨	▨	▨			
	Laurionite	Pb(OH)Cl	0					▨								
			1				++	+	+	+	▨	▨	▨			
Copper minerals	Tenorite	CuO	0	+	+	+										
			1			▨					▨	▨	▨			
	Cuprite	Cu_2O	0	++++	++++	++++										
			1	+++	++++	▨					▨	▨	▨			
	Clinoatacamite	$Cu_2Cl(OH)_3$	0	+		+										
			1			▨					▨	▨	▨			
	Malachite	$CuCO_3Cu(OH)_2$	0	++	+	++										
			1			▨					▨	▨	▨			
	Posnjakite	$Cu_4SO_4(OH)_6H_2O$	0		+											
			1	+		▨					▨	▨	▨			
	Connelite	$Cu_{19}+2Cl_4(SO_4)(OH)_{32}$ $3H_2O$	0	+												
			1			▨					▨	▨	▨			
	Calcite	$CaCO_3$	0	+	++++			▨						+		
			1	++++	++	▨		+			▨	▨	▨	++	+	

Table 8.7 Lead corrosion solids identified in Cu-Pb pipes treated with an increase in pH to 8.3, before and after addition of chlorination ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected. 0-S indicates the pipe disconnected 30 weeks after PLSLR (short-term) and 0-L the pipe disconnected after 156 weeks, both treated with pH 8.3.

	Mineralogy		**Cl_2 (mg/L)**	**Copper pipe**					**Fitting**	**Lead pipe**							
	Name	Formula		Non-galvanic zone (Zone C)			Transition zone (Zone B)	Galvanic zone (Zone A)		Galvanic zone (Zone A)			Transition zone (Zone B)			Non-galvanic zone (Zone C)	
				L1	L2	L3				L1	L2	L3	L1	L2	L3	L1	L2
Lead minerals	Litharge	PbO	0-S		▨	▨			▨		▨	▨	+	▨	▨	+	▨
			0-L								+	++++		+	++++	++	++
			1	▨		▨		▨		+	+	+++	▨	+	+++	++	++
	Cerussite	$PbCO_3$	0-S	++++	▨	▨	+	++++	▨	++++	▨	▨	++	▨	▨	+	▨
			0-L	+			++	++	++	++	+++		++				
			1	▨	+	▨		▨	++++	+++	++		▨	++		++	
	Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	0-S	+++	▨	▨	+	+++	▨	+	▨	▨	++++	▨	▨	++++	▨
			0-L						+++	+++	++++	+	+++	++++	++	++++	++++
			1	▨	+	▨	+	▨	++	+	++++	+	▨	++++	+	+++	++++
	Plumbonacrite	$Pb_5O(OH)_2(CO_3)_3$	0-S		▨	▨			▨		▨	▨		▨	▨		▨
			0-L								+	+		+	+	+	+
			1	▨		▨	+	▨			+	+	▨	+	+		+
	Anglesite	$PbSO_4$	0-S		▨	▨			▨	+	▨	▨		▨	▨		▨
			0-L														
			1	▨		▨		▨	++	+			▨				
	Susannite/ Leadhillite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	0-S	+++	▨	▨	+	++++	▨	++	▨	▨	+	▨	▨	+	▨
			0-L											+			
			1	▨		▨		▨	+	++++		+	▨		+		
	Laurionite	Pb(OH)Cl	0-S		▨	▨			▨	+	▨	▨	+	▨	▨		▨
			0-L														
			1	▨		▨		▨	+	+++			▨				
Copper minerals	Tenorite	CuO	0-S		▨	▨			▨		▨	▨		▨	▨		▨
			0-L		+++	+											
			1	▨	++	▨		▨					▨				
	Cuprite	Cu_2O	0-S		▨	▨	+		▨		▨	▨		▨	▨		▨
			0-L	+	+++	+++											
			1	▨	++++	▨		▨					▨				
	Calcite	$CaCO_3$	0-S	+	▨	▨	++++	++	▨		▨	▨		▨	▨		▨
			0-L	++++			+++	+++	+				+			+	
			1	▨		▨	++++	▨			+		▨	+		++	

Table 8.8 Lead corrosion solids identified in Cu-Pb pipes treated with orthoP, before and after increase in dosage, ++++ represents the major phases present in each sample, +++ moderate presence, ++ minor presence, + traces and D phases that were detected. 1-S indicates the pipe disconnected 30 weeks after PLSLR (short-term) and 1-L the pipe disconnected after 156 weeks, both treated with 1 mg P/L.

	Mineralogy		**orthoP dosage (mg/L)**	**Copper pipe**					**Fitting**	**Lead pipe**					
	Name	Formula		Non-galvanic zone (Zone C)			Transition zone (Zone B)	Galvanic zone (Zone A)		Galvanic zone (Zone A)		Transition zone (Zone B)		Non-galvanic zone (Zone C)	
				L1	L2	L3				L1	L2	L1	L2	L1	L2
Leadn minerals	Litharge	PbO	1-S		▨	▨			▨	++	▨	+	▨	++	▨
			1-L								+	+	+	▨	▨
			1.5							▨	+	▨	+		++
	Cerussite	$PbCO_3$	1-S	+++	▨	▨	+++	++++	▨	++++	▨	++	▨		▨
			1-L	+	+	+	+++	++++	++++	++++	+	+++	++	▨	▨
			1.5	++	+	+++	+++	+++	++++	▨	+++	▨	++	++	
	Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	1-S	++	▨	▨	+	++	▨	++	▨	++++	▨	++++	▨
			1-L				++	++	+++	+		++++	++++	▨	▨
			1.5	+		++	+	++	+++	▨		▨	++++	++++	++++
	Anglesite	$PbSO_4$	1-S		▨	▨			▨	++	▨		▨		▨
			1-L											▨	▨
			1.5						+	▨		▨			
	Susannite/Leadhillite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	1-S		▨	▨		+	▨	++	▨	+	▨		▨
			1-L						+	+	+			▨	▨
			1.5				+	+	++	▨		▨			
	Laurionite	Pb(OH)Cl	1-S		▨	▨		++	▨	++	▨	+	▨		▨
			1-L											▨	▨
			1.5					+	+	▨		▨			
	Hydroxypyromorphite	$Pb_5(OH)(PO_4)_3$	1-S		▨	▨			▨		▨		▨		▨
			1-L					+	+		+		+	▨	▨
			1.5				+	++	+	▨	+	▨	+	+	+
	Lead phosphate	$Pb_9(PO_4)_6$	1-S		▨	▨		++	▨	++	▨	++	▨		▨
			1-L					+	++				+	▨	▨
			1.5			+			+	▨	+	▨	+	+	+
Copper minerals	Tenorite	CuO	1-S		▨	▨			▨		▨		▨		▨
			1-L	++	+	++								▨	▨
			1.5		+	+				▨		▨			
	Cuprite	Cu_2O	1-S	++	▨	▨	++		▨		▨		▨		▨
			1-L	++++	++	++++	++							▨	▨
			1.5	+	++++	++	+			▨		▨			
	Clinoatacamite	$Cu_2Cl(OH)_3$	1-S		▨	▨			▨		▨		▨		▨
			1-L											▨	▨
			1.5		+					▨		▨			
	Malachite	$CuCO_3Cu(OH)_2$	1-S		▨	▨			▨		▨		▨		▨
			1-L											▨	▨
			1.5	++						▨		▨			
	Calumetite	$Cu(OH,Cl)_2\ 2H_2O$	1-S		▨	▨			▨		▨		▨		▨
			1-L											▨	▨
			1.5		+	+				▨		▨			
	Posnjakite	$Cu_4SO_4(OH)_6H_2O$	1-S		▨	▨			▨		▨		▨		▨
			1-L											▨	▨
			1.5	+						▨		▨			
	Calcite	$CaCO_3$	1-S	++	▨	▨	++		▨		▨		▨		▨
			1-L		++++						+			▨	▨
			1.5	++++		++	+			▨		▨			

8.4 Which minerals are present in the galvanic zone of the partial LSL? How do copper minerals differ between the galvanic and non-galvanic zones?

Samples collected in the galvanic zones were often very limited in quantity, mostly for L1, which makes the interpretation of the localized changes in minerals more challenging. In cases when very little material was present in L1 and L2, the samples were blended together in order to have enough materials for PXRD.

8.4.1 Control condition and smaller diameter pipes

8.4.1.1 Galvanic zone

8.4.1.1.1 Control condition

When the Pb pipe was connected to a copper pipe using a brass connector, visual changes were apparent in some pipes and indicative of galvanic corrosion (Figure 8.10). Duplicate pipes, which were disconnected from the pilot at the same time, show visual differences in the galvanic zone, which is reflected in differences in corrosion products observed between pipes.

In the galvanic zone, on the Pb and Cu pipes as well as on the fitting, cerussite is the dominant mineral present, which was not the case in the background zone (Table 8.4). The enhanced presence of cerussite is therefore indicative of a decrease in pH at the fitting and the Pb pipe, which confirms the presence of galvanic corrosion. If a decrease in pH is observed at the connection, it means that the Pb pipe act as the anode in the galvanic couple and is therefore preferentially corroded. Other minerals, also associated with a decrease in pH, were present as secondary products such as: anglesite (PbSO4), susannite/leadhillite and laurionite.

Difference in the minerals present are observed between the galvanic zone of the copper and the lead pipes. Cerussite and hydrocerussite were only present on the copper pipe shortly after the simulation of the PLSLR. Copper oxides (Cu_2O) and carbonates ($CuCO_3Cu(OH)_2$) were also present in the galvanic zone of the copper pipe.

Figure 8.10 Partial LSL of the control condition (A) without visual changes in scale composition at the galvanic zone and (B) with visual changes and for two duplicate pipes of the smaller diameter (C and D).

8.4.1.1.2 Smaller diameter

The galvanic corrosion zone of the control and the smaller diameter condition (Figure 8.10) are visually different as there is much more abundant loose material for the smaller diameter condition. This material, which was white and shiny, was present on the interior and exterior of the pipe wall in the galvanic zone. As it was the case with the control condition, there is a shift from a dominance of hydrocerussite in the non-galvanic zone to a dominance of cerussite in the galvanic zone as well as minor traces of Pb(II) corrosion products containing sulfate and which are associate to lower pH condition (Table 8.5). Similar Pb minerals are present on the Pb and Cu pipes in the galvanic zone.

8.4.1.2 Non-galvanic zone in copper pipe

On the copper pipes of the control condition, for the partial LSLs, cuprite and calcite (Table 8.4and Table 8.5). A minor presence of tenorite was detected in the control condition while it was just observed as traces in the smaller diameter pipes. Corrosion products shifted from the dominance of lead-based to copper-based minerals. For both conditions, duplicate pipes presented similar copper corrosion products.

8.4.2 Sulfate addition

8.4.2.1 Galvanic zone

When sulfate is added to the water, there is no drastic change in composition. This differs from the shift in scale composition from a dominance of hydrocerussite to a dominance of cerussite from the non-galvanic to the galvanic zone for the control condition (Table 8.6). Similar corrosion products are present on the galvanic zones of the lead and copper pipe as well as the fitting. The addition of chlorine to the water yielded the minor presence of anglesite, susannite/leadhillite and laurionite. As it was the case with the smaller diameter pipes, there is also the presence of abundant white powdery material in the fitting in one of the rigs investigated (Figure 8.11).

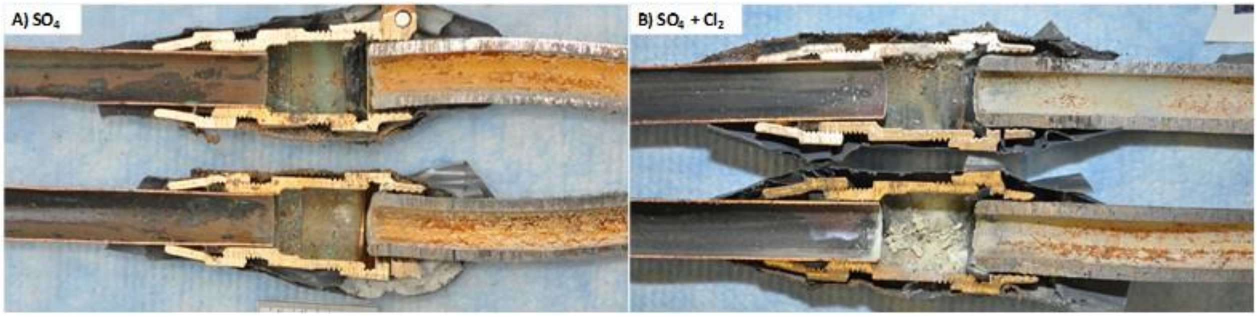


Figure 8.11 Interior of partial LSL treated with sulfate (A) and the combination of sulfate and chlorine (B).

8.4.2.2 Non-galvanic zone in copper pipe

In the non-galvanic zone of the copper pipe, there is a shift from Pb-based corrosion products to Cu-based ones, with cuprite being the dominant form along with the presence of calcite (Table 8.6). Small differences were observed before and after the addition of chlorine, such as the presence of tenorite and malachite in the absence of chlorine.

8.4.3 Increase to pH 8.3

8.4.3.1 Galvanic zone

As it was the case with the control condition, there is an increase in the presence of cerussite towards the galvanic zone, with and without the presence of chlorine (Table 8.7). When chlorine was present, there is a dominance in leadhillite/susannite and laurionite in the corrosion zone. In both condition, the phases present hint at the presence of galvanic corrosion as there is a switch the mineral more likely to be present at lower pH values. In the presence of chlorine, a gradient in the colour of the scale can be observed on both the lead and copper pipes, while it is not seen in the absence of chlorine (Figure 8.12).

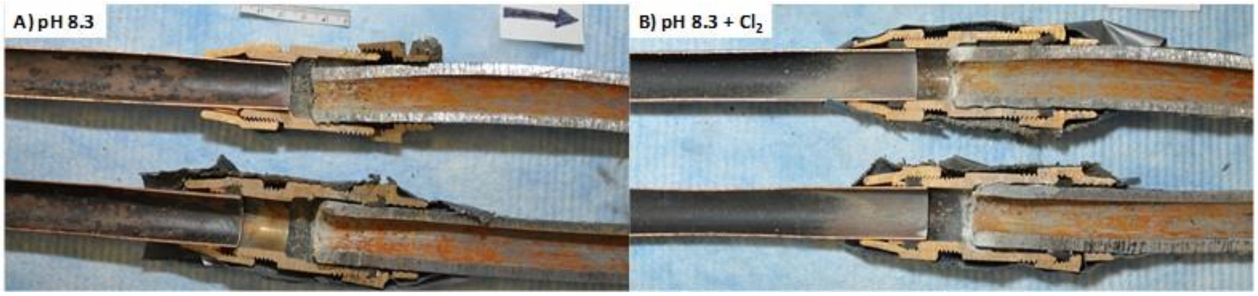


Figure 8.12 Partial LSL treated with an increased pH to 8.3 (A) and the combination of increased pH and chlorine (B).

For these conditions, there are less Pb-based corrosion products on the copper pipe. There was little material in the galvanic zone, therefore limited analysis was possible. Calcite was detected as the major constituent in the galvanic zone of the copper pipe.

8.4.3.2 Non-galvanic zone in copper pipe

With and without the presence of chlorine, the major copper minerals present are tenorite and cuprite, which is in line with observations made in other conditions in the pilot (Table 8.7).

8.4.4 orthoP

8.4.4.1 Galvanic zone

As with the control condition, in the galvanic zone of the Pb pipes treated with the addition of orthoP, there is a dominance of cerussite as well as the presence, to a lesser degree, of minerals also indicative of a decrease in pH at the junction (Table 8.8). These minerals also extend to the galvanic zone of the copper pipe. Pb(II) phosphate are present on the layer L2, as well as in the fitting in the transition and the galvanic zone, similar to observations in the non-galvanic zone. The galvanic zone of the Pb and Cu pipes presented similarities in terms of the presence of Pb(II) corrosion products.

As with other conditions, there is a sharp visual change between the galvanic and non-galvanic zones, with the abundance of white loosely attached deposits in the fitting (Figure 8.13).

8.4.4.2 Non-galvanic zone in copper pipe

No corrosion products of copper including a phosphate component were present on the copper pipe (Table 8.8). Similar to other conditions, tenorite is the dominant phase along with the presence of cuprite.

Figure 8.13 Interior of an orthoP treated partial LSL (A) shortly after PLSLR simulation, (B) before changes in water quality and (C) after an increased in orthoP (1 vs 1.5 mg P/L).

8.5 Can minerals confirm the presence of galvanic corrosion and indicate anodic/cathodic sites?

Based on PXRD analysis of the minerals present in the PLSL, it is possible to determine whether Pb pipes acted as an anode in the galvanic couple, as minerals formed under lower pH conditions should be favoured at the junction. However, in some cases, such evidence could not be seen as there were no clear shift in the minerals present at the junction.

Table 8.9 Evidence of galvanic corrosion of the Pb pipe.

Condition	**Indication of the presence of anodic site on the Pb pipe?**	**Increased corrosion based on Pb concentrations in water?**
Control	Yes	Yes
Smaller diameter	Yes	Yes
Sulfate	No	No
pH 8.3	Yes	Yes
orthoP	Yes	Yes

Relating the pipe minerals to the Pb levels in water (Chapter 5), provides insights to understand why an increase in Pb levels was observed following PLSLR simulations on the pilot. Prior research has shown that galvanic corrosion exacerbates the corrosion rate of Pb pipe and results in increased levels of Pb in the water. When galvanic corrosion occurs, a drop in pH is observed at the surface of the Pb pipe, which acts as the anode in the galvanic couple. Since the drop in pH affects the minerals present in the pipe, it was possible to determine whether galvanic corrosion was taking place or not for each water quality tested (Table 8.9). Interestingly, there is a direct correlation between the presence of galvanic corrosion, confirmed by different corrosion products present at the junction, as well as Pb concentrations in water. The addition of sulfate was the most protective treatment for Pb pipes connected to copper pipe and a bras fitting. In this particular water quality, no trends of decreasing pH were observed. This confirms that decreasing the CSMR, reduces the occurrence of galvanic corrosion.

Also, the scale composition confirms that the non-galvanic zone of the partial LSLs is similar to the full LSL for each specific water quality. This confirms that the hypothesis of similar Pb release from the non-galvanic zone and the full LSLs in the SANMR calculations. It is also important to note that the observations of changes in scale composition were only made over a short distance from the galvanic zone, in line with the assumptions made in the SANMR calculations.

8.6 Concluding remarks

From our observations, we note that:

- Other studies observed Pb(II) and Pb(IV) corrosion products in drinking water distribution systems (Arnold & Edwards, 2012; DeSantis et al., 2018; DeSantis et al., 2009; Wasserstrom et al., 2017). Mostly Pb(II) was observed in the pipes installed in the pilot, considering all the water qualities tested. The fact that chlorine was depleted in the storage tank prior to entering the pilot, probably decreased the ORP of the water to levels insufficient to maintain and form Pb(IV) corrosion products.
- Amorphous corrosion products were detected on the L1 layer, indicated by the presence of a raised background on the PXRD patterns.
- In the galvanic zone, when an increase in Pb concentrations was observed in samples collected after 16 hours of stagnation, the corrosion solids are indicative of a decrease in pH compared to the non-galvanic zone.

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CHAPTER 9 GENERAL DISCUSSION

Main findings of this research project are highlighted in this Chapter. The overall objective was to improve our understanding of dissolved and particulate lead and copper release and the impact of the presence of galvanic corrosion in different types of distribution systems. To achieve this research objective, we focused on the occurrence of Pb and Cu in schools and large buildings' tap water as well as the release of Pb from full and partial lead service lines (LSL).

Figure 9.1 summarizes the different themes of the research conducted. The first step was to understand the sources of lead specific to schools and large buildings as well as how lead and copper are released in service lines. One of the key parameters determining Pb and Cu release in full and partial LSL, is the scale corrosion products present as they drive the solubility of lead and copper. Since the water quality parameters promoting lead and copper leaching are different, as well as the trend each metal follows depending on the stagnation time, appropriate sampling protocols have to be determined. Adequate sampling allows to identify the sources of each metal and determining cases of acute exposure. For identifying the causes of particulate Pb and Cu, it is also important to determine how the water quality impacts leaching. By understanding the sources of lead and factors affecting the release of each metal, adequate mitigation strategies can be determined. It is important to take into account these factors when establishing regulatory guidelines and protocols.

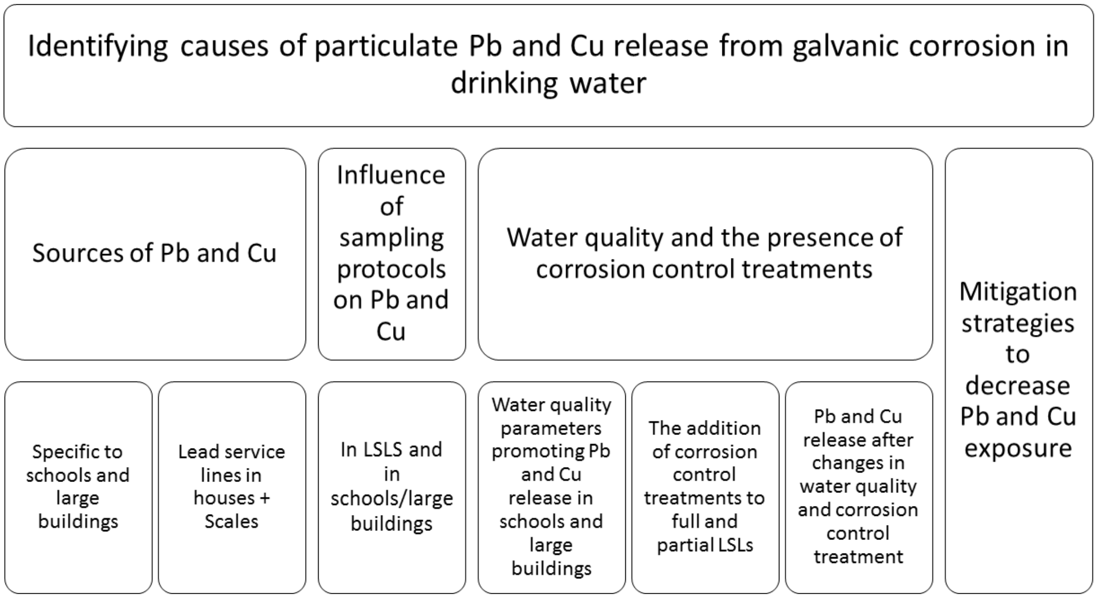

Figure 9.1 Summary of the research conducted.

In relating the impacts of water quality to particulate deposition, scale accumulation and particulate detachment in a lead service line particularly, one can consider an overall schematic of the various mechanisms that are in place. Figure 9.2 presents the various corrosion zones present in a partial LSL showing different factors such as pH, chloride, sulfate and the addition of orthoP. Other important factors such as temperature will also impact of the solubility and formation of different compounds and on the expansion and contraction of materials which can have an impact on the detachment of materials.

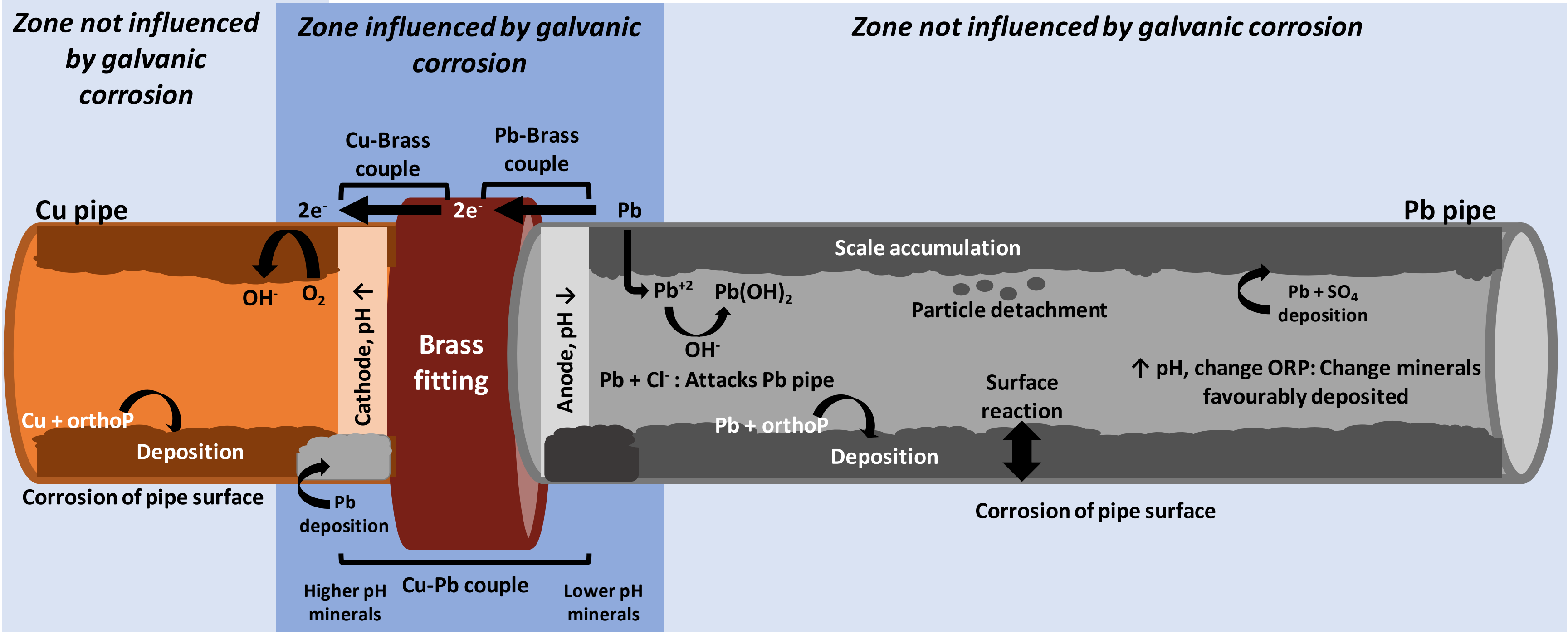

Figure 9.2 Factors influencing Pb release in a lead service line.

9.1 What are Pb and Cu sources in distribution systems?

As lead service lines were installed in Canada until 1975 and that the use of leaded solder continued until 1986, current drinking water systems materials still present sources of lead as legacy materials (Health Canada, 2017). As plumbing components are not readily accessible to identify their composition, sampling of water must be carried out as a proxy to identify lead and copper sources. As presented in Chapter 4, the schools and large buildings investigated present legacy sources of lead that are mostly located at distal ends of the plumbing system. In houses, LSLs are shown to be important sources of Pb in tap water, accounting for 50 to 75% of Pb present in houses (Cartier et al., 2011; Levallois et al., 2013; Sandvig et al., 2008). In Chapter 5, we identified that full and partial LSLs can leach significant Pb levels in tap water. Sources of lead in large buildings and in houses are different, which implies that different strategies should be used for sampling and mitigating Pb exposure.

9.1.1 Schools and large buildings

In Chapter 4, based on our sampling results, we noted that Pb and Cu concentrations were the highest in the first draw samples collected after extended stagnation. Previous research carried out in schools and large non-residential buildings also indicated that the distal end of the premises plumbing of schools and large buildings are the major contributors to Pb in tap water (Barn et al., 2014; Cartier et al., 2012c; Deshommes et al., 2012a; McIlwain et al., 2015). The faucet and its connecting plumbing components, which can contain leaded solder, are therefore the most important sources of Pb in schools and large buildings. This is exemplified by the fact that flushing the taps result in a significant decrease in Pb concentrations, as presented in Chapter 4. Striking results from our investigation conducted in large buildings is the order of magnitude of difference which can be observed between first draw samples within one building, which is in line with observations made in university buildings (McIlwain et al., 2015). Multiple factors are presented in the literature to explain variations between lead concentrations measured at different outlets within one building, including the changing usage patterns or the variety of piping materials used (Deshommes et al., 2012a; McIlwain et al., 2015). Also, lead release from brass devices can come from the friction between the different moving parts, resulting in enhanced lead release (Boyd et al., 2008a; Lytle et al., 1994).

However, even in flushed samples, we measured concentrations >2 µg Pb/L, which is the threshold used to detect LSLs in households (Deshommes et al., 2016b; Deshommes et al., 2017). This highlights the systemic nature of lead in buildings, as valves and solder can also leach significant levels of Pb as found in studies conducted in penitentiary complexes (Cartier et al., 2012c; Deshommes et al., 2012a). This has implications in terms of exposure to Pb from drinking water in schools and large buildings as even flushed water can be at risk of elevated Pb concentrations.

Contrary to lead sources in large buildings, our results in Chapter 4 show that copper sources are more widespread as they also include copper piping. As we could not directly observe the piping in the schools we investigated, we used sampling after stagnation and flushing the water for the determination of copper sources. Since a longer duration of flushing was required to decrease copper concentrations, we hypothesized that copper piping is widespread in large buildings, as found in schools sampled in British-Columbia (Canada) by Barn et al., (2014).

Due to the presence of mixed plumbing materials containing lead, such as leaded-solder or leaded-brass, in the drinking water distribution systems of schools and large buildings, the occurrence of galvanic corrosion, as one of the mechanisms of lead leaching is to be expected. When brass devices are connected to a plumbing component made out of copper, galvanic corrosion can occur between the two metals (Edwards & Triantafyllidou, 2007). The empirical galvanic series predicts that when a galvanic couple forms between brass and copper, brass should be preferentially corroded (Matsukawa et al., 2010). Despite the impossibility to determine the exact configuration of the distribution systems in the buildings, it is still possible to hypothesize that galvanic corrosion played a role in the release of Pb. This hypothesis is based on the construction year of the buildings, discussion with building managers and knowledge of past certification on brass materials. Cartier et al. (2012c) identified leaded-solders as a potential source of Pb in a Canadian penitentiary complex. Galvanic corrosion was also determined to occur in tin-lead solders connected to copper, based on galvanic series (Jones, 1996; Subramanian et al., 1995). The relative importance of galvanic corrosion in large buildings depends on the type of materials present in the buildings.

From the results of our sampling campaign carried out in schools and large buildings, we can conclude that the distal end of the plumbing system represents the most important source of both lead and copper, however copper is found throughout the plumbing system of schools.

9.1.2 Lead service lines

9.1.2.1 Lead sources

For the sources of lead and copper in houses, our research focused on lead service lines (LSL), which we studied extensively at pilot scale for over 2 years. Previous research conducted in distribution systems or at laboratory scale have also shown that LSLs can leach significant Pb levels in houses and highlighted the importance of galvanic corrosion in Pb release (Cartier et al., 2012b; Cartier et al., 2013; Deshommes et al., 2016b; Deshommes et al., 2017; Deshommes et al., 2010; McNeill & Edwards, 2004; Schock & Lytle, 2011; St. Clair et al., 2016; Triantafyllidou & Edwards, 2011; Trueman et al., 2016; Trueman & Gagnon, 2016; Wang et al., 2012; Wang et al., 2013; Xie & Giammar, 2011).

In the short-term, after partial LSL replacements (PLSLR) were simulated on the pilot setup, Cartier et al. (2013) did not observe a decrease in Pb concentrations although only 60 cm of Pb pipes remained out of the 3 meters before partial replacement. During the long-term (155 weeks), increased Pb leaching as a result of PLSLR persisted. This is evident when comparing Pb concentrations from full and partial LSL, adjusted for Pb pipe length for each water quality (Chapter 5). In fact, in the control condition, median Pb concentrations from the 100%Pb configuration were 2.9 and 5.1-fold lower than the Cu-Pb and Pb-Cu configurations, respectively. Our observations are in agreement with field and laboratory experiments (St. Clair et al., 2016; Triantafyllidou & Edwards, 2011; Trueman et al., 2016; Wang et al., 2012).

Following analyses of the scale corrosion products present in the full and partial LSLs in the pilot, we determined that Pb(II) oxides, carbonates and phosphates were present (Chapter 8). Pb levels from the pilot were elevated as the low solubility Pb(IV) oxides could not be identified.

Observations from the partial LSL (Cu-Pb) allowed us to confirm the presence of galvanic corrosion as an added source of lead leaching following PLSLR, as presented in different studies (Cartier et al., 2013; DeSantis et al., 2018; Schock & Lytle, 2011; St. Clair et al., 2016; Triantafyllidou & Edwards, 2011). We identified different lead release mechanisms in full and partial LSL based on the presence/absence of galvanic corrosion (Chapter 8). Also, Pb concentrations, adjusted for pipe length, were higher in the partial LSLs than in the full LSLs (2.9-5.1-fold for the control condition) indicating the important contribution of galvanic corrosion to total Pb release. In the absence of galvanic corrosion, Pb concentrations, adjusted for pipe length, should be within the same range, which was not observed. The addition of sulfate is the conditions for which concentrations adjusted for pipe length are the closer for full and partial LSLs.

The presence of galvanic corrosion was confirmed based on the Pb(II) corrosion products identified. Indeed, when lead is galvanically connected to brass or copper, it is preferentially oxidized (Oldfield, 1988). A drop in pH was observed using micro-electrodes in Pb-bass galvanic couple (Ma et al., 2018; Ma et al., 2017), which confirms that the Pb pipe act as the anode in the galvanic couple. In our study, we used corrosion products as a proxy to confirm the decrease in pH at the surface of the Pb pipe (Chapter 8). Indeed, as pH decreases, hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) switches to cerussite ($PbCO_3$), laurionite ($Pb(OH)Cl$), and then anglesite ($PbSO_4$) at lower pH values (DeSantis et al., 2018). Other specific corrosion products depend also on the DIC of the water (Schock & Lytle, 2011). In the pilot, hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) and cerussite ($PbCO_3$) were the dominant Pb forms present, with an increase dominance in cerussite closer to the galvanic joint. At the junction, we also identified the presence of susannite/leadhillite (Chapter 8).

Furthermore, corrosion products examination and visual observations of changes in scale appearance confirmed the presence of different corrosion zones as sources of Pb release in partial LSLs. The non-galvanic zone of partial LSLs installed in the pilot had similar scale material as the full LSL (Chapter 8). It confirms that our hypothesis of similar surface area normalized mass release rate (SANMR) for full LSL and the non-galvanic zone of partial LSL (Chapter 5) is correct. In the galvanic zone, we identified Pb corrosion products preferentially formed under lower pH values than those formed in the non-galvanic zone, confirming that the lead pipe act as the Pb anode in the galvanic couple, exacerbating Pb release. These observations in the scale are in line with the galvanic SANMR, derived from the Pb concentrations measured in water for partial LSL (Chapter 5).

The addition of the galvanic connection in an LSL as an additional source of Pb raises questions of acute exposure from an elevated mass of Pb present in a small section of the pipe. We calculated that the galvanic connection (Chapter 5), only represents a small volume of about 41-62 mL (1.3-1.6 cm internal diameter pipes respectively). We estimated that very important Pb masses (up to 1,208 µg Pb (Cu-Pb) and 1,563 µg Pb (Pb-Cu)) could be present at the galvanic junction in the 16 hour stagnation samples, in the control condition. If consumed as a slug in a small volume at the tap, this greatly exceeds the reference mass of Pb of 175 µg Pb to determine when toys pose an acute health risk (USCPSC, 2005). The question of the significance of these extreme concentrations merits more investigation. They are likely to be diluted during the transport from the galvanic area to the tap depending on the flow regime and may not be detected by sampling, even by sequential sampling unless small volumes are used.

When increasing the duration of stagnation prior to sampling, there is a sharp increase in lead concentrations when comparing concentrations measuring under flowing conditions and after 16 hours of stagnation (Chapter 6). This sharp increase in concentrations is expected based on solubility models (Kuch & Wagner, 1983; Schock, 1990; Schock et al., 1996). Following the sharp increase in concentrations, after 16 hours of stagnation, a fluctuation in total lead concentrations was observed, as precipitation and dissolution was occurring. The dominant forms of corrosion products present in the LSL (Chapter 8) influence the dissolution and precipitation happening in the LSL. The rate of lead release vary depending on the water quality (Chapter 5), which in turns influences the corrosion products in the LSL (Chapter 8) as well as concentrations measured at different stagnation times (Chapter 6).

Therefore, our observations based on Pb concentrations in water and on corrosion solids present in the full and partial LSLs confirm the lead release from the non-galvanic zone and the significant contribution of the galvanic zone to Pb concentrations in water.

9.1.2.2 Copper sources

In partial LSLs, copper sources include the newly added brass connector and the copper pipe. Higher concentrations are linked to newly added copper materials which have not passivated yet (Schock & Lytle, 2011). In Chapter 6, we presented the passivation of copper over 155 weeks, following the simulation of LSL replacement at pilot scale, under different water qualities. As expected, we demonstrated a decrease in concentrations as passivation occurred between 20 and 155 weeks after simulation of partial LSL replacements. For example, when comparing copper concentrations before and after 104 weeks following partial LSL replacements, for smaller diameter pipes, concentrations decreased by 1.6-fold (Cu-Pb) and 1.7-fold (Pb-Cu). The decrease in copper concentrations is due to the formation of a passivating films at the surface, which are associated to different types of copper corrosion products, with different solubilities, such as the 10-1,000-fold difference in solubility between cupric and cuprous oxides (Lytle & Schock, 2000).

Different changes in copper concentrations were observed depending on the changes in concentrations observed in Chapter 6 are in agreement with prior reports (Edwards et al., 2002; Lagos et al., 2001; Schock et al., 1995; Turek et al., 2011)

However, when sampling after 16 hours of stagnation, concentrations measured at pilot scale did not exceed recommended levels as often as Pb concentrations did.

9.2 What are the impacts of pH, chloride to sulfate mass ratio and orthophosphate on Pb and Cu?

The effect of pH on lead and copper release was evaluated in schools and large buildings (Chapter 4) as well as in LSLs at pilot scale (Chapter 5). The impacts of changing the chloride to sulfate mass ratio (CSMR) and adding orthophosphate (orthoP) were only studied on LSLs (Chapter 5). We also briefly investigated how adding chlorine and changing the orthoP dosage changes Pb concentrations in full and partial LSLs (Chapter 7).

At pilot scale, we observed that the effectiveness of corrosion control treatments depends on pipe configuration (full vs partial LSL), but also on the type of sample collected (flowing or stagnating water). Our results also show that the optimal corrosion control treatment might be different for full and partial LSLs in one distribution system and that the corrosion control treatment which would be effective for all LSL configurations should be chosen (Chapter 5).

9.2.1 pH

One of the groups of schools and large buildings sampled were in a drinking water distribution system using pH increase as a corrosion control treatment. The highest Pb concentrations in the buildings were measured in the low pH (6.6 – 7.8) and low alkalinity (8.5 – 15 $mgCaCO_3/L$) water without corrosion control (Chapter 4). We also sampled buildings with a similar water quality, but with increased pH (8.8 – 9.2) as a corrosion control strategy. Concentrations of Pb and Cu were significantly lower in this water quality, similar to observations made by Murphy (1993). In large buildings, galvanic corrosion is one of the most important source of Pb leaching as there are no free standing Pb pipes. In buildings, Pb is present as part of plumbing components in brass fixtures or as leaded solder. I all of these cases, the Pb is in contact with a different metal, giving the opportunity for galvanic corrosion to occur. We did not investigate the Pb and Cu corrosion products in large buildings, as it would have been too invasive for the scope of this project, but we can hypothesize that the increase in pH resulted in the formation of lower solubility hydrocerussite. Also, in the buildings we studied, a chlorine residual was present in fully flushed (10 minutes) samples collected from dead-ends of the premises plumbing. The presence of residual chlorine could have led to the formation of lower solubility corrosion solids.

A significant decrease in Pb and Cu concentrations in large buildings (Chapter 4) operated at elevated pH was not observed in full and partial LSLs at pilot scale (Chapter 5 and Chapter 6). In the pilot setup, the increase in pH was set at 8.3 as this was the pH expected in Montreal's water following the switch from free chlorine to sodium hypochlorite as disinfectant before distribution. The pH of the water in the large building treated for corrosion inhibitor was of 8.8 – 9.2, which is significantly higher than the pH studied in the pilot setup. Depending on the dissolved inorganic carbon (DIC) and alkalinity of the water, the pH at which formation of hydrocerussite is favoured comparatively to cerussite is around 8.3 (Schock & Lytle, 2011). Both the control condition and the increased pH pipes were dominated by the presence of hydrocerussite as corrosion solids and more cerussite was present in the pH 8.3 than the control condition (Chapter 6).

9.2.2 Decrease of the CSMR

The decrease in CSMR resulted in the most stable concentrations of Pb from the full and the partial LSLs through time (Chapter 5). The effect of CSMR changes are mostly on the galvanic corrosion as it protects the Pb anode in the galvanic couple and prevents it from being oxidized. However, we also observed that the decreased CSMR reduced the presence of particulate Pb in full LSLs. Also, this treatment resulted in the lowest Pb concentrations in the partial LSLs, reducing concentrations by 1.8-fold for the Cu-Pb configuration and by 3.2-fold for the Pb-Cu. The particulate Pb was also better controlled with the reduction in CSMR, as indicated by the lowest galvanic SANMR calculated (839 and 160 µg/m2 for the Cu-Pb and Pb-Cu configurations, vs 7,349 and 9,499 µg/m2 for the control). Our results are in agreement with previous observations at bench and pilot scales (Cartier et al., 2013; Kogo et al., 2017; Nguyen et al., 2010; Nguyen et al., 2011c).

9.2.3 Addition of orthoP

The addition of orthoP (1 mg P/L) was the water quality condition tested in the pilot with the most variability in the Pb concentrations after 16 hours of stagnation, with concentrations spanning over

3 orders of magnitude (Chapter 5). Our observations are coherent with reports by Cartier et al. (2013) at the short-term. However, this treatment resulted in different effects depending on the pipe configuration and therefore on the different types of corrosion occurring.

Concentrations of Pb decreased by 73% after 16 hours of stagnation in the full LSL, which is similar to decreases of 68% and 70% observed by Cartier et al. (2013); Edwards and McNeill (2002). However, despite well controlling total Pb concentrations in full LSLs at pilot scale, peaks of elevated concentrations remained, as this is the issue with orthoP which is highlighted in the literature (Arnold & Edwards, 2012; Cardew, 2009; Xie & Giammar, 2011).

The pipes treated with an addition of orthoP did show a small incorporation of orthoP into the corrosion solids (Chapter 8) as Pb(II) phosphates were less present, mostly in the non-galvanic corrosion zone. The analysis of the scale also demonstrated that the small incorporation of phosphate into scale material resulted in lower Pb concentrations from the non-galvanic zone. In this zone, the SANMR (background) was 15.3-fold lower, and less variable, for the Cu-Pb configuration than the galvanic SANMR.

9.3 Presence of particulate Pb

Elevated particulate Pb concentrations were present in the schools/large buildings sampled, as well as in the pilot setup in full and partial LSLs.

The highest Pb and Cu particulate fractions and concentrations were measured in the schools with the low pH and low alkalinity without the addition of corrosion control treatment (Chapter 4). The highest Pb concentration measured in schools (850 µg Pb/L) was after 30 minutes of stagnation and consisted mostly of particulate Pb (≥99%). Most of the samples with acute Pb concentrations (> 50 µg Pb/L) were from this specific water quality or the particulate Pb fraction was significant and exceeded 87%. Also, the particulate Pb concentration and fraction are influenced by water quality, as highlighted in Chapter 4.

In the pilot setup, it was possible to predict the Pb concentrations depending on stagnation time by calculating a rate of Pb release per hour (Chapter 6). While it was possible to predict dissolved Pb concentrations, the occurrence of particulate Pb could not be predicted because of its variable and sporadic occurrence.

In the pilot setup, after partial LSL replacements, spikes of elevated total Pb concentrations could be explained by spikes in particulate Pb as this accounted for 67% of total Pb, when grouping all the water qualities investigated. In agreement with the studies present in the literature, the addition of orthoP, even in the full LSLs, could not decrease particulate Pb concentrations as they were comparable to concentrations of the control condition.

In the simulated partial LSL replacements, the particulate Pb fraction was greater than in the full LSLs for the control, the orthoP and the pH adjustment conditions (16 hours stagnation samples). However, under flowing conditions, the particulate fractions of all samples were similar, confirming that galvanic corrosion and the increase in particulate Pb is mostly caused after prolonged station, as it was observed in schools and large buildings (Chapter 4).

When discussing these results, one must take into consideration the intrinsic limitations of the procedure to differentiate the particulate fraction from the dissolved fraction. In the present work, the dissolved fraction was defined as the part of the sample which could pass through a 0.45 µm filter. Depending on the definition of the dissolved fraction, a 0.45 µm filter will capture large particulate and small particulate. However, the colloidal cannot be captured by a 0.45 µm filter. The particulate fraction was obtained by subtracting the dissolved concentrations from the total concentrations measured in one sample. One of the considerations to take into account when measuring particulate Pb is the acidification of the sample, to ensure adequate digestion prior to analysis. Insufficient acidification was shown to underestimate the particulate concentration and fraction in samples (Deshommes et al., 2010; Triantafyllidou et al., 2007). Another consideration is the analytical procedure to fully account for the particulate fraction captured on the filter. In this study, we applied a recognized approach (0.45 µm filter) and digestion (at least 24 hours, 0.5-2% HNO_3). The total fraction was quantified by a full bottle digestion, rather than using an aliquot, to fully account for all the metals, which can also adhere to the wall of the sampling bottle. Finally, our current definition of particulate may need to be reviewed to account for more fine and brittle materials which could be broken down during the filtration process. And lastly it has been recently recognized that the role of particulate iron is important in influencing the release of Pb (Camara et al., 2013; Trueman & Gagnon, 2016). We did not account for iron in the current study, as iron levels were quite low in the water entering the pilot setup.

9.4 Is flushing an effective mitigation strategy to decrease Pb and Cu?

Letting the tap run prior to drinking the water is one of the mitigation strategies which can be used to remove the water which was in contact with lead and copper. The Government of Ontario recommends daily morning flush in schools to decrease the exposure of children to elevated Pb concentrations (Government of Ontario, 2010). The effectiveness of such a mitigation strategy, to decrease concentrations throughout the day, has not been properly quantified properly. Extensive flushing should also be carried following partial LSL replacements as well as any modifications which could have disturbed scale deposits within the LSL (AWWA 2017; Lewis et al., 2017).

Despite different sources of lead and copper between houses and large buildings, mechanisms of dissolution and precipitation of Pb and Cu are similar between both, as well as the presence of galvanic corrosion. As a matter of fact, galvanic corrosion present in large buildings and houses is related to the presence or particulate Pb, as we have demonstrated in Chapter 4 and Chapter 5. Therefore, for lead and copper, in large buildings and LSLs, flushing the water prior to consumption is a mitigation strategy which yielded a decrease in concentrations (Chapter 4 and Chapter 6).

9.4.1 Schools and large buildings

Our results show the uttermost importance of not drinking the first 250 mL of water after long and short stagnation, as we measured concentrations up to 850 μg Pb/L after 30 minutes of stagnation (Chapter 4). However, the benefits of flushing the taps do not last throughout the day as concentrations half of those measured in overnight stagnation samples were reached after only 30 minutes of stagnation. Our observations on the impact of flushing on Pb concentrations are in agreement with previous research (Barn et al., 2014; Boyd et al., 2008b; Cartier et al., 2012c; Murphy, 1993; Triantafyllidou et al., 2014).

It is important to mention that the decrease is greater for Pb (81%) than Cu (59%) and that it takes a longer flushing period to decrease Cu concentrations than to decrease Pb concentrations. All samples collected under flowing conditions respected the current maximum acceptable concentration (MAC) of Health Canada. The benefits of avoiding the very first draw are clear but are short lived.

9.4.2 Full and partial LSLs

As it was the case with schools and large buildings, the lowest Pb and Cu concentrations were measured under flowing conditions (Chapter 5 and Chapter 6). In the case of the pilot study, interesting findings on flushing are the impacts of high velocity flushing in decreasing Pb concentrations in subsequent samples collected after 16 hours of stagnation (Chapter 6). The high velocity flushing reduced the particulate Pb concentrations by up to 24-fold. This demonstrate that particulate Pb can easily be detached by a change in hydraulic regime. When disturbances in the scale present inside LSL could have occurred, from partial LSL replacements, to changing a valve or even road repairs, extensive flushing should be mandatory to decrease risks of acute exposure (Del Toral et al., 2013; Deshommes et al., 2017; Lewis et al., 2017).

9.5 What are the regulatory implications of the findings and how to sample for Pb and Cu?

Our results have demonstrated that sampling for lead and copper at the same time might be sub-optimal to detect elevated concentrations of both metals as they have different dissolution kinetics and because their sources are different (Chapters 4 to 6). Therefore, sampling targeted for the detection of Pb sources might miss elevated copper concentrations.

9.5.1 Schools and large buildings

In schools and large buildings, we observed a wide variability in Pb concentrations between taps in the same building. A 415-fold difference in Pb concentrations was also detected between samples collected after extended stagnation and extensive flushing, while the difference was of 39-fold for copper. This highlights the variability in concentrations depending on the type of sampling carried out.

As we have demonstrated in Chapter 4, the sampling protocol should be adapted to the objectives of the sampling: for the determination of acute exposure or the detection of taps at risk of leaching elevated Pb concentrations. Samples with elevated copper concentrations might differ than samples with elevated lead sources. Therefore, in instances when copper is a concern due to the water quality, specific sampling should be applied for copper, and include flushed samples to detect the presence of copper piping.

As such, we recommend that sampling be carried out at every outlet used by children in schools in order to detect taps at risk of leaching elevated Pb concentrations. We also suggest that sampling be conducted in the morning after overnight stagnation as it seems to be the easiest sampling strategy to apply in schools and large buildings, as it can be done before children enter the building and does not hinder daily activities. Also, given the importance of water quality, sampling should first be conducted in low pH and low alkalinity waters.

9.5.2 Lead service line

From our monitoring results in full and partial LSLs (Chapters 4 to 6), we have demonstrated that Pb and Cu concentrations follow different dissolution kinetics, which implies that the highest concentrations of both metals might not occur in samples collected after the same stagnation time. Therefore, utilities should keep in mind that when targeting sampling at the detection of lead sources, they might under quantify the risks of elevated copper concentrations.

Our results on full and partial LSLs also showed the importance of the addition of the galvanic junction as an added source of Pb following partial LSL replacements. In Chapter 5, we presented a decision framework which utilities could follow to manage new and legacy partial LSLs. Our study proved that some corrosion control treatments can be effective at decreasing Pb concentrations in full and partial LSLs, it also demonstrated the elevated exposure which can arise from occurrences of elevated Pb concentrations from partial LSL. The best long-term solution is therefore the removal of all sources of lead in distribution system, which should also include the removal of lead sources from schools and large buildings. We have also highlighted the effectiveness of high velocity flushing as a mean to decrease exposure from particulate Pb.

CHAPTER 10 CONCLUSION AND RECOMMENDATIONS

This project aims to contribute to understanding of Pb and Cu corrosion mechanisms occurring in large buildings and in lead service lines (LSL), which can result in the release of particulate lead. Several questions were initially raised: What are the conditions under which lead and copper sampling should be prioritized in schools and large buildings? How should lead and copper sampling be carried out in schools and large buildings? Are corrosion control treatments as effective in reducing lead concentrations in full lead service lines as in partial lead service lines? How does the water quality affect the scale formation inside the full and partial lead service lines? When does the addition of galvanic corrosion, caused by partial lead service line replacements, increase the lead concentrations at the consumers' tap? Is it possible to use the same stagnation time prior to sampling to detect elevated lead and copper concentrations?

The following conclusions were reached concerning the exposure to lead and copper in schools and large buildings:

- The benefits associated with extensive flushing of the taps in the morning in schools and large buildings are short lived as lead and copper concentrations increase to value representing half of those measured after overnight stagnation. Relying on flushing to prevent elevated lead at the tap is not feasible and morning flushing is not an effective strategy.
- The effectiveness of flushing is different in decreasing lead and copper concentrations as sources of each metal are different in schools and large buildings. Sources of lead are the tap and its connecting plumbing while copper sources are more widespread in large buildings and can also include copper piping.
- Using an aggressivity index including pH and alkalinity as well as the presence of corrosion control treatments can be an effective tool to determine which areas are more at risk of elevated lead concentrations in schools and large buildings.
- Sampling for lead should be prioritized based on water quality, starting with low pH and alkalinity water in which leaded plumbing components are susceptible to be present. Sampling after overnight stagnation can easily be implemented in order to identify high risk outlets.

- Prior to drinking water in schools and large buildings, the first 250 mL should be flushed to remove water at risk of presenting elevated lead concentrations and it should be done every time before drinking the water.

During the study of the long-term (155 weeks) impact of partial lead service line (LSL) replacement on the release of lead and copper and the impact of water quality were investigated under different stagnation times. The contribution of galvanic corrosion to lead concentrations in partial LSL was also quantified.

- Partial LSL released higher Pb concentrations than full LSL through the entire duration of the study, when sampling after 16 hours of stagnation.
- The most effective corrosion control treatments are different depending on the type of corrosion, with the addition of sulfate the most effective to control galvanic corrosion and the addition of orthoP to control corrosion from the non-galvanic zones.
- During the first 16 hours of stagnation, it is possible to predict lead and copper concentrations for the different pipe configurations and water qualities investigated. The increase in dissolved lead and copper concentrations with increasing stagnation times can be better predicted than the particulate lead and copper.
- Vigorous and extended flushing of the LSL at a flow rate of 15 m/min resulted in a significant decrease in total and particulate Pb concentrations in subsequent sampling events after stagnation. Therefore, high velocity flushing should be proscribed prior to sampling as it could underestimate Pb concentrations at the tap. However, in situations of elevated particulate Pb (particulate prone systems of post PLSLR sites), this strategy can decrease the concentrations found at the tap.
- Calculating the surface area normalized mass release (SANMR) quantified the relative contribution of the galvanic and non-galvanic zones to Pb concentrations. Using the SANMR, an estimate of the LSL length which has to be removed in order to offset the addition of galvanic corrosion can be made in a given system. This length varied based on the corrosion control approach tested.
- Scale analysis revealed a change in composition in the galvanic zone, revealing a decrease in pH in the lead pipe compared to the copper pipe. This change in corrosion solids confirms

that the lead pipe acts as the anode in the galvanic couple of all the conditions tested, except for the addition of sulfate and is in line with the increase in Pb release from partial LSLs.

- Lead corrosion solids present in the pilot are almost exclusively Pb(II) carbonates, sulfates and phosphates and no Pb(IV) solids were detected.
- Pilot studies can only be used as a proxy to estimate the effectiveness of corrosion control treatments as they tend to exacerbate Pb release.
- Sampling for lead and copper in houses should not be conducted after similar stagnation times as the kinetic of dissolution of each metal is different as well as conditions representing worst case exposure.

New questions came up as well as means to improve the research presented in this doctoral work arose, and can be separated into 2 categories: (1) studying lead and copper in drinking water in large buildings and (2) investigating lead and copper release from full and partial LSLs at pilot scale. They include interesting avenues for further research.

- Large buildings
    - What proportion of water do children drink at school vs at home?
    - What concentrations of lead and copper do children drink at schools?
    - What is the variation in lead and copper concentrations in one outlet during one day, if sampled according to its typical inter stagnation times?
- Full and partial LSLs at pilot scale
    - How do corrosion products change and at which rate following: (1) partial LSL replacements and (2) following the onset of treatment or water quality change?
    - What are the dynamics of dissolved oxygen in full and partial LSLs and how does it impact copper concentrations in partial LSLs?
    - What is the surface coverage of each scale layer, as it is not homogenous, and how does this uneven coverage influence lead and copper release?
    - What is the influence of flow rate and type of flow (turbulent vs laminar) on the dispersion of the peak of contaminants coming from the LSL?

Also, after completing extensive piloting work, ideas of future work or on how to conduct pilot studies of LSL are also listed:

- Automated operation of the pilot to facilitate sampling following different stagnation times and under flowing conditions.
- Automated modification in the flow rate to have water use patterns that are representative of the use in houses.
- Complete elemental analysis to determine if more corrosion products that those identified by PXRD are present and carry, and use scanning electron microscope (SEM) to see the shape of the scale deposits.

The role of galvanic corrosion in lead release is under scrutiny by regulatory agencies as well as by utilities, as there are evidences of the presence of elevated lead concentrations caused by the increased corrosion of partial lead pipes. As multiple water quality parameters influence lead and copper corrosion, and sometimes in different ways, efforts in research will improve our understanding of these complex interactions.

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APPENDIX A SUPPLEMENTARY INFORMATION, ARTICLE 1: SCHOOLS AND LARGE INSTITUTIONAL BUILDINGS: IMPLICATIONS FOR REGULATION, EXPOSURE AND MANAGEMENT OF LEAD AND COPPER

Supplementary Information

Journal: Water Research

Title: Sampling in schools and large institutional buildings: Implications for regulation, exposure and management of lead and copper

Authors: Evelyne Doré, Elise Deshommes, Robert C. Andrews, Shokoufeh Nour, Michèle Prévost

Table A.1 Overview of Canadian, American and European guidance and regulations on sampling lead and copper in schools are large buildings

Authority / Legislative agency	**Country**	**Pb or Cu**	**Regulation or recom-mendation**	**Concen-tration (µg /L)**	**How to sample**	**# of outlets per building to sample**	**Volume of sample**	**Specific for schools**	**Reference**	
Health Canada (HC) (Current)	Canada	Pb	MAC	10	After 8 hour stagnation, follow up: after flush of 30s[1]	NS	250 mL[1]	No	Health Canada (2009, 2014)	Guidelines for Canadian drinking water quality, Guidance on controlling corrosion in drinking water distribution systems
		Cu	AO	1000						
Health Canada (Proposed)		Pb	MAC	5	RDT	Every outlet used by children or for meal prepartion	125 mL	No	Health Canada and Federal-Provincial-Territorial Committee on Drinking Water (2017)	Lead in drinking water
Alberta	Canada	Pb	MAC	Refers to HC	Flushed, cold water sample	NS	NS	No	Government of Alberta (2012); Province of Alberta (2003)	Potable water regulation (277/2003), Standards and Guidelines for Municipal Waterworks, Wastewater and Storm Drainage Systems
		Cu	Not regulated							
British-Columbia	Canada	Pb	MAC	Refers to HC	NS	NS	NS	Yes	Legislative Assembly of British-Columbia (2016)	M215-2016, Drinking water protection (Safe water for schools), Amendment Act, 2016
		Cu	AO							
Manitoba	Canada	Pb	MAC	10	2-5 minute flush prior to sampling	NS	NS	No	Government of Manitoba (2017a, 2017b)	The drinking water safety act, C.C.S.C c. D101
		Cu	NS	NS						

[1] Recommendations, AL: Action level, AO: Aesthetic objective, MAC: Maximum acceptable level, NS: Not specified

Table A.1. Overview of Canadian, American and European guidance and regulations on sampling lead and copper in schools are large buildings (continued).

Authority / Legislative agency	Country	Pb or Cu	Regulation or recommendation	Concentration (µg /L)	How to sample	# of outlets per building to sample	Volume of sample	Specific for schools	Reference	
New-Brunswick	Canada	Pb	MAC	10[2]	NS	NS	NS	No	Government of New-Brunswick (2017a, 2017b)	Clean Water Act (O.C. 93-979), Public Health Act, Drinking Water Guidelines
		Cu	AO	1000[3]						
Newfoundland and Labrador	Canada	Pb	MAC	10	5 minute flush	NS	NS	No	Government of Newfoundland and Labrador (2009, 2016)	Water Resources Act, Policy for Drinking Water Quality Monitoring and Reporting for Public Water Supplies
		Cu	AO	1000						
Nova-Scotia	Canada	Pb	MAC	Refers to HC	10 minute flush	NS	NS	No	Government of Nova Scotia (2005, 2017)	Water and Wastewater Facilities and Public Drinking Water Supplies Regulation, Guidelines for Monitoring Public Drinking Water Supplies
		Cu	AO							
Ontario	Canada	Pb	MAC	10	After 6 hour or more stagnation and 30 minute stagnation	Every outlet used by children or for meal preparation	1L	Yes	Government of Ontario (2017)	243/07: Schools, private schools and child care centres
		Cu	Not regulated		NS	NS	NS	No	Government of Ontario (2018)	169/03: Ontario drinking water quality standards

[2] Depending on sampling plan submitted to the Minister, [3] Recommendation, AL: Action level, AO: Aesthetic objective, MAC: Maximum acceptable level, NS: Not specified

Table A.1 Overview of Canadian, American and European guidance and regulations on sampling lead and copper in schools are large buildings (continued).

Authority / Legislative agency	Country	Pb or Cu	Regulation or recom-mendation	Concen-tration (µg /L)	How to sample	# of outlets per building to sample	Volume of sample	Specific for schools	Reference	
Northwest territories	Canada	Pb	MAC	Refers to HC	Faucets should be flushed, or as prescribed by health officer	1 per year for all the distribution system	NS	No	Government of Northwest Territories (2011)	Public health act – Water supply system regulations (R-108-2009, 12(1))
		Cu	AO							
Nunavut	Canada	Pb	MAC	50	NS	NS	NS	No	Government of Nunavut (1990)	Public Health Act – Consolidation of public water supply regulations R.R.N.W.T. 1990, C.P-23, 12(3)
		Cu	MAC	1000						
Prince Edward Island	Canada	Pb	MAC	Refers to HC	5 minute flush[4]	NS	250 mL[4]	No	Government of Prince Edward Island (2015)	Environmental protection act – Drinking water and wastewater facility operating regulations, 8
		Cu	AO							
Quebec	Canada	Pb	MAC	10	After 5 minute flush	NS	NS	Yes	Government of Québec (2017)	Environmental Quality Act – Regulation respecting the quality of drinking water
		Cu	MAC	1000						
Saskatchewan	Canada	Pb	MAC	10	Thorouhly flushed	NS	NS	No	Government of Saskatchewan (2015)	The waterworks and serwage works regulations (Chapter E-10.22 Reg 3), 26(1)
		Cu	Refers to HC (2012)		NS					

[4] Not in the Environmental Protection Act, as presented on the website of the Communities, Land and Environment Minister, AL: Action level, AO: Aesthetic objective, MAC: Maximum acceptable level, NS: Not specified

Table A.1 Overview of Canadian, American and European guidance and regulations on sampling lead and copper in schools are large buildings (continued).

Authority / Legislative agency	**Country**	**Pb or Cu**	**Regulation or recommendation**	**Concentration (µg /L)**	**How to sample**	**# of outlets per building to sample**	**Volume of sample**	**Specific for schools**	**Reference**	
Yukon	Canada	Pb	MAC	Refers to HC	NS	NS	NS	No	Government of Yukon (2007)	Public Health and Safety Act – Drinking water regulation, 44(1)
		Cu	AO					No		
US EPA, 3Ts	United States	Pb	Recommendation	20	After 8-18 hour stagnation, follow up: 30s flush	Outlets used for drinking and cooking	250 mL	Yes	USEPA United States Environmental Protection Agency (USEPA) (2006b)	3Ts for Reducing Leand in Drinking Water in Schools
		Cu	Recommendation	1300	NS	NS	NS	Yes		
California	United States	Pb	AL	15	NS	Outlets used for drinking and cooking	NS	Yes	Government of California (2018)	California Safe Drinking Water Act
		Cu	PHG	300	NS	NS	NS	No	California Environmental Protection Agency et al. (2008)	Copper
European Union	NA	Pb	MAC	10	Random day time, or fixed stagnation	NS	1 L	No	(European Commission, 2015)	Commussion Directive (EU) 2015/1787 of October 2015 Amending Annexes II and III to Council Directive 98/83/EC on the quality of water intended for human consumption
		Cu	MAC	2000		NS		No		

AL: Action level, AO: Aesthetic objective, MAC: Maximum acceptable level, NS: Not specified

Table A.2 Overview of studies on lead and copper in drinking water in large buildings, schools and daycares

Reference	**Type of building sampled (n)**	**Type of taps sampled**	**Location of study**	**Volume of samples**	**Lead and copper concentrations** **A = Mean; M = Median; 10th p. = 10th percentile; 90th p. = 90th percentile; R = Range; Max = Maximum**		
					Extended stagnation (>6h)	**Flushed sample (duration)**	**Random day time or 30 minute stagnation**
Deshommes et al. (2016a)	Schools, universities, hospitals, penitentiaries (n=8530)	Fountains, classroom taps, kitchen/cafeteria taps, bathroom taps (n=78,791)	Canada	125 mL, 250 mL, 1L	Children data set M: 1.8 µg Pb/L 90th p.: 11 Max: 13,200	Children data set M: 1.3 µg Pb/L 90th p.: 9.2 Max: 710 (30 second)	Children data set M: 1.0 µg Pb/L 90th p.: 4.7 Max: 3,890 (30 minute)
					Adult data set M: 2.9 µg Pb/L 90th p.: 26 Max: 1,800	Adult data set M: 1.3 µg Pb/L 90th p.: 12 Max: 400 (30 second)	Adult data set M: 1.0 µg Pb/L 90th p.: 5.7 Max: 1,900 (30 minute)
McIlwain et al. (2015)	Non-residential buildings (n=48)	Fountains (n=71)	Halifax, Nova Scotia, Canada	250 mL, 1L	R: 1.2-31 µg Pb/L		
Barn et al. (2014)	Elementary schools and secondary schools (n=5)	Classroom sink and fountains (n=48)	British-Columbia, Canada	Not specified	Elementary schools A: 71.1 µg Pb/L R: 5.9-306 A: 4,900 µg Cu/L R: 400-7,600 Secondary schools A: 94.5 µg Pb/L R: 12-191 A: 3,200 µg Cu/L R: 2,200-4,000	Elementary schools A: 5.0 µg Pb/L R: 0.9-20.8 A: 2,000 µg Cu/L R: 50-10,700 Secondary schools A: 12.3 µg Pb/L R: 1.2-21.0 A: 4,300 µg Cu/L R: 500-7,000 (5 minutes)	

Table A.3 Overview of studies on lead and copper in drinking water in large buildings, schools and daycares (continued)

Reference	Type of building sampled (n)	Type of taps sampled	Location of study	Volume of samples	**Lead and copper concentrations** **A = Mean; M = Median; 10th p. = 10th percentile; 90th p. = 90th percentile; R = Range; Max = Maximum**		
					Extended stagnation (>6h)	**Flushed sample (duration)**	**Random day time or 30 minute stagnation**
Triantafyllidou et al. (2014)	Elementary schools (n=71)	Fountain and sink faucet (n=~3,100)	Seattle, USA	250 mL	A: 24.4 µg Pb/L M: 4.0 R: <1-1,600 19% > 20 µg/L	A: 3.4 µg Pb/L M: 1.0 R: <1-370 3% > 20 µg/L	
	Elementary schools (n=629)	Each water outlets (n=~51,000)	Los Angeles, USA	Not specified	A: 11.0 µg Pb/L M: 5.0 10% < 1.0 µg Pb /L R: 0.2-13,000	A: 4.0 µg Pb /L M: 2.0 R: 0.2-7,400 1% > 20 µg Pb /L	
Bitenc (2013)	Old kindergartens and schools (n=39)	Kitchen	Slovenia	250 mL	M: ~3 µg Pb/L R: 0 – 42 0 µg Pb/L :28.2% 0-5: 66.7% 5.1 – 10: 17.9% 10 and lower: 84.6% >10: 7.7%	All samples below 10 µg Pb/L (30 seconds)	
Deshommes et al. (2012a)	Active federal penitentiary	Water from the utility, bathroom, kitchen, cell taps, drinking fountains, coffee-maker (n=45)	Canada	250 mL	M: 100 µg/L Pb Max: 1,000 M: 1,200 µg/L Cu Max: 3,900 µg/L Cu R. fountains: 1-120 3,900 µg/L Cu		

Table A.3 Overview of studies on lead and copper in drinking water in large buildings, schools and daycares (continued)

Reference	Type of building sampled (n)	Type of taps sampled	Location of study	Volume of samples	Lead and copper concentrations A = Mean; M = Median; 10th p. = 10th percentile; 90th p. = 90th percentile; R = Range; Max = Maximum		
					Extended stagnation (>6h)	**Flushed sample (duration)**	**Random day time or 30 minute stagnation**
Cartier et al. (2012c)	Federal penitentiary complex (n=15)	Fountains, faucets in inmates cells (n=35)	Canada	250 mL	Fountains (n=9) M: 29 µg $Pb_{Diss.}$/L 90th p.: 79 M: 12 µg $Pb_{Part.}$/L 90th p.: 98 M: 1,350 µg $Cu_{Diss.}$/L 90th p.: 2,900 M: 370 µg $Cu_{Part.}$/L 90th p.: 2,720 Old double faucets (n=18) M: 50 µg $Pb_{Diss.}$/L 90th p.: 206 M: 48 µg $Pb_{Part.}$/L 90th p.: 272 M: 877 µg $Cu_{Diss.}$/L 90th p.: 1,220 M: 235 µg $Cu_{Part.}$/L 90th p.: 1,090 Old single faucets (n=8) M: 86 µg $Pb_{Diss.}$/L 90th p.: 127 M: 22 µg $Pb_{Part.}$/L 90th p.: 912 M: 1,015 µg $Cu_{Diss.}$/L 90th p.: 1,220 M: 220 µg $Cu_{Part.}$/L 90th p.: 821		

Table A.3 Overview of studies on lead and copper in drinking water in large buildings, schools and daycares (continued)

Reference	**Type of building sampled (n)**	**Type of taps sampled**	**Location of study**	**Volume of samples**	**Lead and copper concentrations** **A = Mean; M = Median; 10th p. = 10th percentile; 90th p. = 90th percentile; R = Range; Max = Maximum**		
					Extended stagnation (>6h)	**Flushed sample (duration)**	**Random day time or 30 minute stagnation**
Massey and Steele (2012)	Primary schools and preschools		South central Kansas, USA	1L	M: 3.35 µg Pb/L A: 6.16 (non-detectable values not taken into account) R: 1.0 – 27.2		
Elfland et al. (2010)	University building	Drinking fountains, kitchen faucets, bathroom faucets, Devices leaching ≥ 15 µg Pb/L	University of North Carolina at Chapel Hill, USA	1 L	A: 39.4 µg Pb/L M: 27 R: 15 – 98	A: 33.3 µg Pb/L M: 22.5 R: 15-120 (24-72 hour)	
Boyd et al. (2008a)	Elementary, middle and high school (n=4)	Fountains n=22 *Recently remediated (within approximately three weeks of sampling)	Seattle, USA	50 mL or 100 mL, multiple contiguous samples (up to 11 samples/source)	E-1, 5 sources, 1st 50 mL: R: 38-79 µg Pb/L Then: next 50 mL : <1-4 Other 2 sources : 1st and 2nd 50 mL: R: 9-15		

Table A.3 Overview of studies on lead and copper in drinking water in large buildings, schools and daycares (continued)

Reference	**Type of building sampled (n)**	**Type of taps sampled**	**Location of study**	**Volume of samples**	**Lead and copper concentrations** A = Mean; M = Median; 10th p. = 10th percentile; 90th p. = 90th percentile; R = Range; Max = Maximum		
					Extended stagnation (>6h)	**Flushed sample (duration)**	**Random day time or 30 minute stagnation**
Lambrinidou et al. (2010)	Elementary and high schools (n=735)	All drinking water outlets (n=66,000)	Los Angeles, USA	250 mL	92% of schools > 20 µg Pb/L		
	Elementary and high schools (n=16)		Washington D.C., USA	250 mL	77% of taps > 20 µg Pb/L, in one school 75% of schools > 20 µg Pb/L Max: 20,000 µg Pb/L		
	Elementary and high schools	Fountains	Seattle, USA	250 mL	Wedgwood Elementary school : elevated lead levels in all samples, Max: 200 µg Pb/L 2004: 70% of school built before 1997 > 20 µg Pb/L One school A: 175 µg Pb/L Max: 1,600		
	Public schools (n=10)	Drinking water sources (n=48)			A: 2.8 µg Pb/L Max : 19.2	A: 1.70 µg Pb/L Max: 11.0	

Table A.3 Overview of studies on lead and copper in drinking water in large buildings, schools and daycares (continued)

Reference	Type of building sampled (n)	Type of taps sampled	Location of study	Volume of samples	**Lead and copper concentrations** **A = Mean; M = Median; 10th p. = 10th percentile; 90th p. = 90th percentile; R = Range; Max = Maximum**		
					Extended stagnation (>6h)	**Flushed sample (duration)**	**Random day time or 30 minute stagnation**
Cech et al. (2006)	Large public access office complex (n=5)	Drinking fountains (n=45)	Houston, USA	60 mL	*Flush for 10s prior to sampling M: <1 µg Pb/L A: 16 ± 48 (±SD) R: BD – 210 M: 320 µg Cu/L A: 650 ± 958 µg Cu/L R: 2 - 5,043		
Sathyanarayana et al. (2006)	Elementary schools (n=71)	Drinking fountains and faucet (1S>8h n=1905, 30s F n=1850)	Seattle, USA	250 mL	A: 22.85 µg Pb/L Std. Dev. : 65.58 M: 5 R: BD – 1600 90th p.: 49	A: 3.80 µg Pb/L Std. Dev.: 14.80 M: 1 R: BD – 370 90th p.: 7 (30 seconds)	
Costa et al. (1997)	Elementary school (n=1)	Kitchen taps, classroom taps, drinking fountains (n=7)	Utah, USA	Not specified	A: 308.6 µg Pb/L M: 280 R: 12-840	A: 57.9 µg Pb/L M: 8.1 R: 3-270	

Table A.3 Overview of studies on lead and copper in drinking water in large buildings, schools and daycares (continued)

Reference	**Type of building sampled (n)**	**Type of taps sampled**	**Location of study**	**Volume of samples**	**Lead and copper concentrations** **A = Mean; M = Median; 10th p. = 10th percentile; 90th p. = 90th percentile; R = Range; Max = Maximum**		
					Extended stagnation (>6h)	**Flushed sample (duration)**	**Random day time or 30 minute stagnation**
Bryant (2004)	School buildings (n=292, ~58% elementary schools)	Drinking fountains, water coolers, bathroom faucets, classroom faucets, icemaker, kitchen cold-water faucet, and kitchen hot-water faucets	Philadelphia, USA	Not specified	42.5% schools, <20 µg Pb/L, 28.7 % of schools between 20 and 50, 11.6% of schools between 50 and 100, 17.1% >100 µg/L		
				Not specified	Drinking water fountains (250 buildings) 38% of schools, primary mean lead levels > 20 µg Pb/L 20.4% >50 11.6%> 100	Drinking water fountains (68 follow up samples) 30.9% of samples >20 µg/L	
Maas et al. (1994)	Schools and workplace	Water coolers, bubblers, chillers, faucets and ice makers (n= >12,000)	USA	250 mL	All types of taps/faucets 71.6% : 0 to 7.4 ppb 11.4% : 7.5 to 15.0 ppb 17% : > 15 ppb N = 10132	All types of taps/faucets 89.2% : 0 to 7.4 ppb 4.95% : 7.5 to 15.0 ppb 5.84% : > 15 ppb N = 5376 % : 0 to 7.4, 7.5 to 15.0, > 15.0; % Red of % > 15 ppb from first draw	

Table A.3 Overview of studies on lead and copper in drinking water in large buildings, schools and daycares (continued)

Reference	**Type of building sampled (n)**	**Type of taps sampled**	**Location of study**	**Volume of samples**	**Lead and copper concentrations** **A = Mean; M = Median; 10th p. = 10th percentile; 90th p. = 90th percentile; R = Range; Max = Maximum**		
					Extended stagnation (>6h)	**Flushed sample** **(duration)**	**Random day time or 30 minute stagnation**
Murphy (1993)	Schools (n=50)	Fountains (n=100)	New Jersey, USA	Not specified	M: 10 µg Pb/L R: BD-135 M: 260 µg Cu/L R: BD-10,200	M: 5 µg Pb/L R: BD-74 M: 68 µg Cu/L R: BD-7,800 (10 minutes)	M: 7 µg Pb/L R: BD-75 M: 120 µg Cu/L R: BD-8,500
Gnaedinger (1993)	Schools and day care centers	Water coolers, fountains (non-cooled), sinks, icemakers, kitchen/classroom sinks (n=3,332)	Missouri, USA	Not specified			
Singh and Mavinic (1991)	High-rise apartment buildings 12 buildings 72 suites, 3 sampling runs	Kitchen taps	Vancouver, Canada	1st flush : 50 mL 2nd flush : 200 mL 3rd flush : 750 mL 5 minutes running : 125 mL	A(1st L): 20 µg Pb/L A 50 mL : 41 200 mL : 34 750 mL : 14 A 50 mL : 1310 µg Cu/L 200 mL : 1760 750 mL : 1300 1st L (combined) : 1390		

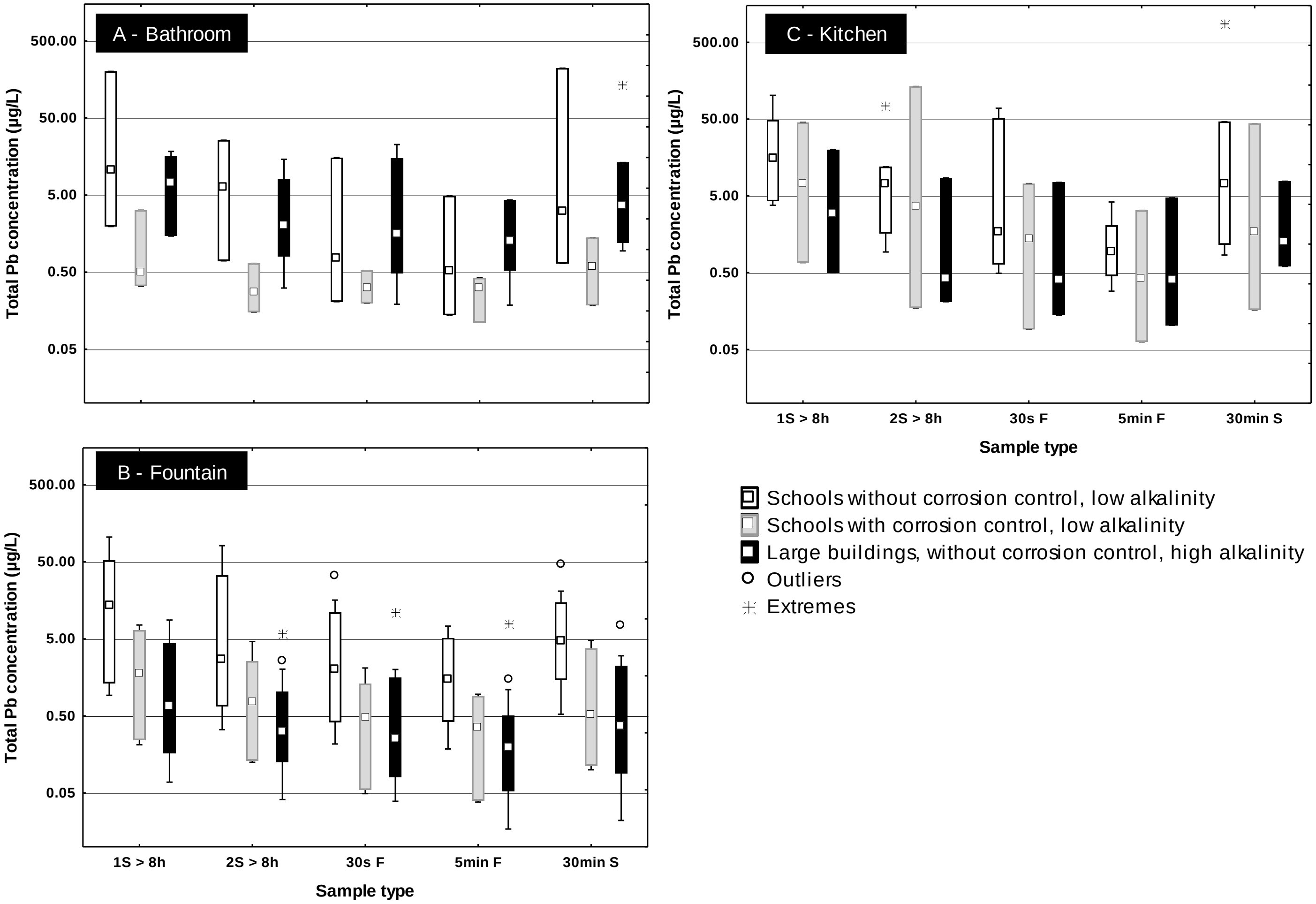

Figure A.1 Total lead concentration per type of tap and building sampled. Schools without corrosion control and with low alkalinity (A n=5, B n=20, C n=12), Schools with corrosion control and with low alkalinity (A n=3, B n=19, C n=7), Large buildings (A n=17, B n=38, C n=9). Whiskers represent minimum and maximum values, boxes the 10th and 90th percentile, white squares the median concentration.

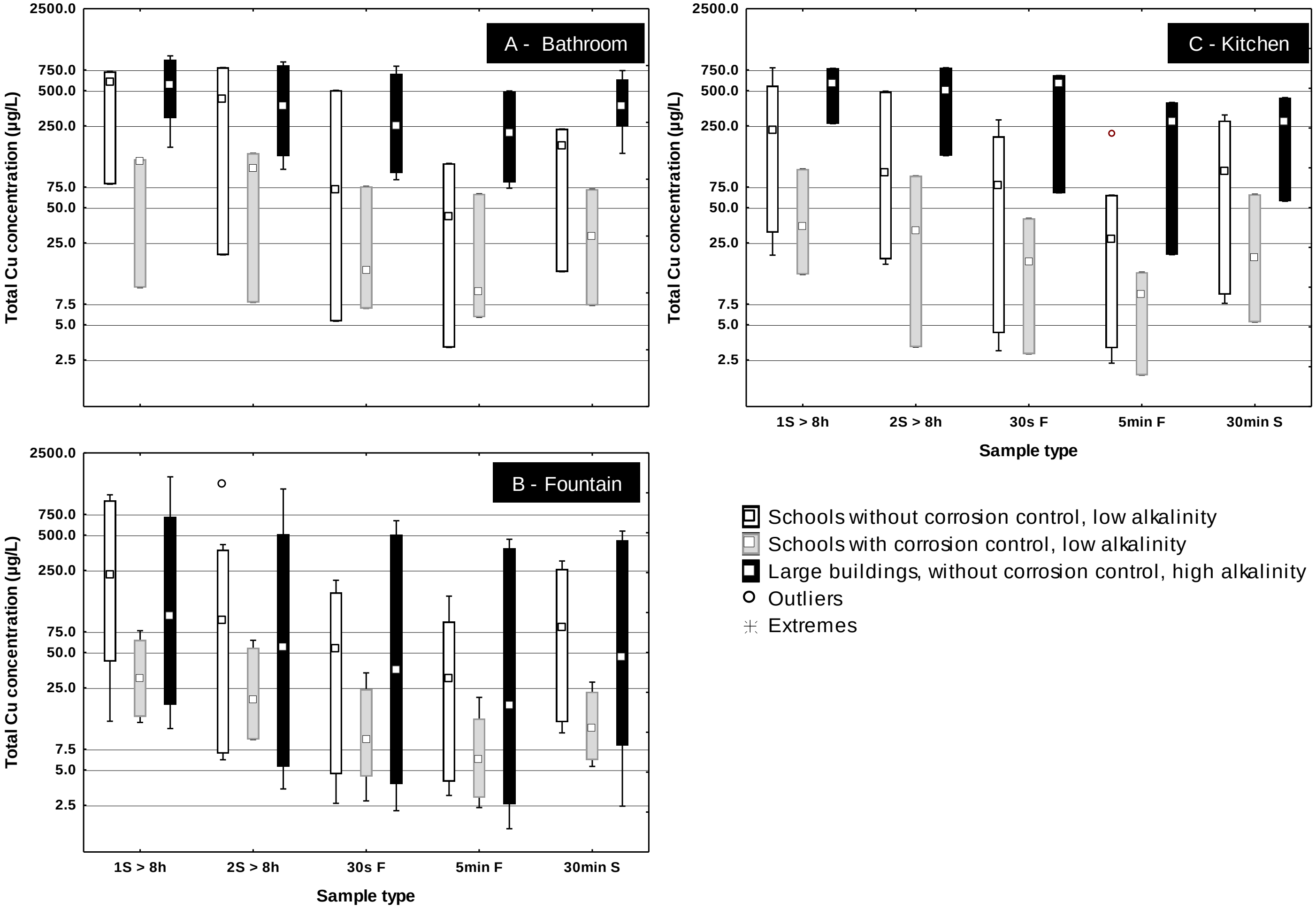

Figure A.2 Total copper concentration per type of and building. Schools without corrosion control and with low alkalinity (A n=5, B n=20, C n=12), Schools with corrosion control and with low alkalinity (A n=3, B n=19, C n=7), Large buildings (A n=17, B n=38, C n=9). Whiskers represent minimum and maximum values, boxes the 10th and 90th percentile, white squares the median concentration.

Table A.3 Percentage of the samples with a total Pb concentration greater than 1 µg Pb/L, all types of samples considered at each types of tap and buildings.

	Mean pH	**Mean alkalinity (mg CaCO$_3$/L)**	**AI**	**Type of outlet**	**1S > 8h (1st 250 mL)**		**2S > 8h (Following 1.75 L)**		**30s F**		**5min F**		**30min S**	
Schools, without corrosion control n=37	7.0	15	9.8	**Bathroom n=5**	97%	100%	86%	80%	68%	40%	59%	40%	92%	80%
				Fountain n=20		95%		85%		70%		70%		95%
				Kitchen n=12		100%		92%		75%		50%		92%
Schools, with pH control n=29	9.1	35	12.4	**Bathroom n=3**	66%	33%	38%	0%	28%	0%	7%	0%	52%	33%
				Fountain n =19		63%		26%		21%		0%		42%
				Kitchen n=7		86%		86%		57%		29%		86%
Large buildings without corrosion control, high alk. n=64	7.7	86	11.7	**Bathroom n=17**	61%	100%	30%	76%	27%	71%	25%	71%	45%	94%
				Fountain n=38		37%		11%		11%		8%		24%
				Kitchen n=9		89%		22%		11%		11%		44%

Table A.4 Multivariate Adaptative Regression (MARSpline) results presenting significant variables for total lead and copper concentrations.

Input – Variables	**Output**		
	Response variable	**Significant variables**	**R^2**
Total Fe, total Cu, total Zn, total Sn, sampling point, flow rate, building, type of taps	Total Pb concentration (1S>8h)	Total Sn (5x), building (4x), sampling point (3x), total Cu (2x), total Zn (1x), flow rate (1x)	0.974
Total Fe, total Cu, total Zn, total Sn, sampling point, building, type of taps	Total Pb concentration (1S>8h), >1 µg Pb/L	Building (4x), sampling point (4x), total Sn (4x), toal Zn (2x)	0.975
Total Fe, total Cu, total Zn, total Sn, sampling point, group of buildings, building, type of taps	Total Pb concentration (1S>8h), >5 µg Pb/L	Sampling point (5x), building (4x), total Sn (4x), total Cu (1x),	0.989
Total Fe, total Cu, total Zn, total Sn, sampling point, group of building, type of taps	Total Pb concentration (1S>8h), >10 µg Pb/L	Samping point (7x), total Sn (2x), type of taps (1x)	0.994
Total Fe, total Cu, total Zn, total Sn, sampling point, building, type of taps		Total Sn (6x), building (5x), sampling point (4x), total Zn (2x), type of taps (1x)	0.997
Particulate Fe, particulate Cu, particulate Zn, particulate Sn, sampling point, group of buildings, building, type of taps	Particulate Pb concentration (1S>8h)	Particulate Cu (5x), particulate Sn (4x), group of buildings (3x), type of taps (3x), sampling point (2x), building (1x)	0.966
Total Fe, total Cu, total Zn, total Sn, sampling point, group of buildings, building, type of taps	Total Pb (30minS)	Total Sn (7x), total Cu (4x), total Zn (4x), sampling point (3x)	0.998
Total Fe, total Cu, total Zn, total Sn, sampling point, group of buildings, building, type of taps	Total Pb (30minS), >5 µg Pb/L	Total Sn (5x), sampling point (3x), total Fe (2x), building (1x), type of taps (1x)	0.999

Table A.4 Multivariate Adaptative Regression (MARSpline) results presenting significant variables for total lead and copper concentrations (continued).

Input – Variables	Output		
	Response variable	Significant variables	R^2
Total Fe, total Cu, total Zn, total Sn, sampling point, group of buildings, building, type of taps	Total Pb (30minS), >10 µg Pb/L	Total Sn (3x), sampling point (1x), group of buildings (1x)	0.999
Particulate Fe, particulate Cu, particulate Zn, particulate Sn, sampling point, group of buildings, building, type of taps, flow rate	Particulate Pb (30minS)	Particulate Sn (3x), sampling point (1x), flow rate (1x), group of buildings (1x)	0.998
Total Fe, total Cu, total Zn, total Sn, sampling point, group of buildings, building, type of taps, flow rate	Total Pb (30sF)	Sampling point (2x), total Zn (1x), total Sn (1x)	0.912
Total Pb, total Fe, total Zn, total Sn, sampling point, group of buildings, building, type of taps	Total Cu (1S>8h)	Total Zn (6x), building (4x), sampling point (3x), total Sn (1x)	0.848
Total Pb, total Fe, total Zn, total Sn, sampling point, building, type of taps	Total Cu (30sF)	Building (5x), sampling point (4x), total Zn (3x), total Fe (1x)	0.719
Total Pb, total Fe, total Zn, total Sn, sampling point, building, type of taps	Total Cu (5minF)	Sampling point (7x), building (3x), total Zn (1x)	0.848

Table A.5 Number of samples required to estimate the true geometric mean total Pb concentrations for each school sampled.

Building ID	**Number of samples to estimate the true GM**	**Type of water/building**	**Number of taps sampled**
B1	30	Schools without corrosion control, low alkalinity	6
B2	25		6
B3	30		9
B4	25		6
B5	20		10
B6	15	Schools with pH control, low alkalinity	10
B7	8		9
B8	10		10

APPENDIX B SUPPLEMENTARY INFORMATION, ARTICLE 2: STUDY OF THE LONG-TERM IMPACTS OF TREATMENTS ON LEAD RELEASE FROM FULL AND PARTIALLY REPLACED HARVESTED LEAD SERVICE LINES

Supplementary Information

Journal: Water Research

Title: Study of the long-term impacts of treatments on lead release from full and partially replaced harvested lead service lines

Authors: Evelyne Doré, Elise Deshommes, Laurent Laroche, Shokoufeh Nour, Michèle Prévost

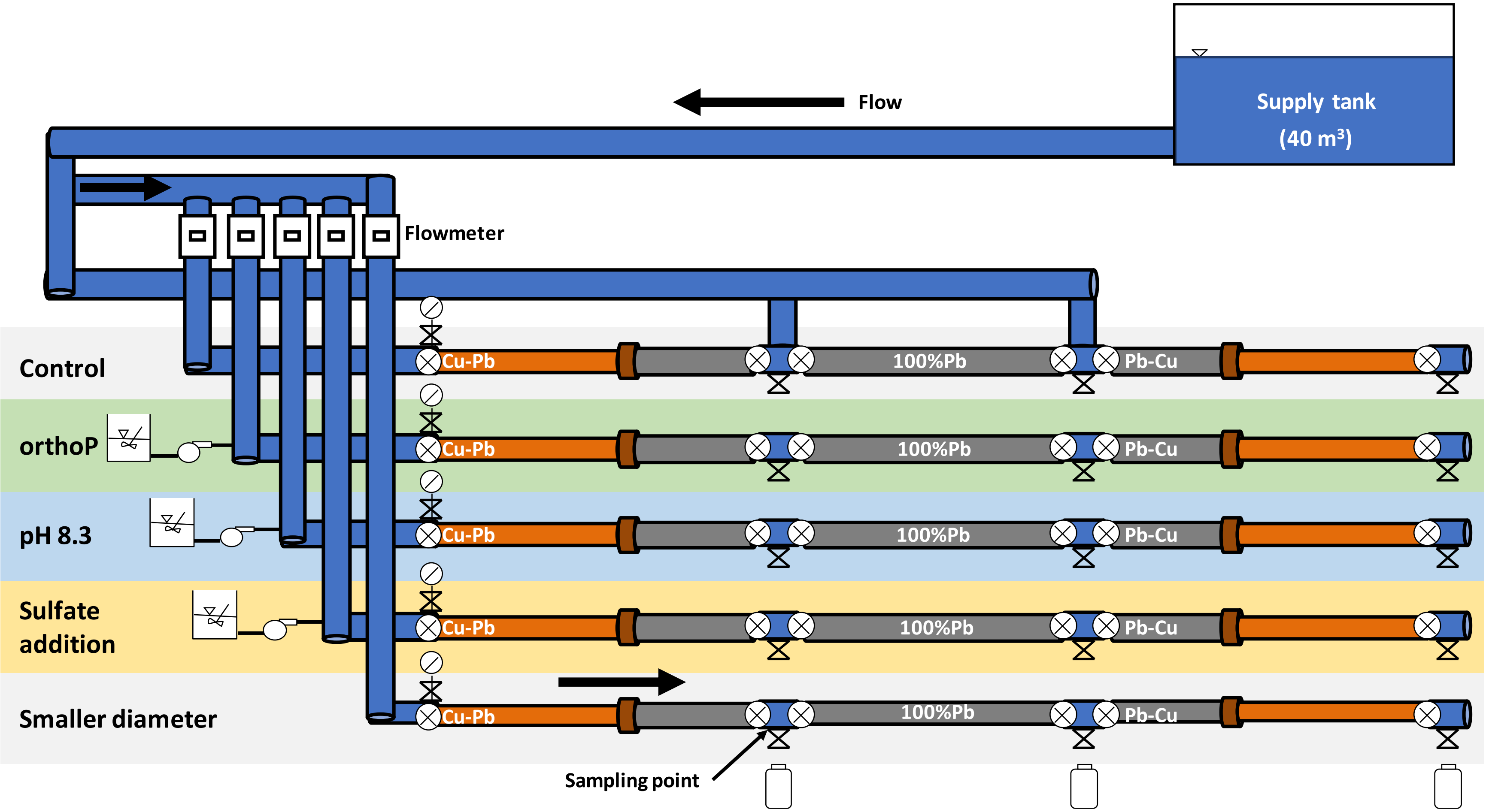

Figure B.1 Schematic of the pilot setup built using aged LSLs from the distribution system of Montreal and new copper pipes connected to the Pb pipes using red brass compression fittings.

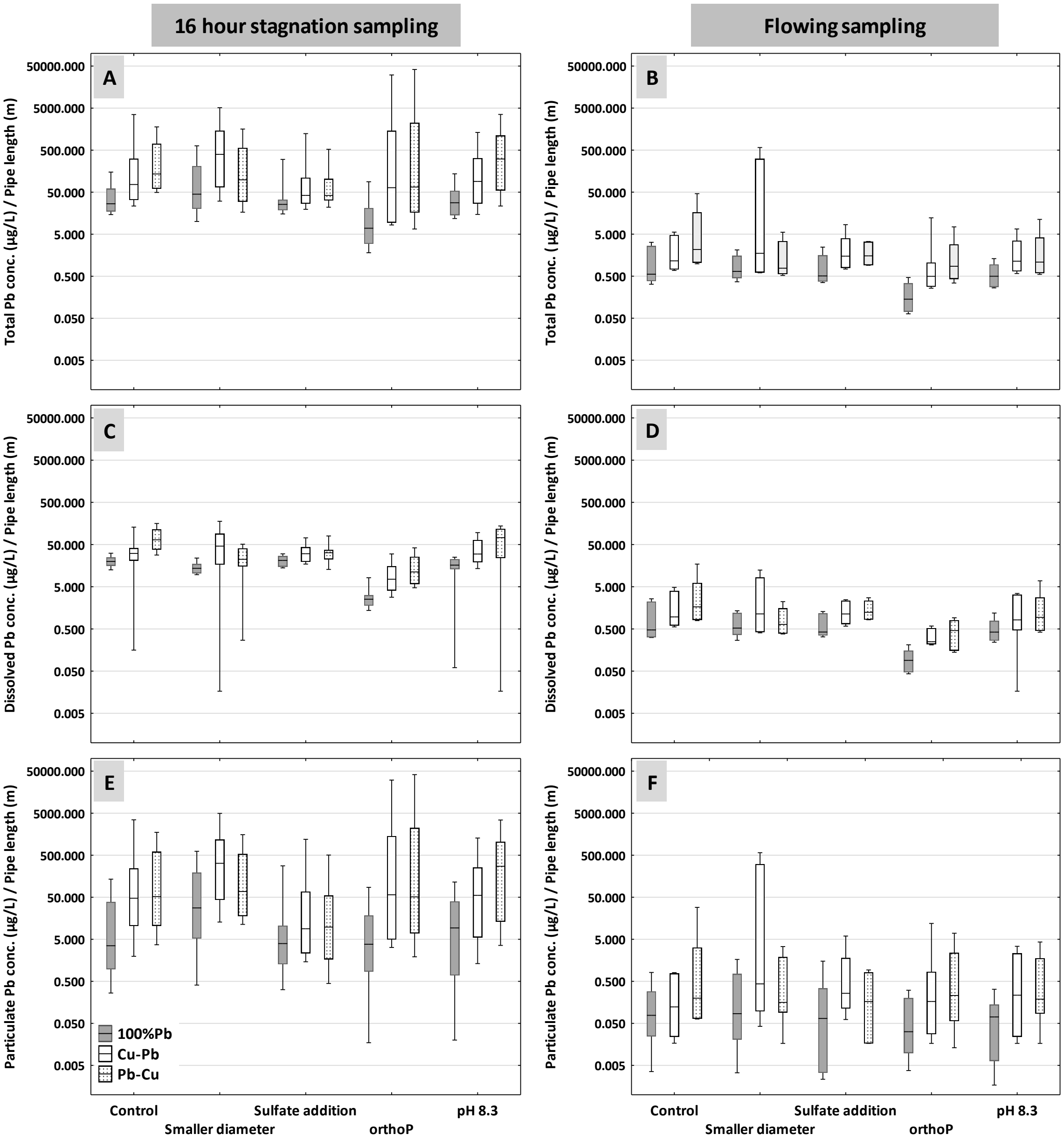

Figure B.2 Total (A-B), dissolved (C-D) and particulate (E-F) lead (Pb) concentrations measured after a 16 hour stagnation period (left) or under flowing conditions (right) normalized for the length of the pipe for the control, smaller diameter, sulfate treatment, orthoP treatment, and pH 8.3 conditions. The 100% Pb pipe configuration is represented in grey, Cu-Pb configuration in white and Pb-Cu configuration with black dots. The line within each box represents the median concentration. The bottom and top of each box represents the 10th-90th percentiles, respectively. The whiskers represent the minimum and maximum values.

APPENDIX C SUPPLEMENTARY INFORMATION, ARTICLE 3: LEAD AND COPPER RELEASE FROM FULL AND PARTIALLY REPLACED HARVESTED LEAD SERVICE LINES: IMPACT OF STAGNATION TIME PRIOR TO SAMPLING AND WATER QUALITY

Supplementary Information

Journal: Water Research

Title: Lead and copper release from full and partially replaced harvested lead service lines: Impact of stagnation time prior to sampling and water quality

Authors: Evelyne Doré, Elise Deshommes, Shokoufeh Nour, Michèle Prévost

Information on sampling for lead and copper

A recent review of guidelines and standards is presented in Table S1. Guidelines and standards are established for Pb and Cu in drinking water covering the acceptable concentrations and the sampling protocols to be applied. In Canada and the European Union, lead concentrations are recommended to be below 10 µg Pb/L, while in the United States 90th percentile values should not exceed 15 µg Pb/L (European Commission, 2015; Health Canada, 2014; USEPA 1991). In Europe, copper concentrations should not be greater than 2,000 µg Cu/L (Official Journal of the European Communities, 1998) and 1,300 µg Cu/L in the United States (USEPA 1991). Current Canadian recommendations set an aesthetic objective of 1,000 µg Cu/L in drinking water (Health Canada, 2014), with a newly proposed health-based maximum acceptable concentration of 2,000 µg Cu/L (Health Canada, 2018) in line with the World Health Organization's (WHO) recommendations (WHO, 2017). California has set a public health goal (PHG) of 300 µg Cu/L in drinking water to protect young children (California EPA, 2008). Regulations and recommendations for lead and copper sampling, in residential sites, vary between countries or even within one country depending on the regulatory agencies (Deshommes et al., 2016b). Health Canada recommends sampling for lead after either random day time (RDT), 1 L sample, or after 30 minute of stagnation, 2 consecutive 1 L samples (Health Canada, 2017). In the Province of Ontario in Canada, lead samples in houses are collected after 30 minute stagnation (two 1 L samples) (Government of Ontario, 2009). However, in the Province of Quebec samples for lead and copper are collected after at least 5 minutes of flushing (MDDELCC 2016). In the European Union, samples must be taken after random stagnation time (RDT), without flushing the taps prior to collecting the 1 L sample (European Commission, 2015). Whereas the USEPA recommends collecting samples after at least 6 hours but less than 24 hours of stagnation (1 L) (USEPA 1991).

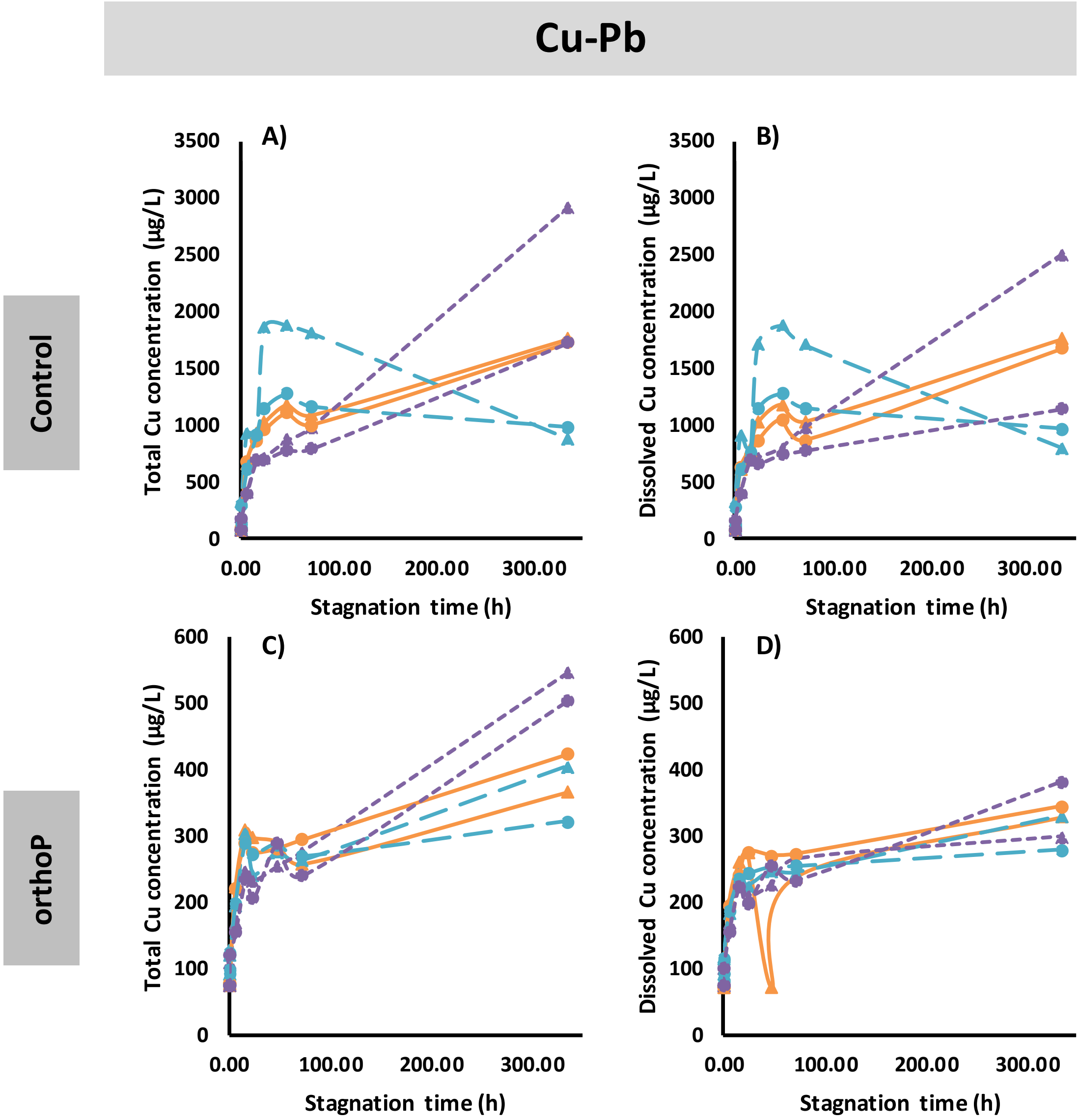

Figure C.1 Total (left) and dissolved (right) Cu concentration (µg/L) in the copper pipe depending on stagnation time for the control condition (A and B) and the orthoP condition (C and D) in Cu-Pb pipe configurations (Cu pipes upstream of Pb pipes). Each colour/type of line represents consecutive sampling events. The full line (orange) is the 1st event, the long dashes (teal) the 2nd event and the short dashes (purple) the 3rd event. The triangles and the circles each represent one pipe.

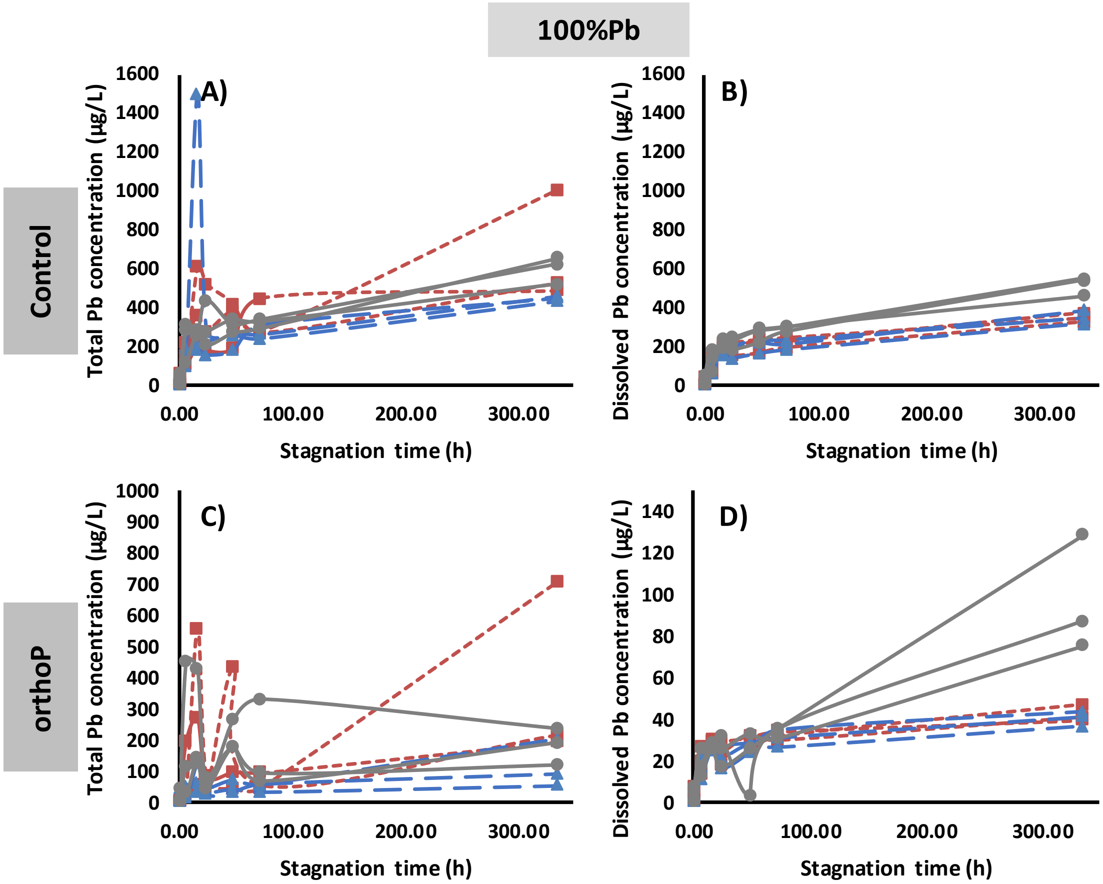

Figure C.2 Total (left) and dissolved (right) Pb concentration (µg/L) in the lead pipe depending on stagnation time for the control condition (A and B) and the orthoP condition (C and D), for the full LSLs (100%Pb). The squares, triangles, and circles each represent one pipe, as well as each colour/type of line.

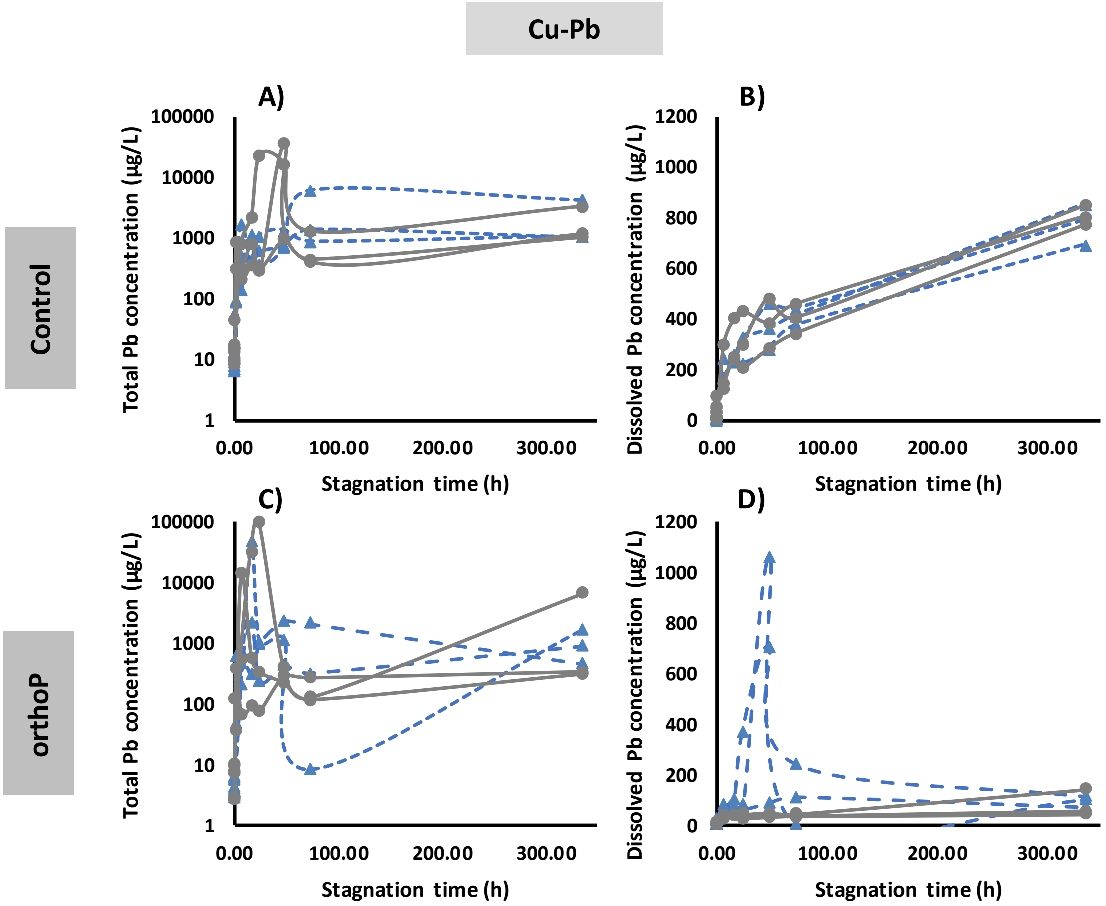

Figure C.3 Total (left) and dissolved (right) Pb concentration (µg/L) in the lead pipe depending on stagnation time for the control condition (A and B) and the pipes dosed with orthoP (C and D), for the partial LSLs in which the Cu pipe is upstream of the Pb pipe (Cu-Pb). The triangles and the circles each represent one pipe, as well as each colour.