



Differentiating natural organic matter roles in freshwater flocc and bed sediment lead dynamics

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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 flocc 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 flocc microbes and extracellular polymeric substances, were the best predictor of flocc Pb solid-solution partitioning, more consistent with cationic Pb behavior, as well as the key flocc 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 flocc (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 flocc 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.

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1. 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-flocc 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 Siers, 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.

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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; Dicaldo 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 surficial 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.

2. Materials and methods

2.1. 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 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 solid-phase 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 ($18.2 \Omega \text{ m cm}^{-1}$, 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.

2.2. Water-column collection/analysis

Water samples for dissolved Pb analysis were collected by an acid washed Van Dorn water sampler, serially filtered through $0.45 \mu\text{m}$ and $0.2 \mu\text{m}$ 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 through 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 $[\text{Pb}]_{\text{D}}$ ($<0.2 \mu\text{m}$) 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 $0.45 \mu\text{m}$ (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).

2.3. 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 ($>2000 \text{ L}$, 6 L min^{-1}) into stainless steel bowls (pre-leached 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.

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