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Characterization of the Physical and Chemical Controls on the Environmental Geochemical Behavior of Beryllium

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Abstract
In this dissertation, we investigate the geochemical controls on the behavior of beryllium to better constrain its use as a geomorphologic and geochronologic tool and to characterize its potential mobility as a toxic environmental contaminant. First, we investigated the effects of soil chemistry on beryllium retention. We find that beryllium sorption varies significantly depending on the pH, complexing ligand and type of mineral present. Overall, sulfur and phosphorus oxides as well as soil acidity exert the strongest control on beryllium sorption. Next, we investigated the relative effect of different chemical perturbations on the desorption of beryllium from organic ligands and minerals that demonstrated particular sorption ability in our first body of work. We determined that reducing the pH promoted the greatest amount of beryllium desorption. Overall, we found that beryllium sorbed to organic compounds was more resistant to desorption relative to mineral-bound beryllium. We estimate that beryllium sorption by the organic ligands tested and illite were governed by inner sphere complexation while outer sphere processes were more prevalent among montmorillonite. Finally, with a new understanding of the chemical controls on beryllium retention from our previous work, we are able to develop a mathematical relationship that predicts the beryllium sorption capacity of a system based on the product of the cation exchange capacity and inverse percent quartz. We can use this relationship to compare beryllium concentrations from field measurements to the total beryllium sorption capacity independent of the specific physical and chemical properties of soil.

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CHARACTERIZATION OF THE PHYSICAL AND CHEMICAL CONTROLS ON THE ENVIRONMENTAL GEOCHEMICAL BEHAVIOR OF BERYLLIUM

Vanessa Lynne Boschi

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CHARACTERIZATION OF THE PHYSICAL AND CHEMICAL CONTROLS ON THE ENVIRONMENTAL GEOCHEMICAL BEHAVIOR OF BERYLLIUM

2016

Vanessa Lynne Boschi

Dedicated to my family and friends who have been my proverbial rock in the storm of life.

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What a journey it has been! A journey that started quite a long time ago actually, when Louis Nicolas Vauquelin first discovered beryllium in 1798. Therefore I would be remiss if I did not include him in my acknowledgements as he influenced five very important years of my life and inspired a love of one very special element.

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ABSTRACT

CHARACTERIZATION OF THE PHYSICAL AND CHEMICAL CONTROLS ON THE ENVIRONMENTAL GEOCHEMICAL BEHAVIOR OF BERYLLIUM

Vanessa L. Boschi

Jane K. Willenbring

In this dissertation, we investigate the geochemical controls on the behavior of beryllium to better constrain its use as a geomorphologic and geochronologic tool and to characterize its potential mobility as a toxic environmental contaminant. First, we investigated the effects of soil chemistry on beryllium retention. We find that beryllium sorption varies significantly depending on the pH, complexing ligand and type of mineral present. Overall, sulfur and phosphorus oxides as well as soil acidity exert the strongest control on beryllium sorption. Next, we investigated the relative effect of different chemical perturbations on the desorption of beryllium from organic ligands and minerals that demonstrated particular sorption ability in our first body of work. We determined that reducing the pH promoted the greatest amount of beryllium desorption. Overall, we found that beryllium sorbed to organic compounds was more resistant to desorption relative to mineral-bound beryllium. We estimate that beryllium sorption by the organic ligands tested and illite were governed by inner sphere complexation while outer sphere processes were more prevalent among montmorillonite. Finally, with a new understanding of the chemical controls on beryllium retention from our previous work, we are able to develop a mathematical relationship that predicts the beryllium sorption capacity of a system based on the product of the cation exchange capacity and inverse percent quartz. We can use this

relationship to compare beryllium concentrations from field measurements to the total beryllium sorption capacity independent of the specific physical and chemical properties of soil.

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CHAPTER 1

INTRODUCTION

Although small in size physically, positioned fourth on the periodic table weighing only 9.012 amu, beryllium is associated with major advancements in science from providing a picture of Earth's evolving surface to peering back to the depths of space. Owing to its unique chemistry, we use beryllium isotopes in a variety of different applications from tracking geomorphologic events large enough to affect global climate to producing state of the art telescopic equipment. In the field of geochronology and geomorphology, beryllium isotopes are important tools that have been used in the last 25 years (Granger et al, 2013). It was not until the advent of accelerator mass spectrometry that ultra-trace quantities of cosmogenic ^{10}Be could be quantitated. 'Meteoric' ^{10}Be and ^{7}Be are formed in the atmosphere through spallation reactions involving the interactions of high energy neutrons with oxygen and nitrogen. These atmospherically derived isotopes of beryllium are deposited onto the Earth's surface through wet or dry deposition and sorbed onto the surface sediments. Accumulating over time, sorbed amounts of meteoric beryllium are used to calculate the residence time of sediments in a landscape over various timescales. In addition, ^{9}Be leached from mineral lattices during weathering processes moves through a landscape adsorbed to soil particles and in solution (Bacon et al., 2012; Willenbring and von Blanckenburg, 2010b; von Blanckenburg and Bouchez, 2014). As such, the flux of ^{9}Be from rivers is indicative of the weathering flux of the catchment. When deposited in ocean sediment along with ^{10}Be, these concentrations of ^{9}Be are thought to record the silicate weathering history of Earth. Aside from sediment tracing, ^{7}Be concentrations have also been used as a proxy for airborne contaminant deposition rates including persistent organic pollutants like polycyclic aromatic hydrocarbons (PAH), polychlorinated bisphenols and metals (Percot et al, 2013).

Sorbed concentrations of beryllium isotopes are used to calculate sediment residence time. Thus, environmental conditions allowing for preferential sorption of beryllium from soil particles complicates the interpretation of such geomorphologic calculations. Processes affecting beryllium desorption are equally important. For example, the analysis of beryllium isotopes in marine sediments bears consideration of the variety of chemical environments these sediments are exposed to during numerous cycles of erosion and deposition. The salinity gradient experienced from source to sink could promote the removal of sorbed beryllium through cation exchange. Therefore, characterization of the physical and chemical controls on beryllium mobility in soils and aquatic environments is integral to the application of geomorphologic techniques.

Although much of this work applies to the use of beryllium as a geomorphologic tracer, it is also worth noting beryllium's industrial uses due to its toxicity and potential as an environmental contaminant. Doted as the 'miracle metal', it is one third lighter than aluminum, yet six times stiffer than steel (Taylor et al, 2003). Commonly alloyed with other metals, a 2% addition of beryllium to copper produces an alloy that is six times stronger than the original material without affecting its thermal and electrical conductivity. Because of its high melting point, heat absorbing capacity, and small neutron cross sectional area, beryllium and its compounds are used in a variety of industrial applications including lasers, x-ray imaging, automotives, nuclear reactors, aeronautical equipment and electronic devises. Beryllium is also the element behind some of NASA's greatest accomplishments, from the beryllium heat shield used for the first manned space expedition in 1961, to the construction of the James Webb Space Telescope in 2010 equipped with 18 large beryllium mirrors allowing humanity to peer deeper into the universe than ever before (Gutro, 2011).

Although useful**,** beryllium is considered one of the most toxic elements on the periodic table. Beryllium is classified as a Class A carcinogen: the highest ranking issued by the US Environmental Protection Agency relating to carcinogenicity (Taylor et al, 2003). Inhalation of beryllium compounds causes a potentially fatal pulmonary condition known as berylliosis which leads to chronic granulomatous disease. Oral consumption can lead to gastrointestinal and skeletal cancers. Beryllium is released into the environment through its industrial use, and its natural abundance in coal emissions which poses a major health risk. There are 339 Superfund sites in the United States contaminated with beryllium, which is considered one of the top 25 most toxic Superfund contaminants (Irwin NFS). Despite its toxicity and prevalence as an environmental contaminant, little information regarding the fate of beryllium and its related compounds has been published (Taylor et al, 2003). Therefore, similar to its applications in geomorphology and geochronology, a better understanding of the geochemical controls on beryllium mobility in the environment is crucial predicting its behavior as a contaminant.

Currently, research on beryllium stems from two very different scientific communities: environmental geochemistry, and inorganic and medicinal chemistry. Both fields contribute unique perspectives on beryllium, and if combined, could provide a more complete understanding of the behavior of beryllium in soils and aquatic environments.

In the field of geochemistry, most studies discuss beryllium in the environment or in the presence of natural materials used to simulate environmental conditions. Their conclusions can be summarized.

1) Beryllium, which is primarily released through the chemical weathering of biotite and sodium feldspars, is particle reactive and readily sorbs to the surface of sediment in the environment (Vesely et al., 2002). It is believed that the chemical nature of soils including its mineralogy and organic matter content can affect the sorption behavior of beryllium. For example, beryllium forms complexes with soil organic matter, possibly by means of carboxylic acid and catechol functionalities and has also been shown to bind preferentially to certain minerals such as illite (Aldahan et al., 1999; Esteves Da Silva et al., 1996; Takahashi et al., 1999; You et al., 1989). However, the role of organic matter as a control on beryllium retention is debated within the geochemical literature. Additionally, the relative strength of beryllium complexation by organic ligands and minerals is not thoroughly discussed.

2) The physical characteristics of soil (e.g. grain size) influence beryllium sorption. In general, the concentration of sorbed beryllium increases with decreasing particle size (Aldahan et al., 1999; Willenbring and von Blankenburg, 2010a). Unfortunately, there is only one published example of beryllium sorption as a function of surface area measured directly (Korte et al, 1976). Other research has attempted to calculate surface area using grain size (Taylor et al, 2014), which provides a poor approximation. Clay minerals are integral to the sorption capacity of soils due to their large, negatively charged surfaces areas. An understanding of

the sorptive behavior of beryllium as a function of surface area needs to be established.

3) Natural concentrations of dissolved beryllium are low, ranging from ng/L to µg/L in soil, ground, stream and lake waters. Dissolved concentrations of beryllium are strongly influenced by pH (Kaste et al., 2002; Measures and Edmound, 1983; Navratil et al., 2000; Vesely et al., 1989; Vesely, 1994). Van Green et al. (1988) and Heath et al. (1988) reported that acidified lakes having a pH of about 4.5 may increase the concentration of dissolved beryllium by 2 to 4 times relative to neutral waters. In addition, dissolved fluoride, aluminum, sulfate, carbonate and organic matter in addition to salinity and suspended particle concentration have been shown to also affect dissolved concentrations of beryllium (Vesely et al., 2002). Several studies suggest that waters with high fluoride and sulfate content act to increase dissolved concentrations of beryllium thus increasing its mobility (Burba et al., 1983; Heath et al., 1988; van Green et al., 1988; Vesely et al., 1989). These studies show a strong linear correlation of dissolved beryllium and fluoride and sulfate concentrations in lakes and stream waters, respectively (Vesely et al., 1989; Vesely et al., 2002). However, further work is needed to determine if species like fluoride correlate with or control beryllium desorption into solution.

4) Suspended particle load also contributes to total sorbed beryllium. Although the concentration of beryllium increases with increasing suspended particle concentration, the overall distribution coefficient, K_d, or the concentration of sorbed beryllium normalized by the mass of sorbent, shows the opposite effect.

This unexpected trend, referred to the as the particle concentration effect, was reported in several studies and is thought to occur due to the aggregation of particles at greater concentrations, thus reducing the effective surface area (Aldahan et al., 1999; Hawley et al., 1986; Olsen et al., 1986; You et al., 1989). Although the results presented in these studies agree regarding the overall relationship between the K_d and particulate concentration, they each exhibited significant scatter in their data.

5) The sorption of beryllium is pH dependent, being present as a divalent cation at low (<6) and high (>11) pH and as insoluble $Be(OH)_2$ around and above neutral conditions. In general, beryllium K_d values increase with increasing pH (Aldahan et al., 1999; Brown et al., 1992; You et al., 1989). As in natural waters, beryllium can be desorbed and mobilized under acidic conditions in soils, particularly those with low buffering capacity or low clay content (Vesely et al., 2002). However, a global meta-analysis investigating the relationship between meteoric ^{10}Be concentrations and the physical and chemical properties of soils found no correlation between ^{10}Be and pH (Graly et al, 2010). Therefore, we need to better understand under how the binding environment, like the type of complexing ligand, affects the influence of pH on beryllium mobility.

Several review papers on beryllium in the field of environmental chemistry summarize these findings (Kaste et al., 2002; Taylor et al., 2003; US DHHS, 2002; Vesely et al., 2002). Thus far, the existing body of literature makes inferences regarding the chemistry of beryllium by observing its behavior in natural systems.

We can derive additional information regarding the behavior of beryllium by combining these findings with research in the field of inorganic chemistry. For example, literature reporting the aqueous coordination chemistry of beryllium has revealed the strength of various beryllium-ligand complexes (Alderighi et al, 1999; Alderighi et al, 2000; Schmidbaur 2001; Wong and Woollins 1994; Mederos et al, 2001). Considering its electronegativity, ionization potential, hydration enthalpy and charge to size ratio, beryllium functions as a hard acid and is capable of forming coordinate covalent complexes and hydrolysates. The most stable interactions are formed between beryllium and bidentate ligands including dihydroxyaromatic and dicarboxylic ligands (Alderighi et al, 2000). Unfortunately, no single study examined the all of the various ligands expected to exist in a soil matrix and at various pH values. Rather, existing studies were intended to understand the behavior of beryllium under physiologic conditions for medicinal applications.

Due to the limited amount of data available on the geochemical behavior of beryllium, fundamental experiments are needed to determine the conditions under which beryllium is most strongly sorbed or could become mobilized. For example, it should be determined how the chemical composition of soil including organic matter content, mineralogy and pH affect the strength of beryllium retention. It is also important to identify under what conditions beryllium is desorbed from soil materials and potentially mobilized into the soil solution.   With a better understanding of the key chemical and physical controls driving beryllium retention, we can develop a standardization method helping to reduce error in sorbed beryllium amounts due to differences in soil sorption capacity so that sorbed beryllium amounts can be more accurately used to assess erosional fluxes. Once these more elemental questions are resolved, field evaluations of beryllium contaminated soils can be examined to determine their potential environmental risk and cosmogenic beryllium concentrations can be better constrained for applications in geomorphology.

In this dissertation we will discuss our approach to these broader questions and present the main findings. In *Chapter 2*, we lay the foundation of this work by investigating the effects of soil composition on beryllium retention, focusing on beryllium sorption amongst various ligands chosen to represent organic matter and minerals at various pH values over time. We conclude that beryllium sorption varies significantly depending on the pH, complexing ligand or minerals present. We also determined that phosphorus and sulfur oxides in addition to soil acidity are strong controls on beryllium mobility. This chapter is published in Environmental Chemistry.

In *Chapter 3*, we investigate the relative effect of different chemical processes including a reduction in pH, an increase in ionic strength (NaCl) and complexation by soluble organic (malonic acid) and inorganic species (NaF) on the desorption of beryllium from organic ligands and minerals that demonstrated particular sorption strength presented in Chapter 2. We determined that a reduction in pH promoted the greatest amount of beryllium desorption. Overall, we found that beryllium sorbed to organic compounds was more resistant to desorption relative to mineral-bound beryllium and that these processes can promote the exchange of beryllium between solid and dissolved phases either through desorption or increased sorption, the extent to which depends on the composition of the system. Resistance to desorption also helped us to predict potential complexation mechanisms dominating sorption among the organic ligands and minerals. We estimate that beryllium sorption by the organic ligands and illite were governed by inner sphere complexation while outer sphere processes were more prevalent among montmorillonite. This chapter is submitted for publication in Chemical Geology.

In *Chapter 4*, we utilized the results from Chapters 2 and 3 relating to the principal controls on beryllium sorption to develop a means of standardizing sorbed beryllium concentrations for more consistent comparison between systems with differing chemical and physical properties. We determined through the correlation of sorbed beryllium amounts with various soil properties including grain size, surface area, percent carbon, percent nitrogen, cation exchange capacity (CEC), sulfur and phosphorus concentration and mineralogical composition that the inverse percent quartz composition of a soil sample most strongly varied with beryllium concentrations. Using a stepwise regression analysis, we determined a model using the product of CEC and inverse percent quartz to predict beryllium sorption capacity was the most theoretically and statistically sound. Plotting the product of these two variables with the percent sorbed beryllium, we were able to develop a mathematical relationship that predicts the beryllium sorption capacity of a system based on these two major properties. This relationship can be applied to beryllium concentrations from field measurements to estimate the total beryllium sorption capacity of system independent of the physical and chemical properties of soil.

Chapter 5 summarizes the main conclusions in this dissertation and provides recommendations when using beryllium isotope concentrations to better understand landscape change and assess its behavior as a contaminant.

CHAPTER 2

THE EFFECT OF PH, ORGANIC LIGAND CHEMISTRY AND MINERALOGY ON THE SORPTION OF BERYLLIUM OVER TIME

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Environmental Context:

Beryllium is a toxic environmental contaminant but has many industrial and scientific applications. Our work explores the effects of soil composition on beryllium retention, focusing on organic matter, mineralogy and pH and concludes that phosphorus and sulfur oxides in addition to soil acidity are strong controls on beryllium mobility. These results aid in future predictions regarding the fate of beryllium in the environment.

Abstract:

Understanding the chemical controls on beryllium sorption is fundamental when assessing its mobility as a pollutant and interpreting its concentration as a geochemical tracer of erosion, weathering and landscape surface stability. In order to evaluate the interactions of beryllium with soil- and aquatic-related materials, we selected model organic compounds and minerals to perform sorption experiments. The retention of beryllium by each of these compounds and minerals was evaluated over a pH range of 3–6 and at various equilibration times to determine which conditions allowed the greatest retention of beryllium. We conclude that most beryllium sorption occurred within 24 h

for both organic and mineral materials. However, equilibration required longer periods of time and was dependent on the solution pH and sorbent material. The pH exhibited a strong control on beryllium sorption with distribution coefficient (K_d) values increasing non-linearly with increasing pH. A system with a pH of 6 is likely to retain 79–2270 % more beryllium than the same system at a pH of 4. Phosphonate retained the greatest amount of beryllium, with K_d values 2–30× greater than all other materials tested at a pH of 6. Therefore, soils containing larger amounts of phosphorus-bearing minerals could result in greater retention of beryllium relative to phosphorus-limited soils. Overall, soil composition, with an emphasis on phosphorus oxide content and pH, is an important property to consider when evaluating the capacity of a system to retain beryllium.

2.1 Introduction

Currently, two very different scientific communities generate beryllium research: environmental geochemistry and inorganic and medicinal chemistry. In the field of environmental geochemistry, beryllium isotopes have been used in the last 25 years as a tool in geochronology and geomorphology for a range of applications from assessing chemical weathering fluxes from continents to understanding the age and stability of topsoils (Granger et al, 2013; Wallbrink and Murray, 1996; Willenbring and von Blanckenburg, 2010a, 2010b). Such isotopes including ‘meteoric’ cosmogenic ^{10}Be and ^{7}Be are produced from high-energy spallation reactions involving oxygen and nitrogen in the atmosphere. ^{10}Be and ^{7}Be fall onto the Earth’s surface through wet or dry deposition, adsorbing onto surface sediments, and can be used to understand sediment redistribution. The concentration of ^{7}Be (half-life $t_{1/2}$ = 53.1 days) and ^{10}Be ($t_{1/2}$ = 1.39 Ma) scales with the residence time of sediments in a landscape (Kaste and Baskaran, 2011). In addition to cosmogenic ^{10}Be and ^{7}Be, recent work indicates ^{9}Be leached from mineral lattices during weathering processes moves through a landscape adsorbed to soil particles and in solution (Willenbring and von Blanckenburg, 2010b; von Blanckenburg et al, 2012). As such, the flux of ^{9}Be from rivers is indicative of the weathering extent of soils within the catchment. When deposited in ocean sediment along with ^{10}Be, these concentrations of ^{9}Be are thought to record the silicate weathering history of Earth (Willenbring and von Blanckenburg, 2010b). Natural conditions that cause beryllium mobilisation or preferential sorption, thus biasing its concentration, would complicate the interpretation of these measurements. A better understanding of the chemical controls affecting the environmental behaviour of beryllium is fundamental to constrain such measurements.

Such information is also essential because of beryllium's toxicity and potential as an environmental contaminant. Beryllium qualifies as a Class A carcinogen – the highest ranking issued by the US Environmental Protection Agency relating to carcinogenicity (Taylor et al, 2003). Anthropogenic sources of beryllium include beryllium ore processing and the combustion of fossil fuels – principally coal, which accounts for 99 % of anthropogenic beryllium emissions into the atmosphere and 93 % of total atmospheric beryllium levels (USDE, 1996; USEPA, 1987). Wet and dry deposition processes deliver atmospheric beryllium to surface soils and water systems (Fishbein, 1981). After deposition, beryllium could potentially be leached from particles in acidic environments and mobilised into the soil profile and possibly the ground water. In addition to atmospheric emissions, wastewaters from industries including metal manufacturing, electric power generation, paint and ink formulation, coal mining and other sources can contain beryllium up to or possibly exceeding 5 mg L^{-1}, or 1250 times the drinking water standard (USEPA, 1981). The behaviour of beryllium and beryllium compounds in soil and water systems proximal to anthropogenic sources provides a cause for environmental concern. Unfortunately, unlike other heavy metals, there is a paucity of data regarding the behaviour of beryllium in the environment despite its toxicity as evidenced by its low drinking-water standard (Figure 2.1) (USEPA, 2000). Therefore, further investigation into its environmental behaviour is needed.

Both fields of environmental geochemistry and inorganic and medicinal chemistry contribute a unique perspective on beryllium and if merged, could provide a more complete understanding of beryllium's behaviour in soils and aquatic environments. In the field of geochemistry, most studies report observations relating to beryllium in the environment or in the presence of natural materials used to simulate environmental conditions. Several review papers have been published and summarise these findings (Kaste and Baskaran, 2011; Taylor et al, 2003; USDHHS, 2002; Vesely et al, 2002).

Although some of these studies report the sorption of beryllium among specific minerals to demonstrate the effect of mineralogy on beryllium retention, none incorporate individual organic ligands into their research design. Additionally, there is a lack of consensus in the geochemical literature regarding the role of organic matter in the retention of beryllium. A study of the geochemical availability of beryllium in lake and river surface sediments did not show significant correlation between organic matter content and beryllium concentration (Lum and Gammon, 1985). A global meta-analysis investigating the relationship between meteoric ^{10}Be concentrations and the physical and chemical properties of soils found no correlation between ^{10}Be and the organic matter concentrations in soils. It has also been reported that the presence of organic matter did not significantly affect beryllium retention to specific minerals (You et al, 1989). However, other studies have concluded that both humic and fulvic acids were able to form stable complexes with beryllium and influenced its speciation and sorption to minerals (Esteves Da Silva and Machado, 1996; Takahashi et al, 1999). In fact, it has been shown that the organic fraction of lake sediments contains ~100× more ^{10}Be atoms per gram than the bulk sediment (Lundberg et al, 1983). The inconsistency in available data has spurred a debate regarding the distribution of beryllium between organic and inorganic phases in the environment. Understanding the relative strength of organoberyllium complexes with ligands like carbonate, sulfate and phosphate and the relative strength of various beryllium–mineral associations can help resolve inconsistencies between data sets and aid in predictions regarding the fate of beryllium in different environments.

Conversely, work published in the field of inorganic and medicinal chemistry discusses the aqueous coordination chemistry of beryllium, particularly the strength of various beryllium–ligand complexes, for medicinal applications related to the toxicity of beryllium (Alderighi et al, 1999; Alderighi et al 2000; Keizer et al, 2005; Mederos et al, 2001; Schmidbaur, 2001; Wong and Woollins, 1994). Many of these studies report the stability constants for various inorganic and organic beryllium complexes. Unfortunately, no single study examined the various ligands and biomolecules expected to exist in natural organic matter and soils with varying acidity and time. Therefore, there is a need to examine such ligands in addition to selected minerals under the same environmental conditions to determine their relative strength in complexing beryllium.

In the present study, we merged these two areas of science and used both approaches by applying chemical principles to environmental materials to understand the behaviour of beryllium in soils and aquatic systems. We performed fundamental experiments to determine how the chemical composition of materials including minerals, organic ligands mimicking organic matter and pH affect the strength of beryllium sorption and under what time scales equilibrium is established between solid and solution phases. Our goals were to (1) determine the relative strength of beryllium sorption among organic ligands and minerals; (2) to estimate the difference in the degree of sorption with pH; and (3) to determine the time scales over which equilibrium occurs between dissolved and sorbed beryllium. With a better understanding of the conditions and materials that affect the sorption of beryllium, we can make predictions regarding the behaviour of beryllium in various soil and aquatic systems for the application of geomorphologic techniques and assessment of its risk as an environmental contaminant.

2.2 Methods

2.2.1 Organic compound selection and preparation

We selected organic compounds on the basis of their environmental availability and individual chemical properties to determine how those properties affect their ability to sorb beryllium. For example, organic molecules containing carboxylic acids are presumed drivers for metal retention in soil organic matter. In order to test whether or not carboxylic acids and other functional groups are responsible for beryllium retention, we selected organic compounds containing a single functional group of interest. These functional groups include (i) an alcohol, (ii) a carboxylic acid, (iii) an amine, (iv) a sulfonate, and (v) a phosphonate. We also used graphite (Acros, New Jersey, USA) as a control because it contains no functionalities that would allow an electrostatic interaction with beryllium.

In order to calculate the proportion of sorbed beryllium, we used a 0.45-µm filter (Pall Life Sciences, Port Washington, NY, USA) to separate non-bound beryllium from beryllium sorbed to the surfaces of the selected materials. All of these compounds with the exclusion of graphite contain polar functionalities, thus making them water soluble. Therefore, the organic compounds used were either insoluble or exceeding 0.45 µm in size so that they could be easily separated through filtration. For example, we selected polystyrene-bound compounds when available with a mesh rating that exceeded 0.45 µm so they could be easily removed through filtration. Benzoic acid (Alfa Aesar, Ward Hill, MA, USA), tris(2-aminoethyl)amine (Sigma Aldrich, St. Louis, MO, USA) and toluenesulfonic acid (Alfa Aesar) bound to a polystyrene resin were selected to represent a carboxylic acid, amine and sulfonate group respectively (Table 2.1). We chose octadecylphosphonic acid (Sigma Aldrich), a large insoluble alkane, to represent a phosphonate group. Phosphonate was used as an analogue for phosphate, the more abundant form of phosphorus in the environment. The complexation of beryllium by these two ligands is very similar (Alderighi et al, 1999; Alderighi et al, 2009). Similarly, sulfonate was used as a representative for sulfate. We also selected cellulose (Sigma Aldrich) and lignin (Tokyo Chemical Industry Co., Tokyo, Japan) because they are the most abundant biopolymers, are insoluble and contain numerous alcohol functional groups.

2.2.2 Mineral selection and preparation

We also selected mineral samples to determine if mineralogy affects the retention of beryllium in soils. We chose (i) illite, (ii) montmorillonite, (iii) kaolinite, and (iv) goethite because of their great abundance in many soils. These minerals were acquired through Ward's Science (Rochester, NY, USA). Each sample's mineralogical purity was verified using X-ray diffraction (XRD) analysis. The samples were then ground using a disc mill. Each sample was rinsed with weakly acidic HCl (Fisher Scientific, Pittsburgh, PA, USA) solution to remove any impurities, then rinsed with ultrapure Millipore (Billerica, MA, USA) water. The ground mineral samples were wet-sieved and dried in an oven overnight. The <20-µm fraction was collected for use in the present experiment. Prior to experimentation, a Beckman–Coulter particle size analyser (Miami, FL, USA) was used to determine the proportion of each mineral's <20-µm fraction that was smaller than 0.45 µm to ensure the filter would be able to remove mineral particles from solution. We found that ~99.5 % of particles were greater than 0.45 µm in size for all mineral samples. As an additional precaution, all mineral samples were centrifuged with the appropriate speed and time interval before filtration to ensure >99.5 % of particles were excluded from the solution.

2.2.3 Solution preparation

We prepared individual organic compound and mineral solutions at a concentration of 250 mg L^{-1}. We selected a sorbent concentration of 250 ppm to ensure the sorbent was in excess over the beryllium concentration and would not limit the extent of beryllium sorption. It is important to note that for organic compounds, 250 mg L^{-1} represents the concentration of the active functional group, not the organic molecule because the ratio of functional group to organic compound mass varies from compound to compound. For example, 250 mg L^{-1} phosphonate (PO_3) was prepared rather than 250 mg L^{-1} of octadecylphosphonic acid ($C_{18}H_{39}O_3P$). Maintaining the same concentration of the active functional group ensures consistent comparison of each beryllium–ligand complex. However, with regard to the mineral samples, 250 mg L^{-1} represents the concentration of the bulk mineral, not the concentration of active binding sites, which unfortunately restricts direct comparison of organic and mineral results. We selected a solution concentration of 1 mg L^{-1} beryllium prepared using a beryllium ICP standard (BDH, Lutterworth, UK) because this magnitude falls in the range of natural, dissolved concentrations of beryllium, which can be as high as ~100 ppb in surface waters and can exceed 5 mg L^{-1} in wastewaters (USDHHS, 2002). This concentration also ensures our ability to resolve small changes in sorbed beryllium amounts. Considering 1 ppm is greater than beryllium's natural abundance in the environment, we used Hyperquad Simulation and Speciation software (Protonic Software, Hanau, Germany) to model the effect of beryllium concentration on its speciation and ligand complex formation. We selected ligands similar to those used in the present experimental study to model beryllium complex formation at different beryllium concentrations using previously determined stability constants published in Alderighi et al., 2000. Beryllium hydrolysis and ligand complexation were modelled using 1 mg L^{-1} and 0.1 µg L^{-1} beryllium. The results will be discussed in the *Results from modelling concentration effects* section.

We prepared each organic compound and mineral solution in triplicate at a pH of 3, 4, 5 and 6 and for each of four different time intervals. The solution pH was adjusted using dilute HCl (Fisher Scientific) and NaOH (Fisher Scientific). An explanation as to why these pH values were selected is provided below in the *Blank spike* filtration results section. Therefore, a total of 48 50-mL solutions were prepared for each compound for a total of 528 individual mineral and organic compound solutions. Each sample was prepared in a solution of 0.1 M KCl (Sigma Aldrich). This was done to maintain constant ionic strength so that the abundance of ions in solution capable of interacting with beryllium, potentially restricting its interaction with the sorbent, was not variable with pH. The solutions were placed on a roller table to allow constant but gentle mixing of the material and beryllium solution.

2.2.4 Blank spike sample preparation

To ensure the beryllium in solution was not adhering to the surfaces of the sample containers or removed during filtration, blank spike solutions containing 1 mg L^{-1} beryllium were carried through the same procedure as the samples. Beryllium precipitates at approximately neutral pH at the concentrations used and it was important to determine if the 0.45-µm filter would remove unbound, precipitated $Be(OH)_2$ in solution. We prepared two sets of solutions containing 1 mg L^{-1} beryllium in 0.1 M KCl for a pH range of 2–12 with each pH solution prepared in triplicate; a total of 60 solutions were prepared. We examined this range to determine under what pH conditions the use of filtration would be suitable for the separation of bound and unbound beryllium remaining in solution. One set of the duplicate solutions was filtered through a 0.45-µm filter and the other set was not. Both the filtered and non-filtered solutions were analysed to determine the amount of beryllium remaining in solution.

2.2.5 Analysis

The pH was monitored throughout the duration of the experiment and before sampling to ensure there were no fluctuations. The change in pH did not exceed ±0.1 pH units. Samples were collected after 1, 7, 14 and 120 days. At the time of sampling, we filtered each solution through a 0.45-µm Pall GHP Acrodisc filter made of polypropylene to ensure low binding potential. Whatman glass-fibre filters (GE Healthcare Bio-Sciences, Pittsburgh, PA, USA) retained ~2 % of beryllium from a blank spike solution and were therefore excluded. We analysed the filtered solutions using an inductively coupled plasma optical emission spectrophotometer (ICP-OES) (Spectro, Mahwah, NJ, USA) to determine the concentration of unbound beryllium remaining in solution.

2.3 Results and discussion

2.3.1 Beryllium speciation

2.3.1.1 Blank spike filtration results

The blank spike filtration data indicated that a 0.45-µm filter is capable of removing most of the precipitated Be(OH)$_2$ at certain pHs. Be(OH)$_2$ precipitates at a pH of ~7, resulting in the removal of 79 % of beryllium from the solution (Figure 2.2). In addition, there is increased removal of beryllium with increasing pH; almost 100 % of the beryllium was filtered from solutions with a pH of 9 and 10. The filtration of beryllium agrees with its speciation under these conditions. Beryllium is expected to exist as insoluble $Be(OH)_2$ in solutions with a pH of ~7 to 12 when its concentration is 1 mg L^{-1}. The speciation of beryllium, and thus the pH at which $Be(OH)_2$ is formed, is dependent on the concentration of beryllium in solution. Therefore, it is strongly encouraged when using filtration that blank spike solutions be prepared using the same solution matrix, pH range and concentration of metal as expected in the samples to determine if the filter restricts precipitated metal oxide or hydroxide.

Unfortunately, this result affects the pH range for which we were able to study the behaviour of beryllium. Non-bound $Be(OH)_2$ would be removed under neutral conditions and mistakenly calculated as beryllium sorbed by either the mineral or organic material. Thus, the pH range used in this investigation was 3–6. These pH values are most relevant to soil chemistry while also ensuring accurate use of filtration to differentiate between bound and non-bound beryllium.

2.3.1.2 Results from modelling concentration effects

After modelling various ligands in aqueous solutions ranging in pH from 2 to 7 and with different beryllium concentrations, we conclude that beryllium concentration has minimal effect on beryllium complexation under the conditions studied. For each beryllium–ligand system we modelled, beryllium speciation as a function of pH for a system containing 0.1 ppb was similar to a system containing 1 ppm beryllium. Although the beryllium concentration affects the pH at which it precipitates as a hydroxide, considering $Be(OH)_2$ does not form until a pH of 7 under our experimental conditions, the beryllium–ligand complexes tested in the present study were not in competition with hydroxide formation. This would become even less of a concern at natural beryllium concentrations, where $Be(OH)_2$ is formed at even higher pH. At natural concentrations, beryllium could remain complexed by a ligand over a greater pH range, under even more basic conditions but the relative abundance of beryllium–ligand species would not differ significantly from the same system containing 1 ppm beryllium at the pH range studied. Therefore, the relative order of ligand preference is maintained at lower, natural beryllium concentrations under our experimental conditions and the pH range studied.

2.3.2 Distribution coefficient calculations

It should be noted that in the current study, the term 'sorption' can refer to any of three possible mechanisms including adsorption, absorption or complexation. We report the extent of beryllium sorption among the various organic ligands and minerals as the distribution coefficient (K_d). The K_d represents the ratio of sorbed beryllium normalised by the sorbent concentration, to non-sorbed beryllium at equilibrium (Equation 2.1):

$$\textbf{\textit{(Eq. 2.1)}} \qquad K_d = S/C$$

where K_d is reported in units of millilitres per gram, where S represents the concentration of sorbed beryllium normalised by the concentration of sorbent and C represents the concentration of non-sorbed beryllium remaining in solution.

In order to calculate the amount of sorbed beryllium, we calculated the difference between the initial concentration of beryllium and the concentration of beryllium remaining in solution at the time of sampling. However, rather than using an initial concentration of 1 mg L^{-1} of beryllium in solution, we calculated its activity. Although the use of a 0. 1 M KCl matrix normalised the ionic strength of solutions with differing pH, the abundance of potassium and chloride ions affects the ability of beryllium to form associations with the sorbent material. Therefore, we accounted for beryllium's reduced chemical potential by calculating its effective concentration, or activity, in solution. In order to calculate activity (a), the concentration of beryllium in solution (c) is multiplied by an activity coefficient (γ) (Equation 2.2).

$$\textbf{\textit{(Eq. 2.2)}} \qquad a = c\gamma$$

We derived the activity coefficient from the extended Debye–Hückel Equation where A and B are constants, I represents the ionic strength, α represents the ionic radius and z represents the ionic charge (Equation 2.3):

$$\textbf{\textit{(Eq. 2.3)}} \qquad \log\gamma = -\frac{Az^2 I^{0.5}}{1 + B\alpha I^{0.5}}$$

where $A = 0.51$, $B = 0.00328$ pm^{-1}, $I = 0.10$ M, $z = 2$ and $\alpha = 35$ pm.

Applying the activity coefficient 0.239, the effective concentration of beryllium in solution, as represented by C in the K_d equation, was adjusted for each sample to account for the reduced ability of beryllium to interact with the sorbent due to the ionic strength of the solution. These corrected values were used to calculate the K_d.

2.3.3. Beryllium sorption as a function of pH

2.3.3.1 Organic compound results

The distribution coefficients reported for most organic ligands demonstrate a clear dependence on solution pH (Figure 2.3). With the exception of graphite, cellulose and benzoic acid, which showed very little to no retention of beryllium, there is a positive correlation between the amount of beryllium sorbed and the pH: as pH increases, more beryllium is retained. This relationship is non-linear and is unique for each organic ligand. For example, K_d values reported for phosphonate and sulfonate differed significantly from pH 3 to 6 relative to the other organic ligands like lignin and the trisamine group in tris(2-aminoethyl)amine (will be referred to as 'trisamine' in the remainder of the paper), which exhibited a smaller increase in K_d with increasing pH.

Overall, pH exhibits a significant control on beryllium retention and is an important variable to consider when comparing beryllium concentrations in differing environments because it can have an effect on the amount of beryllium complexed by organic matter. Table 2.2 reports the percentage increase in the amount of retained beryllium from a pH of 4 to 6 after 14 days for each organic compound. (Note: a pH of 4 was used to calculate percentage change rather than 3 because soil with a pH of 4 is more common.) The combined results for the organic compounds indicate a sorbent–solution mixture with a pH of 6 is capable of retaining 79–475 % more beryllium than the same mixture with a pH of 4. Lignin and trisamine exhibit the greatest percentage increase in the amount of sorbed beryllium, retaining 350 and 475 % more beryllium at a pH of 6 respectively. Phosphonate and sulfonate also demonstrate a significant percentage increase in sorbed beryllium of 86 and 98 % respectively. Although having larger K_d values, sulfonate and phosphonate exhibit a smaller percentage increase in the amount of complexed beryllium relative to lignin and trisamine because they are able to complex beryllium more effectively over the entire pH range studied. Cellulose, benzoic acid and graphite exhibited smaller percentage increases relative to lignin and trisamine because they provided little retention of beryllium at any pH.

We expect this behaviour in view of each ligand's charge dependence on the pH. Acid dissociation constants, represented as K_a, approximate the availability of each ligand to attract and form an association with beryllium as a function of pH (Table 2.3). These values describe the extent of protonation at any pH and thus the charge on the active functional group. The pK_a represents the pH at which half of the acidic functional groups are deprotonated, making them more capable of complexing metals. With increasing pH, more acidic functional groups become deprotonated, explaining the increase in sorption and K_d values. Beryllium exhibited strong retention in the presence of toluenesulfonic acid and octadecylphosphonic acid, representing the sulfonate and phosphonate functional groups respectively. Their low pK_a values indicate that most of the organic species in solution were deprotonated and negatively charged at the pHs used, thus allowing a stronger attraction of beryllium. Toluenesulfonic acid has a lower p$K_{a,}$ and more readily complexes beryllium at a pH of 3 compared with octadecylphosphonic acid, which has a slightly higher pK_a. However, above a pH of 3, octadecylphosphonic acid complexes larger amounts of beryllium relative to toluenesulfonic acid and the other organic ligands. This reflects the chemical nature of the phosphonate–beryllium complex and will be further discussed in the *Beryllium sorption as a function of organic matter composition* section.

The K_d values for trisamine are significantly lower (Figure 2.3). Considering the pK_a value for trisamine is 8.5, the extent to which the primary amine groups are deprotonated is minimal even at a pH of 6. Therefore, there is a large difference in the amount of beryllium retained by trisamine at a pH of 6 versus a pH of 4. According to the Henderson–Hasselbalch equation, ~0.28 % of the amine groups would be deprotonated at a pH of 6, rendering a lone electron pair available for complexation compared with 0.0028 % at a pH of 4. Thus at a pH of 6, 0.28 % or 750 ppb of the total amine groups would be available for complexation. Beryllium typically assumes a four-coordinate, tetrahedral geometry. Therefore, we assume that beryllium is coordinated by a single trisamine -molecule, owing to steric hindrance, and two water molecules. Assuming it is thermodynamically favorable for both primary amines to chelate a single beryllium, we could approximate the amount of complexed beryllium to be 344 ppb, applying a 2:1 amine–beryllium ratio. We observed that 340 ppb of beryllium was retained by trisamine after 14 days at a pH of 6, which is very close to the estimated value. Lignin behaves similarly to trisamine in that its pK_a value falls within the pH range studied and therefore with increasing pH, there is an increase in the amount of retention.

The smaller K_d values reported for cellulose can also be explained by its pK_a value. Within the pH range of interest, the hydroxyl groups of cellulose are protonated, providing little attraction towards beryllium. Although the pK_a value for benzoic acid suggests we should observe greater K_d values, we see very little retention. This indicates that in some instances the chemical nature of the ligand provides an additional control on beryllium complexation other than pH. This effect will be further discussed in the following section.

2.3.3.2 Mineral results

Similarly to the trends observed in organoberyllium complexation, K_d values representing beryllium–mineral associations show a non-linear increase with increasing pH (Figure 2.4). Beryllium–illite mixtures exhibited the greatest change in K_d with increasing pH whereas goethite demonstrated the smallest variation. The percentage increase in sorbed beryllium from a pH of 4 to 6 was also evaluated for each mineral (Table 2.4). The combined results for all minerals demonstrate that a mineral–solution mixture with a pH of 6 is capable of retaining 121–2270 % more beryllium than the same mixture with a pH of 4. Illite exhibited the largest percentage increase, 2270 %, in the amount of complexed beryllium between a pH of 4 and 6.

Similarly to pK_a values, the pH of zero point charge, pH_zpc, can be used to determine the overall surface charge of a mineral at a given pH (Table 2.5). The pH_zpc accurately predicts that beryllium would form the weakest association with goethite relative to the other minerals. At the pH values of interest, the overall surface charge is predominantly positive. However, the pH_zpc and the estimated cation exchange capacity still fail to explain the overall trend in sorbed amounts of beryllium. These values suggest that montmorillonite should exhibit the greatest amount of sorbed beryllium. Instead, illite was the strongest mineral sorbent under our experimental conditions. We hypothesise that the abundance of ions in solution could result in increased interlayer spacing, preferentially affecting the illite mineral, allowing increased penetration of beryllium ions. Additionally, this could be a result of particle aggregation predominantly occurring within the montmorillonite samples, resulting in reduced surface area and effective surface charge available for sorption. We are further investigating this result.

There is a significant increase in the amount of beryllium retained by each mineral species with increasing pH and overall, these differences in sorption from a pH of 4 to 6 are greater than those observed for the organic compounds. This indicates that changes in pH have a greater effect on the ability of minerals to sorb beryllium than the organic compounds evaluated in the present study. Again, this suggests the importance of considering pH when evaluating the sorption potential of a system and the behaviour of beryllium.

These results have implications specifically for the geomorphologic community using beryllium isotopes to compare denudation in areas with differing environmental conditions. For example, if we were using beryllium isotopes to assess total denudation within a highly weathered landscape, we might expect less beryllium to accumulate in the soil over time owing to reduced soil pH and sorption capacity. Chemical weathering leaches calcium and magnesium, typically lowering soil buffering capacity and ultimately reducing soil pH. Acidic environments would also reduce the ability of organic matter to complex beryllium. Therefore, more weathered, acidic soils may have reduced sorption capabilities, thus unfavorably affecting the results of geomorphologic investigations using beryllium isotopes.

2.3.3.3 Considerations for beryllium complexation as a hydroxide

As stated previously, the sorptive behaviour of beryllium could not be determined above a pH of 6 because at a concentration of 1 ppm, beryllium exists as an insoluble hydroxide, which would be removed by filtration. Although our filtration method limited our ability to study beryllium under these conditions, it is worth noting the various inorganic chemistry papers that do report beryllium–ligand interactions around neutral pH values. Many of these studies utilise ^{9}Be nuclear magnetic resonance (NMR) and potentiometry to characterise beryllium–ligand complexation with varying pH. An excellent review paper produced by Alderighi et al., concluded that most beryllium–ligand complexes are not thermodynamically stable enough to compete with hydrolysis and the eventual precipitation of $Be(OH)_2$ (Alderighi et al, 2000). In fact, both enthalpy and entropy favor the hydrolysis of beryllium and aggregate formation, with thermodynamic favorability increasing as each additional hydroxyl bridge is formed (Alderighi et at, 2000; Mattock, 1954). Only few ligands are capable of competing with hydrolysis. Of the monodentate ligands reviewed (not including sulfonates), only fluoride and phosphonates can compete with water for Be^{2+} (Alderighi et al, 2000). Dihydroxyaromatic and hydroxylcarboxylic bidentate ligands are also capable of forming complexes that are stable enough to suppress the formation of $Be(OH)_2$. Additional research is needed to better understand the behaviour of beryllium hydroxide under environmental conditions and is the focus of our future work.

2.3.4 Beryllium sorption as a function of organic matter composition

Although helpful in determining the charge of each organic compound as a function of pH, the pK_a values do not fully explain the difference in the degree of complexation. For example, although phosphonic and sulfonic acids have similar acidities, phosphonic acid exhibited K_d values two times greater than sulfonic acid. Benzoic acid showed very little retention of beryllium despite being negatively charged at a pH of 5 and 6. In addition to benzoic acid, cellulose and graphite also exhibited little to no retention of beryllium. We expected little sorption of beryllium on graphite. However, cellulose and benzoic acid contain oxygen-containing functionalities that could form stable interactions with beryllium. Although beryllium's electronegativity and charge-to-size ratio allow it to form stable interactions with hard donors like oxygen, as predicted by hard acid–base theory, the oxygen-containing hydroxyl groups in cellulose and carboxylic acid group in benzoic acid do not complex beryllium at the pH values studied. Thus, the chemical nature of the organic ligand provides additional control on beryllium sorption and can be further explained using beryllium coordination chemistry.

Previous research in this area reveals weak associations between beryllium and monocarboxylic acid groups like those in benzoic acid (Alderighi et al, 2000). Most monodentate ligands, both organic and inorganic, do not form stable complexes with beryllium in aqueous conditions (Keizer and McCleskey, 2011). However, beryllium does form stable complexes with dicarboxylic, dihydroxyaromatic and hydroxylcarboxylic ligands, all of which are bidentate ligands capable of chelation (Figure 2.5). The chelation effect provides added stability to a complex by lessening the reduction in entropy that typically accompanies complexation with multiple ligands. Monodentate ligands like the monocarboxylic acid in benzoic acid are not capable of chelation, which explains their weak coordination with beryllium. Although cellulose contains multiple hydroxyl groups, they are sterically hindered from chelating beryllium. Combined with their poor acidity as evidenced by their large pK_a, we also observe little retention of beryllium by cellulose. Conversely, lignin contains aromatic hydroxyl groups resembling a polymer of catechol. Its aromaticity enhances the acidity of the hydroxyl groups, providing lower pK_a values. This would explain its enhanced retention over cellulose. Lignin complexation with beryllium resulted in K_d values almost 10 times greater than cellulose and benzoic acid.

Even though oxygen donors form the most stable interactions with beryllium, nitrogen coordination can occur as well. Although weak, it has been shown that the amino group in amino acids are capable of complexing beryllium. These compounds have been studied extensively because of their potential involvement in beryllium retention in the body, specifically in identifying the mechanism and cause for beryllium's toxicity. The trisamine compound used in the present study provided greater retention than benzoic acid and cellulose, exhibiting K_d values similar to lignin. This greater retention may be a result of beryllium chelation by the two primary amine groups, which would provide enhanced retention over a single primary amine, like those found in amino acids and proteins that contribute to organic matter content.

Of all the ligands, beryllium appeared to bind most efficiently with phosphonic acid. Beryllium's enhanced affinity for complexation with phosphonic acid even over sulfonic acid can be explained by examining the thermodynamics of each system. Owing to its large charge-to-size ratio, beryllium is capable of polarising and strongly orienting water molecules around it (Everest, 1964). However, owing to their lower charge-to-size ratio, sulfonate groups are less capable of ordering surrounding water molecules. These differences in hydration entropies provide a weaker metal–ligand association between sulfonate and beryllium relative to phosphonate (Everest, 1964).

There are several studies that have investigated the unique relationship between beryllium and phosphonate and phosphate ligands. It has been discovered that their strong associations are due to the fact that they are both able to displace the highly arranged water ligands surrounding beryllium and form stable complexes (Alderighi et al, 1999 and 2000). The interaction between beryllium and phosphonate is so favorable that it provides more stability than that gained through chelation. In fact, a study by Alderighi et al reports a larger formation constant for methylphosphonic acid, a monodentate ligand, when complexed with beryllium than for malonic acid, which actually chelates beryllium to produce a sterically desired six-membered ring (Alderighi et al, 1999). Interestingly, phosphonate groups are even capable of complexing beryllium without being fully deprotonated. Diphosphonic acid, which contains two phosphonic acid groups capable of chelation, provides even greater stability, having a formation constant two times greater than that reported for malonic acid complexes (Alderighi et al, 1999).

It is important to assess the abundance and availability of phosphates and phosphonates in soils of interest owing to their strong ability to complex beryllium. Phosphonates are much less abundant in soils but their biosynthesis is more common than previously believed (Yu et al, 2013). They are of growing interest in environmental science and play an important role in the global phosphorus cycle. Both phosphonates and phosphates are capable of strongly binding to the surfaces of minerals and organic material (Nowack and Stone, 2006). In addition, phosphates are sequestered by biota and held in organic forms. Therefore, very little phosphorus exists in the soil solution. Its accessibility is greatly dependent on pH, with peak availability occurring at pH ~6–7.5 (Tisdale et al, 1993). Above a pH of 7.5, it forms complexes with calcium and below a pH of 6, it complexes with aluminum and iron. Aluminum and iron phosphates are insoluble in water and calcium phosphates are only partially soluble. Therefore, depending on the environmental conditions and soil composition, phosphates can greatly affect the mobility of beryllium and should especially be considered in areas affected by agricultural activity where phosphate-containing fertiliser is frequently applied.

2.3.5 Beryllium sorption as a function of mineral composition

Similarly to the organic ligand results, mineralogical composition also influences the amount of sorbed beryllium. Illite exhibited the largest beryllium K_d values relative to the other minerals. Although it was expected for montmorillonite to provide the greatest amount of surface charge to form electrostatic associations with beryllium, illite was capable of sorbing almost twice the amount at a pH of 6. Our results are supported by the findings of You et al. who performed similar sorption experiments using ^{7}Be and various minerals including montmorillonite, kaolinite and illite (You et al, 1989). Their results also demonstrated larger K_d values for illite than montmorillonite (Table 2.6). The K_d values reported by You et al. were two orders of magnitude greater than the values reported in the present study (You et al, 1989). However, their experiment was conducted at a higher pH and lower ionic strength, both of which favor greater sorption of beryllium.

Iron and manganese oxides are important minerals when evaluating the sorption potential of the soil. Because of their large surface area and surface charge, Fe and Mn oxides have long been evaluated for their ability to sorb heavy metals in the soil (McCleskey et al, 2007). Our observation is that at the pHs studied, goethite sorbed smaller amounts of beryllium relative to the other aluminosilicate minerals. As previously discussed, part of goethite's reduced sorption is due to its pH_{zpc}. However, other studies have also found that beryllium is more highly associated with aluminosilicates than iron oxides in river sediments (Lum and Gammon, 1985). Lum and Gammon found that gentle acid leaching of beryllium showed no significant correlation with iron but a strong correlation, $R^2=0.79$, with aluminum. They concluded that beryllium is more highly correlated with aluminosilicate phases similarly to copper, molybdenum and vanadium whereas cadmium, zinc, cobalt, lead, chromium, nickel, manganese and phosphorus were more highly associated with iron oxides.

2.3.6 Beryllium sorption as a function of time

The sorption of beryllium was evaluated at different time intervals to determine how quickly beryllium complexation occurred. The rate at which beryllium is sorbed to the surface of particles is very important because it affects the degree of beryllium mobility. The faster it is able to form interactions with soil material, the more quickly it is removed from the soil solution, preventing its movement through the soil column. Beryllium sorption for each organic compound and mineral was examined after 1, 7, 14 and 120 days. Unfortunately without the use of buffers, the pH could not be controlled over the 120-day time interval. Although the drift in pH was slight, causing samples with an original pH of 5 and 6 to increase in alkalinity, it was indiscernible if sorption amounts were attributable to the removal of $Be(OH)_2$, known to form above a pH of 6. Therefore, these results were omitted. However, we can still derive useful information from the sorption data reported for 1, 7 and 14 days.

2.3.6.1 Organic compound results

We reviewed the K_d values at each time interval and pH and observed for most compounds, there was little change in the amount of beryllium absorbed, with some exceptions (Figure 2.6). To better understand the overall change in beryllium concentration over time, we calculated the difference in the percentage of beryllium sorbed between 1 and 14 days as a function of pH for each organic compound (Figure 2.7). Although it is accepted that beryllium sorption occurs very rapidly, it appears that for some of the organic compounds, it required 14 days or more to establish equilibrium for a given pH. Therefore, the time required to reach equilibrium is dependent on the pH of the solution as well as the nature of the organic compound. We can classify the behaviour of the organic compounds into three categories. The first category includes compounds that exhibit little change in the amount of beryllium retained over the 14-day time period because they provided little to no retention of beryllium overall. This category includes graphite, cellulose and benzoic acid. The second category consists of compounds that readily establish equilibrium after 1 day regardless of solution pH. There is no change in the amount of beryllium sorbed by lignin after 1, 7 and 14 days, indicating beryllium readily establishes equilibrium with lignin. The third category includes compounds that at certain pHs continue to sorb beryllium after 14 days had passed. These compounds include trisamine and phosphonate. Both phosphonate– and trisamine–beryllium complexation rates were dependent on the pH. For trisamine, the greater the pH, the greater the amount of time required to reach equilibrium. Even after 14 days, trisamine continued to sorb increasing amounts of beryllium when the solution pH was 5 or 6. For example, 31 % more beryllium was retained by trisamine over the entire 2-week time period relative to the first 24 h. Phosphonate exhibited similar behaviour at pH 4–6. After 2 weeks, phosphonate complexed 50, 80 and 26 % more beryllium at a pH of 4, 5 and 6 respectively relative to the first 24 h. The ionic strength of the solution may reduce the rate of beryllium complexation by impeding beryllium's ability to form strong hydrogen bonds with the active functional groups on these ligands (McCleskey et al, 2007).

Sulfonate exhibits unique behaviour, particularly at a pH of 5 and 6, in that the concentration of beryllium fluctuates with time (Figure 2.6). It appears that the concentration of sulfonate-bound beryllium increases up to 7 days and then decreases after. More resolved time intervals would be needed to further understand the behaviour of beryllium–sulfonate complexation with time. Overall, the ligands that are capable of sorbing beryllium, including lignin, trisamine, sulfonate and phosphonate, appear to sorb the majority of beryllium in ~24 h, with some ligands continuing to sorb beryllium after 14 days had passed.

2.3.6.2 Mineral results

Similarly to the organic compound results, beryllium readily sorbed to each of the minerals, exhibiting retention in less than 1 day but requiring longer time periods to reach equilibrium. We also observed that like the organic compounds, the pH affected the rate of sorption of beryllium to certain minerals. For example, beryllium sorption more readily approached equilibrium with montmorillonite, kaolinite and goethite at a pH of 6 and with illite at a pH of 3 (Figure 2.8). Goethite was the only mineral unaffected by pH, exhibiting little change in the K_d constant over time, which reflects its higher pH_{zpc}. For minerals other than goethite, depending on the pH, the concentration of sorbed beryllium was changing even after 14 days had passed. Although the difference in the percentage of sorbed beryllium between 1 and 14 days was small overall (under 6 %), it indicated that equilibrium was not established after 14 days (Figure 2.9).

Similarly, equilibration times were reported by You et al. for beryllium sorption to montmorillonite and kaolinite (You et al, 1989). After ~12–20 days, there was negligible change in the amount of beryllium sorbed by either mineral. Rates of sorption onto biotite and albite as reported by Aldahan et al. also revealed equilibration times on the scale of days; the concentration of beryllium remaining in solution appeared constant after ~4–10 days (Aldahan et al, 1999). The faster equilibration times reported by Aldahan et al. can be explained by the significantly lower ionic strength of their prepared solutions because they did not maintain a constant ionic strength for solutions of differing pH (Aldahan et al, 1999).

We also observed a reduction in beryllium K_d values associated with montmorillonite over time, which increased with decreasing pH (Figure 2.9). To ensure the increase in beryllium concentration in solution was not due to mineral dissolution, we monitored changes in major ion concentrations in solution using ICP-OES, and determined that dissolution was not occurring. Therefore, we believe the reduction in beryllium K_d values over time could be attributed to beryllium desorption under acidic conditions or a result of the mineral's behavior at lower pHs causing reduced sorption capacity.

2.4 Conclusions

Overall, we conclude that pH exhibits a strong control on beryllium retention among the mineral and organic compounds. The increased amount of sorbed beryllium at a pH of 6 relative to the same system at a pH of 4 is significant (79–2270 %) and should be considered when evaluating the potential for sorption of beryllium in the environment. With increasing pH, K_d values increased non-linearly for both organic ligands and minerals. The composition of organic matter also affects the extent of beryllium complexation and retention. Phosphonates and sulfonates exhibited the largest K_d values of all materials tested, indicating they could be a major driving force in beryllium sequestration in soils and aquatic environments. Not only are the K_d values associated with phosphonate large, phosphonate continues to complex beryllium over the 14-day time span. Thus, sulfur and phosphorus oxide abundances may be important variables to consider when estimating the sorption potential of soils. Lignin, an abundant biopolymer and component of natural organic matter, was also associated with large K_d values. Beryllium retention also varied depending on mineral composition, with illite exhibiting the highest sorption of those measured. For both organic and mineral materials, sorption occurred within 24 h. However, longer periods of time were required for equilibration to occur between beryllium and the sorbent. Equilibration time was dependent on the solution pH and sorbent material. Overall, soil pH, mineralogy and organic matter composition, with a specific emphasis on phosphorus and sulfur oxides, are important properties to consider when evaluating the capacity of a system to retain beryllium and when comparing beryllium concentrations in different environments.

2.5 Safety Considerations

The inhalation of beryllium compounds can result in serious illness. Inhalation of beryllium compounds causes a potentially fatal pulmonary condition known as berylliosis, which leads to chronic granulomatous disease. All beryllium-containing compounds should be handled in a fume hood and with the proper respiratory equipment, such as a properly rated mask. Beryllium exposure to the skin should also be avoided through the use of gloves.

2.6 Acknowledgements

Research reported in this publication was supported by the National Institute of Environmental Health Sciences (NIEHS) of the National Institutes of Health (NIH) under award number P42 ES023720 Penn Superfund Research Program Center Grant. The content is solely the responsibility of the authors and does not necessarily represent the official views of the NIH. We thank the University of Pennsylvania for providing the facilities and instrumentation necessary for this work as well as David Vann and Peter Gans for their technical assistance. We also thank Alain Plante and Art Johnson for their support.

Table 2.1: Structural formulas for each model organic compound

The grey circles represent the polystyrene backbone for compounds that were resin-bound. There is no defined structure for lignin; however, it is believed to consist of aromatic rings and alcohol functionalities

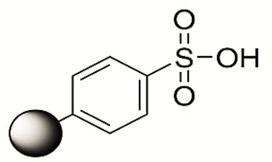
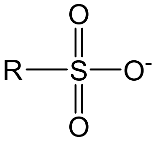
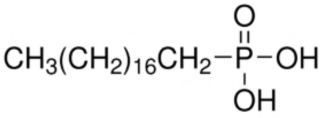
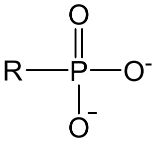
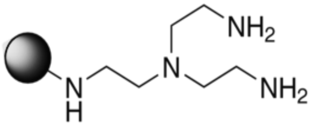
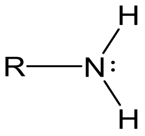
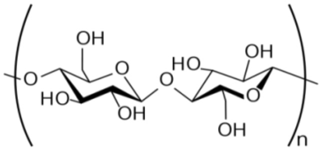
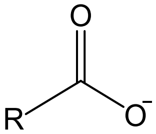
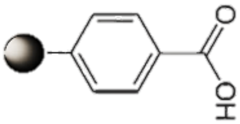
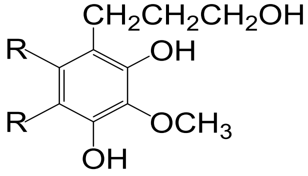
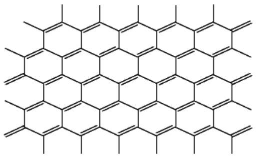
Toluenesulfonic acid		 $R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-$
Octadecylphosphonic acid	 $CH_3(CH_2)_{16}CH_2-\overset{\overset{O}{\|}}{\underset{OH}{P}}-OH$	 $R-\overset{\overset{O}{\|}}{\underset{O^-}{P}}-O^-$
Tris(2-aminoethyl) amine		
Benzoic acid		
Cellulose		$R-O^-$
Lignin		$R-O^-$
Graphite		None (control)

Table 2.2: The percent increase in the amount of retained beryllium from a pH of 4 to a pH of 6 after 14 days for selected organic compounds

Cellulose	79 %
Phosphonate	86 %
Sulfonate	98 %
Benzoic acid	105 %
Lignin	350 %
Trisamine	475 %

Table 2.3: List of the model organic compounds, the functional groups they represent and their associated pK_a values

Compound	Functional group	Approximate pK_a
Toluenesulfonic acid	$–SO_3H,SO_3^–$	–2. 8
Octadecylphosphonic acid	$–PO_3H_2,PO_3H^–,PO_3^{2–}$	2. 6, 8. 5
Benzoic acid	$–CO_2H,CO_2^–$	4. 2
Lignin	$–OH,O^–$, CO2H, CO2-	6. 0–11
tris(2-Aminoethyl)amine	$–NH_3^+,NH_2$	8. 6
Cellulose	$–OH,O^–$	15
Graphite	–C=C	43

Table 2.4: The percentage increase in the amount of retained beryllium from a pH of 4 to a pH of 6 after 14 days for selected minerals

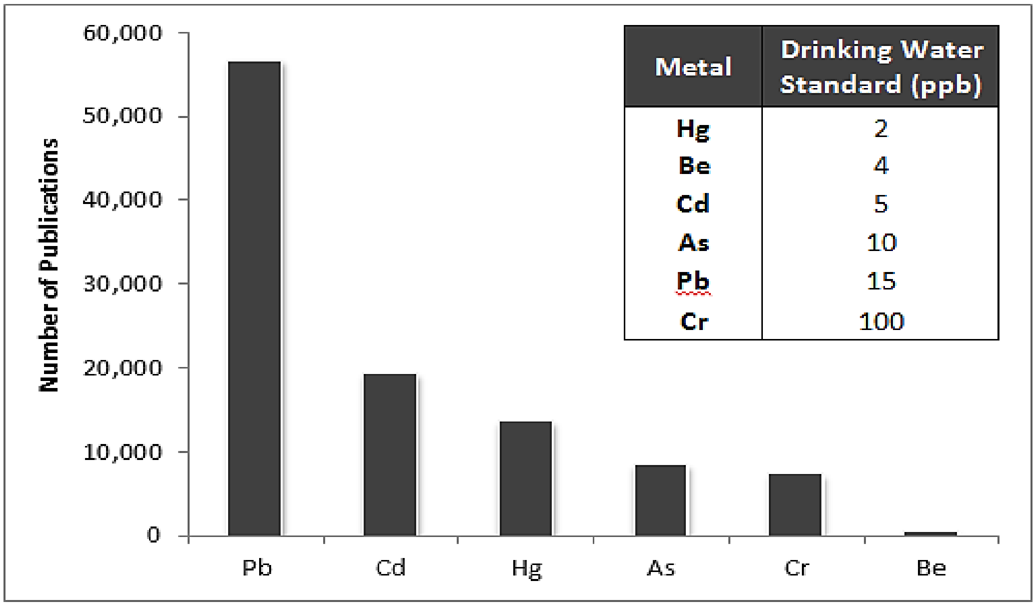
Mineral	% increase in Be
Goethite	121
Kaolinite	120
Montmorillonite	223
Illite	2270

Table 2.5: Minerals and their corresponding cation exchange capacities (CEC) (meq 100 g^{-1}) and pH of zero point charge (pH$_{ZPC}$) (Brady and Weil, 2008)

Mineral	CEC	pH$_{ZPC}$
Goethite	4–100	7. 8
Kaolinite	3–15	4. 6
Montmorillonite	80–120	2. 5
Illite	20–50	3. 2

Table 2.6: K_d values reported by You et al., 1989 and the present study. I represents the ionic strength and $[S]$ represents the solid concentration

Mineral	Study parameters	
	You et al.	Present study
	pH = 7. 8	pH = 6
	$I \approx 0.\ 05$M	$I = 0.\ 1$M
	$[S]$ = ~200 mg L^{-1}	$[S]$ = 250 mg L^{-1}
	K_d values (mL g^{-1}, ×10^{3})	
Illite	220	5. 32
Montmorillonite	210	3. 23
Kaolinite	160	2. 82



Metal	Drinking Water Standard (ppb)
Hg	2
Be	4
Cd	5
As	10
Pb	15
Cr	100

Figure 2.1: The number of environmentally related papers published on various heavy metals and their respective drinking water standards as established by the US EPA.

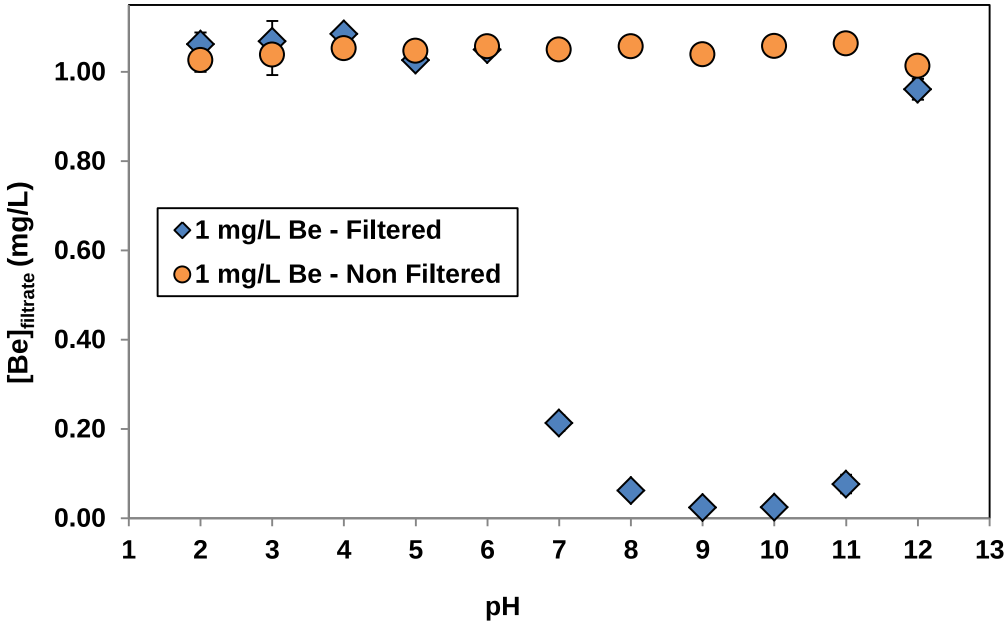


Figure 2.2: The concentration of beryllium remaining in solution after filtration using a 0.45 µm filter as a function of pH for a solution containing 1 mg/L Be. A non-filtered solution containing 1 mg/L Be was used as a control for comparison.

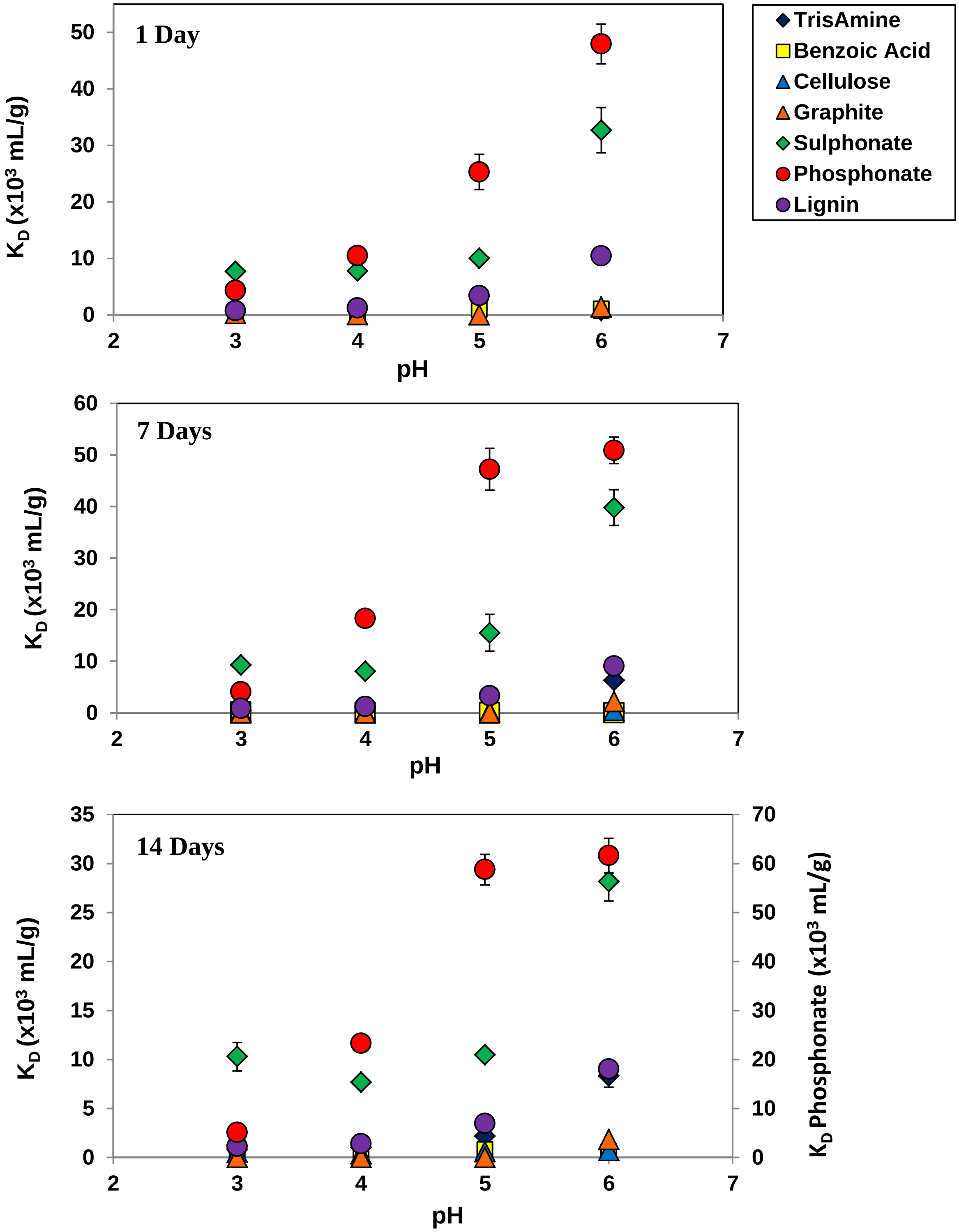


Figure 2.3: Distribution coefficient for Be for each model organic compound expressed as a function of pH after 1 day, 7 days and 14 days.

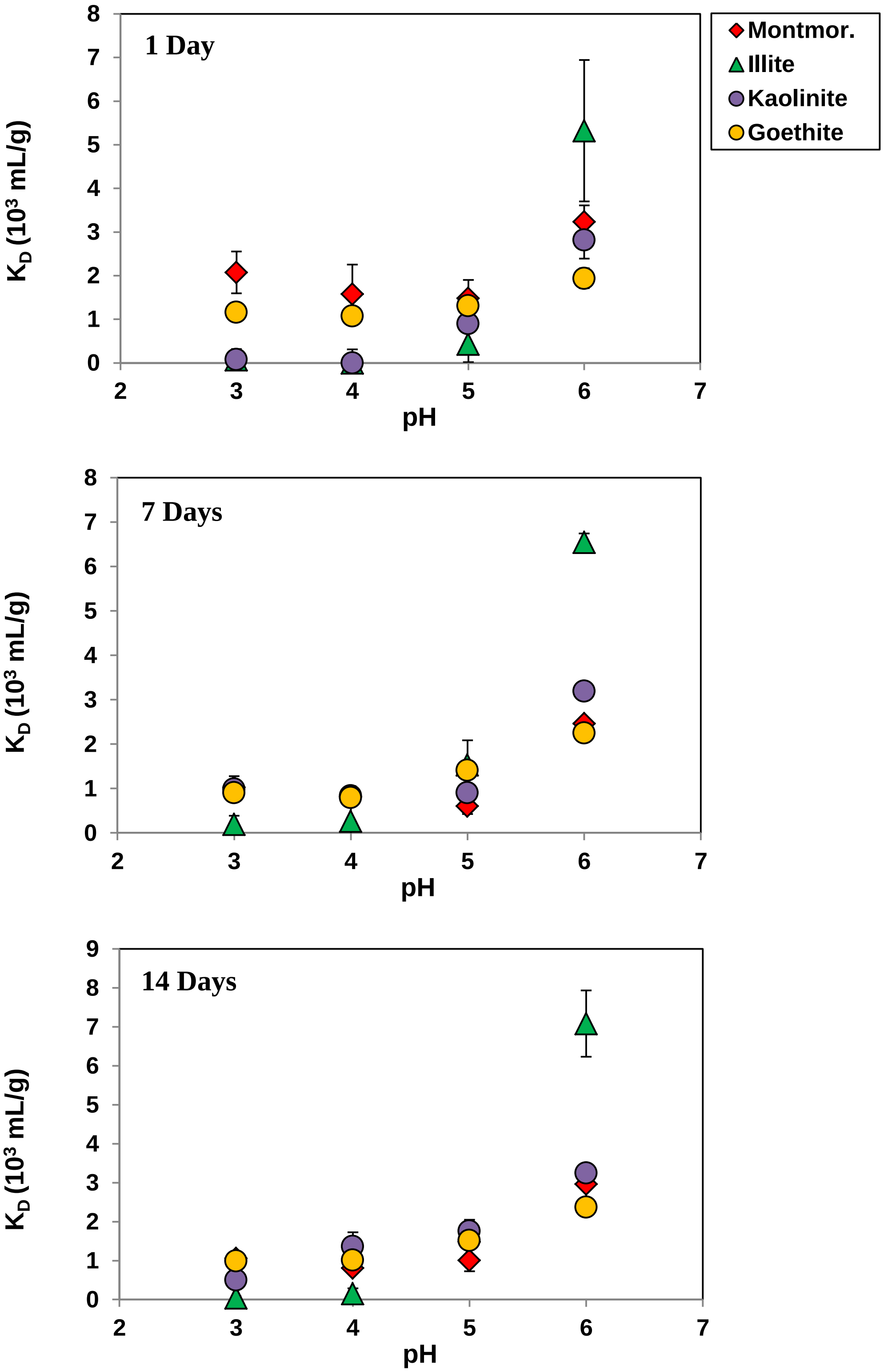
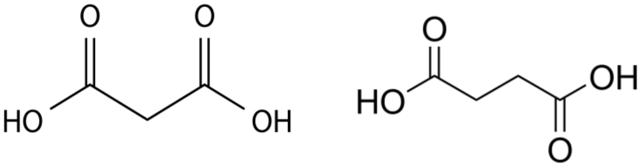
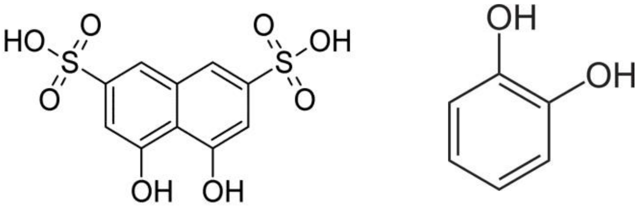


Figure 2.4: Distribution coefficient for Be for each model mineral expressed as a function of pH after 1 day, 7 days and 14 days.



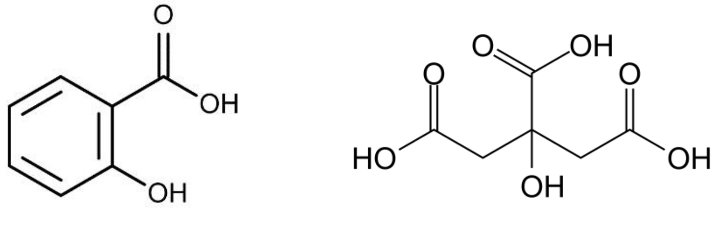
malonic acid *succinic acid*

Dicarboxylic ligands



chromotropic acid *catechol*

Dihydroxyaromatic ligands



salicylic acid *citric acid*

Hydroxylcarboxylic ligands

Figure 2.5: Structural formula examples of dicarboxylic, dihydroxyaromatic and hydroxycarboxylic ligands.

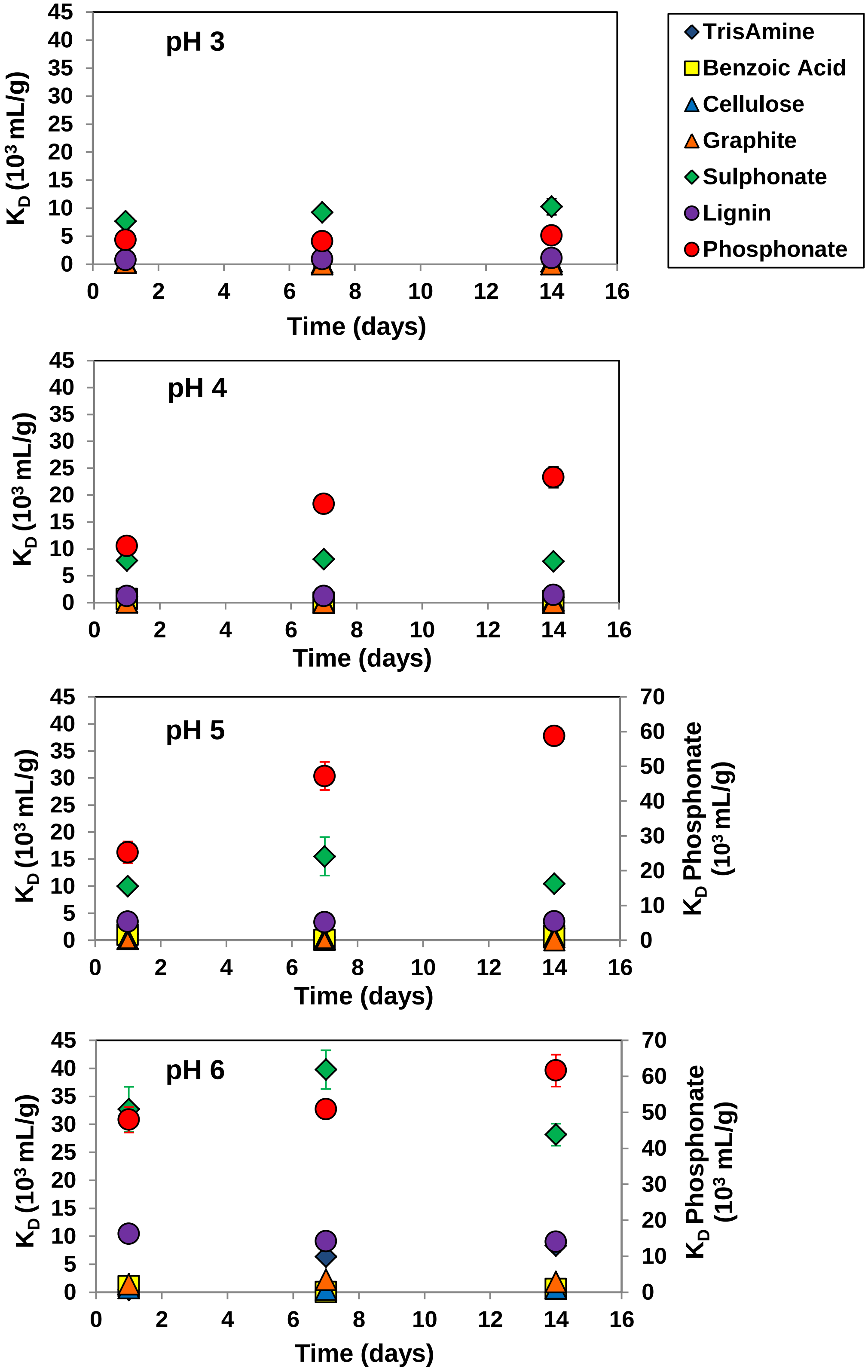


Figure 2.6: Distribution coefficient for each organic compound expressed as a function of time for solutions with a pH of 3, 4, 5 and 6.

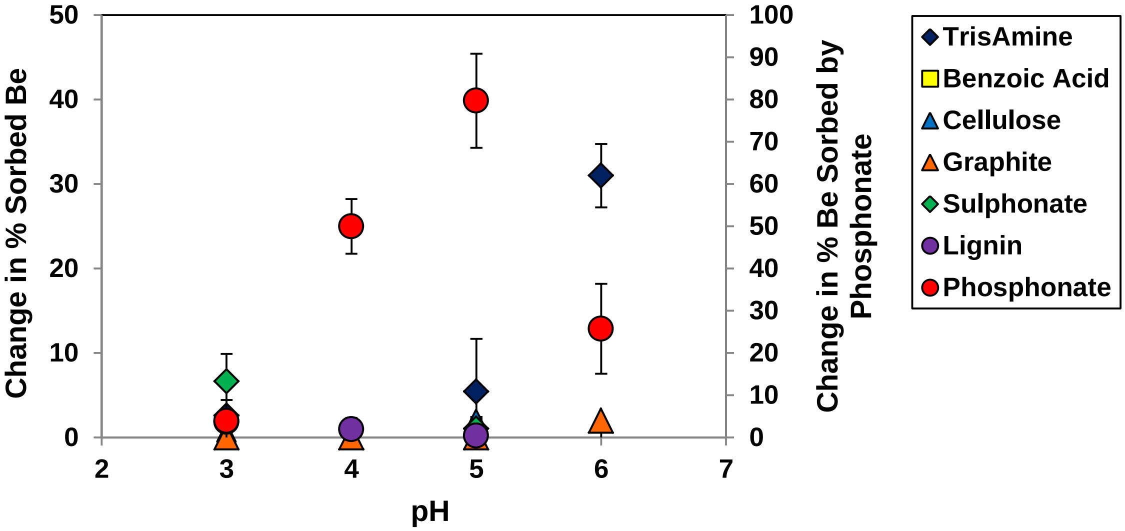


Figure 2.7: The change in the percentage of total beryllium retained by each organic compound between 1 and 14 days.

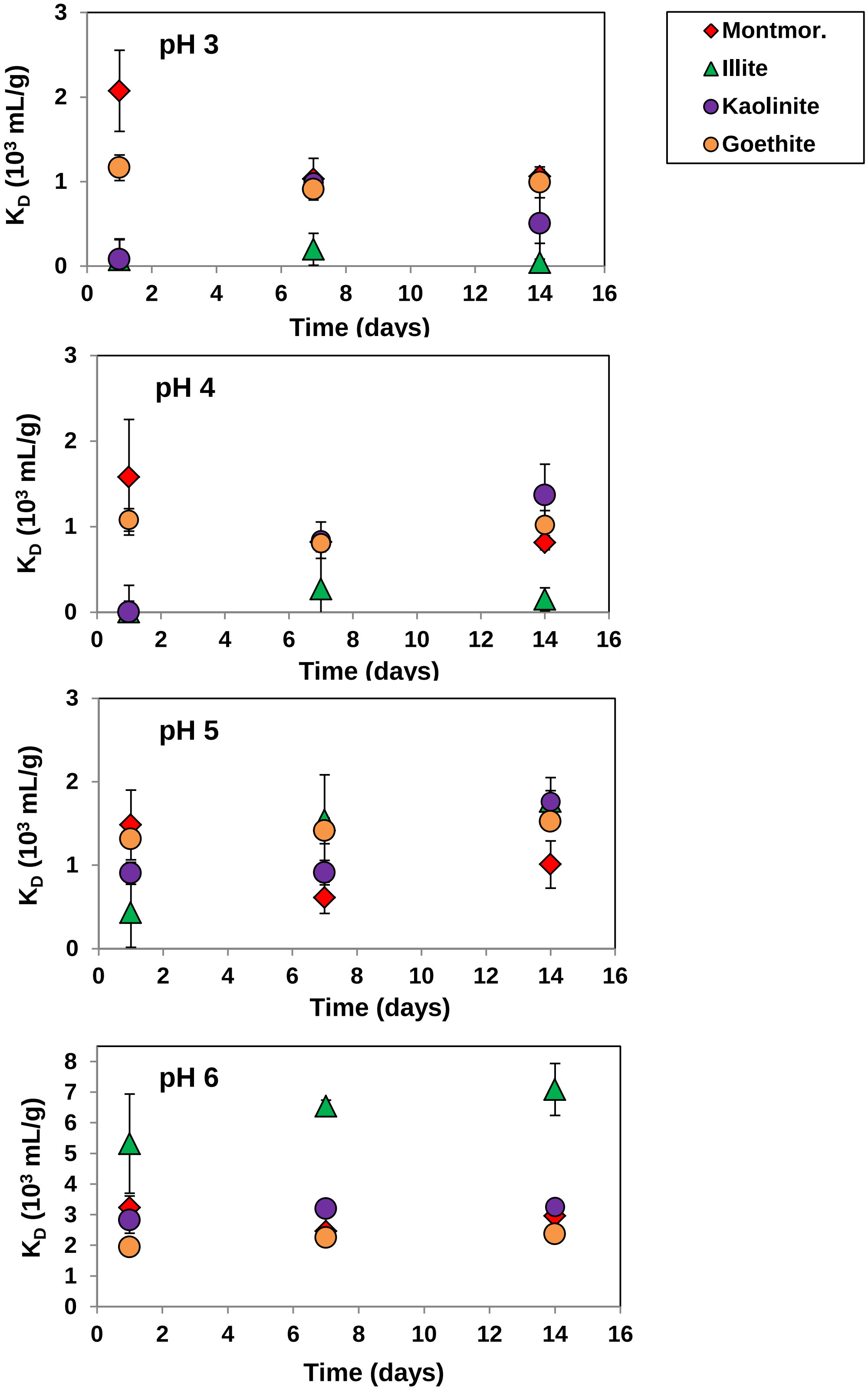


Figure 2.8: Distribution coefficient for each mineral expressed as a function of time for solutions with a pH of 3, 4, 5 and 6.

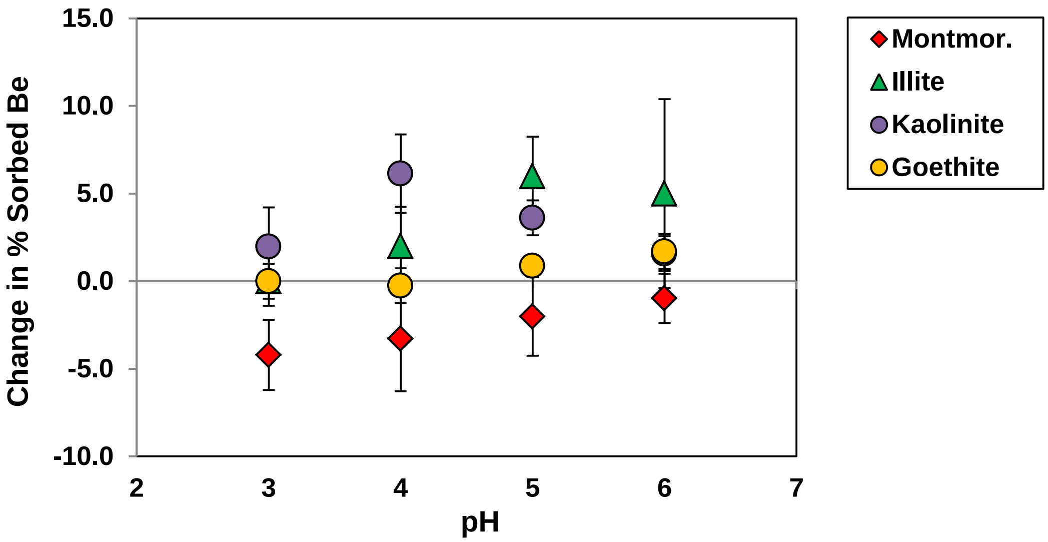


Figure 2.9: The change in the percentage of total beryllium retained by each organic compound between 1 and 14 days.

CHAPTER 3

BERYLLIUM DESORPTION FROM MINERALS AND ORGANIC LIGANDS OVER TIME

Submitted to: Chemical Geology

Environmental Context:

The use of beryllium isotopes to assess erosion in a landscape relies on the assumption that beryllium sorbed to the surface of sediments is undisturbed during transport and over large timescales. However our results conclude that different chemical processes can alter sorbed beryllium concentrations through desorption and even increased sorption. Therefore we emphasize caution when relying on sorbed beryllium isotope concentrations to make such calculations.

Abstract:

Beryllium isotopes sorbed to sediments have provided useful tools in the field of geochronology and geomorphology over the last few decades. The use of beryllium isotopes relies on the premise that beryllium sorbed to sediments is unaltered over large timescales. Changes in the environmental chemistry, either *in-situ* or *en route* from soil to fluvial system, to the ocean, can cause beryllium desorption and may preclude some beryllium isotopic applications.

Four mechanisms were tested to determine the desorption potential of beryllium including a reduction in pH, an increase in ionic strength (NaCl) and complexation by soluble organic (malonic acid) and inorganic species (NaF). To quantify their effect on beryllium desorption from both organic and mineral fractions, we prepared separate

solutions of beryllium bound to minerals and organic compounds and measured beryllium concentrations in solution before and after each chemical perturbation. We conclude that a reduction in pH resulted in the greatest amount of desorption, removing 97% and 75% of sorbed beryllium from illite and montmorillonite, respectively. The addition of malonic acid also resulted in desorption from montmorillonite by 46%. Although increasing the ionic strength did remove 32% and 8.4% of beryllium from montmorillonite and sulfonate, respectively, the presence of sodium significantly enhanced sorption to illite. Overall, beryllium sorbed to organic compounds was more resistant to desorption relative to mineral-bound beryllium.

We can relate differences in beryllium desorption behavior to complexation mechanisms driving retention among organic and mineral species. Inner sphere complexation is believed to control beryllium sorption among the organic ligands tested due to the minimal amounts of desorption. Because beryllium sorption was reversible due to changes in pH, ionic strength and organic acid complexation, we hypothesize that outer sphere processes, driven by weaker electrostatic attractions, govern beryllium-montmorillonite associations. Beryllium exhibited a unique relationship with illite in that sorption appears to be dominated by not only inner sphere processes but also physical inclusion within collapsed interlayer spaces. Our results not only suggest potential complexation mechanisms among various sorbents but also show that various processes can promote the exchange of beryllium between solid and dissolved phases, the extent to which depends on the composition of the system.

3.1 Introduction

In the past few decades, beryllium isotopes have been used in the field of geomorphology and geochronology to determine the residence time of sediments in landscapes ranging from several weeks to millions of years (Granger et al, 2013; Wallbrink and Murray, 1996; Willenbring and von Blanckenburg, 2010a and 2010b). These methods use concentrations of beryllium isotopes sorbed to sediments and often rely on the assumption that these concentrations are unchanged over such large timescales. However various biotic and abiotic processes could influence beryllium's behavior in soils and aquatic environments. As sediment is transported, undergoing various cycles of erosion and deposition, beryllium sorbed to these particles is exposed to a variety of different chemical environments and is susceptible to transformations along the path from source to sink. For example, marine core sediments used to measure ^{10}Be/^{9}Be ratios for estimating total denudation in a landscape can experience a salinity gradient during their transport from fresh to saline waters. Such changes in the ionic strength could result in competition for sorption sites and subsequent desorption of beryllium. Additionally, within a single soil profile, *in-situ* processes like plant and microbial production of chelating organic acids can stimulate beryllium mobilization altering its natural distribution with depth. Beryllium desorption poses a problem for the environmental scientist and the geomorphologist, both of whom rely on the retention of beryllium to sediment to prevent the contamination of ground water, preserve a landscape's erosional signature and for tracking particle movement. Therefore, although the sorption behavior of beryllium is important to understand, it is equally important to consider processes that cause desorption.

In this study, we investigate four major processes known to stimulate metal desorption including a reduction in pH, an increase in the ionic strength and complexation by soluble organic and inorganic species. A decrease in pH reduces available sorption sites encouraging the exchange of sorbed cations for protons. Increasing the ionic strength also enhances competition between cations for reactive sites on the surfaces of particles, resulting in desorption of ions previously bound to the surface. Additionally, low molecular weight organic acids (LMWOA) that are excreted by biota are capable of chelating cationic species like beryllium, mobilizing them into the soil solution (Qin, et al, 2004; Vanhees et al, 1999; Vranova et al, 2013). Examples of such acids include oxalic, malonic, succinic and other dicarboxylic acids. In addition to organic ligands, beryllium is also complexed by inorganic species such as fluoride. Previous studies determined that dissolved, unsorbed beryllium concentrations were dependent on the amount of fluoride in fresh water systems and that the presence of fluoride can increase the mobility of beryllium (Vesely et al, 1989; Vesely et al, 2002; Kram et al, 1998).

Although these chemical perturbations are intended to provide us with a greater understanding of processes driving beryllium desorption, the rate and extent of desorption can also provide information relating to the predominant complexation mechanism among the organic ligands and mineral tested. Sorption processes can be characterized as specific and non-specific. Non-specific sorption, or outer sphere complexation, involves the electrostatic interactions of hydrated metal ions with sorption sites. Considering these interactions are driven simply by differences in charge, there is less specificity among ligand type. Conversely, specific sorption, also referred to as inner sphere complexation, involves an actual chemical reaction between the metal and sorption site. The term ‘specific’ refers to the thermodynamic preference of a metal ion to form a covalent bond with particular ligands. Considering specific, inner sphere complexation involves the formation of chemical bonds, it produces a stronger metal-ligand association compared to outer sphere complexation. These inner sphere complexation mechanisms are therefore more resistant to chemical disturbances affecting the electrostatic interactions between metal and ligand like changes in ionic strength or pH. Therefore, the ease of beryllium desorption from organic and mineral sorbents can be used to estimate dominant sorption types, with outer sphere complexation allowing for greater desorption at faster rates. We can use this knowledge to estimate how beryllium chemically associates with organic ligands and minerals.

Understanding how these four variables affect the equilibrium of beryllium between sorbed and dissolved phases is central in understanding not only the potential for beryllium desorption and mobilization but the predominant complexation mechanism among organic and mineral sorbents. The goals of this paper are to 1) establish the relative strength of each chemical perturbation on beryllium desorption, 2) to determine the relative strength of beryllium desorption from organic ligands versus mineral sorbents and 3) to indirectly estimate the predominant sorption mechanism by observing their responses and determine how those mechanisms may differ among organic ligands and minerals.

3.2 Methods

3.2.1 Sorption of Beryllium to Sorbent Materials

In order to test the ability of different processes to desorb beryllium, we initially needed to sorb beryllium to organic and inorganic sorbents. We selected two clay minerals to represent the mineral fraction and two organic compounds to represent the organic matter fraction of soils. We chose to use standard, model materials in order to identify how different chemical perturbations individually affect the retention of beryllium by either mineral or organic fractions. By observing their behavior separately we are able to better approximate the extent each chemical perturbation has on a natural soil depending on its organic or clay mineral content. Using model materials also removes any uncertainty that results from the complex and heterogeneous nature of using an actual soil sample and can allow us to better elucidate differences in the desorption behavior of beryllium between organic and inorganic soil materials.

We selected mineral and organic materials based on their ability to complex beryllium as determined from previous experiments (Boschi and Willenbring, 2016). Of the minerals tested, illite and montmorillonite exhibited the greatest amount of beryllium sorption. We obtained these minerals through Ward science (Rochester, NY, USA) and confirmed their mineralogical purity using x-ray diffraction (XRD). The samples were ground using a disc mill and rinsed with a weakly acidic HCl (Fisher Scientific, Pittsburgh, PA, USA) solution and ultrapure Millipore (Billerica, MA, USA) water to remove impurities. The minerals were then wet sieved and dried in an oven overnight. The <20 µm fraction was collected for use in this experiment. A Beckman-Coulter Particle Size Analyzer (Miami, FL, USA) was used to determine the proportion of each mineral sample that was smaller than 0.45 µm to ensure the filter removed mineral particles from solution. It was determined that less than 0.5% of the sample was smaller than 0.45 µm. As an additional precaution in order to ensure particles were not escaping through the filter, all mineral samples were centrifuged at the appropriate speed and time interval prior to filtration to ensure the >99.5% of particles were excluded from the filtrate.

Similarly to the mineral samples, we selected phosphonic and sulfonic acid bearing compounds because they formed the most stable complexes with beryllium relative to other organic compounds tested in previous experiments (Boschi and Willenbring, 2016). Octadecylphosphonic acid (Sigma Aldrich, St. Louis, MO, USA), a large insoluble alkane and toluenesulfonic acid bound to a polystyrene resin (30-60 mesh size) (Alfa Aesar, Ward Hill, MA, USA) were selected to represent a phosphonate and sulfonate group respectively. These compounds were selected so that they could be easily separated from solution by filtration using a 0.45 µm filter. By selecting organic ligands and minerals with larger stability constants relative to other materials, our results will provide a conservative estimate of beryllium desorption from ligands physically available to do chemistry in natural environments.

For each mineral or organic material, we prepared 72 beryllium-sorbent solutions, which allowed a sufficient number for triplicate analysis at 6 different time intervals for each of the four chemical treatments. We prepared an additional 21 beryllium-sorbent solutions for each sorbent material to function as controls. These 21 solutions (three designated for each time interval plus an additional three for time ‘0’ to determine the initial amount of sorbed beryllium) would not be perturbed by any of the chemical amendments and would act to monitor the amount of beryllium in solution over the entire duration of the experiment. Following each chemical treatment, we compared beryllium concentrations in solution to the concentration of beryllium in the control sample at the same time interval. The six time intervals included 1 hour, 3 hours, 6 hours, 12 hours, 1 day and 7 days. Therefore, we made a total of 372 solutions.

We prepared individual organic compounds and mineral solutions at a concentration of 250 mg L^{-1}. It is important to note that for organic compounds 250 mg L^{-1} represents the concentration of the active functional group, not the entire organic molecule because the ratio of functional group to organic compound mass varies from compound to compound. For example, 250 mg L^{-1} phosphonate (PO_3) was prepared rather than 250 mg L^{-1} of octadecylphosphonic acid ($C_{18}H_{39}O_3P$). However, for the mineral samples, 250 mg L^{-1} represents the concentration of the bulk mineral. We used a beryllium concentration of 1 mg L^{-1} to mimic its average abundance in natural soils and to ensure its instrumental detection (Taylor et al, 2003; USDHHS, 2002). We prepared our beryllium stock solution using a beryllium ICP standard (BDH, Lutterworth, UK). The solutions were prepared in ultrapure Millipore water and initially adjusted to a pH of 6 to ensure maximum sorption. We could not exceed a pH of 6 considering the dependence of beryllium speciation on pH. At a concentration of 1 mg L^{-1}, beryllium is present as a divalent cation at low (<6.5) and high (>11) pH's and as insoluble $Be(OH)_2$ in-between. For example at a pH of 7, 79% of $Be(OH)_2$ is removed from the solution via filtration with a 0.45 µm filter (Boschi and Willenbring, 2016). The solutions were placed on a roller table to allow constant mixing of the material and beryllium solution for 14 days.

3.2.2 Solution Alteration

After 14 days, control samples representing time ‘0’ were measured to determine the amount of beryllium sorbed to each of the four materials. At this time, each of the beryllium-sorbent mixtures, excluding the control samples, underwent chemical alteration through the addition of 0.25 mL of a NaF (Acros, New Jersey, USA), NaCl (Fisher Scientific), HCl (Fisher Scientific) and malonic acid (Fisher Scientific) solution. A small volume was used to ensure that the beryllium-sorbent solution was not diluted, thus affecting the system’s equilibrium. Each of the chemical treatments was added to separate solutions so that a total of 18 solutions (for the 6 sampling events in triplicate) were prepared for each beryllium-sorbent mixture for each treatment. The final concentration of NaF, NaCl and malonic acid in the beryllium-sorbent mixture represented that found in natural environments. Malonic acid was prepared so the final concentration was 5 mg L^{-1} (Harter and Naidu, 1995). The final concentration of NaF was 0.2 mg L^{-1}, representing the median dissolved fluoride concentration in freshwaters as reported in previous work showing strong correlation with dissolved beryllium concentrations (Vesely et al, 1989). The final concentration of NaCl was 2.2 g L^{-1} which falls within the range of brackish waters (NOAA, 2012). To test the effect of increased acidity on desorption, the pH was adjusted to a pH of 3 using HCl. Considering the addition of malonic acid reduced the solution pH to 4, we chose an even lower pH to simulate an acidic environment.

3.2.3 Sampling and Analysis

At each time interval the solutions were filtered using a 0.45 µm filter (Pall Life Sciences, Port Washington, NY, USA) to separate the amount of beryllium in solution from the amount of sorbed beryllium. The pH was monitored throughout the duration of the experiment and before each sampling event to ensure that the pH did not exceed 6. The filtered solutions were analyzed using an inductively coupled plasma optical emission spectrophotometer (ICP-OES) (Spectro, Mahwah, NJ, USA) to determine the concentration of unsorbed beryllium in solution. The results are reported as percent desorption which represents the concentration of beryllium remaining in solution after treatment relative to the concentration of beryllium in the control sample at the same time interval.

3.3 Results and Discussion

3.3.1 Increase in Solution Ionic Strength

By changing the ionic strength of the solution so that the final concentration of NaCl was 2.2 g L^{-1}, we observe different responses between both mineral and organic compounds (Figure 3.1). In order to gauge the change in beryllium concentration, we calculated the overall percent desorption or increased sorption after the 7-day time period for each material (Table 3.1). The addition of NaCl caused sulfonate and montmorillonite to desorb 8.4% and 32%, respectively, of the original amount of sorbed beryllium after 7 days (Figure 3.1, Table 3.1). Conversely, it caused illite and phosphonate to sorb additional amounts of beryllium by 96% and 17% of what was originally sorbed, respectively.

The change in the ionic strength of the solution can affect both the behavior of the beryllium and the behavior of the sorbent. For montmorillonite and, to a lesser extent, sulfonate, the increased concentration of competing ions for sorption sites lead to the displacement of beryllium by sodium cations. The difference in the magnitude of desorption relates to the nature of the beryllium-ligand complex formed by either the hydroxyl groups on the surface of montmorillonite particles or the sulfonate group of the toluene sulfonic acid compound. As shown in Boschi and Willenbring 2016, sulfonate is able to form stronger interactions with beryllium compared to the various organic ligands studied. Previously reported stability constants, a metric for metal-ligand strength, indicate that among organic and inorganic ligands, sulfonate is able to form some of the strongest interactions with beryllium (Alderighi et al, 2000). Therefore it is less thermodynamically favorable to disrupt a sulfonate-beryllium complex.

Despite having a large surface area containing negatively charged hydroxyl groups, the significant amount of beryllium desorption from montmorillonite can infer two possible scenarios relating to complexation type. If complexation is dominated by inner sphere processes by which beryllium directly interacts with hydroxyl groups on mineral edge sites, then we might assume that beryllium is being complexed by a single hydroxyl group given the reversibility of the reaction as shown in Equation 3.1 where SOH represents a surface hydroxyl group, M^{2+} represents a divalent metal cation such as Be^{2+} and SOM^{+} represents the metal-hydroxyl complex. However, we are aware from previous work that few monodentate ligands are able to compete with hydrolysis for beryllium complexation (Harter and Naidu, 1995). Additionally, reported stability constant values (log K_1) for bidentate, dihydroxy containing ligands are as high as 16.2, indicating they form very stable complexes with beryllium and would not be as susceptible to desorption under the given conditions (Alderighi et al, 2000). Therefore, it seems less likely that beryllium would be directly complexed by a single or multiple hydroxyl groups on the surface of montmorillonite.

Conversely, it may be more likely that beryllium is retained through outer sphere complexation which involves the indirect sorption of beryllium to a surface by means of water molecules (Equation 3.2). Water molecules are electrostatically held to the surface while also hydrating beryllium cations. It is also generally accepted that outer sphere complexation occurs primarily on interlayer surfaces (Poinssot and Geckeis, 2012). Previous studies have shown that outer sphere complexation dominates when the ionic strength of the solution influences the amount of sorption unlike inner sphere complexation which is considered less susceptible to cation exchange (Sparks, 2003). This effect was investigated by Hayes and Leckie who used a modified version of the Triple Layer Model (TLM) to indirectly characterize the nature of metal-ligand complexation. The TLM is a surface complexation model that defines three separate electrical layers, the distribution of ions amongst these layers, as well as the surface charge and potential between planes (Figure 3.2) (Hayes and Leckie, 1987). Hayes and Leckie modified the original TLM to include inner sphere metal complexation rather than previously assuming metals where only complexed through outer sphere processes. They determined which process dominates metal sorption by performing sorption isotherms under different ionic strengths and comparing the empirical data to modeled outcomes representing inner and outer sphere complexation. Metal complexation dominated by outer sphere processes, occurring at the *β*-plane, is affected by the ionic strength of the solution whereas inner sphere complexation, occurring at the *o*-plane, is not. Therefore the equation characterizing outer sphere complexation accounts for the concentration of background electrolyte whereas the equation representing inner sphere complexation does not, as shown in equations 3.3-3.6 (Hayes and Leckie, 1987). Here, *K* represents the thermodynamic equilibrium constant for either inner sphere ($K_{I.S.}$) or outer sphere processes ($K_{O.S.}$), *F* represents Faraday constant in C mol^{-1}, ψ_i represents the potential in the *i*th surface plane in V, *R* represents the gas constant in J mol^{-1} K^{-1}, σ_d is the charge of the bulk solution that balances the surface charge also known as the dissociate charge, *C* is the concentration of 1:1 background electrolyte (e.g. NaCl), ε_r represents dielectric constant of water and ε_o represents the permittivity of vacuum.

Inner Sphere Complexation

(Eq. 3.1) $$SOH + M^{2+} \leftrightarrow \ SOM^{+} + H^{+}$$

Outer Sphere Complexation

(Eq. 3.2) $$SOH + M^{2+} \leftrightarrow \ SO^{-} - M^{2+} + H^{+}$$

Equilibrium Expressions

(Eq. 3.3) $$K_{I.S.} = \frac{[SOM^{+}][H^{+}]}{[SOH][M^{2+}]}\exp[-F\varphi_o /RT]$$

(Eq. 3.4) $$K_{O.S.} = \frac{[SO^{-}-M^{2+}][H^{+}]}{[SOH][M^{2+}]}\exp\left[-F(\varphi_o - 2\varphi_\beta)/RT\right]$$

(Eq. 3.5) $$\varphi_\beta = \left(\frac{\sigma_d}{C_2}\right) + \varphi_d$$

(Eq. 3.6) $$\sigma_d = -(8RTC\varepsilon_o\varepsilon_r)^{1/2}\sinh\left(\frac{F\varphi_d}{2RT}\right)$$

Outer sphere complexation is affected by the ionic strength of the solution because it affects the electrical potential between the β and the diffuse layer. Therefore we can deduce that if metal sorption is affected by the electrolyte concentration, complexation is dominated by outer sphere processes. Considering beryllium is able to desorb from montmorillonite due to changes in ionic strength, it may indicate that beryllium sorption is dominated by outer sphere complexation under our experimental conditions including a solution pH of 6.

This hypothesis is further supported when we consider the strong association between beryllium and water molecules. Beryllium has a large charge to size ratio and is capable of strongly orienting water molecules around it forming polymeric hydrolysate products in an aqueous media (Walsh and Vidal, 2009). Of all divalent ions, beryllium is the most heavily hydrated and has the highest solvation energy (Martell and Hancock, 1996). The hydrolysis reaction of beryllium is described in Equations 7 and 8. It involves the initial hydration of beryllium by four water molecules, covalently bound having tetrahedral geometry (Equation 3.7).

(Eq. 3.7) $$Be^{2+} + 4H_2O \leftrightarrow [Be(H_2O)_4]^{2+}$$

Beryllium is capable of strongly polarizing water molecules, orienting the negatively charged oxygen towards itself and causing strong repulsion amongst hydrogen atoms. This allows water molecules to more easily deprotonate with increasing pH resulting in a network of beryllium atoms bridged by hydroxyl groups (Equation 3.8). The bridging results in the initial formation of a trimer species (Figure 3.3).

(Eq. 3.8) $$[Be_a(H_2O)_b]^{2a+} + cOH^- \leftrightarrow [Be_a(H_2O)_{b-c}(OH)_c]^{2a-c} + cH_2O$$

With increasing concentrations, these trimers gradually accumulate and form higher aggregates (Alderighi et al, 2000). These aggregates increase in size to become colloidal, eventually precipitating as insoluble $Be(OH)_2$ depending on the concentration of beryllium in solution (Mattock, 1954). The strong arrangement and preference of beryllium for water ligands may result in an increased preference for outer sphere complexation mechanisms in the absence of more thermodynamically preferred ligands.

Considering beryllium's behavior in response to changes in ionic strength combined with what we already understand regarding beryllium hydrolysis, we hypothesize that beryllium sorbed to montmorillonite is dominated by outer sphere processes. Typically, we would employ x-ray absorption spectroscopy to characterize and confirm metal complexation type. Unfortunately, these techniques are limited for light weight elements like beryllium. Therefore our future work will involve using additional solution based experiments and surface modeling techniques to confirm dominate complexation mechanisms for beryllium.

Unlike montmorillonite, changes to the ionic strength of the solution caused an increase in the sorption of beryllium by illite which could be the result of changes in the structure of illite. Illite is a 2:1 aluminosilicate clay that is characterized as an intermediate between mica and smectite clays (Sparks, 2003). It differs from true micas in that only 1/6 versus 1/4 of the silicon atoms are replaced with aluminum atoms in the tetrahedral layer (Rolfe et al, 1960). Illite interlayers are occupied and tightly held together almost entirely by potassium ions. However previous work has shown that the edge sites of illite are void of potassium ions due to chemical weathering and are susceptible to infiltration and subsequent expansion by other hydrated cations such as sodium, calcium and magnesium (Fuller et al, 2015). The increase in the interlayer spacing of illite due to cation exchange and has been well documented (Smith, 1967). With the addition of sodium in attempts to increase the ionic strength of the solution, the subsequent lattice expansion would allow beryllium atoms to diffuse further into the interlayers thus enhancing its sorption potential relative to the amount initially sorbed. The exchange of cations at edge sites can also cause them to collapse, physically enveloping the metal and preventing it from desorbing back into solution. Increased sorption and resistance to desorption may suggest that beryllium is more physically protected by occupying the collapsed frayed edges of illite upon exchange with other interlayer cations as is observed with other metals like cesium (Fuller et al, 2015). Illites' planar surfaces are otherwise tightly held by potassium ions and less accessible relative to the hydrated interlayers of montmorillonite, thus frayed edge sites may be more readily populated. This mechanism would help to explain beryllium's physical protection and thus resistance to exchange with the solution over time. Further work involving the use of transmission electron microscopy will be employed to better understand the behavior of illite including the formation of collapsed edges in the presence of beryllium under various environmental conditions.

Similarly to illite, the fluctuation in beryllium sorption by phosphonate may be a result of the effect of ionic strength on the behavior of octadecylphosphonic acid itself. Although increasing the ionic strength of the solution initiated beryllium desorption from phosphonate, after 7 days equilibrium is established resulting in a net increase of beryllium sorption. Octadecylphosphonic acid contains a hydrophilic, polar functional group with a large, hydrophobic hydrocarbon tail, which allows it to function as a surfactant. Thus, it is strongly affected by changes in ionic strength. Increasing the concentration of ions in solution dampens repulsions between polar, phosphonate head groups resulting in the formation of globular aggregates of individual molecules (Palladino and Ragone, 2011). Dissolved organic matter is also amphiphilic in nature and previous work has shown that its macromolecular structure is capable of forming aggregates in response to changes in solution chemistry including pH and ionic concentration (Ghosh and Schnitzer, 1980; Piccolo, 2001). These structural changes may affect the accessibility of the phosphonate groups, or other polar functionalities in the case of natural organic matter, therefore explaining fluctuations in the concentration of complexed beryllium over time.

3.3.2 Reduction in Solution pH

There is a marked difference in the response between the minerals and organic compound with changes in solution pH. The decrease in pH caused little to no desorption among the organic compounds. It actually caused an increase in the amount of beryllium to be sorbed by phosphonate after 7 days by 44% (Figure 3.4) (Table 3.1). Beryllium desorbed more easily from the minerals tested, with 75% and 97% of beryllium removal from montmorillonite and illite, respectively.

The reduction in pH did not desorb beryllium from sulfonate as its pKa, -2.8 for toluene sulfonic acid, is much lower than the pH of the solution. Therefore, it remained deprotonated and able to complex beryllium preventing desorption. For phosphonate, we observed that it continues to complex beryllium over time and sorbs 44% more beryllium than what was originally complexed. Longer equilibration times were required for beryllium complexation by phosphonate as previously reported in Boschi and Willenbring (2016). Similar to changes in the ionic strength, the reduction in pH may not only affect protonation of polar functional groups but it may also affect the aggregate behavior of octadecylphosphonic acid and thus the rate at which beryllium is complexed.

Conversely, desorption of beryllium from mineral species upon decreasing the pH can be attributed to the expected reduction in surface charge from increased protonation of the negatively charged surface sites. The point of zero charge, pzc, or the pH at which the surface charge of a mineral is equal to zero has been previously established as 2.5 and 3.2 for montmorillonite and illite, respectively. Therefore, by adjusting the pH to 3, we observed greater amounts of desorption from illite. Montmorillonite has a greater pzc and it is able to maintain a more negatively charged surface at even lower pH's, which resulted in relatively smaller amounts of desorption compared to illite.

3.3.3 Addition of Organic Acid

Similarly to the reduction in pH, malonic acid caused negligible desorption of beryllium from the organic ligands after 7 days (Figure 3.5, Table 3.1). Malonate is able to chelate beryllium and gains additional stability through the formation of the desired 6 member ring (Alderighi et al, 2000). However, stability constants previously determined for phosphonate- and sulfonate-beryllium complexes are greater than that of malonate helping to explain the small amount of desorbed beryllium. Additionally, the reduction in pH due to the addition of malonic acid did not exceed the pKa of either ligand leaving them both predominantly deprotonated and available for complexing beryllium.

The potential for beryllium desorption from organic ligands upon addition of a LMWOA will depend on the chemical properties and composition of the sorbed versus dissolved organic matter fractions in a given system. For example, in addition to phosphonate and sulfonate, other organic ligands associated with organic matter including aromatic dihydroxyl, hydroxycarboxylate and biscarboxylic functionalities similar to what is found in lignin, are also able to form strong interactions with beryllium having stability constants (log K_1 values) exceeding 12 (Alderighi et al, 2000). Conversely, soluble, LMWOA most commonly abundant in soils including acetic, citric, formic, oxalic, malonic, malic and succinic acids have stability constants lower than 6 (Alderighi et al, 2000). These types of LMWOA would not be able to compete for beryllium complexation with the aforementioned ligands. Therefore, the type of ligands comprising the dissolved organic matter fraction will influence the potential for beryllium desorption from the sorbed organic fraction. The types of ligands found in either fraction will differ depending on many factors making it difficult to predict the potential for beryllium desorption unless both are sufficiently characterized.

Similar to the other treatments, the mineral fraction was more susceptible to beryllium mobilization. However, there was a difference in the response of beryllium desorption amongst montmorillonite and illite. The addition of malonic acid resulted in desorption of 46% of the original amount of beryllium sorbed by montmorillonite after 7 days. Conversely, it caused an initial increase in beryllium sorption by illite which was then released over time, resulting in a net zero desorption. Although illite has a higher pzc compared to montmorillonite and is therefore more sensitive to a reduction in solution pH, the addition of malonic acid caused a greater amount of desorption from montmorillonite than from illite. Therefore, we can again hypothesize that beryllium sorbed onto the surface of montmorillonite and illite is controlled by different mechanisms.

The lack of desorption observed from illite helps support our hypothesis that the majority of beryllium sorption occurs at edge sites and thus inner sphere mechanisms dominate beryllium complexation by illite. As previously discussed, access to the interlayer spacing of illite is restricted due to the abundance of tightly held potassium ions. This limits beryllium sorption to exterior basal surfaces or edge sites. The resistance to desorption upon addition of an organic complexing agent suggests inner sphere complexation may be the dominant mechanism thus supporting the occurrence of sorption at edge sites. Although we do observe desorption of beryllium from illite when we reduced the pH to 3, the resultant pH was equivalent to the pzc of illite and thus we would expect to see significant removal of beryllium. Conversely, the addition of malonic acid only reduced the pH to 4. Unlike planar sites which maintain a constant delocalization of negative charge among the basal oxygen atoms due to isomorphic substitution within the tetrahedral layer, protonation of edge hydroxyl groups are dependent on pH (Strawn and Sparks, 1999). Therefore sorption reversibility can occur but is most favorable at pHs similar to the pzc.

Unlike illite, the availability of interlayer spacing relative to the edge sites in montmorillonite combined with the observed reversibility of beryllium sorption, suggests that beryllium retention is dominated by outer sphere complexation on basal surfaces of montmorillonite. This is supported by other work that reported outer sphere complexation was most common on interlayer sites of montmorillonite at lower pH's like those experienced from the addition of malonic acid reducing the solution pH to 4 (Gu et al, 2010; Strawn and Sparks, 1999). Therefore although montmorillonite may have greater surface area due to the accessibility of interlayer binding sites, outer sphere complexation processes appear to dominate in these regions creating weaker associations with beryllium. Again, the dominate complexation mechanism for either mineral would have to be confirmed through additional sorption experiments and modeling techniques.

3.3.4 Addition of Fluoride (NaF)

The addition of sodium fluoride caused increased sorption among illite and slight increase in sorption among montmorillonite but did not have any effect on the beryllium complexed by sulfonate (Figure 3.6) (Table 3.1). Although initially 38% of the total sorbed beryllium was able to desorb from phosphonate, after seven days there was a net zero desorption. The increased absorption for illite may again be explained by its sensitivity to changes in sodium concentrations, albeit small, helping to increase the interlayer spacing via ion substitution. However overall, increased amounts of fluoride do not appear to promote beryllium desorption from either organic ligands or minerals.

3.4 Conclusions

Although previously believed that beryllium sorbed to the surfaces of sediment or organic matter was resistant to desorption, our results show that various processes can promote the exchange of beryllium between solid and dissolved phases. Of all four treatments, a decrease in pH caused the greatest amount of desorption which was only observed for the minerals studied; the organic ligands were unaffected by changes in pH. Montmorillonite was more susceptible to beryllium desorption considering the addition of malonic acid removed 46% of beryllium from montmorillonite but did not affect illite. As such, it is hypothesized that outer sphere processes are more dominate for montmorillonite whereas inner sphere complexation and physical inclusion is more common with illite due to differences in their clay structure. Additionally, illite exhibited an enhanced sorption capacity in the presence of sodium which may also be a result of illite's chemistry and structure. Our future work will focus on confirming the dominant complexation type and the physical behavior of beryllium in the presence of these two minerals using additional sorption experiments and surface complexation modeling.

Because of beryllium's resistance to desorption in the presence of organic ligands relative to the mineral fraction, we conclude that certain organic ligands can play an important role relating to beryllium mobility in soil and aquatic environments. The organic ligands tested were less susceptible to chemical perturbations. This emphasizes the importance of organic matter, its chemical composition and response to changes in solution chemistry when making predictions regarding beryllium mobility.

3.5 Acknowledgements

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Table 3.1: Percent desorption or increased sorption for each sorbent material 7 days after the addition of HCl, Malonic Acid, NaCl and NaF

	HCl		**Malonic Acid**		**NaCl**		**NaF**	
	% D	***% S***	***% D***	***% S***	***% D***	***% S***	***% D***	***% S***
Illite	97	0	0	0.6	0	96	0	77
Mont.	75	0	46	0	32	0	0	0
Sulfonate	0	0	0.2	0	8.4	0	0	0
Phosphonate	0	44	1.4	0	0	17	0	2.1

Table 3.2: Stability constants associated with low molecular weight organic acids most commonly identified in soils

	Log K_1
Malonic	5.73
Oxalic	4.87
Succinic	4.69
Maleic	4.33
Fumaric	4.33
Citric	4.31
Malic	2.49
Tartaric	1.69
Acetic	1.62
Propionic	0.30
Formic	0.15

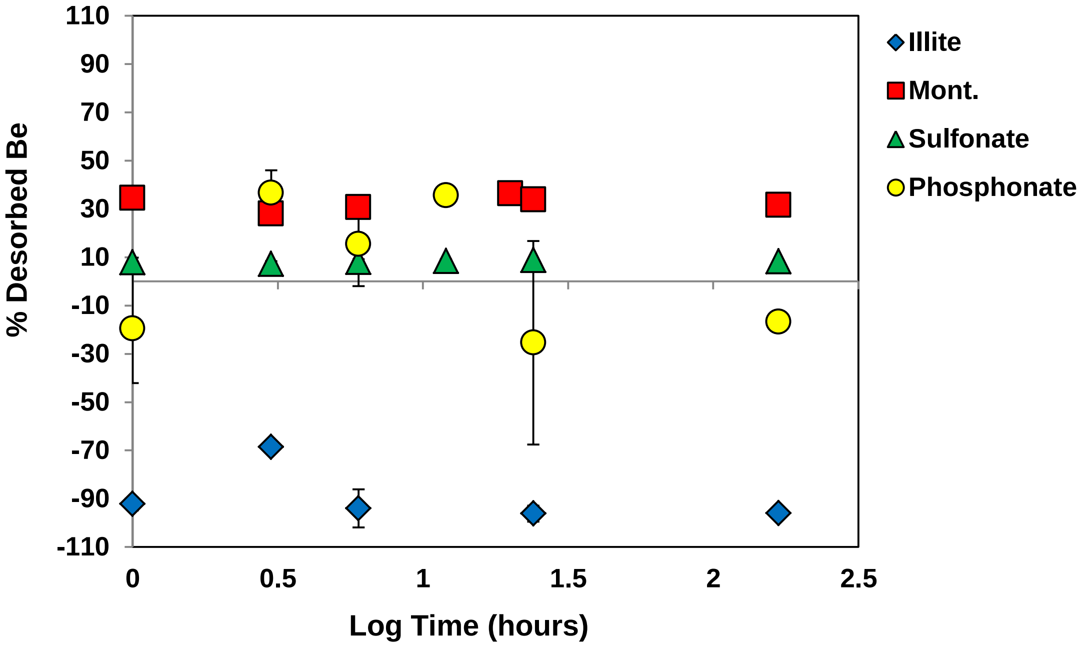

Figure 3.1: Percent desorbed beryllium from each sorbent material as a function of time after the addition of NaCl to produce a final concentration of 2.2 g L^{-1}.

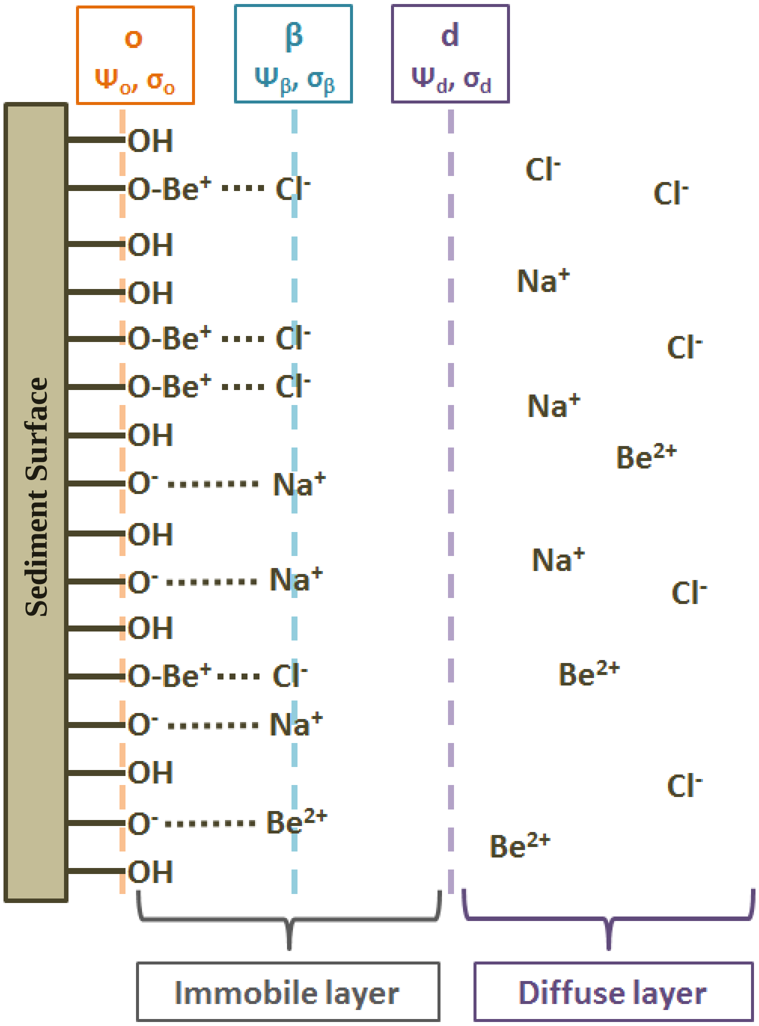

Figure 3.2: Triple Layer Model Schematic adapted from Hayes and Leckie, 1987 where *o*, *β* and *d* represent the three electrostatic planes with *ψ* potential and a bulk solution charge of σ. Ions within the *o* and *d* boundaries have limited mobility while ions within the diffuse layer are more readily exchanged.

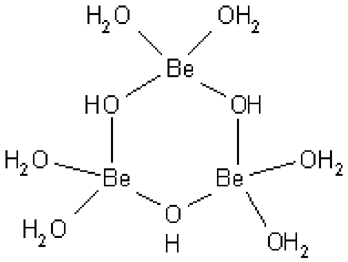

Figure 3.3: Structural formula for the trimeric beryllium hydrolysis product.

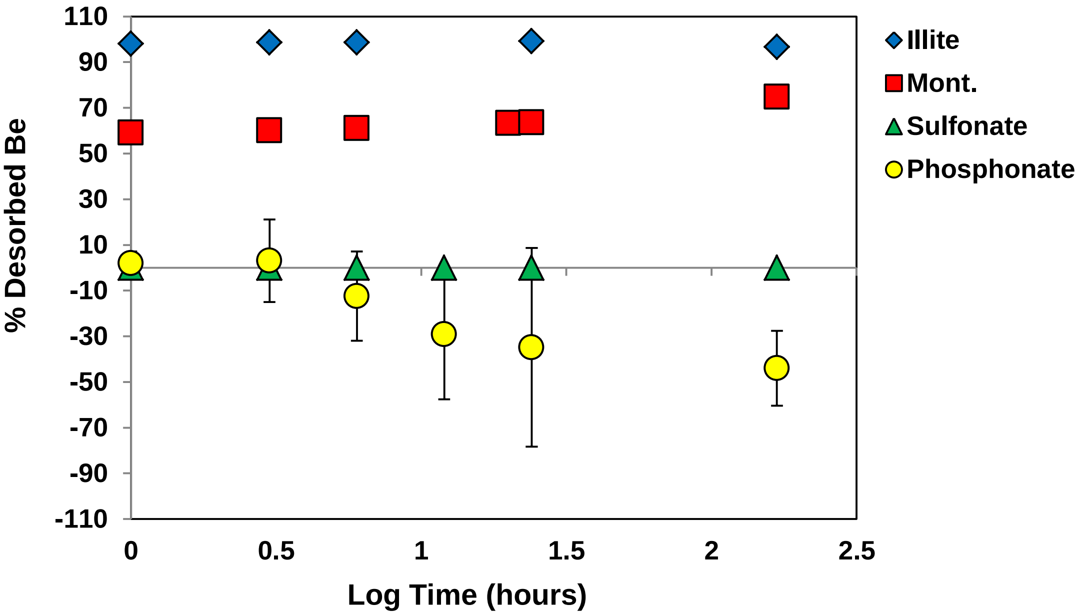

Figure 3.4: Percent desorbed beryllium from each sorbent material as a function of time after the solution pH was lowered to 3.

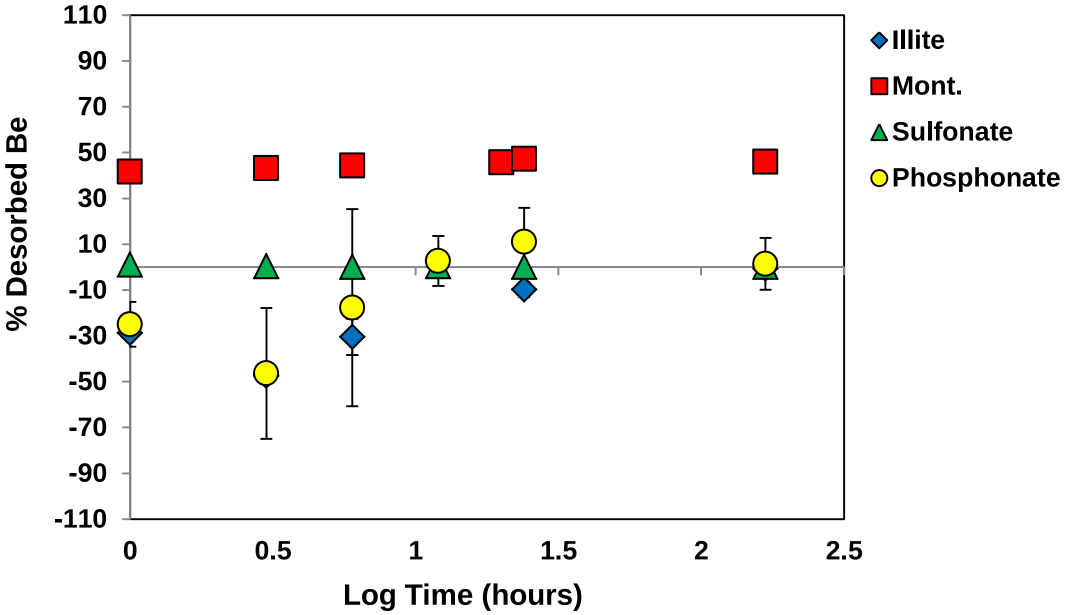

Figure 3.5: Percent desorbed beryllium from each sorbent material as a function of time after the addition of malonic acid to produce a final concentration of 5 mg L^{-1}. Negative desorption means the material actually sorbed more beryllium as a result of the addition of malonic acid.

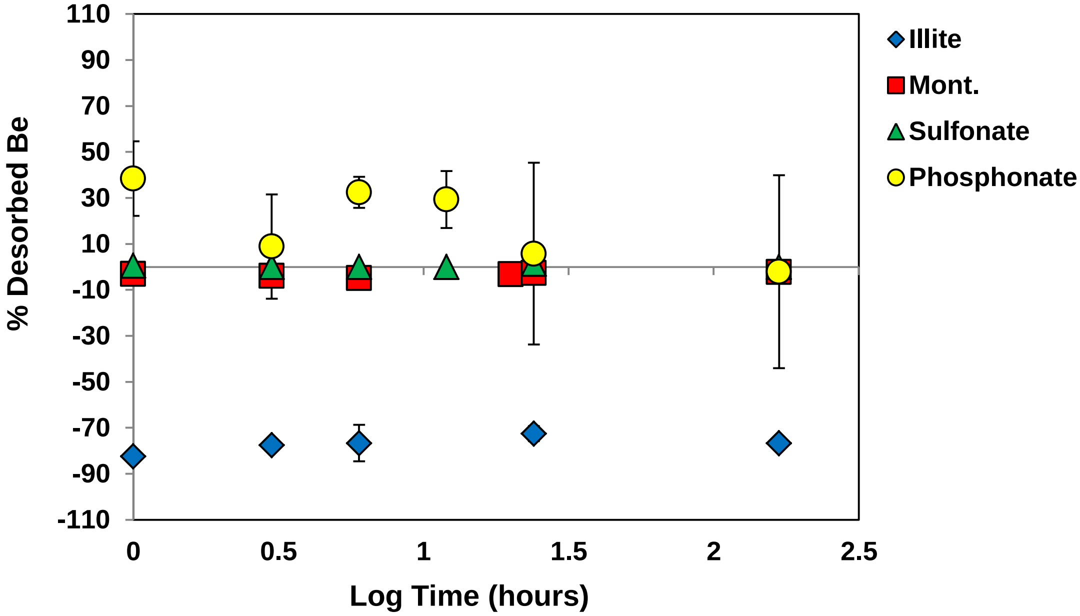

Figure 3.6: Percent desorbed beryllium from each sorbent material as a function of time after the addition of NaF to produce a final concentration of 0.2 mg L^{-1}. Negative desorption means the material actually sorbed more beryllium as a result of the addition of sodium fluoride.

CHAPTER 4

STANDARDIZATION METHOD FOR BERYLLIUM SORPTION DATA

For Submission to: Chemical Geology

Abstract:

The field of geomorphology relies on the use of beryllium isotope concentrations to calculate erosion and weathering fluxes. Meteoric ^{10}Be and ^{7}Be produced in the atmosphere from high-energy spallation reactions are deposited onto the Earth's surface through wet and dry deposition and sorb onto the surfaces of particles. Their sorbed concentrations scale with the residence time of sediments in a landscape. Additionally, the amount of native ^{9}Be, leached from minerals, scales with the chemical weathering of soils within a catchment. Previous work has shown that sorbed beryllium concentrations are also affected by the chemical and physical properties of soils and sediments. Therefore, the magnitude of sorbed beryllium concentrations may be more representative of the sorption capacity of the system rather than its erosional or weathering signal.

In order to account for differences in sorbed beryllium concentrations due to soil composition, we developed a standardization method by identifying which properties best predicted the beryllium sorption capacity of a system. We selected two samples with differing compositions, separated them on the basis of grain size and carefully characterized key variables known to influence sorbed beryllium concentrations including surface area, mineralogy, organic carbon content, sulfur and phosphorus concentrations, and cation exchange capacity. We determined that the inverse percent abundance of quartz and the CEC best predict beryllium sorption potential in soils. By

deriving a mathematical relationship between percent of sorbed beryllium and the product of these two variables, we were able to predict the sorption capacity of the system. We can use the percent of sorbed beryllium calculated from measured amounts of quartz and the CEC and combine it with actual, beryllium concentrations measured in field samples to estimate total beryllium sorption potential independent of the physical and chemical properties of soil. We estimate this standardization method reduces error in sorbed beryllium amounts due to differences in soil sorption capacity by about 50%. However, additional soils samples should be incorporated in future work to determine if our derived mathematical relationship predicting percent sorption is maintained over a greater variety of soil properties.

4.1 Introduction

Many applications in geomorphology rely on isotopic techniques to quantify the erosional and weathering fluxes that alter landscapes. Among them, cosmogenic beryllium isotopes including 'meteoric' ^{10}Be and ^{7}Be are produced in the atmosphere from high-energy spallation reactions, are deposited onto the Earth's surface through wet and dry deposition, and are then sorbed to the surfaces of particles (Kaste and Baskaran, 2011; Willenbring and von Blanckenburg, 2010a). These sorbed isotopes track sediment redistribution and increased concentrations of ^{7}Be (half-life $t_{1/2}$ = 53 days) and ^{10}Be ($t_{1/2}$ = 1.39 Ma) scale with the residence time of sediments in a landscape on the order of months to thousands of years, respectively (Willenbring and von Blanckenburg, 2010a). Additionally, the flux of native ^{9}Be in rivers, leached from minerals, scales with the chemical weathering of soils within a catchment (von Blanckenburg et al., 2012). When deposited in ocean sediment along with ^{10}Be, these concentrations of ^{9}Be are thought to record the silicate weathering history of Earth. Although these methods rely on sorbed beryllium concentrations, we know from previous work that the physical and chemical properties of soil and aquatic environments affect the magnitude of beryllium sorption and thus its concentration on sediment surfaces, potentially hindering erosion rate calculations (Boschi and Willenbring, 2016). For example, grain size differences between samples with the same erosion and weathering rates will impart a difference in sorbed isotope concentrations (Willenbring and von Blanckenburg, 2010a). Past work has used ^{9}Be concentrations to standardize ^{10}Be concentrations in river sediments of different grain sizes (Wittmann et al, 2012). However, this use of ^{9}Be precludes the use of ^{9}Be as a proxy for weathering fluxes because it cannot be used for both purposes simultaneously. Therefore this work is intended to develop a means of standardizing sorbed beryllium concentrations so that data collected from differing systems is compared consistently and ^{10}Be and ^{9}Be concentrations can be used in both chemical weathering and erosion rate calculations.

The concentration of absorbed beryllium is most commonly reported per mass of sediment analyzed. However, mass does not represent the nature of the sediment, nor the actual properties that affect sorption capacity. Rather than standardizing by mass, it may be more accurate to standardize sorbed beryllium concentrations by other properties known to affect beryllium sorption. Our previous work has shown that certain chemical variables including pH, organic matter content and mineralogy can affect such sorption capacity (Boschi and Willenbring, 2016). Sorbed beryllium concentrations also increase with decreasing grain size and increasing specific surface area (Aldahan et al, 1999; Shen et al, 2004; Wallbrink and Murray, 1996; Willenbring and von Blanckenburg, 2010a). It is of particular interest to characterize the sorption behavior of beryllium as a function of grain size because different sized particles exhibit different transport behaviors. Sediment fining processes involving the preferential mobility of smaller particles both along a downstream transect from river to ocean as well as within a soil profile have the potential to distort the erosional signal derived from beryllium measurements. Colloid mediated transport is also a major mechanism by which inorganic and organic pollutants alike are preferentially moved large distances, potentially causing ground and surface water contamination. Considering beryllium is one of the top 25 most toxic superfund site contaminants and one of the 126 priority pollutants as designated by the US EPA, knowledge of how beryllium concentration varies with particle size and surface area will improve our understanding of beryllium contaminant transport and provide a more accurate means of quantifying surface processes.

Soil mineralogy also influences beryllium sorption both indirectly through its influence on soil texture and directly through its contribution to surface charge. For example, the extent of soil development, and thus the proportion of smaller to larger sized grains, depends on the chemical stability of the parent material being more or less susceptible to various types of weathering. Perhaps more importantly, mineralogy also influences the total surface charge and its dependence on soil pH. Phyllosilicate clays are known for their large, negatively charged surface areas as a result of isomorphic substitution within the mineral lattice resulting in a surface charge independent of pH. Other minerals including amorphous metal oxides and hydroxides are also known for their significant surface areas, but with a surface charge that is dependent on soil pH. Conversely, minerals like quartz have little surface area and charge and contribute less to the sorption capacity of a soil. Therefore, the mineralogical content of soils can be a major driver of its ability to sorb metals and other cationic species. We know from previous work that beryllium sorption is dependent on mineralogy (Aldahan et al, 1999; Boschi and Willenbring, 2016; You et al, 1989). Both our work and the work of You et al., 1989 determined that illite preferentially sorbs beryllium relative to other 2:1 and 1:1 aluminosilicates as well as goethite. Thus, it is important to characterize the various minerals within a sample as it may correlate beryllium sorption capacity.

Sorption of organic matter and other ligands onto mineral surfaces also plays an important role in the enhanced retention of metals onto sediment surfaces. Beryllium is known to form stable associations with soil organic matter due to the availability of negatively charged functionalities capable of forming strong interactions with beryllium, in particular dicarboxylic, dihydroxyaromatic and hydroxylcarboxylic ligands (Alderighi et al, 2000; Boschi and Willenbring, 2016a and *in review*; Esteves Da Silva and Machado, 1996; Lundberg et al, 1984; Takahashi et al, 1999). These stable chemical associations have the potential to influence the retention of beryllium in soils containing organics. Previous work has shown that not only are organic ligands capable of complexing beryllium, but their interactions with beryllium are stronger than beryllium-mineral associations as evidenced by its greater resistance to chemically instigated desorption (Boschi and Willenbring, *in review*). Although these studies report a correlation between sorbed beryllium amounts and organic matter content, other published work reported no significant relationship (Graly et al, 2010; Lum and Gammon, 1985; You et al, 1989). Therefore it is important to determine how beryllium sorption scales with organic matter concentration to assess whether organic content can provide an effective method for standardizing sorbed beryllium concentrations.

In addition to organic matter content, phosphorus and sulfur oxides are important complexing agents that strongly influence beryllium retention (Boschi and Willenbring, 2016; Alderighi et al, 1999 and 2000). Phosphorus oxides are particle reactive and are commonly found bound to the surface of sediments, particularly clays and metal oxides, or found incorporated in organic matter (Gerke, 2010; Hinkle et al, 2015; Nowack and Stone, 2006). The poor solubility of phosphorus oxides combined with their ability to form strong metal complexes has aided in its development as a remedial device for the immobilization of metal contaminants in solution (Bolan et al, 2003). These compounds are known to increase the sorptive capacity of sediment and form particularly stable interactions with beryllium. In fact, monophosphonate is one of the only monodentate ligands capable of forming thermodynamically favorable complexes with beryllium (Alderighi et al, 1999). Large stability constants are also associated with sulfates which may also play a major role in beryllium retention. Despite their strong interactions with beryllium, sulfur and phosphorus oxides are not typically considered as a control for beryllium sorption in geochemical analyses. Therefore, the concentration of phosphorus and sulfur should be measured to determine how well they relate with sorbed beryllium concentrations in field samples.

Although surface area, grain size, mineralogy, total organic carbon, phosphorus and sulfur oxide content are important parameters to consider for standardization, the cation exchange capacity (CEC) or the ability of a system to retain cationic species like beryllium could potentially encompass the total contribution of the other variables on the availability of negative charge. The CEC also indirectly accounts for the effects of pH as the two are inversely related. For example, more highly weathered soils with smaller abundances of base cations like Ca, Mg, Na and K have a smaller CEC. These types of soils having low buffering capacities would typically have a lower pH. By taking into account CEC, the effects of pH are indirectly addressed. Therefore the use of the CEC as a proxy for the abundance of negatively charged surface sites may prove the most efficient means of standardizing beryllium concentrations.

Although we have been able to identify various controls affecting beryllium sorption, it is uncertain which of these variables exhibit the greatest control on beryllium sorption and thus provide the most accurate means of standardizing sorbed beryllium concentrations. Understanding the relative control each of these variables has on beryllium sorption will help construct a standardization method. Therefore, our goals for this work were to 1) select two samples with varying properties, 2) separate them on the basis of particle size, 3) fully characterize the surface area, percent carbon and nitrogen, sulfur and phosphorus concentrations, CEC, and mineralogy in each size fraction for both soils and 4) determine how sorbed beryllium concentrations correlate with each of these variables. Using this information, our final objective was to determine which variables provide the most effective means of standardizing sorbed beryllium concentrations for more consistent comparison of samples from different environments.

4.2. Methods

4.2.1 Sample Selection

To examine how different soil properties influence sorbed beryllium amounts, we selected two soils with differing soil properties. Using two soil endmembers ensures that we can observe the sorption behavior of beryllium over a range of soil textures, mineralogies, organic carbon, phosphorus and sulfur abundances and cation exchange capacities to ensure the development of a comprehensive standardization method. Both soils were collected from the Luquillo Critical Zone Observatory (LCZO) in Puerto Rico. The unique geography of the northeastern region of Puerto Rico where LCZO research is focused insures control on specific variables including topography, vegetation, climate and bedrock composition to determine their effect on soil development. The Luquillo Mountains are comprised of two major lithologies including andesitic sedimentary volcanoclastics and quartz diorite. The volcanoclasitics and quartz diorite produce two different soil types characterized as an oxisol and inceptisol, respectively. Two samples were selected, one from each soil regime, for use in this study. The oxisol soil is the more chemically weathered of the two soil types, consisting of a greater abundance of secondary clay minerals, including kaolinite, metal oxide/hydroxides including goethite and gibbsite and smaller amounts of quartz and other primary minerals. Conversely, the inceptisol sample, as insinuated by its classification, is a ‘newer’, less chemically weathered end-member containing greater amounts of quartz and feldspars and smaller amounts of secondary minerals and metal oxide/hyroxides. These differences in mineralogy amount to differences in the physical and chemical nature of the soil. As such, these two soils differ in the properties that we are attempting to evaluate including texture, percent carbon, sulfur and phosphorus content and cation exchange capacity. Both soils were sampled at a depth of 0-20 cm where we would expect the greatest concentration of organic matter in order to assess its effects on beryllium sorption. For the purposes of meteoric beryllium, this depth range is also most relevant considering both are atmospherically deposited onto the surface. In order to determine how individual properties contributed to beryllium sorption, both samples were physically separated by particle size. This separation was done not only to observe the behavior of beryllium with particle size and surface area but subsequently with all of the other select variables that also scale with particle size.

4.2.2 Sample Separation

We applied Stokes Law in order to separate both soil samples by particle size. According to this principle, the rate at which particles fall out of suspension is dependent on their particle size. We were able to calculate the amount of time required for particles of a certain size to settle at a given sampling height according to Equation 4.1 where t is the settling time in seconds, η represents the temperature dependent solution viscosity in kg m^{-1} s^{-1}, h represents the sampling height in meters, g represents the gravitational force in m s^{-2}, ρ_s and ρ_l represent the temperature dependent density of the soil and solution, respectively, in Mg m^{-3} and χ represents the particle diameter in meters:

(Eq. 4.1)

$$t = \frac{20\eta h}{g(\rho_s - \rho_l)\chi}$$

4.2.3 Dispersion and Sedimentation

Prior to the sedimentation experiment, soil samples were suspended in water (1:20 soil to water ratio) and shaken with glass beads overnight to help break up aggregates in preparation for sieving. We avoided using chemical dispersants like sodium hexametaphosphate. These types of ligands are capable of complexing beryllium and residual amounts might affect sorption of beryllium to the sediment. Both samples were wet sieved and the >250 µm, 53-250 µm and <53 µm fractions were collected. The >250 µm and 53-250 µm were placed in a 40°C oven until dry. The <53 µm fractions for both samples were distributed into several one liter settling columns. It is important to ensure that the proportion of water to soil is great enough to limit interactions between particles or the surface of the settling container as is a primary assumption when applying Stokes Law in order to ensure the natural descent of a particle is not hindered. The application of Stokes Law also assumes that particles are spherical and have the same density, that terminal velocity is achieved as soon as settling begins, temperature is constant and resistance is only influenced by the viscosity of the fluid rather than other variables like surface roughness. Although some of these assumptions are violated, best approximations are used to achieve accurate separation by grain size. The columns are filled to the one liter mark with deionized water and allowed to sit several hours to allow the system to come to equilibrium and assure that the temperature is stable.

The settling times were calculated for various particle size fractions including 20-53 µm, 5-10 µm, 1-2 µm and <1 µm using a sampling height of 10 cm. The columns were thoroughly shaken end over end for several minutes and the solution temperature was noted to determine if the solution had warmed upon shaking. After the appropriate amount of time had lapsed for the columns to sit completely undisturbed, the temperature was noted again and a 10 mL aliquot was carefully extracted at the sampling height. This process was repeated until ample sample had been collected for each size fraction. With the exclusion of the <1 µm fraction, each size fraction collected had to undergo additional rinses to remove smaller sized particles. This was done in separate columns where particles of the intended size range were allowed to settle to the bottom of the column after a calculated amount of time and the solution was carefully siphoned off. Once each size fraction had been collected and rinsed, it was placed in a 40^{o}C oven until dry.

4.2.4 Size Fraction Characterization

4.2.4.1 Surface Area

Surface area analysis was completed using a Micromeritics TriStar BET surface area analyzer. The BET surface area was determined.

4.2.4.2 Grain Size

Prior to grain size analysis, approximately 10 mg of each size fraction were suspended in 5 mL of water and placed on a shaker overnight. This helped disperse particles for a more accurate grain size distribution measurement. Grain size analysis was performed using a Beckman-Coulter LS 13 320 Particle Size Analyzer. The mean grain size was determined.

4.2.4.3 Elemental Analyzer

The percent carbon and nitrogen content was determined using a Costech ECS4010 Elemental Analyzer.

4.2.4.4 X-ray Diffractometer (XRD) Analysis

The sample mineralogy was determined using a PANalytical X'Pert Powder X-ray Diffractometer. PANalytical High Score software was used to analyze the XRD spectra through the assignment of mineral phases and execution of the Rietveld analysis for the quantitative determination of the mineral composition.

4.2.4.5 Mehlich 3 Extraction

In order to determine the concentration of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, P and S content, we performed a Mehlich 3 extraction. This method is intended to mimic the extraction of plant available nutrients by plant roots and is a proxy for total major and minor nutrient content in acidic to slightly alkaline soils. The Mehlich solution contains 0.2 N CH_3COOH, 0.25 N NH_4NO_3, 0.015 N NH_4F, 0.013 N HNO_3 and 0.001M ethylenediaminetetraacetic acid (EDTA). The use of acetic acid is representative of a root exudate and combined with diluted nitric acid is intended to lower the solution pH to about 2 to both facilitate the exchange of cationic species and prevent the formation of CaF_2 precipitate. The presence of fluoride in the form of NH_4F is intended to disrupt Fe and Al-phosphate/sulfate associations while the ammonium component of NH_4F and NH_4NO_3 promotes cation exchange, liberating major and minor nutrients. EDTA, a hexadentate ligand, is able to chelate cationic species and thus has an enhanced ability to extract more strongly sorbed metals including micronutrients like Mn and Zn. The combined reactants in the Mehlich 3 procedure provide a precise means of extracting Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, P and S and is widely accepted as the preferred method for the determination of such extractable species.

For the Mehlich extraction, 0.5 g of soil sample was placed in a 15 mL polypropylene centrifuge tube. It is important to avoid the use of glass as trace amounts of Na can be leached into solution upon contact with the extractant solution. A soil to extractant ratio of 1:10 should be used. As such 5 mL of extractant was added to each soil sample. The samples were immediately placed on a 200 rpm shaker table and were agitated for 5 minutes. Afterward, samples were filtered using a 0.45 µm filter, making sure to complete filtration within 3 minutes of removing the sample from the shaker. The filtrate was then analyzed using Spectro Genesis inductively coupled plasma optical emission spectrophotometer (ICP-OES) to determine the concentration of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, P and S. Soil pH was also determined for each size fraction prior to extraction using a pH meter.

To calculate the CEC, we first converted the concentration of each metal including Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}, as determined by the Mehlich analysis, from mg L^{-1} to cmol positive charge (+) per kg. We also converted the pH to the same units of cmol (+) kg^{-1}. We then calculated the sum of the cmol (+) kg^{-1} for these four metals and the pH to determine the soil CEC.

4.2.5 Beryllium Sorption

In order to determine the sorption of beryllium amongst the various soil fractions, 10 mg of soil sample was measured into a 50 mL polypropylene centrifuge tube. To reduce particle concentration effects in which greater concentrations of suspended soil can lead to increased aggregate formation, decreased effective surface area and thus reduced sorption capacity, we used a soil to water ratio of 0.2 g L^{-1} as referenced in previous work (Aldahan et al, 1999). As such, each soil sample was suspended in 50 mL solution of 50 ppb beryllium in ultrapure water. The pH of each solution was adjusted to 5.5, around the natural pH of the soil, as the addition of beryllium to solution caused a reduction in pH. The beryllium spike was prepared using an acidic beryllium ICP standard. The beryllium-soil solutions were allowed to equilibrate for 14 days based on previous work (Boschi and Willenbring, 2016). After two weeks, the pH was remeasured to assess potential drift; the maximum change in solution pH was only by 0.2 units. All samples were centrifuged for several hours at 5,000 revolutions per minute to ensure the removal of particles from solution. The supernatant was carefully pipetted off of the pellet and filtered using a 0.45 µm filter. The filtered solutions were analyzed using an ICP-OES to determine the concentration of unsorbed beryllium in solution. From this, sorbed beryllium concentrations were calculated and compared with the other characterized variables.

4.3 Results and Discussion

4.3.1 Grain Size and Surface Area

4.3.1.1 Grain Size versus Surface Area

As expected, as grain size decreases, the surface area of particles in either soil increased (Figure 4.1). The relationship between grain size and surface area for both soils is non-linear and is best represented by a logarithmic trend. This varies from the expected power law relationship between grain size and surface area that would result if all particles assumed a spherical geometry according to the relationship in Equation 4.2 where *SSA* represents the specific surface area in g m^{-2}, ρ represents particle density in g cm^{-3} and *D* represents particle diameter or grain size in µm:

(Eq. 4.2)

$$SSA = \frac{6}{\rho D}$$

This approximation has been used in previous work to derive a relationship between sorbed beryllium amounts and surface area calculated from grain size (Taylor et al, 2014). However, if we use the grain size values measured in this study to calculate the surface area for each sample size fraction, we find that the theoretical surface area is several orders of magnitude smaller than the actual surface area in the oxisol and inceptisol samples. We know from a general knowledge of soil texture that clay minerals deviate from sphericity and have large surface areas due to collective layers of crystalline metal oxides. This makes it very difficult to approximate surface area using the relationship in Equation 4.2. Interestingly however, the greatest deviation between the theoretical and actual surface area is evident in the larger grain size fractions. This indicates that the larger particle size fractions, consisting mostly of quartz, also deviate from sphericity due to pitting and the formation of microfractures resulting from greater rates of chemical weathering in the tropical environment of Luquillo (Schulz and White, 1999). This causes the larger particle size fractions to have greater surface areas than otherwise expected according to their particle size. Considering the oxisol had a greater abundance of quartz in the larger sized fractions relative to the inceptisol sample, it would explain the greater difference between the theoretical and actual surface area in this soil type. The theoretical surface area not only deviates in its mathematical relationship with grain size, it is also orders of magnitude less than the actual surface area. Therefore, the use of grain size to calculate surface area is a poor approximation and should be avoided.

Overall, the actual surface area of the oxisol soil was at least two times greater than that of the inceptisol. Also the oxisol sample exhibited a greater range in surface area with respect to grain size. The large abundance of clay minerals including kaolinite and iron and aluminum oxides present in the oxisol soil relative to the inceptisol contributes to it having a greater surface area.

4.3.1.2 Beryllium Sorption vs Grain Size and Surface Area

As expected, beryllium behaves like other metal species in that sorbed beryllium concentrations increase with surface area and decrease with grain size. This finding is consistent with previous work that reported grain size dependency on sorbed beryllium concentrations (Aldahan et al, 1999; Graly et al, 2010; Taylor et al, 2014; Shen et al, 2004b; Wallbrink and Murray, 1996; Willenbring and von Blanckenburg, 2010a). When comparing beryllium sorption with grain size and surface area, it appears that beryllium sorption more strongly correlates with surface area than grain size within a given soil type (Figure 4.2 and 4.3). This result is understandable considering sorption is a surface phenomenon and grain size does not predict the total amount of available surface for beryllium to form an association. Certain minerals, particularly aluminosilicate clays, have numerous layers attributing to their large surface areas which cannot be accurately quantified using grain size. Work previously published by Graly et al. (2010) also concluded when trying to standardize beryllium concentrations with depth using grain size approximations that other factors were probably influencing beryllium distribution. Although beryllium sorption does not correlate as strongly with grain size within a given soil type, the relationship between sorbed beryllium amounts and grain size is more consistent relative to surface area when considering all soil samples; there appears to be a less precision with beryllium sorption amongst samples with similar surface areas. Not only is there little agreement in sorbed beryllium amounts for samples with similar surface areas, greater concentrations of sorbed beryllium are associated with smaller surface area. For example, although the oxisol soil has a greater surface area, up to eight times more beryllium is sorbed per unit surface area by the inceptisol soil. The lack of correlation between total beryllium and surface area when considering both soils reflects the differences in the relationship between surface area and grain size for either soil. The difference in beryllium sorption with surface area relates to differences in the distribution of organic matter, mineralogy and other chemical properties with each size fraction for either soil. This indicates that although surface area is an important control, it is not the dominant control on beryllium sorption. It also suggests that the chemical composition also influences a soil’s sorption capacity with respect to beryllium sorption.

Unfortunately, although there is data available reporting good correlation between sorbed beryllium amounts and grain size similar to this work, there is little published data relating sorbed beryllium concentrations to surface area. Recent work by Taylor et al. (2014) investigated the distribution of ^{7}Be among various particle size fractions for two different soils. Unlike in the present work, they first sorbed beryllium to either soil and then separated each into size fractions using sedimentation columns. Although they did not measure surface area directly but rather approximated it from grain size measurements, they also observed an overall greater beryllium sorption among the more coarsely textured soil with a lower surface area. Additionally, work done by Korte et al. (1976) demonstrated a significant correlation ($R^2 = 0.81$) between the surface area measured for 11 different soils and the sorbed beryllium concentration. However they used ethylene glycol monomethyl ether (EGME) to quantify surface area which unlike N_2 gas adsorption, estimates both external and internal rather than only the external surface area (Chiou et al, 1993). As such, EGME methods will report greater surface areas than gas adsorption methods. Perhaps being smaller, beryllium is capable of diffusing into the interior of the bulk solid and thus its sorption is better approximated by EGME methods.

4.3.2 Percent Carbon and Nitrogen

Overall, there is a greater amount of carbon and nitrogen associated with the inceptisol sample. The carbon to nitrogen ratio, which can be broadly related to the composition of the organic matter, appears relatively consistent between both soils types. Beryllium sorption increases logarithmically with increasing percent carbon and percent nitrogen (Figure 4.4 and 4.5). This positive relationship between soil carbon content and sorbed beryllium concentration is supported in other geochemical studies (Barg et al, 1997; Lundberg et al, 1983; Takahashi et al, 1999; Vesely, 1998; Vesely et al 2002).

However, the dependence of beryllium sorption on carbon and nitrogen content is inconsistent between soils types. Beryllium concentrations correlate well with percent carbon and nitrogen in the inceptisol soil but not in the oxisol soil. This result reflects the poor correlation of either nutrient with surface area in the oxisol sample; the carbon and nitrogen content increases with increasing surface area with the exception of the smallest size fraction (Table 4.1). One explanation is that the smallest clay-sized particles form larger aggregates with a reduced surface area and thus reduced amounts of organic coatings. When those aggregates are broken down during the separation process, the collective surface area increases while the percent carbon and nitrogen remain constant thus distorting the relationship between both variables. Conveniently, through the process of separating the soil by size fractions, we were able to disrupt the relationship between surface area and percent carbon content which helped to elucidate whether beryllium sorption co-varied with percent carbon, both of which scale with surface area, or was actually dependent on the percent carbon.

Unfortunately, we are limited at the data we can derive from percent carbon and nitrogen content. Although this information provides quantitative information, it fails to provide a qualitative assessment of the organic matter in either soil. The differences in beryllium sorption amongst the two soil types and soil size fractions could also be a result of differences in the chemical nature of the organic matter. For example, beryllium is known to form stronger associations with certain types of organic functionalities including aromatic dicarboxylic and dihydroxyl groups relative to more aliphatic, less oxygenated organic matter (Esteves da Silva et al, 1996, Alderighi et al, 2000). Previous work conducted by Stone (2014) characterized the organic matter chemistry of both soil types using nuclear magnetic resonance (NMR) to determine the type and relative abundance of functional groups. Although she noted no major differences in the soil organic matter (SOM) chemistry between soil fractions, she did note an overall abundance of alkyl and *O*-alkyl functional groups like those found in polysaccharides. The composition of SOM is correlative with the chemistry of tropical plant litter and roots (Stone, 2014). The abundance of aliphatic compounds is also consistent with preferred stabilization and recalcitrance of compounds like cutin, suberin and lipids in tropical soils having larger amounts of iron oxides. Because mineralogy changes with particle size, the quality of organic matter may also scale with particle size. For example, in the oxisol sample, the abundance of iron and aluminum oxides increased with decreasing particle size and then decreased significantly in the smallest size fraction which was mimicked by the percent carbon. If aliphatic compounds are more preferentially stabilized by metal oxides, then the difference in mineralogical composition in the smallest fraction may also relate to a change in the organic matter composition. Although smaller in abundance, aromatic functional groups, which are associated with large beryllium stability constants, were also reported in these soils. If these aromatic functionalities were more highly associated with the smallest size fraction it would explain the larger amount of sorbed beryllium despite having a lower percent carbon. Beryllium forms highly stable complexes with dicarboxylic, dihydroxyaromatic and hydroxylcarboxylic ligands, all of which are bidentate ligands capable of chelation

(Alderighi et al, 2000). Therefore, although the percent carbon was low in the smallest size fraction, the quality of organic matter in terms of beryllium sorption may have been more favorable supporting the deviation in correlation with percent carbon. This indicates that a more representative metric, opposed to the commonly reported percent carbon or total organic carbon (TOC), may be needed to assess organic matter when comparing it to sorbed beryllium concentrations.

Additionally, correlations between beryllium sorption and organic carbon are challenging to assess because there are compounding factors affecting the sorption capacity of the organic fraction. This may also help to explain the lack of consensus in the geochemical literature regarding the role of organic matter in the retention of beryllium. For example, a study by Lum and Gammon (1985) on the geochemical availability of beryllium in lake and river surface sediments did not show significant correlation between organic matter content and beryllium concentration yet a separate study conducted by Lundberg et al. (1983) reported that the organic fraction of lake sediments retains approximately 100x more ^{10}Be/g than the bulk sediment. Additionally, a global meta-analysis investigating the relationship between meteoric ^{10}Be concentrations and the physical and chemical properties of soils found no correlation between ^{10}Be and the organic matter concentrations in soils (Graly et al, 2010). Such large data analyses are difficult to interpret because in addition to the organic carbon content, chemical factors including pH and ionic strength can affect the behavior of organic matter. For example, a soil containing a higher percent carbon may still exhibit lower beryllium retention if the soil pH is below its collective acid dissociation constant, K_a. However, that same soil at higher pH above its K_a where acidic functional groups are deprotonated and available to complex beryllium would potentially sorb a greater amount of beryllium. This effect was demonstrated by Takahashi et al. (1999) in which complexation of beryllium by humic and fulvic acids reducing its sorption to minerals was dependent on the solution pH. Additionally, environments with greater ionic strength can promote the aggregation of organic matter and the occupation of negatively charged functional groups by cationic species affecting the accessibility of binding sites. This occurrence may explain the negligible influence of dissolved organic matter on beryllium among illite samples in seawater (You et al, 1989). Therefore, the composition, acidity and changes in the physical behavior of organic matter with respect to the environmental chemistry will affect its sorption capacity, which is poorly predicted by the percent carbon although frequently used as a metric. Although organic matter is able to complex beryllium and therefore is a control for beryllium retention in soils, external factors affecting its ability to complex beryllium can arise resulting in inconsistencies between sorbed beryllium concentrations and percent carbon content. Therefore, a better metric such as the abundance of dicarboxylic and dihydroxyl aromatic functionalities as well as an understanding of the organic matter chemistry including the K_a would aid in our knowledge of the relationship between sorbed beryllium amounts and organic carbon.

4.3.3 Cation Exchange Capacity

As predicted, sorbed beryllium concentrations increase with increasing cation exchange capacity (CEC) (Figure 4.6). The inceptisol soil has a greater range and magnitude of CEC values compared to the oxisol sample and the correlation of sorbed beryllium amounts with the oxisol soil is weaker. However, of all variables tested, the relationship between CEC and sorbed beryllium concentrations was the most consistent among both soil samples. Much of the association between beryllium and CEC can be attributed to its significant correlation with magnesium and calcium concentrations which are the drivers of CEC in both soils (Table 4.2). The greater CEC observed with the inceptisol sample helps to explain the larger proportion of sorbed beryllium.

Positive correlations between sorbed beryllium amounts and CEC are also reported in previous work (Korte et al, 1976; Taylor et al, 2012). Taylor et al. (2012) characterized four soils exposed to ^{7}Be fallout and the total activity of beryllium exhibited a significant, positive correlation with CEC (R^2=0.67). Similar correlation (R^2=0.62) was reported for sorbed beryllium amounts and CEC by Korte et al. (1976). Even a large compilation of global ^{10}Be data revealed a positive, albeit weak, statistically significant correlation with the CEC (Graly et al, 2010).

The strong correlation shown in the current study between beryllium and the CEC, or labile cation concentrations, may indicate that a significant portion of beryllium is associated with weakly to moderately exchangeable binding sites. This hypothesis is corroborated by the work of Taylor et al. (2012) where they reported approximately 50% of total beryllium was removed in the first step of the optimized BCR sequential extraction procedure that targets weak acid soluble, exchangeable and carbonate-bound metals. It should be noted that although small, their work indicates that with increasing residence time beryllium becomes increasingly more associated with less labile bonding sites. For example, analysis of ^{10}Be in soils by Wittman et al. (2012) and Barg et al. (1997) revealed beryllium is more highly associated with stronger, less reversible binding sites. Therefore, longer residence times than the 14 day sorption time interval used in the current study may slightly affect its association with CEC. Longer sorption time intervals would be needed to test the influence of residence time on sorbed beryllium concentrations with CEC.

The CEC is also representative of soil pH which in previous work has shown considerable influence on beryllium sorption among various organic ligands and minerals (Aldahan et al, 1999; Boschi and Willenbring 2016; You et al, 1989). Acidic soils have smaller concentrations of base cations as they have been chemically weathered and exchanged with protons. Conversely, soils with greater amounts of base cations, and thus a greater CEC, are higher in pH. Therefore, CEC can be directly related to pH in that CEC increases with increasing pH. Prior to the addition of the acidic beryllium spike, it was determined that the oxisol samples were more acidic than the inceptisols which correlates with it having a lower overall CEC. Therefore although we did not directly assess the influence of pH on beryllium sorption, the relationship between sorbed beryllium amounts and CEC indirectly accounts for this variable.

Not only does beryllium correlate well with CEC but it is also explains why greater amounts of beryllium are sorbed by the inceptisol sample. Unlike the other variables, there is a better agreement in sorbed beryllium concentrations for a given CEC between both soils types. This result indicates that CEC is viable option for standardizing beryllium sorption between differing soil types.

4.3.4 Phosphorus and Sulfur

Sulfur concentration showed a strong, positive correlation with sorbed beryllium amounts within a given soil type and also correlated well between soil types (Figure 4.7). This supports previous work that showed strong complexation of beryllium by sulfur oxides relative to other ligands, highlighting their potential importance to beryllium retention in soils (Alderighi et al, 2000; Boschi and Willenbring, 2016 and *in review*). Unlike sulfur, there is poor correlation with phosphorus concentration not only between soil type but within individual soils (Figure 4.8). Although beryllium positively correlates with phosphorus in the inceptisol soil, the reverse trend is apparent in the oxisol sample. Similar to percent carbon, the lack of correlation in the oxisol sample is due to a lack of correlation between phosphorus concentration and grain size. Rather the phosphorus concentration positively correlated with the with the aluminum oxide concentration which did not scale with grain size.

Phosphorus and sulfur oxides are important ligands that influence the sorptive behavior of metals in soil environments. Phosphorus and sulfur oxides can act to enhance metal retention either through increased sorption by enhancing the negative charge density on the surface of soils or through precipitation mechanisms (Violante et al, 2008). Of the phosphorus in soils, most exists in its oxidized form as phosphate. Phosphates are predominantly associated with organic matter as monoesters ($R\text{-}O\text{-}PO_3^{2-}$), with smaller abundances in the form of diester phosphates ($R\text{-}O\text{-}PO_2^{-}\text{-}O\text{-}R$) and phosphonate ($R\text{-}PO_3^{-}$) (Frossard et al, 2012). Hedley extractions performed on these soils by Mage and Porder (2013) reveal that 75 and 94% of the labile phosphorus extracted with 0.5 N $NaHCO_3$ is organically associated in the bulk inceptisol and oxisol soils, respectively (Table 4.3 and 4.4). Even 73% and 74% of the more stably phosphorus extracted with 0.1 N NaOH was characterized as organically bound in the bulk inceptisol and oxisol soils, respectively.

It is worth noting that according to the results reported by Mage and Porder (2013), the weakly sorbed phosphorus fraction only accounted for approximately 4% and 6% of the total phosphorus stock in the oxisol and inceptisol soil, respectively. Although we used a different phosphorus extraction technique than Mage and Porder (2013), our extraction procedure (Mehlich) is designed to remove weakly bound, non-recalcitrant phosphorus. We can roughly estimate that the concentrations of phosphorus we report are only a small fraction of the total available phosphorus in the soil (McCray et al, 2012). It is likely that we extracted more than just the weakly extractable phosphorus fraction using the Mehlich procedure because we report phosphorus concentrations greater than the total phosphorus content reported using the Hedley analysis. For example, the Hedley procedure extracted a total of 205 ppm of phosphorus in the inceptisol sample although we report phosphorus concentrations as high as 373 mg kg^{-1} in the individual size fractions. However, we report greater phosphorus concentrations because we are examining amounts in separate size fractions where, especially in smaller fractions, phosphorus concentrations are not diluted by larger grains (the >250 µm fraction) that most likely have lower amounts of sorbed phosphorus. Therefore, our phosphorus concentrations will be greater than what was reported for the bulk soil. However, because the phosphorus concentrations we report are such a small proportion of the total phosphorus in these soils, it could explain why we observe poor correlation with sorbed beryllium. It also helps to explain why we see a weaker correlation with beryllium sorption and phosphorus in the oxisol sample; less phosphorus is removed from the labile and non-labile phosphorus fractions of the oxisol sample during the Hedley extraction. The oxisol sample has greater amounts of goethite that is not found in the inceptisol sample. Changes in mineralogy affect the physiochemical association of phosphorus with soil surfaces, and thus its extractability. Even if the Mehlich procedure removed a portion of what would be extracted by step two of the Hedley procedure involving 0.1 N NaOH, as estimated in method comparison studies, there would still remain a large amount of phosphorus strongly bound to the surfaces of aluminum oxides and organics which beryllium has the potential to bind to but is not accounted for (McCray et al, 2012).

The poor correlation with beryllium can also relate to the speciation of phosphorus. Even if we are able to better estimate the availability of phosphorus in each soil fraction, it would be ideal to characterize its speciation including the proportion of reduced and oxidized phosphorus as well as the ratio of phosphate to phosphonate using ^{31}P nuclear magnetic resonance. Although most phosphorus exists as phosphate, we know from previously published stability constants that beryllium sorbs more strongly to phosphonates and therefore quantifying its abundance would be useful. In fact, phosphonates are one of the few ligands that can compete with hydrolysis for beryllium complexation (Alderighi et al, 2000). There are many examples in the literature discussing the thermodynamic favorability of beryllium-phosphonate complexes (Alderighi et al 1999; Alderighi et al 2000; Boschi and Willenbring 2016). It has been shown that monophosphonate, a monodentate ligand, provides a more stable complex with beryllium relative to malonic acid, a bidenate ligand capable of chelating beryllium.

Although phosphonate is not as abundant as phosphate in soils, stability constants associated with monophosphonate-beryllium complexes are about three orders of magnitude greater than monophosphate-beryllium complexes (Alderighi et al, 2000). Therefore a small abundance can have a big impact on beryllium sorption. Knowing the relative concentrations of phosphorus species may also help to better characterize the relationship between sorbed beryllium amounts and phosphorus in soils.

Similarly to phosphorus, the majority of sulfur, >90%, is associated with the organic fraction of soils, particularly well aerated and drained surface soils (Frossard et al, 2012). Sulfur is able to exist in a range of oxidation states (S^{2-} to S^{6+}), greater than any other geochemically abundant element. As such, organic sulfur can exist in a reduced state as sulfides, an intermediate oxidation state in the form of sulfoxides and sulfonates and as strongly oxidized ester sulfate (Solomon, 2003). Inorganic sulfur is almost entirely in the form of sulfate in aerated soils and as sulfide under anaerobic conditions (Freney and Williams, 1983). Although the relative magnitude of each species depends on the redox conditions and microbial activity, the various forms of sulfur have the potential to complex beryllium either electrostatically or covalently.

Sulfur inputs to a system include atmospheric deposition of sulfate containing aerosols, direct sorption of SO_2 gas, mineral weathering and organic matter degradation (Edwards, 1998). Atmospheric input of sulfates and SO_2 are particularly substantial in industrialized regions and could have a significant impact on beryllium retention in soils. In the region of the El Yunque National Forest where the soils were collected, the majority of sulfur found in the surface soils originates from the wet and dry deposition of atmospheric sources opposed to bedrock weathering (Yi-Balan et al, 2014). According to research done by Yi-Balan et al. (2014), atmospheric contributions of sulfate are mostly marine in origin with slightly less originating from non-sea salt sources. Considering these soils are slightly acidic and contain an abundance of clay minerals, they are able to retain the atmospheric inputs of sulfur species as evidenced by minimal loss of sulfur to stream systems in parts of the watershed (Yi-Balan et al, 2014).

Sulfate retention in soils is highly dependent on several factors including pH, with smaller amounts sorbed in neutral or alkaline soils (Edwards, 1998). Sulfate sorption is rapid and is enhanced in soils containing iron and aluminum oxides and 1:1 clays like kaolinite as opposed to montmorillonite which has a greater net negative charge. However, kaolinite is typically associated with lower organic matter retention therefore proving less favorable for ester sulfate linkages. Specific sorption processes which involve ligand exchange with sulfate on the surfaces of iron and aluminum oxides resulting in a strong chemical association are believed to be the predominant sorption mechanism of sulfur in soils opposed to weaker electrostatic sorption mechanisms (Edwards, 1998). In addition to sorption, immobilization, or the assimilation and conversion of inorganic sulfur to organic forms by plants and microbes, is another key mechanism in sulfur retention in soils. As such, the majority of sulfur is found in organic forms. Considering immobilization is biotically driven, rates are controlled by temperature, moisture and soil carbon content. Therefore, greater amounts of organic sulfur are found in upper soil horizons where there is adequate soil moisture and carbon to foster microbial activity, although these processes can also occur deeper in the soil profile.

Mechanisms promoting the release of sulfur from these reservoirs include desorption and sulfur mineralization that involves the depolymerization of large organic sulfur molecules into smaller, sulfur containing molecules or sulfate as a result of microbial and plant mediated degradation of organic matter. The rate of mineralization is also dependent on several environmental variables including temperature, moisture, organic matter content and sulfur limitation, all of which control microbial activity. Although not as significant, it should be noted that a portion of sulfur mineralization is independent of microbial activity considering plants and extracellular enzymes are also capable of hydrolyzing ester sulfates. If sulfur concentrations are below the demands of the system, any sulfur that enters the soil is quickly immobilized by incorporation into organic matter as a reserve for microbial requirements. However, mineralization will occur in systems with adequate sulfur supply. Therefore, when sulfur is in supply and conditions favor microbial activity, greater rates of mineralization will occur. A generally accepted rule is that plant material containing a C:S ration of 200:1 or less will result in sulfate mineralization while a ratio of 400:1 promotes immobilization (Edwards, 1998). Speciation of organic sulfur is also dependent on sulfur limitation with greater depletion of ester sulfates in sulfur limited soils as this form of sulfur is most easily metabolized by cleavage of the C-O-S linkage. Storm events appear to trigger the biggest loss of sulfate and other soluble, low molecular weight organic compounds containing sulfur to surface and ground waters, the extent of which depends on system properties like hydraulic conductivity and the magnitude and frequency of rainfall.

Sulfur is a dynamic pool, thus it is important to consider how its transformations driven by various biotic and abiotic processes affect the net beryllium sorption capacity in soils. It is unclear how sulfur complexed beryllium is affected by chemical reactions involving sulfurous compounds both due to processes involving plants and microbes and changes in redox conditions. Additionally, environmental conditions promoting the leaching of sulfates from soils may also enhance the mobilization of complexed beryllium. Previous, unpublished work has demonstrated a positive correlation between dissolved beryllium and sulfate concentrations in stream water that originated from soils exposed to an inflow of water with high sulfate concentrations causing beryllium mobilization (Vesely et al, 2002). Although there is some potential for beryllium mobilization as a result of sulfur cycling, the bulk of sulfur (>90%) is immobilized through incorporation in the organic matter fraction and only a small portion (1-3%) is converted to inorganic sulfate annually (Freney and Williams, 1983). We also know from previous work that beryllium complexation by sulfur oxides is strong and resistant to chemical disruption. Therefore, it may be possible that beryllium losses due to sulfur cycling are less significant. Additional work would be required to determine if the strength of the relationship between beryllium and sulfur is maintained in soils with various chemical and physical properties and under different environmental conditions.

4.3.5 Mineralogy

The difference in parent material is reflected in the respective mineralogies of the sols the form from the bedrock (Table 4.5). The oxisol sample, which was produced from volcaniclastics, has a greater abundance of kaolinite and goethite as a result of extensive chemical and physical weathering that occurred over long time scales. Conversely, hornblende, feldspar and larger amounts of gibbsite were identified in the inceptisol. The mineralogical composition is consistent with expected weathering products of the quartz diorite bedrock in this region (Buss et al 2008). Similar amounts of quartz were observed for both soils which is most likely the result of fractionation by grain size. The abundance of quartz decreased non-linearly with decreasing grain size. Conversely, kaolinite increased with decreasing grain size.

Of all minerals, sorbed beryllium concentrations scaled with kaolinite and quartz abundances. Therefore, their relationships will be more closely examined. Although iron and aluminum oxides are known to affect the sorption of metals in soils, there was no correlation with gibbsite and goethite. This result is supported by previous work which has shown little sorption of beryllium onto goethite, especially in acidic soils like those in the present study where the pH is below its point zero charge of 7.8 (Boschi and Willenbring, 2016). Additionally, we found no correlation with feldspar minerals although previous work has shown strong retention of ^{7}Be by crushed diorite (Kaste et al, 2013). We hypothesize that the exposure of reactive surfaces through physical abrasion and fracturing provided larger K_d values than may be typically observed for physically unaltered diorite material.

Sorbed beryllium concentrations correlated most strongly with the percent kaolinite in each of the individual soils relative to all other variables tested (Figure 4.9). In fact, correlation between sorbed beryllium and percent kaolinite was the strongest in the oxisol soil relative to all of the other variables characterized indicating that the abundance of clays, specifically kaolinite, has significant control on beryllium sorption in the oxisol sample. This is expected considering kaolinite represents a larger portion of the total oxisol mineralogy relative to the inceptisol. The percent kaolinite also correlates strongly with beryllium sorption in the inceptisol sample, although we still observe a significant amount of beryllium sorption even when zero kaolinite is reported. Therefore, although there is a strong correlation, kaolinite abundance is not the only influence on beryllium sorption in the inceptisol. In addition, there is less agreement in sorbed beryllium amounts with respect to the abundance of kaolinite between both soils. For example, similar amounts of beryllium were sorbed by the inceptisol soil containing no kaolinite and the oxisol soil containing about 50% kaolinite. This result indicates that although beryllium correlates well with kaolinite, it does not explain the greater amount of beryllium sorbed by the inceptisol and is not a consistent proxy between different soil types.

Conversely, there is a very strong, inverse correlation of sorbed beryllium concentration with quartz abundance both within individual soil type and between both soils (Figure 4.10). In fact, among all of the variables characterized in this study, beryllium sorption scales most strongly with quartz abundance. Beryllium concentrations are inversely proportional and scale non-linearly with percent quartz. Quartz is resistant to weathering due to its chemical stability. Thus, its abundance would decrease with decreasing grain size and correlates very strongly with grain size ($R^2 > 0.99$). Although beryllium also correlates strongly with grain size, it relates more strongly with quartz abundance. We do not expect that beryllium is sorbed to quartz because of its low surface charge. Rather, quartz abundance is inversely proportional to properties that directly affect beryllium sorption like surface area and clay amounts which control the type and abundance of sorption sites. Considering the strong, inverse relationship between quartz and beryllium, the percent inverse quartz is a key variable when comparing beryllium amounts in different soils.

4.3.6 Sorption Standardization Methods

When attempting to standardize the effects of various chemical and physical properties on beryllium sorption potential, it is important to include variables in our model that correlate consistently with beryllium among different soil types. Therefore, we considered variables more strongly associated with sorbed beryllium concentrations among the total soil results, not just individual soil types. Pearson correlation coefficients and their statistical significance were reported for each variable to get a general understanding of the relationship with sorbed beryllium amounts (Table 4.6). Considering sorbed beryllium varies non-linearly with each of the variables as demonstrated in Figures 4.3-4.10, a correlation matrix was also calculated using the log transformation of each variable to demonstrate how this preparation provided a stronger model. We see that for all variables, with the exclusion of sulfur and phosphorus concentrations, the log transformation provides a stronger correlation coefficient and is more statistically significant than using a linear relationship to predict sorbed beryllium amounts. However, we would argue that even for sulfur, using a log scale is preferable considering within individual soil types, the concentration of sorbed beryllium relates more strongly to the log of the sulfur concentration. Therefore it would be inconsistent and less accurate to assume a linear relationship when combining both soil data sets if it scales logarithmically with sulfur concentration among individual soil types and with all other variables. Therefore we used log transformed variables to predict sorbed beryllium amounts in our model. We expect a logarithmic relationship based on the separation of soil samples by grain size and its logarithmic relationship with the chemical variables tested. As expected, most chemical properties increase non-linearly with decreasing grain size. If beryllium retention is driven by those chemical variables, it will also mimic a similar logarithmic profile based on the availability of charge and binding sites.

To produce a more rigorous model, we eliminated certain variables based on their poor ability to predict beryllium sorption. Although phosphorus may be significant in other systems, it poorly correlates with beryllium in our system showing a positive correlation in one soil type and a negative correlation in the other. This is potentially due to its speciation and availability as discussed in the previous section. Unfortunately, the phosphorus concentration does not quantify the more reactive forms of phosphorus and is perhaps a poor metric for beryllium's association with phosphorus containing compounds. Additionally, the correlation with surface area was poor and insignificant between both soil samples. This is supported by lack of correlation between beryllium and minerals like goethite that largely contribute to surface area but provide little beryllium retention, particularly under acidic conditions. Therefore surface area is not representative of surface charge, as evidenced by its very poor correlation with CEC (R=0.07), which is the chemical means by which beryllium is retained by soil materials. Beryllium sorption is driven by chemical interactions with soil materials and variables better characterizing the potential for complexation will better predict sorption amounts. Therefore on a theoretical and statistical basis, we chose to exclude phosphorus concentration and surface area from our model as they do not accurately predict sorbed beryllium amounts.

We also eliminated any variables that were collinearly related which would bias multiple regression calculations. For example, variables like percent quartz have a dependency on grain size. Considering the inverse percent quartz demonstrates the strongest correlation with sorbed beryllium amounts, we chose to exclude grain size from our model rather than eliminating quartz. Similar to surface area, grain size is not directly representative of the chemical composition of soil systems which is more strongly related to beryllium retention. Therefore we believe other variables will have better predictive capabilities.

Of all variables considered in this study, the percent quartz among both soil types was most highly associated with sorbed beryllium amounts (Figure 4.10). Conveniently quartz is the most abundant and ubiquitous silicate mineral and is measureable in most soils (Molina, 2013). We know from our work and the work of others that beryllium sorption onto quartz in negligible (Aldahan et al, 1999).   However the strong inverse relationship between sorbed beryllium amounts and the abundance of quartz can be described as a dilution effect. The greater the amount of quartz, which provides negligible sorption capacity, the smaller the abundance of materials like clay minerals and organic substances capable of strongly retaining beryllium. Therefore, we can use the mathematical relationship between percent beryllium sorption and inverse quartz abundance to make predictions regarding the total beryllium sorption capacity of different soil systems (Figure 4.11). For example, if we were to determine the meteoric beryllium concentration in a soil and wanted to estimate the total potential beryllium sorption based on the inverse percent quartz in the sample we could apply the equation presented in Figure 4.11. We can then divide the measured meteoric concentration by the percent sorbed beryllium to estimate the total beryllium sorption capacity of the system. Unfortunately, the best fit equation only accounts for approximately 77% of the observed variance in sorbed beryllium amounts.

However, we can improve our model by incorporating additional variables. In order to test which variables produce the most accurate representation of the data, we performed stepwise regression analysis. Stepwise regression analysis is a process by which a set of predictor variables are successively added to a model in order to improve its predictive ability until the addition of variables fails to enhance the model based on a set of criteria. In our calculations, we defined the dependent variable as percent sorbed beryllium and the independent variables as the log percent quartz, log CEC, log percent carbon, log percent nitrogen and log sulfur concentration. The results from the regression analysis combined with our theoretical understanding of system variables revealed that the inverse percent quartz and CEC were the best subset of predictors. Table 4.7 lists variables representing model fitness including the R^2, the Akaike information criterion (AIC) and p values. The AIC predicts the simplest model with the best goodness of fit; the most favorable model having the smallest relative AIC value. As predicted by our stepwise regression analysis, the inverse percent quartz and CEC model has a low AIC relative to the other models, with both variables bearing statistical significance and strong predictive abilities (R^2=0.89) (Table 4.7). As seen in table 4.7, we also show that a model including percent inverse quartz and percent carbon yield similar statistical results.

However, as previously demonstrated, percent carbon only indicates the amount of carbon in soils but does not quantify the amount of reactive functional groups capable of complexing beryllium. As discussed in previous sections, it has been shown that TOC or percent carbon is an inconsistent predictor of beryllium concentrations. It is not to say that organic carbon does not play an important role in beryllium sorption; rather, percent carbon is not quantifying what gives organic matter its retentive capability. Although the percent carbon and inverse percent quartz model may be slightly more significant in *this* environment, it could easily fail when applying this relationship to other environments where the organic matter composition is very different. For example, let us consider two hypothetical soil systems with the same percent carbon but different organic matter chemistry. In soil A, most of the organic matter is aliphatic carbon, similar to the samples used in this study. Conversely in soil B, there is a larger abundance of more aromatic, lignin like material. We can easily defend using complexation constants that soil B will complex more beryllium even though it has the same abundance of carbon. Therefore, percent carbon is not a precise metric.

Conversely, CEC is not limited by type of minerals or organic carbon and quantifies the portion of either material that is actually contributing to retention. CEC also indirectly accounts for soil pH, which, as established in the previous chapters, exhibits a strong influence on beryllium retention and would be imperative to include in the model. None of the other variables tested account for the effect of pH. Therefore, we predict that the inverse percent quartz and CEC model more directly represents the availability of charge, both indirectly and directly, and thus provides a more robust model that can be more universally applied. It is important to note that including the phosphorus concentration and surface area into our calculations did not affect our results, validating our initial reasoning to exclude them from the model.

Although the addition of a third variable improved the correlation, an expected consequence of overfitting, it did not improve the statistical strength of the model as demonstrated with the AIC values. To emphasize this, we also report the R^2, AIC and p values for various models that implemented three terms. The addition of a third variable increased the AIC and decreased the statistical significance of variables within the model. Thus, the use of percent quartz and CEC provide the best predictive model for beryllium sorption capacity. The use of this two component model rather than quartz abundance alone improves our ability to predict sorbed beryllium concentrations (Figure 4.12).

This work was useful in identifying the physical and chemical properties of soils that best correlate with sorbed beryllium concentrations and agreed with our findings in previous work. In order to ensure that the mathematical relationship derived between percent beryllium sorption and these three variables is maintained over a variety of soil compositions, additional soils would need to be analyzed using the procedure in this study. Although the soils used in this study vary in their chemical and physical properties, soils with an even greater range of properties including samples from different soil orders and climate regimes with varying amounts of primary minerals, clays and sulfur concentrations should be included in future work.

It is worth noting that stable beryllium concentrations can be used to standardize sorbed ^{10}Be concentrations under the assumption that ^{9}Be will have the same sorption behavior as meteoric beryllium and account for preferred sorption and desorption. However, there are uncertainties that limit the use of this method. For example, differences in chemical weathering patterns at the saprolite boundary resulting in greater inputs and thus greater sorbed concentrations of ^{9}Be will act to dilute the ^{10}Be signal. Additionally, contributions of sorbed ^{10}Be and ^{9}Be concentrations to the soil are the result of different mechanisms, the former originating from processes in the atmosphere the ladder from sediment weathering. It is unclear if their associations with soil material are similar. For example, ^{10}Be may be more highly complexed by organic matter upon interacting with surface sediments. However ^{9}Be, which is weathered from bedrock material at depth, may be more highly associated with the mineral fraction. Differences in complexation binding energies can lead to preferential sorption or desorption of either isotope. This would alter the ratio of ^{10}Be/^{9}Be and the use of ^{9}Be to standardize differences in sorption amounts due to differences in soil chemistry.

4.4 Conclusions

We determined through the characterization of physical and chemical soil properties and their correlation with sorbed beryllium amounts that the inverse percent abundance of quartz and the CEC best predict beryllium concentrations. By determining the mathematical relationship between percent sorbed beryllium and the product of these two variables, we were able to predict the sorption capacity of the system and account for differences in beryllium sorption due to differences in soil properties. By measuring the CEC using the Mehlich 3 extraction method and determining the percent quartz using XRD analysis, the percent sorbed beryllium concentration could be estimated and combined with measured beryllium concentrations to determine the total beryllium concentration. Although this work provides us with a method for standardizing beryllium concentrations, a larger number of soils samples should be incorporated in future work to determine if our derived mathematical relationship predicting percent sorption is maintained with a greater variety of sample properties.

Table 4.1: Characterization of soil carbon and nitrogen content, surface area and grain size for either soil type

Soil	Surface Area ($m^2\ g^{-1}$)	Grain Size (μm)	%N	%C	C/N
Inceptisol	2.09	99	0.13	2.6	20
	4.23	47	0.13	2.6	20
	13.3	20	0.57	8.9	16
	18.2	5	0.78	10.4	13
	26.5	4	0.79	9.1	12
Oxisol	19.2	101	0.04	1.2	30
	30.7	37	0.25	4.1	16
	40.5	17	0.29	4.4	15
	47.7	4	0.66	8.8	13
	59.9	2	0.21	2.8	13

Table 4.2: Correlation coefficient for sorbed beryllium concentrations (mg kg^{-1}) and extracted cation concentrations (mg kg^{-1})

	K	Na	Ca	Mg
Inceptisol	0.65	0.45	0.80	0.73
Oxisol	0.31	0.46	0.62	0.73
Total	0.56	0.43	0.63	0.67

Table 4.3: Results from Hedley sequential phosphorus extractions for either bulk soil as reported by Mage and Porder, 2012. Total extracted phosphorus and the percent of phosphorus extracted in each step including step 1) 0.5 N $NaHCO_3$; step 2) 0.1 N NaOH; step 3) 1.0 N HCl and the remaining, residual amount are listed

	Total P (ppm)	%P $NaHCO_3$	%P NaOH	%P HCl	% P Residual
Oxisol	445.33	4.07	50.34	0.76	44.83
Inceptisol	205.20	5.93	76.88	1.14	16.05

Table 4.4: Results from Hedley sequential phosphorus extractions for either bulk soil differentiating the percent inorganic (%P_i) and percent organic (%P_o) phosphorus quantified of the total phosphorus (P_t) extracted in step 1) 0.5 N $NaHCO_3$ and step 2) 0.1 N NaOH as reported by Mage and Porder (2012)

	P_t (ppm) NaHCO3	**%P_o NaHCO3**	**%P_i NaHCO3**	**P_t (ppm) NaOH**	**%P_o NaOH**	**%P_i NaOH**
Oxisol	18.10	94.04	5.96	224.19	76.44	23.56
Inceptisol	12.16	75.125	24.87	157.76	72.92	27.08

Table 4.5: Mineralogical composition, surface area (SA) and grain size (GS) for each sample fraction. Each mineral is reported as a percent.

Soil	**SA (m^2 g^{-1})**	**GS (μm)**	**Quartz**	**Horne-blend**	**Feldspar**	**Gibbsite**	**Goethite**	**Kaolinite**
Inceptisol	2.09	99	75	9	16	0	0	0
	4.23	47	33	20	36	11	0	0
	13.3	20	13	8	3	24	0	52
	18.2	5	4	0	0	16	0	80
	26.5	4	1	0	0	16	0	83
Oxisol	19.2	101	90	0	0	9	0	1
	30.7	37	45	0	0	9	0	47
	40.5	17	17	0	0	16	2	65
	47.7	4	6	0	0	8	14	72
	59.9	2	1	0	0	2	13	85

Table 4.6: Summary of correlation coefficients and significance of correlation (P values) for sorbed beryllium amounts with each variable for total soil results. Statistically insignificant correlations are shown in red.

	R	R^2	P		R	R^2	P
%Quartz^{-1}	-0.85	0.73	0.002	Log (%Quartz^{-1})	-0.88	0.77	0.001
CEC	0.81	0.65	0.005	Log (CEC)	0.85	0.73	0.002
S	0.87	0.76	0.001	Log (S)	0.84	0.71	0.002
GS	-0.81	0.65	0.005	Log (GS)	-0.83	0.68	0.003
%N	0.78	0.61	0.007	Log (%N)	0.82	0.67	0.004
%C	0.74	0.55	0.014	Log (%C)	0.76	0.58	0.010
SSA	0.29	0.09	0.410	Log (SSA)	0.37	0.13	0.296
P	-0.24	0.06	0.504	Log (P)	-0.06	0.04	0.865

Table 4.7: Summary of stepwise regression analysis model fit parameters including the correlation coefficient, AIC and P values. Statistically insignificant values are shown in red.

Model	R^2	AIC	P Value
Log %Quartz^{-1}	0.89	99.0	0.0164
Log CEC			0.0313
Log %Quartz^{-1}	0.89	98.5	0.0028
Log %C			0.0248
Log %Quartz^{-1}	0.82	104	0.08022
Log S			0.22404
Log %Quartz^{-1}	0.91	106	0.1603
Log CEC			0.0489
Log S			0.2733
Log %Quartz^{-1}	0.93	103	0.0141
Log CEC			0.1324
Log %C			0.1066
Log %Quartz^{-1}	0.89	107	0.02619
Log S			0.83754
Log %C			0.08063

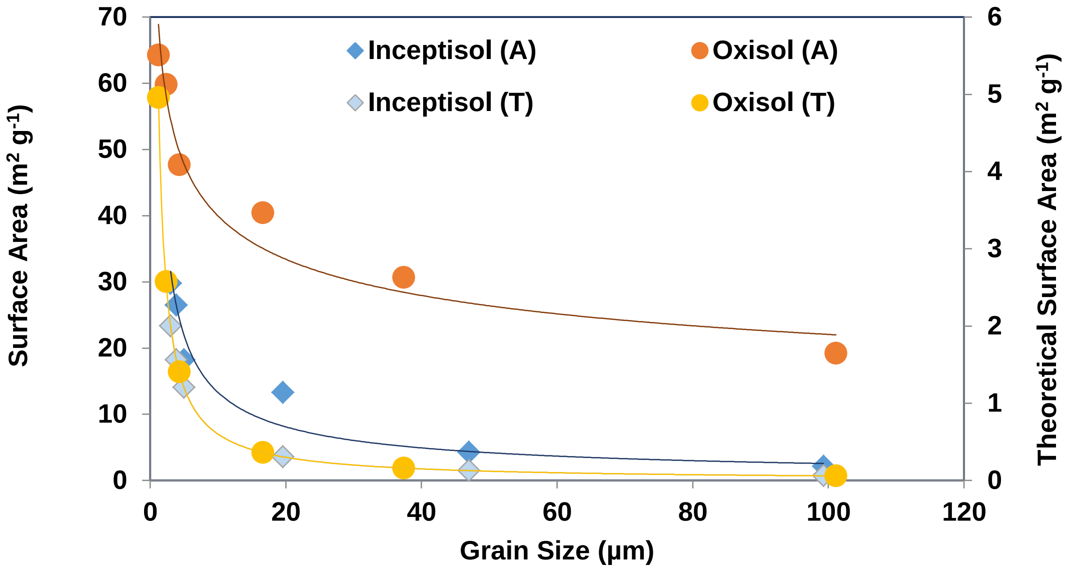

Figure 4.1: Relationship between the actual surface area (A) and theoretical surface area (T) and grain size for both the oxisol (orange) and inceptisol (blue) soils. The surface area of the oxisol was over two times greater than that of the inceptisol.

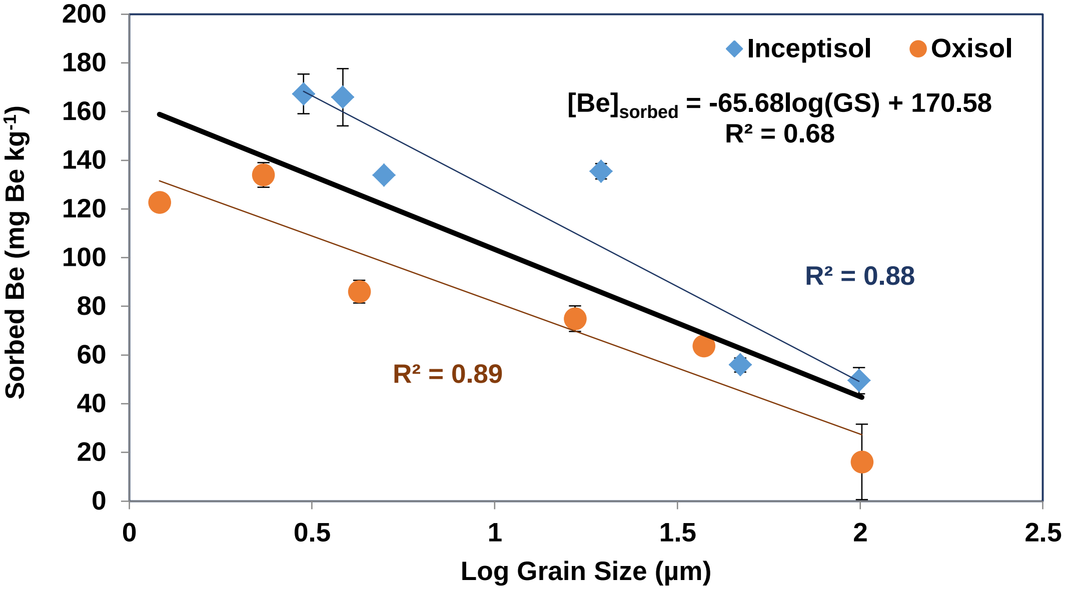

Figure 4.2: Dependence of sorbed beryllium concentrations on the log grain size for the oxisol (orange), inceptisol (blue) and combined soil types (black).

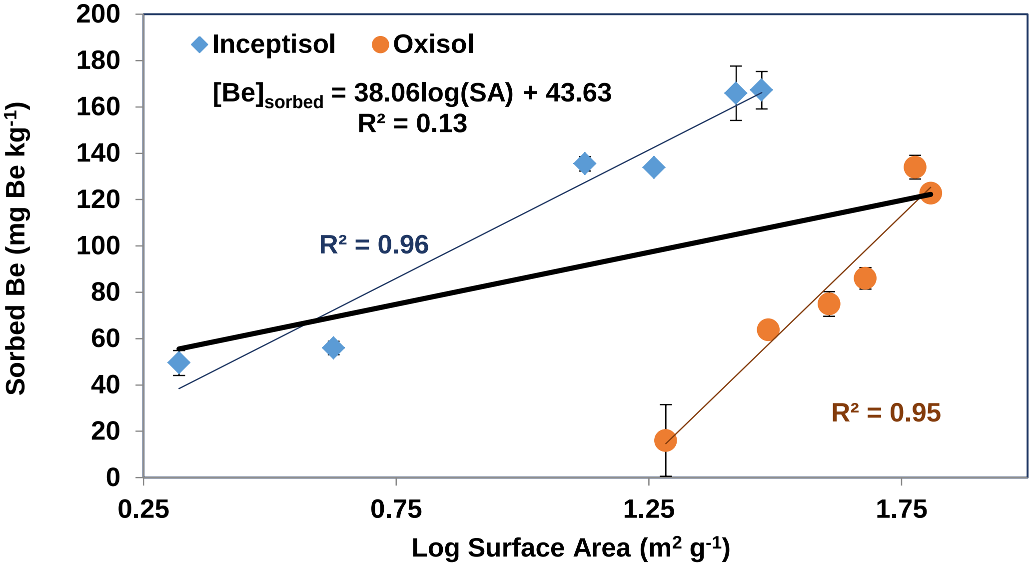

Figure 4.3: Dependence of sorbed beryllium concentrations on the log surface area for the oxisol (orange), inceptisol (blue) and combined soil types (black).

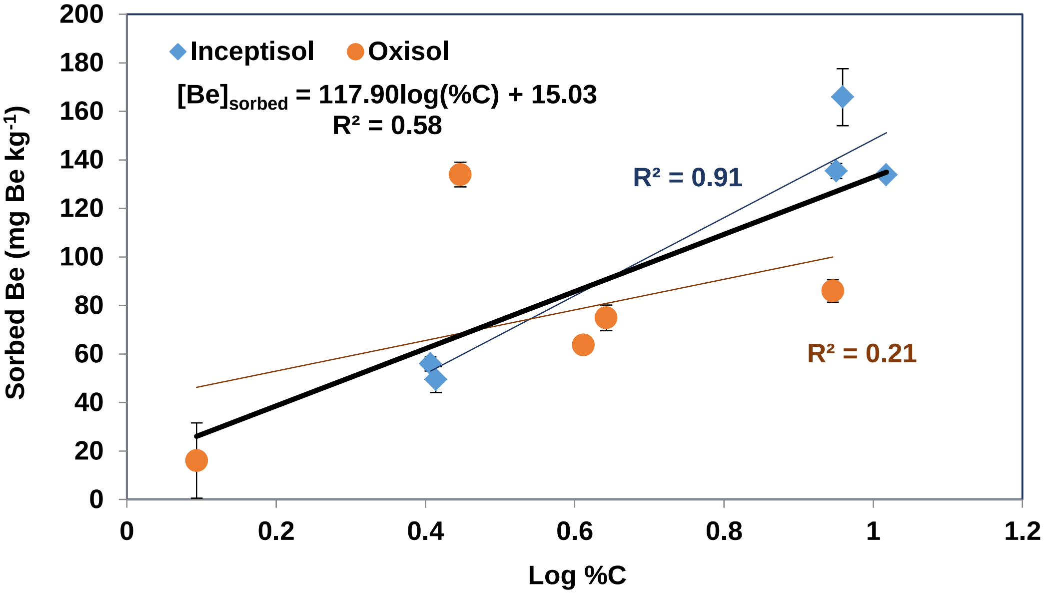

Figure 4.4: Dependence of sorbed beryllium concentrations on the log percent carbon for the oxisol (orange), inceptisol (blue) and combined soil types (black).

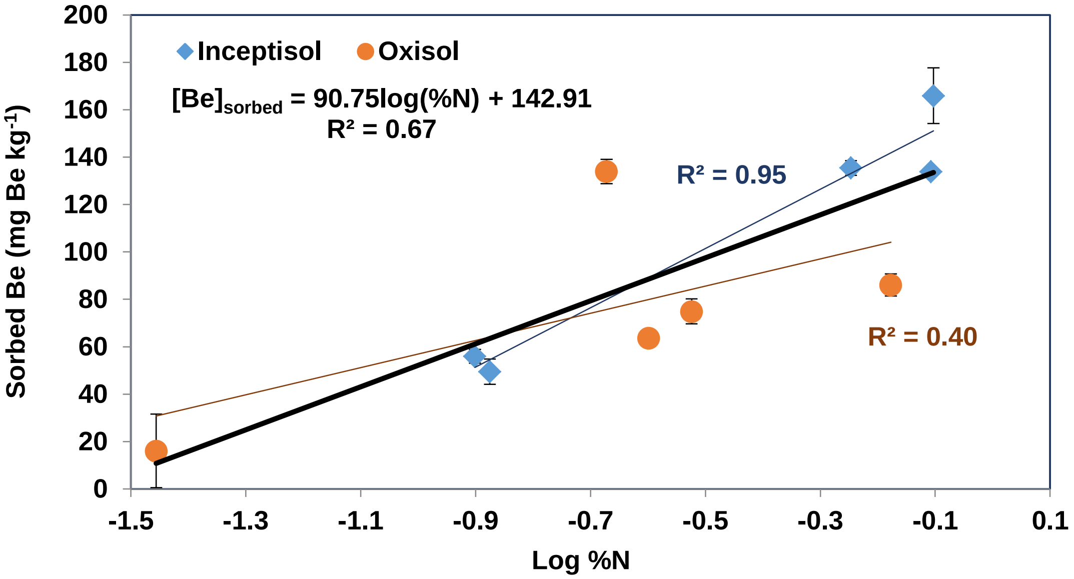

Figure 4.5: Dependence of sorbed beryllium concentrations on the log percent nitrogen for the oxisol (orange), inceptisol (blue) and combined soil types (black).

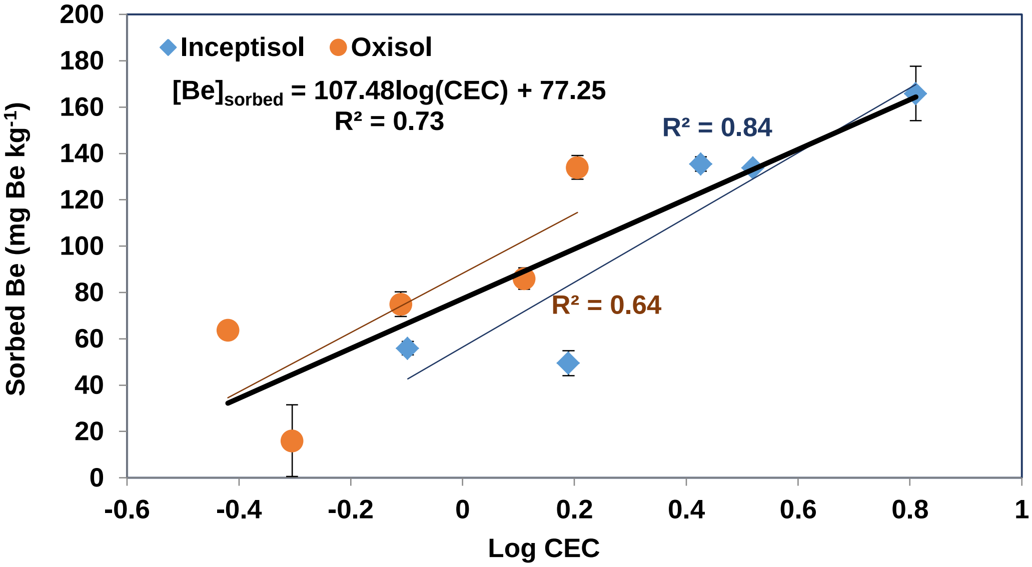

Figure 4.6: Dependence of sorbed beryllium concentrations on the log CEC for the oxisol (orange), inceptisol (blue) and combined soil types (black).

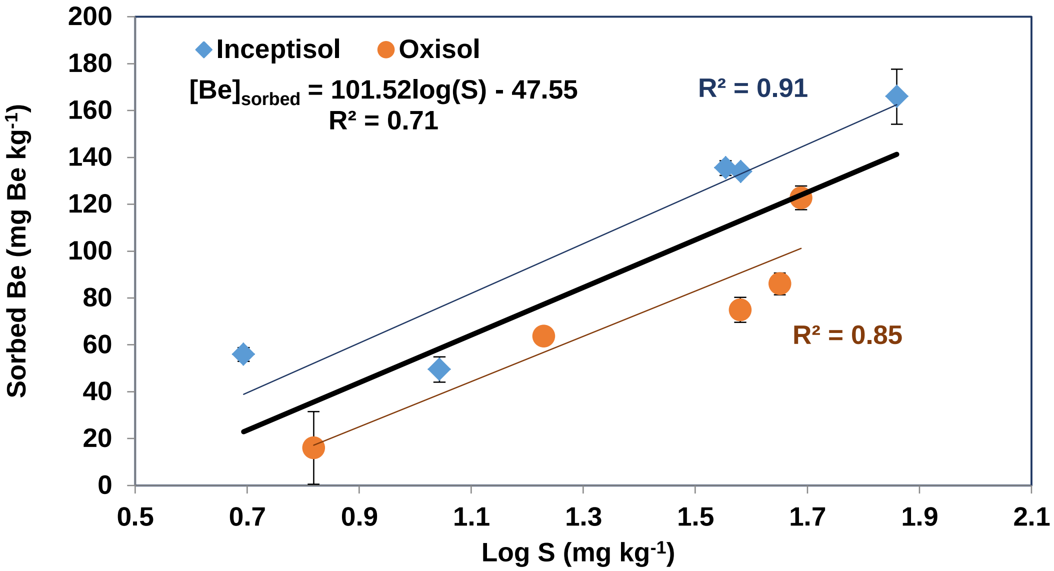

Figure 4.7: Dependence of sorbed beryllium concentrations on the log sulfur concentration for the oxisol (orange), inceptisol (blue) and combined soil types (black).

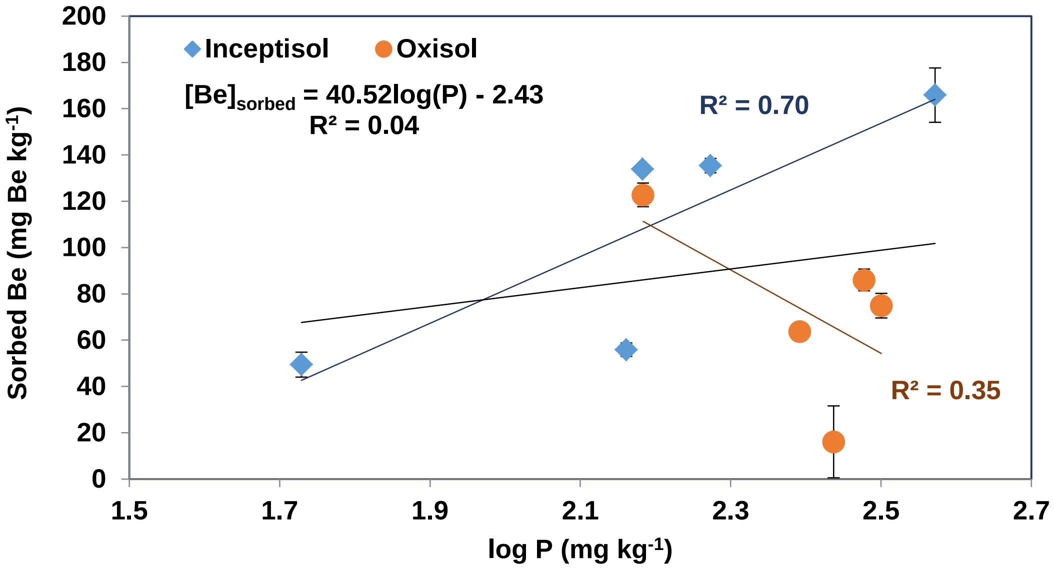

Figure 4.8: Dependence of sorbed beryllium concentrations on the log phosphorus concentration for the oxisol (orange), inceptisol (blue) and combined soil types (black).
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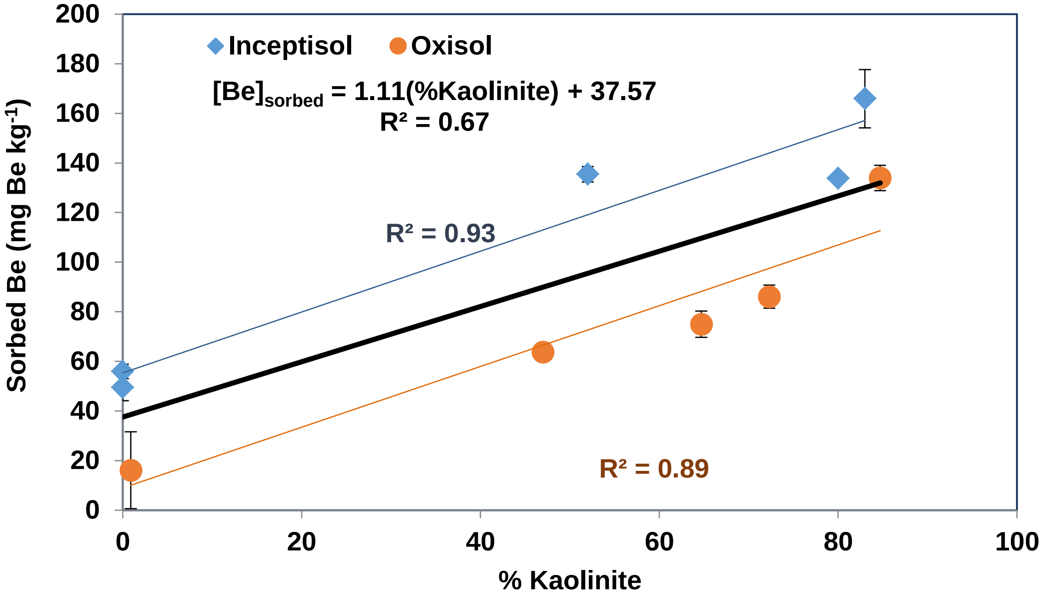

Figure 4.9: Dependence of sorbed beryllium concentrations on percent kaolinite for the oxisol (orange), inceptisol (blue) and combined soil types (black).

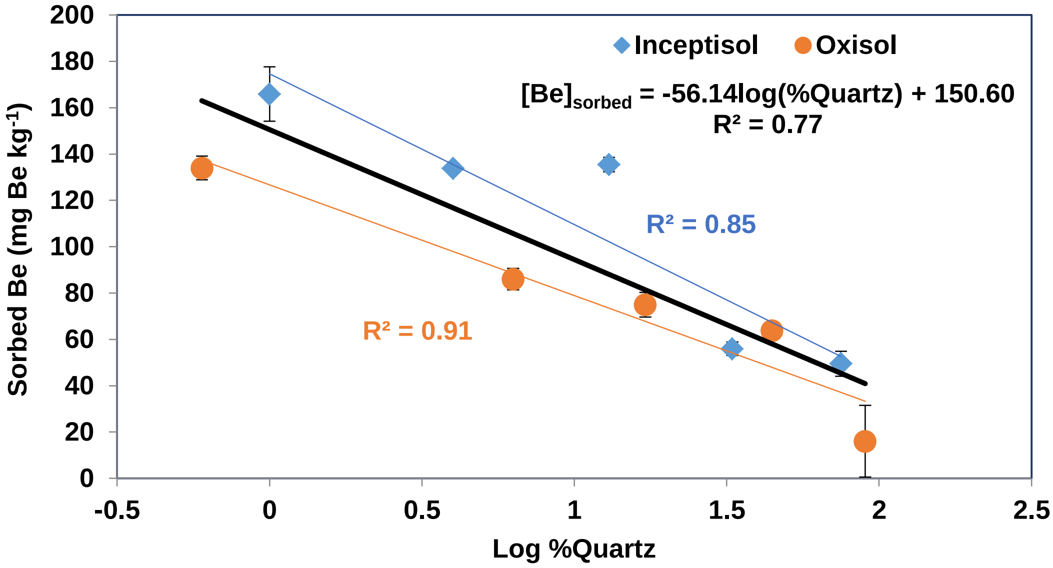

Figure 4.10: Dependence of sorbed beryllium concentrations on the log percent quartz for the oxisol (orange), inceptisol (blue) and combined soil types (black).

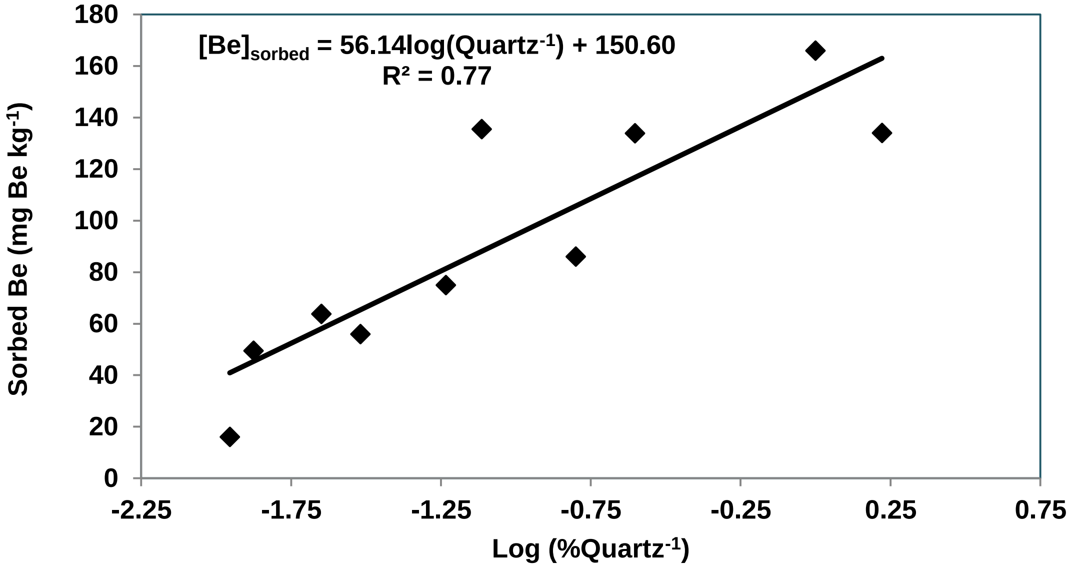

Figure 4.11: Dependence of percent sorbed beryllium on the log percent quartz^{-1}.

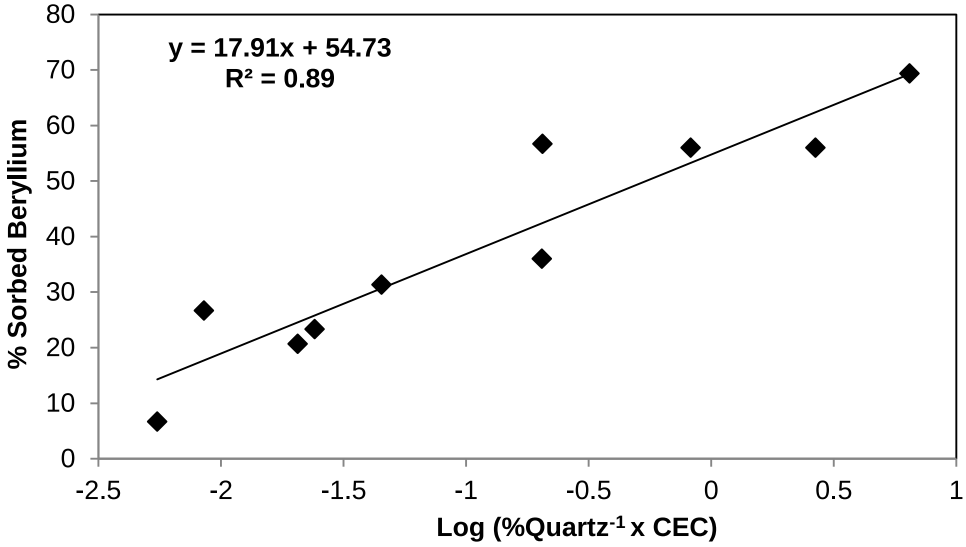

Figure 4.12: Dependence of percent sorbed beryllium on the log of the product of percent quartz^{-1} and CEC.

CHAPTER 5

CONCLUSIONS

This body of work improves our understanding of the major controls on the geochemical behavior of beryllium in soil and aquatic systems. The use of beryllium isotopes for geomorphologic applications hinges on knowledge of environmental factors affecting beryllium concentrations and thus sediment flux calculations. Additionally, beryllium contamination as a result of industrial activity combined with its severe toxicity necessitates an understanding of conditions that enhance sorption or mobilization into solution. Through the use of various controlled experiments, we determined the chemical and physical properties that best explain and predict the behavior of beryllium in a system.

In Chapter 2, we demonstrated that certain organic ligands and minerals are able to more strongly complex beryllium indicating that soil chemistry does matter and can significantly influence the beryllium sorption capacity of a system. Phosphonates and sulfonates exhibited the largest K_d values of all materials tested, indicating they could be a major driving force of beryllium mobility in soils and aquatic environments. Beryllium retention also varied depending on mineral composition, with illite exhibiting the greatest sorption relative to the other minerals surveyed. Overall, we conclude that pH exhibits a strong control on beryllium retention among the mineral and organic compounds with a significant increase in the amount of sorbed beryllium at a pH of 6 relative to the same system at a pH of 4.

Having gained a better understanding of which minerals and ligands most strongly sorb beryllium in Chapter 3, we used desorption experiments to not only determine which processes promoted the greatest amount of beryllium mobility but to estimate complexation mechanisms amongst select organic ligands and minerals. Although previously assumed that beryllium sorbed to the surfaces of sediment or organic matter was resistant to desorption, our results show that various processes can promote the exchange of beryllium between solid and dissolved phases. Of all four treatments, a decrease in pH caused the greatest amount of desorption which was only observed for the minerals studied. The addition of malonic acid and increasing the ionic strength also caused beryllium to desorb from montmorillonite but not illite. In fact, increasing the ionic strength caused additional beryllium to sorb to illite. This result suggests that different complexation mechanisms are controlling the sorption of beryllium among either mineral. Considering the reversibility of beryllium sorption due to changes in pH, ionic strength and organic acid complexation, we hypothesize that outer sphere processes driven by weaker electrostatic attractions govern beryllium-montmorillonite associations. Beryllium’s increased sorption and resistance to desorption from illite indicates complexation may be dominated by not only inner sphere processes but also physical inclusion within collapsed interlayer spaces. It is also estimated that inner sphere complexation dominates beryllium sorption among the organic ligands tested as evidenced by the minimal amounts of desorption. Overall, our results not only suggest potential complexation mechanisms among various sorbents but also show that various processes can promote the exchange of beryllium between solid and dissolved phases, the extent to which depends on the composition of the system.

Now having a better foundation in the chemical controls on beryllium sorption as established in Chapters 2 and 3, we were able to better develop a standardization method in Chapter 4 to estimate differences in beryllium sorption capacity due to differences in soil properties. We determined that the product of the percent inverse quartz and the CEC best predict beryllium concentrations in soils. By deriving a mathematical relationship between percent of sorbed beryllium and the product of these two variables, we were able to predict the sorption capacity of the system. The sorption capacity can be applied to sorbed concentrations of beryllium from field measurements to estimate the total potential for sorbed beryllium independent of the physical and chemical properties of soil. However additional soils samples should be incorporated in future work to determine if our derived mathematical relationship predicting percent sorption is maintained over a greater variety of soil properties and environments.

Using the information that we gained from these three bodies of work, we can now make recommendations when assessing beryllium concentrations in differing environments.

1) The system pH should be strongly considered as differences in sorbed beryllium amounts up to orders of magnitude can be observed for systems differing in pH. Additionally, decreases in pH most effectively result in removal of beryllium from sorption sites relative to other chemical processes.

2) Specific ligands demonstrate an enhanced ability to complex beryllium and should be measured in addition to sorbed beryllium amounts. Sulfur and phosphorus oxides not only sorb greater amounts of beryllium, they are more resistant to beryllium desorption. However, considering both phosphorus and

sulfur are dynamic reservoirs, it is important to consider how their transformations, driven by various biotic and abiotic processes, affect the net beryllium sorption. For example, landscapes affected by agricultural activity involving both the use of phosphate for fertilization and phosphonate as a fungicide and herbicide or contamination due to phosphorus in wastewater effluent from its various industrial uses and agricultural effluence should be given particular attention. The effect of increased phosphorus loads due to anthropogenic activity on beryllium retention could present an issue particularly in the use of ^{7}Be sediment concentrations considering its short half-life and more current application. Now that we understand the relative magnitude of beryllium complexation by phosphonate, more work is required to quantify potential effects of phosphonate on beryllium mobility on a larger scale.

There is some potential for beryllium mobilization as a result of sulfur cycling. However, the bulk of sulfur is immobilized by incorporation in the organic matter fraction and only a small portion (1-3%) is converted to inorganic sulfate annually. Therefore, it may be possible that beryllium losses due to sulfur cycling are less significant.

3) Although we found that beryllium correlation with percent carbon varied in significance with soil type, organic matter contributes to the CEC of a system which is able to strongly predict sorbed beryllium concentrations. We also know that certain organic ligands, in addition to sulfur and phosphorus functionalities, are able to form very strong associations with beryllium including dicarboxylic,

dihydroxyaromatic and hydroxylcarboxylic ligands as evidenced by some of the largest reported beryllium stability constants. Large pools of phosphorus and sulfur are also present in the organic fraction, although total amounts vary depending on environmental conditions, and contribute significantly to the sorption capacity of organic carbon. Beryllium complexed by such ligands is also more resistant to desorption. Therefore sorbed organic carbon can have a major influence on the retention of beryllium, the degree of which is dependent on its chemical composition.

4) Of all minerals evaluated in this work, beryllium demonstrated a unique relationship in the presence of illite. This result is of particular importance in environments with increasing ionic strength, which promotes increased beryllium sorption due to the expansion of edge sites. There is also the potential for physical exclusion of beryllium due to the collapse of these frayed edges, preventing beryllium from exchanging back into solution. In addition to physical protection, we propose that sorption onto the surface of illite is dominated by inner sphere complexation. Not only does beryllium form stable associations with illite, the sorption capacity of illite can change with solution chemistry. Thus sample mineralogy should be considered especially in environments with large amounts of illite.

5) Overall, it appears that the product of the percent of inverse percent quartz and CEC best predict the sorption capacity of soils. Although additional work is required to confirm whether the mathematical relationship used to estimate the

percent of sorbed beryllium is maintained amongst an even greater suite of samples, what we conclude from Chapters 2 and 3 supports these findings. For example, more highly weathered soils will have a greater abundance of clays, which are drivers of sorption in soils due to their large, negatively charged surface area, and less quartz. Therefore, the inverse abundance of quartz accounts for clay mineral abundances and other materials associated with clay minerals including organic matter. Additionally, the CEC represents the exchangeable binding sites associated with both organic and mineral fractions. The CEC is inversely related to pH, which also strongly influences sorbed beryllium amounts. Therefore, the use of these three variables to predict percent beryllium sorption is supported by our work and the work of others studying the geochemical behavior of beryllium.

In conclusion, the previous method of standardizing sorbed beryllium concentrations using sample mass should be avoided as it does not take into account the chemical and physical properties of a soil that we have now come to understand strongly control the sorption behavior of beryllium. When comparing beryllium concentrations in differing environments, it is imperative to characterize soil properties, especially those previously highlighted. Unfortunately, it is more difficult to account for desorbed amounts of beryllium, which are more likely than previously assumed. However, we are now aware of the relative influence of different chemical perturbations on beryllium mobility, with increasing pH exerting the greatest control. With a greater understanding of the variables affecting the geochemical behavior of beryllium, we can more accurately measure erosional fluxes as well as better predict the potential mobility of beryllium contamination through the environment.

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