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ASSESSMENT OF Pb MOBILITY FROM SPENT BULLETS IN THREE DIFFERENT SOIL TYPES: APPLICATION OF LEACHABILITY TEST TO THE SPENT BULLETS

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ABSTRACT

Leaching of lead (Pb) from spent bullets in soil, especially around shooting range is a threat to the environment at large which could be as a result of soil condition. Available Pb in soil could bio-accumulate in the food web through phyto-extraction by crops, which could be consumed by animals and humans. The Pb could also contaminate surface water through run-offs and percolate into underground water, causing risk to human health when the source of water is exploited for domestic use such as bore-hole and well. The study therefore investigated the mobility potential of Pb from spent bullet fragments obtained within a military shooting range, on three different soil types (Loamy, Sandy, & Clay). Similarly, a leachability test was applied to the spent bullets to determine their leaching pattern of the spent bullets.

Three soil types; Loamy-25kg, Sandy-25kg, Clay-25kg, were each obtained from locations of less likely Pb contamination, within the Ibadan metropolis. Specimen of spent bullet fragments were also collected from a military shooting range and separated into corroded and less corroded fragments. For the mobility study; 80g of each soil types were weighed into 250ml container respectively and 8g of corroded bullet fragments were added to each. Conditions were simulated within the sample to natural environment. This process was repeated for less corroded bullets in all soil types. The sample was digested after a week and taken for Pb analysis using FAAS. Replicate samples were prepared for 24 weeks' subsequent analysis. A total of 144 samples were prepared for the study. For the leachability test; three types of leachate solutions were prepared in a 250ml container; ASTM(100ml), SPLP(40ml) and TCLP(40ml). 10g of corroded bullet fragments were added into each leachate solution and the samples were taken for Pb analysis after a week using FAAS. The same procedure was repeated for less corroded bullets. Replicate samples were prepared to cover up for 24 weeks' subsequent analysis making a total of 144 samples. Preliminary studies were carried out on the different soil types such as heavy metal speciation (Tessier *et. al.*), mechanical properties, phosphates, nitrates, sulphate, TOC, pH and moisture content. Analar grade reagents and deionised water were used for the analysis. Also sample blanks were prepared. Statistical analysis was carried out using ANOVA.

The results showed an elevated concentration of lead (Pb) in the soil samples and leachate solutions. The total concentration of heavy metals in the soil samples gave a sequence of Loamy>Sandy>Clay, while the total heavy metal concentration in the leachate solution gave a sequence of TCLP>SPLP>ASTM.

The study was objectified towards the development of a model which shows the trend of available Pb in different soil types at elevated concentrations. Thus, the toxicity potential of Pb on human health and environment is of high significance.

LIST OF ABBREVIATIONS

USEPA	United States Environmental Protection Agency
ASTDR	Agency for Toxic Substances and Disease Registry
CERCLA	Comprehensive Environmental Response, Compensation, and Liability
NPL	National Priorities List
EPA	Environmental Protection Agency
PbB	Blood Lead
NSSF	National Shooting Sport Foundation
μ-XRF	Micro-X-Ray Fluorescence
μ-XANES	Micro-X-Ray Absorption Near Edge Structure
SPLP	Synthetic Precipitation Leaching Procedure
TCLP	Toxic Characteristics Leaching Procedure
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrophotometer
IDEM	Indiana Department of Environmental Management
RCRA	Resource Conservation and Recovery Act
TCLP	Toxicity characteristic leaching procedure
AAS	Atomic Absorption Spectrometer
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrophotometer
ASTM	American Society for Testing and Materials
DOC	Dissolved Organic Carbon
XRPD	X-ray powder diffraction
SEM	scanning electron microscopy
SET	sequential extraction test
FAAS	Flame Atomic Absorption spectrophotometer

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CHAPTER ONE
INTRODUCTION

1.1 Background to the study

The contamination of shooting range soil with lead (Pb) emanating from shots and bullets has received increased attention due to the elevated amounts of Pb in these places and the adverse health effects associated with the exposure to Pb (Dermatas *et. al*., 2004). The adverse effects to humans are more pronounced in children. Low levels of Pb, as low as 0.01mgdl^{-1}, in children's bodies can lead to conditions such as damage to the brain and nervous system, behaviour and learning problems (e.g hyperactivity and aggressions), slowed growth, learning problems, headaches and impairment of vision and motor skills (USEPA, 2001). Exposure to Pb in adults can cause difficulties during pregnancy, reproductive problems in both men and women (such as low birth weight, birth defects and decreased fertility), high blood pressure, digestive problems, neurological disorders, memory and concentration problems, muscle and joint pain, and kidney dysfunction.

In the past few years, studies have shown that there is an elevated amount of Pb contamination in the soil of shooting ranges (Hin, et al., 2002). To highlight that environmental pollution from Pb at shooting ranges is a worldwide concern, approximately 58,300 tonnes of Pb is accumulated into the United States' soils annually and 300gkg^{-1} of lead has been documented in the topsoil of clay-shooting range in the Netherlands (Luo, et al., 2015; Van Bon & Boerserna, 1988).

1.2 Bullet composition and characteristics

A bullet is a kinetic projectile and the component of firearm ammunition that is expelled from the gun barrel during shooting. The term is from Middle French and originated as the diminutive of the word *boulle* (*boullet*), which means "small ball" (Meriem-Webster, 2017). Bullets are made of a variety of materials such as copper, lead, steel, polymer, rubber and even wax. They are available either singly as in muzzle loading and cap and ball firearms (Hornady, 2017) or as a component of paper cartridges, but much more commonly in the form of metallic cartridges. Bullets are made in a large number of shapes and constructions depending on the intended applications, including specialized functions such as hunting, target shooting, training and combat.

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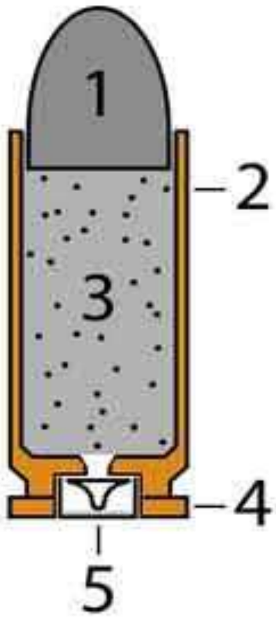

Figure 1.1 A modern Centrefire Cartridge

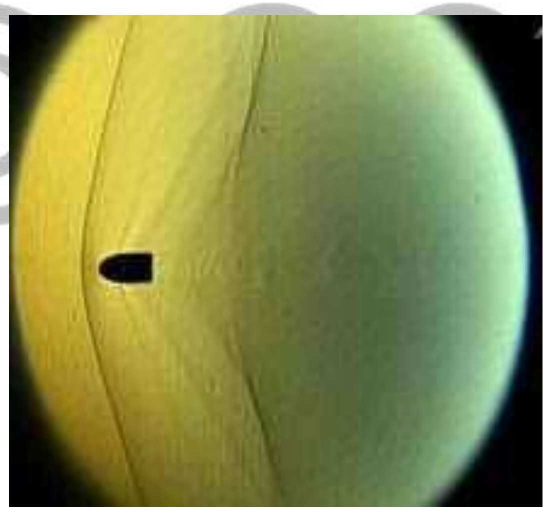

Figure 1.2 Schlieren image of a bullet travelling in free-flight demonstrating the air pressure dynamics surrounding the bullet.

The modern centrefire cartridge consists of;

1. the bullet, as the projectile;
2. the metallic case, which holds all parts together;
3. the propellant, for example, gun powder or cordite;
4. the rim, which provides the extractor on the firearm place to grip the case to remove it from the chamber once fired;
5. the primer, which ignites the propellant.

Bullet sizes are expressed by their weights and diameters (referred to as "calibres") in both imperial (Firearm guide, 2017) and metric measurement systems. For example: 55 grams .223mm calibre bullets are of the same weight and calibre as 3.56 gram 5.56mm calibre bullets. The bullets used in many cartridges are fired at muzzle velocities faster than the speed of sound (Handgun ballistics, 2017; Ballistics, 2017) about 343 meters per second (1,130 ft/s) in dry air at 20 °C (68 °F) and thus can travel a substantial distance to a target before a nearby observer hears the sound of the shot. The sound of gunfire (i.e. the muzzle report) is often accompanied with a loud bullwhip-like crack as the supersonic bullet pierces through the air creating a sonic boom. Bullet speeds at various stages of flight depend on intrinsic factors such as its sectional density, aerodynamic profile and ballistic coefficient, and extrinsic factors such as barometric pressure, humidity, air temperature and wind speed (Inspireme, 2016). Subsonic cartridges fire bullets slower than the speed of sound so there is no sonic boom. This means that a subsonic cartridge can be substantially quieter than a supersonic cartridge such as the .223 Remington, even without the use of a suppressor (Silencershop, 2017). Bullets do not normally contain explosives (Swift & Rutty, 2017) but damage the intended target by transferring kinetic energy upon impact and penetration.

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Figure 1.3 Minnie Ball ammunition

Figure 1.4 Modern Bullets

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1.3 Aim of the study

The aim of the study is to assess the leaching of spent bullets in shooting range soil and to apply leachability test to the spent bullets.

1.4 Objectives of the study

i. Assessment of the nature, corrosion pattern and contamination level of lead from spent bullets in different types of soil.
ii. Determination of the leachability pattern and percentage toxicity of lead from spent bullets.
iii. Development of a model to predict the contamination pattern of lead in soil.

1.5 Scope of study

The scope of this study covers the assessment of lead, leaching out from spent bullets into shooting range soil, and the application of leachability test to the spent bullets. The pre-selected shooting range was the Adekunle Fajuyi Army Cantonment, Ojoo, Ibadan, Oyo state. The scope of this study is therefore limited to this shooting range.

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CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy metal contamination of shooting range soil

The spatial distribution and speciation of Pb in the weathering crust and soil surrounding corroding metallic Pb bullets in a shooting range soil is known to pose a great risk to the soil environment (Delphine *et. al.*, 2005). A soil with a neutral pH could be highly contaminated with Pb with a concentration as high as 68,000 $mgkg^{-1}$. This mostly occur on the surface of the soil. In this study, undisturbed soil samples containing corroding bullets, collected and embedded in resin, polished sections and prepared for micro-X-ray fluorescence (μ-XRF) elemental mapping, micro-X-ray absorption near edge structure (μ-XANES) spectroscopy and X-ray diffraction analysis showed a steep decrease in total Pb concentrations from the bullet weathering crust into the surrounding soil matrix. The weathering crust consisted of a mixture of litharge [R-PbO], Hydrocerussite [$Pb_3(CO_3)_2$-$(OH)_2$], and Cerussite [$PbCO_3$], with litharge dominating near the metallic Pb core and Cerussite dominating in the outer crust, which is in contact with the soil matrix.

On the basis of these results and thermodynamic considerations, it was proposed that the transition of Pb species after oxidation of Pb(0) to Pb(II) follows the sequence litharge, hydrocerussite to cerussite. Consequently, the solubility of cerussite limits the activity of Pb^{2+} in the soil solution in contact with weathering bullets to $\leq 28 \times 10^{-6}$ at pH 7, assuming that the CO_2 partial pressure (P_{CO2}) in the soil is equal or larger than in the atmosphere ($P_{CO2} \geq 0.000\ 35$ atm).

2.2 Toxicity of lead (pb)

For lead to be toxic to animals or humans, it must enter the body. The exposure pathways of concern for lead are inhalation and ingestion (IDEM 2012). Inhalation can be a factor when significant amount of airborne lead dusts and fumes are present, such as around lead smelters and recycling centres. Small, poorly ventilated indoor ranges firing large volumes of non-jacketed lead bullets into steel backstops have occasionally presented risks from inhalation for range employees upon long-term exposure. Excavation of the impact areas of a range could possibly generate lead dusts, so dust control measures should be used.

Normally, lead inhalation at outdoor ranges has not been found to present a problem, because the amount of lead dust produced by outdoor firing ranges is very limited. This leaves ingestion as the

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major pathway for toxic lead effects from a firing range. Drinking water is seldom affected by firing ranges because of the low solubility and restricted migration of metallic lead. Therefore, eating of lead or lead contaminated soils is the health risk normally encountered. Pre-school children are the most vulnerable to lead toxicity because lead absorption in the gastrointestinal tract is greater for children than adults, children's nervous systems are more susceptible to neurotoxic effects, and children are much more likely to be in contact with, and eat, soil. If there is no contact, then there is no possibility of ingestion. A good vegetative cover helps prevent contact, but children should not be allowed to play in range impact areas.

The use of lead bullets and shot at shooting ranges is under increasing scrutiny as a potentially significant source of Pb pollution (Xinde *et. al.*,2003). The study assessed Pb contamination in the soils of two shooting ranges (TRR and MPR) in Florida. Soil samples were collected from the two ranges and analysed for total Pb to determine Pb contamination. Selected spent bullets and berm soil samples were mineralogically characterized to identify Pb transformation. Total Pb in the range soils was significantly elevated with the highest (up to 4.84% by weight) in the berm soils.

Most soils failed the synthetic precipitation leaching procedure (SPLP) test. Also, at the MPR shooting range, a substantial amount of Pb migrated down in the subsurface soil, possibly due to the enhanced solubilisation of organic Pb complexes at alkaline pH, whereas high cation exchange capacity of the profile soil may be responsible for Pb retention in the subsoil. The weathering products on the surface of the spent bullets were predominantly hydrocerussite and cerussite ($PbCO_3$). Hydrocerussite was mainly found in the MPR range soils, whereas Pb was transformed into hydroxypyromorphite in the TRR range soils because of the presence of more Pb. Sequential extraction and lead activity ratio modelling showed that the soil Pb solubility was controlled by Pb carbonate minerals in the MPR shooting range, and by less soluble Pb phosphate minerals in the TRR shooting range.

Forms of Lead Exposure

Most of the cases of severe lead poisoning in children are due to exposure to lead based paints or leaded gasoline residues, and this is the focus of much of the research and articles on lead toxicity (Xintaras, 1992; Mielke, 1999). These reports cannot be related to firing ranges. Lead from a firing range is much less toxic because there are direct relationships between toxicity and lead particle

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size, plus chemical form. Firing range lead is in metallic form, mostly as whole or fragmented bullets, with only a small amount of dust-sized particles. The larger particles are not as readily absorbed (Colorado Dept of Health, 1990). Leaded paints normally form dusts from the paints' flaking, weathering, and chalking, which are readily absorbed into the body. Also, the lead in paints exists in the form of oxides or salts, which can be over ten times more absorbable than metallic lead (Xintaras, 1992). Lastly, lead from paint concentrates in and around the house, where contact is unavoidable, and ingestion common.

Ecological Risks

Smaller lead particles (shot or fragments) can be ingested by wildlife, usually when mistaken for seeds or consumed by fowl looking for gizzard grit. Even one pellet may prove toxic to some birds, so precautions should be taken to make range impact areas uninviting to wildlife. This is a particular problem for waterfowl feeding in ponds, which is why there is a ban on lead shot for waterfowl hunting, and why firing ranges should not have open water in or near impact areas.

Fruit trees, grains, and other vegetation providing wildlife foods should not be located on firing ranges. Even grasses may prove a problem as ducks and geese prefer to graze in close-cropped grasses and may dig several inches into the soil. Range impact areas should not be closely mowed. Denser, low shrubs and bushes should be encouraged. If grasses are planted, they should be allowed to grow knee to waist high to discourage rooting wildlife.

2.3 Leachability test

In order to establish a valid method for determining the possible extent of lead impacts on areas surrounding shooting ranges, it is necessary to use appropriate analytical models. Although lead is basically immobile in the environment, there are certain forms which can be mobilized, and therefore, have the potential to impact areas other than the immediate vicinity of the shooting range.

A commonality of these forms of lead is their solubility in water or acids. Leach modelling is the most appropriate method to assess the mobility of lead. Leach models act as a gauge of the totality of mobile lead. For the purposes of truly assessing mobility and contaminant risk in a site specific area, several other factors must be identified and accounted for. Average rainfall amounts, infiltration rates, soil cation exchange capacities, existence of lead-reactive ionic species, total

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volume of the area of interest, etc., must be considered in order to determine the level of risk associated with a shooting range site. The model most commonly considered for use is the toxicity characteristic leaching procedure (TCLP), EPA SW-846 method 1311.

This model is used to determine whether leachable lead levels exceed regulatory thresholds, and are considered hazardous for the purposes of disposal. This model was designed to mimic leachate generated in a solid waste landfill, which accepts organic and inorganic wastes. These organic wastes may decompose, with attendant acid formation, which increases the likelihood of metal ion solubility. The premise behind the model makes it a poor candidate for assessing the level of leachable lead at a firing range, because the amount and type of acids the model uses typically would significantly exceed those types and amounts found naturally. Water leach models, similar to the Indiana Neutral Leaching Method or the ASTM Water Leach Method, are more appropriate than TCLP, as they tend to reflect a more real estimate of the acidity encountered in the environment.

The main shortcoming of these models is their use of distilled, deionized water, which does not exactly mimic the buffered water systems found in the environment. For shooting ranges over a standing body of water, such as some shotgun ranges, this would be the most appropriate leach model to assess the amounts of lead which may become mobile. Although rain would feed the standing water body, directly or indirectly, the size and buffering capacity of the standing water body and its matrix would cause the pH of the influx water to rapidly approach neutral. Given the acidic nature of rainfall in Indiana, the leach model which could be considered appropriate for most shooting ranges would be the Synthetic Precipitation Leaching Procedure (SPLP), SW-846 method 1312.

The vast majority of water that would be in contact with lead from the majority of shooting ranges would be encountered as rainfall. The pH of rainfall in Indiana ranges from around 4.5 to 5 standard units. The leach fluids stipulated for this model simulate the acidity and types of acids noted in rain. The leach fluid appropriate for determining lead mobility in Indiana has a pH of 4.2 ± 0.05 standard units, and would effectively model a worst-case scenario of lead mobilized by the effects of acid rain.

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2.3 Lead mobility

A number of factors affect the mobility of lead in the environment. A partial list of the factors which affect lead in the environment follows:

➢Lead oxidation is very slow (100 to over 300 years) for bullets, depending on site conditions.

➢Cation exchange capacity: In soils, the ability to exchange cations binds lead into the soil matrix, but the process is reversible when new cations are introduced into the system.

➢Sulphides: Sulphur has a high affinity for lead, which, after reacting to form lead sulphide, precipitates out, moving contamination from water into the sediments. In sediments, sulphides cause free lead to become effectively insoluble, preventing transfer into water resources by dissolution.

➢Sulphites and Sulphates: In the presence of water-soluble sulphites/sulphates, lead tends to precipitate out of solution. Soils high in sulphites/sulphates will cause lead to become effectively insoluble, preventing transfer into water resources by dissolution. Depending on the amount of free oxygen present, sulphites tend to slowly oxidize to the sulphate species.

➢Phosphates: Phosphate ion sources tend to be quite effective in immobilizing lead. Lead phosphate is insoluble, and is quite stable. Phosphate fertilizers can help immobilize lead.

➢Hydroxides: Free lead, in the presence of hydroxide ions, forms lead hydroxide, which is insoluble.

➢Humic substances: Lead forms complexes with these high molecular weight compounds, reducing their mobility and solubility.

➢Carbonates: Lead/carbonate interactions decrease the solubility of lead.

➢Acids: Lead is soluble in dilute acids.

➢Clays, and iron or manganese oxides (all very common in southern and central Indiana), are highly lead absorbent, which restricts mobility.

According to the Agency for Toxic Substances and Disease Registry, and the U.S. Environmental Protection Agency (USEPA) priority list of hazardous substances, lead has been ranked as the

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number two priority hazardous substance. Serious human health risks, particularly for children under 6 years of age, are associated with lead poisoning (Xintaras, 1992). In recent years, lead contamination of soils at shooting ranges from the use of lead bullets is under increasing scrutiny as a potentially significant source of lead contamination (Rooney *et al.*, 1999; Craig *et al.*, 1999).

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CHAPTER THREE

MATERIAL AND METHOD

3.1 Study Design

This study entailed the assessment of spent bullet fragments in three types of soil and also, three types of leachate solutions. Three soil types; Sandy, Loamy, and Clay, were collected from a location of less likely Pb contamination, within the Ibadan metropolis. Also, bullets fragments were collected from a military shooting range. Three types of leachate solutions (SPLP, TCLP, ASTM) were also prepared. Each sample was encoded using the following parameters:

Soil type:

1. Loamy – **L**
2. Sandy – **S**
3. Clay – **C**

Bullet fragment type:

1. Corroded bullet fragments - *
2. Less-corroded bullet fragments - **#**

Leachate solution type:

1. ASTM leachate solution – **A**
2. SPLP leachate solution – **S**
3. TCLP (USEPA) leachate solution – **U**

Week – Number 1-24

Example: A sample code of *L_2 indicated a loamy soil, containing corroded bullet, to be analysed in the second week.

The experimental set-up was done cover 24 weeks of Pb analysis, making up a total of 288 samples. Blanks were also prepared for the sample and the reagents. The experimental procedure was divided into two phases:

1. the leaching of the spent bullet fragments into three different soil types;

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2. the application of leachability test to the spent bullets.

3.2 Soil sampling and pre-treatment

The three types of soil that were collected were:

- Loamy soil, from the botanical garden of UI.
- Sandy soil, from a location at Akobo
- Clay soil (Laterite), from the Abdulsalami Abu-Bakr Hostel, University of Ibadan.

The closest in soil property to the shooting range soil was the clay soil obtained, as the soil type found on the shooting range was also of clay properties. The selected soil samples were air-dried for seven days to remove every field moist from them. They were then recovered and pulverised to pass through a 2mm sieve. This was done to ensure that the particle size distribution of the soil, allows the easy flow of the leachate from the spent bullet fragments into the soil, giving room for more surface area distribution of the leachate around the soil sample.

80g of the pre-treated soil was then weighed into 250ml pre-cleaned container. Each sample container was then assigned a sample code based on the type of soil, the nature of the bullet to be added and the week of analysis. After this, there was an addition of forty mil (40ml) of water to the sample to simulate environmental conditions.

3.3 Bullet collection and segregation

Composite bullet fragments were collected from the military shooting range and transported to the laboratory in a glass jar, that had been pre-cleaned. The bullets were washed and air dried in the laboratory. After drying, the bullet fragments were then separated into corroded and less-corroded types. This was done by observing the smoothness of the bullet after washing and air-drying. After separation, each bullet fragments were weighed. For bullets whose weights were far lesser than the selected weight (8g for soil; 10g for leachate solution), a combination of two or more fragments of the same nature (corroded/less corroded) was used to arrive at about the exact weight.

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Figure 3.1 Corroded bullet fragments

Figure 3.2 Less-corroded bullet fragments

3.4 Mobility Experiment Set-up

The first phase of the study involved the collection of 80g of each soil types in a 250ml container and the addition of 8g of corroded bullet fragments (bullet-to-soil ratio; 1:10) to each soil type. This same procedure was repeated for less corroded bullets. The sample was then simulated to natural environment by the initial addition of 40ml of water and subsequently, 8ml to keep the soil moist. Replicate samples were prepared to extend to 24 weeks for each sample types. 24 samples were prepared for corroded bullets in each soil type, and also 24 samples for less-corroded bullets in each soil type, making a total of 144 samples for the study. The samples were kept in the dark to avoid photochemical reactions and exposed to the atmosphere to prevent anaerobic reactions. One of each sample type was then retrieved after a week, digested using HNO_3 (1:1 v/v), and the digest was taken for Pb analysis using FLAME ATOMIC ABSORPTION SPECTROPHOTOMETER (FAAS). Subsequent samples were analysed continuously on a weekly basis.

3.5 Leaching experiment

The second phase of the study involved the preparation of leachate solutions; ASTM (100ml), TCLP (40ml), SPLP (40ml). 10g of bullet fragments, which could be about 2 to 3 fragments were added to each leachate solution. Replicate samples were prepared to extend to 24 weeks for each sample types. 24 samples were prepared for corroded bullets in each leachate solution, and also 24 samples for less-corroded bullets in each leachate solution. Altogether, there were 144 samples for the leachate study. One of each sample type was then retrieved after a week, digested using HNO_3 (1:1 v/v), and the digest was taken for Pb analysis using FLAME ATOMIC ABSORPTION SPECTROPHOTOMETER (FAAS). Subsequent samples were analysed continuously on a weekly basis. The leachate solutions were:

1. The American Society for Testing and Materials (ASTM)
2. The United States Environmental Protection Agency's Synthetic Precipitation Leaching Procedure (SPLP)
3. The United States Environmental Protection Agency's Toxic Characteristic Leaching Procedure (TCLP)

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3.5.1 ASTM Test

The test involves the use of reagent water as the leachate solution. This was done by weighing about ten grams (10g) of the bullet into a sample container, and adding hundred millilitres (100ml) of distilled water, to make the final bullet-to-leachate ratio of 1:10. This was done both for corroded and less corroded bullets.

3.5.2 TCLP Test

This test involved the preparation of a leachate solution, using Acetic acid, buffered with 1.0M NaOH. To this effect, 11.4ml of the Concentrated Acetic Acid (17.4M) was added to about 1000ml of distilled water to make a final concentration of 0.19836M. A solution of 1.0M NaOH was also prepared and used to buffer the solution of the acetic acid till a pH of 4.93 was reached. This was then made up to mark of 1000ml. A known weight of about ten grams (10g) of the bullets was weighed into a sample container and forty-millilitres (40ml) of the leachate solution was added to make the final bullet-to-leachate ratio 1:4. This was done both for corroded and less corroded bullets, making up 24 samples each for both corroded and less corroded bullets.

3.5.3 SPLP Test

This test involves the preparation of a buffer solution of sulphuric and nitric acid in ratio of 60/40 (v/v). The solution was prepared by measuring 2ml of nitric acid and adding it to 3ml of sulphuric acid. This was then diluted into about 2500ml to make a final concentration of 0.0216M for sulphuric acid and 0.01248M of nitric acid. The solution was then diluted with distilled water till a pH of about 4.22 was reached, and then made to mark. About ten grams of bullets was weighed into forty millilitres (40ml) of the leachate solution and these was done for twenty-four samples of corroded bullets and another twenty-four samples of less corroded bullets. All the leachate solutions were left to stand for a week before analyses commenced and this was subsequently carried out every seven days for twenty-four weeks.

3.6 Pb analysis in soil

After the first week, the first samples of each set was collected, and a total of nine (9) samples were collected which included;

- Six soil samples;
- Three soil blank samples, for both the soil

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The soil samples were homogenised and about 2.0g of the soil was taken as wet weight. This was then digested with 20ml of Nitric acid solution, prepared from Nitric acid and distilled water (1:1 v/v). The solution was then boiled over a hot plate for three hours. The resultant solution was then filtered and transferred into a 50ml standard flask which was then made up to mark with distilled water. Afterwards, 1ml of the solution was then taken and diluted in another 100ml standard flask to make a final dilution ratio of 1:100. These were then taken for analyses using the FLAME ATOMIC ABSORPTION SPECROPHOTOMETER (FAAS).

Formula for calculating % contamination

$$\textbf{\% contamination} = \left(\frac{\textit{weight of bullet}}{\textit{weight of soil}} \times \frac{\textit{metal concentration in sample}}{\textit{Initial soil concentration}}\right) \times \mathbf{100}$$

3.7 Analysis of Pb in leachate solution

For the leachate solutions, the solution was homogenised by shaking the container, transferred into a beaker, and digested with 5ml concentrated Nitric acid, till a clear solution was obtained. This was then filtered and made up to mark in a 100ml standard flask. One millilitre (1ml) of the solution was then taken and diluted with distilled water to make up to a 100ml mark. For the SPLP and TCLP solution, they were collected and digested using concentrated nitric acid. The resultant solution was digested and made up to 100ml mark. A mil of the solution was then diluted to 100ml, making a dilution ratio of 1:100. These were then taken for analyses using the FLAME ATOMIC ABSORPTION SPECROPHOTOMETER (FAAS).

3.8 Preliminary studies

Soil analysis was carried out on all the sample soils that were used and the following parameters were determined:

1. Phosphates, Nitrates and Sulphates.
2. Heavy metal speciation
3. Mechanical properties
4. Organic carbon
5. Cation Exchange Capacity
6. Moisture content
7. pH

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All the sequential extractions 1-4 were carried out in a 50ml polypropylene centrifuge tubes. Heavy metal analysis was determined using Flame Atomic Absorption Spectrophometer (FAAS).

3.9 Quality control

1. Analar grade reagents were used for all the analysis.
2. Deionised water was used for all sample and reagent preparations, dilution and blanks.
3. Sample and reagent blanks were prepared and also analysed alongside samples.

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Table 3.1 Initial metal concentration in soil

Blank	Pb concentration (mg/kg)	Cu concentration (mg/kg)
Loamy soil	432.67±38.7	2.92±0.37
Sandy soil	299.50±34.65	7.41±8.01
Clay soil	386±52.33	7.48±0.20

Soil weight: 5g

Table 3.2 Initial metal concentration of leachate solution

Leachate solution	Volume (ml)	pH	Pb concentration (mg/L)	Cu concentration (mg/L)
TCLP	40	4.93	1.02	0.007
SPLP	40	4.22	1.07	0.004
ASTM	100	7.00	1.00	0.007

Table 3.3 Initial metal concentration in bullets

Nature of Bullet	Total weight (g) of bullet	Used weight (g) of bullet	Pb concentration (mg/kg)	Cu concentration (mg/kg)	% composition
Corroded	7.6786	0.1388	547,235.0	497.12	1.81
Less-corroded	8.8603	0.4918	390,400.0	3678.3	5.55

Table 3.4 Metal concentration of blank used for weekly analysis

Blank	Time Interval (weeks)	Pb concentration (mg/L)	Cu concentration (mg/L)
H_2O	1	0.010	0.007
	2	0.011	0.005
	3	0.012	0.005
	4	0.007	0.034
	5	0.006	0.002
	6	0.007	0.003
	7	0.013	0.000
	8	0.014	0.000
	9	0.002	0.000
	10	0.002	0.060
	11	0.007	0.007
	12	0.007	0.007

Volume of Water 100ml

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CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results

Table 4.1 Physicochemical properties of soil

Parameters	Loamy soil	Clay soil	Sandy soil
pH	4.7	5.8	4.7
Organic carbon (%)	11.07	3.09	1.80
Moisture content (%)	2.5	6.3	1.4
Phosphate (mg/g)	10.66	10.42	10.32
Sulphate (mg/kg)	82.0	256.0	140.0
Nitrate (µg/g)	48.62	50.60	46.50

Table 4.2 Speciation study of Pb in soil

Fractions	Loamy soil (% Geochemical Phases)	Clay soil (% Geochemical Phases)	Sandy soil (% Geochemical phases)
Exchangeable metals	27.62	7.75	10.64
Bound to carbonate	2.32	2.75	7.09
Bound to Fe-Mn oxide	0.87	4.25	7.09
Bound to organic matter	6.98	64.25	63.12
Residual metals	62.21	21.00	12.06

Soil weight 5g
Total Pb concentrations; Loamy - 6880±2.404 mg/kg, Sandy - 2820±3.055 mg/kg, Clay – 16,000±1.404 mg/kg

Table 4.3 Speciation study of Cu in soil

Fraction	Loamy soil (% Geochemical Phases)	Clay soil (% Geochemical Phases)	Sandy soil (% Geochemical Phases)
Exchangeable metal	0.00	0.00	0.00
Bound to carbonate	3.32	0.83	9.76
Bound to Fe-Mn oxide	4.37	10.01	24.07
Bound to organic matter	28.51	44.58	23.23
Residual metals	63.80	44.58	66.16

Soil weight 5g
Total Cu concentrations; Loamy - 13.26±0.887 mg/kg, Sandy – 23.76±1.029 mg/kg, Clay – 16.96±0.492 mg/kg

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4.2 Discussions

All the soil types studied were contaminated with Pb. For the Loamy soil, week 9 had the highest Pb concentration of 4975±0.012 mg/kg using the corroded bullet fragments; while week 10 had the highest Pb concentration of 3650±0.052 mg/kg using the less-corroded bullet fragments (Fig. 4.1). This shows an anomaly in the geometric increase in Pb mobility around the soil with time. This could be attributed to the surface area of the bullet, soil pH, or soil moisture (Nicholas *et. al.*, 2017). However, the highest total Pb concentration of 36,898±0.755 mg/kg was observed using corroded bullet fragments, which was higher than the highest total Pb concentration of 32,100±0.796 mg/kg observed using the less-corroded bullet fragments. This means the corroded bullet fragments were more leached than the less-corroded bullet fragments. Also, week 12 has the lowest Pb concentration of 1850±0.073 mg/kg using the corroded bullet fragments; while week 5 has the lowest Pb concentration of 1425±0.021 mg/kg using the less-corroded bullet fragments (Fig. 4.1). This shows that there is a correlation between the overall concentrations of Pb and the nature of the bullet fragments.

For the Sandy soil, the highest Pb concentration of 4225±0.029 mg/kg using the corroded bullets was observed in week 9; while the highest Pb concentration of 3650±0.019 mg/kg using less-corroded bullets was observed in week 10 (Fig. 4.2). The highest total Pb concentration that was leached from the corroded bullet fragments was 31,900±0.985 mg/kg; while the highest total Pb concentration that was leached from the less-corroded bullet fragments was 28,350±1.145 mg/kg. The lowest Pb concentration of 1350±0.192 mg/kg using the corroded bullet fragments was observed in week 5; while 1475±0.027 mg/kg of Pb concentration was observed in week 5 using less-corroded bullets. The overall concentration of Pb in all the bullet types shows that the corroded bullet fragment was more leached in the sandy soil, than the less corroded bullet fragments. There is a possibility that the Pb could be dispersed farther apart in the soil mixture during homogenisation. This could have affected the decrease in concentration of the aliquot collected from the soil mixture for digestion.

The clay soil also showed a similar trend like the previous soil types. The highest Pb concentration of 3825±0.137 mg/kg was observed in week 9 for the corroded bullet fragment; while the highest Pb concentration of 3575±0.086 mg/kg was observed in week 10 for the less-corroded bullet fragments (Fig. 4.3).

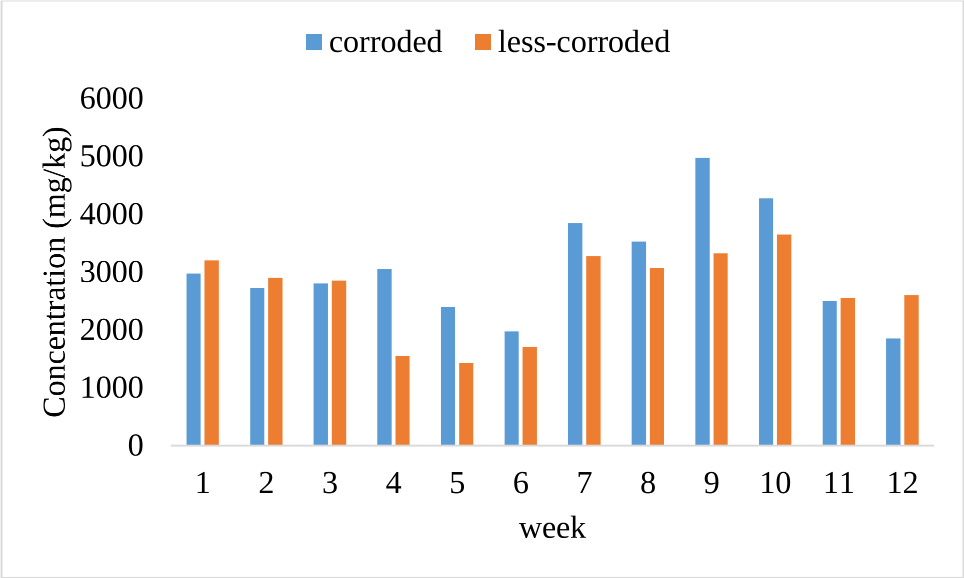

Figure 4.1 Pb mobility in Loamy soil

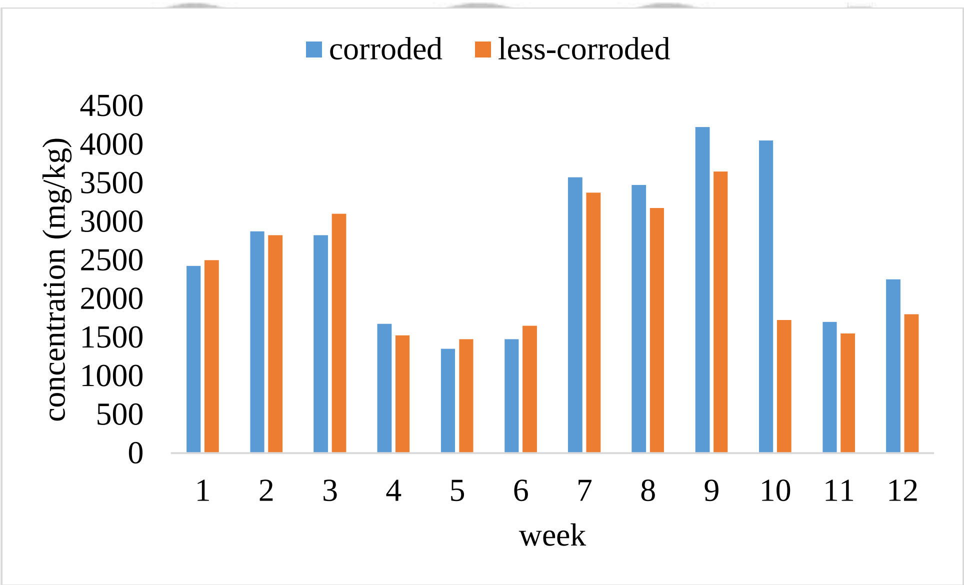

Figure 4.2 Pb mobility in Sandy Soil

The lowest Pb concentration of 1125±0.132 mg/kg (7.8984g) using the corroded bullet fragments was observed in week 5, while week 4 had the lowest Pb concentration by a slight margin of 1325±0.037 mg/kg below week 5, using the corroded bullet fragments. The proximity of the Pb concentration between week 4 and week 5 (1350±0.189 mg/kg; 8.5009g) shows that there is no correlation between the weight of the spent bullet fragments and its leachability. The total Pb concentration for Clay soil was highest using corroded bullet fragments (30,875±1.104 mg/kg) compared to the use of less-corroded bullet fragments (30,450±1.109 mg/kg). The overall Pb mobility for corroded bullets in the three types of soil; Loamy- 36,898±0.755 mg/kg; Sandy – 31,900±0.985 mg/kg; Clay – 30,875±1.104 mg/kg; shows that Loamy soil was the most contaminated (Fig. 4.4). This could be attributed to the nature of the soil, the organic matter bound (from the speciation study), and the form in which the Pb exists in the soil (Cerrusite, Hydrocerrusite or massicot).

The leachate solutions appeared to have leached the spent bullet fragments. The mobility of Pb in the soil due to acid rain was simulated using the SPLP method. Also, TCLP and ASTM methods were used. The TCLP leachate solution had the highest Pb concentration at 4213±0.747 mg/kg, followed by SPLP at 2656±1.062 mg/kg, and ASTM at 1152±0.944 mg/kg. the lowest TCLP concentration was recorded at 3455±1.146 mg/kg which is still higher than the highest concentration of SPLP and ASTM. There were outliers in week 8 for SPLP and weeks 9 and 10 for TCLP, due to outrageous concentration values. The SPLP and ASTM solutions appeared to have higher Pb concentration for less corroded bullets.

Speciation study is commonly used to ascertain the chemical mobility, availability, leaching and distribution of metals in the soil (Fayiga, *et. al.*, 2011). The partitioning of Pb in the different fractions is largely dependent on the chemistry and geochemistry of the soil. The availability of the exchangeable Pb fraction and carbonate bound fractions, shows that the Pb contamination is of environmental significance. The Pb availability in carbonate form (Cerrusite and Hydrocerrusite) could easily undergo uptake by crops and could be introduced into surface water, groundwater and even atmosphere (massicot). The loamy soil had the highest Pb concentration for exchangeable at 1900±0.112 mg/kg, while the carbonate had the highest Pb concentration for the carbonate bound at 440±0.742 mg/kg.

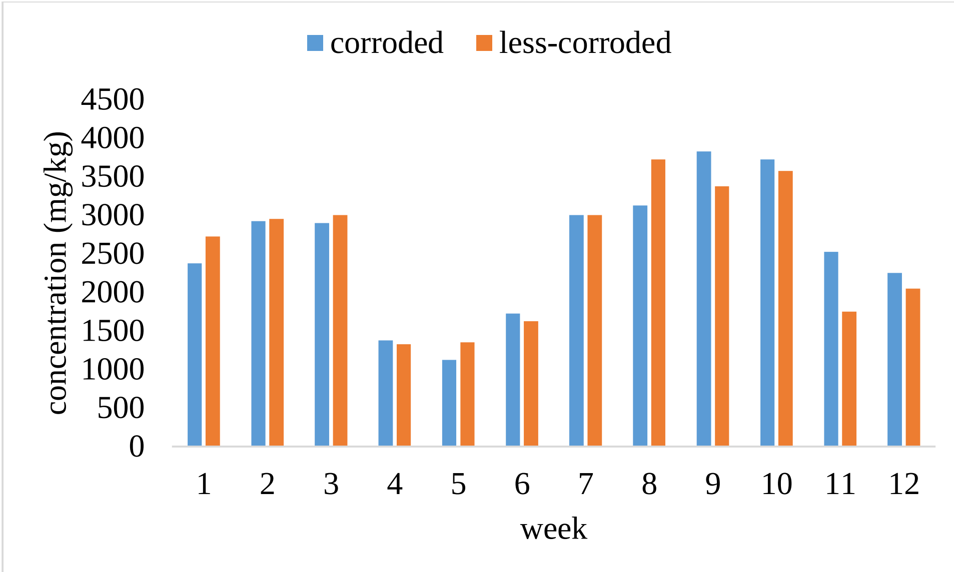

Fig. 4.3 Pb mobility in Clay Soil

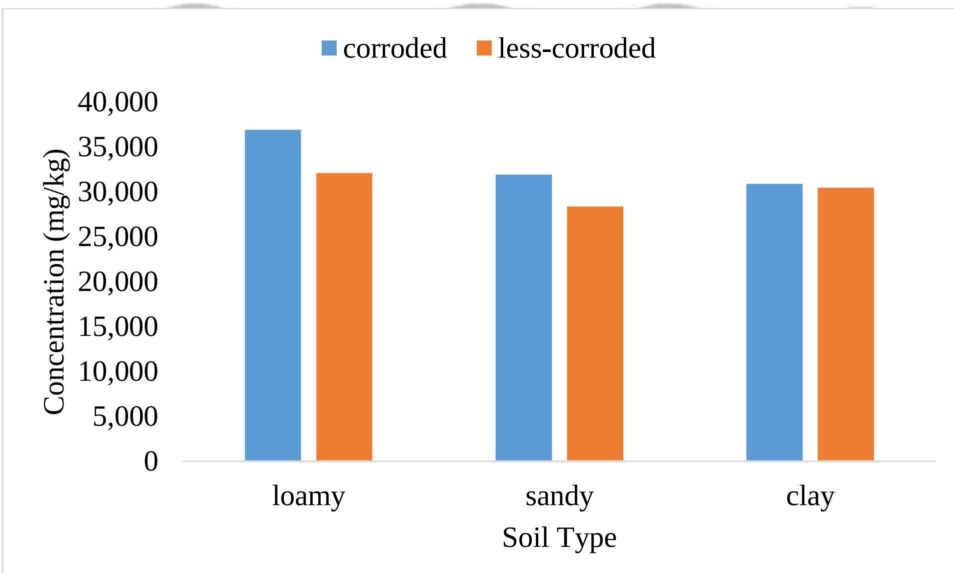

Figure 4.4 Total Pb mobility in three soil types

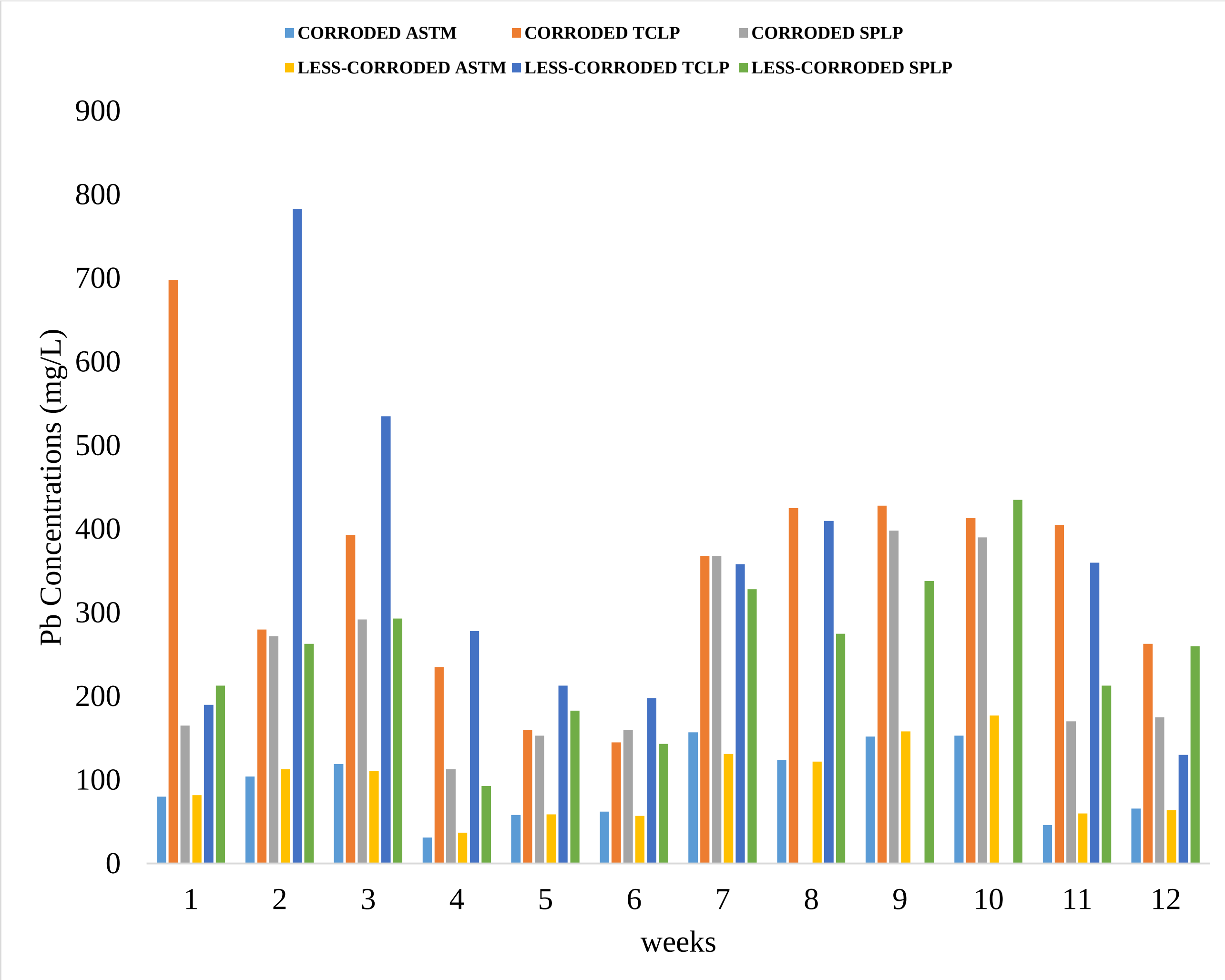

Figure 4.5 Pb mobility in leachate solutions

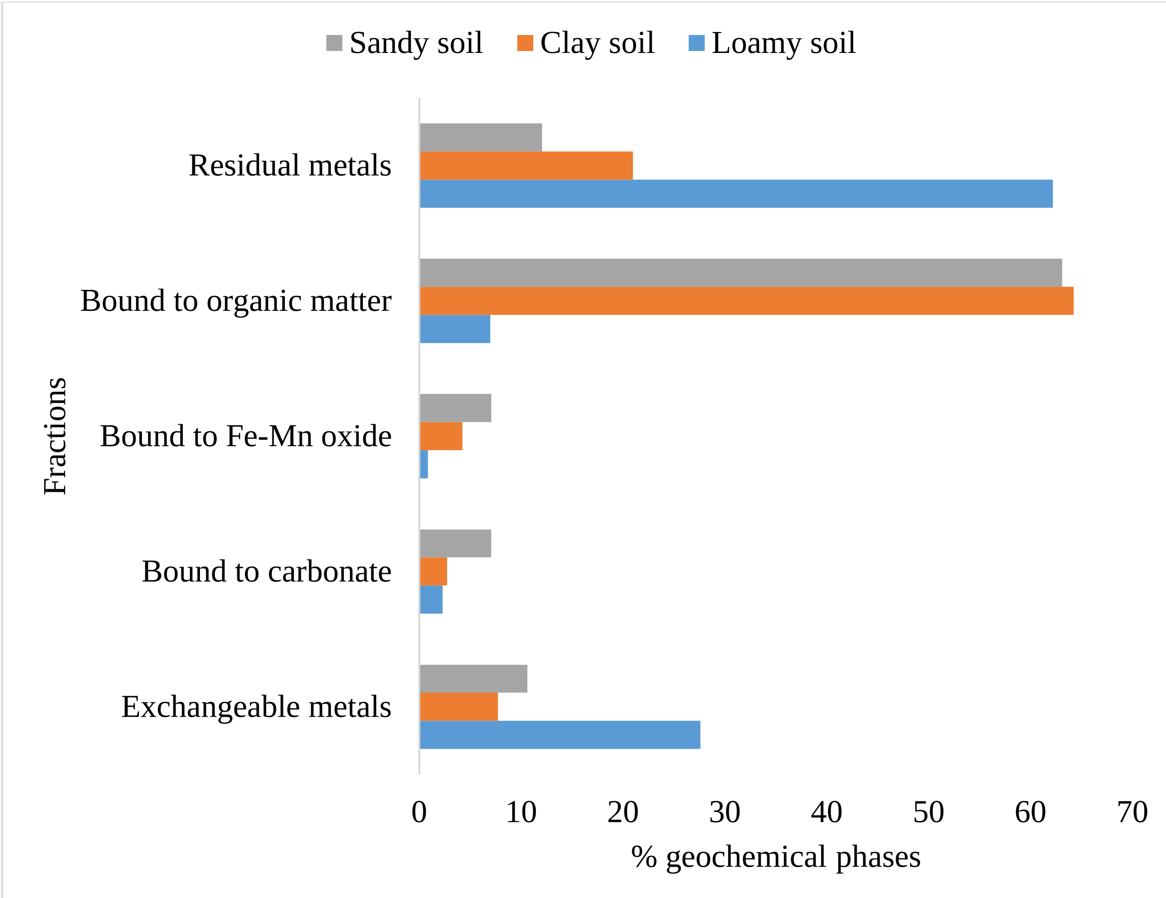

Figure 4.6 Speciation Study of three soil types; Loamy, sandy and Clay

Metallic Pb is unstable under typical soil conditions (Cao, 2003). It could be clearly stated from the study that bullet fragments in soil, especially around shooting range, are rapidly transformed into lead compounds which may be found as surface coatings on the pellets or in the surrounding soil. This transformation is accelerated when the pellets are mixed with the upper soil layers by ploughing and other agricultural treatment. In an acidic sandy soil, the transformation products are soluble and may be mobile in the soil. In soils with a high pH and/or a high content of organic matter such has loamy soil, the transformation products are only sparingly soluble and may stick to the pellet surface or remain in the upper soil layers. The following processes are important for the transformation of metallic lead into lead compounds in soil and, eventually, for the dissolved lead to enter drainage and groundwater: oxidation of Pb to Pb^{2+}; precipitation of sparingly soluble lead compounds such as carbonates, sulphate, and phosphates; and retention of lead by soil components. In soils that do not contain free strong acids or bases, which is seldom the case, the oxidation of lead may be written as:

Oxidation of Pb to Massicot,

$$PbO;\ Pb + O_2 + H_2O \rightarrow PbO + 2OH-$$

Formation of cerussite,

$$PbCO_3;\ PbO + HCO^-_3 \rightarrow PbCO_3 + OH^-$$

Formation of hydrocerussite,

$$Pb_3(CO3)_2(OH)_2;\ 3PbCO_3 + 2H_2O \rightarrow Pb3(CO3)_2(OH)_2 + H_2CO_3$$

Dissolution of cerussite,

$$PbCO_3 + 2H^+ \rightarrow Pb^{2+} + H_2O + CO_2$$

Dissolution of hydrocerussite,

$$Pb_3(CO3)_2(OH)_2 + 6H^+ \rightarrow 3Pb^{2+} + 4H_2O + 2CO_2$$

According to the Environmental Science Department of the University of Illinois, the natural occurrence of Pb in soil is between a concentration of 10-50 mg/kg. The New Jersey Administrative code remediation Standards has established the ingestion-dermal health based criterion for lead consumption at 800 mg/kg; the inhalation health based criterion at 12,000 mg/kg; the soil PQL at 1 mg/kg and the Non-residential direct contact soil remediation standard at 800 mg/kg. Corrosion of the metallic lead continues until a more stable corrosion product, like hydrocerussite, coats the surface, in effect passivating the shot and reducing the corrosion rate (Black and Allen 1999; Graedel 1994).

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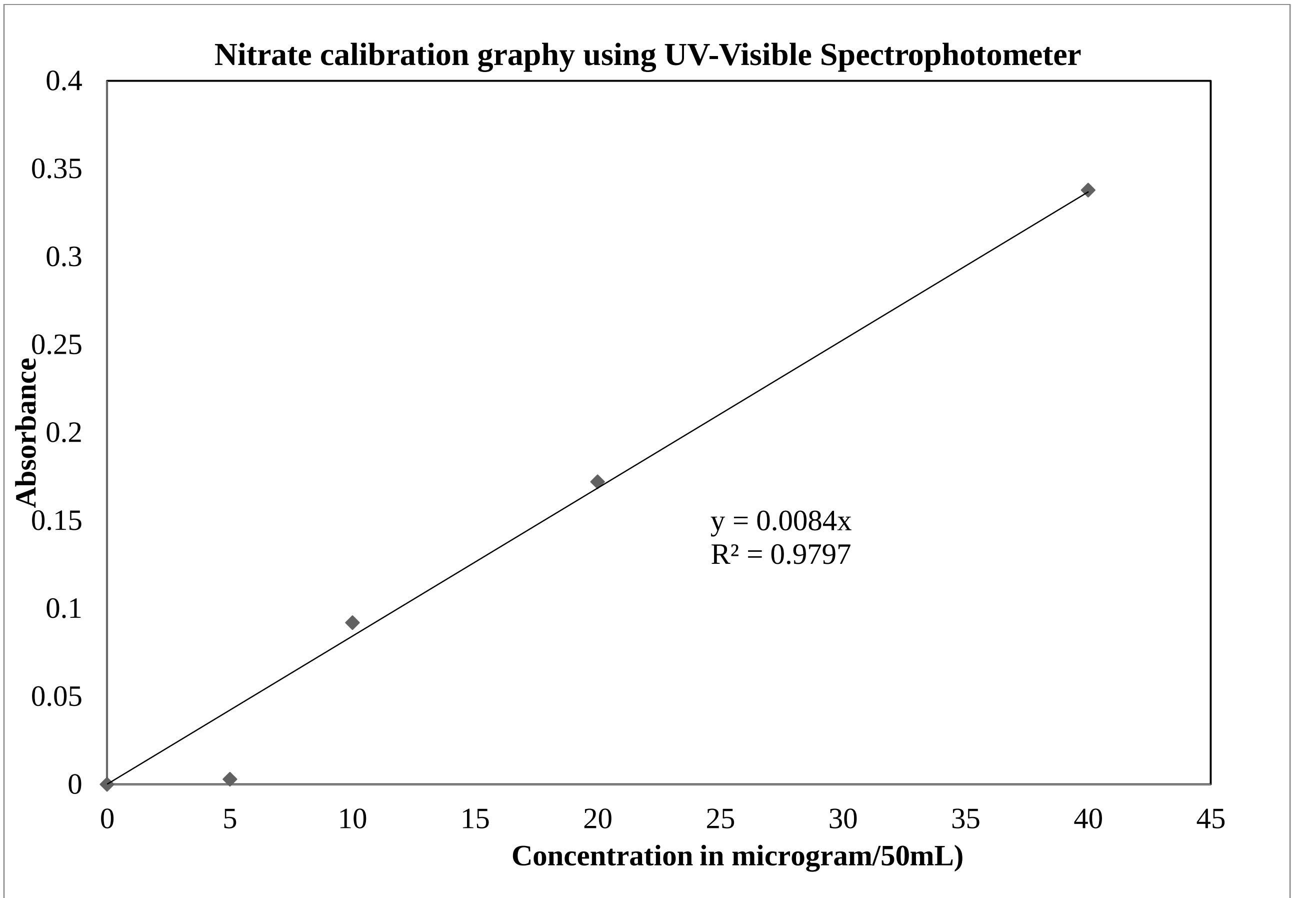
APPENDIX



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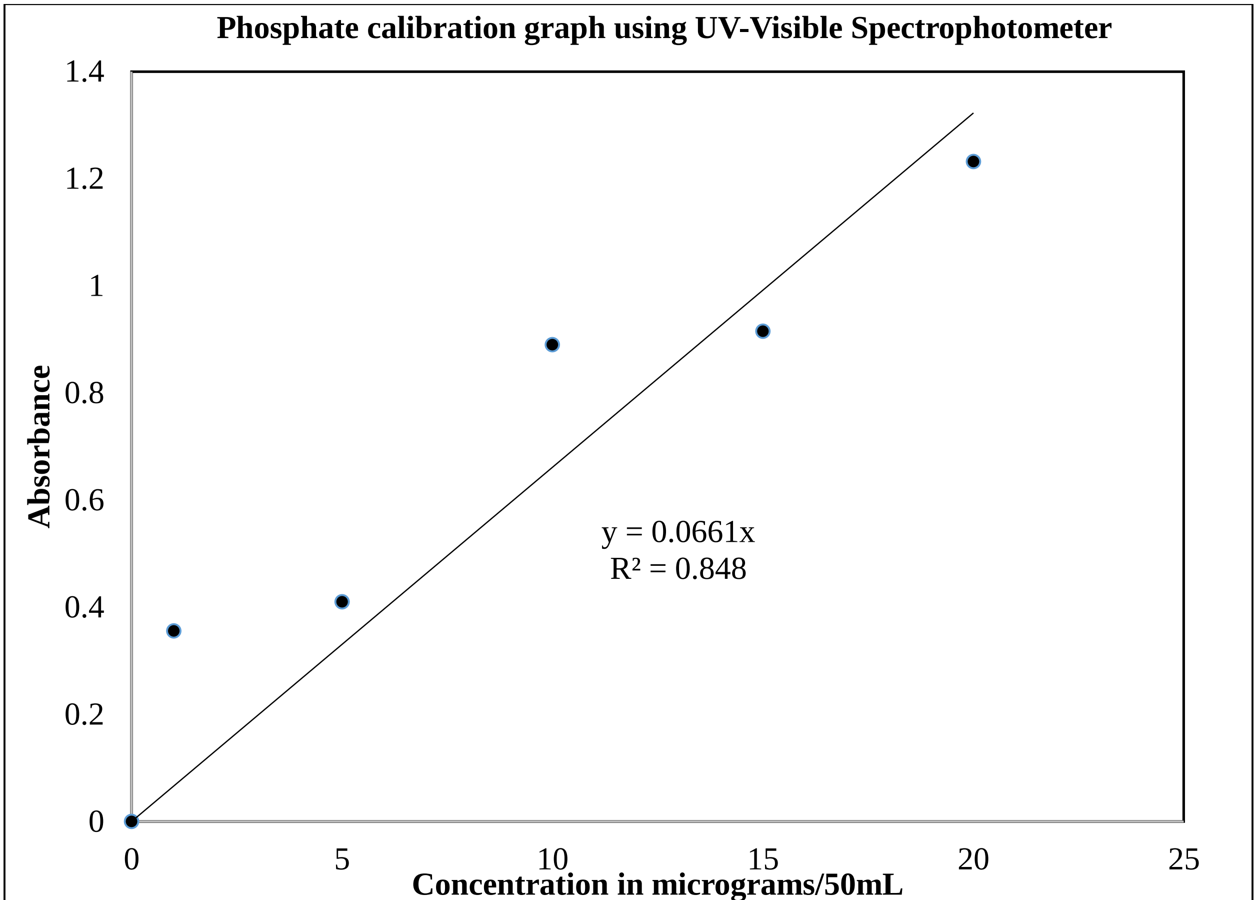
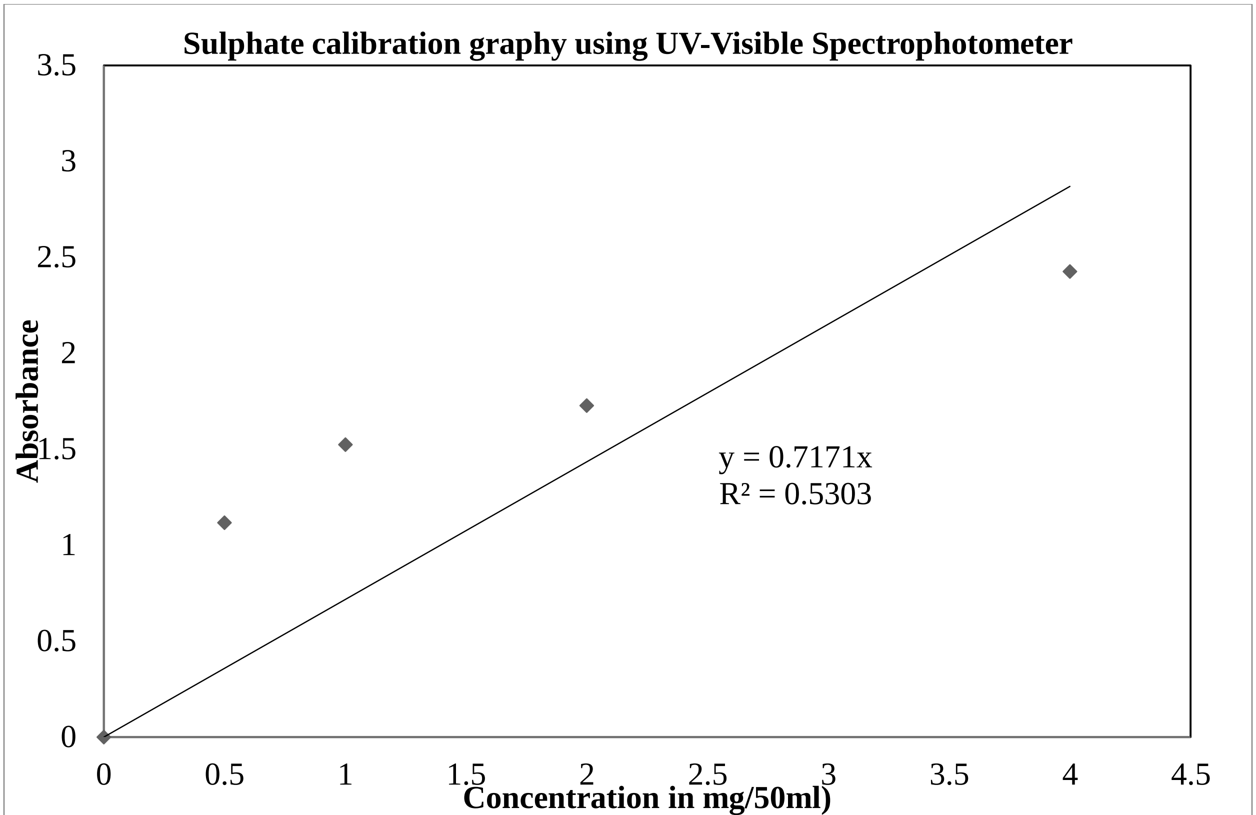

Phosphate calibration graph using UV-Visible Spectrophotometer
Absorbance
1.4
1.2
1
0.8
0.6
0.4
0.2
0
y = 0.0661x
R² = 0.848
0
5
10
15
20
25
Concentration in micrograms/50mL


Sulphate calibration graphy using UV-Visible Spectrophotometer
Absorbance
3.5
3
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
Concentration in mg/50ml)
y = 0.7171x
R² = 0.5303

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MOISTURE CONTENT

Crucible	Initial weight (g)	1st weight (g)	2nd weight (g)	Final weight (g)	Samples	Crucible + sample weight (g)	Sample weight (g)	Dry weight of Crucible + Sample (g)	Moisture content	% moisture content
1	55.9922	55.9875	55.9846	55.9846	Clay	106.0242	50.0396	102.8818	3.1424	6.3
2	76.2451	76.2449	76.2351	76.2351	Loamy	126.2831	50.0480	125.6134	0.6697	2.5
3	56.2488	56.2475	56.2451	56.2451	Sandy	106.6813	50.0714	105.4362	1.2451	1.4

ORGANIC CARBON

STANDARDIZATION

Burette reading (ml)	Rough (ml)	First (ml)	Second (ml)	Third (ml)
Final	5.90	5.90	5.90	6.00
Initial	0.00	0.00	0.00	0.00
Volume	5.90	5.90	5.90	5.90

Average Titre: 5.93ml

LOAMY

Burette reading (ml)	Rough (ml)	First (ml)	Second (ml)	Third (ml)
Final	13.30	13.90	15.00	14.45
Initial	0.00	0.00	0.00	0.00
Volume	13.30	13.90	15.00	14.45

Average Titre: 14.45ml

SANDY

Burette reading (ml)	Rough (ml)	First (ml)	Second (ml)	Third (ml)
Final	20.10	20.20	20.00	20.10
Initial	0.00	0.00	0.00	0.00
Volume	20.10	20.20	20.00	20.10

Average Titre: 20.10ml

CLAY

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Burette reading (ml)	Rough (ml)	First (ml)	Second (ml)	Third (ml)
Final	18.50	18.70	18.20	18.45
Initial	0.00	0.00	0.00	0.00
Volume	18.50	18.70	18.20	18.45

Average Titre: 18.45ml

BLANK

Burette reading (ml)	Rough (ml)	First (ml)	Second (ml)	Third (ml)
Final	20.50	20.70	20.20	20.45
Initial	0.00	0.00	0.00	0.00
Volume	20.50	20.70	20.20	20.45

Average Titre: 20.45ml

Mechanical properties

Sample	**Location**	**Organic matter**	**Clay <2 µm**	**Silt 2-20 µm**	**Fine sand 20-200 µm**	**Coarse sand 200-2000 µm**
Loamy	Botanical Garden U.I.	3.1	9.7	11.3	71.7	4.2
Sandy	Akobo	1.4	3.6	11.0	60.3	23.7
Clay	PG Hall U.I.	2.3	10.3	10.9	63.3	13.2

Speciation study of Pb in soil

Fractions	Loamy soil (mg/kg)	Clay soil (mg/kg)	Sandy soil (mg/kg)
Exchangeable metals	1900±0.112	1240±0.284	300±0.51
Bound to carbonate	160±1.000	440±0.742	200±1.00
Bound to Fe-Mn oxide	60±1.000	680±0.278	200±1.00
Bound to organic matter	480±0.268	10280±0.042	1780±0.06
Residual metals	4280±0.024	3360±0.058	340±0.485

Soil weight 5g

Speciation study of Cu in soil

Fraction	Loamy soil (mg/kg)	Clay soil (mg/kg)	Sandy soil (mg/kg)

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Exchangeable metal	0.00±0.757	0.00±0.05	0.00±1.0
Bound to carbonate	0.44±0.097	0.14±0.424	2.32±0.005
Bound to Fe-Mn oxide	0.58±0.007	1.7±0.005	5.72±0.016
Bound to organic matter	3.78±0.018	7.56±0.005	5.52±0.006
Residual metals	8.46±0.008	7.56±0.008	15.72±0.002

Soil weight 5g

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