

# INVESTIGATING THE EFFECT OF AGING AND TIME ON THE FATE AND TRANSPORT OF LEAD IN ARTIFICIALLY CONTAMINATED TROPICAL SOILS

by

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## ABSTRACT

Incubation and Batch desorption experiments were conducted on ultisol and a mollisol to assess the effect of aging temperature and contact time on Pb sorption in soils A and B horizon ultisol and Mollisol from Humboldt and San Luis Obispo County, California were incubated at room temperature, 50 and 70 °C for 3 hours, 4 weeks and 2 months in the laboratory. After each aging period, samples were extracted with  $10^{-4}$  M H<sub>2</sub>SO<sub>4</sub> solution, equilibrated for 24 hours, centrifuged and filtered through a 0.45 µm filter. A separate subsample of the B-Horizon supernatant was passed through 0.22 µm filter. Increase in aging temperature and fixation time was observed to enhance Pb solubility and bioavailability in the A horizon soils. Mobility of Pb in the B horizon was greatly retarded. XRD analysis showed no phase change upon heating; while K<sub>d</sub> computations showed partitioning of Pb in the solid phase of the mollisol was greater. This allows for assessing the risk associated with mobility of Pb in tropical soils, and shows that ground water in areas overlain by ultisols are probably more liable to Pb contamination.

INDEX WORDS: Pb sorption, Tropical soil, Mollisol, Soil Horizons, Thermal aging, ICP-MS, pH, Mobility, Distribution coefficient.

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## **DEDICATION**

This Thesis is dedicated to my parents, Prof. and Mrs. F.A. Balogun for their continued financial, emotional and spiritual support; and to all scientists who are relentlessly pursuing the “truth”.

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## 1 INTRODUCTION

### 1.1 General Overview

Contamination of soils by heavy metals from anthropogenic sources has become a source of major environmental problems since the advent of the industrial revolution. This is partly due to their ability to persist in the environment by partly being retained in the solid phase components of the soil as well as dissolved Pb in soil waters (Rodriguez-Maroto et al., 2003; Sipos et al., 2008). As a result of the increase in human population over last two centuries, there has also been a commensurate increase in the demand for energy (Adriano 1986; Appel and Ma, 2002). In the quest to meet this growing energy demand, humans have engaged in various developmental activities which have resulted in the introduction of heavy metals to the environment. Mining is a quintessential example of a source which could release high doses of heavy metals into the environment. Others include peat mining, application of fertilizers and animal manure for the purpose of agricultural yield, smelting, gasoline additives, and car battery repair facilities (Alloway, 1995; Rodrigo-Maroto et al., 2002; Walraven et al., 2014). In the course of these various developmental activities, huge quantities of waste materials are generated. Also, various unsustainable waste disposal methods have been adopted, which have resulted in accumulation and localization of toxic, deleterious heavy metals such as Pb, As and Cd in the environment (Jalali and Khanlari, 2007, Mahar et al., 2015). Soils and hydrologic systems are major reservoirs for the accumulation of these toxic, heavy metals.

Soils are heterogeneous mixture of both solid phase, fluid and gaseous phase components, interactions between these phases are important in understanding the fate and transport of heavy metal contaminant which enter the system. These interactions determine the ability of soils to adsorb heavy metals, which has huge consequences in the area of waste disposal, nutrient transport

in agriculture, soil fertility, remediation of polluted soils and wastewater (Bradl, 2014). Solid-liquid phase interactions leading to heavy metal sorption and desorption, are affected by soil components and their properties, environmental factors such as Eh and pH, as well as the quantity of metal added either by anthropogenic or pedogenic sources (Jalali and Khanlari, 2007). Several soil components and properties such as organic constituents, surface active mineral, presence of primary and secondary mineral phases are important controlling factors in metal retention and mobility in the solid phase (Sipos et al., 2008). These factors have been extensively studied in the last few decades (Abollino et al., 2002; Ronkard et al., 2007). Most importantly, other abiotic factors such as organic matter, carbonate content, clay mineral, Fe, Al and Mn Oxides, Eh and pH, play a pivotal role in metal retention in soils (Rieuwerts et al., 1998; Rodrigo-Maroto et al., 2002; Sipos et al., 2009). The role of these aforementioned controlling factors is well acknowledged and extensively studied in Temperate soils, however, tropical soils are less understood (Davies, 1997; Kookana and Naidu, 1998; Naidu et al., 1998; Onyatta and Huang, 1999; Mbila et al., 2001; Appel and Ma, 2002; Herpin et al., 2002; Campos et al., 2003; Reeves, 2003; Bertonecini et al., 2004; de Alcantara and de Carmago, 2004; Udom et al., 2004, Rieuwerts, 2007). An area where a knowledge gap exists is, the role of pH in sorption of heavy metals in tropical soils, because of the variable nature of their surface charge. Also, the effect of aging time and incubation on sorption of heavy metals in tropical soils hasn't been extensively researched; this work aims to consider both areas. Understanding the role of aging and incubation will allow for better assessment of soil behavior, and health risk associated with mobility of Pb in the tropics. In addition to understanding this basic soil behavior, and health risks it is important to look into common mining practices in the underdeveloped countries of West Africa, in order to understand the pathways of heavy metals into soils in mining areas.

## **1.2 Artisanal Mining practices in Sub-Saharan West Africa**

Artisanal mining is widely practiced in Sub-Saharan West Africa, and one of its major environmental impacts is the production of heavy-metal wastes as by-products. Artisanal mining is broadly defined as mining by individuals or companies, using little or no mechanization (Hentschel, et al., 2002). In West Africa, it has been estimated that over 600,000 people are engaged in Artisanal mining, with gold being the primary mineral mined (Hentschel, et al., 2002). Ghana is currently the second largest producer of gold in Africa, and ninth largest producer of gold in the world, while Nigeria and Sierra Leone are ranked 22<sup>nd</sup> and 23<sup>rd</sup> respectively (Carson et al., 2005; Bloch et al., 2012; USGS Minerals Resource Program, 2012). In these countries, artisanal exploration of mineral resources lacks proper legal authorization. Mining involves the use rudimentary techniques, laborious processes, and hazardous working conditions, which frequently results in negative human health and environmental impacts (Hilson, et al., 2002, Tschakert et al., 2007; Van Bockstael, 2014). The method of mining used involves crude open cut (Open pit mining), whose construction sometimes can be mechanically assisted (Tubosun, et al., 2014). Some heavy metals mined using this technique include Zn and Pb, which also are constituents of gangue minerals like Cerussite and Sphalerite (wastes) from Gold mining. Mine wastes from unsustainable artisanal mining practices are piled in heaps. Contaminants usually leach and infiltrate into the soil and aquatic ecosystems, resulting in environmental pollution, which causes serious health challenges in humans (Ogbonna et al., 2012; Garcia-Lorenzo, et al., 2014).

### **1.3 Health effects of Lead Contamination**

(Pb) is a major heavy metal in Galena and Gold mining districts, which leaches out of mine tailings and can cause significant health problem in humans, especially in pregnant women and children. In many developing countries, children have been known to work, play and eat at these mine sites (Lar, et al., 2013). Though there is no known safe level of Pb exposure, however, a substantially high blood Pb level can result in adverse health effects (U.S CDC Advisory Committee, 2012, Zahran, et al., 2013). The average concentration of Pb in surface soils worldwide is 32 ppm but varies from 10 ppm to 67 ppm (Pendias, et al., 2001; Wuana et al., 2011; Gunatilake, et al., 2014). Studies have shown that plants do not readily take up Pb from soils, however, in soils that have high Pb content, significant levels of Pb have been found in roots of plants growing in such soils (Wuana, et al., 2011; Alvarez-Ayuso, et al., 2012). Ingestion of contaminated food and inhalation of dust are the main routes of exposure (Sharma, et al., 2007; Wuana, et al., 2011 and Alvarez-Ayuso, et al., 2012). Pregnant women and children are at a higher predisposition to Pb poisoning than men.

The worst affected group are children below six years of age, and common health effects associated with this group include; intellectual deficits, low birth weight, nervous system, red blood cell and kidney damage (Needleman et al., 2004, Oulhote et al., 2013; Zahran, et al., 2013; Gunatilake et al., 2014). A typical example of the effect of Pb poisoning in children is the incident which occurred in June 2010, in Zamfara state, Northwestern Nigeria. Here, the ingestion and inhalation of Pb dust from gold mining, caused the death of about 400 children (Lar et al., 2013, Taylor-Mejia, 2015). Adults, on the other hand, exhibits symptoms that range from sterility to some form of cancer. (Mandal et al., 2002; Alvarez-Ayuso, et al., 2012 and Gunatilake et al., 2014). In the light of these health hazards associated with Pb contamination, it is of great



importance to examine the occurrence of the various Pb phases, which could lead to Pb contamination of soils.

#### 1.4 Occurrence and Speciation of Pb in the Environment

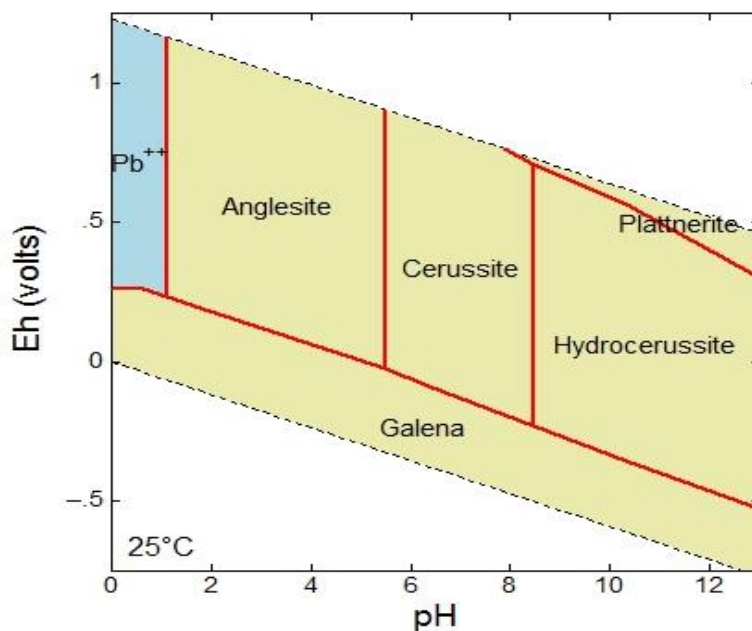
Chemical weathering of Pb minerals plays a significant role in the bioavailability and bioaccessibility of Pb from different phases. In nature, the occurrence of Pb in its native state is rare (Cheng and Hu 2009). It occurs in minerals such as Galena (PbS), Cerussite (PbCO<sub>3</sub>), Anglesite (PbSO<sub>4</sub>), Pyromorphite (Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl and Mimetesite (PbCl<sub>3</sub>Pb<sub>3</sub>(AsO<sub>4</sub>)<sub>3</sub>) (Ponizovsky et al., 2001; Cheng, 2009). When Galena is exposed to the right conditions such as abundant oxygen and water (rainfall), it weathers to form Anglesite (PbSO<sub>4</sub>), which is partially stable and bioaccessible (Razo et al., 2004; Lara et al., 2011). Galena and Cerussite are the most common phases, but others frequently occur in nature (Cheng et al., 2009).

Due to the unstable nature of Anglesite, it can weather further to form cerussite, which is more bioaccessible and hazardous than Galena and Anglesite put together (Fuerstenau et al., 1986; Lara et al., 2011, Taylor-Mejia et al., 2015).  $\text{PbSO}_4 + 3\text{OH}^- \rightarrow \text{Pb(OH)}_3^- + \text{SO}_4^{2-}$  (1)



Of all these Pb phases, Cerussite appears to be the most toxic. The mineral cerussite is an indicator mineral in silver mining. Cerussite is a mineral which can be colorless, white, gray, light yellow and green. It has a white streak and a hardness of 3-3.5, with an orthorhombic crystal system (Wikipedia). It exhibits a conchoidal fracture, cleavage in 1 direction and has specific gravity of 6.5-6.6g/cm<sup>3</sup>. Whereas cerussite is a carbonate mineral, and anglesite is a sulfate, the soil environments that favor thermodynamically stability of one over the other are quite different with cerussite favored by alkaline, higher-pH soils (Deocampo, 2010). The retention of Pb from cerussite and Pb mineral phases in soils depends on certain characteristic properties of the soil.

The Figure 1 below shows the Eh-pH diagram of different Pb phases.



**Figure 1:** Eh-pH speciation diagram for different Pb species  
[\\*http://www.coalgeology.com/lead-geochemistry-eh-ph-solubility-and-remedial-technologies/21720/](http://www.coalgeology.com/lead-geochemistry-eh-ph-solubility-and-remedial-technologies/21720/)

### 1.5 Background Knowledge on Characteristics of Tropical Soils

Several soil types with different physical, chemical characteristics and varying Pb retention capabilities can be found in Sub Saharan West Africa. Some of them are Oxisol, Ultisol, Mollisol. Oxisol, Ultisol are characterized by their low base saturation, while mollisol on the other hand, has a high base saturation of >50%. The two most abundant soil types in West Africa are Ultisols and Mollisols. (FAO Database, 2008). However, the most prominent soil in Galena mining districts in Nigeria, where base metals such as Cu, Zn, and Pb are mined, are Ultisol and Alfisol (USDA Global soil map 2005). In order to have an adequate understanding of heavy metal sorption to tropical soils, important characteristics of tropical soils must be examined.

Generally, there are about three distinct features which distinguish Western African tropical soils from other soil types. These are: (i) domination of Kaolinite clay fractions over 2-1

clays; (ii) low organic matter content; (iii) Presence of Fe and Al oxides (Rieuwerts, 2007). Tropical soils are a product of intense leaching and weathering of soils at the tropics, leading to enrichment in two-layer clay minerals and secondary alteration products such as Fe and Al rich minerals (Wilcke et al., 1999a after Duchaufor, 1977). The minerals resulting from this process usually exhibit little isomorphic substitution, which is a reason why tropical soils exhibit low cation exchange capacity (CEC) (Davies, 1997).

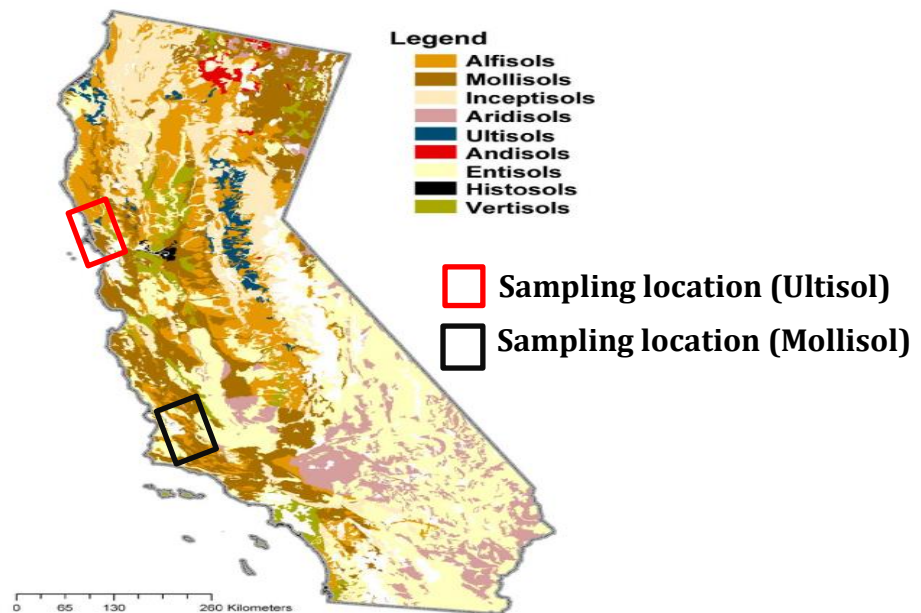
Though kaolinite has a low cation exchange capacity, however, there are about two binding sites which could interact with metals. Firstly, the  $\text{Si}^{4+}$  in the tetrahedral sheet can be substituted for by a  $\text{Al}^{3+}$  which leaves a net negative charge of -1 (Rieuwerts, 2007). A metal such as  $\text{K}^+$ ,  $\text{Ca}^{2+}$  or  $\text{Pb}^{2+}$  can make up for the deficiency in charge, depending on its ionic radii; the likelihood of this is rare. Secondly, based on empirical evidence, Kaolinite has a point of Zero Charge (PZC) of about 2-4 (Appel and Ma, 2002; Peter Ryan, 2005). The importance of  $\text{H}^+$  and  $\text{OH}^-$  in the determination of surface charge in soil system cannot be overemphasized, because they ultimately determine the types of ion sorbed by the soil (Van Olphen 1997, Appel and Ma, 2002). Given that kaolinite has relatively small surface charge, the importance of pH in determining sorption of ions in soil dominated by kaolinite becomes relatively insignificant. However, Davies (1997) has shown that other tropical soils consists of 2:1 clays, which have high permanent negative charges and high CEC. Furthermore, findings by Naidu et al., 1997 in a study on the mobility of trace metals in tropical soils, points out that magnitude of negative surface charge of a typical tropical soil like Ultisol increases with increasing pH and organic matter, however, most tropical soils are deficient in organic matter due to high rate of mineralization of humus. The study concludes that, due to the low surface charge density on the surface of tropical soils, the mobility of trace metals

increases, so does their bioavailability. In the light of these findings, the need to examine characteristics of some tropical soils become pertinent.

Ultisols are one of the twelve soils order in the USDA Soil Taxonomy system, and they have some peculiar characteristics which distinguishes them from temperate soils. They are usually acidic, clay-rich, low in organic matter, common in subtropical regions and have low base saturation (USDA Soil Taxonomy). Mollisols are intermediate between Ultisols and Aridisols, also known as “black soils and are organic matter rich, and have high base saturation and high pH value (Xing et al., 2004, Veenstra, 2012). They are characteristics of grassland areas (USDA Soil Taxonomy). Aridisols on the hand are dry, poor in Calcium rich organic matter, have high pH and are usually found in semi-arid to arid regions. Due to the variability in these properties, it is expected that these soils will have different Pb retention capabilities. Oxisols are characteristic of tropical and subtropical regions of the world. They are highly weathered soils which typically have low physical and chemical activity of minerals like (Kaolinite, Fe, Al and Mn Oxides, Zircon and Quartz (<http://www.nrcs.usda.gov>). Oxisols are known to be relatively acidic with soil pH ranging from 4.5-6.5. For this work Pb sorption in Ultisol and Mollisol will be considered. Figures 1 and 2 shown below are pictures of the soils and locations from which they were obtained.



**Figure 2:** A picture showing Ultisol (Left) and Mollisol (Right)



**Figure 3:** General map of soil orders in California (Adapted from USDA-NRCS STATGO Database).

\*<https://casoilresource.lawr.ucdavis.edu/projects/pedology-and-soil-survey/gis-and-digital-soil-survey-projects/>

### 1.5.1 Soil Properties Affecting Pb Sorption in Topical Soils

Several physical and chemical factors such as pH, organic matter, clay mineralogy, carbonate content, temperature, and time, are known to aid in Pb sorption and retention in different soils. Clayey soil has been found to retain Pb, two and a half times better than sandy soils; however, on addition of organic matter to the soil, Pb retention was similar (Heil and Deocampo, 2011). This is probably due to the high surface area of clay minerals compared to that of sand-sized particles. Therefore, particle size (soil texture) and Organic matter are important factors in soil Pb retention (Vega, et al., 2009; Heil and Deocampo 2011; Garcia-Lopez, et al., 2014). Also, varying quantities of carbonate and soil pH have been found to support Pb retention as well. Increasing the concentration of calcium carbonate and pH has been reported to increase Pb retention in soils,

especially clayey soils (Businelli and Tombesi, 2009; Cerqueira et al., 2011; Garcia-Lopez et al., 2014). Also, the availability of oxides and hydroxides of Fe and Mg greatly influences sorption of Pb in soils (Vega et al., 2009; Arenas-Lago et al., 2014, Garcia-Lopez et al., 2014).

The significance of the effects of these factors is that it determines the speciation and bioavailability of these Pb species (Vega et al., 2009). For instance, cerussite is highly soluble at pH of less than 6 and low  $\text{CaCO}_3$  concentration; Anglesite is soluble at pH higher than 4.5 (Wilkin et al 2007). The effect of climate is yet another important factor. Precipitation enables the formation of Iron hydroxides which reacts with Pb to form Pb-hydroxide, thereby sequestering Pb from the soil (John and Leventhal, 1995). These factors vary in different soils. Therefore, it is essential to examine in detail, some roles played by these physical and chemical properties, in Pb sorption in tropical soils.

### ***1.5.2 Impact of pH and Organic Matter in the Sorption of Pb in Soils***

The role of pH in heavy metal sorption has been extensively studied in the field of soil sciences, and is arguably the most important soil parameter which contributes metal sorption. Results from empirical investigations has revealed that, at low pH there is a decrease in metal sorption and vice versa (Temminghoff et al., 1994, Semu et al., 1987; Barrow et al., 1992; Yin et al., 1996; Bradl et al., 2004; Rieuwerts, 2007). Consequently, there is a corresponding increase in both bioavailability and mobility of the heavy metals. Several authors have investigated the effect of pH on metal sorption in soil. Stated below are some of their findings.

Appel and Ma (2002) examined the sorption characteristic of two heavy metals (Cd and Pb) in three tropical soils as a function of pH, while varying metal concentration. The result of their experiment showed that the concentration of Pb released in solution, increased with decreasing pH. The experiment also showed that Ultisol absorbed a higher concentration of Pb

than the Mollisol. This is counter intuitive, because Mollisol is expected to sorb more Pb in the solution. However, this was attributed to the unusually high proportion of organic matter present in the Ultisol relative to the Mollisol. Due to the mineralogy of these three tropical soils, these soils are mainly composed of amorphous colloids which have amphoteric surfaces, therefore pH becomes very important.

Bradl (2004) studied the adsorption of heavy metal ions on soils and its constituents using empirical and mechanistic model approaches for heavy metal sorption. EXAFS was used to evaluate several ligands and some ternary complexes. Humic acid was one of the ternary complexes examined. The presence of humic acid on mineral surfaces was found to have a profound effect on heavy metal mobility. The research posited that at high pH values, anionic forms of humic acid increased in solution. With an increase in the concentration of this type of acid, the rate of desorption of heavy metals into ground water systems becomes pronounced.

Vega et al. (2009) in another study, used linear regression and tree regression statistical tool, for the analysis of influence of soil properties on the sorption of Cd, Cu and Pb in 20 soils from Northwestern Spain. The result of the linear regression statistical modelling revealed that, non-competitive Pb sorption and retention capabilities for the soils are similar. A regression coefficient of 0.33 and 0.29 was obtained for CEC, pH and organic matter respectively. In conclusion, the work showed that, the soil horizons sorbed Pb in the order  $Cd < Cu < Pb$ . Also, the soil parameters responsible for >60% of sorption and retention of these heavy metals were exclusively, CEC and pH. This again goes to show; the pertinent role pH plays in heavy metal sorption and retention in soils.

In a study conducted by Li et., al (2014) on the release of Cd, Cu and Pb in the urban soils of Copenhagen, 1mM  $Ca(NO_3)_2$  and 10Mm  $HNO_3$  were used as leaching solutions to assess the

shifts in metal leachability as a function of soil acidification. It was concluded that, over a period of 15 weeks, 78%, 18% and 15% of total Cd, Cu and Pb were released into solution. A 10 fold the rate of desorption increase for Cd and Pb was observed when the pH was decreased by 2 and 3 units respectively. Based on the ongoing discussion, pH of the soil solution plays a major role in the cation sorption in soils. However, the presence of organic matter in the soil, especially humic and fluvic acids which have functional groups such as (-COOH, -OH and -NH<sub>3</sub>) greatly influences the soil ability to sorb and retain, and make heavy metals like Pb bioavailable (Ahmed et al., 2015). However, other pertinent soil properties such as the proportion of Organic matter, Cation Exchange Capacity and Clay mineral content play important roles in heavy metal sorption in all types of soils. Pb sorbs onto organic matter because of the formation of chemical bonds with -COOH and OH<sup>-</sup> functional groups.

In recent times, studies have been conducted to assess sorption of Pb by organic matter which is partitioned in either the solid or liquid phase. It was observed that at a pH of around <5, the solubility of Pb increased, which is expected because solubility increases with decreasing pH (Elder; 1989, Ahmed et al; 2015). Low concentration of organic ligands inhibited this process. However, increased concentration of organic ligands increased Pb desorption at low pH again. (Ashworth and Alloway, 2008). The interaction of organic matter and heavy metals results in the formation of organo-metal complexes which usually aids the mobility and bioavailability of Pb in soils. Also, the effect of organic matter (solid phases and liquid phases) on Pb sorption and desorption has been extensively studied.

Yang et al. (2006) studied the effects of pH, organic acids, and inorganic ions on Pb desorption from variable charge soils in China. For this study, citric, acetic, malic and oxalic acids were used as chelating agents. It was found that, the rate of desorption of Pb in these soils decreased



by 5 times its original value within a pH range of 1-4. However, this decline diminished at pH values >4. The explanation given to this phenomenon was that, at low pH and concentration of organic acid, the desorption process was slightly inhibited, but at higher concentrations of organic acid, and high pH,  $\text{Pb}^{2+}$  desorption was enhanced.

(Seul-Ji Lee et al., 2013) amended a characterized soil with 1%, 5%, and 10% peat moss, and recorded 37.9%, 87.1% and 95.4% immobilization of Pb. This lends further credence to the fact that organic matter, in the solid form, can sorb Pb in soils. The use of brown coal, peat moss in the immobilization/sorption of Pb has also been extensively studied. Brown coal “lignite” is a good source of organic matter because it undergoes slow mineralization and greatly enhances soils ability to sorb Pb and other heavy metals (Sklodowski et al., 2006). Given the ongoing discussion, a good background has been established on how pH and Organic matter can affect the bioavailability and speciation of Pb in soils.

### ***1.5.3 Role of Clay Minerals in Pb sorption in soils***

It is of little surprise that, the predominant mineral in most tropical soils is the 1:1 clay mineral, kaolinite. This is probably due to the intense weathering which has worked and reworked the soil over extended periods of time. The Point of Zero Charge of Kaolinite varies between 2-4 (P. Ryan, Environmental and low temperature geochemistry). Direct assessment of surface charges via non-specific ion adsorption as a function of pH, yielded a PZC of 2.3-3.7 for ultisol and 3.9-4.4 for oxisol from Puerto Rico (Appel et al., 2002). On the other hand, investigations on the mineralogy of Mollisol, showed that a large proportion of its clay mineralogy is made up the 2:1 clays Vermiculite, Smectite and Illite.

Based on results from empirical studies, kaolinite has a layer charge of zero. Its ability to act as a cation or anion absorber in soil systems has been highly downplayed. Again, the

fundamental role of pH in determining the mobility and availability of heavy metal contaminants comes into the fold here. As mentioned earlier on, kaolinite is a “low activity” mineral, results from cesium adsorption method has been able to delineate that kaolinite under natural conditions carry a net negative surface charge and thus have a limited ability to sorb cation (Khawmee et al., 2013). Also, it is believed that kaolinite has a heterogeneous surface charge based on prevailing soil conditions; therefore, the mechanism of the development of charge is subject to some dispute in some quarters (Ma and Eggleton, 1999).

Some research works have suggested that the basal ditrigonal structure carries this negative charge due to the isomorphous substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$ . The charge on the mineral edges is believed to be due to the exposed  $\text{OH}^-$  group, which sorb cations depending on pH (Mc Bride; 1976, Rand and Melton; 1977; Williams and William, 1976, Ma and Eggleton, 1999). Works done by Bolland et al., (1979) shows that the negative charge is developed because of isomorphous substitution, while Grim (1968) favored the exposed  $\text{OH}^-$  at the mineral edge site scenario. (Ma and Eggleton, (1999) corroborates the finding that, exposed  $\text{OH}^-$  groups are mainly responsible for the charge, this in turn is highly dependent on pH. In other words, pH and PZC charge play a very crucial role in the development of surface layer charge either in the basal siloxane ditrigonal hole or at the mineral edge sites of kaolinite.

The adsorption of Pb on Ferrihydrite and iron oxides is quite similar. This is because, the mechanism by which they sorb divalent cations is also pH dependent. Experimental analysis has shown that, these divalent metals form inner sphere complexes on the surface of clay minerals with variable surface and inner layer charges (Violante et al., 2002). Also, data from Dzombak and Morel (1990) shows that sorption of cations onto the ferrihydrite is a function of pH, with a preferred sorption pattern being set up with smaller radius trivalent cations being sorbed first.

Based on the ongoing discussion, it is emphatic that Clay minerals with the aid of changes in pH of the soil and solution are the major controlling factors for heavy metal speciation and bioavailability

#### ***1.5.4 Effect of contact time and aging temperature on heavy metal sorption***

Empirical results from batch sorption experiments by authors such as Cline et al., (1994), Martinez et al., (2008), Jalali and Khanlari (2007) have shown that contact time and temperature do have an effect on the bioavailability of heavy metals in soils. It has been established that the residence time of heavy metals in soils is directly related to the bioavailability. Also, research work by various researches have shown that bioavailability is usually at its highest immediately after the application of the metals to the soil. Elucidated below are some of the key finding by these various authors.

In their investigation of the effects of aging process on the fractionation of heavy metals on some calcareous soils in Iran, Jalali and Khanlari (2007) studied the effect of contact time on the availability of Pb, Zn, Cd, and Cu. The soil samples were spiked with 500 mg/kg of Pb, Zn, Cu, and 8 mg/kg in chloride form, and incubated for 3hr, 1, 7, 14, 21 and 28 days at 25 °C and constant moisture. The amended soils were fractionated by sequential extraction method to obtain metals bound to carbonate, Mn and Fe Oxide, organic, residual and exchangeable fractions of the soil. The result of their experiment showed that Cd and Pb which associated with the weakly bounded exchangeable fraction are most labile within the first 3 hours, and become less mobile with increasing contact time. This shows that there is a heightened risk of heavy metal contamination of lower horizons and run off water through leaching at the onset of pollution.

Martinez et al. (2003) in a study to determine the effect of aging and temperature on dissolved organic matter and elemental release from metal contaminated soils. The soil samples

were equilibrated using 30ml, and incubated at 10, 28, 45, 70 and 90 °C for 2 days, 2 weeks and 2 months. Dissolved organic carbon (DOC), total soluble elements (by ICP-MS), and labile metal concentrations by differential pulse anodic stripping voltammetry (DPASV) were determined in the supernatants filtered through 0.22µm (10-90 °C), and supernatants filtered through 0.45µm (90 °C only). The results of the experiment showed that concentration of total soluble metal increased as the time and temperature increased. Also, it was observed that a corresponding increase in DOC resulted in a commensurate increase in total soluble metal released in solution. However, at 90 °C, DPASV analysis showed a marked sharp decline in concentrations of Cu and Al. The experiment was conducted for an extended period of (550 days); results still showed a decrease in concentration of Cu and Al at lower temperature of 23 °C and 70 °C. It was concluded that the breakdown of soil Organic Matter is enhanced by increased aging temperature and time, and the process is believed to be element specific. This again shows the importance of soil organic matter in metal retention and speciation. Furthermore, aging temperature and time has clearly been demonstrated to influence heavy metal mobility in aqueous systems.

Cline et al. (1994) examined the effect of aging on contaminant mobility for Pb contaminated soils. Four soil samples (2 sand, 2 sandy loam) were contaminated at two different concentrations of Pb (1000 mg/kg and 10000mg/kg) and aged for 2 and 20 months respectively. 25ml of tap water, EDTA (0.01M and 0.1M), HCl (0.1N and 1.0N), HNO<sub>3</sub> (0.1N and 1.0N), CH<sub>3</sub>COOH (0.1N and 1.0N), and CaCl (0.1M and 1.0M) were used as washing solutions to examine the effect of aging on washing efficiencies. 10 ml of each supernatant was vacuum-filtered through a 0.45µm filter and analyzed for soluble Pb. Results from AAS analysis showed that for samples (sandy loam) washed with HNO<sub>3</sub>, EDTA, and CaCl, at 20 months of aging, there was a slight increase in concentration of Pb that was released in solution relative to samples aged at 2 months. This trend

was observed for soils aged at lower concentration, while a slight decrease was observed for those aged at higher levels of Pb. Though enough data wasn't gathered from the experiment to yield a thorough statistical analysis, the results showed that aging had an effect on the efficiencies of the washing process.

## **1.6 Justification for the Study**

Many studies around the world have focused on Pb retention in calcareous soil, however, not enough has been on tropical soils (Kaschl et al., 2002; Jalali and Khanlari, 2007; Li et al., 2013; Santiago-Martin et al., 2014). Ultisol and Mollisol are predominant in many mining districts of Sub-Saharan Africa, and in several other tropical areas of the world. Data on the factors and mechanisms responsible for sorption of heavy metals such as Pb, Cd, and As onto soil constituents have been well articulated and documented in the literature. However, not nearly enough research work has been done on the effect of some of these factors on heavy metal sorption in Tropical soils. This work aims to examine the speciation and mobility of Pb as a function of pH, temperature and contact time in variably charged tropical soils from two different horizons. To assess the role of thermal aging and fixation time in heavy metal sorption in these soils, dilute Sulfuric acid ( $\ll 1\text{M}$ ) has been used as a proxy for acid rain fall, extracting solution. Also, this work aims to elucidate upon the transport of Pb between soil fractions in the  $0.45\mu\text{m}$  and  $0.22\mu\text{m}$  size range. To evaluate the impact of increasing temperature and time on Pb sorption in the tropical soils used in this work, quantitative measurement of Pb recovered from batch dissociation experiments were examined. Furthermore, probable phase transformation of mineralogical constituents of the soils was examined to further ascertain the role of temperature in Pb sorption.

## 2 METHODOLOGY

### 2.1 Experimental Procedures

The surface horizon A (0-36cm) and B horizon (36-203cm) of two soils obtained by Dr. Chip Appel (department of Environmental Soil Chemistry, California Polytechnique) from California were used for this study. An Ultisol (Fine, parasesquic, isomesic Typic Palehumults), a Mollisol (Fine, smectitic, thermic Typic Argixerolls) were obtained by) from the Trailhead series, Humboldt County, and Los Osos Series, San Luis Obispo County respectively. Mineralogical characterization was performed by Dr. Willie Harris' group (Department of Soil and Water sciences, Univ. of Florida, Gainesville). Presented in **tables 1& 2** are the physical and chemical properties of the soils used in this experiment. A cobble-sized Quartz crystal obtained from the Mineralogy Laboratory of Georgia State University was pulverize and used as control experiment.

About 500 grams of each soil type was passed through <2 mm (ASTM 10) sieve to remove roots and coarse-grained particles. The resulting soil fraction was oven dried at 60 °C for 24 hours, and ground in a ceramic casket using a ball pestle impact motor grinder for 15 minutes. This was done to ensure that the grain sizes were within a range <0.5mm, because heavy metals have the greatest affinity for small grain sizes with high surface area. Resulting samples were collected in acid washed 1 L Pyrex beakers, and three, 20-gram replicate of each soil type (B-Horizon) were prepared for spiking experiment at concentrations of 2000 mg/kg and 4000 mg/kg, and subsequently for aging at 0days, 4 weeks and 8 weeks respectively.

*Table 1: Empirical Physical and Chemical Characteristics of A Horizon soils by (Dr. Harris)*

Soil Order	Horizon	Sampling Depth (cm)	% Organic Carbon	pH	USDA CEC (cmolc/kg)	Mineralogy
Ultisol	A	0-13	3.96	4.2	15.4	HIV, HIS and Kaolinite
Mollisol	A	0-36	3.55	6.5	27.3	Vermiculite

Table 2: Empirical Physical and Chemical Characteristics of Bt Horizon Soils (Dr. Harris)

Soil Order	Horizon	Sampling Depth (cm)	% Organic Carbon	pH	USDA CEC (cmolc/kg)	Mineralogy
Ultisol	Bt	69-203	0.27	4.5	21.4	HIV, HIS and Kaolinite
Mollisol	Bt	36-81	0.97	6.5	55.0	Vermiculite

### 2.1.1 Preparation of Spiking agent and washing solution

The Pb carbonate used as spiking agent for this experiment was ACS chemical grade obtained from Fisher Scientific. deionized water (18.2 MΩ) was used in the preparation of dilute H<sub>2</sub>SO<sub>4</sub> stock solutions used as washing solution to simulate rainwater. Provided below are the computational methods used for the calculation of quantity of spiking agent (PbCO<sub>3</sub>) and washing solutions used in this experiment. To achieve a concentration of 2000 mg Pb/kg of soil; about 2.6 grams of PbCO<sub>3</sub>/kg must be added according to the formulation:

$$\frac{2000\text{mg Pb}}{1\text{kg soil}} \times \frac{1\text{mmol Pb}}{207\text{mg Pb}} \times \frac{1\text{mmol PbCO}_3}{1\text{mmol Pb}} \times \frac{267\text{mg PbCO}_3}{1\text{mmol PbCO}_3}$$

$$= 2579.7 \text{ mg PbCO}_3/\text{kg Soil}$$

Therefore, 0.052gram of PbCO<sub>3</sub> will be needed to achieve a concentration of 2000mg Pb /kg in 20 grams of soil.

Conversely, to achieve a concentration of 4000 mg Pb/kg soil, the formulation below was used

$$\frac{4000\text{mg Pb}}{1\text{kg soil}} \times \frac{1\text{mmol Pb}}{207\text{mg Pb}} \times \frac{1\text{mmol PbCO}_3}{1\text{mmol Pb}} \times \frac{267\text{mg PbCO}_3}{1\text{mmol PbCO}_3}$$

$$= 5159.4 \text{ mg PbCO}_3/\text{kg Soil}$$

Based on the calculation above, 0.103 gram of PbCO<sub>3</sub> will be required to achieve a concentration of 4000 mg Pb /kg in 20 grams of soil.

For the batch experiment conducted to determine the sorption capacity of both soils, 1.2 Liters of  $10^{-4}$  M  $\text{H}_2\text{SO}_4$  was used as washing/extracting agent. This was prepared by modifying the method of (Beyer et al., 2006) by diluting 6.6  $\mu\text{L}$  18M  $\text{H}_2\text{SO}_4$  against  $\approx 1.2$  Liters of D.I Water. The final pH of resulting solution was 3.94 and was adjusted to 4 by adding an appropriate volume of 0.001M NaOH solution. (Furthermore, in an effort to study the variation in sorption characteristics at pH. 4, different solutions with pH 3, 4, 5, 6 were prepared). Solutions with pH 3 and 4 were prepared by diluting  $10^{-3}$  M and  $10^{-4}$  M  $\text{H}_2\text{SO}_4$  respectively against 1 L of D.I water. Final solution pH of 2.71 and 3.67 were achieved and were adjusted to 3 and 4 by adding an appropriate volume of NaOH. However, solutions with pH 5 and 6 were prepared by adding 5-10  $\mu\text{L}$  of 1M NaOH to a solution of dilute  $\text{H}_2\text{SO}_4$  with a pH of 4.

### ***2.1.2 Incubation and batch extraction experiment***

Incubation experiments were conducted and modified, following the method of Tai and McBride (2013). Two analytical 20-gram replicate samples of each soil type were placed in 16 different petri dishes and spiked with 2000 mg/kg and 4000 mg/kg of Pb respectively. The powdered cerussite was dispensed in 5 mL of 0.05 M  $\text{NaNO}_3$  (background electrolyte) and sprayed evenly over the soil. A background concentration of 0.005 M was used because, the ionic strength of most tropical soils varies between 0.005 – 0.01 M (Gillman and Bell, 1978; Dolling and Ritchie, 1985; Naidu et al 1994). The soils were then homogenized using a 15 cm glass rod for about 5 minutes. The unaged samples were allowed to stand for 3 hours, before they were subjected for 24 hours of equilibration and subsequent centrifugation and filtration. Other sets of samples were aged in an oven at 4 weeks and 8 weeks, at a temperature of 50 °C and 70 °C respectively. Presented below is the quantity of  $\text{PbCO}_3$  added to each 20 grams of soil replicate samples.



*Table 3: Soil prepared for unaged sample and dilute Acid extraction (A Horizon)*

Spiked Soil (20 Grams)	Sample ID	PbCO <sub>3</sub> added (Grams)
Ultisol + PbCO <sub>3</sub>	UdoC1	0.0529
Ultisol + PbCO <sub>3</sub>	UdoC2	0.1053
Mollisol + PbCO <sub>3</sub>	MdoC1	0.0573
Mollisol + PbCO <sub>3</sub>	MdoC2	0.1088

*Table 4: Soil prepared for 8 weeks sample and dilute acid extraction (A Horizon)*

Spiked Soil (20 Grams)	Sample ID	PbCO <sub>3</sub> added (Grams)
Ultisol + PbCO <sub>3</sub>	UW8C1	0.0566
Ultisol + PbCO <sub>3</sub>	UW8C2	0.1074
Mollisol + PbCO <sub>3</sub>	MW8C1	0.0558
Mollisol + PbCO <sub>3</sub>	MW8C2	0.1059

*Table 5: Soils prepared for unaged sample and dilute acid extraction (Bt Horizon)*

Spiked Soil (20 Grams)	Sample ID	PbCO <sub>3</sub> added (Grams)
Ultisol + PbCO <sub>3</sub>	UVdo	0.0513
Ultisol + PbCO <sub>3</sub>	UWdo	0.0535
Mollisol + PbCO <sub>3</sub>	MVdo	0.0584
Mollisol + PbCO <sub>3</sub>	MWdo	0.0531
Ultisol + PbCO <sub>3</sub>	UXdo	0.1046
Ultisol + PbCO <sub>3</sub>	UYdo	0.1044
Mollisol + PbCO <sub>3</sub>	MXdo	0.1075
Mollisol + PbCO <sub>3</sub>	MYdo	0.1041

*Table 6: Soils prepared for aging at 4 weeks and dilute acid extraction (Bt Horizon)*

Spiked Soil	Sample ID	PbCO <sub>3</sub> added (Grams)
Ultisol + PbCO <sub>3</sub>	U4V	0.0585
Ultisol + PbCO <sub>3</sub>	U4W	0.0592
Mollisol + PbCO <sub>3</sub>	M4V	0.0579
Mollisol + PbCO <sub>3</sub>	M4W	0.0581
Ultisol + PbCO <sub>3</sub>	U4X	0.1081
Ultisol + PbCO <sub>3</sub>	U4Y	0.1103
Mollisol + PbCO <sub>3</sub>	M4X	0.1034
Mollisol + PbCO <sub>3</sub>	M4Y	0.1073

*Table 7: Soils prepared for aging at 8 weeks and dilute Acid extraction (Bt Horizon)*

Spiked Soil	Sample ID	PbCO <sub>3</sub> added (Grams)
Ultisol + PbCO <sub>3</sub>	U8V	0.0562
Ultisol + PbCO <sub>3</sub>	U8W	0.0537
Mollisol + PbCO <sub>3</sub>	M8V	0.0538
Mollisol + PbCO <sub>3</sub>	M8W	0.0553
Ultisol + PbCO <sub>3</sub>	U8X	0.1064
Ultisol + PbCO <sub>3</sub>	U8Y	0.1041
Mollisol + PbCO <sub>3</sub>	M8X	0.1052
Mollisol + PbCO <sub>3</sub>	M8Y	0.1067

UV= 20 grams of soil spiked with of 2000 mg Pb/kg of soil

UW= 20-gram replicate of Ultisol (UV) at 2000 mg Pb/kg of soil

MX= 20 grams of soil spiked with a concentration of 4000 mg Pb/kg of soil

MY= 20-gram replicate of Mollisol (MX) at 4000 mg Pb/kg of soil.

After the completion of each period of incubation, the soils were extracted from the incubation chamber for further analysis. For the A horizon soils, Three, 5-gram samples were taken from each batch of 20 grams for batch desorption. For the B horizon, 7 analytical sample measurements weighing 2.5 grams each were taken from each 20-gram batch of soil. 3 out these 7 samples were used in the batch desorption experiment, while the remaining 4 were used in a separate pH Vs desorption experiment where. The first 3 soil samples for the batch desorption experiment were extracted with a H<sub>2</sub>SO<sub>4</sub> solution of pH 4, while the remaining 4 samples were extracted using solutions with pH ranging from 3-6.

### ***2.1.3 Determination of Initial Spiking Concentration (C<sub>0</sub>) by Acid Digestion***

Acid digestion in accordance with EPA Method 3050B was employed in a fume hood to determine the initial concentration of Pb which was successfully applied in spiking the soil. Approximately 1-gram sample (dry weight) of incubated soils were transferred to a digestion vessel (Teflon Beaker), and 10 mL of 70%w/v HNO<sub>3</sub> was added. The slurry was mixed and

covered with a ribbed watch glass; heated on a hot plate at  $95\text{ }^{\circ}\text{C} \pm 5$  for 15 minutes. The samples were to cooled for a period 20 minutes after which an additional 5ml of  $\text{HNO}_3$  was added. The sample was again returned to the heating source and heated until brown fumes were minimal. During this period, the samples were heated for a period of 1 hour until approximately 5ml of digestate was left in the vessel. Covering over the solution was maintained always using a ribbed watch glass.

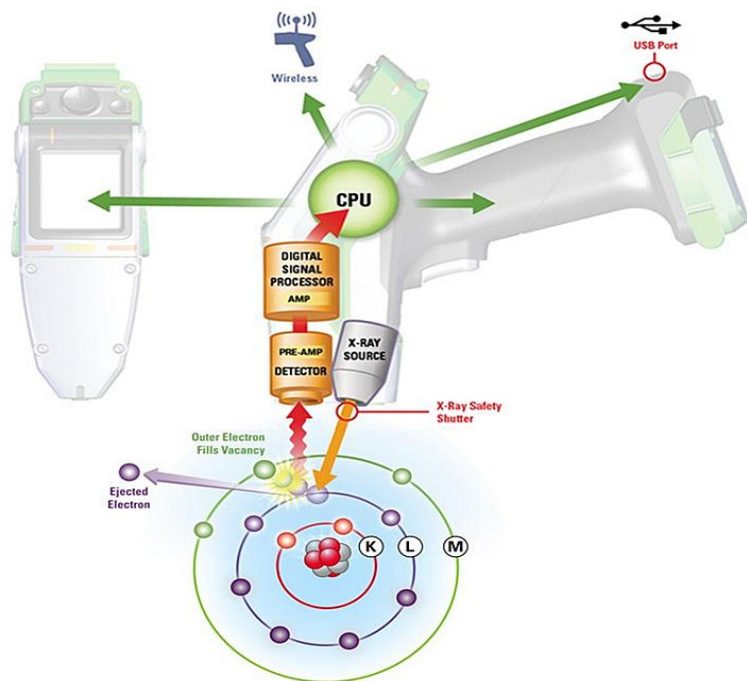
After this step, the heating vessels were removed from the heating source and allowed to cool for another 20 minutes. Then, 2 mL of  $\text{H}_2\text{O}$  and 3mL of 30%  $\text{H}_2\text{O}_2$  was added to the 5mL digestate in a 1ml aliquots respectively. The samples were returned to the heating source, covered with a ribbed watch glass and the acid-peroxide digestate was allowed to evaporate and reduce to approximately 5mL. This reduction in volume was achieved after 1 hour of heating without boiling. After this step, the digestate was cooled for 15 minutes, then 1 ml of the digestate was withdrawn and diluted with 19 mL of D.I water to achieve a dilution factor of 20. The diluted samples were subjected to centrifugation at a speed of 3000rpm for 15minutes; the supernatants were decanted and filtered using a  $0.45\mu\text{m}$  syringe filter. The samples were subsequently sent for ICP-MS analysis at the Laboratory for Environmental Analysis University of Georgia, Athens. Provided below is a flow chart showing the setup for this experiment.

#### ***2.1.4 Determination of Initial Spiking Concentration by (XRF)***

X-Ray fluorescence hand analyzer was also used as a reconnaissance tool in determining initial concentration of Pb which successfully contaminated the soil. The X-ray fluorescence spectroscopy is a fast, non-destructive, safe and clean analytical technique used in the quantitative determination of the elemental composition of materials. The handheld XRF analyzer employs the

use of Energy Dispersive X-ray fluorescence for its operation by measuring secondary X-rays which are emitted from a sample.

Like most analytical techniques, the underpinning XRF analytical technique is based on the interaction of radiation with matter; in the case of this technique the X-ray portion of the light Spectrum is used in the analysis. Primary X-rays generated from the X-ray source interacts with atoms of the elements in the material of interest, thus some electrons are knocked off from the inner shells of these atoms. Specifically, the energy of the incident primary electrons must be greater than the binding energy of the K or L shells for these electrons to be dislodged. The vacant space vacated by the dislodged electron is then filled by another electron from the atoms outer orbital shell. This electron from the outer higher energy shell, fills the vacant void, thereby emitting characteristic fluorescence radiation ( $k\beta$ ) which is indicative of elements in the material of interest. The energy distribution of the emitted secondary characteristics radiation is measured by a detector equipped with a preamplifier. The digital signal processor which is equipped with multistage electronic circuits processes the measured signal and send the output to the CPU; the final result is then displayed on the readout screen attached to the XRF gun. Figure 3 shows the schematics of a handheld XRF analyzer.



*Figure 4: Schematics of the Energy Dispersive XRF handheld analyzer*

\* <https://www.thermofisher.com/us/en/home/industrial/spectroscopy.html>

### **2.1.5 X-Ray Diffraction (XRD)**

There are numerous analytical techniques used in determining structural changes across variety of different surfaces. The X-ray Diffraction is a nondestructive technique which investigates structures of amorphous and crystalline materials. It can also be used in the semi quantification and identification of mineral phases in powdered samples. The selected samples were hydrolyzed, and subjected to 5 mins of ultrasonic disaggregation, centrifuged for 10 mins at 3500 rpm, and the clay portion was collected and applied to labeled glass slides. They were left to dry for 24hrs, then run through the EXPERT PRO diffractometer with the PANalytical measurement program to obtain the “air-dried diffraction pattern. After this, they were immersed in an ethyl-glycol chamber for vapor saturation for another 24hrs. The samples were again analyzed using a scan angle range of 5 – 40 ° for 30 minutes with nickel monochromator to

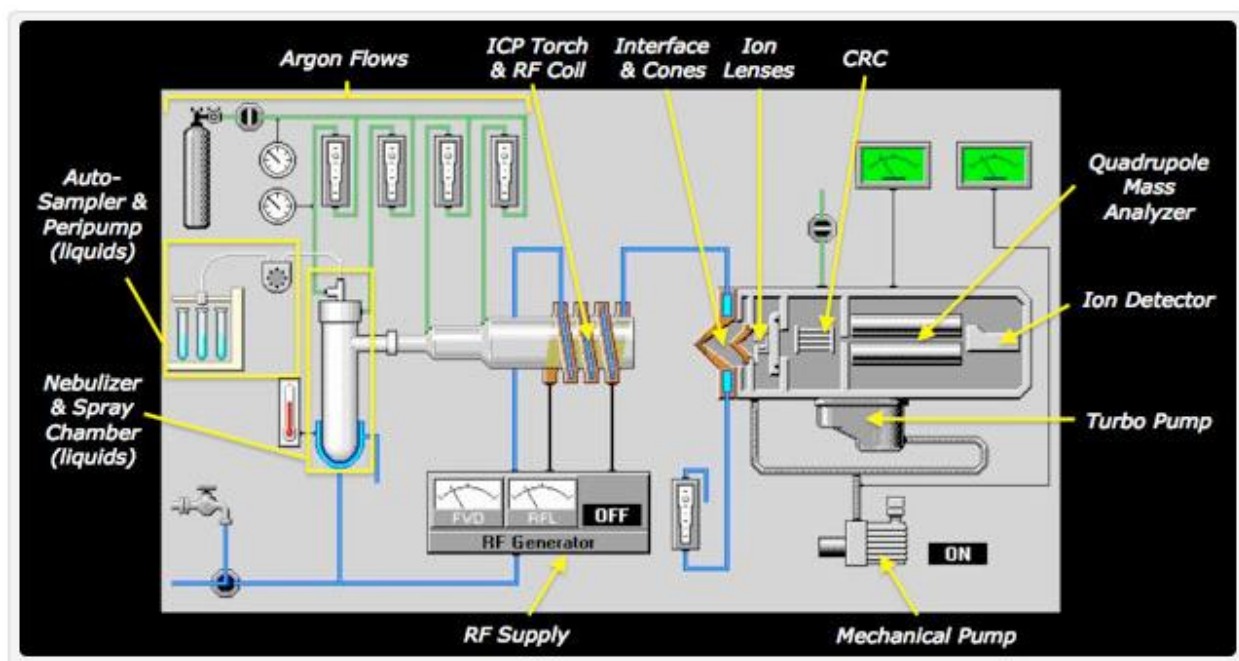
attenuate Iron fluorescence. The source of radiation and detector are Cu K $\alpha$  X-ray and PIXcel 1D detector respectively (Mejia, 2015). Some mineral phases were identified using the ICDD identification data base software embedded in the software program, while others were identified based on d-spacing.

### ***2.1.6 The Inductively coupled Plasma-Mass Spectrometer (ICP-MS)***

The Inductively Coupled Plasma Mass Spectrometry is one of the fastest and most reliable elemental analysis technique available to the scientific world due to major advances in technology. The major technological advancements which gives the ICP-MS a major advantage over other analytical techniques include: a stable plasma source which can excite virtually most atoms of trace, minor and major elements in the periodic table. Also, about 30-40 element's spectra line can be isolated using a single grating spectrometer. The ICP-MS has multiple scan modes to detect different mass to atomic number  $m/z$  ratios due to different elements. Lastly, the ICP-MS has a high resolving power, such that two close peaks from different elements can be better resolved. Although other hardware components are integrated into the instrument, the ICP-MS is essentially made up of six crucial parts which are; a sample introduction system, a plasma source, the mass analyzer, detector, signal processor and, readout.

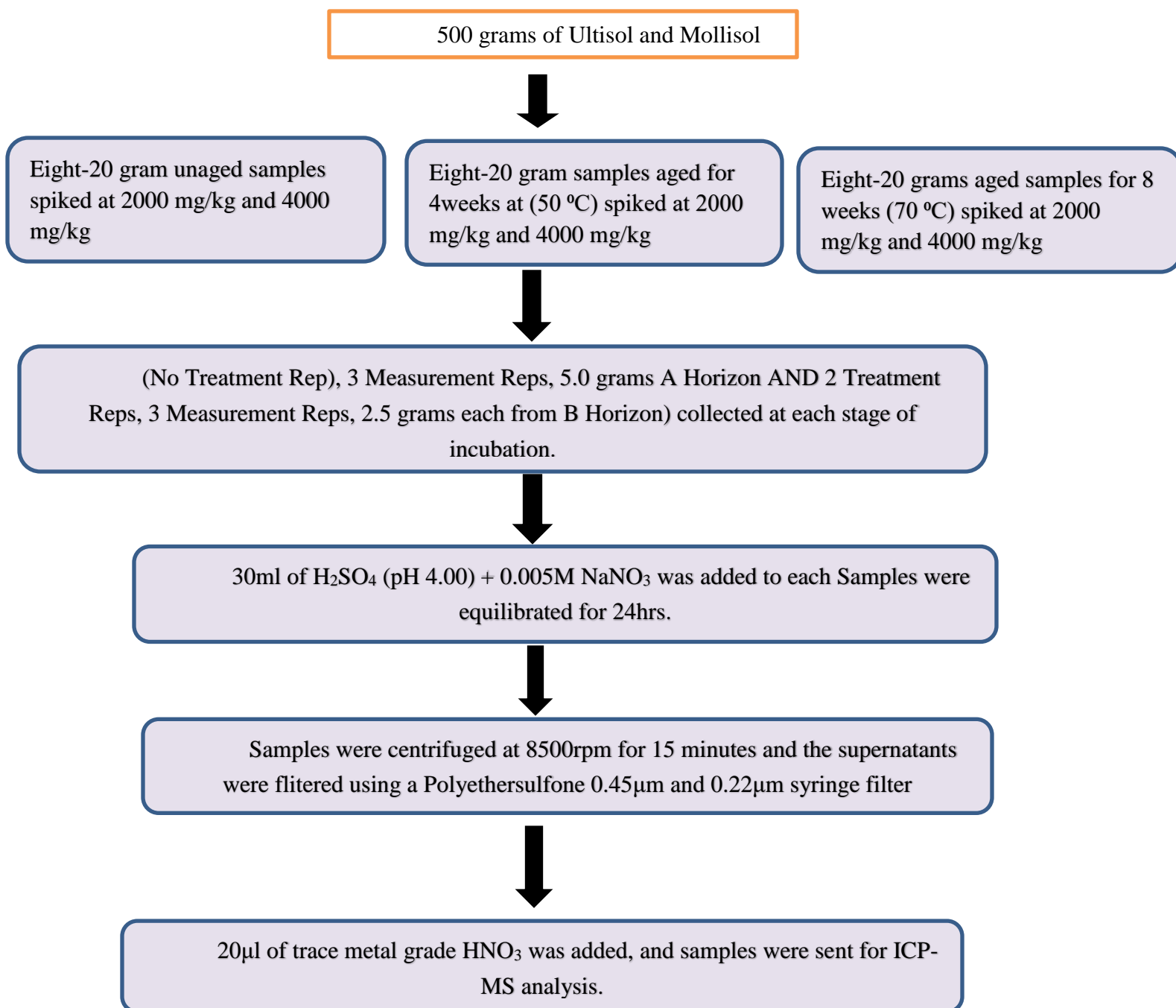
The plasma for the analysis is generated by flowing Argon gas through a Tesla induction coil which is powered by a Radio Frequency Generator. The RF generator generates high frequency oscillating current which causes a magnetic field to be set up. The oscillating current then initiates electric fields which creates a spark and ignites the tesla coil and ionizes the Argon gas. The sample is then introduced into the Plasma by the sample inlet system. In the plasma, the sample is vaporized into a gaseous state, by bombarding it with photons from the already atomized

Ar gas. The resultant sample is a stream of positively and negatively charged ions which are then accelerated into the mass analyzer which separates the various ions based on their different mass to charge ratio ( $m/z$ ). Ions of certain ( $m/z$ ) ratios are then collected, converted to electrical signal which is then detected by a detector (Skoog et al 2014). ICP-MS instrument used for this work had a Quadrupole mass analyzer, and a photomultiplier detector with a detection limit of  $< 20$  ng/l.



\* <http://www.jsg.utexas.edu/icp-ms/icp-ms/>

Figure 5: Schematics of the ICP-MS



*Figure 6: Flow diagram depicting the Experimental Procedure for Batch Experiment*



### 3 RESULTS AND DISCUSSION

The results obtained from ICP-Mass Spectroscopy, XRF and XRD analytical technique is discussed and interpreted in this chapter. **Tables 9 and 10** shows concentration of Pb measured by the ICP-MS in 30ml of dilute H<sub>2</sub>SO<sub>4</sub> filtrate from batch experiments for horizon A and Bt soils respectively. However, concentrations of Pb shown in Table 9 shows values for the end members of the batch experiment (unaged and samples aged for 8 weeks at 70 °C); while table 10 shows concentrations for batch experiments for unaged, samples aged at 50 °C for 4 weeks, and samples aged for 8 weeks at 70°C). Several challenges were encountered during the experimental stage of this research work; these challenges could have significant impacts on the results obtained. Some of the challenges and methods applied to navigate around them are also elucidated in this chapter

Initial concentration/original spiking concentration data ( $C_0$ ) obtained through acid/peroxide digestion and XRF shows that for most samples, the target concentrations of 2000 mg/kg and 4000 mg/kg of Pb in the soils were not met. This discrepancy could have resulted from a couple of scenarios; firstly, the use of powder/solid spiking agents in spiking experiments makes achieving a desired spiking concentration very difficult. This is because, Powder spiking agents present a challenge in sample homogenization. Secondly, during the application of the powdered cerussite to the soils, there is a high probability that some fraction of the powdered got airborne, thus reducing the target concentration. Again, systematic errors could have been introduced while weighing the powdered cerussite; this could have also resulted in failure to meet the concentration target. Back calculations to obtain an approximate concentration of Pb recovered by 30ml of solution from the solid phase will be computed and included in this chapter.

Another challenge encountered was that, most of the dissolved Pb concentration values reported for B-horizon soils are below the (ICP-MS) Instrument Detection Limit of  $0.42 \pm 1.28$

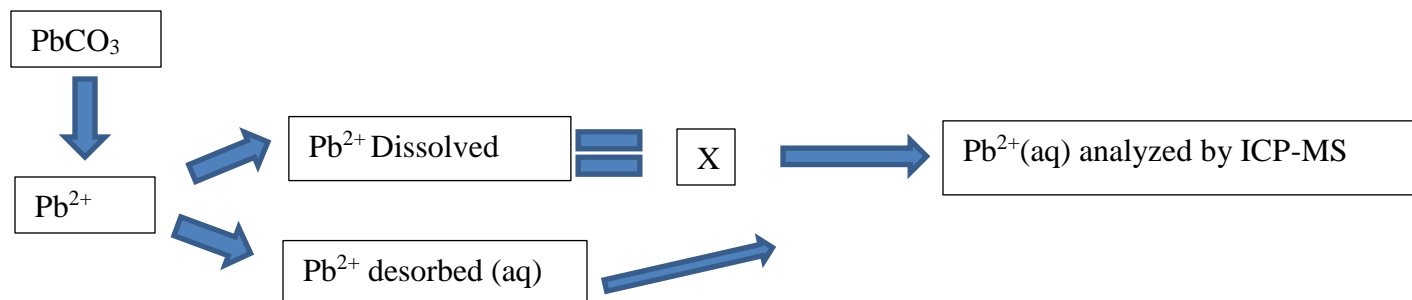
$\mu\text{g/l}$ . Therefore, in reporting the results from the ICP-MS analysis (in tables), the raw concentration values ( $R_c$ ) have been normalized by the concentration of cerussite which has been reported in 100ml of  $\text{H}_2\text{O}$  at  $20^\circ\text{C}$  i.e. equilibrium concentration at saturation (EQ) ( $0.00011\text{g}/100\text{ml}$ ). Therefore, the ratio  $R_c/\text{EQ}$  represents an *Index ratio*. It should also be noted that the supernatants were filtered using a  $0.45\mu\text{m}$  syringe filter. The only exception were samples filtered with  $0.22\mu\text{m}$  for the colloidal facilitated investigation.

### 3.1 Results for Batch Desorption Experiments on A Horizon Soils

Table 8: Initial spiking concentration ( $C_0$ ) in the A Horizon soils by portable XRF

ID	0 weeks (unaged) (ppm)	4 weeks(ppm)	8 weeks (ppm)	Uncontaminated (ppm)
UC1	1846	NA	2093	12
UC2	3457	NA	3770	
MC1	1425	NA	1960	25
MC2	3829	NA	4579	

For this work, the term “desorption” has been replaced by “recovered” because, it is suspected that not all Pb bound to mineral surfaces were “desorbed”. It is likely that some Pb which were not associated with mineral grains/ clay surfaces in these soils could also have been dissolved and collected as part of the Pb analyzed by the ICP-MS. However, in the body of this work, for technicality and reference to research work by other authors, the process of stripping the soils of Pb has been referred to as desorption. Below is an illustration of the usage of both terms. X is recovered Pb.



### 3.1.1 Desorption results for unaged samples from A Horizon soils

Table 9: Dissolved Pb in solution for unaged samples ( $d_0$ )

Sample ID Label	Raw Concentration (Rc) (mg/l)	Index Ratio	Mean of Index Ratio	SD of Rc ( $\pm$ )
U1doC1	1.12	1.02	<b>0.97</b>	0.05
U2doC1	1.06	0.96		
U3doC1	1.02	0.93		
U1doC2	3.90	3.55	<b>3.36</b>	0.39
U2doC2	3.95	3.59		
U3doC2	3.24	2.95		
M1doC1	0.22	0.20	<b>0.18</b>	0.02
M2doC1	0.17	0.15		
M3doC1	0.19	0.17		
M1doC2	0.27	0.25	<b>0.25</b>	0.01
M2doC2	0.26	0.24		
M3doC2	0.29	0.26		

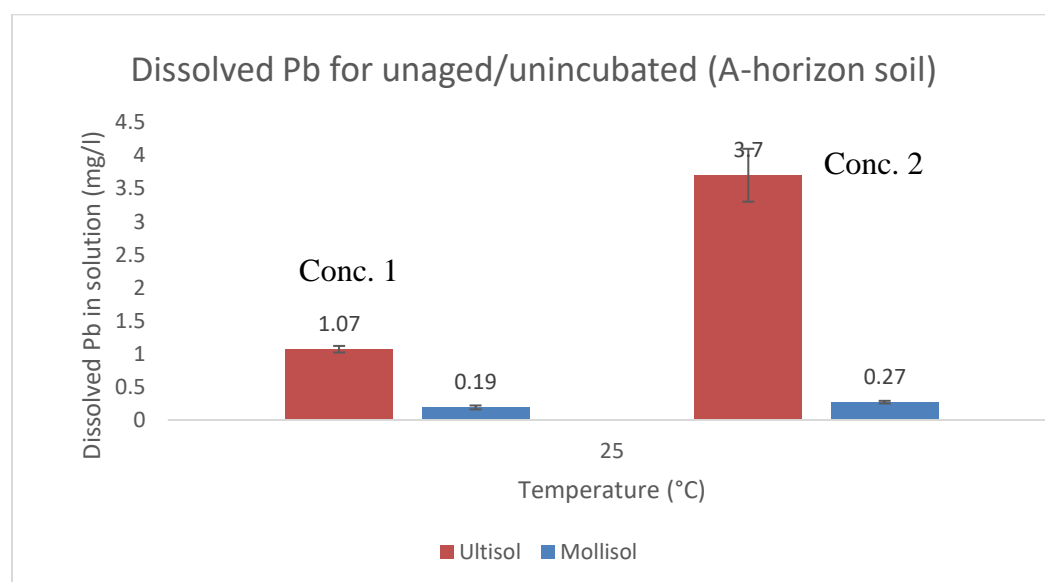


Figure 7: Concentration (C1 & C2) of soluble Pb in 30ml solution from unaged samples (Standard deviations were obtained from 3 measurements; no reps)

Based on Tables 9 and 10, which shows data of both normalized ratio  $R_c/EQ$ , and raw concentration data  $R_c$  (at different initial spiking concentrations) of dissolved Pb for both unaged and aged samples; a clear distinction in the ability of both soils to retain/absorb Pb at the two different doses, and contact time can be observed. At a supposed initial concentration ( $C_1$ ) of 1846 mg/kg and ( $C_2$ ) 3457 mg/kg Pb; the ultisol released 1070  $\mu\text{g/l}$  of Pb, and 3700  $\mu\text{g/l}$  of Pb in solution respectively. However, at supposed initial concentrations ( $C_1$ ) of 1425 mg/kg and ( $C_2$ ) 3829 mg/kg, about 190  $\mu\text{g/l}$  and 270  $\mu\text{g/l}$  Pb were recovered in solution from the Mollisol. Expressing the removal efficiencies of Pb from the ultisol in terms of percentages, at Concentrations ( $C_1$  and  $C_2$ ), an average removal efficiency of 0.06 % and 0.11 % respectively was obtained. The removal efficiency in the ultisols shows that recovery in samples spiked at a higher level of Pb is greater than that for samples spiked at a lower concentration of Pb. This trend agrees with results obtained from empirical data from Banin et al., (1987), Cline et al., (1994), Yang et al., (2006), Ipeaiyeda 2014 and Tesi (2014), Etoh et al., (2015) and Ahmed et al., (2015) which has shown that Pb is less tightly bound to adsorption sites when present at an initial higher level of Pb. This is because at low concentrations, Pb is preferably sorbed in high energy binding sites. With increasing concentrations of Pb, the capacity of the high binding sites to retain Pb decreases significantly, thus making the selectivity coefficient of the Pb to decrease because the high-energy sites have already been occupied at low Pb levels. When a cation ion exchange site in a soil accepts an ion, invariably, cation exchange site is lost thereby decreasing the effective cation exchange capacity of the soil, and consequently the rate of adsorption decreases (Ahmed et., al 2015). Conversely, for the mollisol, an average removal efficiency of 0.01 % and 0.007% was obtained at both initial spiking concentrations ( $C_1$  &  $C_2$ ) respectively. A close observation of the desorption values obtained from mollisol clearly shows a decrease in the recovery rate at higher Pb dosage which

directly contradicts the trend observed in the ultisol; this could be because the clay content of mollisol is dominated by 2:1 clay mineral vermiculite, hence has high CEC value of 27.29 cmolc/kg which is about two times the CEC value 15.39 cmolc/kg as obtained for the ultisol. This could also result in the mollisol have more “high affinity sites”, thus giving it the capacity to sorb more Pb. Furthermore, a comparison of the pH values of both soils reveals that the ultisol and mollisol has pH values of 4.24 and 6.49 respectively. It is an established fact that most metals are soluble at low pH values, hence there is a decrease in adsorption; also, there is a competition between  $H^+$  and  $Al^{3+}$  for adsorption sites resulting in decreased metal sorption in the ultisol (Garcia-Miragaya and Page, 1978; Farrah and Pickering, 1979; Ram and Verloo, 1985; Elliott et al., 1986; Eriksson, 1989; Basta and Tabatabai, 1992; Rieuwerts et al., 2007). Therefore, the higher pH value of the mollisol could also be partly responsible for the decreased recovery rates observed at a low and high initial spiking concentrations. Surprisingly, the ultisol has a significantly high organic Matter (OM) content of 3.96% which is 0.41% (4100ppm) higher than that of the mollisol; the synergistic effect of both the high CEC and pH values could just be enough to give the mollisol a higher Pb sorption capacity.

### 3.1.2 Desorption Results for A Horizon Soils aged at 70°C for 8 weeks.

Table 10: Normalized recovered Pb concentration values for aged samples (8weeks)

Sample Label	Raw Pb Concentration in leachate (Rc) (mg/l)	Mean of Raw Concentration (mg/l)	Index Ratio	Mean of Index Ratio	SD of Rc ( $\pm$ )
U1W8C1	5.80	<b>3.79</b>	5.27	<b>3.45</b>	1.75
U2W8C1	3.02		2.75		
U3W8C1	2.55		2.32		
U1W8C2	3.87	<b>4.62</b>	3.52	<b>4.20</b>	1.24
U2W8C2	6.05		5.50		
U3W8C2	3.93		3.57		
M1W8C1	1.43	<b>1.37</b>	1.30	<b>1.25</b>	0.19
M2W8C1	1.53		1.39		
M3W8C1	1.16		1.05		
M1W8C2	1.78	<b>1.70</b>	1.62	<b>1.55</b>	0.16
M2W8C2	1.52		1.38		
M3W8C2	1.80		1.64		

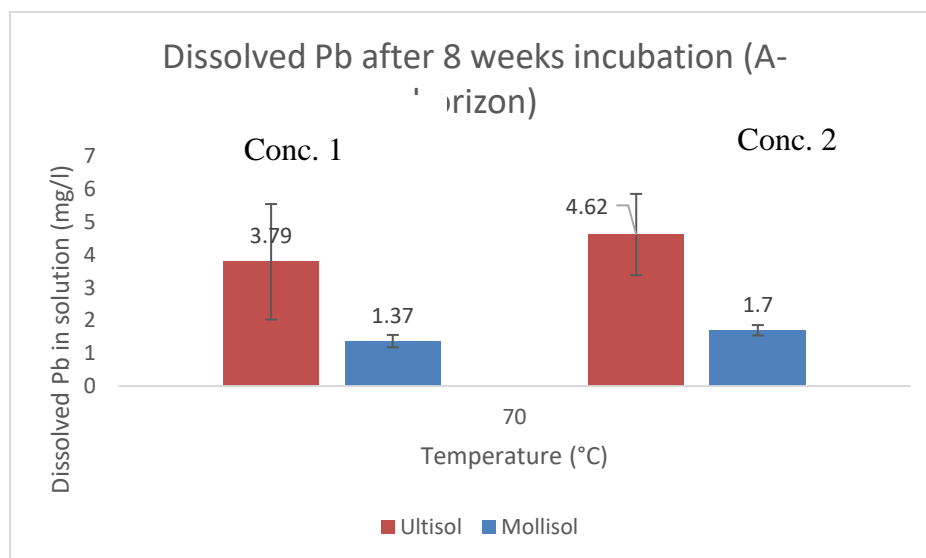


Figure 8: Concentration (C1 & C2) of soluble Pb in 30ml solution from sample aged 8 weeks (Standard deviations were obtained from 3 measurements; no reps)

Data presented in table 10 shows that, concentrations of Pb recovered from both soils after a fixation time of 8 weeks and incubation temperature of 70 °C at two different concentrations, is higher than values obtained for unaged samples. The set of data obtained at this fixation time and incubation temperature closely follows the trend of results obtained for the unaged soil samples; however, the data shows marked increase in the concentration of recovered Pb in solution; the probable reason will be discussed subsequently. Given an initial low (C1) and high (C2) spiking level of 2093 mg/kg and 3770 mg/kg, 3790 µg/l and 4620 µg/l were recovered respectively from 5 grams of ultisol. Again, expressing the concentration of Pb recovered at both low and high Pb levels yielded 0.18% and 0.12% respectively. Considering the data obtained for the mollisol, at an initial spiking concentration of 1960 mg/kg and 4579 mg/kg; 1370 µg/l and 1700 µg/l Pb was recovered from 5 grams of soil. In terms of removal efficiency, this translates to 0.07 % and 0.04 % respectively. For the ultisol, the removal at 2093 mg/kg (C1) is marginally greater than at 3770 mg/kg (C2) by 0.06 %, While a difference of 0.03 % was obtained for removal of Pb between C1 and C2 for the mollisol.

Though, it is expected that, because of the high-energy sites being quickly filled up at a higher Pb dose, the ultisol should desorb more Pb. However, this is not the case for both soils after incubating at 70 °C for 8 weeks. The probable reason for experiencing this reverse could be because of the effect of initial spiking concentration. Comparing both low and high initial Pb concentration for the ultisol reveals that C2 is greater than C1 by 1677 mg/kg, and by 2619 mg/kg for the mollisol. In the case of the ultisol, the measured initial concentration C1 is greater than theoretical initial concentration of 2000 mg/kg, whereas, the measured initial concentration C2 is lesser than the target theoretical concentration of 4000 mg/kg. The reverse is the case for the mollisol. This discrepancy could have been responsible for the lesser recovery rate at Concentration C2. Findings

by Cline et., al (1994) in a study to determine the effect of aging process on metal removal also suggest that variations in initial spiking concentrations could influence heavy metal removals in acid washed soils.

To succinctly elucidate the role of aging temperature and contact time on the variations in recovery patterns observed between the unaged and aged soils examples, the soils physico-chemical properties such as pH, organic matter, CEC, clay minerals and sorption mechanism should be critically considered. In a study conducted by Yanai et al., (2010) four soils; dune soil, alluvial soil, red soil, and volcanic soils were spiked with nitrates of Cd, Pb, Zn, Ni and Cu, aged at 25°C for 1 day, 1, 2, 4 weeks, 6 month, and washed with ammonium acetate to assess the risk associated heavy metal contamination with reference to aging. The study concluded that, for all the soils, especially for the red soils, there was a significant decrease in the exchangeable metal availability after 4 weeks of aging, this decrease was attributed to the high proportions of Fe oxides in the red soil to which Pb could bind. Also, in a similar study conducted by Jalili and Khanlari (2008), on the effect of aging process on the fractionation of heavy metals (Pb, Zn, Cd, and Cu) in some calcareous soils using sequential extraction procedure, the soils were incubated at 25 °C for 3 hours, 1, 3, 7, 14, 21 and 28 day. The findings concluded that the extractability of the heavy metals in the soil decreased with increasing time. This phenomenon was also attributed to the fact that the exchangeable metal fraction (soluble) were fixed in more stable fractions such as the carbonate, Fe-Mn oxides bound, adsorption on surfaces and residual fractions with increasing time.

Comparison between the findings of the studies stated above, and the results deduced from this research work shows a direct contradiction because a crucial variable was omitted in the former. Both aging studies were conducted at 25 °C. This appears to be the most likely explanation why more heavy metals were sequestered in the solid phase as opposed to being released into the



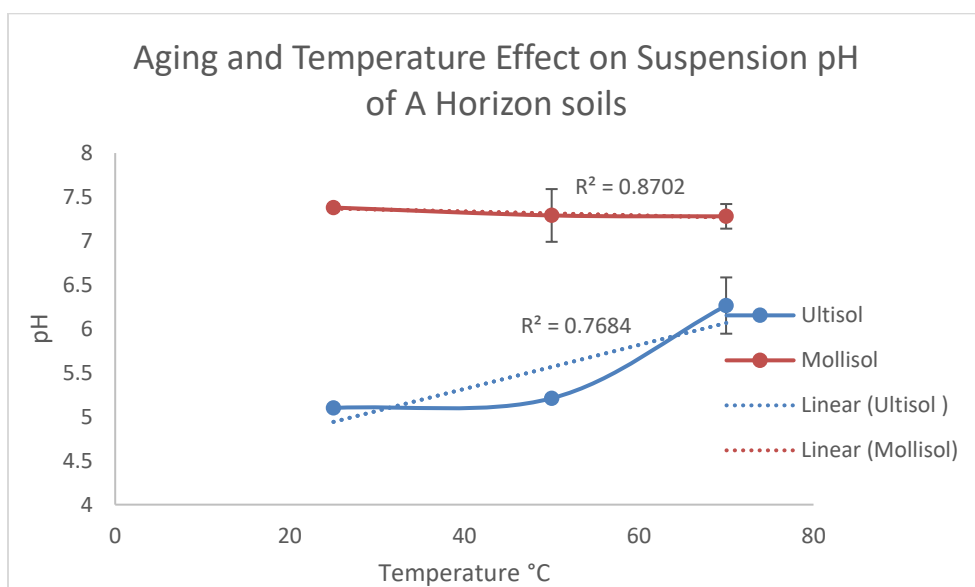
liquid phase, which was the observed in this work. To support this claim, Martinez et., al (2008) in a research work to determine the effect of aging process and temperature on dissolved organic carbon (DOC) and elemental release from metal contaminated soils, added 30ml of 1mM KNO<sub>3</sub> solution to 10g of contaminated soil containing Zn, Pb, Cd, Ni, Cu, Mn Mo, P and S. The soils were subsequently aged for a period ranging from 2 hours to 2 months at temperatures ranging from 10 – 90 °C. The results of the experiment unequivocally showed that, with increasing temperature and concentration of DOC, the concentration of metals in solution also increased, with Cu being the only exception at an elevated temperature of 90 °C. Also, Martinez and McBride (1998) showed the effect of thermal treatment on metal solubility and solid phase transformation of iron oxides. Metals such as Cd, Cu, Pb and Zn were coprecipitated with Fe and were aged at room temperature for 200 days, and later heated at 70 °C for 60 days. The results of the research revealed a decrease in Soluble Cd and Zn, whereas the solubility of Pb increased with increasing temperatures as revealed by anodic stripping voltammetry.

Thermal treatments have been well documented in the literature as one of the techniques employed in immobilizing most inorganic and organic contaminants in soils. However, most of these studies focused on the use of very high temperatures (600-900 °C) Cocarta et al., 2013 demonstrated that, subjecting Pb-contaminated soils to very elevated temperatures of about 800 °C for 60minutes could increase the removal efficiency by as much as 61%. In a similar experiment conducted by Sorensen et., al (2000), it was posited that thermal treatment in the temperature range mentioned above, greatly altered the leachability if some heavy metals like Cd, Ni, Pb and Zn. All these metals were observed to show marked high concentrations in solutions in low pH range. Also, they found that, the surface area of ferrihydrite onto which these metals sorb, reduced drastically with increasing temperature, thus further aiding in the recovery process.

Considering the supporting types of evidences, the recovery trend in this research work models the results of those cited above. Within an 8-week aging period, the difference in recovery efficiency for the ultisol at Concentration C1, is 0.12%; which is an increase in recovery rate of about two orders of magnitude (200%). At a Concentration C2, the difference is 0.11%, corresponding to a recovery efficiency rate increase of 9.1%. This difference suggests that more Pb is lost at a lower Pb dose with increase in time and ageing period. For the mollisol, at C1, a difference of 0.06%, corresponding to a recovery rate of 600% (6 orders of magnitude recovery rate), while a difference of 0.03%, (4.7 orders of magnitude; recovery rate increase of 470%) was obtained at C2. From tables 9 and 10, and recovery rates, it's clear that the mollisol sorbs more pb than the ultisol; probably due to its high CEC as established by the dominant clay mineral vermiculite, and its organic carbon content. Though, it is expected that at a lower concentration, the recovery efficiency should be lower, the drastically high rate of recovery in the ultisol for C1 samples at 0-8 weeks is 200% (2 orders of magnitude), and 9.1% for samples at C2 could be because of the effect of initial spiking concentration, again, could be due to the effect of a decrease in the effective surface area of Fe oxide minerals as temperature was increased, thereby resulting in an increase in rate of recovery, as observed in the case of ultisol at C1 (0-8 weeks) (Sorensen et., al 2000). The recovery efficiency of the mollisol is several orders greater than of the ultisol; this again points towards the physico-chemical characteristics of the soil. The probable explanation for this could lie in the kinetics of metal ion adsorption; there is a possibility that the retention capacity of the mollisol wasn't reached during the 24hr equilibration period. Furthermore, In Figure 8 below, the pH value of supernatants shows a slight increase with ageing temperature with a regression coefficient ( $R^2$ ) value of 0.870 and 0.764 for the mollisol and ultisol respectively. The variation in pH of the supernatant for the mollisol varies between (7.23-7.38); but from a pH of 6

and beyond, surface precipitation appears to be the most prevalent retention mechanism (Cline et al 1994; Rieuwerts 1998, Wang et., al 2009). Therefore, this data suggests that the high rate of recovery of the mollisol could also have been caused by surface precipitation which is a slower retention mechanism than Specific Adsorption and Cation exchange.

In conclusion, from the set of empirical data and manipulations made, there has been a difference in the Pb retention of both soils at different aging temperature and contact time. pH has been established as the most likely variable to affect the heavy metal retention capacity of soils, but an extracting solution ( $\text{H}_2\text{SO}_4$ ) with a fixed pH value of 4 was used in the experiment, therefore other ions in solution could have contributed to the observed changes in recovery pattern. Other variables which could affect the result of the experiment are the nature of the soil, which includes (mineralogy, grainsize, other ions in the soils, and organic matter), initial spiking concentration. However, the other parameters which are not inherent properties of the soils are the variations in temperature and time. Therefore, it can be concluded that temperature and contact time has influenced some of the soil properties which in turn has affected recovery of Pb in the soils.



*Figure 9: A scatter plot of supernatant pH Vs Temperature in A horizon soils. (Standard deviations were obtained from 3 measurements; no reps)*

### 3.2 Batch Desorption Experiment Result for B Horizon Soils at C1 & C2

Table 11: Initial spiking concentration ( $C_0$ ) in the B Horizon soils by XRF

ID	0 weeks (unaged) (ppm)	4 weeks(ppm)	8 weeks (ppm)	Uncontaminated (ppm)
UV&W	1484	1596	1455	10
UX&Y	2135	1983	2991	
MV&W	2486	1745	1550	22
MX&Y	2784	2974	2491	

Table 12: Averages of Normalized Concentrations for aged & unaged samples at C1 (B Horizon)

Incubation Time	Sample ID (Treatment) replicates	Mean recovered Pb for each Rep ( $\mu\text{g/l}$ )	Mean Index Ratio ( $\times 10^{-4}$ )	Mean of 2 replicates ( $\mu\text{g/l}$ )	Standard Deviation Both reps ( $\pm$ )
0 weeks	UVdo	2.01	18.30	<b>2.03</b>	0.03
	UWdo	2.05	18.67		
	MVdo		-		
	MWdo		-		
4 weeks	U4V	0.91	8.25	<b>0.75</b>	0.22
	U4W	0.60	5.44		
	M4V	0.27	2.41		
	M4W	0.30	2.61		
8 weeks	U8V	0.88	7.99	<b>0.92</b>	0.06
	U8W	0.96	8.70		
	M8V	1.32	11.97		
	M8W	1.06	9.61		

Tables 12 shows concentration values normalized to the quantity of  $\text{PbCO}_3$  that can dissolve in 100 ml of water; the mean of the normalized concentration value for 2 analytical replicates (V and W) treatments are reported in the table. For the unaged samples, the average value of mean normalized concentration of two analytical replicates of ultisol was computed to be  $2.03\mu\text{g/l}$ . Due to abnormally high concentration values of, the average value for the mollisol has

not been included in this report. The anomaly has been attributed to either inhomogeneity in the spiking process or interference due to incomplete atomization of high molecular weight organic acids in the ICP. For ultisol and mollisol samples aged at 4 and 8 weeks, the average values of the mean concentrations are 0.75 µg/l, 0.29 µg/l and 0.92 µg/l, 1.19 µg/l. The initial lower limit spiking concentrations of the ultisol and mollisol at 4 and 8 weeks are 1596, 1745 and 1455, 1550 mg/kg respectively. Dividing the released metal concentration by the initial spiking concentration, and multiplying by 100% will again yield the recovery efficiency.

The computed recovery efficiency for the unaged, 4 weeks and 8 weeks aged ultisols samples are  $1.37 \times 10^{-4}$ ,  $4.70 \times 10^{-5}$  and  $6.32 \times 10^{-5}\%$ . For the mollisol, only data for samples aged at 4 weeks and 8 weeks are presented in this work due to some errors mentioned above. The recovery efficiencies after 4 and 8 weeks incubation period are  $1.66 \times 10^{-5} \%$  and  $7.68 \times 10^{-5} \%$ . These set of results shows a decreasing trend of recovery in the unaged ultisol to samples aged for 8 weeks, however a slight increase in recovery is experienced between 4-8 weeks, but the general trend is that of a decrease as noticed from 0-8 weeks. A definitive trend couldn't be established for the mollisol because of the error in the recovery data for the unaged samples. However, a similar trend as observed in the ultisol is predicted.

The availability and mobility of metals in batch reaction experiments may differ considering from what is obtained under field situations in natural soil profiles due to heterogeneity in the soil. Intuitively, it is expected that as soil organic matter is being broken down at high temperature, there should be an increase in the mobility of heavy metals (Martinez et., al 2003). However, this is metal specific; studies on the fate and transport of metals in tropical soils has suggested that some metals like Ni, Zn, Cd and Cu are mobile in tropical soils, while mobility Cr and Mo is mainly confined to the A horizon, but is readily immobile in the B horizon. The mobility

of Pb between different soils has also been studied, but no unanimous decision has been reached on its mobility in tropical soils, majority of the studies have implied that Pb is mostly retained in the A horizon. The difference in mobility of Pb may be related to the transformation in organic matter content in these different soil profiles.

The breakdown of organic matter with increasing temperature, time and depth usually results in the formation of insoluble humic and fulvic acids. Humic and fulvic acids are usually derived from terrestrial organic matter, and they are a mixture of weak aliphatic and aromatic organic acids which are not soluble under acidic conditions; on the other hand, fulvic acids are soluble under all pH conditions (Pettit, 2004). Humic acid is a complex high molecular weight organic acid which increases in proportion with increasing depth of burial. Its OH-, -COOH and -NH<sub>2</sub> functional groups make it well suited to sorb heavy metals like Pb, Cu, Zn and Cd (Tissot and Welte, 1984, Wu et al., 2003). The -COOH functional group depletes with increasing depth while the phenol group with its attached -OH functional group is dominant below the A horizon. Experimental data from; Martinez et al., (2003); Yang et al., (2006) and Ahmed et al., (2015) has showed that low concentration of dissolved organic acid inhibits metal desorption. pH also appears to be a controlling factor in the ability of humic acid to bind heavy metals. Takahashi et al., (1999) and Montavon et al., (2002) have reported that, at pH <6, humic substances enhance the adsorption of metals. Abaete and Masini (2005) in a study on sorption of Pb onto vermiculite found that at pH range 5.0- 6.0 there is an increase in adsorption, but at 7.0 and beyond, the adsorption decreases due to the formation of stable organo-metal complexes in solution. However, other authors such as Wang et al., (2009) have reported an increase in Pb sorption with increasing concentration of humic acid. Similar results were obtained by Kim et al., (2005) in a study of the application of

humic acids in sequestration of Cobalt. It should be noted that Pb sorbs to organic matter probably by Hydrogen bonding.

Comparing the proportions of organic matter in the B horizon of both soils, it can be observed that the mollisol has 0.97%, while the Ultisol has 0.27%. Temperature and pH are major factors controlling OM in soils. From Figure 9 below which shows the variation of pH with aging temperature, the  $R^2$  value shows a good correlation of 0.976 and 0.684 for the ultisol and mollisol respectively. Therefore, with decreasing soil solution pH and increasing temperature, it is expected that the solubility of Pb in solution will increase, however this is not the case. This may be explained by the release of OM In solution. It is expected that these values of organic matter could yield low concentrations of humic and fluvic acid in solution which could have inhibited the recovery of Pb at low pH, thus reducing Pb recovery as shown in Fig 9. Due to the lack of desorption data for the unaged mollisol samples, a certain conclusion could not be reached about which of the two soils sorbed more Pb. Notwithstanding, it can be seen that at 4 weeks, there is a significant difference the Pb sorption between the soils; the mollisol appears to adsorb more within the first four weeks. Nevertheless, the effect of the high CEC capacity of the mollisol over ultisol cannot be ignored. The overriding factor affecting Pb sorption in the B horizon appears to be the temperature dependent influence of organic matter on the mobility and availability of Pb in the B horizon.

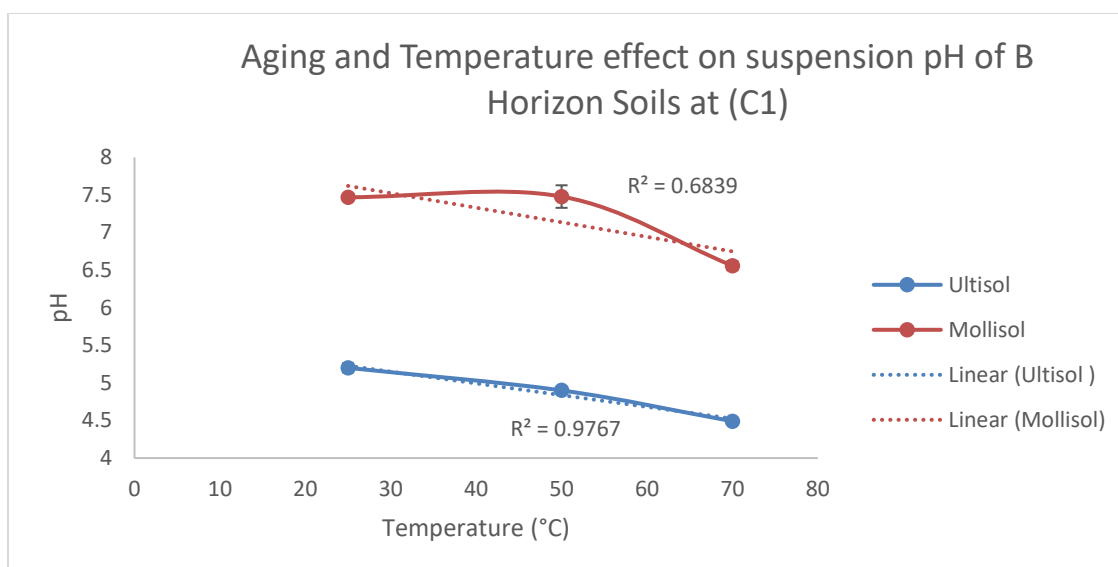


Figure 10: A scatter plot of supernatant pH Vs Temperature in B horizon soils at C1 (Each data point is an average 6 measurements from 2 analytical replicates)

Table 13: Averages of Normalized Concentrations for aged & unaged samples at C2 (B Horizon)

Incubation Time	Sample ID (Treatment) replicates	Mean recovered Pb for each rep (µg/l)	Mean Index Ratio (x10 <sup>-4</sup> )	Mean of 2 (Treatment) replicates (µg/l)	Standard Deviation of both reps (±)
0 weeks	UXdo	0.62	5.69	<b>0.62</b>	0.00
	UYdo	0.62	5.60		
	MXdo	0.68	6.15	<b>*0.68</b>	-
	MYdo	NA	NA		
4 weeks	U4X	0.53	4.87	<b>0.54</b>	0.01
	U4Y	0.54	4.88		
	M4X	0.69	6.26	<b>0.73</b>	0.06
	M4Y	0.77	7.01		
8 weeks	U8X	0.47	4.31	<b>0.47</b>	0.01
	U8Y	0.46	4.22		
	M8X	0.46	4.19	<b>0.48</b>	0.03
	M8Y	0.50	4.56		



Results presented in table 13 above models those of both soils as presented in table 12. The unaged, 4, and 8 weeks ultisol samples have recovered Pb concentration of 0.62, 0.54 and 0.47  $\mu\text{g/l}$ . The replicate for the unaged mollisol sample produced a gross error, therefore it has not been reported here. However, the average of 2 measurements from (MXdo) has been used for the sake of completion. Therefore, Pb recovery values of 0.68  $\mu\text{g/l}$ , 0.73  $\mu\text{g/l}$  and 0.48  $\mu\text{g/l}$  after 0, 4 and 8 weeks of aging have been used here. An initial spike concentration C2 of 2135, 1983 and 2991 mg/kg Pb was measured for the ultisol at 0 (unaged), 4 weeks and 8 weeks of aging. Also, for the mollisol, an initial spike concentration of 2784, 2974 and 2491 mg/kg was recorded for the unaged, 4 and 8 weeks samples. Computing recovery efficiencies at each fixation time for the ultisol yielded  $2.90 \times 10^{-5} \%$ ,  $2.73 \times 10^{-5} \%$  and  $1.57 \times 10^{-5} \%$  respectively. At a fixation time of 0, 4 and 8 weeks, recovery efficiencies of  $2.44 \times 10^{-5} \%$ ,  $2.45 \times 10^{-5} \%$  and  $1.92 \times 10^{-5} \%$  have been calculated for the mollisol.

The results presented above show a decrease in Pb recovery with increasing temperature and fixation time, though there is a very slight increase in Pb recovery for mollisol at C2 between the unaged and samples aged for 4 weeks. This observed trend at a higher Pb concentration C2, can also be accounted for by reasons given for samples spiked at a lower Pb level C1 (i.e. effect of both initial concentration and transformation of organic matter in the B horizon). A comparison of Pb recovery efficiencies between the soils at different Pb level suggested that, more Pb is recovered at a lower Pb dosage than at higher dose. This prompted a calculation of the relative recovery rates at different spike concentrations C1 & C2. A decrease in Pb recovery of 54% and 46% at C1 and C2 was obtained for the ultisol. This shows that within the 8-week period, more Pb is being bound to the soil at a lower Pb dose. A recovery rate couldn't be obtained at C1 for the Mollisol, because of the erroneous desorption data for the unaged mollisol sample. However, a

21% decrease in Pb recovery was derived at C2. These results suggest yet again that, the ultisol appears to sorb more Pb at both high and low doses than the mollisol. To corroborate this observation, fig 10 below shows the variation of supernatant pH with temperature of aging. From the figure, there was a significant drop in pH in both soils, however, the ultisol's pH is more acidic, suggesting faster surface adsorption. This again shows that, the retention mechanism here is probably by adsorption which suggests inner sphere complexation as opposed to outer sphere, slower surface precipitation which appears to be the sorption mechanism for the mollisol.

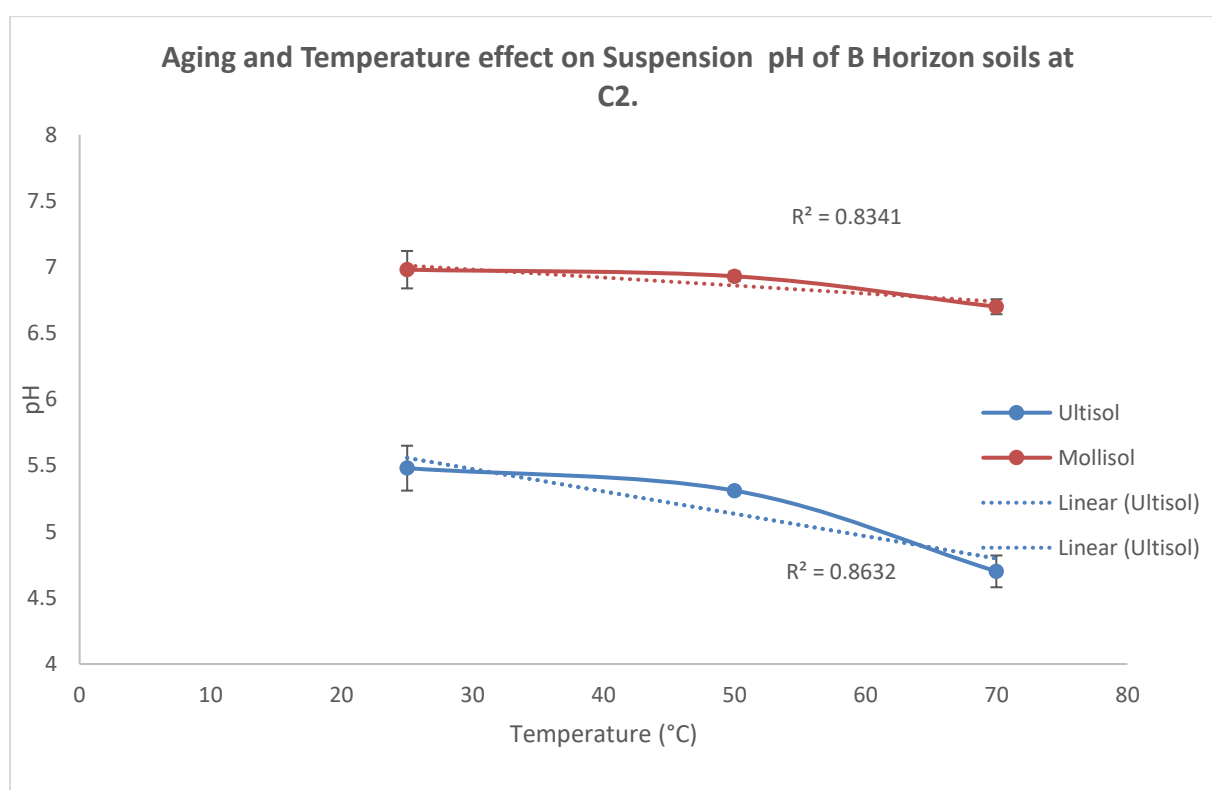
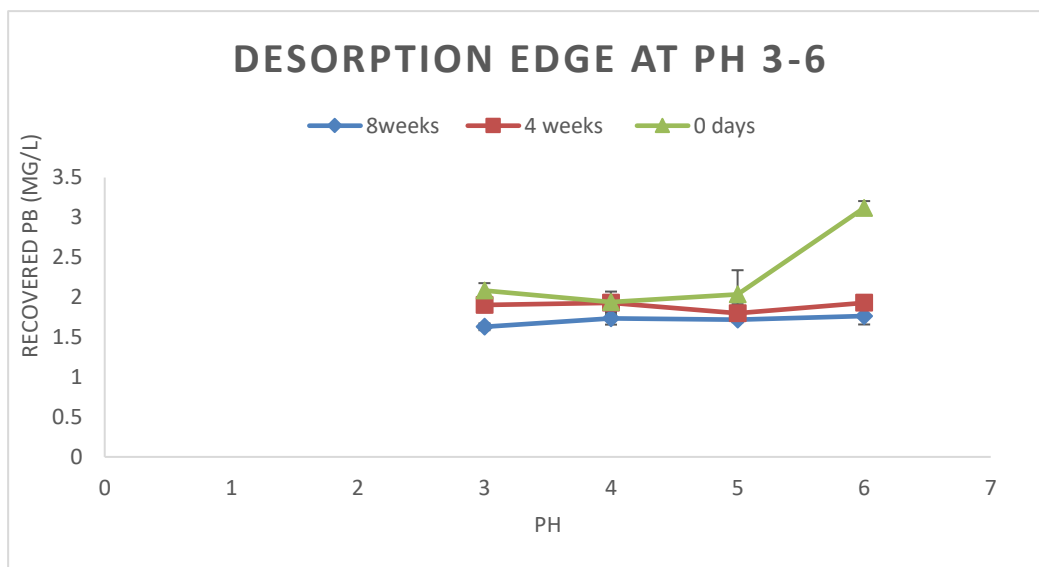


Figure 11: A scatter plot of supernatant pH Vs Temperature in B horizon soils at C2 (Each data point is an average 6 measurements from 2 analytical replicates)

### 3.3 Investigation of the effect of pH on adsorption edge of Ultisol

Though soil properties such as CEC, Organic matter content, FeO and MnO oxides, etc. play vital roles in the interaction of heavy and trace metals with the variably charged soils. In the field of soil science, the role of pH on sorption/desorption of heavy metals has been extensively studied. For most metals, with the exception of Mo, it has been widely established that at low pH, there is a decrease in in metal sorption which leads to an increase in metal mobility and bioavailability. This is probably due to competition between H and other Pb for sorption sites. Several research works have been conducted on the effect pH on metal sorption in tropical soils, with many of the conclusions corroborating the theory stated above. However, some other research works have reported that a decrease in pH does not necessarily correlate with an increase in metal desorption and vice Versa. The result of the experiment is presented in figure 11.



*Figure 12: Pb recovery as a function of pH in ultisol.*  
(Each data point is an average of two measurements from 2 analytical replicates)

An investigation was conducted within a sorption edge of 3-6 with the objective of determining the effect of pH on Pb sorption in ultisols. A Pb recovery trend which closely models the trend observed for Ultisol of the B horizon was observed across the pH range used for this study. From Figure 11 above, apart from the effect of pH on metal desorption, the effect of aging can also be observed. The highest rate of increase in Pb recovery between the selected pH range was calculated to be 49% for the unaged soils. The lowest increase of 1% was obtained after 4 weeks of aging, while 8% increase was computed after 8 weeks.

These results show that, Pb recovery in the variably charged soil does not conform with the theory of Pb desorption at low pH. Instead, more desorption is occurring at high pH values. It could be that the soil is retaining more Pb below its PZNC which suggests inner sphere complexation or adsorption onto phases with high layer charge e.g. Hydroxy-interlayer Vermiculite, Smectite and Illite. Another possible explanation could be because of the various ionic species in solution. Gonzales-Batista et al., (1982) reported that, the point of zero net charge (PZNC) should be equal to point of zero charge for soils devoid of permanent charge, but soils where permanent and variable charges are available, PZNC may differ from the PZC. This scenario has been reported in soils such as Entisols and Inceptisols, where PZNC is lower than its PZC (Moghini et al., 2013). In highly weathered soils such as Oxisols and Ultisols PZNC is higher than PZC (Taubaso et al., 2004). In variably charged soils, the negative charge density is low between pH 4-5, and they have been reported to have low affinities for heavy metals at these pH (McBride 1994; Appel et al., 2002; Moghini et al., 2013). A lower negatively charged sites could mean more desorption at between this pH range. These findings could be used to explain the phenomenon of significant recovery with increasing pH observed in this work.

### 3.4 Colloid Facilitated Transport

Table 14: Concentration of Pb in supernatants filtered with 0.22  $\mu\text{m}$  filter

Incubation Time	Sample ID (Treatment) replicates	Mean recovered Pb for each rep ( $\mu\text{g/l}$ )	Mean Index ratio ( $\times 10^{-4}$ )	Mean of 2 analytical replicates ( $\mu\text{g/l}$ )	Standard Deviation Measurement ( $\pm$ )
0 weeks	UXdoz	0.82	7.46	<b>0.83</b>	0.01
	UYdoz	0.83	7.54		
	MXdoz	0.93	8.49		
	MYdoz		NA	-	-
4 weeks	U4Xz	0.77	7.02	<b>0.76</b>	0.02
	U4Yz	0.74	6.73		
	M4Xz		-		
	M4Yz	1.02	9.23	-	-
8 weeks	U8Xz	0.74	6.72	<b>0.69</b>	0.07
	U8Yz	0.64	5.85		
	M8Xz	0.68	6.14		
	M8Yz	0.67	6.11	<b>0.68</b>	0.01

The Table 14 presented above shows the concentration of Pb derived from filtering samples in Table 13 with 0.22  $\mu\text{m}$  syringe filter. The trend of decreasing Pb in solution with increasing temperature and time holds once again. However, interestingly, an increase in Pb concentration was observed with a decrease in filter size. Research work done by Yin et al., (2009) on the effect of ionic strength and flow rate on both colloids and Pb release in columns filled with Pb contaminated soils from two shooting range in Florida showed that, about 87% of measured Pb were associated with coarse colloid fractions (0.45-8  $\mu\text{m}$ ). However, after filtration, it was observed that 66% of the Pb was found in them 0.1  $\mu\text{m}$  fraction.

The increase in the concentration of soluble Pb in the 0.22  $\mu\text{m}$  fraction could have been a result of some of the processes during the execution of the experiment. Firstly, the result above was derived from filtration of the 0.45  $\mu\text{m}$  samples from table 13. These samples were acidified with 20  $\mu\text{l}$  of concentrated nitric acid, after which they filtered with a 0.22  $\mu\text{m}$  filter almost immediately; It is likely that there was an incomplete reaction between the  $\text{HNO}_3$  and the supernatant before filtration. This could have resulted in the desorption of Pb which had already been bound to colloids or formed stable complexed with organic acids. Since the syringe probably only contacted the top layer of the supernatant during filtration, this suggest that, only the topmost portion in which  $\text{HNO}_3$  had reacted was taken up for filtration, thereby resulting in these abnormally high Pb values. Secondly, there is a probability that the process of filtration could have resulted in this aberration as well. During filtration, a great amount of force per unit area was applied to the piston of the syringe, which in turn was transferred to the filter. The pressure applied might be responsible for dislodging Pb bound to the 0.45  $\mu\text{m}$  fraction. These suggestions are not affirmative, but in the ultisol, there has been a 32% and 47% increase in Pb for the 0.22  $\mu\text{m}$  fraction at 0 weeks and 8 weeks respectively when compared with the 0.45  $\mu\text{m}$  fraction. Similarly, an increase of 37% and 42% were observed for the 0.22  $\mu\text{m}$  fraction of the mollisol colloids within times stated above. Though, these results do not follow the expected trend of decrease in Pb associated with a smaller fraction of colloids, however, some vestige of colloidal facilitated transport of Pb within the 0.45  $\mu\text{m}$  and 0.22  $\mu\text{m}$  fractions is evident.

### 3.5 Comparison of Coefficient of Distribution between the two soils

Pb is ubiquitous in the terrestrial ecosystem, and it is known to bound to Fe and Mn Oxides, Organic matter, Clay minerals and surfaces of aluminosilicate minerals. Total metal concentration has been used to quantify the metal bioavailability in the different portions of the soil profile. However, this has been to be unreliable due to the fact total concentrations are affected by geochemical and biogeochemical factors which reorders heavy metals across different soil profile (Rieuwerts et al., 2007). Therefore, partitioning of heavy metal between solid and liquid phase has been proposed as an alternate way of assessing the bioavailability and mobility of heavy metals into liquid phase. The partition coefficient,  $K_d$  is defined as the ratio of metal sorbed per unit weight of soil (MS), to the amount of metal in solution per unit volume of liquid (ML) (USEPA, 1999, Rieuwerts, 2002). In this work, an attempt has also been made to compare the coefficient of distribution of Pb in both soils used in the experiments. The equation for the computation of  $K_d$  is

$$\text{given as; } K_d (\text{partition coefficient}) = \frac{MS (\mu g/g)}{ML (\mu g/l)}$$

MS = ( $C_0$  - Mass of Pb recovered/gram of soil). An example of the derivation of MS is give below;

$C_0$ =initial concentration. At 0 days  $C_0$  at  $C_1$  =1846 mg/kg Pb

$$= \frac{1846 \text{mg Pb}}{L} \times \frac{1L}{1000 \text{ml}} \times 30 \text{ml} \times \frac{1000 \mu g}{1 \text{mg}} \Rightarrow 11076 \mu g \text{ Pb/grams of soil} = \text{sorbed Pb}$$

per gram of soil

$$\frac{1120 \mu g \text{ Pb}}{L} \times \frac{1L}{1000 \text{ml}} \times 30 \text{ml} = 33.6 \mu g \text{ Pb} \Rightarrow 33.6 \mu g \text{ Pb/5grams of soil} = 6.72 \mu g$$

recovered Pb per gram of soil.

Table 15: partition coefficient of the A Horizon unaged soils (0.45  $\mu\text{m}$  fraction)

Sample Label	MS ( $\mu\text{g/g}$ ) $\times (10^2)$	ML ( $\mu\text{g/l}$ ) $\times (10^2)$	Kd (L/g)	Mean Kd	SD ( $\pm$ )
U1doC1	111	11.20	9.88	<b>10.4</b>	<b>0.5</b>
U2doC1	111	10.60	10.4		
U3doC1	111	10.20	10.9		
U1doC2	207	39.00	5.31	<b>5.65</b>	<b>0.6</b>
U2doC2	207	39.50	5.24		
U3doC2	207	32.40	6.39		
M1doC1	85.5	2.20	38.9	<b>44.7</b>	<b>5.7</b>
M2doC1	85.5	1.70	50.3		
M3doC1	85.5	1.90	44.9		
M1doC2	230	2.70	85.1	<b>88.4</b>	<b>4.6</b>
M2doC2	230	2.60	88.4		
M3doC2	230	2.90	79.2		

Table 16: partition coefficient of the A Horizon soils aged for 8 weeks (0.45  $\mu\text{m}$ )

Sample Label	MS ( $\mu\text{g/g}$ ) $\times (10^2)$	ML ( $\mu\text{g/l}$ ) $\times (10^2)$	Kd (L/g)	Mean Kd	SD ( $\pm$ )
U1W8C1	125	58.0	2.16	<b>3.74</b>	<b>1.42</b>
U2W8C1	125	30.2	4.15		
U3W8C1	125	25.5	4.92		
U1W8C2	226	38.7	5.84	<b>5.10</b>	<b>1.19</b>
U2W8C2	226	60.5	3.73		
U3W8C2	226	39.3	5.74		
M1W8C1	118	14.3	8.22	<b>8.68</b>	<b>1.29</b>
M2W8C1	118	15.3	7.68		
M3W8C1	118	11.6	10.1		
M1W8C2	275	17.8	15.4	<b>16.25</b>	<b>1.58</b>
M2W8C2	275	15.2	18.1		
M3W8C2	275	18.0	15.3		



Observing the distribution/partition coefficient above, Pb is more partitioned in the solid phase for the mollisol than in the ultisol. In the Ultisol, at a low Pb dose, Pb is about 2.8 orders of magnitude less partitioned in the solid phase after an eight-week period of aging. At a higher Pb dose C2, not much of a difference in the Kd values could be observed, but Pb appears to be slightly more mobile after the eight weeks of incubation. Conversely, for the Mollisol, at a lower initial spike concentration, the Kd value after incubation for 8 weeks was 5 orders of magnitude lower than that of the unaged sample. For mollisol samples spiked at a higher Pb dose, more Pb was retained in the solid phase just as it was for the other soil samples, but the partition coefficient reduced by an order of magnitude of about 5 and a half, after eight weeks of incubation.

From the ongoing discussion, it is discernable that the set of data present above agrees with the recovery rates and desorption data presented earlier in this chapter. Both soils partition Pb more in the solid phase as opposed to the liquid phase, however, due the high CEC, clay type, and temperature induced breakdown of organic matter at different stages of incubation, the mollisol sorbs more Pb than the Ultisol in the A horizon.

Table 17: partition coefficient of the B Horizon soils aged for 0-8 weeks (C1)

Sample Label	M <sub>S</sub> (µg/g) x (10 <sup>2</sup> )	M <sub>L</sub> (µg/l)	K <sub>d</sub> x (10 <sup>2</sup> ) (l/g)	Mean K <sub>d</sub> x (10 <sup>2</sup> )	SD x (10 <sup>2</sup> ) (±)
U1doV	178	1.62	110	<b>90.5</b>	<b>17</b>
U2doV	178	2.11	84.4		
U3doV	178	2.31	77.1		
U1doW	178	2.31	77.1	<b>90.7</b>	<b>26</b>
U2doW	178	1.48	120		
U3doW	178	2.37	75.1		
M1doV	298	56.4	ND	<b>ND</b>	<b>ND</b>
M2doV	298	2.25			
M3doV	298	76.5			
M1doW	298	36.8	ND	<b>ND</b>	<b>ND</b>
M2doW	298	90.2			
M3doW	298	94.3			
U1W8V	175	0.89	196	<b>198</b>	<b>6</b>
U2W8V	175	0.90	194		
U3W8V	175	0.85	205		
U1W8W	175	1.07	163	<b>184</b>	<b>18</b>
U2W8W	175	0.89	196		
U3W8W	175	0.91	192		
M1W8V	186	1.24	150	<b>142</b>	<b>8</b>
M2W8V	186	1.38	135		
M3W8V	186	1.33	140		
M1W8W	186	0.43	430	<b>235</b>	<b>171</b>
M2W8W	186	1.23	151		
M3W8W	186	1.51	123		

From the tables 16 & 17 above, very significant differences can be observed in the K<sub>d</sub> values of Pb in both aged and unaged soils of the A and B horizon. The K<sub>d</sub> value of Pb in the Ultisol of the B horizon is about 900 orders of magnitude greater than that of the A horizon at C1, and after 8 weeks of aging it increased by 5.5 times that order. A direct comparison couldn't be

made between the unaged mollisol for the A and B horizon due to gross error in the results from the B horizon. Similarly, the difference in  $K_d$  for the Mollisol after the 8-week aging period for both A and B horizon soils appears to be greater than 2000 orders of magnitude.

More data sets are required to validate these results, however, they show that Pb appears to be more mobile in the A horizon, whereas it is highly sequestered in the B horizon. The reasons for these have been discussed earlier in this chapter, and this resolves mainly around the interplay between the soils physico-chemical properties. The Pb is more mobile in the A horizon probably because of the abundance of organic matter. The fraction of soluble Pb and  $K_d$  values of Pb in ultisol and mollisol of the A horizon suggest that Pb is less strongly bound to the functional groups of the organic matter, clay minerals, Mn and Fe-Oxides. However, in the B horizon, probably due to temperature maturation of the organic matter coupled with release presumed low concentrations of humic substances, Pb appears to have highly immobilized.

### 3.6 Additional data from XRD and Control sample

To determine the effect of temperature on Pb sorption in the soils used for this study, the X-Ray Diffractometry was used as an investigative tool to probe for phase changes in the unaged and aged ultisol and mollisol of the B horizon. The results yielded the presence of clay mineral expected in these soils such as Illite, smectite, vermiculite, and probably some chlorite. (Data presented in appendix). The control sample (quartz) also appeared to sorb a very significant amount of Pb when compared to the soils used in this experiment. This is probably due to sorption of Pb onto the apical oxygen in the cleaved  $\text{SiO}_2$  crystal structure or  $\text{OH}^-$  (Ahmed et al., 2015).



#### 4 CONCLUSIONS

Though this research work did not generate enough data to make the results of the experiments statistically thorough; however, the results obtained do provide a good illustration of the effect of aging and contact time in both soils used in this study. Despite the inherent errors associated with experimental protocols, and perhaps the analytical technique, a difference in sorption capacities of the soil is evident especially between the unaged soils, and those that aged for 8 weeks. ICP-MS analysis of supernatant from A horizon showed that mollisol clearly sorbs more Pb than the variably charged ultisol. This is probably due to the virtue of the soils physico-chemical properties such as CEC, pH, Organic matter and weight of the absorbent material (soil).

Within a single aging period, less Pb was recovered from the mollisol in comparison to the ultisol. Holistically, combining the 8-week incubation period, the Mollisol recovered Pb at about 2 orders of magnitudes more than that of the ultisol. pH Vs aging temperature diagram was plotted for the A horizon soils and a decrease in pH was observed with increasing temperature and time. A slight pH decrease was observed at around the neutral range for the mollisol. This suggests that the retention mechanism of the mollisol is probably surface precipitation as opposed to specific adsorption for the ultisol, and the retention capacity was probably not achieved in the mollisol within the 8 weeks aging period.

Batch experiments on the B horizons soils however, revealed an entirely different recovery trend to what was observed in the A horizon. The partitioning of Pb in the B horizon were about 900-5000 orders more than what was obtained in the A horizon soils. This unexpected observation was suggested to have resulted from temperature-catalyzed breakdown of the small quantity of organic matter present in the B horizon. This thermal breakdown has been shown by other research to have resulted into the release of low concentrations of dissolved organic Carbon, which can

inhibit the recovery of Pb when in present in very low concentrations. With increasing temperature, the proportions of phenol and hydroxyl anion groups attached are expected to increase; these groups have been well documented to sorb higher levels of heavy metals than carboxylic group in humic substances. Furthermore, organic acids such as humic acids are very insoluble and can form stable organo-metal complexes at  $\text{pH} > 5$ , which happens to be the range most of the sample lie. Conversely, desorption data revealed that, within a single aging period and a combined 8-week period the ultisol appear to sorb more Pb compared to the mollisol. Investigation into the sorption edge of Pb on Ultisol at  $\text{pH}$  3-6 revealed an unexpected increase in recovery with increasing  $\text{pH}$ . This phenomenon has been attributed to the low negative charge density associated with variably charged soils in the tropics. A subset of the supernatants from the  $0.45\ \mu\text{m}$  fraction was also filtered through  $0.22\ \mu\text{m}$  filters to investigate the prospect of colloidal facilitated transport. It was observed that Pb was enriched in the  $0.22\ \mu\text{m}$  fraction than in the  $0.45\ \mu\text{m}$ . This is counterintuitive, but suggests that Pb is tightly bound to the  $0.22\ \mu\text{m}$  fraction due to its low surface area. However, this could also be due to errors in the experimental protocol.

Lastly, to determine the bioavailability and mobility of Pb in soils of the A and B horizon, the distribution coefficient values were computed. As expected Pb appeared to be readily retained in the solid phase as opposed to the liquid phase. Mollisol retained more Pb in the solid phase than the ultisol in both horizon. However, the results show that Pb is more mobile at different concentrations in the A horizon, while it's mobility is severely retarded in the B horizon by an order of several thousands. Though, the abnormally high  $K_d$  values in the B horizon may not be fully justified; however, these results show that with increasing temperature and residence time, Pb could be more mobile. This could have a huge significance on ground water contamination in shallow aquifer systems underlain by ultisols, especially in coastal mining areas of Africa.

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## APPENDICES

### *Appendix A: Weight and pH of unaged samples, 4 and, 8 weeks aged samples for Incubation*

#### *Batch experiment (A Horizon)*

##### *Appendix A.1: Weight and pH for unaged samples*

Sample Label	Sample Weight (grams)	pH	Mean pH	SD ( $\pm$ )
U1doC1	5.0011	5.03	5.11	0.15
U2doC1	5.0018	5.29		
U3doC1	5.0005	5.02		
U1doC2	5.0030	5.06	5.10	0.06
U2doC2	5.0080	5.07		
U3doC2	5.0048	5.16		
M1doC1	5.0015	7.32	7.35	0.07
M2doC1	5.0013	7.29		
M3doC1	5.0001	7.43		
M1doC2	5.0009	7.25	7.41	0.17
M2doC2	5.0029	7.41		
M3doC2	5.0011	7.58		

##### *Appendix A.2: Weight and pH for samples aged for 4 weeks at 50°C, C1, C2.*

Sample Label	Sample Weight (grams)	pH	Mean pH	SD ( $\pm$ )
U1W4C1	5.0167	5.18	5.23	0.05
U2W4C1	5.0175	5.27		
U3W4C1	5.0242	5.25		
U1W4C2	5.0072	5.25	5.19	0.10
U2W4C2	5.0225	5.24		
U3W4C2	5.0237	5.07		
M1W4C1	5.0191	7.05	7.07	0.02
M2W4C1	5.0106	7.07		
M3W4C1	5.0075	7.09		
M1W4C2	5.0139	7.47	7.50	0.20
M2W4C2	5.0072	7.32		
M3W4C2	5.0249	7.71		

*Appendix A.3: Weight and pH for samples aged for 8 weeks at 70°C, C1, C2.*

Sample Label	Sample Weight (grams)	pH	Mean pH	SD ( $\pm$ )
U1W8C1	5.0180	6.10	6.04	0.09
U2W8C1	5.0058	6.08		
U3W8C1	5.0039	5.93		
U1W8C2	5.0158	6.75	6.49	0.42
U2W8C2	5.0039	6.72		
U3W8C2	5.0142	6.01		
M1W8C1	5.0125	7.07	7.38	0.28
M2W8C1	5.0025	7.47		
M3W8C1	5.0144	7.61		
M1W8C2	5.0238	7.16	7.18	0.05
M2W8C2	5.0177	7.23		
M3W8C2	5.0037	7.14		

**Appendix B: Weight and pH for 0, 4, 8 weeks aged sample for Batch/Incubation experiment**

**(Bt Horizon)**

**Appendix B.1: Weight and pH for samples aged for Unaged samples at C1**

Sample Label	Sample Weight (grams)	pH	Mean pH	SD ( $\pm$ )
U1doV	2.5053	5.23	5.22	0.14
U2doV	2.5101	5.08		
U3doV	2.5043	5.35		
U1doW	2.5086	5.12	5.13	0.03
U2doW	2.5018	5.11		
U3doW	2.5032	5.16		
M1doV	2.5067	7.53	7.50	0.04
M2doV	2.4950	7.45		
M3doV	2.5107	7.52		
M1doW	2.5189	7.44	7.44	0.03
M2doW	2.5079	7.41		
M3doW	2.5055	7.46		

**Appendix B.2: Weight and pH for samples aged for 4 weeks, 50 °C at C1**

Sample Label	Sample Weight(grams)	pH	Mean pH	SD ( $\pm$ )
U1W4V	2.5120	4.87	4.91	0.05
U2W4V	2.5023	4.96		
U3W4V	2.5124	4.89		
U1W4W	2.5144	4.88	4.88	0.01
U2W4W	2.5189	4.87		
U3W4W	2.4995	4.88		
M1W4V	2.5174	7.37	7.37	0.02
M2W4V	2.5052	7.39		
M3W4V	2.5048	7.36		
M1W4W	2.5054	7.68	7.59	0.13
M2W4W	2.5291	7.44		
M3W4W	2.5212	7.64		

***Appendix B.3: Weight and pH for samples aged for 8 weeks, 70°C at C1***

Sample Label	Sample Weight(grams)	pH	Mean pH	SD (±)
U1W8V	2.5064	4.46	4.49	0.04
U2W8V	2.5096	4.54		
U3W8V	2.522	4.47		
U1W8W	2.5047	4.49	4.50	0.03
U2W8W	2.5098	4.53		
U3W8W	2.5135	4.47		
M1W8V	2.5119	6.68	6.60	0.10
M2W8V	2.5116	6.49		
M3W8V	2.5023	6.63		
M1W8W	2.5063	6.53	6.51	0.08
M2W8W	2.5105	6.42		
M3W8W	2.5229	6.58		

***Appendix B.4: Weight and pH for unaged samples at (C2).***

Sample Label	Sample Weight (grams)	pH	Mean pH	SD (±)
U1doX	2.5014	5.14	5.36	0.28
U2doX	2.5117	5.26		
U3doX	2.5055	5.67		
U1doY	2.5038	5.25	5.60	0.42
U2doY	2.505	6.07		
U3doY	2.512	5.47		
M1doX	2.5035	7.08	6.88	0.18
M2doX	2.5647	6.75		
M3doX	2.5105	6.80		
M1doY	2.5199	7.16	7.08	0.08
M2doY	2.5069	7.00		
M3doY	2.5084	7.09		



***Appendix B5: Weight and pH for samples aged for 4 weeks at 50°C C2.***

Sample Label	Sample Weight (grams)	pH	Mean Ph	SD (±)
U1W4X	2.5131	5.27	5.32	0.12
U2W4X	2.5118	5.24		
U3W4X	2.5013	5.46		
U1W4Y	2.5095	5.27	5.30	0.05
U2W4Y	2.5019	5.27		
U3W4Y	2.5010	5.35		
M1W4X	2.5144	6.91	6.95	0.06
M2W4X	2.5287	6.92		
M3W4X	2.5082	7.01		
M1W4Y	2.5127	6.95	6.90	0.08
M2W4Y	2.5072	6.81		
M3W4Y	2.5043	6.95		

***Appendix B6: Weight and pH for samples aged for 8 weeks at 70 °C C2***

Sample Label	Sample Weight(grams)	pH	Mean pH	SD (±)
U1W8X	2.5101	4.6	4.61	0.01
U2W8X	2.5054	4.61		
U3W8X	2.5005	4.62		
U1W8Y	2.5013	4.79	4.78	0.02
U2W8Y	2.5002	4.76		
U3W8Y	2.5018	4.79		
M1W8X	2.5003	6.81	6.65	0.23
M2W8X	2.5098	-		
M3W8X	2.5062	6.48		
M1W8Y	2.5050	6.66	6.73	0.06
M2W8Y	2.5081	6.75		
M3W8Y	2.5096	6.78		

**Appendix C: Raw data for unaged, 4, 8 weeks aged sample for Batch experiment (Bt Horizon)**

**Appendix C.1: Pb desorption data for unaged samples (do) at C1 filtered with .45 $\mu$ m**

Sample Label	Raw Concentration ( $\mu$ g/l)	Index Ratio x ( $10^{-4}$ )	Mean Index Ratio (x $10^{-4}$ )	SD measurements ( $\pm$ )
U1doV	1.62	14.73	<b>18.30</b>	<b>0.36</b>
U2doV	2.11	19.18		
U3doV	2.31	21.00		
U1doW	2.31	21.00	<b>18.67</b>	<b>0.50</b>
U2doW	1.48	13.50		
U3doW	2.37	21.55		
M1doV	56.4			
M2doV	2.25	-	-	-
M3doV	76.5			
M1doW	36.8			
M2doW	90.2	-	-	-
M3doW	94.3			

\*W=Replication on the treatment level at C1 (Analytical replicate of V)

V= Replication on the measurement level at C1

*Appendix C.2: Pb desorption data for samples aged at 50° C (4 weeks) at C1*

Sample Label	Raw Concentration (µg/l)	Index Ratio (x10 <sup>-4</sup> )	Mean Index Ratio (x10 <sup>-4</sup> )	SD measurements (±)
U1W4V	1.38	12.55	<b>8.25</b>	<b>0.56</b>
U2W4V	0.28	2.58		
U3W4V	1.06	9.64		
U1W4W	1.16	10.55	<b>5.44</b>	<b>0.49</b>
U2W4W	0.35	3.16		
U3W4W	0.29	2.61		
M1W4V	0.25	2.30	<b>2.41</b>	<b>0.01</b>
M2W4V	0.28	2.52		
M3W4V	0.27	2.42		
M1W4W	0.33	2.95	<b>2.61</b>	<b>0.04</b>
M2W4W	0.27	2.42		
M3W4W	176	-		

*Appendix C.3: Pb desorption data for samples aged at 70° C (8weeks) at C1*

Sample Label	Raw Concentration (µg/l)	Index Ratio (x10 <sup>-4</sup> )	Mean Index Ratio (x10 <sup>-4</sup> )	SD measurements (±)
U1W8V	0.89	8.09	<b>7.99</b>	<b>0.03</b>
U2W8V	0.90	8.20		
U3W8V	0.85	7.68		
U1W8W	1.07	9.73	<b>8.70</b>	<b>0.10</b>
U2W8W	0.89	8.06		
U3W8W	0.91	8.31		
M1W8V	1.24	11.27	<b>11.97</b>	<b>0.07</b>
M2W8V	1.38	12.55		
M3W8V	1.33	12.09		
M1W8W	0.43	3.93	<b>9.61</b>	<b>0.56</b>
M2W8W	1.23	11.18		
M3W8W	1.51	13.73		

**Appendix C.4: Pb desorption data for unaged sample ( $d_0$ ) at C2**

Sample Label	Raw Concentration ( $\mu\text{g/l}$ )	Index Ratio $\times (10^{-4})$	Mean Index Ratio ( $\times 10^{-4}$ )	SD of samples ( $\pm$ )
U1doX	0.74	6.73	<b>5.69</b>	<b>0.10</b>
U2doX	0.56	5.09		
U3doX	0.57	5.18		
U1doY	0.61	5.55	<b>5.60</b>	<b>0.30</b>
U2doY	0.59	5.36		
U3doY	0.65	5.91		
M1doX	0.75	6.82	<b>6.15</b>	<b>0.10</b>
M2doX	56.8	-		
M3doX	0.61	5.55		
M1doY	56.5	-	-	-
M2doY	60.5	-		
M3doY	55.1	-		

\*Y=Replication on the treatment level at C2 (Analytical replicate of X)

X= Replication on the measurement level at C2

**Appendix C.5: Pb desorption data for samples aged at 50° C (4weeks) at C2**

Sample Label	Raw Concentration ( $\mu\text{g/l}$ )	Index Ratio ( $\times 10^{-4}$ )	Mean Index Ratio ( $\times 10^{-4}$ )	SD of samples ( $\pm$ )
U1W4X	0.49	4.45	<b>4.87</b>	<b>0.04</b>
U2W4X	0.54	4.91		
U3W4X	0.57	5.18		
U1W4Y	0.52	4.73	<b>4.88</b>	<b>0.04</b>
U2W4Y	0.50	4.55		
U3W4Y	0.59	5.36		
M1W4X	0.72	6.55	<b>6.26</b>	<b>0.05</b>
M2W4X	0.71	6.45		
M3W4X	0.63	5.73		
M1W4Y	0.78	6.64	<b>7.01</b>	<b>0.01</b>
M2W4Y	0.76	6.91		
M3W4Y	0.78	7.09		

**Appendix C.6: Pb desorption data for samples aged at 70° C (8weeks) at C2**

Sample Label	Raw Concentration (µg/l)	Index Ratio (x10 <sup>-4</sup> )	Mean Index Ratio (x10 <sup>-4</sup> )	SD of samples (±)
U1W8X	0.57	5.18	<b>4.31</b>	<b>0.09</b>
U2W8X	0.43	3.91		
U3W8X	0.42	3.82		
U1W8Y	0.55	5.00	<b>4.22</b>	<b>0.08</b>
U2W8Y	0.45	4.09		
U3W8Y	0.39	3.55		
M1W8X	0.43	3.91	<b>4.19</b>	<b>0.02</b>
M2W8X	0.48	4.36		
M3W8X	0.47	4.27		
M1W8Y	0.49	4.45	<b>4.56</b>	<b>0.01</b>
M2W8Y	0.52	4.73		
M3W8Y	0.49	4.45		

**Appendix C.7: Raw Pb desorption data for pH Experiment (B Horizon/ Concentration C2)**

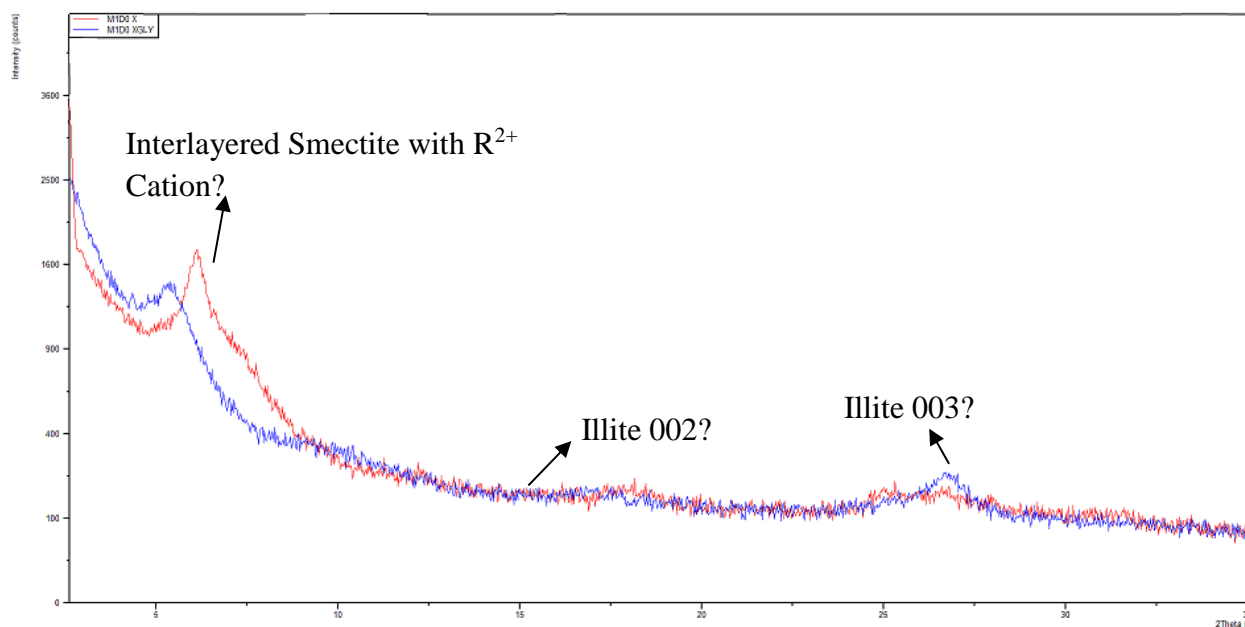
Sample ID	Conc. ppb	SD (±) reps of X&Y	Sample ID	Conc.(ppb)	SD (±) reps of X&Y	Sample ID	Conc. (ppb)	SD (±) reps of X&Y
U1w8Xp	1.66	0.04	U1W4Xp	1.84	0.09	U1doXp	2.15	0.09
U2W8Xp	1.68	0.07	U2W4Xp	2.03	0.14	U2doXp	1.96	0.02
U3w8Xp	1.72	0.00	U3W4Xp	1.72	0.11	U3doXp	1.82	0.30
U4W8Xp	1.84	0.10	U4W4Xp	1.9	0.04	U4doXp	3.06	0.08
U1w8Yp	1.6		U1W4Yp	1.97		U1doYp	2.02	
U2w8Yp	1.79		U2W4Yp	1.83		U2doYp	1.92	
U3w8Yp	1.72		U3W4Yp	1.88		U3doYp	2.25	
U4W8Yp	1.69		U4W4Yp	1.96		U4doYp	3.18	
M1W8Xp	1.9		M1W4Xp	60.9		M1doXp	71.8	
M2W8Xp	2.31		M2W4Xp	47		M2doXp	34.2	
M3W8Xp	2.16		M3W4Xp	58.4		M3doXp	73.4	
M4W8Xp	2.52		M4W4Xp	57.6		M4doXp	56.4	
M1W8Yp	141		M1W4Yp	43		M1doYp	62.7	
M2W8Yp	132		M2W4Yp	49.8		M2doYp	95.1	
M3W8Yp	125		M3W4Yp	67.2		M3doYp	39.4	
M4W8Yp	106		M4W4Yp	89.2		M4doYp	48	

*Appendix C.8: Mean Pb concentration for analytical reps for pH Experiment (B Horizon/  
Concentration C2)*

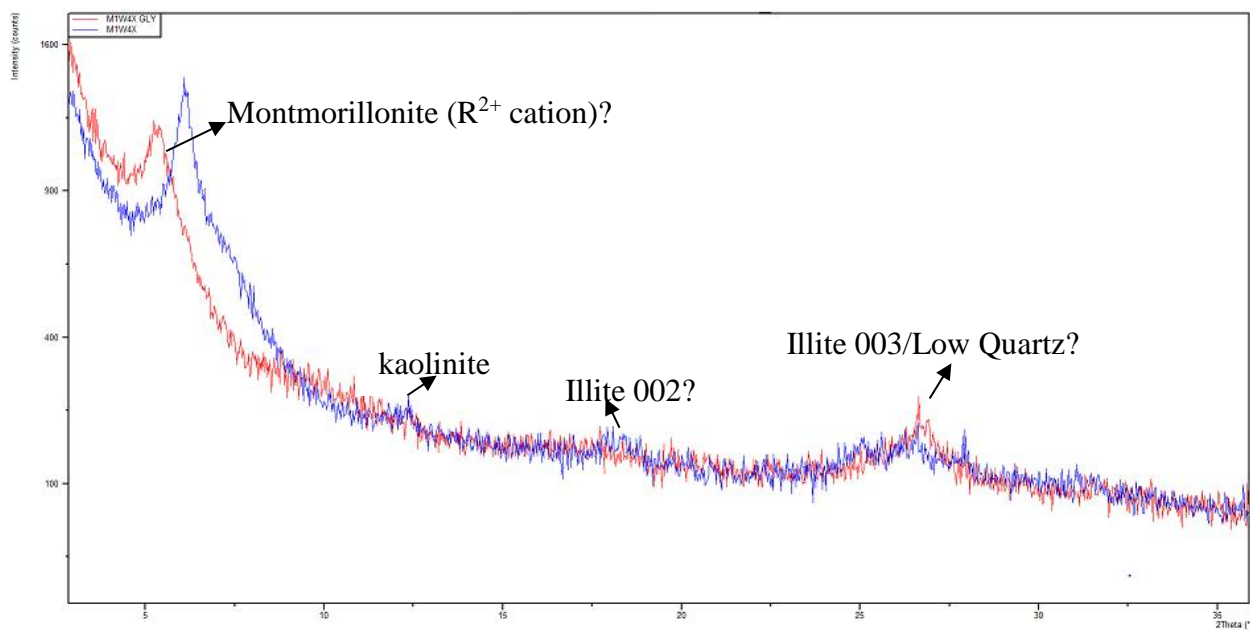
pH	8weeks (ppb)	4 weeks (ppb)	0 days (ppb)
3	1.63	1.91	2.09
4	1.74	1.93	1.94
5	1.72	1.80	2.04
6	1.77	1.93	3.12
	SD = 0.06	SD = 0.06	SD = 0.55

## Appendix D: X-Ray Diffraction patterns for unaged, 4 and, 8 weeks aged samples.

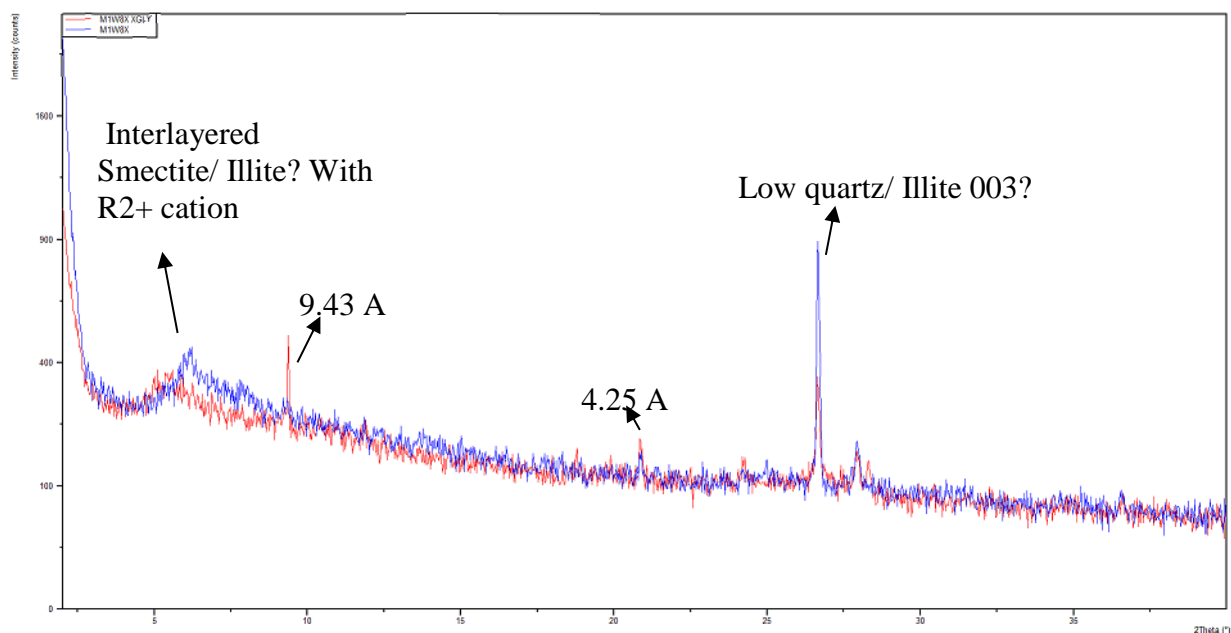
### Appendix D.1: Diffractogram of M1doX (unaged Mollisol sample)



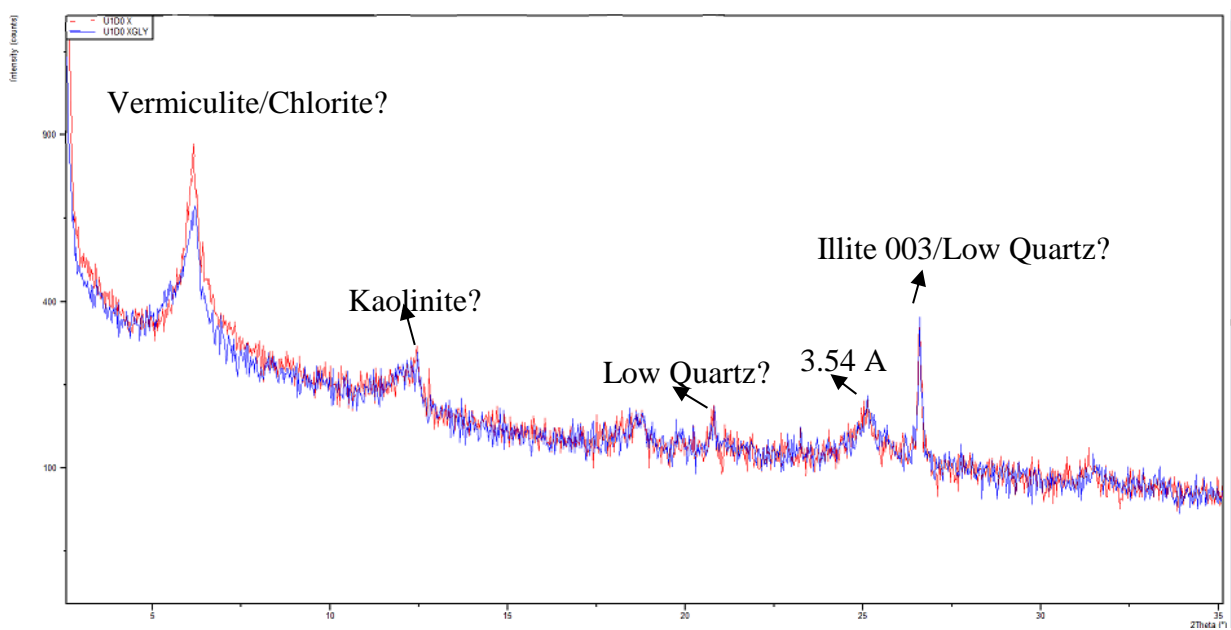
### Appendix D.2: Diffractogram of M1W4X (Mollisol aged for 4 weeks at 50°C)



**Appendix D.3: Diffractogram of M1W8X (Mollisol aged for 8 weeks at 70°C)**

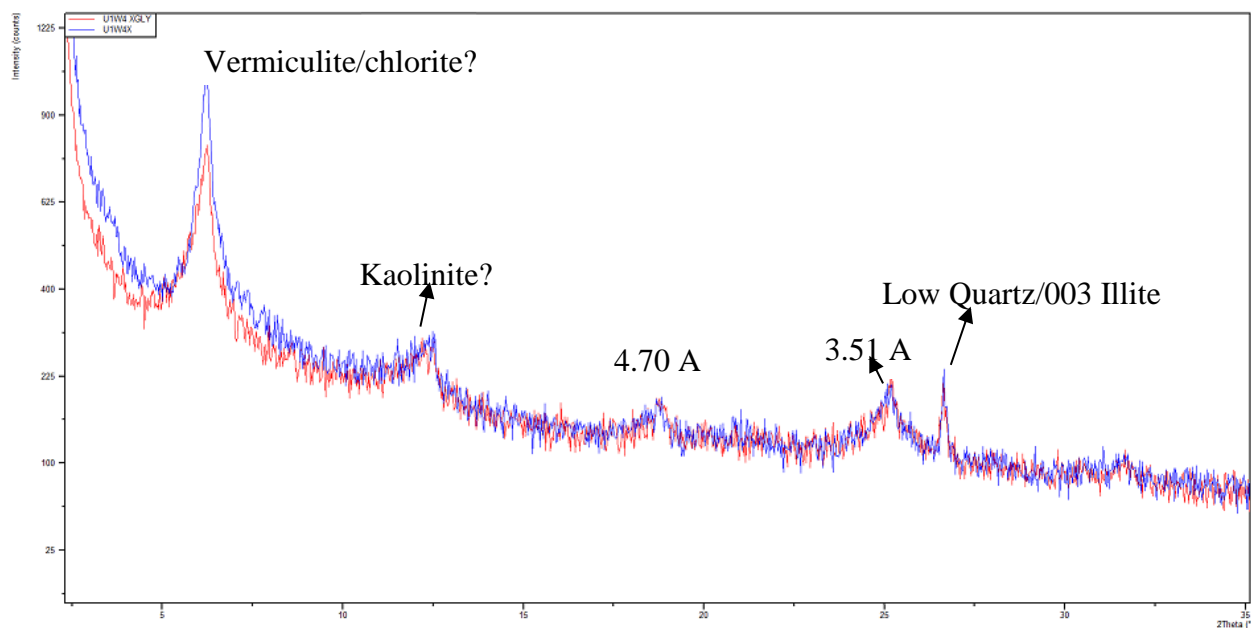


**Appendix D.4: Diffractogram of U1doX (unaged Ultisol sample)**

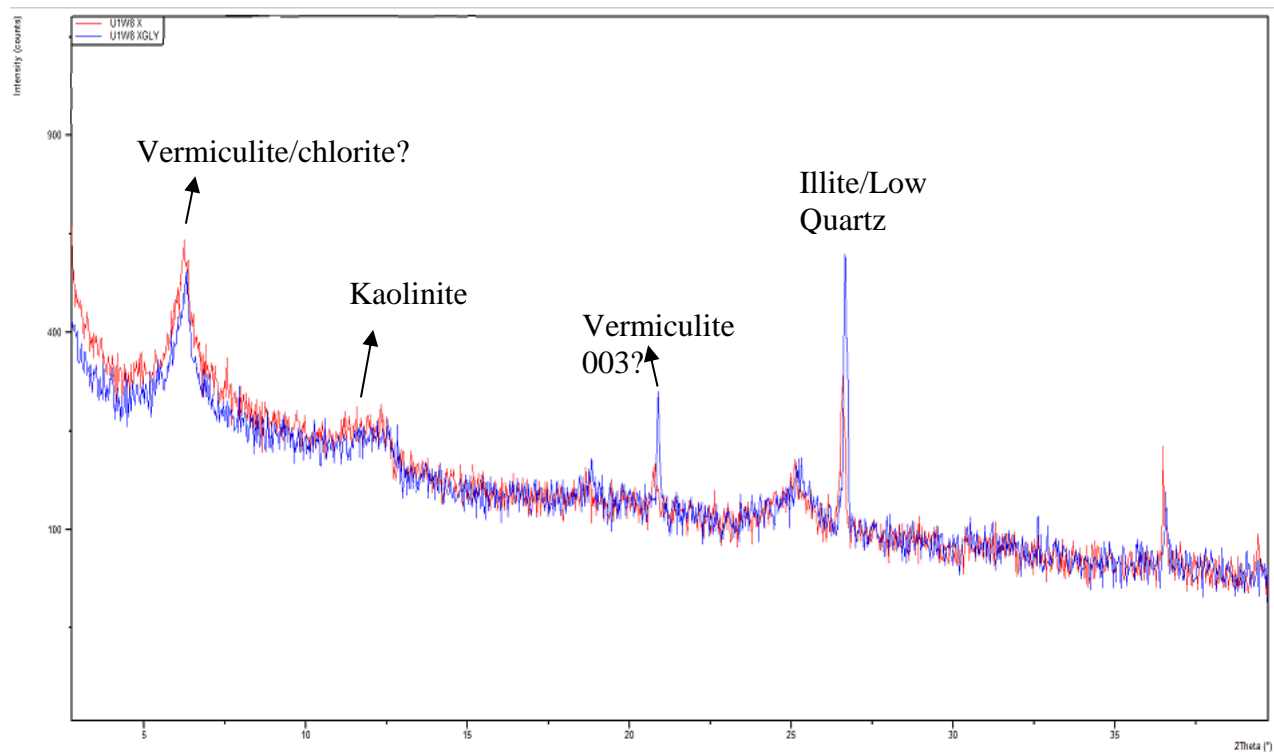




**Appendix D.5: Diffractogram of U1W4X (Ultisol aged for 4 weeks at 50°C)**



**Appendix D.6: Diffractogram of U1W8X (ultisol aged for 8 weeks at 70°C)**



*Appendix E: Miscellaneous Data (Picture, desorption data for quartz, acid digestion data for soils, and Pb speciation curves).*



Sample ID	Conc. ppb	Sample ID	Conc. ppb	Sample ID	Conc. ppb
Q1doV	2.05	Q1W4V	2.13	Q1W8V	2.23
Q2doV	2.15	Q2W4V	2.15	Q2W8V	2.12
Q3doV	2.08	Q3W4V	2.26	Q3W8V	2.36
Q1doW	2.06			Q1W8W	2.42
Q2doW	2.3			Q2W8W	2.47
Q3doW	2.05			Q3W8W	2.38

Sample ID	Conc. ppb	Sample ID	Conc. ppb	Sample ID	Conc. ppb
DoUX1	2.45	D4UX1	2.67	D8UX1	2.38
DoUX2	2.43	D4UX2	2.333	D8UX2	2.55
DoMX1	2.86	D4MX1	2.68	D8UV1	3.01
DoMX2	2.38	D4MX2	2.58	D8UV2	2.41
				D8MX1	2.71
				D8MX2	2.72
				D8MV1	2.41
				D8MV2	2.38

