

CHEMICAL TRANSFORMATION AND FATE OF LEAD IN SHOOTING RANGE SOILS FOUND IN EASTERN AND NORTHERN BOTSWANA

By

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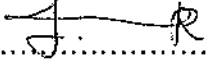
A thesis presented to the graduate school of the Botswana International University of Science and Technology in partial fulfilment of the requirements for the Degree of Master of Science

BIUST

September 2017

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CERTIFICATION

The undersigned certifies that he has read and hereby recommends for acceptance by the College of Science a dissertation/thesis titled: '**Chemical Transformation and Fate of Lead in Shooting Range Soils Found in Eastern and Northern Botswana**' in fulfilment of the requirements for the degree of Master of Science in Analytical Chemistry of the BIUST.



Dr. Pogisego Dinake
(Supervisor)

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Special thanks to my hubby and daughter for putting up with me and my crazy schedules. You two are my rock.... ♥

Last but not least I will forever be grateful to BIUST for the sponsorship of this project.

DEDICATION

This work is dedicated to my great grandmother, **Kukuwe 'Hams' Bosepetseng**. You will forever be treasured Mosele!!

“Is there
anything
more wonderful
than a grandmother's
love for
her grandchildren?
It's just pure
love, nothing
but pure
love.”

Warmly, Susan
Tuesday - Oct. 16, 2012(10:20 pm)

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ACRONYMS

BOBS: Botswana Bureau of Standards

BMP: Best Management Practices

CEC: Cation Exchange Capacity

ICP-OES: Inductively Coupled Plasma- Optical Emission Spectrometer

MAT R1: Matsiloje Rifle Range 1

MAT R2: Matsiloje Rifle Range 2

MCL: Maximum Contaminant Limit

OC: Organic Carbon

OM: Organic Matter

P/LEBO: Pandamatenga Lebolobolo Rifle Range

P/TSHU: Pandamatenga Tshukudu Rifle Range

S/PIST: Selibe Phikwe Pistol Range

SE: Sequential Extraction

SEM: Scanning Electron Microscope

SP R1: Selibe Phikwe Rifle Range 1

SP R2: Selibe Phikwe Rifle Range 2

SPLP: Synthetic Precipitation Leaching Procedure

USEPA: United States Environmental Protection Agency

WHO: World Health Organization

XRD: X-Ray Diffraction

ABSTRACT

Ammunition used for military training and exercises has been found to contain high content of lead (Pb). The Pb present in the ammunition projectiles undergoes an array of transformation and weathering reactions when it reaches the shooting range soils. Seven military shooting ranges in the eastern and northern Botswana were used for this study. Soil samples were collected at each of the seven shooting ranges at the berm (stop butt), target line, 50 and 100 m from the berm. Pb concentrations were determined using ICP-OES and in all of the shooting ranges investigated, the highest concentrations were found in the berm soils. The weathering products of the Pb bullets and shots at all the seven shooting ranges studied were predominantly carbonates: specifically, cerussite (PbCO_3) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$). The XRD results agreed well with the fractionation studies which showed that the carbonate bound Pb was the most predominant in all the seven shooting ranges investigated. The presence of high concentrations of carbonate bound Pb culminated in high concentrations of Pb in the shooting range soils due to dissolution of carbonate Pb at lower pH ranges. MAT R2 berm soils accumulated the highest concentrations of total Pb of up to 20882 ± 5419 mg/kg. In all the shooting ranges studied, total Pb concentrations far exceeded the United States Environmental Protection Agency (USEPA) critical level of 400 mg/kg. All the seven shooting ranges studied also failed the Synthetic Precipitation Leaching Procedure (SPLP) with SPLP-Pb concentrations exceeding the USEPA 0.015 mg/kg critical level of hazardous waste, posing a pollution threat to surface and groundwater. Mobility of Pb in the berm soils in all the shooting ranges was found to be over 90% implying high Pb lability. The bioavailability index of Pb was found to be in the range 60-90%, an indication that most of the Pb was available for plant uptake in all the shooting ranges studied.

CHAPTER 1

INTRODUCTION

Lead is a naturally occurring, corrosion resistant, malleable, ductile and easy to process soft metal. It accounts for 15-20 mg/kg of the Earth's crust ¹. Its most important ores/minerals are galena (PbS), cerussite (PbCO₃) and anglesite (PbSO₄) ^{1,2}.

Lead has been known to man since 4000 BC; The Egyptians, Hebrews and Romans were some of the early users of lead in pottery glazing, water pipes and cooking utensils manufacture ³. It was also used in Mexican folk remedies azarcon and greta for colic treatment while some Middle Eastern communities used it in cosmetics ⁴.

1.1 Physical and Chemical Properties of Lead

Elemental lead (Pb) is an ubiquitous bluish or silvery-grey soft metal, with atomic number 82, atomic weight 207.19, a specific gravity of 11.34, a melting point of 327.5 °C and a boiling point at atmospheric pressure of 1740 °C. It has four naturally occurring isotopes with atomic weights 208, 206, 207 and 204 (in decreasing order of abundance). Lead exists in four valence states (0, +1, +2 and +4). Even though lead has four electrons on its valence shell, its chemistry in the environment is dominated by the plumbous ion Pb²⁺ rather than Pb⁴⁺, since only two of the four electrons ionize easily ⁵.

Owing to its numerous exceptional properties, lead is still being used today in a wide range of applications ⁶; thereby increasing its concentration in our environment over time. Current uses of lead include cable sheathing, pigments, chemicals, storage batteries, petrol, alloys and ammunition worldwide ^{2,5,7}.

All these lead industries lead to exposure of humans and the environment at large to high amounts of lead in these lead smelting plants, battery manufacturing plants, firing ranges, construction sites etc. This exposure poses a serious risk to the health and general wellbeing of people and animals.

1.2 Health, Biological and Physical Effects of Lead

However useful in our daily lives; lead is an element of particular environmental concern because of its toxicity to all living things. It has been described as a known toxin with cumulative properties, that impairs the renal, hematopoietic and nervous systems ^{1,5,8,9}. Human exposure to lead is brought about by a number of factors such as inhalation of the contaminated soil dust, ingestion and skin adsorption. Children have the highest risk of exposure due to their countless hand to mouth activities of putting hands, toys, and other non-food items in their mouths. In children, concentrations as little as 10 µg/dL lead to damage to the brain and nervous systems, slowed growth, behavioural and learning problems, impairment of vision and motor skills whilst adults experience high blood pressure, neurological disorders, kidney dysfunctions and reproductive health problems such as low birth weight, birth defects and decreased fertility as a result of exposure to lead ¹⁰. Figure 1 below summarises the health effects of lead in children and adults.

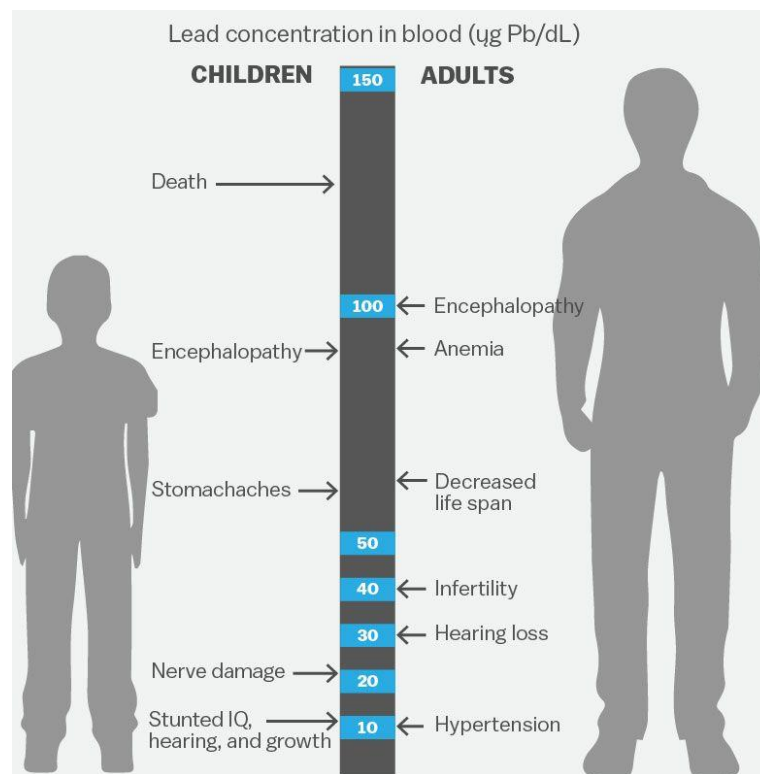


Figure 1: Health effects of Lead exposure ¹¹

1.2.1 Lead pollution in other species

Lead contamination is not only limited to human beings but affects wild birds and animals also. The effects of lead from ammunition have primarily been studied in birds. Birds are exposed to lead via direct ingestion of spent gunshot as they mistake it for food while predators and scavengers are exposed to fragments of lead, in the flesh of their prey. Numerous studies carried out in the UK and other areas over the last 65 years show that lead poisoning from ammunition sources is geographically widespread and causes substantial suffering and mortality in many avian taxa ¹²

Other species such as plants and fungi also absorb lead from soil, a study carried out through a 2-year incubation of sporocarps in growth bags at a shooting range show some variability in the Pb load ¹³. And since animals feed on plants and human beings in turn feed on both plants and animals; there are increased chances for the lead to move higher in the food chain ¹⁴ posing serious health threats to life.

In attempts to reduce these detrimental effects of lead, some of its uses in gasoline, paint, solder and many other lead-containing products have been banned ¹⁰. Limits for allowable amounts in water and soils have been put in place as shown in table below

Table 1: Allowable limits of lead in soil and water

Organization	Soil Limits	Water Limits
Botswana Bureau of Standards as noted in BOS32:2005 ¹⁵		10 µg/L
United States Environmental Protection Agency (USEPA) ¹⁶⁻¹⁸	400 mg/kg	15 µg/L
World Health Organization (WHO) ¹⁹		10 µg/L

It is therefore imperative to continue to diligently monitor anthropogenic activities that increase the concentrations of lead in the environment. One such activity is the use of firearms by police and military personnel as well as recreational shooters. An average lead shot contains lead (97%), antimony (2%), arsenic (0.5%), and sometimes nickel (0.5%) whilst lead bullets are composed of lead (90-99%), antimony (1-10.5%), and copper (0.1%) ²⁰

Figures 2 and 3 below depict the structure and composition of bullets that end up in the soils at the firing ranges.



Figure 2: Structure of a Bullet ²¹

Projectiles

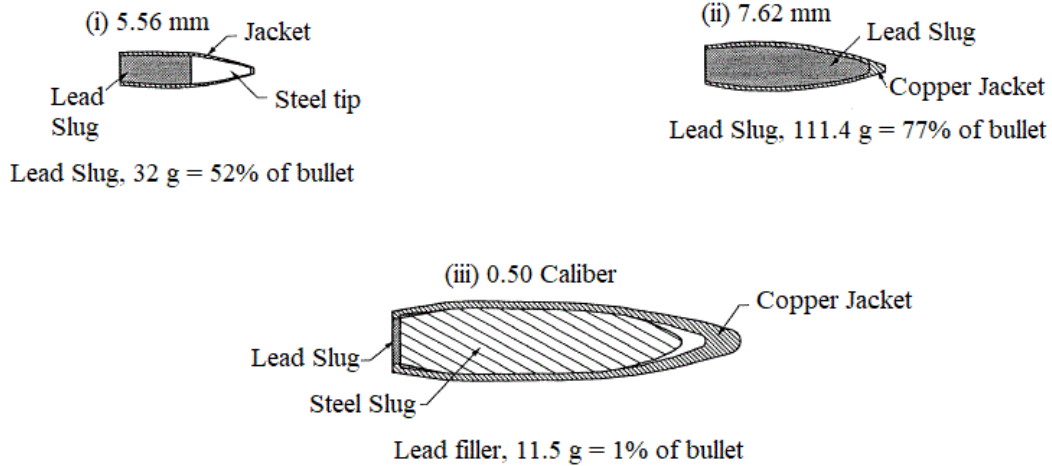


Figure 3: Lead Bullets Projectile Composition ²²

Since these shooting activities concentrate spent and intact lead bullets onto very small pieces of land, they are a source for Pb contamination in many soils worldwide making shooting ranges areas of interest where issues of environmental lead pollution are concerned ²³.

Below is a diagram of the layout of a shooting range where most of the shooting takes place during target practice and training in marksmanship by the shooters. A shooting range is an enclosed area designated for various shooting exercises ^{8,24}.

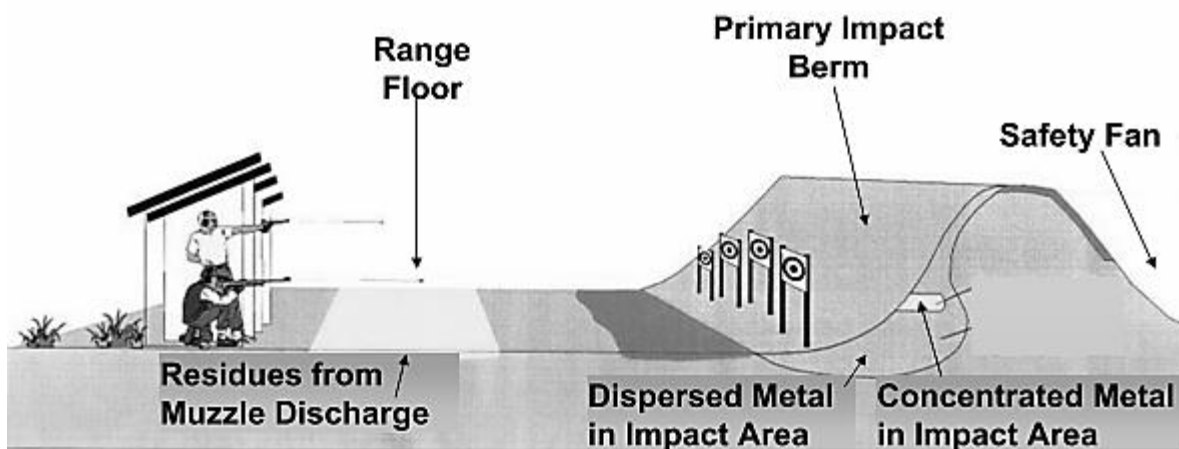


Figure 4: Shooting range layout ²⁵

Shooting ranges are structured in such a way that shooters stand on one side and shoot at targets on the other side of the range. The berm as shown in Figure 4 above, serves as a wall that traps the fired bullets to prevent them from going any further. Over time, the berm becomes an area of high concentration of lead as it lies just behind the target line. The lead is found as spent bullets, shattered fragments, small particles, and lead smears on larger sand grains ²⁶ in the soil.

Therefore, like many other countries with shooting ranges, Botswana needs to face the issue of lead pollution in shooting range soils and come up with ways to manage it. Remediation techniques such as phosphate addition ²⁷⁻²⁹ have been praised by many researchers as it forms an insoluble compound; pyromorphite, thereby immobilising the lead in the soil. Other techniques employed include building sand/steel traps, liming of the soil, hand raking/sifting and soil washing ¹⁰.

Botswana presents an unparalleled setting for this kind of study as ever since the inception of the Botswana Defence Force (BDF) in 1977 and its shooting ranges more than 30 years ago, no such effort has been made to quantify the extent of pollution from the lead found in ammunition as well as the mobility, transformation and bioavailability of lead after deposition into our environment.

This study is therefore a necessary move in order to aid in policy making and implementation of best management practices for the affected areas going forward.

1.3 Statement of the Problem

Metals used in ammunition manufacture are a concern at firing ranges worldwide. Lead is however a metal of particular concern because of its adverse health effects and the fact that it is the principal component of the projectiles in bullets. Also, depending on the depth of groundwater, climate, soil chemistry, or proximity to surface water at the ranges, lead contamination could reach groundwater or surface waters. If left unmanaged, lead contamination could pose serious health risks to wildlife or people who are exposed to affected areas.

1.4 Objectives of this study:

1. To determine extent of lead pollution by quantifying the total concentrations of lead in seven (7) shooting ranges found in Northern Botswana.
2. To identify the major lead weathering products in these range soils
3. To investigate the factors that contribute to the weathering and migration of lead in the range soils
4. To give feedback to stakeholders, in particular, the government of the Republic of Botswana, to assist in policy formulation, suggest best management practices for shooting ranges operators/employees, visitors and area inhabitants

CHAPTER 2

BACKGROUND

2.1 Lead in Shooting Ranges

Lead pollution at shooting ranges is a worldwide concern. Accumulation of lead from bullets occurring at shooting ranges depends on the rate of use, type of ammunition used and the age of the shooting range. United States Environmental Protection Agency; USEPA estimates that about 72 600 metric tons of lead shot and bullets are deposited annually into the environment at outdoor shooting ranges ¹⁰. A number of other researchers in different countries such as the Netherlands, Switzerland, Sweden, Finland, Denmark, Canada and UK, have also reported an annual deposition of metallic Pb ranging between 200 and 6000 tonnes ³⁰⁻³².

Ammunition calibres also differ when it comes to their lead content. For example, a 7.62 mm calibre is made up of 77% Pb and a 5.56 mm up to 52% Pb. Coupled with the high velocities and pressures the bullet exits the gun muzzle with, means that those containing larger lead percentages will cause large surface areas of exposure of the soils to the lead ³³.

Table 2: Chamber pressure values for modern ammunition ³⁴

Cartridge	Velocity (ft/s)	Bullet weight (g)	Pressure (psi)
0.22'' LR	1200	40	15300
9 mm	1200	125	35500
5.56 mm M16	3250	56	52000

Above is a table illustrating some chamber pressure figures for modern ammunition. As shown, lead bullets used at these firing ranges exit rifles at high velocities, experience some friction and even heating and then undergo fragmentation, smearing and/or pulverization upon impact with the ground, berms or targets ³⁵. All these processes lead to distribution of lead powder, fragments and even whole projectiles in the shooting range soils and weathering of these fragments eventually results in elevated lead contamination of the environment. It has been estimated that one whole pellet would take between 100-300 years to be fully transformed into secondary lead compounds ³⁰. It is therefore important to understand the soil

chemistry and how it affects the weathering of lead in order to better manage or even reduce contamination at these shooting ranges.

2.2. Distribution of lead in Shooting Ranges

2.2.1 General outlay of the shooting ranges

Shooting ranges generally comprise of a backstop or berm soil that lies behind the target line and various firing lines. The target line is where the targets are set up then shooters stand at various distances; 50 m and 100 m away to practice their marksmanship. Below is a diagram showing the described areas and at each of these areas there are various processes that occur that lead to the soil being contaminated with lead from the bullets used.

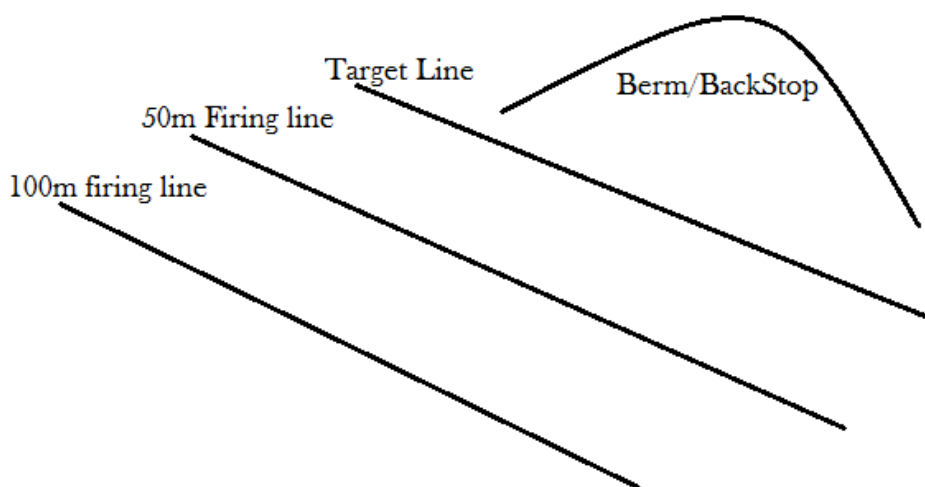


Figure 5: Schematic diagram of a shooting range with firing lines

Lead content of soils at shooting ranges varies both down the soil profile and horizontally within each range as it will be proved by the following researches;

According to previous studies carried out in Florida, USA; lead concentrations have been reported to increase as distance from the firing line increased. The TRR and MPR ranges had the following (as shown in Table 3) lead concentrations as one moved away from the firing line.

Table 3: Lead concentration patterns from the berm soil ³¹

Range	Distance from firing lines (m)	Total Pb (mg/kg)
TRR	1.5	7.3
	31.5	22.6
	61.5	21.7
	91.5	736
	Berm Soil	12710
MPR	1.5	1066
	31.5	562
	61.5	1018
	91.5	2715
	Berm Soil	48400

This study was conducted in 2003 when TRR range was only operational for 3 years and MPR operational for 16 years; this also shows how age of a range affects lead pollution.

As shown, substantial amounts of lead in surface soils closer to the firing line may be caused by fine particulate lead that is generated during weapon discharge especially for older ranges like the MPR range; whilst the berm/backstop contains the highest density of lead in shooting ranges ^{18,31,33,36} as this is where most bullets are deposited and trapped. Soils closer to the berm i.e. at 91.5 m from the firing line also show large amounts of lead pollution.

Concentrations of lead in the soils adhering to the bullets and in the stop-butt area from a shooting range in China were found to exceed the control sample by up to 161 times ³⁷. Elevated lead concentrations ranging between 1025 to 24417 mg/kg were found in the berm soil in a shooting range in USA ³⁸ whilst an Australian berm soil contained 81000 mg/kg and subsurface concentrations were up to 21000 mg/kg ³⁹.

A Finland study at various soil depths in shooting ranges also revealed that the environmental lead contamination is not only confined to pellet shot fall areas as it discovered abnormally high lead levels at some distance outside the clay pigeon ranges that were studied ⁴⁰. In

Nigeria mean concentrations of lead in the berm soil were 5680 ± 2700 mg/kg in a shooting range in Ibadan ⁴¹. Even small arms ranges exhibit high levels of lead pollution; e.g. Some Canadian small arms firing range was found to contain 27100 mg/kg of lead ⁴².

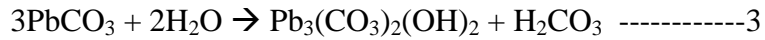
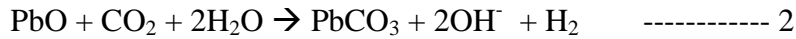
According to Ma *et al* findings, the high total soil Pb, TCLP-Pb and SPLP-Pb concentrations in the shooting ranges raises serious health concerns for the shooters, range workers, their families (as the Pb ridden dust is carried to the shooters' and range workers' homes through their boots and gear). Animals in the vicinity of the ranges could also be affected ⁴³.

All the total Pb concentrations in the surface soils of areas studied were far above USEPA limit of 400 mg/kg ³⁸ meaning that there is far too much lead available for weathering and transformation in the shooting range soils.

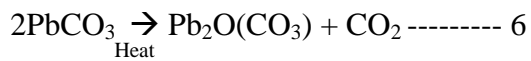
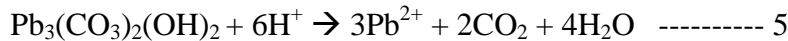
2.2.2 Weathering and transformation of lead in Shooting Ranges

Even though metallic lead is deemed unstable under typical soil conditions, upon deposition into the environment it undergoes weathering ³¹; both physical weathering and chemical weathering and transformation. Physical weathering involves breaking down of new bullets into smaller fragments and even powder. Upon discharge, the bullet undergoes massive heating and experiences high friction whilst exploding from the gun barrel. It also experiences some abrasions on impact with the target or other bullets and upon striking and getting lodged in the berm soil. All these processes lead to the deposition of lead into the soil. To corroborate this, bullets of known mass were fired into boxes of compacted sand which was then passed through a 2 mm sieve immediately after firing and analysed for total lead. The results showed that 41 mg per bullet (1.5% of the bullet mass) was abraded as the bullet passed through the sand ³³.

Chemical weathering involves chemical transformation of metallic lead. Below is a series of reactions that lead to the transformation of lead in the environment as proposed by Chen ¹⁸. A study in China went a step further to suggest that for extremely arid soil conditions like those of Baicheng shooting range in China, cerussite may undergo thermal decomposition after migrating to the surrounding soil due to frequent heating conditions generated by bombs, which may be the explanation for the presence of shannonite in Baicheng soils detected by XRD accounted for by equation 6 below ³⁷.



The products of equation (2) and (3) are easily dissolved by acid rain thereby mobilising Pb^{2+} as shown below:



Fangyan shooting range also in China was found to be semi-arid and so the moisture levels were insufficient to aid the formation of hydrocerussite on the lead layer leaving the cerussite as the main weathering product ³⁷. Weathering products including minerals like cerussite, hydrocerussite, pyromorphite, galena and anglesite have also been reported ⁴⁴. Weathering of lead bullets elevates the amount of lead available to organisms in polluted soils through formation of secondary minerals which are more bio-accessible than metallic lead ²⁹. It also accelerates the release of lead from the soil by converting it into ionic and more mobile species ³¹.

2.2.3 Effect of soil properties on mobility, bioavailability, weathering and transformation of lead in Shooting Ranges

Despite lead being an immobile element in the soil, its migration within shooting range soils and offsite has been reported in literature ^{23,31,44}. Elevated lead concentrations have been found to be uniform up to a depth of 200 mm down the soil profile at shooting range soils in New Zealand and Denmark ^{23,30} and this was after passing the samples through a 2 mm sieve; meaning that the ‘un-weathered’ lead shot was not accounted for. The intact lead shot still poses a threat of further elevation of lead contamination which poses a potential risk for underground water contamination via subsequent downward movement of lead ²³. A number of researches have been conducted to study the structure and make-up of the weathering crust that forms on lead bullet surfaces under various environmental conditions ³⁷. Once these crusts exist in soil they are susceptible to a number of geochemical reactions, which include

oxidation, reduction, precipitation, dissolution, adsorption, desorption and complexation/chelation. Various soil properties have a significant influence on these transformation processes³¹. Therefore soil properties such as pH, organic matter content, Cation exchange capacity (CEC), electrical conductivity and rainfall amounts (moisture) are all important factors which must be studied to determine their effect in metal distributions in surface soils.

2.2.3.1 Effect of pH

Soil pH plays a vital part in lead solubility in shooting range soils^{30,44}. It has been recommended that soil pH at shooting ranges should lie between 6.5 and 8.5, as outside this range the mobility of lead increases¹⁰ this is because low pH affects the mobilisation intensity of heavy metals in soils. Mobility is much higher in acidic than neutral and alkaline soils⁴⁵.

High soil pH's have been associated with soils contaminated with lead shot at a shooting range in Denmark and were ascribed to the corrosion of the Pb bullets⁴⁶. In another investigation, strong positive correlations were found between soil pH and concentrations of total lead, as well as TCLP-Pb at a rifle range in Central Florida, implying that the elevated soil pH could be a result of the soil contaminated with lead bullets¹⁷. Rooney and McLaren, 2007⁴⁷ incubated lead shot for up to 24 months in soils at field moisture capacity content, 25°C and at four different pH levels of 4.9, 5.2, 6.3 and 7.5. They found that crusts developed on all samples but larger ones developed on samples under higher pH's than the others. Minerals such as cerussite, hydrocerussite, thuriosite and galena were contained in all these crusts but cerussites dominated especially at higher pH. These findings were aligned with previous ones that found that at pH 7.4 there was more cerussite than at pH 5.5³⁰

Lead weathering products in shooting ranges have been found to be site specific, for example: only hydrocerussite was detected at the MPR shooting range in Florida with pH 7.36 whereas both hydrocerussite and cerussite were found in the TRR range which had a pH of 5.76. Massicot and cerussite have been found to be stable in soils with high pH, but these may become soluble and more mobile in acidic sandy soils³¹.

High concentrations of lead have been found in shooting range soils with acidic soils by researchers, for example: Elevated lead concentrations were found in slightly acidic (pH

ranging between 6.11-6.72) soils in three Florida shooting ranges. Range G, Range O and Range L had total lead concentrations of 12689 mg/kg, 70350 mg/kg and 10 068 mg/kg respectively ³⁶. In another study on lead transformations and distribution still in Florida, two ranges TRR of soil pH 5.53 and the MPR range of pH 6.73 were found to contain concentrations of lead up to 12710 mg/kg and 48400 mg/kg respectively ³¹.

2.2.3.2 Effect of Organic Matter and Organic Carbon Content

Other factors such as the presence of organic matter also accelerate weathering of metals such as lead in the soil. Since soil organic matter is composed of living organisms, soluble biochemicals (amino acids, proteins, carbohydrates and organic acids) and insoluble humic substances. The bio-chemicals provide sites for metal sorption thus forming water soluble complexes that increase metal mobility ⁴⁸. Organic matter not only increases the soil's cation holding capacity in solid form, but also the lead mobility caused by increased solubilisation of organo-Pb complexes in alkaline pH's ³¹. Acidic forest soils in ranges studied showed that organic matter leads to the accumulation of lead as it acted as a main sink for lead but as the lead concentrations increase due to further weathering of bullets, the organic lead complexes become unstable and the lead is easily leached ⁴⁰.

Since the presence of soil organic matter is required for the transformation of metallic lead to more reactive lead compounds in the soil. Soil with little amounts of organic matter (0.15%) showed no evidence of secondary lead minerals even after 12 days of incubation. These findings suggest that low organic matter levels hinder the transformation of metallic lead to lead oxides and carbonates ²⁹.

Organic carbon also plays a significant role on interactions between metal concentrations and microbial parameters ⁴⁹. A study conducted on five shooting range soils over five years in storage revealed that the total inorganic carbon increased whilst total organic carbon decreased. This suggests a conversion of organic carbon into inorganic carbon. This was confirmed by the presence of primary lead carbonates which were the predominant products found in soils. This therefore means that soil organic matter does play a vital role in bullet weathering and also controls lead migration within the soil ⁵⁰.

2.2.3.3 Effect of moisture

Soil moisture content and temperature also affect the availability of lead in soils⁵¹. The water layer that forms on the lead surface though non-corrosive to metals facilitates the corrosion of lead as it acts as a means of diffusion of atmospheric gases such as oxygen and carbon dioxide that attack the surface of the metal to form secondary minerals.

The transformation of metallic lead to more reactive species in the soil was found to be a speedy process that is influenced by soil moisture. After five days of incubation both hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] and litharge (PbO) were formed and evidenced by their peaks in the XRD patterns obtained in a study carried out in Florida, USA²⁹.

In another study using a water leach test, lead was shown to be retained by soils at field moisture content in exactly the insoluble form it was introduced in. Results of this study revealed that 71-99% of lead added was indeed retained. This retention of lead is however also influenced by the initial Pb addition, total sand content, effective clay porosity and soil pH⁵².

A combination of high moisture content of soil (high rainfall) with other factors such as low soil pH, low clay and organic matter which accelerate lead weathering rate causes concern worldwide especially for areas with shallow groundwater levels¹⁷.

2.2.3.4 Effect of soil Cation Exchange Capacity (CEC)

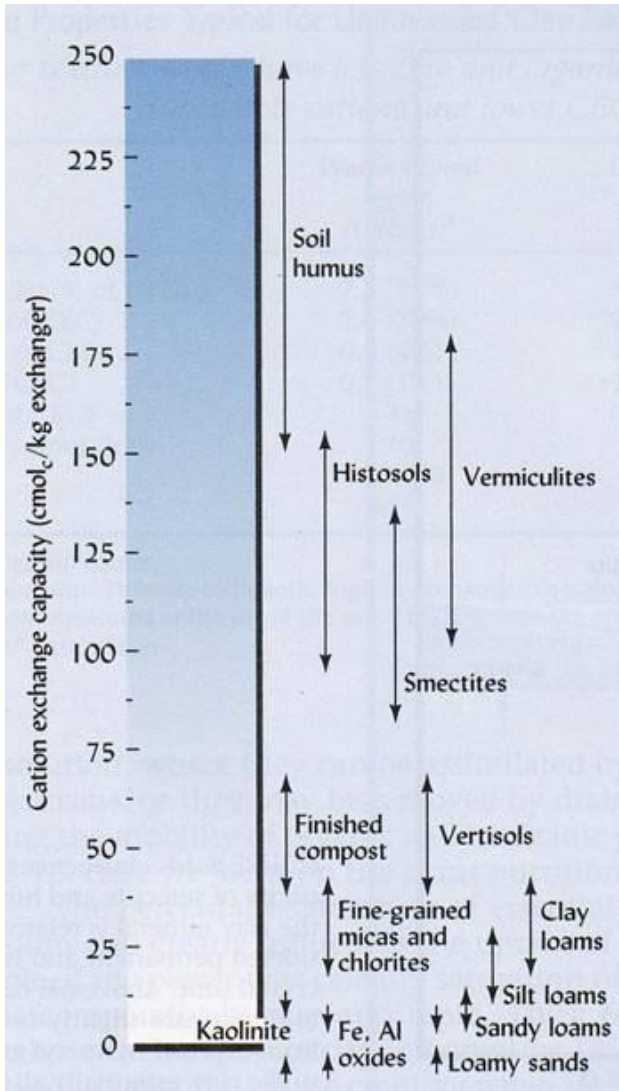


Figure 6: CEC values of different soil types, media and minerals⁵³

Cation exchange capacity (CEC) is another property of soil that affects the mobility and bio availability of lead in soils. Soils with high CEC values have a high binding ability and vice versa³¹. Soils with high amounts of organic matter and moderately weathered clays tend to have high CEC's. And as soils become highly weathered, their CEC decreases. Sandy soils generally have low CEC because of the lesser surface area of sandy particles when compared to clay minerals. This therefore decreases the capacity of the sand particles to hold and retain nutrients and to adsorb positive metal cations from solution. Dissolved lead generally exists in

the form Pb^{2+} and will therefore adsorb to cation exchange sites. Soil types do play a part in immobilizing metal ions; Endoleptic Luvisol and Humic Cambisol strongly retain Pb^{2+} and Cu^{2+} ions⁵⁴

Cationic metal binding increases with increase in valence, atomic weight and ionic potential. The affinity of metal cations relative to clay minerals is arranged in a series of $Cu^{2+} > Cd^{2+} > Fe^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+}$ ⁴⁵.

Soils with high pH, CEC, Fe/Mn content and a wide variety of minerals in their clay fractions, have shown the highest sorption capacities for Pb^{2+} and Cu^{2+} ions⁵⁴. Also, lead shot incubated in Temuka silt loam soil of CEC 31 cmol/kg displayed greater corrosion as compared to lead shot in Waimakariri sandy loam soil of CEC 11 cmol/kg and this was attributed to the high sorption capacity as indicated by the sorption values⁴⁷.

2.4 Best Management Practices (BMP's) for lead at shooting ranges

To help minimise or curb the mobility and bioavailability of lead in soils at these shooting ranges and by extension the adverse effects of lead, there are measures that can be put in place. These include the four-step system proposed by USEPA in 2005 ¹⁰:

- i) Controlling and containing lead- lead bullets and bullet fragments by using earthen backstops, sand traps, steel traps and reducing shotfall zones.
- ii) Preventing Lead Migration- via monitoring and adjusting soil pH by liming, immobilization using phosphates and controlling run off using vegetative cover
- iii) Removal of lead from the ranges and recycling- hand raking, sifting, vacuuming, soil washing, reclamation and recycling.
- iv) Documentation- keep records of number, size and type of rounds fired; keep records for the life of the range and up to 10 years after closing and evaluate effectiveness of the BMP's employed at ranges.

Further studies recommend more or less the same BMP's as the USEPA;

2.4.1 Liming

Addition of lime, CaCO_3 raises the soil pH thereby lowering the concentration of the H^+ ion concentration in the soil which reduces the hydrocerussite and cerussite minerals solubility ³². Liming was discovered to be efficient in reducing water soluble lead due to the formation of lead carbonate ²⁹. However, though liming soils to raise the pH increases metal retention; in soils with significant amounts of dissolved organic matter/carbon, liming leads to an increase in soil pH which may mobilize metal due to complex formation ^{48,55}.

2.4.2 Phosphate Addition

Phosphate treatment of the soil has become a widely-accepted remedy for lead contaminated soils as Phosphate has been found to have the highest affinity to lead over other metals in soil. It induces the formation of a highly insoluble mineral flouropyromorphite which immobilises lead ^{27,31}. Pyromorphite is much more insoluble than the other lead compounds that have been found in lead contaminated soils such as galena, anglesite and lead carbonates ³¹. However, care must be taken especially around water bodies when applying this treatment as it can lead to eutrophication ⁵¹.

2.4.3 Berm Soil Replacement

Replacing berm soils with sand is another option as it has been shown that sand is a better choice as its low organic matter, low moisture content and high pH can deter or at least decrease mobility of the lead in the soils at the ranges ⁵⁶.

2.4.4 Mechanical Sieving

Other proposed BMP's such as mechanical sieving have been found to increase lead concentrations in soils. This is due to the fact that the sieving action is abrasive and therefore adds significant amounts of lead powder back into the soil ⁵⁶.

Even though other countries have started implementing these BMP's, our country is still lagging behind. There is no requirement set for shooting ranges to undergo remediation to immobilise lead and its subsequent weathering products at both operational and obsolete shooting ranges in Botswana, this study could be useful to manage existing ranges and also to help in future when selecting locations for new shooting ranges as far as how soil chemistry and other environmental conditions affect lead breakdown and weathering. This study of the is going to gauge where we are as a country concerning lead pollution in shooting ranges and map the way forward.

CHAPTER 3

EXPERIMENTAL/METHODOLOGY

3.1 Chemicals and Reagents

All reagents used in this project were of analytical grade. Orthophosphoric Acid (85%) was purchased from Merck (Darmstadt, Germany); Hydrofluoric Acid, Perchloric Acid, Acetic Acid (99.8%), and Nitric Acid (65%) were supplied by LabChem (Johannesburg, South Africa). Ethanol (99.9%) and Hydroxylamine hydrochloride (99%) were both purchased from Sigma Aldrich (St. Louis, USA). Isopropyl Alcohol (99%), 30% Hydrogen Peroxide, Sodium Chloride (99%), Sodium Hydroxide pellets (99%) and Calcium Chloride dihydrate (99%) were supplied by Rochelle Chemicals Company (Johannesburg, South Africa). Magnesium Chloride hexahydrate (99%) 1,10 Phenanthroline indicator (99.8%), Potassium Dichromate (99%) and Sulphuric Acid (96%) were all purchased from Minema Chemicals Company (Johannesburg, South Africa) and Ferrous Ammonium Sulphate (99%) was purchased from Alpha Chemika (Mumbai, India).

Double deionized water was also used for dilutions of samples to be analysed with ICP OES. Working standards solutions used for calibration were prepared from 10 ppm of multi elemental standard stock supplied by Perkin Elmer Inc.

3.2 Glassware

Glassware used such as measuring cylinders, conical flasks, beakers, volumetric flasks, funnels, burettes were purchased from Pyrex and Borosilicate Companies. All glassware was washed with soap and tap water, soaked in HNO₃ acidified water, rinsed with distilled water and dried in an oven at 110°C prior to use.

3.3 Analytical Instruments

Inductively Coupled Plasma Optical Emission Spectrometer Optima 7300 DV fitted with an auto sampler was purchased from Perkin Elmer. Manual performance tests were performed using 10 ppm Mn solution to ensure %RSD was always $\leq 1.00\%$. The drying Oven was purchased from Thermo Fisher Scientific (Johannesburg, South Africa). Scanning Electron Microscope (JSM-7100F) purchased from JEOL USA, Inc. And a D8 Advance X-Ray Diffractometer was purchased from Bruker.

3.4 Description of sampling points

Seven shooting ranges located in the eastern and north eastern part of Botswana were used in this study. The S/P Pistol, S/P R1 and S/P R2 sampling areas are situated near the town of Selibe Phikwe, GPS Coordinates: $-21^{\circ} 58' 19.79''$ South, $27^{\circ} 50' 14.39''$ East. The MAT R1 and MAT R2 are found in Matsiloje Village in an area with GPS coordinates: $21^{\circ} 22' 12.00''$ South, $27^{\circ} 52' 12.00''$ East. On the other hand, the LEBO and TSHU shooting ranges are located in the Pandamatenga area at GPS coordinates: $18^{\circ} 31' 57.01''$ South, $25^{\circ} 39' 14.22''$ East. These are military shooting ranges used for shooting practices using military rifles of 0.50", 5.56 mm and 7.62 mm calibres.

Figures 7 and 8 below depict the location of the shooting ranges in Botswana and the Location of Botswana in Africa respectively

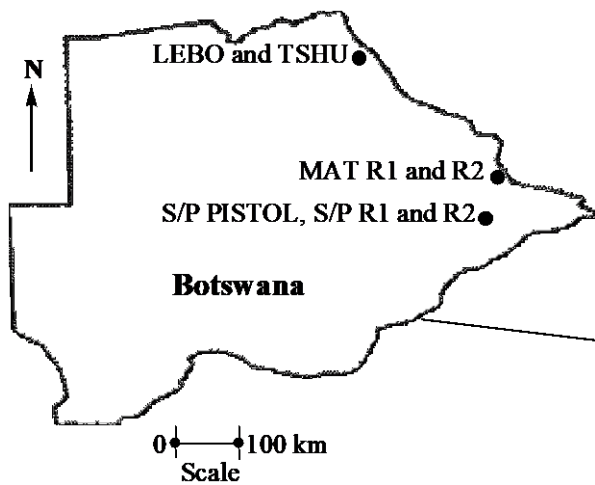


Figure 7: Location of Shooting Ranges Sampled in the Northern and Eastern Parts of Botswana.

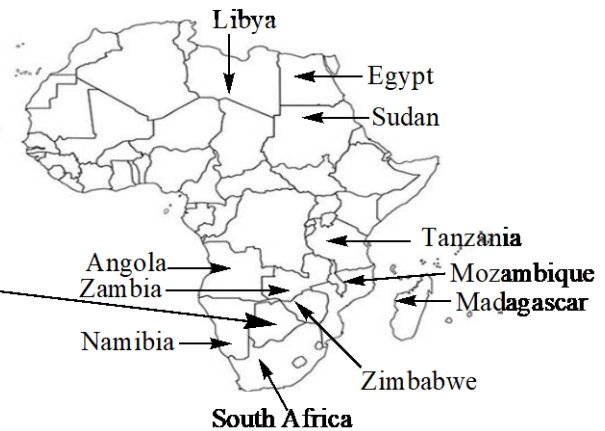


Figure 8: Map showing African countries.

3.5 Sampling

A total of 48 samples were collected from each range up to a depth of 20 cm from the soil surface using a soil recovery probe and a slide hammer. The samples were collected in quadruplicates at four sampling areas: The Backstop/Berm, Target line, 50 m and 100 m firing lines as shown in Figure 8 below. Each sampling point was circular with a radius of 150 cm. Composite samples of the berm were obtained by mixing the upper, middle and bottom berm samples whilst for the other sampling points (Target line, 50 m and 100 m); the left, centre and right portions were mixed together using a mortar and pestle.

Background samples to be used as control samples were collected from areas 200 m outside the shooting ranges.

Samples were stored in labelled butyrated zip-lock bags. The samples were then transported to the laboratory for pre-treatment and analysis

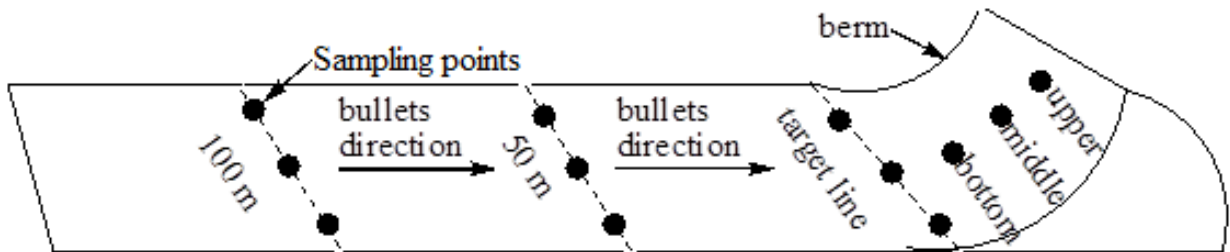


Figure 9: Schematic diagram showing sampling points at the shooting ranges

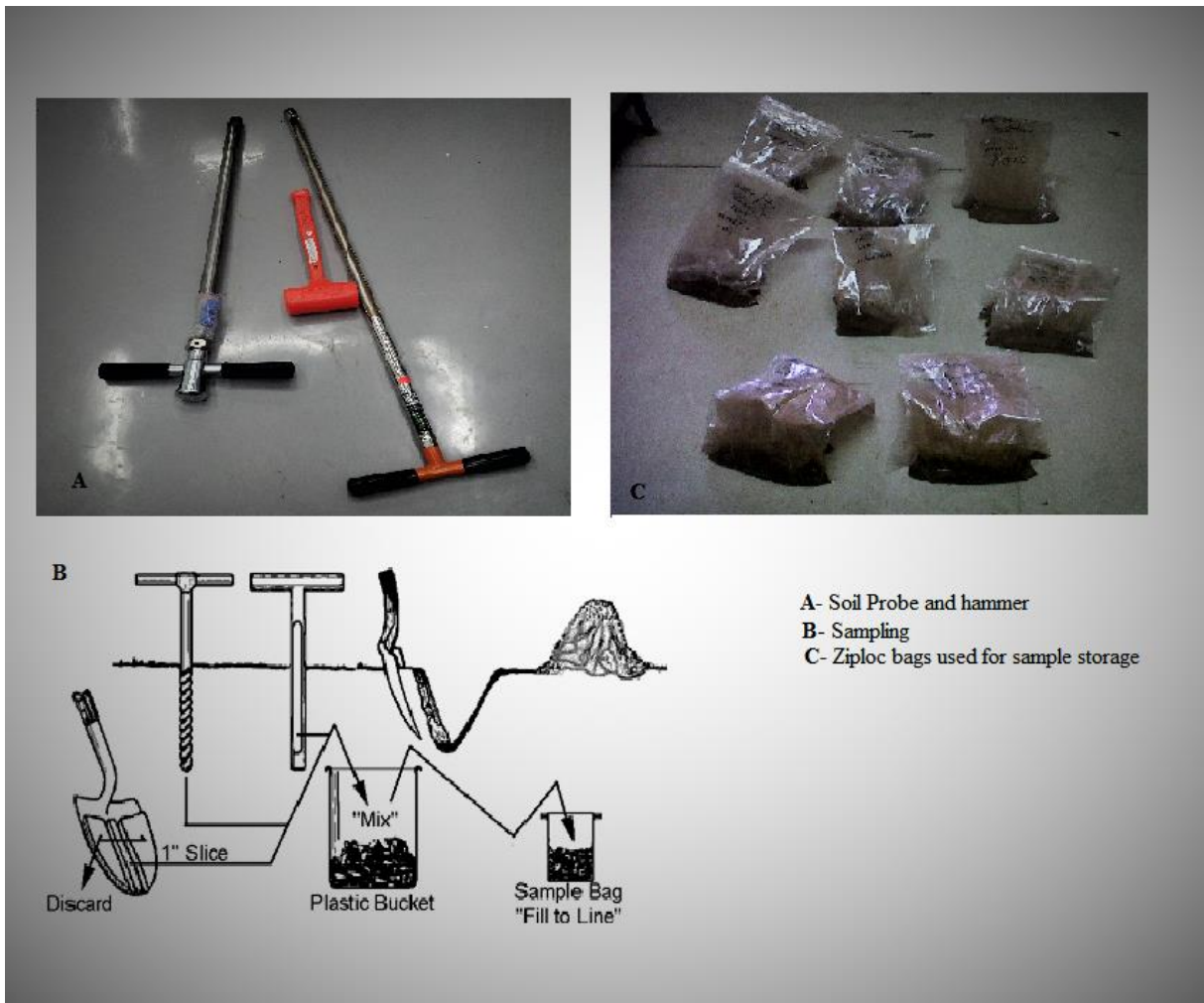


Figure 10: Sampling tools used for sample collection- soil recovery probe, hammer and Ziploc bags used for sample storage

3.6 Sample Pre-treatment

Composite samples were air dried then all visible lead shot, bullets, rock fragments and tree matter were removed by hand and the remaining sample was ground with a mortar and pestle and passed through a 2 mm stainless steel sieve. Then using an electric rotary splitter, the soil samples were homogenized as shown in the Figure below and stored them in appropriately labelled Ziploc bags.



Figure 11: Visibly corroded bullets were witnessed upon sieving with a 2 mm sieve (a) and the electric rotary splitter was used for homogenising the soil samples as shown in (b) above.

A portion of the samples was pulverized using a manually operated, Retsch RS 200 Vibratory Disk Mill at 700 rpm for 3 minutes and then stored in sample envelopes for X-Ray Diffraction and Inductively Coupled Plasma-Optical Emission Spectroscopy analysis. Non-pulverized samples were used for soil properties such as pH and electrical conductivity.

3.7 Sample Preparation and Analysis

After removing tree matter, bullets, rocks and leaves. Samples were now ready to undergo analysis. Below is a diagram that gives an overview of the tests the samples underwent.

Details of these tests are then outlined one by one below the diagram.

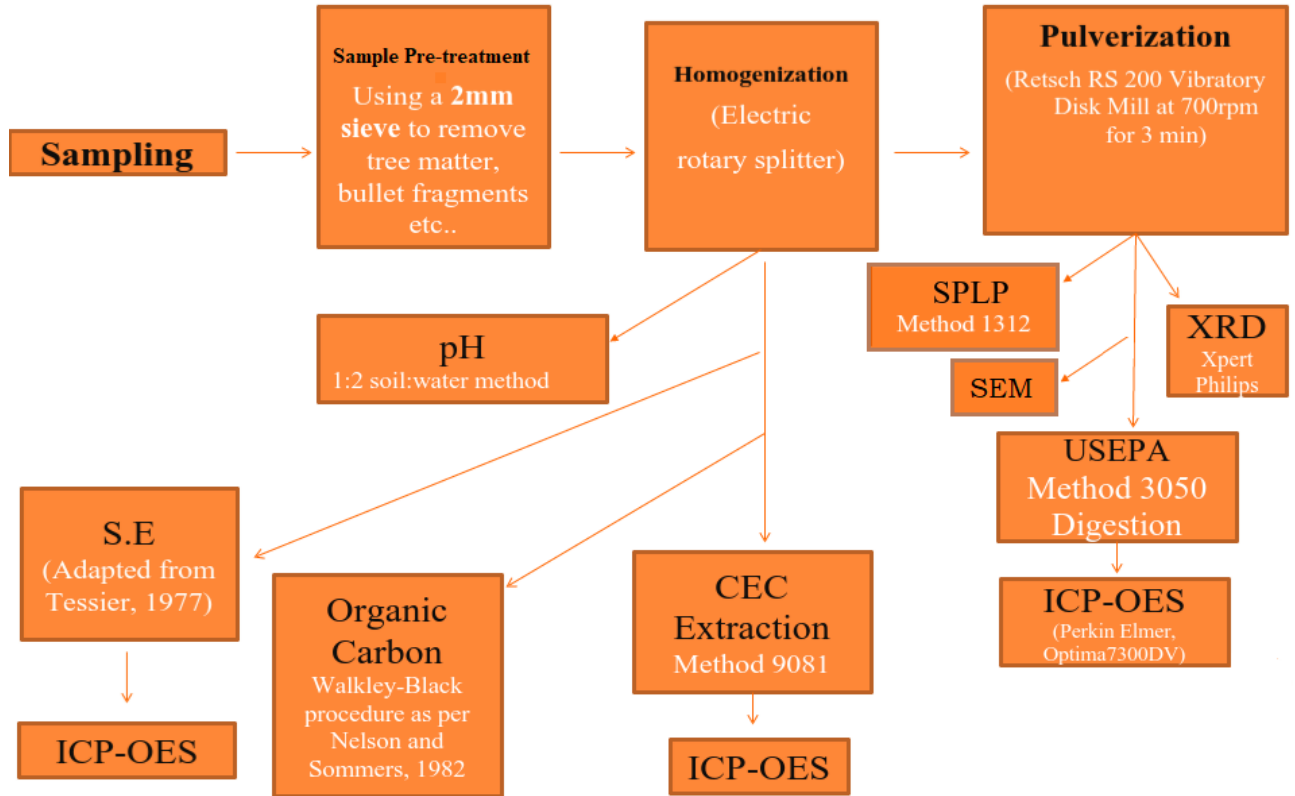


Figure 12: Figure showing the sample preparation and analysis procedure

3.7.1 pH Measurement

40 ml of distilled water was added to a 100 ml Pyrex beaker containing 20 g of soil. The mixture was stirred well using a stirring rod and allowed to stand for an hour at room temperature. The pH of the mixture was then measured using a calibrated pH meter. Calibration of the pH meter was done using buffers near 4.7 and 10 at 25°C. Measurements for each shooting range were done in triplicates.

3.7.2 Electrical Conductivity Determination

Using an analytical balance 10 g of air dried soil (2 mm) was weighed out into a 100 ml polyethene bottle. Then 50 ml distilled water was added to the bottle and the solution was shaken for an hour at 50 rpm to dissolve soluble salts. Then using a calibrated HACH SensION +EC5 portable conductivity meter, the electrical conductivity of the samples were measured.

3.7.3 Organic Carbon Determination^{31,57,58}

Between 1.00 to 2.00 g dried soil (ground to <60 mesh) was weighed out and transferred to a 500 ml Erlenmeyer flask, then 10 ml of 0.167 M $K_2Cr_2O_7$ was added by means of a pipette. Using a dispenser 20 ml of concentrated H_2SO_4 was added to the mixture and the flask swirled gently to mix. The solution was allowed to stand 30 minutes with the flask placed on an insulation pad during this time to avoid rapid heat loss. After 30 minutes the suspension was diluted with about 200 ml of water to provide a clearer suspension for viewing the endpoint. Then 10 ml of 85% H_3PO_4 and 0.2 g NaF was added to complex Fe^{3+} which would interfere with the titration endpoint. Then 10 drops of ferroin indicator was added just prior to titration to avoid deactivation by adsorption onto clay surfaces.

The mixture was then titrated with 0.5 M Fe^{2+} to a burgundy endpoint. Use of a magnetic stirrer with an incandescent light makes the endpoint easier to see in the turbid system. A reagent blank was also run using the above procedure without soil. The blank was used to standardize the Fe^{2+} solution daily.

3.7.4 Cation Exchange Capacity Determination⁵⁹

4 g of pulverized soil was weighed out into a 50 ml polypropylene centrifuge tube and 33 ml of 1.0 N sodium acetate solution was added to the sample. The tube was then stoppered and shaken in a mechanical shaker for 5 minutes and then centrifuged until the supernatant liquid was clear. The clear liquid was then decanted and discarded and the process repeated three times. The above procedure was also repeated using isopropyl alcohol. Then finally using a 1.0 N solution of Ammonium acetate the process was repeated and the three washings were transferred to a 100 ml clean, dry volumetric flask and made up to the mark with 1.0 N ammonium acetate and the mixture was analysed with ICP-OES.

3.7.5 Total Pb analysis

Samples were digested using the USEPA Method 3050: Using an Analytical balance 0.1000 g of each homogenous sample was weighed into a 30 ml Teflon vial. Then under a fume hood 25 ml of HNO₃ was added to the vial and heated for 16 hours in a dry block digester. Sample vials were then removed from the block and allowed to stand and for 25 minutes. After cooling samples were transferred to appropriately labelled 50 ml polypropylene vials and topped to the mark with distilled water. Then 5 ml of each sample was pipetted to a 15ml vial and 5 ml 10% HNO₃ added to make a x1000 dilution. Vials were then recapped and homogenized before analysis with ICP-OES. A certified reference material, NCS DC 73320, of known concentration of 20 mg/kg was using for quality control checks with a percent recovery of 89.7%. The accuracy of measurements was < 3% RSD, an indication of accuracy of the analytical methodology.

3.7.5.1 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) also known as Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) is a multi-element technique widely used to determine the concentration of various elements in a variety of sample matrices⁶⁰.

This technique uses a high temperature argon plasma to excite atoms to the point where they emit their characteristic wavelengths of light (emission lines). The intensity of the emitted light is directly proportional to the concentration of the elements of interest in the sample. Like AAS, one needs to establish a calibration curve using light emitted by known and varying concentrations (which serve as standards) of an element before measuring emissions of unknown samples. ICP-OES has also been used for the determination of lead in soil samples^{31,37,61}. In ICP-OES the sample is transported into the instrument as a stream of liquid where it is converted into an aerosol via nebulisation. The aerosol is then carried into the plasma at temperatures of above 6000 K where it is desolvated, vaporised, atomised and excited. The excited atoms in turn emit their characteristic radiation which is sorted according to wavelength and sent to the detector. The signals detected are then converted into electronic signals further converted to concentration information for the analyst⁶². Figure 13 below shows a representation of the ICP-OES instrument.

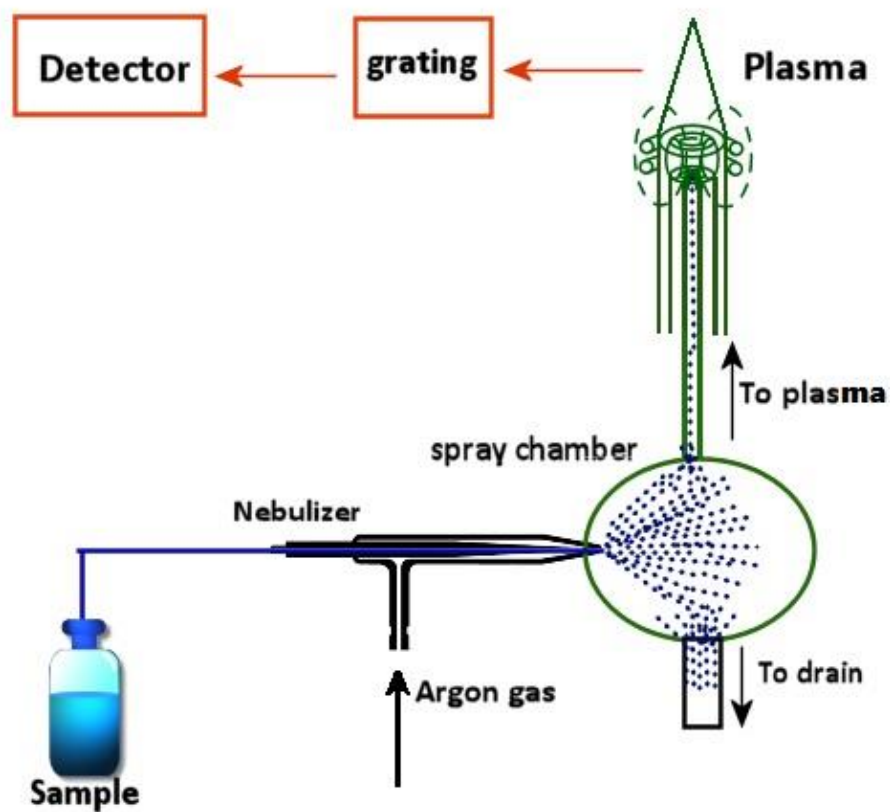


Figure 13: ICP- OES Schematic diagram ⁶³

3.7.6 Fractionation Studies of lead in soil samples

1 g of processed soil for each sampling point was weighed out into sterile 50ml polypropylene centrifuge tube

Water Soluble/Exchangeable Fraction

1 g of soil was extracted with 8 ml of 1 M $MgCl_2 \cdot 6H_2O$ at pH 7.0. Extraction with continuous agitation on the wrist action shaker was done for 1 hour at room temperature. The sample was then centrifuged for 30 minutes at 2750 rpm. The supernatant solution was decanted, five drops of 10% HNO_3 added to it and stored in the refrigerator until ICP-OES analysis. The residue was washed with 8 ml of deionized water by vigorous hand shaking followed by 30 minutes in the centrifuge at 10 000 rpm. The supernatant was decanted and discarded whilst the residue was saved for the next extraction step.

Bound-to-Carbonates Fraction

8 ml of 1 M CH_3COONa adjusted to pH 5.0 with acetic acid was added to the residue collected from the exchangeable fraction. Extraction with continuous agitation on the wrist action shaker for was done for 5 hours at room temperature. The sample was then centrifuged for 30 minutes at 10 000 rpm. The supernatant solution was decanted, five drops of 10% HNO_3 added to it and stored in the refrigerator until ICP-OES analysis. The residue was washed with 8 ml of deionized water by vigorous hand shaking followed by 30 min in the centrifuge at 10 000 rpm. The supernatant was decanted and discarded whilst the residue was saved for the next extraction step.

Bound-to-Fe & Mn Oxides Fraction

20 ml 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) acetic acid was added to the residue collected from the bound-to-carbonate fraction and extracted with occasional hand agitation for 6 hours in a water filled beaker on a hot plate at $96 \pm 3^\circ \text{C}$. The sample was then centrifuged for 30 minutes at 10 000 rpm. The supernatant solution was decanted, five drops of 10% HNO_3 added to it and stored in the refrigerator until ICP-OES analysis. The residue was washed with 8 ml of deionized water by vigorous hand shaking followed by 30 min in the centrifuge at 10 000 rpm. The supernatant was decanted and discarded whilst the residue was saved for the next extraction step.

Bound-to-Organic Matter Fraction

3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 (adjusted to pH 2 with HNO_3) were added to the residue collected from the bound-to-Fe & Mn oxide fraction and the mixture heated in a water bath at $85 \pm 2^\circ \text{C}$ for 2 hours. Then a second aliquot of 5 ml of 30% H_2O_2 (adjusted to pH 2 with HNO_3) was added to the mixture and further heated in a water bath at 85°C for 3 hours with intermittent agitation. The extraction mixture was then allowed to cool to room temperature and 5 ml of 3.2 M $\text{CH}_3\text{COONH}_4$ in 20% (v/v) HNO_3 was added to prevent adsorption of extracted metals onto oxidized sediment and diluted to 20 ml with deionized water. The sample was then centrifuged for 30 minutes at 10 000 rpm. The supernatant solution was decanted, five drops of 10% HNO_3 added to it and stored in the refrigerator until ICP-OES analysis. The residue was washed with 8 ml of deionized water by vigorous hand

shaking followed by 30 min in the centrifuge at 10 000 rpm. The supernatant was decanted and discarded whilst the residue was saved for the next extraction step

Residual Fraction

Residue from Bound-to-Organic matter fraction was digested with Hydrofluoric and Perchloric acids in a 5:1 mixture, followed by a 10:1 mixture and evaporated to near dryness in a Platinum Crucible until white fumes started to appear. The residue was then diluted with 12 M HCl and diluted to 25 ml using distilled water and stored in a refrigerator until ICP-OES analysis.

3.7.6.1 Fractionation Studies using Sequential Extraction ⁶⁴

The mobility and bioavailability of Pb in soils is dependent on many physical, chemical and biochemical factors such as physical weathering, oxidation-reduction, association-dissociation, precipitation-dissolution and sorption-desorption ⁶⁵. Most studies have dealt with total concentration of Pb in soil which does not provide a good measure for the mobility and bioavailability of Pb in soils failing to give a true picture of the potential environmental, vegetation and human health hazards. To better understand the risk posed by elevated levels of Pb in the environment, it is important to understand the different chemical species in which Pb exist in the shooting range soils (free metal, metal-organic complexes and salts). The different forms of heavy metals and their reactivity with the specific target constituents of the soils help ascertain for their solubility, mobility, bioavailability, fate and Eco toxicological importance in the environment ⁶⁶.

The method of sequential extraction was first coined by Tessier et al in 1979 and has been widely applied in trying to ascertain for the solubility, mobility and bioavailability of heavy metals in the environment ⁶⁴. The same method has been widely used to assess the distribution of Pb in shooting range soils arising from Pb shots and bullets ^{29,67,68}. Tessier et al also found out that heavy metals exist predominantly in five different chemical species in the soil.

The successive extraction procedures account for four well defined compartments and a residual. These include heavy metal as components of the water soluble and exchangeable (WE), organic-bound (OM), carbonate-bound (CB), Fe-Mn oxides bound (FM) and residual fractions (RS). The binding of heavy metals to the water-soluble and exchangeable fraction is

considered weak as compared to other fractions with the binding more strongly in the residual fraction. Therefore, in terms of mobility, the heavy metals in the WE fraction are considered mobile while the fractions in the OM, CB, and FM fractions are considered mobilizable. The RS fraction on the other hand is referred to as the immobile fraction. The Fe-Mn oxides bound and organic-bound compartments are also referred to as the reducible and oxidizable fractions respectively ⁶⁹. The residual fraction refers to the soil component with heavy metals embedded in the crystal lattice of minerals (detrital) ⁷⁰. Under normal environmental conditions, heavy metals present in the RS fraction have restricted mobility and are unreachable by living organisms. It is also important to note the assumption that the bioavailability of the heavy metals diminishes with each successive fractionation step ⁷⁰.

The bioavailability and non-bioavailability of Pb can be further divided into two types of soil fractions through which heavy metals in the shooting range soils can be confined to, being; (1) the inert fraction and (2) the labile fraction ⁷¹. The inert fraction is considered to be the chemically inactive form of heavy metal compounds and is believed to be non-toxic whilst the labile fraction is considered hazardous and toxic. For example, shooting range soils in which Pb exists in residual fractions such as lead phosphate ($Pb_3(PO_4)_2$), lead sulphate ($PbSO_4$), lead sulphite (PbS) and lead chloride phosphate ($Pb_5(PO_4)_3Cl$) makes lead unreachable and therefore less potential risk to the biota. On the other hand, the chemically active fraction of Pb-particulate matter such as lead nitrate ($PbNO_3$), lead acetate ($PbCOOCH_3$) and lead chloride ($PbCl_2$) has the potential to be translocated into plants and contaminating both surface and underground water sources leading to their presence in the food chain. As a result, the mobile toxic Pb metal can end up in plants, animals and human beings' systems ^{72,73}. The bioavailability of the active fraction chemical species is dependent on the soil physical and chemical properties such as pH, cation exchange capacity (CEC) and organic matter content ⁷⁴.

Sequential extraction procedure has been extensively studied in the analysis of trace metals including Cd, Co, Cr, Cu, Fe, Mn Ni, Pb and Zn in both river sediments and marine sediments. It has also been used in fractionation of Lead in shooting range soils ^{31,38,75,76}

3.7.7 Pb mobility, bioavailability and leaching risks at shooting ranges

3.7.7.1 Pb mobility and bioavailability Potential

The absolute and relative content of fractions weakly bound to components may be used to evaluate the mobility and fate of Pb in shooting range soils. A method by Kabala and Singh ⁷⁷ for the calculation of mobility factor was used to ascertain for the relative index of metal mobility and fate. The mobility factor was calculated based on the following expression;

$$\text{Mobility Factor (MF)} = \frac{F_{WE} + F_{CB} + F_{FM} + F_{OM}}{F_{WE} + F_{CB} + F_{FM} + F_{OM} + F_{RS}} \times 100\%$$

Where, F_{WE} = water soluble fraction

F_{CB} = carbonate-bound fraction

F_{FM} = Fe-Mn oxides fraction

F_{OM} = organic-bound fraction

F_{RS} = residual fraction

The strength of binding of Pb to different soil components determines its bioavailability and the risk associated with its presence in the ecosystem. The risk assessment was carried out through calculating the bioavailability factor (BF). The bioavailability factor represents the potential of Pb from the shooting range soil matrix to enter the soil solution from which it can be adsorbed and accumulate in plants. The bioavailability factor is calculated as the ratio of the available Pb in a fraction to its total concentration as given in the following expression,

$$\text{Bioavailability Factor (BF)} = \frac{\text{Available concentration of Pb in a fraction}}{\text{Total concentration of Pb}} \times 100\%$$

3.7.7.2 Leaching test: Synthetic Precipitation Leaching Procedure (SPLP) ⁷⁸

The synthetic precipitation leaching procedure (SPLP) extraction technique is widely applied in to evaluate the possible underground water contamination. The extraction fluid is used to simulate acid rain and this involves the use of acidified de-ionized water.

100 g of each sample was weighed out into 2 L polyethene bottles. Then 2 L of extraction fluid (Distilled water adjusted to pH 5.0 using a mixture of H₂SO₄:HNO₃ in a 60:40 ratio) was added to the bottles that were rinsed out with the extraction fluid. Using Teflon tape, the

bottle lids were secured in place and the bottles were shaken in an end-over-end shaker for 18 hours at 28 rpm. Samples were then allowed to stand before filtration with 0.7 μ m borosilicate glass fibre filter and the filtrate was analysed for Pb amounts using ICP OES.

3.7.8 Characterization Studies

3.7.8.1 Characterization using X-Ray Diffraction (XRD) Analysis

A powder XRD analysis was employed to investigate the crystalline structure of the weathering products found in the soils from shooting ranges as well as the bullets recovered from the soil. A Bruker D8 Advance Powder X-Ray Diffractometer with a 3.0 kW generator, a Cu tube X-ray source, and a LynxEye XE energy-dispersive strip detector was used.

The radiation used was a cu-K α with a wavelength of 1.54056 Å within the values of 2θ between 5-90 degrees. The intensity of collected radiation at each angle, ($^{\circ}$ Theta) 5.00 – 90 degrees was measured. Each sample took about 10 minutes to run. The machine was run at 40 V and 40 mA. The interplanar spacing d , peak intensities and position of peak (2θ $^{\circ}$) were obtained directly from the captured XRD data. Then Bruker software EVA, was used for data analysis, including phase identification, structure refinement and quantitative phase analysis.

3.7.8.1.1 Principle of XRD

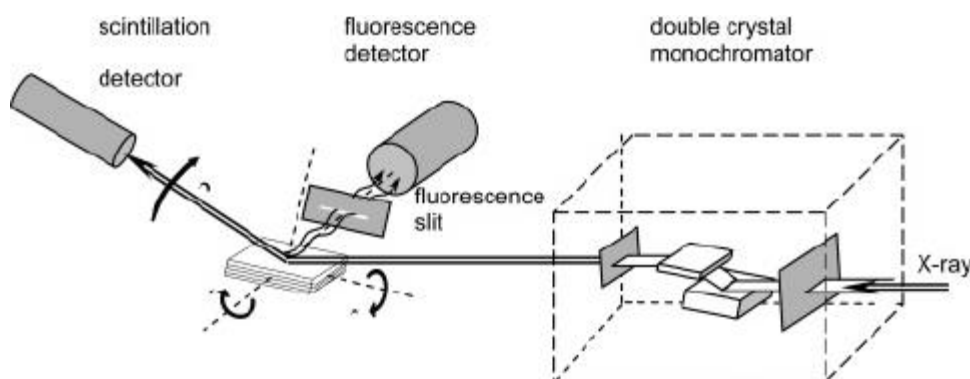


Figure 14: X-Ray Diffraction Diagram ⁷⁹

An X-ray diffraction pattern is a plot of the intensity of X-rays scattered at different angles by a sample. The detector moves in a circle around the sample –The detector position is recorded

as the angle 2θ (2θ). The detector records the number of X-rays observed at each angle 2θ . The X-ray intensity is usually recorded as “counts” or as “counts per second”. To keep the X-ray beam properly focused, the sample will also rotate. On some instruments, the X-ray tube may rotate instead of the sample. A representation of an XRD instrument is shown in figure 14 above.

The X-ray diffraction pattern is like a fingerprint that lets one figure out what one’s sample is composed of. It determines; what crystallite structures are in the sample; how much each crystalline structure is in the sample and there is any amorphous material is present in the sample. The resulting peaks correspond to directions at which x-rays undergo constructive interference from planes within crystals. These directions are given by Bragg’s Law below:

$$n\lambda = 2d\sin\theta$$

Where d is the lattice spacing of the crystal and θ is the angle of incidence. The Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) from a copper target is the most common X-ray source for the diffraction measurement.

3.7.8.2 Characterization using the Scanning Electron Microscope (SEM)

Soil sample was placed on one side of the double sided sticky carbon tape and coated with carbon. After drying, mounting tweezers for SEM lifts were used to stick the other side of the tape to the aluminium stub. Then using mounting tweezers, the stub was placed in the holder and the screws on the holder were tightened. The holder was then placed on the stage, ensuring that the flat edge of the mount was against the flat area of the stage. The desired working distance of 10 mm and probe current of 15.0 kV were selected.

3.7.8.2.1 Principle of SEM

SEM provides images of the surface of the sample by using a high-energy electron beam. As shown on figure 15 below; it consists of an electron gun that generates the electron beam; a column that serves as a path in which the electron beam travels and a series of lenses to guide and shape the electron beam. It also has a chamber that houses the sample, and entire system is kept under vacuum by a series of pumps.

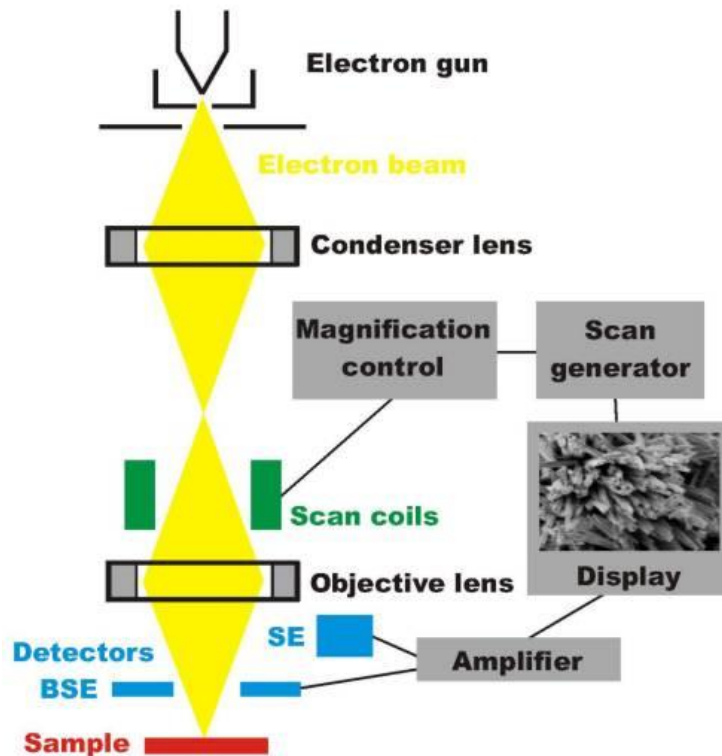


Figure 15: SEM schematic diagram⁸⁰

For samples to be imaged, their surfaces must be electrically conductive, non-conductive samples are therefore coated with a layer of either a metal or carbon in order to curb accumulation of static electric charges on the sample surface during electron irradiation. During irradiation, the electrons interact with the atoms in the sample to produce signals that contain information about the morphology and composition of the sample surface. SEM can be coupled with energy dispersive X-ray analysis (EDX), to determine the elemental composition of the elements of sample precisely.

Using this technique has advantages which include good resolution at high magnification; chemical quantification analysis, crystallography, magnetic and electrical characteristics of a sample. The only snag is that it operates under vacuum and that the sample must be conductive in order to be imaged.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Rainfall amounts, soil types and dates of establishment of the shooting ranges

All the seven shooting ranges under study have been operational for more than 15 years with the oldest being the Pandamatenga Tshukudu Range established in 1984 as shown in Table 4 below.

Table 4: Shooting ranges dates of establishment as supplied by the Botswana Defence Force

Range Name	Year of establishment	Soil Classification
S/P PISTOL	2001	Haplic luvisols
S/P R2	2001	Haplic luvisols
S/P R1	2001	Haplic luvisols
MAT R2	1985	Chromic luvisols
MAT R1	1985	Chromic luvisols
LEBO	1987	Pellic vertisols
TSHU	1984	Pellic vertisols

The soils in the shooting ranges investigated are mostly luvisols and vertisols (Table 4). The haplic luvisols have a shallow topsoil cover with subsoil materials being mainly weathered and decomposed granites. The soils found in this area have been found to be less suitable for arable agriculture. The pellic vertisols on the other hand are fertile black cotton clay rich soils and these soils are mostly used for arable agriculture in the studied region ⁸¹. The chromic luvisols are moderately deep to very deep and slightly excessively drained, strong brown to dark red, sandy loams to clay loams. The soil type strongly affects the soil cation exchange capacity. Sandy soils in comparison to clay soils have been found to have low cation exchange capacity ⁸².

Rainfall is an influencer of lead corrosion and mobility in the soil because lead bullets corrode, solubilise and move down the soil profile as it rains. Even though it's a slow process, there is always some downward movement of lead in the soil ²². Rainfall amounts as supplied by the Botswana Meteorological Services show that the shooting ranges receive rainfall between the months of October and April as depicted in Figure 16 below. All the ranges experience no rainfall at all during the winter season: between May and August, in summer

rainfall amounts of more than 150mm can be received by the Selibe Phikwe and Matsiloje areas.

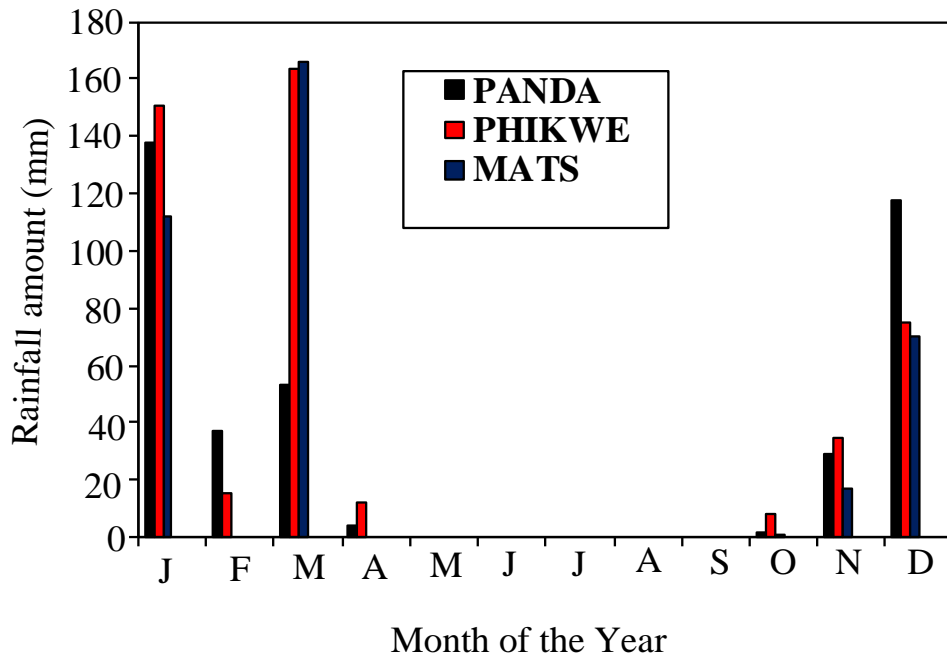


Figure 16: Rainfall amounts of the areas sampled for the period: July 2013-June 2014

4.2 Distribution of total lead contamination in the shooting range soils

All the seven shooting ranges studied were found to be contaminated with lead as shown in Figures 17 (i-iv) below. Berm soils had the highest lead concentrations as this is where the highest density of bullets is found ⁴⁶. This is consistent with other studies by Cao et'al, 2003 ³¹ who found concentrations of up to 48 400 mg/kg in the berm soil in the MPR range in Florida. In another study, concentrations of lead ranging between 10 068 mg/kg to 70350 mg/kg in three ranges were registered ⁵⁷. These high concentrations in the berm is attributed to the berm being the point where almost all the bullets end up save for the ricochet and off target ones.

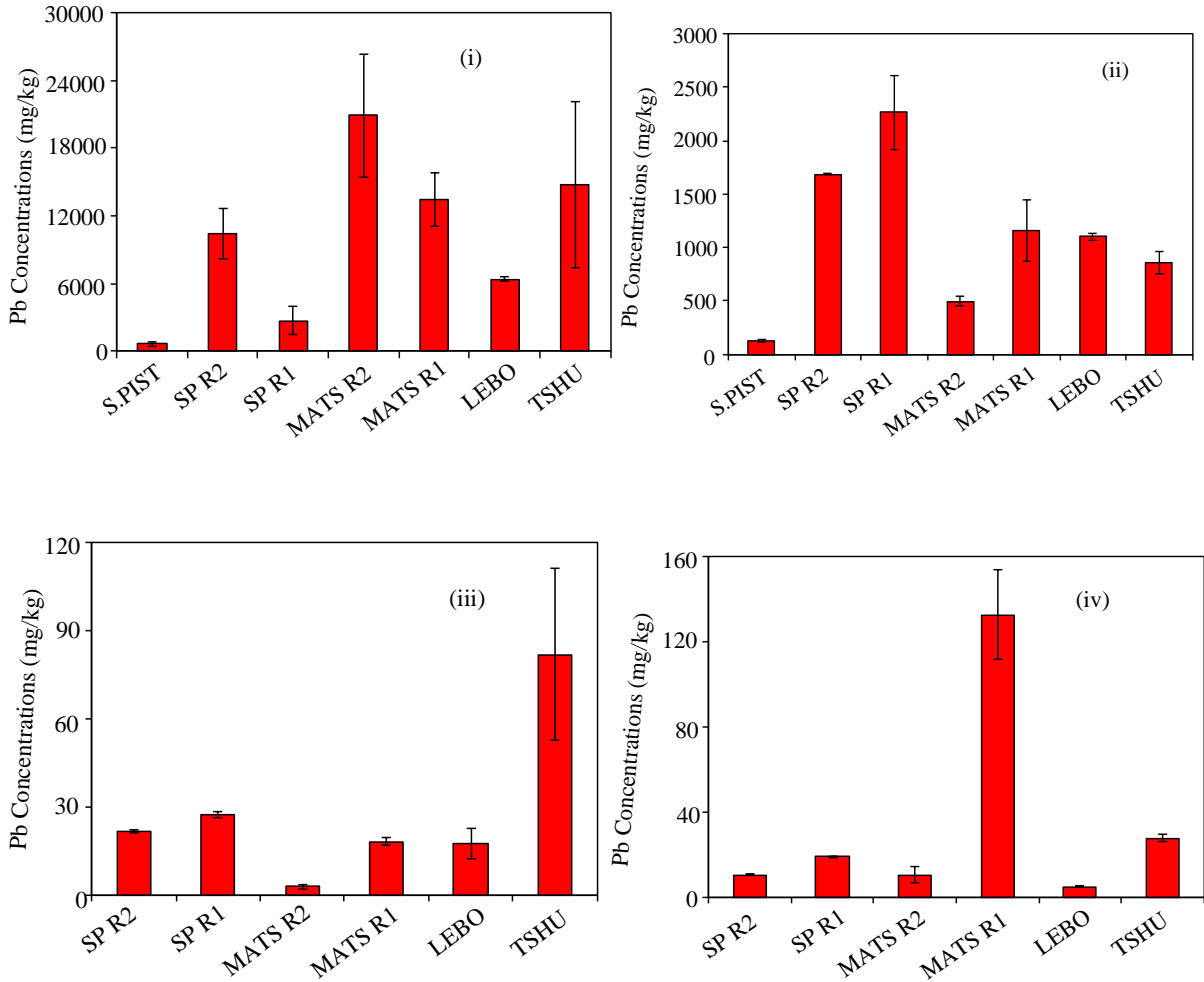


Figure 17: Total Pb concentrations of composite (i) Berms soils, (ii) Target line soils, (iii) 50m from the target line and (iv) 100m from the target line at the 7 shooting ranges in the Northern and Eastern parts of Botswana. Mean of $n=3$; Standard error of the mean = δ/\sqrt{n} , where δ is standard deviation

Matsiloje R2 had the highest lead concentrations of $20\ 882.55 \pm 5419.27$ mg/kg. All the other ranges had lead concentrations exceeding 2000 mg/kg except the Selibe Phikwe Pistol range which had 685.42 ± 218.95 mg/kg which still exceeded the 400 mg/kg USEPA limit. This low concentration in the pistol range can be explained by the fact that pistol ammunition contains small content of Pb slug as compared to the rifles used in the other six shooting ranges. According to pistol ammunition contains less amount of Pb slug of about 52% as compared to assault rifles with over 80% Pb slug content²². In addition, pistol shooting practices are only carried out by military officers who are few in numbers and thereby less accumulation of Pb shots in shooting ranges berm.

There are many reasons contributing to the elevated levels of Pb at MAT R2 shooting range. This shooting range has been in operation for more than 20 years. This implies that Pb bullets and shots have been accumulating in this shooting range since 1985. The TSHU shooting range is the oldest of all the shooting ranges studied, established in 1984. It had total Pb concentrations of 14731 ± 7353 mg/kg. However, total Pb concentration at TSHU shooting range was less than that at MAT R2. There are several reasons to this difference, according to military personnel; intense shooting practices take place at MAT R2 than any other range studied. The MAT R2 is used mostly by the infantry units who are the foot soldiers and backbone of the Botswana Defence Force. These military personnel carry out their shooting practices frequently using this shooting range. The berm total Pb concentrations of other shooting ranges were as follows: 13449 ± 2375 mg/kg, 10386 ± 2248 mg/kg, 6413 ± 253 mg/kg and 2741 ± 1291 mg/kg at MAT R1, S/P R2, LEBO and S/P R1 respectively.

Total lead concentrations for all the ranges except the Matsiloje ranges, decrease as one moves away from the berm soils as expected. This may be explained by that in the Matsiloje ranges most firing is done from the 100 m firing line, therefore this means all the processes that a bullet undergoes when exiting the gun (heating and friction) cause some deposition of lead powder at this line. The target line being closer to the berm accumulated the higher concentrations of Pb than at 50 m and 100 m firing lines (Figure 17(ii)). The target line total Pb concentrations were highest for the S/P R2 (3169 ± 479 mg/kg) followed by S/P R1 (3169 ± 479 mg/kg) and the lowest the S/P Pistol range as expected (180 ± 13 mg/kg). We found out that the two ranges S/P R1 and S/P R2 are located at the foot of a hill with the hill acting as the berm. This we assume greatly increased the mobility of Pb due to rain runoff water travelling down the hill. One other important point to note is that the target line total Pb concentration at S/P R1 (2741 ± 1291 mg/kg) was higher than the berm concentration, an indication that most of Pb on the berm soils had migrated down to the foot of the berm.

In addition to runoff from water down the berm, the target line Pb concentrations are higher than at 50 and 100 m firing lines because of the physical abrasion of Pb bullet from friction between the bullet and target as the bullet pierced through the target. Most of the shooting ranges showed contamination less than the USEPA critical level of 400 mg/kg at the 50 and 100 m firing lines. This implies that most of the contamination is restricted to the berm soils

and the target line soils. However, it should be noted that the total Pb concentrations at the 50 and 100 m firing lines are still higher than the USEPA maximum contaminant limit (MCL) in water which is 15 µg/L and the Botswana and World Health Organization MCL limit of 10 µg/L. This may still pose a threat to both surface and underground water.

Background samples used a control samples were collected from areas 200 m outside the ranges to assess the migration of lead to the surrounding villages.

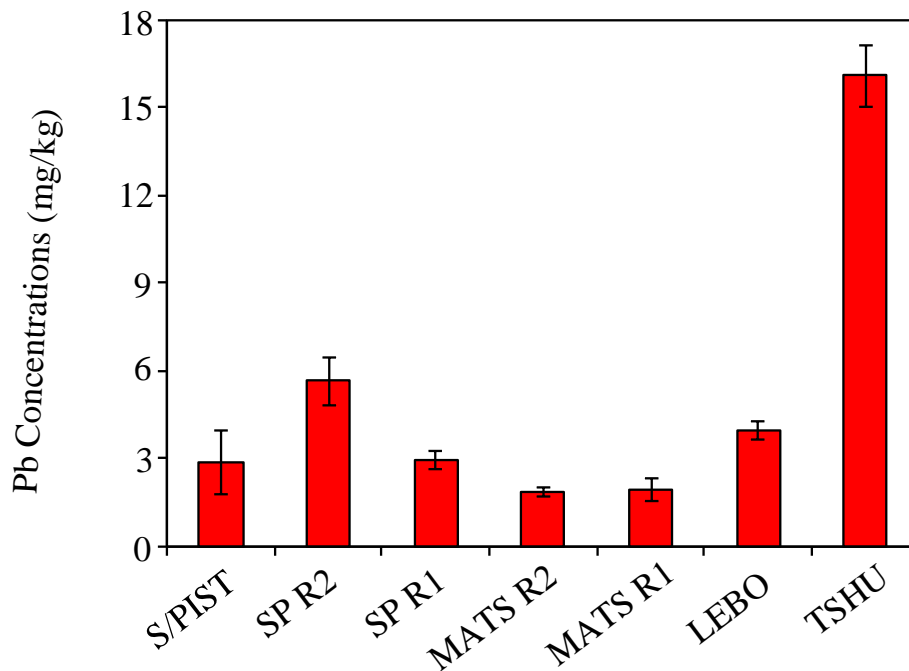


Figure 18: Graph showing lead concentrations of background samples

As seen in Figure 18 above, all the background samples show that for now the pollution is still confined to the shooting range soils, concentrations were less than 20 mg/kg in all the samples. The background soils showed Pb concentrations in the range of the earth's crust of 15-20 mg/kg¹.

The synthetic precipitation leaching procedure (SPLP), a method used to simulate the leaching of heavy metals into the soils due to acid rain; was employed to check the leachability of lead. SPLP-Pb concentrations were found to be highest in the berm soils of the Pandamatenga Tshukudu range with 267.45 ± 2.80 mg/kg, followed by the Selibe Phikwe range 1 with 125.63 ± 1.60 mg/kg. The lowest SPLP-Pb concentrations were found in the

Matsiloje ranges with Mats R1 having 0.89 ± 0.32 mg/kg and Mats R1 with 1.23 ± 0.33 mg/kg as depicted by Figure 19 below:

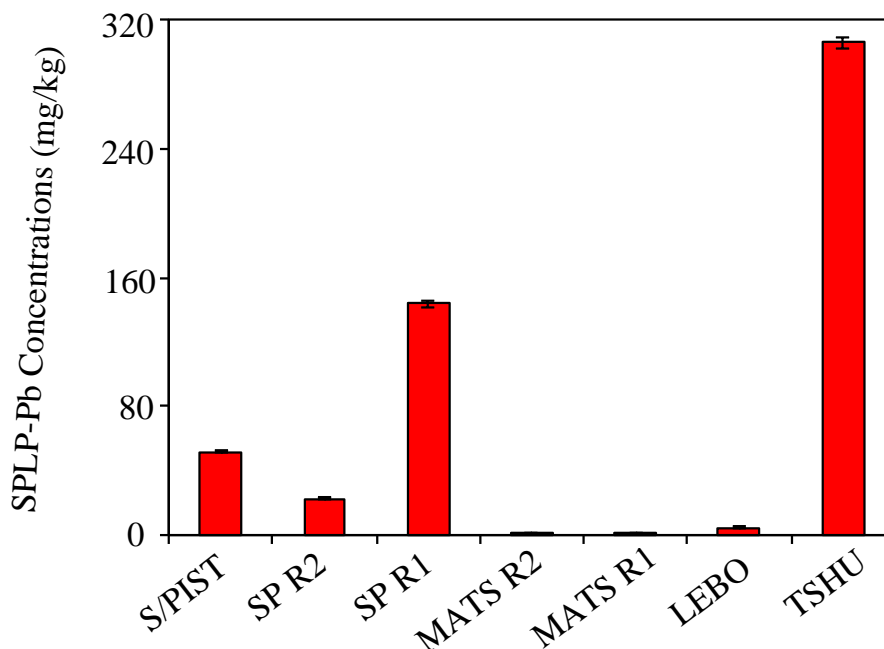


Figure 19: SPLP-Pb concentrations in the Northern/Eastern Botswana shooting ranges

All the SPLP-Pb concentrations in the seven ranges under study exceeded the USEPA critical limit of 0.015 mg/kg. This therefore is an indication of a possibility of lead leaching from the shooting range soils and contaminating both surface and groundwater.

4.3 Lead Fractionation and Partitioning in the shooting range soils

Sequential extraction (SE) is a process used to determine the mobility, leaching potential and distribution of lead in the soil. SE is effective for monitoring shooting range soils^{18,76} as the use of total Pb concentration as a criterion to assess its potential effects to the shooting range soils may imply that all its forms have equal impact to the environment but this is not the case⁶⁴. SE assesses the retaining, chemical mobility, leaching and distribution of Pb in the different soil compartments. It assumes that with each extractant, different fractions of lead in soils can be determined. It is a five-step process: the water extractable, organic bound, Carbonate bound, Fe-Mn bound and the residual fraction. Metals in the Water Extractable

fraction are readily available in the environment, whilst the metals in the Residual Fraction are held tightly and are not easily released under natural conditions⁵⁷.

It is important to note that the partitioning of Pb in the different soil fractions is largely dependent on the chemical and physical characteristics of the soils such as the soil pH, organic matter and cation exchange capacity. In all the seven shooting ranges studied, Pb existed mostly in the carbonate fraction (CB), 36-53% (Figure 20) followed by OB (2-41%)>FM (0-28%)>WE (1-27%)>RS (0-3%).

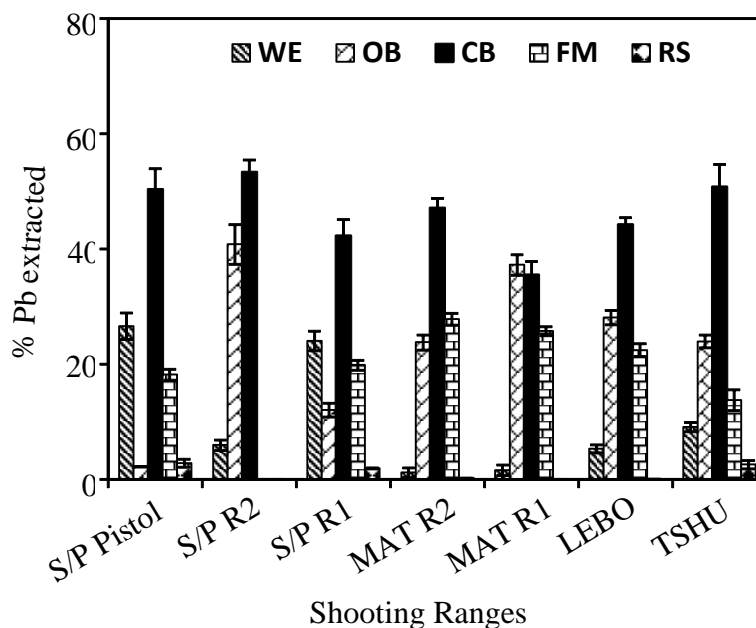
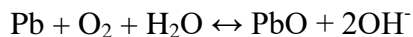


Figure 20: Fractionation of lead in soils at the Northern and North Eastern shooting ranges in Botswana. WE- Water Extractable, OB- Organic Bound, CB- Carbonate Bound, FM- Fe-Mn Oxides Bound and RS- Residual Fraction.

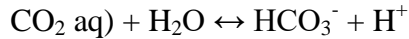
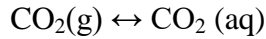
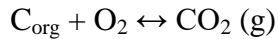
The high percentages of lead in the carbonate fraction have been explained by the reactions that lead bullets undergo upon leaving the gun. The lead is oxidised by air to form PbO, which is then acted upon by carbon dioxide and moisture to give rise to Lead carbonates³¹; cerussite and hydrocerussite.

The following is a series of reaction of how these carbonates are formed⁵⁰

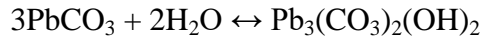
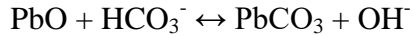
1. Oxidation of metallic lead



2. Oxidation and conversion of organic carbon



3. Formation of cerussites



The pH of the soil plays an important role in the stability of the Pb fractions. At high pH (alkaline), the Pb oxides and carbonates become more stable and inert to chemical reactions and dissolutions. In all the ranges studied, ranges that experienced the highest carbonate-bound Pb such as TSHU, S/P R2, MAT R2 and MAT R1 possessed soil pH in the range 7.55 – 8.69 as shown in Table 5 below. According to previous studies high soil pH stabilizes the lead carbonates formed in the soils and thereby limits their migration ⁴⁶. Our findings of the pH dependent existence of the carbonates have also been described elsewhere. It was found out that the Pb carbonates (cerussites) and Pb hydroxyl carbonates (hydrocerussites) were the most prevalent species at high pH in the shooting ranges studied ⁸³.

Table 5: Soil properties of the seven shooting ranges studied

Range	pH _w ± δ ^a	Organic Matter (%) ± δ	CEC ^b ± δ
S/P PISTOL	6.81 ± 0.01	0.52 ± 0.11 ^c	8.20 ± 0.11
S/P R2	8.20 ± 0.01	0.88 ± 0.15	10.24 ± 0.22
S/P R1	7.30 ± 0.01	0.65 ± 0.01	11.93 ± 0.21
MAT R2	8.36 ± 0.02	2.13 ± 0.02	21.87 ± 0.07
MAT R1	8.69 ± 0.01	1.32 ± 0.01	20.60 ± 0.24
LEBO	7.50 ± 0.01	1.10 ± 0.11	27.05 ± 0.31
TSHU	7.55 ± 0.01	0.31 ± 0.08	9.26 ± 0.22

^aδ = Standard deviation

^bCation exchange capacity

^cMean ± standard deviation (*n* = 3)

Other soil properties such as organic matter and cation exchange capacity are also vital in the weathering of lead in soils. Organic matter acts a cumulative primary sink for lead in surface soils, but as the lead load increases the stability of the Pb-Complexes reduces and makes the lead bound by the organic matter susceptible to leaching especially in soils with low pH⁴⁰. Increasing soil pH can help with inhibiting the lead downward movement.

Ma's research group was able to find that the removal of soil organic matter prevented the weathering and transformation of Pb shots and bullets into Pb-oxides and Pb-carbonates²⁹. The micro-organisms in the soil rich in organic matter produce CO₂ and make it available for the transformation of lead bullets and shots into Pb oxides and carbonates⁸⁴. The humic and fulvic acids present in the organic matter can bind with Pb on the surface of the Pb shots and bullets and thereby accelerating the weathering of the Pb shots and bullets by exposing new surfaces to weathering processes³⁰.

All of the seven shooting ranges studied contained substantial amount of organic matter in the range 0.31-2.13% OM. The elevated levels of organic matter in the shooting range berm soils corroborated well with the partitioning of Pb in OM fraction. The amount of organic matter present at MAT R2 was 2.13% OM and this shooting range contained the highest organic matter than any other range in this study. Typical for such high content of organic matter, the MAT R2 accumulated the highest total Pb concentration of 20882.55 ± 5419.27 mg/kg in the

berm soil corroborating the above-mentioned theory of organic matter acting as a sink for lead in surface soils (Figure 20). This implies that most of the Pb shots and bullets that accumulated into the MAT R2 berm soil weathered away and the metallic Pb in the bullets was transformed into more reactive Pb complexes in the soil thereby increasing the mobility and bioavailability of Pb in the soil. The high pH's of the Matsiloje ranges and Selibe Phikwe range 2 mean that the lead bound to the OM fraction in these ranges can be assumed to be immobile. Problem is these are areas that receive the highest amounts of rainfall (Figure 16) during the rainy season which poses serious threats of leaching and downward migration as mentioned by Bricka, 2000²²

The soil cation exchange capacity (CEC) was also found to be an important factor in the weathering, transformation, mobility and bioavailability of Pb. The binding capacity of metals such as lead in soils is governed by the soil's CEC, which is a measure of the amount of exchangeable cations that can be retained by a given mass of soil (Cheng et al, 2012). The higher the CEC the higher the soils binding capacity leading to reduced Pb mobility and bioavailability³¹. LEBO, MATS R1 and MATS R2 had high CEC values reaching 27.05 cmol/kg in the LEBO range (Table 5). S/PIST had the lowest CEC and pH values of 8.20 cmol/kg and 6.81 cmol/kg respectively. The low CEC and slightly acidic conditions provide a conducive environment for lead mobility in this range. As for the MAT R2 range the combination of high CEC (21.87 cmol/kg) and other factors such as high pH and high soil organic matter implies that the soils at this range are able to retain high concentrations of Pb. Cao and colleagues found total Pb concentration in berm soils of MPR shooting range as high as 48 400 mg/kg with the corresponding high CEC of 43.2 cmol/kg compared to the total Pb concentration of 12 710 mg/kg with corresponding CEC of only 8.51 cmol/kg at TRR shooting range³¹.

4.4 Lead mobility and bioavailability Potential

The mobility of Pb in shooting range soils describes its potential to become mobile and thereby posing a danger to the ecosystem. All the seven shooting ranges studied experienced the highest Pb mobility of over 90% (Figures 21 a-b below).

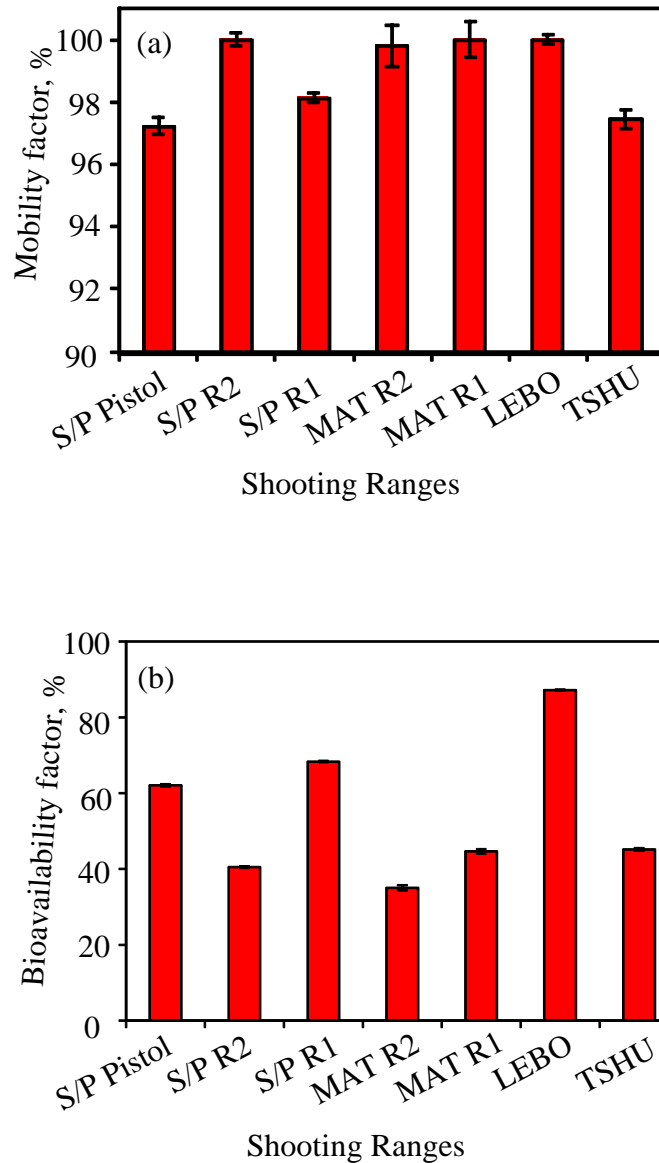


Figure 21 (a) Mobility factor (%) and (b) Bioavailability factor (%) of Pb in the berm soils of 7 shooting ranges found in Eastern and Northern Botswana

The high Pb mobility signals the high Pb lability in the shooting range soils. The high mobility of Pb in the shooting ranges studied corroborates our sequential extraction findings in which most of the Pb is restricted to the carbonate fraction which can easily dissolve under favourable environmental conditions. Other factors such as pH, organic matter content and cation exchange capacity affect the mobility of Pb. It has been found that soils with high content of other metals present unfavourable conditions for Pb mobility⁸⁵. The toxicity and bioavailability of Pb in the soil is highly dependent on the chemical species that Pb exists in. The bioavailability index of Pb in the shooting range soils was evaluated. The bioavailability index was calculated in the range 35-87% for all the seven shooting ranges studied. More than 50% of Pb was found to be bioavailable in three of the seven shooting ranges. Pb in LEBO shooting range had the greatest chance of being accumulated in plants with bioavailability index of 87% and MAT R2 Pb was the least bioavailable at 35%. Aikpokpodion and colleagues were able to determine that the uptake of heavy metals by cocoa plants was greatly affected by the chemical speciation of the heavy metals in the soil⁸⁶

4.5 Mineralogical and chemical transformation of lead in shooting range soils

Almost all the seven shooting ranges studied were characterised by lead carbonates (cerussite and hydrocerussites) as the predominant weathering products as depicted in Figures 22-27 below.

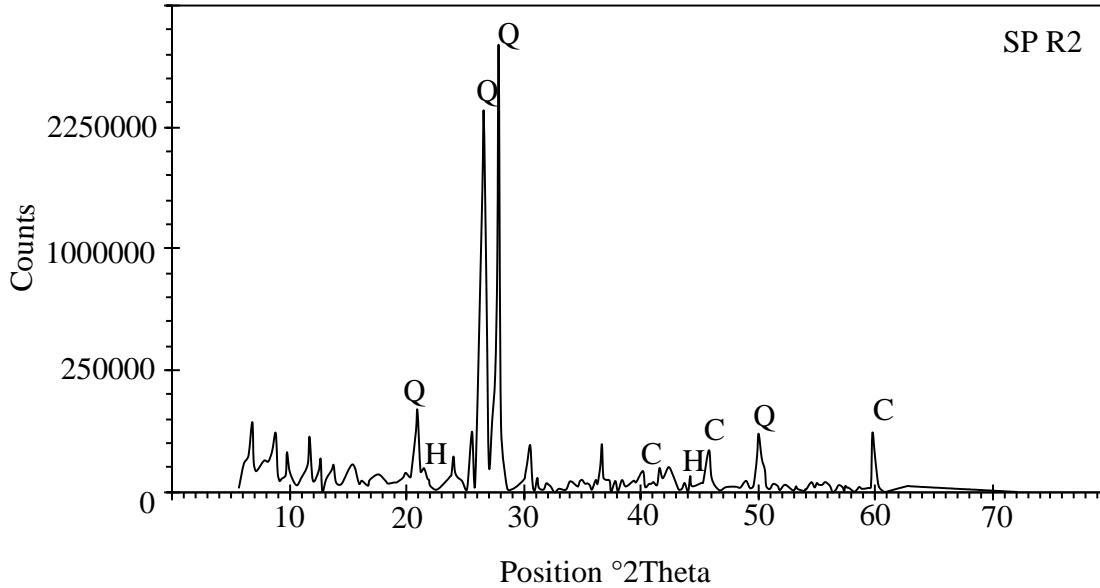


Figure 22: XRD pattern showing the weathering products of Pb bullets at SP R2

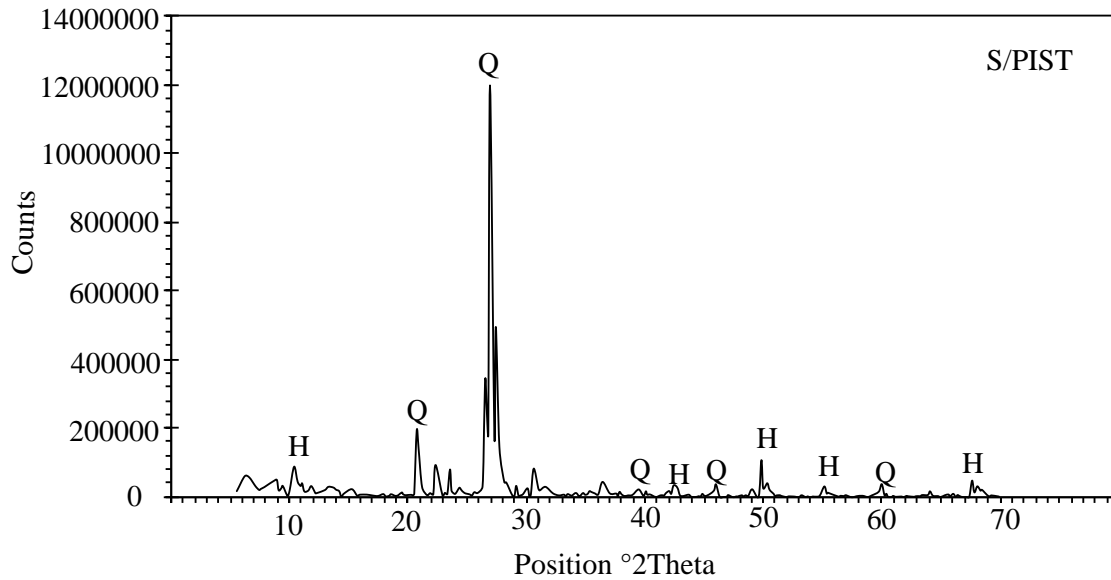


Figure 23: XRD pattern showing the weathering products of Pb bullets at S/PIST

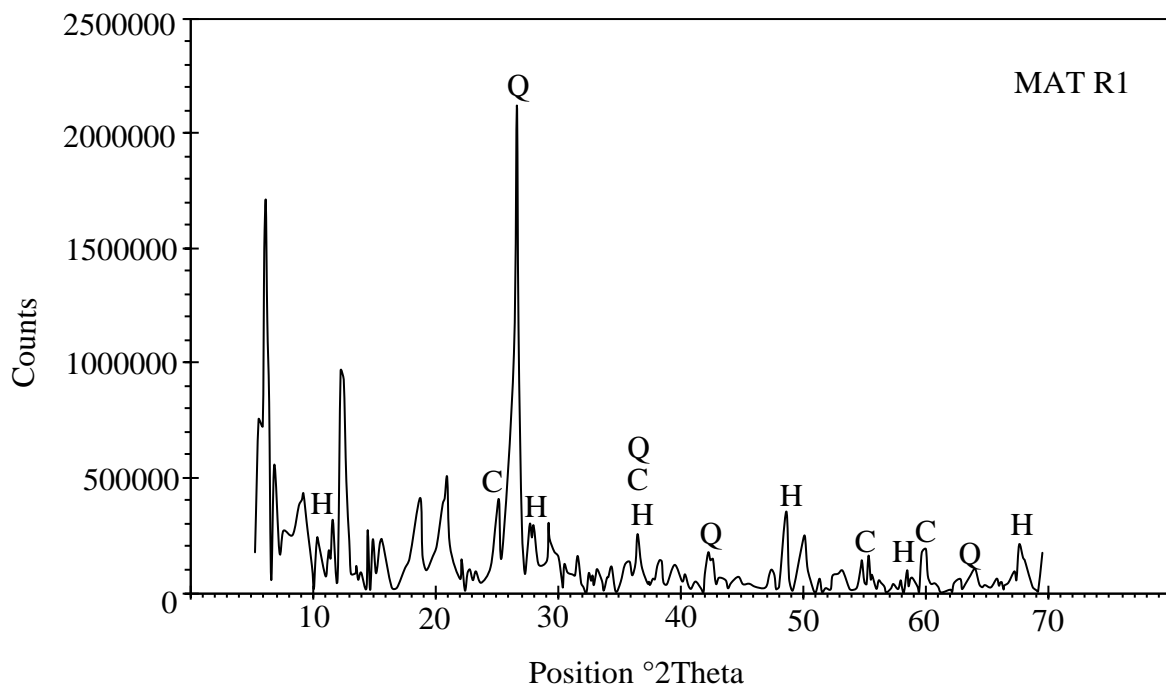


Figure 24: XRD pattern showing the weathering products of Pb bullets at MAT R1

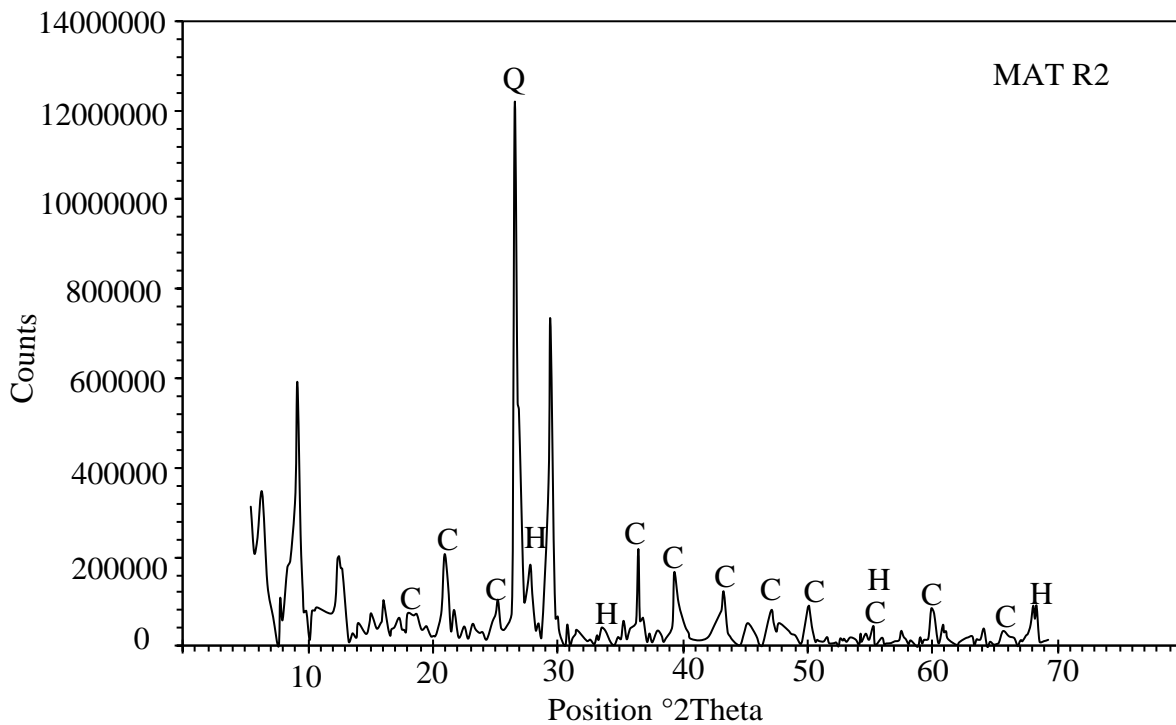


Figure 25: XRD pattern showing the weathering products of Pb bullets at MAT R2

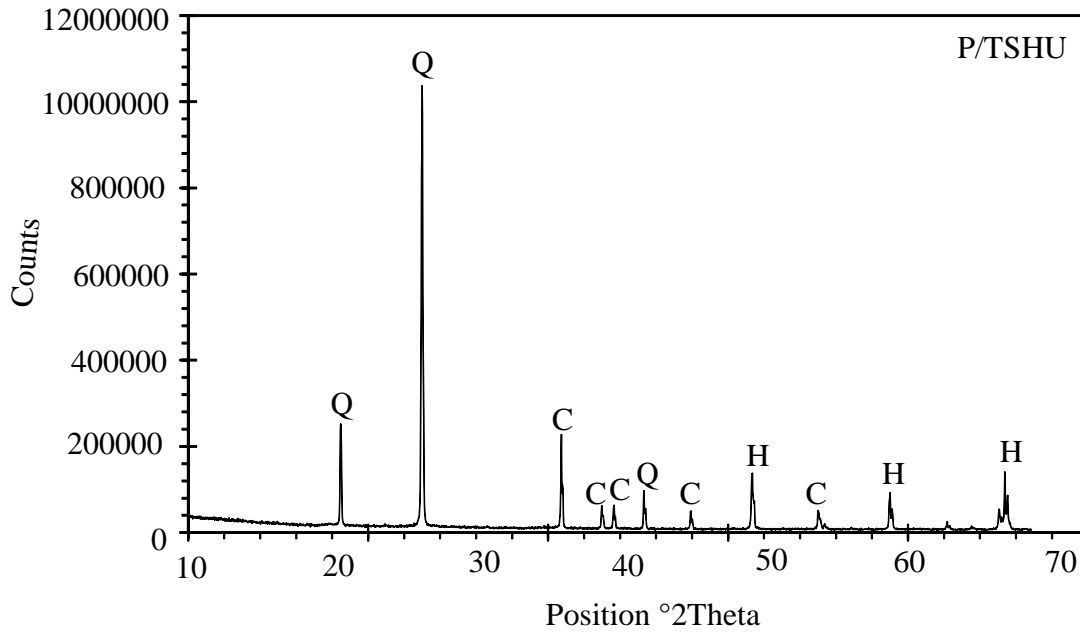


Figure 26: XRD pattern showing the weathering products of Pb bullets at P/TSHU

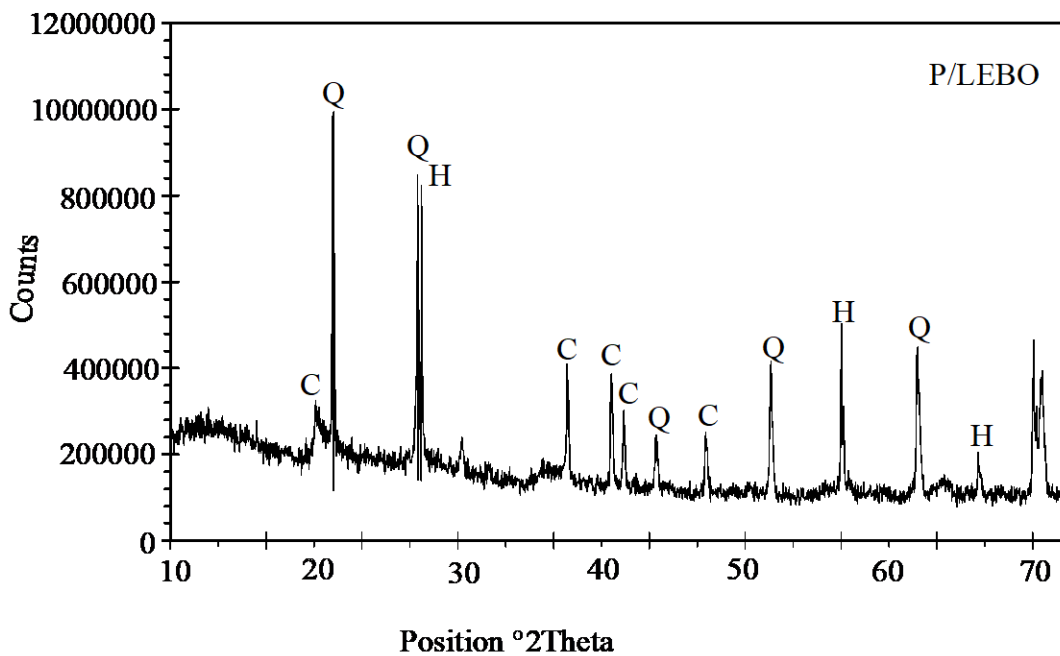


Figure 27: XRD pattern showing the weathering products of Pb bullets at P/LEBO

At the S/PIST shooting range, hydrocerussite was the only dominant Pb carbonate weathering product with no trace of other Pb carbonates. The other six shooting ranges had a mixture of both cerussite and hydrocerussite as predominant weathering products. A study carried out by Dermatas et al. ³⁵ showed that the carbonates are some of the dominant weathering products of Pb bullets and shots in shooting range soils

The elevated levels of carbonate bound Pb in the berm soils, has been explained to be due mainly to the oxidation of metallic Pb bullets and shots and the conversion (by action of carbon dioxide and moisture) of the oxidised Pb (PbO) to Pb carbonates such as cerussites and hydrocerussites ^{18,31}. These results corroborate the fractionation study (Figure 20) which showed that most of the lead in these soils is carbonate bound.

4.6 SEM images of the sampled areas

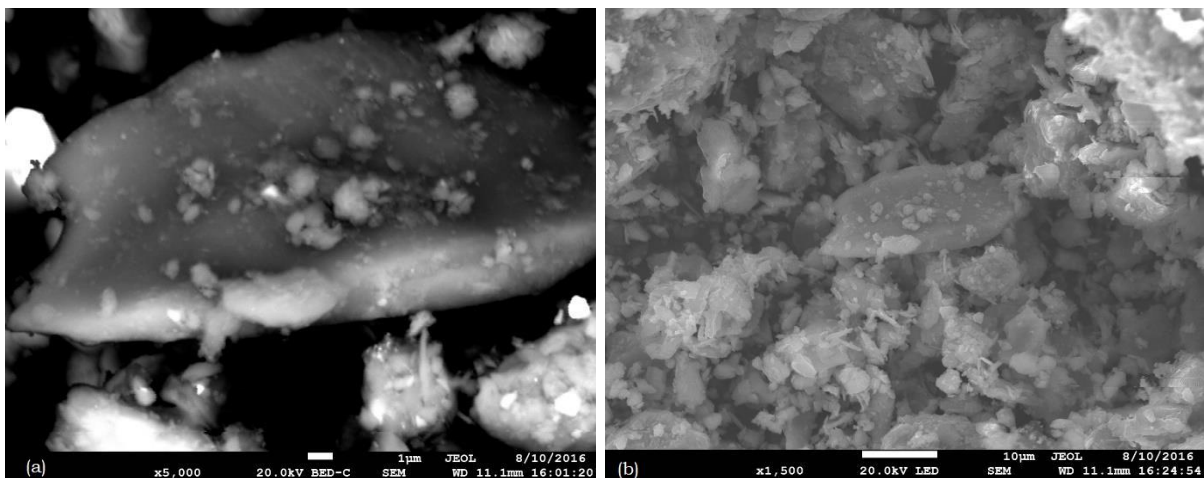


Figure 28: SEM images of the soil samples

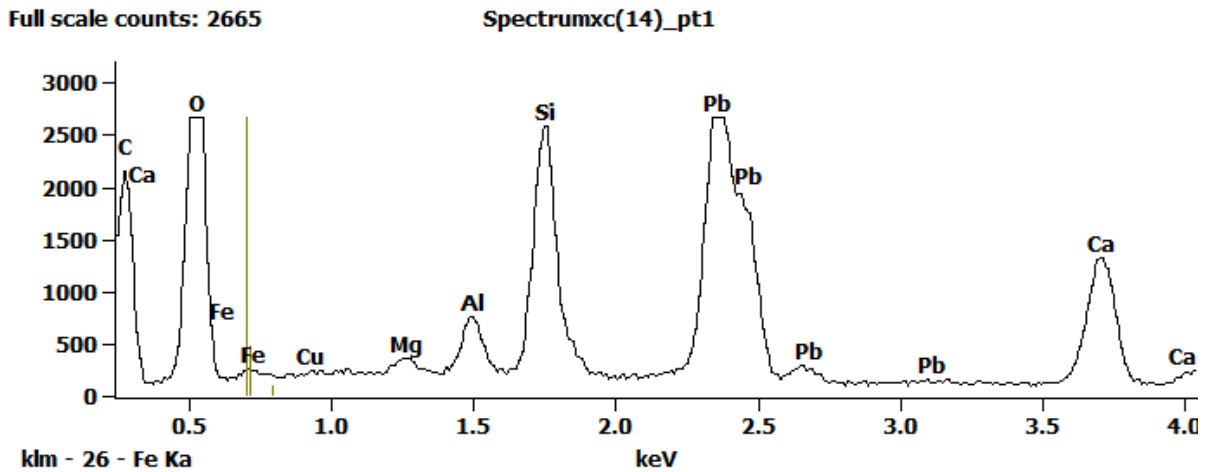


Figure 29: Spectrum showing the quantification of elements in the shooting range soils

Wed Aug 10 16:20:22 2016

Filter Fit Chi² value: 2.817

Correction Method: Proza (Phi-Rho-Z)

Acc. Voltage: 20.0 kV

Take Off Angle: 31.1°

SEM analysis showed that these soils at the shooting ranges contain lead, carbon and oxygen. These corroborate the fractionation (SE) and XRD results which showed that most lead at these shooting ranges is in the form of carbonates.

CONCLUSIONS

Total Pb pollution in all the seven shooting ranges studied far exceeded the USEPA critical value of 400 mg/Kg. Total Pb concentrations in the berm soils were in the range 600–21000 mg/kg. MAT R2 experienced the highest pollution compared to other shooting ranges due to favourable environmental conditions such pH, organic matter and cation exchange capacity. The elevated Pb pollution in these shooting ranges pose adverse effects to human beings living in close proximity of the shooting ranges. Plants growing near the shooting ranges are also at risk from Pb poisoning and eventual death due to uptake of Pb by these plants as shown by the high bioavailability index (up to 87%) of the shooting range soils studied. The mobility factors were all over 90% in all the shooting ranges studied. Both ground and underground water run the risk of being contaminated. All the seven shooting ranges studied failed the synthetic precipitation leaching procedure (SPLP). The SPLP Pb concentrations in all the seven shooting ranges exceeded the USEPA critical level of 0.015 mg/kg. The fractionation studies showed that most of the Pb in all the shooting ranges was confined in the carbonate fraction. To remedy soil pollution in shooting ranges, best shooting range management practices should be enforced. Remedial measures such as soil cleaning and immobilization of Pb to reduce its solubility; mobility and bioavailability have been found to greatly reduce the impact on Pb in shooting range soils.

RECOMMENDATIONS

1. Remedial actions such as monitoring and adjusting soil pH by liming; immobilization of Pb using phosphates and controlling run off using vegetative cover to be implemented in Botswana.
2. Removal of lead from the ranges via hand raking, sifting, vacuuming and soil washing for reclamation and recycling could also be implemented.
3. Shooting range workers, inhabitants and visitors to be vigilant in their health and safety measures especially the use of protective clothing such as masks to prevent inhalation of Pb-ridden dust during training exercises. Also, protective clothing such as boots, gloves and coveralls to be washed/cleaned on site to prevent transference of Pb into homes and other places.
4. Blood lead level tests to be offered to shooting range users for monitoring purposes.
5. Documentation of number, size and type of rounds fired; keep records for the life of the range and up to 10 years after closing and evaluate effectiveness of the BMP's employed at ranges. This could also assist in policy formulation for better management of Pb pollution in shooting ranges.

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