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Iron cycling in a littoral freshwater beach: Implications for floc trace metal dynamics

Janina M. Plach [a], Sean Lin [a], Ian G. Droppo [b], Lesley A. Warren [a,*]

[a] School of Geography and Earth Sciences, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4K1, Canada
[b] National Water Research Institute, Environment Canada, P.O. Box 5050, Burlington, Ontario L7R 4A6, Canada

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ABSTRACT

This field-based study demonstrates that highly dynamic trace metal (Ag, Co, Cu and Pb) behavior in suspended floc and the sediment surface fine-grained lamina (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 trace 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, resulting 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 SFGL 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 trace 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 trace metal uptake. Taken together, these findings demonstrate highly dynamic linkages between energy regime and physico-chemistry impacted Fe mineral cycling resulting in observable compartment-specific trace metal partitioning patterns for littoral floc and surficial sediments in beach environments.

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 trace metals and metalloids. Iron exists as diverse amorphous oxyhydroxides and crystalline oxides in circumneutral well-oxygenated waters (Cornell and Schwertmann, 2003; Fortin et al., 1993; Perret et al., 2000). These are important solid phases for the sequestration of trace metals in aquatic sedimentary compartments i.e. suspended and bed sediments (Priadi et al., 2011; Tessier et al., 1996). Amorphous Fe oxyhydroxides (FeOOH) (e.g. ferrihydrite) have poorly ordered mineral structures and large surface areas, making them highly reactive minerals for uptake of trace metals from solution (Jambor and Dutrizac, 1998). Ferrihydrite is typically unstable and tends to transform into more crystalline (FeOx) forms (e.g. goethite, hematite) 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). As such, mineral transformations from ferrihydrite to goethite would decrease surface area and density of sorption sites (Trivedi and Axe, 2001), contributing to the release of FeOOH-sorbed trace metals back into solution or to be scavenged by other reactive constituents (e.g. organic matter). In addition, reactions between ferrihydrite and Fe(II) can induce nucleation of goethite (Hansel et al., 2003) which may result in the incorporation of trace metals originally associated with the FeOOH into more crystalline FeOx forms (Cooper et al., 2006; Ford et al., 1997). As such, the abundance and reactivity of differing Fe minerals in suspended versus bed sediments will have a direct impact on the distribution of trace metals within an aquatic system.

FeOOH exists in highly complex associations with natural organic matter (e.g. microbial cells, extra cellular substances (EPS)) in suspended flocs (Buffle and Leppard, 1995; Droppo, 2001; Liss et al., 1996; Ongley et al., 1981), synonymous with suspended particulate matter (SPM) (as referred to elsewhere in the literature), forming a unique aggregate of greater affinity for trace metals than bed sediments (Hua et al., 2012; Santiago et al., 1994; Stecko and Bendell-Young, 2000). Floc Fe minerals may originate from adsorption of Fe nanoparticulates onto reactive sites on EPS (Liu et al., 2013) and/or FeOOH precipitation onto cells/EPS induced by floc-microbial Fe redox cycling

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* Corresponding author. Tel.: +1 905 525 9140x27347.
E-mail address: warrenl@mcmaster.ca (L.A. Warren).

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(Elliott et al., in press) within the diffusive floc microenvironment (Liss et al., 1996). Research has shown that floc-FeOOH controls floc trace metal sequestration (Elliott et al., 2012) while crystalline oxides tend to dominate bed trace 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 trace metal partitioning may thus be an effective marker of floc/bed interactions, directly relevant for tracking trace metal mobility within high energy environments where constantly changing hydrologic 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. photosynthetic induced pH changes, biological uptake of dissolved Fe) are likely to cause frequent mixing of floc/sediment material and alter floc-FeOOH concentrations and trace metal sorption behavior. High-energy waves can erode sediment crystalline oxides and associated trace 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 have a larger reactive surface area and a higher metal affinity (Garnier et al., 1991; Laurent et al., 2009), variation in floc particle size due to water turbulence is also expected to 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 (Grassi et al., 1997; Lead et al., 1999; Lion et al., 1982; Plach and Warren, 2012), largely attributed to pH-dependent adsorption behavior of floc associated-FeOOH (Benjamin and Leckie, 1981; Gadde and Herbert, 1974). Therefore, daily shifts in water-column pH should affect floc trace 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 trace metal mobility is directly relevant to improving 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/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 surficial fine-grained lamina (SFGL) (Droppo and Stone, 1994). Floc settling would provide a transport mechanism for Fe and trace 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 trace metal accumulation in the SFGL. Although previous studies have investigated floc settling/sediment erosion (Droppo et al., 2007; Garcia-Aragon et al., 2011; Milligan and Hill, 1998; Stone et al., 2008) and associated trace metal mobilization under controlled laboratory energy regimes (Cantwell et al., 2002; Theis et al., 1988), to date none have directly investigated Fe and trace metal dynamics of freshwater flocs and surficial sediments under varying spatial and time-dependent energy regimes in the environment. As such, the objectives of this field-based study were to investigate: 1) Fe distributions between suspended floc, SFGL and bed sediments; 2) reactive solid phases for trace metal sequestration, and 3) potential spatial and temporal variation in physicochemical conditions affecting Fe abundance and trace metal behavior of flocs and surficial sediments along a spatial transect from nearshore to offshore, within an urban freshwater beach.

Methods

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) (Fig. 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 trace 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 metals (Ag, Co, Cu, and Pb), selected because they are known to occur in urban runoff (Davis et al., 2001; Gromaire-Mertz et al., 1999; Joshi and Balasubramanian, 2010) and sewage treatment and combined sewer effluent (STP/CSO) which are likely important sources of contaminants to Sunnyside Beach. In addition, this particular suite of trace metals was chosen to represent a range in element affinity for Fe minerals (e.g. Ag showing strong affinity for floc oxyhydroxides (Plach et al., 2011) while Cu is largely bound by floc organic matter (Gagnon et al., 2009)) as well as varying biogeochemical behavior and toxicity of these elements in the environment. 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 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 energy conditions, i.e. high energy nearshore and low energy offshore (Fig. 1B).

Water-column collection/analysis

Water sample collection and physicochemical profiling were carried out upstream (~5 m distance) from bulk suspended floc collection (Floc/bed collection section). All sampling equipment was acid-cleaned with 10% HCl for >24 h and subsequently rinsed eight times with ultrapure water (18.2 Ω m 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 (within 48 h) at McMaster University, Hamilton ON, Canada. Analysis for dissolved (<0.2 μm) trace metals $[M]_D$ used inductively coupled plasma mass spectrometry (ICP-MS (Ag, Cu, Co, and Pb)) (PerkinElmer SCIEX ELAN 6100, Woodbridge ON, Canada). Dissolved (<0.2 μm) iron $[Fe]_D$ was determined colorimetrically using the FerroVer HACH method (Ultroscpec 2000, UV/visible spectrophotometer, Pharmacia Biotech, Cambridge, U.K.). Field blanks (i.e. filtering/