TRACE METAL BIOGEOCHEMISTRY OF FRESHWATER FLOC

TRACE METAL BIOGEOCHEMISTRY OF FRESHWATER FLOC

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ABSTRACT

Water-quality in freshwater ecosystems is linked to metal contaminant sequestration and transport by suspended aquatic floc. This doctoral thesis investigates the combined microscale biogeochemical processes as well as macroscale hydrodynamic mechanisms controlling trace metal dynamics of freshwater floc, through comparative assessments of floc versus bottom bed sediment metal(loid) (Ag, As, Co, Cu, Ni and Pb) sequestration/mobilization across aquatic ecosystems ranging in physico-chemistry (e.g. pH, organic carbon, Fe/trace metal concentrations) in the Boreal Forest Region of Ontario and under variable energy-regimes (i.e. calm, windy, prolonged-storm) in a shallow wave-dominated urban beach in Lake Ontario, Canada.

The results establish differential biogeochemical controls in suspended floc versus bed sediments influencing the abundance, reactivity and type of Fe minerals affecting trace metal abundance and solid-phase partitioning patterns between these two compartments. Specifically, this work demonstrates a microbial underpinning to floc collection of amorphous Fe oxyhydroxides (FeOOH) controlling floc metal sorption, retention and overall metal concentrations that are significantly greater in suspended floc than bed sediment. In contrast, crystalline Fe oxides (FeOx) dominate sediment metal retention, due to reductive dissolution and/or mineral aging of FeOOH, where sediment solid-solution metal partitioning is more influenced by system physico-chemistry (i.e pH). Further, rapid fluctuations in energy regime influencing re-suspension/settling of floc and sediment (i.e. surficial fine-grained lamina (SFGL) versus underlying consolidated sediments) result in temporal and spatial hydrodynamic-dependent mixing of Fe mineral phases, altering metal abundance and solid-phase metal partitioning in each compartment.

Collectively, findings of this innovative integrated thesis work provide new understanding of the physical and biogeochemical controls on Fe cycling/mineral transformations between floc and bed sediments, ultimately affecting trace metal behaviour between these compartments and fate in freshwater environments. This insight has important implications for policy development in improving risk management of aquatic systems under varying physico-chemical and hydrodynamic conditions.

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"It's not what the world holds for you, it's what you bring to it" - L.M. Montgomery

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To my family and friends, you are my foundation and inspiration.
~ I dedicate this thesis to you ~

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LIST OF ACRONYMS

%LOI	Percent Loss on Ignition
CFC	Continuous Flow Centrifugation
EPS	Extracellular Polymeric Substances
FeOOH	Amorphous Fe Oxyhydroxides
FeOx	Crystalline Fe Oxides
SFGL	Surficial Fine Grain Lamina
TEM	Transmission Electron Microscopy
XRD	X-ray Diffractometry

PREFACE

This thesis contains six chapters, consisting of three manuscripts for peer-review publication. Chapter 3 and 4 have been published as:

Plach, J.M and Warren, L.A. 2012. Differentiating natural organic matter roles in freshwater floc and bed sediment lead dynamics. *Chemical Geology*. 304-305, 97-105. (Chapter 3)

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The author of this thesis carried out all field-based and laboratory data collection, data analysis, microscopy imaging, literature review, writing and revisions presented in this thesis under the guidance of Dr. Lesley Warren in partial fulfillment of a Ph.D degree. Collaborations with other authors of the published papers consisted of combined efforts in field sampling and laboratory data collection with Amy Elliott in Chapter 4. Field sampling and data collection of the sediment transect presented in Chapter 5 was carried out by Sean Lin. Editorial comments for this thesis were provided by Dr. Ian Droppo (Chapter 4 and 5), Dr. Graeme Batley (Chapter 5), Amy Elliott (Chapter 4) and Dr. Lesley Warren.

CHAPTER 1: FLOC- TRACE METAL INTERACTIONS IN FRESHWATER ENVIRONMENTS

1.1 Introduction

Trace metal/metalloid contamination is highly prevalent globally in urban lake and river systems (Liu et al 2008; Gobeil et al 2005; Jain et al 2007) and a concern for pristine aquatic environments due to airborne transport/deposition of anthropogenic emissions (Blais et al., 1993). Water-quality assessment of freshwater ecosystems requires an understanding of the interacting physical, chemical and biological processes controlling contaminant behaviour of suspended floc, an important metal sequestering solid compartment in aquatic environments. Natural floc are highly mobile particulates for metal transport (Hodder 2009) and an important link between water column and bed sediment compartments (Figure 1.1). Trace metal behaviour of suspended floc has received a great deal of attention in the last several decades due to the ability of floc to sequester large quantities of metal contaminants relative to bottom bed sediments (Stecko and Bendell-Young, 2000; Sondi et al., 1994; Santiago et al., 1994; Hua et al., 2012). Although floc has been shown to be a significant metal sorbent, little is known about the specific biogeochemical mechanisms driving its metal dynamics relative to bed sediments. Bottom sediments are long-term sinks of metal contaminants. However, the upper few millimeters of surficial sediments (surficial fine-grained lamina; SFGL) in contact with the overlying water column are relatively reactive zones where floc settling, mineral formation, and microorganism decomposition processes occur. Frequent sediment disturbance events, such as wind-driven waves or boat traffic, have the potential to re-mobilize bed material into the water column. Therefore, surficial bed sediments are important for trace metal cycling in the short-term.

Because trace metal bioavailability, toxicity and fate depend on speciation (both in solution and solid phases), identifying the key biogeochemical and physiochemical mechanisms controlling metal sequestration by floc and hydrodynamic influences on floc/bed interactions (i.e. floc settling/sediment re-suspension) is imperative to assess metal distributions, cycling and ecological impacts in the environment. Characterizing these processes within urban aquatic systems, such as municipal public beaches, is particularly relevant given the potential for water quality degradation and contaminant exposure to both humans and aquatic organisms. The objective of this introductory chapter is to summarize peer-reviewed literature providing an overview of natural floc characteristics as well as relevant biogeochemical and hydrodynamic processes as they influence floc trace metal dynamics in the environment. In addition, this chapter outlines detailed thesis research objectives, specifically formulated to address current knowledge gaps in floc trace metal biogeochemistry.

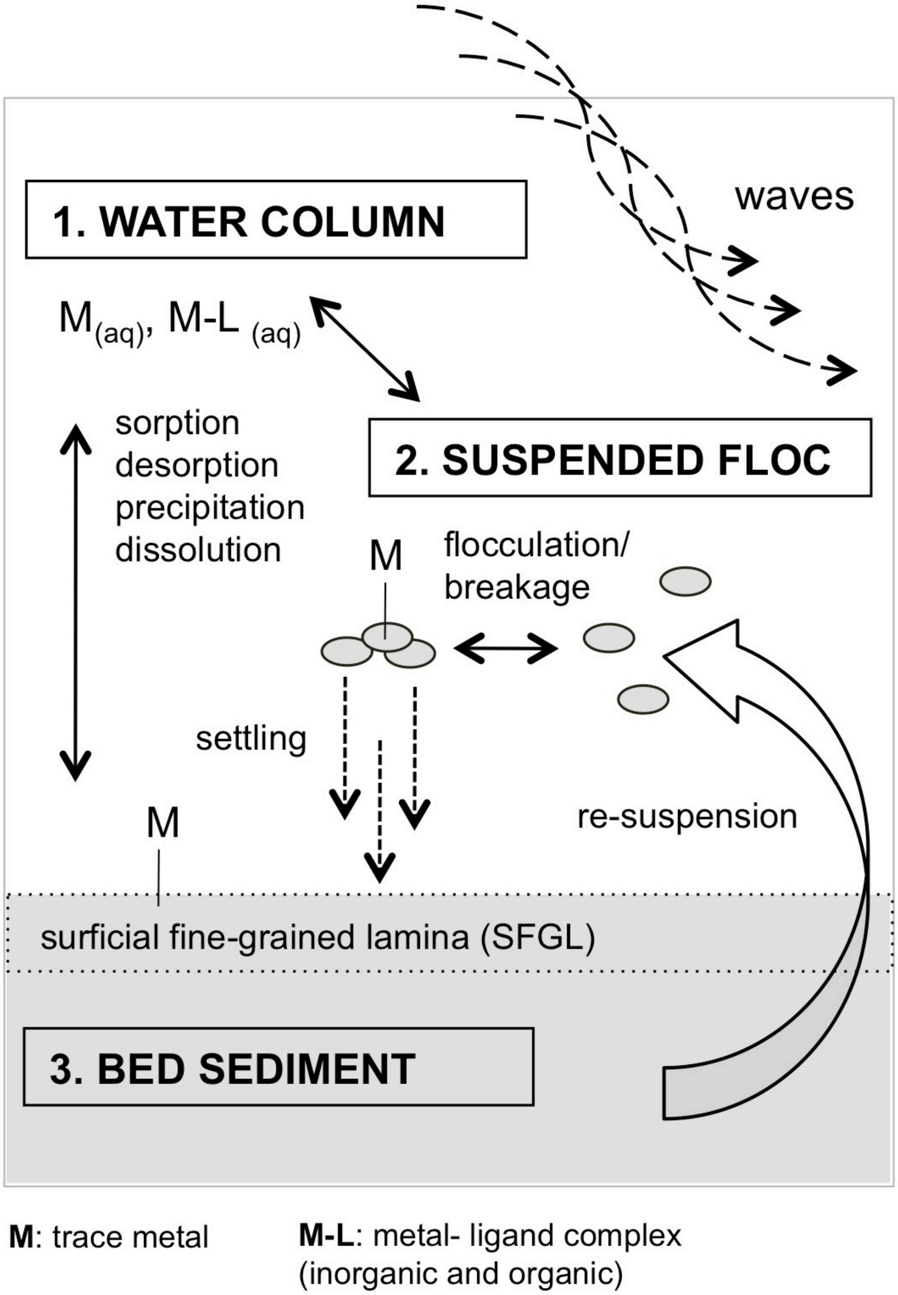


Figure 1.1 Aquatic compartments: 1) water column, 2) suspended floc and 3) bed sediments. Trace metal distribution between each compartment is influenced by dynamic and reversible reactions driven by interacting biogeochemical parameters (e.g. solid-phase inorganic/organic composition, water-column physico-chemistry) and hydrodynamic processes (e.g. floc settling/ sediment re-suspension).

1.1 Suspended Aquatic Floc

Suspended particulate matter is considered to exist as biologically flocculated particles (Azetsu-Scott and Johnson, 1992; Phillips and Walling, 1995; Droppo et al., 1997), referred to as 'floc', that are highly mobile in aquatic environments (Hodder 2009). There are four major components that characterize natural floc: (1) inorganic particles, (2) organic material, (3) water and (4) pores (Droppo, 2001). These constituents interact to influence floc physical behaviour through size/density differences affecting transport/settling (Milligan and Hill, 1998; Hodder 2009), chemical behaviour through the sorption of contaminants (Hua et al., 2012) and biological behaviour through providing surfaces for microorganisms to colonize (Costerton et al., 1987). The inorganic particles, including clays, carbonates and oxide/oxyhydroxide minerals, are held together by an extensive network of microbially produced exopolymeric substances (EPS) (Figure 1.2), which are hydrophobic organic polymers of proteins, carbohydrates, uronic acids, and DNA (Bura et al., 1998). These fibrils are small in diameter (4-6 nm; Liss et al, 1996) and have large surface-areas allowing for the sorption of nutrients, contaminants and the retention of water (Leppard et al., 2003). The architecture of suspended floc aggregates is complex and biologically regulated, similar to that of surface-adhered biofilms (Neu and Lawrence, 1997).

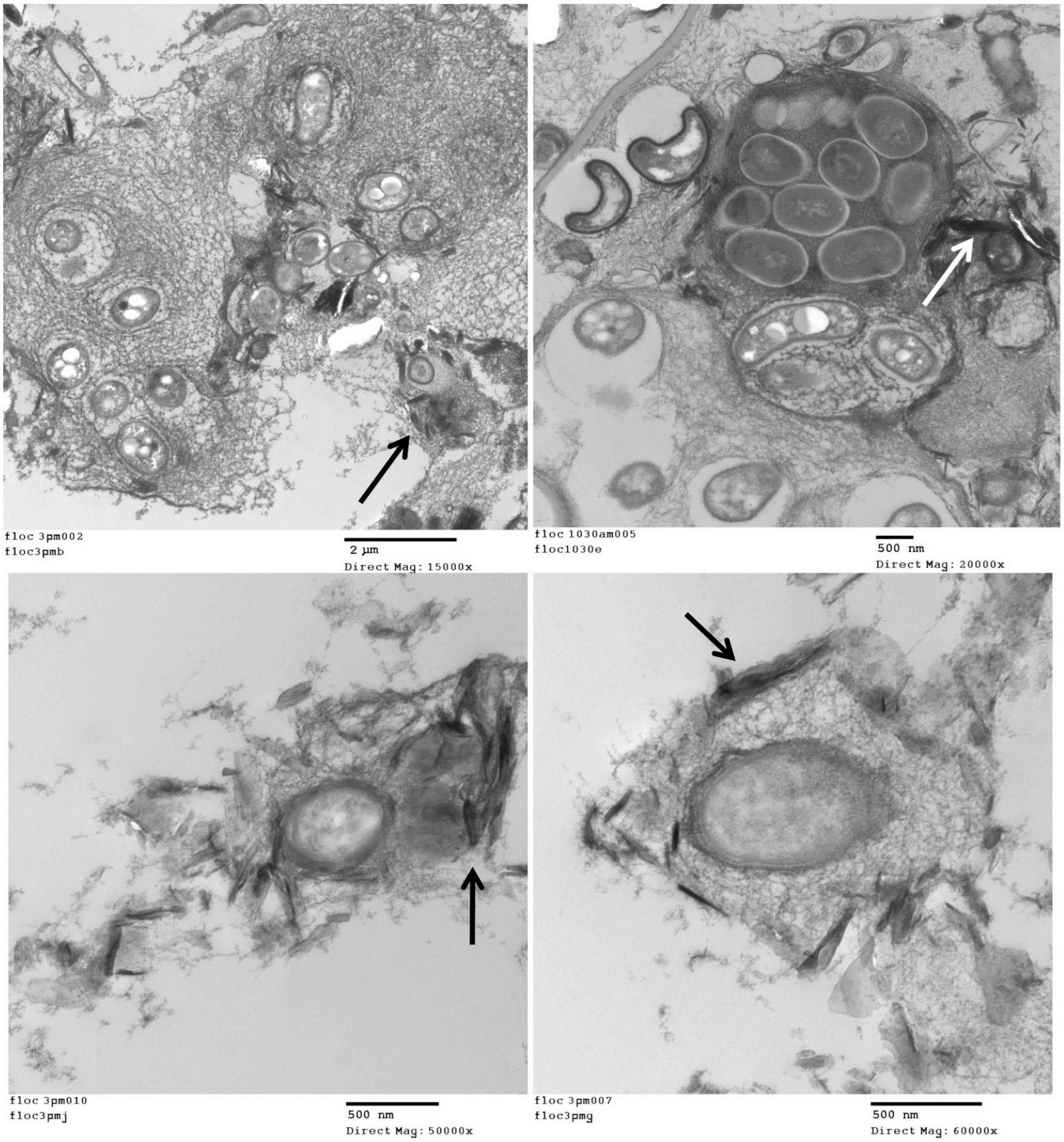


Figure 1.2 Transmission electron microscopy (TEM) images of suspended floc. The architecture is complex and biologically regulated by microbial cells and associated produced EPS network that trap inorganic minerals (arrows). Floc shown here was collected from Lake Ontario (field sampling campaign in Chapter 5). Top right image is included in Elliott et al, 2013 [submitted Chemical Geology 16/06/13].

Flocculation alters the overall size of the individual particles thereby altering the overall shape, density, and surface area of floc aggregates. Surface area exerts a major control on particle surface chemistry (Hochella and Madden, 2005) and is known to influence floc sorptive capacity for metals (e.g. Laurent et al., 2009). Small-sized particles have larger surface area to volume ratios, hence greater surface reactivity (Wigginton et al., 2007). However, there is a lack of clear trends within in the literature relating natural floc particle size to overall metals loads (e.g. Warren and Zimmerman, 1994a). For example, trace metal sorption experiments carried out by Lead et al., (1999) on natural floc particulates showed a lack of correlation between metal binding surface area and particle size. This suggests that particle composition (i.e. concentration of reactive sorbent-phases) may be more important in determining floc metal binding than overall particulate size. Evidence in the literature clearly indicates the importance of substrate geochemical controls, particularly the key role of Fe/Mn oxide/oxyhydroxide sorbent-phases, for floc metal retention (Gagnon et al., 2009; Stecko and Bendell-Young, 2000; Tessier et al., 1996; Warren and Zimmerman, 1994b). Oxides/oxyhydroxides are known to be highly effective metal scavengers on their own (Section 1.3). However, their coexistence with natural organic matter in the environment (Section 1.4) leads to complex interactions with trace metals that few have investigated within natural floc (Hua et al., 2012; Muller and Sigg, 1990). Further, there remains a discrepancy as to their combined influence on floc trace metal dynamics observed in the environment. This may be due to a largely biological control on floc morphology influencing its geochemical behaviour not considered to date. Further, changes in energy regime (e.g. wind driven waves) can mobilize bed sediments, potentially altering the physical, chemical and biological properties of floc particulates in suspension and associated trace metal behaviour (Section 1.5).

1.3 Geochemical Reactivity of Oxide/Oxyhydroxides

1.3.1 Trace Metal Solid-Solution Partitioning

Partitioning of metal contaminants from solution to solid phases plays a key role in determining metal behaviour in the environment given that not all metal forms are equally reactive, mobile or toxic. In fact, total metal concentration is not a good indicator of metal behavior. The dissolved free hydrated metal ion is the most toxic and bioavailable form of a metal (Luoma, 1983; Hare, 1992). This is in direct contrast to organic contaminants where the more broken down the molecule, the less toxic it becomes (Bacci, 1993). Therefore, removing dissolved metals from solution can reduce metal toxicity. Partitioning of metals from solution to solid phases will depend on interacting parameters of the metal properties (e.g. positively charged cations versus negatively charged anions), the solution chemistry (e.g. pH, ionic strength (Puls, et al., 1991), chelating molecules (Section 1.4), temperature (Scheckel and Sparks, 2001) and the availability of reactive substrates such as organic matter (Section 1.4) and Fe/Mn oxides/oxyhydroxides.

Metal partitioning with Fe/Mn oxides/oxyhydroxide solid phases is of particular importance due to the highly reactive nature of these mineral surfaces and their ubiquitous presence in the environment, including floc and bed sediment compartments (Dong et al., 2007; Jambor and Dutrizaz, 1998; Perret et al., 2000; Hua et al., 2012). Oxides/oxyhydroxides typically exist as nanoparticulates that have large surface areas relative to their volume resulting in their considerable metal scavenging ability (Waychunas et al., 2005). Aqueous metal to oxyhydroxide partitioning reactions include ion exchange, specific adsorption and precipitation into solid mineral phases (Warren and Haack, 2001). Direct trace metal-oxide precipitation is not common in the water-column due to generally under-saturated conditions for these minerals. More commonly, trace metals are removed from solution by sorption reactions between charged solution metal ions and charged solid oxide/oxyhydroxide surfaces.

1.3.2 pH Control on Sorption

Metal sorption to oxide/oxyhydroxide minerals is both pH and element dependent. Net surface charge on any solid results from protonation or deprotonation of surface functional groups at a given solution pH. Reported pH_{zpc} values for the Fe oxyhydroxide ferrihydrite are typically in the vicinity of ~7.5 (Hendershot et al 1983), consistent with the pH range of the circumneutral conditions of the field sites in this thesis (Chapter 3-5). In contrast, reported Mn oxyhydroxide pH_{zpc} values are lower, in the vicinity of 2.3 (Catts and Langmuir 1986), which predicts higher scavenging ability of Mn oxyhydroxides for metal cations within lower pH aquatic systems (Haack and Warren, 2003). As such, any fluctuations in pH would likely change the net surface charge on Fe oxide/oxyhydroxides, hence alter the mineral metal scavenging efficiency. This is directly relevant to floc trace metal geochemistry whereby changes in water column pH, such as cycles of photosynthetic activity in littoral waters (Fuller and Davis, 1989), has the potential to influence metal scavenging efficiency of floc-associated Fe oxide/oxyhydroxides and influence overall floc trace metal partitioning. In fact, controlled laboratory sorption studies demonstrated a pH control on river and estuarine floc metal uptake (Lead et al., 1999; Lion et al., 1982; Grassi et al., 1997), supporting pH changes in the water column may influence floc metal sequestration in the environment.

1.3.3. Mineral Crystallinity

Metal sorption to Fe oxide/oxyhydroxides can be further influenced by the degree of mineral crystallinity (Brown et al., 1999). Amorphous Fe oxyhydroxides e.g. ferrihydrite are characteristically more reactive than crystalline Fe(III) forms (e.g. goethite) due to their poorly ordered crystal structure and greater density of exposed surface sites (Jambor and Dutrizaz, 1998). Under well-oxygenated circumneutral pH conditions, amorphous Fe oxyhydroxides are unstable and tend to age into more crystalline forms (Cudennec and Lecerf 2006; Das et al., 2011) while anaerobic conditions lead to reductive dissolution (e.g. microbial mediated iron reduction) and the re-crystallization of amorphous iron (Hansel et al., 2003). These mineral transformations control metal distribution between amorphous and crystalline mineral forms (Cooper et al., 2006; Ford et al., 1997) as well as the partitioning of sorbed metals between solid and solution phases due to the changing mineral surface properties. While the importance of oxide/oxyhydroxides for metal sequestration in floc has been demonstrated (Tessier et al., 1996; Warren and Zimmerman, 1994b; Stecko and Bendell-Young, 2000; Gagnon et al., 2009), few studies have investigated amorphous versus crystalline oxide/oxyhydroxides controls on metal retention comparing floc and bed sedimentary compartments, particularly in freshwater environments (e.g. Linge and Oldham, 2002). Metals bound to an easily reducible amorphous rather than crystalline phase may show more dynamic behaviour reflecting changing redox conditions. For example, under anaerobic conditions the rate of microbial Fe(III) reduction is influenced by mineral surface area and crystallinity (Roden and Zachara, 1996, Lovley and Phillips, 1986) hence, less crystalline oxyhydroxide minerals (e.g. Ferrihydrite) are generally more susceptible to microbial reduction (Thamdrup, 2000). As such, if suspended floc was removed from an oxygenated water column and subjected to anaerobic conditions (e.g floc settling and burial within bottom bed sediments) any floc-associated amorphous oxyhydroxides may be reductively dissolved, releasing bound metals back into the overlying water column, increasing toxicity in the environment and/or sequestered by other reactive sorbent phases such as natural organic matter in sediments.

1.4 Geochemical Reactivity of Natural Organic Matter

1.4.1. Dissolved Organic Carbon

Similar to oxide/oxyhydroxide minerals, natural organic matter (NOM) is ubiquitous in freshwater environments and a geochemically reactive substrate for binding trace metals. NOM consists of both living (e.g. microorganisms, EPS) and non-living (e.g. detritus, humic and fulvic acids) material. Much aquatic NOM research has focused on dissolved organic carbon (DOC), refractory organic compounds i.e. humic acids (HA) and fulvic acids (FA) that are highly effective at binding metal ions forming stable organic-metal complexes in solution (Davis, 1984. Gondar et al., 2006; Pandey et al., 2000). Dissolved organo-metal complexes are significant transporters of aqueous metals in the environment (Landre et al., 2009; Dawson et al., 2010). Understanding the mechanisms controlling solid-solution partitioning of organic-metal complexes with floc and sediment compartments is directly relevant for assessing trace metal cycling in NOM rich aquatic environments (e.g. wetlands, rivers and lakes of the Boreal Forest Region). In terrestrial systems, sorption studies demonstrate a strong pH control on organo-metal complex solid-solution partitioning with organic soils (Wang and Benoit, 1996; Jordan et al., 1997; Sauve et al., 1998) opposite to that expected for metal cation partitioning. This is largely attributed to an overall negative charge of soil DOC molecules masking positively charged metal cations in the organic complex. If a similar pH control exists on aquatic organic-metal complex solid-solution partitioning, then trace metal sequestration by floc/surfical sediments may occur very differently in NOM rich ecosystems (e.g. Boreal Forest Region) compared to NOM poor environments (e.g. Great Lakes).

1.4.2. Bacteria Surface Reactivity

Bacteria are prevalent in aquatic systems and display analogous metal interactions at their cell surfaces as inorganic minerals (Warren and Ferris, 1998). Bacteria surface charge is determined by the presence of a variety of functional groups on their cell walls and in their extracellular polymeric substance (EPS) matrix (Parmar et al*.,* 2000) including carboxyl, phosphoryl and amine groups with pKa values within the ranges 4.5 - 6, 6.5 -7.8 and 9.9 -10.2, respectively (Plette et al., 1995; Cox et al., 1999; Fein et al., 1997; Daughney et al., 1998) and as such bacterial cells (whether viable, non-viable or even lyzed) can be highly reactive across a range of pH conditions. Reactions that occur at biological surfaces play an important role in the distribution of iron oxyhydroxides and trace metal in aquatic environments, as cell surfaces and associated EPS act as effective nucleation sites for the precipitation of oxyhydroxide minerals (Ferris et al., 1999; Chan et al., 2004). Iron oxyhydroxide precipitation may be enhanced in the presence of bacteria (Warren and Ferris, 1998) and in turn the cell associated iron oxyhydroxide coatings create new reactive surfaces available for metal sorption. However, mineral coatings may simultaneously mask underlying reactive surfaces on bacterial cell walls (Small et al., 1999). While the sorptive capacity of isolated bacterial cells and iron oxyhydroxide surfaces are well characterized, the combined reactivity of heterogeneous bacterial-oxides is still not well understood, despite the prevalent occurrence of organic-iron minerals composites in the environment (Dong et al., 2000; Ferris, 2005; Fru et al., 2012). Moreover, few studies have specifically investigated the combined role these bacteriogenic-iron oxides play in suspended floc metal sorption dynamics (Hua et al., 2012; Muller and Sigg, 1990).

1.4.3. Microbial Metabolisms

Microorganisms impact all element cycles important for metal behaviour through utilization of environmental redox pairs to drive their diverse metabolisms. Particularly relevant for surficial sediments, where the accumulation of settled floc occurs, are microorganisms that catalyze metal dependant redox reactions like the reduction of Fe(III) oxide/oxyhydroxides and re-oxidation of Fe^{2+}. In undisturbed bed sediment compartments with an oxic or suboxic surficial layer, the cycling of Fe can concentrate metal contaminants at the sediment-water interface and limit metal release into the water column (Burdige, 1993). In addition, any microbial driven metabolic process that induces change to the surrounding microenvironment, such as pH changes during oxidation/reduction reactions or photosynthetic activity, will affect protonation and deprotonation of metal reactive functional groups, hence influence mineral and organic matter surface metal binding. Furthermore, microbes will directly uptake and assimilate a variety of essential trace metal elements (e.g. Mn, Fe, Co, Ni, and Cu) that are required for their natural function and growth (Warren and Haack, 2001). As such aquatic microorganisms are highly dynamic NOM constituents that have a significant influence on mineral and ultimately trace metal behavior in the environment.

1.5 Disturbance Events

Published literature on suspended floc and sediment trace metal geochemistry has focused primarily on undisturbed compartments. However, sediment disturbance events are frequent in aquatic environments occurring naturally by wind-driven waves, storms and currents as well as by anthropogenic activities such as dredging, ship traffic and recreational activities. Sediment re-suspension is an important mechanism which, depending on the intensity and duration of the disturbance event(s), can introduce substantive concentrations of very different sedimentary substrates and contaminants into the water-column and suspended floc compartment. For example, bed sediments typically contain an easily erodible surficial fine-grained lamina (SFGL; Droppo and Amos, 2001) at the sediment water interface characterized by recently settled floc. In contrast, underlying bulk sediments are less easily erodible, and contain different sized particulates with differing geochemical composition and affinity for trace metals (Bothner et al., 1998). As such, the impact of mobilized bed material on suspended floc trace metal behaviour highly depends on the hydrodynamic conditions.

This scenario was demonstrated in a laboratory re-suspension experiment whereby total metal concentrations of suspended particulates decreased with increasing mobilization of bottom sediments (Kalnejais et al., 2007). Under low shear stress conditions, suspended particulate metal concentrations were high which was attributed to the remobilization of a metal enriched surfical layer, likely analogous to the SFGL as described by Droppo and Amos (2001). In contrast, increasing shear stress resulted in a decrease in total suspended metal loads, which was attributed to the remobilization of bulk sediment of lower metal content. This study demonstrated that floc total metal concentrations can be highly variable due to the energy dependent depth of bed erosion and sediment mobilization. Further, water column chemical conditions (e.g. pH, O_2) play an important role in influencing the trace metal sorptive behaviour of mobilized particulates during disturbance events. For example, Atkinson et al., (2007) showed rapid Fe(II) oxidation and oxide/oxyhydroxide precipitation when anaerobic pore waters from marine sediments were exposed to a circumneutral oxygenated water column during disturbance events, creating new reactive mineral surfaces that increased trace metal uptake from the water column. Although laboratory studies such as these provide valuable insight into the nature of sediments mobilized and physico-chemical controls on suspended particulate metal sorption under laboratory settings, few field-based studies have attempted to characterize the impact of sediment re-suspension on suspended particulate metal loads under variable energy conditions in the environment (i.e. quiescent conditions versus disturbance events) (e.g. Birch and O'Hea 2007; Millward et al., 1998). Further, a particular lack of in situ geochemical assessments comparing floc and sediment trace metal partitioning and key metal scavenging phases (e.g. oxide/oxyhydroxide, organic matter) under differing energy regimes precludes determination of the relative effect of hydrodynamic driven sediment- floc interactions on temporal floc geochemistry in the environment.

The majority of sediment contaminant re-suspension studies have focused on marine (Birch and O'Hea 2007; Cantwell et al., 2002; Millward et al., 1998) and river sediments (Theis et al., 1988; Hwang et al., 2011; Garcia-Aragon et al., 2001). Little is known about sediment disturbance events influencing trace metal dynamics in freshwater urban beaches where rapidly fluctuating wave-driven energy regimes also have the potential to mobilize contaminants significantly degrading water-quality posing increased risk to both aquatic organisms and human health. For example, current water quality assessments by cities typically involve sampling beach surface waters during the early morning hours when water-column conditions are typically very calm. As such, this sampling strategy does not capture the potential impact of turbulence on the exchange of contaminant-laden suspended floc and bed sediments on beach water quality during higher energy conditions, generated by wind-driven waves or recreational activities that typically occur later in the day. This is particularly relevant as most recreational swimmers including young children, are likely to be directly exposed to contaminants (through skin contact or ingestion of sediments) during these more turbulent conditions. The intensity of disturbance events vary temporally but also spatially in beach environment (e.g. shallow water nearshore versus deep waters offshore; Carper and Bachmann, 1984) thus, sediment erosion/re-suspension impacts on contaminant mobility will likely differ depending on location of sampling. In addition, changing water-column chemical conditions throughout the day (e.g. pH, O_2) may influence metal scavenging efficiency of floc substrates (e.g. Fe/Mn oxide/oxyhydroxides), thereby further altering metal floc metal sorption dynamics. Therefore, predicting contaminant mobility and fate in municipal public beaches requires characterizing metal partitioning of key metal scavenging phases of floc and sediment under varying water column chemical and energy regimes at different spatial locations and timescales.

1.6 Research Objectives

This integrated study is designed to investigate microscale biogeochemical processes underpinning floc trace metal sequestration/mobilization as well as a broader macroscale assessment of system physico-chemical and energy regime on overall floc metal dynamics. The aim is to examine potential Fe cycling/mineral transformations between floc and bed sediments and identify the biogeochemical controls affecting abundance, reactivity and type of Fe minerals influencing trace metal behaviour in these two compartments. Further, this work evaluates the importance of physical parameters affecting re-suspension/settling of floc and sediment (i.e. SFGL versus underlying consolidated sediment) overlaying Fe dynamics and ultimately, trace metal dynamics in each compartment. The outcome of this work has important implications for predicting trace metal distributions, mobility and fate in the environment that will direct future research into the ecological risks associated with floc contaminant behaviour in freshwater ecosystems (Chapter 6). The overall objectives of this study were to:

1. Establish the role of living (i.e. microbial cells; EPS) versus refractory natural organic matter (e.g. DOM) on suspended-floc and surficial bed sediment trace metal (i.e. Pb) sequestration behaviour, linking changes in water-column physico-chemistry (e.g. pH) to NOM and Pb solid-solution partitioning from these two sedimentary compartments

Chapter 3 examines Pb partitioning behaviour of suspended floc versus bed sediments and implications for NOM impacting Pb mobility in various freshwater ecosystems types in the Boreal Forest and the Great Lakes Regions of Ontario. The specific objectives of this combined field-based and laboratory study were to: (1) investigate Pb and NOM distributions among suspended floc, surficial bed sediment and water-column compartments, (2) identify the important solid phases for Pb sequestration in floc and surfical bed sediments, and (3) determine the role of pH impacting DOC and Pb solid-solution partitioning from natural limnetic floc, compared to surficial sediments in lake, stream and wetlands.

2. Comparatively assess in situ metal sequestration of suspended floc versus bed sediments by establishing the important solid-phases for metal retention (i.e. role of amorphous versus crystalline Fe oxides in each compartment) and the potential for interactions of floc and sediment reactive substrates impacting metal behavior within each sedimentary compartment under varying energy-regimes.

Chapter 4 presents the field results investigating trace metal dynamics of suspended floc and bed sediments at Sunnyside Beach, Toronto, an urban public beach in Lake Ontario, and discuss implications for water-quality assessments of freshwater beaches. The specific objectives of this field based study were to determine: (1) metals Ag, Cu, Co, Ni, Pb, and metalloid As concentrations within suspended floc, bed sediment, and water-column aqueous compartments and (2) the important reactive solid-phases for metal sequestration in floc and bed sediment compartments under i) quiescent ii) storm and iii) post-storm conditions.

3. Investigate temporal floc trace metal dynamics by assessing metal partitioning in suspended floc compared to settled-floc (SFGL) and bed sedimentary compartments under diel-linked changes in hydrodynamic conditions (i.e. wind driven waves) and physcio-chemistry both in nearshore and offshore locations.

Chapter 5 presents the field-based results assessing in situ Fe mineral and trace metal dynamics of floc and surficial bed sediments in Sunnyside Beach, Lake Ontario and implications for dynamic contaminant cycling at short timescale in shallow littoral zones of lakes. The specific objectives of this field-based study were to investigate: (1) Fe oxide/oxyhydroxide distributions between suspended floc, SFGL and bed sediment compartments, (2) reactive solid phases for metal sequestration, and (3) potential spatial and temporal variation in physico-chemical conditions affecting Fe oxide/oxyhydroxide abundance and metal behaviour of floc and surficial sediments along a spatial transect from nearshore to offshore.

CHAPTER 2: STUDY SITES, SAMPLING PROTOCOLS AND LABORATORY METHODS

2.1 Introduction

This study evaluates freshwater floc trace metal dynamics by utilizing a variety of aqueous and solid phase geochemical analysis and imaging techniques through an integrated field-based and laboratory experimental approach. Although specific methods sections are included in each data chapter (Chapter 3, 4 and 5), the purpose of this chapter is to provide a more detailed rationale and description of the standard field and laboratory methodologies used and the environmental field sites characterized in this thesis. Identifying the important biogeochemical controls on floc trace metal behaviour required strategic sampling/analysis of the three interacting aquatic compartments (1) water column; (2) suspended floc and (3) bed sediments (i.e. bulk consolidated sediments and surfical fine grained lamina; SFGL) under various hydrodynamic and system chemical conditions. Solid-phase sampling techniques and analysis were specifically targeted to evaluate floc/sediment geochemical composition (e.g. amorphous versus crystalline oxide/oxyhydroxide, organic matter) and trace metal concentrations in key reactive substrate phases. Aqueous phase sampling was designed to capture potential changes in water column chemistry (e.g. pH, [DOC]) expected to influence floc trace metal sequestration. Sampling campaigns spanned a four-year period (2008- 2011) and were carried out across a wide range of freshwater ecosystem types (e.g. wetland, stream and lakes) ranging in physcio-chemistry and hydrodynamic energy regimes (i.e. quiescent, turbulent). Field site descriptions are presented in Section 2.2. Details on specific field sampling techniques and laboratory analysis are provided in Section 2.3.

2.2 Field Study Sites

Field sites were specifically selected along surface water flow paths i) to capture natural variations in water-column physico-chemistry in a watershed (i.e. upstream acidic NOM/Fe rich wetlands to downstream circumneutral NOM/Fe poor lakes) as well as ii) detailed sampling in a littoral beach to capture fluctuations in energy regime at different temporal scales and spatial locations (e.g. shallow high-energy nearshore versus deep low-energy offshore) (Figure 2.1). Chapter 3 of this thesis explores floc and bed sediment Pb dynamics across the full range of physico-chemical system sites that included a range of pristine aquatic ecosystems (e.g. wetlands, streams and lakes) in Algonquin Provincial Park (Section 2.2.1). Chapter 4 and 5 investigate floc/sediment interactions (i.e. settling and re-suspension) influencing floc trace metal (Ag, As, Cu, Co, Ni and Pb) behaviour under variable hydrodynamic and water column chemical conditions in a shallow littoral wave-dominated beach in Lake Ontario (Section 2.2.2).

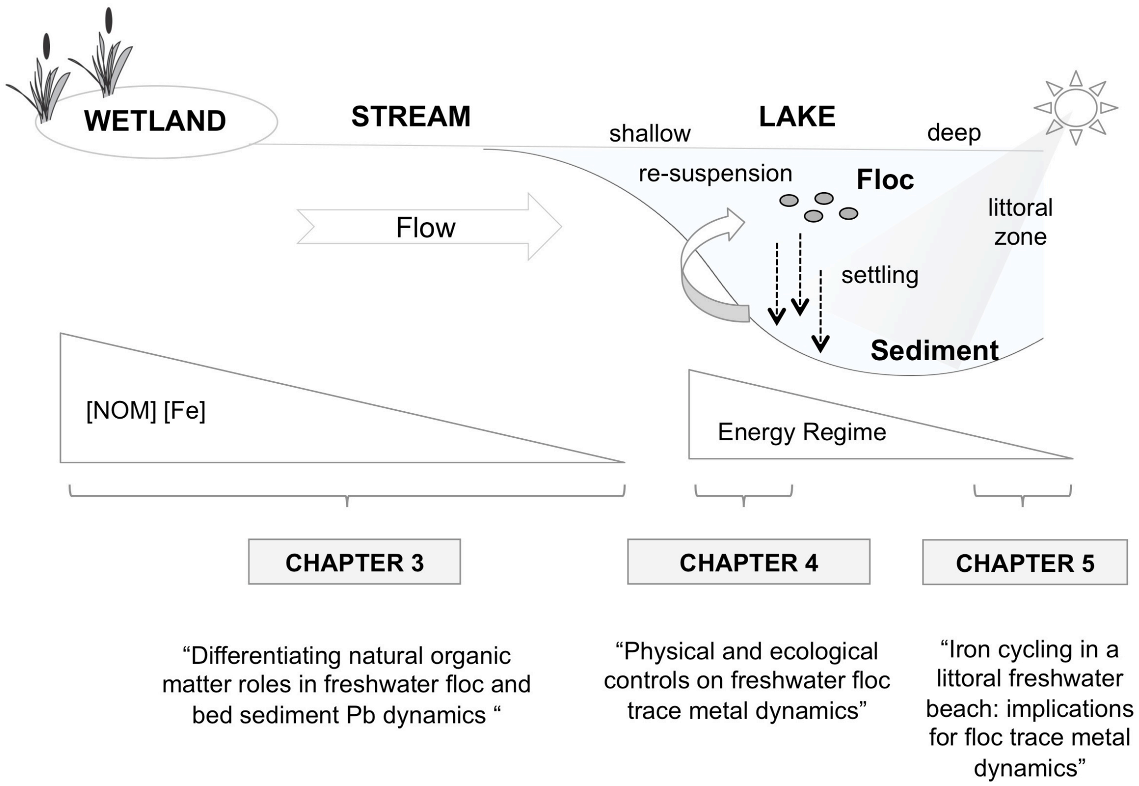


Figure 2.1 Conceptual framework linking study sites. Comparative assessment of suspended floc versus bed sediment trace metal sequestration across a gradient of NOM/Fe rich ecosystems (Chapter 3) as well as under various temporal and spatial energy regimes (i.e. quiescent, windy, prolonged storm) in an urban littoral beach (Chapter 4 and 5).

2.2.1 Pristine Aquatic Ecosystems

2.2.1.1 Algonquin Park- Wetlands, Streams and Lakes

Seven study sites ranging in ecosystem type (i.e. wetland, stream and lake) were selected in the Boreal Forest Region of Ontario in Algonquin Provincial Park (Figure 2.2A). The field sites consisted of Brewer Lake, Brewer Wetland, Costello Creek, Costello Lake, Coldspring Lake, Coldspring Wetland, Cache Lake Wetland. The location coordinates and physico-chemical conditions of these sites are provided in Chapter 3 in Table 3.1. These sites were chosen in Algonquin Park to represent relatively pristine aquatic ecosystems compared to systems located in Southern Ontario Great Lakes region that are more directly impacted by anthropogenic activities (Section 2.2.2). For example, Coldspring Lake and Wetland sampling sites were located in a protected Nature Reserve in Algonquin Park and therefore accessible only by floatplane (Figure 2.2B). Sites were selected, where possible, to include ecosystems with connecting surface water flow paths (e.g. Coldspring Wetland and Lake Figure 2.2B) to capture natural variations in water column chemistry (e.g. NOM, Fe, pH). Sites in Algonquin Park were sampled for suspended floc (where possible), bulk bed sediments and water over multiple years (when possible) during sampling campaigns in 2008- 2010, between May and August. Results of floc, sediment and aqueous Pb dynamics within these relatively pristine aquatic environments are presented in Chapter 3.

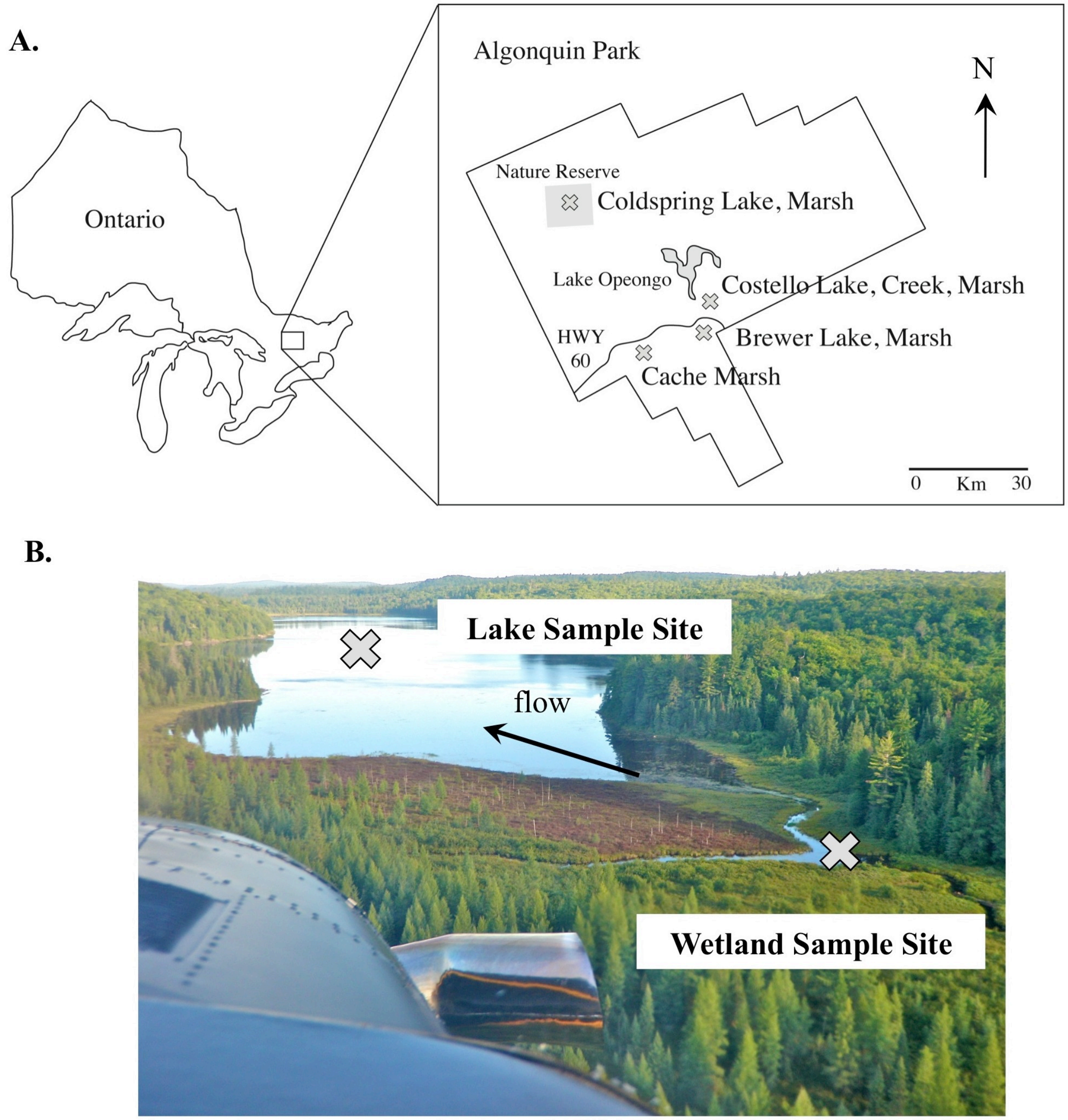


Figure 2.2 Pristine aquatic ecosystems. Map (A.) indicates location of sampling sites within the boundary of Algonquin Provincial Park. Photograph (B.) showing two sampling sites that are connected by surface water flow, Coldspring Wetland and Coldspring Lake (high to low [NOM] and [Fe], respectively).

2.2.2. Anthropogenic Impacted Aquatic Ecosystems

2.2.2.1 Guelph- Agricultural Stream

Agriculture is a major land-use of watersheds draining into the Great Lakes (Baker, 1993). The application of fertilizers, pesticides and sewage sludge are major source of metal contamination (e.g. As, Cu, Ni, Pb) in agricultural regions (Belon et al., 2012). In this study, a rural stream near Guelph, Ontario (43°39'24"N 80°24'06"W) was sampled for bulk suspended floc, bulk bed sediments and water Pb dynamics on July 29, 2008. In contrast to the relatively pristine sites of Algonquin Park, this site was selected to represent an ecosystem with high NOM and Fe concentrations and vulnerability to metal contaminates through runoff from agriculture activities.

2.2.2.2 Lake Ontario- Urban Beach

Sunnyside Beach is an erosive, manufactured sandy beach located on the north shore of Lake Ontario (43°3802100N 079°270210W). This site was selected to identify the important metal sorbent-phases in floc and sediments within a NOM and Fe poor system that is directly impacted by anthropogenic contaminants. This public beach is 1.7 km long in the urbanized West end of the City of Toronto (Figure 2.3A). Sunnyside beach is impacted by road sediment runoff, combined sewer overflow (CSO) and wastewater (WW) treatment effluent discharge, all known sources of metal contaminates including Ag, As, Cu, Co, Ni and Pb (Toronto Water, Annual Report 2008; Elliott et al., 2012; Irvine et al., 2009). Situated at the west end of the beach is the outflow of the Humber River (Figure 2.3A), a major river system that drains a watershed of 903 square kilometers into Lake Ontario, consisting of 27% urbanized, 40% rural land use (e.g. agricultural) and 33% natural landscapes (e.g. wetland) (TRCA, 2008).

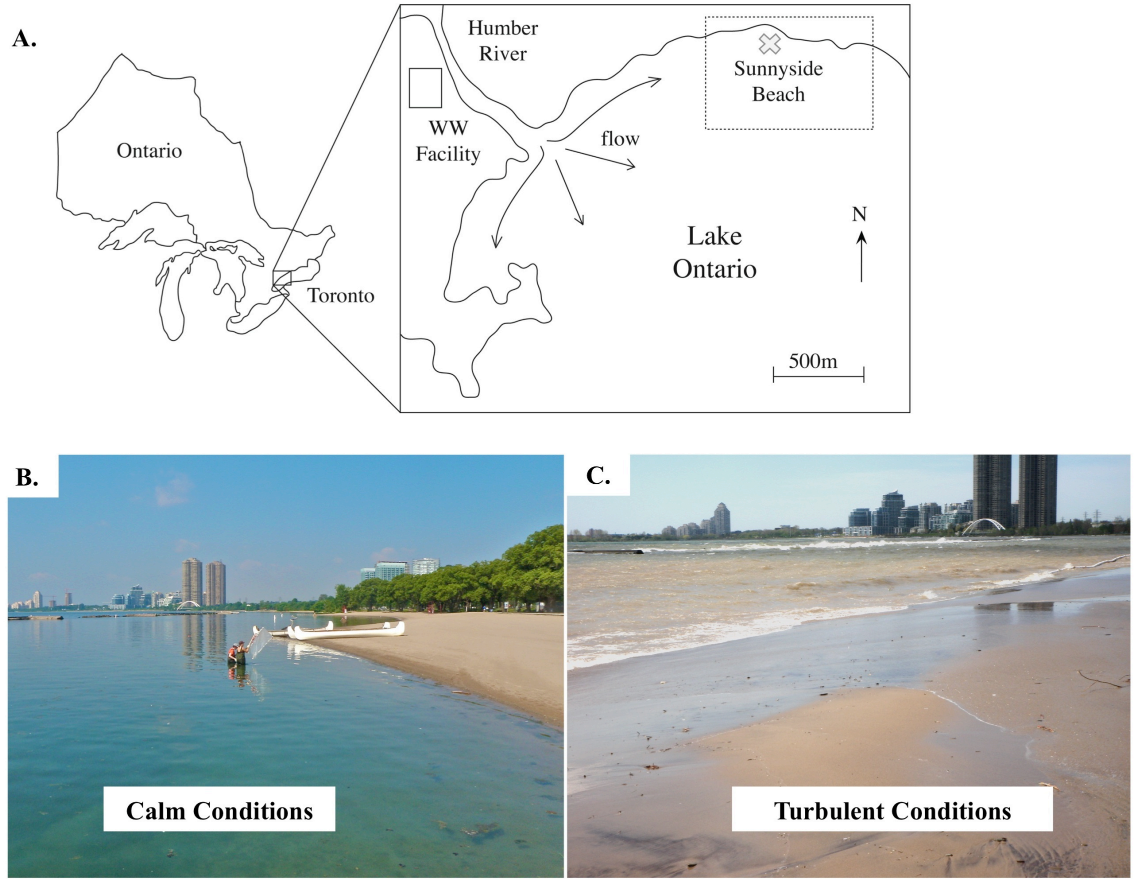


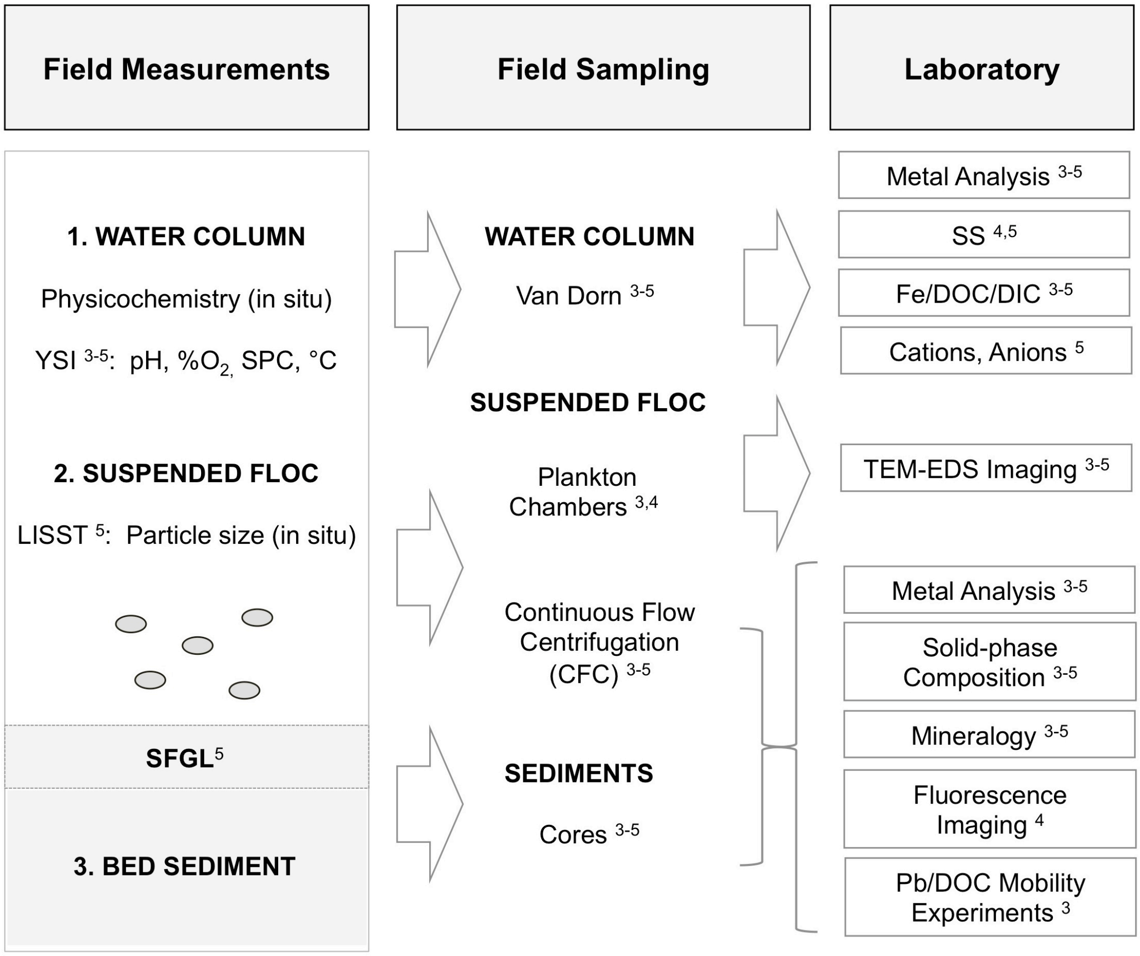
Figure 2.3 Sunnyside Beach, Lake Ontario. Map (A) indicates study site location in relation to outflow from the Humber River and Humber Wastewater (WW) treatment facility. Photographs showing nearshore sampling site under calm (B) and (C) turbulent energy conditions.

To characterize the influence of water turbulence on the interaction of floc/sediments, discrete integrated “snapshots” of in situ chemistry were analyzed at Sunnyside Beach during periods of varying degrees of turbulence (i.e. calm, windy, prolonged storm). Sampling campaigns were designed to investigate temporal trends of floc and bulk bed sediment trace metal concentrations and key metal scavenging phases. Bulk floc, bed sediment, water samples were collected during calm (May 13, 2009, July 21, 2009; Figure 2.3B), storm (May 14, 2009; Figure 2.3C) and post-storm conditions (May 13, 2008) to capture any associated changes in floc metal partitioning associated with high energy storm wave disturbances nearshore (Chapter 4).

To further investigate potential spatial and short term temporal trends of floc geochemistry linked to hydrodynamic mixing with SFGL and bulk sediments, two in depth daily sampling campaigns were carried out at two separate locations: nearshore (shallow) on July 21, 2010 and offshore (deep) on August 15, 2011 (Chapter 5). Bulk floc was collected during three sampling periods during daylight hours at both onshore/offshore sites, capturing daily fluctuations in wind-driven water turbulence and water column chemistry. To evaluate changes in floc physical characteristics associated with turbulence, floc particle size was evaluated in situ during each of the three collection periods at the nearshore shallow site. Bottom sediments (i.e. SFGL and bulk sediments) were collected several times through the day nearshore and along a transect from shallow to offshore sites to evaluate temporal and spatial impacts of bed disturbance on SFGL composition and associated trace metal partitioning. Water samples were collected several times through the day to monitor changes in water column chemical conditions (e.g. pH, O_2) that may influence floc metal sorption behaviour. Surface water was also collected from the mouth of the Humber River to evaluate potential river metal inputs into Sunnyside Beach.

2.3 Field Sample Collection and Analysis

Measurements, sample collection and analysis of the water column, suspended floc and bed sediment compartments followed established field and laboratory protocols. Water column geochemical characterization consisted of in situ physico-chemical profiling (temperature, pH, dissolved oxygen and specific conductivity (Datasonde-Surveyor 4A, Hydrolab Corporation, TX) and sample collection involving: (1) collection of water samples by Vandorn for dissolved-phase trace metal/Fe analysis, cations and anions, dissolved organics (DOC) and dissolved inorganics (DIC) suspended sediment concentrations, (2) diver retrieved plankton chambers (Droppo et al, 1996) collected for suspended floc imaging, (3) bulk suspended sediment (continuous field flow centrifugation (CFC), and (4) collection of bed sediment (diver retrieved or hand cored) for solid-phase metal analysis, mineralogy, solid-phase composition (e.g. Fe/Mn oxide/oxyhydroxides, organic matter), imaging and sorption experiments (Figure 2.4).



^{3,4,5} indicate chapter of field sampling and laboratory analysis

Figure 2.4 Method schematic summarizing field sampling procedures and laboratory analysis for the three aquatic compartments: i) water column, ii) suspended floc and iii) bed sediments.

2.3.1 Water Sample Collection/Analysis

All sampling containers for chemical analysis of water samples (i.e. trace metal, iron, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), suspended sediments (SS), major cations and anions) were extensively cleaned in the laboratory prior to use. Sampling containers were scrubbed using Extran 300 and rinsed with eight rinses of MiliQ ultra pure water (18.2 Ωm cm^{-1}, Mili-Q, Millipore). Subsequent sample container preparations were prepared according to Table 2.1. All containers were rinsed three times with sample water prior to being filled (to the brim) and sealed. Samples were collected in triplicate and placed on ice in the dark until return to the laboratory where they were stored and processed according to Table 2.1. Field blanks consisted of processing ultra pure water following the sample protocols during each sampling campaign. All water samples were collected at the same depth of bulk floc collection.

Table 2.1 Summary of water sample container preparation, sample collection, storage and analysis.

Analyte	Container Preparation	Sample Collection	Sample Storage	Analysis
Trace Metals Ag, As, Co, Cu, Ni, Pb	High-density polyethylene Nalgene bottles (30 mL) soaked in 10% (v/v) HNO_3 acid bath for >24 h followed by 8 rinses MiliQ	Water filtered serially through 0.45 µm and 0.2 µm sterile inline syringe filters Preserved with trace metal grade (TMG) 2% (v/v) HNO_3	Stored in dark 4°C	ICP-MS (Section 2.3.6.1)
Iron	High-density polyethylene Nalgene bottles (30 mL) soaked in 10% (v/v) HNO_3 acid bath for >24 h followed by 8 rinses MiliQ	Water filtered serially through 0.45 µm and 0.2 µm sterile inline syringe filters Preserved with TMG 2% (v/v) HNO_3	Stored in dark 4°C	Colorometric FerroVer Method (Method 8008) using UV/visible spectorophotometer
DOC/ DIC	Glass bottles (100 mL) soaked with 5 mL of 10% H_2SO_4 filled to the brim with MiliQ for 3 days followed by 4 rinses MiliQ	Water filtered using glass Millipore filtration apparatus (cleaned with 10% H_2SO_4 and ultrapure water between samples) and cellulose acetate filters.	Stored in dark 4°C	UV-persulfate TOC analyzer (by NLET staff, CCIW)
Cations Ca^{2+}, K^+, Mg^{2+}, Na^+ Anions Fl^-, Cl^-, SO_4^{2-}	Polyethylene containers (500 mL) soaked with 25 mL of 10% HCl filled to the rim with de-ionized water (DI) for 3 days followed by 3 rinses DI	Unfiltered water samples	Stored in dark 4°C	Atomic absorption spectroscopy (by NLET staff, CCIW)
SS	Polyethylene containers (1L)	Water filtered using glass Millipore filtration apparatus on glass-fiber Whatman filters	Stored in dark 4°C	Dry weight (by NWRI Staff, CCIW)

NLET: National Laboratory for Environmental Testing
CCIW: Canadian Center for Inland Waters
NWRI: National Water Research Institute Staff

2.3.4 Suspended Floc Collection

2.3.4.1. Bulk Suspended Floc

In situ continuous flow centrifugation (CFC) was utilized in this thesis for the effective removal of bulk floc from suspension. This method allows for instantaneous and rapid floc collection directly from the water-column at the depth of interest. This method was necessary to collect enough bulk floc material for geochemical, mineralogy, trace metal analysis, and pH experiments. Suspended floc was collected at 0.5m above the sediment-water interface (unless otherwise specified) using CFC (Westfalia Model KA) by National Water Research Institute Staff (NWRI) staff. Water was pumped into stainless steel bowls that were pre-leached with 10% ETDA solution and rinsed 8 times with ultra pure water. Bulk floc samples were collected over 4- 8hour intervals (depending on specific research objectives). After each collection period, the bowls were removed from the centrifuge and placed on ice onsite for transport back to the laboratory. Bowls were kept closed at all times in the field. Floc was immediately removed from the bowls upon return to the laboratory using acid washed silicon spatulas. Bulk floc material was put into acid washed 50 mL Falcon polypropylene tubes that were stored at -20˚C until analysis and pH experiments.

2.3.4.2. Particle Size Distribution

Since floc particle size influences floc physical characteristics and sporptive capacity (Chapter 1, Section 1.1), suspended floc particle size distributions were determined using a laser in situ scatter and transmissometry (LISST) particle-size analyzer (Blake et al, 2009). This technique provides an instantaneous snapshot of suspended floc particle size distribution directly in situ. Chapter 5 investigates temporal trends in floc particle size distributions at Sunnyside Beaches under changing hydrodynamic conditions. Measurements were carried out at the same depth of CFC bulk floc collection and were taken once during each of the bulk floc collection periods.

2.3.5 Bed Sediment Collection

Bed sediments were collected using acid washed silicon core tubes by SCUBA divers (where possible) as to minimize sediment disturbances and by hand at shallow sites (i.e. wetlands, streams). Cores were sub-sampled immediately onshore at the surface and at depth (depending on the specific objectives) using acid washed silicon spatulas and put into Whirlpak sample bags. Whirlpaks were subsequently placed into a bag of mud to minimize oxygen diffusion. If a 'fluffy' layer of settled- floc (SFGL) was present on the core surface (Chapter 5) it was sampled separately with an acid-washed wide-mouth pipette and transferred into 50 mL acid-washed Falcon polypropylene tubes. All sediment samples were immediately frozen in the dark on dry ice onsite and stored at -20°C until back at the laboratory until analysis.

2.3.6 Metal Analysis

Six metals were quantified in this study: Ag, As, Cu, Co, Ni and Pb. This particular suite of metals was chosen to represent a range in abundance across the various anthropogenic-impacted aquatic ecosystems investigated in this thesis (Section 2.2) as well as varying biogeochemical behaviour and toxicity of these elements in the environment. For example, Ag and Pb are highly toxic at low concentrations, while Cu and Co are micronutrients at low concentrations and required for biological growth (Warren and Haack, 2001).

2.3.6.1 Dissolved Trace Metal Analysis

Dissolved metal concentrations (Ag, As, Cu, Co, Ni and Pb) were quantified using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS; (ICP-MS; Perkin Elmer SCIEX ELAN 6100, Woodbridge, ON, Canada) in the Stable Isotope Biogeochemistry Laboratory (SIBL) at McMaster University, Hamilton. Preserved acidified samples were run in triplicate and the average concentrations are reported herein.

2.3.6.3 Solid Phase Metals

Total metal concentrations of natural solid samples (e.g. floc, sediments) indicate the extent to which these materials are contaminated but provide little information about potential metal mobility from these solids under changing physical, chemical or biological processes in the environment (Filgueiras, et al., 2002). Therefore, determining metal solid-phase partitioning (i.e. sorbed versus precipitated) to different reactive solids within the heterogeneous mixed-material of natural solids is key for predicting their mobility and fate. To evaluate the reactive metal phases associated with suspended floc and bed sediments, floc/sediment samples were processed using a microwave digestion sequential extraction procedure from Haack and Warren (2003). This method was designed to rapidly quantify metals in natural surface biofilm samples, a useful tool to characterize metal partitioning within natural suspended floc. This method is a modified version of the Tessier et al., (1979) extraction procedure that differentiates between amorphous and crystalline oxide/oxyhydroxides. The selective extraction and distinction between these two solid-phases is valuable, given the difference in their reactivity for metals (Chapter 1, Section 1.3). Details on the development and optimization of this scheme are described in Haack (2004). Using this method, floc/sediment trace metals are extracted from six operationally defined reactive phases: (1) exchangeable, (2) carbonates, (3) amorphous iron/ manganese oxides, (4) crystalline Fe/ Mn oxides, (5) organic matter and (6) residual fractions (Table 2.2).

Table 2.2 Procedure was developed by Haack and Warren (2003). This scheme is based on a 20:1 ratio of reagents to dry-weight of sediment. Sediment/floc samples were homogenized and extracted in triplicate. Total metal abundance was determined by summing metal concentrations within the six extraction steps.

Fraction	**Reagents**	**Conditions**
Step 1: Exchangeable "Loosely Bound"	1M sodium acetate, pH 8.2 (with HOAc)	1hr shaking, room temperature
Step 2: Carbonates "Acid Soluble"	1M sodium acetate, pH 5.0 (with HOAc)	Microwave Program 1 (MP-1): Heat to 150°C over 8 minutes. Maintain temperature for 5 minutes. 30 minute cool-down.
Step 3: Amorphous Fe/Mn Oxyhydroxides "Easily Reducible"	0.25M Hydroxylamine hydrochloride in 0.25M HCl	MP-1
Step 4: Crystalline Fe/Mn Oxyhydroxides "Reducible"	1.0 M Hydroxylamine hydrochloride in 25% (v/v) acetic acid	MP-1
Step 5: Organics and Sulfides "Oxidizable"	3:2 ratio 30% H_2O_2: 0.02M HNO_3 + 1:4 ratio 3.2M NH_3OAc:UPW	MP-1
Step 6: Residual	Concentrated HNO_3	Microwave Program 2 (MP-2): Heat to 180°C over 20 minutes. Maintain temperature for 10 minutes. 45 minute cool-down.

The exchangeable fraction refers to metals “loosely bound” by electrostatic attraction and therefore easily influenced by changes in ionic strength and pH in the environment. Step 1 of the extraction scheme liberates exchangeable metals by adjusting the ionic strength. The carbonate fraction refers to metal adsorption or co-precipitation with carbonate minerals. Carbonates are susceptible to dissolution with decreasing pH thus Step 2 lowers solution pH, referred to as the “acid soluble” fraction. Iron and manganese oxide/oxyhydroxides are unstable under reducing conditions. Steps 3 and 4 of the scheme target the reductive dissolution of less stable “easily reducible” amorphous Fe/Mn oxide/oxyhydroxides first, followed by more crystalline oxide/oxyhydroxides. Organic matter (both living and detrital,) and sulphides will decompose under oxidizing conditions. Step 5 releases metal bound to organics/sulphides through oxidization. Trace metals held within mineral crystal lattices. They are not relevant for release under the environmental conditions and time scales of this study. These low reactive “residual” metals were liberated in Step 6 by a concentrated acid digestion. Total metal concentrations in floc/sediments were determined by summing the metal concentration released from these six extraction steps [Eq 1].

$$\text{Total Metal}\{M\}_T = \text{exchangeable}\{M\}_E + \text{carbonate}\{M\}_C + \text{amorphous oxyhydroxides}\{M\}_A + \text{crystalline oxides}\{M\}_C + \text{organic/sulphides}\{M\}_O + \text{residual }\{M\}_R \quad \text{[Eq 1]}$$

The supernatant from the six fractions were diluted (10x minimum) using TMG 2% (v/v) HNO_3. Trace metal concentrations (Ag, As, Cu, Co, Ni and Pb) were quantified using ICP-MS. Matrix matched external standard curves for each fraction was used to correct for any matrix affects. The molar concentration of trace metals in floc and sediment samples are expressed as a gram dry-weight (μmol g^{-1}) by using wet:dry ratios (Table 2.3) to convert the metal concentrations extracted from wet floc/sediment material.

2.3.6.4 Comparison of Sediment Metal Concentrations to Guidelines

The Ministry of the Environment (1993) has set three metal contaminant guidelines for aquatic sediments in Ontario, Canada (Table 2.3). These guidelines are based on the long-term effects that metal contaminants may have on aquatic benthic organisms. Currently, there are no guidelines in Ontario for suspended floc metal concentrations. However, these sediment guidelines were applied to total metal concentrations in suspended- and settled-floc in Chapter 4 and 5 at Sunnyside Beach as a relative indicator of floc metal contamination and potential requirement for further floc analysis and water management.

Table 2.3 Three levels of aquatic sediment quality guidelines in Ontario, Canada

Level	**Guidelines**
No Effect Level	No affect on fish/sediment-dwelling aquatic organisms or water quality is expected by metal concentrations
Lowest Effect Level	Ecotoxic effects become apparent. Contamination that exceeds the Lowest Effect Level may require further testing and a management plan
The Severe Effect Level	Sediments are heavily polluted and likely to affect health of benthic organisms. Contamination that exceeds the Severe Effect Level requires further testing and potential management plan

2.3.6.5 Solid Phase Analysis

Solid-phase organic matter and inorganic minerals are highly reactive sorbents for solution trace metals and are important geochemical constituents of natural floc and bed sediments (Chapter 1). An estimate of the per-gram dry-mass of floc and bed sediment organic matter, Fe/Mn oxides/oxyhydroxide and carbonate content as well as bulk mineralogy was determined according to the methods summarized in Table 2.4.

Table 2.4 Solid-phase composition. Floc and sediment samples were homogenized manually by stirring prior to processing. Samples were processed and analyzed in triplicate.

Parameter	**Sample Preparation**	**Analysis**
Wet: Dry Ratio	Dry samples 80°C until constant weight	Divide the weight of the wet floc/sediment by the dry sample weight
Organic Matter	Dry samples according to Wet: Dry	Loss on ignition (LOI) 550°C for 2h
Carbonates	Further heating post LOI analysis	950°C for 1h
Fe Oxide/Oxyhydroxides	Supernatant from the amorphous and crystalline oxyhydroxide sequential extraction fractions (Step 3 and 4, respectively in Table 2.2)	Colorometric FerroVer Method (Method 8008) using UV/visible spectorophotometer
Mn Oxides/Oxyhydroxides	Supernatant from the amorphous and crystalline oxyhydroxide sequential extraction fractions (Step 3 and 4, respectively in Table 2.2)	ICP-MS
Bulk Mineralogy	Dry samples 40°C until constant weight	X-ray power diffractrometry (XRD)

2.3.7 Laboratory Floc/Sediment Pb Mobility Experiments

Solution pH is considered to be the dominant control on solid-solution sorption reactions (Chapter 1). Investigating the influence of pH on trace metal (i.e. Pb) and organic matter solid-solution partitioning from suspended floc and bed sediments was carried out in a series of controlled laboratory experiments from floc/bed samples collected from a range of NOM concentrations and metal contaminated ecosystems. Specific experimental methodology is described in detail in Chapter 3 and therefore will not be repeated here.

2.3.8 Floc Imaging

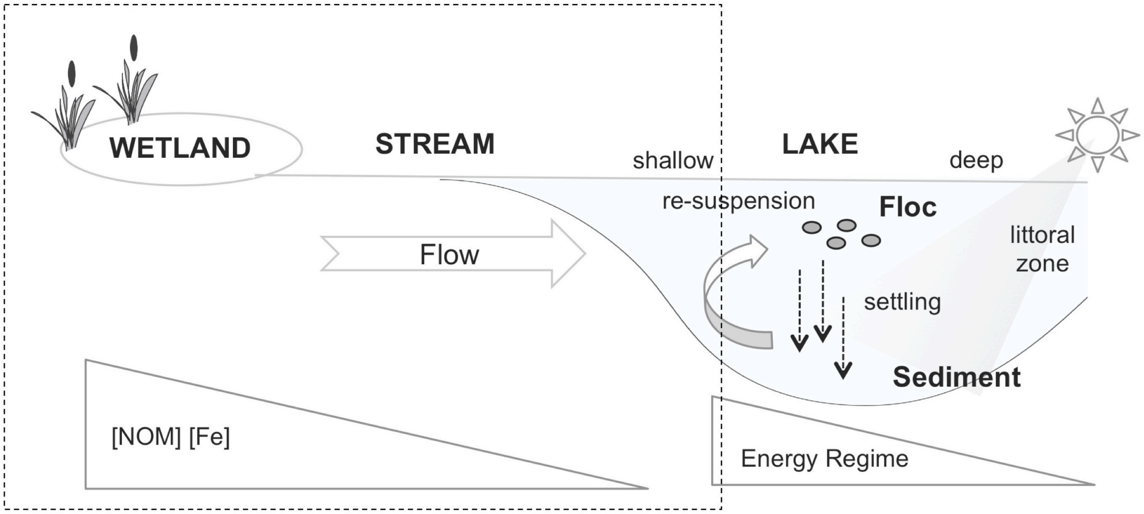
2.3.7.1 Transmission Electron Microcopy

Floc architecture is a highly complex intricate matrix of organic matter, inorganic minerals and pore spaces that combine to influence floc biogeochemistry (Chapter 1 Section 1.2). Transmission Electron Microscopy (TEM) allows for the two-dimensional visualization of the internal spatial arrangement of floc associated microbial cells, associated network of extracellular polymeric substances (EPS) and mineral components within the suspended aggregates. Diver collected plankton chambers (Droppo et al, 1996) were used, when possible, to collect floc at the same depth as the CFC, for nondestructive observation of floc aggregates. If divers were not available (Chapter 5), bulk water samples were hand collected into 4 L polyethylene containers. Floc aggregates were subsequently stored in the dark at 4°C and processing began within 24 hrs of collection. A fourfold multipreparatory technique was utilized (Liss et al., 1996) by staff at the Electron Microscopy Facility at the Health Sciences Centre, McMaster to prepare floc samples for visualization using a JEOL 1200 Ex II TEMSCAN TEM. Elemental composition of floc- associated minerals (e.g. Fe, Mn) within the EPS fibrils and on cell wall surfaces were analyzed using an X-ray energy dispersive analyses (EDS).

2.3.7.1 Epifluoresence Microscopy

Bacterial reactive surfaces (i.e. cells, EPS) and diverse metabolic activity make them highly dynamic organic constituents in the environment and likely to influence floc trace metal dynamics (Chapter 1, Section 1.4). To compare the bacterial viability in suspended floc versus bottom bed sediments, LIVE/DEAD BacLight^{TM} Bacterial Viability Kit L7012 (Invitrogen Canada Inc., Burlington, ON, Canada) and epifluoresence microscopy was utilized on bulk floc and sediments. Approximately 10 mg of floc and sediments were re-suspended separately in 1 mL of 0.085% NaCl solution, and 0.5 μL of LIVE/DEAD BacLight^{TM} staining solution was added and incubated for 15 min in the dark at room temperature. Each stained sample mixture was applied (5 μL) to a gelatine-coated slide [ethanol-sterilized slides that were coated in a 50°C filter sterilized solution of 0.1% (w/v) gelatin and 0.01% (w/v) $CrK(SO_4)_2$ in distilled water and UV- irradiated for 30 mins). A glass coverslip was applied to each sample slide. Prepared slides were imaged using a Leica LEITZ DMRX epifluorescence microscope equipped with an HBO 100-W mercury arc lamp (Leica Microsystems Canada, Richmond Hill, ON, Canada) in the Aquatic Microbial Geochemistry Lab, McMaster University. Fluorescence imaging was performs using GFP (Alexaflour 488) and TX2 (TexasRed) filter cubes. Digital imaging was carried out using Openlab Software Version 5.5.0 (Improvision, Coventry, UK). Overlay of live and dead images were performed using Adobe Photoshop CS4 software.

CHAPTER 3: DIFFERENTIATING NATURAL ORGANIC MATTER ROLES IN FRESHWATER FLOC AND BED SEDIMENT LEAD DYNAMICS



CHAPTER 3: DIFFERENTIATING NATURAL ORGANIC MATTER ROLES IN FRESHWATER FLOC AND BED SEDIMENT LEAD DYNAMICS

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3.1 Abstract

Natural organic matter (NOM) is shown to be an important determinant of Pb dynamics across nine highly variable freshwater (wetland, stream, lake) ecosystems of Ontario, Canada. Soluble organic–Pb complexes emerged as the dominant Pb aqueous species (68–99%) in NOM-rich ecosystems; while distinct surficial sediment and suspended floc Pb sequestration and solid-solution partitioning patterns were observed across sites, driven by differential roles of living versus refractory NOM respectively within these two compartments. Field results suggest organo-Pb complexes dominate bed sediment Pb solid-solution partitioning, as sites with the highest pH values showed the greatest Pb mobilization, despite site-specific solid-phase Pb sequestration patterns. Contrasting bed sediment results, amorphous Fe oxyhydroxides (FeOOH) collected by floc microbes and extracellular polymeric substances, were the best predictor of floc Pb solid-solution partitioning, more consistent with cationic Pb behavior, as well as the key floc Pb sequestration phase (43–82%) across systems.

Laboratory batch experiments assessed Pb solid-solution dynamics as a function of pH (5, 6, 6.5, 7 and 8) for surficial bed sediments (wetland, stream and lake) and limnetic floc (pH 5 and 8) varying in NOM concentrations. Results confirmed the occurrence of stable organo-Pb complexes in NOM-rich sediments, as mobilization of dissolved organic carbon (DOC) and Pb occurred with increasing pH, while Pb release decreased with increasing pH from NOM poor sediment. The most organic rich, wetland surficial sediments showed the greatest mobilization rate of organo-Pb complexes, indicating dynamic DOC and Pb export is likely from such NOM-rich ecosystems under

changing pH conditions. In contrast, experimental floc pH dependent Pb mobilization showed no correlation to DOC concentrations and was consistent with FeOOH-cationic Pb solid-solution behavior, rather than anionic organo-Pb complexes, as suggested in field observations. Results of this combined field and laboratory study demonstrate that establishing the nature of NOM and differential processes impacting NOM abundance/reactivity in each aquatic compartment across intrinsically connected aquatic ecosystems is fundamental to understanding Pb migration in freshwater catchments from upstream NOM-rich wetlands through to downstream NOM-poor littoral lake environments.

3.2 Introduction

Natural organic matter (NOM) is a fundamental component of freshwater environments and a geochemically significant substrate for lead (Pb) transport, retention and fate in watersheds. Despite a decline in atmospheric Pb sources into the environment associated with major reductions in leaded gasoline consumption since the 1970s, concern remains whether Pb remobilization from highly organic sediments and subsequent transport by soluble organo-Pb complexes and organic– floc aggregates continues to pose risk to freshwater ecosystems.

Aquatic NOM comprise a broad spectrum of highly complex and variable carbon compounds with differential surface reactivity for trace elements, that are traditionally operationally classified by filtration; particulate organic carbon (POC) >0.45 μm and dissolved organic carbon (DOC) <0.45 μm. DOC is known to be a significant carrier of soluble Pb in surface waters (LaZerte et al., 1989; Shafer et al., 1997; Taillefert et al., 2000; Kerr et al., 2008; Landre et al., 2009; Dawson et al., 2010). DOC comprises humic acids (HA) and fulvic acids (FA), refractory organic compounds largely derived from plant litter, root exudates, microbial biomass and products of microbial decomposition (e.g. Smith, 1976; Guggenberger et al., 1994; McKnight and Aiken, 1998), that contain acidic functional groups (e.g. phenolic and carboxylic groups; Stevenson, 1994) important for complexation of trace elements including Pb (e.g. Cd, Cu, Co, Ni, and Zn, Davis, 1984; Gondar et al., 2006; Pandey et al., 2000; Temminghoff et al., 1997). Although variation in DOC concentrations in freshwater lakes and streams has been partially linked to hydrologic mechanisms from catchment runoff (Hinton et al., 1997; Raymond and Saiers, 2010; Laudon et al., 2011) and export from upstream wetlands (Freeman et al., 2001; Strack et al., 2008; Koehler et al., 2009); the potential of DOC mobilization from limnetic surficial sediments and subsequent impact on Pb mobility remains largely un-described.

Solution pH is considered a master variable driving NOM solubility (e.g. Kalbitz et al., 2000), trace element solid-solution behavior (e.g. Petrovic et al., 1999; Trivedi et al., 2003) as well as complex formation of trace elements with dissolved organic ligands (e.g. Liu and Gonzalez, 2000; Pehlivan and Arslan, 2006). Previous laboratory studies have demonstrated a significant positive correlation between pH and NOM solubility within terrestrial organic soils (Tipping and Hurley, 1988; Kennedy et al., 1996; Sauve et al., 1998; Shen, 1999; Impellitteri et al., 2002), largely attributed to surface charge repulsions of negatively charged organic molecules from increasingly negatively charged solid matter (e.g. Fe-oxides; Tipping, 1981) in the soil matrix. Further, some studies have linked Pb mobilization from organic soils with increasing pH to the formation of soluble organo-Pb complexes with DOC (Wang and Benoit, 1996; Jordan et al., 1997; Sauve et al., 1998). Although pH is known to play an important role in interactive DOC and Pb solubility within the terrestrial environment, the potential for such interactions within freshwater systems has not been elucidated to date.

As aquatic sediments are often considered sinks for atmospheric Pb, they are commonly used to develop a chronology of lead contamination into the environment (Heyvaert et al., 2000; Yohn et al., 2004; Gallon et al., 2006). However, if some fraction of aquatic sediment Pb occurs as anionic organo-Pb complexes that may be weakly sorbed to sediments (El Bilali et al., 2002), similar to within terrestrial environments, then pH changes may affect Pb solid-solution partitioning and potentially mobilize organo-Pb complexes to the overlying water column. This is particularly relevant given the substantial pH variations that can occur associated with photosynthesis within euphotic zones of aquatic environments (Beck et al., 2009; Dicataldo et al., 2011), long term pH alterations from anthropogenic liming (Driscoll et al., 1996) as well as common pH alterations observed as water moves from wetland regions to downstream lakes (e.g. Stecko and Bendell-Young, 2000). As such, establishing the importance of soluble organo-Pb complexes in aqueous Pb dynamics across aquatic system types that vary in NOM abundance, and linking pH effects on DOC and Pb re-mobilization from aquatic sediments are relevant for both short and long term assessments of water quality of our freshwater ecosystems.

Transport of Pb in surface waters also occurs by suspended aquatic floc, commonly referred to as suspended particulate matter (SPM) elsewhere in the literature (Warren and Zimmerman, 1994; Stecko and Bendell-Young, 2000; Audry et al., 2006). Floc are complex aggregates of inorganic particles (e.g. clays and oxyhydroxides) and organics (e.g. detritus, bacteria, algae) (Droppo et al., 1997), that are known to significantly concentrate trace elements in the environment (As, Ag, Co, Cu, and Ni, Elliott et al., 2012) including Pb (Plach et al., 2011). Floc NOM is largely living material dominated by microbial communities and associated extracellular polymeric substances (EPS) (Liss et al., 1996; Droppo, 2001). This is in direct contrast to bed sediment associated NOM that more often consists of fewer living cells than floc (Droppo et al., 2009; Plach et al., 2011), and more detrital and refractory in nature (Godshalk and Wetzel, 1984). Recent work (Plach et al., 2011; Elliott et al., 2012) suggests that the living organic components of floc (i.e. cells and EPS) facilitate floc trace element concentration above that of bed sediments, through the collection and/or templating of amorphous Fe oxyhydroxide (FeOOH) minerals, the key substrate for trace element retention within floc. However, few studies have specifically investigated suspended floc

Pb behavior (Stecko and Bendell-Young, 2000; Taillefert et al., 2000; Plach et al., 2011); particularly none to date have evaluated the key biogeochemical controls on floc Pb uptake within natural freshwater systems that range in physico-chemical characteristics (e.g. pH) and Pb and NOM concentrations (e.g. DOC). Given that floc comprises a highly mobile compartment that can move between aquatic environments, understanding floc Pb behavior is imperative for modeling Pb transport through watersheds. As such, the objectives of this study are to: (1) investigate Pb and NOM distributions among suspended floc, surficial bed sediment and water-column compartments; (2) identify the important solid phases for Pb sequestration in floc and surfical bed sediments; and (3) determine the role of pH impacting DOC and Pb solid-solution partitioning from natural limnetic floc, as well as lake, stream and wetland sediments both in situ and under controlled laboratory settings.

3.3 Materials and methods

3.3.1 Study site/sampling protocol

Seven study sites (wetland, stream and lake systems) located in the boreal forest and Great Lakes regions of Ontario, Canada and two sites (stream, lake) in agricultural/urbanized regions of southern Ontario ranging in physico-chemical parameters, DOC and Pb concentrations were selected (Table 3.1). In situ water-column measurements and sample collection occurred during 2008, 2009 and 2010 between May and August. Geochemical characterization and sample collection involved (1) in situ physico-chemical water-column profiling (temperature, pH, dissolved oxygen and specific conductivity; Datasonde- Surveyor 4A, Hydrolab Corporation, TX); (2) collection of bed sediments and bulk suspended floc (at four sites; <0.5 m above bed) for solidphase trace element analysis and bulk mineralogy; and (3) collection of water samples (<0.5 m above bed) for dissolved Pb and DOC analyses. All sampling equipment and sample containers for Pb analysis were prepared by soaking in 10% (v/v) HCl for >24 h followed by eight rinses with ultra pure water (18.2 Ω m cm^{-1}, Milli-Q, Millipore). All sample containers for DOC collection were pre-soaked in 10% H_2SO_4 for >24 h followed by eight rinses with ultra pure water.

Table 3.1 Physico-chemical characteristics of sample sites (<0.5 m water-column above sediments)

Site	Sample Date	Coordinates	pH	Temperature (°C)	Oxygen (mg L^{-1})	SPC μScm	DIC[c] (mg L^{-1})	DOC[c] (mg L^{-1})	$[Pb]_D$ (nmol L^{-1})	$[Fe]_D$[c] (mg L^{-1})
Algonquin Park, ON										
Brewer Lake Site 1	26-Jun-08	45°35'15"N 78°18'07"W	5.88	15.7	8.5	101	2.2	5.4	0.4	0.05
Brewer Lake Site 1[b]	18-Jun-09	45°35'15"N 78°18'07"W	6.01	15.38	8.85	101	1.3	5.5	1.5	-
Brewer Lake Site 2	18-Jun-09	45°35'30"N 78°18'36"W	5.70	4.46	0.25	176	1.2	5.3	1.8	0.40
Brewer Wetland[a]	18-Jun-09	45°35'37"N 78°19'23"W	6.72	19.89	2.64	701	1.3	48	8.7	0.45
Costello Lake[a]	18-Jun-09	45°35'52"N 78°19'07"W	5.85	5.06	4.71	70	1.7	5.7	2.1	0.39
Costello Creek[a]	18-Jun-09	45°37'01"N 78°20'39"W	6.94	20.9	6.52	58	0.9	21.6	4.0	0.40
Costello Creek	09-Aug-10	45°37'01"N 78°20'39"W	6.45	23.81	2.03	76	0.8	10.2	1.1	0.70
Coldspring Lake	18-Aug-09	45°85'28"N 78°82'17"W	6.30	19.71	4.03	25	1.7	7.23	1.9	0.07
Coldspring Wetland	12-Aug-10	45°50'49"N 78°48'38"W	6.30	20	-	25	3.2	21.5	3.3	6.20
Cache Lake Wetland	13-Aug-10	45°33'10"N 78°35'31"W	6.72	24.03	6.16	326	3.1	14.8	1.0	1.10
Urbanized Region, Southern ON										
Sunnyside Beach, Lake Ontario	13-May-08	43°38'14"N 79°27'20"W	7.66	8.5	12.2	341	21.6	2.4	0.7	0.01
Sunnyside Beach, Lake Ontario[a,b]	21-Jul-09	43°38'14"N 79°27'20"W	7.94	13.95	12.9	305	23.5	2.97	0.3	0.02
Agricultural Stream, Guelph	29-Jul-08	43°39'24"N 80°24'06"W	7.55	14.85	8.5	75	65.3	8.97	1.1	0.05

[a] bed sediments [b] floc used for experiments

[c] values are means (n=3) and standard deviation: DIC/DOC, $[Fe]_D$= 10^{-1}

3.3.2 Water-column collection/analysis

Water samples for dissolved Pb analysis were collected by an acid washed Van Dorn water sampler, serially filtered through 0.45 μm and 0.2 μm sterile inline syringe filters and subsequently preserved with trace metal grade (TMG) HNO_3 to 2% (v/v) (Fisher). Procedural blanks consisted of Milli-Q water run though an acid-cleaned Van Dorn followed by syringe filtration. Samples were kept in the dark and stored at 4 °C until analysis. Dissolved Pb concentrations $[Pb]_D$ (<0.2 μm) were quantified by inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer SCIEX ELAN 6100, Woodbridge ON, Canada). Limit of quantification (LOQ) for Pb was 0.3 nmol L^{-1}. Water samples for DOC analysis (collected <0.5 m above sediments) were filtered through 0.45 μm (cellulose acetate filters) and kept in the dark at 4 °C until analysis using a UV-persulfate TOC analyzer following the methods at the National Laboratory for Environmental Testing (NLET) Environment Canada (1979).

3.3.3 Bed sediment and floc collection/Pb analysis

Bed sediments were collected by coring, either diver retrieved, or hand collected in shallow sites, in acid washed polycarbonate core tubes (6 cm diameter, 45 cm length). Cores were capped underwater to the keep sediment water-interface intact. Sediment cores were immediately extruded on site and sub-sectioned samples (0–0.5 cm depth) were stored in Whirlpack bags. Samples were immediately frozen on dry ice and stored in the dark at −20 °C until analysis. Bulk suspended floc was collected using continuous flow centrifugation (CFC, Westfalia Model KA) whereby water (0.5 m above sediments) was pumped (>2000 L, 6 L min^{-1}) into stainless steel bowls (preleached with 10% EDTA solution prior to collection) over a 6–8 h period according to Plach et al. (2011). Greater than 90% of the floc was recovered (assessed by weight comparison of CFC inflow and outflow filtered water samples on glass-fiber Whatman filters following the standard method 2540D; Eaton et al., 2005) and was stored in acid washed 50 mL falcon tubes at −20 °C until analysis.

Samples were homogenized and processed in triplicate using a modified Tessier sequential extraction method (Haack and Warren, 2003). Sediment associated Pb was partitioned into six operationally defined sediment fractions: exchangeable (loosely bound); acid soluble; amorphous Fe/Mn oxyhydroxides (easily reducible); crystalline Fe/Mn oxides (reducible); organics/sulfides (oxidizable); and residual (concentrated HNO_3 digestion). Reagents blanks were included during digestion to correct for procedural contamination and matrix effects associated with ICP-MS were corrected using matrix-matched standard curves. Blank analysis indicated negligible contamination. Analytical accuracy of the extraction method was assessed by the co-extraction of certified reference materials (Buffalo River 8047, Bovine Liver 1577b: NIST Standard Reference Materials). Mean total sediment Pb concentrations $\{Pb\}_T$ (µmol g^{-1} dry weight) were determined by summing Pb concentrations from the six sediment fractions.

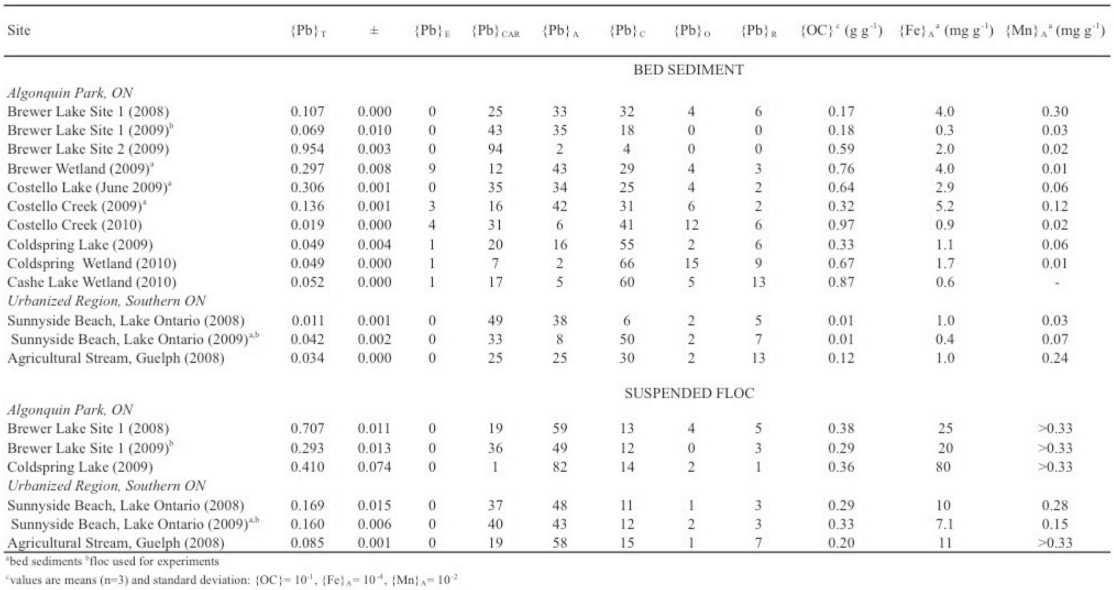
3.3.4 Sediment and floc composition

Mean floc and sediment weights were determined by drying at 80 °C in triplicate until consistent weight. Mean bulk organic content {OC} of floc/sediment samples was estimated by loss on ignition (%LOI, 550 °C 2 h). Total Fe and Mn from extraction step 3 were used to estimate the concentration of amorphous Fe oxyhydroxides $\{Fe\}_A$ (quantified colorimetrically using FerroVer HACH method (Ultrospec 2000, UV/visible spectorophotometer, Pharmacia Biotech, Cambridge, U.K.)) and amorphous Mn oxyhydroxides $\{Mn\}_A$ (quantified by ICP-MS) substrates, respectively. X-ray diffractometry (XRD) was used to determine bulk mineralogical composition (Siemens D5005 X-ray diffractometer). Bulk XRD analysis identified the main crystalline components were similar for both bed sediments and floc (Table S.3.1).

3.3.5 Sediment and floc experiments: influence of pH on Pb solid-solution behavior

Experiments were designed to specifically assess the impact of pH on sediment and floc Pb solid-solution behavior associated with varying NOM and pH concentrations. Four surficial sediment samples (from wetland, stream and lake systems) were selected for experimentation from sites that ranged in NOM and Pb concentrations (Table 3.2), which we hypothesized, reflected variations in the relative occurrence of Pb–DOC complexes within the sediment/floc. Samples were titrated to five pH values between 5 and 8, and DOC and Pb solution concentrations were determined at each pH titration point. We hypothesized that sites with higher NOM concentrations (i.e. wetlands) would contain a greater proportion of organo-Pb complexes in sediments, and further, that these complexes are highly stable. Thus, the greatest Pb remobilization, i.e. as organo-Pb (anionic) complexes, with increasing pH would be observed in organic rich systems. Batch experiments were replicated on two limnetic-floc samples collected from NOM rich and NOM-poor sites (Table 3.2). Concentrations of solution DOC and Pb were determined at pH 5 and 8 for both floc samples. These values were chosen to reflect the pH conditions of the two sites and the limited experimental range that could be assessed due to sample volume.

Table 3.2 Mean Pb concentrations $\{Pb\}_T$ (μmol g^{-1})of floc and surficial sediments and percent (%) Pb in six sediment fractions; exchangeable $\{Pb\}_E$, carbonates $\{Pb\}_{CAR}$, amorphous Fe/Mn oxyhydroxides $\{Pb\}_A$, crystalline Fe/Mn oxyhydroxides $\{Pb\}_C$, organics $\{Pb\}_O$ and residual $\{Pb\}_R$. Sediment and floc constituents; organic carbon {OC}, amorphous Fe $\{Fe\}_A$ and Mn $\{Mn\}_A$.



Site	$\{Pb\}_T$	±	$\{Pb\}_E$	$\{Pb\}_{CAR}$	$\{Pb\}_A$	$\{Pb\}_C$	$\{Pb\}_O$	$\{Pb\}_R$	$\{OC\}^c$ ($g\ g^{-1}$)	$\{Fe\}_A{}^a$ ($mg\ g^{-1}$)	$\{Mn\}_A{}^a$ ($mg\ g^{-1}$)
						BED SEDIMENT					
Algonquin Park, ON											
Brewer Lake Site 1 (2008)	0.107	0.000	0	25	33	32	4	6	0.17	4.0	0.30
Brewer Lake Site 1 (2009)[b]	0.069	0.010	0	43	35	18	0	0	0.18	0.3	0.03
Brewer Lake Site 2 (2009)	0.954	0.003	0	94	2	4	0	0	0.59	2.0	0.02
Brewer Wetland (2009)[a]	0.297	0.008	9	12	43	29	4	3	0.76	4.0	0.01
Costello Lake (June 2009)[a]	0.306	0.001	0	35	34	25	4	2	0.64	2.9	0.06
Costello Creek (2009)[a]	0.136	0.001	3	16	42	31	6	2	0.32	5.2	0.12
Costello Creek (2010)	0.019	0.000	4	31	6	41	12	6	0.97	0.9	0.02
Coldspring Lake (2009)	0.049	0.004	1	20	16	55	2	6	0.33	1.1	0.06
Coldspring Wetland (2010)	0.049	0.000	1	7	2	66	15	9	0.67	1.7	0.01
Cashe Lake Wetland (2010)	0.052	0.000	1	17	5	60	5	13	0.87	0.6	-
Urbanized Region, Southern ON											
Sunnyside Beach, Lake Ontario (2008)	0.011	0.001	0	49	38	6	2	5	0.01	1.0	0.03
Sunnyside Beach, Lake Ontario (2009)[a,b]	0.042	0.002	0	33	8	50	2	7	0.01	0.4	0.07
Agricultural Stream, Guelph (2008)	0.034	0.000	0	25	25	30	2	13	0.12	1.0	0.24
						SUSPENDED FLOC					
Algonquin Park, ON											
Brewer Lake Site 1 (2008)	0.707	0.011	0	19	59	13	4	5	0.38	25	>0.33
Brewer Lake Site 1 (2009)[b]	0.293	0.013	0	36	49	12	0	3	0.29	20	>0.33
Coldspring Lake (2009)	0.410	0.074	0	1	82	14	2	1	0.36	80	>0.33
Urbanized Region, Southern ON											
Sunnyside Beach, Lake Ontario (2008)	0.169	0.015	0	37	48	11	1	3	0.29	10	0.28
Sunnyside Beach, Lake Ontario (2009)[a,b]	0.160	0.006	0	40	43	12	2	3	0.33	7.1	0.15
Agricultural Stream, Guelph (2008)	0.085	0.001	0	19	58	15	1	7	0.20	11	>0.33

[a]bed sediments [b]floc used for experiments

[c]values are means (n=3) and standard deviation: $\{OC\}= 10^{-1}$, $\{Fe\}_A= 10^{-4}$, $\{Mn\}_A= 10^{-2}$

Homogenized sediment samples for experimentation were gamma irradiated to remove any potential living microbial influence on NOM and/or Pb partitioning. Gamma irradiation was selected for sterilization, rather than chemical or autoclaving methods, to minimize release of soluble of organic matter (Berns et al., 2008) and to preserve the chemical and physical properties of the natural samples (McNamara et al., 2003). Experimental systems were set up in 50 mL acid washed polyethylene bottles using ~3 g (dry weight equivalent) surficial sediments or ~0.5 g (dry weight equivalent) floc samples and 30 mL 0.01 M KNO_3 solution, loosely capped to allow for gas exchange. The experimental-systems were initially placed on a reciprocal shaker for 30 min to equilibrate and then each bottle was manually titrated using TMG HNO_3 or KOH to each of the five pH values being examined (5, 6, 6.5, 7 and 8) for bed sediments and at pH 5 and 8 for the two floc samples; these values were specifically selected to mimic the pH range of the study sites as well as encompassing critical pH points in cationic/anionic trace element and amphoteric substrates (i.e. pHzpc of Fe oxyhydroxide/oxides) sorption dynamics. Samples were maintained at each pH value (+ − 0.1) for 30 min, and then sacrificed for sampling. Sample bottles were centrifuged at 8000 rpm (9733xg) for 15 min and supernatant filtered (<0.2 μm). Supernatant samples from each pH treatment for each experimental system were analyzed for (1) Pb using ICP-MS (acidified to 2% (v/v) TMG HNO_3) and (2) DOC (<0.2 μm; for comparison with soluble Pb) by colorimetric approach, measuring absorbance at λ=330 nm (Ultrospec 2000, UV/visible spectrophotometer, Pharmacia Biotech, Cambridge, U.K.) and correcting for any Fe release (FerroVer® HACH) according to Moore (1985). Sensitivity of the colorimetric approach was assessed along a concentration gradient of DOC and by the co-analysis of samples with values recovered by UV-persulfate TOC analyzer (Figure S.3.1 and Table S.3.2). No additions of organic matter or Pb were made to the natural floc or bed sediment samples prior to pH treatment.

3.3.6 Microscopy

Field samples of suspended floc collected in situ by diver-retrieved plankton chambers (Droppo et al., 1996) were prepared following a 4-fold multi-step technique to enhance visualization of cells and EPS (Liss et al., 1996). Ultra-thin sections for ultrastructure imaging and elemental analysis were imaged in transmission mode at an accelerated voltage of 80 kV using a using a JEOL 1200 Ex II TEMSCAN scanning transmission electron microscope (TEM-ES) (McMaster University, Hamilton, ON, Canada).

3.3.7 Data analysis

Concentrations of organic and inorganic species of Pb in the water-column at each site were predicted using Visual MINTEQ speciation program (Gustafsson, 2011).

Details on modeling parameters are described in Supplementary Information (Table S.3.3 and Table S.3.4). Statistical analyses were performed using PASW version 18.0 (SPSS Inc., Chicago, Illinois, USA). Multiple regression analysis was performed to identify key variables (floc/sediment constituent phase concentrations and water-column physcio-chemistry i.e. [DOC], pH, temperature, O_2, specific conductance) influencing trends in $[Pb]_D$, bed sediment $\{Pb\}_T$, floc $\{Pb\}_T$ and individual sediment/floc reactive fractions. T-tests were applied to test for significant differences of mean $\{Pb\}_T$ between floc and surfical bed sediment. Significance was assessed at a level of $p \leq 0.05$.

3.3 Results and discussion

3.3.1. Field results

3.3.1.1. Water-column and bed sediment Pb dynamics

Dissolved Pb concentrations $[Pb]_D$ showed significant positive correlation with DOC concentrations [DOC] across sites (Figure 3.1A). The highest $[Pb]_D$ and [DOC] values were observed in Brewer Lake wetland (8.7 nM and 48 mg L^{-1}, respectively) while the lowest concentrations were observed in the littoral waters of Lake Ontario (0.3 nM and 2.97 mg L^{-1}, respectively). Significant correlations between $[Pb]_D$ and [DOC] have previously been observed in the natural environment (Kerr et al., 2008; Landre et al., 2009; Dawson et al., 2010) suggesting soluble organo-Pb complexes are important transport vectors of Pb in surface waters.

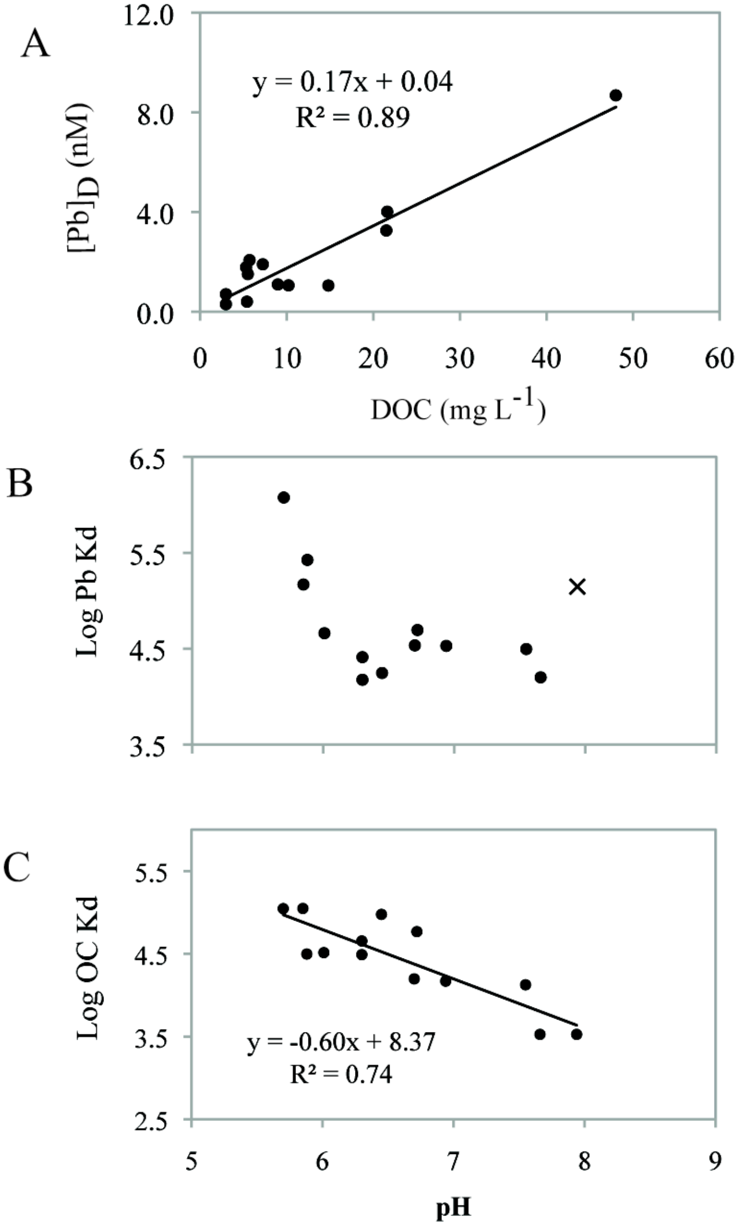


Figure 3.1 (A) Dissolved organic carbon [DOC] and aqueous Pb $[Pb]_D$ concentrations in the water column (<0.5 m above bed sediments). $[Pb]_D$ showed significant positive correlation with [DOC]. (B) Surficial bed sediment Pb distribution coefficients (Kds; L kg^{-1}) as a function of water-column pH (<0.5 m above sediments). (x) indicates outlier, organic poor beach, Lake Ontario. (C) OC distribution coefficients (Kds; L kg^{-1}) as a function of water-column pH (<0.5 m above sediments).

The observed variation in water-column $[Pb]_D$ within proximity of the sediment water interface (<0.5 m above sediments), did not correlate with mean total surficial bed sediment Pb concentrations $\{Pb\}_T$ (µmol g^{-1}) across sites. However, a pH control on Pb partitioning between water-column ($[Pb]_D$ values <0.5 m above bed) and surficial bed sediment compartments, assessed by distribution coefficients (Kd L/Kg: $\{Pb\}_T/[Pb]_D$; mol kg^{-1}/mol L^{-1}) (Stumm and Morgan, 1996), was evident across the large range of $[Pb]_D$ (0.3–8.7 nM) and bed sediment $[Pb]_T$ (0.011–0.954 mol g^{-1}) concentrations measured across the nine systems investigated. Pb distribution coefficients (Kds) decreased with increasing system pH (Figure 3.1B), i.e. lower Pb Kd values were observed for the higher pH sites (pH>6) indicating a relatively larger distribution of Pb to the overlying water-column solution phase with increasing pH values (exception to this trend was organic poor littoral Lake Ontario site in 2009). These results do not fit with solid-solution behavior of cationic Pb^{2+} with increasing pH (e.g. Wang et al., 1997; Petrovic et al., 1999; Hu et al., 2010) whereby Pb^{2+} sorption to organic matter, oxyhydroxide and clay mineral surfaces increases with higher pH. The relative increase in soluble Pb with pH across field sites observed here may reflect; (1) Pb carbonate complexes dominating aqueous Pb species (34–53%) in the two NOM-poor urbanized systems and (2) increased strength of organo-Pb complexes (Liu and Gonzalez, 2000) which dominate aqueous Pb species (68–99%) in the seven NOM-rich Algonquin sites (Table S.3.5). Consistent with observed results, these anionic organo-Pb species in the NOM-rich sites could desorb from sediments at higher pH conditions associated with greater charge repulsion between increasingly negatively charged organo-Pb complexes and solid surfaces in sediments.

3.3.1.2. Water-column and bed sediment NOM dynamics

Differential DOC abundances are inherent across natural aquatic systems, from upstream NOM-rich wetlands to downstream NOM poor lakes. Dissolved organic carbon concentrations across the nine sites ranged from 48 mg L^{-1} (Brewer Lake wetland, Algonquin Park, ON) to 2.97 mg L^{-1} (Lake Ontario, beach environment, Toronto, ON)

(Figure 3.1). Similar to the pH trend observed for Pb Kd values (Figure 3.1B), organic matter distribution coefficients ((i.e. Kd={OC}/DOC); DOC values from <0.5 m above the sediment) also decreased with increasing water-column pH (Figure 3.1C) suggesting desorption and/or minimized sediment sorption of DOC is occurring. In contrast, higher OC Kd values in the low pH systems indicate greater relative retention of DOC within the surficial bed compartment. These field results recapitulate laboratory findings of pH dependent soil organic matter solubility (Sauve et al., 1998; Impellitteri et al., 2002) and are the first demonstrating a potential pH control on organic solid solution partitioning from aquatic sediments in situ.

Solubility of DOC has been linked to Pb mobilization and pH from organic terrestrial soils (Wang and Benoit, 1996; Jordan et al., 1997; Sauve et al., 1998). Our combined field results showing; (1) correlation between $[Pb]_D$ and [DOC], (2) lower Pb and OC Kds at higher pH systems and (3) organo-Pb complexes dominating Pb species in NOM-rich sites, indicate that DOC may also play an important role driving Pb mobility/retention from organic aquatic sediments. Based on these field results we hypothesized that organo-Pb complexes are important and highly stable Pb species in organic rich sediments and that such organo-Pb complexes would cycle between surficial sediments and the overlying water-column associated with pH changes in exactly the opposite manner to cationic Pb^{2+}.

3.3.1.3 Floc Pb dynamics

Floc collected within the vicinity of the surficial sediments (<0.5 m above bed) significantly concentrated Pb compared to surficial bed sediments across the four sites of floc collection (Table 3.2). Mean floc $\{Pb\}_T$ ranged from 0.707 μmol g^{-1} (highest observed in Brewer Lake, Algonquin Park) to 0.085 μmol g^{-1} (lowest observed in Guelph, agricultural stream). The ability of floc to significantly concentrate Pb compared to bed sediments is consistent with recent findings of floc sequestration of other trace elements (Ag, As, Ag, Cu, Co and Ni, Elliott et al., 2012).

Floc Pb distribution coefficients (i.e. Floc Kds: $\{Pb\}_T/[Pb]_D$) did not correlate with water-column physico-chemical parameters (pH, DOC, $[Pb]_D$, °C, O_2 (mg L^{-1}), specific conductance) commonly observed to be important for bed sediment solid-solution partitioning of trace elements, and as observed for the bed sediment results discussed earlier. Rather, floc Pb Kd values were significantly correlated with the scavenging efficiency of floc-associated FeOOH across all four sites (Figure 3.2A). Scavenging efficiency of amorphous Fe oxyhydroxides was estimated using concentration factors CFs (i.e. CF: $\{Pb\}_A/\{Fe\}_A$; μmol g^{-1}/g g^{-1}) which normalize the amount of Pb bound to the easily reducible "amorphous oxyhydroxides" phase $\{Pb\}_A$ (Table 3.2) to the concentration of Fe within the easily reducible "amorphous oxyhydroxides" phase $\{Fe\}_A$ (Table 3.2). The significant positive correlation between floc $\{Fe\}_A$ CFs and floc Pb Kds (not observed for amorphous $\{Mn\}_A$ i.e. $\{Pb\}_A/\{Mn\}_A$) indicate that Pb retention within floc is specifically determined by floc FeOOH scavenging ability and that this scavenging ability increases with increasing pH, consistent with cationic Pb interactions with increasingly negatively charged amorphous Fe oxyhydroxides. Consistent with floc results observed for other trace elements (As, Elliott et al., 2012 and Ni, Co, Cu, Plach et al., 2011), reactivity of FeOOH controlling floc Pb uptake appears linked to the living floc NOM (i.e. live microbial cells and associated EPS fibrils) which act as organic frameworks for trapping and/or precipitating FeOOH (Figure 3.2B). Similarly, Taillefert et al. (2000) reported a significant correlation between limnetic particulate organic matter, hydrous iron oxides, and particulate Pb, which also suggested that Pb scavenging was linked to the formation of suspended Fe-rich EPS aggregates. In fact, floc in this study containing higher {OC} also displayed greater FeOOH scavenging efficiency for Pb (i.e. CFs) and overall higher total floc Pb uptake (i.e. Kds).

Consistent with the important role of floc-FeOOH in floc Pb retention, assessment of floc solid-phase Pb partitioning indicated that the amorphous oxyhydroxides phase retained the largest proportion of floc Pb, up to 82% (Table 3.2), similar to findings of

Stecko and Bendell-Young (2000) where the greatest proportion of Pb was generally bound to the easily reducible SPM-fraction. In contrast, results observed for the surficial sediments in these systems indicate site specific Pb solid-phase partitioning, with no single substrate consistently accounting for the majority of $\{Pb\}_T$ (Table 3.2). Results of this study provide broader evidence across a range of aquatic systems to support the premise of previous floc studies (Plach et al., 2011; Elliott et al., 2012), namely that floc comprises a distinctly different solid compartment than bed sediments in aquatic systems, whereby controls on trace element uptake are linked specifically to living floc NOM components (i.e. cells and EPS) which drives floc FeOOH concentrations, the key floc trace element sequestration phase.

The field results indicate NOM plays an important role on Pb behavior across a physico-chemical spectrum of aquatic ecosystems (i.e. wetland, stream and lakes) and aquatic compartments (i.e. water-column, bed sediments and suspended floc). The observed pH driven effects on sediment Pb solid-solution partitioning depend on DOC, while the unique microbial nature of floc NOM likely conserve floc Pb partitioning patterns through accumulation of Pb reactive FeOOH. Intrinsic hydrologic linkages between wetland-stream-lake ecosystems in the natural environment indicate that Pb mobility/transport through catchments will depend on differential processes impacting NOM abundances/reactivity within each aquatic compartment.

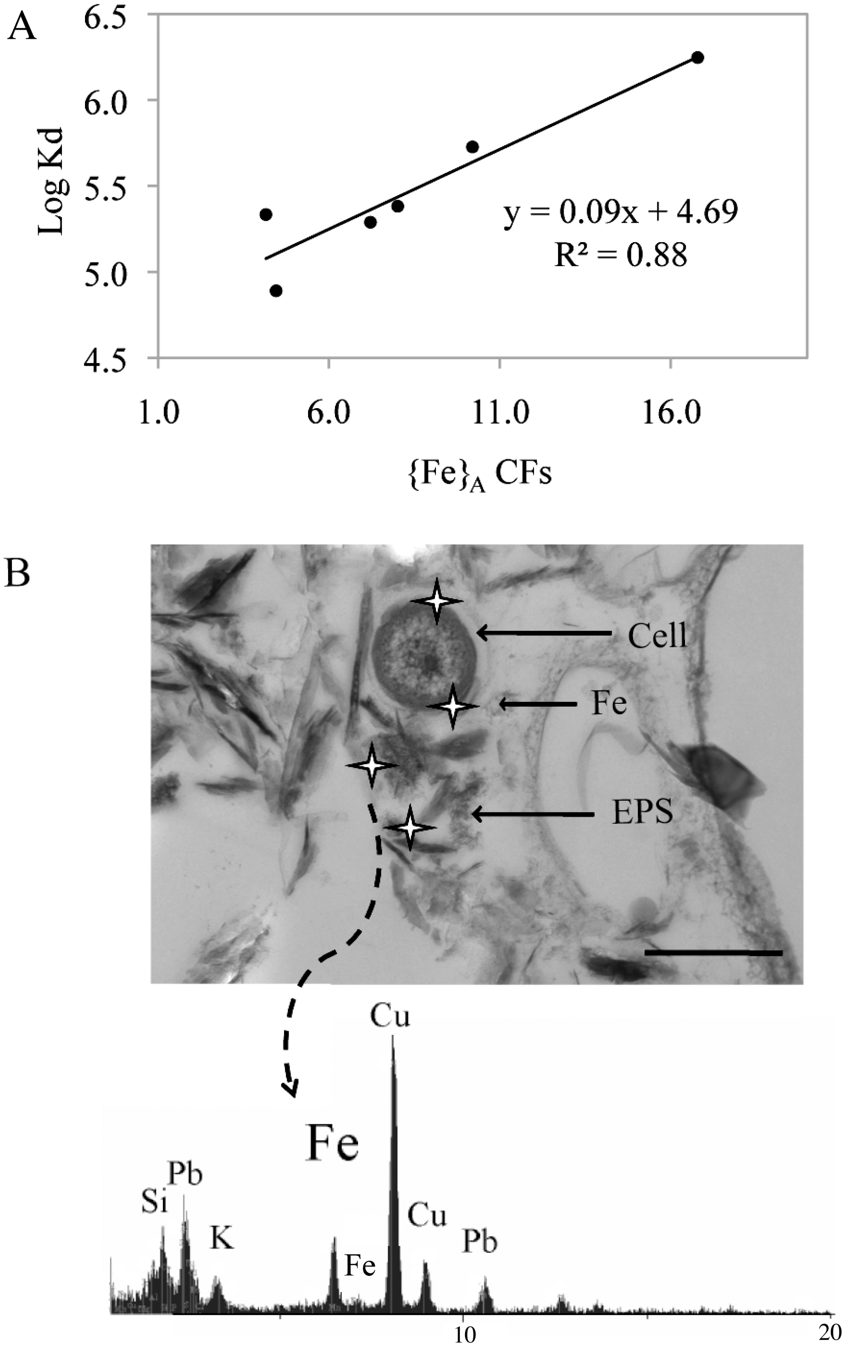


Figure. 3.2 (A) Floc Pb distribution coefficients (Kds; L kg^{-1}) and floc amorphous Fe oxyhydroxide concentration factors $\{Fe\}_A$ CF (μmol g^{-1}). (B) TEM-EDS of in situ collected floc showing Fe associated with cells and EPS material. Scale represents 500 nm. Peaks of Pb and Cu are an artifact of sample preparation.

3.3.2 Laboratory results

3.3.2.1 Sediment Pb–DOC mobility

The field-based results identified a strong pH effect on bed sediment Pb dynamics that is more consistent with organo-Pb complexes, rather than cationic Pb species, dominating Pb species in organic rich sediments. Organic carbon concentrations and pH are commonly correlated in systems, i.e. wetlands are highly organic rich and often lower in pH, while many lakes are more circumneutral and organic poor relative to wetland systems confounding field assessment of the individual effects of pH and organic carbon concentration on Pb behavior. Therefore, experiments were designed to specifically assess the impacts of pH on surficial sediment and floc Pb and DOC behavior across a spectrum of wetland, stream and lake environments. In order to confirm our hypothesis that Pb solid-solution behavior is linked to organo-Pb complexes in organic sediments, experiments investigated both Pb and DOC release from sediment (four sites) and floc (two sites) ranging in both NOM and Pb concentrations (Table 3.2), assessing $[Pb]_D$ and [DOC] (within the same size fraction <0.2 μm) over a suite of pH values 5, 6, 6.5, 7 and 8 that encompass potential shifts in solid surface net charge (i.e. Fe oxyhydroxides) as well as the pH range of the study sites.

In the experimental batch systems, release of sediment DOC and Pb was observed with increasing pH in the three organic rich lake, stream and wetland sediment samples (Figure 3.3A & B). For example, solution [DOC] and $[Pb]_D$ were ~3 and 5 times greater at pH 8 compared to pH 5, respectively for the stream bed sediment (organic rich) experimental system. These experimental results indicate (1), that some fraction of Pb in these surficial sediments forms stable complexes with negatively charged organic molecules and (2), these anionic, organo-Pb complexes can be mobilized from sediments with increasing pH, suggesting sorption behavior is important in their bed sediment uptake.

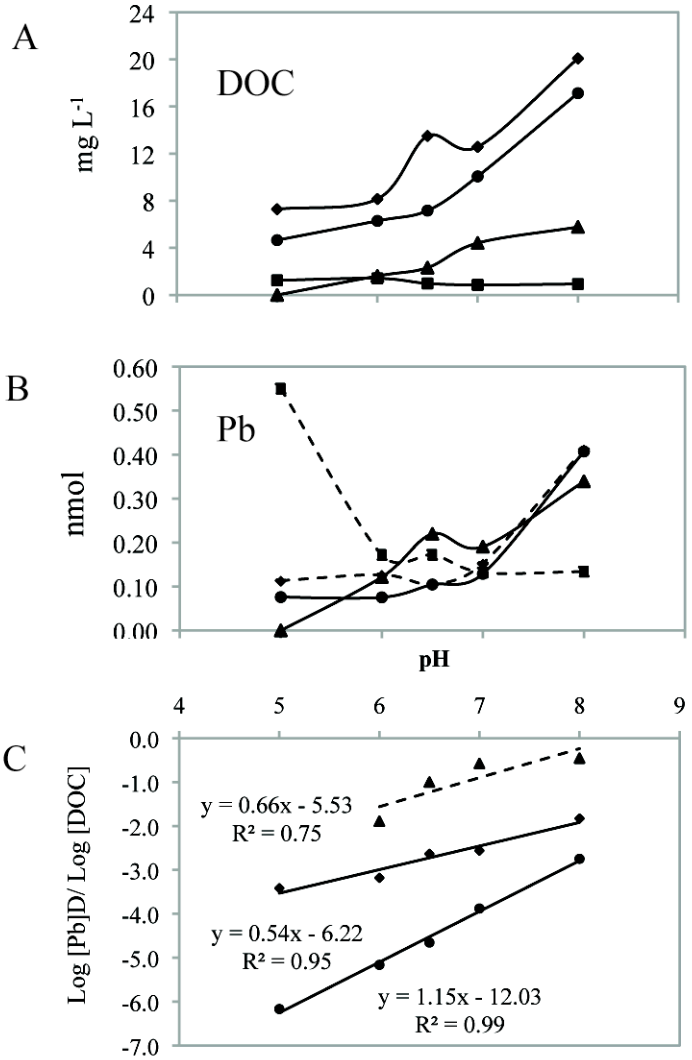


Figure 3.3 (A) Aqueous Pb $[Pb]_D$ and (B) dissolved organic carbon [DOC] release (per gram dry weight) as a function of pH for organic rich (Δ wetland {OC}=0.76 g g^{-1}); (● streambed {OC}=0.32 g g^{-1}); (◆ lake sediment {OC}=0.64 g g^{-1}) and organic poor (■ lake sediment {OC}=0.01 g g−1). (C) Ratio $\log[Pb]_D/\log[DOC]$ (μmol g^{-1}/mg L^{-1}) estimates relative mobility of Pb–DOC complexes. Only four ratio points were generated for the wetland (Δ) since no DOC release at pH 5. For each panel (— – –) values/5, (– – –) values/10, (- - -) values/50.

The observed correlation between DOC and Pb in the 3 organic rich experimental systems is consistent with the known high affinity of DOC for Pb compared to other cationic trace metals (e.g. Cu, Zn, Ni, Beveridge and Pickering, 1980; Giesy, 1983; Gao et al., 1999). Peat derived humic acids have one of the highest reported stability constants for Pb among transition metals (Gao et al., 1999) which suggests wetland peat sediments may display the largest DOC affinity for Pb and have the greatest influence on Pb mobilization compared to sediments of other aquatic ecosystems (e.g. limnetic). This hypothesis was assessed by comparing the slopes of the regressions of $[Pb]_D$ to [DOC] (i.e. mobility rate of Pb–DOC complexes; the higher the slope, the greater the release of Pb–DOC complexes per unit increase in pH) from the three organic rich Algonquin sediment samples across pH treatments (Figure 3.3C). Results are consistent with this notion, the highest slope (6.61) was observed for the most organic rich wetland sediments, followed by the wetland-draining streambed (1.15) and surficial lake sediments (0.54). Further, Pb-partitioning results indicate that the wetland sediment sample had the largest exchangeable fraction (i.e. loosely bound Pb) of these 3 sediment batch treatments at 9% (Table 3.2) that we suggest reflects a greater proportion of soluble organo-Pb complexes. Together, these results indicate that wetlands may be dynamic source environments for mobile organo-Pb complexes with shifting water-column pH, and that not only hydrological mechanisms but also in situ physico-chemical processes (e.g. diel photosynthetic driven pH cycles) may contribute to DOC and associated $[Pb]_D$ export to downstream river and lake ecosystems. This has important implications for wetlands in the context of watershed carbon and trace element biogeochemistry, particularly for the Canadian Boreal forest region that is a major global carbon pool containing the world's largest density of wetland, river and lake ecosystems (Lehner and DÖll, 2004).

Although higher pH facilitated DOC and Pb mobilization from the three organic rich sediments (Algonquin ON) in the batch experiments, results for the organic poor sediments (Lake Ontario) showed no correlation between pH and [DOC], or $[Pb]_D$ and

[DOC]. In fact, $[Pb]_D$ decreased with higher solution pH (Figure 3B), indicating that the formation of organo-Pb complexes is not important for Pb mobilization from NOM-poor sediments. Rather, Pb desorption with decreasing pH is more consistent with charge repulsion of positive cationic Pb species (i.e. Pb^{2+} or $PbOH^+$) at oxides/clay/organic surfaces within the sediment matrix. These experimental results identify that within NOM-rich aquatic environments (i.e. wetlands), DOC plays a critical role in Pb behavior through the formation of stable organo-Pb complexes; while within NOM-poor environments downstream (e.g. lacustrine littoral beaches), Pb solid-solution partitioning is more reflective of typical cationic sorption behavior (Summary Figure S.3.2).

3.3.2.2 Floc Pb–DOC sorption experiments

While results indicated that DOC facilitated bed sediment Pb mobilization with pH, experimental floc Pb mobility was found to be independent of DOC concentrations. Results for the floc experimental systems (Brewer Lake (high [DOC])) and Lake Ontario (low [DOC])) revealed that increasing pH inhibited Pb mobilization and resulted in negligible DOC release for both systems (Table 3.3). For example, $[Pb]_D$ released by Brewer Lake floc was more than 2 times greater at pH 5 compared to pH 8. These results suggest that Pb is not retained within floc as mobilizable organo-Pb complexes (as would be predicted based on [DOC]). These experimental findings are consistent with the sequential extraction results identifying no exchangeable Pb for floc in any of the study sites, in contrast to the surficial bed sediments where an exchangeable fraction (up to 9%) was often present (Table 3.2). However, these results do not conclusively rule out the possibility of organo-Pb complex scavenging by metabolically active floc. Organo-Pb complexes would represent a highly labile and accessible NOM source to floc heterotrophs. We hypothesize that if scavenged by floc, heterotrophic consumption of DOC from sorbed organo-Pb complexes would result in cationic Pb release and potential scavenging by floc FeOOH. Thus, the living microbial nature of floc NOM may help explain the lack of any exchangeable Pb, and the dominance of amorphous oxyhydroxides on floc Pb sequestration, observed in the field floc results.

Table 3.3 Pb and DOC release as function of pH for floc collected from OC rich (Brewer L.) and OC poor (L.ON) environment.

pH	Brewer Lake	Lake Ontario
	Pb ($nmolg^{-1}$)[a]	
5	1.2	5.3
8	0.5	2.6
	DOC (mgL^{-1})[a]	
5	15	31
8	13	32

[a] 1 standard deviation Pb= 10^{-2} and DOC= 10^{-1}

Further, the observed relative scavenging efficiency of floc FeOOH supports the importance of FeOOH for floc Pb sequestration. Floc $\{Fe\}_A$ CF were the most important control on floc Pb uptake observed in situ (Figure 2A) and were also linked to observed floc Pb mobilization with pH in the experimental floc batch treatments. For example, field results indicated that Lake Ontario floc had a higher $\{Fe\}_A$ scavenging efficiency (CF=10.7) than Brewer Lake floc (CF=7.2) which also corresponded to more efficient Pb uptake as indicated by 2.7 nmol g^{-1} Pb uptake (between pH 5–8) by Lake Ontario floc compared to 0.7 nmol g^{-1} of Brewer Lake floc in the experiments. Further investigation into potential biogeochemical processes occurring at the floc micro-scale influencing the scavenging efficiency of floc FeOOH (e.g. microbial induced redox gradients (Norlund et al., 2009) and/or pH differences) would enhance understanding of the potential role floc microbial ecology plays in floc specific Pb geochemistry.

3.4 Conclusion

Results of this combined field and laboratory study demonstrate that the high affinity of NOM for Pb imparts a significant control on Pb dynamics within each aquatic compartment (water-column, surficial sediments and suspended floc) across natural wetland, stream and lake freshwater ecosystem types. Soluble, stable organic complexes dominated aqueous Pb species in NOM-rich systems and were responsible for significant Pb mobility from surficial sediments in these environments. Laboratory batch sorption experiments confirmed field observation of a pH dependent release of DOC and Pb from NOM-rich sediments, whereby the greatest mobilization rate occurred within the wetland sediment. Results suggest stable organo-Pb complexes occur within natural aquatic organic sediments, similar to terrestrial organic soils, and that pH can mobilizes these anionic Pb complexes, most effectively from NOM-rich wetland sediments, in the exact opposite manner expected to that of cationic Pb observed by NOM-poor sediments. Thus, in addition to known hydrological mechanisms, pH may also plays an important role driving DOC and Pb export from wetland environments.

In contrast, field and experimental floc Pb behavior showed no evidence of stable organo-Pb complexes occurring in floc and a pH dependent Pb solid-solution behavior that was most consistent with cationic Pb species. While overall solid-phase Pb partitioning of bed sediments was site-specific, a conserved amorphous FeOOH was shown to be the best predictor of floc Pb uptake, independent of bulk physico-chemical conditions across sites. In contrast to the refractory nature of sediment NOM, suspended floc NOM is predominantly living cells and EPS. These results indicate that even if DOC trace element complexes, such as organo-Pb, are scavenged by floc, they are likely rapidly processed by heterotrophic metabolism, releasing cationic Pb which may then be scavenged by floc FeOOH. Our results demonstrate that establishing the processes impacting NOM abundance/reactivity within suspended floc versus bed sediments is imperative for understanding migration of Pb through surface–water catchments between upstream NOM-rich wetlands to downstream NOM-poor lake ecosystems.

3.5 Supporting Information

Table S.3.1 Bulk mineralogical composition floc and surfical bed sediments (Siemens d5005 x-ray diffractometer)

	Algonquin Park, ON						*Urbanized Region, Southern ON*					
%	Brewer Lake Site 1(2009)		Brewer Lake Site 1 (2008)		Coldspring Lake (2009)		Sunnyside Beach, L. ON (2008)		Sunnyside Beach, L. ON (2009)		Agricultural Stream, Guelph (2008)	
	Floc	Bed	Floc	Bed	Floc	Bed	Floc	Bed	Floc	Bed	Floc	Bed
Magnetite	2	3		3	1	1	1	1	1	3		
Quartz	7	11	25	30	1	29	14	26	21	14	32	31
Calcite		2					13	12	17	15	15	13
Anorthite/albite	6	12	22	20	1	22	19	18	11	24	20	19
Microcline	3	4	5	7		8	7	7	4	5	6	6
Mica	2	3		5		4			5			
Dolomite/ankerite	2	3					8	9	4	4	6	18
Chlorite/Chloride	1			4			11	9	4		3	3
Amphibole	2	4	2	7	1	2	2	2	3	2		
Smectite	2			4	1				6			
Gypsum				2								
Bassanite	1		1						2			
Anhydrite			3	2								
NaCl			2									
Zeolite 2(KAlSiO4).3H2O												
Illite							12	10			5	3
Amorphous	6	6	7	6	6	6	5	4	5	4	5	4
Kaolinite		3										
Pyrite	5	2										
Hematitie					1	4						
Talc						2						
Ankerite									1			

Table S.3.2 Comparison of DOC analysis methods

Method	DOC (<0.45μm)
UV-persulfate TOC analyzer	21.5 ± 0.4 mg L^{-1}
Colorimetrically (Moore, 1985)	26.7 ± 0.8 mg L^{-1}

values are means (n=3) and ± 1 standard deviation

Pb Speciation Modeling

Pb speciation at each sampling site was modeled in Visual MINTEQ (Gustafsson, J. P., 2011). The following water-column parameters were used to formulate input files; pH, temperature, DIC, DOC, $[Fe]_D$ and $[Pb]_D$ (see Table 3.1). Total concentration of cations (Ca^{2+}, K^+, Mg^{2+}, Na^+; Table S.3.3) and anions (Cl^-, SO_4^{2-}; Table S.3.3) at location of floc collection were included in input parameters for those sites (Brewer Lake 2008 and 2009, Coldspring Lake 2009, Lake Ontario 2008 and 2009, agricultural stream 2008). Default model paramaters were used for the Gaussian DOM model at all sites (Table S.3.4).

Table S.3.3 Major cations and anions at sites of floc collection

Site of floc Collection	Ca^{2+} (mg L^{-1})	K^+ (mg L^{-1})	Mg^{2+} (mg L^{-1})	Na^+ (mg L^{-1})	Cl^- (mg L^{-1})	SO_4^{2-} (mg L^{-1})
Algonquin Park, ON						
Brewer Lake Site 1 (2008)	3.82	0.52	0.93	23.6	38	5.47
Brewer Lake Site 1 (2009)	2.64	0.42	0.72	14.4	22	4.63
Coldspring Lake (2009)	3.54	0.44	1.04	0.89	0.19	2.05
Urbanized Region, Southern ON						
Sunnyside Beach, Lake Ontario (2008)	37.4	1.84	8.91	23	40.3	28.3
Sunnyside Beach, Lake Ontario (2009)	35.9	1.69	8.86	15.6	26.5	26.4
Agricultural Stream, Guelph (2008)	88.7	2.63	25	25.5	50.8	16.3

Table S.3.4 Gaussian DOM model parameters

Parameter	Value
DOM Component	DOM1
DOC Concentration	varied
Fixed Database Values	selected
Speciation Based Values	unselected

Table S.3.5 Summary of Pb species and percent (%) total $[Pb]_D$ modeled in Visual MINTEQ (only species >1% abundance shown).

Ecosystem Type	Site	Pb Species	% of total concentration
LAKE	Brewer Lake Site 1 2008	Pb DOM	68.4
		Pb^{+2}	28.6
		$PbSO_4$ (aq)	1.6
	Brewer Lake Site 1 2009	Pb DOM	74.7
		Pb^{+2}	23.2
		$PbSO_4$ (aq)	1.2
	Brewer Lake Site 2 2009	Pb DOM	89.1
		Pb^{+2}	10.8
	Coldspring Lake 2009	Pb DOM	78.1
		Pb^{+2}	20.3
	Costello Lake 2009	Pb DOM	91.8
		Pb^{+2}	8.1
	Lake Ontario 2008	PbCO3 (aq)	34.3
		Pb^{+2}	31.0
		$PbOH^+$	16.3
		Pb DOM	6.5
		$PbSO_4$ (aq)	6.5
		$PbHCO_3^+$	4.1
	Lake Ontario 2009	$PbCO_3$ (aq)	34.8
		$PbSO_4$ (aq)	22.2
		$PbOH^+$	17.1
		Pb^{+2}	16.6
		Pb DOM	5.0
		$PbHCO_3^+$	2.3
		$Pb(SO4)_2^{-2}$	1.0
WETLAND	Brewer Wetland 2009	Pb DOM	99.5
	Coldspring Wetland 2010	Pb DOM	98.5
		Pb^{+2}	1.4
	Cache Wetland 2010	Pb DOM	98.8
STREAM	Costello Creek 2009	Pb DOM	99.4
	Costello Creek 2010	Pb DOM	97.9
		Pb^{+2}	2.0
	Agricultural Stream 2008	$PbCO_3$ (aq)	53.2
		Pb^{+2}	19.4
		$PbOH^+$	9.3
		$PbHCO_3^+$	8.3
		Pb DOM	7.1
		$PbSO_4$ (aq)	1.7

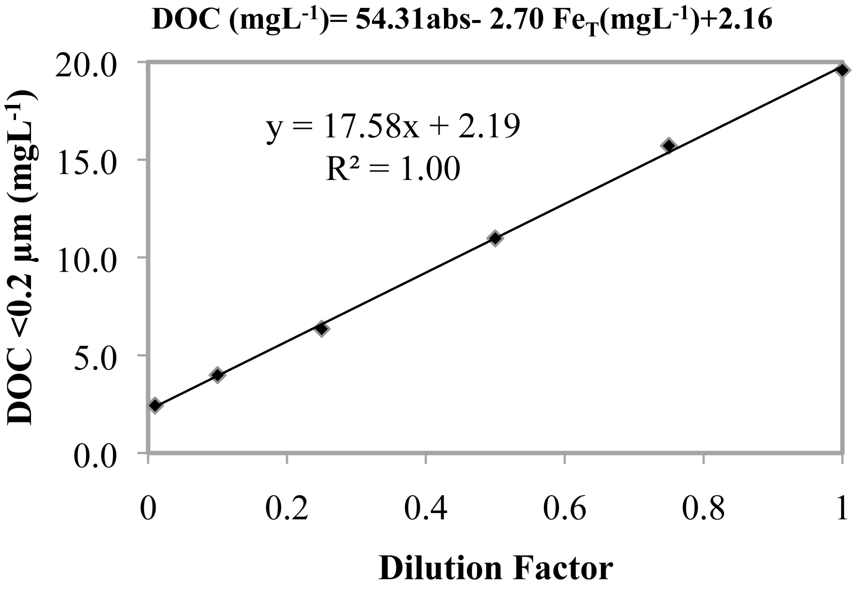


Figure. S.3.1 [DOC] measured colorimetrically of Coldspring wetland 2010 water sample.

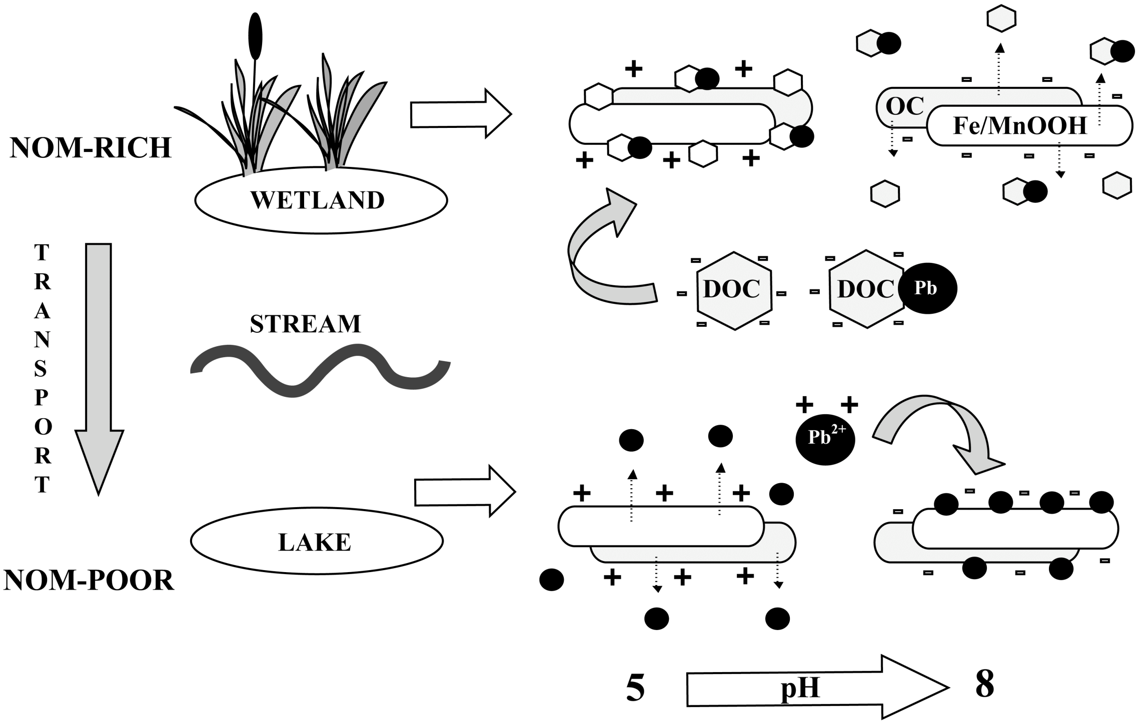


Figure S.3.2 pH driven solid-solution partition of DOC, DOC-Pb complexes and Pb^{2+} across variability NOM-rich aquatic ecosystems. Rising pH promotes de-sorption of DOC and DOC-Pb complexes from NOM-rich sediments in contrast to Pb^{2+} sorption into NOM-poor sediments.

3.6 Acknowledgments

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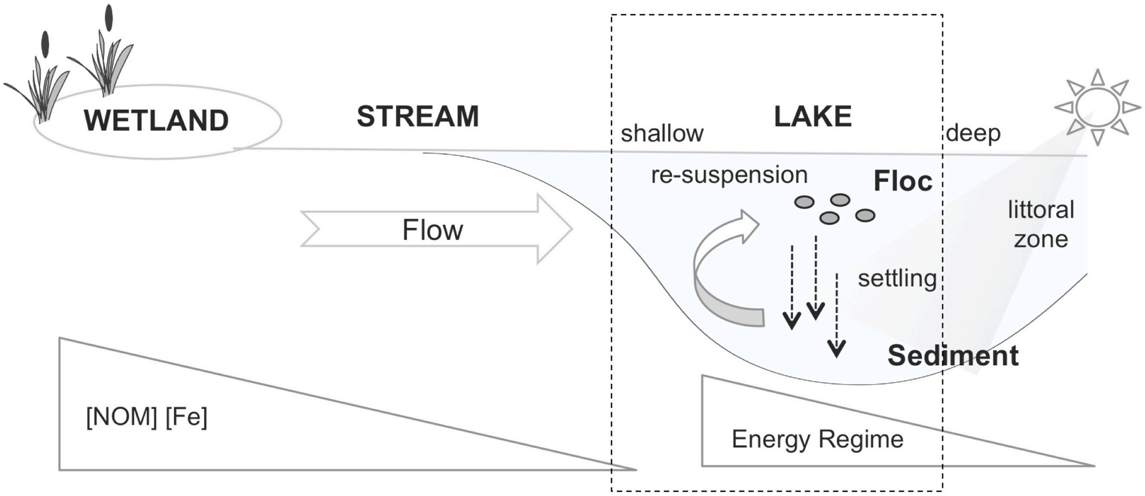
CHAPTER 4: PHYSICAL AND ECOLOGICAL CONTROLS ON FRESHWATER FLOC TRACE METAL DYNAMICS



CHAPTER 4: PHYSICAL AND ECOLOGICAL CONTROLS ON FRESHWATER FLOC TRACE METAL DYNAMICS

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4.1 Abstract

Significantly higher concentrations of Ag, As, Cu, Co, Ni, and Pb are found in suspended floc compared to surficial bed sediments for a freshwater beach in Lake Ontario. Contrasting observed element-specific bed sediment metal partitioning patterns, floc sequestration for all elements is dominated by one substrate: amorphous oxyhydroxides. More specifically, floc metal scavenging is controlled by floc biogeochemical architecture. Floc organics, largely living microbial cells and associated exopolymeric substances (EPS), act as scaffolds for the collection and/or templating of amorphous Fe oxyhydroxides. While interactions between floc organics and amorphous Fe oxyhydroxides affected floc sorption behavior, specific element affinities and competition for these limited substrates was important for overall floc partitioning. Further, assessment of metal dynamics during stormy conditions indicated energy-regime driven shifts in floc and bed sediment partitioning that were specifically linked to the exchange of floc and bed sedimentary materials. These novel results demonstrate that the microbial nature of floc formation exerts an important control on floc metal dynamics distinguishable from surficial bed sediments and that hydrodynamic energy-regime is an important factor to consider in overall floc metal behavior, especially in beach environments.

4.2 Introduction

Trace metal behavior in aquatic environments is controlled by dynamic interactions between aqueous and sedimentary compartments that reflect interactive environmental, substrate, and element specific influences. While many studies have assessed metal abundance and substrate associations in bed sediments (e.g., refs 1), few have investigated suspended floc metal dynamics.

Aquatic floc is a complex aggregate of fine-grained inorganic particles (e.g., clays, oxyhydroxide minerals, carbonates) held together by a network of extracellular polymeric substances (EPS) generated by floc-associated biological communities (e.g., bacteria, algae, fungi).[2,3] These suspended microbial microecosystems constantly interact with the surrounding watercolumn sequestering nutrients, organic material (e.g., detritus, humic and fulvic acids), and chemicals for development and growth.[2] Floc comprises the majority of suspended particulate matter (SPM) in aquatic environments[3] enabling comparison of our floc results with those determined for "SPM" referred to elsewhere in the literature. Although floc has been shown to be a significant metal sorbent,[4,5] its metal dynamics relative to bed sediments has not been assessed to date.

Microorganisms and associated EPS are important metal sorbents with the potential to significantly influence trace metal behavior (mobility, bioavailability, and toxicity) and contaminant cycling in the environment.[6,7] Internal redox gradients, within the diffusive microenvironment of floc,[8] may facilitate microbial catalysis of redox sensitive mineral precipitation-dissolution reactions (i.e., Fe/Mn oxides[9,10]) that could profoundly affect metal cycling, similar to sulfur redox cycling observed in other environmental microbial consortia.[11] Fe and Mn oxyhydroxides are well recognized to influence metal behavior in the environment.[12] Oxyhydroxides are ubiquitous in aquatic systems and tend to precipitate as surface coatings on other minerals and organic material including bacterial surfaces.[13,14] These minerals typically exist as nanoparticulates that have large surface areas relative to their volume resulting in considerable metal scavenging.[15] Although Fe/Mn oxyhydroxides and organic matter are both highly effective metal scavengers, these reactive substrates typically coexist and interact resulting in collective impacts on metal cycling, interactions that will be especially important within suspended floc. The underlying microbial nature of floc formation, its differing substrate composition, and its suspension within the water-column collectively suggest that floc metal abundances and partitioning will differ from that observed within bed sediments.

Further, interactive exchanges between suspended floc and bed sediment compartments driven by energy-regime will affect solution and sedimentary compartment metal dynamics and are likely to be particularly important in shallow beach environments. The role of sediment remobilization on floc metal concentrations has been investigated within marine coastal sediments (e.g., refs 16). However, very little is known about temporal chemistry and in situ metal partitioning of floc and its interactions with bed sediments within freshwater beach environments where the potential remobilization and exchange of contaminants may significantly degrade water quality and increase risk to aquatic organisms and public health.[17,18] While it is well-known that the energy-regime mediates interactions between suspended floc (i.e., SPM) and bed sediment compartments,[19] the subsequent fate of metal contaminants associated with any exchange of sedimentary reactive constituents in freshwater aquatic systems remains undescribed.

The objectives of this field based study were to determine 1) metals Ag, Cu, Co, Ni, Pb, and metalloid As concentrations (collectively referred to as metals from here on) within suspended floc, bed sediment, and water-column aqueous compartments and 2) important reactive solid-phases for metal sequestration in suspended floc and bed sediment compartments under variable energy-regimes specifically within an urban freshwater beach.

4.3 Materials and Methods

4.3.1 Study Site/Sampling Protocol

The study site, Toronto Sunnyside Beach, is an erosive manufactured sandy beach located on the north shore of Lake Ontario, Canada (43°3802100N, 079°270210W); an urbanized region of more than 5 million people. The sampling campaign was designed to investigate temporal trends of suspended floc and bed sediment metal concentrations with associated geochemistry. In situ water-column measurements and sample collection occurred ~10 m from the shoreline on four sampling days under varying hydrodynamic conditions: July 21, 2009 (Calm-1), May 13, 2009 (Calm-2), May 14, 2009 (Storm), and May 13, 2008 (Post-Storm). For the purpose of this study, conditions at the beach were considered 'calm' when average and maximum wind speeds were less than 26 Km h^{-1}.[20] Mean and range of wind speeds on each sampling day and 48 h prior are outlined in Table S.4.1, Supporting Information. Geochemical characterization and sample collection involved 1) in situ physicochemical profiling (°C, pH, O_2, and specific conductivity; Datasonde-Surveyor 4A, Hydrolab Corporation, TX) of the 1.2 m deep water-column; 2) collection of bed sediment (diver retrieved cores) and bulk floc (continuous field flow centrifugation (CFC), 0.5 m above sediment-water interface) for solid-phase metal analysis and mineralogy; 3) diver retrieved plankton chambers[21] used to collect floc from the same depth for ultrastructural imaging; and 4) collection of water samples (0.5 m above bed) for dissolved metal analysis and dissolved inorganic and organic carbon (DIC/DOC).[22]

4.3.2 Water-Column Collection/Analysis

All sampling equipment and sample containers for trace metal analysis were prepared by soaking in 10% (v/v) HCl for >24 h followed by eight rinses with ultra pure water (18.2Ωm cm-1, Mili-Q, Millipore). Water samples for dissolved metal analysis were collected into acid washed syringes from an acid washed van dorn water sampler, filtered serially through a 0.45 and 0.2 μm sterile inline syringe filters and subsequently preserved with trace metal grade (TMG) HNO3 to 2% v/v (Fisher). Field blanks were collected by flushing ultra pure water through an acid washed van dorn as well as serially syringe filtering (Acrodisc 0.45 and 0.2 μm) and acidifying ultra pure water during each sampling period. Samples were kept in the dark and stored at 4 °C until analysis. Dissolved metal (<0.2 μm) concentrations $[M]_D$ were quantified by inductively coupled plasma mass spectrometry (ICP-MS (Ag, As, Cu, Co, Ni, Pb) PerkinElmer SCIEX ELAN 6100, Woodbridge, ON, Canada). $[M]_D$ are summarized in Table S.4.1, along with procedural limits of quantification. Field blank analysis indicated no contamination for all elements. Unfiltered iron [Fe] was determined colorometrically using the FerroVer HACH method (Ultrospec 2000, UV/visible spectorophotometer, Pharmacia Biotech, Cambridge, U.K.). DIC/DOC samples were analyzed using a UV-persulfate TOC analyzer following the methods at the National Laboratory for Environmental Testing (NLET) Environment Canada (2009).

4.3.3. Floc Collection

Bulk suspended floc was collected using a continuous flow centrifuge (CFC, Westfalia Model KA). Water (>2000 L) was pumped (6 L min^{-1}) into stainless steel bowls, preleached with 10% EDTA solution prior to collection, with a rotational speed of 9470 rpm where >90% of the floc was recovered (assessed by weight comparison of CFC inflow and outflow filtered water samples on glass-fiber Whatman filters following the standard method 2540D23) and placed into acid clean 50 mL Falcon tubes. Floc samples were collected over 6-8 h 0.5 m above the sediment-water interface. Although centrifugation may facilitate colloid aggregation, unfiltered centrifuge inflow and outflow [M] showed no differences for detectable elements in solution (As, Co, Cu, Ni, Pb; $p < 0.05$), indicating no significant CFC associated colloidal artifacts were induced.

4.3.4. Bed Sediment Collection

Bed sediments were collected in acid washed polycarbonate core tubes (6 cm diameter, 45 cm length) and capped underwater by SCUBA divers to the keep sediment water-interface intact and to retain pore waters. Cores were collected within the vicinity but downstream of the CFC inflow to minimize sediment disturbance. Sediment cores were immediately extruded onshore and subsamples collected from the surface (0-0.5 cm) and mid core (5-7 cm) were immediately frozen on dry ice and stored at -20 °C until analysis. All bed sediment samples were composed of >98% sand sized particles on each sampling campaign and likely well-aerated at these surficial depths.[24]

4.3.5. Solid-Phase Sediment Metal Analysis

Floc and bed sediment samples were processed using a modified Tessier sequential extraction method using microwave digestion that distinguishes between amorphous and crystalline oxides.[25] Samples were homogenized prior to digestion and run in triplicate. Sediment associated metals were partitioned into six operationally defined sediment fractions: exchangeable (loosely bound); carbonates; amorphous Fe/Mn oxyhydroxides (easily reducible); crystalline Fe/Mn oxides (reducible); organics/sulfides (oxidizable); and residual (concentrated HNO_3 digestion). Reagents blanks were included during digestion to correct for procedural contamination. Matrix effects associated with ICP-MS were corrected using matrix-matched standard curves. Mean total floc and bed sediment metal concentrations $\{M\}_T$ (μmol g^{-1} dry weight) were determined by summing metal concentrations from the six sediment fractions. Variation in relative aqueous metal sorption by bulk floc was assessed by relative solid-solution distribution coefficients (Kd)

$$Kd = \{M\}_T/\{M\}_D \qquad (1)$$

where $\{M\}_T$ is the total metal concentration (mol kg^{-1}) within the bulk sediment, and $[M]_D$ is the dissolved metal concentration (mol L^{-1}) within the water-column.[26] Bed sediment porewater concentrations were not available, thus Kds for the surficial bed sediments were not calculated for comparison. $[M]_D$ below detection on particular sampling periods were assigned the limit of quantification to generate Kds (Co, Pb; Table S.4.1). $[Ag]_D$ was consistently below detection limits, thus no floc Ag Kds were calculated.

4.3.6. Statistical Analysis

All statistical analyses were performed using PASW version 18.0 (SPSS Inc., Chicago, Illinois, U.S.A). Multiple linear regression analysis identified the main variables influencing $\{M\}_T$ (floc and bed), metal concentration within individual solidphase fractions, and $[M]_D$. T-tests were applied to test for significant differences of mean $\{M\}_T$ between floc and surfical bed sediment. Unless otherwise indicated, for all statistical tests a sample size of n = 6 and a significance level of R = 0.05 was applied.

4.3.7. Sediment Composition

Mean sediment weights were determined by drying (80 °C) triplicates of sediment samples until consistent weight. Mean bulk organic content {OM} of floc/ sediment samples was estimated by loss on ignition (%LOI, 550 °C 2 h) and carbonate content {carbonate} estimated by further heating (%carbonates, 950 °C 1 h). Total extracted Fe and Mn from extraction steps 3 and 4 (Fe quantified by colorimetric analysis; Mn quantified by ICP-MS) were used to estimate the concentration of amorphous Fe/Mn oxyhydroxide $\{Fe\}_A/\{Mn\}_A$ and crystalline Fe/Mn oxide $\{Fe\}_C/\{Mn\}_C$ substrates, respectively. The relative metal scavenging efficiency of each specific sediment substrate was assessed through calculation of concentration factors CF

$$CF = \{M\}_{\text{sediment fraction}}/\{\text{substrate}\} \qquad (2)$$

where {M} sediment fraction is the metal concentration (µmol g^{-1}) within a specific sediment fraction, and {substrate} is the estimated concentration of that substrate within the bulk sediment (g g^{-1}).

X-ray diffractometry (XRD) was used to determine bulk mineralogical composition of floc and bed sediments (Siemens D5005 X-ray diffractometer). Bulk XRD analysis identified the main crystalline components of both floc and bed sediments as silicates (quartz and albite) and calcite minerals on each sampling campaign.

4.3.8 Microscopy

Diver retrieved plankton chambers samples were prepared following a 4-fold multistep technique to enhance visualization of cells and EPS material[8] for ultrastructure using transmission electron microscopy (TEM). Ultrathin sections were imaged in transmission mode at an accelerated voltage of 80 kV using a JEOL 1200 Ex II TEMSCAN scanning transmission electron microscope. Floc and bed sediment microbial viability was assessed using the LIVE/DEADBacLight nucleic acid staining technique. Bulk floc and sediments (~10 mg) were resuspended in 1 mL of 0.085% NaCl solution, and 0.5 μL of LIVE/DEAD BacLight staining solution was added to the mixture, incubated for 15 min in the dark and spotting on gelatin-coated slides [0.25% gelatin and 0.01% $KCr(SO_4)_2$]. Slides were viewed using Leica LEITZ DMRX epifluorescence microscope equipped with an HBO 100-W mercury arc lamp [Leica Microsystems (Canada), Richmond Hill, ON] equipped with 525/50, 645/75 nm barriers and 470/40, 560/40 nm excitation filters.

4.4 Results and Discussion

(A). Suspended Floc and Bed Sediment Metal Dynamics

Suspended floc metal concentrations $\{M\}_T$ were significantly higher than those of bed sediments for all elements analyzed during four sampling campaigns (Table 4.1) despite their close proximity (floc collected here <0.5 m above bed). Mean floc $\{M\}_T$ ranged across the six elements analyzed (four sampling campaigns) from Cu (highest observed concentrations) to Ag (lowest observed concentrations): $\{Cu\}_T$ (1.0 µmol g^{-1}) > $\{Ni\}_T$ (0.58 µmol g^{-1}) > $\{As\}_T$ (0.23 µmol g^{-1}) > $\{Pb\}_T$ (0.20 µmol g^{-1}) > $\{Co\}_T$ (0.17 µmol g^{-1}) > $\{Ag\}_T$ (0.01 µmol g^{-1}) exceeding provincial sediment quality guidelines (SQG) at the lowest effect level as well as natural Great Lake background levels for metals.[27] In contrast, surficial bed sediment mean $\{M\}_T$ did not exceed SQG: $\{Ni\}_T$ (0.12 µmol g^{-1}) > $\{Cu\}_T$ (0.06 µmol g^{-1}) > $\{As\}_T$ (0.04 µmol g^{-1}) > $\{Co\}_T$ = $\{Pb\}_T$ (0.03 µmol g^{-1}) > $\{Ag\}_T$ (0.003 µmol g^{-1}). Floc thus concentrated metals 4-18 times that observed in the surficial bed sediments. These results suggest discretely different metal scavenging behavior between these two sediment compartments that exist in close proximity. This ability of floc to sequester large quantities of metal contaminants relative to bottom sediments has been demonstrated in the literature.[28-30]

Table 4.1. Floc, Surface and Mid Sediment Total Metal Concentrations $\{M\}_T$ (μmol g^{-1}) (1 Standard Deviation and Percent (%) {M} in Each of Six Operationally Defined Sediment Fractions (Exchangeable $\{M\}_E$, Carbonates $\{M\}_{CAR}$, Amorphous Fe/Mn Oxyhydroxides $\{M\}_A$, Crystalline Fe/Mn Oxides $\{M\}_C$, Organics $\{M\}_O$, Residual $\{M\}_R$).

		Ag			**As**			**Co**			**Cu**			**Ni**			**Pb**		
		Floc	**Sur**	**Mid**	**Floc**	**Sur**	**Mid**	**Floc**	**Sur**	**Mid**	**Floc**	**Sur**	**Mid**	**Floc**	**Sur**	**Mid**	**Floc**	**Sur**	**Mid**
Calm-1	$\{M\}_T$	**0.011**	**0.002**	**0.002**	**0.252**	**0.055**	**0.024**	**0.137**	**0.044**	**0.027**	**0.879**	**0.109**	**0.062**	**0.749**	**0.281**	**0.087**	**0.160**	**0.042**	**0.025**
	±	0.001	0.000	0.000	0.009	0.007	0.007	0.006	0.002	0.001	0.039	0.011	0.003	0.065	0.016	0.005	0.006	0.002	0.001
	$\{M\}_E$	0	0	0	8	0	0	2	0	0	4	3	0	2	0	0	0	0	0
	$\{M\}_{CAR}$	0	0	0	18	5	11	19	16	13	2	5	5	11	26	30	40	33	20
	$\{M\}_A$	75	0	0	17	6	8	29	5	6	15	2	2	17	13	13	43	8	13
	$\{M\}_C$	17	84	83	12	70	57	32	37	33	24	53	59	55	30	27	12	50	56
	$\{M\}_O$	3	6	7	8	4	7	5	7	15	40	14	15	6	6	8	2	2	2
	$\{M\}_R$	5	10	10	37	15	17	13	35	33	15	23	19	9	25	22	3	7	9
Calm-2	$\{M\}_T$	**0.012**	**0.006**	**0.003**	**0.137**	**0.045**	**0.050**	**0.148**	**0.028**	**0.050**	**0.603**	**0.048**	**0.071**	**0.492**	**0.074**	**0.101**	**0.140**	**0.010**	**0.027**
	±	0.000	0.001	0.000	0.010	0.005	0.005	0.009	0.002	0.001	0.019	0.003	0.004	0.028	0.005	0.002	0.002	0.001	0.001
	$\{M\}_E$	0	0	0	4	0	0	0	0	0	2	2	0	1	0	0	0	0	0
	$\{M\}_{CAR}$	0	0	0	11	8	9	6	9	8	1	6	4	11	15	15	7	24	31
	$\{M\}_A$	80	5	2	39	13	13	60	16	13	36	8	5	50	23	26	76	29	22
	$\{M\}_C$	17	60	88	36	68	65	21	45	38	18	57	52	20	38	33	14	38	39
	$\{M\}_O$	1	11	6	7	4	5	2	8	12	22	10	15	5	6	8	0	2	1
	$\{M\}_R$	2	24	4	3	7	8	11	22	29	21	17	24	13	18	18	3	7	7
Storm	$\{M\}_T$	**0.009**	**0.003**	**0.003**	**0.289**	**0.018**	**0.039**	**0.217**	**0.007**	**0.033**	**1.094**	**0.010**	**0.012**	**0.523**	**0.055**	**0.088**	**0.340**	**0.067**	**0.025**
	±	0.001	0.001	0.000	0.028	0.004	0.001	0.022	0.002	0.002	0.065	0.001	0.001	0.047	0.006	0.003	0.039	0.013	0.001
	$\{M\}_E$	0	0	0	1	1	0	0	0	0	0	0	0	1	0	0	0	0	0
	$\{M\}_{CAR}$	0	0	0	5	12	9	7	5	10	2	0	5	10	17	15	7	22	22
	$\{M\}_A$	0	0	0	5	14	16	3	4	9	1	0	0	10	25	19	18	31	26
	$\{M\}_C$	87	89	92	79	56	66	31	63	53	61	0	0	49	33	45	67	45	42
	$\{M\}_O$	6	7	4	2	7	3	48	15	8	17	36	22	7	9	7	2	0	3
	$\{M\}_R$	7	4	4	8	10	6	11	13	20	19	64	73	23	16	14	6	2	7
Post-Storm	$\{M\}_T$	**7.347**[a]	**0.387**[a]	**0.112**[a]	**0.228**	**0.046**	**0.014**	**0.165**	**0.021**	**0.010**	**1.454**	**0.059**	**0.017**	**0.544**	**0.079**	**0.043**	**0.169**	**0.011**	**0.009**
	±	0.367[a]	0.029[a]	0.012[a]	0.012	0.002	0.001	0.008	0.001	0.001	0.202	0.008	0.001	0.030	0.005	0.001	0.015	0.001	0.001
	$\{M\}_E$	0	0	0	18	0	0	4	0	0	6	19	0	3	0	0	0	2	0
	$\{M\}_{CAR}$	0	0	0	19	4	10	12	19	23	3	7	17	11	37	51	37	47	49
	$\{M\}_A$	64	39	23	38	37	46	47	37	39	32	25	49	43	30	29	48	37	38
	$\{M\}_C$	19	18	26	12	51	30	24	16	14	11	11	12	23	12	8	11	7	6
	$\{M\}_O$	8	8	14	9	5	8	5	7	6	29	20	4	5	6	2	1	2	2
	$\{M\}_R$	9	35	37	4	3	6	8	21	18	19	18	18	15	15	10	3	5	5

[a] values in nmolg^{-1}

4.4.1 Floc Metal Sorption Behavior

The observed variation in mean floc $\{M\}_T$ were not correlated with system physicochemical parameters ($[M]_D$, pH, temperature, O_2, specific conductivity, DIC/DOC) commonly observed to control solid-phase metal concentrations.[28,31,32] However, solution physico-chemistry within the floc environment (0.5 m above bed sediments) remained relatively constant across the four sampling periods (i.e., circumneutral pH, oxygenated water, <5 °C variation; Table S.4.1). Under these static conditions typically important controlling physicochemical parameters, floc metal uptake was instead found to be strongly correlated to the mass of two key floc sorbent-phases: 1) amorphous Fe oxyhydroxides $\{Fe\}_A$ and 2) organic matter $\{OM\}$. Distribution coefficients (Kd) were significantly and positively correlated with either floc $\{Fe\}_A$ (Cu, Ni, and Co) or floc $\{OM\}$ (Pb and As) (Figure S.4.1, Supporting Information). This indicates a greater sorption of these elements to floc from solution with increasing concentrations of these two floc substrates. Although Mn amorphous oxyhydroxides are important sorbents for metal sequestration,[25,33,34] floc $\{Mn\}_A$ did not predict floc metal distribution coefficients in this study. The importance of Fe oxyhydroxides and organic matter in controlling solid-solution metal distributions has been widely reported in literature,[35-37] and thus our results are entirely consistent with the metal reactive nature of these substrates. Organic components are commonly reported to be important metal sorbents in aquatic systems.[33,38] However, in contrast to bed sedimentary organics which typically contain a greater proportion of dead, decomposing organic matter, our results indicate that floc organics were largely comprised of a viable microbial community and associated EPS fibrils as evidenced by Live/Dead (Figure S.4.2, Supporting Information) and high-resolution TEM imaging (Figure 4.1). This finding is consistent with previous investigations of floc organics, where microbial cells and EPS dominate floc structure[3,8] and exhibit reactive surfaces that are efficient at scavenging trace metals.[4,6] The highly "viable" nature of floc organic matter contrasts organic matter within the bed sediments that reveals far fewer living cells (Figure S.4.2). Thus floc organics may be playing several roles facilitating floc metal scavenging such as provision of greater surface area to volume ratio and thus exposure of reactive metal sorption sites as well as collection/ templating of reactive amorphous Fe oxyhydroxide minerals and metabolically induced microenvironments.

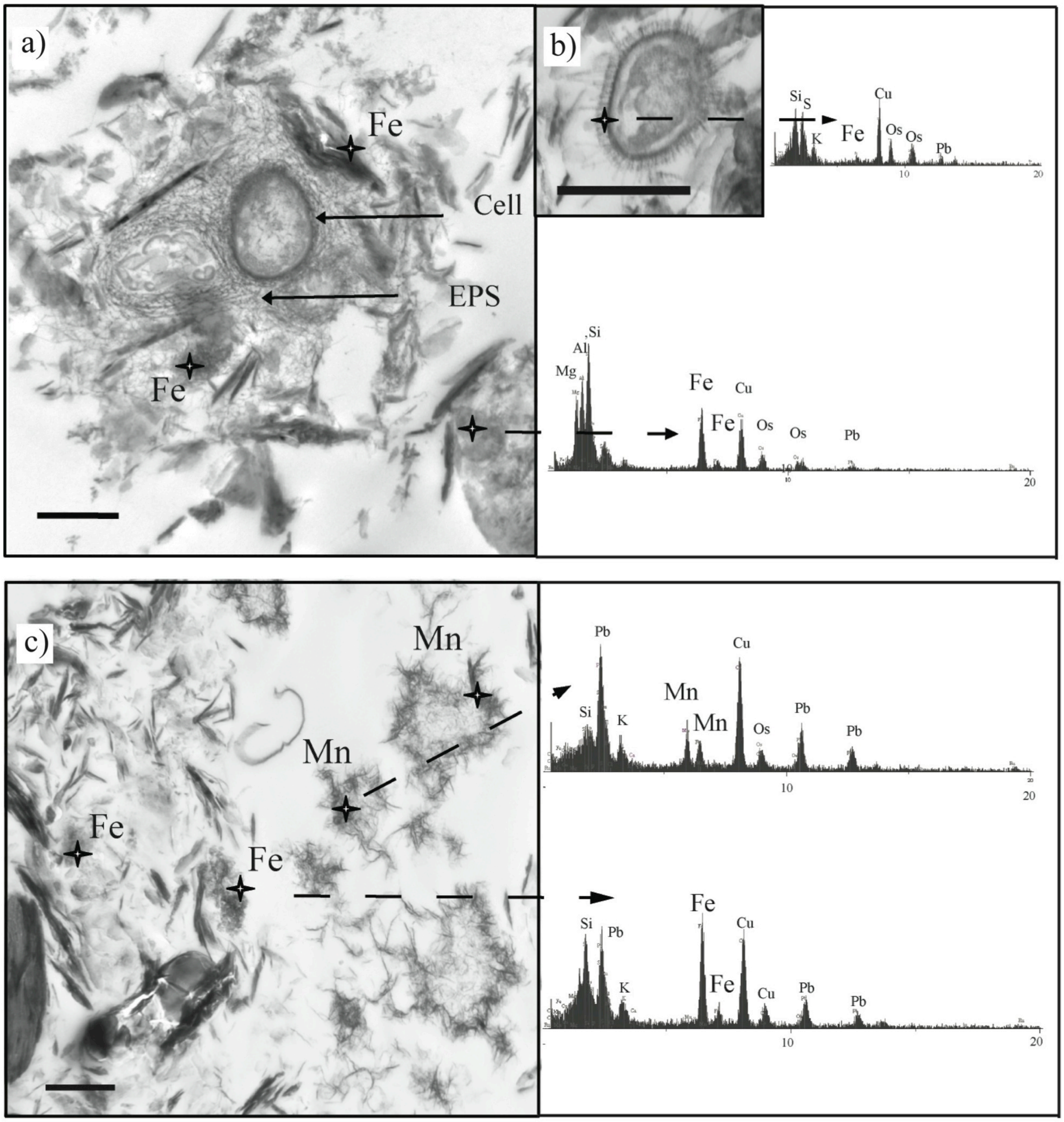


Figure 4.1 TEM image of calm-floc (a) exhibiting bacteria (species unknown) with EPS and cell walls (b) associated with Fe. TEM image of storm-floc exhibiting large mineral component rich in Mn and Fe (c). Scale represents 500 nm. Peaks of Cu, Os, and Pb are an artifact of sample preparation and grid.

4.4.2 Floc-Metal Partitioning

Assessment of metal partitioning of floc metal-reactive phases indicated that floc amorphous oxyhydroxides retained the largest proportion of Ag, Pb, Co, Ni, As, and Cu, up to 80%, 76%, 60%, 50%, 39%, and 36% of floc $\{M\}_T$ across the four sampling campaigns, respectively (Figure 4.2; Table 4.1). Further, floc $\{M\}_A$ were an order of magnitude greater than within the bed (Table 4.1) and generally exhibited a greater $\{Fe\}_A$ scavenging efficiency (CF) 50-100% of the time, depending on the element (Table S.4.2, Supporting Information). For example, a gram of floc Fe amorphous oxyhydroxides retained up to 32 times the amount of Cu compared to the observed Cu concentration associated with a gram of amorphous Fe oxyhydroxides within surficial bed sediments. This result highlights factors contributing to a higher relative scavenging capacity of floc amorphous oxyhydroxides, such as the relative degree of amorphicity, the physical nature of the oxyhydroxides, i.e. surface coatings,[13,14] the relatively higher surface area to volume ratio of floc [4,8] and the occurrence of floc suspended within an oxygenated, circumneutral water-column, which collectively favor greater amorphous Fe oxyhydroxides abundances within floc and greater associated metal sorptive capabilities. In contrast, amorphous Fe oxyhydroxides within bed sediments are likely to be consumed by Fe reducing bacteria and/or aged into more crystalline Fe oxide minerals, such as hematite and/or goethite,[10,39] which are relatively less reactive[40] but tend to dominate bed sediment geochemistry. Indeed, in contrast to the floc, the crystalline Fe/Mn oxides were the most important metal sequestration phase in the surficial bed sediment compartment (Figure 4.2; Table 4.1). While previous studies have demonstrated the importance of oxides and oxyhydroxides for scavenging metal,[33,38,41] this study is the first to our knowledge to identify a compartment dependent control on metal sequestration of floc amorphous oxyhydroxides and surficial bed sediment crystalline oxides.

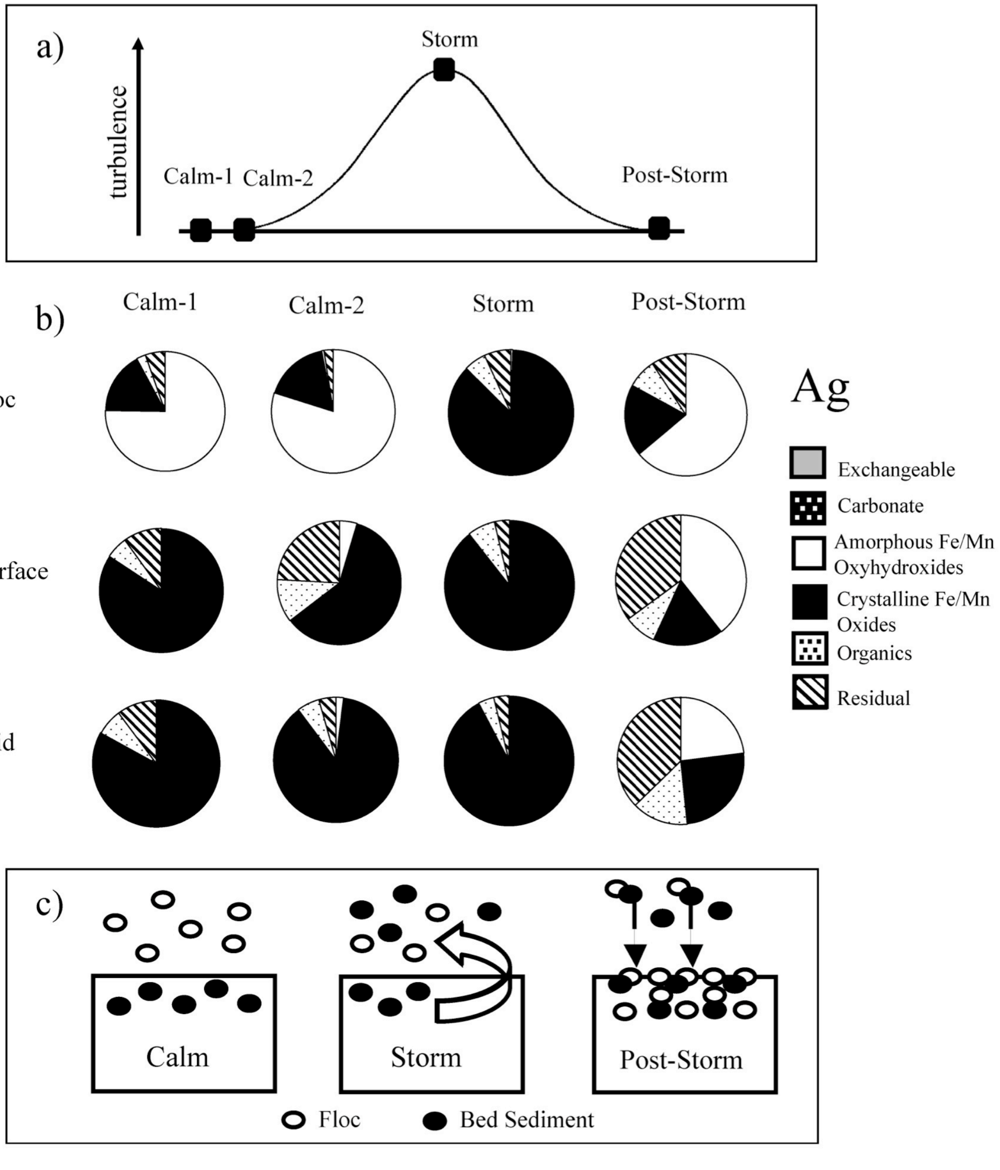


Figure 4.2 Under variable energy-regimes (a), relative proportion of Ag observed in each of six extraction steps of floc and bed sediments (b). Schematic diagram of floc-bed interactions (c).

Consistent with a more favorable sorptive environment of suspended floc relative to bed sediments, our results indicate the exchangeable fraction (metal loosely held by electrostatic attraction) sequestered floc Ni, Co, Cu, and As (Table 4.1). Floc $\{Ni\}_E$, $\{Cu\}_E$, and $\{As\}_E$ (up to 0.016, 0.087, and 0.041 μmol g^{-1}, respectively) were within the same magnitude as bed $\{Ni\}_T$, $\{Cu\}_T$, and $\{As\}_T$. Further, $\{As\}_E$ are among the first reported for floc and are important as they indicate higher labile As concentrations within the water-column than those reported for $\{As\}_E$ in bed sediments (e.g., ref 42). Bed sediment $\{M\}_E$ observed in this study were negligible for all elements analyzed (Table 4.1). Given that suspended floc is a highly mobile compartment, an exchangeable fraction has important ecological and human health implications for floc as a transport vector of easily liberated metal contaminants within freshwater beach environments. Our results also indicate that prediction of solution metal behavior likely requires characterization of floc metal abundances and distributions.

Organic matter was a major constituent of floc, comprising 10-33% by mass versus 1% within the bed (Table S.4.1). Although floc {OM} was an important predictor of aqueous-floc distribution, sequential extraction results somewhat surprisingly indicated that the organic fraction was generally not responsible for significant metal retention (Table 4.1). Cu was the sole exception to this trend. The organic fraction retained up to 49% of floc $\{Cu\}_T$, an association previously documented in both floc and bed sediments.[38,43] In contrast to the results observed for amorphous Fe oxyhydroxides, a gram of floc organic matter was generally not more reactive than a gram of surficial bed sediment organic carbon. In fact, a gram of floc organic carbon was often less effective at concentrating metal compared to bed organic carbon (bed CF exceeded floc CF 75% of the time, exception of Cu; Table S.4.2). We interpret these results as indicating floc organics (mostly live cells and EPS) act as a scaffold for the accumulation of the key floc metal reactive sorbent-phase, amorphous Fe oxyhydroxides, rather than as a direct metal scavenging phase. Consistent with this hypothesis, TEM-EDS analysis revealed peaks of

Fe specifically localized to surfaces of floc EPS fibrils and surrounding microbial cells (Figure 4.1). Associations of Fe with organics within floc have been commonly observed.[4,8] Here, however, our results demonstrate potential linkages between floc organics, Fe entrapment, and metal dynamics. Moreover, results show that flocs with greater {OM} generally contained greater $\{Fe\}_A$ abundances (Table S.4.1) consistent with our suggested scaffolding role of floc organic matter enabling the formation and/or collection of amorphous Fe oxyhydroxides rather than direct metal sequestration. However, when combined with our results for floc Kds, these partitioning results indicate that interactions between floc organics and amorphous Fe oxyhydroxides occur that affect initial metal uptake from solution and sorbent sequestration. For instance, while the distribution of Cu between suspended floc and the solution phase is significantly controlled by the abundance of floc $\{Fe\}_A$ (Figure S.4.1), the partitioning results indicate that it is bound by the floc organics themselves (Table 4.1). Based on these results, we hypothesize competitive binding for limited substrate sites within floc either by other elements outcompeting Cu for limited amorphous Fe oxyhydroxide sites or Cu out competing other elements for limited organic sites. Interestingly while both floc Pb and As Kds are best predicted by floc {OM} indicating that the greater the floc organic concentrations (Figure S.4.1), the greater sorption of these elements to the floc from solution occurs; neither of these elements are significantly bound to the floc organics themselves (Table 4.1). The intimate and, we believe, architectural association of floc organics and amorphous Fe oxyhydroxides drives overall floc metal uptake; however, variation in element concentrations and specific element affinities for these likely limited substrates within this competitive sorptive environment are also apparent.

(B). Energy-Regime Metal Dynamics.

Given the substantive differences in both abundance and substrate associations of metals observed between floc and surficial bed sediments, it would be expected that interactions of these two sedimentary compartments would lead to dynamic shifts in metal behavior. Indeed, a comparison of floc and bed sediment metal partitioning observed during low-energy and storm conditions indicated that interactions of these two compartments led to shifts in substrate composition and associated metal behavior both when energy regimes were sufficient to mobilize bed sediments into suspension as well as post storm, when materials subsequently settled out of suspension into the surficial bed sedimentary compartment. Low-energy periods (Calm-1, Calm-2) revealed distinctly different metal partitioning patterns between floc and bed sediments (Figure 4.2; Table 4.1). For these sampling periods, metal sequestration in floc was dominated by the amorphous oxyhydroxide fraction while the crystalline oxide fraction controlled bed metal dynamics, as discussed previously. In contrast, under storm-conditions, floc-partitioning patterns resembled that of bed sediments i.e. loss of the floc-signature in suspension. Metal sequestration in both floc and bed sediments was dominated by the crystalline oxide fraction (Figure 4.2; Table 4.1) indicating that hydrodynamic driven mobilization of bed sediments, and associated crystalline oxide-signature, overwhelmed the distinct floc amorphous Fe oxyhydroxide metal signature observed under low-energy periods. Mobilization of bed sediments was evidenced not only by a 100 times increase in suspended sediment concentrations during the storm but also increased $\{Fe\}_C$ and $\{Mn\}_C$ within storm collected floc (Table S.4.1). TEM visualization of storm-floc revealed a greater proportion of inorganic particles compared to that of calm-floc (Figure 4.1), and TEM-EDS analysis indicated a distinct Mn marker within the inorganic particles. Further, imaging revealed far less biological structure to storm-floc aggregates, in particular fewer EPS fibrils associated with microbial cells. Together, these results reflect a distinct shift in floc aggregate structure, substrate composition, and associated metal-partitioning behavior during periods of hydrodynamic mixing of floc-bed sedimentary compartments.

Storm-floc (i.e., including mobilized surficial bed sediments in the floc compartment) Kds were also distinctly different from that of calm-floc in that they were greater for all metals, with the exception of Co, and did not correlate with either $\{Fe\}_A$ or

{OM} (Figure S.4.1). These results indicate that nonsaturated differentially metal reactive substrates from the bed sediments are present in storm-floc altering both Kds as well as partitioning patterns to that of calm-floc. Specifically, crystalline Fe oxides mobilized from the bed increased floc metal uptake, as evidenced by storm-floc $\{Fe\}_C$ CFs that were substantively greater than those determined for the previous day calm-floc (Table S.4.2). These results indicate energy-regime driven mobilization of nonmetal-saturated bed sedimentary crystalline Fe oxide provides a dynamic mechanism for enhanced floc metal uptake during high energy-regimes in nearshore beach environments.

Further, mobilized crystalline oxides also provide new surfaces for flocculation during periods of mixing. Flocculation, through physical collision, chemical (electrochemical) and/or biological means,[44,45] generates new aggregates of combined floc-bed substrates that would likely settle together when energy levels subsides. Newly generated floc deposition appears evident in our results by the emergence of a floc amorphous-partitioning signature in the bed compartment (Figure 4.2; Table 4.1), along with an observed spike of $\{Fe\}_A$ in the surficial bed sediments poststorm consistent with formation and entrainment of this more amorphous material once energy-regimes drop, settling this material into the surficial bed sediments (Table S.4.1). As bed sediments remain undisturbed, the new supply of floc amorphous Fe oxyhydroxides may age into more crystalline oxide minerals, incorporating any bound metals into its solid structure[39] thus regenerating the crystalline oxide signature characteristic of the bed compartment under low-energy conditions. In contrast, regeneration of amorphous-partitioning in the floc compartment poststorm (Figure 4.2; Table 4.1) indicates return of "microbial floc" dominated by EPS-amorphous Fe oxyhydroxides and distinct metal behavior (substrate control on Kds and amorphous-partitioning signature) as larger particles quickly redeposit. Therefore, floc collected under low-energy conditions is a unique microbially controlled sedimentary compartment in aquatic systems that cannot be regarded simply as bed sediments in suspension. It is the largely living microbial cells and EPS components that play a key structural role in floc metal behavior specifically through the biomineralization and/or collection of amorphous Fe oxyhydroxides, ultimately creating a distinctly different solid with different metal partitioning than bed sedimentary materials. These results indicate that floc is an important metal repository in aquatic systems that will not be well modeled by bed sediments, even when floc is in close proximity to surficial bed sediments (0.5 m above bed in this study). Further, the exchange of floc and bed sedimentary materials driven by hydrodynamic energy-regime will dynamically impact metal behavior of these two compartments, and, as such, freshwater beach environments are likely highly active metal systems.

4.5 Supporting Information

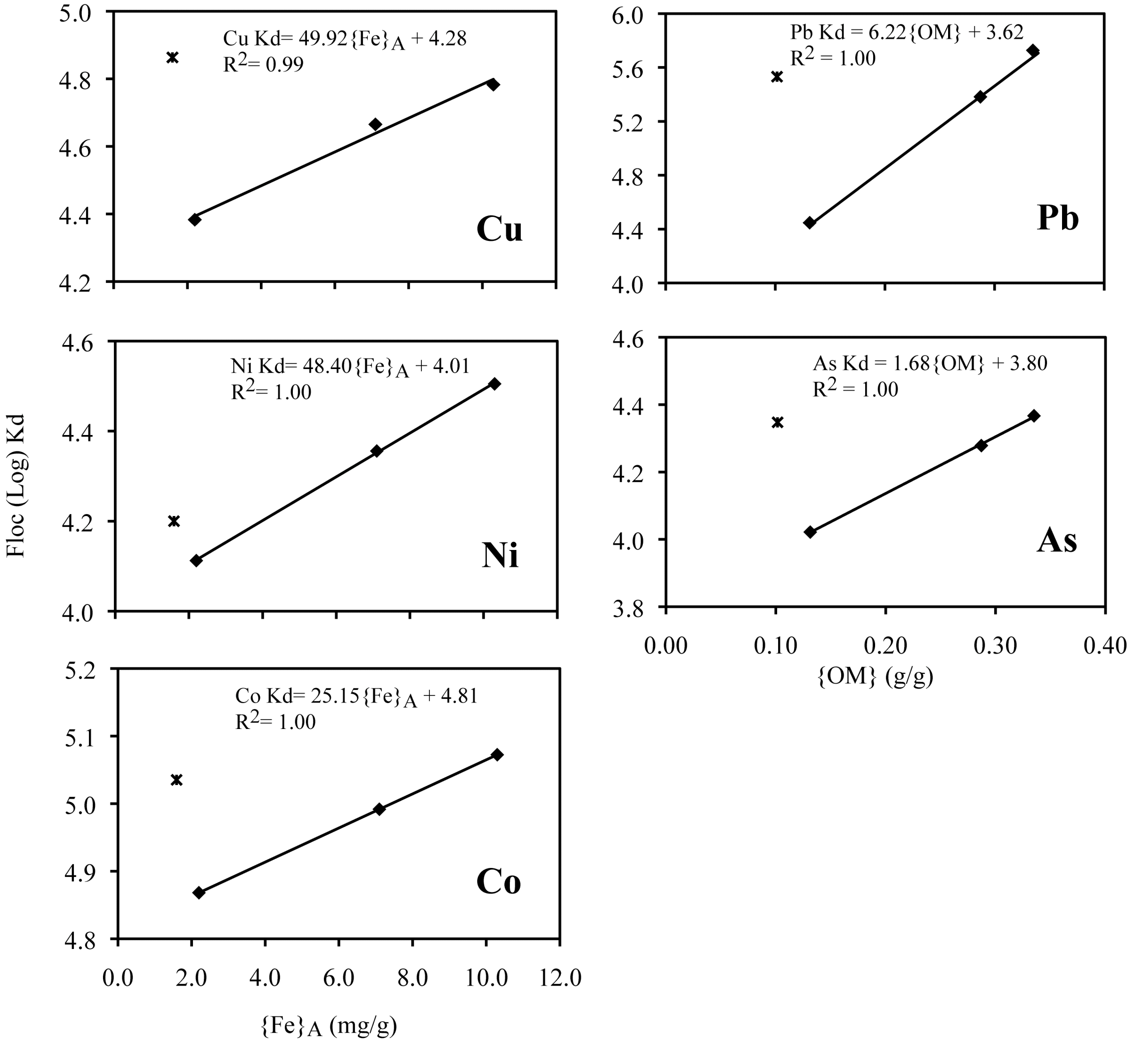


Figure S.4.1 Distribution coefficients (Kd) versus floc $\{Fe\}_A$ and {OM}. Calm-floc (◆) and storm-floc (✖).

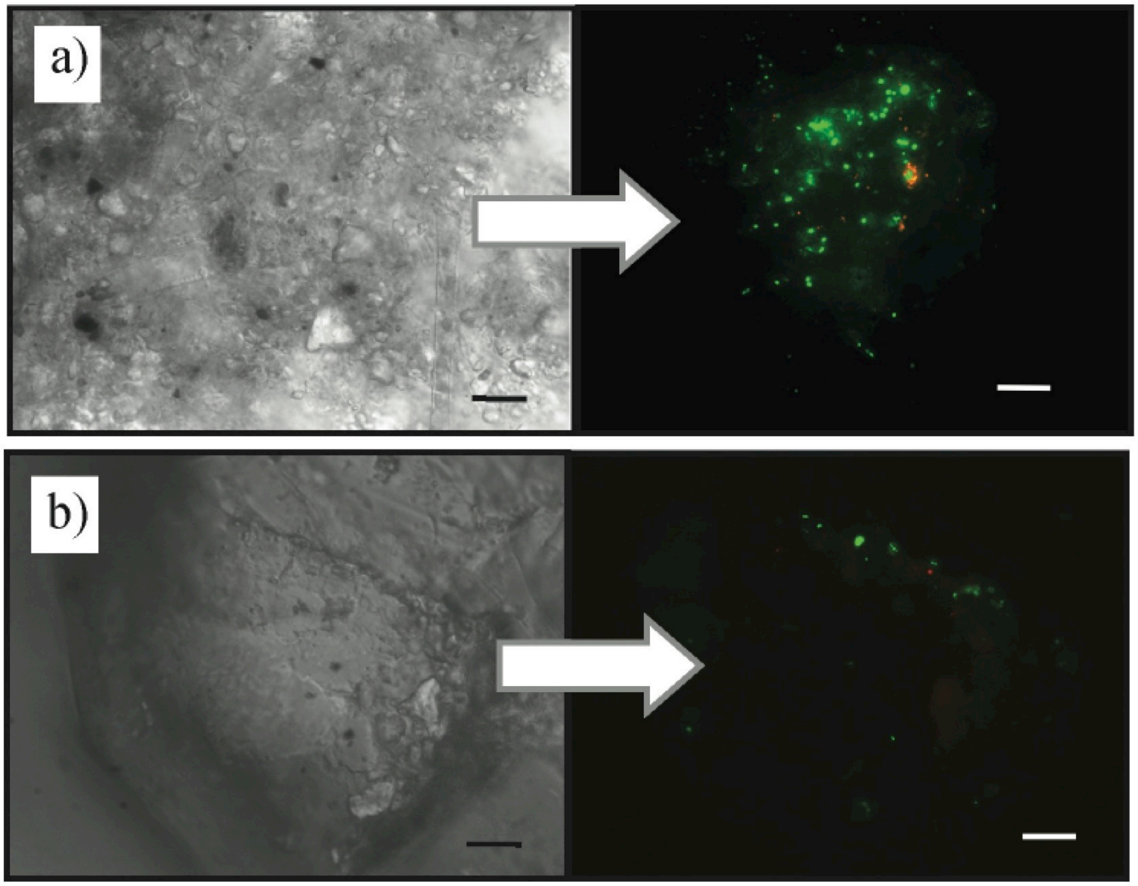
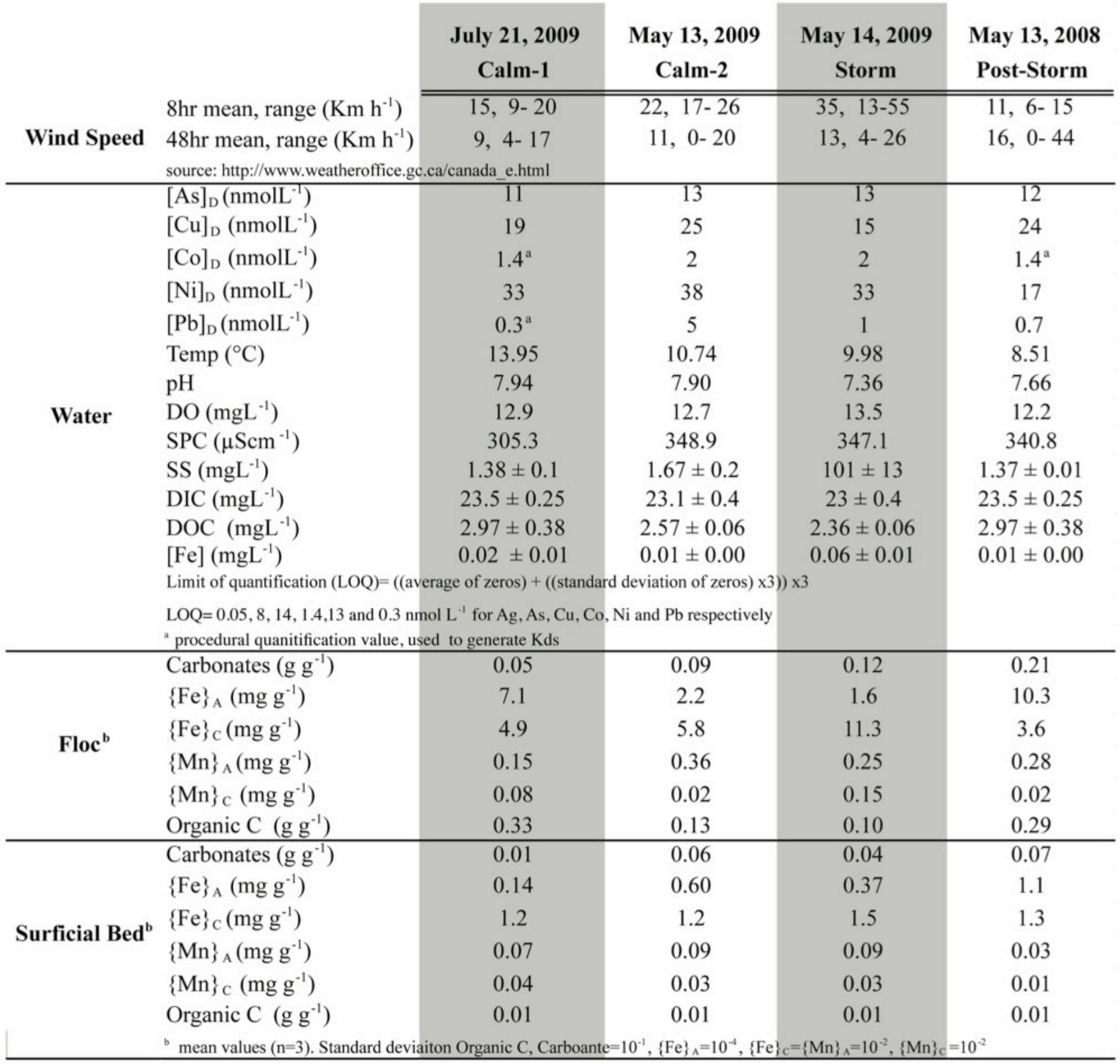


Figure S.4.2 Live (green) and dead (red) microbial community of floc (a) and bed sediments (b). Scale represents 10µm.

Table S.4.1 Physico- chemical conditions of floc environment (0.5 m above sediment-water interface) and mean metal- reactive constituent of floc and surficial bed sediments



		July 21, 2009 Calm-1	May 13, 2009 Calm-2	May 14, 2009 Storm	May 13, 2008 Post-Storm
Wind Speed	8hr mean, range (Km h^{-1})	15, 9- 20	22, 17- 26	35, 13-55	11, 6- 15
	48hr mean, range (Km h^{-1})	9, 4- 17	11, 0- 20	13, 4- 26	16, 0- 44
	source: http://www.weatheroffice.gc.ca/canada_e.html				
Water	$[As]_D$ (nmolL^{-1})	11	13	13	12
	$[Cu]_D$ (nmolL^{-1})	19	25	15	24
	$[Co]_D$ (nmolL^{-1})	1.4[a]	2	2	1.4[a]
	$[Ni]_D$ (nmolL^{-1})	33	38	33	17
	$[Pb]_D$ (nmolL^{-1})	0.3[a]	5	1	0.7
	Temp (°C)	13.95	10.74	9.98	8.51
	pH	7.94	7.90	7.36	7.66
	DO (mgL^{-1})	12.9	12.7	13.5	12.2
	SPC (μScm $^{-1}$)	305.3	348.9	347.1	340.8
	SS (mgL^{-1})	1.38 ± 0.1	1.67 ± 0.2	101 ± 13	1.37 ± 0.01
	DIC (mgL^{-1})	23.5 ± 0.25	23.1 ± 0.4	23 ± 0.4	23.5 ± 0.25
	DOC (mgL^{-1})	2.97 ± 0.38	2.57 ± 0.06	2.36 ± 0.06	2.97 ± 0.38
	[Fe] (mgL^{-1})	0.02 ± 0.01	0.01 ± 0.00	0.06 ± 0.01	0.01 ± 0.00
	Limit of quantification (LOQ)= ((average of zeros) + ((standard deviation of zeros) x3)) x3				
	LOQ= 0.05, 8, 14, 1.4,13 and 0.3 nmol L^{-1} for Ag, As, Cu, Co, Ni and Pb respectively				
	[a] procedural quanitification value, used to generate Kds				
Floc[b]	Carbonates (g g^{-1})	0.05	0.09	0.12	0.21
	$\{Fe\}_A$ (mg g^{-1})	7.1	2.2	1.6	10.3
	$\{Fe\}_C$ (mg g^{-1})	4.9	5.8	11.3	3.6
	$\{Mn\}_A$ (mg g^{-1})	0.15	0.36	0.25	0.28
	$\{Mn\}_C$ (mg g^{-1})	0.08	0.02	0.15	0.02
	Organic C (g g^{-1})	0.33	0.13	0.10	0.29
Surficial Bed[b]	Carbonates (g g^{-1})	0.01	0.06	0.04	0.07
	$\{Fe\}_A$ (mg g^{-1})	0.14	0.60	0.37	1.1
	$\{Fe\}_C$ (mg g^{-1})	1.2	1.2	1.5	1.3
	$\{Mn\}_A$ (mg g^{-1})	0.07	0.09	0.09	0.03
	$\{Mn\}_C$ (mg g^{-1})	0.04	0.03	0.03	0.01
	Organic C (g g^{-1})	0.01	0.01	0.01	0.01
	[b] mean values (n=3). Standard deviaiton Organic C, Carboante=10^{-1}, $\{Fe\}_A=10^{-4}$, $\{Fe\}_C=\{Mn\}_A=10^{-2}$, $\{Mn\}_C=10^{-2}$				

Table S.4.2 Floc and surficial sediment concentration factors (CF)

		Calm-1	**Calm-2**	**Storm**	**Post-Storm**
Ag	Floc {Fe}$_A$	14	4.5	*	0.47
	{Fe}$_C$	0.38	0	0.70	0.39
	{OM}	*	*	0.01	*
	Bed {Fe}$_A$	*	0.46	*	0.01
	{Fe}$_C$	1.5	2.2	1.5	0.05
	{OM}	0.01	0.06	0.02	*
As	Floc {Fe}$_A$	6.0	25	9.0	8.7
	{Fe}$_C$	6.2	8.5	20	7.6
	{OM}	0.06	0.07	0.06	0.07
	Bed {Fe}$_A$	2.3	9.9	6.8	1.7
	{Fe}$_C$	32	21	6.7	18
	{OM}	0.22	0.18	0.13	0.23
Co	Floc {Fe}$_A$	5.6	42	4.1	7.8
	{Fe}$_C$	9.0	5.3	6.0	11
	{OM}	0.02	0.02	1.0	0.03
	Bed {Fe}$_A$	1.6	7.5	0.79	0.75
	{Fe}$_C$	14	8.4	3.1	2.6
	{OM}	0.31	0.22	0.11	0.15
Cu	Floc {Fe}$_A$	19	103	6.8	47
	{Fe}$_C$	43	19	59	44
	{OM}	1.1	1	1.9	1.5
	Bed {Fe}$_A$	1.6	6	*	1.4
	{Fe}$_C$	48	18	*	5.0
	{OM}	1.5	0.48	0.34	1.2
Ni	Floc {Fe}$_A$	18	117	33	23
	{Fe}$_C$	84	17	23	35
	{OM}	0.14	0.19	0.37	0.09
	Bed {Fe}$_A$	26	29	37	2.3
	{Fe}$_C$	70	19	12	7.3
	{OM}	2	0	0.49	0.47
Pb	Floc {Fe}$_A$	9.7	51	38	8.1
	{Fe}$_C$	3.9	3.4	20	5.2
	{OM}	0.01	*	0.07	0.01
	Bed {Fe}$_A$	2.4	4.8	56	0.4
	{Fe}$_C$	17	2.5	20	0.6
	{OM}	0.08	0.02	*	0.02

* no metal associated with sediment fraction

4.6 Acknowledgements

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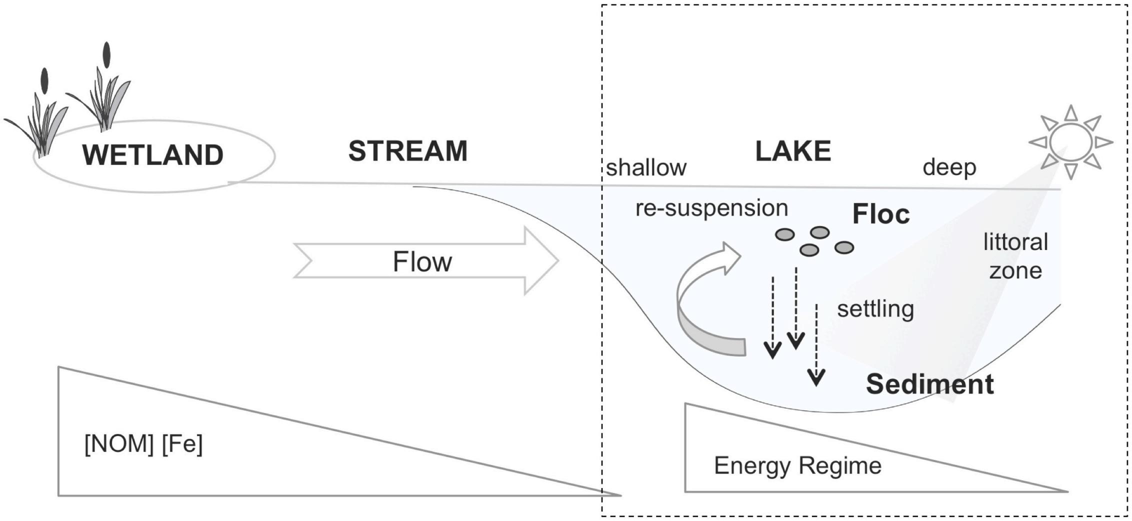
CHAPTER 5: IRON CYCLING IN A LITTORAL FRESHWATER BEACH IMPLICATIONS FOR FLOC TRACE METAL DYNAMICS



CHAPTER 5: IRON CYCLING IN A LITTORAL FRESHWATER BEACH IMPLICATIONS FOR FLOC TRACE METAL DYNAMICS

Submitted by Plach, J.M., Lin, S., Droppo, I.G., and Warren, L.A. to
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5.1 Abstract

Results reveal that highly dynamic trace metal (Ag, Co, Cu and Pb) behavior in suspended floc and the sediment surface fine-grained layer (SFGL) is linked specifically to Fe mineral cycling between these two compartments driven by rapidly fluctuating energy regimes in a shallow, littoral beach of Lake Ontario. Results reveal distinct, Fe mineral controls on metal sequestration patterns under quiescent conditions. Higher metal sequestration occurred in floc associated with amorphous Fe oxyhydroxides (FeOOH), while less reactive crystalline Fe oxides (FeOx) dominated bed metal sequestration. Spatial shifts in energy regime governing floc settling and sediment erosion controlled the mixing of FeOOH and FeOx, and thus resulted in discernible, hydrodynamic-dependent floc and SFGL trace metal associations. Low turbulence offshore limited compartment mixing, resulting in enrichment of FeOOH and metals in floc and SFLG over bulk bed sediments. In contrast, higher turbulence nearshore increased bed erosion resulting in less distinct floc and SFGL-FeOOH/metal abundances and partitioning.

Diurnal shifts in energy regime impacting floc and SFGL geochemistry were observed nearshore. Accumulation of FeOOH and metals occurred in the SFGL under calm morning conditions, while diurnal wind-induced waves rapidly re-cycled the SFGL back into the overlying water-column. Post mixing, re-suspended FeOOH and smaller floc particulates entrained within a higher photosynthetically-induced pH water-column increased overall floc metal uptake. This field-based investigation demonstrates highly dynamic linkages between energy regime and physico-chemistry impacted Fe mineral cycling, resulting in observable compartment-specific metal partitioning patterns for littoral floc and surficial sediments in beach environments.

5.2 Introduction

Iron (Fe) cycling, influenced by both microbial and physico-chemical parameters, is fundamental to the water quality of aquatic ecosystems, as it directly affects the mobility, cycling and fate of metal contaminants. Iron exists as diverse amorphous oxyhydroxide and crystalline oxides in circumneutral well-oxygenated waters (Perret et al., 2000; Cornell and Schwertmann, 2003; Fortin et al 1993). These are important solid phases for the sequestration of metals in aquatic sedimentary compartments (Tessier at al., 1996; Priadi et al., 2011). Amorphous Fe oxyhydroxides (FeOOH) have poorly ordered mineral structures and large surface areas, making them highly reactive minerals for uptake of solution metals (Jambor and Dutrizaz, 1998). Iron oxyhydroxides are typically unstable and tend to age into more crystalline forms under oxic conditions and neutral pH (Cudennec and Lecerf 2006; Das et al., 2011) or reductively dissolve and re-crystallize under anaerobic conditions (Hansel et al., 2003). Such transformations alter the surface properties and control the incorporation of metals originally associated with the FeOOH into more crystalline Fe oxide forms (Cooper et al., 2006; Ford et al., 1997). The lower binding capacity of crystalline Fe oxides may also facilitate the release of sorbed metals back into solution or to be scavenged by other reactive constituents (e.g. organic matter). As such, the abundance and reactivity of differing Fe minerals in suspended versus bed sediment compartments will have a direct impact on the distribution of metal contaminants within an aquatic system.

FeOOH exists in highly complex associations with natural organic matter (e.g. microbial cells, extra cellular substances) in suspended flocs (Droppo, 2001a; Liss et al., 1996; Ongley et al., 1981; Buffle and Leppard, 1995), synonymous with suspended particulate matter (SPM) (as referred to elsewhere in the literature), forming a unique aggregate of greater affinity for metals than bed sediments (Hua et al., 2012; Stecko and Bendell-Young, 2000; Santiago et al., 1994). Research has shown that floc-FeOOH, controls floc metal sequestration (Elliott et al., 2012) while crystalline oxides tend to dominate bed metal retention (Stecko and Bendell-Young, 2000) due to mineral aging and/or reductive dissolution limiting FeOOH. This differentiated Fe mineral control on floc versus sediment metal partitioning may thus be an effective marker of floc/bed interactions, directly relevant for tracking metal mobility within high energy environments where constantly changing hydrodynamic conditions (i.e. waves and currents) can lead to rapid mixing of flocs and bed sedimentary materials.

Shallow littoral beaches are dynamic environments where diurnal variations in hydrodynamics as well as water-column chemistry (e.g. pH) are likely to cause frequent mixing of floc/sediment material and alter floc sorption behaviour. High-energy waves can erode sediment crystalline oxides and associated metals into suspension altering floc partitioning (Plach et al., 2011), while quiescent conditions typically limit sediment mobilization. As such, flocs should show differences in amorphous and crystalline Fe-phase abundance and thus trace metal partitioning associated with temporal and spatial changes in energetic regime within a beach environment. Water turbulence can also affect floc particle size (Biggs and Lant, 2000; Bouyer et al., 2004), which in turn influences the surface properties and sorptive capacity of flocs. Given that smaller floc particulates can have a larger reactive surface area and a higher metal affinity (Laurent et al., 2009), variation in floc particle size due to water turbulence may also affect floc trace metal uptake. Further, diurnal variability in water-column chemistry (Nimick et al., 2011), particularly photosynthetic-driven cycles in pH typical of littoral waters (Fuller and Davis, 1989), would affect floc sorption dynamics over short timescales within shallow littoral beaches. Water-column pH is known to affect floc metal uptake/release (Lead et al., 1999; Lion et al., 1982; Grassi et al., 1997; Plach and Warren, 2012), largely attributed to pH-dependent adsorption behaviour of floc associated-FeOOH (Gadde and Laitinen, 1974; Benjamin and Leckie, 1981). Therefore, daily shifts in water-column pH should affect floc metal uptake, and be reflected in the scavenging efficiency of floc-FeOOH. Further, variation in light intensity driving photoreduction of Fe (McKnight et al., 1988) and the potentially rapid Fe(II) re-oxidation/precipitation of FeOOH expected in circumneutral oxygenated waters should contribute to the proliferation of abundant reactive FeOOH minerals within littoral beach waters. Although several studies have observed temporal variations in floc Fe and trace metal abundances within marine coastal environments (Birch and O'Hea, 2007) and river systems (Carter et al 2006), the potential for diurnal variation in floc geochemistry within shallow littoral beach systems remains undescribed. Given that human exposure to contaminants can occur at urban public beaches, characterizing the role of physicochemical parameters on the cycling of Fe and associated metal mobility is directly relevant to helping improve the risk assessment and water-quality management needs of these highly active systems.

Surface bed sediment geochemistry is also likely to be dynamic in littoral beach environments given exposure to variations in pH/O_2 conditions, and periodic erosion and reworking of sedimentary layers. Deeper water limits the translation of wind energy into waves and water momentum that reaches the bed; therefore sediment erosion typically decreases with increasing distance from shore (Carper and Bachmann, 1984). Lower energy-regimes offshore should facilitate floc settling, forming a low-density ''fluffy'' surface deposit of flocs on surficial sediments, referred to as the surface fine-grained lamina (SFGL) (Droppo and Stone, 1994). Floc settling would provide a transport mechanism for Fe and metals from the water-column to the lakebed (Sigg et al., 1987). Further, oxidation and precipitation of FeOOH at the oxic sediment-water interface of undisturbed sediments may also contribute to Fe and metal accumulation in the SFGL. Although previous studies have investigated floc settling/sediment erosion (Droppo et al., 2007; Milligan and Hill, 1998; Garcia-Aragon et al., 2011; Stone et al., 2008) and associated metal mobilization under controlled laboratory energy regimes (Theis et al., 1988; Cantwell et al., 2002), to date none have directly investigated Fe and metal dynamics of freshwater flocs and surfical sediments under varying spatial and time-dependent energy regimes directly in situ. As such, the objectives of this field-based study were to investigate: 1) Fe distributions between suspended floc, SFGL and bed sediment compartments; 2) reactive solid phases for trace metal sequestration, and 3) potential spatial and temporal variation in physicochemical conditions affecting Fe abundance and trace metal behaviour of flocs and surficial sediments along a spatial transect from nearshore to offshore, within an urban freshwater beach.

5.3 Methods

5.3.1 Field Site and Sampling

Suspended/settled-floc, water and bed sediments samples were collected at Toronto Sunnyside Beach, Lake Ontario Canada (43°38’21’N, 079°27’21”W) (Figure 5.1A). This highly utilized freshwater beach is located within an urbanized region, home to more than 5 million people. The sampling campaign was designed to investigate both spatial and temporal trends in suspended floc, SFGL and bed-sediment Fe and metal geochemistry. Suspended floc samples were collected at two sites within the littoral zone at 0.5 m sampling depths, comprising a nearshore (1 m total depth) and an offshore (3 m total depth) location, during two separate 12-h sampling campaigns on July 21, 2010 (nearshore floc collected 0.5 m above bed) and August 15, 2011 (floc collection 2.5 m above bed). Samples were analyzed for Fe and trace metal analysis (Ag, Co, Cu, and Pb), selected since they are known to occur in urban runoff (Gromaire-Mertz et al., 1999; Davis et al., 2001; Joshi and Balasubramanian, 2010) and sewage treatment and combined sewer effluent (STP/CSO), which are likely important sources of contaminants to Sunnyside Beach. For the purpose of this study, the shallow nearshore site was characterized as “high energy” and deep offshore as “low energy” due to differences in suspended sediment concentrations [SS] at peak wind speed, i.e. 18 mg L^{-1} and 7 mg L^{-1}, respectively (Table 5.1). Settled-floc (SFGL) and bulk bed sediments were collected along a transect from the shallow to deep site to capture potential spatial variation in hydrodynamic energy conditions, i.e. high energy nearshore and low energy offshore (Figure 5.1B).

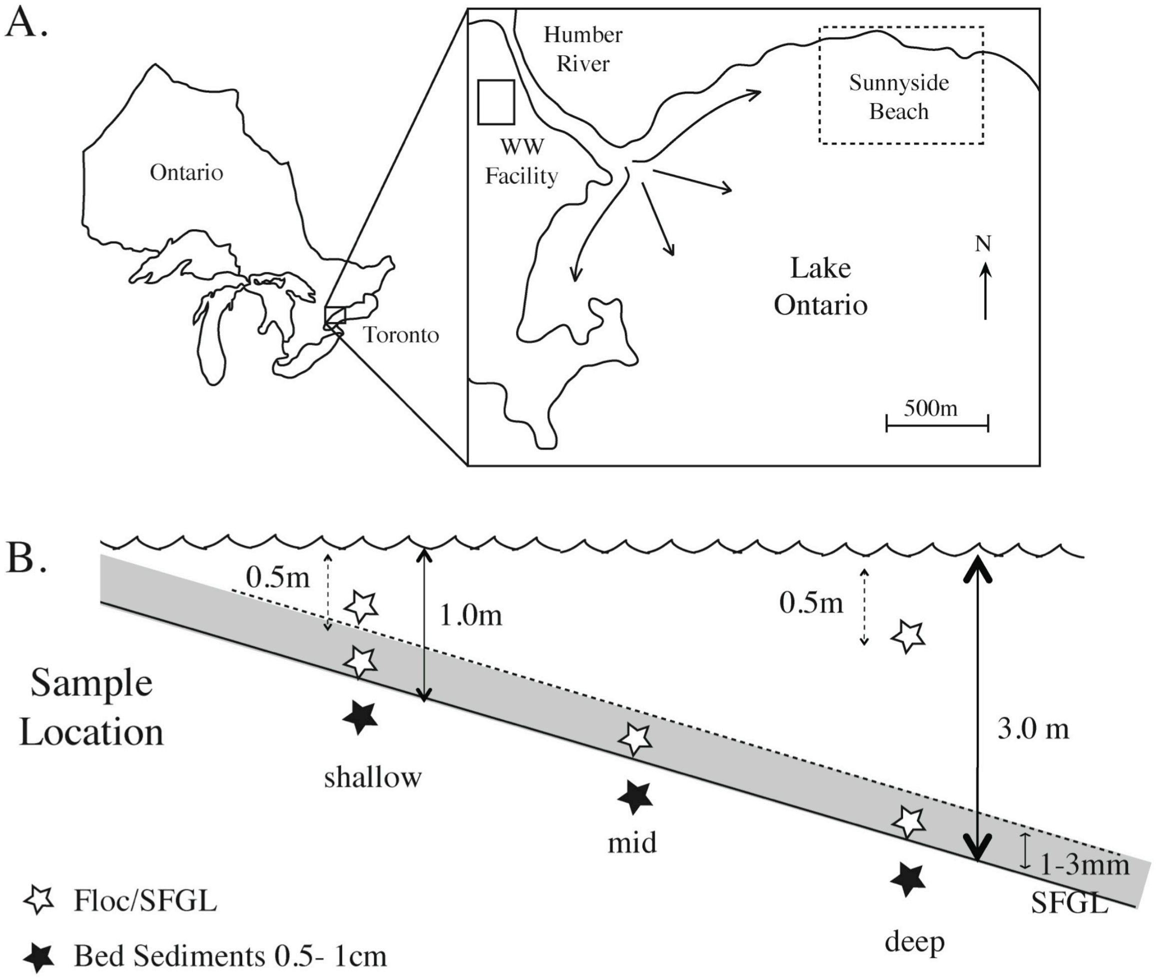

Figure 5.1 Site map depicting Sunnyside Beach, the Humber River and nearby waste water facility (WW) (A). Suspended floc, SFGL and bed sediment sampling locations along a shallow to deep transect (B).

5.3.2 Water-column Collection/Analysis

All sampling equipment was acid-cleaned with 10% HCl for >24 h and subsequently rinsed eight times with ultrapure water (18.2 Ωm cm^{-1}, Mili-Q, Millipore). Water samples were collected using an acid-washed Van Dorn Sampler and filtered serially through 0.45 and 0.2 µm sterile in-line syringe filters. Samples were preserved with trace metal grade (TMG) HNO_3 to 2% v/v (Fisher) in acid-washed 50 mL Falcon tubes, and stored at 4°C until analysis. Analysis for dissolved trace metals $[M]_D$ used inductively coupled plasma mass spectrometry (ICP-MS (Ag, Cu, Co, and Pb)) PerkinElmer SCIEX ELAN 6100, Woodbridge ON, Canada). $[Fe]_D$ was determined colorimetrically using the FerroVer HACH method (Ultroscpec 2000, UV/visible spectrophotometer, Pharmacia Biotech, Cambridge, U.K.) Field blanks (i.e. filtering/acidifying ultrapure water on site at each sampling time) and analytical blanks revealed negligible contamination for all elements analyzed. Dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and the major cations (Ca^{2+}, K^+, Mg^{2+}, Na^+) and anions (Fl^-, Cl^-, SO_4^{2-}) were analyzed following the methods at the National Laboratory for Environmental Testing (NLET) Environment Canada (2009) and are reported in Table S.5.1.

Water-column parameters (pH, dissolved oxygen (DO), temperature and specific conductivity) were measured using a Datasonde-Surveyor 4A (Hydrolab Corporation, TX) at nearshore/offshore locations (0.5 m depth site of bulk floc collection). Bulk water samples were analyzed on site for suspended sediment (SS) concentration, using a HACH photometric method. Temporal variations in floc particle size were quantified in situ at the nearshore site (11:00, 13:00 and 16:00) using a LISST-100X (Laser In Situ Scatter and Transmissometry) particle size analyzer (Blake et al., 2009).

Table 5.1 Physicochemical conditions of the water-column nearshore and offshore at depth of floc collection (0.5 m) and at the outflow of the Humber River (HR) at 0.5 m depth.

	pH	Temp °C	Wind Speed[a] Km h^{-1}	SS mg L^{-1}	DO %	SPC μScm^3	$[Fe]_T$ mg L^{-1}	[Fe] (aq) mg L^{-1}	[Co](aq) nM	[Cu] (aq) nM	[Pb] (aq) nM
Nearshore											
10:30	8.21	19.5	17	7	SAT	353	0.03	0.00	2.5	24	2.4
15:00	8.39	21.27	33	18	SAT	379	0.06	0.01	6.4	31	0.5
19:30	8.72	21.41	21	6	SAT	361	0.03	0.01	2.0	15	0.3
Offshore											
11:00	8.35	22.81	9	3	SAT	539	0.09	0.01	1.3	57	*
15:30	8.26	23.15	17	7	SAT	627	0.09	0.01	1.4	72	*
19:30	8.70	22.72	15	6	99.3	589	0.16	0.01	1.4	61	*
HR	-	-	-	-	-	-	0.88	0.02	2.8	77	*

Limit of Quantification (LOQ)= ((average of zeros) + ((standard deviation of zeros) x3)) x3

LOQ= 0.05, 1.4, 14 and 0.3 nM for Ag, Co, Cu and Pb respectively

* below LOQ

[a] source: http://www.weatheroffice.gc.ca/canada_e.html

Mean values (n=3) ± 1 standard deviation [Fe],[Pb]=10^2, [Co],[SS]=10^{-1}, [Cu]=1

5.3.3 Floc/Bed Collection

Bulk suspended floc samples were collected using field-flow centrifugation (CFC, Westfalia Model KA, stainless-steel bowls pre-leached with 10% ETDA) during four-h intervals (i.e. 8:00-12:00, 12:00-16:00 and 16:00-20:00) for solid-phase Fe/metal analysis and mineralogy. Greater than 2000 L of water (6 L min^{-1}) was centrifuged both nearshore and offshore (0.5 m depth). Bulk floc samples (> 90% recovery of suspended sediment as assessed according to Eaton et al. (2005)) were collected from the stainless-steel bowls (kept sealed on ice at the field site) into acid-cleaned 50 mL Falcon tubes back at the laboratory and were stored frozen at -20˚C until analysis.

SFGL and bulk bed sediments were hand collected in acid-washed polycarbonate core tubes (6 cm diameter, 45 cm length). Sediment cores were collected along the shallow to deep water transect (16:00) as well as temporally at the nearshore site, i.e. 8:00, 13:00, 16:00 and 19:30. Previous characterization of sediments at Sunnyside Beach indicate a composition of > 98% sand sized particles (Plach et al., 2011). Cores were immediately extruded onshore and subsamples collected from the surface (i.e. settled-floc 0-3 mm, SFGL) using 25 mL sterile pipettes and underlying bulk sediments (0.5-1 cm) using acid washed spatulas into Whirlpak bags. The SFGL/sediment samples were stored within a separate mud lined Ziplock bag to limit oxygen diffusion and frozen immediately on dry ice at the field site. Upon return to the laboratory, the samples were stored at -20˚C until analysis.

5.3.4 Solid Phase Metal Analysis

Suspended floc, SFGL and bed sediment metal solid-phase partitioning was determined using a modified Tessier sequential-extraction method optimized for natural organic rich biofilm samples (Haack and Warren, 2003) to determine metals associated in six operationally defined sediment fractions: exchangeable (loosely bound $\{M\}_E$); carbonates $\{M\}_{CAR}$; amorphous Fe/Mn hydrous oxyhydroxides (easily reducible $\{M\}_A$); crystalline Fe/Mn oxides (reducible $\{M\}_C$); organics/sulfides (oxidizable $\{M\}_O$); and residual fractions $\{M\}_R$. Samples were homogenized prior to digestion and each subsample was run in triplicate. Reagents blanks were included in each digestion to account for procedural contamination. Metal concentrations for each sediment fraction were quantified by an ICP-MS using matrix-matched standard curves to correct for matrix effects. Mean total floc/sediment metal concentrations $\{M\}_T$ were determined by summing concentrations from each of the six fractions.

5.3.5 Mineralogy/ Solid Phase Composition

The bulk mineralogical composition of floc and sediment was determined by X-ray diffractometry (XRD) (Siemens D5005 X-ray diffractometer). Bulk XRD analysis identified Fe oxyhydroxide/oxides minerals in floc and sediment as Ferrihydrite/Feroxyhite and Magnetite (Fe_3O_4), as well as Hematite (Fe_2O_3) in floc (Table S.5.2). Organics and amorphous minerals dominated floc abundance, while Quartz, Calcite and Plagioclase were the main mineral components of sediments (Table S.5.2).

Mean floc/sediment weights were determined by drying samples at 80°C in triplicate until consistent weight. Mean bulk organic matter content {OM} was estimated by loss on ignition (%LOI, 550°C for 2 h). Oxyhydroxide content was estimated by quantifying the total Fe extracted from the amorphous $\{Fe\}_A$ and crystalline $\{Fe\}_C$ oxide (referred to here on as FeOOH and FeOx, respectively) fractions by colorimetric analysis using FerroVer HACH method (Ultrospec 2000, UV/visible spectrophotometer, Pharmacia Biotech, Cambridge U.K.), and $\{Mn\}_A$ and $\{Mn\}_C$ quantified by ICP-MS.

5.3.6 Statistical Analysis

Statistical analyses were performed using PASW version 18.0 (SPSS Inc., Chicago, Illinois, U.S.A). T-tests were applied to test for significant differences of mean FeOOH, $\{M\}_T$ and $\{M\}_A$ between suspended floc, SFGL and bed sediments. Unless otherwise indicated, for all statistical tests a sample size of n =6 and a significance level of R = 0.05 was applied.

5.3.7 Imaging

Suspended flocs were visualized for internal structure and elemental analysis using transmission electron microscopy (TEM-EDS). Ultra-thin sections of suspended-floc collected from bulk water samples (at depth of CFC floc collection) were prepared according to Liss at al. (1996) and imaged in transmission mode at an accelerated voltage of 80 kV using a JEOL 1200 Ex II TEMSCAN (McMaster University) scanning transmission electron microscope.

5.4 Results and Discussion

5.4.1 Spatial Variability

Differences in suspended-floc partitioning were observed for shallow versus deep waters, reflecting spatially dependent hydrodynamic mixing of floc and bed material and thus relative amorphous and crystalline Fe oxide mineral floc abundances.

5.4.1.1 Suspended-Floc Offshore

Amorphous Fe oxyhydroxides (FeOOH) was the most important substrate controlling floc metal sequestration in deep waters offshore. Average floc FeOOH concentration (2.5 m above bed) was 8.83 mg g^{-1} compared to 0.06 mg g^{-1} in the underlying bed sediment (0.5-1cm depth). The amorphous oxyhydroxides phase dominated floc partitioning at 56, 36, and 47% of floc Ag, Co, and Pb respectively (Figure 5.2/Table 5.2). In contrast, limited FeOOH abundance within sediments resulted in crystalline oxides retaining the largest proportion of metals at 66, 36, 53 and 52% of bed Ag, Co, Cu and Pb, respectively. Although floc Cu was an exception to the trend with the largest proportion of Cu retained by the organic fraction (35%), an association previously reported in natural flocs and sediments (Gagnon et al., 2009; Koretsky et al., 2006), Cu bound to the amorphous FeOOH phase $\{Cu\}_A$ was significantly greater in floc than sediments, demonstrating the specific importance of reactive FeOOH minerals for floc metal scavenging. The high metal retention by FeOOH was reflected in significantly higher total floc metal concentrations $\{M\}_T$, compared to bed sediments for all elements analyzed (Table 5.2 and 5.3). These littoral floc metal results resemble those observed for limnetic pelagic flocs that are known to concentrate FeOOH and associated metals over those of bulk bed sediments, and have a characteristic amorphous FeOOH partitioning signature (Elliott et al., 2011). These results suggest that the relatively lower energetic conditions in deeper waters away from shore (as indicated by [SS], Table 5.1) limits mixing of flocs and sediments and thus the exchange of amorphous and crystalline Fe minerals, leading to compartment-specific partitioning signatures, i.e. amorphous oxyhydroxide in flocs and crystalline oxides in bed sediments (Figure 5.2). These results reflect the different controls on FeOOH abundance within each compartment related to their biogeochemical characteristics. For example, flocs suspended in the oxygenated water-column accumulate Fe within the organic-rich aggregate ({OM} 0.74 g g^{-1}) of microbial cells and extracellular polymeric substances (EPS) (Figure S.5.1; Elliott et al., 2011), while greater abundances of FeOx than FeOOH in the bed sediments reflect mineral aging and/or microbial reductive dissolution of FeOOH (Table S.5.3).

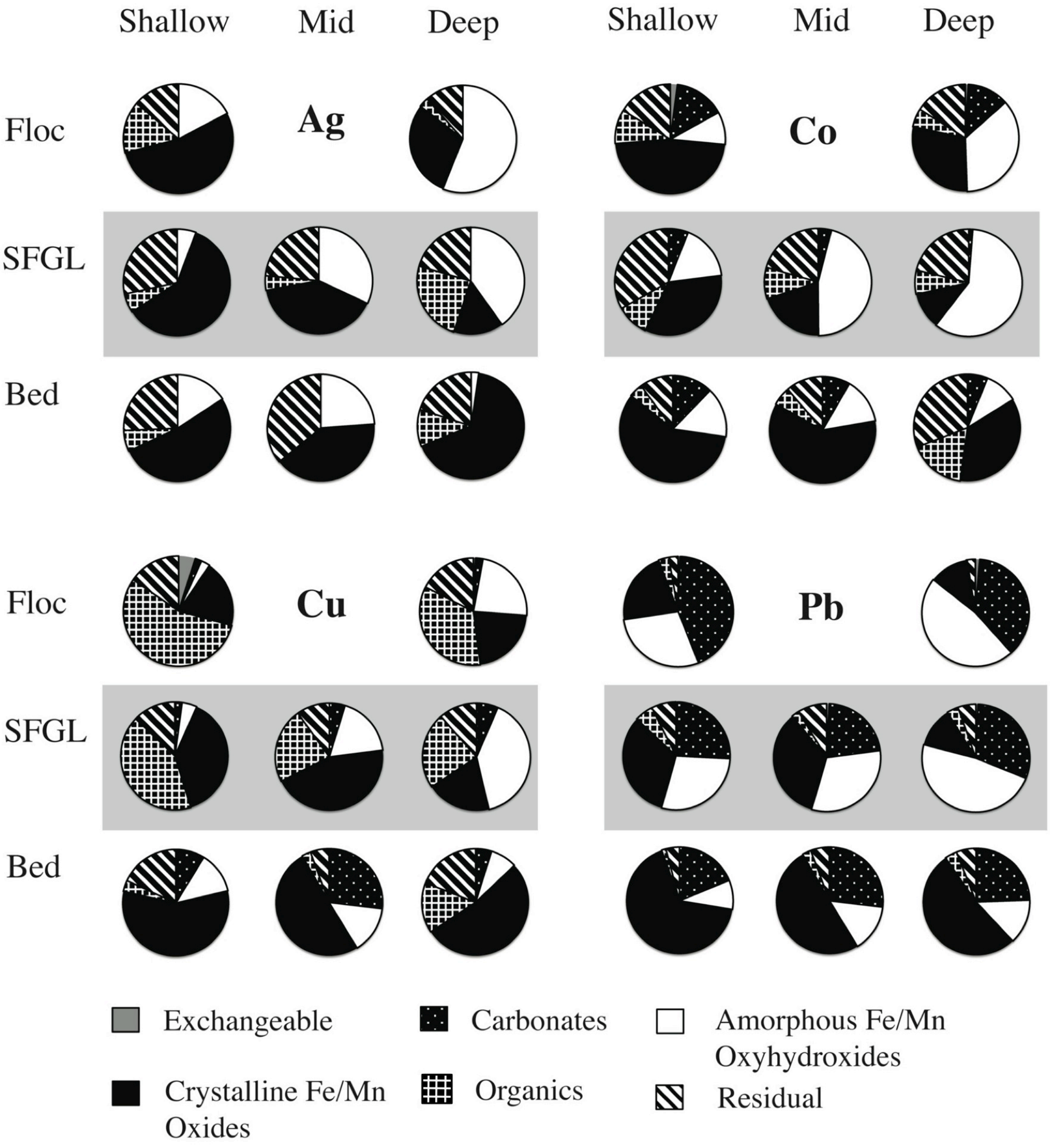

Figure 5.2 Relative proportion of Ag, Co, Cu and Pb observed in each of six extraction steps of suspended floc, SFGL and bed sediment along the shallow to deep transect.

Table 5.2 Suspended floc (nearshore and offshore) temporal total metal concentrations $\{M\}_T$ (µmolg^{-1}) ± 1 standard deviation and percentage (%) of metal in six operationally defined solid phases (exchangeable $\{M\}_E$, carbonates $\{M\}_{CAR}$, amorphous oxyhydroxide $\{M\}_A$, crystalline oxides $\{M\}_C$, organic $\{M\}_O$ and residual $\{M\}_R$) .

		Ag		**Co**		**Cu**		**Pb**	
		NS	**OS**	**NS**	**OS**	**NS**	**OS**	**NS**	**OS**
Morning	$\{M\}_T$	0.005	0.012	0.077	0.108	0.626	2.802	0.159	0.179
	±	0.000	0.001	0.010	0.006	0.051	0.099	0.016	0.007
	$\{M\}_E$	0	0	2	1	0.000	2	0	2
	$\{M\}_{CAR}$	0	0	19	17	3	7	46	41
	$\{M\}_A$	3	39	7	20	1	24	20	42
	$\{M\}_C$	62	48	32	36	21	26	25	13
	$\{M\}_O$	19	3	9	7	75	28	4	0
	$\{M\}_R$	15	11	32	19	0	12	3	2
Afternoon	$\{M\}_T$	0.008	0.018	0.171	0.136	0.982	1.288	0.243	0.192
	±	0.000	0.002	0.014	0.024	0.046	0.136	0.034	0.017
	$\{M\}_E$	0	0	2	0	7	0	1	2
	$\{M\}_{CAR}$	0	0	11	11	2	0	35	41
	$\{M\}_A$	2	58	9	29	2	21	32	41
	$\{M\}_C$	61	26	54	35	15	27	26	13
	$\{M\}_O$	17	3	11	6	52	32	3	0
	$\{M\}_R$	20	13	13	20	22	20	2	3
Evening	$\{M\}_T$	0.008	0.020	0.114	0.155	1.206	0.893	0.185	0.193
	±	0.000	0.001	0.007	0.004	0.116	0.075	0.009	0.010
	$\{M\}_E$	0	0	2	1	6	0	1	0
	$\{M\}_{CAR}$	0	0	18	10	2	0	51	29
	$\{M\}_A$	40	72	12	59	4	25	31	59
	$\{M\}_C$	41	15	48	16	24	11	12	9
	$\{M\}_O$	11	2	10	4	47	44	2	1
	$\{M\}_R$	7	11	11	10	18	20	3	2
Day Average	$\{M\}_T$	0.007	0.017	0.121	0.133	0.938	1.661	0.196	0.188
	±	0.000	0.001	0.010	0.011	0.071	0.103	0.020	0.011
	$\{M\}_E$	0	0	2	1	4	1	1	1
	$\{M\}_{CAR}$	0	0	16	13	2	2	44	37
	$\{M\}_A$	15	56	9	36	2	23	28	47
	$\{M\}_C$	55	29	45	29	20	22	21	12
	$\{M\}_O$	16	3	10	6	58	35	3	0
	$\{M\}_R$	14	12	18	16	13	17	3	3

5.4.1.2 Suspended-Floc Nearshore

In contrast to the observed offshore unique partitioning patterns of floc versus bed sediments, compartment-specific signatures and distinct FeOOH abundances were not observed in shallow waters nearshore. Flocs collected nearshore (0.5 m above the bed, high energy) were far less enriched in FeOOH, $\{M\}_A$ and overall trace metals compared to bed sediments as indicated by lower enrichment factors (EF= e.g. (Floc$\{M\}_T$ / Bed$\{M\}_T$) – 1); Table 5.4). Relative to offshore (low energy), floc nearshore showed a strong crystalline oxide signature for each element analyzed that was more reflective of bed sediment suspension (Figure 5.2). For example, the crystalline oxides were the most important phase for Co in sediments (58%) and contained almost half (45%) of total floc Co collected nearshore compared to only 29% of total floc Co offshore. The low floc-FeOOH abundance and crystalline oxide signature resembles that of floc collected under turbulent conditions when wind-driven waves mobilize bulk bed sediments into suspension (Plach et al., 2011). These results indicate that the relatively higher-energy conditions in shallow waters (as indicated by [SS] Table 5.1) increase bed erosion and sediment mobilization altering floc metal partitioning (Figure 5.2). Thus, spatially variable energy regimes within beach environments can have a significant impact on floc FeOOH abundance and metal behaviour, demonstrating that the compartment-specific partitioning is a useful marker of floc/bed mixing and associated contaminant mobilization within these hydrodynamic aquatic systems.

Table 5.3 Along a transect from nearshore (shallow) to offshore (deep), SFGL and bed sediment total metal concentrations $\{M\}_T$ (μmolg^{-1}) ± 1 standard deviation and percentage (%) of metal in six operationally defined solid phases (exchangeable $\{M\}_E$, carbonates $\{M\}_{CAR}$, amorphous oxyhydroxide $\{M\}_A$, crystalline oxides $\{M\}_C$, organic $\{M\}_O$ and residual $\{M\}_R$) .

		Ag^a		**Co**		**Cu**		**Pb**	
		SFGL	**Bed**	**SFGL**	**Bed**	**SFGL**	**Bed**	**SFGL**	**Bed**
Shallow	$\{M\}_T$	1.185	0.714	0.026	0.026	0.194	0.064	0.039	0.032
	±	0.097	0.283	0.002	0.005	0.028	0.008	0.003	0.006
	$\{M\}_E$	0	0	0	0	0	0	0	0
	$\{M\}_{CAR}$	0	0	6	12	2	9	25	19
	$\{M\}_A$	6	18	17	15	4	13	29	9
	$\{M\}_C$	60	46	34	58	39	57	33	67
	$\{M\}_O$	6	7	10	4	42	3	6	1
	$\{M\}_R$	28	29	33	10	13	18	7	4
Mid	$\{M\}_T$	0.656	0.431	0.026	0.027	0.143	0.066	0.037	0.029
	±	0.125	0.090	0.001	0.005	0.006	0.006	0.002	0.004
	$\{M\}_E$	0	0	0	0	0	0	1	0
	$\{M\}_{CAR}$	0	0	4	8	5	28	22	28
	$\{M\}_A$	32	24	46	14	18	11	32	11
	$\{M\}_C$	40	40	20	61	45	53	34	53
	$\{M\}_O$	4	0	10	6	23	3	2	3
	$\{M\}_R$	23	36	21	11	10	6	9	6
Deep	$\{M\}_T$	0.716	0.313	0.034	0.016	0.088	0.031	0.026	0.014
	±	0.081	0.012	0.002	0.002	0.008	0.003	0.003	0.004
	$\{M\}_E$	0	0	0	0	0	0	1	0
	$\{M\}_{CAR}$	0	0	1	6	6	5	30	24
	$\{M\}_A$	40	2	59	10	40	8	48	14
	$\{M\}_C$	15	66	11	36	19	53	12	52
	$\{M\}_O$	24	11	7	17	23	15	3	4
	$\{M\}_R$	21	20	21	31	11	19	5	6

[a] values nmolg^{-1}

Table 5.4 Enrichment factors (EFs) of suspended floc versus bed sediments for FeOOH, total metal concentrations $\{M\}_T$ and metal associated with carbonates $\{M\}_{CAR}$, amorphous oxyhydroxides $\{M\}_A$, crystalline oxides $\{M\}_C$ and organic $\{M\}_O$ fractions. Positive EF values indicate metal enrichment in suspended floc.

		Ag	**Co**	**Cu**	**Pb**	**FeOOH**
Nearshore	$\{M\}_T$	9.1	3.7	14	5.1	8.7
	$\{M\}_{CAR}$	0.0	4.7	2.3	13	
	$\{M\}_A$	8.7	2.7	3.3	8.3	
	$\{M\}_C$	29	17	32	6.0	
	$\{M\}_O$	7.6	2.9	92	0.0	
Offshore	$\{M\}_T$	52	7.1	52	12	$15\text{x}10^1$
	$\{M\}_{CAR}$	0.0	15	42	19	
	$\{M\}_A$	$14\text{x}10^2$	30	$15\text{x}10^1$	45	
	$\{M\}_C$	21	5.3	23	1.9	
	$\{M\}_O$	13	1.6	$11\text{x}10^1$	0.0	

5.4.1.3 Surfical Bed Sediments Offshore

Consistent with the importance of the energy regime affecting the geochemistry of the suspended floc compartment, surficial bed sediments also showed distinct Fe mineral abundances and metal behaviour associated with the impacts of variable energetic conditions on bed erosion and floc-settling. Greater concentrations of FeOOH (26x) and associated metals (up to 40x) were observed in the offshore surfical fine-grained layer (SFGL, 0-3 mm) compared to the underlying bed sediments (0.5- 1 cm). This is consistent with recent settlement of floc-FeOOH onto the undisturbed bed surface as well as oxidation of Fe(II) diffused up from deeper sediments and precipitation of FeOOH at the oxic sediment-water interface.

The amorphous oxyhydroxides were the important phase for SFGL metal sequestration retaining 40, 59, 40 and 48% of total offshore SFGL Ag, Co, Cu and Pb, respectively (Figure 5.2/Table 5.3). The importance of FeOOH for overall SFLG metal retention was also reflected in $\{M\}_A$ and total metal concentrations $\{M\}_T$ that were enriched in the SFLG compared to underlying sediments for all elements analyzed (Table 5.3). Enrichment of Fe and metals is frequently observed at oxic sediment-water interfaces of undisturbed sediments (e.g. Feyte et al., 2010).

The strong amorphous oxyhydroxide signature to offshore SFGL partitioning was similar to that of offshore suspended floc, however, the abundances of SFGL-FeOOH, $\{M\}_A$ and total metal $\{M\}_T$ were lower. This result illustrates the importance of the SFGL as a transitional, layer whereby diagenetic processes occurring in the undisturbed sediments lead to the cycling of Fe and associated metals over likely small spatial and rapid temporal scales. For example, anaerobic conditions are typically reached within millimeter depths from an oxic water-column of undisturbed sediments (e.g. Gerhardt and Schink, 2005). As such, FeOOH deposited in the SFGL would be rapidly buried, reductively dissolved and/or aged, resulting in the re-partitioning of metals originally associated within FeOOH into FeOx as well as the mobilization of metals into the overlying water column reflecting the decreased reactivity of FeOx relative to FeOOH. Further, local lowering of pH due to Fe(II) oxidation at the oxic-anoxic boundary may also facilitate desorption of metals bound by Fe minerals and contribute to the observed reduced metal retention in the SFGL compared to floc.

5.4.1.4 Surfical Bed Sediments Nearshore

While distinct FeOOH abundances and partitioning between SFLG and underlying sediments were observed at the sediment-water interface offshore (i.e. amorphous FeOOH in SFGL versus FeOx in the bed), limited FeOOH and metal accumulation was observed in the SFGL nearshore (Table S.5.3). Along the sediment transect from deep to shallow waters, the concentration of SFGL-FeOOH (i.e. indicative of settled-floc), not observed for SFGL-$\{Mn\}_A$, were highest offshore and decreased towards shore (1.57, 1.31 and 0.77 mg g^{-1}). In contrast, SFGL-FeOx (i.e. indicative of bulk bed sediments) was lowest offshore and increased at shallower water depths (Table S.5.3). Lower nearshore SFGL-FeOOH resulted in less $\{M\}_A$ which was reflected in reduced partitioning towards the amorphous oxyhydroxide phase for all elements analyzed (Figure 5.2/Table 5.3). Rather, the nearshore SFGL showed a greater $\{M\}_C$ and partitioning towards the crystalline oxide phase, that was more reflective of bulk bed sediments. For example, SFGL Ag partitioning decreased from 40 to 6% in the amorphous oxyhydroxide phase and increased in the crystalline oxide phase from 15 to 60% towards shore. These results highlight that the relatively higher energy-regime occurring in shallow waters limits floc settling and FeOOH deposition and thus affects SFGL metal dynamics. Further, increased bed erosion would broaden the oxic zone of surface sediments and result in a slower Fe(II) oxidation rate (Gerhardt and Schink, 2005), contributing to limited FeOOH accumulation and associated metals observed in the SFGL nearshore.

Increased sediment layer mixing nearshore was evidenced by SFGL/bed enrichment factors (EF= i.e. (SFGL{FeOOH} / Bed{FeOOH}) – 1)) which were lower for SFGL-FeOOH compared to offshore; i.e. lower SFGL-FeOOH abundance compared to underlying bed due to greater erosion results in lower EF values (Figure 5.3). Despite element specific affinities for different fractions (e.g. Cu for organics), metal $\{M\}_A$ EFs were also lower nearshore than offshore for all elements analyzed and showed lower overall metal enrichment (Table S.5.4). The exception to this trend was total Cu EFs, which increased towards shore, likely due to organic matter rather than FeOOH dominating overall Cu retention.

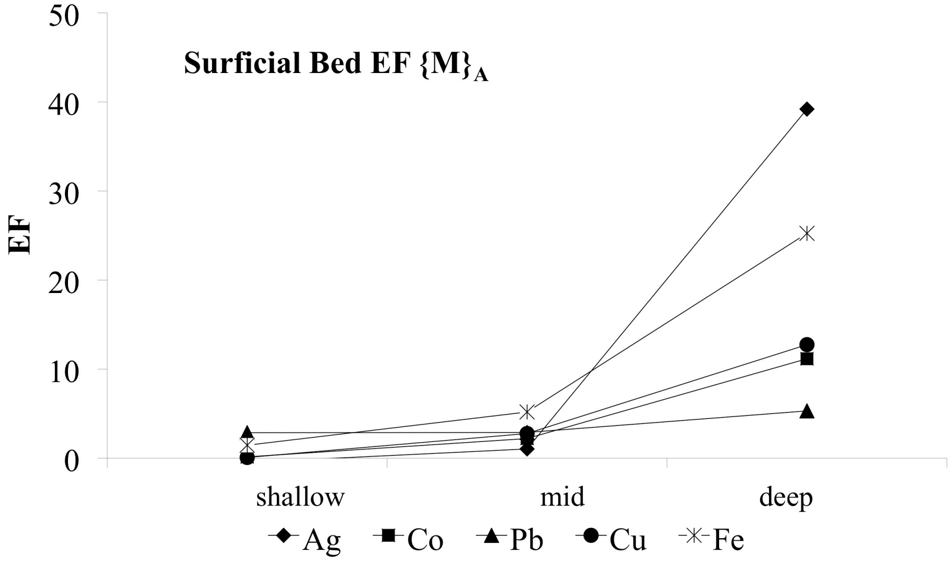

Figure 5.3 Enrichment factors (EFs) at the sediment-water interface (i.e. SFGL versus bed) for $\{Ag\}_A$, $\{Co\}_A$, $\{Pb\}_A$, $\{Cu\}_A$ and $\{Fe\}_A$ along the shallow to deep transect. Values greater than 0 indicate enrichment of element in the SFGL.

5.4.2 Diurnal Variability

5.4.2.1. Suspended Floc Offshore

Given the importance of FeOOH for floc metal retention, the potential temporal variation in floc-FeOOH abundance and/or reactivity driven by daily changes in water-column physico-chemistry would be expected to alter floc metal behaviour. Indeed, FeOOH concentrations in floc collected offshore increased through the day from 5.56, 7.19 to 13.74 mg L^{-1} over three 4-h collection intervals (i.e. 8:00-12:00, 12:00-16:00 and 16:00-20:00). Increased floc-FeOOH abundance correlated with increased floc $\{M\}_A$, as well as an overall increase in total floc metal $\{M\}_T$ (Table 5.2 and S.5.3). For example, mean total floc $\{Co\}_T$ increased from 0.108 to 0.157 μmol g^{-1}, $\{Co\}_A$ increased from 0.021 to 0.093 μmol g^{-1} and overall floc Co partitioning towards the amorphous oxyhydroxides phase from 20 to 59% throughout the day. The exception to the trend was for Cu where partitioning was largely retained in the organic fraction (28-44%). Given that dissolved Fe concentrations (<0.2 μm) showed minimal variation throughout the day (Table 5.1), transport mechanisms of particulate FeOOH likely play a key role on the observed temporal variation in floc-FeOOH abundance. For example, rising floc-FeOOH concentrations may reflect FeOOH carried by long-shore currents from the Humber River, i.e. a source of particulate Fe to this system (Figure 5.1/ Table 5.1) as well as longitudinal and vertical transport of SFGL-FeOOH from surficial sediments driven by diurnal variability in wave action and currents.

5.4.2.2 Suspended Floc Nearshore

Vertical transport and the exchange of FeOOH minerals between floc and surficial sediments were evident through a temporal assessment of floc and SFGL geochemistry nearshore (i.e. SFGL collected morning 8:00, afternoon 13:00 and 16:00 and evening 19:30). For example, accumulation of FeOOH in the SFGL under quiescent early morning conditions (as indicated by low [SS] Table 5.1), resulted in the highest SFLG $\{M\}_A$ for all elements analyzed (Table S.5.3 and S.5.5). The high SFGL-FeOOH and associated metal during the morning is suggestive of floc-settling as well as Fe(II) oxidation/FeOOH precipitation sequestering metals at the oxic sediment surface. As turbulence increased mid-day, a decrease in FeOOH abundance, $\{M\}_A$ and a strong crystalline oxide signature reflective of bed sediments was observed in the SFGL. In contrast, suspended floc showed an increased in FeOOH and $\{M\}_A$ mid-day suggesting the remobilization of SFGL-FeOOH and associated metals into the water-column driven by turbulence (Table S.5.3 and S.5.5). Further, higher FeOx and $\{M\}_C$ concentration in floc mid-day also suggests some re-suspension of bulk bed material. The subsequent increase of FeOOH and $\{M\}_A$ in the SFGL under calm evening conditions (as indicated by low [SS] Table 5.1) suggested partial FeOOH/metal re-settlement as well as FeOOH precipitation/metal sequestration at the undisturbed sediment surface.

Suspended floc entrained in the water-column post turbulent mixing was enriched in FeOOH and metals over that of SFGL as evidenced by enrichment factors (e.g. Floc$\{M\}_A$ / SFGL$\{M\}_A$) – 1) that were highest at the end of the day for FeOOH, Ag, Co, and Cu (Figure 5.4 and Table S.5.6). Enrichment of floc Fe and metals over surfical sediments post re-suspension is commonly observed under laboratory conditions (e.g. Kalnejais et al., 2007; Cantwell et al., 2002), and is consistent with in situ floc metal EFs observed by this study. The preferential re-settlement of more dense FeOx minerals rather than FeOOH post mixing, as indicated by a subsequent decreased in Floc-FeOx abundance in the evening (Table S.5.3), would lead to the observed enrichment of floc-FeOOH at the end of the day. Changing water-column physicochemical conditions likely play a key role in the observed floc metal enrichment. For example, water turbulence can alter floc particle size and thus surface area, which will impact floc reactivity for trace metal uptake (Biggs and Lant, 2000; Bouyer et al., 2004; Laurent et al., 2009). Further, floc metal enrichment may also be linked to the preferential association of metals with fine-grained particles in sediments (Bothner et al., 1998) that remain entrained in the water column after mixing. Results of this study show that floc particle size decreased during the day (Figure S.5.2), suggesting the formation of a relatively greater floc surface area, and sorptive capacity for solution metals. Indeed, an assessment of mean total floc solid-solution distribution coefficients (Kd values; $\mathrm{Log}\{M\}_T/[M]_D$; Stumm and Morgan, 1996) indicated that the greatest floc solution metal uptake (i.e. largest Kd values) occurred at the end of the day for all elements analyzed (Table S.5.7).

Consistent with the importance of FeOOH for floc metal sequestration, floc metal solid-solution distribution coefficients in the amorphous oxyhydroxide phase (i.e. $\{M\}_A$ Kd; $\mathrm{Log}\{M\}_A/[M]_D$; Table S.5.6) and floc EFs in the amorphous oxyhydroxide fraction (i.e. $\mathrm{Floc}\{M\}_A$ / $\mathrm{SFGL}\{M\}_A) - 1$)) were highest in the evening post-mixing (Figure 5.4). A photosynthetic-driven rise in water-column pH (8.16 to 8.72) may also contribute to the observed increased floc-FeOOH metal uptake, given that FeOOH sorptive capacity is highly pH dependent (Gadde and Laitinen, 1974; Benjamin and Leckie, 1981) and overall floc metal retention has been shown to increase under higher pH conditions (Plach and Warren, 2012; Lead et al., 1999; Theis et al., 1988).

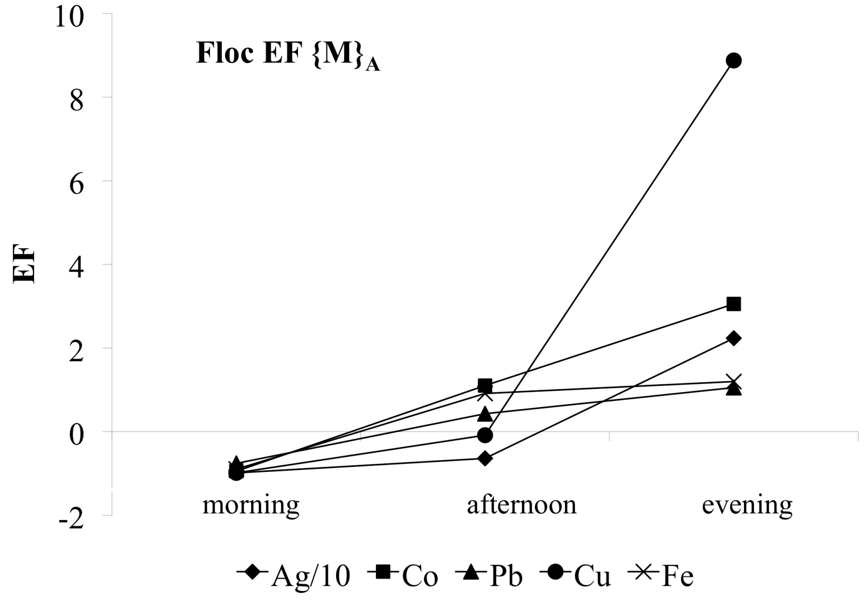

Figure 5.4 Floc enrichment factors (EFs) (i.e. suspended floc versus SFGL) for $\{Ag\}_A$, $\{Co\}_A$, $\{Pb\}_A$, $\{Cu\}_A$ and $\{Fe\}_A$ during the morning, afternoon and evening nearshore. Values greater than 0 indicate enrichment of element in floc.

5.5 Summary

Together, these results demonstrate that floc is a highly dynamic compartment within shallow littoral waters, with metal behaviour linked specifically to shifts in floc-FeOOH abundance and reactivity, dependent on rapidly changing physicochemistry over relatively short timescales. A summary of spatial and temporal floc, SFGL and bed sediment Fe mineral cycling and associated metal behaviour are presented as a conceptual model in Figure 5.5.

Results suggest a spatial energy-dependent exchange of differentially metal-reactive amorphous and crystalline Fe minerals between floc and bed compartments (Figure 5.5A). Limited compartment mixing under quiescent conditions offshore resulted in distinct compartment-specific partitioning of floc from sediments i.e. FeOOH in floc and FeOx in the bed. Settling of floc as well as Fe(II) oxidation/FeOOH precipitation at the undisturbed sediment-water interface lead to the accumulation of FeOOH and associated metals in the SFGL. Subsequent burial, reductive FeOOH dissolution and/or mineral aging limited bed-FeOOH abundance, resulting in the re-partitioning of metals originally associated with FeOOH into FeOx as well as metal mobilization towards the overlying water-column. In contrast, greater turbulent conditions and compartment mixing in shallow waters nearshore resulted in bed sediment FeOx mobilization leading to less distinct floc, SFGL and bed-FeOOH/metal abundances and metal partitioning.

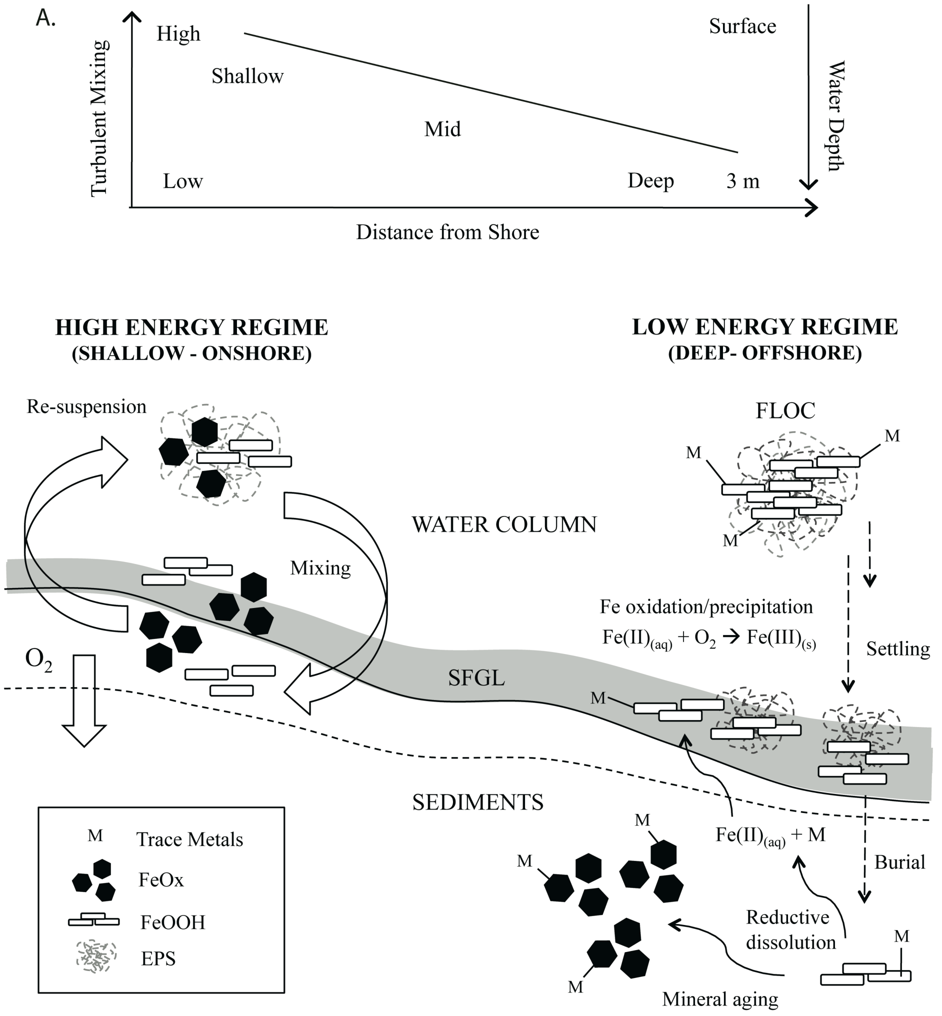

Figure 5.5 (Part 1/2): Schematic diagram of proposed Fe cycling and associated metal behaviour of suspended floc, SFGL and sediments under varying spatial (A) and temporal (B) physico chemical conditions.

Diurnal changes in wind-driven waves and water-column pH nearshore resulted in temporal shifts in floc and SFGL Fe mineral abundance/reactivity and associated metal behaviour (Figure 5.5B). Calm morning conditions lead to enrichment of FeOOH and associated metals in the SFGL, while afternoon turbulent mixing re-cycled SFGL-FeOOH/bed-FeOx and associated metals into the floc compartment. Increased floc breakage and entrainment of fine-grained sediment particulates likely contributed to the decrease in floc particle size through the day. Post-mixing, preferential settlement of dense FeOx minerals lead to FeOOH enrichment in small floc particulates in higher pH conditions, increasing floc-FeOOH reactivity and overall sorption of metals by flocs.

Given that floc metal concentrations consistently exceeded provincial sediment quality guidelines (SQG) at the lowest effect level (LEL) as well as natural Great Lake background levels for metals (Ontario Ministry of Environment and Energy, 1993), understanding the physicochemical controls on Fe cycling affecting floc metal behaviour has direct implications for predicting metal mobility and potential water quality degradation in urban freshwater beach environments.

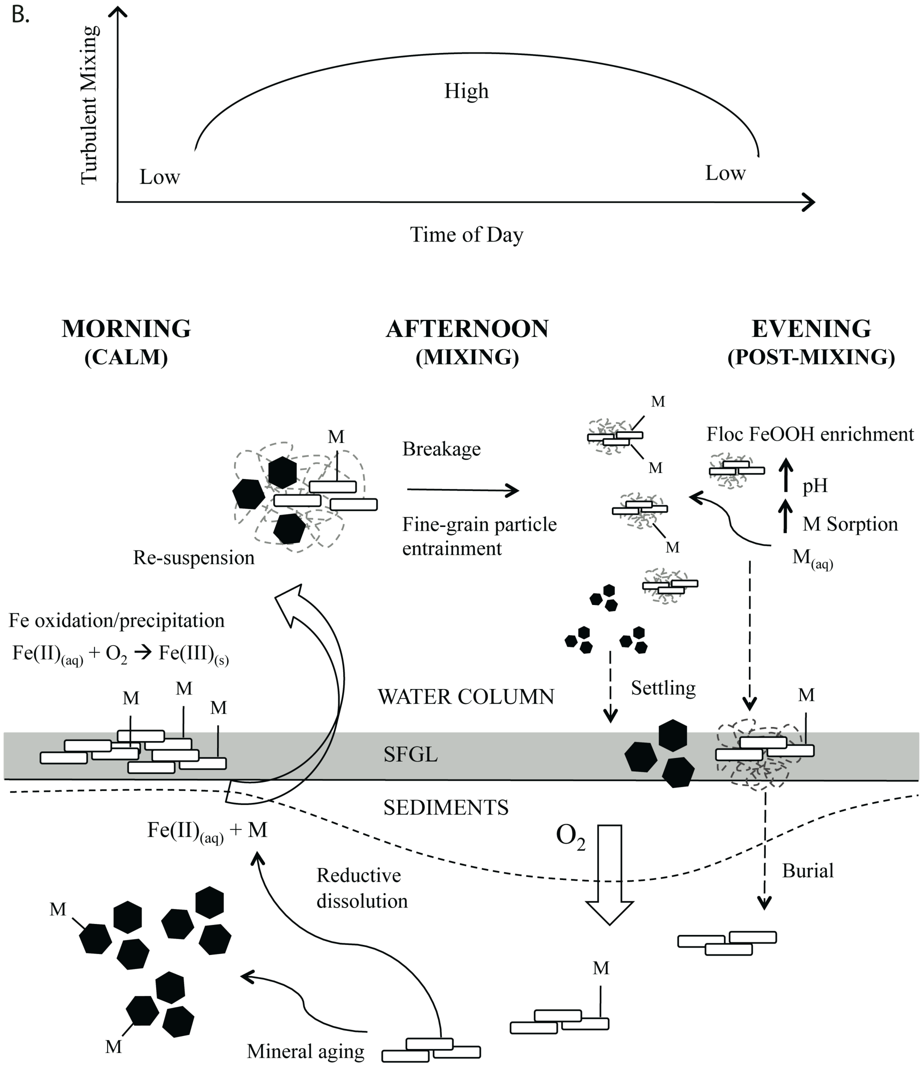

Figure 5.5 (Part 2/2): Schematic diagram of proposed Fe cycling and associated metal behaviour of suspended floc, SFGL and sediments under varying spatial (A) and temporal (B) physico chemical conditions.

5.6 Conclusion

This field investigation demonstrates that the high affinity of FeOOH for trace elements imparts a significant control on floc metal retention, and that changing hydrodynamic and water column chemistry (i.e. pH) dynamically affects floc-FeOOH abundance and metal behaviour within a littoral freshwater beach. Establishing the spatial and temporal controls on abundance and reactivity of differing Fe minerals within suspended floc and bed sediment compartments is imperative for understanding contaminant distribution within these shallow systems. Results of this study further identify that physicochemical parameters also play an important role on cycling of Fe in aquatic environments, dynamically affecting floc and surficial sediment metal behaviour over short timescales in littoral zones of lakes.

5.8 Supplementary Information

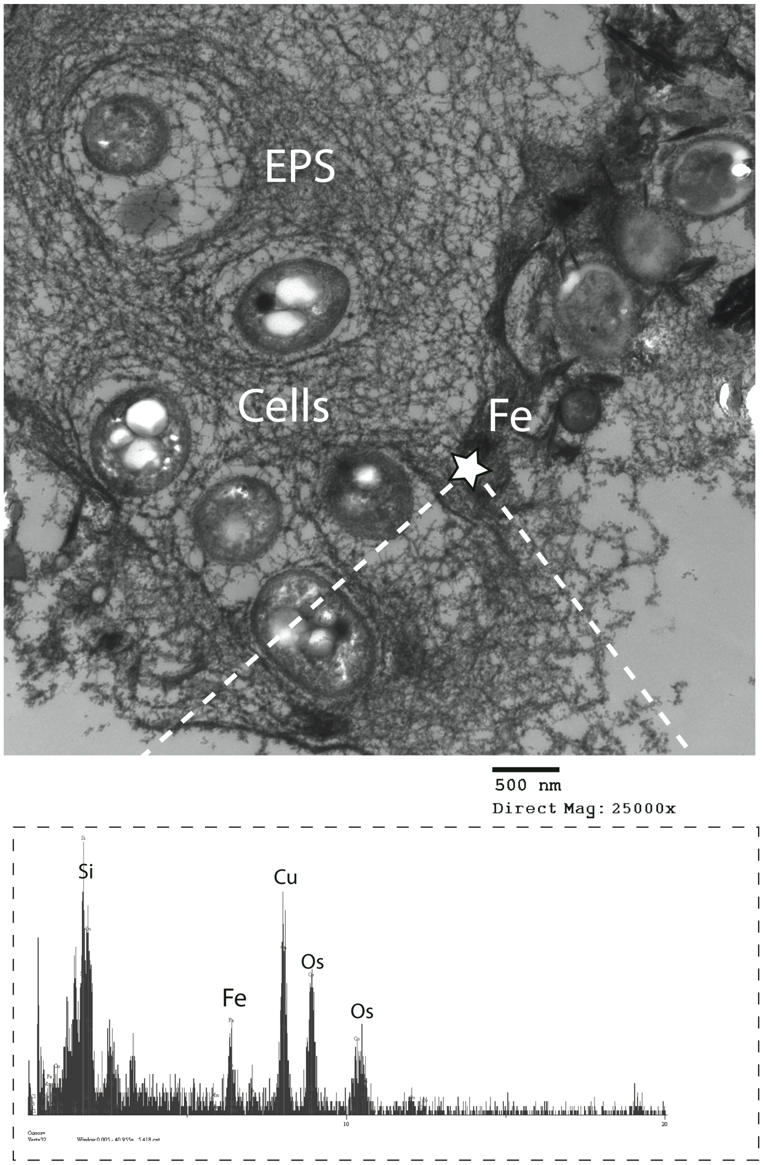

Figure S.5.1 TEM image of suspended floc depicting bacteria (species unknown) with EPS and associated Fe. Peaks of Cu and Os are an artifact of sample preparation and grid.

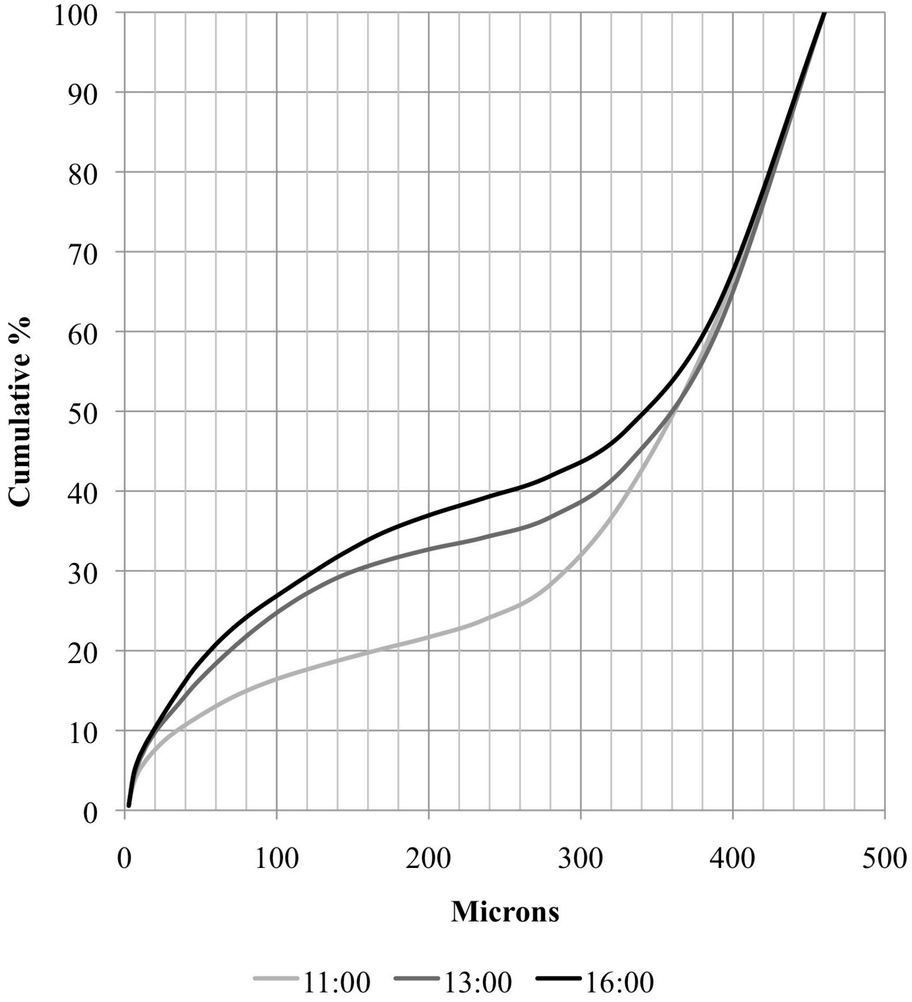

Figure S.5.2 Suspended floc particle size cumulative distribution in the morning (11:00), afternoon (13:00) and evening (16:00) nearshore.

Table S.5.1 Major cations and anions, dissolved inorganic and organic carbon at site of nearshore floc collection (0.5m depth).

	Ca mg L^{-1}	Mg mg L^{-1}	Na mg L^{-1}	K mg L^{-1}	F mg L^{-1}	Cl mg L^{-1}	SO_4^{2-} mg L^{-1}	DIC mg L^{-1}	DOC mg L^{-1}
Nearshore									
10:30	34.6 ± 0.25	8.94 ± 0.05	16.5 ± 0.06	1.77 ± 0.01	0.11 ± 0	28.6 ± 0.12	26.1 ± 0	20.7 ± 0.1	2.5 ± 0.1
15:30	34.4 ± 0.1	8.93 ± 0.03	16.4 ± 0.06	1.75 ± 0.02	0.11 ± 0	28.1 ± 0.06	26 ± 0.06	19.9 ± 0.15	2.6 ± 0.25
7:30	33.7 ± 0.06	8.89 ± 0.01	16.3 ± 0.06	1.78 ± 0.03	0.11 ± 0	28.1 ± 0.06	25.9 ± 0.06	19.1 ± 0.06	2.6 ± 0.12

Table S.5.2 Bulk mineralogy (XRD) of suspended floc and offshore SFGL and bed sediment.

MINERAL	**SEDIMENT**		**FLOC**	
	Bed	**SFGL**	**Nearshore**	**Offshore**
Quartz	~34%	33%	6%	7%
Calcite	21%	~23%	18%	9%
Plagioclase	23%	22%	3%	~6%
Alkali K- feldespars	2%	2%	-	1%
Dolomite/ankerite	3%	3%	3%	2%
Amphibole	4%	3%	-	-
Hematite	-	-	1%	1%
Magnetite	2%	2%	2%	3%
Micas	1%	1%	-	-
Illite	-	-	1%	1%
Chlorite	-	1%	-	1%
Zeolite	1%	1%	-	-
Ferrihydrite/feroxyhite	1%	1%	3%	4%
Talc	-	-	-	-
Smectite	-	-	4%	2%
Nacrite	1%	-	-	-
Gehlenite	2%	3%	1%	1%
Organic and amorphous	-	-	~53%	57%
Other materials	5%	5%	5%	5%

Table S.5.3 Mean metal reactive constituents of suspended floc, SFGL and bed sediments

	FeOOH **mg g^{-1}**	**FeOx** **mg g^{-1}**	**$\{Mn\}_A$** **mg g^{-1}**	**$\{Mn\}_C$** **mg g^{-1}**	**OM** **g g^{-1}**
Nearshore					
Suspended Floc					
Morning	1.65	4.74	0.08	0.11	0.19
Afternoon	3.66	6.40	0.11	0.07	0.30
Evening	3.83	5.44	0.11	0.08	0.27
Day Average	3.05	5.53	0.10	0.09	0.25
SFGL (0- 3 mm)					
8:00	15.9	9.10	0.41	0.12	0.95
12:00	1.91	10.7	0.29	0.17	0.93
16:30	0.66	8.33	0.08	0.08	0.79
19:30	1.74	5.82	0.11	0.09	0.74
Bed (0.5- 1 cm)					
8:00	0.03	0.69	>0.01	>0.01	0.00
12:00	0.06	1.11	0.00	0.00	0.04
16:30	0.18	0.71	N/A	N/A	0.01
19:30	0.21	0.94	N/A	N/A	0.01
Offshore					
Suspended Floc					
Morning	5.56	5.68	0.52	0.07	0.62
Afternoon	7.19	3.71	1.20	0.09	0.47
Evening	13.7	3.62	1.10	0.04	0.74
Day Average	8.83	4.34	0.94	0.07	0.61
Sediment Transect					
SFGL (0- 3 mm)					
shallow	0.77	1.70	0.06	0.02	0.01
mid	1.31	1.20	0.07	0.03	0.01
deep	1.57	0.88	0.07	0.01	0.01
Bed (0.5- 1cm)					
shallow	0.31	1.69	0.02	0.01	0.02
mid	0.21	1.59	0.02	0.04	0.01
deep	0.06	1.06	0.03	0.04	0.01

Mean values (n=3). Standard deviation $\{Fe\}_A$ $\{Fe\}_C=10^{-1}$, $\{Mn\}_A$ $\{Mn\}_C$ $\{OM\}=10^{-2}$

Table S.5.4 Transect enrichment factors (EFs) of SFGL versus bed sediments for FeOOH, total metal concentrations $\{M\}_T$ and metal associated with carbonates $\{M\}_{CAR}$, amorphous oxyhydroxides $\{M\}_A$, crystalline oxides $\{M\}_C$ and organic $\{M\}_O$ fractions. Positive EF values indicate metal enrichment in SFGL.

		Ag	**Co**	**Cu**	**Pb**	**FeOOH**
Shallow	$\{M\}_T$	0.7	0.0	2.0	0.2	1.5
	$\{M\}_{CAR}$	0.0	-0.5	-0.2	0.6	
	$\{M\}_A$	-0.5	0.2	0.1	2.9	
	$\{M\}_C$	1.2	-0.4	1.0	-0.4	
	$\{M\}_O$	0.3	1.4	37	4.3	
Mid	$\{M\}_T$	0.5	0.0	1.2	0.3	5.2
	$\{M\}_{CAR}$	0.0	-0.5	-0.6	0.0	
	$\{M\}_A$	1.0	2.2	2.8	2.9	
	$\{M\}_C$	0.5	-0.7	0.8	-0.2	
	$\{M\}_O$	0.0	0.6	17	0.1	
Deep	$\{M\}_T$	1.3	1.1	1.8	0.8	25
	$\{M\}_{CAR}$	0.0	-0.6	2.8	1.2	
	$\{M\}_A$	39	11	13	5.3	
	$\{M\}_C$	-0.5	-0.4	0.0	-0.6	
	$\{M\}_O$	4.0	-0.1	3.2	0.7	

Table S.5.5 Temporal (8:00, 12:00, 16:30 and 19:3) nearshore SFGL and bed sediment total metal concentrations $\{M\}_T$ (μmolg^{-1}) ± 1 standard deviation and percentage (%) of metal in six operationally defined solid phases (exchangeable $\{M\}_E$, carbonates $\{M\}_{CAR}$, amorphous oxyhydroxide $\{M\}_A$, crystalline oxides $\{M\}_C$, organic $\{M\}_O$ and residual $\{M\}_R$).

		Ag		**Co**		**Cu**		**Pb**	
		SFGL	**Bed**	**SFGL**	**Bed**	**SFGL**	**Bed**	**SFGL**	**Bed**
8:00	$\{M\}_T$	0.016	0.211[a]	0.274	0.020	1.536	0.038	0.482	0.019
	±	0.001	0.030	0.009	0.002	0.039	0.003	0.012	0.002
	$\{M\}_E$	0	0	1	0	5	1	1	0
	$\{M\}_{CAR}$	0	0	26	9	10	5	63	16
	$\{M\}_A$	72	1	37	5	24	2	28	4
	$\{M\}_C$	11	68	21	28	17	40	6	55
	$\{M\}_O$	8	0	6	8	35	13	2	6
	$\{M\}_R$	10	32	9	50	10	38	2	19
12:00	$\{M\}_T$	0.010	0.016	0.227	0.039	1.520	0.040	0.429	0.068
	±	0.001	0.004	0.008	0.004	0.067	0.003	0.013	0.019
	$\{M\}_E$	0	3	1	1	2	0	0	0
	$\{M\}_{CAR}$	0	0	18	7	5	7	43	46
	$\{M\}_A$	5	7	3	2	2	1	13	4
	$\{M\}_C$	70	89	30	58	37	1	25	11
	$\{M\}_O$	14	0	9	5	38	40	5	9
	$\{M\}_R$	11	0	21	26	16	53	3	29
16:30	$\{M\}_T$	0.006	0.134[a]	0.131	0.013	0.650	0.040	0.234	0.061
	±	0.000	0.012	0.003	0.000	0.014	0.004	0.005	0.011
	$\{M\}_E$	0	0	0	0	1	0	0	0
	$\{M\}_{CAR}$	0	0	8	19	2	10	15	41
	$\{M\}_A$	1	27	1	1	0	2	5	17
	$\{M\}_C$	42	0	25	46	18	50	24	38
	$\{M\}_O$	7	32	5	7	19	8	2	3
	$\{M\}_R$	7	42	8	28	2	31	3	1
19:30	$\{M\}_T$	0.005	0.287[a]	0.101	0.017	0.647	0.073	0.232	0.066
	±	0.000	0.025	0.002	0.005	0.014	0.022	0.002	0.010
	$\{M\}_E$	0	0	0	0	2	0	0	0
	$\{M\}_{CAR}$	0	0	8	13	2	4	22	22
	$\{M\}_A$	3	1	3	1	1	1	12	6
	$\{M\}_C$	38	0	17	9	16	47	11	56
	$\{M\}_O$	7	63	3	10	15	22	2	7
	$\{M\}_R$	7	37	5	68	7	27	2	10

[a] values in nmolg^{-1}

Table S.5.6 Temporal enrichment factors (EFs) of nearshore suspended floc versus SFGL for FeOOH, total metal concentrations $\{M\}_T$ and metal associated with carbonates $\{M\}_{CAR}$, amorphous oxyhydroxides $\{M\}_A$, crystalline oxides $\{M\}_C$ and organic $\{M\}_O$ fractions. Positive EF values indicate metal enrichment in suspended floc.

		Ag	Co	Cu	Pb	FeOOH
Morning	$\{M\}_T$	-0.7	-0.9	-0.6	-0.7	-0.9
	$\{M\}_{CAR}$	*	-0.8	-0.9	-0.8	
	$\{M\}_A$	-1.0	-0.9	-1.0	-0.8	
	$\{M\}_C$	1.0	-0.6	-0.5	0.5	
	$\{M\}_O$	-0.1	-0.6	-0.1	-0.3	
Afternoon	$\{M\}_T$	-0.2	-0.9	-0.4	-0.4	0.9
	$\{M\}_{CAR}$	*	-0.5	-0.8	-0.5	
	$\{M\}_A$	-0.6	1.1	-0.1	0.4	
	$\{M\}_C$	-0.3	0.3	-0.7	-0.4	
	$\{M\}_O$	-0.1	-0.1	-0.1	-0.7	
Evening	$\{M\}_T$	0.6	0.1	0.9	-0.2	1.2
	$\{M\}_{CAR}$	*	1.4	0.6	0.9	
	$\{M\}_A$	22	3.1	8.9	1.1	
	$\{M\}_C$	0.7	2.3	1.8	-0.1	
	$\{M\}_O$	1.4	2.2	4.8	0.1	

* metal concentrations below LOQ

Table S.5.7 Distribution coefficients (Log Kds; MKg^{-1}) of nearshore suspended floc during morning, afternoon and evening sampling periods for total metal concentrations $\{M\}_T$ and operationally defined solid phases (carbonates $\{M\}_{CAR}$, amorphous oxyhydroxide $\{M\}_A$, crystalline oxides $\{M\}_C$, and organic $\{M\}_O$). Kds not calculated for Ag because $[Ag]_D$ were below LOQ.

		Co	**Cu**	**Pb**
$\{M\}_T$	Morning	4.5	4.4	4.8
	Afternoon	4.4	4.5	5.7
	Evening	4.8	4.9	5.7
$\{M\}_{CAR}$	Morning	2.8	2.8	4.5
	Afternoon	2.8	2.8	5.2
	Evening	3.1	3.1	5.4
$\{M\}_A$	Morning	3.3	2.4	4.1
	Afternoon	3.4	2.9	5.2
	Evening	3.8	3.5	5.2
$\{M\}_C$	Morning	4.0	3.7	4.2
	Afternoon	4.2	3.7	5.1
	Evening	4.4	4.3	4.8
$\{M\}_O$	Morning	4.3	4.3	3.4
	Afternoon	4.2	4.2	4.1
	Evening	4.6	4.6	4.1

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CHAPTER 6: SUMMARY, CONCLUSIONS and FUTURE RESEARCH

6.1 Summary

Results of this thesis have advanced the understanding of combined microscale biogeochemical processes as well as macroscale hydrodynamic mechanisms influencing trace metal (Ag, As, Co, Cu, Ni and Pb) sequestration/mobilization of freshwater floc (Figure 6.1). In particular, it establishes for the first time the importance of differential biogeochemical controls in suspended floc versus bed sediments affecting abundance, reactivity and type of Fe minerals resulting in distinct metal solid-phase partitioning between these two compartments (i.e. amorphous oxyhydroxides versus crystalline oxides, respectively). Specifically, results provide a new understanding of the microbial links (i.e. extracellular polymeric substance (EPS) structural framework) underpinning floc's accumulating reactive type Fe minerals controlling floc metal sorption, distinguishable from that of bed sediments whereby metal solid-solution dynamics are more influenced by system physico-chemistry (i.e pH) (see summary Section 6.2). Further, the importance of energy regime (i.e. quiescent, windy, prolonged-storm conditions) influencing re-suspension/settling of floc and sediment (i.e. surficial fine grained lamina (SFGL) versus underlying consolidated sediments) lead to temporal and spatial hydrodynamic-dependent cycling of Fe mineral phases that affect trace metal abundance and solid-phase partitioning of each compartment (see summary Section 6.3). Together, the outcome of this innovative integrated work provides new insights into the physical and biogeochemical controls on Fe cycling/mineral transformation between floc and bed sediments, ultimately impacting metal distributions and fate in the environment. This insight has important implications for policy development in improving risk management of exposure to metal-laden floc and sediment material to aquatic organisms and/or humans under varying physico-chemical and hydrodynamic conditions.

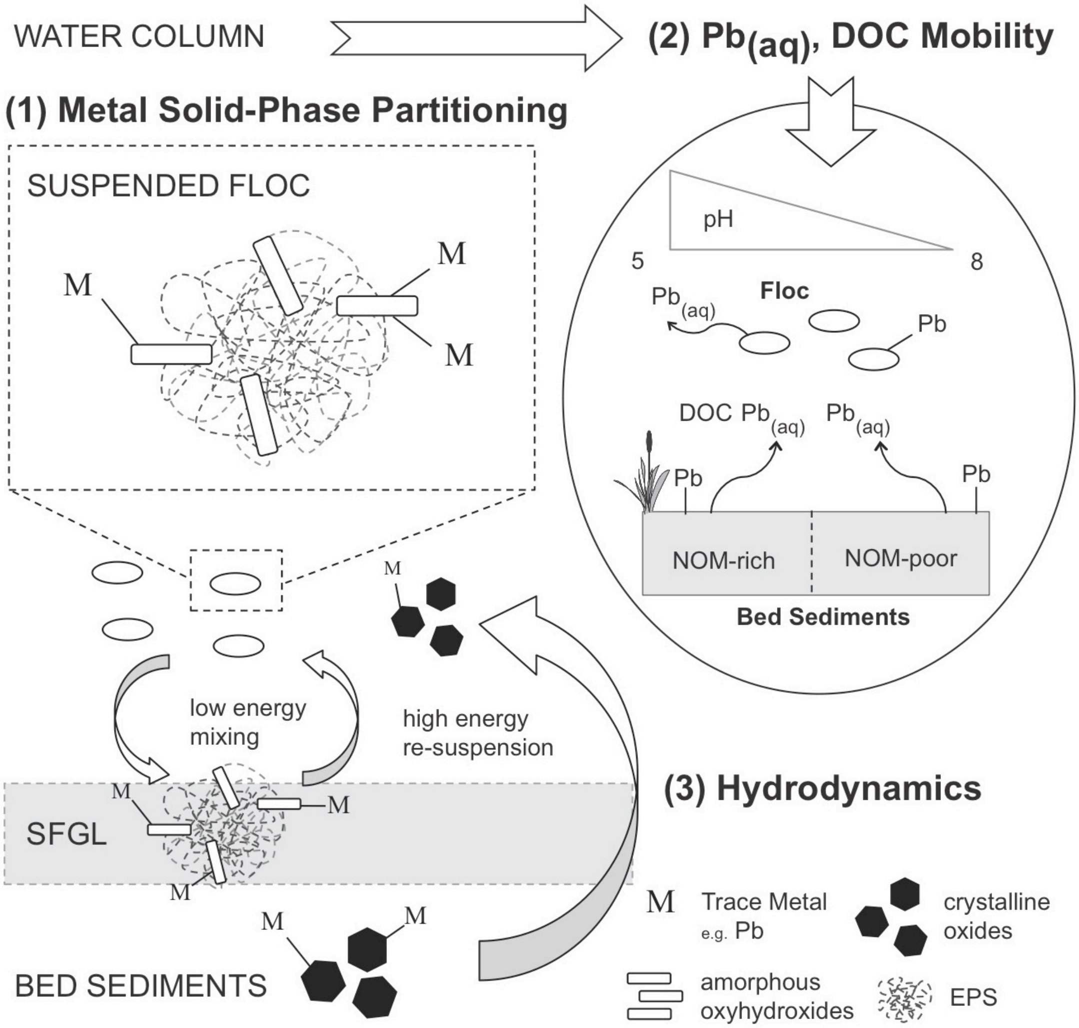

Figure 6.1 Summary of Key Findings

(1) Metal Solid-Phase Partitioning: Different Fe mineral controls on suspended floc (amorphous oxyhydroxides) versus bottom bed sediment (crystalline oxides) trace metal retention

(2) Pb and DOC Mobility: Increasing pH mobilizes anionic Pb-DOC complexes, most effectively from NOM-rich sediments, opposite to that of cationic Pb solid-solution paritioning observed by NOM-poor sediments and floc

(3) Hydrodynamics: Energy-dependent exchange of floc and sediment (SFGL versus bulk bed) Fe mineral phases lead to dynamic shifts in trace metal behaviour in both compartments

6.2 Advances in Floc Trace Metal Biogeochemistry

Significantly higher metal concentrations (Ag, As, Co, Cu, Ni and Pb) in suspended floc over bed sediments were linked specifically to amorphous Fe minerals (FeOOH) that were trapped and/ mineralized onto floc-associated microbial cell surfaces and extensive sticky extracellular polymeric substance (EPS) network (Chapters 3- 5). Floc-FeOOH abundance and reactivity were the dominant controls on floc metal sorption and solid-phase partitioning dynamics. In contrast, crystalline oxides dominated bottom bed sediments metal retention attributable to the dissolution of FeOOH and/or mineral aging within the diffusive environment of undisturbed sediments. Although floc is known to be an important metal repository in the environment, results of this thesis clearly demonstrate floc to be a distinct solid with different metal sequestration and partitioning dynamics compared to that of bed sediments. This has important implications for predicting metal contaminant distributions in aquatic systems given that floc will not be well modeled by dynamics of bed sediments.

This distinction was demonstrated by solid-solution partitioning results in Chapter 3 whereby a laboratory pH dependent release of Pb from organic-rich flocs was opposite to that of organic-rich sediments. The data suggested that stable organo-Pb complexes were relatively scarce within floc. The predominantly living floc microbial community may rapidly process sorbed soluble organic matter for heterotrophic metabolic growth, thereby liberating cationic Pb to be scavenged by floc-FeOOH. Future investigation into floc microbial metabolisms and potential biogeochemical processes at the floc micro-scale modifying scavenging efficiency of floc-FeOOH (e.g. microbial induced redox gradients and/or pH differences) would advance understanding of floc microbial ecology in floc FeOOH and trace metal geochemistry (see Section 6.4). In contrast to the largely living nature of floc organics (i.e. cells, EPS), the detrital nature of bed sediments showed occurrence of stable organo-Pb complexes. This was reflected by pH dependent mobilization of organic matter and Pb from organic-rich surficial sediments (e.g. wetland) into solution opposite to that expected for cationic Pb, hence distinct from Pb mobility observed in floc.

Results demonstrate that predicting solution metal behavior requires appreciation of the unique nature of organic matter and differential biogeochemical processes impacting Fe mineral abundances/reactivity in floc versus surficial sediments. This has important implications for pH related metal re-mobilization from surficial sediments and floc metal migration in predicting metal distributions within freshwater catchments (e.g. organic-rich wetlands to downstream organic-poor lakes). For example, in situ solid-solution Pb partitioning with surficial sediments correlated with system pH (i.e. relatively larger distribution of Pb in the overlying water-column solution phase at higher pH) across organic-rich ecosystems (Chapter 3), consistent with laboratory findings of pH dependent organic-Pb mobilization from these sediments. Therefore natural processes (e.g. photosynthetic activity) and/or anthropogenic interventions (e.g long-term application of lime for acidification remediation) that increase pH may increase toxicity in organic rich environments (e.g. Boreal Forest Region) due to pH related release of organo-metal complexes from sediments. Mobilized organo-metal complexes may subsequently be sequestered and transported by floc-FeOOH such that ultimately, the fate of the metal will depend on water column chemical and hydrodynamic conditions impacting floc-FeOOH abundance/reactivity in downstream shallow lake zones.

6.3 Hydrodynamic Controls on Floc Trace Metal Dynamics

The discovery of differing Fe mineral controls on floc versus bed sediment metal solid-phase partitioning (i.e. amorphous in floc versus crystalline in bed) were shown to be an effective marker of floc/bed interactions, directly relevant for tracking metal mobility within high energy shallow littoral lake environments where constantly changing hydrodynamic conditions (i.e. waves and currents) lead to rapid mixing of floc and bed sedimentary materials. Field investigations at Sunnyside Beach, Lake Ontario in Chapter

4 and 5 demonstrate for the first time that temporal and spatially variable hydrodynamic-dependent Fe-mineral cycling between floc and bed sediments can lead to dynamic shifts in solid-phase metal partitioning in both compartments. Re-mobilized bulk sedimentary material (i.e. crystalline oxides) during a high-energy storm event was shown to substantially alter the amorphous oxyhydroxide- metal partitioning floc signature nearshore. In contrast, calm conditions (e.g. morning hours, deep offshore waters) increased floc-FeOOH settling and entrainment in surficial sediments, contributing to greater FeOOH abundance and associated metals at the sediment-water interface. Re-cycling of FeOOH in the surficial fine-grained layers (SFGL) to the floc compartment and decreased floc particulate size during afternoon wind-driven turbulence resulted in floc-FeOOH and trace metal enrichment over that of surficial sediments.

Collectively, this in situ study provides a valuable and relatively rare real-world evaluation of floc and surfical sediment geochemical composition and associated metal behaviour to changing energy conditions, supporting previous laboratory-based findings of differential sediment re-suspension and metal mobilization under varying disturbance intensities (e.g. Kalnejais et al., 2007, Cantwell et al., 2002). Given that suspended and settled-floc metal concentrations consistently exceeded provincial sediment quality guidelines at the lowest effect level (LEL), understanding the relative distribution of floc (i.e. water column versus surficial bed) and interacting biogeochemical/hydrodynamic mechanisms influencing Floc-FeOOH abundance in these locations has important implications in predicting ecological impacts of floc-metals in an aquatic system. For example, accumulation of metal-laden floc settling at the sediment-water interface during calm conditions (e.g. offshore, morning periods) may increase risk of metal exposure to benthic aquatic organisms. In addition, reductive dissolution of FeOOH under anaerobic conditions of undisturbed sediments may release a portion of the floc FeOOH-bound metals into the overlying water column, thereby increasing metal toxicity. In contrast, settled-floc re-mobilization from wind-driven waves can increase particulate contaminants in suspension thereby increase risk of exposure to fish and humans through contact/ingestion of floc material during more turbulent conditions.

Although the focus here was a wave-dominated freshwater beach, results of this work are applicable across a range of high-energy aquatic ecosystems (e.g. rivers, coastal estuaries, harbors), where natural (e.g. tides, currents) and anthropogenic disturbance events (e.g. dredging operations, ship traffic) also cause frequent mixing of floc material and re-mobilization of sediments, thereby altering floc metal concentrations and geochemical patterns. Results of this thesis highlight the importance for careful consideration of hydrodynamic energy regime when predicting metal contaminant distributions and interpreting floc metal dynamics in the natural environment.

6.4 Future Research

Realizing the complex interactions between floc-minerals, microbes and hydrodynamics influencing floc metal sequestration is a large step forward in understanding the role of floc on metal cycling in the environment. The current challenge is to further identify and quantify the biogeochemical processes (e.g. redox and/or pH gradients), solid particle and microbial-metal interactions that occur at finer scales (i.e. μm and nm) in floc aggregates, to better predict floc metal behaviour observed at the ecosystem scale. For example, recent collaborative work isolating floc microbial Fe redox cycling consortia capable of influencing floc Fe mineral precipitation dynamics (Elliott et al., 2013 [submitted Chemical Geology 16/06/13]) demonstrates that complex microbial-mineral interactions occur within floc (Figure 6.2). This work supports the hypothesis of Chapter 3 that floc metabolic activity within the diffusive floc microenvironment can influence overall floc geochemistry. These results underscore that much greater understanding of the living microbial communities and the impact of their collective ecology in the context of FeOOH, organic carbon and trace metal biogeochemical dynamics is needed.

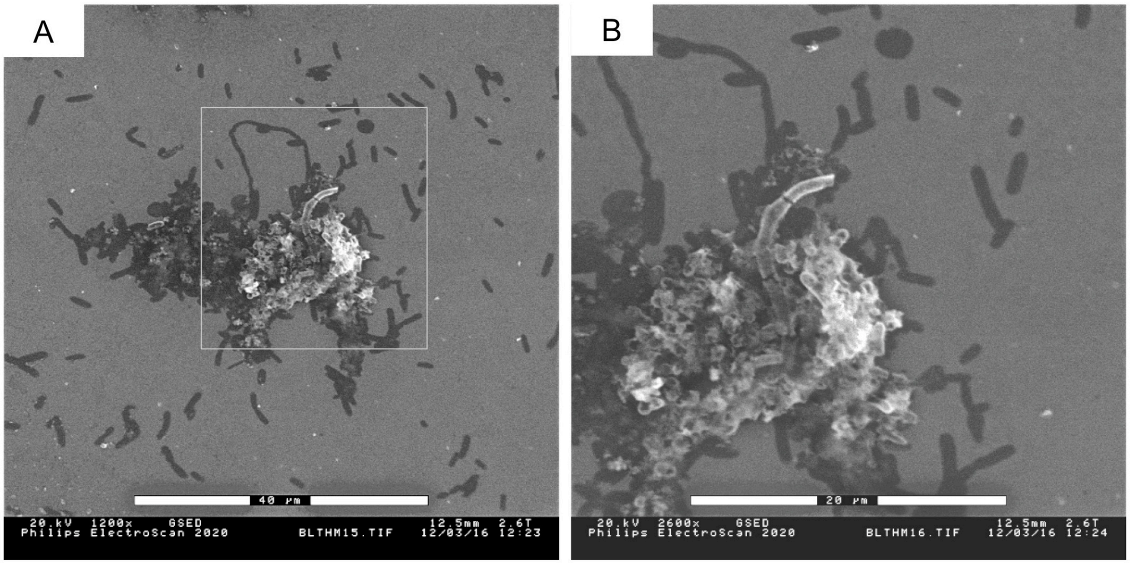

Figure 6.2. Scanning electron microscopy image of floc microbial Fe redox cycling consortia (A). Enlargement showing complex microbial-mineral (white) arrangements (B). Image B is reported in Elliott et al., 2013 [submitted Chemical Geology 16/06/13].

Advances in microscopy and spectrometry technologies such as the application of synchrotron radiation (e.g. scanning transmission X-ray microscopy (STXM); Hunter et al., 2008 and X-ray absorption spectrometry (XAS); Trivedi et al., 2003) allow for the integrated study of geochemical and biological controls on metal behavior at the microscale. These technologies could be applied to heterogeneous floc aggregates to directly probe mineral surfaces and individual bacterial cells, identifying cell arrangements within EPS (e.g. polysaccharides, protein and lipids), metal distributions and iron speciation (e.g. Fe (II) and (III)) that influence floc metal sequestration in both controlled laboratory or complex environmental settings. This would provide valuable information, complementing analytical transmission electron microscopy and sequential chemical extractions applied in this thesis, on identification of key mineral and organic matter substrates and potential for dynamic microscale microbial-mineral-metal interactions influencing floc trace metal biogeochemistry under changing physcio-chemical and hydrodynamic conditions.

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