ASSESSMENT OF LEAD AND BERYLLIUM SORPTION TO EXPOSED STREAM CHANNEL SEDIMENT UNDER VARYING FRESHWATER CHANNEL CONDITIONS

A THESIS
SUBMITTED TO THE FACULTY OF
UNIVERSITY OF MINNESOTA
BY

ETHAN DAVID PAWLOWSKI

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE

ADVISER: DR. DIANA L. KARWAN

JUNE 2019

Acknowledgements

Dedication

From an early age my parents took my siblings and I on frequent trips and planned activities centered around and on the water. This upbringing cultivated and developed my keen interest in hydrology and sediment transport. I am truly grateful for those experiences. I am also thankful for the support and encouragement I have received from my wife and children at various stages in completing this work. For all of these things, I dedicate this thesis to my family.

Abstract

Purpose: Beryllium (Be) and lead (Pb) sorption is important to the utility of the radioisotopes of these elements for sediment fingerprinting. I examined the sorption of Be and Pb to exposed fluvial sediment under varying chemical conditions representative of freshwater streams draining two distinct Critical Zone environments in the eastern United States: the mid-Atlantic piedmont and heavily glaciated Great Lakes region.

Materials and Methods: Batch experiments were completed using well-characterized in-stream deposit sediments collected from these two systems and varying solutions to reflect background and elevated levels of iron oxide in the form of goethite across times ranging from 0.25 to 360 h. The mid-Atlantic piedmont sediment had further treatments testing dissolved organic carbon (up to 11.86 mg L^{-1}) and increased sediment to solution ratio (up to 8000 mg: 1 L) effects on Pb and Be sorption.

Results and Discussion: Beryllium partition coefficients (K_d) ranged from a log K_d of 1.46 to 3.48 L kg^{-1} and Pb ranged from 0 to 5.03 L kg^{-1} across all treatments displaying several noticeable patterns. Two-stage sorption was observed such that sorption increased over time across all treatments and substrates. Goethite additions either enhanced or reduced sorption relative to the base treatment depending on the original sediment and mixing time. Lead sorption with the addition of 100 mg of goethite increased during shorter mixing times before being surpassed by the base treatment at longer mixing times for both the mid-Atlantic piedmont and glaciated Great Lakes sediment. Beryllium sorption was increased with the mid-Atlantic piedmont sediment whereas it was primarily decreased with the

glaciated Great Lakes sediment. The 1 mg of goethite generally showed equal to or slightly enhanced sorption relative to the base treatment of both Pb and Be with the exception of Pb sorption to the Great Lakes sediment. The highest DOC concentration that I tested (11.86 mg L^{-1}) retained a greater amount of Be and Pb in solution compared to other treatments after 360 h. Increasing the sediment to solution ratio showed decreased partition coefficients across all analogous times for Be compared to the base treatment whereas Pb sorption surpassed the unaltered treatment after 24 h.

Conclusions: It is not recommended to use either ^{7}Be or ^{210}Pb in fluvial systems with high background concentrations of DOC because the DOC was shown to inhibit sorption to sediment surfaces and it could produce erroneous results in sediment fingerprinting studies unless that inhibition or loss is accounted for. The goethite treatments produced mixed results and further research is needed to parse out conditions that enhance or inhibit the sorption of fallout radionuclides in the presence of stream sediments with varying amounts of organic matter occlusion of surface binding sites. Increased sediment to solution ratios increased sorption of Pb suggesting that Pb would be a conservative tracer in fluvial systems with high sediment delivery. These results suggest that fluvial sediment mineralogy, organic matter concentration, and biogeochemical cycling of common stream chemical constituents may play a role in the mobilization or retention of these two trace metals and alter their utility for sediment fingerprinting.

Table of Contents

List of Tables

List of Figures

1 Introduction

Disentangling the source and transport phenomenon of fine sediment fluxes to streams and rivers entails a multifaceted approach. Chemical fingerprints that differentiate sediment sources provide one toolkit by which to accomplish this task by taking advantage of the physical and chemical characteristics found within a watershed. Fingerprints can come from a variety of sources within the 3-dimensional space of the watershed Critical Zone providing insights into processes throughout space and time (Koiter et al. 2013; Walling 2013). For example, geogenic tracers detailing lithology and mineralogy indicate specific substrates while modifications to the substrates by weathering and soil formation processes unique to specific land uses may provide further sediment source differentiation (Collins et al. 1997; Gellis et al. 2016). Isotope fractionation gives insight into flow paths and biogeochemical cycling (McDonnel 2014; Ohkouchi et al. 2015; Sprenger et al. 2016). Fallout radionuclides (FRNs) utilizing isotopes with various decay rates can also act as chronometers that parameterize sediment delivery based on depth from the sediment surface (Belmont et al. 2011; Gellis et al. 2017).

Beryllium-7 (^{7}Be) and lead-210 (^{210}Pb) are two FRNs (half-lives 53.3 days and 22.0 years, respectively) that have been used to quantify erosion, fingerprint sediment source, and assess sediment age in streams and fluvial environments on individual event to decadal timescales (Matisoff et al. 2005; Sepulveda et al. 2008; Blake et al. 2009; Liu et al. 2011; Smith and Blake 2014; Belmont et al. 2014; Underwood et al. 2015). That quantification relies on the propensity of both radionuclides to bind readily to particle surfaces through sorption processes. Several questions remain regarding the conditions under which surface particles are "tagged" (e.g. sorption) and, hence, their utility as fingerprints of sediment

source in stream materials (Koiter et al. 2013; Taylor et al. 2013; Walling 2013; Smith and Blake 2014; Mabit et al. 2014).

1.1 Review of sorption and aqueous behavior

Lead and beryllium isotopes are considered readily sorbed by particles (Kaste 2002, You 1989, Mabit et al 2014). In this study sorption is defined as both adsorption and absorption where the sorbing chemical species may bind to the surface or be incorporated into the crystal lattice of the sorbent. Sorption of metal cations is dependent on many variables such as pH, ionic strength, the presence of organic material, sorbent chemical composition, and the chemical composition of the solution (Essington 2015). In natural waters, Be and Pb speciation is likely to be found as a divalent cation, inorganic ligand, or organic ligand in solution or bound to sediment surfaces. Therefore, the next two sections highlight basic chemistry of both Be and Pb in conditions pertinent to this research and provides context for the interpretation of the results presented later in this manuscript.

1.1.1 Beryllium

Beryllium is a group two alkaline earth metal with an atomic number of 4. It is primarily found as a divalent cation with an ionic radius of 0.31 (Railsback 2003) giving it a high charge density. It is amphoteric, acting as both a base and acid during reactions depending on the pH of the solution, and favors a tetrahedral geometry. These chemical characteristics influence the aqueous and non-aqueous behavior of Be.

The aqueous speciation of Be is primarily found as a divalent cation [Be^{2+}] or bonded to a hydroxide (Hawley et al. 1986; Wong and Woolins 1994; Schmidbauer 2000). Above a pH of 5.5 Be dissolved in pure water begins to form polymeric Be hydroxide

[Be(OH)$_2$]$_n$ that is insoluble leading to the precipitation of Be out of solution. In natural waters between a pH of 4 and 8 the dominant Be species are Be$_3$(OH)$_3$$^{3+}$, Be^{2+}, and Be(OH)$_2$ (Hawley et al. 1986; Kaste et al. 2002; Keizer et al. 2015). Fluoride has been shown to compete for Be with hydroxide in solution and the resulting complex [BeF$_2$] is highly soluble in water (Wong and Woolins 1994; Keizer et al. 2015). There are only a few organic ligands that can compete with the formation of Be(OH)$_2$ (solubility product (K$_{sp}$) = 1 x 10^{-20}) at a higher pH (Wong and Woolins 1994; Keizer et al. 2015). Acetate [CH$_3$COOH] will form polynuclear species such as Be$_4$(O-Acetate)$_6$ that forms a tetrahedral Be$_4$O core. Citric acid [C$_6$H$_8$O$_7$] will solubilize Be across a wide range of pH values. Citramalic acid [C$_5$H$_8$O$_5$] , malic acid [C$_4$H$_6$O$_5$] , and 3-hydroxy-3-methylglutaric acid [C$_6$H$_{10}$O$_5$] behave similarly to citric acid and primarily form six membered rings with Be although some five membered rings also exhibit stability (Wong and Woolins 1994, Alderighi et al. 1998, Alderighi et al. 1999). Be ligands with carboxylates such as acetate and dicarboxylic acids such as oxalic [C$_2$H$_2$O$_4$] and malonic [C$_3$H$_4$O$_4$] acids are thermodynamically favorable because these ligands preserve the tetrahedral geometry. Of these ligands, malonic acid preserves the tetrahedral geometry and creates the most stable O-Be-O angle (Wong and Woollins 1994). In general, unidentate ligands usually bind weakly to Be and are often replaced by hydroxyls whereas bidentate catecholate and salicylates have some of the most favorable properties forming five and six membered rings respectively (Wong and Woolins 1994).

Other solution properties such as salinity, ionic strength, and pH influence aqueous speciation and Be sorption to sediment. pH is the most influential variable determining the aqueous speciation and sorption of Be on primary and secondary minerals which has been

found to increase with increasing pH (You et al. 1989; Takahashi et al. 1999; Aldahan et al. 1998; Boschi and Willenbring 2016). However, limited research exists at or above a neutral pH due to the uncertainty that removal of Be^{2+} from solution was due to sorption rather than precipitation of $[Be(OH)_2]_n$. Only Takahashi et al. (1999) and You et al. (1989) tested Be sorption above a neutral pH, but Takahashi et al. (1999) is the only study to take into account Be speciation above a pH of 7 and its effects on sorption results. Other studies test the sorption of Be to different minerals below a pH of 7 to avoid complications arising from precipitation reactions. In research looking at Be sorption to sediments composed of several mineralogies, these mixed sediments have been shown to sorb similarly to pure minerals and clays with greater sorption occurring with increasing fine sediment fractions and increasing pH (Hawley et al. 1986; You et al. 1989; Taylor et al. 2012; Ryken et al. 2018). High salinity and ionic strength slowed sorption to sediments when compared to freshwater and increasing temperature accelerated sorption (You et al. 1989). You et al. (1989) showed that there was not a significant difference on Be partition coefficients (K_d) in the presence of dissolved organic matter (DOM) in seawater. Partition coefficients are a way to report the division of a chemical species bound to a particle surface and what remains in solution; greater K_d values indicate that more of a chemical species is sorbed to a particle surface. In contradiction to You et al. (1989), the work of Baskaran et al. (1997) found positive correlations between particulate organic carbon and K_d in addition to observing lower K_d values in the presence of dissolved organic carbon (DOC), albeit the DOC concentration of the estuary studied is greater than the equivalent seawater dissolved organic matter (DOM) concentrations used in You et al. (1989). The distinction between DOM and DOC is operationally defined by methodology. In both studies the measure of

DOM and DOC is an indication of the presence of organic compounds in solution. Of these studies, the results in Baskaran et al. (1997) are the most applicable to riverine systems. Takahashi et al (1999) surmised that hydrolysis and absorption are important mechanisms for Be in solution. Observations from that study show that solid surfaces (kaolinite and silica) and humic acid compete as Be binding sites with partitioning dependent upon pH. Boschi and Willenbring (2016) wanted to test different functional groups thought to be environmentally relevant to metal sorption and showed increasing sorption of Be to lignin, phosphonate, and sulfonate with increasing pH. Those results suggest that preferential sorption or the binding affinity of a chemical species to specific compounds may exist between these functional groups. This preferential sorption was also observed by Yang et al. (2013) who found that Be was preferentially sorbed in descending order to silicon dioxide [SiO_2], manganese dioxide [MnO_2], ferric oxide [Fe_2O_3], aluminum oxide [alpha-Al_2O_3], kaolinite, and calcium carbonate [$CaCO_3$] in ocean water. However, the differences in sorption exhibited in that study showed a smaller range compared to Pb, and additions of macro-organic molecules (humic acid, acid polysaccharides (APS) and protein (bovine serum albumin, BSA) did not significantly affect Be sorption suggesting those macro-organic molecules did not influence Be sorption. This added further validation of Be's usefulness as a bulk particle tracer (Yang et al. 2013). These results were significantly different from Pb which varied over 2 orders of magnitude depending on particle type and macro-organic molecule added to the experiment suggesting that sediment composition is important (Yang et al. 2013) when considering Be to Pb ratios in deposition.

1.1.2 Lead

Lead is a group 14 post-transition p-block heavy metal with the atomic number 82 and an ionic radius of 1.75. Lead is polarizable with coordination geometries ranging from 1 to 12 that can lead to large interatomic distances (Swadzba-Kwasny 2015). The differences in observed bond lengths is partially due to the "inert pair" effect resulting from an intact 6s orbital that creates stability at the 2^+ oxidation state (Drago 1958, Schwerdtfeger et al. 1992). Thus Pb(IV) bonds covalently with defined geometries and these bonds are primarily composed of Pb-C bonds (Schwerdtfeger et al. 1992) whereas ionic metal-ligand bonding favors Pb(II) speciation. This allows Pb to react and bind to a variety substrates.

Pb(II) species are primarily present in aqueous environments. Pb(II) forms hydrates $[Pb(H2O)n]^{2+}$, and hydroxolead(II) complexes in equilibrium with Pb(II) complexes of other anions present in solution. Lead (II) will form complexes with oxoacids, oxygen donor ligands, halides, pseudohalides, oxides, chalocogenides, and others (Powell et al. 2009). Hu et al. (2011) shows an expansive coordination chemistry of Pb(II) compounds with carboxylate ligands. Lead (II) has the ability to form stable complexes with both soft and hard donors, but under similar coordination environments, the affinity of Pb^{2+} is higher toward S-donors compared to O-, or N-donors. This preferential behavior suggests that organic composition impacts Pb speciation and could alter the partitioning of Pb between sediment surfaces and the solution.

With a few exceptions Pb has been shown to be highly immobile and accumulate in the upper soil layers, binding well to a wide variety of sorbents ranging from chemically pure oxides to mixed sediments (Davies 1995; Gerritse and Driel 1984; Wang and Benoit

6

1996; Du and Hayashi 2005; Fernandez and Sordo 2006; Degryse et al. 2009; Yang et al. 2013). As was the case with Be, increasing pH augments Pb sorption to mineral surfaces (Davies 1995; Appel and Ma 2002; Anagu et al. 2009). However, increasing pH tends to increase DOC concentrations in the interstitial waters within sediments which has been found to be positively correlated to Pb mobility in sediments (Davis and Leckie 1978; Gerritse and Driel 1984; Wang and Benoit 1996; Strawn and Sparks 2000). Wu et al. (2003) found similar trends during research that tested how the additions of ethylenediaminetetraacetic acid (EDTA) and citric acid affected Pb sorption on humic acid, goethite, and montmorillonite and found that sorption was inversely related to EDTA and citric acid concentration under most of the experiments. However, the results in that study also showed that citric acid enhanced Pb sorption onto humic acid showing that preferential tendencies of sorbates and interactions between organic molecules can either enhance or hinder sorption depending on the composition of organic material in solution. One study that demonstrated an increase in sorption with organics showed that humic acid may form cation bridges between Pb and mineral surfaces with increasing ionic strength (Liu and Gonzalez 1999). Preferential sorption may also influence Pb sorption; Yang et al. (2013) observed that polysaccharides aided binding of $CaCO_3$ to Pb. Carbonates such as gypsum and lime industrial by-products have been shown to immobilize Pb in contaminated soils (Illera et al. 2004). Besides organic molecules, other cations in solution may also influence Pb sorption to mineral surfaces. Ponizovsky and Tsadilas (2003) demonstrated near equal displacement of calcium and hydrogen ions to sorbed Pb suggesting that increasing ionic strength could potentially decrease metal sorption through ion exchange processes and binding site competition.

This review indicates that pH is the most influential variable determining sorption and is influenced to a lesser extent by ionic strength, the presence of organic material, and preferential binding to specific mineral compositions (Davis and Leckie 1978; Gerritse and Driel 1984; You et al. 1989; Wong and Woolins 1994; Wang and Benoit 1996; Aldahan et al. 1998; Takahashi et al. 1999; Strawn and Sparks 2000; Wu et al. 2003; Du and Hayashi 2005; Degryse et al. 2009; Taylor et al. 2012; Yang et al. 2013; Boschi and Willenbring 2016). All of these factors affect solid and solution partitioning but there is a need to address sorption as it relates to factors influencing biogeochemical cycles and conditions found within stream channels that are tested in combination and not isolation.

1.2 Pairing sorption to sediment fingerprinting applications: environmental considerations

The most prevalent applications of [7]Be and ^{210}Pb focus on the delivery of sediment from terrestrial environments into the stream channel (Wallbrink and Murray 1996; Matisoff et al. 2002; Huisman and Karthikeyan 2012; Gellis et al. 2017) and rely on sediments being tagged prior to entering the stream channel. Applications have focused in areas with extensive agricultural practices and locations with high relief that are susceptible to high sediment delivery from terrestrial environments into the river channel. However, in catchments with low sediment delivery ratios, such as forested catchments or locations with low relief, direct precipitation of FRNs onto the stream channel and the tagging of exposed and resuspended fluvial sediments during storm events cannot be ignored (Kaste et al. 2014; Underwood et al. 2015; Karwan et al. 2018). While partition coefficients generated from sorption experiments are not directly applied to sediment fingerprinting

studies, these coefficients provide a critical evaluation of assumptions surrounding conservative behavior (Taylor et al. 2013; Mabit et al. 2014). Due to the historical focus of sediment fingerprinting studies on the delivery from terrestrial to aquatic environments, previous sorption research has largely focused on Pb and Be sorption to terrestrial sediments and soils (Welp and Brummer 1999; Strawn and Sparks 2000; Degryse et al. 2009; Taylor et al. 2012; Ryken et al. 2018). This has left a large gap in the understanding of how direct channel input of FRN's and within channel sorption processes may influence sediment fingerprinting applications in fluvial settings and when assessing sediments stored in deposits and channel margins as a possible suspended sediment source. Some of this knowledge gap can be inferred from remobilization literature focused on desorption and subsequent sorption of trace metals. Such work suggests that the fraction of reducible oxides and hydroxides along with organic matter may play a crucial role in the retention or mobilization of trace metals by stream sediments (Gerringa 1990; Caille et al. 2003; Cappuyns et al. 2006; Atkinson et al. 2007; Di Nanno et al. 2007; Du Laing et al. 2008; Du Laing et al. 2009; Monnin et al. 2018). However, studies observing the remobilization of Be are rare and the limited number of sorption papers involving Be (Taylor et al. 2013 and references within) have not focused on assessing sorption to reducible fractions, mixed organic compounds, and chemically heterogeneous fluvial sediments in contrast to Pb which has been more thoroughly evaluated (Mabit et al. 2014 and references within). This, along with uncertainties associated with FRN spatial distribution and deposition rates, particularly during individual storm events, are unknown constraints that limit their use as sediment fingerprints within the Critical Zone (Koch 1998; Zhang et al. 2001; Duenas et al. 2004; Arkian et al. 2010; Kaste et al. 2014; Krmar et al. 2016; Itoh and Narazaki 2017).

In this study, we seek to fill that void by quantifying Be and Pb sorption with time to collected stream sediments under a series of stream-like conditions. We examined the concentrations of DOC, particulate iron, and increased sediment to solution ratios as a means to test the efficacy of these two trace metals for sediment fingerprinting applications within the Critical Zone in settings where direct deposition onto streams is a key input.

2 Methods

2.1 Sediment collection sites

2.1.1 Difficult Run, VA

Difficult Run is located in the crystalline Piedmont region of Virginia and is a tributary to the Potomac River and the Chesapeake Bay (Figure 1) (Drake and Morgan 1981). Difficult Run flows through urban and suburban land use areas. The riparian area consists of second-growth forest and is managed primarily for natural resource protection and recreation (Hupp et al. 2013). It has been instrumented since 2007 at its upstream gage (14.2 km^2 drainage area) and has a median discharge of 0.34 $m^3 s^{-1}$, pH of 7.2, and water temperature of 13.5 °C (USGS 2018). The stream bed is composed primarily of gravel and coarse clastic sediments with predominantly micaceous fine material originating from metasedimentary, metavolcanic, and transported metaigneous rocks within the Peters Creek Schist and Piney Complex that include: ultramafic quartz, mica gneiss, calc-silicate layering, plagioclase, metagraywacke and semipelitic schists in addition to large blocks of serpentinite associated with chlorite-tremolite-epidote, talc-chlorite, and talc-chlorite-actinolite schists (Drake and Morgan 1981). The watershed is situated in a temperate

climate with average monthly temperatures ranging from 0 to 32 °C and receives an average rainfall of 113 cm and 53 cm of snowfall per year (Diamond et al. 2013).
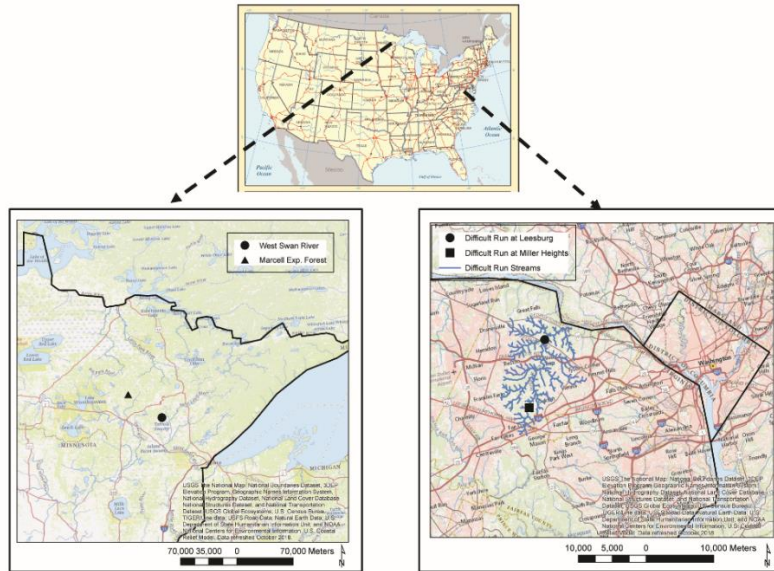
Figure 1 Spatial locations of dissolved organic carbon collection (Marcell Experimental Forest, MN) and channel substrate material (West Swan River, MN and Difficult Run, VA)

2.1.2 West Swan River, MN

The West Swan River is a tributary to the St. Louis River and Lake Superior flowing through rural forests and wetlands. The last glaciation, the Wisconsinan Episode, deposited stratified layers of sediment characterized by the last two glacial advances.. The Rainy-Superior Lobe (20,000 y BP) advanced from the northeast bringing igneous and metamorphic rock fragments primarily derived from the Canadian Shield that are rich in iron, non-calcareous, and defined by red and brown coloration. The St. Louis sublobe of the Des Moines lobe brought gray, highly calcareous deposits with shale fragments from North Dakota and Central Canada (16,000- 12,000 BP). The melting and retreat of the Des Moines lobe created glacial Lake Upham. As glacial meltwater flowed into Lake Upham

settling sediment formed the stratified clay layers found throughout the West Swan River's watershed (Lusardi and Dengler 1994). Climate records for Hibbing, MN, located approximately 24 km north of the West Swan River indicate a temperate climate with average monthly temperatures ranging from -2.4 to 9.3 °C (Diamond et al. 2013). Annually, Hibbing receives an average rainfall of 63 cm and an average snowfall depth of 166 cm (data record from 1988 to 1999) that typically accumulates as a snowpack from November through April (Diamond et al. 2013).

2.2 Sediment collection

Stream deposits on bars, banks, log deposits, and behind woody debris were identified as possible sediment sources and sinks on an event-time scale. Selected in-channel deposits were collected by carefully scraping sediment from the surface of in-channel deposits until roughly 1000 cm^3 was collected. Only the surface, within the top few centimeters of the deposits were collected. These sediment deposits can act as sinks for FRNs falling on the stream channel via direct precipitation and are more likely to be transported with increases in discharge during precipitation events (Kaste et al. 2014; Underwood et al. 2015). This sampling strategy targets FRNs that are deposited to the stream channel deposits via atmospheric deposition and not brought into the stream with eroded sediment. In total, seven samples were collected: five from Difficult Run and two from West Swan.

2.3 Sediment characterization

Upon collection, sediments were oven dried at 45 °C, sieved to less than 2 mm, and homogenized. Physical and chemical characteristics were tested on the less than 2 mm size class sediments. Grain size analysis was performed using a laser diffraction particle size analyzer (Mastersizer 3000, University of Minnesota, St. Paul, MN) in triplicate by preparing 0.31 cm^3 of sediment with 5 mL sodium hexametaphosphate, 5 mL of 3-8% sodium hypochlorite solution, and deionized water that was then shaken overnight. Three measurements were taken on each 1 mm wet sieved sample to define clay, silt, and sand size fractions.

Specific surface area (SSA) was determined using the Brunauer-Emmett-Teller (BET) method (Brunauer et al. 1938) utilizing nitrogen gas adsorption (Micrometrics TriStar II 3020, University of Minnesota, St. Paul, MN). Approximately 5 to 7 g of each sediment was oven dried at less than 60 °C, organic debris removed, lightly ground to break up aggregates, and stored in a desiccator until analysis. BET SSA was analyzed on sediments combusted at 350 °C for 12 h to minimize alteration of less-crystalline mineral phases and on non-combusted sediments (Wagai et al. 2009). For each sediment, a glass test tube was weighed and had 1.5 g poured into it. The test tube was placed in a sonicator to facilitate the downward movement of fine sediment into the bulbous bottom. A brush slightly wetted with isopropyl alcohol was then used to brush the inside of the test tube. The test tube with sediment was then weighed. A carbon black standard for BET SSA analysis was prepared with 0.5 g of carbon black in the same way as the sediment samples. The samples were then degassed for 6 h to overnight using Nitrogen Flow at 150 °C with the flow of N_2 gas measured at 1.5 bubbles per second as measured in a beaker of water.

The Nitrogen Flow gas probes were cleaned and checked for blockages before being inserted into the test tubes at an angle of 5 to 10° to ensure no sediment entered the bottom of the probe. An aluminum insulator was placed over the tube and placed in the heating well to remove moisture. After a minimum of 6 h, if the test tubes were free of visible moisture they were placed in the cooling well with the gas flow remaining and a rubber stopper placed in the top of the tube. Once cool, the gas probe and rubber stopper were removed ensuring no sediment was stuck to the probe, immediately weighed, and placed on the surface area analyzer. Cloth or anti-static gloves were used during all stages of sample preparation to avoid static build-up and changes in mass due to dust or fingerprints. After a leak test, the N_2 absorption is measured on the analyzer and BET SSA (m^2 g^{-1}) is computed within the instrument specific software. Organic occlusion of mineral surfaces defined as the fraction of the total mineral surface area not accessible to N_2 gas in the non-combusted sediment was calculated following Mayer and Xing (2001):

$$\%SSA_{organic\ occlusion} = \left[\frac{(SSA_{combusted} - SSA_{non-combusted})}{SSA_{combusted}} \right] \times 100 \quad (1)$$

where SSA$_{combusted}$ and SSA$_{non-combusted}$ refer to the specific surface area of combusted and non-combusted sediment respectively.

Mineral composition was determined using XRD analysis (Bruker D8 Discover 2D) using a cobalt (Co) Kα radiation point source at the University of Minnesota Characterization Facility, Minneapolis, MN, and was analyzed using Jade software and the mineral databases therein. The Co Kα radiation point source was used to eliminate error associated with iron containing sediments analyzed with standard copper Kα radiation point sources. Based on all of these characteristics, one representative sediment from each

site was chosen for the sorption experiments, selecting sediments with lower BET SSA with the idea that those sediments would provide conservative results.

2.4 Batch experiments

Batch experiments were designed to determine the sorption of Pb and Be to stream sediments from our field collection sites. Experiments followed guidelines set by the OECD (2000), Roy et al. (1991), and the US EPA V1 (1999) and were informed by prior findings from numerous trace metal sorption studies (Gerritse and Driel 1984; You et al. 1989; Aldahan et al. 1998; Welp and Brummer 1999; Strawn and Sparks 2000; Grybos et al. 2007; Gustafsson et al. 2011; Taylor et al. 2012). Experimental treatments varied in time of experiment, sediment to solution ratio, iron oxide fraction, and amount of dissolved organic carbon (DOC) (Figure 2).

Sorption experiments were carried out in parallel using duplicates that contained 0.5 g of sediment and a background electrolyte solution (0.01 M calcium nitrate $[Ca(NO_3)_2]$) to form a sediment to solution ratio of 1:500. The $Ca(NO_3)_2$ background solution was synthesized in the laboratory and chosen to avoid Pb precipitation with chloride salts. A background concentration of 0.01 M was selected to align with existing sorption literature (Roy et al. 1991; US EPA V1 1999; OECD 2000). The samples containing 0.5 g of sediment and 0.01 M $Ca(NO_3)_2$ without further alteration is referred to as the base or unaltered treatment. Individual modifications to this base treatment included the addition of 1 and 100 mg goethite (99+% α-FeOOH Alfa Aesar) to the sediment, adding dissolved organic carbon (DOC) to the solution at concentrations of 2.38 and 11.86 mg L^{-1} and increasing the sediment to solution ratio to 1:125 (Figure 2). Only the Difficult Run

sediment was tested with the DOC and increased sediment to solution ratio modifications due to budgetary constraints. The base treatment and any modifications were well mixed and allowed to equilibrate while shaking for 12 h or overnight on a table shaker in glass containers. After the equilibration period, nitric acid [HNO_3] and sodium hydroxide [$NaOH$] were then used to adjust the solution pH to 6.5. A pH of 6.5 was chosen to avoid possible precipitation of [$Be(OH)_2$]$_n$ (Wong and Woolins 1994). This step was followed by spikes of beryllium sulfate [$BeSO_4 \cdot 4H_2O$] or lead nitrate [$Pb(NO_3)_2$] that were added to achieve an initial metal concentration of 100 $\mu g\,L^{-1}$ and a final solution volume of 250 mL. Subsequently, supernatant was collected and centrifuged at 3000 rpm for 25 min after time intervals of 0.25, 1, 12, 24, 120, and 360 h. Supernatant with added DOC was filtered using 0.45 μm polyethersulfone filters from Foxx Life Sciences followed by centrifuging at 3000 rpm for 25 min to remove suspended particulate matter. A sampling time interval of 0.25, 0.50, 0.75, 1, 4, 12, 24, and 48 h followed by centrifugation at 3000 rpm for 25 mins was used on the samples with an increased sediment to solution ratio. Background concentrations of Be and Pb were assessed using blanks containing the sediment and background electrolyte in the absence of the spikes. These were allowed to run for 0.25, 1, 24, 120, and 360 h. Beryllium and Pb concentrations in the blanks were below detection limits thereby eliminating the possibility that desorption of existing Be and Pb influenced the results. Sorption to vessel walls was determined by running blanks that contained the spikes of $Pb(NO_3)_2$ and $BeSO_4 \cdot 4H_2O$ along with the background electrolyte. These spiked blanks were shaken for 360 h after which the measured concentration of the solution compared to the measured spike concentration differed by less than 1%. All samples and blanks were analyzed by ICP-MS (Perkin Elmer, Elan DRC-e) for Be and Pb

concentrations with lower detection limits of 1 $\mu g\, L^{-1}$ for each solute at the Yale Analytical and Stable Isotope Center, New Haven, CT. The initial concentrations of Be and Pb were higher than those found in natural freshwater streams but allowed Be and Pb to remain detectable in all treatments (Figure 2). Out of the 112 duplicates tested, 90% of the pairs differed by less than 10% of the spike concentration with an average spike concentration percent difference between pairs of 4.3%.
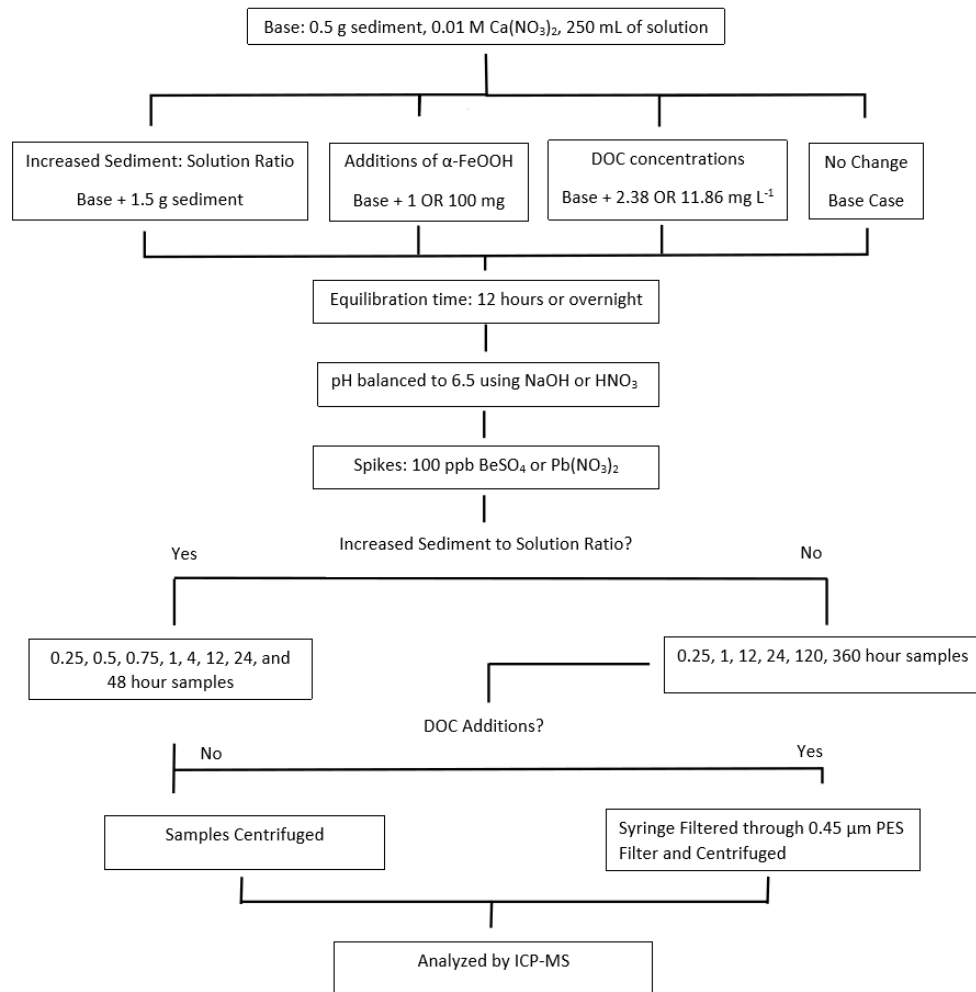
Figure 2 Batch layout and methodology

Modifications to the base treatment were chosen for several reasons. Iron oxides provide a high specific surface area with variably charged sites to sediments but are

seasonally affected by aerobic and anaerobic bacterial respiration (Yu et al. 2009; Gault et al. 2012; Hegler et al. 2012; Stuckey et al. 2015; Sulu-Gambari et al. 2016). Goethite was a relatively conservative choice for iron oxides due to its low solubility in water, availability, and its nearly balanced charge at circumneutral pH (Kosmulski et al. 2003). DOC concentration was increased because of the lack of available literature on the sorption of Be to a heterogeneous organic matter relevant to freshwater streams. Additional DOC for use in experiments was collected from the outlet stream of a zero-order basin, immediately downstream of an ombrotrophic bog (S2), in the Marcell Experimental Forest, MN, a site with known high concentrations of DOM that could be added without pre-concentration to increase the DOC concentration of experiments with Difficult Run sediment (Figure 1). Water from the S2 outlet stream was previously characterized by ^{13}C NMR spectroscopy. The carbon percent was primarily aliphatic (34.0 and 23.3%), carbohydrate (17.3 and 18.3%), aromatic (12.2 and 18.3%), carboxylic (20 and 14.2%), methoxy-amino (5.6 and 6.0%), anomeric (2.9 and 5.7%), phenolic (3.9 and 7.8%), and carbonyl (4.1 and 6.4%) by DEAE and XAD8 extraction respectively (Brezonik et al. 2015). This DOC source was chosen as a more accessible alternative to commercially available products with similar organic characterization and required a simple dilution to incorporate into the treatments. In our experiments, DOC was added to the background electrolyte solution in order to approximate the range found in Difficult Run stream water: 2.38 and 11.86 mg L^{-1} based on personal communication with Dr. Judson Harvey, USGS. The chemical composition of this catchment water was assessed for other elements capable of forming precipitates or complexes that may have influenced the results. Typical concentrations of inorganic ligands capable of forming a precipitate were found to have a

concentration well below solubility limits. DOC concentrations were at least three orders of magnitude greater than any inorganic ligand capable of forming a complex with Pb or Be. Due to chelation effects in addition to the affinity of both cations for organic species (Wong and Woolins 1994; Strawn and Sparks 2000), the influence of complexation reactions to inorganic ligands on the sorption of Pb and Be in these experiments was determined to be minimal. Increasing the sediment to solution ratio to 1:125 and changing the sampling time interval was done to mimic observed sediment export response following a precipitation event observed from Difficult Run USGS data (2016).

2.5 Partition coefficient calculation

Partition coefficients, K_d, values were calculated using:

$$q = \frac{V(C_i - C_{eq})}{m_{sorbent}} \tag{2}$$

$$K_d = \frac{q}{C_{eq}} \tag{3}$$

Where V is the volume of liquid (L) in the container, C_i is the initial concentration ($\mu g\ L^{-1}$), C_{eq} is the equilibrium concentration after a time interval ($\mu g\ L^{-1}$), and $m_{sorbent}$ is the mass of sediment (kg) in the container. Eq. (2) yields q which is placed into the numerator of Eq. (3) to produce the K_d (L kg $^{-1}$). Isotherms were plotted to show the change in K_d value with time. Reporting results in this manner follows how the partitioning between metals and sediments have previously been reported in the literature. However, even between studies that publish K_d values, methodological differences can alter partitioning results. Consequently, the variation in experimental design and other metrics that exist for quantifying partitioning make direct cross study comparisons of partitioning data difficult.

3 Results

3.1 Sediment characteristics

3.1.1 Difficult Run

Four of Difficult Run (DR) sediments were sampled near Miller Heights (MH) and were associated with a wood deposit (DRMHW), two different morphological features (DRMHM1 & DRMHM2), and a gravel bar (DRMHG). The final sediment was a morphological feature collected at Leesburg Pike (DRLPM) (Figure 1). The sediments from Miller Heights ranged from 48.5% to 71.2% sand, 20.7% to 35.8% silt, and 8.1% to 15.7% clay. Leesburg Pike contained coarser sediments composed of 80.6% sand, 14.5% silt, and 5% clay (Table 1, Figure 3). BET SSA ranged from 1.70 to 3.89 $m^2 g^{-1}$ (Table 2). The percent organic occlusion of the BET SSA ranged from 19.5% to 45.6% (Table 2). Mineralogy by x-ray diffraction of the five Difficult Run sediments was found to be primarily quartz in all of the spectra with other minerals enriched in magnesium and iron such as pyrope/almandine, tremolite, forsterite, antigorite, talc/pyrophyllite, and bixbyite. Muscovite and, to a lesser extent, biotite were the primary clay minerals detected.

Table 1 Average percent grain size for collected sediments. Grain size ranges were defined as clay (0.1, 8) µm, silt (8, 50) µm, and sand (50, 2000) µm.

Sediment	Clay (%)	Silt (%)	Sand (%)
WSU	6.8	15.1	77.2
WSL	13.3	38.6	48.1
DRMHW	8.1	20.7	71.2
DRMHM1	15.7	35.8	48.5
DRMHM2	14.8	33.9	51.3
DRMHG	10.7	24.8	64.5
DRLPM	5	14.5	80.6

Table 2 BET SSA measured for sediments pre and post combustion at 350 °C along with the percent organic matter coverage of the specific surface area.

Sediment	Non-combusted sediment ($m^2\,g^{-1}$)	Combusted at 350 °C ($m^2\,g^{-1}$)	Organic occlusion (%)
WSU	1.4498	3.7979	61.8
WSL	3.2791	6.8689	52.3
DRMHW	2.6335	3.2729	19.5
DRMHM1	3.8263	7.0323	45.6
DRMHM2	3.8934	6.7258	42.1
DRMHG	3.3441	4.7353	29.4
DRLPM	1.6980	2.2626	25.0
α-FeOOH	13.0088		
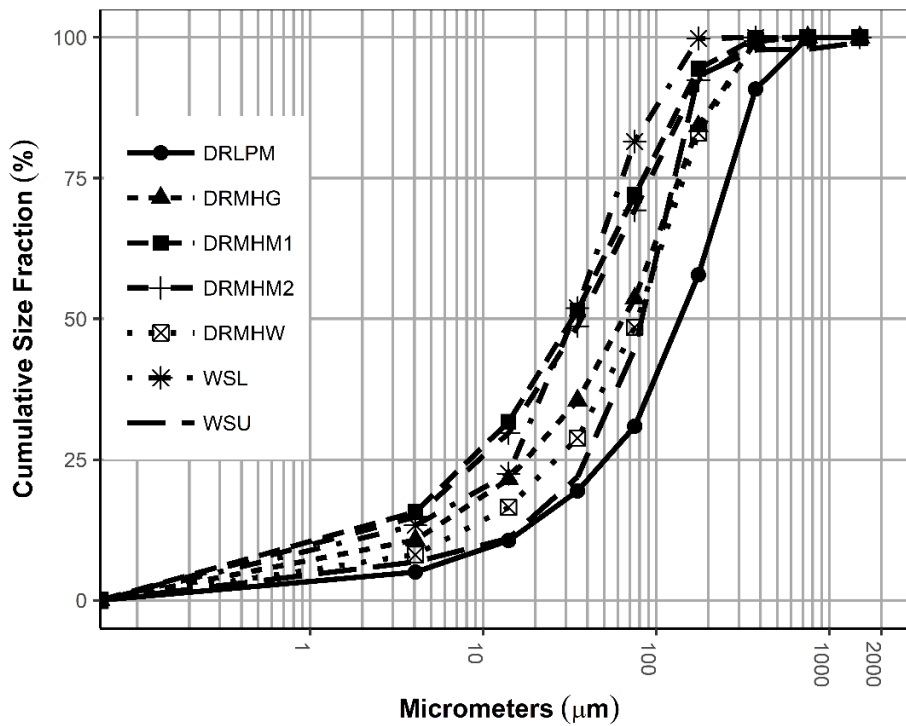
Figure 3 Cumulative grain size distribution. For reference, WSU and DRMHW were the two sediments used in batch experiments

3.1.2 West Swan River

The West Swan River upper channel bar deposit (WSU) is composed 77.2% sand, 15.1% silt, and 6.8% clay whereas the deposit associated with coarse woody debris at the West Swan River lower (WSL) site was composed of 48.1% sand, 38.6% silt, and 13.3% clay (Table 1, Figure 3). The increase in silt and clay fractions of WSL compared to WSU is most likely due to the physical features and location of the deposit. The WSL deposit was located closer to the channel margins than WSU and the WSL deposit sat within a depositional zone that allowed fine material to settle and accumulate. BET SSA of the WSU and WSL deposits measured 1.45 and 3.28 $m^2\,g^{-1}$ respectively (Table 2). Organic matter covered 62% of BET SSA at WSU and 52% at WSL. X-ray diffraction yielded mineralogy consisting of quartz, albite, muscovite, gehlenite, labradorite, pyrope, and dolomite amongst others aligning with expected mineralogy from the last glaciation.

3.2 Batch chemical distributions

3.2.1 Difficult Run

The partition coefficients, K_d, varied over a larger range for Pb (log K_d: 1.93 to 4.48 $L\,kg^{-1}$) than Be (1.46 to 3.43 $L\,kg^{-1}$) (Figure 4, Table 3). Both species show rapid sorption within the first 24 to 48 h before beginning to plateau (Figure 4) between 120 and 360 h. Three Be treatments using the DRMHW sediment had higher sorption relative to the base treatment (100 mg α-FeOOH, 1 mg α-FeOOH, and 2.38 mg L^{-1} DOC) with decreases in log K_d observed for the increased sediment to solution ratio and 11.86 mg L^{-1} DOC manipulations during the first 24 h (Figure 4, Table 3). The 11.86 mg L^{-1} DOC treatment had the lowest Be sorption with a log K_d of 2.52 $L\,kg^{-1}$ after 360 h (Figure 4, Table 3).

Lead sorption to the Difficult Run sediment had several unique features. The 0.25 h and 1 h samples for the 100 mg α-FeOOH, 11.86 mg L^{-1} DOC, and 2.38 mg L^{-1} DOC tests had greater log K_d values than the base treatment (Table 3) that represented an average percent increase in sorbed Pb of 88.6, 58.0, and 42.5 respectively. After 12-h mixing, the base treatment partition coefficient was exceeded by the following treatments: 1 mg α-FeOOH, 8 g L^{-1} sediment, and 100 mg α-FeOOH trials (Figure 4, Table 3). By 24 h only the increased sediment ratio had larger log K_d values than the base treatment with 22.0% more Pb sorbed but at longer mixing time intervals no treatment surpassed the amount of sorbed Pb to the base treatment for Pb sorption.
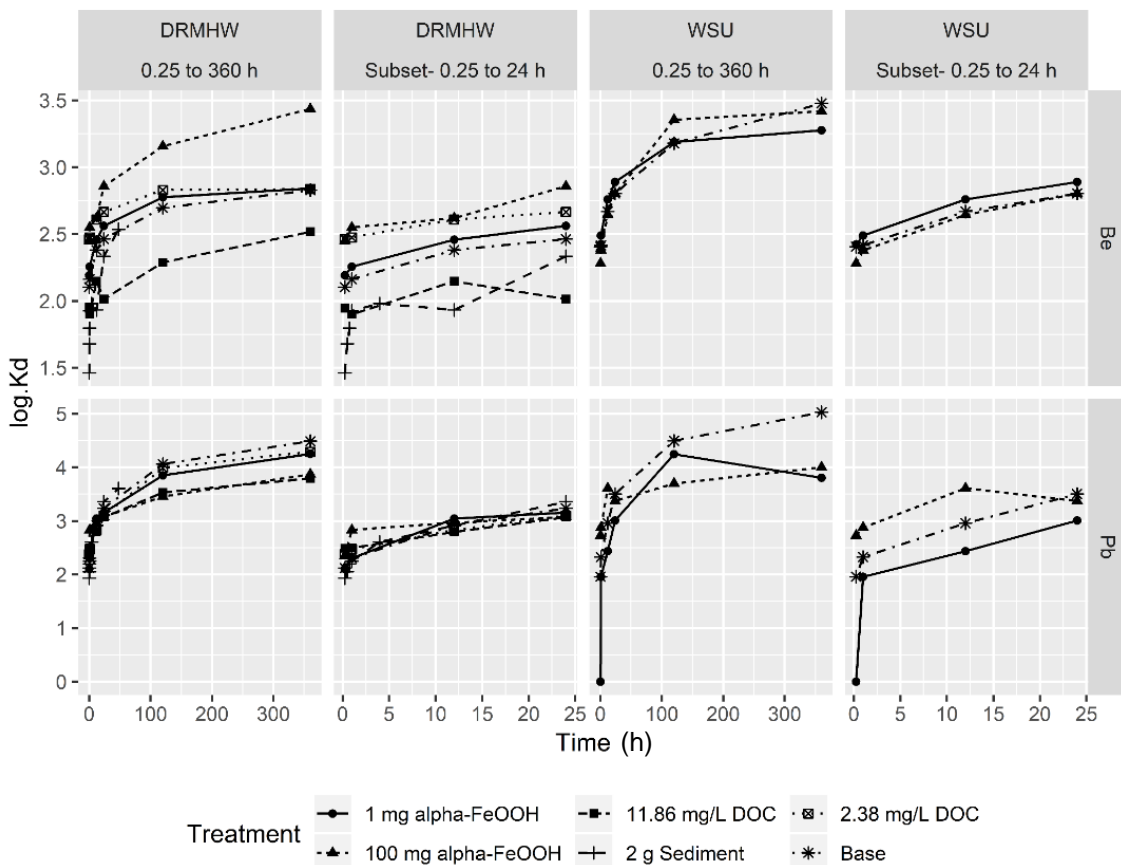
Figure 4 Lead and beryllium log K_d over time for the Difficult Run and West Swan River sediments with all treatments. The subset labeled plots are presented with a rescaled time axis from 0.25 to 24 h using the same data found in the 0.25 to 360-h plots.

Table 3 Log K_d and percent metal sorbed by treatment and time.

Time (h)			0.25		0.5		0.75		1		4		12		24		48		120		360	
Sediment	Pb/Be	Treatment	log Kd	% Sorbed	log Kd	% Sorbed	log Kd	% Sorbed	log Kd	% Sorbed	log Kd	% Sorbed	log Kd	% Sorbed	log Kd	% Sorbed	log Kd	% Sorbed	log Kd	% Sorbed	log Kd	% Sorbed
West Swan	Pb	Base	1.96	15.4					2.33	29.6			2.96	64.4	3.50	86.4			4.49	98.4	5.03	99.5
West Swan	Be	Base	2.41	33.7					2.42	34.3			2.67	48.2	2.80	55.8			3.18	75.1	3.48	85.7
Difficult Run	Pb	Base	2.12	20.9					2.31	28.8			2.92	62.6	3.24	77.5			4.06	95.4	4.49	98.3
Difficult Run	Be	Base	2.10	20.2					2.16	22.5			2.38	32.4	2.46	36.7			2.70	49.8	2.83	57.4
West Swan	Pb	100 mg α-FeOOH	2.73	48.4					2.87	59.3			3.61	87.8	3.37	81.3			3.70	92.1	4.00	95.9
West Swan	Pb	1 mg α-FeOOH	0.00	-5.3					1.96	12.9			2.44	35.2	3.01	67.1			4.24	97.0	3.80	92.7
West Swan	Be	100 mg α-FeOOH	2.28	31.5					2.38	36.5			2.64	51.5	2.80	60.3			3.35	84.2	3.42	86.3
West Swan	Be	1 mg α-FeOOH	2.42	34.6					2.49	38.2			2.76	53.5	2.89	60.6			3.19	75.5	3.28	78.8
Difficult Run	Pb	100 mg α-FeOOH	2.35	35.1					2.83	60.3			2.97	68.6	3.07	72.9			3.45	84.9	3.87	89.8
Difficult Run	Pb	1 mg α-FeOOH	2.10	20.3					2.30	28.6			3.04	68.8	3.16	74.1			3.85	93.3	4.25	97.2
Difficult Run	Be	100 mg α-FeOOH	2.45	40.5					2.55	46.1			2.62	50.0	2.86	63.4			3.16	77.3	3.44	86.8
Difficult Run	Be	1 mg α-FeOOH	2.19	23.8					2.26	26.6			2.46	36.5	2.56	42.2			2.78	54.5	2.84	58.2
Difficult Run	Pb	11.86 mg L^{-1} DOC	2.49	38.0					2.50	38.6			2.79	55.4	3.07	69.9			3.53	87.1	3.79	92.3
Difficult Run	Pb	2.38 mg L^{-1} DOC	2.38	32.5					2.47	37.3			2.83	57.5	3.10	71.1			3.99	95.1	4.29	97.5
Difficult Run	Be	11.86 mg L-1 DOC	1.95	14.9					1.90	13.7			2.15	21.9	2.01	17.1			2.29	27.9	2.52	39.7
Difficult Run	Be	2.38 mg L^{-1} DOC	2.46	36.6					2.48	37.4			2.61	44.8	2.67	48.0			2.83	57.5	2.84	57.9
Difficult Run	Pb	2 g Sediment	1.93	40.6	2.05	47.4	2.20	55.7	2.25	58.7	2.61	76.4	2.91	86.8	3.36	94.5	3.61	96.9				
Difficult Run	Be	2 g Sediment	1.46	18.8	1.68	27.6	1.80	33.3	1.93	40.4	1.98	43.4	1.93	32.4	2.33	63.3	2.54	73.3				

3.2.2 West Swan River

WSU sediment was assessed for Be and Pb sorption using the base treatment and iron treatments. The base treatment showed a steady increase in log K_d values from 1.96 to 5.03 L kg^{-1} for Pb over 0.25 to 360 h respectively with most of the sorption occurring within the first 24 h (Figure 4, Table 3). That same treatment's sorption isotherm did not plateau over the 360-h period whereas the goethite treatments both plateaued following 120 h (Figure 4). After 24 h the iron treatments exhibited reduced sorption relative to the base treatment (Figure 4, Table 3) with a 5.8 and 22.3% reduction in the amount of Pb sorbed for the 100 mg goethite and 1 mg goethite additions respectively. The 100 mg goethite addition corresponded to higher log K_d values (2.73, 2.87, and 3.61 L kg^{-1}) during the 0.25, 1, and 12-h intervals compared to the base treatment (1.96, 2.33, 2.96 L kg^{-1}) (Figure 4, Table 3) exhibiting 214.0, 100.6, and 36.3% more Pb sorbed. The addition of 1 mg of goethite decreased Pb sorption at all sampling times. Beryllium sorption ranged from 2.41 to 3.48 L kg^{-1} across all mixing times for the base treatment (Figure 4, Table 3). Mixing intervals from 0.25 to 24 h showed that the 1 mg goethite addition had the greatest sorption between treatments (Figure 4, Table 3) with 2.5, 11.3, 10.9, and 8.5% more Be sorbed. All Be treatments exhibited similar behavior with graphically similar increases in log K_d values (Figure 4).

4 Discussion

Both Pb and Be exhibited two-stage sorption defined by rapid increases in sediment bound metals followed by slower increases and plateaus at longer mixing periods. This aligns well with the findings of You et al. (1989) and Taylor et al. (2012), who both

surmised that the rapid period of fast sorption could be attributed to sorption to exchangeable mineral sites such as inner and outer sphere complexation followed by the slower movement to sites of greater stability such as within the crystal lattices of sediments. It is an inherently complex process driven by kinetics and defined by sediment characteristics, metal properties, the environment in which reactions take place, and how those variables change with time (McKinley and Jenne 1991).

Goethite was chosen to represent iron oxyhydroxides because of its stability and conservative nature compared to other phases of FeOOH. Iron oxyhydroxides and hydroxides are particles with high specific surface areas containing variable charge sites that are pH dependent and may act as a mechanism through which binding may remove trace metals directly or may serve as a facilitator of co-precipitation or flocculation that can also remove metals from solution (Murphy et al. 1992; Tang et al. 2014 and references within). This suggests that these minerals have the ability to easily sorb Pb and Be from solution. The relative affinity of iron compounds for various metals is directly related to pH controls on speciation but is also dependent on the redox potential. Bacterial respiration utilizing these iron compounds has been demonstrated as a source of metal mobility when conditions turn from oxic to anoxic (Cantwell et al. 2002; Cappuyns et al. 2006; Hwang et al. 2011; Monnin et al. 2018). Resuspension may also affect the release and sequestration of metals depending on the initial sediment conditions. Anoxic or subanoxic sediment when suspended into oxic conditions demonstrate a rapid release of iron to solution followed by a removal through precipitation or readsorption (Saulnier and Mucci 2000; Caille et al. 2003; Monnin et al. 2018) whereas oxidized sediments show no to minor releases of metals (Gerringa 1990). Thus, testing the sorption of Pb or Be bound to

oxyhydroxide and hydroxide particles with other fluvial sediments is vitally important to assess their conservative behavior. While this study does not directly look at desorption, examining sorption and the partitioning of Pb and Be to fluvial sediments with an increased fraction of iron hydroxides may help indicate to what degree that increased fraction changes sorption behavior and in what settings the speciation and cycling of reducible sediments could influence conservative behavior as sediments are transported through stream channels. The 100 mg addition of goethite enhanced Pb sorption for both the West Swan and Difficult Run sediments during the short mixing times. Beryllium sorption was increased with the 1 mg goethite additions for both sediments and the 100 mg addition with the Difficult Run sediment. This agrees with other studies in the literature (McKenzie 1980; Boschi and Willenbring 2016). The Pb and Be may have sorbed directly to the goethite or the goethite may have become bound to the sediment and facilitated the binding of metals to the sediment. This difference was not determined in the current study, but if this sediment were to be deposited or buried within a stream channel after being "tagged" by ^{210}Pb or ^{7}Be, these particles would be subject to the changes in speciation determined by oxygen content and pH which could be a source of mobility and release back into solution, hence the sediment could release some of its ^{7}Be or ^{210}Pb fingerprint.

One intriguing result was that the West Swan sediment showed a decreased sorption for Be with the 100 mg goethite addition and Pb with the 1 mg addition whereas on the Difficult Run sediments both Pb and Be sorption was enhanced or near equal to the base treatment (Figure 4, Table 3). Sediment characterization revealed that the WSU sediment had the highest organic surface coverage characterized at 61.8%. In contrast, DRMHW, had the least surface coverage of any of the Difficult Run sediments at 19.5%. Organic

matter on the surface of sediments, can play a role in the sorption or repulsion of other chemical species in solution (Lang and Kaupenjohann 2003; Wang et al. 2008), modify the charge characteristics at mineral surfaces, and/or occlude inner binding sites decreasing the available surface area for sorption (Wagai et al. 2009). One explanation for our results is that Pb may have experienced increased sorption with the 100 mg goethite addition to the Difficult Run sediment due to Pb's affinity to bind to iron oxides and a simultaneous increase in available binding sites upon addition of the goethite. In contrast, binding to the West Swan sediment may have resulted in aggregation or further occlusion of binding sites catalyzed by the organic material. These complex interactions may have accounted for the fact that the majority of duplicate pairs that differed by greater than 10 μg L^{-1} were WSU sediments with goethite additions. The Pb interaction cannot be confirmed without further analysis, but this example highlights one of the complexities of using metals for sediment fingerprinting that is rarely mentioned in the literature.

The addition of DOC to the background solution also provides a complexity to these experiments beyond that associated with sediment surfaces. Beryllium had enhanced sorption at 2.38 mg L^{-1} yet decreased sorption at 11.86 mg L^{-1} during the short and long mixing times (Figure 4). Lead had increased sorption with the low and high DOC concentration for the 0.25 h (55.3% and 81.8% more Pb sorbed than the base treatment, respectively) and 1 h (29.7% and 34.1% more Pb sorbed than the base treatment, respectively) time intervals before showing a decreased sorption at time intervals 12 h and longer. The low DOC concentration inhibited sorption relative to the base treatment the least at longer time intervals (-0.3% reduction at 120 h and -0.8% reduction at 360 h) compared to the other treatments. However, during all time intervals for the high and low

DOC concentrations, Be and Pb partitioning still increased, but not to the degree of the base treatment. The decreased sorption, compared to the base treatment, suggests that DOC is in competition with sediment for binding Pb and Be resulting in a greater proportion of both metals remaining in solution at higher DOC concentrations. This aligns well with the work of Takahashi et al. (1999) who demonstrated this competition for Be and in other studies that have demonstrated the affinities of Pb and Be to various organic species (Wong and Woolins 1994; Powell et al. 2009; Hu et al. 2011).

The increase in Be sorption with the 2.38 mg L^{-1} addition across all times could be emblematic of a scenario where organic matter may serve as a way for ligands to come out of solution. Yang et al. (2015) found that preferential sorption occurred between cations and that Be sorption was highest on Fe_2O_3 and lowest on $CaCO_3$ nanoparticles while ^{210}Pb showed preferential sorption for Fe_2O_3 and TiO_2 compared to the other minerals and oxides. When organics were introduced to solutions the amounts of both Pb and Be attached to nanoparticles significantly increased. More specifically, ^{210}Pb binding was augmented by the presence of polysaccharides and ^{7}Be by the presence of humic acid (Yang et al. 2015). These results suggest that organics may aid sorption under the right mixing conditions.

Increasing the sediment to solution ratio did not result in a proportional increase in partitioning and instead K_d values were lower relative to all treatments containing less sediment. The particle concentration effect is a decline in partition coefficients as the quantity of sediment increases and has been found in numerous studies (McKinley and Jenne 1991 and references within; Benoit and Rozan 1999). Cantwell et al. (2002) offered the conclusion that the amount of sediment is not nearly as important as the sediment

characteristics and chemical characteristics of the reaction environment. Taylor et al. (2012) experimented with a sediment to solution ratio of 1:10 that (described as a "slurry") found rapid sorption to sediment in short time frames and reported the results as percent sorbed across time. The observations from the current study saw similar patterns with low K_d values associated with an increased sediment ratio yet this treatment had some of the highest percent of sorbed material for Pb across all treatments and time intervals (Table 3). This suggests that more sediment equates to increased Pb sorption to mineral surfaces. The lowered K_d values should be expected based on the mathematical model because the mass normalization (Eq. 2) may be disguising this result when the volume is held constant. In contrast to Pb, Be showed similar percent sorption compared to other treatments. These results suggest that Be sorption is limited by its affinity for specific binding sites and transport time to those binding sites. This disparity between Pb and Be may be related to the need for Be to fit within a tetrahedral position whereas Pb, with its large range of coordination numbers (Swadzba-Kwasny 2015), may not be as limited to binding sites. This is also a possible reason why Pb has higher K_d values compared to Be in the literature.

5 Conclusions

In order to assess the importance of multiple stream environment factors contributing to metal sorption to channel sediments, sediments were characterized and batch experiments were performed testing the sorption of Pb and Be in the presence and absence of varying amounts of goethite, DOC, and a higher sediment to solution ratio on two sediments with different mineralogy and organic matter coverage. Sorption increased with time across all treatments, but treatments had different effects relative to the base

treatment at each time interval. A two-stage process was observed with rapid increases in log K_d values at shorter time intervals and a decreasing rate of log K_d growth at longer time intervals. High concentrations of DOC hinder sorption for both Be and Pb. Additional goethite had a positive influence on the sorption to Difficult Run sediments but negatively affected Be with the 100 mg addition and Pb with the 1 mg addition. Increasing the sediment to solution ratio saw a decrease in log K_d values consistent with the "particle concentration effect" but had the largest percentage of Pb sorbed over the short time intervals.

The goal of this work was to assess the sorption of Be and Pb to fluvial sediments in the presence of goethite or DOC to assess the conservative behavior of ^{7}Be and ^{210}Pb. Acknowledging varying environmental conditions throughout time and across the Critical Zone can lead to divergence of patterns and trends in sorption observed on river sediments. This work highlights one subset of those conditions. It showed that the binding of Be and Pb cations increased with time exhibiting similar patterns and ranges on two regionally different sediments, suggesting that these cations may be used in a wide variety of places. Critical Zone systems experiencing fast export of delivered fallout radionuclides during storm events may have reduced sorption and experience tracer export. Increasing levels of DOC may export a significant fraction of deposited ^{210}Pb and ^{7}Be in solution along with any cations subjected to the redox chemistry of various oxides and hydroxides. However, time is a critical component of sorption and with increasing mixing time and slower transport processes the exported fraction will be reduced.

The results may help to explain the effectiveness of using ^{7}Be and ^{210}Pb as tools for sediment fingerprinting, particularly when in-channel tagging and channel sediment

redistribution contribute to watershed export. The results of this study show researchers should continue to be cognizant of the complexities found within stream channel environments. Thus, when assessing the utility of Pb and Be isotopes for sediment fingerprinting prior knowledge of system complexities and behavior can help to determine suitability. Further exploration of these unknowns will not only benefit sediment fingerprinting but our understanding of the Critical Zone and its response to storm events.

6 References

Anagu I, Ingwersen J, Utermann J, Streck T (2009) Estimation of heavy metal sorption in German soils using artificial neural networks. Geoderma 152:104-112. doi:10.1016/j.geoderma.2009.06.004.

Aldahan A, Haiping Y, Possnert G (1998) Distribution of beryllium between solution and minerals (biotite and albite) under atmospheric conditions and variable pH. Chem Geol 156:209-229

Alderighi L, Bianchi A, Mederos A, Midollini S, Rodriguez A, Vacca A (1998) Thermodynamic and multinuclear NMR study of beryllium (II) hydrolysis and beryllium (II) complex formation with oxalate, malonate, and succinate anions in aqueous solution. European Journal of Inorganic Chemistry:1209-1215.

Alderighi L, Vacca A, Cecconi F, Midollini S, Chinea E, Dominguez S, Valle A, Dakternieks D, Duthie A (1999) Interaction of beryllium(II) in aqueous solution with bidentate ligands containing phosphonate groups. Inorganica Chimica Acta 285:39-48.

Appel C, Ma L (2002) Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils. J. Environ. Qual. 31:581-589.

Arkian F, Meshkatee AH, Bidokhti AA (2010) The effects of large-scale atmospheric flows on beryllium-7 activity concentration in surface air. Environmental Monitoring and Assessment 168:429-439. doi: 10.1007/s10661-009-1124-1

Atkinson CA, Jolley DF, Simpson SL (2007) Effect of overlying water pH, dissolved oxygen, salinity and sediment disturbances on metal release and sequestration from metal contaminated marine sediments. Chemosphere 69:1428-1437

Baskaran M, Ravichandran M, Bianchi TS (1997) Cycling of ^{7}Be and ^{210}Pb in a high doc, shallow, turbid estuary of south-east Texas. Estuarine, Coastal, and Shelf Science 45:165-176.

Belmont P, Gran KB et al (2011) Large shift in source of fine sediment in the upper Mississippi River. Environ Sci Technol 45:8804-8810

Belmont P, Willenbring JK, Schottler SP, Marquard J, Kumarasamy K, Hemmis JM (2014) Toward generalizable sediment fingerprinting with tracers that are conservative and nonconservative over sediment routing timescales. J Soils Sediments 14:1479-1492

Benoit G, Rozan TF (1999) The influence of size distribution on the particle concentration effect and trace metal partitioning in rivers. Geochimica et Cosmochimica Acta 63(1):113-127

Blake WH, Wallbrink PJ, Wilkinson SN, Humphreys GS, Doerr SH, Shakesby RA, Tomkins KM (2009) Deriving hillslope sediment budgets in wildfire-affected forests using fallout radionuclide tracers. Geomorphology 104:105-116. doi:10.1016/j.geomorph.2008.08.004

Boschi V, Willenbring JK (2016) The effect of pH, organic ligand chemistry and mineralogy on the sorption of beryllium over time. Environ Chem 13:711-722. http://dx.doi.org/10.1071/EN15107

Brezonik PL, Bloom PR, Sleighter RL, Cory RM, Khwaja AR, Hatcher PG (2015) Chemical differences of aquatic humic substances extracted by XAD-8 and DEAE-cellulose. J Environ Chem Eng 3:2982-2990. http://dx.doi.org/10.1016/j.jece.2015.03.004

Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. J Am Chem Soc 60(2):309-319. doi: 10.1021/ja01269a023

Caille N, Tiffreau C, Leyval C, Morel JL (2003) Solubility of metals in an anoxic sediment during prolonged aeration. Sci Total Environ 301:239-250

Cantwell MG, Burgess RM, Kester DR (2002) Release and phase partitioning of metals from anoxic estuarine sediments during periods of simulated resuspension. Environ Sci Technol 36(24):5328-5334

Cappuyns V, Swennen R, Deviver A (2006) Dredged river sediments: potential chemical time bombs? A case study. Water Air Soil Poll 171:49-66

Collins AL, Walling DE, Leeks GJL (1997) Sediment sources in the Upper Severn catchment: a fingerprinting approach. Hydrology and Earth System Sciences 1(3):509-521

Davies BE (1995) Lead, In: Alloway, B.J. (Ed.), Heavy metals in soils, 2nd ed. 206-223 (Chapter 9)

Davis JA, Leckie JO (1978) Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. Environ Sci Technol 12(12):1309-1315

Degryse F, Smolders E, Parker DR (2009) Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications- a review. Eur J Soil Sci 60:590-612. doi: 10.1111/j.1365-2389.2009.01142.x

Diamond HJ, Karl TR, Palecki MA et al (2013) U.S. Climate Reference Network after one decade of operations: status and assessment. Bull Am Meteor Soc 94:489-498. doi: 10.1175/BAMS-D-12-00170.1

Di Nanno MP, Curutchet G, Ratto S (2007) Anaerobic sediment potential acidification and metal release risk assessment by chemical characterization and batch resuspension experiments. J Soils Sediments 7(3):187-194. http://dx.doi.org/10.1065/jss2007.04.220

Drago RS (1958) Thermodynamic evaluation of the inert pair effect. Journal Physical Chemistry 62:353

Drake AA, Morgan BA (1981) The piney branch complex- a metamorphosed fragment of the central Appalachian ophiolite in northern Virginia. American Journal of Science 281:484-508

Du YJ, Hayashi S (2005) Investigation on some factors controlling the sorption of heavy metals on ariake clay. Lowland Technology International 7(1):43-49

Duenas C, Fernandez M.C, Carretero J, Liger E, Canete S (2004) Long-term variation of the concentrations of long-lived Rn descendants and cosmogenic ^{7}Be and determination of the MRT of aerosols. Atmos Environ 38:1291-1301. doi: 10.1016/j.atmosenv.2003.11.029

Du Laing G, Meers E, Dewispelaere M, Rinklebe J, Vandecasteele B, Verloo MG, Tack FMG (2009) Effect of water table level on metal mobility at different depths in wetland soils of the Scheldt Estuary (Belgium). Water Air Soil Poll 202:353-367. doi: 10.1007/s11270-009-9982-2

Du Laing G, Rinklebe J, Vandecasteele B, Meers E, Tack FMG (2008) Trace metal behavior in estuarine and riverine floodplain soils and sediments: A review. Sci Total Environ 407:3972-3985

Essington ME (2015) Soil and water chemistry: an integrative approach. CRC Press Taylor & Francis Group 2nd ed. Boca Raton, FL:383-486

Fernandez JSC, Sordo J (2006) Lead: chemistry, analytical aspects, environmental impact and health effects. Elsevier 1st ed. Amsterdam, The Netherlands

Gault AG, Langley S, Ibrahim A et al (2012) Seasonal changes in mineralogy, geochemistry and microbial community of bacteriogenic iron oxides (BIOS) deposited in circumneutral wetland. Geomicrobiology Journal 29:161-172. doi: 10.1080/01490451.2010.532196

Gellis A, Fitzpatrick F, Schubauer-Berigan J (2016) A manual to identify sources of fluvial sediment. EPA/600/R-16/210. U.S. EPA, Washington, DC

Gellis AC, Fuller CC, Van Metre PC (2017) Sources and ages of fine-grained sediment to streams using fallout radionuclides in the Midwestern United States. Journal of Environmental Management 194:73-85. https://doi.org/10.1016/j.jenvman.2016.06.018

Gerringa LJA (1990) Aerobic degradation of organic matter and the mobility of Cu, Cd, Ni, Pb, Zn, Fe and Mn in marine sediment slurries. Mar Chem 29:355-374

Gerritse RG, Van Driel W (1984) The relationship between adsorption of trace metals, organic matter, and pH in temperate soils. J Environ Qual 13(2):197-204

Grybos M, Davranche M, Gruau G, Petitjean P (2007) Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? Journal of Colloid and Interface Science314:490-501. doi: 10.1016/j.jcis.2007.04.062

Gustafsson JP, Tiberg C, Edkymish A, Kleja DB (2011) Modelling lead(II) sorption to ferrihydrite and soil organic matter. Environ Chem 8:485- 492. http://dx.doi.org/10.1071/EN11025

Hawley N, Robbins JA, Eadie BJ (1986) The partitioning of 7 beryllium in fresh water*. Geochimica et Cosmochimica Acta 50:1127-1131.

Hegler F, Losekann-Behrens T, Hanselmann K, Behrens S, Kappler A (2012) Influence of seasonal and geochemical changes on the geomicrobiology of an iron carbonate mineral water spring. Appl Environ Microbiol 78(20):7185-7196. doi: 10.1128/AEM.01440-12

Hu M, Morsali A, Aboutorabi L (2011) Lead(II) carboxylate supramolecular compounds: coordination modes, structures and non-structures aspects. Coordination Chemistry Reviews 255:2821-2859. doi: 10.1016/j.ccr.2011.05.019

Huisman NLH, Karthikeyan KG (2012) Using radiometric tools to track sediment and phosphorus movement in an agricultural watershed. Journal of Hydrology 450-451:219-229. http://dx.doi.org/10.1016/j.jhydrol.2012.05.007

Hupp CR, Noe GB, Schenk ER, Benthem AJ (2013) Recent and historic sediment dynamics along Difficult Run, a suburban Virginia Piedmont stream. Geomorphology 180-181:156-169

Hwang K-Y, Kim H-S, Hwang I (2011) Effect of resuspension on the release of heavy metals and water chemistry in anoxic and oxic sediments. Clean-Soil Air Water 39(10):908-915. doi: 10.1002/clen.201000417

Illera V, Garrido F, Serrano S, Garcia-Gonzalez MT (2004) Immobilization of the heavy metals Cd, Cu and Pb in an acid soil amended with gypsum-and lime-rich industrial by-products. European Journal of Soil Science 55:135-145. doi:10.1046/j.1365-2389.2003.00583

Itoh H, Narazaki Y (2017) Meterological notes for understanding the transport of beryllium-7 in the troposphere. Jpn J Health Phys 52(2):122-133. doi: 10.5453/jhps.52.122

Karwan DL, Pizzuto JE, Aalto R, Marquard J, Harpold A, Skalak K, Benthem A, Levia DF, Siegert CM, Aufdenkampe AK (2018) Direct channel precipitation and storm characteristics influence short-term fallout radionuclide assessment of sediment source. Water Resources Research 54:4579-4594. https://doi.org/10.1029/2017WR021684

Kaste JM, Magilligan FJ, Renshaw CE, Fisher GB, Dade WB (2014) Seasonal controls on meteoric beryllium-7 in coarse-grained river channels. Hydrological Processes 28:2738-2748

Kaste JM, Norton SA, Hess CT (2002) Environmental chemistry of beryllium-7. Reviews in Mineralogy and Geochemistry 50:271-289. doi:10.2138/rmg.2002.50.6

Keizer TS, Scott BL, McCleskey TM (2015) Beryllium: inorganic chemistry. Encyclopedia of Inorganic and Bioinorganic Chemistry:1-9. doi: 10.1002/9781119951438.eibc0276.pub2

Koch D (1998) Beryllium 10/beryllium 7 as a tracer of stratospheric transport. J Geophys Res 103(D4):3907-3917

Koiter AJ, Owens PN, Petticrew EL, Lobb DA (2013) The behavioural characteristics of sediment properties and their implications for sediment fingerprinting as an approach for identifying sediment sources in river basins. Earth-Science Reviews 125:24-42

Kosmulski M, Maczka E, Jartych E, Rosenholm JB (2003) Synthesis and characterization of goethite and goethite-hematite composite: experimental study and literature survey. Advances in Colloid and Interface Science 103:57-76

Krmar M, Mihailovic DT, Arsenic L, Radnovic D, Pap I (2016) Beryllium-7 and ^{210}Pb atmospheric deposition measured in moss and dependence on cumulative precipitation. Sci Total Environ 541:941-948. doi: 10.1016/j.scitotenv.2015.09.0830048-9697/

Lang F, Kaupenjohann M (2003) Immobilisation of molybdate by iron oxides: effects of organic coatings. Geoderma 113: 31-46

Liu A, Gonzalez RD (1999) Adsorption/desorption in a system consisting of humic acid, heavy metals, and clay minerals. Journal of Colloid and Interface Science 218:225-232

Liu G, Yang M, Warrington D, Liu P, Tian J (2011) Using beryllium-7 to monitor the relative proportions of interrill and rill erosion from loessal soil slopes in a single rainfall event. Earth Surf Proc Land 36:439-448. doi: 10.1002/esp.2057

Lusardi BA, Dengler EL (1994/2017) Minnesota at a glance. Minnesota Geological Survey

Mabit L, Benmansour M, Walling DE (2008) Comparative advantages and limitations of the fallout radionuclides 137 Cs, 210 Pbex and 7 Be for assessing soil erosion and sedimentation. J Environ Radioactiv 99:1799-1807

Mabit L, Benmansour M, Abril JM, Walling DE, Meusburger K, Iurian AR, Bernard C, Tarjan S, Owens PN, Blake WH, Alewell C (2014) Fallout 210Pb as a soil and sediment tracer in catchment sediment budget investigations: A review. Earth-Science Reviews 138:335-351. http://dx.doi.org/10.1016/j.earscirev.2014.06007

Matisoff G, Bonniwell EC, Whiting PJ (2002) Soil erosion and sediment sources in an Ohio watershed using beryllium-7, cesium-137, and lead-210. J Environ Qual 31:54-61

Matisoff G, Wilson C G, Whiting P J (2005) The7Be/210Pbxs ratio as an indicator of suspended sediment age or fraction new sediment in suspension. Earth Surf Proc Land 30(9):1191–1201. https://doi.org/10.1002/esp.1270

Mayer LM, Xing B (2001) Organic matter-surface area relationships in acid soils. Soil Sci Soc Am J 65:250-258. doi: 10.2136/sssaj2001.651250x

McDonnel JJ (2014) The two water worlds hypothesis: ecohydrological separation of water between streams and trees? Wiley Interdisciplinary Reviews: Water 1(4):323-329

McKenzie RM (1980) The adsorption of lead and other heavy metals on oxides of manganese and iron. Australian J Soil Res 18:61-73

McKinley JP, Jenne EA (1991) Experimental investigation and review of the "solids concentration" effect in adsorption studies. Environ Sci Technol 25:2082-2087

Monnin L, Ciffroy P, Garnier JM, Ambrosi JP, Radakovitch O (2018) Remobilization of trace metals during laboratory resuspension of contaminated sediments from a dam reservoir. J Soils Sediments 18:2596-2613

Murphy EM, Zachara JM, Smith SC, Phillips JL (1992) The sorption of humic acids to mineral surfaces and their role in contaminant binding. Sci Total Environ 117/118:413-423

OECD (Organization for Economic Co-Operation and Development) (Ed.) (2000): OECD- Guideline for testing of chemicals 106: Adsorption/Desorption, pp 1-45

Ohkouchi N, Ogawa N.O, Chikaraishi Y, Tanaka H, Wada E (2015) Biochemical and physiological bases for the use of carbon and nitrogen isotopes in environmental and ecological studies. Prog Earth Planet Sci 2:1. doi: 10.1186/s40645-015-0032-y

Ponizovsky AA, Tsadilas CD (2003) Lead(II) retention by alfisol and clinoptilolite: cation balance and pH effect. Geoderma 115:303-312. doi:10.1016/S0016-7061(03)00069-7

Powell KJ, Brown PL, Byrne RH et al (2009) Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: the Pb^{2+} + OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} systems (IUPAC Technical Report). Pure Appl Chem 81(12):2425- 2476. doi: 10.1351/PAC-REP-09-03-05

Railsback LB (2011) An earth scientist's periodic table of the elements and their ions. Geology 31:737-740. doi: 10.1130/G19542.1

Roy WR, Krapac IG, Chou SFJ, Griffin RA (1991) Batch-type procedures for estimating soil adsorption of chemicals. EPA 530-SW-87-006-F. U.S. EPA, Washington, DC

Ryken N, Al-Barri B, Blake W, Taylor A, Tack FMG, Van Ranst E, Bode S, Boeckx P, Verdoodt A (2018) Rapid and irreversible sorption behavior of ^7Be assessed to evaluate its use as a catchment sediment tracer. Journal of Environmental Radioactivity 182:108-116. https://doi.org/10.1016/j.jenvrad.2017.11.018

Saulnier I, Mucci A (2000) Trace metal remobilization following the resuspension of estuarine sediments: Saguenay Fjord, Canada. Appl Geochem 15(2):191-210. https://doi.org/10.1016/S0883-2917(99)00034-7

Schmidbaur H (2000) Recent contributions to the aqueous coordination chemistry of beryllium. Coordination Chemistry Reviews 215:223-242

Schwerdtfeger P, Heath GA, Dolg M, Bennett MA (1992) Low valencies and periodic trends in heavy element chemistry. A theoretical study of relativistic effects and electron correlation effects in group 13 and period 6 hydrides and halides. J Am Chem Soc 114:7518-7527

Sepulveda A, Schuller P, Walling DE, Castillo A (2008) Use of ^7Be to document soil erosion associated with a short period of extreme rainfall. J Environ Radioactiv 99:35-49

Smith HG, Blake WH. (2014) Sediment fingerprinting in agricultural catchments: a critical re-examination of source discrimination and data corrections. Geomorphology 204:177-191

Sprenger M, Leistert H, Gimbel K, Weiler M (2016) Illuminating hydrological processes at the soil-vegetation-atmosphere interface with water stable isotopes. Rev Geophys 54:674-704. doi: 10.1002/2015RG000515

Strawn DG, Sparks DL (2000) Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil. Soil Sci Soc Am J 64:144-156

Stuckey JW, Schaefer MV, Kocar BD, Benner SG, Fendorf S (2015) Arsenic release metabolically limited to permanently water-saturated soil in Mekong Delta. Nature Geoscience 9:70-78. doi: 10.1038/NGEO2589

Sulu-Gambari F, Seitaj D, Meysman FJR, Schauer R, Polerecky L, Slomp CP (2016) Cable bacteria control iron-phosphorus dynamics in sediments of a coastal hypoxic basin. Environ Sci Technol 50:1227- 1233. doi: 10.1021/acs.est5b04369

Swadzba-Kwasny M (2015) Lead: inorganic chemistry. Encyclopedia of Inorganic and Bioinorganic Chemistry. doi: 10.1002/9781119951438.eibc0111.pub2

Takahashi Y, Minai Y, Ambe S, Makide Y, Ambe F (1999) Comparison of adsorption behavior of multiple inorganic ions on kaolinite and silica in the presence of humic acid using the multitracer technique. Geochimica et Cosmochimica Acta 63(6):815-836

Tang WW, Zeng GM, Gong JL, Liang J, Xu P, Zhang C, Huang BB (2014) Impact of humic/fulvic acid on the removal of heavy metals from aqueous solutions using nanomaterials: a review. Sci Total Environ 468-469:1014-1027. http://dx.doi.org/10.1016/j.scitotenv.2013.09.044

Taylor A, Blake W, Couldrick L, Keith-Roach M (2012) Sorption behaviour of beryllium-7 and implications for its use as a sediment tracer. Geoderma 187-188:16-23

Taylor A, Blake WH, Smith HG, Mabit L, Keith-Roach MJ (2013) Assumptions and challenges in the use of fallout beryllium-7 as a soil and sediment tracer in river basins. Earth-Science Reviews 126:85-95. http://dx.doi.org/10.1016/j.earscirev.2013.08.002

Underwood JW, Renshaw CE, Magilligan FJ, Dade WB, Landis JD (2015) Joint isotopic mass balance: a novel approach to quantifying channel bed to channel margins sediment transfer during storm events. Earth Surf Proc Land 40(12):1563-1573

US EPA (Environmental Protection Agency) (1999) Understanding variation in partition coefficient K_d values. Volume 1: The K_d model, methods of measurement and application of chemical reaction codes. EPA 402-R-99-004A. U.S. EPA, Washington, DC

U.S. Geological Survey (2016) National Water Information System data available on the World Wide Web (USGS Water Data for the Nation), accessed [April 10, 2016], at URL https://waterdata.usgs.gov/usa/nwis/uv?01645704

U.S. Geological Survey (2018) National Water Information System data available on the World Wide Web (USGS Water Data for the Nation), accessed [June 10, 2018], at URL https://waterdata.usgs.gov/usa/nwis/uv?01645704. http://dx.doi.org/10.5066/F7P55KJN

Wagai R, Mayer LM, Kitayama K (2009) Extent and nature of organic coverage of soil mineral surfaces assessed by a gas sorption approach. Geoderma 149:152-160

Wallbrink PJ, Murray AS (1996) Distribution and variability of [7]Be in soils under different surface cover conditions and its potential for describing soil redistribution processes. Water Resources Research 32(2):467-476. doi: 10.1029/95WR02973

Walling DE (2013) The evolution of sediment source fingerprinting investigations in fluvial systems. J Soils Sediments 13:1658-1675

Wang EX, Benoit G (1996) Mechanisms controlling the mobility of lead in the spodosols of a northern hardwood forest ecosystem. Environ Sci Technol 30:2211-2219

Wang X, Lu J, Xu M, Xing F (2008) Sorption of pyrene by regular and naoscaled metal oxide particles: influence of adsorbed organic matter. Environ Sci Technol 42:7267- 7272

Welp G, Brummer GW (1999) Adsorption and solubility of ten metals in soil samples of different composition. J Plant Nutr Soil Sci 162:155-161

Wong CY, Woolins JD (1994) Beryllium coordination chemistry. Coordination Chemistry Reviews 130:243-273

Wu Z, Gu Z, Wang X, Evans L, Guo H (2003) Effects of organic acids on adsorption of lead onto montmorillonite, goethite and humic acid. Environ Pollut 121:469-475

Yang W, Guo L, Chuang CY, Schumann D, Ayranov M, Santschi PH (2013) Adsorption characteristics of ^{210}Pb, [210]Po and [7]Be onto micro-particle surfaces and the effects of macromolecular organic compounds. Geochimica et Cosmochimica Acta 107:47-64. https://doi.org/10.1016/j.gca.2012.12.039

Yang W, Guo L, Chuang CY, Santschi PH, Schumann D, Ayranov M (2015) Influence of organic matter on the adsorption of ^{210}Pb, [210] Po and [7]Be and their fractionation on nanoparticles in seawater. Earth Planet Sci Lett 423:193-201. http://dx.doi.org/10.1016/j.epsl.2015.05.007

You C, Lee T, Li YH (1989) The partition of Be between soil and water. Chem Geol 77:105-118

Yu R, Gan P, MacKay AA, Zhang S, Smets BF (2009) Presence, distribution, and diversity of iron-oxidizing bacteria at a landfill leachate-impacted groundwater surface water interface. FEMS Microbiology Ecology 71:260-271

Zapata F (2003) The use of environmental radionuclides as tracers in soil erosion and sedimentation investigations: recent advances and future developments. Soil Till Res 69:3-13

Zhang XC, Friedrich JM, Nearing MA, Norton LD (2001) Potential use of rare earth oxides as tracers for soil erosion and aggregation studies. Soil Sci Soc Am 65:1508-1515

7 Appendix 1

Table 4 Batch Data

Sediment	Sorbate	Time (h)	Treatment	$m_{sediment}$ (g)	$m_{\alpha-FeOOH}$ (g)	$m_{sorbent}$ (kg)	V(L)	C_i (µg L^{-1})	C_{eq} (µg L^{-1})
WSU	Pb	0.25	Base	0.50	0	0.0005000	0.2500	100.0000	85.7000
WSU	Pb	0.25	Base	0.50	0	0.0005000	0.2500	100.0000	83.5000
WSU	Pb	1	Base	0.50	0	0.0005000	0.2500	100.0000	74.2000
WSU	Pb	1	Base	0.50	0	0.0005000	0.2500	100.0000	66.7000
WSU	Pb	12	Base	0.50	0	0.0005000	0.2500	100.0000	35.8000
WSU	Pb	12	Base	0.50	0	0.0005000	0.2500	100.0000	35.4000
WSU	Pb	24	Base	0.50	0	0.0005000	0.2500	100.0000	12.9000
WSU	Pb	24	Base	0.50	0	0.0005000	0.2500	100.0000	14.4000
WSU	Pb	120	Base	0.50	0	0.0005000	0.2500	100.0000	1.8000
WSU	Pb	120	Base	0.50	0	0.0005000	0.2500	100.0000	1.4100
WSU	Pb	360	Base	0.50	0	0.0005000	0.2500	100.0000	0.4360
WSU	Pb	360	Base	0.50	0	0.0005000	0.2500	100.0000	0.5070
WSU	Pb	0.25	100 mg α-FeOOH	0.50	0.1022	0.0006022	0.2500	100.0000	31.3000
WSU	Pb	0.25	100 mg α-FeOOH	0.50	0.1027	0.0006027	0.2500	100.0000	72.0000
WSU	Pb	1	100 mg α-FeOOH	0.50	0.1035	0.0006035	0.2500	100.0000	26.3000
WSU	Pb	1	100 mg α-FeOOH	0.50	0.1004	0.0006004	0.2500	100.0000	55.1500
WSU	Pb	12	100 mg α-FeOOH	0.50	0.1025	0.0006025	0.2500	100.0000	18.2000
WSU	Pb	12	100 mg α-FeOOH	0.50	0.1037	0.0006037	0.2500	100.0000	6.1950
WSU	Pb	24	100 mg α-FeOOH	0.50	0.1030	0.0006030	0.2500	100.0000	26.9500
WSU	Pb	24	100 mg α-FeOOH	0.50	0.1018	0.0006018	0.2500	100.0000	10.4000
WSU	Pb	120	100 mg α-FeOOH	0.50	0.1005	0.0006005	0.2500	100.0000	6.7000
WSU	Pb	120	100 mg α-FeOOH	0.50	0.1029	0.0006029	0.2500	100.0000	9.0300
WSU	Pb	360	100 mg α-FeOOH	0.50	0.1007	0.0006007	0.2500	100.0000	4.8400
WSU	Pb	360	100 mg α-FeOOH	0.50	0.1009	0.0006009	0.2500	100.0000	3.4100
WSU	Pb	0.25	1 mg α-FeOOH	0.50	0.0010	0.0005010	0.2500	100.0000	115.0000
WSU	Pb	0.25	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	95.6000

WSU	Pb	1	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	72.3000
WSU	Pb	1	1 mg α-FeOOH	0.50	0.0014	0.0005014	0.2500	100.0000	102.0000
WSU	Pb	12	1 mg α-FeOOH	0.50	0.0015	0.0005015	0.2500	100.0000	68.4000
WSU	Pb	12	1 mg α-FeOOH	0.50	0.0012	0.0005012	0.2500	100.0000	61.3000
WSU	Pb	24	1 mg α-FeOOH	0.50	0.0015	0.0005015	0.2500	100.0000	33.7000
WSU	Pb	24	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	32.1000
WSU	Pb	120	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	3.8300
WSU	Pb	120	1 mg α-FeOOH	0.50	0.0015	0.0005015	0.2500	100.0000	2.1600
WSU	Pb	360	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	8.1300
WSU	Pb	360	1 mg α-FeOOH	0.50	0.0015	0.0005015	0.2500	100.0000	6.5500
WSU	Be	0.25	Base	0.50	0	0.0005000	0.2500	100.0000	66.7673
WSU	Be	0.25	Base	0.50	0	0.0005000	0.2500	100.0000	65.8233
WSU	Be	1	Base	0.50	0	0.0005000	0.2500	100.0000	65.9810
WSU	Be	1	Base	0.50	0	0.0005000	0.2500	100.0000	65.4784
WSU	Be	12	Base	0.50	0	0.0005000	0.2500	100.0000	52.3526
WSU	Be	12	Base	0.50	0	0.0005000	0.2500	100.0000	51.2034
WSU	Be	24	Base	0.50	0	0.0005000	0.2500	100.0000	47.0694
WSU	Be	24	Base	0.50	0	0.0005000	0.2500	100.0000	41.2855
WSU	Be	120	Base	0.50	0	0.0005000	0.2500	100.0000	25.1396
WSU	Be	120	Base	0.50	0	0.0005000	0.2500	100.0000	24.6238
WSU	Be	360	Base	0.50	0	0.0005000	0.2500	100.0000	14.2615
WSU	Be	360	Base	0.50	0	0.0005000	0.2500	100.0000	14.3059
WSU	Be	0.25	100 mg α-FeOOH	0.50	0.1015	0.0006015	0.2500	100.0000	67.1000
WSU	Be	0.25	100 mg α-FeOOH	0.50	0.1044	0.0006044	0.2500	100.0000	69.9000
WSU	Be	1	100 mg α-FeOOH	0.50	0.1022	0.0006022	0.2500	100.0000	63.3000
WSU	Be	1	100 mg α-FeOOH	0.50	0.0998	0.0005998	0.2500	100.0000	63.7000
WSU	Be	12	100 mg α-FeOOH	0.50	0.1033	0.0006033	0.2500	100.0000	48.2000
WSU	Be	12	100 mg α-FeOOH	0.50	0.1011	0.0006011	0.2500	100.0000	48.9000
WSU	Be	24	100 mg α-FeOOH	0.50	0.1003	0.0006003	0.2500	100.0000	41.3000
WSU	Be	24	100 mg α-FeOOH	0.50	0.1018	0.0006018	0.2500	100.0000	38.1000
WSU	Be	120	100 mg α-FeOOH	0.50	0.1033	0.0006033	0.2500	100.0000	18.3000

WSU	Be	120	100 mg α-FeOOH	0.50	0.1035	0.0006035	0.2500	100.0000	13.4000
WSU	Be	360	100 mg α-FeOOH	0.50	0.1028	0.0006028	0.2500	100.0000	13.1000
WSU	Be	360	100 mg α-FeOOH	0.50	0.1037	0.0006037	0.2500	100.0000	14.3000
WSU	Be	0.25	1 mg α-FeOOH	0.50	0.0015	0.0005015	0.2500	100.0000	67.6000
WSU	Be	0.25	1 mg α-FeOOH	0.50	0.0012	0.0005012	0.2500	100.0000	63.3000
WSU	Be	1	1 mg α-FeOOH	0.50	0.0007	0.0005007	0.2500	100.0000	63.2000
WSU	Be	1	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	60.5000
WSU	Be	12	1 mg α-FeOOH	0.50	0.0014	0.0005014	0.2500	100.0000	46.7000
WSU	Be	12	1 mg α-FeOOH	0.50	0.0011	0.0005011	0.2500	100.0000	46.3000
WSU	Be	24	1 mg α-FeOOH	0.50	0.0009	0.0005009	0.2500	100.0000	36.0000
WSU	Be	24	1 mg α-FeOOH	0.50	0.0010	0.0005010	0.2500	100.0000	42.9000
WSU	Be	120	1 mg α-FeOOH	0.50	0.0014	0.0005014	0.2500	100.0000	23.2000
WSU	Be	120	1 mg α-FeOOH	0.50	0.0011	0.0005011	0.2500	100.0000	25.8000
WSU	Be	360	1 mg α-FeOOH	0.50	0.0010	0.0005010	0.2500	100.0000	24.0000
WSU	Be	360	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	18.5000
DRMHW	Pb	0.25	Base	0.50	0	0.0005000	0.2500	100.0000	77.1000
DRMHW	Pb	0.25	Base	0.50	0	0.0005000	0.2500	100.0000	81.1000
DRMHW	Pb	1	Base	0.50	0	0.0005000	0.2500	100.0000	72.3000
DRMHW	Pb	1	Base	0.50	0	0.0005000	0.2500	100.0000	70.2000
DRMHW	Pb	12	Base	0.50	0	0.0005000	0.2500	100.0000	38.6000
DRMHW	Pb	12	Base	0.50	0	0.0005000	0.2500	100.0000	36.3000
DRMHW	Pb	24	Base	0.50	0	0.0005000	0.2500	100.0000	23.3000
DRMHW	Pb	24	Base	0.50	0	0.0005000	0.2500	100.0000	21.8000
DRMHW	Pb	120	Base	0.50	0	0.0005000	0.2500	100.0000	6.0100
DRMHW	Pb	120	Base	0.50	0	0.0005000	0.2500	100.0000	3.2000
DRMHW	Pb	360	Base	0.50	0	0.0005000	0.2500	100.0000	1.2800
DRMHW	Pb	360	Base	0.50	0	0.0005000	0.2500	100.0000	2.1400
DRMHW	Pb	0.25	100 mg α-FeOOH	0.50	0.1026	0.0006026	0.2500	100.0000	62.7000
DRMHW	Pb	0.25	100 mg α-FeOOH	0.50	0.0993	0.0005993	0.2500	100.0000	67.2000
DRMHW	Pb	1	100 mg α-FeOOH	0.50	0.1039	0.0006039	0.2500	100.0000	31.3000
DRMHW	Pb	1	100 mg α-FeOOH	0.50	0.1032	0.0006032	0.2500	100.0000	48.2000

DRMHW	Pb	12	100 mg α-FeOOH	0.50	0.0993	0.0005993	0.2500	100.0000	34.8000
DRMHW	Pb	12	100 mg α-FeOOH	0.50	0.1030	0.0006030	0.2500	100.0000	28.0000
DRMHW	Pb	24	100 mg α-FeOOH	0.50	0.1032	0.0006032	0.2500	100.0000	32.8000
DRMHW	Pb	24	100 mg α-FeOOH	0.50	0.1035	0.0006035	0.2500	100.0000	21.4000
DRMHW	Pb	120	100 mg α-FeOOH	0.50	0.1045	0.0006045	0.2500	100.0000	9.0700
DRMHW	Pb	120	100 mg α-FeOOH	0.50	0.1024	0.0006024	0.2500	100.0000	21.2000
DRMHW	Pb	360	100 mg α-FeOOH	0.50	0.1007	0.0006007	0.2500	100.0000	17.2000
DRMHW	Pb	360	100 mg α-FeOOH	0.50	0.1021	0.0006021	0.2500	100.0000	3.1400
DRMHW	Pb	0.25	1 mg α-FeOOH	0.50	0.0012	0.0005012	0.2500	100.0000	81.2000
DRMHW	Pb	0.25	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	78.3000
DRMHW	Pb	1	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	69.5000
DRMHW	Pb	1	1 mg α-FeOOH	0.50	0.0012	0.0005012	0.2500	100.0000	73.3000
DRMHW	Pb	12	1 mg α-FeOOH	0.50	0.0011	0.0005011	0.2500	100.0000	32.4000
DRMHW	Pb	12	1 mg α-FeOOH	0.50	0.0014	0.0005014	0.2500	100.0000	30.0000
DRMHW	Pb	24	1 mg α-FeOOH	0.50	0.0011	0.0005011	0.2500	100.0000	27.6000
DRMHW	Pb	24	1 mg α-FeOOH	0.50	0.0014	0.0005014	0.2500	100.0000	24.3000
DRMHW	Pb	120	1 mg α-FeOOH	0.50	0.0011	0.0005011	0.2500	100.0000	5.9600
DRMHW	Pb	120	1 mg α-FeOOH	0.50	0.0011	0.0005011	0.2500	100.0000	7.3600
DRMHW	Pb	360	1 mg α-FeOOH	0.50	0.0012	0.0005012	0.2500	100.0000	3.1600
DRMHW	Pb	360	1 mg α-FeOOH	0.50	0.0014	0.0005014	0.2500	100.0000	2.4100
DRMHW	Pb	0.25	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	61.0000
DRMHW	Pb	0.25	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	57.9000
DRMHW	Pb	0.5	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	50.8000
DRMHW	Pb	0.5	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	54.5000
DRMHW	Pb	0.75	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	44.6000
DRMHW	Pb	0.75	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	44.1000
DRMHW	Pb	1	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	40.8000
DRMHW	Pb	1	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	41.9000
DRMHW	Pb	4	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	24.4000

DRMHW	Pb	4	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	22.8000
DRMHW	Pb	12	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	13.9000
DRMHW	Pb	12	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	12.6000
DRMHW	Pb	24	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	6.8500
DRMHW	Pb	24	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	4.2000
DRMHW	Pb	48	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	2.5000
DRMHW	Pb	48	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	3.7800
DRMHW	Pb	0.25	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	64.6000
DRMHW	Pb	0.25	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	59.4000
DRMHW	Pb	1	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	62.2000
DRMHW	Pb	1	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	60.7000
DRMHW	Pb	12	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	46.4000
DRMHW	Pb	12	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	42.9000
DRMHW	Pb	24	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	27.8991
DRMHW	Pb	24	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	32.2171
DRMHW	Pb	120	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	12.0674
DRMHW	Pb	120	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	13.8264
DRMHW	Pb	360	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	8.9664
DRMHW	Pb	360	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	6.3788
DRMHW	Pb	0.25	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	67.7000
DRMHW	Pb	0.25	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	67.4000
DRMHW	Pb	1	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	64.0000
DRMHW	Pb	1	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	61.4000
DRMHW	Pb	12	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	44.4000
DRMHW	Pb	12	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	40.6000
DRMHW	Pb	24	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	32.5000

DRMHW	Pb	24	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	25.4000
DRMHW	Pb	120	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	5.2700
DRMHW	Pb	120	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	4.6000
DRMHW	Pb	360	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	2.5900
DRMHW	Pb	360	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	2.4300
DRMHW	Be	0.25	Base	0.50	0	0.0005000	0.2500	100.0000	80.3935
DRMHW	Be	0.25	Base	0.50	0	0.0005000	0.2500	100.0000	79.1180
DRMHW	Be	1	Base	0.50	0	0.0005000	0.2500	100.0000	78.4425
DRMHW	Be	1	Base	0.50	0	0.0005000	0.2500	100.0000	76.5669
DRMHW	Be	12	Base	0.50	0	0.0005000	0.2500	100.0000	67.8914
DRMHW	Be	12	Base	0.50	0	0.0005000	0.2500	100.0000	67.2159
DRMHW	Be	24	Base	0.50	0	0.0005000	0.2500	100.0000	62.2403
DRMHW	Be	24	Base	0.50	0	0.0005000	0.2500	100.0000	64.3137
DRMHW	Be	120	Base	0.50	0	0.0005000	0.2500	100.0000	49.4382
DRMHW	Be	120	Base	0.50	0	0.0005000	0.2500	100.0000	50.8626
DRMHW	Be	360	Base	0.50	0	0.0005000	0.2500	100.0000	42.2871
DRMHW	Be	360	Base	0.50	0	0.0005000	0.2500	100.0000	42.9115
DRMHW	Be	0.25	100 mg α-FeOOH	0.50	0.1043	0.0006043	0.2500	100.0000	61.1000
DRMHW	Be	0.25	100 mg α-FeOOH	0.50	0.1028	0.0006028	0.2500	100.0000	58.0000
DRMHW	Be	1	100 mg α-FeOOH	0.50	0.1027	0.0006027	0.2500	100.0000	53.0000
DRMHW	Be	1	100 mg α-FeOOH	0.50	0.1019	0.0006019	0.2500	100.0000	54.9000
DRMHW	Be	12	100 mg α-FeOOH	0.50	0.1004	0.0006004	0.2500	100.0000	51.8000
DRMHW	Be	12	100 mg α-FeOOH	0.50	0.1007	0.0006007	0.2500	100.0000	48.3000
DRMHW	Be	24	100 mg α-FeOOH	0.50	0.0996	0.0005996	0.2500	100.0000	36.9000
DRMHW	Be	24	100 mg α-FeOOH	0.50	0.1000	0.0006000	0.2500	100.0000	36.4000
DRMHW	Be	120	100 mg α-FeOOH	0.50	0.1000	0.0006000	0.2500	100.0000	24.8000
DRMHW	Be	120	100 mg α-FeOOH	0.50	0.1003	0.0006003	0.2500	100.0000	20.6000
DRMHW	Be	360	100 mg α-FeOOH	0.50	0.1028	0.0006028	0.2500	100.0000	12.6000
DRMHW	Be	360	100 mg α-FeOOH	0.50	0.1007	0.0006007	0.2500	100.0000	13.9000
DRMHW	Be	0.25	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	76.7360

DRMHW	Be	0.25	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	75.7605
DRMHW	Be	1	1 mg α-FeOOH	0.50	0.0010	0.0005010	0.2500	100.0000	73.1849
DRMHW	Be	1	1 mg α-FeOOH	0.50	0.0012	0.0005012	0.2500	100.0000	73.7094
DRMHW	Be	12	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	65.6339
DRMHW	Be	12	1 mg α-FeOOH	0.50	0.0014	0.0005014	0.2500	100.0000	61.4072
DRMHW	Be	24	1 mg α-FeOOH	0.50	0.0014	0.0005014	0.2500	100.0000	56.1317
DRMHW	Be	24	1 mg α-FeOOH	0.50	0.0011	0.0005011	0.2500	100.0000	59.5562
DRMHW	Be	120	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	45.8806
DRMHW	Be	120	1 mg α-FeOOH	0.50	0.0013	0.0005013	0.2500	100.0000	45.2051
DRMHW	Be	360	1 mg α-FeOOH	0.50	0.0010	0.0005010	0.2500	100.0000	41.8296
DRMHW	Be	360	1 mg α-FeOOH	0.50	0.0010	0.0005010	0.2500	100.0000	41.7540
DRMHW	Be	0.25	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	82.5000
DRMHW	Be	0.25	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	79.9000
DRMHW	Be	0.5	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	74.0000
DRMHW	Be	0.5	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	70.8000
DRMHW	Be	0.75	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	68.8000
DRMHW	Be	0.75	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	64.6000
DRMHW	Be	1	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	59.4000
DRMHW	Be	1	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	59.9000
DRMHW	Be	4	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	57.3000
DRMHW	Be	4	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	56.0000
DRMHW	Be	12	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	91.2081
DRMHW	Be	12	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	43.9406
DRMHW	Be	24	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	37.4000
DRMHW	Be	24	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	36.0000
DRMHW	Be	48	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	26.3000
DRMHW	Be	48	8 g L^{-1} Sed:Sol	2.00	0	0.0020000	0.2500	100.0000	27.1000

DRMHW	Be	0.25	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	81.8000
DRMHW	Be	0.25	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	88.4000
DRMHW	Be	1	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	84.4450
DRMHW	Be	1	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	88.2409
DRMHW	Be	12	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	76.9432
DRMHW	Be	12	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	79.2738
DRMHW	Be	24	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	82.5000
DRMHW	Be	24	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	83.3000
DRMHW	Be	120	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	73.7000
DRMHW	Be	120	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	70.5000
DRMHW	Be	360	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	61.3000
DRMHW	Be	360	10 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	59.3000
DRMHW	Be	0.25	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	64.9527
DRMHW	Be	0.25	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	61.8260
DRMHW	Be	1	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	63.6505
DRMHW	Be	1	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	61.5750
DRMHW	Be	12	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	55.1994
DRMHW	Be	12	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	55.1239
DRMHW	Be	24	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	52.8483
DRMHW	Be	24	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	51.0728
DRMHW	Be	120	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	42.3973
DRMHW	Be	120	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	42.6217
DRMHW	Be	360	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	41.9231
DRMHW	Be	360	2 mg L^{-1} DOC	0.50	0	0.0005000	0.2500	100.0000	42.2098