CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

FACULTY OF ENVIRONMENTAL SCIENCES

THE USE OF STABLE METAL ISOTOPES IN ENVIRONMENTAL GEOCHEMISTRY

DIPLOMA THESIS

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THESIS SUPERVISOR: Ing. Zuzana Michálková, Ph.D.

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DIPLOMA THESIS ASSIGNMENT

Robert Zachary Porter

Environmental Geosciences

Thesis title

The use of stable metal isotopes in environmetal geochemistry

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Objectives of thesis

The aim of the review part of the study is to summarize basic concepts and knowledge concerning stable metal isotopes in the environment, i.e., their types, properties and occurence. Analytical methods used for determination of isotopic composition will be mentioned together with the applications of these analyses in the field of environmental geochemistry.

In the experimental part of the thesis, the pH-dependence of adsorption of Cd and Zn onto different representatives of various soil phases (e.g., Fe oxides, Mn oxides, clays) will be determined and corresponding adsorption edges will be constructed and model using various surface complexation models. If the TIMS technique at the Department of Environmental Geosciences will be available, isotopic fractionation before and after sorption at chosen pH levels will be evaluated to estimate the influence of sorption processes on the isotopic fractionation of Cd and Zn in soil.

Methodology

Review part is based on appropriate literature sources, eg., mainly scientific books and articles.

In the experimental part of the thesis, a set of batch adsorption experiments will be performed to evaluate the pH dependence of Cd and Zn adsorption onto goethite, ferrihydrite, birnessite and illite. The experiments will be performed under nitrogen atmosphere with initial concentration of Zn/Cd set to 10-4 M in a background eletrolyte (0.1, 0.01 or 0.001 M NaNO3). When the adsorption edges will be constructed, chosen points will be analyzed concerning Cd/Zn isotopic fraction before and after sorption using thermal ionization mass spectrometry (TIMS), if this technique will be available at that time at the department. If not, discussion of published literature dealing with the processes of isotopic fractionation during sorption will be included as a part of the thesis Discussion.

Obtained data will be processed, summarized and statistically evaluated. Student will discuss the results with existing literature and summarize main conclusions of the work.

The proposed extent of the thesis

about 50 pages as need

Keywords

zinc; cadmium; adsorption; isotopic fractionation; soil; geochemistry

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Recommended information sources

Guinoseau, D., Gélabert, A., Moureau, J., Louvat, P., Benedetti, M.F., 2016. Zn isotope fractionation during sorption onto kaolinite. Environ. Sci. Technol. 50, 1844-1852.

Juillot, F., Maréchal, C., Ponthieu, M., Cacaly, S., Morin, G., Benedetti, M., Hazemann, J.L., Proux, O., Guyot, F., 2008. Zn isotopic fractionation caused by sorption on goethite and 2-Lines ferrihydrite. Geochim Cosmochim Acta 72, 4886-4900.

Wiederhold, J.G., 2015. Metal Stable Isotope Signatures as Tracers in Environmental. Environ. Sci. Technol. 49, 2606-2624.

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The Diploma Thesis Supervisor

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Electronic approval: 24. 3. 2019

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Prague on 25. 03. 2019

DECLARATION

I hereby declare that I have written this diploma thesis titled "*The use of stable metal isotopes in environmental geochemistry*" independently under the direction of Zuzana Michálková. I have listed all literature and publications from which I have acquired information in the reference section.

In Prague, Czech Republic of April 18th, 2019

X ZP

R. Zachary Porter, BSc.

R. Zachary Porter

ACKNOWLEDGEMENTS

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Cheers,

R. Zachary Porter

ABSTRACT

Zinc and cadmium are naturally occurring elements but are also present at increased levels in the environment as a result anthropogenic activity. Both elements, specifically cadmium are potentially toxic from an environmental standpoint and is it vital to identify the pathways these contaminants may take and in what form they are present. Advances in instrumentation and technologies such as the development of TIMS (Thermal Ionization Mass Spectrometry) and MC-ICPMS (Multi-Collector Inductively Coupled Plasma Mass Spectrometry) have made it possible to analyze non-traditional isotopes. Traditionally, zinc and cadmium isotopes were unable to be readily analyzed in terms of isotopic fractionation. To help understand the processes in which these two elements become either isotopically enriched or depleted, it is essential to know how they react with soil phases in question.

The primary objective of this thesis was to evaluate the pH and ionic strength's influence on the adsorption of zinc and cadmium on four representative soil phases, i.e., varying crystalline Fe oxides, Mn oxides and clay minerals. As the representatives, synthetic 2-line ferrihydrite, goethite, synthetic birnessite, and illite clay were chosen for the purpose of our experiment. The main aim of the work was to provide a more in-depth view into the interaction between each soil phases' surface chemistry with zinc and cadmium, respectively. Experiments were performed to construct adsorption edges of $1x10^{-4}$M solutions of both Zn and Cd at varying ionic strengths of 0.1M, 0.01M, and 0.001M $NaNO_3$. The adsorption was evaluated by adjusting the pH of each solution through a progressive range of pH values under an inert atmosphere. The adsorption of both Zn and Cd was highly dependant on the specific mineral phase; it is worth noting that the influence of pH on each minerals adsorption also varied on the respective element, inferring that although both metals share similar properties, they behave differently. Birnessite exhibited the smallest range of pH required to transition from minimal to maximum adsorption of Zn, and for Cd, ferrihydrite was found to be the most dependant. Experimental research provided by this thesis offers access to parameters essential to imminent isotopic fractionation studies regarding the preferential adsorption of Zn and Cd on each soil phase. Results from this study will help provide additional insight into the surface chemistry of these representative phases. To conclude, the comparison of these experimental results can aid in the fitting of experimental parameters to equilibrium models. As visible from the literature review dealing with fractionation of Cd/Zn during the sorption onto the various soil mineral phases, there are still significant gaps in knowledge. Because of that, this study will serve as a basis for large study aiming to elucidate the isotopic fractionation of Zn/Cd during the sorption on various soil phases and its connection with the types of surface complexes formed.

Key words: zinc; cadmium; adsorption; isotopic fractionation; soil; geochemistry

CONTENTS

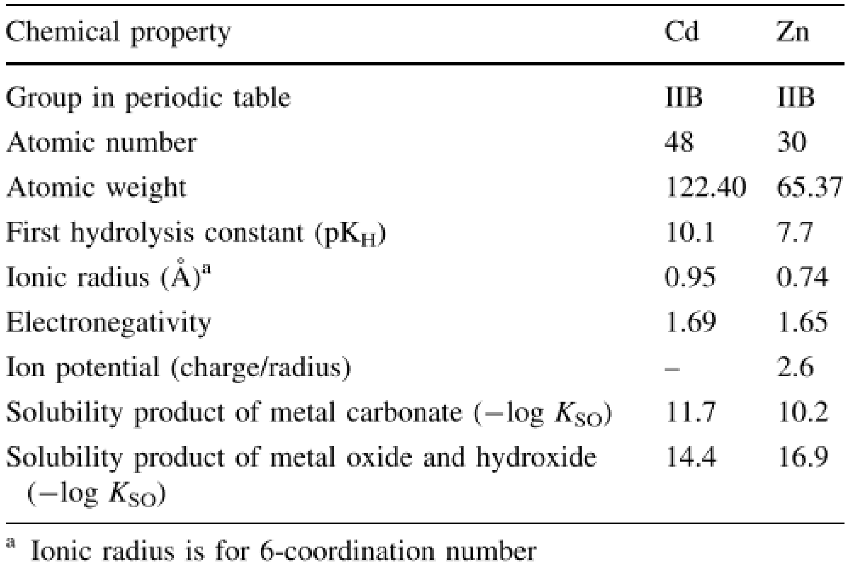
1. **INTRODUCTION**

1.1 BACKGROUND

Stable metal isotope analysis exists within the realm of isotopic studies that are concerned with ‘non-traditional isotopes’; these isotopes are often trace elements, potentially volatile, and commonly redox sensitive (Baskaran 2012; White 2014). These isotopes are continuing to be used as tracers, employed to analyze environmental cycling of any relevant species. The introduction of modern analytical technology (TIMS; Thermal Ionization Mass Spectrometry, and MC-ICP-MS; Multi-Collector Inductively Coupled Plasma Mass Spectrometry) has allowed the isotopic analysis of heavier isotopes, such as the transition and post transitional metals; whereas previously it was difficult to ionize these metallic elements (Teng et al. 2017; Wiederhold 2015). Within the realm of geochemistry, and more specifically this project, the behavior of cadmium and zinc is of great interest. The element cadmium (Cd) is an extremely toxic element, whereas zinc (Zn) is a common trace metal within numerous biological processes and species - most important of which, are humans (De Leon & Aragon 2012). Both elements share several similar properties as they are both located within elemental group 12IIB (see Table 1); due to these properties there are additional environmental risks involved in their interactions. Within the scope of the soil environment, these elements may be present in natural states in mineral constituents, or via anthropogenic insertion due to pollution. Regarding soils, the movement of such cationic metals is highly determined by specific soil phases, and their ability to preferentially bind or adsorb contaminants (Baskaran 2012; Chrastný et al. 2015; Strawn et al. 2015). The adsorption of metallic cations by soil phases results in isotopic fraction; both Zn and Cd only exhibit one natural oxidation state, and when these species become complexed, they are highly susceptible to the process of isotopic fractionation (Baskaran 2012; Hoefs 2015; Pokrovsky et al. 2005). According to Baskaran (2012), the isotopic fractionation is highly related to the structural coordination of specific soil phase minerals. The adsorption processes associated with isotopic fractionation also differ, depending on the state of equilibrium within the solution (Wiederhold 2015). Any environment in which adsorption processes occur and can reach an equilibrium state depend highly on several different factors.

The relationship regarding the isotopic fractionation of Cd and Zn within aqueous solutions in the presence of specific soil phases is an area where there is not extensive pre-existing research. The functionality of this data can be utilized by several different disciplines of environmental research; the results from data may be used to optimize different surface complexation modelling methods, and even provide more insight into the processes regarding specific fractionation. The specific fractionation of both Cd and Zn isotopes may both help identify the transformation of these elements through their formation, and even more so their fates within the environment. These determinations may prove to increase knowledge about the solubility and possible bioavailability, as well as provide insight into the relative toxicity of present compounds.

Table 1 General physio-chemical properties of cadmium (Cd) and zinc (Zn) (Kim 2014)



Chemical property	Cd	Zn
Group in periodic table	IIB	IIB
Atomic number	48	30
Atomic weight	122.40	65.37
First hydrolysis constant (pK_H)	10.1	7.7
Ionic radius (Å)[a]	0.95	0.74
Electronegativity	1.69	1.65
Ion potential (charge/radius)	–	2.6
Solubility product of metal carbonate ($-\log K_{SO}$)	11.7	10.2
Solubility product of metal oxide and hydroxide ($-\log K_{SO}$)	14.4	16.9

[a] Ionic radius is for 6-coordination number

1.2 AIMS OF THESIS

The primary aim of this thesis is to summarize basic concepts concerning stable metal isotopes in the environment as well as analytical methods used for the determination of isotopic fractionation and surface complexation. The application of these topics will be observed from their application to environmental geochemistry.

From an experimental point of view, the aim of this thesis is to determine the pH-dependence of adsorption of zinc and cadmium on the representative soil phases. In further studies the isotopic fractionation will be evaluated before and after sorption equilibrium in attempts to estimate the influence of these processes on the isotopic fractionation of zinc and cadmium in soils.

2. REVIEW OF LITERATURE

2.1 STABLE ISOTOPIC FRACTIONATION

Stable isotopic fractionation of metals has been utilized as a functional tool in hopes to understand more thoroughly the processes associated with the specific interest. Within any isotope there is a variation in the number of neutrons present in its atomic structure. In this sense, the weight of the specific isotope can be significantly different, resulting in varying reactivity and slight discrepancies in physio-chemical properties (Hoefs 2015; White 2014). Any given element that has numerous isotopes allows the scientific community to gather information regarding the possible environmental cycling. The fact that many metallic stable isotopes can have multiple isotopic variants allows them to be much better indicators of environmental process; particularly processes within geochemistry, cosmology, and biology (De Leon & Aragon 2012; Loganathan et al. 2012). Specifically, metal stable isotopic fractionation has been a more modern introduction to the studies of stable isotopic fractionation. The variations within any elements isotopic fractionation must be accurately relative to a given reference material, so that the results may have a comparative baseline. This results in complicating requirements for global scientific communities, due to the difficulty of acquiring reference material. Pokrovsky et al. (2005) established the notion that, although numerous different isotopes have turned out to be varied across different natural phenomena, these processes are not well understood. Additionally, work by Wombacher et al. (2003) has stated that variation of isotopic fractionation within terrestrial samples is extremely low; although samples measured from extra-terrestrial bodies, specifically meteorites are exposed to a significant temperatures and pressures resulting in a higher variation. Mechanisms involving the use of adsorption processes to analyse the fractionation of an element’s isotopes have provided an interesting trend (see Figure 1). Pokrovsky et al. (2005) have claimed that within lighter metal stable isotopes there is preferential portioning of lighter isotopes onto the adsorbed phase in solution, and the heavier proportion is relegated to the dissolved portion of solution.

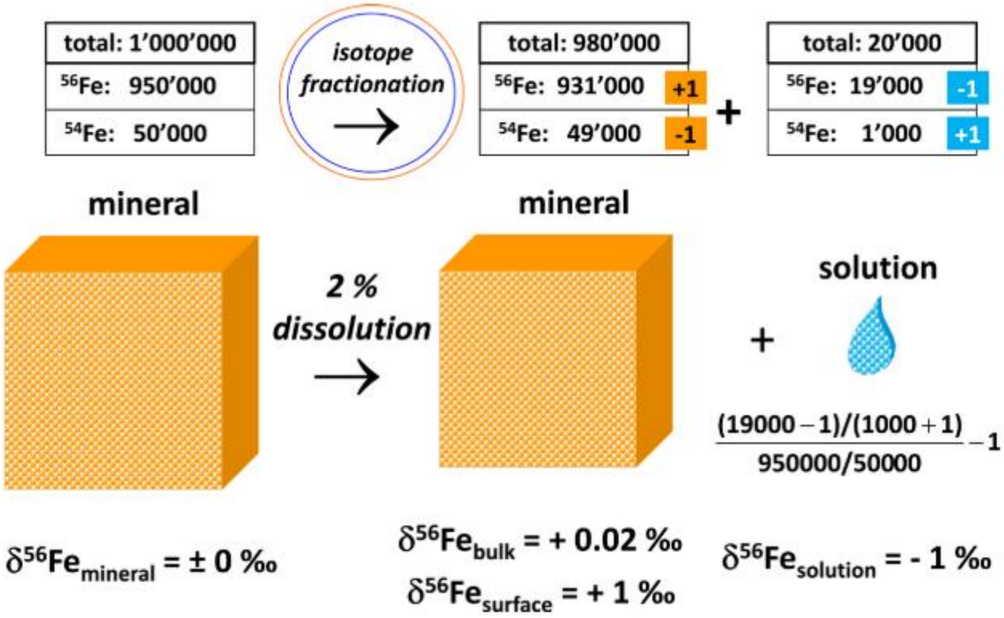


Figure 1 Example of isotopic fractionation due to mineral dissolution (Wiederhold 2015)

When using stable isotopic fractionation information as environmental tracers, there are specific applications in which the data is frequently separated into, either source or process tracing. Source tracing of isotopic fractions attempts to use well defined systems to determine the initial source of a specific isotope within its own defined complicated system (Wiederhold 2015), whereas process tracing attempts to track a specific process that was able to transform an isotope one species into a second identifiable isotopic signature. More recent studies by Wiederhold (2015) has stated studies of isotopic enrichment within adsorption experiments shows that cationic metals such as Zn had the tendency for the heavier isotopic enrichment within the adsorbed phase; whereas conversely, certain cationic metal species such as Cd had lighter isotopic species enriched on the adsorbed phase present in solution (White 2014; Wiederhold 2015; Wombacher et al. 2003).

2.2 CHARACTERISTICS OF ZN & CD

Cadmium (Cd) and zinc (Zn) are two post-transition metals naturally occurring with a dominant oxidation state of +2. Currently zinc has five stable isotopes and cadmium six at regular atmospheric conditions (Guinoiseau et al. 2016; Wei et al. 2016; Zhu et al. 2015). Due to their very similar chemical properties, Cotton and Wilkinson (1966) expected that both would behave very similarly within soil.

Zinc is the 25th most abundant element within the earth's crust and cadmium the 64th, with the difference of abundance numerous orders of magnitude apart. Most primary figures comparing the natural abundance of earth's crust have been evaluated numerous decades prior with figures of 0.87µmol g^{-1} and 0.0045µmol g^{-1} respectively; these estimated figures are still considered valid based upon more modern estimates (Goldschmidt 1958; Wedepohl 1969). Although the relative abundance of each is significantly different, the origin of both elements can be found in similar minerals and compounds. Both zinc and cadmium are commonly extracted from the mineral sphalerite (ZnS) (Sposito 2008; Wedepohl 1969; Zhu et al. 2015). During its formation, some samples of sphalerite may convert to CdS instead of ZnS due to Zn and Cd's similar physio-chemical properties. These metals only have subtle differences within them due to their electron arrangement in which exchanged electrons are located within their d-orbitals instead of their s or p-orbitals (Strawn et al. 2015). CdS, as a fully naturally occurring mineral, takes the form of Greenockite, which is the mineral that is known to have the largest proportion of cadmium present (Wedepohl 1969).

In terms of environmental concern, both elements represent their own specific problems. Zinc can become one of the most toxic metals in terms of affecting plants within the environment, even at low levels (Al-Asheh & Banat 2001). Both elements may enter the environmental sphere via both natural and anthropogenic means (see Table 2). However, the anthropogenic sources are often a more significant problem as presented by Loganathan et al. (2012), presenting that these sources are often more unstable due to increased solubility and bio-availability. There is a complicated relationship between zinc in the environment as its effects are vary relative to the specific organisms (Fan et al. 2018). For most other organisms, especially animals and humans, it is deficiency in zinc that is the indicator of health problems, such as weakening of senses, cell division, and strength of the body's ability to recover from injuries (Cotzias et al. 1961). Certain areas of the planet, especially soils may become highly abundant in zinc, but the areas experiencing vast deficiencies are those under aggressive agricultural practices; although some crops only extract small amounts of zinc, it is the quick turnover and vast quantity of produce that is able to absolutely deteriorate soils of zinc (Strawn et al. 2015). Cadmium has a much higher apparent toxicity that is associated with even basic contact. In contrast to zinc, cadmium is regarded as a non-essential element for all environmental spheres, except a very specific types of algal species (Cao et al. 2006; Schroeder et al. 1967). The largest concern for humans regarding cadmium toxicity is its preferential solubility as it is extremely toxic to almost any species that filters or uses water within its organism (Cao et al. 2006). Notably, cadmium is one of the few toxic inorganic pollutants that may cause extreme adverse environmental effects even at very low concentrations within solution (Soon-An et al. 2013). Although each element separately has potentially toxic environmental effects, one of the more interesting interactions takes place when both are present in a bio-available form. When both elements are present within the same soil environment, the two elements can produce what Fan et al. (2018) refer to as antagonistic effects. This interaction allows an increased uptake of zinc to potentially toxic levels when in the presence of cadmium. The damage done to these plant species will evidentially be further exacerbated by the presence of additional cadmium in solution (Fan et al. 2018).

Table 2 Characteristic uses, health effects and sources of Zn and Cd (Strawn et al. 2015)

Metal:	Uses:	Health Effects:	Sources (Industrial):	Sources (Natural):
Zinc (Zn)	Batteries, coating compounds, crops, die-casting alloys.	Stomach cramps, skin irritations, nausea, respiratory disorders, anaemia and mental fever.	Smelting, electroplating, pig and poultry manures.	Surface water, soil and rock.
Cadmium (Cd)	Electroplating, Ni-Cd batteries, cell-phones, laptop computers.	Carcinogenic, lung fibrosis, dyspnoea, chronic lung disease and testicular degeneration.	Zinc smelting's, waste batteries, e-waste, paint sludge, incinerations and fuel combustion.	Coal combustion, iron and steel production, phosphate fertilizer, zinc production, volcanoes and anthropogenic sources.

2.3 INNERSPHERE VS. OUTTERSPHERE COMPLEXATION

Sorption processes involve a numerous amount of interactions that occur at the interface between both solution and solids. The two specific processes that are of most important to this thesis research are inner and outer-sphere complexation; also referred to as specific and non-specific adsorption, respectively. Although a solution may exhibit properties of varied sorption processes, it is the mechanisms controlling these phenomena are crucial to understanding the mechanics and driving factors. If we can deeply understand the phenomena of surface complexation and sorption process, we can more accurately predict contaminant release and potential remediation efforts (Komárek et al. 2018; Schaller et al. 2009). The process of outer-sphere complexation or adsorption occurs when there is at least one molecule of water remaining between the sorbate ions or material and the physical surface species (see Figure 2); these types of processes are driven by electrostatic forces and are categorized as physisorption (Davis & Kent 1990). Conversely, inner-sphere complexation occurs when adsorbate constituents can form direct covalent or ionic bonds with the surface species (Strawn et al. 2015).

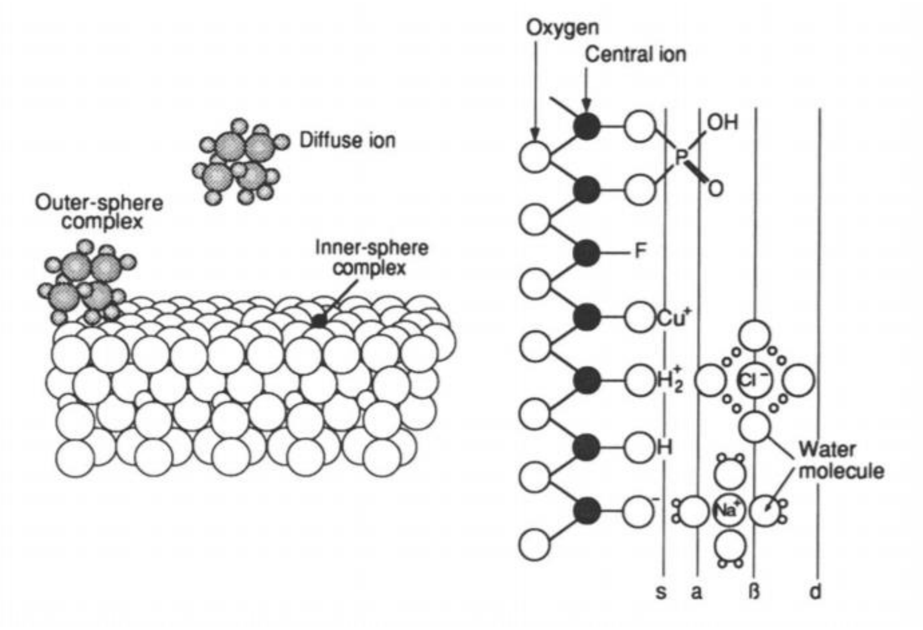


Figure 2 Representation of inner & outer-sphere complexation (3D & 2D representations) (Huang et al. 1995)

When evaluating the formation of surface complexes within a study it is important to understand the underlying chemical make up and geologic structuring of any given sorbent materials. The tendency for the formation of these two types of complexation relies upon a variety of factors; in a simplified environment the most important characteristics preventing or promoting the formation of specific complexes are: (I) sorbent parent material, (II) solution pH, (III) available functional groups, (IV) background electrolyte presence, (V) organic matter presence, and (VI) cation exchange capacity (Bradl 2004; Strawn et al. 2015). As sorbate materials, both zinc and cadmium ions have experimentally been shown that they are preferentially able to form inner-sphere bonds most regularly with aluminosilicate edge surfaces, as well as oxide mineral surfaces (Benjamin 1981; Bradl 2004; Davis & Kent 1990). Strawn et al. (2015) states that for successful inner-sphere complexation to occur, the sorbate material must have appropriate conditions regarding water solubility, ionization energy and proficient energy in which to create bonds. Outer-sphere complexes naturally occur within soil phases where minerals frequently bind base cations used within soil organic processes and for later uptake from plants (Bradl 2004; Vodyanitskii 2010). Amorphous phase minerals are subject to higher rates of adsorption due to the higher proportion of surface functional groups, which is due to their irregular structures, and larger surface areas (Mathur & Dzombak 2006; Sposito 2008).

2.4 EFFECTS OF PH ON ADSORPTION

Adsorption processes have been utilized historically but are now becoming increasingly popular as a technology used to deal with an assortment of environmental issues. Adsorptions popularity is highly attributed to its particularly low cost and high efficiency (Yong-Gui et al. 2011). As previously mentioned in the section on inner-sphere and outer-sphere adsorption, these processes are highly revolved around either electrostatic or chemical interactions to exist (Zhong et al. 2010). The intrinsic pH is an extremely important factor regarding adsorption processes. This is due to the charge of functional group’s heavy reliance on the present pH, therefore without appropriate pH values, certain types of adsorption simply would not be possible (Strawn et al. 2015). The pH is quite crucial for sorption processes because of pH’s influence on surface charges and charges of relevant materials. Particularly concerning divalent metals and heavy metals the increasing influence of pH on adsorption is mentioned by Yu et al. (2005) as well as the influence of external cations. Regarding many experiments conducted with both Zn^{+2} and Cd^{+2} it is found that at lower values of pH the dominant adsorption processes will be outer-sphere, whereas at higher pH values the dominant process is either inner-sphere adsorption or surface precipitation (Chesne & Kim 2014; Fan et al. 2018; Yong-Gui et al. 2011). The distribution of surface charges can be observed relative to a material point of zero charge (pH_{pzc}). The pH_{pzc} of a material indicates the pH in which the net surface charge of a material is zero; if $pH > pH_{pzc}$ there will be a resultant negatively charged surface and vice versa (Sposito 2008). According Strawn et al. (2015) a specific pH sensitive coefficient referred to as the distribution coefficient (K_d) can be used to estimate the favoured type of adsorption by any given system. If the given K_d value is smaller than the concentration of metal in solution, it is more likely to find chemical precipitation and sorption, and the opposite is true (see Figure 3) (Strawn et al. 2015).

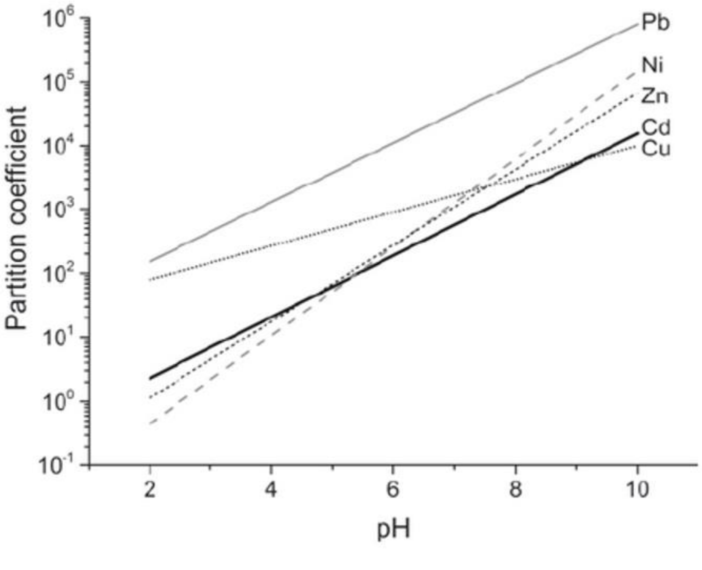


Figure 3 Partition coefficients of divalent metals as influenced by pH; high partition coefficients indicate the metal is present in a solid state opposed to an aqueous state. (Strawn et al. 2015)

The relative importance of pH is clearly present when considering the available amount of potential binding sites. Depending on the pH and availability of hydrogen ions (H^+) can restrict or create excess binding sites for metallic ions to access (He et al. 2000). Both surface charge and pH are highly influential on each other which presents a complex issue when determining the relative influence of either, since these values can differ extremely based on their region. It is also important to mention, most soils that are present within the temperate regions of North America and the European Union are influenced by negatively charges soils (Kim 2014; Niu et al. 2018; Strawn et al. 2015). These major intrinsic negative charges are highly related to the large amount of 2:1 clay that is present throughout the soil profile fractionation; whereas in tropical regions there is significantly more soil weather that takes place and, therefore these soils are more likely to exhibit a positive surface charge. The reason this is such an issue is that a large proportion of the experiments and studies on adsorption are focused on negatively charged soils; from a more realistic point of view, their interactions are global and there are possibilities of positive, negative, as well as variable charged soils. Concerning clay minerals, most adsorption process occur on edge surfaces, which depending on pH are dominated by amphoteric binding sites; the amphoteric nature is related to the function groups being highly influenced by the binding of hydroxide (OH^-) or hydrogen ions (H^+) (Gaskova 2009).

2.5 CHARACTERISTIC SOIL PHASES

2.5.1 INTRODUCTION

Within naturally occurring soils there are numerous different elements present due to any number of pedogenetic processes, such as through primary weathering, biological deposition, or climatic influence. Soil acts as a dynamic system in which the earth can cycle many organic and inorganic substances and involves naturally occurring processes to deal with externalities such as pollutants which can be attenuated via adsorption (Strawn et al. 2015). In common soils about half of its volume is comprised of solid materials; which are often present in the form of soil minerals made of relatively simplistic chemical compounds (Sposito 2008). Based upon pure abundance, the most present elements within soils are oxygen (O) and silicon (Si) which form the key structure of many silicate minerals. The most widespread soil minerals take form of some primary groups such as silicates, oxides, carbonates, and sulphides. Each of these families are represented by numerous subspecies of mineral forms. Regarding this thesis the focus of soil mineral phases was put on four specific soil mineral phases that were thought to be of significance to temperate regions. All four of the minerals also have specific important factors that make them interesting species to evaluate and test from a chemical standpoint. The first mineral phase established was a manganese oxide, birnessite [$[Na,Ca,Mn(II)]Mn_7O_{14}\cdot 2.8H_2O$]; although samples used within this thesis is a synthetic potassium based birnessite (K-OL-1) (Ching et al. 1997; Post 1999). The second mineral phase represents the aluminosilicate family in the form of a secondary mineral known as illite (K,H_3O) $(Al, Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$ (Bibi et al. 2016). The last two minerals are both iron oxy(hydroxide) minerals goethite (α-FeO(OH)) and ferrihydrite ($(Fe3^+)_2O_3\cdot 0.5H_2O$)); ferrihydrite was selected to represent amorphous and slightly crystalline Fe minerals whereas goethite was chosen to represent a more crystalline state (Cornell & Schwertmann 2003; Ponthieu 2006). Each one of the established minerals has an extensive background of properties each can highly influence their ability to act as potential sorbents. The main purpose of choosing these target mineral phases is due to their widespread occupancy and general abundance in the natural environment.

2.5.2 BIRNESSITE

Birnessite as a mineral was discovered in Scotland in 1956 and in a natural state is the most abundantly occurring manganese oxide mineral, and one of the most abundance oxide minerals in general (Sposito 2008). Geologically this mineral phase forms via precipitation within bodies of waters that have many base cations such as groundwater or lakes; the origins of the mineral itself are of a biogenic source initially (Strawn et al. 2015; White 2014). Within soils this mineral is often found coating the external edges of other particle surfaces. Within its mineral structure there is a significant amount of empty cationic sites which expresses itself as a negative net surface charge, allowing the mineral phase to adsorb a variety of cations (Post 1999). Literature states that although there are structural issues associated with the mineral birnessite, often these regions are rapidly occupied via isomorphic substitution; although in the case of adsorption processes stronger cations may be able to occupy these sites (Strawn et al. 2015). Structurally birnessite forms poorly structured crystals which explain these charge gaps within the structure. Historically it was relatively impossible to specific the structure of naturally occurring birnessite samples. Naturally occurring birnessite often exists with a poorly crystalline structure and is extremely fine grained which resulted in numerous analytical issues (Post 1999; Sposito 2008). Originally it was not possible to analyse natural samples instead birnessite ‘like’ phases had to be chemically synthesized to do analysis (Post 1999). According to Post (1999) until advanced XRD (X-Ray Diffraction) and XANES (X-ray Adsorption Near Edge Structures) were being used the true structure of natural birnessite could only be estimated. This mineral exhibits a few properties that make it a mineral of interest when analysing adsorbent potentials for minerals. The cationic gaps within the structure readily allow strong electronegative metallic cations to become bound within the structure itself rendering them unavailable biologically (see Figure 4). Lastly, the poor crystalline structure of this mineral allows for more irregular surface charge which provides more possible active binding sites for metallic cations from solution (Sposito 2008).

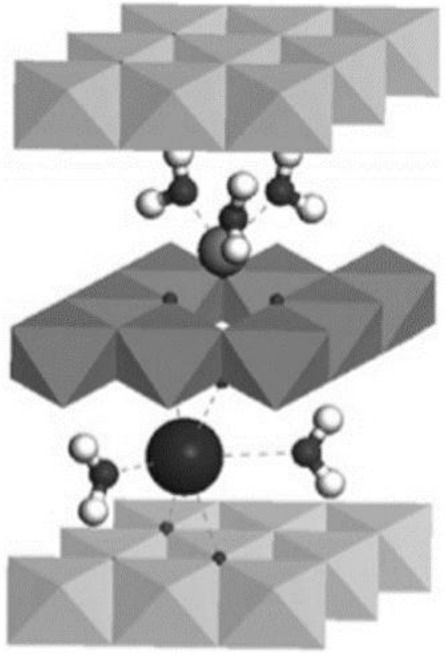


Figure 4 Polyhedral depiction of atomic structure of birnessite, exhibiting the cation vacancy relative to charge balance (Mn^{3+} on top and K^{+} on the bottom) (Spositio 2008)

2.5.3 ILLITE

The secondary aluminosilicate illite is phyllosilicate three-layer clay mineral which occurs naturally in structured sheets in a 2:1 alternating silica-tetrahedrons and alumina-octahedrons arrangement (Sposito 2008). To secure the clay structure together there is a potassium ion (K+) between intermediate layers of the mineral phase (Bibi et al. 2016; Strawn et al. 2015). The formation of this mineral is most commonly a result of the weathering of primary silicate materials such as feldspar or the degradation of weathered muscovite. The actual process of formation occurs more often in alkaline conditions as opposed to acidic environments; these processes do not prevail in acidic soils due to their tendency to leach major constituents and cations out of the soil solution preventing some major frameworks of clay minerals (Bergaya et al. 2006; Bibi et al. 2016). Clay minerals are essential for environmental stabilization due to their large surface areas and ability to buffer pH (Bibi et al. 2016). Illite clays are highly susceptible to isomorphic substitution which highly influences the surface charge; the dominant negative charge that the mineral normally exhibits is due the tetrahedral substitution of aluminium (He et al. 2000)

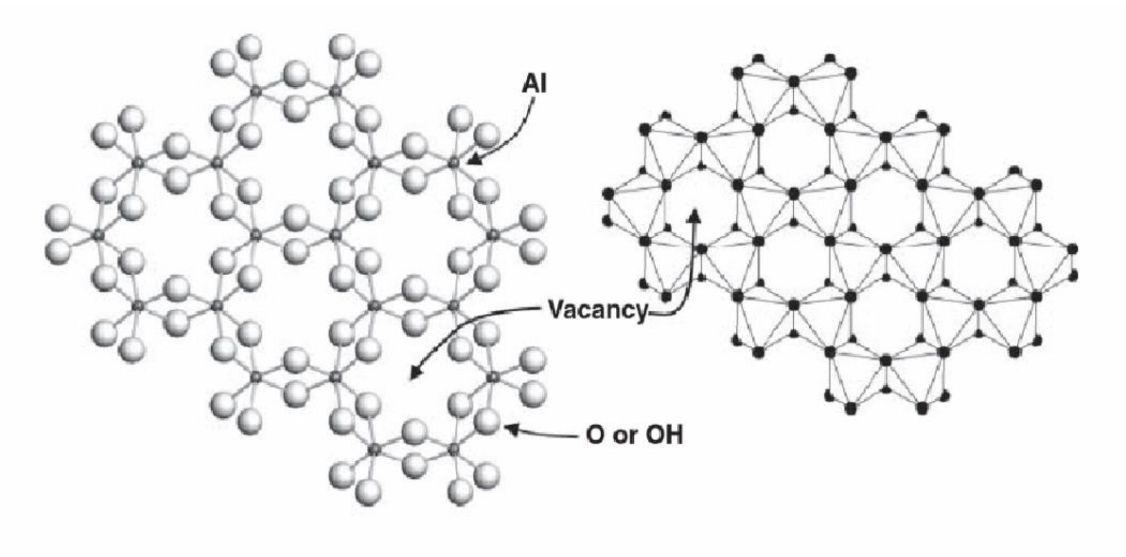


Figure 5 Generic 2:1 phyllosilicate cationic vacancy; in tri-octahedral sheets, Mg+2 or Fe2+ often occupy such vacancies (Strawn et al. 2015)

Clay minerals in general can perform adsorption processes through two major processes, often referred to selective and non-selective adsorption processes in literature (Gaskova 2009; Strawn et al. 2015). Illite clay can perform selective adsorption through direct chemical bonding within the surface layers; due to the large presence of hydroxide sites that are accessible on the edge geometry (Bergaya et al. 2006). The non-selective adsorption is what often occurs on the basal faces of illite due to the negative surface charges (see Figure 5); these adsorption processes are exclusively electrostatically driven in the form of outer-sphere complexes. Clay minerals in general have potential as efficient adsorbents as they are very mechanically stable, high cation exchange capacities (CEC) and have high specific surface (Sposito 2008; Yong-Gui et al. 2011). Regarding clays, a high cation exchange capacity is one of the quantifiable characteristics that allows them to be good adsorbent materials, although Gaskova (2009) proved experimentally that a high cation exchange capacity is only as relevant as the amount of background electrolyte. The ability for a mineral surface to adsorb or bind new cations relies heavily on the adsorbates' ability to compete or be forced onto the surface structure (Gaskova 2009). Although birnessite and illite are both entirely different minerals they share a few characteristics that allow them to be viable adsorbent materials. Both minerals are comprised of a poorly crystalline structure, allowing for isomorphic substitutions within their geometry as well as a high proportion of negatively charged surfaces. These two minerals occur over a vast region of the earth and so far, have high potential in becoming adsorbents for both heavy metals and transition metals or metalloids.

2.5.4 FERRIHYDRITE & GOETHITE

Unlike the other two soil phase minerals, goethite and ferrihydrite share a specific relationship with each other due to their chemical composition and potential origins. Goethite is regarded as the most naturally occurring iron oxide mineral present on earth's surface, most commonly occurring in temperate regions, and especially in humid regions (Perelomov et al. 2011). Goethite forms as a by-product of weathering as a secondary mineral of magnetite, pyrite, and siderite (Cornell & Schwertmann 2003; Vodyanitskii 2010). In aquatic oxygenated conditions the metastable ferrihydrite minerals may transform into a more stable goethite; the reduction of ferrihydrite is able to heavily accelerate the adsorption of divalent candidate heavy metals which can be associated into newly formed goethite (Vodyanitskii 2010). Ferrihydrite formation often occurs in highly acidic soils that are hosts to a variety of excess organic matter and microorganisms (Vodyanitskii & Shoba 2016). Goethite and ferrihydrite are both susceptible to high rates of isomorphic substitution and are often observed with impurities containing calcium oxides or manganese oxides according to Cornell and Schwertmann (2003). Ferrihydrite is considered the more reactive and active iron hydroxide phase (Cornell & Schwertmann 2003). Due to the specific requirements of formation and high reactivity of the mineral, ferrihydrite is extremely rare to find in pure mineral form; ferrihydrite found in the environment is often combined with other molecules or ions.

Within the topic of mineral soils, iron oxides and iron hydroxides can retain heavy metals and transitional metals, but it is worth noting that within organic soils the iron competes with present metals for organic functional sites (Vodyanitskii & Shoba 2016). Iron based minerals are efficient adsorbents of transitional or heavy metals due to their disorderly structure, high charge density, and larger than average surface areas (Perelomov et al. 2011). Structurally the iron ions (Fe^{3+}) within goethite are incompletely coordinated on the edge structures of the mineral resulting in a net charge imbalance; the results in complexation of hydrogen (H^+) or hydroxide (OH^-) complexation resulting in additional valid binding sites (see Figure 6) (Strawn et al. 2015). Like goethite, ferrihydrite is a highly disordered mineral in both synthetic and naturally occurring variants (Cornell & Schwertmann 2003). Structurally ferrihydrite occurs in nanoparticles, and the fact that the mineral is unorganized allows for the complexation of most divalent cations (Hiemstra 2013; Vodyanitskii & Shoba 2016). The ephemeral nature of ferrihydrite as a mineral is due to its short existence as a pure mineral, the amorphous structure can exist in several different forms. Until the introduction of synchrotron X-ray absorption spectroscopy (XAS) there was not a significant amount of knowledge about the true crystalline structure (Vodyanitskii & Shoba 2016). Iron oxides and hydroxides in general are effective adsorbents, but goethite and ferrihydrite specifically have intrinsic characteristics like birnessite and illite that allow them all to be increasingly effective.

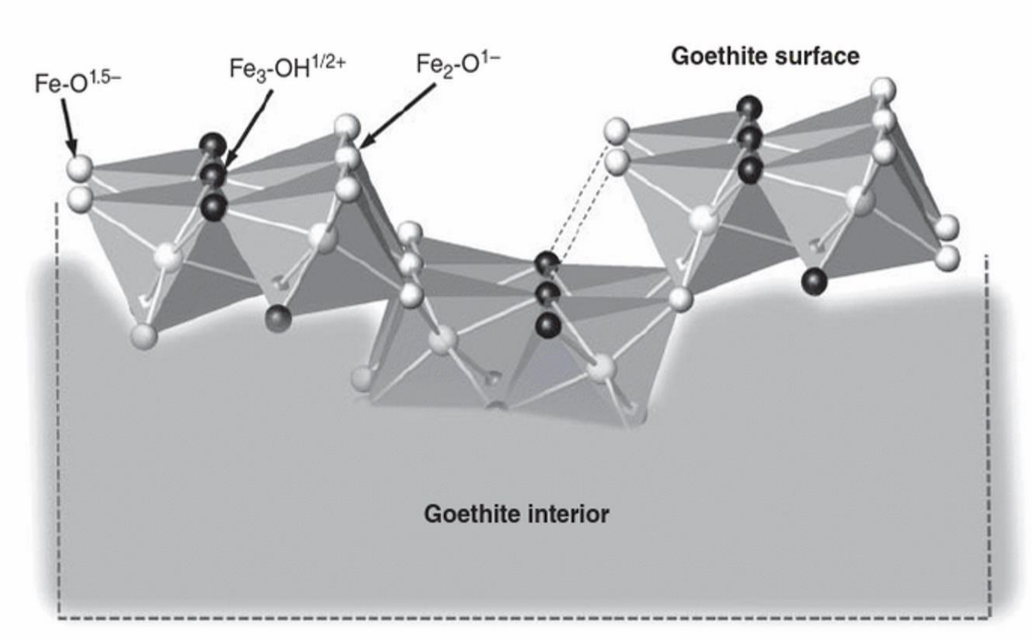


Figure 6 Surface functional groups of goethite (α-FeOOH) edge; reactivity is due to uncoordinated edge surfaces (Strawn et al. 2015)

3. MATERIALS & METHODS

3.1 MATERIALS

The materials for adsorption experiments were chosen in order to cover the main mineral phases playing a role in soil sorption processes, i.e., Fe (hydr)oxides (FeOx), Mn oxides (MnO) and clay minerals. Concerning the FeOx, ferrihydrite was chosen to represent amorphous and slightly crystalline FeOx phases, while goethite was chosen as a representative of more crystalline FeOx phases. Ferrihydrite (namely a 2-Line Ferrihydrite) was synthesized according to Schwertmann and Cornell (2000), when 40g of $Fe(NO_3)•9H_2O$ dissolved in 500 mL of deionized water reacted with 330 mL of 1 M KOH under vigorous stirring to reach the final pH between 7 and 8. Resulting solid precipitates were filtered, washed several times with deionized water and dried at 35°C. Goethite was purchased in a form of Bayoxide® E F 20 (Lanxess). Birnessite was chosen as one of the most common types of Mn (hydr)oxides occurring in soil environment (Post 1999). It was prepared using the sol-gel method for synthesis of potassium birnessite (Ching et al. 1997). Here, 250 mL of 0.38 M $KMnO_4$ was added quickly to 100 mL of 1.4 M glucose solution. The resulting mixture was stirred vigorously for 15 s and then allowed to stand. The originated brown gel was allowed to cool down to room temperature (its temperature was higher due to the exothermic nature of reaction), the exceeding liquid was decanted, and the gel was dried at 45 °C. After that, it was calcinated at 400 °C for 2 h and resulting ash was finely milled, washed 4 times with deionized water and dried at 40 °C overnight. Concerning clay minerals, illite was chosen as the most commonly occurring clay type in soil (Bergaya et al. 2006). The samples of illite (denoted by producer as Imt-2) were acquired from The Clay Minerals Society (CMS®) sourced from Cambrian Shale in Silver Hill, Montana, USA.

3.2 EXPERIMENTAL PROCEDURES

A set of batch adsorption experiments was performed to determine the dependence of Cd/Zn adsorption on the pH (so called adsorption edges) at varying ionic strength. All solutions produced had a concentration of metal ions 1×10^{-4}M according to the agreed upon protocol. Ionic strengths varied between three different values (0.1 M, 0.01M, and 0.001M) with the background electrolyte of $NaNO_3$. The preparation of solutions was highly dependent on the number of experiments that were done in a single lab session. The metal solutions should not be stored and worked on at later dates. These solutions should be used experimentally as soon as possible after their preparation.

The solutions of (1×10^{-4}M) Zn or Cd were prepared out of certified ICP-standards for Zn and Cd (ANALYTIKA®). In addition to the Zn or Cd ions within the flask an additional amount of solid sodium nitrate ($NaNO_3$) was accurately weighed and added via a distilled water (H_2O) washing; the addition of sodium nitrate is to alter the background concentration of electrolytes, resulting in different magnitudes of ionic strength (IS). The solution was completed via the addition of deionized H_2O acquired by our Smart2Pure system (Thermo Fisher Scientific®). In order to prevent the precipitation of carbonates, the experimental processes occurred under a controlled nitrogen environment (N_2 (g)); the deionized water used in the solution was also over boiled in order to prevent such formations. After the solution was completed and corked it was agitated or shaken manually to ensure complete mixing; it was necessary to mix the solution until completely homogenous. After the completion each solution was appropriately marked and used for the experimental process.

3.3 SET UP & APPARATUS

Once each solution was prepared it was possible to proceed with the experimental procedure. Firstly, the solution was transferred to an appropriately sized beaker in which proper physical mixing can take place. In order to prevent the formation of carbonates and oxidation, the solution was sparged with pure nitrogen gas ($N_2(g)$) during the whole experimental process (see Figure 7). Before proceeding with the experiment, it was considered optimal to let the solution proceed to equilibrium with the entering nitrogen gas. Therefore, it was best to let the solution sparge for an excess amount of time; the function of this step was to allow the soil phases interact simply with either Zn or Cd ions.

Figure 7 Apparatus for introduction of nitrogen atmosphere (left), Gas sparging the metal solutions until all additional gasses are sparged (right) (Porter 2019)

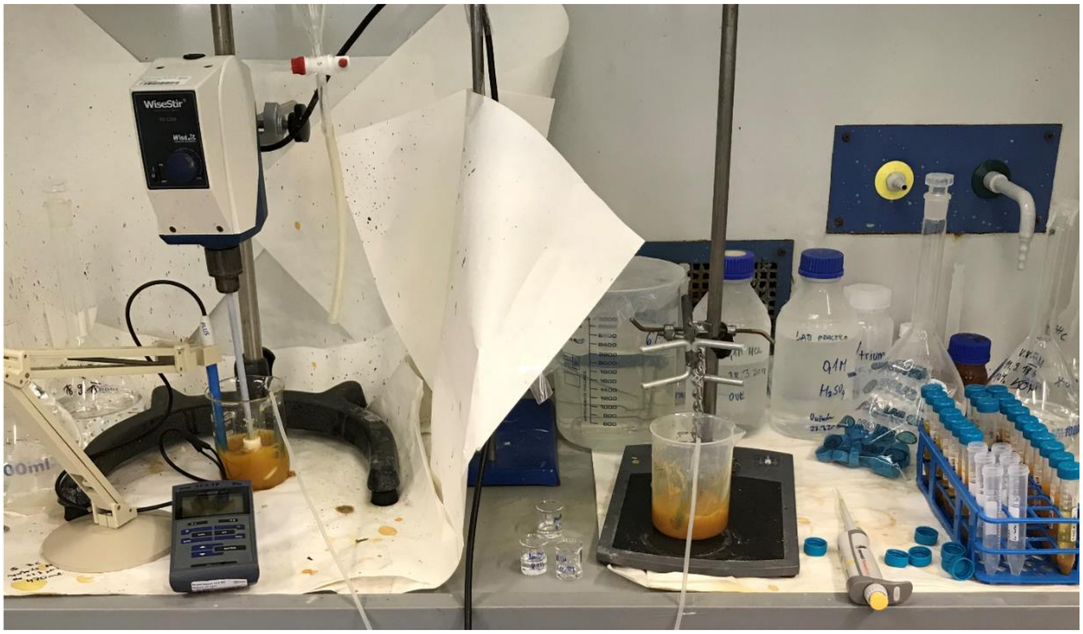


Figure 8 Full experimental apparatus including pH probe, physical mixer, nitrogen sparging, pipettes, and sample test tubes (Porter 2019)

Once the solution was prepared and thoroughly flushed by nitrogen gas, initial samples were extracted for the purpose of creating blanks. Extraction of blanks was necessary to determine what the background concentrations of the final solutions were measured against. After an appropriate number of blanks were extracted it was necessary to affix a physical stirring apparatus. The use of Teflon or other relatively inert materials was essential due to the potential reactivity of ions in solution. It was important not to use a magnetic inducing automatic stirrer as some of the interactions and soil minerals can be influenced by the induction of a magnetic field, especially ferrihydrite and goethite due to the content of iron (Cornell & Schwertmann 2003). Accompanying the physical stirring apparatus, a pH probe was affixed to the apparatus containing at least one of the solutions (see Figure 8). The pH probe was a glass electrode probe affixed to an electrode holder; before introduction into the solution it was important to functionally calibrate the device and to thoroughly clean it before introduction into solution. After the addition of the pH probe, nitrogen sparging equipment and physical mixer the experiment process may proceed.

3.4 EXPERIMENTAL PROCESS

Once the apparatus was fully set up and the solution had been left to bubble with nitrogen for an adequate amount of time the introduction of the soil minerals was performed to the individual solution. After each soil mineral was introduced, the solution was left until the initial pH of solution stabilizes. The specific soil mineral phases being used for this experiment were birnessite, illite, ferrihydrite and goethite (see Figure 9); each mineral phase was applied in differing concentrations due to the relative sorption strength; birnessite (0.5 g/L), illite (10.0 g/L), ferrihydrite (1.50 g/L), and goethite (2.0 g/L).

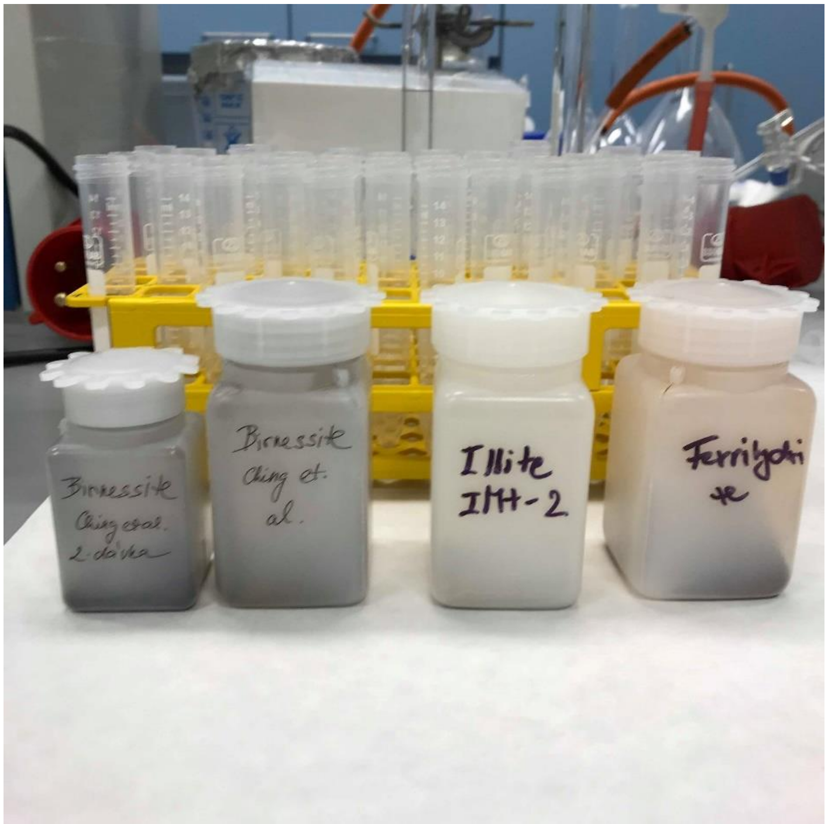


Figure 9 Samples of birnessite, illite, and ferrihydrite used in adsorption experiments (Porter 2019)

Once the solution pH stabilized, initial samples were extracted for ICP-OES (inductively coupled plasma optical emission spectrometry) analysis before the pH adjustment occurred. Two different ranges of pH were utilized, for Zn a pH range of pH

3 to pH 9 and for cadmium Cd pH 4 to pH 10. The range of pH values used throughout the sampling process was used to create a spread of data while still considering more realistic pH values from soil ranges. The solutions were adjusted by dosing 0.01M, 0.1M or 1M sodium hydroxide (NaOH) or nitric acid (HNO_3) (see Figure 10). While adjusting the pH it was essential to be precise and attempt to use as small a volume or acid or base as possible. Within the spectrum of pH values associate with each metal it was determined that 15 sampling points would provide an appropriate adsorption edge. The distribution of these 15 sample points would consist of the initial sample and 14 evenly spaced extractions within the respective ranges; for Zn (initial, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5) and Cd (initial, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5). These values of pH were subject to change after reaching full equilibrium with solution. Once an appropriate number of samples are extracted these samples were subject to 24-hours on either an orbital or end over end shaker in order to make sure equilibrium within the system is achieved.

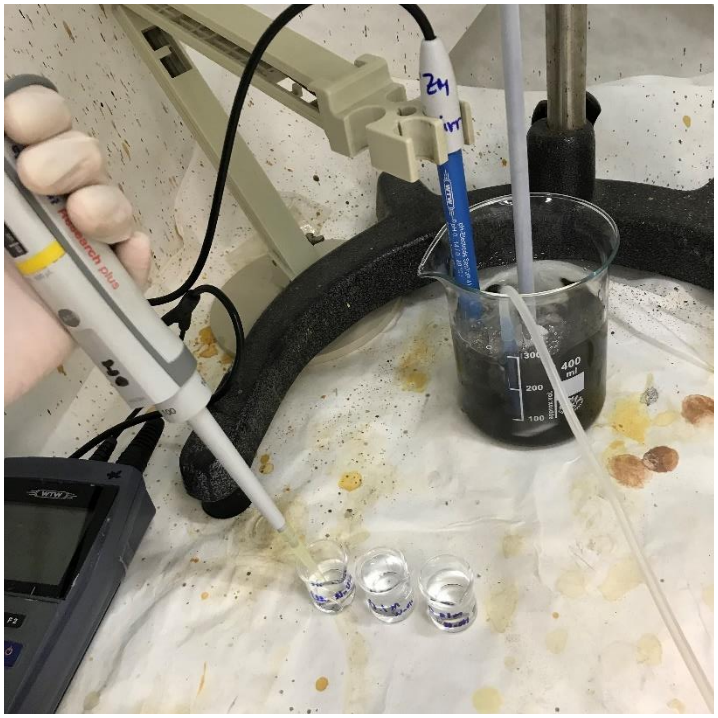


Figure 10 Adjusting of pH via dosing of NaOH from beakers containing (0.01M, 0.1M or 1M) (Porter 2019)

3.5 SAMPLE COLLETION

After 24-hours of agitation, the samples achieved equilibrium within solution. These samples will be remeasured for pH; it was vital to clean the probe in-between each measurement to avoid sample cross contamination. The measurements were repeated for every extracted sample. Following pH measurements, all samples were required to be filtered (see Figure 11). The filtration of samples should be done with 0.45μm cellulose filters. Samples were centrifuged prior to filtration using a Hettich® Universal 320 centrifuge, one or two rounds at 3500rpm at 10 minutes was adequate to facilitate proper filtration techniques. Following the filtration of all relevant samples, samples must be prepared for storage and further analysis. These samples were sent to be analyzed using ICP-OES (Agilent ® 720, USA) for analysis of metals within solution. In order to prepare samples for both storage and analysis they were acidified. The acidification of samples prior to storage was done by pipetting 100μL of concentrated HNO_3 in order to prevent the precipitation within the solution.

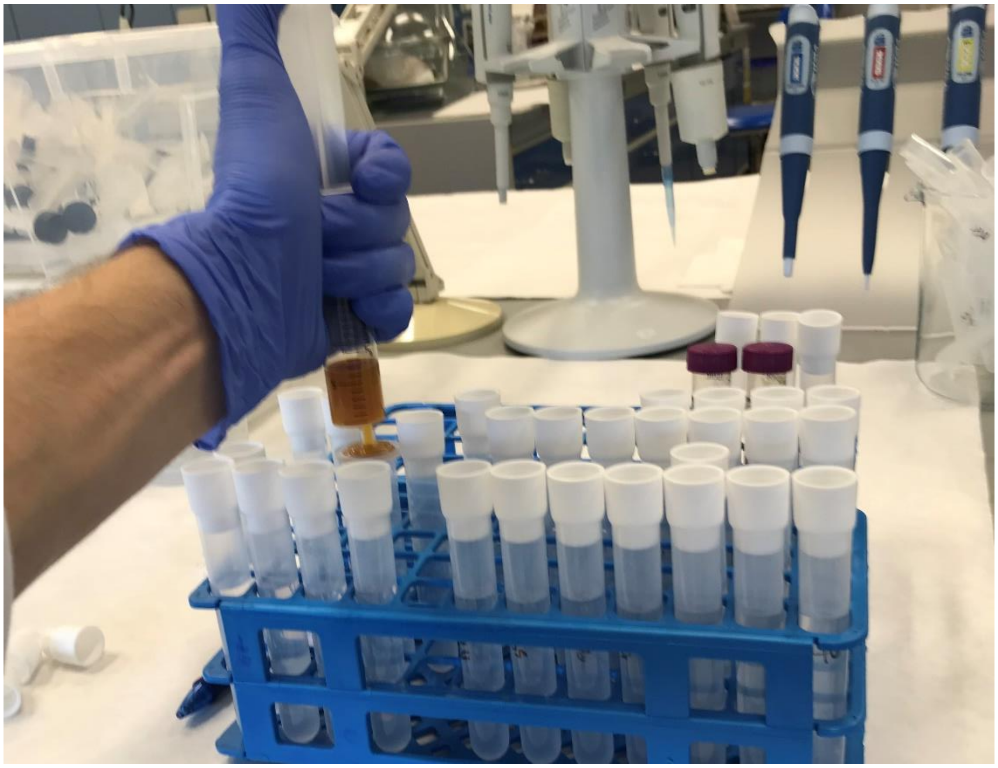


Figure 11 Filtration of samples done via syringe filters into 15mL ICP-OES test tubes (Porter 2019)

3.6 ANALYSIS

In order to evaluate the amount of Zn or Cd that had become complexed by the specific soil phases, it was essential to establish the concentration remaining in solution after sorption and filtration. From a theoretical standpoint the comparison of initial blank sample may be compared to any of the 15 samples. The adsorbed amount of the metals was calculated as a difference between the initial concentration and concentration in solution after sorption.

3.7 ADSORPTION EDGES

With the appropriate ICP-OES data it was possible to construct adsorption edges for both Zn and Cd. Firstly, all concentration data was adjusted for the volume associated with the acidification of the samples. After these concentration values are adjusted, plots can be created comparing adsorbed amount (%) against pH. The concentrations in solution were compared to the blanks from the initial extraction of samples. Calculating the percent difference of the samples against their initial blanks provided information regarding how much of the Zn or Cd was adsorbed via the sorption processes. Resulting adsorption edges were formulated from each metal, ionic strength, and soil phase combination; resulting in a total of 24 separate adsorption edges. Each group of metal and solid phase should have three ionic strengths which can all be used for ideal visual graphical comparison.

3.8 MODELLING

The surface complexation modeling (SCM) was applied to experimental data to elucidate more the observed sorption processes. All models created for SCM were all produced on Visual MINTEQ version 3.0 (Gustaffson 2013). All models were constructed utilizing parameters provided through previous literature (see Table 3). Models being utilized were CCM (Constant Capacitance) and DLM (Double Layer Models); specifically, 2-pK DLM, 2-pK CCM, and HFO DLM. Inputting all the initial solution conditions coupled with the adsorbent physical properties of each specific mineral phase resulted in each respective adsorption data across specified pH ranges. All models if suitable will be included along side figures of the actual collected experimental results along side their respective data sets.

Table 3 Literature sources of modeling parameters for surface complexation

Mineral Phase:	Parameters for Zn:	Parameters for Cd:
Birnessite	(Tonkin et al. 2004)	(Tonkin et al. 2004)
Illite	(Gu & Evans 2007)	(Gu & Evans 2007)
Ferrihydrite	(Dzombak & Morel 1990)	(Dzombak & Morel 1990)
Goethite	(Mathur & Dzombak 2006)	(Buerge-Weirich et al. 2003)

4. RESULTS

4.1 ADSORPTION EDGES – ZINC

4.1.1 ADSORPTION EDGES – ZINC / BIRNESSITE

Adsorption edges for Zn sorption onto birnessite were constructed within the pH range of 3 to 9 at the ionic strengths of 0.1, 0.01 and 0.001 M $NaNO_3$ used as background electrolyte. The range of significant adsorption (25% to 100%) of Zn on birnessite occurred between a pH of 3 to 7.5; where the maximum adsorption (100%) occurred across all three ionic strengths around a pH of ~6.5. The Zn-birnessite solution with background electrolyte concentration of 0.001M resulted in full adsorption at the lowest pH of 6.3. Samples with an ionic strength of 0.001M expressed some negative adsorption values which was theoretically impossible, this error was likely due to Zn contamination of the solution before the initial sample extractions (see Figure 12A). One common introduction of sample contamination can originate from nitrile, latex, and neoprene gloves (Balter et al. 2016). Birnessite exhibited a narrow pH range of (5 to 6.5 pH) regarding significant adsorption of Zn (25% to 100%). According to generalized SCM's (Surface complexation models) for birnessite the double layer model exhibited similar shape to the experimental values with only slight variation. Most of the variation can be attributed to lacking material parameters (site density, log K etc.), which were not available for exactly the same type of birnessite we used. For that, we had to use the data from the literature although they may not correspond precisely to our material. Trends in the 2pK-DLM (SCM) indicate that the 0.001M solution reaches maximum adsorption before the after the two others which is contradictory to the experimental results.

4.1.2 ADSORPTION EDGES – ZINC / ILLITE

Adsorption edges for Zn sorption onto illite were constructed within the pH range of 3 to 9 at the ionic strengths of 0.1, 0.01 and 0.001 M $NaNO_3$ used as background electrolyte. The range of significant adsorption of Zn on illite occurred between pH of 3 to 7.5; where maximum adsorption was reached at ~pH of 7.5 at all ionic strengths. There is an extremely low variation between adsorption edges pertaining to ionic strengths (see Figure 12B). Although illite samples did express similar adsorption preference for lower ionic strengths, they were not affected strongly by the influence of ionic strength on adsorption. The required pH for maximum adsorbance followed the conventional standard of effect of ionic strength on adsorption (0.001M ≤ 0.01M ≤ 0.1M) (Strawn et al. 2015). Illite exhibits a wide range of pH (3 to 7.5 pH) regarding moderate adsorption (10% to 100%) of Cd. CCM-SCM (Constant Capacitance Model) models for examining the adsorption of Zn on illite were generally inconclusive and did not provide any meaningful insights.

4.1.3 ADSORPTION EDGES – ZINC / FERRIHYDRITE

Adsorption edges for Zn sorption onto ferrihydrite were constructed within the pH range of 3 to 9 at the ionic strengths of 0.1, 0.01 and 0.001 M $NaNO_3$ used as background electrolyte. The range of significant adsorption (20%+) within the Zn-ferrihydrite solution existed between pH of 5 to 8; where it reached maximum adsorption upwards of 99%. Maximum adsorption was reached in these samples between pH of 6.8 to 7(see Figure 12C). The Zn-ferrihydrite solution had expressed the inverse relationship with ionic strength that would be expected. Where maximum adsorption was achieved by the solution with a higher ionic strength more rapidly. The required pH for maximum adsorbance did not follow the conventional standard of effect of ionic strength on adsorption (0.001M > 0.01M > 0.1M) (Strawn et al. 2015). Although, these results may be more indicative of a systematic error, as some results also presented a negative adsorption, indicating a higher presence of Zn higher than the blank sample (i.e., original Zn solution without solid adsorbent). Ferrihydrite exhibited a narrow range (5 to 7.5 pH) regarding significant adsorption (20%+) of Zn. HFO-TLM models with parameters provided by Mathur and Dzombak (2006) provided a relatively good fit for the conditions regarding the experimental data; it is worth regarding that this approximation follows the expected ionic strength separation, as previously mentioned.

4.1.4 ADSORPTION EDGES – ZINC / GOETHITE

Adsorption edges for Zn sorption onto goethite were constructed within the pH range of 3 to 9 at the ionic strengths of 0.1, 0.01 and 0.001 M $NaNO_3$ used as background electrolyte. The range of significant adsorption (20%+) occurred within the Zn-goethite solution primarily between pH 4.5 to 8; where the maximum adsorption occurred around pH of 6.9 for all ionic strengths. A clear distinction between horizontal edge shifting was due to the ionic strength that was indicative of the literature (Strawn et al. 2015); the pH required to reach maximum adsorption was decreasing proportionally to ionic strength (0.001M < 0.01M < 0.1M) (see Figure 12D). Goethite exhibited a relatively narrow pH range (5.5 to 7 pH) regarding significant adsorption (20% to 100%) of Zn. SCM used to model the adsorption of Zn was 2-pK DLM (Double Layer Model); the fit of the model to the experimental data would be considered relatively accurate although, the observed trend from experimental results proves contradictory. This is because modelled results exhibited relations which contradict the general relation of ionic strength and required pH for maximum adsorption. In the case of Zn-goethite solution, the 0.1M and 0.01M edges had a better fit than the 0.001M data.

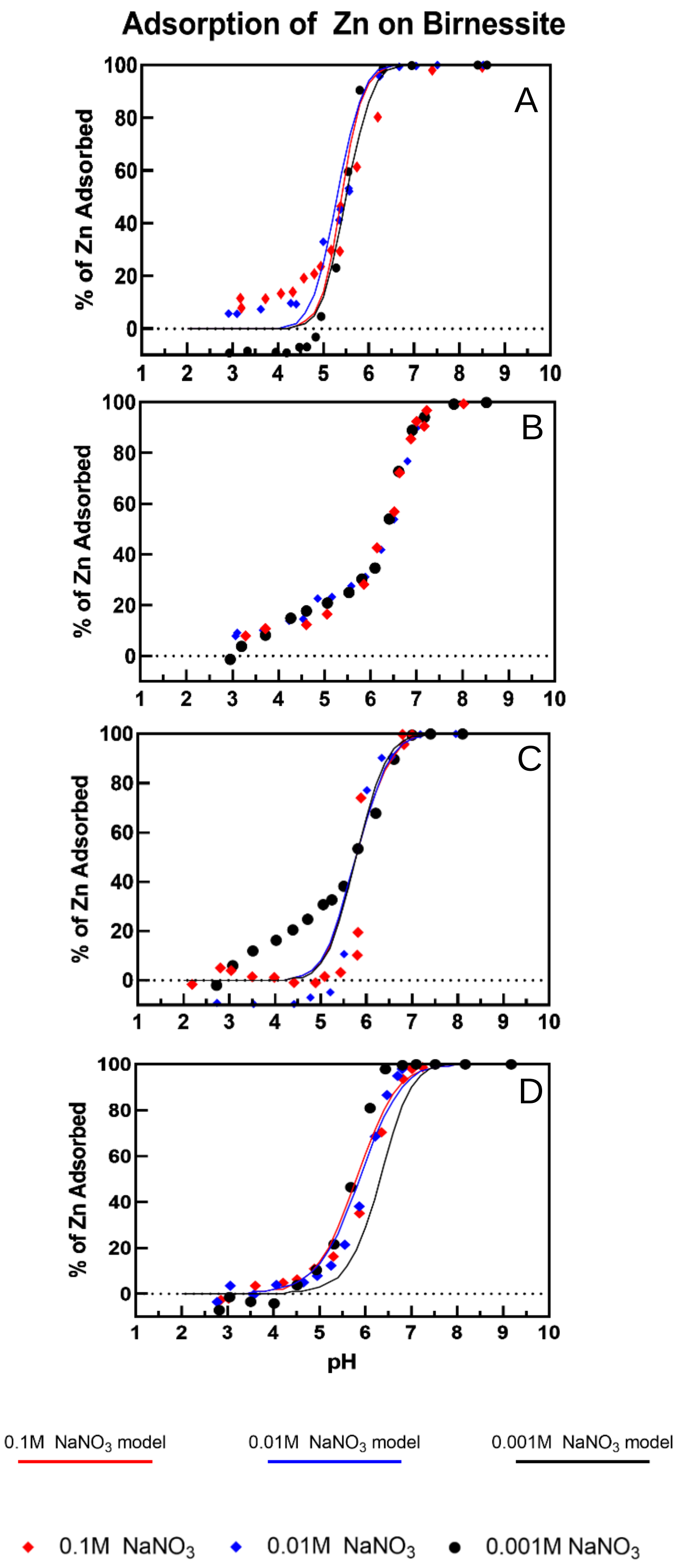


Figure 12 Adsorption edges of Zn on birnessite (A), illite (B), ferrihydrite (C), and goethite (D)

4.2 ADSORPTION EDGES – CADMIUM

4.2.1 ADSORPTION EDGES – CADMIUM / BIRNESSITE

Adsorption edges for Cd sorption onto birnessite were constructed within the pH range of 4 to 10 at the ionic strengths of 0.1, 0.01 and 0.001 M $NaNO_3$ used as background electrolyte. The range of adsorption of Cd on birnessite ranged between pH ~2 to 7; where the maximum adsorption occurred across all three ionic strengths at pH of 7. The effect of ionic strength on the Cd-birnessite sample was low according to the result; there was only a very minute shift essential pH for maximum adsorption (see Figure 13A). Within this sample the weakest ionic strength resulted in the lowest required pH for maximum adsorption, which was expected but there was a slight anomaly regarding Cd-birnessite (0.01M); according to the collected data the point in which samples (0.01M & 0.001M) reach 99% is almost identical. Required pH for maximum adsorption within the Cd-birnessite sample did not follow an expected trend as 0.001M required the lowest followed by 0.1M and 0.01M (Strawn et al. 2015). Although the shape of the figure was deceptive there were minute differences. Birnessite exhibited a relatively large range (2.5 to 7 pH) regarding the significant adsorption (25% to 100%) of Cd. The experimental results did not represent the typical adsorption edge provided by most mineral phases. Experimental results when compared to the 2pK-DLM model exhibits some major differences. The modeled results are indicative of parameters extracted from samples which were analyzed by Tonkin et al. (2004). Both DLM and experimental results expressed the same response to pH changes, but the proportionality of this effect was highly exaggerated by the models.

4.2.2 ADSORPTION EDGES – CADMIUM / ILLITE

Adsorption edges for Cd sorption onto illite were constructed within the pH range of 4 to 10 at the ionic strengths of 0.1, 0.01 and 0.001 M $NaNO_3$ used as background electrolyte. The range of significant adsorption (25%+) of Cd on illite occurs between pH 4.5 to 10; where the maximum adsorption occurred across all three ionic strengths around a pH of ~9.7. The effect of ionic strength on the Cd-illite solution was more immediately apparent; there was a more significant horizontal variance between the three independent trials (see Figure 13B). The required pH for maximum adsorbance followed the conventional standard of lower ionic strength requiring a lower pH to achieve a maximum (0.001M < 0.01M < 0.1M) (Strawn et al. 2015). These adsorption edges do not show any major observable irregularities compared to other samples regarding trends. Illite exhibited a wide range (2.5 to 7 pH) regarding moderate adsorption (10% to 40%) of Cd. CCM-SCM's did not provide any relevant fit to the data according to the parameters included by Gu and Evans (2007). Models were not able to be accurately constructed with pre-existing literature parameters.

4.2.3 ADSORPTION EDGES – CADMIUM / FERRIHYDRITE

Adsorption edges for Cd sorption onto ferrihydrite were constructed within the pH range of 4 to 10 at the ionic strengths of 0.1, 0.01 and 0.001 M $NaNO_3$ used as background electrolyte. The range of significant adsorption (25%+) of Cd on ferrihydrite occurred between pH 5 to 10; where maximum adsorption occurred across all three ionic strengths at a pH of ~7.8. The effects of ionic strength on adsorption for ferrihydrite with regards to ionic strengths were tough to detect with the graphical visualization alone (see Figure 13C); although coupled with the data it was easier to see that there were minute discrepancies. The required pH for maximum adsorbance followed the conventional standard of effect of ionic strength on adsorption (0.001M < 0.01M < 0.1M) (Strawn et al. 2015). Samples extracted from the lower range of pH in the 0.001M samples indicated there may have been traces of contamination resulting in negative sorption in some cases. Ferrihydrite exhibits a narrow range (6.5 to 8 pH) regarding the significant adsorbance (25% to 100%) of Cd. HFO-SCM models were used to establish a general fit regarding the experimental results. The results of this model were effective at expressing the Cd-ferrihydrite solutions. The HFO model not only accurately fits the experimental data, it also was able to exhibit the same trends as the laboratory results.

4.2.4 ADSORPTION EDGES – CADMIUM / GOETHITE

Adsorption edges for Cd sorption onto goethite were constructed within the pH range of 4 to 10 at the ionic strengths of 0.1, 0.01 and 0.001 M $NaNO_3$ used as background electrolyte. The range of significant adsorption (25%+) of Cd on goethite occurred between pH 5.5 to 10; where maximum adsorption occurred across all three ionic strengths at a pH of ~ 8. All observed data from each different ionic strength exhibited seemingly similar results; each respective sample from lowest to highest ionic strength reached maximum adsorption capacity at pH values of 7.6, 7.9, and 8.5 (see Figure 13D). Ionic strength cannot be clearly indicated from the respective figure; although values extracted from samples approaching maximum adsorption capacity were distinctly separate. Goethite exhibited a narrow range (6 to 7.5 pH) of pH regarding the significant adsorption (25%+) of Cd. 2-pK DLM's used to produce models for the Cd-goethite solutions also were able to provide a good fit to the experimental results. Maximum adsorption was projected by the model to be almost identical to that of the preliminary experimental results. Overall, the model can be regarded as successful as it is indicative of both the experimental and theoretical results.

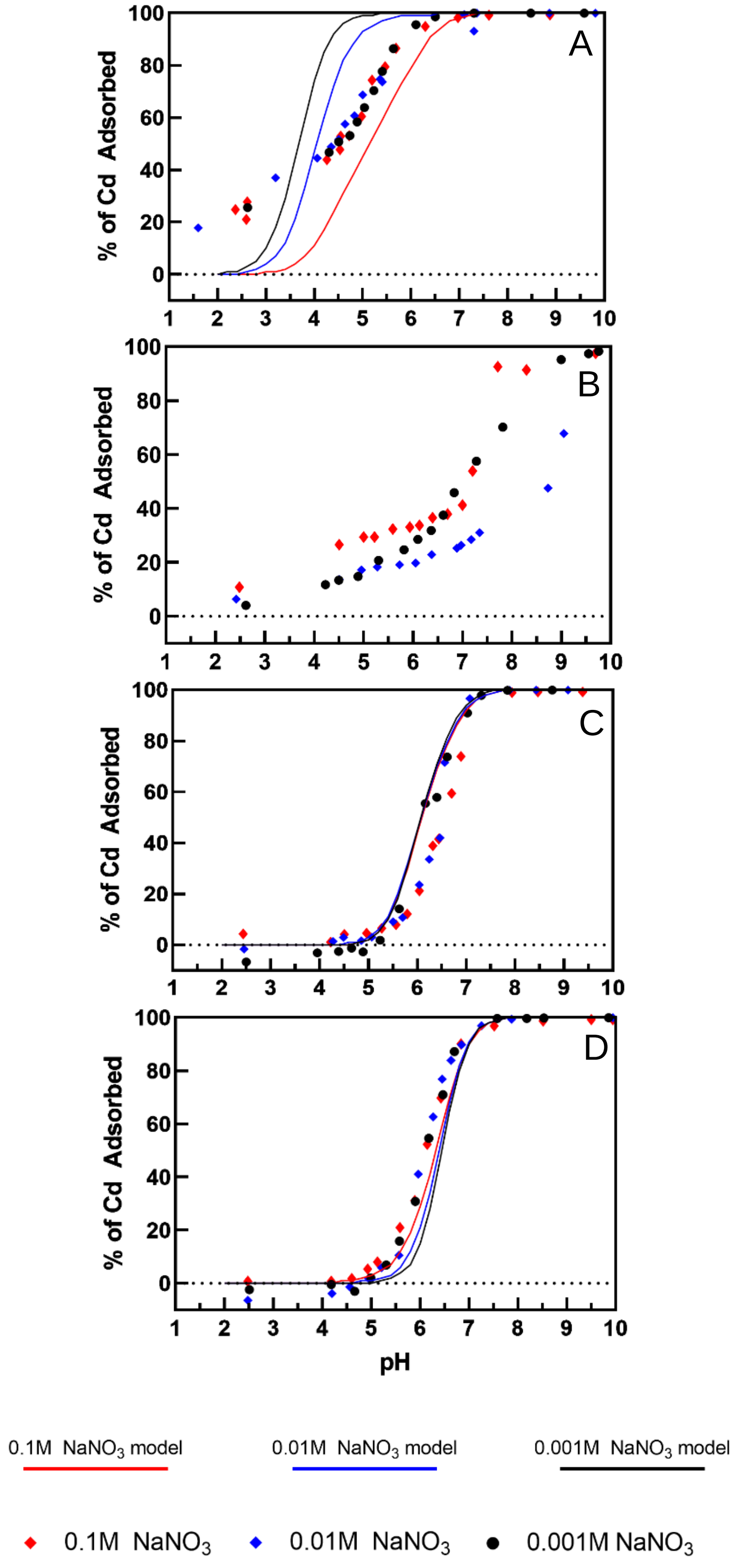


Figure 13 Adsorption edges of Cd on birnessite (A), illite (B), ferrihydrite (C), and goethite (D)

4.3 MINERAL PHASE COMPARISSONS – ZN & CD

4.3.1 BIRNESSITE

The behavior of both Zn and Cd differ in solution with birnessite; there were obvious differences regarding their respective adsorption edge diagrams. According to experimental results there was more significant variation between respective ionic strengths present in the Zn-birnessite solution compared to the Cd-birnessite solution. In both solutions the relation of ionic strength to adsorption remained within conventional standards (Strawn et al. 2015); in both Zn-birnessite and Cd-birnessite solutions with the lowest ionic strength achieved maximum adsorption at a lower pH (0.001M < 0.01M < 0.1M). Both metals reached maximum adsorption at a pH of 6.5 to 7 which should be revealing of material properties of birnessite itself. The relative range of significant adsorption (25%+) was comparable for both metals. Both Zn and Cd were adsorbed to a substantial level at pH values of pH 2 to 7; in which increasing adsorption occurred with increasing pH. Although the ranges of adsorption were similar, birnessite experienced the highest levels of Zn adsorption across a smaller internal range of pH values; whereas Cd exhibited a larger range of significant adsorbance with its lowest adsorbance rates exceeding 15%. Models were established for both Zn and Cd sorption onto birnessite. In both models' parameters such as site density, specific surface area, and solid concentration remain the exact same regarding the material parameters. Although exactly similar material parameters the chemical interactions between the individual divalent ions and surface structures varied highly, as can be seen in Cd-birnessite adsorption curves.

4.3.2 ILLITE

The samples of Zn-illite and Cd-illite exhibited several different qualities regarding total sorption potential. Both adsorption edge diagrams differed quite apparently, but in general both solutions expressed a wide range (4 to 9 pH) of values that can actively promote significant adsorption of these metals. Regarding ionic strength both solutions expressed the conventional standard of inverse proportionality with metal adsorption (0.001M < 0.01M < 0.1M) which often regulates both physisorption and chemisorption respectively (Strawn et al. 2015). Where these solutions differ is in regard to pH required to achieve maximum adsorbance; all three Zn trials achieved maximum adsorbance at pH 7.5 where as Cd samples required a more alkaline environment of pH 9.7. Although both solutions exhibited significant adsorption (25%+) between pH 5 to 10, illite is also able to adsorb empirically significant amounts of Cd at pH 3 to 5.5 but is not as effective regarding Zn. CCM models for both Zn and Cd resulted in very poor estimations of the chemical system and therefore were omitted from the report, all available parameters or materials information appeared to be too varied according to literature (Gu & Evans 2007).

4.3.3 FERRIHYDRITE

Solutions containing ferrihydrite as the primary mineral phase were able to adsorb both Zn and Cd effectively albeit within a narrow range (6 to 8 pH). Both solutions were able to effectively adsorb Zn and Cd within a range of pH 5 to 9. Both solutions were subject to rare negative adsorption values which were due to Zn or Cd contamination; these contaminations have skewed the lower portion of both distributions but still allow for the interpretation of the most vital information from the figure, the location of maxima and range. Experimentally the Cd-ferrihydrite solution exhibited results conventional to ionic strength, but the Zn-ferrihydrite variants exhibited the complete opposite of what was expected; instead of (0.001M < 0.01M < 0.1M) the results expressed a trend of (0.001M > 0.01M > 0.1M) in which a higher ionic strength solution was able to adsorb more Zn at lower pH (Strawn et al. 2015). Overall, according to these experimental results in an inert atmosphere both Cd and Zn are adsorbed similarly by ferrihydrite. HFO models produced for ferrihydrite are almost identical to experimental results. There were no major discrepancies and the fit of the data and trends were extremely cohesive with one another.

4.3.4 GOETHITE

Adsorption edges for goethite solutions were able to clearly indicate the relationship between Zn and Cd adsorption. The range at which both solutions effectively adsorbed Zn and Cd were extremely narrow but similar; both solutions were able to adsorb the most amount of metals between the ranges of pH 5 to 8. Zn-ferrihydrite and Cd-ferrihydrite variants both achieved highest adsorption at a lower pH when ionic strength was respectively at its lowest value (0.001M < 0.01M < 0.1M). Although there was not major variation within each adsorption edge, there was a clear horizontal shift in pH between Zn-goethite and Cd-goethite. While there was a horizontal shift regarding the pH required for maximum adsorption, the shape of the adsorption edges was almost identical. The overall fit of both models was accurate and representative of the experimental data, however the model for Zn explicitly expresses a trend within the data that is not representative of the experimental data. This inaccuracy is due to primality to the imprecisions within the model regarding the weak 0.001M Zn-goethite solution.

5. DISCUSSION

5.1 SURFACE COMPLEXATION MODELLING

According to results from these experiments general adsorption parameters obtained from literature were established that were considerably close for some materials and lacking for others. For each experimental sample a corresponding model was attempted. Comparing experimental results to numerical models requires the acceptance of predetermined parameters established by specific protocols and individuals. Depending on the specific model being utilized to exhibit the specific metal/mineral combination there can be varied outputs. Certain reactions within SCM (Surface Complexation Modeling) are only included within specific models. In order to encapsulate all of these specific reactions you must run a complex combination model of different variants. All modeling done within this thesis was constructed via Visual MINTEQ (Gustaffson 2013). The specific type of model being utilized for each specific situation depends highly on the pre-existing literature. If previous literature exists containing all the specific parameters required to produce such a model it can be utilized. If there is no pre-existing information about a mineral phase or aqueous solution reaction, studies must be performed in order to measure the necessary parameters.

There were a few categories of surface complexation modelling that were available options. The initial options for modelling these complexation reactions in solution were CCM, DDL, and TL; all of which are forms of EDL (Electrical Double Layer) models. The CCM or CC (Constant Capacitance Model) has a relatively limited range of application; the model essentially allows the user to estimate charge density as a function of both pH and ionic strength, where the ionic strength remains relatively constant (Somasundara 2015). CCM models are only able to consider inner-sphere complexes (Lützenkirchen 1999). CCM models incorporate four adjustable parameters which are log K^+, Log K^-, N_s, and c_1 ; where Log K^+ and Log K^+ represent equilibrium constants of complexation reactions, N_s represents site density, and c_1 represents capacitance (Hayes et al. 1991). The secondary option to consider for the modeling of interactions was the DDL/DLM (Diffuse Double Layer / Diffuse Layer Model) which is often regarded as one of the simpler models, as there are less parameters involved in its formulation. Double layered models incorporate three adjustable parameters log K^+, Log K^-, and N_s

(Hayes et al. 1991). Like CCM's, DDL models only consider inner-sphere complexes; strictly pertaining to covalent bonds. Lastly, there is TLM (Triple Layer Models) which are the most complicated of the three common options. TLM's incorporate six adjustable parameters which are log K^+, Log K^-, N_s, c_1, Log K_{An}, and Log K_{Cat} ; where Log K_{an} and Log K_{Cat} represent the log of solubility constants of both anions and cations (Hayes et al. 1991). TLM's can consider both inner and outer-sphere complexes within a given solution.

Due to time and resource constraints, many parameters and resources that were integral to modelling were acquired from a third party compiling database RES^3T (Stockmann et al. 2019). The Rossendorf Expert System for Surface and Sorption Thermodynamics© has compiled a large database of technical parameters measured and provided in historical literature alongside surface complexation reaction equations. Since parameters may vary based on their experimental purpose, it is important to thoroughly examine the presented literature. Each specific combination of mineral and solution may have numerous different models available in the database (see Table 4). It must be determined which type of reaction is being modeled for example monodentate, or bidentate surface complexation.

Problems that arose during the actual modeling of all solutions were acquisition of data, variation in results, and complexity of surface interactions. Although some literature provides extremely accurate parameters regarding their specific results and materials, these results may only be appropriate or representative of their specific samples. The overall variation between each individual's samples can vary by numerous factors of magnitude; these variations result in extreme differences between the literature and an external study. Originally when fitting the models for the included figures there were numerous variants before the finalized versions. In some combinations of Zn or Cd and the respective mineral phase there were numerous literature sources all providing different modeling parameters. In regards to illite specifically there was only one applicable paper regarding material parameters and surface complexation chemistry (Gu & Evans 2007). Regarding the included figures, there was often a combination of literature material parameters coupled with experimental variables measured by the lab, or by the material provider. In order to maximize the viability of each model it was essential to combine parameters and adjust complexation databases. Models were produced for six out of the eight mineral phases; in which models for illite were omitted.

These models were specifically omitted due to their lack of utility or validity. The true complexity of surface complexation of clay minerals resulted in highly over exaggerated models which did not account for multitudes of binding sites (Bergaya et al. 2006; Gu & Evans 2007).

Table 4 Different models available for each surface complexation combination (Stockmann et al. 2019)

Zn Adsorbed by:	Types of Models:	Cd Adsorbed by:	Types of Models:
Birnessite	CC: Constant Capacitance DDL: Diffuse Double Layer NE: Non-electric	Birnessite	DDL: Diffuse Double Layer NE: Non-electric
Illite	CC: Constant Capacitance	Illite	CC: Constant Capacitance ECC: Extended Constant Capacitance
Ferrihydrite	CC: Constant Capacitance DDL: Diffuse Double Layer TL: Triple Layer	Ferrihydrite	BS: Basic Stern CC: Constant Capacitance DDL: Diffuse Double Layer NE: Non-electrostatic TL: Triple Layer
Goethite	CC: Constant Capacitance DDL: Diffuse Double Layer NE: Non-electrostatic TL: Triple Layer	Goethite	CC: Constant Capacitance CDM: CD-MUSIC DDL: Diffuse Double Layer

5.2 MINERAL PHASE SORPTION

Regarding the analysis of adsorption edges for each respective mineral phase there was a variety of literature to consult, which varied based on the mineral. The adsorption of Zn was relatively well categorized data, in particular literature sources regarding Zn adsorption on birnessite, illite, ferrihydrite and goethite were all well comparable to the results from the experiments (Gu & Evans 2007; Komarek et al. 2018; Pokrovsky et al. 2005; Ponthieu et al. 2008). Most of the literature expressed adsorption curves very similar to those acquired through this experimentation. Regarding the adsorption of Zn, illite was a very unpredictable mineral phase which expresses highly variable adsorption across differing ionic strengths according to Gu & Evans (2007); resulting in differing outcomes. Due the many adsorption sites present on the clay mineral illite, the pH required for deprotonation and subsequent adsorption of cations should be maximized between a pH of 6.5 and 7; however, the beginning of this deprotonation begins as early as pH of 2 (Gu & Evans 2007). This property of gradual deprotonation explains the relatively gradual adsorption edges expected for clay minerals (Fan et al. 2018); similar gradual curves are seen in other clay minerals such as bentonite as mentioned in work by Yong-Gui et al. (2011). For Cd the available data is rarer to come across but there were still some available resources. Adsorption data was available regarding birnessite, illite, ferrihydrite, and goethite (Gu & Evans 2007; Huang et al. 2017; Kim 2014; Komarek et al. 2018; Tiberg 2016). Adsorption edges provided by Tiberg (2016) and Komarek et al. (2018) regarding cadmium adsorption onto ferrihydrite and goethite respectively fit the trends observed from this studies experimental results. There are discrepancies between experimental and literature results regarding Cd adsorption edges for birnessite and illite (Gu & Evans 2007; Huang et al. 2017). It is important to note that the comparison between literature sources should not be taken as identical comparisons; experimental procedures are often different and preformed on not identical materials. Six of the eight total adsorption edges exhibited trends reflective of the scientific literature (Kim 2014), whereas Cd-birnessite and Zn-illite illustrated irregular trends according to the literature (Gu & Evans 2007; Huang et al. 2017).

Each combination of either Zn or Cd alongside each mineral phase is controlled by specific adsorption mechanisms. The mechanism is often determined by either specific mineralogical structure or pH (Strawn et al. 2015). Regarding birnessite, there is a consensus that the primary mechanism for adsorption is inner-sphere complexation although this depends highly on the environmental conditions. According to Pokrovsky et al. (2005) the primary mechanisms of adsorption regarding Zn and birnessite are primarily inner-sphere complexes; where sorption sites are composed of structural vacancies surround by oxygen atoms resulting in a bidentate site (Apello & Postma 2002). In comparison, Huang et al. (2017) indicate that with regards to Cd adsorption onto birnessite there were two primary mechanisms indicated; according to their experimental results adsorption mechanism highly depends on the systems pH, at pH less than 5 the driving mechanism of adsorption is outer-sphere complexation and at a pH higher than 6 there is mostly inner-sphere complexation. For illite, the mechanisms of adsorption for both Zn and Cd identified by Gu and Evans (2007) were nonspecific ion-exchange at lower pH which occurred on basal surfaces and edges, and secondly specific adsorption at higher pH’s that occurred primarily on mineral edges. Work by both Ponthieu et al. (2008) and Tiberg (2016) found that for Zn and Cd respectively the main mechanism of adsorption onto ferrihydrite was inner-sphere complexation; More specifically Cd adsorption by ferrihydrite was identified as inner-sphere bidentate complexes to the ferrihydrites surface (Tiberg 2016). Lastly, goethite was found to predominantly form inner-sphere complexes but outer-sphere complexes are also a possibility under more conditions with lower pH (Buerge-Weirich et al. 2003; Dzombak & Morel 1990). Inner-sphere bonds involving both ferrihydrite and goethite primarily involve covalent bonds from the deprotonation of these iron oxy(hydroxides) minerals (Benjamin & Leckie 1981). Estimations regarding adsorption mechanism may be estimated based off of visual analysis of Figures 12 and 13; in general, adsorption on mineral phase is less dependant on pH for outer-sphere complexes compared to inner-sphere complexes due to the amount of available functional groups (Strawn et al. 2015).

5.3 ISOTOPIC FRACTIONATION IN LITERATURE

Due to the long-term malfunction of TIMS (Thermal Ionization Mass Spectrometer) used by the research group of Department of Environmental Geochemistry, the specific isotopic fractionation of Zn/Cd during sorption onto different mineral materials used could not be analyzed within a time frame of this study, although it was originally planned. Therefore, the discussion portion of this topic will mainly focus on the results and evidence provided by already published literature. Regarding the fractionation of stable isotopes there is a relative tendency for heavier isotopes to become enriched in solution, although this is not always the case (White 2014; Wiederhold 2015). Regarding Zn and Cd, they will commonly exhibit both of these behaviours respectively (Wiederhold 2015). There are numerous factors that influence the overall preferential fractionation of these elements within their systems.

It is important to note that in experimental papers working with fractionation and adsorption there are two common notations that are used, either enrichment of mineral surface (1) or solution (2). In environmental systems it is imperative to recognize that adsorption and fractionation can be vary in intensity between organic and inorganic systems. This is the case of Zn isotope fractionation where the variation of $\delta^{66/64}$ Zn can be between -0.4 ‰ and 1.4 ‰ regarding the liquid phase (Cloquet et al. 2008). For iron oxy(hydroxide) minerals, Guinoiseau et al. (2016) stated that heavy Zn isotopes were preferentially enriched on the surface of these minerals $\delta^{66/64}$Zn of 0.29 ± 0.07‰ for goethite and 0.53 ± 0.07 ‰ for ferrihydrite. Iron, aluminum, and manganese oxides are susceptible to quite varied fractionation due to a number of influential factors; minerals such as goethite preferentially adsorb lighter Zn isotopes, whereas birnessite often adsorb heavier isotopes (Bryan et al. 2015; Ponthieu et al. 2008). The fractionation of Zn when adsorbing onto birnessite is considered highly variable depending on ionic strength; low ionic strength results in extremely limited fractionation, while at high ionic strengths there is enrichment of heavy isotopes on mineral surfaces where $\delta^{66/64}$Zn can vary between 0.52 ‰ to 0.77 ‰ (Bryan et al. 2015; Guinoiseau et al. 2016). Lastly, illite which is one of the most, if not the most abundant clay mineral especially in more temperate regions. According to the research of the literature and academic journals, there is research pertaining to adsorption experiments involving illite clays such as work done by Gaskova (2009), Gu and Evans (2007) and He et al. (2000). Although there is several adsorption and SCM's (Surface Complexation Modeling) done for illite, there appears to be almost no research regarding the isotopic fractionation during Zn complexation with illite clays.

There is a large gap of knowledge regarding the isotopic fractionation of Cd, and cadmium enrichment regarding three mineral phases identified in this study. Most of the research regarding Cd fractionation in the present literature often pertains to oceanic and extraterrestrial samples. A large portion of these samples take the form in the fractionation of Cd isotopes present in meteorites, aquatic plants, sea water, and more recently waste materials (Martinková et al. 2016; Wei et al. 2016; Zhu et al. 2015). There is a similar problem with Zn as there is with Cd, which refers to the relative abundance of studies; there is a large influx of studies regarding adsorption trends, but the effects of surface complexation on isotopic fractionation are lacking. Although there were no sufficient studies done regarding the isotopic fractionation of Cd adsorbing to many mineral phases, there were studies done by Wasylenki et al. (2014) covering fractionation related to manganese oxy(hydroxides). The study was performed to analyze the fractionation of Cd^{2+} on marine birnessite, these experiments were conducted at both high and low ionic strengths. High ionic strength experiments resulted in $\delta^{114/12}$Cd values of 0.27 ± 0.07 ‰ which is significantly higher than the values observed at low ionic strengths which averaged $\delta^{114/12}$Cd of 0.12 ± 0.03‰ (Wasylenki et al. 2014). In a weaker ionic strength solution, birnessite preferentially sorbed lighter isotopes of cadmium, whereas the heavier isotopes became enriched within the solution (Wasylenki et al. 2014).

6. CONCLUSION

The influence of pH and ionic strength was analyzed by subjecting each selected mineral phase to $1x10^{-4}$M solutions of Zn and Cd with background electrolyte concentrations of 0.1M, 0.01M, and 0.001M. The pH of the solutions was adjusted according to each respective element, pH 3 to 9 for Zn and a pH of 4 to 11 for Cd. Birnessite, illite, ferrihydrite, and goethite were all significantly influenced by varying ranges of pH with regards to their adsorption capacity. Experimental results indicate that the influence of pH on Zn adsorption exhibited the following trend where birnessite > ferrihydrite > goethite > illite; where birnessite appeared to be the have smallest pH range required to reach maximum adsorption, which can be caused by its poor crystalline structure and susceptibility to isomorphic substitution. Regarding Cd solutions lead to the following trend where ferrihydrite > goethite > birnessite > illite; where ferrihydrite in this case exhibited the smallest range of pH required to achieve total adsorption. Even though Zn and Cd share many properties that allow them to behave similarly in numerous physical and biological processes, they do not appear to behave identically with regards to adsorption onto various soil mineral phases; as is the case according to these experimental results where the trends although similar, do not share identical results. Contributions from this research provide three major insights into future problems in the sphere. Firstly, access to these experimental and modeled adsorption edges allows for several of the necessary parameters for studying isotopic fractionation due to adsorption processes regarding Zn and Cd; where it is vital to know the range of pH where maximum adsorption occurs within respective mineral phases. Secondly, the difference in pH sensitivity for both Zn and Cd between differing mineral phases offers more opportunity to study the individual surface chemistry and the cationic interactions of each respective element and its respective mineral phase. Lastly, the results coupled with SCM aid in estimating the overall accuracy of pre-existing models or material parameters currently in circulation; for example, the tendency to include either inner-sphere or outer-sphere complexes. As visible from the literature review dealing with fractionation of Cd/Zn during the sorption onto the various soil mineral phases, there are still significant gaps in knowledge in some cases. Because of that, this study will serve as a basis for large study aiming to elucidate the isotopic fractionation of Zn/Cd during the sorption on various soil phases and its connection with the types of surface complexes formed.

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