QUANTITATIVE ASSESSMENT OF STATIC VERSUS DYNAMIC ENVIRONMENTAL POLLUTION RISK FROM LEAD POLLUTION AT SHOOTING RANGES

By

Nicholas Sehube

14100208

BSc, (UB)

Department of Chemical and Forensic Sciences
Faculty of Science
Botswana International University of Science and Technology

Email: nicholas.sehube@studentmail.biust.ac.bw Cell: (+267)74970218

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 Degree in Chemistry

Supervisor: Dr Pogisego Dinake
Department of Chemical and Forensic Sciences
Faculty of Science
Botswana International University of Science and Technology
Email: dinakep@biust.ac.bw Contact No.: (+267) 4931538
Signature:
Date: 08/07/2020

February, 2020

PEER REVIEW PUBLICATIONS

[1] Pogisego Dinake, Rosemary Kelebemang, **Nicholas Sehube**, Tsotlhe Trinity Kereeditse and Obakeng Motswetla. Dynamic risk assessment of lead pollution of shooting range soil by applying the delayed geochemical hazard model – A case study in Botswana, *Soil and Sediment Contamination: An International Journal.* **Accepted Manuscript, 2020**.

[2] Pogisego Dinake, Rosemary Kelebemang and **Nicholas Sehube**. A Comprehensive Approach to Speciation of Lead and Its Contamination of Firing Range Soils: A Review, *Soil and Sediment Contamination: An International Journal.* **2019**;2:431–459. https://doi.org/10.1080/15320383.2019.1597831.

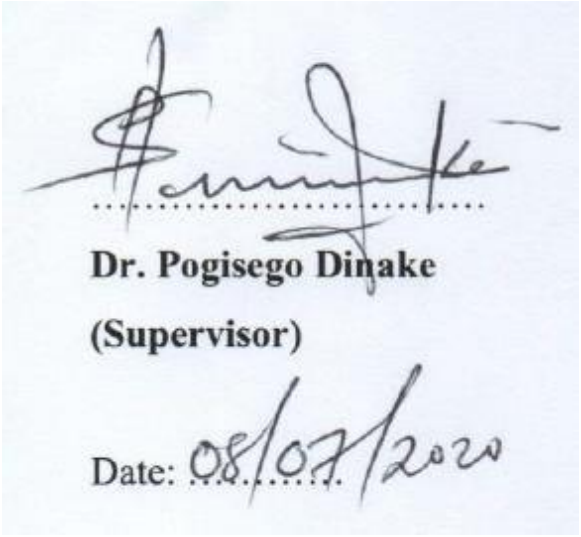
[3] Pogisego Dinake, Rosemary Kelebemang, **Nicholas Sehube**, Obed Kamwi and Masego Laetsang. Quantitative assessment of environmental risk from lead pollution of Shooting range soils, *Chemical Speciation & Bioavailability.* **2018**;30:76–85. https://doi.org/10.1080/09542299.2018.1507689.

[4] **Nicholas Sehube**, Rosemary Kelebemang, Otlogetswe Totolo, Masego Laetsang, Obed Kamwi and Pogisego Dinake. Lead pollution of shooting range soils. *South African Journal of Chemistry*. **2017**;70:21–28. http://dx.doi.org/10.17159/0379-4350/2017/v70a4.

[5] Rosemary Kelebemang, Pogisego Dinake, **Nicholas Sehube**, Boniface Daniel, Otlogetswe Totolo and Masego Laetsang. Speciation and mobility of lead in shooting range soils. *Chemical Speciation & Bioavailability*. **2017**;29:143–152. https://doi.org/10.1080/09542299.2017.1349552

CERTIFICATION

The undersigned certifies that he has read and hereby recommends for acceptance by the Faculty of Science a thesis titled: **'Quantitative assessment of static versus dynamic environmental pollution risk from lead pollution at shooting ranges'** in fulfilment of the requirements for the degree of Master of Science in Analytical Chemistry of the BIUST.



ACKNOWLEDGEMENTS

I would love to acknowledge All Mighty God for giving me strength and opportunity to finish this project. My special appreciation goes to my supervisor Dr Pogisego Dinake, for his unwavering support throughout this project. He has been very patient and supportive both academically and morally. I thank Rosemary Kelebemang, Department of Chemical and Forensic Sciences staff at BIUST, Botswana Defence Force, Botswana Geoscience Institute chemistry staff for the different roles they played in this project.

DEDICATION

I dedicate this thesis to my lovely grandmother, Ms Bonno Sehube, who is celebrating her 90th birthday this year.

SUMMARY

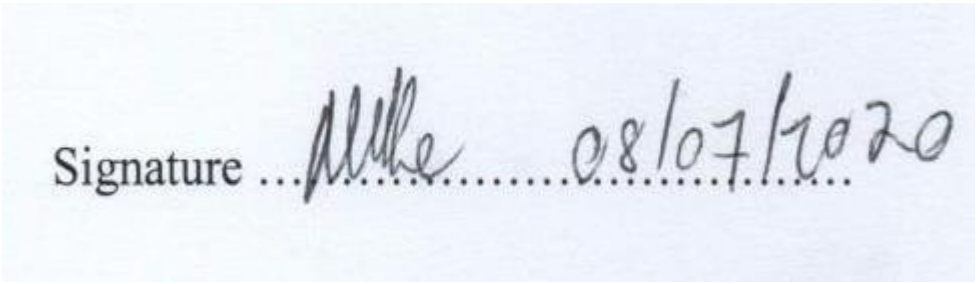
This research study investigated Pb pollution of soils in eight shooting ranges found in Botswana. Many studies have considered total Pb concentration in the soil as a measure of the degree of pollution in the soil. However, total Pb concentration does not give any information on the possible chemical and mineralogical forms of Pb in the soil nor does it give quantitative data on pollution risk to the environment posed by such high total Pb concentrations in the soil. As a result, methods such as sequential extraction procedures were also carried out in this study in order to determine the different chemical forms of Pb in the soil which gives insight into their reactivity and solubity states. This also helps establish the different chemical forms of Pb present in the soil and whether they are inert or labile which gives appreciation of the degree of mobility and biovailability of Pb in the soil. Pollution risk assessment indices such as contamination factor (*CF*), enrichment factor (*EF*) and potential ecological risk index (*PERI*) were used to quantify Pb pollution risk to biota. In addition, total Pb concentration in the soil views environmental pollution as a static process whereas by its nature it is a dynamic process which is dependent on the physicochemical properties of the environment and the holding capacity of the environment. The delayed geochemical hazard (DGH) model was used to map the environmental pollution risk from Pb as a dynamic process as opposed to static. The DGH model describes the potential transformation and release of Pb partitioned in the different fractions of the soil that may be inert but becoming reactive when the conditions of the soil such as pH, moisture and organic matter become favourable or when the Pb deposited into the soil exceeds the soil holding capacity. Soil reclamation and remediation strategies have been suggested for controlling and managing Pb pollution at military shooting ranges found in Botswana.

ANTI-PLAGIARISM REPORT

This Thesis has been checked using the TURNITIN Plagiarism software provided by Botswana International University of Science and Technology with a score of less than 16%.

DECLARATION AND COPYRIGHT

I, **Nicholas Sehube**, declare that this thesis is my own original work and that it has not been presented and will not be presented to any other university for a similar or any other degree award.



This thesis is copyright material protected under the Berne Convention, the Copyright Act of 1999 and other international and national enactments, in that behalf, on intellectual property. It must not be reproduced by any means, in full or in part, except for short extracts in fair dealing; for research, private study, critical scholarly review or discourse with an acknowledgement, without the written permission of the office of the Provost, on behalf of both the author and the BIUST.

TABLE OF CONTENTS

TITLE PAGE i

PEER REVIEW PUBLICATIONS ii

CERTIFICATION iii

ACKNOWLEDGEMENTS iv

DEDICATION v

SUMMARY OF THE CONTENTS vi

ANTI-PLAGIARISM REPORT vii

DECLARATION AND COPYRIGHT viii

TABLE OF CONTENTS ix

LIST OF TABLES xiii

LIST OF FIGURES xiv

ACRONYMS xvi

ABSTRACT xviii

CHAPTER 1 1

1. INTRODUCTION 1

1.1. Physicochemical Characteristics of Lead (Pb) 1

1.2. Occurrence of Pb in nature and its uses 1

1.3. Toxicity associated with exposure to Pb 3

1.4. Ammunition as a source of Pb pollution at shooting ranges 7

1.4.1. General layout of a shooting range and Pb distribution patterns *7*

1.4.2. Structure of ammunition *8*

1.4.3. Environmental pollution risk from Pb in ammunition *11*

1.5. Static environmental pollution risk versus dynamic pollution risk 12

1.6. Assessment of soil pollution from Pb-containing ammunition used in Botswana 14

1.7. Statement of the problem 14

1.8. Objectives of the study 15

1.8.1. **General Objective** 15

1.8.2. **Specific Objectives** 15

CHAPTER 2: 16

2. BACKGROUND 16

2.1. Pollution of shooting range soils from Pb shots and bullets 16

2.2. Spatial Pb loading and distribution in shooting range soils 18

2.3. Effect of soil physicochemical properties on Pb weathering and transformation 30

2.3.1. The effect of soil pH *30*

2.3.2. The effect of soil organic matter *32*

2.3.3. The effect of soil cation exchange capacity *32*

2.3.4. The effect of soil moisture *33*

2.3.5. The effect of soil type and texture *34*

2.4. Speciation and fractionation of Pb in the soil 35

2.5. Simulation of potential underground water contamination – synthetic precipitation leaching procedure (SPLP) 37

2.6. Quantitative evaluation of pollution risk to the environment from Pb deposition 38

2.6.1. Evaluation environmental pollution risk using contamination factor *39*

2.6.2. Quantitative assessment of environmental pollution risk using the enrichment factor *40*

2.6.3. Assessment of ecological risk using potential ecological risk index *41*

2.7. Evidence of uptake of Pb by vegetation 43

2.8. Soil reclamation and remediation techniques applied to Pb polluted shooting range soils 45

2.8.1. Chemical amendments applied to polluted shooting range soils *46*

2.8.1.1. Phosphate addition… *48*

2.8.1.2. Liming *53*

2.8.1.3. Iron based sorbents… *55*

2.8.2. Phytoremediation *57*

2.8.3. Other Soil Remediation Strategies *58*

CHAPTER 3 59

3. EXPERIMENTAL/METHODOLOGY 59

3.1. Description and characteristics of sampling locations 59

3.2. Sampling of shooting range soils 61

3.3. Chemicals and reagents used in the study 62

3.4. Glassware used in the project 63

3.5. Sample preparation and analysis 63

3.6. Lead fractionation studies 64

3.7. Simulation of acid rain – leaching test 65

3.8. Physicochemical properties of shooting range soils 65

3.9. Soil sampling scheme at TAB shooting range for application of the delayed geochemical hazard (DGH) model 65

CHAPTER 4 67

4. RESULTS AND DISCUSSION 67

4.1. Physicochemical properties of shooting range soils 67

4.2. Spatial distribution of Pb in shooting range soils 68

4.3. The Tessier method of sequential extraction for determination of Pb partitioning shooting range soils 71
4.4. Chemical transformation of Pb shots and bullets 73
4.5. Simulation of acid rain through the synthetic precipitation leaching procedure 76
4.6. Quantification of environmental risk from Pb pollution 77
4.6.1. Quantification of environmental pollution risk using contamination factor (CF) *77*
4.6.2. Quantification of environmental pollution risk using enrichment factor (EF) *78*
4.6.3. Quantification of environmental pollution risk using potential ecological risk index (PERI) 79
4.7. Static risk assessment of Pb pollution at TAB shooting range soils 80
4.8. Delayed geochemical hazard (DGH) Model 82
4.8.1. Description of the delayed geochemical hazard model 82
4.8.2. Dynamic risk assessment of Pb pollution using the delayed geochemical hazard (DGH) Model 84
4.8.3. The pathway and mechanism of the DGH Model 88
5. RECOMMENDATIONS AND FUTURE STUDIES 89
6. CONCLUSIONS 90
7. REFERENCES 92

LIST OF TABLES

Table 1.1 Physical properties of Pb…..... 1
Table 1.2 Different Pb compounds and their use 3
Table 1.3 Maximum contaminant level (MCL) of Pb in soil, drinking water and livestock drinking water 6
Table 2.1 Comprehensive research studies for the past 35 years on contamination of shooting range soils from Pb… 19
Table 2.2 Classification of contamination factor from Pb pollution…..... 39
Table 2.3 Categories of enrichment factor 41
Table 2.4 Potential Ecological risk index and the corresponding ecological risk level…..... 42
Table 3.1 Location of shooting ranges and types of soils found at each range..... 60
Table 3.2 Five steps sequential extraction procedure as adapted from Tessier *et al.* (1979). 64
Table 4.1 Soil chemical properties…..... 67
Table 4.2 Pb concentration in different chemical fractions…..... 81
Table 4.3 Fitting nonlinear polynomials and the corresponding DGH characteristics for Pb in the studied area 85

LIST OF FIGURES

Figure 1.1 Lead blast furnace..... 2

Figure 1.2 Toxicity of Pb in adults 4

Figure 1.3 Toxicity of Pb in children… 5

Figure 1.4 (a) Lead sinker, fishing tackle and gizzard stones removed from loon gizzard. (b) Radiograph showing ingested lead fragments in the ventricles of a bald eagle….....6

Figure 1.5 Schematic layout of the shooting range..... 7

Figure 1.6 Structure of ammunition showing the cartridge and projectile containing Pb slug.9

Figure 1.7 Ore heads or projectiles that collect into shooting range soils indicating presence of Pb and Sb as the main slug components… 9

Figure 1.8 Processes taking place when a rifle is being fired… 10

Figure 1.9 The effect on the bullet/ore head/projectile upon hitting the impact berm/stop butt 11

Figure 3.1a Location of shooting ranges in Botswana.....60

Figure 3.1b Location of Botswana in southern africa..... 60

Figure 3.2 The rainfall amounts at the sampled sites for the period July 2013 to June 2014….....61

Figure 3.3 Schematic diagram of shooting range showing sampling points.....62

Figure 3.4 Schematic layout of a shooting range indicating sampling points….....66

Figure 4.1 Concentrations of Pb in soil collected from; (a) berm; (b) target line; (c) 50 m and (d) 100 m from target line at eight shooting ranges found in Botswana, Mean of n = 3; Standard error of the mean, $\delta = \delta/\sqrt{n}$, where δ = standard deviation… 70

Figure 4.2 Concentrations of Pb in Background soils taken 200 m from eight shooting ranges in Botswana. Mean of $n = 3$; Standard error of the mean, $\delta_x = \delta/\sqrt{n}$, where δ = standard deviation…..... 71

Figure 4.3 Different chemical fractions of Pb in shooting range soils found in Botswana. WE (water-soluble and exchangeable), OB (organic-bound), CB (carbonate-bound), FM (Fe-Mn oxides) and RS (residual)…..... 73

Figure 4.4 X-ray diffraction patterns showing mineralogical and transformation products of Pb shots and bullets in shooting range soils. Q (Quartz), C (Cerussite) and H (Hydrocerussite)…..... 75

Figure 4.5 Concentration of Pb measured after simulation of acid rain procedure (SPLP) at eight shooting ranges found in Botswana. Mean of $n = 3$; Standard error of the mean,

$\delta_x = \delta/\sqrt{n}$, where δ = standard deviation… 76

Figure 4.6 Determination of contamination factor (CF) of Pb in the berm soils.

Mean of n = 3; Standard error of the mean, δ= δ/√n, where δ = standard deviation… 77

Figure 4.7 Determination of Pb enrichment of the berm soils. Mean of n = 3; Standard error of the mean, δ= δ/√n, where δ = standard deviation… 79

Figure 4.8 Determination of potential ecological risk index (*PERI*) of Pb in the berm soils. Mean of n = 3; Standard error of the mean, δ= δ/√n, where δ = standard deviation… 80

Figure 4.9 Graphical representation of the DGH model and its digital characteristics… 83

Figure 4.10 Fitting curve for the relationship between $TCAS_{Pb}$ ($Pb_{(E)}$) and $TRCP_{Pb}$ ($Pb_{(E+C+F+O)}$) at TAB shooting range 88

Figure 4.11 Geochemical release routes of DGH_{Pb} at TAB shooting range 89

ACRONYMS

BCR: Bureau Communautaire de Reference

BOBS: Botswana Bureau of Standards

BMP: Best Management Practices

CB: Carbonate bound

CEC: Cation Exchange Capacity

CF: Contamination factor

DGH: Delayed geochemical hazard

EF: Enrichment factor

FM: Fe–Mn oxides bound

ICP-OES: Inductively Coupled Plasma- Optical Emission Spectrometer

MAK: Makanke shooting range

MCL: Maximum Contaminant Limit

MOG: Mogoditshane shooting range

OB: Organic bound

OM: Organic Matter

PAJ R1: Paje shooting range 1

PAJ R2: Paje shooting range 2

PERI: Potential ecological risk index

RAC: Risk assessment code

RS: Residual fraction

SHO R1: Shoshong shooting range 1

SHO R2: Shoshong shooting range 2

SPLP: Synthetic Precipitation Leaching Procedure

TAB: Thebephatshwa shooting range

TCAS: Total concentration of active species

TRCP: Total releasable content of pollutant

TSH: Tshele shooting range

USEPA: United States Environmental Protection Agency

WE: Water soluble and exchangeable

WHO: World Health Organization

XRD: X-Ray Diffraction

ABSTRACT

Lead pollution of soil arising from use of leaded ammunition in shooting ranges has received considerable attention from researchers, scientists, policy makers and legislatures. This is due to the adverse health effects associated with exposure to Pb. Eight military shooting ranges found in Botswana were used in this research project. All the eight shooting range soils were polluted with Pb with total Pb concentrations in the range 13-38 386 mg/kg. TAB shooting range soils accumulated the highest concentration of Pb. Most of the shooting ranges studied had Pb loading of over 1000 mg/kg, far surpasing the United States Environmental Protection Agency (USEPA) set maximum contaminant limt (MCL) value of 400 mg/kg. Fractionation studies established that Pb existed mostly in the carbonate form and the X-ray diffraction (XRD) patterns showed higher proportions of the cerussite ($PbCO_3$) and hydrocerussite ($PbCO_3H_2O$). The SPLP-Pb concentrations in all the eight shooting ranges were higher than the USEPA set critical limit of 0.015 mg/kg, which indicates possible contamination of water sources. Determining total Pb concentration in shooting range soils only gives information on the amount of Pb stored in the soil but does not quantify the pollution risk to the environment. The amount of Pb deposited in shooting range soil may be in inert form, posing low risk to biota. To quantify the environmental pollution risk, pollution risk indices have been found to be suitable for this task. Contamination factor (*CF*), enrichment factor (*EF*) and potential ecological risk index *(PERI)* provided a good quantitative measure of environmental pollution risk posed by Pb accumulated in shooting range soils compared to total Pb concentration. TAB shooting range posed the highest risk to environmental pollution with highest *CF* of over 40000 indicating very high contamination and this correlated well with the amount of Pb deposited into the shooting range. In contrast, TSH shooting range experienced lower total concetration of Pb compared to MAK shooting range. However, TSH shooting range displayed a higher contamination factor (*CF*~9360) compared to MAK with CF ~ 3585 and corresponding total Pb concentrations of 13309.06 mg/kg and 25,193.19 mg/kg respectively. Similarly, TSH experienced higher enrichment factor (*EF*) than MAK with *EF* ~ 4916 and 2432 respectively.

This means that TSH shooting range posed higher environmental pollution risk than MAK even though it accumulated lower total Pb concentration compared to MAK. It should be appreciated that total Pb concentration alone does not give a complete assessment of the environmental pollution risk posed by Pb in shooting range soils. Total concentration gives a static assessment of the pollution risk and does not provide insight into the effects of physicochemical properties of the environment or its holding capacity on total Pb

concentration. Therefore, it is important to treat environmental pollution risk as a dynamic evolution process such that concentration of Pb in the environment would change with changing soil physicochemical properties and the holding capacity of the environment. The delayed geochemical hazard (DGH) model was used to show that environmental pollution risk from Pb is a dynamic process as opposed to static. The DGH model describes the potential transformation and release of Pb partitioned in the different fractions of the soil that may be inert but becoming reactive when the conditions of the soil such as pH, moisture and organic matter become favourable or when the Pb deposited into the soil exceeds the soil holding capacity. This model was applied to the TAB shooting range which is highly polluted with Pb. The findings indicated that TAB shooting range may be classified as high-risk area of Pb DGH with over 65% of Pb capable of being transformed into the mobile and bioavailable chemical forms. The high Pb deposition into shooting range soils calls for immediate remedial action. The use of chemical amendments, Pb accumulating plants and physical techniques such as soil sieving have proven to minimize Pb pollution at shooting ranges.

CHAPTER 1

1. INTRODUCTION

1.1. Physicochemical characteristics of lead (Pb)

Lead with symbol Pb (from Latin: plumbum) is a soft and heavy transition metal with high density of 11.34 g/cm^3 and malleable.[1] It has the atomic number 82, which is the highest atomic number of all stable elements. It has four stable isotopes which are Pb-204, Pb-206, Pb-207 and Pb-208. Two oxidation states of lead have been defined as Pb^{2+} and Pb^{4+}, with the latter being the more stable of the two. The physical properties of Pb are given in Table 1.1 below.

Table 1.1 Physical properties of Pb.[2]

Physical property	**Effect**
Color	Bluish-White
Malleability	Capable of being shaped or bent
Conductivity	Poor transmission of heat or electricity
Softness	Relatively Soft
Tensile	It can be stretched without breaking
Luster	A shine or glow
Crystalline structure	Face-centered cubic crystalline structure

1.2. Occurrence of Pb in nature and its uses

Lead is one of the abundant heavy metals in the earth crust and the 36th most abundant element in the environment. It rarely occurs as a pure element in the Earth crust. It occurs mostly as ores of galena or lead sulphide (PbS), anglesite or lead sulphate ($PbSO_4$), cerrusite or lead carbonate ($PbCO_3$) and mimetite ($PbCl_2 \cdot Pb_3(AsO_4)_2$).[3] It is found in the soil worldwide with mean concentrations ranging from 10 to 84 mg/kg.[4] Pb used in the industry is obtained from its ores through a smelting process. The ore is heated in a blast furnace, transforming the ore into a compound of Pb and oxygen (PbO_2) as shown in Figure 1.1 below. The lead oxide is then heated with charcoal to remove the oxygen so that pure Pb metal is obtained.

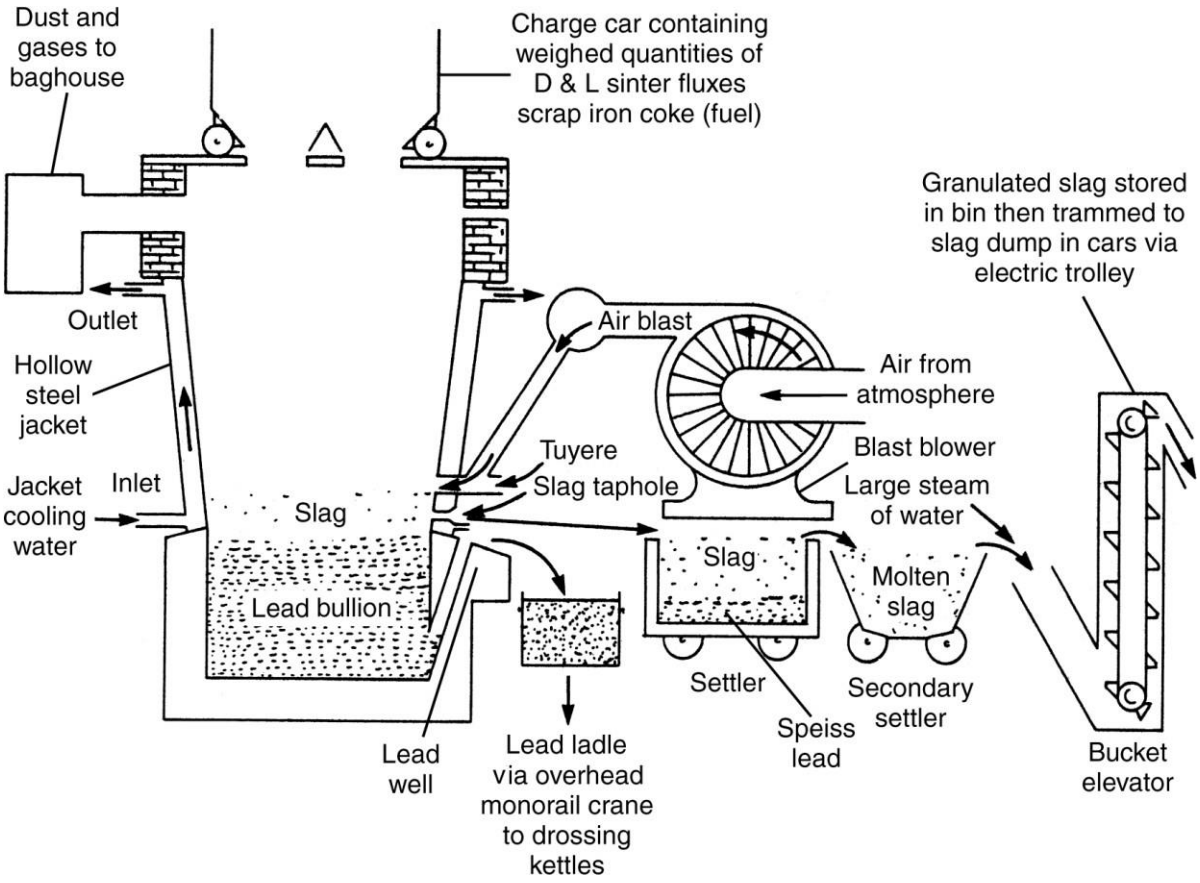


Figure 1.1 Lead blast furnace.[5]

The mining of Pb has been taking place for more than 6000 years and its compounds have been in use for a very long time.[6] The Greeks have used Pb since 650 by converting the metal into a white Pb powder and adding it to paint to give it a good covering power.[6] The Romans have also produced lead on a large scale and applied it in making water pipes, coffins, pewter tableware, to debase their silver coinage, as pottery glazes and printing type. Pb later found its use as fuel additive.[7] Pb has also been used to make Pb compounds, which were used for different applications as shown in Table 1.2 below.

Table 1.2 Different Pb compounds and their use.[8]

Pb Compound	**Use**
Lead acetate ($(Pb(C_2H_3O_2)_2$	Insecticides, waterproofing, varnishes, dyeing of cloth, production of gold and hair dye
Lead antimonate ($Pb_3(SbO_4)_2$)	Staining of glass, porcelain and other ceramics
Lead azide ($Pb(N_3)_2$)	Igniter in explosives
Lead chromate ($PbCrO_4$)	Industrial paint due to its yellow colour
Lead fluoride (PbF_2)	Lasers and specialized optical glasses
Lead iodide (PbI_2)	Photography and cloud seeding to produce rain
Lead naphthenate ($Pb(C_7H_{12}O_2)$)	Wood preservative, insecticide, additive for lubricating oil, paint and varnish drier
Lead phosphite ($2PbO \cdot PbHPO_3$)	Screens out ultraviolet radiation in plastics and paints
Lead stearate ($Pb(C_{18}H_{35}O_2)_2$)	Makes soaps, greases, waxes, paints lubricants and drier for paints and varnishes
Lead telluride (PbTe)	Makes semiconductors, photoconductors, and other electronic equipment

1.3. Toxicity associated with exposure to Pb

Anthropogenic activities such as mining and manufacturing industries increase concentration of Pb in the environment. Sources of lead exposure include products made from Pb compounds such as lead-based paint, batteries, roofing materials, toys, pottery, mining and smelting, traditional remedies and cosmetics.[9,10] Lead particles that settle on the soil from leaded gasoline around urban areas and highways lead to accumulation of Pb in the soil.

Heavy metals have the ability to accumulate in delicate parts of human beings once absorbed into the body.[11] Pb contamination is of major concern because of the dangers it poses to humans and animals. Exposure to Pb can cause a wide array of health problems in children and adults as shown in Figures 1.2 and 1.3 below.[12] The adverse health effects in humans are more pronounced in children since low levels of Pb, as low as 10 μg/dL, in children's bodies

can lead to adverse health conditions as depicted in Figure 1.3.[12]

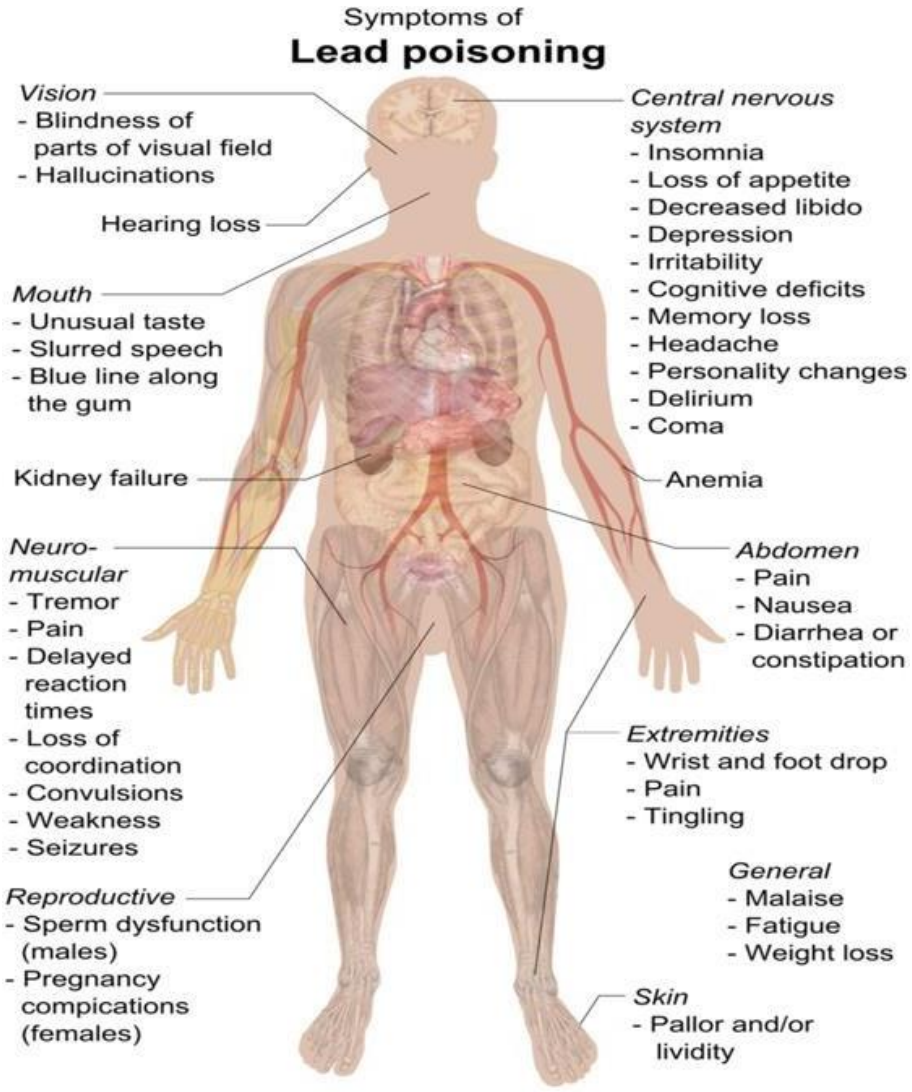


Figure 1.2 Toxicity of Pb in adults.[13]

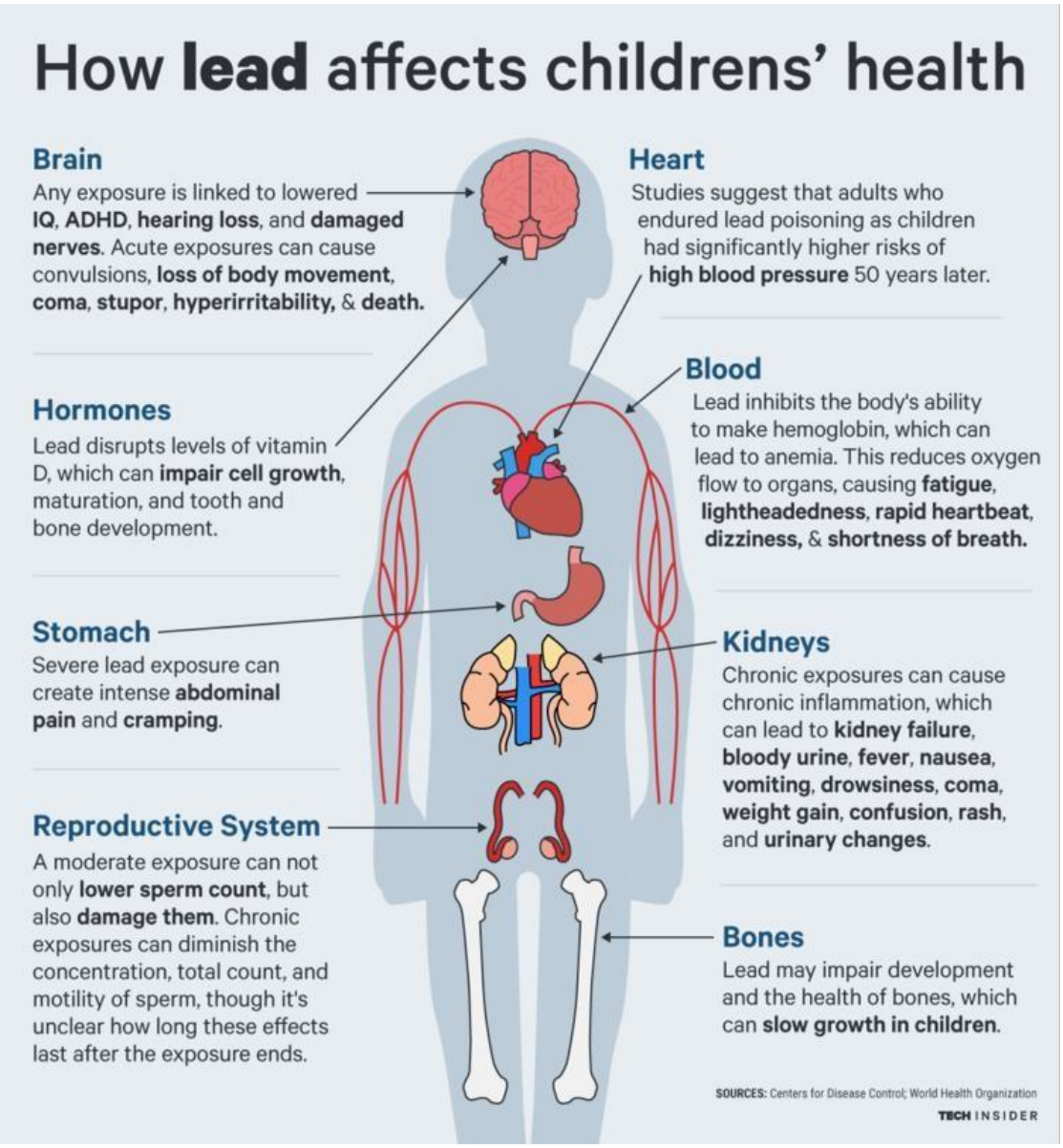


Figure 1.3 Toxicity of Pb in children.[14]

Heavy metals are dangerous to human health because they cause shortage of important nutrients to the bodies of organisms. Once heavy metals are ingested, organisms reduce their ability to absorb important nutrients which in turn weakens their immunity systems. Cancer causing symptoms have also been linked to lead ingestion.[15] Lead poisoning and toxicity is not only limited to humans, even plants and animals are also in danger. [16,17] Lead poisoning in birds emanates from various sources such as lead pellets, ingestion of lead fishing weight, eating contaminated prey animals, plant materials such as fruits, flowers and roots and contaminated water.[18,19] Lead poisoning in birds affects their nervous system, kidneys, intestines and blood cells (Figure 1.4).[19] Some of the symptoms of birds lead poisoning

include neurological signs such as blindness and head tilting may occur or a wing droop or leg paralysis. The presence of blood in birds' droppings, which is not actually blood but the breakdown product of blood, may also occur.[19] The bird starts to sit quietly with fluffed feathers. The bird may also start to exhibit noticeable weakness and depression. Loss of control and coordination of its body movements are also signs of lead poisoning in birds. Constant thirst and regurgitation of water, seizures and muscle tremors indicate lead poisoning in birds.[18,19]

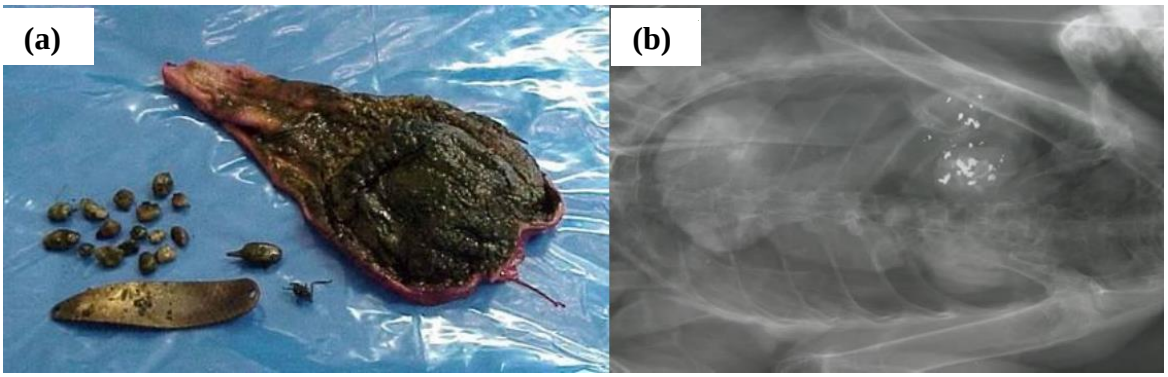


Figure 1.4 (a) Lead sinker, fishing tackle and gizzard stones removed from loon gizzard. (b) Radiograph showing ingested lead fragments in the ventricles of a bald eagle.[18,19]

Due to the toxicity associated with exposure to Pb, some countries and independent bodies regulating health issues such as the world health organization (WHO) have set maximum contaminant limits of Pb in soil, waste water and drinking water (Table 1.3).[20-24]

Table 1.3 The maximum contaminant level (MCL) of Pb in soil, drinking water and livestock drinking water.[20-24]

Regulating Body	**Soil MCL**	**Drinking Water MCL**	**Livestock Drinking Water MCL**
Botswana Bureau of Standards as noted in BOS32:2005[20]		0.01 mg/L	
United States Environmental Protection Agency (USEPA) [21-23]	400 mg/kg	0.015 mg/L	0.05 mg/L
World Health Organization (WHO) [24]	100 mg/kg	0.01 mg/L	

1.4. Ammunition as a source of Pb pollution at shooting ranges

Contamination of shooting range soils with Pb from spent bullets and shots is of environmental concern. As described earlier Pb is known to be toxic even at low concentrations below the required minimum guidelines due to its accumulative nature.[12] Heavy metals such as Pb have high affinity to the body system with minute concentrations likely to cause harm to the body.[25] It is noteworthy that Pb in ammunition is not well regulated even though the toxic characteristics of Pb are well known with some restrictions in its use. However, shooting ranges have been found to be one the main sources of Pb pollution in the environment, coming second to the battery manufacturing industry.[26] As a result, the contamination of shooting range soils 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 exposure to Pb.

1.4.1. General layout of a shooting range and Pb distribution patterns

The general layout of a shooting range includes a backstop berm, target lines and firing lines or firing bay (Figure 1.5). The firing line is usually a certain distance from the target line and it is the point where shooters stand and discharge bullets and shots towards the targets.[27] The target line on the other hand is an area closest to the impact berm where targets are erected. The berm is normally a hip of soil used to absorb and contain bullets and shots that have penetrated the targets. The schematic diagram in Figure 1.5 below shows the layout of a shooting range.

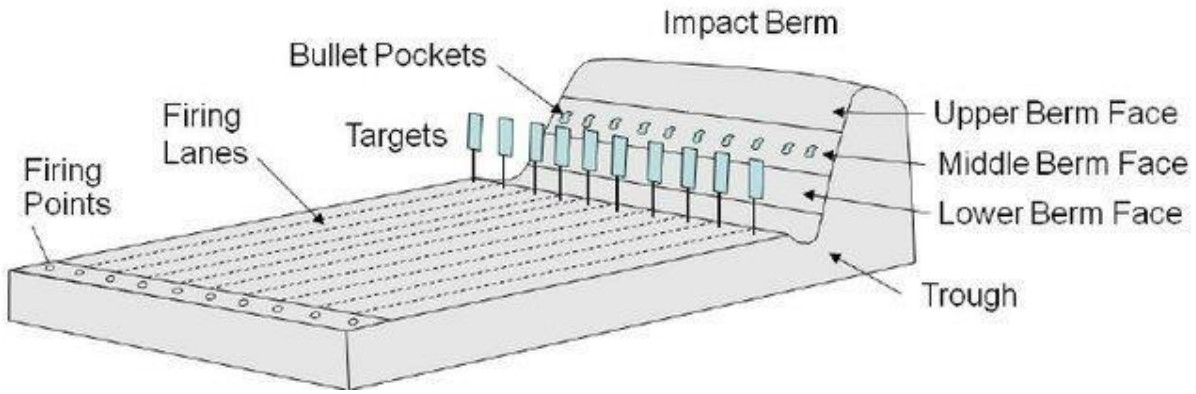


Figure 1.5 Schematic layout of the shooting range[28]

The Pb may be found as spent bullets, shattered fragments, small particles, and lead smears on larger soil particles.[29] Studies have shown that the berm soils contain the highest concentrations of Pb mainly because this section of the shooting range acts as storage for spent bullets and shots.[22,30,31]

1.4.2. Structure of ammunition

Shooting ranges contribute significantly to soil Pb pollution due to the fact that ammunition contains an excess of 80% Pb slug and small traces of As, Sb, Cd, Cu, Ni, Mn and Zn whose environmental impact is rarely studied.[32] Ammunition shots and bullets have been found to contain 95-97% metallic Pb by weight, 0.4-2.0% Sb, 0.2-0.8% As and mean concentrations of Sn, Se, Mn, Cd, Cr, Cu, and Ni greater than 30 mg/kg.[33] Pb is mainly found in the core of bullets and shots while Cu, Zn and Sb are constituents of bullet ore heads and cartridges as shown on Figures 1.6 and 1.7.[34,35]



Figure 1.6 Structure of ammunition showing the cartridge and projectile containing Pb slug.[36]

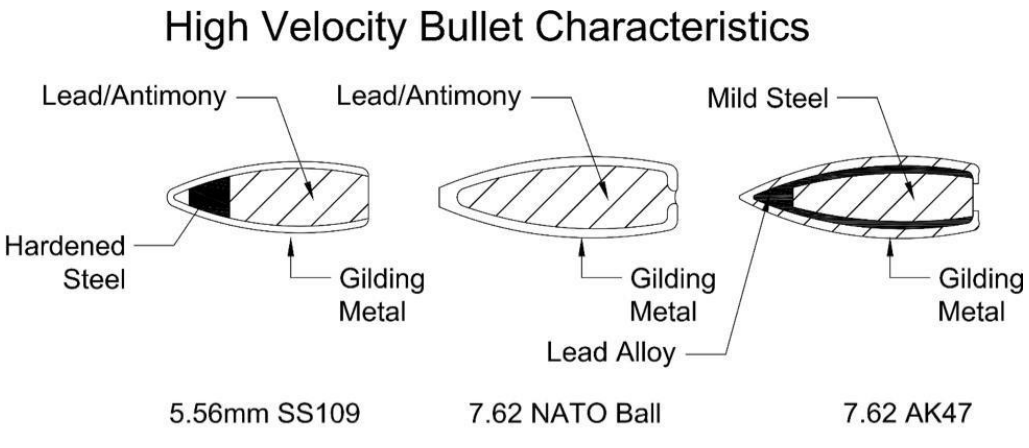


Figure 1.7 Ore heads or projectiles that collect into shooting range soils indicating presence of Pb and Sb as the main slug components.[37]

The bullet/ore head or projectile leaves the rifle barrel travelling at high speed towards the target. There are some physical processes that take place when the rifle trigger is pulled. Pulling the trigger causes firing pin to strike and explode the primer in the base of the cartridge or shotshell. Fire from the primer ignites the gunpowder that burns rapidly, converting to a gas. Gas rapidly expands and drives the bullet/projectile/ore head through the barrel with such a great force (Figure 1.8 a-c).[38]

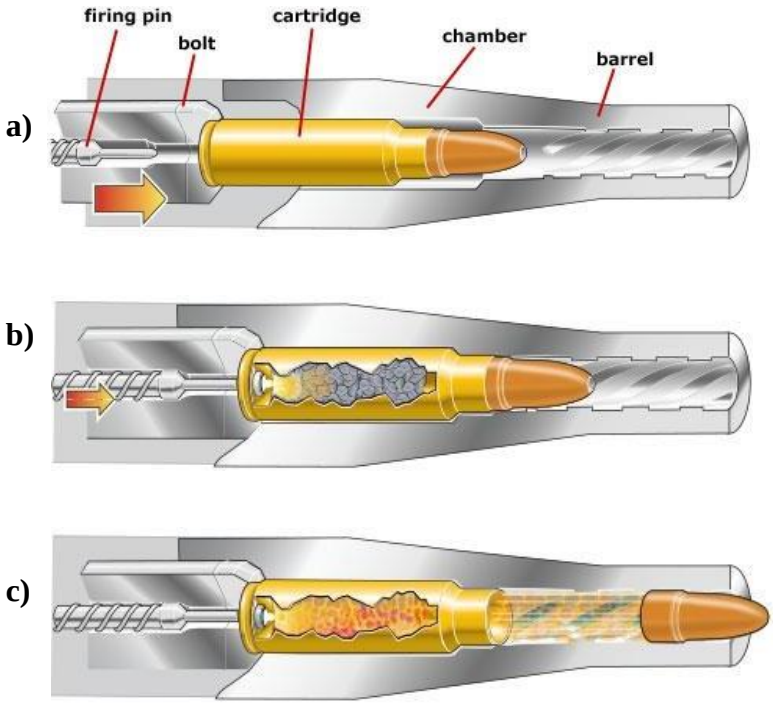


Figure 1.8 Processes taking place when a rifle is being fired.[38]

The bullets and shots then travel across the bed of the shooting range towards the target upon leaving the barrel of the rifle. The bullets and shots will then penetrate the targets placed at the target zone and accumulate on the impact berm. There are many possible processes that can take place upon bullets and shots hitting the impact berm such as bullet penetrating the berm soil, fragmentation of bullets, bullet agglomeration, smearing and ricochet. Figure 1.9 below shows impact on the bullet upon hitting the impact berm/stop butt.[39]



Figure 1.9 The effect on the bullet/ore head/projectile upon hitting the impact berm/stop butt.[39]

1.4.3. Environmental pollution risk from Pb in ammunition

Once the bullets have accumulated into the impact berm, physicochemical processes such as physical weathering, redox reactions, association followed by dissociation and precipitation accompanied by dissolution will start working on the Pb bullets and shots leading to the transformation, migration, mobility, bio-accessibility, bioaccumulation and bioavailability of Pb.[40] As a result, Pb contamination has not only been restricted to shooting range soils but pollution in water has also been detected in surface water samples at places close to shooting ranges.[41-44] In addition to soil and water contamination, elevated levels of Pb in plants found in the vicinity of shooting ranges have also been reported. High quantities of Pb have been found in the roots of plants.[45] Pb in plants has also been reported to reduce plant dry weight, photosynthesis, water absorption and root growth.[46]

1.5. Static environmental pollution risk versus dynamic pollution risk

The environmental risk assessment of soil pollution from Pb has focused mainly on the total concentration of Pb in shooting range soils.[47,48] This risk assessment is based on the amount of Pb stored in contaminated sites and fails to give details on Pb species that are mobile, bioavailable, bio-accessible, non-degradable and bio-accumulative.[49] In addition, this approach does not give a broader understanding and appreciation of the environmental impact and ecological ramifications of Pb deposition over time. As a result, the method of total Pb concentration in soil has increasingly become limited as it does not take into account the interactions of the various forms of Pb in the soil and as a result leading to the overestimation of the potential risk.[50] Speciation studies have provided insight into the environmental risk posed by Pb accumulation in shooting range soils giving a comprehensive perspective into ecotoxicology of Pb to biota.[51,52]

The speciation analysis has been carried out based on methods such as the Tessier sequential extraction procedure[53] and the the Bureau Communautaire de Reference (BCR)[54] sequential extraction method. The speciation methods such as Tessier sequential extraction procedure outlines the existence of Pb according to five different chemical fractions in the soil being water soluble and exchangeable (WE), organic-bound (OB), carbonate-bound (CB), Fe–Mn oxides bound (FM) and residual fractions (RS). Speciation techniques are able to ascertain for the existence of these different chemical forms of Pb in the soil. It has been found that some of these chemical species such as Pb-acetate ($PbCOOCH_3$) and Pb-nitrate ($PbNO_3$) are quite chemically active making them highly mobile and bioavailable.[55] Similarly, speciation procedures have identified other chemical species of Pb such Pb-sulphate ($PbSO_4$), Pb-phosphate ($Pb_3(PO_4)_2$ and Pb-sulphite (PbS) that are insoluble and immobile under normal environmental conditions.[56] Studies on the soil chemical and physical properties such as temperature, pH, organic matter, soil electrode potential and soil cation exchange capacity properties have been effective in estimating the mobility and bioavailability of Pb in the soil.[57] However speciation techniques and soil property studies focus on the various chemical forms and total concentration of Pb statically and unilaterally giving only the static pollution risk assessment overlooking the transformation between the chemical species in the soil that result in dynamic risk potential to the ecosystem.[50]

The delayed geochemical hazard (DGH) concept was coined by Ming *et al.* (2005).[58] It describes the ecological and environmental pollution threat emanating from the unexpected

reactivation and abrupt release of pollutants that accumulated over a long period of time.[58] There are two important characteristics of the DGH model; (1) "total releasable content of pollutant" (TRCP) and "total concentration of active species" (TCAS). As the DGH process takes place, it overcomes a series of critical points in the soil where the total releasable characteristic of pollutants (TRCP) exceeds the environmental holding capacity of pollutants. The DGH concept takes into account the dynamic transformation of the chemical species from one sequential extraction soil fraction to another.[50] This model takes into consideration the accumulation of inactive chemical species in the soil over a long period of time that can become labile when soil chemical and physical properties such as pH, moisture, soil redox potential, organic matter, soil electrical conductivity and cation exchange capacity become favourable. Once activated, these species can be released into the environment increasing the ecological pollution risk. It is important to note that the focus on total concentration of Pb in the soil implies the linearity of its ecotoxicity.

On the other hand, the DGH model emphasizes that the geochemical hazard in the soil presents itself in a nonlinear manner, such that the contribution of external pollutants may be insignificant as the system has the capability to self-implosion.[58] Under the DGH model, chain reactions are possible due to changes in physicochemical conditions of the soil, leading to the formation of new highly toxic chemical species and thereby exacerbating the environmental pollution risk. The implication of these chain reactions is the possibility of temporal and spatial hazard migration.[59] The DGH model rupture arises from two reasons (1) the nonelinear deposition of Pb (TRCP) into the soil to the point where the accumulated Pb concentration far exceeds the holding capacity of the environment (2) the total releasable content of Pb pollutant is constant but changes in environmental physicochemical conditions lead to a shrink in the holding capacity of the environment.[58] This implies that the DGH model is a result of; the persistent deposition of contaminants into the environment, the changes in the use of the environment and changes in the physicochemical condition of the soil. Some Pb chemical species making up the TRCP may not be readily available for direct uptake by plants and animals under certain environmental conditions. Based on the Tessier method of sequential extraction, the heavy metal species in the water-soluble and exchangeable (WE) fraction are considered weakly bound and readily available making this fraction the most active component of the TCAS.[60,61] Therefore, heavy metals in the WE fraction are considered highly labile and have high mobility and are readily bioavailable under normal environmental conditions. On the other hand, chemical species in the OM, CB and FM can be activated and mobilized under suitable environmental conditions.[60]

1.6. Assessment of soil pollution from Pb-containing ammunition used in Botswana

The extent of Pb contamination of shooting range soils has never been ascertained in Botswana, this was the first attempt in evaluating the deposition of Pb into the soils emanating from munitions. Botswana should not be an exception to Pb pollution in shooting ranges since it uses ammunition regularly for training at shooting ranges by the Botswana Defence Force (BDF), Botswana Police Service (BPS), Botswana Prisons Service (BPS) and the Department of Wildlife and National Parks including private shooting clubs. However, since their inception there has not been a single research study on the environmental impact of Pb at shooting ranges used by these government bodies. The only research on pollution from Pb that has been done focused on vehicular emissions.[62,63]

1.7. Statement of the problem

Currently there is no baseline data on Pb concentrations in shooting range soils found in Botswana even though Pb emanating from ammunition is considered to be the second largest contributor to Pb pollution in the world after the battery industry. There are adverse health effects to humans associated with exposure to Pb. Pollution from Pb has also been found to negatively affect plant growth and as such the concentrations of Pb in the soil should be kept in check. Possible contamination of both surface and underground water should also be assessed to ascertain that water for human and livestock consumption is not polluted, posing a health risk. It is also important to understand the physicochemical processes taking place on Pb bullets and shots so as to understand the degree of pollution risk to biota. It is therefore imperative that Pb pollution of shooting ranges from ammunition should always be kept in check to avoid the irreversible consequences that can arise from exposure to this toxic heavy metal.

1.8. Objectives of the study

1.8.1. General Objective

To assess the static pollution risk from Pb pollution of shooting range soils and its comparison to the dynamic risk.

1.8.2. Specific objectives

The objectives of this study are

(1) To determine the extent of Pb pollution in shooting range soils in Botswana.

(2) To determine the various chemical species of Pb present in shooting range soils.

(3) To assess and quantify environmental pollution risk from Pb pollution of shooting range soils.

(4) To explore a new method based on delayed geochemical hazard (DGH) for the assessment of potential and dynamic ecotoxicological risks emanating from Pb pollution of shooting range soils as opposed to static pollution risk assessment.

(5) To establish possible contamination of surface and underground water sources by applying the synthetic precipitation leaching procedure (SPLP).

CHAPTER 2

2. BACKGROUND

2.1. Pollution of shooting range soils from Pb shots and bullets

Lead (Pb) has been used in the production of bullets and shots for many years due to its intrinsic physical and chemical properties such as high density contributing to the bullets and shots pronounced momentum and making them travel long distances and possess considerable destruction force. Pb can easily be moulded into bullets and shots because of its its low melting point of 327.4 °C. Other properties of Pb that make it suitable for ammunition manufacture include high malleability, corrosion resistance and affordabibility. There is no other fiting metal that has been found to carry all these properties making Pb to be the best metal for drawing and swaging bullets.[64] This has led to a heavy reliance in the use of Pb for ammunition production for example; Sweden uses about 500-600 tonnes of Pb annually in the manufacture of bullets and shots.[65] In the years 2011 and 2012 alone, the United states of America has used about 75,100 and 73,900 tonnes of Pb respectively, in the production of ammunition.[66] The deposition of bullets and shots occurs mainly in the berm and can remain intact in the shooting range soils for many years. When bullets and shots reach the impact berm, they can exist in various forms; 1) the projectiles can remain in the soil as complete rounds containing metallic Pb; 2) projectiles can fragment into small pieces upon hitting the impact berm; 3) agglomeration of the projectiles can occur; 4) some bullets and shots can ricochet; 5) while others will undergo chemical transformation in the berm soils into oxidized forms of Pb.[67] Soil physicochemical conditions such as moisture, pH, organic matter, cation exchange capacity (CEC) can work on these bullets and shots by oxidising, carbonating and hydrating them and thereby making Pb mobile, bioavailable and bioaccessible to biota. Many scientists and researchers have published the devastating effects of Pb to the environment and constantly calling for strict regulatory measures for the control and management of Pb pollution arising from ammunition. For example, studies have shown that 58,300 tonnes of Pb are deposited into the soil annually in the United States of America (USA) alone.[68] In other countries such as England, Sweden, Finland and Denmark, total Pb concentrations in the range 10,000–100,000 mg/kg have been reported.[30,44,69,70]

Exposure to Pb has been reported to have detrimental effects to human and animal health. The adverse health effects of Pb are normally more prominent in young children than adults because children's bodies can absorb more Pb (up to 50%) compared to adults (10%).[71] It is thefore, important that the chemistry and biochemical reactions that take place on Pb ammunition are well established, understood and appreciated. Previous research studies have centred around determining total Pb concentrations in shooting range soils which fails to give an accurate quatitative measure of the pollution risk posed by Pb to the environment. [31] The determination of total Pb concentration in the soils gives information on the amount of Pb accumulated into shooting range soils but fails to account for physical and chemical processes that accelerate the mobility, bioavailability, fate and ecotoxicity of Pb to biota.[51] Speciation studies have been used to determine the different chemical species of Pb that exist in the soil in order to establish the types Pb species present in the soil and their degree of solubility, inertness or lability.[51] This provides a good estimate of the environmental pollution risk posed by Pb deposition into shooting range soils.[51,52,72] In addition, environmental pollution risk indices have been used to give a quantitative measure of the degree of hazard posed by Pb accumulated into shooting range soils.[51,72] Modelling strategies such as the delayed geochemical hazard (DGH) models have helped shed light that environmental pollution risk from Pb is a dynamic evolution process rather than static risk.[58] As a result a holistic approach to evaluating pollution of shooting range soils should involve; (1) assessment of total Pb concentration deposited into shooting range soils; (2 Speciation of Pb in shooting range soils in order to establish the degree of Pb mobility and fate; (3) Use pollution risk indices to quantify pollution risk posed by Pb to the environment as opposed to total Pb concentration and (4) showing that the environmental pollution risk from Pb pollution is a dynamic rather than static process.

2.2. Spatial Pb loading and distribution in shooting range soils

Research studies have reported that shooting ranges come only second to the battery industry as a source of Pb pollution in the environment.[72,73] The continuous use of small arms ammunition in shooting exercises has drawn the attention of researchers and environmentalists to shooting ranges in order to assess contribution to soil pollution from Pb used in ammunition.[31,51,74-76] Once deposited into the soil, the bullets and shots would undergo a variety of chemical and physical transformation that increase the mobility and bioavailability of Pb in the soil. Over time, these processes have the potential to elevate concentrations of Pb in shooting range soils. Studies have shown that most shooting ranges accumulate Pb in concentrations of many fold compared to the natural concentration of Pb which normally occurs at 10–30 mg/kg.[45] Table 2.1 below shows the different studies that have been carried out for the past 35 years in order to assess the level of shooting range soil pollution from total Pb concentration.

Table 2.1 Comprehensive research studies for the past 35 years on contamination of shooting range soils from Pb.[174]

Location, Year of study and Reference	Number of shooting ranges studied	Number of years in operation at time of study	Total Pb concentration (mg/kg)	Sampling Depth (cm)	Maximum contaminant limit (MCL) for Pb referred to in the study (mg/kg)
Denmark (1983)[77]	1	14	0.2-3 kg per m^2	-	-
Denmark (1987)[78]	3	12-26	274-1000	0-5	7-12 (reference area)
Netherlands (1988)[79]	1	-	300-300,000	0-5	600 (critical value for soil sanitation)
Netherlands (1989)[80]	1	12	360-70,000	0-5	0.001-1.1 (control area)
Germany (1990)[81]	1	-	5000	0-50	-
Finland (1991)[82]	1	-	10,500	0-70	-
USA (1992)[42]	8	-	838	0-7.5	-
USA (1993)[83]	1	78	11-345	0-800	5.0 mg/L (Toxicity characteristic leaching procedure (TCLP) Pb benchmark
Finland (1993)[84]	1	29	4700-54,000	0-40	240 (reference area)
England (1994)[16]	1	-	10,620	0-150	-
Netherlands	-	-	7390	-	-

(1995)[85]					
USA (1995)[86]	8	-	1000	-	-
USA (1995)[87]	1		11-4675		5 mg/l (TCLP USEPA regulatory level)
Sweden (1996)[65]	8	26	687-24,500	5-10	23-191 (reference soils)
USA (1996)[88]	1	-	75,000	0-75	-
Switzerland (1997)[89]	1	-	29,550	-	50 (official tolerance level)
USA (1997)[90]	1	-	2256	5-15	25 (background soil level)
New Zealand (1998)[45]	3	60	4000-8300	0-75	300 (Australia and New Zealand set limit for soil)
Denmark (1999)[30]	1	30	60,000	0-40	5-15 (as reference soils)
USA (1999)[70]	1	-	400	-	-
New Zealand (2000)[91]	3	7–51	15,370-206,600	1-7.5	300 (as per Australia and New Zealand set limit for soil)
USA (2000)[92]	1	-	856.9	-	-
Finland (2000)[93]	1	-	9804	5-20	-
USA (2000)[94]	1	-	110-27,000	0-3	-
Switzerland (2001)[95]	2	-	3110-33,600	-	50 (Swiss official Pb tolerance level
USA (2001)[22]	1	14	875-4448	0-10	400 (USEPA soil screening level)
USA (2001)[87]	1	-	13,525-37,174	10-25	294 (adjacent areas)

South Korea (2002)[96]	1	45	78-165	0-10	53 (reference soil)
USA (2002)[23]	1	14	330 – 17,850	0-10	400 (USEPA soil screening level)
USA (2002)[68]	1	-	16,200	0-15	22.1-60.5 (background soil)
USA (2003)[44]	2	3-16	12,710-48,400	0-10	400 (USEPA soil screening level)
Switzerland(2003)[97]	1	38	80,900	0-10	23 (background soil)
USA (2004)[98]	2	0.25 (3 months)	193–1142	0-15	-
USA (2004)[99]	1	-	385-12,400	3-20	0.3 (World Health Organization (WHO) of Pb in fish
USA (2004)[100]	2	-	134.9-144.6	-	14.7 (reference site)
Italy (2004)[101]	1	-	212-1898	-	100 (Italian soil Pb threshold)
Switzerland (2005)[102]	1	90	1045-67,860	0-5	10-30 (natural background concentration)
England (2005)[103]	1	45	6410	-	296 (control site)
USA (2006)[104]	4	-	1025-49,228	-	400 and 1000 (Regulatory Pb screening levels set by the states of California and New Jersey
USA (2006)[104]	6	-	1025-49,228	-	400 and 1000 (California's Code of

			(3196 and 10542 included in this study)		Regulations for the Total Threshold Limit Concentration (TTLC)
Finland (2006)[105]	1	23	2500-49,700	0-5	75 (background soil)
Canada (2007)[106]	3	3-5	16,400-27,600	0-5	-
Germany (2007)[107]	1	-	16,760	-	-
USA (2007)[108]	2	-	406-22,333	-	64-85 (reference areas)
Finland (2007)[109]	1	16	28,700	0-6	-
USA (2007)[110]	12	5-60	54.9-68,519	2-20	5mg/L (TCLP hazardous limit)
Finland (2007)[111]	3	33-44	350-19,800	0-20	300 (Finish limit value of Pb in soil)
USA (2007)[112]	1	60	19.8-7915	0-15.24	69 (background soil)
Switzerland (2008)[113]	1	-	100,000	2-10	530 (Dutch Intervention Value)
USA (2008)[114]	2	-	2520-35868	0-20	5 mg/l (TCLP USEPA regulatory level)
Finland (2009)[115]	2	16-20	15,500-41,800	0-8	750 (upper guideline value for Pb)
USA (2009)[116]	9	-	990-97,600	0-5	6-119 (background soils)
USA (2009)[117]	1	16	340	0-50	12 (background soil)
Poland (2009)[118]	2	-	640–4600	0-10	400 (USEPA Pb critical level)

USA (2009)[67]	8	-	4549 – 24,484	-	-
Japan (2009)[119]	1	10	29,200	0-10	-
South Korea (2010)[120]	1	-	3529	0-30	400 (Korean standard limits for non-residential area)
Czech Republic (2010)[121]	1	30	573-694	0-30	300 (critical limit for agricultural soils by the EC Council Directive 86/278/EC (1986))
Switzerland (2010)[122]	2	-	500-620	0-30	200 (Swiss Pb trigger value)
USA (2010)[123]	1	9	4694- 11,479	-	5mg/L (TCLP hazardous limit)
USA (2010)[123]	2	24	2096-29,900	0-30	0.18-450 (background soils)
Canada (2010)[124]	4	-	16,485-43,113	0-30	1000 (MDDEP[1] commercial level) 600 (CCME[2] industrial level)
South Korea (2010)[125]	1	-	8684	-	100 (Korean warning standard)
Norway (2010)[126]	1	-	22,000	-	1-50 (Background soil)
Switzerland (2011)[127]	1	-	500	0-30	-
Canada (2011)[128]	4	-	14,400-27,100	0-30	1000 (MDDEP commercial level) 600 (CCME industrial level)

USA (2011)[129]	3	7-38	10,068-70,350	-	5 mg/L (TCLP hazardous limit)
Switzerland (2012)[130]	2	-	466-644	0-40	40 (maximum allowed trace element concentrations in fodder DW)
South Korea (2012)[131]	1	-	4626	-	700 (Korean hazard standard)
Finland (2012)[132]	2	22-25	19,100-50,300	5-8	750 (ecological risk guideline value)
Canada (2012)[133]	1	-	423-66,972	0-90	1000 (MDDEP commercial level) 600 (CCME industrial level)
Australia (2012)[72]	4	42-52	399-10,403	0-20	400 (USEPA critical level) 600 (ecological investigation level (EIL)) 600(health investigation level (HIL))
South Korea (2013)[134]	1	-	7996	0-30	200 (Korean warning standard)
Czech Republic (2013)[135]	1	40	4800	0-5	60 (guideline for agricultural soils)
Norway (2013)[136]	5	-	2000-30,000	-	60 (Norwegian soil quality guidelines)
Canada (2013)[137]	1	-	18,600-44,100	0-20	140 (criteria for residential soils) 600 (criteria for industrial soils)
South Korea (2013)[134]	1	-	11,885	0-30	-

South Korea (2013)[134]	1	-	11,900	0-30	100 (residential warning standard)
China (2014)[138]	1	20	153.7-2763	0-20	34.97 (background soil)
Argentina(2014)[139]	1	-	80	0-5	-
Netherlands (2014)[140]	1	-	47-2398	-	-
Netherlands (2014)[141]	1	-	355-2153	0-20	-
China (2015)[73]	3	-	2019.75-9160.25	0-10	-
Finland (2015)[141]	2	22-28	19,000-28,000	1-6	-
Australia (2015)[142]	4	45-55	233-12,167	0-10	5 mg/l (TCLP regulatory limit)
Netherlands (2015)[143]	1	-	2153–2398	-	-
Norway (2016)[144]	1	16	356–1112	0-30	60 (Norwegian soil quality guideline)
Nigeria (2016)[145]	1	60	17,500	0-15	400 (USEPA guideline)
South Korea (2016)[146]	1	-	5715.4	-	200 (Korean standard)
South Korea (2016)[147]	2	20-30	3918-18,609	0-30	200 (Korean regulation value)

Australia (2016)[148]	4	46-56	177-2545	-	-
Spain (2016)[149]	1	30	82.36-724.85	0-15	100 (generic reference level)
Spain (2016)[150]	1	-	55-6309	0-15	100 (generic reference Level) 400 (USEPA guideline)
South Korea (2017)[151]	1	30	3436	0-30	700 (Korean standard level)
Norway (2017)[152]	1	-	1400	-	-
Norway (2017)[35]	1	139	410-2700	2-3	130 (reference sediments)
Norway (2017)[153]	7	50-80	260-13,000	0-15	20 (background soil)
Nigeria (2017)[154]	1	-	2333-16,976	0-15	-
Switzerland (2017)[47]	2	-	500-620	0-30	-
Spain (2017)[155]	1	-	160-720	0-15	100 (Spanish Generic Reference Level(GRL) 400 (USEPA guideline)
Botswana (2017)[31]	8	19-40	85-38,386	0-20	400 (USEPA guideline)
Botswana (2017)[51]	7	16-33	685-20,882	0-20	400 (USEPA guideline)
Switzerland (2018)[156]	1	-	471	0-30	40 (regulatory values for fodder plants)
Norway (2018)[157]	1	-	450	0-10	300-700 (Norwegian quality class 4 soil

					criteria)
Norway (2018)[158]	4	-	580-33,000	-	0.17-3.6 (reference soil)
Norway (2018)[159]	3	123	41-7189	-	60 (soil quality guideline for sensitive land use)
Belgium (2018)[76]	7	28	23.4-2167	-	139 (control sample)
Nigeria (2018)[160]	1	53	14.85	0-15	4.99 (unpolluted site)
Norway (2018)[161]	2	-	450-3200	0-10	300-2500 (Norwegian quality class 3-5 soil criteria)

[1]MDDEP – Ministere du Developpement Durable, de l'Environnement et des Parcs.

[2]CCME – Canadian Council of Ministers of the Environment.

As shown in Table 2.1 above, Pb pollution of shooting range soils arising from continuous use of Pb containining ammunition has been experienced by every continent on the world map. Total Pb concentrations have been determined in shooting ranges around the world over time, for example; 300,000 mg/kg in the Netherlands, 206, 600 mg/kg (New Zealand), 97,600 mg/kg in the USA, 66,972 mg/kg (Canada), 38, 386 mg/kg (Botswana), 29,200 mg/kg in Japan.[31,116,133] The initial study on pollution of shooting range soils by Pb was first carried out by Adsersen *et al.* (1983), more than three decades ago and discovered 200,000-300,0000 mg of Pb per square meter in a shooting range that had been operational for only 14 years.[77] The years that followed have seen an acute increase in the amount of Pb deposited into shooting range soils with concentrations of up to 200,000 and 300,000 mg/kg.[79,91] In some instances, the rate of shooting range use has been found to be directly proportional to the amount of Pb deposited into shooting range soils. Rooney *et al*. (2000), were able to confirm this assumption whereby total Pb concentration of 1632 mg/kg was determined at a shooting range that experienced the highest rate of shooting activity.[91] In another study, total Pb concentration of 38,386 mg/kg was measured at a 22 year old shooting range where shooting practices take place frequently compared to low concentration of 6163.15 mg/kg that accumulated at shooting range that was 7 years older.[31] However, the duration the shooting range has been in use plays a crucial role such that when shooting practices take place at an equivalent rate, the age of the range will greatly influence the amount of Pb deposited in the soil. This assertion was verified by a study in Florida where total Pb concentration of 48,400 mg/kg was measured at MPR shooting range that is 16 years old compared to a younger 3 years old TRR shooting range that accumulated only 12,710 mg/kg of Pb. [44] Similarly, total Pb concentration of 41,800 mg/kg was determined at 20 year old shooting range in Finland compared to 15,500 mg/kg found in a 16 year old shooting range soil.[115] The length of time bullets and shots spend in shooting range soils allows for ample opportunity for oxidative reactions to take place leading to weathering and transformation of the metallic projectiles into soluble secondary mineral species such as cerussites ($PbCO_3$) and hydrocerussites ($PbCO_3H_2O$).[31] The weathering of Pb shots and bullets into soluble Pb minerals elevates the mobility, leaching and bioavailability of Pb in shooting range soils.

The different sections of the shooting range have been found to accumulate varying concentrations of Pb based on the amount of Pb projectiles that collect and accumulate in these sections. The highest concentrations of Pb have been found in the berm soils because of high density of spent Pb shots and bullets that pierce through the targets and deposit into the berm soils. For example, in Florida (USA) around 180 g bullets per kg of soil were retrieved from the berm soils.[22] In Denmark, about 70 kg of Pb projectiles were collected in the berm soils.[68] Similar studies such as the one in California, USA, 1620 Pb pellets per kg of soil were recovered from the shooting range berm soils.[68] In the same way, Jorgensen *et al*. (1987) were able to measure total Pb concentrations of up to 1000 mg/kg in one of their infacy studies on Pb contamination of shooting ranges. Other studies that followed have determined concentrations as high as 33,000 mg/kg[158] and 38,386 mg/kg[31] in the berm soils of shooting ranges in Norway and Botswana respectively. As one moves away from the berm towards the firing lines, the concentration of Pb has been found to decrease. In a study by Cao *et al.* (2003), it was established that total Pb concentration decreased as one moved away from the target line towards the firing zones.[44] The lowest Pb concentration of 7.3 mg/kg 12,710 mg/kg was determined at 1.5 m from the firing zone and the concentration increased as one moved from the firing zone towards the target line at levels of 22.6 mg/kg (31.5 m from firing line) and 736 mg/kg furthest away from the firing line and closer to the berm.[44]

The vertical distribution of Pb in shooting range soils was found to be mainly confined to the surface and subsurface soils of 0-30 cm deep. [91,97] In a study by Chen *et al.* (2001), it was demonstrated that total Pb concentration decreased drastically with depth in which total Pb concentration of 2357 mg Pb/kg was measured in the 0-10 cm soil profile and only 9.0-9.8 mg Pb/kg was recovered in the 51-200 cm depth of the berm soils in Florida.[22] In a similar study, TRR shooting range experienced the highest Pb loading of 736 mg/kg in the 0-30 cm soil profile, followed by 17 mg/kg (10-30 cm), 2.60 mg/kg (30-50 cm) and 1.80 mg/kg (50-100 cm), a substantial decrease of 99.8% from the 0-30 cm soil profile to the 50-100 cm.[44] Knechtenhofer *et al.* (2003) have also shown a huge difference between the concentration of total Pb of 80,935 (0-10 cm) compared to 78 mg/kg in the 60-70 cm soil compactment.[97]

In other studies, Murray *et al*. (1997) were able to measure 2256.0 mg/kg of total Pb in the 0-30 cm soil profile that was five times higher than in the 90-100 cm (472 mg/kg) soil profile.[90] It is important to note that total Pb concentrations determined in the studies indicated in Table 2.1 alarmingly exceeded the set regulatory maximum contaminant limits (MCLs). In a more recent study by Johnsen *et al*. (2018), total Pb concentration of 7189 mg/kg was determined at one of the shooting ranges found in Norway which in effect exceded the Norwegian soil quality guideline of 60 mg/kg 120 times.[159] In the same country, Norway, total Pb concentrations 500 times higher than the set soil quality guideline have been recorded.[136] The type of firearm used at shooting ranges has significant impact on the amount of Pb deposited into shooting range soils.[134] This is due to the fact that firearms of different calibres conatin varying amounts of Pb in their ammunition. For example, pistol ammunition containes less Pb slug (52%) compared to rifle ammunition that can carry up to 99% of Pb.[134]

2.3. Effect of soil physicochemical properties on Pb weathering and transformation

The physicochemical characteristics of the soil play a pivotal role and control the chemical reactions that take place inside the soil that ultimately affect the vertical and spatial distribution of Pb. The soil pH, texture, organic matter, moisture and cation exchange capacity contribute significantly to the mobility, immobility, bioavailability and fate of Pb in shooting range soils. Soil chemical characteristics such as moisture content accompanied by low soil pH and high organic matter can significantly accelerate the disintegration, weathering and transformation of metallic Pb shots and bullets into labile secondary Pb minerlas.[98] Examples of Pb mineralogical chemical species that Pb shots and bullets get transformed into include; massicot (PbO), cerussite ($PbCO_3$), hydrocerussite [$Pb_3(CO_3)_2(OH)_2$] and anglesite ($PbSO_4$). The changes in the soil physicochemical properties can favour or inhibit the weathering of Pb shots and bullets in shooting range soils.

2.3.1. The effect soil pH

The mobility, leaching and bioavailability of Pb in shooting range soils is to a large extent controlled by the soil pH.[22,23,30,31] Acidic soils have been found to favour the weathering and transformation of Pb while alkaline soils help immobilise Pb and restrict its mobility.[57] Astrup *et al.* (1999), demonstrated that high total Pb concetrations were recovered in alkaline soils because of the restricted transformation of Pb into soluble Pb minerals and their

subsequent leaching deep into the soil or being washed away by runoff water.[30] The studied soils accumulated Pb concentration of 96,800 mg/kg and corresponding soil pH of the range 6.0 to 7.0 while acidic soils of pH 4.7-5.4 collected only 13,300 mg/kg of Pb. [30] In Florida, USA, total Pb concentration of 17,850 mg/kg was determined in shooting range soils bearing pH of 7.7 relative to 10,138 mg/kg in soil of pH 6.8.[23] As mentioned earlier, alkaline soils stabilize Pb oxides and carbonates leading to slowed reactivity of these Pb compounds and reduced leaching and slowed mobility resulting elevated levels of Pb concentrations being retained in the soil.[31]

In addition, X-ray diffraction patterns on shooting range soil collected from MPR shooting range in the USA indicated high proportions of hydrocerussite [$Pb_3(CO_3)_2(OH)_2$] at corresponding elevated soil pH of 7.36 while the TRR shooting range soil accumulated both hydrocerussite and cerussite ($PbCO_3$) at acidic soil pH of 5.76.[44] The acidic soils to a large extent influence the rate of solubility of metallic Pb projectiles.[162] In a study by Dermatas *et al.* (2006), it was observed that the alkaline soils slowed the transformation of Pb bullets and shots and favoured the immobilization of Pb.[104] In a similar study by Ma *et al*. (2007), the abration and transformation of Pb pellets were carried out in a simulation environment where the effect of varying soil pH were probed.[57] The soils were spiked by 5% metallic Pb powder and incubated for nine days at pH 4.8 after which X-ray diffraction analysis was carried out and found that Pb immediately transformed into hydrocerussite under these conditions. Conversely, in alkaline soils of pH 8.5, the XRD patterns indicated mostly the metallic Pb and less of the weathered and transformed Pb.[57]

2.3.2. The Effect soil organic matter

The soil organic matter is another characteristic of the soil that has significant impact on the weathering and transformation of Pb and can dictate the mobility and fate of Pb in shooting range soils. Organic matter increases soil cation holding capacity and exchange rate of Pb in the soil.[44] In some cases, the presence of organic matter in the soil can assist in the formation of organo-Pb complexes which stabilize Pb in the soil leading to elevated concentrations of Pb being retained in the soil.[44]

Cao *et al*. (2003), discovered high content of organo-Pb complexes at the MPR shooting range with elevated levels of organic carbon (OC) content of 16.1-107 g/kg and high dissolved organic carbon (DOC) content (89.3-267 mg/kg).[44] In addition, the alkaline soil p(H 6.73-7.69) provided a favourable condition for the transformation of formed organo-Pb complexes leading to high concentrations of Pb in the MPR shooting range soils.[44] Sequential extraction studies have demonstrated that Pb restricted to the organic fraction is labile and therefore can weather easily resulting in increased bioavailability of Pb in the soil.[57] In a related study, shooting range soil with organic carbon of 4.3% exhibited high Pb loading of 644 mg/kg comapared to soil with organic carbon of only 0.9% (466 mg/kg).[130]

Duggan *et al.* (2007) have demonstrated that high organic carbon content in the soil can result in high Pb loading as shown by elevated concentrations of 7915 mg/kg in soil with organic carbon content of 38.8% compared to 19.8 mg/kg with corresponding organic carbon content of 2.1%.[112] The effect of soil organic matter on its ability to alter the soil redox potential arising from the transformation of soil organic matter has not been extensively explored.[163]

2.3.3. The Effect of soil cation exchange capacity

The soil cation exchange capacity (CEC) describes the quantity of exchangeable cations that can be absorbed by a given mass of soil and it governs the binding capacity of the soil.[164] Shooting range soils with high CEC have increased binding capacity of Pb leading to reduced Pb mobility and leaching.[44] Cao *et al.* (2003) have demonstrated the impact of CEC whereby the MPR shooting range soils with elevated CEC of 43.2 cmol/kg deposited high total Pb concentration of 48,400 mg/kg whereas TRR shooting range soils accumulated only 12,710 mg/kg with lower CEC of 8.51 cmol/kg.[44] Similarly, elevated total Pb concentration of 60,600 mg/kg was determined in shooting range soils with 50.1 meq/100g CEC compared to 5040 mg/kg in soils with corresponding CEC of 1.05 meq/100g.[165]

In most cases, the soil CEC works in conjuction with other soil chemical properties such as soil pH, moisture and organic matter to effectively and efficiently transform Pb shots and bullets to secondary Pb ninerals. It is important to note that the impact of other soil chemical properties such as pH towards weathering of Pb projectiles can supersede that of the CEC. For example; Sanderson *et al.* (2012), discvored elevated total Pb concentration of 10,403 mg/kg at the Murray Bridge (MB) shooting range with corresponding lower CEC of 5.3 cmol/kg but high soil pH of 9.3. On the other hand the RAAF Darwin (DA) shooting range soils experienced high CEC of 33.2 cmol/kg and accumulated lower total Pb concentration of 399 mg/kg and the determining factor at this range was the low pH of 5.4.[72] As mentioned earlier, acidic soils accelerate the weathering and transformation of Pb pellets into secondary Pb chemicals species that may be soluble resulting in the leaching and mobility of Pb in shooting range soil.

2.3.4. Effect of soil moisture

Soil moisture provides a medium through which chemical reactions can take place on the surface of the Pb shots and bullets leading to their erosion and corrosion and thereby enhancing the mobility and leaching of Pb in shooting range soils.[57] It lubricates the surfaces of Pb projectiles through formation of an aqueous layer on the Pb shot surface which facilitates the diffusion of labile gases such as oxygen and carbon dioxide from the environment across to the metal surface leading to the formation of secondary Pb mineral species such as Pb carbonates, sulphates, oxides and phosphates and their concomitant solubilisation and dissolution.[31] In china, the Fenghuang shooting range (FH) that is located in a humid environment was found to accumulate more secondary Pb minerals such as cerussite and hydrocerussite compared to the formation of cerussite minerals at Baicheng (BC) and Fangyan (FY) shooting ranges which are located in a dry area.[73] The mechanism for the formation of a layer of hydrocerussite on the Pb shot surface in the presence of moisture has been thought to occur through to occur via reaction of cerussite with moisture as indicated in equation (1) below;

$$3PbCO_3(s) + H_2O(l) \longrightarrow \underset{\text{(hydrocerussite)}}{4Pb_3(CO_3)_2(OH)_2(s)} + CO_2(g) \qquad (1)$$

This leads to a chain of events as the dissolution of the cerussite and hydrocerussite layers on the Pb projectile surfaces re-expose the Pb shot surface to further weathering and transformation. It is worth noting that moisture alone cannot corrode metallic Pb shots but rather facilitates corrosion and weathering of such Pb shots and bullets by providing a membrane for the oxidizing gases to diffuse through to metallic Pb shot and subsequent reaction with the metallic Pb shot results in the formation of secondary Pb minerals that can be soluble and mobile.[98]

2.3.5. Effect of soil type and texture

It is imperative that soil texture should be considered in trying to have a complete grasp of the chemical reactions that transform metallic Pb shots into secondary reactive Pb chemical species. Soil texture describes relative amounts of soil matter of varying dimensions such as clay, silt and sand that compose the mineral fraction of the soil. In a study by Hardison Jr *et al*. (2004), the effect of soil texture was investigated in a simulation study where the weathering and transformation of small particles of metallic Pb powder was carried out under varying conditions of soil moisture. The XRD patterns indicated the appearance of the hydrocerussite and small peaks for cerussite ($PbCO_3$) and massicot (PbO) and the disappearance of the metallic Pb peaks.[98] It was established after seven days that, the small metallic Pb particles were transformed into secondary Pb minerals at a faster rate than larger Pb shot particles. However, it is worth noting that in a non-ideal situation of a shooting range, the weathering and transformation of a typical Pb pellet can take many years to erode and corrode into soluble secondary Pb minerals compared to the metallic Pb powder used in the simulation experiment Hardison Jr *et al*. (2004). Jorgensen and Willems, (1987),[78] were able to demonstrate that it can take a time period of 6-13 years to transform just 5-17% of Pb shotgun pellets and Lin *et al*. (1995)[166] reported transformation rates of 2.8-15.6% over a period of 20-25 years. It has been discovered that the weathered Pb shots and bullets once in the soil, are enveloped in a thin layer of crust of the formed secondary Pb mineral forming a protecting layer and preventing the diffusion of reactive gases from reaching the Pb shot surface and thereby slowing down any further erosion and transformation.

2.4. Speciation and fractionation of Pb in soil

The speciation of Pb in shooting range soils is dependent on the physical weathering and soil chemistry of the soil such as oxidation-reduction, association-dissociation, sorption-desorption and precipitation-dissolution.[51] In order to better understand the toxicity and environmental pollution risk posed by Pb, it is important to have a good appreciation of the different Pb minerals that exist in shooting range soils. It has been observed in the literature that most studies carried out so far have concentrated more on detecting total Pb concentration in shooting range soils which does not give a good measure for the mobility and bioavailability of Pb in the environment and thereby not giving an accurate picture on the environmental and human health risk posed by exposure to Pb. In consequence, it is important to have a good grasp of the different chemical species of Pb that exist in shooting range soils, be it the free Pb metal, Pb salts and Pb organic complexes. These different chemical species of Pb in shooting range soils cause distinct reactivity with particular target components of the soils which contributes to their solubility, mobility and their ultimate ecotoxicological impact to the environment.[57,121,167]

Different methods have been used in determining the partitioning of the different chemical species of Pb in shooting range soil compartments with the sequential extraction techniques being popular. Two such sequential extraction methods include; (i) the European Community Bureau of Reference (BCR)[54] method and (ii) the sequential extraction method by Tessier *et al*. (1979).[53] The Tessier method is the most widely used technique because it provides for a five stage sequential extraction procedure relative to the BCR procedure that combines stages one and two of the Tessier method. The Tessier method of sequential extraction has been extensively used for establishing the chemical speciation of Pb in shooting range soils.[51,87] The sequential extraction procedure outlines the presence of heavy metals such as Pb in five different chemical species in shooting range soils. These include the water soluble and exchangeable (WE), organic-bound (OM), carbonate-bound (CB), Fe-Mn oxides bound (FM) and residual fraction (RS).[51] The mobility and bioavailability of Pb in shooting range soils largely depend on the partitioning of Pb in these compartments. The strength of binding of Pb to the water-soluble and exchangeable fraction is regarded as being weak in relation to the binding to other fractions. In contrast, the binding of Pb to the residual fraction is considered the strongest of all the other fractions. As a result, the migration rate of Pb is the highest in the WE fraction and lowest in the RS fraction. In addition, Pb in the mobilisable fractions poses a greater environmental hazard than when associated with the immobilisable phases.

In a study by Chen and Daroub, (2002) in a Florida shooting range, 91.3% (16,289 mg/kg) of Pb was partitioned in the carbonate fraction and therefore mobilisable, followed by the organic bound at 4.5% (803 mg/kg) and only 0.37% (66 mg/kg) of Pb was locked up in the residual fraction and therefore immobile.[23] The partitioning of Pb in the different soil fractions was in the order of CB > OM > Fe-M > WE > RS. In a similar study in two shooting ranges found in Florida, it was determined that 59.8% of Pb in MPR shooting range was primarily associated with the carbonate fraction and followed the order OM > Fe-Mn > RS > WE.[44] In contrast to the MPR shooting range, Pb in the TRR shooting range soils predominantly existed in the residual fraction (20.7%) with less than 22.3% associated with the water soluble and exchangeable and carbonate fractions. This implies that Pb in the MPR shooting range soils posed a greater hazard as it was associated mainly with the mobilisable fractions as compared to Pb in the TRR soils which exhibited low mobility. In a study of four shooting ranges, Pb was found to be predominantly partitioned in the carbonate fraction in three (Goldstone Site (FIGS), the Armaments Technology Facility (PATF), and Fort Dix Range 15 (FDR15)) of the four studied shooting ranges whereas Pb in the Marine Range (PAMR) soils was bound to the Fe-Mn oxide (70%).[104] At the FIGS shooting range, the partitioning of Pb in the soil compartments was in the order CB > FM > OS > EX > RS with more than 95% of Pb existing in the CB and FM fractions. In this case, it was postulated that the association of Pb with the Fe-Mn oxide fraction in the FIGS soils occurred due to the presence of high concentrations of Fe and Mn as amorphous ferromanganese oxides as corroborated by the X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM).[104] Similarly, the predominant existence of over 90% of Pb in the carbonate fraction in the PATF soil was also confirmed using the XRPD which was dominated by the Pb carbonate (cerussite) peaks and the SEM image which showed the cerussite crystals formed on the surface of the Pb shots and bullets. On the other hand, Pb in the FDR15 shooting range was mostly partitioned in the WE fraction (21%) due to the leaching out of Pb from the quartz surfaces.[104] In other studies, such as the one by Isaacs, (2007), it was found that 79.8% of Pb was restricted to the residual fractions in all of the twelve shooting ranges investigated.[110] This means that Pb in all the twelve shooting range soils studied was immobile and not bioavailable.

It is important to note that speciation of Pb in shooting range soils is largely dependent on the soil physicochemical properties such as soil pH, soil organic matter and soil redox potential. For example, in a study by Scheetz and Rimstidt, (2009), redox potential versus pH diagrams (Eh-pH) for the Pb–CO_3–H_2O system were used to interpret the layers of Pb chemical species found on the surface of Pb shots and bullets.[117] They were able to establish that metallic Pb is stable at low redox potentials and moderately acidic to highly basic pH conditions. The weathering of metallic Pb uses up the oxygen and hydrogen ions as depicted in the following equation (2);

$$Pb(s) + \frac{1}{2}O_2 + 2H^+ \longrightarrow Pb^{2+} + H_2O \qquad (2)$$

They were also able to find that the weathering product hydrocerussite is stable at high redox potential and slightly alkaline pH conditions. As a result, the interface between the thin layer of hydrocerussite and the metal surface would have a low redox potential and high pH.

2.5. Simulation of potential underground water contamination – synthetic precipitation leaching procedure (SPLP)

The synthetic precipitation leaching procedure (SPLP) is a technique used to simulate possible underground water pollution in areas highly contaminated with Pb.[31,168,169] It simulates acid rain at pH 4.0 that has the ability to mobilize high concentrations of Pb and leach to underground water sources. By extension, the SPLP helps assess the mobility, bioavailability and toxicity of Pb in shooting range soils. The United States Environmental Protection Agency (USEPA) has set 15 µg/l as the critical level for Pb mobility in soils. SPLP Pb concentration that exceeds this limit poses a pollution risk to underground water. The SPLP Pb concentrations were 6850 and 19,910 ug/l at TRR and MPR shooting ranges respectively.[44] The SPLP Pb concentrations were more than 400 and 1000 times the USEPA set critical limit at the TRR and MPR shooting ranges respectively.[44] These findings mean that Pb mobility was high at TRR and highest in MPR shooting range soils with possible leaching to and contamination of underground water.

An investigation into the pollution status of agricultural soils in the vicinity of a shooting range discovered that total Pb concentration ranged from 573 to 694 mg/kg and SPLP Pb concentration of up to 24.0 μg/l.[121] The SPLP Pb concentration exceeded the USEPA set critical limit, an indication of possible contamination of underground water which could lead to metal uptake by crops planted in the polluted soil and water. This could also lead to the presence of Pb in the food chain when contaminated crops and vegetables are consumed by animals and human beings. Fayiga *et al*. (2011) also observed that underground water at three shooting ranges was at risk of being polluted as the determined SPLP Pb concentrations at Range-G, Range-O and Range-L were 1.19×10^3 μg/l, 3.62×10^3 μg/l and 3.80×10^3 μg/l respectively and exceeding the set USEPA critical limit by a factor of up to 200.[129] It can also be deduced from the SPLP experiments at the three shooting ranges that Pb found at these three shooting ranges was highly mobile and therefore of great hazard. Other studies have been carried out that revealed that acidic precipitation has the ability to leach sufficient amounts of Pb from shooting range soils and thus pose a significant risk to both surface and underground water sources.[98,110,114,128,133,137] The high SPLP Pb concentration found in shooting range soils suggest that the Pb chemical species that form thin layers on the surface of Pb shots and bullets are instantly bioavailable and are susceptible to leaching.

2.6. Quantitative evaluation of pollution risk to the environment from Pb deposition

Quantification of pollution risk posed by Pb accumulation into shooting range soils gives insight into the degree of hazard to biota from this highly toxic heavy metal.[170] Unfortunately, many studies have focused on total Pb concentration deposited into shooting range soils. Total Pb concentration approach gives clear picture on how much Pb is contained and stored in shooting range soils but does not give information on how much of this stored Pb poses pollution risk to the ecosystem. In fact, determination of total Pb concentration alone falls short of giving details of Pb mobility, speciation, bioavailability, bio-accessibility and fate in shooting range soils. Therefore, in addition to determining total Pb concentration and chemical species of Pb present in shooting range soils it is of paramount importance that the toxicity of these Pb minerals to biota be quantified. As a result, evaluation of environmental pollution risk helps in coming up with the best shooting range management practices for the control and remediation of polluted soils.

Pollution risk formulae and methods have been used to assess and quantify shooting range soils pollution.[35,47,87,147,151,170] Such environmental pollution risk assessment methods include; (i) contamination factor (*CF*), (ii) enrichment factor *(EF)* and (iii) potential ecological risk index (*PERI*).[170] The interpretation of results obtained using these pollution indices provide a better understanding of the pollution risk posed by the accumulation into shooting range soils of Pb used in the manufacture of ammunition.

2.6.1. Evaluation environmental pollution risk using contamination factor

The contamination factor (*CF*) relates the degree of Pb deposition into shooting range soils to the background concentration of Pb.[170] The background Pb concentration usually comes from nearby unpolluted sites that act as controls. It is estimated using Equation (3) given below,

$$CF = C_i/C_b \qquad (3)$$

where C_i and C_b denote mean concentrations of the target heavy metal in the soil (Pb) and background respectively. The environmental pollution risk levels of the calculated contamination factors are given in Table 2.2 below. Soils with a contamination factor of less than 1 are classified as being less contaminated while *CF* of greater than 6 implies very high soil contamination.

Table 2.2 Classification of contamination levels from Pb pollution.[170]

Contamination Factor (CF)	Contamination level
$CF < 1$	Low contamination
$1 \leq CF < 3$	Moderate contamination
$3 \leq CF \leq 6$	Considerable contamination
$CF > 6$	Very high contamination

In a study by Dinake *et al*. (2018), the soils found in all the seven shooting ranges studied experienced contamination factors *(CF) g*reater than 6 (*CF* = 238-11,255) implying 'very high contamination' from Pb.[170] The highest *CF* determined was more than 1800 times the set threshold for soils with very high contamination, which indicated that the corresponding shooting range soil was extremely contaminated with Pb. It is also important to note that the highest *CF* value determined at the MAT R2 shooting range correlated well with the amount of Pb (20888 ± 5419 mg/kg) accumulated in the soil found in this shooting range.[170]

2.6.2. Quantitative assessment of environmental pollution risk using the enrichment factor

Shooting ranges are anthropogenic activities that lead to the accumulation of toxic heavy metals such as Pb into soil and water. The enrichment factor *(EF)* is a tool used to quantify the degree of pollution from such anthropogenic activities as shooting ranges.[170] Enrichment factor gives an understanding of how shooting range soils and their immediate environment is impacted by the Pb emanating from ammunition used for shooting practices relative to original undisturbed state of the soil. A formulae given in Equation (4) below is used to estimate *EF*

$$EF = \frac{C_{Pb}}{[\text{Median } C_{Pb} \text{ Background} + (2 \times \text{MAD } C_{Pb} \text{ Background})]} \qquad (4)$$

where C_{Pb} is the concentration of Pb in shooting range soil; median C_{Pb} Background is the concentration of Pb in background soil and MAD C_{Pb} Background is the median absolute deviation from median given by the following equation (5),

$$\text{MAD} = \text{median}(\left| C_{pb} \text{ Background} - \text{median}(C_{pb} \text{ Background}) \right|) \qquad (5)$$

The equation given above is read as; find the mean of replicate Pb background concentration in unpolluted soil; then subtract the median from each background Pb concentration; take the absolute value of the differences between the individual background Pb concentrations and their median and finally obtain the median of these absolute differences. The degree of shooting range soil enrichment can be categorized as in Table 2.3 below. *EF* of greater than 50 means there is extreme soil enrichment with Pb toxic pollutant.

Table 2.3 Categories of enrichment factor.[170]

EF	Level of enrichment
<1	No enrichment
1≤ *EF* <3	Minor enrichment
3≤ *EF* <5	Moderate enrichment
5≤ *EF* <10	Moderately severe enrichment
10≤ *EF* <25	Severe enrichment
25≤ *EF* <50	Very severe enrichment
EF ≥50	Extreme enrichment

In Pantex shooting range soils (Texas, USA) total Pb concentration of 4675 mg/kg was determined with corresponding enrichment factor *(EF)* of 277. Such high *EF* value depicted soils with extreme Pb enrichment. The soil in this shooting range was highly contaminated with Pb exceeding the USEPA set critical limit of 400 mg/kg by a factor of more than 10.[87] In another study in Kesariani, Greece, an enrichment factor of 115 indicated extreme Pb Pb enrichmenet of shooting range soils.[35] Similarly a study in seven shooting ranges found in Botswana established extreme Pb enrichment of *EF* ranging from 146 to 7467.[170] The *EF* values determined corroborated the high concentrations of Pb deposited in the seven shooting range soils studied. Establishing the extent of Pb enrichment in shooting range soils can assist in pollution management and control strategies to employ in order to curb such contamination.

2.6.3. Assessment of ecological risk using potential ecological risk index

On the other hand, potential ecological risk index *(PERI)* accounts for both ecological and environmental effects emanating from Pb pollution of shooting range soils.[170] This concept was first coined by Hakanson in 1980.[171] It consists of three components; (i) degree of contamination *(CD)*, (ii) toxic-response factor *(TR)* and (iii) potential factor *(ER)*. Three components can be incorporated into the potential ecological risk index as shown in equations (6) and (7) below.

$$C^{Pb}{}_F = C^{Pb}{}_D / C^{Pb}{}_R \quad (6)$$

$$E^{Pb}{}_R = T^{Pb}{}_R \times C^{Pb}{}_F \quad (7)$$

Where $C^{Pb}{}_D$ denotes the concentration of Pb in each sampling point; $C^{Pb}{}_R$ is the reference concentration of Pb as measured in unpolluted control areas; $C^{Pb}{}_F$ represents the pollution coefficient of Pb and $E^{Pb}{}_R$ indicates the potential ecological risk index from Pb deposited into shooting range soil. The $T^{Pb}{}_R$ signifies the biological factor of Pb as determined by Hakanson, (1980) and it is 5 for this heavy metal.[171] The ecological toxicity levels emanating from Pb pollution of shooting range soils can be arrived at using information given on Table 2.4 below.

Table 2.4 Potential Ecological risk index and the corresponding ecological risk level.[170]

Ecological risk index	Ecological risk level
<40	Low
40< $E_r \leq$80	Moderate
80< $E_r \leq$160	Considerable
160< $E_r \leq$ 320	High
$E_r \geq$320	Very high

Potential ecological risk indices *(PERI)* of 3446 and 725 at Cho-do and We-rye respectively, were determined in the two shooting range soils found in South Korea.[147] It can be seen that the PERI values at the two shooting ranges exceeded the set limit of $E_r \geq$320 by a huge magnitude indicating very high risk to the ecosystem. Similarly, Dinake *et al*. (2018) determined the Pb potential ecological risk indices in the range 1192–56,272 in the seven shooting range soils studied, indicating extreme risk to biota.[170] These extremely high ecological risk indices for Pb in shooting range soils require for urgent remedial and pollution control strategies to be adopted and applied mitigating Pb pollution of shooting range soils.

2.7. Evidence of uptake of Pb by vegetation

There is evidence that most of military shooting ranges in use and those decommissioned are not fenced yet act as grazing fields for domestic animals. Plants and grass growing in polluted shooting range soils have been found to uptake Pb from the soil which can be transported through the food chain when animals graze on these polluted grasses and plants.[113,127,130] Previous studies have shown that plants growing in soils contaminated with Pb were able to absorb Pb from the soil with the concentration of Pb absorbed by plants directly proportional to the concentration of Pb in the soi.[44] In a study by Cao *et al*. (2003), it was established that Pb concentrations in the bermuda grass growing close to the berm were high compared to the grass far away from the berm. Pb concentrations of up to 1342 mg/kg were found in the roots of the Bermuda grass growing near the berm soils.[44] In addition, Pb concentrations were also determined in the shoots of the bermuda grass (806 mg/kg) increasing the possibility of Pb exposure to animals grazing on the polluted bermuda grass. The findings by Cao *et al.* (2003) were consistent with the study by Mellor and McCartney (1994)[16] who found highest concentrations of Pb (over 400 mg/kg) in oilseed rape (*Brassica napus L.*) plants in the area containing the greatest Pb shot deposition compared with less than 14 mg/kg in oilseed plants growing some 300 m away from the area of intense Pb shot deposition. The bioaccumulation of Pb in plants had also been established earlier in shooting ranges in Helsinki, Finland, where Pb concentrations of 38-70 mg/kg were determined in the leaves of three plant species; *Betula pendula*, *Tussilago farfara* and *Equisetum sylvaticum.*[84] The Lingonberries growing in the polluted soils contained Pb concentrations of 0.3 mg/kg and were considered not suitable for consumption in accordance with the Finnish food safety regulations. Earlier studies by Rooney *et al.* (1999), found Pb uptake by radish roots and stem of up to 3825 and 100 mg/kg respectively, relative to soil Pb concentration of 5900 mg/kg.[45] The contribution of dust to Pb in plants should also be considered versus root uptake to clearly understand the ecological impact and Pb transference in the food chain where herbivores are the main receptors. Pb concentrations were found to be 42% lower than in unwashed plants, implying that adsorbed dust arising from Pb shot impact contributed immensely to the Pb loading of in situ plants.[106] An assessment of Pb absorption by the leaves of 10 plant species growing in the berm soils has been carried out by Robinson *et al.* (2008).[113] In soils that contained total Pb concentrations of more than 60000 mg/kg, some plant species such as *Equisetum arvense* and *Tussilago farfara* were able to absorb more than 1000 mg/kg Pb into their leaves.[113] It is worth noting that the concentration of Pb in plant leaves correlated with the concentration of

Pb in the soil. Robinson and co-researchers also found that the maximum bioaccumulation coefficient of Pb increased at elevated concentrations of soil Pb. The implications of these findings were that the risk of Pb moving through the food chain via plant update, to a large extent exceeded threshold concentrations. Most of the plants in the studies referred to in this section failed the world health organization (WHO) guideline for Pb in edible plants, fruits and vegetables set at 0.3 mg/kg dry weight (DW).[45] The solubility of Pb minerals absorbed by plants is very crucial, since high soluble Pb minerals can harm plant roots, allowing direct entrance of soil solution into the xylem and thus enhancing diffusion processes of Pb from the soil into the plant.[113] The detrimental effect of Pb to plant growth and well-being was established in a study by Mellor and McCartney (1994) in which concomitant reduction in growth of ryegrass with increasing soil Pb concentration was observed.[16] Mellor and McCartney (1994) also reported a reduction in the crop density and stem diameter of oilseed rape plants growing in the soil containing Pb concentrations of 1500 to 10 500 mg/kg.[16]

In addition, it is of critical importance that there is distinction between Pb in aboveground biomass portions of plants that came about due to surface deposition and Pb up-taken by the roots and subsequent translocation to the shoots.[113] When a decommissioned shooting range gets heavily vegetated, the uptake of Pb by plant roots can help suppress the production of wind-borne dust and redistribution of pollutants by ran-off water. As a result, Pb uptake from the soil will be the only source of aboveground Pb concentration in plants and hence the only potential Pb exposure to grazing animals. Farmers growing crops near highly Pb polluted shooting ranges should be encouraged to avoid cultivation of root crops in which high levels of Pb are absorbed in the edible part of the plant. In such soils, cultivation of cereal plants should be considered where the risk of Pb contamination is likely to be reduced because the edible parts of the plants are above the ground.[16]

The ability of plants to uptake Pb in shooting range soils has seen the rise in their application in soil amendments to remediate polluted shooting range soils through a process called phytoremediation.[52,172,173] This method makes use of vegetation for the absorption and uptake of Pb from shooting range soils to mitigate the spread of Pb pollution through a process called phytostabilisation in which plants are able to immobilize Pb through its uptake and accumulation in the plant roots and precipitation in the rhizosphere.[149,174] Moreover, this remediation technique helps slow down the mobility and migration of Pb and its abrasion from shooting range soils.[175] Furthermore, this strategy has been found to be environmentally

friendly since it does not produce toxic by-products and metabolites that can add new pollutants to the soil.

2.8. Soil reclamation and remediation techniques applied to Pb polluted shooting range soils

Presently, management and remediation of shooting ranges is largely dependent on written manuals and guidance documents such as the United States Environmental Protection Agency (USEPA)'s 'Best management practices of lead outdoor ranges' manual.[12] Management of pollution of shooting range soils is based on four management strategies; (i) control and containment of bullets, (ii) prevention of migration of contaminants, (iii) removal and recycling of bullets, and (iv) documentation and evaluation of environmental management plans.[12] The control and containment strategies involve use of bullet curtains and traps that are used to collect Pb shots and bullets and prevent the accumulation of these Pb shots and bullets into shooting range soils. The trapped Pb shots and bullets can then be collected and taken away for safe disposal or recycling of the Pb metal. Other strategies include chemical stabilisation agents and phytoremediation. Chemical stabilisation entails the use of a chemical agent to immobilise and restrict migration, leaching and bioavailability of Pb in shooting range soil. This include addition of chemical stabilisers such as phosphate, Fe and Al oxides, lime, red mud, MgO, mussel shell, cow bone, biochar and carbon nanotubes.[75] Phosphate stabilization strategy has been applied for the control and management of Pb mobility and bioavailability in shooting range soils for many years. The choice for the phosphate was made because of its ability to make insoluble precipitates of Pb-phosphates that are stable over a wide pH range.[142,176] Examples of these phosphates that have been used to control the migration of Pb in shooting range soils include hydroxyapatites, rock phosphate and phosphate salts.

Fayiga and Saha (2017) were able to show that application of phosphate rock and phosphoric acid to polluted shooting range soils reduced the toxicity leaching procedure (TCLP) of Pb from 800 mg/l to less than 1 mg/l.[177] A study by Sanderson *et al*. (2015) was able to establish that phosphate amendments of polluted shooting range soils caused a drastic decrease in Pb bio-accessibility by up to 55%.[142] Another study involving coating of Pb shots and bullets surfaces with phosphate based salts saw a dramatic decrease in the leaching and weathering of Pb shots by up to 98%. In another study, the application of phosphoric acid to contaminated shooting range soil was able to convert most of the eroded Pb to about 38% of

pyromorphite and reduction of bio-accessibility by 25%.[176] More studies have successfully used phosphate based stabilizers to control the mobility and bioavailability of Pb in shooting range soils.[178,179]

In a study by Ahmad *et al*. (2014), 5% of mussel shell, cow bone and biochar were able to reduce the uptake of Pb by maize planted in the polluted soils by 71% and this is evident that modified living organism waste has the capability to remediate polluted shooting range soils.[180] The use of only 10% biochar was also able to immobilize Pb in shooting range soils reducing the amount of Pb in the labile exchangeable fraction (WE) by 88.08%.[181] A combination of biochar and carbon nanotubes effectively lowered the concentration of Pb in shooting range soil by 17.6%.[182] The effectiveness of biochar in Pb immobilisation is highly dependent on the chemical constituent of the matter. Phosphorous-rich biochar have been found to be potent in stabilising Pb in shooting range soil.[75]

Other shooting range soil amendments such as MgO, lime, iron oxyhydroxides, red mud and silver nano particles have been successfully used to stabilise and control Pb pollution of shooting range soils.[47,144,183]

Management of Pb pollution in shooting range soils must take into account the physicochemical properties of the soil such as type of soil, soil pH, soil organic matter and soil cation exchange capacity because such strategies are site specific.[75] Depending on the physical and chemical properties of a shooting range soil, particular remediation method may work in one particular shooting range while for the next shooting range a completely different strategy would have to be employed.

2.8.1. Chemical amendments applied to Pb polluted shooting range soils

Addition of chemicals to polluted shooting range soils in order to arrest and contain pollution from Pb has been on-going for many decades and it is still being practiced to this day.[57,131,142,184,185] Some of these amendments have been found to be cost effective with the possibility of being applied on a large scale. It is worth noting that critical cognizant of important factors have to be taken into consideration such as in situ viability, environmental impact and sustainability of the applied chemical amendment.[186]

Chemical amendments have been shown to possess the ability to lower the mobility, bioavailability, bioaccessibility, leaching and ecotoxicity of Pb in shooting range soils.[109,123,172] The process through which chemical amendments stabilize and immobilize Pb in shooting range soils stems mainly from the transformation of Pb chemical and mineralogical forms.[107] Pb speciation, valence and soil properties such as sorption capacity and buffering potential play a pivotal role in chemical stabilization of Pb in shooting range soils.[107] In addition, the chemical additives intensify physical and chemical processes which restrict the mobility and bioavailability of Pb through formation of insoluble Pb minerals. Another important factor to consider about chemical amendments is that they are in situ stabilization techniques and their use in the soil does not alter the total Pb concentration of the shooting range soil.[183] The Chemical additives that have been applied to shooting range soils comprises of both organic and inorganic chemicals that may be synthetic or natural. Some inorganic chemicals that are a source of phosphate such as phosphate rock and hydroxyapatite have been excellent in immobilizing and stabilizing Pb in shooting range soils.[57,119] Magnesium oxide (MgO), ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$), natural iron oxides (Fe_2O_3), calcium carbonate ($CaCO_3$) and zero-valent iron have also been used as chemical amendments.[109,142,158,174] In most cases organic chemical additives have been preferred over inorganic chemical amendments because of their low cost and are readily available.[180-183] Most of the organic chemical amendments are derived from waste which can be transformed into biochar for optimization of the stabilizing ability of the organic chemical amendment.[187]

Biochar is a carbon-rich matter that is derived from combustion of biomass in a sealed container under inadequate oxygen conditions.[187] Examples of biochar material that have been used to immobilize Pb in shooting range soils include; oak wood biochar,[180,183] soy bean stover biochar,[181] green waste biochar[185] and biodegradableethylenediamine-N,N′-disuccinic acid (EDDS).[188] It is imperative that the ecological and environmental risks from use of these chemical amendments are well appreciated and addressed.[72] As mentioned earlier, chemical remediation is an in situ soil remedial strategy and one of the shortfalls about chemical amendments is that they do not remove contamination from the soil such that the pollutant will still be in the soil after remediation exercise has been completed. It is therefore important that there is proof that the chemical amendment has reduced the environmental pollution risk from Pb to an acceptable regulatory level that is comparable with proposed land use.[72]

2.8.1.1. Phosphate Amendment

The application of phosphate toward Pb stabilization and immobilization was first suggested by Nriagu in 1974 while doing research study on the formation and chemical properties of Pb-orthophosphates.[189] The findings by Nriagu has opened opportunities for further studies involving application of different phosphate containing substances towards Pb immobilization in shooting range soils and landfill sites.[72] The United States Environmental Protection Agency (USEPA) lists phosphate chemical amendments in the shooting range best management practices (BMPs) manual as one of the suitable options for soil pollution remediation and management strategies.[12,190] The proposed mechanisms through which phosphate stabilizes Pb in soils is through the formation of the thermodynamically stable Pb-phosphates such as pyromorphites ($Pb_5(PO_4)_3X$ where X = Cl^-, OH^-, F^-) and plumbogummite ($PbAl_3(PO_4)(PO_3OH)(OH)_6$) which are not readily soluble over a wide range of pH and redox potential (Eh).[190] For example, the thermodynamic chloro-pyromorphites are the most stable over a wide range of pH 3–11).[189]

The implementation of phosphate remediation methods should take into consideration the pH and redox potential dependence of the Pb-phoshate end product and its reaction kinetics that are mainly affected by factors such as moisture availability, solution chemistry and particle size of Pb and phosphate compounds.[186] In addition, a clear understanding of the solubility of the original phosphate chemical amendment materials should be made.[186] The remediation strategy should also account for the environmental and ecological risks of Pb in the soil that was not able to be immobilized and stabilized. Scientists and researchers have successfully experimented and achieved immeasurable results through the use of different sources of phosphates towards Pb immobilization and stabilization in soil. Such sources of phosphate include chemicals such as phosphate rock, mono-calcium phosphate, di-calcium phosphate, tri-calcium phosphate, triple super phosphate, phosphoric acid, diammonium phosphate, hydroxyapatite, Apatite II, phosphatic clay, commercial fertilisers, bone meal, poultry waste and bone char.[186]

The different sources of phosphate can be classified into three major categories based on their solubility: (i) readily soluble phosphates (e.g. phosphoric acid); (ii) moderately soluble phosphates (e.g. mono-, di- and tricalcium phosphate); and (iii) less soluble phosphate (e.g. synthetic hydroxyapatite and phosphate rock).[186]

Soil physicochemical properties such as soil pH, moisture and redox potential have a significant impact on the transformation, precipitation, dissolution and insolubility of Pb minerals and phosphate chemical amendments.[191] Under acidic conditions, the dissolution of Pb minerals and phosphate chemical amendments is favoured compared to conditions of alkaline pH in which the Pb minerals and phosphate chemical amendments become less soluble.[191] Soil remediation techniques have employed the use of commercially available phosphate chemicals such as diammonium phosphate (DAP: $(NH_4)_2HPO_4$) and calcium phosphate monobasic (CPM: $Ca(H_2PO_4)_2$) in shooting range soils with high Pb loading resulting in significant decrease in concentrations of labile Pb minerals by 45% and 99% for DAP and CPM respectively.[107] It was established in this study by Spuller *et al.* (2007) that the mechanism for Pb stabilization occurred through the transformation of Pb in shooting range soil into insoluble Pb-phosphates; $Pb_3(PO_4)_2$ and $Pb_4O(PO_4)_2$.[107] The Pb stabilization effect of CPM was determined to be superior over that of DAP due to a more pronounced availability of phosphate in CPM compared to DAP. In addition, there was high dissolution of organic carbon in DAP chemical amendment which resulted in the transformation of Pb into soluble organo-Pb complexes.[107] The scarcity of phosphate in DAP was found to be caused by the conversion of DAP into the semi soluble calcium hydrogen phosphate in soils with high concentrations of calcium. The calcium hydrogen phosphate would finally dissolve generating phosphoric acid as shown in equations (8) and (9) below:

$$(NH_4)_2HPO_4 + Ca^{2+} + 2H_2O \rightarrow CaHPO_4 \cdot 2H_2O + 2NH_4^+ \quad (8)$$

$$4CaHPO_4 \cdot 2H_2O + H_2O \rightarrow Ca_4H(PO_4)_3 \cdot 3H_2O + H_3PO_4 \quad (9)$$

In a study by Sanderson *et al.* (2015), three substances containing phosphate (soft rock phosphate (10% phosphorus), phosphoric acid (85% H_3PO_4) and commercial phosphorus) were employed for stabilization and immobilization of Pb in soils sampled from four shooting ranges (Murray Bridge, Townsville, Darwin and Perth) of different physicochemical properties.[142]

Water-extractable Pb was measured in all soil samples obtained from the four shooting ranges and it was established that water-extractable Pb decreased by over 90% at the Murray Bridge shooting range after application of soft rock phosphate with less effect at Darwin and Perth shooting ranges.[142] On the other hand, phosphoric acid was found to be more efficient in lowering water-extractable Pb in soils obtained from Murray Bridge, Townsville and Darwin than at Murray Bridge.[142] Conversely, mobilisation of Pb was observed at Perth shooting range after application of phosphoric acid.

Commercial phosphorus was also found to be effective in reducing the concentration of water-extractable Pb at Murray Bridge and Townsville shooting ranges. The concentration of Pb determined using the toxicity characteristic leaching procedure (TCLP) was found to be up to 200 mg/l in the four shooting range soils studied, exceeding by 40 times the 5 mg/l USEPA regulatory set limit in untreated soils. It was established that the application of soft rock phosphate chemical amendment was able to lower TCLP-Pb concentrations significantly to concentrations below the regulatory set limit of 5 mg/l.[142] Furthermore, physiologically based extraction test (PBET) was able to demonstrate that the phosphate chemical amendments effectively lowered bio-accessible Pb by over 50%.[142] In a related study, Ogawa *et al.* (2015) used hydroxyapatite ($Ca_5(PO_4)_3OH$) to immobilise and stabilise Pb in a shooting range polluted with over 23 000 mg/kg of Pb and water-extractable Pb concentration of over 100 mg/kg.[178] The application of hydroxyapatite was able to lower the concentration of water exchangeable Pb by 99.2 % (0.9 mg/kg), an indication that this chemical amendment remarkably transformed Pb from its labile and soluble form into the inert and insoluble Pb minerals.[178] The sequential extraction procedure showed a decrease from 78.4% of the labile water exchangeable and carbonates fractions to 45.4% of the unreactive forms of Pb. The effectiveness of the phosphate chemical amendments have also been tracked using X-ray absorption spectroscopy whereby researchers are able to identify and monitor the main Pb minerals in un-amended soils compared to the chemicals that they have been transformed into in the remediated shooting range soils.[176] The transformation of soluble Pb minerals into inert minerals was followed using X-ray absorption spectroscopy before and after addition of phosphate chemical amendment in which Pb minerals litharge (PbO), humic acid bound Pb and iron-oxide bound Pb were observed in untreated soils whereas the remediated soils contained 17% of the inert pyromorphite.[176] In a similar study the X-ray diffraction (XRD) spectrum showed that soil amendment using hydroxyapatite transformed over 95% of Pb into pyromorphite.[178]

Many scientists and researchers are working tirelessly to find cost effective yet efficient soil chemical amendments because most of the chemical amendments recommended by the USEPA can be quite costly when applied at a large scale such as an outdoor shooting range. In consequence, researchers have shifted their attention to cheap industry by-products and waste that are a good source of phosphate such as poultry waste, cow bone and biomass.[134,172,183,192] Many researchers have found poultry waste to be good source of hydroxyapatite ($Ca_5(PO_4)_3OH$) and it has been observed to perform superiorly over the commercially available hydroxyapatite.[193]

Poultry waste has been found to be effective towards Pb immobilization in shooting range soils in which a 43% decrease in water-extractable Pb was observed after application of poultry waste.[172] In addition an increase of 20% in the concentration of Pb in the residual fraction was observed while a reduction by 20% was noted for the concentration of Pb in the water exchangeable and carbonates labile fractions.[193] Other studies have been confirmed in which soil remediation of Pb pollution of shooting range soils using poultry waste resulted in an increase in the inert residual fractions.[178,194-196] As mentioned earlier, it is important to take into consideration the soil physicochemical properties such as the soil pH for optimal performance of the chemical amendment. It has been determined that at elevated pH levels, the dissolution kinetics of poultry waste took place at a faster rate resulting in the liberation of phosphate ions and an enabling environment for the transformation of Pb minerals into insoluble chloropyromorphite precipitates.[119] The mechanism through which poultry waste immobilized Pb was proposed by Hashimoto *et al.* (2009) in which an ionic exchange process between Ca in poultry waste and Pb in shooting range soil leading to the formation of insoluble Pb-phosphate mineral.[119] It was also established that the solubility of the Pb-phosphate mineral decreased with increasing pH of the solution leading to the immobilization of Pb. Hashimoto *et al.* (2009) proposed the following two steps mechanism in which Pb is exchanged for Ca in hydroxyapatite found in the poultry waste (equation (10)) followed by the dissolution of the hydroxyapatite releasing the dihydrogen phosphate anion ($H_2PO_4^-$) (equation (11)) and eventually the precipitation of Pb-phosphate takes place (equation (12)).

$$Ca_{10}(PO_4)_6(OH)_2 + xPb^{2+} \rightarrow [Ca_{(10-x)}Pb_x](PO_4)_6(OH) + xCa^{2+} \quad (10)$$

$$Ca_{10}(PO_4)_6(OH)_2 + 4H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2H_2O \quad (11)$$

$$10Pb^{2+} + 6H_2PO_4^- + 2H_2O \rightarrow Pb_{10}(PO_4)_6(OH)_2 \quad (12)$$

The application of waste cow bone which has a high content of phosphorus (18.5 wt. % P_2O_5) combined with calcined oyster shells (84.3 wt. % CaO) towards Pb stabilization in shooting range soils led to a major reduction in Pb leachability (99%) compared to the untreated soil sample.[134] To be specific, total concentration of Pb in the untreated soil was determined to be 3613 mg/kg and after combined application of waste cow bone and calcined oyster shells only 16.2 mg/kg (>99% reduction) was measured in the treated soil, an indication that most of the Pb had transformed into the inert insoluble Pb minerals.[134] In a similar study by Ahmad *et al.* (2014) cow bone has been shown to lower bioavailable and exchangeable Pb in shooting range soil by 93% compared to untreated soil.[180] In addition, the application of cow bone to the Pb polluted soil significantly lowered the phytoavailability of Pb by 70.47%.[180]

Other studies have investigated the efficacy of biochar towards stabilization of Pb in shooting range soils because of its low cost and it is readily available.[183,192] In a study by Rajapaksha *et al.* (2015), the effectiveness of buffalo weed (*Ambrosia trifida L.)* biomass towards Pb stabilization of shooting range soils was compared with that of its biochar pyrolysed at 300 and 700 ^oC. Phosphate (PO_4^{3-}) concentration in the buffalo weed biomass was determined to be 3.89 mg/kg while its pyrolytic biochars contained phosphate concentrations of 79.96 mg/kg (300 ^oC) and 70.72 mg/kg (700 ^oC).[183] The efficacy of these chemical amendments towards Pb stabilisation were evaluated in shooting range soil contaminated with over 17 468 mg/kg of Pb. Biochar pyrolysed at 300 ^oC displayed superiority towards Pb immobilization (94.7%) followed by the biochar pyrolyzed at 700 ^oC (92.6%) while the original biomass only managed to stabilize 35.5% of Pb in the soil.[183] Moreover, the concentration of TCLP-Pb was also decreased by 77.2% upon application of biochar indicating possible transformation of soluble Pb into insoluble Pb minerals by biochar.

In recent years many other studies have also focused on the application of pyrolytic biochar towards Pb stabilisation and immobilisation in shooting range soils due to its potency, low cost and ease of availability.[180,181] The effectiveness of pyrolytic biochar is an indication that conversion of biomass into biochar improves the stabilisation and immobilisation properties of this material.[180] The pyrolysis temperature plays a pivotal role in converting the original biomass into highly effective and efficient pyrolytic biochar for Pb stabilization in soil. An increase in pyrolysis temperature causes a decrease in the mobile components which provides enhances the formation of the stable matter arising from loss of volatile components during the pyrolysis process of biomass.[180]

During thermal decomposition of biomass, elevated levels of ash in biochar are observed because of the deposition and accumulation of inorganic minerals and organic matter as pyrolysis temperature increases.[180]

Additionally, an increase in surface areas is observed as result of the creation of micropores.[180] It has also been established that the large quantity of carboxyl functional groups in biochar can form strong complexes with Pb in the soil and thereby restricting its mobility and leachability.[197] In addition, studies have also shown that the surfaces of the biochar materials usually carry a negative charge that can attract the positively charged Pb via electrostatic force of attraction.[197] In addition to the electrostatic attraction between Pb and the negative charge layer on surface of biochar, there is also π-π electron donor-acceptor interaction the positively charged Pb in the soil and electron rich graphene in the biochar.[198,199]

2.8.1.2. Liming soil amendment

In addition to phosphate chemical amendment, the USEPA has also recommended the application of lime towards Pb stabilization and immobilization. The application of liming to shooting range soil has been found to have an effect on the pH of acidic soils by increasing its pH as shown in equation 13 below;[12]

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + 2OH^- + CO_2 \qquad (13)$$

(In the soil) (Increases pH)

The solubility of the Pb-carbonates minerals has been observed to be slow in the presence of lime due to a decrease in the concentration of the proton (H^+) providing an unfavorable alkaline environment that inhibits the solubility of the formed Pb carbonates.[57] The application of lime into shooting range soils has also been reported to lead to the formation of pozzolanic minerals which are formed through sorption, phase mixing and substitution.[134] The pozzolanic products normally contain calcium silicon hydrates, calcium aluminium hydrates and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) as shown in equations 14–17 below;

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \qquad (14)$$

$$Ca^{2+} + 2OH^- + SiO_2 \rightarrow \quad CSH \qquad (15)$$

(Calcium silicate hydrate)

$$Ca^{2+} + 2OH^- + Al_2O_3 \rightarrow \quad CAH \qquad (16)$$

(Calcium aluminate hydrate)

$$6Ca^{2+} + 2Al(OH)_4^- + 4OH^- + 3(SO_4^{2-}) + 26H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O \qquad (17)$$

(ettringite)

The mechanism through which pozzolanic minerals immobilize Pb in shooting range soil involves entrapping Pb in their chemical lattice.[131] Examples of studies that involve lime amendment include a study by Levonmaki and Hartikainen (2007) in which the ability of two liming agents, calcium carbonate ($CaCO_3$) and blast furnace slag, to immobilize and stabilize Pb was tested.[109] It was discovered that the concentration of water extractable Pb was substantially reduced by 69% after applying $CaCO_3$ and 61% when blast furnace slag was used.[109] Sanderson *et al.* (2015) used 5% lime for Pb stabilization in shooting range soil with moisture holding of 60% and over 90% of water extractable Pb was immobilized.[142] In the United States of America, a study by Yin *et al.* (2010), demonstrated that liming was effective towards Pb stabilization in which total Pb concentration was reduced by 20-80%.[123]

As observed with phosphate sources, scientists and researchers are also continuously searching for other sources of lime that are cost effective and efficient.[131,134,180] Industrial and household wastes with high content of lime have been applied towards Pb immobilization and stabilization in shooting range soils. These materials include such materials as cow bone,[180] Mussell shell,[180] egg shel,[131] and oyster shells.[134] The application of 5 weight percent of calcined oyster shells has seen a 99% decrease in total concentration of Pb from 3613 mg/kg in the untreated soil to 16.2 mg/kg after chemical amendment.[134] Ahmad *et al.* (2012) used eggshells and calcined eggshells in a Korean shooting range in which TCLP-Pb was found to be eight times higher than the USEPA set regulatory guideline and observed a reduction in the concentration of TCLP Pb by up to 68.8%.[131] The SEM-EDS, XAFS and elemental dot mapping patterns showed interaction between Pb and Si and Ca, supporting the proposed mechanism that Pb was embedded and immobilized inside the calcium silicate hydrate lattice.[131] In addition, it was also established that Pb had been transformed into the insoluble compounds $Pb(OH)_2$ and lanarkite ($Pb_2O(SO_4)$).[131] It was also established that the application of lime containing industrial and household wastes also has an impact on the soil pH as shown by an increase in the soil pH after soil amendment using eggshell and calcined eggshell, demonstrating a similar effect when commercial $CaCO_3$ and CaO were used.[131] As mentioned in previous sections, the increase in pH raises the number of the negative charges on the soil particles and provides a conducive environment for the precipitation of Pb carbonates and oxides. However, both short and long term environmental effects should be taken into consideration in the continuous application of these liming amendments to Pb polluted shooting range soils.[200]

2.8.1.3. Iron based sorbents soil amendments

The immobilization and stabilization of Pb in shooting range soils has also been achieved through the use of iron based chemical additives and these chemicals are favoured becaused of their non-intrusive nature.[178,201] Scientists and researchers have proposed a mechanism for the immobilization of Pb using iron based sorbents in which sorption of Pb occurs by iron (III) hydroxides that are embedded in iron sorbents ferrihydrite, goethite and gibbsite.[107] Additional sorption sites are formed through the oxidation of zerovalent iron (Fe^0) in the presence of moisture into more iron(hydr)oxides as depicted in 18-20 below.[144]

$$Fe(0) + 2H_2O + 1/2O_2 \rightarrow Fe(II) + H_2O + 2OH^- \quad (18)$$

$$Fe(II) + H_2O + 1/4O_2 \rightarrow Fe(III) + 1/2H_2O + OH^- \quad (19)$$

$$Fe(III) + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad (20)$$

An ion exchange process will then take place between the proton (H^+) liberated in equation (20) and Pb that is adsorbed onto the kaolinite minerals in the soil leading to the removal of Pb from the kaolinite surfaces. The sites created by the removal of Pb in the minerals will be replaced by the iron (oxy)hydroxide precipitates. The continuous ion exchange between Pb and the proton (H^+) leads to the adsorption of more Pb by Fe(III) and formation of more ferric (oxy)hydroxides such as ferrihydrite ($Fe(OH)_3$), goethite (α-FeO(OH)) and akaganeite (with the formula $Fe(OH)_{2.7}Cl_{0.3}$ in the presence of chloride).[146] The chemical formation of ferric hydroxide akaganeite is given in the reaction equation 21 below;

$$Fe(III) + 2.7H_2O + 0.3Cl^- \rightarrow Fe(OH)_{2.7}Cl_{0.3} + 2.7H^+ \quad (21)$$

In similar studies, Pb has been immobilized in the cavities formed by iron hydroxides containing hydroxyl groups such as $\equiv FeOH^0$, $\equiv FeOH_2^+$ and $\equiv FeO^-$.[136,202]

One of the examples of Pb stabilization in shooting range soils by iron based sorbents include a study by *Spuller et al.* (2007), in which application of goethite and deferrisation sludge produced significant decline in total concentration of water extractable Pb by 97% compared to Pb concentration of water-extractable Pb in un-amended soil.[107] These iron sorbents immobilized Pb through the sorption mechanism and the higher surface area of deferrisation sludge (262.9 m^2/g) adsorbed more Pb compared to goethite with a surface are of only 23.5 m^2/g.[107] In Japan, soil amendment using ferrihydrite in a skeet shooting range drastically reduced the concentration of water extractable Pb from 100 mg/kg to 3.6 mg/kg giving 96.8% decrease of water extractable Pb compared to untreated soils.[107] In addition, most of the Pb in the skeet shooting range soils was transformed into the inert Pb minerals as seen by the decrease in the percentage of 62.8% representing the reactive Pb species of the water exchangeable and the carbonate fractions to 27.2% denoting the inert and non-reactive inert Fe-Mn oxide bound fraction.

This immobilization of Pb into the non-reactive Pb fractions translates into low mobility and bioavailability of Pb and hence reduced environmental pollution risk. The effectiveness of iron oxide towards Pb stabilization in shooting range soil was also evaluated by Rajapaksha *et al.* (2015) in a military shooting range in Gangwon-do, South Korea in which natural iron oxide chemical additive lowered ammonium acetate extractable Pb by 13.6% in the highly polluted shooting range soil with Pb concentration of 17 468 mg/kg.[183] In other studies, the use of ferric oxyhydroxide powder and zerovalent iron in a Norwegian military shooting range led to a 54% decrease in Pb leachability after application of ferric oxyhydroxide compared to un-amended soils. On the other hand, the zero valent iron exhibited more potency towards Pb stabilization where up to 98% reduction of Pb leachability was realized.[158]

In a similar approach as with other chemical amendments, scientists and researchers are finding options in materials and substances are a good source of iron and yet cost effective.[142] Iron rich substances such as red mud have been found as substitute for Pb immobilizatio in polluted shooting range soils over costly commercially available sources of iron.[142] Sanderson *et al.* (2015) investigated the efficacy of red mud that contained 28-45% iron oxide towards Pb stabilization in shooting range soils and discovered a drastic reduction in the concentration of water-extractable Pb by 99% in four shooting ranges that had accumulated 341–51,820 μg/kg of Pb.[142] Moreover, this chemical additive lowered TCLP-Pb concentration from 15 mg/L to around 7 mg/L.[142]

2.8.2. Phytoremediation

Phytoremediation is another strategy that has been employed for the remediation of Pb pollution in shooting range soils.[173] This technique utilizes vegetation for the adsorption and uptake of Pb from shooting range soils in order to reduce the degree of Pb loading through a process called phytostabilisation.[75] Phytostabilization describes the ability of plants to immobilize Pb through uptake and accumulation in the roots or precipitation in the rhizosphere.[150] Rodríguez-Seijo *et al*. (2016) have used the grass *Agrostis capillaris L.* to adsorb Pb deposited in a trap shooting range soil. It was found that high concentration of Pb (1107 mg/kg) accumulated in the roots of the grass and to a less extent in the shoots (135 mg/kg).[150]

Phytomanagement techniques have also been investigated in other previous studies such the one by Sneddon *et al*. (2009) who discovered up to 38 mg/kg Pb in the shoots of *L. perenne* sampled in shooting ranges in the United Kingdom.[203] Phytoremediation studies have also been explored by many scientists in their quest to find environmentally friendly methods and techniques for the control and management of Pb pollution in shooting range soils.[204,205] In addition, phytoremediation helps slow down the mobility of Pb and its erosion from shooting range soil.[175]

2.8.3. Other Soil Remediation Strategies

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 Pb in the soils at the ranges.[206] In addition, the weathering rate of Pb in sandy soils is quite low compared to clay and silt soils. Other proposed BMP's such as mechanical sieving have been found to increase Pb concentrations in soils due to the fact that the sieving action is abrasive and therefore adds significant amount of Pb powder back into the soil.[206] The weathering rate of Pb powder is quite high compared to Pb shot and bullet.

CHAPTER 3

3. EXPERIMENTAL/METHODOLOGY

3.1. Description and characteristics of sampling locations

A total of eight shooting ranges were selected in the southern and central Botswana. The eight sampling sites were located in or near the villages of Mogoditshane (MOG, GPS Coordinates: -24° 37' 36.98" South, 25° 51' 56.02" East), Mochudi (TSH, GPS Coordinates: -24° 24' 59.99" South 26° 08' 60.00" East), Makanke (MAK, GPS Coordinates: 24° 33' 11.00" South 25° 48' 14.00" East), and Thebephatshwa (TAB, GPS Coordinates: 24° 13' 18.40" South 25° 20' 53.80" East) in Southern Botswana and other shooting ranges such as Shoshong (SHO R1 and SHO R2, GPS Coordinates: -23° 01' 60.00" South 26° 30' 59.99" East) and Paje (PAJ R1 and PAJ R2, GPS Coordinates: -22° 16' 12.00" South 26° 47' 14.39" East) in the central Botswana as shown in the map below (Figure 3.1a).[31] For each shooting range, a background soil sample was collected 200 m outside the shooting range. The shooting activities taking place at these sites involve use of small arms assault rifles mainly of the 0.50", 5.56 mm and 7.62 mm calibres.

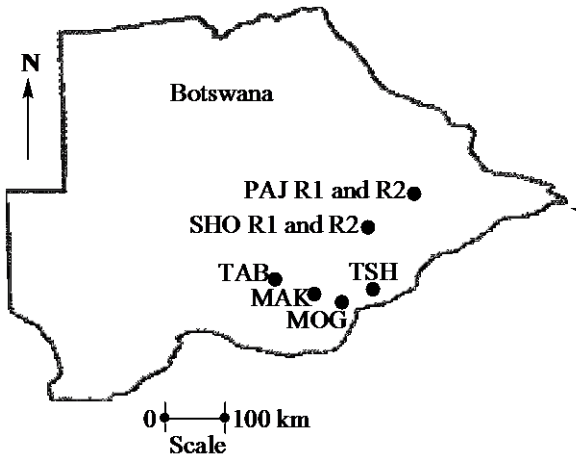


Figure 3.1a. Location of shooting ranges sampled in the map of Botswana.

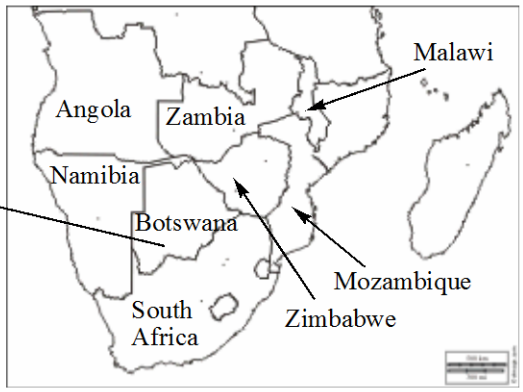


Figure 3.1b. Map showing southern african countries.

All the shooting ranges investigated have been in operation for over 20 years as provided in Table 3.1. The soils found in the sampled shooting ranges occur mostly into three classes (Table 3.1). The chromic luvisols which are moderately deep to very deep and moderately well to slightly excessively drained, strong brown to dark red, sandy loams to clay loams. There are also luvic arenasols which may be deep to very deep, well to somewhat excessively drained, yellowish brown to red, fine and fine-medium sands to loamy fine sands. The ferric luvisols were also found in most of the shooting ranges studied and this class of soils is moderately deep to very deep, imperfectly to moderately well drained, dark brown to red, sandy clay loams to clays.[31]

Table 3.1 Shooting ranges years of establishment and the corresponding soil types found at these shooting ranges.[31]

Range Location	Year of establishment	Soil Classification
MOG	1977	Ferric Luvisols
TSH	1998	Ferric Luvisols
MAK	1983	Chromic Luvisols
TAB	1995	Chromic Luvisols
SHO R1 and SHO R2	1995 and 1988 respectively	Chromic Luvisols
PAJ R1 and PAJ R2	1996 (both)	Luvic Arenosols

The rainfall patterns indicate that most of the shooting ranges receive more rainfall during the months of October to March as shown in Figure 3.2 below. These sites experience high amounts of rainfall in the summer and little to no rain during the winter season. The summer season covers the months of September to April with only four months of winter, May to August. The summer seasons can record high amounts of rainfall, as much as over 300 mm, as experienced by SHO shooting ranges during the month of December.

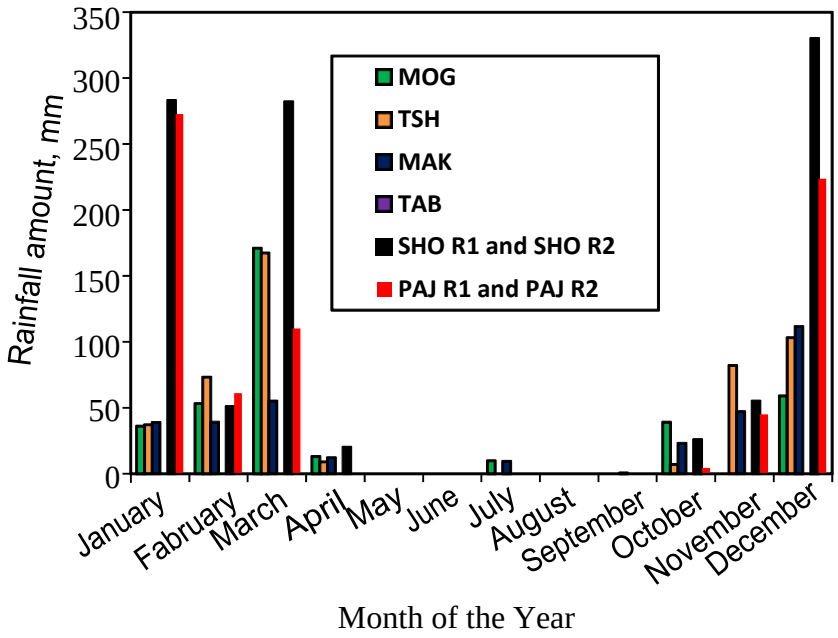


Figure 3.2 Rainfall amounts at the sampled sites for the period July 2013 to June 2014.

3.2. Soil Sampling of Shooting range soils

A total of 48 soil samples were collected from each shooting range to a depth of 20 cm from the earth surface using a soil recovery probe. The soil samples were collected in quadruplicates at three sampling areas on the berm, target line, 50 and 100 m from the target line along a central transect (Figure 3.3). Each sampling area was circular with a radius of 150 cm. Background soils were collected from the areas that were not impacted by lead bullets outside the shooting range at a distance of 200 m from the shooting range. Butyrated zip-lock plastic bags were used to store the soil samples. The field soil samples were then transported to the laboratory to start the sequence of analyses.

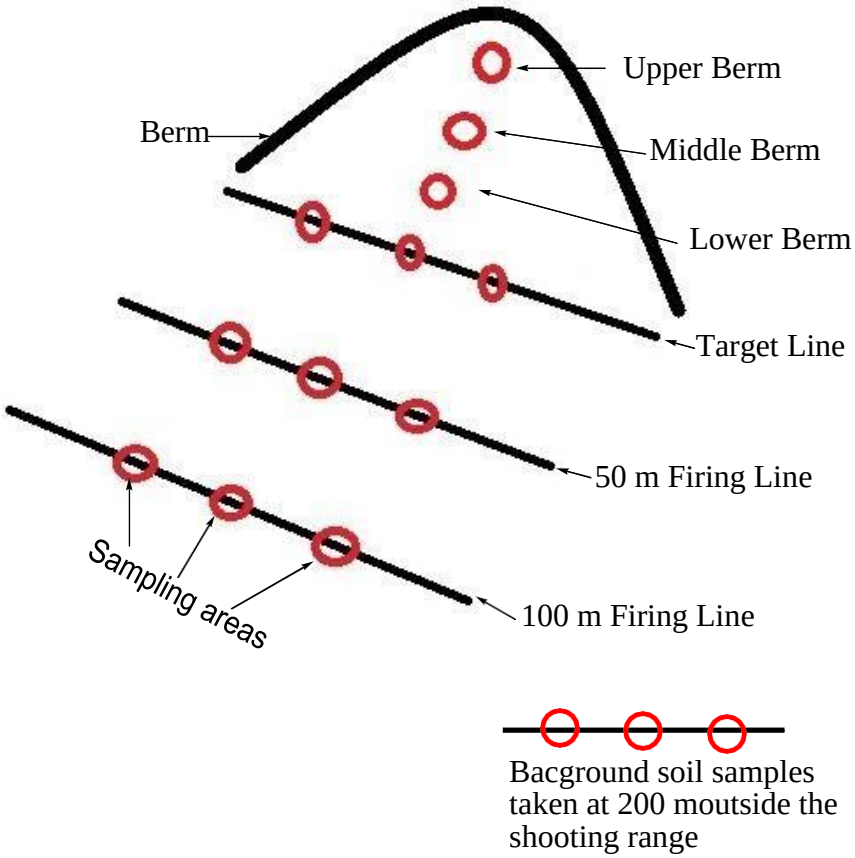


Figure 3.3 Schematic diagram of shooting range showing sampling points.

3.3. Chemicals and Reagents

All chemicals and reagents used were of analytical grade. Hydrofluoric Acid, Perchloric Acid, Acetic Acid (99.8%), and Nitric Acid (65%) were purchased from LabChem (Johannesburg, South Africa). Orthophosphoric Acid (85%) was acquired from Merck (Darmstadt, Germany); Ethanol (99.9%) and Hydroxylamine hydrochloride (99%) were both acquired 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 purchased from Rochelle Chemicals (Johannesburg, South Africa). Magnesium Chloride hexahydrate (99%) 1,10 Phenanthroline indicator (99.8%), Potassium Dichromate (99%) and Sulphuric Acid (96%) were purchased from Minema Chemicals (Johannesburg, South Africa) and Ferrous Ammonium Sulphate (99%) was procured from Alpha Chemika (Mumbai, India). The certified reference material (CRM) of soil (NCS DC

73320) was received from the Botswana Geoscience Institute (BGI) Chemistry Laboratory, in Lobatse, Botswana. Double deionized water obtained from the chemistry department at Botswana International University of Science and Technology (BIUST). Working standards solutions used for calibration were prepared from 10 ppm of multi elemental standard stock supplied by Perkin Elmer Inc.

3.4. Glassware used in the project

Glassware used in this research study include test-tubes, measuring cylinders, beakers, conical flasks, volumetric flasks, burettes, pipets and funnels purchased from Pyrex and Borosilicate Companies. All glassware was washed with liquid soap and tap water, soaked in HNO_3 acidified water overnight, rinsed with distilled water. All glassware except, volumetric flasks, burettes and pipette were dried in an oven at 110°C prior to use.

3.5. Sample Preparation and Analysis

The quadruplicate soil samples collected from the three sampling areas at the berm (bottom, middle and upper), target line, 50 and 100 m position line were mixed together to make three composite soil samples that are a representative of each position line. The soil samples were air dried and passed through a 2 mm stainless steel sieve to remove large particles such as rock pebbles, spent lead bullets and tree matter. A portion of the soil samples was pulverized using a manually operated Retsch RS 200 Vibratory Disk Mill at 700 rpm for 3 minutes and then stored for X-Ray Diffraction (XRD) analysis (X'pert Philips Electronic Instruments, Inc). The X'pert data high score software was used to identify Pb minerals present in the soils. The pellet was prepared using pulverized soil samples. The current used was 30 mA and tension 45kV using CuKα radiation and taking measurements from 5 to 70^o 2Θ.[31] A series of 0.100 g of soil samples were digested in 25 mL of 10% HNO_3 for 16 hours using the dry heating-block digestion procedure (USEPA Method 3050).

Analysis of soil samples was carried out using inductively coupled plasma optical emission spectrometer (ICP-OES; Perkin Elmer, Optima7300DV) found at Botswana Geoscience Institute (BGI) and atomic absorption spectrometry (AAS; Analytik Jena, ContrAA 700). The ContrAA 700 is equipped with a xenon short-arc lamp that is one continuum source of radiation (from 185 nm to 900 nm) with multi element analysis capability and detection limits in the parts per billion range (ppb). The best sensitivity and signal-to-noise ratio is achieved by using the absorbance of 5 pixels (peak volume selected absorbance, PVSA, $A_{\Sigma 5,int}$).[207] The limits of detection (LOD) and limits of quantification (LOQ) were evaluated using the IUPAC recommended methods, LOD = $3\delta/s$ and LOQ = $10\delta/s$, where δ is the standard deviation of blank solutions and s is the slope of the calibration curve. The soil CRM (NCS DC 73320) contained Pb concentration of 20 mg/kg.

3.6. Lead Fractionation Studies in Shooting Range Soils

A sequential extraction process adapted from Tessier *et al.* (1979) was used to separate the berm soil Pb into different fractions so as to determine the mobility and availability of Pb.[53] The fractions of the soil are in the forms: water-soluble and exchangeable (WE); carbonate bound (CB); Fe-Mn oxides (FM); organic matter bound (OM) and the residual (RS) fractions. The five steps of the sequential extraction procedure as adapted from Tessier *et al.* (1979) are shown on Table 3.2.[53]

Table 3.2 Five step sequential extraction procedure as adapted from Tessier *et al.* (1979).[53]

Fractions	Composition of extracting solution
Water soluble and exchangeable (WE)	1.0 M $MgCl_2$, pH = 7.0, room temperature
Bound to carbonate (CB)	1.0 M CH_3COONa, pH = 5.0, room temperature
Bound to Fe/Mn oxides (Fe-Mn)	0.04 M $NH_2OH{\cdot}HCl$, 96 ^oC
Bound to organic matter (OM)	0.02 M HNO_3 + 30% H_2O_2, pH = 2.0, 85 ^oC
Residual (RS)	Aqua regia (96 ^oC)

To better understand the potential health hazards from contamination with Pb, the different chemical species in which Pb exist in the shooting range soils (free metal, metal-organic complexes and salts) were determined. The different Pb species and their reactivity with the

specific target constituents of the soils help ascertain for their mobility and bioavailability in the environment.

3.7. Simulation of acid rain – leaching test

The synthetic precipitation leaching procedure (SPLP) involves the use of a slightly acidified de-ionized water extraction fluid to simulate the acid rain.[168,169] The acidification of de-ionized water was done using a mixture of 60/40 H_2SO_4/HNO_3 to achieve the appropriate pH of 4.2±0.05.[168,169] The SPLP Pb in the shooting range soils was extracted using this extraction fluid in the ratio of solid to liquid of 1:20 and determined using the USEPA method 1312.[208]

3.8. Physicochemical properties of shooting range soils

The physical and chemical properties of the shooting range soils such as pH, organic matter (OM), cation exchange capacity (CEC) and metal content were all determined using standard methods. The pH measurements were carried out by adding to 20 g of the homogenized soil sample 40 mL of deionized water and 0.01 M $CaCl_2$ solution. The solutions were stirred vigorously. The slurry was allowed to settle for 30 minutes. A calibrated crimson basic 20 pH meter was used for pH measurements at 25 ^oC. The Walkley-Black procedure was used to measure the organic matter (OM) content of the soil samples.[209] Cation exchange capacity (CEC) of the soils was determined using method 9081.

3.9. Soil sampling scheme at TAB shooting range for application of the delayed geochemical hazard (DGH) model

Soil sampling was carried out as shown in Figure 3.4. The shooting range was divided into four sections being the berm, target line, 50 m from target line and 100 m from target line. The berm was further divided into three parts being the upper, middle and lower berms. Taking samples in all these three sections of the berm eliminated biasness and errors since in essence samples had been taken in the three different regions of the berm. This gave a true representative soil sample of the berm. The sampling method adopted was along a central transect from the upper berm right through to the 100 m firing line on the shooting range floor bed. This was important considering the fact that bullets and shots follow a similar trajectory when fired onto the berm soils. Each sampling area was circular with a radius of 150 cm from which four soil samples were taken using a soil recovery probe to a depth of 20

cm. By making the sampling area within each central transect circular and collecting four samples within the circumference helped cover more area for sample collection such that not only one area that may be concentrated with bullets and shots was picked. After taking four samples within the three circular sampling points and mixing them, these were then further mixed with samples obtained on the left and centre of the line in order to get a true sample representation of the upper berm. The same sampling strategy was followed at middle, lower berm, target line, 50 and 100 m firing lines. This sampling method was adopted from Cao *et al*. (2003).[44] In total, eighteen composite samples were collected at TAB shooting range for analysis. The DGH model and concept was carried out on only one shooting range as a preliminary and case study in Botswana. The TAB shooting range was used for this investigation of this model and application because of all the shooting ranges studied, TAB was the most polluted even though it was not the oldest.

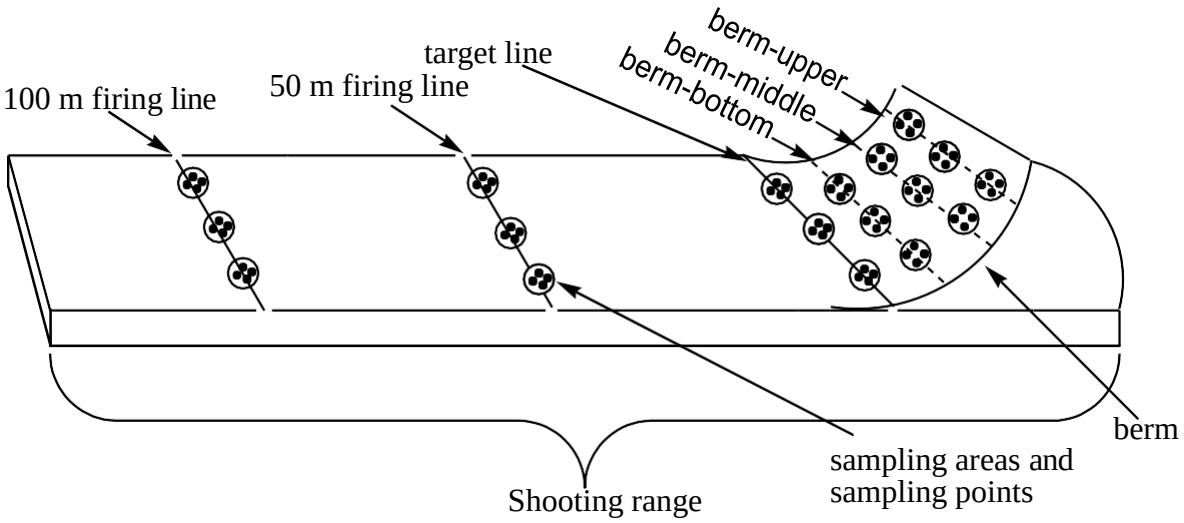


Figure 3.4 Schematic layout of a shooting range indicating sampling points.

CHAPTER 4

4. RESULTS AND DISCUSSIONS

4.1. Physicochemical properties of shooting range soils

The pH of the soils in the eight shooting ranges studied ranged between 6.64 to 8.70 and PAJ R2 contained mildly alkaline soils compared to the other shooting ranges while the soil at MAK and TSH were mildly acidic (Table 4.1). Soil pH plays a pivotal role in the dissolution, mobility and bioavailability of Pb. Acidic soil pH favours Pb mineral dissolution while Pb minerals are immobilized in alkaline soils.[31,51] Organic matter was measured in the range 0.35- 1.62% and MAK shooting range soils experienced high orgnic matter content compared to the other shooting ranges. On the other hand, TAB recorded the lowest organic matter. The highest cation exchange capacity value was determined at PAJ R2 shooting range (11.95 cmol/kg) while SHO R2 experienced the lowest CEC value of 3.50 cmol/kg. The distribution and migration of Pb in shooting range soils is highly dependent on these soil physicochemical properties as illustrated in the subsequent sections.

Table 4.1 Soil chemical properties.[31]

Range	pH_w	Organic Matter (%) ± δ[a]	CEC[b] ± δ (cmol/kg)
TAB	8.25	0.35±0.08[c]	10.75±0.16
MAK	6.64	1.62±0.02	8.00±0.20
TSH	6.80	0.69±0.08	5.34±0.58
MOG	7.07	0.62±0.11	5.01±0.05
PAJ R1	6.95	0.81±0.15	5.95±0.13
SHO R1	7.15	0.66±0.12	7.07±0.15
SHO R2	7.20	0.58±0.02	3.50±0.02
PAJ R2	8.70	0.77±0.08	11.95±0.38

[a]δ = Standard deviation

[b]Cation exchange capacity

[c]Mean ± standard deviation (n = 3)

4.2. Spatial distribution of Pb in shooting range soils

All the shooting ranges studied were contaminated with Pb (Figure 4.1 (a-d)). The highest total Pb concentrations were found in the berm soils. It is worth noting that the soils analysed for total Pb concentration are the soil particles of less than 2 mm in diameter obtained by sieving the soil samples through the 2 mm stainless steel sieve. TAB shooting range berm soils accumulated the highest total Pb concentration of 38386±10197 mg/kg followed by MAK at 25193±3338 mg/kg (Figure 4.1 (a)). The highest total Pb concentration experienced by TAB (established in 1995) shooting range can be attributed more to the frequency of use of the shooting range. The TAB shooting range belongs to the special force unit (Commando unit) of the Botswana Defence Force. The special force unit carries out intensive shooting practices to sharpen their marksmanship skills. These shooting practices can occur as often as once a week to more than once in a week. The MAK shooting range, even though older than the TAB range (established in 1983), has accumulated less concentration of Pb on its berm soils. This does show that the overall concentrations of Pb are more closely related to the frequency of shooting at each shooting range. These findings are consistent with the results obtained by Rooney and McLaren (2000) who found that the shooting range soil that accumulated the highest concentration of Pb was the one that was used frequently.[91]

The lowest total Pb concentrations were measured at the berm soil of PAJ R2 shooting range (85±42 mg/kg) and SHO R2 (728±527 mg/kg) as displayed in Figure 4.1 (a). The PAJ R2 is a pistol range while the SHO R2 is an obsolete rifle range that has not been used for many years. According to military personnel, pistol firing is only restricted to use by military officers who are normally few in numbers, this may be a contributing factor to the small concentration of total Pb at the PAJ R2 shooting range. Pistol ammunition contains less amount of Pb slug of about 52% as compared to assault rifles with over 80% Pb slug content. The less Pb content in pistol projectiles could be a contributing factor to the low pollution in pistol shooting range soils. The SHO R2 has not been in use for some few years. There is a high possibility that the weathered Pb has leached further underground with some of the Pb having been washed off the surface of the ground by runoff water from rain. In all the 8 shooting ranges studied, the highest total Pb accumulation occurred in the berm soils (Figure 4.1). The highest total Pb concentration in the berm soils can be attributed to accumulation of lead bullets, projectiles and shots into the berm. Cao et al. (2003) found that the total Pb

concentration in the berm soils was directly related to the build-up of bullets, shots and projectiles in the berm corroborating our results.[44]

In contrast total Pb concentrations decreased as one moved away from berm to the target line, 50 and 100 m shooting lines. The target line soils total Pb concentrations are second highest to the berm soils total Pb concentrations (Figure 4.1 (b)). Target line total Pb concentrations were measured at 1200±320, 149±17, 45±3, 1554±35, 13204±2408 and 13±6 mg/kg for MAK, PAJ R1, MOG, SHO R1, SHO R2, TAB and PAJ R2 respectively. The target line is closest to the berm, there is high possibility that some of the weathered Pb might have mobilised and migrated down the berm slope contributing to the high concentration of total Pb at the target line. Another contributing factor to the high concentrations of total Pb in the target line soils could be the Pb powder emitted due to the friction between the bullet and the target as the bullet pierced through the target. It is important to note that the total Pb concentrations at the 100 m shooting line were higher compared to the 50 m shooting line for most of the shooting ranges such as the TSH (2681 mg/kg), TAB (896 mg/kg), MAK (647 mg/kg) and SHO R1 (442 mg/kg) at the 100 m shooting line compared to TSH (105 mg/kg), TAB (71 mg/kg), MAK (605 mg/kg) and SHO R1 (19 mg/kg) at the 50 m shooting line. According to military personnel, most of the shooting practice takes place at the 100 m shooting line implying that as bullets, shots and projectiles move through the barrel of the rifle there is friction created between the bullets and the barrel riffling's leading to the discharge of Pb powder into the 100 m shooting line soils leading to higher concentrations of total Pb at 100 m than at 50 m shooting lines. The background total Pb concentrations were less than 10 mg/kg in all the shooting ranges studied (Figure 4.2). This implies that Pb mobility may be restricted within the shooting ranges and their immediate surroundings. Quality assurance was carried out through analysis of certified reference material, NCS DC73320 of known concentration of 20 ppm (20 mg/kg). The CRM was subjected to the same experimental condition as the soil samples with average measurement of 17.3 ± 0.6 mg/kg (mean ± standard error of the mean). The accuracy of measurements was < 3% RSD, an indication of accuracy of the analytical methodology.

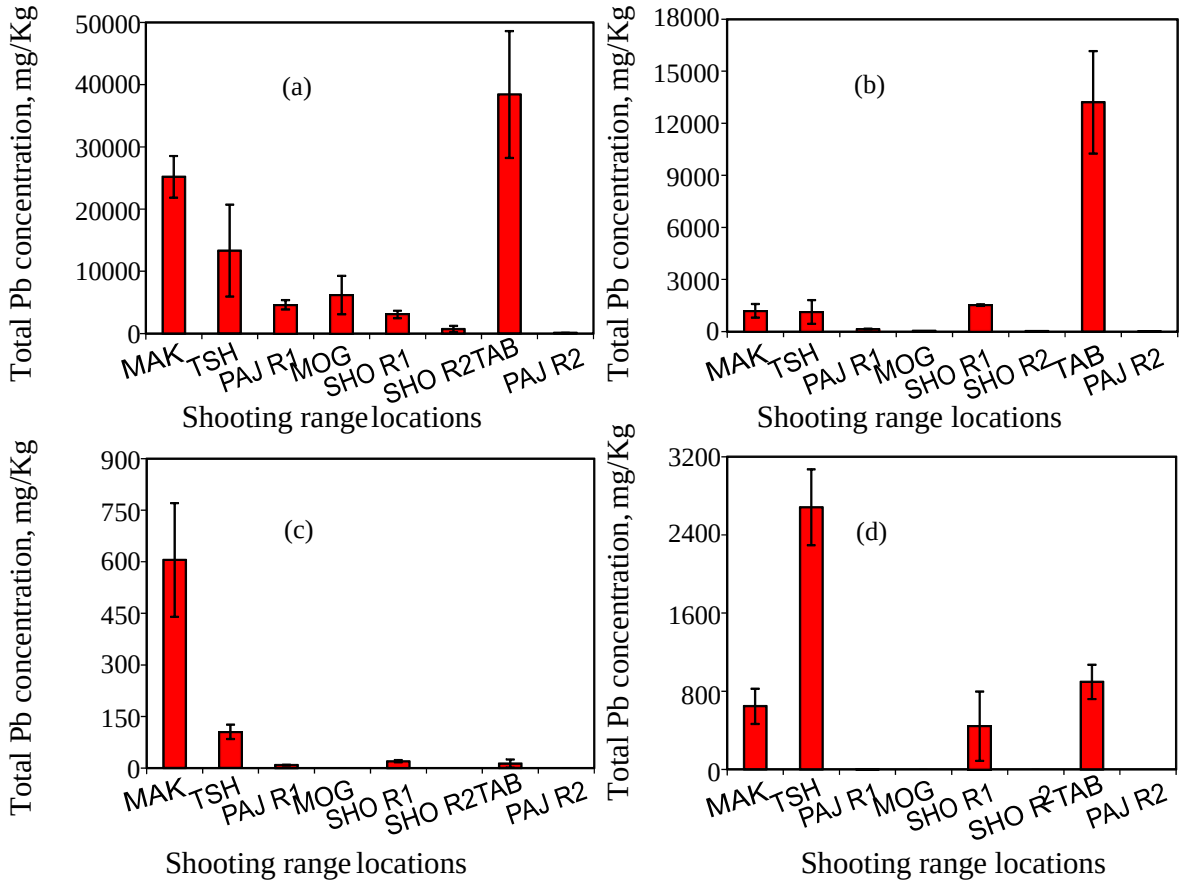


Figure 4.1 Concentrations of Pb in soil collected from; (a) berm; (b) target line; (c) 50 m and (d) 100 m from target line at eight shooting ranges found in Botswana, using ICP-OES.
Mean of $n = 3$; Standard error of the mean, $\delta = \delta/\sqrt{n}$, where δ = standard deviation.

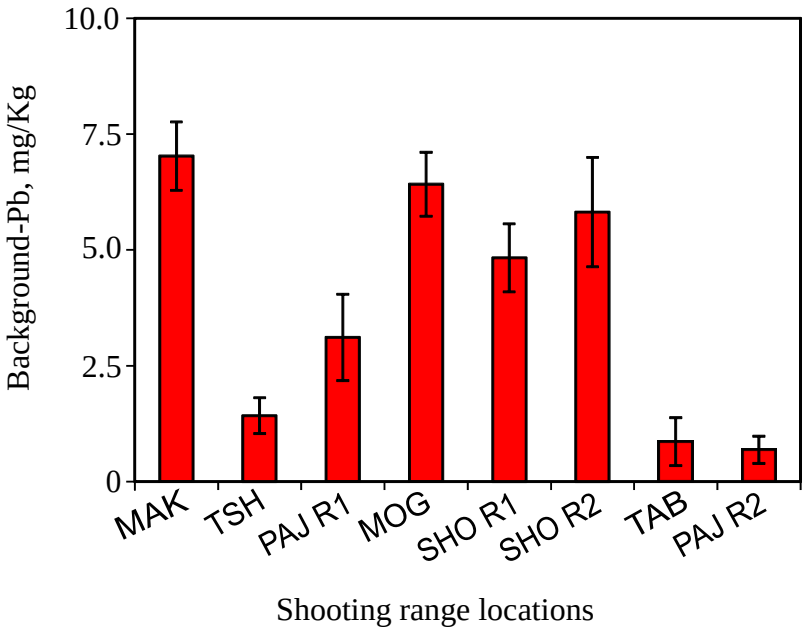


Figure 4.2 Concentrations of Pb in Background soils taken 200 m from eight shooting ranges in Botswana using ICP-OES. Mean of $n = 3$; Standard error of the mean, $\delta_x = \delta/\sqrt{n}$, where δ = standard deviation.

4.3. The Tessier method of sequential extraction for determination of Pb partitioning in shooting range soils

Sequential extraction procedure is commonly used to ascertain the chemical mobility, availability, leaching and distribution of metals in the soil.[53] The partitioning of Pb in the different soil fractions is largely dependent on the chemistry and geochemistry of the soil such as its pH, cation exchange capacity, organic matter content and presence of other chemicals in the soil. The sequential extraction method takes place with the assumption that the partitioning of the metal within each fraction is lowered with each successive extraction step.[53] All the Pb in the shooting range berm soils were found to be linked to the carbonate fraction (CB), 46-68% (Figure 4.3). The berm soil Pb associated with the organic matter (OB) was also found to be in substantial amounts of 2-47% followed by the Fe-Mn oxides (FM) bound Pb (1-37%), water-soluble and exchangeable (WE) (0-19%) and lastly the residual Pb (0-5%). The existence of Pb in the berm soils bound mainly to the carbonate fraction (CB) can be attributed to the weathering processes of Pb bullets and shots such as oxidation of metallic Pb and carbonation of the oxidised Pb (PbO).[44,53] There was a

correlation between the soil pH and the total Pb concentrations found in the shooting range soils studied.

As displayed in Table 4.1, TAB shooting range with the alkaline pH of 8.25 experienced the highest accumulation of total Pb in its soil. The alkaline pH is regarded as a favourable condition for the stability of Pb oxides and carbonates. This corroborates the fractionation results (Figure 4.3) where considerable amounts of Pb were associated with the carbonate fraction. Soil moisture has been reported to play a crucial role in the weathering of Pb bullets and shots. The soil moisture helps in the erosion and corrosion of Pb bullets and shots through the formation of a water layer on the Pb bullets and shots surfaces making it easy for the diffusion of atmospheric gases to reach and attack the metal surfaces leading to the formation of Pb weathering products such as Pb oxides, sulphates and carbonates and subsequent dissolution of these Pb compounds into the shooting range soils.[44] The areas studied have a good annual rainfall supply as shown in Figure 3.2. Rainfall amounts have been recorded to as high as 103 mm (December 2013) for TAB (with total Pb concentration of 38386±10197 mg/kg) shooting range for the year June 2013 to July 2014. Other months in the same year for TAB shooting range have recorded rainfall amounts of as high as 50 mm (November 2013 and March 2014). Other shooting ranges such as SHO R1, SHO R2, PAJ R1 and PAJ R2 have experienced rains as high as 230-320 mm (Figure 3.2). Even though the frequency of shooting in these ranges was not high, significant amounts of total Pb concentrations were found at SHO R1 and PAJ R1 measured at 3075±611 and 4608±748 mg/kg respectively (Figure 4.1). Organic matter has been found to be an important factor in the weathering of Pb bullets and shots. The presence of organic matter in the soil accelerates the transformation of metallic Pb into its Pb oxides and carbonates. This takes place through the production of CO_2 by microbial organisms in the soil rich in organic matter making the CO_2 available for the weathering of lead bullets and shots into Pb oxides and carbonates.[166] Organic matter was high in all of the shooting ranges studied, 0.35-1.62% (Table 4.1), a favourable condition to the weathering of Pb in soil leading to increased mobility and availability of Pb in the shooting range soils. The soil cation exchange capacity (CEC) plays a crucial role in the mobility and bioavailability of Pb. The higher the CEC of the soil the higher the binding capacity of Pb leading to significant reduction in Pb mobility and bioavailability and vice versa.[44] TAB and PAJ R2 experienced the highest CEC values of 10.75 and 11.95 cmol/kg respectively and SHO R2 recorded the least CEC of 3.50 cmol/kg. Coupled with other factors such as higher pH of 8.25 and frequency of use, the highest total

Pb concentrations in berm soils were recorded in TAB shooting range (Figure 4.1). Total Pb concentrations of PAJ R2 were the lowest even though this range has high soil CEC and high soil pH. The main reason for this lower Pb concentration is that, PAJ R2 is a pistol range used to fire 5.56 mm ammunition that contains the least amount of Pb, about 56% compared to other ranges whereby all bullets of 7.62 mm, 5.56 mm and 0.50 mm with Pb content of 77%, 56% and 1% are shot into the berm soils.[31] In addition this range is situated in a military training camp and it is used less frequently for training military officers in shooting pistol firearms, about four to seven times in a month for six months in a year. SHO R2 soils have the lowest CEC with pH values in the neutral region (7.15). This range is obsolete and the low soil CEC may have provided a favourable condition for the solubility and mobility of Pb.

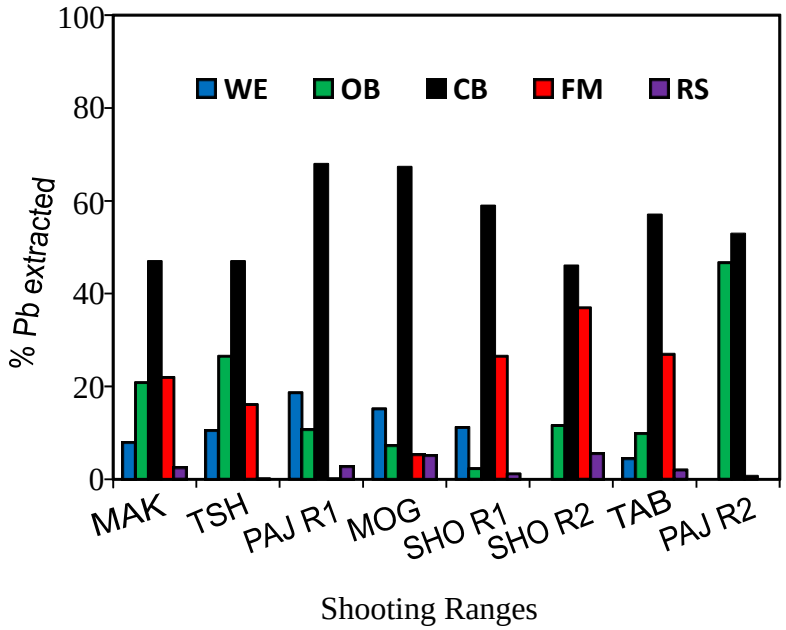


Figure 4.3 Different chemical fractions of Pb in shooting range soils found in Botswana. WE (water-soluble and exchangeable), OB (organic-bound), CB (carbonate-bound), FM (Fe-Mn oxides) and RS (residual).

4.4. Chemical transformation of Pb shots and bullets

The weathering products of Pb bullets and shots at all the eight shooting ranges studied were predominantly carbonates specifically cerussite ($PbCO_3$) and hydrocerussite ($PbCO_3H_2O$) as shown on the XRD plots on Figure 4.4. Cao *et al.* (2003) study on Pb transformation in shooting range soils has shown that the abrasion process of Pb bullets and shots takes place via a two steps mechanism involving the oxidation of metallic Pb and hydration and

carbonation in the presence of H_2O and CO_2.[44] The XRD results agree well with the fractionation studies (Figure 4.3) which showed that the carbonate bound Pb was the most predominant in all the eight shooting ranges investigated. The soil pH plays an important role in the corrosion of Pb shots and bullets and formation of weathering products. At MOG shooting range, hydrocerussite was the only dominant Pb carbonate weathering product with no trace of other Pb carbonates. This could be due to the favourable high pH which is slightly above neural into the alkaline region. The other seven shooting ranges had a mixture of both cerussite and hydrocerussite. A study by Dermatas *et al.* (2006) was able to show that the carbonates are some of the dominant weathering products of Pb bullets and shots in shooting range soils.[104] As mentioned earlier in this study, when Pb shots and bullets accumulate into shooting range soils, there are various chemical reactions that the Pb inside these bullets and shots would undergo. Examples of such reactions include equations 23-27 below;[51]

Oxidation of Pb to Massicot, PbO; $Pb + O_2 + H_2O \longrightarrow PbO + 2OH^-$ (23)

Formation of cerussite, $PbCO_3$; $PbO + HCO_3^- \longrightarrow PbCO_3 + OH^-$ (24)

Formation of hydrocerussite, $Pb_3(CO_3)_2(OH)_2$; $3PbCO_3 + 2H_2O \longrightarrow Pb_3(CO_3)_2(OH)_2 + H_2CO_3$ (25)

Dissolution of cerussite, $PbCO_3 + 2H^+ \longrightarrow Pb^{2+} + H_2O + CO_2$ (26)

Dissolution of hydrocerussite, $Pb_3(CO_3)_2(OH)_2 + 6H^+ \longrightarrow 3Pb^{2+} + 4H_2O + 2CO_2$ (27)

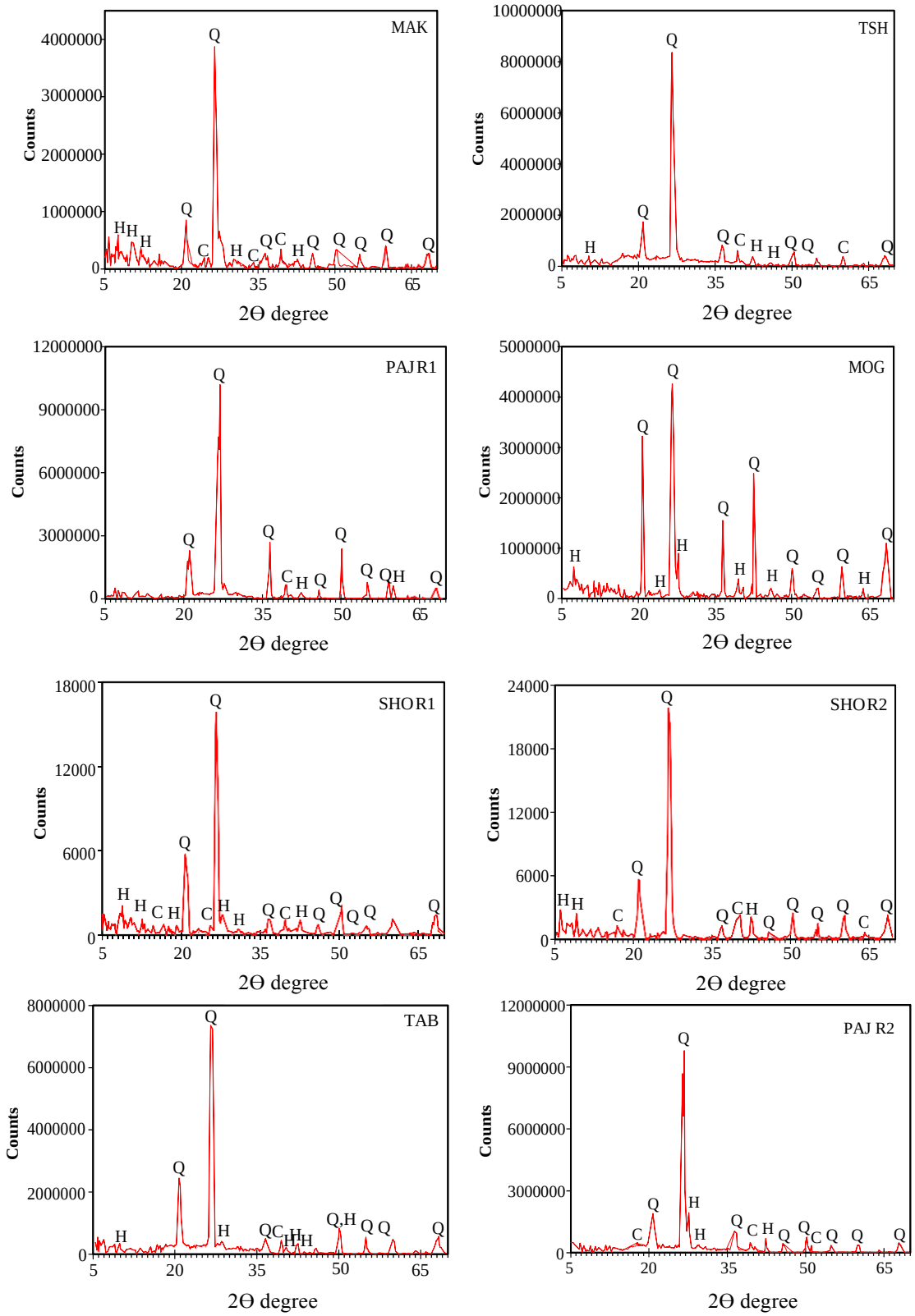


Figure 4.4 X-ray diffraction patterns showing mineralogical and transformation products of Pb shots and bullets in shooting range soils. Q (Quartz), C (Cerussite) and H (Hydrocerussite).

4.5. Simulation of acid rain through the Synthetic Precipitation Leaching Procedure

The mobility of Pb in the soil due to acid rain was simulated using the SPLP procedure.[168] The SPLP Pb concentration was highest in the berm soils of TSH range at 787±8 mg/kg followed by PAJ R2 and TAB ranges at 448±4 and 398 mg/kg respectively (Figure 4.5). The lowest SPLP Pb concentration was recorded in the PAJ R2 soils with a concentration of 0.1±0.08 mg/kg. In all of the eight shooting ranges studied the SPLP Pb concentrations exceeded the USEPA 0.015 mg/kg critical level of hazardous waste.[208] This indicates that some of the Pb may have leached out from the shooting range soils giving rise to possibility of surface and groundwater contamination.

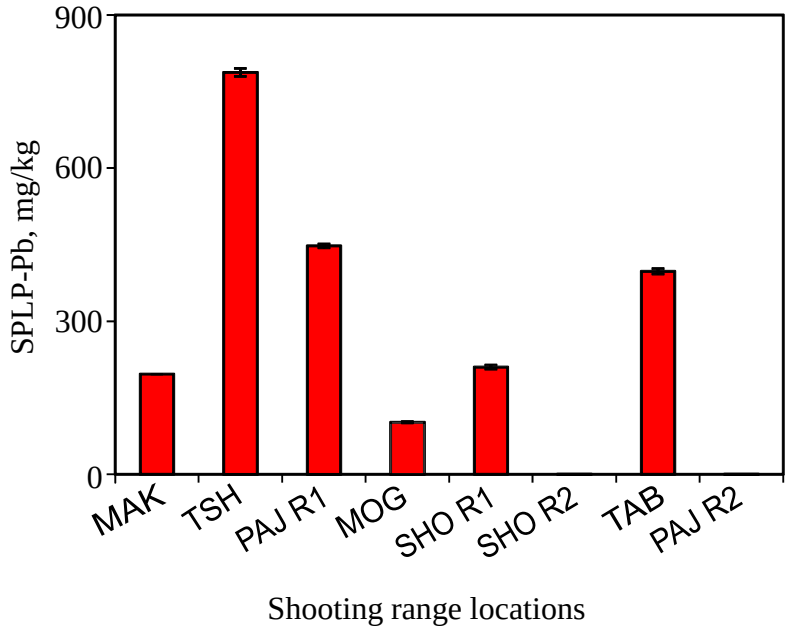


Figure 4.5 Concentration of Pb measured using ICP-OES after simulation of acid rain procedure (SPLP) at eight shooting ranges found in Botswana.
Mean of $n = 3$; Standard error of the mean, $\delta_x = \delta/\sqrt{n}$, where δ = standard deviation.

4.6. Quantification of Environmental Risk from Pb Pollution

The assessment of shooting range soils contamination was carried out using three pollution risk assessment methods, namely; (i) contamination factor (*CF*), (ii) enrichment factor (*EF*), and (iii) potential ecological risk index (*PERI)*

4.6.1. Determination of level of pollution through the contamination factor (CF)

The contamination factors (*CB*) were found to be high for the soils in all the eight shooting ranges studied indicating very high contamination (Figure 4.6). In all the eight shooting ranges investigated, TAB shooting range was found to have accumulated the highest amount of Pb relative to the background Pb concentration in the area with a contamination factor (*CF*) of over 40 000 and more than 6000 times higher than minimum set value for a contamination factor corresponding to very high contamination (Figure 4.6). The high *CF* in these shooting ranges implies elevated retention of Pb in the soil and increased risk to the ecosystem.[209] The high *CF* in the eight shooting ranges studied correlates well with the large total concentrations of Pb which pose a risk to animals, range users and both surface and underground water sources.

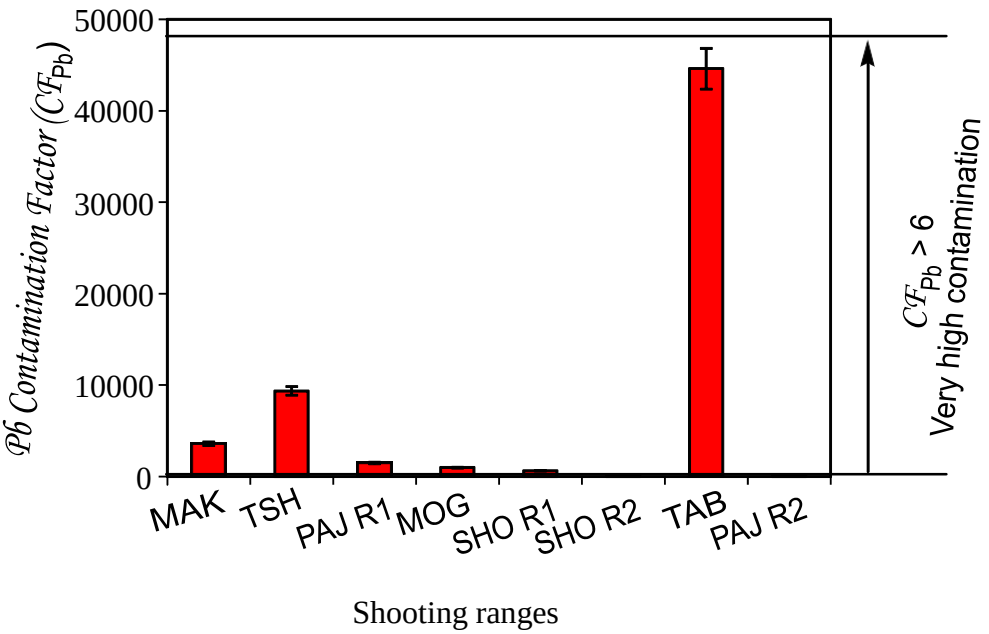


Figure 4.6 Determination of contamination factor (*CF*) of Pb in the berm soils. Mean of $n = 3$; Standard error of the mean, $\delta = \delta/\sqrt{n}$, where δ = standard deviation.

4.6.2. Evaluation of the anthropogenic impact of Pb in the soil using the enrichment factor (EF) approach

Anthropogenic activities such as military shooting exercises contribute significantly to the amount of that accumulates in the environment. The environmental impact of Pb in the eight shooting ranges soils was evaluated using the enrichment factor (*EF*) approach. The concentrations of total Pb in the shooting ranges arising from shooting activities were compared with the background Pb concentrations in order to determine the degree of pollution arising from shooting events. Enrichment factors higher than 50 indicate extreme enrichment (Figure 4.7). The enrichment factors in the soils sampled from the eight shooting ranges were in the range 106 to 22200 and TAB experienced the greatest Pb enrichment in accordance with the highest total Pb accumulated in this area. The enrichment factor results correlate well with the *CF* risk assessment index, an indication of high level of pollution of shooting ranges and potential risk to biota. Our results correlate well with studies performed in a Pantex shooting range in Texas USA where enrichment factor of over 277 and total Pb concentration of up to 4675 mg/kg were determined.[187] In Kesarian, Greece, extremely high Pb enrichment have been reported in a military shooting range soils where enrichment factor of over 115 was measured.[35] The degree of Pb enrichment of the soil can provide insight when selecting the appropriate soil amendment techniques and strategist to employ for managing the pollutant.

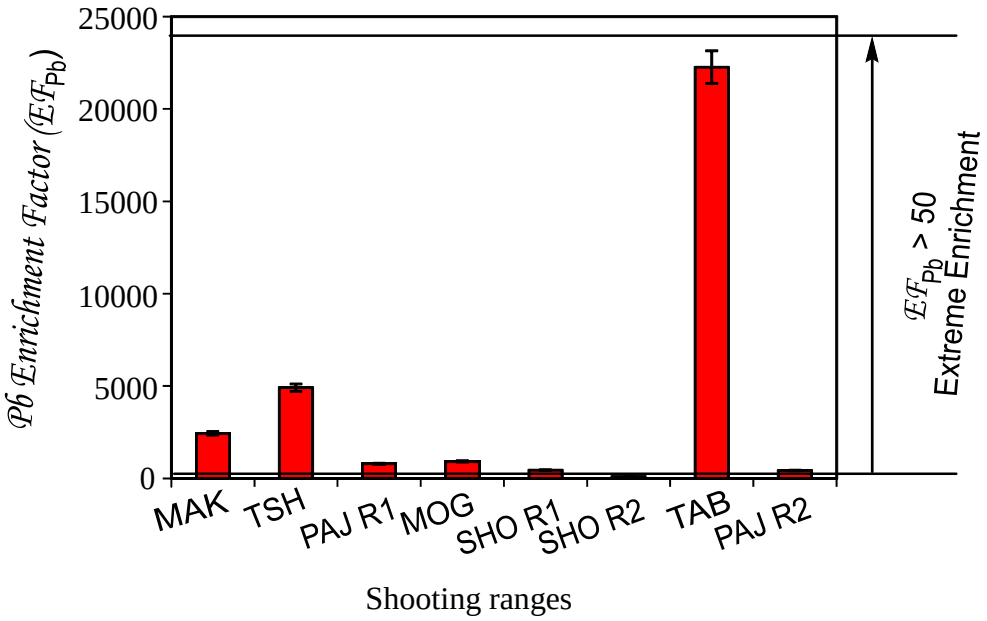


Figure 4.7 Determination of Pb enrichment of the berm soils. Mean of $n = 3$; Standard error of the mean, $\delta = \delta/\sqrt{n}$, where δ = standard deviation.

4.6.3. Assessment of the ecological and environmental effects of Pb pollution using the potential ecological risk index (PERI)

All the eight shooting ranges investigated failed the ecological risk assessment since they all recorded the highest values of ecological risk index (>>320) (Figure 4.8). The high values of *PERI* indicate high loading of Pb in the shooting range soils studied. Potential ecological risk indices were in the range 430-600 000 which exceeded the set limit by an extreme amount. The TAB shooting range exhibited the highest potential ecological risk than all the other shooting ranges studied with an ecological risk index of over 600 000. The lowest ecological risks were recorded at SHO R2 (439) and PAJ R2 (433). There are possible reasons why this could be the case, firstly SHO R2 is a decommissioned shooting range which has not been in use for some time and there are possibilities of Pb having leached deep into the soil or washed away by water runoff from rainfall. The PAJ R2 on the other hand is a pistol shooting range and it is well know that pistol ammunition does not contain substantial amounts of Pb.[31] The findings from our study corroborate the results obtained in previous studies such as the study by Shen *et al.* (2017) in China whereby potential ecological risk index of up to 1158 for heavy metals such as Cd in soils was recorded.[210] In another study by Islam *et al.* (2016) the ecological potential risk indices of Pb in shooting range soils were determined to be 3446 and 725 at Cho-do and We-rye shooting ranges respectively, indicating a very high

environmental pollution risk from Pb.[147] It is important to note that *PERI* assesses the relative sensitivity of the living organisms to toxic Pb and quantifies the potential ecological risk caused by the toxic Pb element.

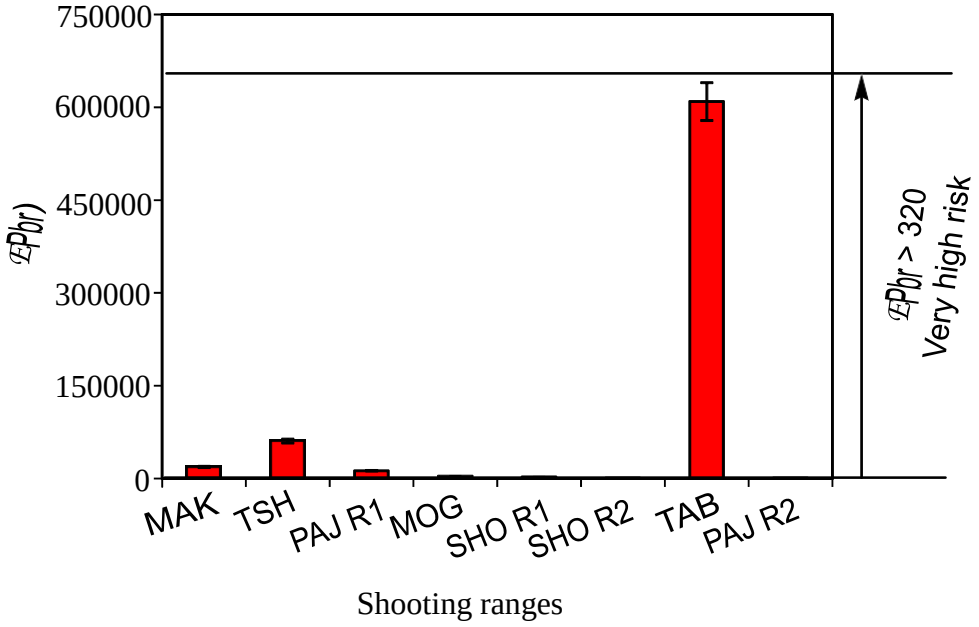


Figure 4.8 Determination of potential ecological risk index (*PERI*) of Pb in the berm soils. Mean of $n = 3$; Standard error of the mean, $\delta = \delta/\sqrt{n}$, where δ = standard deviation.

4.7. Static risk assessment of Pb pollution at TAB shooting range soils

Static risk assessment describes the total amount of Pb accumulated into shooting range soils and disregards the influence of factors such as changes in the physicochemical properties of the environment or changes in the holding capacity of the environment with continued deposition of Pb pollutant. The average total Pb concentration in the berm soils of this shooting range has been determined in our previous study and was found to be 38 406.87 mg/kg.[31] The total concentration of Pb accumulated in TAB shooting range soil was found to be close to 100 times higher than the USEPA set critical limit of 400 mg/kg for Pb concentration in soil. The summation of the concentrations of Pb in the different soil fractions obtained in the current study were comparable to the total Pb concentration determined in our previous study after the aqua regia single extraction procedure as shown in Table 4.2.[31]

Table 4.2 Pb concentration in different chemical fractions.

Soil Sample	Pb_{WE} (mg/kg)	Pb_{CB} (mg/kg)	$Pb_{Fe\text{-}Mn}$ (mg/kg)	Pb_{OB} (mg/kg)	Pb_{RS} (mg/kg)	$Total_{Pb}$ Sum[a] (mg/kg)	Determined[b] mg/kg (Sehube *et al.* (2017))
Berm	1420±107[c]	6448±128	2760±211	15668±252	1243.6±160	27 539±402	38406.87±10197
Target line	1110±25	5042±330	1434±150	8053±1886	156±39	15795±1921	13204 ± 2408
50 m	53±14	145±43	26±7	128±33	26±6	378±57	12.21±2.4
100 m	85±19	254±53	81±25	411±137	92+23	922±152	896±175

[a]Sum of the Pb concentrations in the five different fractions obtained by the Tessier method of sequential extraction.
[b]Total Pb concentration obtained by aqua regia single extraction.

[c]Standard error of the mean, $\bar{\delta} = \delta/\sqrt{n}$, mean of n = 3 and δ = standard deviation.

However, it has been found that the deposition of heavy metals such as Pb into the soil does not provide a good measure of the pollution risk posed by this toxic metal to the environment.[30,68,170] Studies on Pb speciation have helped recognize the importance of the different chemical species of Pb in so far as pollution risk is concerned.[51] Some chemical species of Pb such as $Pb(CO_3)_2$ have been found to be readily soluble in the soil under favourable soil conditions while others such as $PbSO_4$, and $Pb_3(PO_4)_2$ can stay in the soil for a very long time without being transformed and making them less available and of low pollution risk to the environment.[55] In addition, Pollution risk assessment indices such as contamination factor (*CF*), enrichment factor (*EF*) and potential ecological risk index *(PERI)* have been found to be useful in establishing and ascertaining the pollution risk presented by Pb to the environment.[170,211] However, these pollution risk indices provide a static risk assessment of pollution from Pb and leave a gap on the dynamic evolution process of risk from Pb pollution when environmental conditions change. The total amount of Pb deposited into TAB shooting range soils, provides the static risk assessment of Pb pollution at this shooting range without taking into consideration the changes in the environmental conditions that can accelerate the release of Pb chemical forms that were considered inert and thereby exacerbating the environmental pollution risk from this heavy metal. Delayed geochemical hazard (DGH) model provides a dynamic approach to assessment of pollution risk emanating from the deposition of Pb into shooting range soils.

4.8. Delayed geochemical hazard (DGH) Model

4.8.1. Description of the delayed geochemical hazard (DGH) model

The DGH model mainly consists of two factors; (1) total releasable content of pollutant (*TRCP*) and (2) total concentration of active species (*TCAS*). There is a direct relationship between *TRCP* (*C*) and *TCAS* (*Q*) which is used to experimentally study the rupture of the hazard under suitable soil conditions of moisture, pH, organic matter, soil redox potential, and cation exchange capacity (CEC). The DGH plot is made up of the *TRCP (C)* as the independent variable and makes the *X*-axis of the DGH plot while the *TCAS (Q)* is the dependent variable and makes the *Y*-axis of the DGH plot (Figure 4.9). The fitting curve shows changes in trend of *TCAS* which is dependent on changes of the *TRCP*. An increase in the *TRCP* causes increase in the *TCAS*. There are very important points that can be drawn from the DGH model plot; (1) at the beginning, the plot shows that an increase of *TRCP (*ΔC*)*

causes little increase of *TCAS* (ΔQ_1), (2) as the deposition of pollutants reach a certain level, the same *TRCP* (ΔC) causes a significant increase of *TCAS* (ΔQ_2) and it can be shown from the DGH model on Figure 4.9 that $\Delta Q_2 > \Delta Q_1$.[58] It has been shown experimentally using the Tessier method of sequential extraction, that the dynamic evolution activity could be quantitatively expressed using a nonlinear polynomial of three cubed as shown in equation 22;

$$Q = F(C) = a_0 + a_1C + a_2C^2 + a_3C^3 + \ldots \qquad (22)$$

Given that the first and second order derivatives of equation (22) are zero, three special and crucial points can be derived from the model: (1) critical point of burst, (2) burst point and (3) critical point of accumulation. The critical point of burst occurs when the first and second derivatives of equation (22) are zero and this is represented by the beginning of the curve as it moves from being concave at the foot of the curve to still being concave as it rises representing the beginning of the hazard. The burst point takes place when the first derivative of equation (22) reaches maximum and the second derivative is zero. At this point the fitting curve is rising at a sharp slope and reaching its greatest steepness. This point represents the beginning of the delayed geochemical hazard (DGH). Lastly, there occurs a point where the second derivative of equation (22) is at minimum, this point constitutes the critical point of accumulation. It depicts the beginning of the deposition of contaminants for the next DGH.

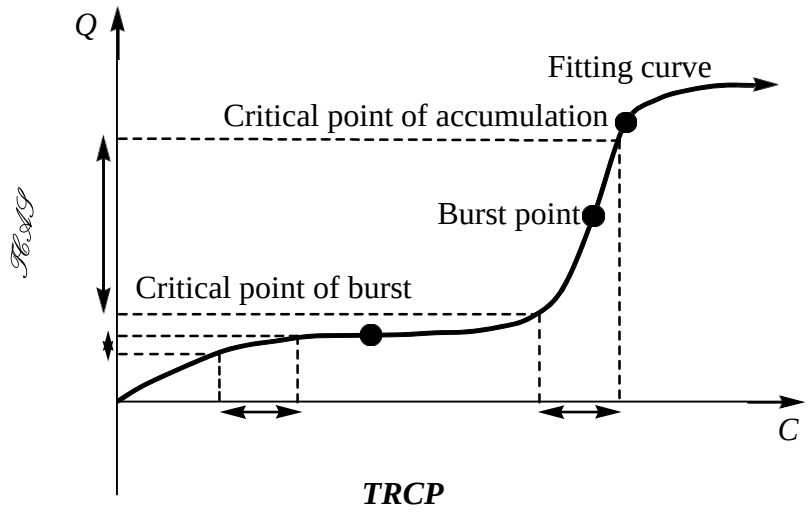


Figure 4.9 Graphical representation of the DGH model and its digital characteristics.

4.8.2. Dynamic risk assessment of Pb pollution using the delayed geochemical hazard (DGH) Model

The fractionation experiments show that Pb was partitioned mostly in the carbonate and organic compartments in TAB shooting range soil. This describes the static risk to the environment from Pb pollution since no insight is given into whether inert and immobile Pb minerals can be re-activated and be bioavailable under favourable conditions of the soil. However, other Pb chemical forms may also be transformed and made mobile under strong oxidizing and acidic conditions of the soil. This is the breakpoint of accumulated pollutants whereby the environment can no longer contain the amount of pollutant that has built up within it and therefore reactivation and release of the accumulated pollutants takes place. The concept has been shown by previous studies that chemical speciation of heavy metal in the soil is dynamic.[50,58,59] Therefore, the idea of DGH has been employed to take into consideration the abrupt reactivation, transformation and discharge of Pb chemical species that had accumulated in the soil for an extended period of time due to decreased holding capacity of the environment towards the Pb chemical species. A sudden change in the soil and environmental physicochemical conditions can also lead to the reactivation of the inert Pb chemical forms and their transformation resulting in their increased mobility, bioavailability and potential environmental pollution risk. The Tessier sequential extraction procedure was used to fit data to each equation such that $TRCP_{Pb}$ should contain all the five components in the Tessier procedure (Table 4.3).[53] In agreement with the DGH model, our findings present that Pb in TAB shooting range soils was quantitatively expressed and well fitted to the nonlinear polynomials with high correlation coefficients (R^2) and large F values at probability value, $p < 0.05$ (Table 4.3).

Table 4.3 Fitting nonlinear polynomials and the corresponding DGH characteristics for Pb in the studied area.

Pb Fraction Pairs	DGH models $y = TCAS_{Pb}$ and $x = TCRP_{Pb}$ (mg/kg)	y'' (2nd Derivative of y for calculating $TRCP_{Pb}$ and $TCAS_{Pb}$)	Statistical Characteristics			Critical points of DGH burst (mg/kg)	
			R^2	F	P	$TRCP_{Pb}$	$TCAS_{Pb}$
Pb_E and Pb_{E+C+F}	$y = 2\times10^{-8}x^3 - 0.0001x^2 + 0.3102x$	$y'' = 1.2\times10^{-7}x - 0.0002$	0.915	54	2×10^{-11}	1666.67	331.81
Pb_E and Pb_{E+C}	$y = 5\times10^{-8}x^3 - 0.0002x^2 + 0.3793x$	$y'' = 3\times10^{-7}x - 0.0004$	0.912	29	3×10^{-9}	1333.33	268.70
Pb_E and Pb_{E+F}	$y = 9\times10^{-8}x^3 - 0.0003x^2 + 0.593x$	$y'' = 5.4\times10^{-7}x - 0.0006$	0.915	9	2×10^{-5}	1111.11	411.98
Pb_{E+F} and Pb_{E+C+F}	$y = 3\times10^{-8}x^3 - 0.0001x^2 + 0.4865x$	$y'' = 1.8\times10^{-7}x - 0.0002$	0.968	6	3×10^{-4}	1111.11	458.25
Pb_{E+C} and $Pb_{E+C+F+O}$	$y = 1\times10^{-9}x^3 - 5\times10^{-5}x^2 + 0.6314x$	$y'' = 6\times10^{-9}x - 0.0001$	0.972	10	7×10^{-6}	16666.67	1264.07
Pb_{E+C} and Pb_{E+C+O}	$y = 2\times10^{-9}x^3 – 7\times10^{-5}x^2 + 0.7305x$	$y'' = 1.2\times10^{-8}x - 0.00014$	0.967	8	4×10^{-5}	11666.67	2170.65
Pb_{E+C} and Pb_{E+O+R}	$y = 2\times10^{-8}x^3 - 0.0002x^2 + 1.3034x$	$y'' = 1.2\times10^{-7}x - 0.0004$	0.917	5	1×10^{-3}	3333.33	2863.19
Pb_{E+C} and Pb_{E+F+O}	$y = 1\times10^{-8}x^3 - 0.0002x^2 + 1.1142x$	$y'' = 6\times10^{-8}x - 0.0004$	0.947	6	3×10^{-4}	6666.67	1502.07
Pb_{E+C} and $Pb_{E+F+O+R}$	$y = 7\times10^{-9}x^3 - 0.0001x^2 + 1.0169x$	$y'' = 4.2\times10^{-8}x - 0.0002$	0.938	7	2×10^{-4}	4761.90	3330.67
Pb_{E+C} and $Pb_{C+F+O+R}$	$y = 2\times10^{-9}x^3 - 6\times10^{-5}x^2 + 0.6746x$	$y'' = 1.2\times10^{-8}x - 0.00012$	0.965	10	1×10^{-5}	10000.00	2746.00
Pb_{E+C} and Pb_{C+F+O}	$y = 3\times10^{-9}x^3 - 7\times10^{-5}x^2 + 0.7156x$	$y'' = 1.8\times10^{-8}x - 0.00014$	0.969	9	2×10^{-5}	7777.78	2742.73
Pb_{E+C} and Pb_{C+O+R}	$y = 3\times10^{-9}x^3 - 8\times10^{-5}x^2 + 0.7989x$	$y'' = 1.8\times10^{-8}x - 0.00016$	0.958	8	5×10^{-5}	8888.89	2887.34

Pb_{E+C} and Pb_{F+O+R}	$y = 1\times10^{-8}x^3 - 0.0002x^2 + 1.1872x$	$y'' = 6\times10^{-8}x - 0.0004$	0.925	6	4×10^{-4}	6666.67	1988.74
Pb_{C+F} and $Pb_{E+F+O+R}$	$y = 6\times10^{-9}x^3 - 0.0001x^2 + 1.0821x$	$y'' = 3.6\times10^{-8}x - 0.0002$	0.938	5	1×10^{-3}	5555.56	3954.05
Pb_{C+F} and Pb_{E+F+O}	$y = 5\times10^{-9}x^3 - 0.0001x^2 + 1.0955x$	$y'' = 3\times10^{-8}x - 0.0002$	0.945	4	2×10^{-3}	13333.33	8680.74
Pb_{C+F} and Pb_{F+O+R}	$y = 1\times10^{-8}x^3 - 0.0002x^2 + 1.2846x$	$y'' = 6\times10^{-8}x - 0.0004$	0.930	4	3×10^{-3}	6666.67	2638.07
Pb_{C} and Pb_{E+O}	$y = 2\times10^{-8}x^3 - 0.0002x^2 + 1.1392x$	$y'' = 1.2\times10^{-7}x - 0.0004$	0.927	415	7×10^{-19}	3333.33	2315.85
Pb_{C} and Pb_{E+F+O}	$y = 7\times10^{-9}x^3 - 0.0001x^2 + 0.8766\,x$	$y'' = 4.2\times10^{-8}x - 0.0002$	0.944	556	6×10^{-20}	4761.90	2662.57
Pb_{C} and Pb_{E+O+R}	$y = 1\times10^{-8}x^3 - 0.0002x^2 + 1.0315\,x$	$y'' = 6\times10^{-8}x - 0.0004$	0.912	462	3×10^{-19}	6666.67	950.74
Pb_{C} and Pb_{F+O+R}	$y = 8\times10^{-9}x^3 - 0.0001x^2 + 0.9412\,x$	$y'' = 4.8\times10^{-8}x - 0.0002$	0.924	538	8×10^{-20}	4166.67	2764.26
Pb_{C} and $Pb_{E+F+O+R}$	$y = 4\times10^{-9}x^3 - 0.0001x^2 + 0.8021x$	$y'' = 2.4\times10^{-8}x - 0.0002$	0.934	611	3×10^{-20}	8333.33	2054.54

For example, the fitting curve for the fractionation path $Pb_{(E)}$ *vs* $Pb_{(E+C+F+O)}$ using the Tessier method is represented in Figure 4.10 and the corresponding regression equation is given in equation (28).

$$y = 1E\text{-}09x^3 - 5E\text{-}05x^2 + 0.6314x \ (R^2 = 0.972) \quad (28)$$

This is one of the many Pb fractionation paths of the DGH model and can be used to describe the dynamic pollution risk from Pb at the TAB shooting range because of the chain reactions that can emanate from $Pb_{(E+C+F+O)}$ to the exchangeable and more reactive and mobile $Pb_{(E)}$ fractions when DGH takes place. Let *y''*, the second derivative of equation (28) above, be zero ($y'' = 0$), then $TRCP_{Pb}$ ($Pb_{(E+C+F+O)}$ is determined to be 1666.67 mg/kg and $TCAS_{Pb}$ ($Pb_{(E)}$) at 331.81 mg/kg. The three important points of the plot are clearly visible in Figure 4.10. The critical point of burst appears at TRCPPb = 1666.67 mg/kg where the plot changed from concave downward at $TRCP_{Pb}$ values lower than 1666.67 mg/kg to upwards at $TRCP_{Pb}$ values larger than 1666.67 mg/kg. This portion of the curve indicates an increase in the discharge and transformation of the inert $Pb_{(E+C+F+O)}$ to the more reactive and mobile $Pb_{(E)}$. It is important to note that at $TRCP_{Pb}$ range of 10000-1666.67 mg/kg, the slope of the curve in Figure 4.10 is almost zero and this section of the curve indicates that an increase in $TRCP_{Pb}$ will not result in the mobile and reactive $TCAS_{Pb}$. This implies that, for as long as the $TRCP_{Pb}$ is greater than the critical point, DGH burst would happen, irrespective of the chemical forms and reaction phases of the components in the Tessier method. Another crucial point in the curve is the burst point where the slope of the curve reaches a maximum. The burst point occurred after $TRCP_{Pb}$ of 20000 mg/kg whereby the transformation and release of reactive Pb components became more and more intense. When considering total Pb concentration (T_{Pb}), it was established that T_{Pb} was higher than the $TRCP_{Pb}$ by 65.3%, indicating a high-risk of DGH burst where the transformation and release of Pb may be frequent.

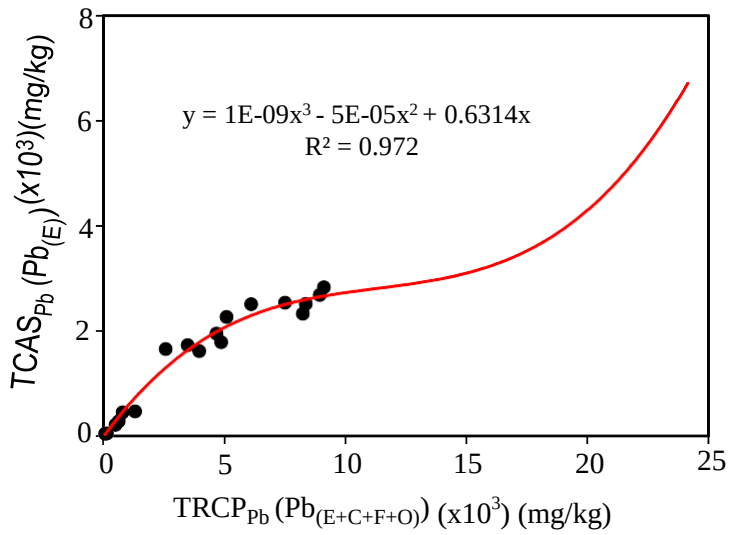


Figure 4.10 Fitting curve for the relationship between $TCAS_{Pb}$ ($Pb_{(E)}$) and TRCPPb ($Pb_{(E+C+F+O)}$) at TAB shooting range.

4.8.3. The pathway and mechanism of the DGH Model

The DGH model can help establish the release and transformation pathways of Pb at TAB shooting range as shown in Figure 4.11. The pairs of Pb fractions that fitted the DGH model depict the various chain reactions that lead to the transformation and release pathway of Pb from $Pb_{E+C+F+O}$ to Pb_E. The Pb transformation mechanism shows that the reactive organic bound and carbonate bound fractions contributed more to the release of Pb in the exchangeable fraction indicating the dominance of these fractions in the DGH_{Pb} model. Examples of the chain reactions include $Pb_{E+C+F+O} \rightarrow Pb_{E+C} \rightarrow Pb_E$ and $Pb_{E+C+F} \rightarrow Pb_E$ and these chain reactions can take place simultaneously. The release of Pb due to these chain reactions can occur at any stage of the DGH model for as long as $TRCP_{Pb}$ is greater than the critical point of burst. The DGH model has helped establish that more than 65% of Pb at TAB shooting range was classified as high-risk of DGH whereas total Pb concentration only shed light on the total amount of Pb deposited into the shooting range soil and failed to provide information on the potential environmental risk.

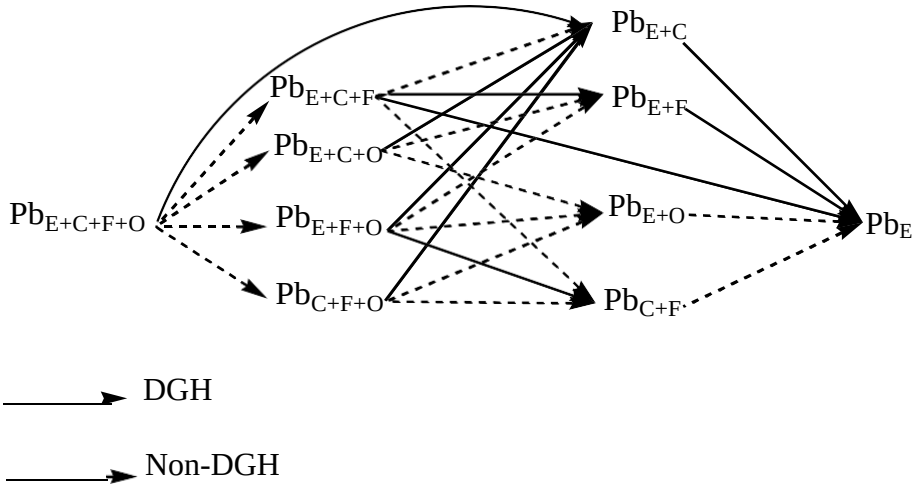


Figure 4.11 The geochemical release routes of DGH_{Pb} at TAB shooting range.

5. RECOMMENDATIONS AND FUTURE STUDIES

The high content of Pb in shooting range soils and elevated ecological risk indices demand that soil remediation and reclamation efforts should be employed in order to mitigate the pollution situation. As mentioned earlier in this study, scientists and researchers are continuously looking for new cost effective and yet efficient methods to immobilize and reduce the mobility and bioavailability of Pb in shooting range soils. Immobilization strategies and methods such as chemical amendments,[47,212] phytoremediation[213] and hydrothermal treatment[151] have been used to reduce the environmental pollution risk from Pb at shooting ranges. Future studies may include assessment of pollution risk from Pb pollution in water sources near shooting range sites. In addition, most of the shooting ranges studied are not enclosed and serve as grazing fields for livestock and source of wild fruits and vegetables for communities within their close proximity. Therefore, other future studies may include determination of accumulation of Pb in vegetation growing in these shooting ranges and nearby environment.

6. CONCLUSIONS

Shooting ranges have become increasingly hazardous and huge potential environmental pollution risks due to continuous deposition of Pb in shooting range soils arising from use of Pb shots and bullets. The concentrations of Pb deposited into seven of the eight shooting ranges studied far exceeded the USEPA set critical limit of 400 mg/kg for Pb in soils. Some shooting ranges such as TAB, accumulated Pb measuring more than ninety times the set USEPA set maximum contaminant limit. The higher Pb loading in shooting range soils increases the risk of pollution of nearby agricultural fields due to migration of Pb from runoff water. There is also increased potential for pollution of both surface and underground water sources. This can lead to Pb finding its way into the food chain after livestock consume contaminated vegetation and water. Pb may also find its way into the human body through consumption of contaminated water, crops and livestostock products such as milk and meat.

Only one shooting range, PAJ R2 specifically, accumulated Pb concentration below the set USEPA critical limit. The main reason for the low content of Pb at PAJ R2 is that shooting practices taking place at this shooting range involve mainly pistols and it is a known fact that pistol ammunition contains about 52% of Pb slug compared to assault rifles that can contain over 80% of Pb. In addition, all the eight shooting ranges studied failed the synthetic precipitation leaching procedure (SPLP) since the SPLP-Pb concentrations were in the range 0.1–784 mg/kg, which were all higher than the USEPA set limit of 0.015 mg/kg. This implies that there is high possibility of underground water contamination at these eight shooting ranges.

It is aslo important that the different Pb mineralogical species that predominate in the studied shooting range soils are identified which provides a qualitative measure of the Pb mobility, bioavailability and fate. The sequential extraction procedure and XRD technique established that Pb existed mostly in the carbonate fraction in all the eight shooting ranges studied and that cerussite and hydrocerussite were the predominate minerals in ther soils. It is important to note that total Pb concentration gives a quantitative measure of the amount of Pb accumulated in shooting range soils but falls short in quantifying the environmental pollution risk posed by Pb. To get a quantitative measure of the pollution risk to environment, pollution risk assessment indices have been used widely. All of the eight shooting ranges studied failed the pollution risk assessment, an indication that these shooting ranges are a danger to the environment, animals and human beings. Contamination and enrichment factors

were found to be very high, indicating very high contamination (CF_{Pb} > 6) and extreme Pb enrichment (EF_{Pb} > 50). In addition, total Pb concentration provides the static risk assessment of Pb pollution in the environment and does not take into consideration the changes in the conditions of the environment such as the diminishing holding capacity of the environment and changes in the chemical and physical properties of the soil. The delayed geochemical hazard (DGH) model gives a clear picture of the dynamic risk assessment of Pb pollution in the environment by relying on the nonlinear relationship between the inactive 'total releasable content of pollutant' and the labile 'total concentration of active species'. The DGH model was able to show that more than 65% of Pb displayed a high-risk of DGH which indicated probable chain reactions that could lead to the release and bioavailability of Pb in the environment. The application of the DGH model indicates that the environmental pollution risk of Pb could be underestimated under static risk assessment techniques.

As a consequence of high Pb pollution in the shooting ranges studied, it is recommended that management and pollution control strategies be implemented to arrest this situation before it spirals out of control. Various soil remediation techniques have been employed to help reduce and contain pollution of shooting range soils from Pb such as physical, chemical and phytoremediation methods. Physical methods include trapping of Pb bullets and shots for safe disposal. Chemical stabilisation and immobilization techniques have been used to minimize the weathering rate of Pb bullets and shots through the formation of insoluble Pb chemical species on the surface of Pb shots. Pb pollution has also been reduced through planting plants that can take up Pb chemical species from the polluted soils and thereby significantly reducing leaching of Pb to underground water. Research and investigation into simple, easily available and cost effective methods for Pb pollution management, control and remediation are ongoing.

7. REFERENCES

1. Haynes WM. *Handbook of Chemistry and Physics*, CRC Press/Taylor and Francis, Boca Raton, FL, 95th Edition, Internet Version. 2015.
2. Abadan H, Ashizawa A, Stevens YW. Toxicological profile for lead. US Public Health Service and Agency Toxic Substance and Disease, 2007; p. 582.
3. Flora G, Gupta D, Tiwari A. Toxicity of lead: a review with recent updates. *Interdiscip. Toxicol.* 2012;5:582.
4. McBride MB. Environmental chemistry of soils. Oxford University Press, Inc., New York. 1994.
5. Cowperthwaite JE, Dugdale PJ, Landry CJF, Morris DR, Steward FR, Wilson TCW. Energy aspects of a lead blast furnace. *Metall. Trans. B.*1980;11:291–299.
6. Hernberg S. Lead poisoning in a historical perspective. *Am. J. Ind. Med.* 2000;38:244–254.
7. Danilov AM. Fuel additives: evolution and use in 1996-2000, *Chem. Tech. Fuels Oils.* 2000;37:200.
8. Emsley J. Nature's Building Blocks: An A-Z Guide to the Elements, Oxford University Press, New York, Thomas Jefferson National Accelerator Facility - Office of Science Education. 2nd Ed. 2011.
9. Graham BWL. Survey of lead in the environment-sources and concentrations. In Lead in the New Zealand Environment. Environmental Occasional Publication No 9. Proceedings of a workshop, University of Auckland, New Zealand. 1988.
10. Wixon BG, Davies BE. Lead in soil: Recommended guideline. Society for Environmental Geochemistry and Health publication. Science Reviews, Northwood. 1993.
11. Ikeda M, Zhang ZW, Shimbo S, Watanabe T, Nakatsuka H, Moon CS, Matsuda Inoguchi N, Higashikawa K. Urban population exposure to lead and cadmium in east and south-east Asia. *Sci. Total Environ.* 2000;249:373–384.

12. US Environmental Protection Agency (USEPA), EPA-902-B01-001: Best management practices for lead at outdoor shooting ranges: United States Environmental Protection Agency Region 2. EPA-902-B01-001. 2001.

13. Centers for Disease Control and Prevention. Lead: prevention tips. Symptomatic lead toxicity can manifest in a variety of ways. ADHD, attention-deficit/hyperactivity disorder. http://www.rifuture.org/lead-poisoning-in-rhode-island/.

14. Jung, JM, Peddinti R. Lead Toxicity in the paediatric patient with sickle cell disease: unique risks and management. *Pediatr. Ann.* 2018;47:e36 –e40.

15. Trichopoulos D. Epidemiology of cancer. In: DeVita, V.T. (Ed.), Cancer: Principles and Practice of Oncology. Lippincott Company, Philadelphia. 1997. p. 231–258.

16. Mellor A, McCartney C. The effects of lead shot deposition on soils and crops at a clay pigeon shooting site in northern England. *Soil Use Manage.* 1994;10:124–129.

17. Lewis LA, Poppenga RJ, Davidson WR, Fischer JR, Morgan KA. Lead toxicosis and trace element levels in wild birds and mammals at a firearms training facility. *Arch. Environ. Contam. Toxicol.* 2001;41:208–214.

18. Haig SM, D'Elia J, Eagles-Smith C, Fair JM, Gervais J, Herring G, Rivers JW, Schulz, JH. The persistent problem of lead poisoning in birds from ammunition and fishing tackle. *The Condor: Ornithological Applications.* 2014;116:408–428.

19. Strom SM, Langenberg JA, Businga NK, Batten JK. Lead exposure in Wisconsin birds. In R. T. Watson, M. Fuller, M. Pokras, and W. G. Hunt (Eds.). Ingestion of Lead from Spent Ammunition: Implications for Wildlife and Humans. The Peregrine Fund, Boise, ID. 2009. Pg. 194-201. http://www.peregrinefund.org/Lead_conference/PDF/0205%20Strom.pdf

20. Botswana Bureau of Standards. *BOS 32:2015*. 3rd Edition. Gaborone, Botswana; 2015.

21. Shen G, Dadachov M, Dutko P, Menounou N, Arienti P. Weathering of lead in Fort Irwin firing range soils. *Glob. Nest Int. J.* 2004;6:167–175.

22. Chen M, Ma LQ, Harris WG. Distribution of Pb and As in soils at a shooting facility in central Florida. Soil and Crop Science Society of Florida Proceedings. 2001;60:15–20.

23. Chen M, Daroub SH. Characterization of lead in soils of a rifle/pistol shooting range in central Florida. Soil Sediment Contam. 2002;7:1–17.

24. World Health Organisation. *Guidelines for Drinking-Water Quality*. 3rd edition Geneva,Switzerland: Geneva, World Health Organization. 2008.

25. Duruibe JO, Ogwuegbu MDC, Egwurugwu JN. Heavy metal pollution and human biotoxic effects. *Int. J. Phys. Sci.* 2007;2:112–118.

26. Li Y, Zhu Y, Zhao S, Liu X. The weathering and transformation process of lead in China's shooting ranges. *Environ. Sci. Processes Impacts.* 2015;17:1620–1633.

27. Bricka RM, Rivera YB, Deliman PN. Vertical migration potential of metal contaminants at small arms firing ranges, Camp Edwards Military Reservation, MA. US Army Corps of Engineers. Technical Report IRRP-98-3. 1998.p.1–91.

28. Clausen, JL, Georgian T, Bednar A. Cost and performance report of incremental sampling methodology for soil containing metallic residues, environmental science and technology certification program, environmental security technology certification program (ESTCP) arlington, VA 22203, ERDC TR-13-10, Project ER-0918, 2013.

29. Tardy BA, Bricka RM, Larson SL. Chemical stabilization of lead in small arms firing range soils–Environmental Quality and Technology Program; U.S. Army Corps of Engineers, ERDC/EL TR-03-20; Vicksburg, Mississippi; 2003. p.1–67.

30. Astrup T, Boddum JK, Christensen TH. Lead distribution and mobility in a soil embankment used as a bullet stop at a shooting range. *J. Soil Contam.* 1999;8:653–665.

31. Sehube N, Kelebemang R, Totolo O, Laetsang M, Kamwi O, Dinake P. Lead pollution of shooting range soils. *S. Afr. J. Chem.* 2017;70:21–28.

32. Hockmann K, Tandy S, Lenz M, Reiser R, Conesa HM, Keller M, Studer B, Schulin R. Antimony Retention and Release from Drained and Waterlogged Shooting Range Soil under Field Conditions. *Chemosphere* 2015;134: 536–543.

33. Fayiga AO, Saha UK. 2016. Review: Soil Pollution at Outdoor Shooting Ranges: Health Effects, Bioavailability and Best Management Practices. *Environ. Pollut.* 2016;216:135–145.

34. Mariussen E, Johnsen IV, Stromseng AE. Distribution and mobility of lead (Pb), copper (Cu), zinc (Zn), and antimony (Sb) from ammunition residues on shooting ranges for small arms located on mires. *Environ Sci. Pollut. Res. Int.* 2017;24:10182–10196.

35. Urrutia-Goyes R, Argyraki A, Ornelas-Soto N. Assessing lead, nickel, and zinc pollution in topsoil from a historic shooting range rehabilitated into a public urban park. *Int. J. Environ. Res. Public Health* 2017;14:698–712.

36. Barnes FC. Cartridges of the World. 9th ed. Ed. McPherson ML. Lola, WI: Krause Publications. 2000.

37. Blast and Ballistics Ltd. 2020. http://www.blastandballistics.com/services/ballistic-technology.php

38. Carlucci DE, Jacobson SS. Ballistics: Theory and Design of Guns and Ammunition. 3rd Ed. CRC Press, Taylor and Francis Group. London. 2018. P. 109–160.

39. Golden NH, Warner SE, Coffey MJ. A review and assessment of spent lead ammunition and its exposure and effects to scavenging birds in the United States. *Rev. Environ. Contam. Toxicol.* 2015;237:123–191.

40. Violante A, Cozzolino V, Perelomov L, Caporale AG, Pigna M. Mobility and bioavailability of heavy metals and metalloids in soil environments. *J. Soil Sci. Plant Nutr.* 2010;10:268–292.

41. Craig JR, Rimstidt JD, Bonnaffon CA, Collins TK, Scanlon PF. Surface water transport of lead at a shooting range, *B. Environ. Contam. Tox.*1999;63:312-319.

42. Stansley W, Widjeskog L, Roscoe DE. Lead contamination and mobility in surface water at trap and skeet ranges. *B. Environ. Contam. Tox.* 1992;49:640–647.

43. Hoch JM, Bruce M. Metal contamination hotspots at unregulated firearm target shooting sites in the Everglades. *J. Environ. Qual.* 2019;48:755–761.

44. Cao X, Ma LQ, Hardison Jr D, Harris WG, Weathering of lead bullets and their environmental effects at outdoor shooting ranges. *J. Environ. Qual.* 2003;32:526–534.

45. Rooney CP, McLaren RG, Cresswell RJ. Distribution and phytoavailability of lead in a soil contaminated with lead shot. *Water Air Soil Poll.* 1999;116:535–548.

46. Koeppe DE, The uptake, distribution and effect of cadmium and lead in plants, *Stevens report, Stevens Institute of Technology*. 1977;**7**:197–206.

47. Tandy S, Meier N, Schulin R. Use of soil amendments to immobilize antimony and lead in moderately contaminated shooting range soils. *J. Hazard. Mater.* 2017;324:617–625.

48. Etim EU, Onianwa PC. Lead contamination of soil in the vicinity of a military shooting range in Ibadan, Nigeria. *Toxicol. Environ. Chem.* 2012;94:895–905.

49. Zhang J, Yang B, Chen T, Sun X, Chen C. Metal speciation and pollution assessment of Cd and Pb in intertidal sediments of Donghai Island, China. *Reg. Stud. Mar. Sci.* 2016;6:37–48.

50. Dong H, Lin Z, Wan X, Feng L. Risk assessment for the mercury polluted site near a pesticide plant in Changsha, Hunan, China. *Chemosphere* 2017;169:333–341.

51. Kelebemang R, Dinake P, Sehube N, Daniel B, Totolo O, Laetsang M. Speciation and mobility of lead in shooting range soils. *Chem. Speciat. Bioavailab.* 2017;29:143–152.

52. Mana SC, Fatt NT, Ashraf MA. The fate and transport of arsenic species in the aquatic ecosystem: a case study on Bestari Jaya, Peninsular Malaysia. *Environ. Sci. Pollut. Res.* 2016;23:1–9.

53. Tessier A, Campbell PGC, Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 1979;51:844–851.

54. Mossop KF, Davidson CM. Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead manganese and zinc in soils and sediments. *Anal. Chimi. Acta.* 2003;478:111–118.

55. Ashraf MA, Maah MJ, Yusoff I, Ghararibreza, M. Speciation of heavy metals in the surface waters of a former tin mining catchment. *Chem. Speciat. Bioavailab.* 2012;24:1–12.

56. Ashraf MA, Maah MJ, Yusoff I. Speciation of heavy metals in the sediments of former tin mining catchment. *Iran J. Sci. Technol.* 2012;36:163–180.

57. Ma LQ, Hardison Jr D, Harris WD, Cao X, Zhou Q. Effects of soil property and soil amendment on weathering of abraded metallic Pb in shooting ranges. *Water Air Soil Poll.* 2007;178:297–307.

58. Ming C, Liu F, Yvon J. Delayed geochemical hazard: Concept, digital model and case study. *Sci. China Ser. D Earth. Sci.* 2005;48:311–316.

59. Zheng M, Feng L, He J, Chen M, Zhang J, Zhang M, Wang J. Delayed geochemical hazard: A tool for risk assessment of heavy metal polluted sites and case study. *J. Hazard. Mater.* 2015;287:197–206.

60. Vodyanitskii YN. Methods of sequential extraction of heavy metals from soils: new approaches and the mineralogical control (a review). *Eurasian Soil Sci.* 2006;39:1074–1083.

61. Ma LQ, Rao GN. Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. *J. Environ. Qual.* 1997;26:259–264.

62. Zhai M, Totolo O, Modisi MP, Finkelman RB, Kelesitse SM, Menyatso M. Heavy metal distribution in soils near Palapye, Botswana: An evaluation of the environmental impact of coal mining and combustion on soils in a semi-arid region, *Environ. Geochem. Health.*, 2009;31:759–777.

63. Mbongwe B, Barnes BR, Shabane J, Zhai M, Rajaram S, Mpuchane S, Exposure to lead among children aged 1-6 years in the city of Gaborone, Botswana, *J. Environ. Health Res.*, 2010;10:17–26.

64. Thornton I, Rautiu R, Brush S. Lead: The Facts, Prepared by IC Consultants Ltd London, UK, December. 2001. pp. 20–30.

65. Lin Z. Secondary mineral phases of metallic lead in soils of shooting ranges from Orebro County. Sweden. *Environ. Geol.* 1996;27:370–375.

66. Guberman DE. U.S. Department of the Interior, United States Geological Survey (USGS), 2012 Minerals year book – Lead. 2016. p. 42.8.

67. Bannon DI, Drexler JW, Fent GM, Casteel SW, Hunter PJ, Brattin WJ. Evaluation of small arms range soils for metal contamination and lead bioavailability. *Environ Sci Technol.* 2009;43:9071–9076.

68. Hui CA. Lead distribution throughout soil, flora and an invertebrate at a wetland skeet range. *J. Toxicol. Environ. Health A.* 2002;65:1093–1107.

69. Camobreco VJ, Richards BK, Steenhuis TS, Peverly JH, McBride MB. Movement of heavy metals through undisturbed and homogenized soil columns. *Soil Sci.* 1996;161: 740–750.

70. Bruell R, Nikolaidis NP, Long RP. Evaluation of remedial alternatives of lead from shooting range soil. *Environ. Eng. Sci.* 1999;16:403–414.

71. Greenway JA, Gerstenberger S. An evaluation of lead contamination in plastic toys collected from day care centers in the Las Vegas Valley, Nevada, USA. *Bull. Environ. Contam. Toxicol.* 2010;85:363–366.

72. Sanderson P, Naidu R, Bolan N, Bowman M, Mclure S. Effect of soil type on distribution and bioaccessibility of metal contaminants in shooting range soils. *Sci. Total Environ.* 2012;438:452–462.

73. Li Y, Zhu Y, Zhao S, Liu X. The weathering and transformation process of lead in China's shooting ranges. Environ Sci Processes Impacts. 2015;17:1620–1633.

74. Chun HJ, Nam SM, Cho IH. Study of the heavy metals in fume of buckshot, blood lead concentration and self-rated health status of national clay shooting athletes. *Korean J. Sports Med.* 2018;36:84–91.

75. Sanderson P, Fangjie QF, Seshadri B, Wijayawardena A, Naidu R. Contamination, fate and management of metals in shooting range soils—a Review. *Curr. Pollution Rep.* 2018;4:175–187.

76. Vandebroek E, Haufroid V, Smolders E, Hons L, Nemery B. Occupational exposure to metals in shooting ranges: A biomonitoring study. *Saf. Health Work.* 2018;10:87–94.

77. Adsersen H, Storgaard S, Jorgensen H, Pedersen F, Willems M. Blyforurening omkring flugtskydningsbaner. *Miljostyrelsen*, Copenhagen. 1983. pp. 1–46.
78. Jorgensen SS, Willems M. The fate of lead in soils: The transformation of lead pellets in shooting range soils. *Ambio*. 1987;6:11–15.
79. Van Bon J, Boersema JJ. Sources, effects and management of metallic lead pollution: the contribution of hunting, shooting and angling. *Contam Soil.* 1988;3:269–271.
80. Ma WC. Effect of soil pollution with metallic lead pellets on lead bioaccumulation and organ/body weight alterations in small mammals. *Arch. Environ. Contam. Toxicol.* 1989;18:617–622.
81. Fahrenhorst C, Renger M. Verband Deutscher Landwirtschaftlicher Untersuchngs und Forschungsanstalten. *Reihe Kongressberichte.* 1990;32:827–830.
82. Tanskanen H, Kukkonen J, Kaija J. Heavy metals pollution in the environment of a shooting range. *Geological Survey Final Special Paper* 1991:12:187–193.
83. Pott DB, Shephard BK, Modi A. Lake Michigan sediment contamination from 73 years of trap and skeet shooting. *Wat. Sci. Tech.* 1993:28:383–386.
84. Mannenin S, Tanskanen N. Transfer of lead from shotgun pellets to humus and three plant species in a Finnish shooting range. *Arch. Environ. Contam. Toxicol.* 1993;24:410–414.
85. Merrington G, Alloway BJ. Soils contaminated with lead and antimony from sports shooting. In *Fifth International Conference on Contaminated Soil*. Maastricht, The Netherlands.(Eds van der Brink, Bosman and Arendt). (Kluwer Academic Publishers). 1995. pp. 631-632.
86. Murray KS, Bazzi A. The use of geology and chemistry in determining the buildup of lead in the soil of outdoor shooting ranges (abstr.) *Mich. Acad.* 1995:6.

87. Basunia S, Landsberger, S. Contents and leachability of heavy metals (Pb, Cu, Sb, Zn, As) in soil at the Pantex firing range, Amarillo, Texas. *J. Air Waste Manag. Assoc*. 2001;51:1428–1435.

88. Stansley W, Roscoe DE. The uptake and effects of lead in small mammals and frogs at a trap and skeet range. *Arch. Environ. Contam. Toxicol.* 1996;30:220–226.

89. Braun U, Pusterla N, Ossent P. Lead poisoning of calves pastured in the target area of a military shooting range. *Schweiz. Arch. Tierheilk.* 1997;139:403–407.

90. Murray K, Bazzi A, Carter C, Ehlert A, Harris A, Kopec M, Richardson J, Sokol H. Distribution and mobility of lead in soils at an outdoor shooting range. *J. Soil Contam.* 1997;6:79–93.

91. Rooney CP, McLaren RG. Distribution of soil Pb contamination at clay target shooting ranges. ,*Australas. J. Ecotoxicol.* 2000;6:95–102.

92. Peddicord RK, Lakind JS. Ecological and human health risks at an outdoor firing range. *Environ. Toxicol. Chem.* 2000;19:2602–2613.

93. Turpeinen R, Salminen J, Kairesalo T. Mobility and bioavailability of lead in contaminated boreal forest. *Soil. Environ. Sci. Technol.* 2000;34:5152–5156.

94. Vyas NB, Spann JW, Heinz GH, Beyer WN, Jaquette JA, Mengelkoch JM. Lead poisoning of passerines at a trap and skeet range. *Environ. Pollut.* 2000;107:159–166.

95. Mozafar A, Ruh R, Klingel P, Gamper H, Egli S, Frossard E. Effect of Heavy metal contaminated shooting range soils on mycorrhizal colonization of roots and metal uptake by leek. *Environ. Monit. Assess.* 2002;79:177–191.

96. Lee IS, Kim OK, Chang YY, Bae B, Kim HH, Baek KH. Heavy metal concentrations and enzyme activities in soil from a contaminated Korean shooting range. *J. Biosci. Bioeng.* 2002:94:406–411.

97. Knechtenhofer LA, Xifra IO, Scheinost AC, Fluhler H, Kretzschmar R. Fate of heavy metal in a strongly acidic shooting-range: small scale metal distribution and its relation to a preferential water flow. *J. Plant Nutr. Soil Sci.* 2003;166:84–92.

98. Hardison Jr DW, Ma LQ, Luongo T, Harris WG. Lead contamination in shooting range soils from abrasion of lead bullets and subsequent weathering. *Sci. Total Environ.* 2004;328:175–183.

99. Labare MP, Butkus MA, Riegner D, Schommer N, Atkinson J. Evaluation of lead movement from the abiotic to the biotic at a small arms firing range. *Environ. Geol.* 2004;46:750–754.

100. Johnson MS, Major MA, Casteel SW. Lead accumulation in woodchucks (Marmota monax) at small arms and skeet ranges. *Ecotoxicol. Environ. Saf.* 2004;59:232–236.

101. Migliorinia, M., Pigino, G., Bianchi, N., Bernini, F. and Leonzio, C. The effects of heavy metal contamination on the soil arthropod community of a shooting range. *Environ. Pollut.* 2004;129:331–340.

102. Vantelon D, Lanzirotti A, Scheinost AC, Kretzschmar R. Spatial distribution and speciation of lead around corroding bullets in a shooting range soil studied by micro-X-ray fluorescence and absorption spectroscopy. *Environ. Sci. Technol.* 2005;39:4808–4815.

103. Reid BJ, Watson R. Lead tolerance in Aporrectodea rosea earthworms from a clay pigeon shooting site. *Soil Biol. Biochem.* 2005;37:609–612.

104. Dermatas D, Menounou N, Dadachov M, Dutko P, Shen G, Xu X, Tsaneva V. Lead leachability in firing range soils. *Environ. Eng. Sci.* 2006;23:88–101.

105. Rantalainen ML, Torkkeli M, Strömmer R, Setälä H. Lead contamination of an old shooting range affecting the local ecosystem — A case study with a holistic approach. *Sci. Total Environ.* 2006;369:99–108.

106. Bennett JR, Kaufman CA, Koch I, Sova J, Reimer KJ. Ecological risk assessment of lead contamination at rifle and pistol ranges using techniques to account for site characteristics. *Sci. Total Environ.* 2007;374:91–101.

107. Spuller C, Weigand H, Marb C. Trace metal stabilisation in a shooting range soil: Mobility and phytotoxicity. *J. Hazard. Mater.* 2007;141:378–387.

108. Johnson MS, Wickwire WT, Quinn Jr MJ, Ziolkowski Jr DJ, Burmistrov D, Menzie CA, Geraghty C, Minnich M, Parsons PJ. Are songbirds at risk from lead at small arms ranges? An application of the spatially explicit exposure model. *Environ. Toxicol. Chem.* 2007:26:2215–2225.

109. Levonmaki M, Hartikainen H. Efficiency of liming in controlling the mobility of lead in shooting range soils as assessed by different experimental approaches. *Sci. Total Environ.* 2007;388:1–7.

110. Isaacs LK. Lead leaching from soils and in storm waters at twelve military shooting ranges. *J. Hazard. Subst. Res.* 2007;6:1–30.

111. Sorvari J. Environmental risks at Finnish shooting ranges—A case study. *Hum. Ecol. Risk Assess.* 2007;13:1111–1146.

112. Duggan J, Dhawan A. Speciation and vertical distribution of lead and lead shot in soil at a recreational firing range. *Soil Sediment Contam.* 2007;16:351–369.

113. Robinson BH, Bischofberger S, Stoll A, Schroer D, Furrer G, Roulier S, Gruenwald A, Attinger W, Schulin R. Plant uptake of trace elements on a Swiss military shooting range: Uptake pathways and land management implications. *Environ. Pollut.* 2008;153:668–676.

114. Cao X, Dermatas D, Xu X, Shen G. Immobilization of Lead in shooting range soils by means of cement, quicklime, and phosphate amendments. *Env. Sci. Pollut. Res.* 2008;15:120–127.

115. Hartikainen H, Kerko E. Lead in various chemical pools in soil depth profiles on two shooting ranges of different age. *Boreal Environ. Res. (Suppl. A).* 2009;14:61–69.

116. Clausen J, Korte N. The distribution of metals in soils and pore water at three U.S. military training facilities. *Soil Sediment. Contam.* 2009;18:546–563.

117. Scheetz CD, Rimstidt JD. Dissolution, transport, and fate of lead on a shooting range in the Jefferson National Forest near Blacksburg, VA, USA. *Environ. Geol.* 2009;58:655–665.

118. Rauckyte T, Zak S, Pawlak Z, Oloyede A. Lead leachability from shooting range soils. *Ecol. Chem. Eng. A.* 2009;16:419–426.

119. Hashimoto Y, Taki T, Sato T. Sorption of dissolved lead from shooting range soils using hydroxyapatite amendments synthesized from industrial by-products as affected by varying pH conditions. *J. Environ. Manag.* 2009;90:1782–1789.

120. Lee KY, Kim K.W. Heavy metal removal from shooting range soil by hybrid electrokinetics with bacteria and enhancing agents. *Environ. Sci. Technol.* 2010;44:9482–9487.

121. Chrastny V, Komarek M, Hajek T. Lead contamination of an agricultural soil in the vicinity of a shooting range. *Environ. Monit. Assess.* 2010;162:37–46.

122. Conesa HM, Wieser M, Gasser M, Hockmann K, Evangelou MWH, Studer B, Schulin, R. Effects of three amendments on extractability and fractionation of Pb, Cu, Ni and Sb in two shooting range soils. *J. Hazard. Mater.* 2010;181:845–850.

123. Yin X, Saha UK, Ma LQ. Effectiveness of best management practices in reducing Pb-bullet weathering in a shooting range in Florida. *J. Hazard. Mater.* 2010;179: 895–900.

124. Laporte-Saumure M, Martel R, Mercier G. Evaluation of physicochemical methods for treatment of Cu, Pb, Sb, and Zn in Canadian small arm firing ranges backstop soils. *Water Air Soil Pollut.* 2010;213:171–189.

125. Moon DH, Cheong KH, Kim TS, Khim J, Choi SB, Ok YS, Moon OR. Stabilization of Pb contaminated army firing range soil using calcined waste oyster shells. *Korean Soc. Environ. Eng.* 2010;32:185–192.

126. Heier LS, Meland S, Ljones M, Salbu B, Stromseng AE. Short-term temporal variations in speciation of Pb, Cu, Zn and Sb in a shooting range runoff stream. *Sci. Total Environ.* 2010;408:2409–2417.

127. Conesa HM, Wieser M, Studer B, Schulin R. Effects of vegetation and fertilizer on metal and Sb plant uptake in a calcareous shooting range soil. *Ecol. Eng.* 2011;37:654–658.

128. Laporte-Saumure M, Martel R, Mercier G. Characterization and metal availability of copper, lead, antimony and zinc contamination at four Canadian small arms firing ranges. *Environ. Technol.* 2011;32:767–781.

129. Fayiga AO, Saha U, Cao X, Ma LQ. Chemical and physical characterization of lead in three shooting range soils in Florida. *Chem. Speciat. Bioavailab.* 2011;23:148–154.

130. Evangelou MWH, Hockmann K, Pokharel R, Jakob A, Schulin R. Accumulation of Sb, Pb, Cu, Zn and Cd by various plants species on two different relocated military shooting range soils. *J. Environ. Manag.* 2012;108:102–107.

131. Ahmad M, Hashimoto Y, Moon DH, Lee SS, Ok YS. Immobilization of lead in a Korean military shooting range soil using eggshell waste: An integrated mechanistic approach. *J. Hazard. Mater.* 2012;209–210:392– 401.

132. Selonen S, Liiri M, Strommer R, Setala H. The fate of lead at abandoned and active shooting ranges in a boreal pine forest. Environ Toxicol Chem. 2012;31:2771–2779.

133. Laporte-Saumure M, Martel R, Mercier G. Pore water quality in the upper part of the vadose zone under an operating Canadian small arms firing range backstop berm. *Soil Sediment Contam.* 2012;21:739–755.

134. Moon DH, Cheong KH, Khim J, Wazne M, Hyun S, Park JH, Chang YY, Ok YS. Stabilization of Pb^{2+} and Cu^{2+} contaminated firing range soil using calcined oyster shells and waste cow bones. *Chemosphere* 2013;91:1349–1354.

135. Ash C, Tejnecky V, Sebek O, Nemecek K, Zahourova-Dubova L, Bakardjieva S, Drahota P, Drabek O. Fractionation and distribution of risk elements in soil profiles at a Czech shooting range. *Plant Soil Environ.* 2013;59:121–129.

136. kkenhaug G, Amstatter K, Bue HL, Cornelissen G, Breedveld GD, Henriksen T, Mulder J. Antimony (Sb) contaminated shooting range soil: Sb mobility and immobilization by soil amendments. *Environ. Sci. Technol.* 2013;47:6431−6439.

137. Lafond S, Blais JF, Martel R, Mercier G. Chemical leaching of antimony and other metals from small arms shooting range soil. *Water Air Soil Pollut.* 2013;224:1371–1385.

138. Liu Y, Fang Z, Xie C, Li J. Analysis of existing speciation and evaluation of heavy metals pollution of soil in a shooting range. *Nature Environ. Pollut. Technol.* 2014;13:449–456.

139. Rubio M, Germanier A, Mera MF, Faudone SN, Sbarato RD, Campos JM, Zampar V, Bonzi E, Perez CA. Study of lead levels in soils by weathering of metallic Pb bullets used in dove hunting in Cordoba, Argentina. *X-Ray Spectrom*. 2014;43:186–192.

140. Luo W, Verweij RA, van Gestel, CAM. Contribution of soil properties of shooting fields to lead biovailability and toxicity to Enchytraeus crypticus. *Soil Biol. Biochem.* 2014;76:235–241.

141. Selonen S, Setala H. Soil processes and tree growth at shooting ranges in a boreal forest reflect contamination history and lead-induced changes in soil food webs. *Sci. Total Environ.* 2015;518–519:320–327.

142. Sanderson P, Naidu R, Bolan N. Effectiveness of chemical amendments for stabilisation of lead and antimony in risk-based land management of soils of shooting ranges. *Environ. Sci. Pollut. Res.* 2015;22:8942–8956.

143. Luo W, Verweij RA, van Gestel CAM. Toxicity of Pb contaminated soils to the oribatid mite Platynothrus Peltifer. *Ecotoxicol.* 2015;24:985–990.

144. Okkenhaug G, Gebhardt KAG, Amstaetter K, Bue HL, Herzel H, Mariusseni E, Almas AR, Cornelissen G, Breedveld GD, Rasmussen G, Mulder J. Antimony (Sb) and lead (Pb) in contaminated shooting range soils: Sb and Pb mobility and immobilization by iron based sorbents, a field study. *J. Hazard. Mater.* 2016;307:336–343.

145. Etim EU. Distribution of soil-bound lead arising from rainfall-runoff events at impact berm of a military shooting range. *J. Environ. Prot.* 2016;7:623–634.

146. Yoo JC, Shin YJ, Kim EJ, Yang JS, Baek K. Extraction mechanism of lead from shooting range soil by ferric salts. *Process Saf. Environ.* 2016;103:174–182.

147. Islam MN, Nguyen XP, Jung HY, Park JH. Chemical speciation and quantitative evaluation of heavy metal pollution hazards in two army shooting range backstop soils. *Bull. Environ. Contam. Toxicol*. 2016;96:179–185.

148. Sanderson P, Naidu R, Bolan N. The effect of environmental conditions and soil physicochemistry on phosphate stabilisation of Pb in shooting range soils. *J. Environ. Manag.* 2016;170:123–130.

149. Rodríguez-Seijo A, Alfaya MC, Andrade ML, Vega FA. Copper, chromium, nickel, lead and zinc levels and pollution degree in firing range soils. *Land Degrad. Dev.* 2016;27:172–1730.

150. Rodriguez-Seijo A, Lago-Vila M, Andrade ML, Vega FA. Pb pollution in soils from a trap shooting range and the phytoremediation ability of Agrostis capillaris L. *Environ. Sci. Pollut. Res.* 2016;23:1312–1323.

151. Islam MN, Park JH. Immobilization and reduction of bioavailability of lead in shooting range soil through hydrothermal treatment. *J. Environ. Manag.* 2017;191:172–178.

152. Okkenhaug G, Smebye AB, Pabst T, Amundsen CE, Saevarsson H, Breedveld GD. Shooting range contamination: mobility and transport of lead (Pb), copper (Cu) and antimony (Sb) in contaminated peatland. *J. Soils Sed.* 2017;18:3310–3323.

153. Mariussen E, Heier LS, Teien HC, Pettersen MN, Holth, TF, Salbu B, Rosseland BO. Accumulation of lead (Pb) in brown trout (Salmo trutta) from a lake downstream a former shooting range. *Ecotoxicol. Environ. Saf.* 2017;135:327–336.

154. Etim EU. Lead removal from contaminated shooting range soil using acetic acid potassium chloride washing solutions and electrochemical reduction. *J. Health Pollut.* 2017;7:22–31.

155. Rodríguez-Seijo A, Cachada A, Gavina A, Duarte A C, Vega FA, Andrade ML, Pereira R. Lead and PAHs contamination of an old shooting range: A case study with a holistic approach. *Sci. Total Environ.* 2017;575:367–377.

156. Hockmann K, Tandy S, Studer B, Evangelou MWH, Schulin R. Plant uptake and availability of antimony, lead, copper and zinc in oxic and reduced shooting range soil. *Environ. Pollut.* 2018;238:255–262.

157. Pedersen KB, Jensen PE, Ottosen LM, Barlindhaug J. Influence of electrode placement for mobilising and removing metals during electrodialytic remediation of metals from shooting range soil. *Chemosphere* 2018;210:683–691.

158. Mariussen E, Johnsen IV, Stromseng AE. Application of sorbents in different soil types from small arms shooting ranges for immobilization of lead (Pb), copper (Cu), zinc (Zn), and antimony (Sb). *J. Soil Sediment.* 2018;18:1558–1568.

159. Johnsen IV, Mariussen E, Voie O. Assessment of intake of copper and lead by sheep grazing on a shooting range for small arms: a case study. *Environ. Sci. Pollut. Res.* 2019;26:7337–7346.

160. Magaji Y, Ajibade GA, Yilwa VMY, Appah J, Haroun AA, Alhaji I, Namadi MM, Sodimu AI. Concentration of heavy metals in the soil and translocation with phytoremediation potential by plant species in military shooting range. *World Sci. News.* 2018;92:260–271.

161. Pedersen KB, Jensen PE, Ottosen LM, Barlindhaug J. The relative influence of electrokinetic remediation design on the removal of As, Cu, Pb and Sb from shooting range soils. *Eng. Geol.* 2018;238:52–61.

162. Darling CTR, Thomas VG. 2003. The distribution of outdoor shooting ranges in Ontario and the potential for lead pollution of soil and water. *Sci. Total Environ.* 2003;313:235–243.

163. Zheng G, Xu S, Liang M, Dermatas D, Xu X. Transformations of organic carbon and its impact on lead weathering in shooting range soils. *Environ. Earth Sci.* 2011;64:2241–2246.

164. Nelson DW, Sommers LE. Total carbon, organic carbon, and organic matter. In: Page AL, Miller RH, Keeney DR. editors. Methods of soil analysis, part 2 chemical and microbiological properties 9. Madison (WI): ASA; 1982 pp. 539–577.

165. Cao X, Dermatas D. Evaluating the applicability of regulatory leaching tests for assessing lead leachability in contaminated shooting range soils. *Environ. Monit Assess.* 2008;139:1–13.

166. Lin Z, Comet B, Qvarfort U, Herbert R. The chemical and mineralogical behavior of Pb in shooting range soils from central Sweden. *Environ. Pollut.* 1995;89:303–309.

167. Van Vleek B, Amarasiriwardena D, Xing B. Investigation of distribution of soil antimony using sequential extraction and antimony complexed to soil-derived humic acids molar mass fractions extracted from various depths in a shooting range soil. *Microchem. J.* 2011;97:68–73.

168. Peddicord RK. Synopsis of applications and limitations of TCLP and SPLP at outdoor shooting ranges. Newtown, CT: Facility development series No. 4, National Shooting Sports Foundation. 1998; pp. 1–12.

169. Reid S, Cohen SZ. A new tool to predict lead mobility in shooting range soils: Predicting SPLP results. Amherst, University of Massachusetts: The 16th Annual International Conference on Contaminated Soils, Sediments and Water. Massachusetts. 2000.

170. Dinake P, Kelebemang R, Sehube N, Kamwi O, Laetsang M. Quantitative assessment of environmental risk from lead pollution of shooting range soils. *Chem. Speciat. Bioavailab.* 2018;30:76–85.

171. Hakanson L. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Res.* 1980;14:975–1001.

172. Hashimoto Y, Matsufuru H, Sato T. Attenuation of lead leachability in shooting range soils using poultry waste amendments in combination with indigenous plant species. *Chemosphere* 2008;73:643–649.

173. Bandara T, Vithanage M. Phytoremediation of shooting range soils. In: Ansari AA, Gill SS, Gill R, Lanza GR, Newman L. (Editors). Phytoremediation. Cham: Springer International Publishing. 2016 pp. 469–488.

174. Dinake P, Kelebemang R, Sehube N. A Comprehensive approach to speciation of lead and its contamination of firing range soils: A Review. *Soil Sed. Contam.* 2019;28:431–459.

175. Tariq SR, Ashraf A. Comparative evaluation of phytoremediation of metal contaminated soil of firing range by four different plant species. *Arab. J. Chem.* 2016;9: 806–814.

176. Sanderson P, Naidu R, Bolan N, Limb JE, Ok YS. Chemical stabilisation of lead in shooting range soils with phosphate and magnesium oxide: Synchrotron investigation. *J. Hazard. Mater.* 2015;299:395–403.

177. Fayiga AO, Saha UK. Effect of phosphate treatment on Pb leachability in contaminated shooting range soils. *Soil Sed. Contam.* 2017;26:115–126.

178. Ogawa S, Katoh M, Sato T. Simultaneous lead and antimony immobilization in shooting range soil by a combined application of hydroxyapatite and ferrihydrite. *Environ. Technol.* 2015;36:2647–2656.

179. Yan Y, Qi F, Seshadri B, Xu Y, Hou J, Ok YS, Dong X, Li Q, Sun X, Wang L, Bolan N. Utilization of phosphorus loaded alkaline residue to immobilize lead in a shooting range soil. *Chemosphere* 2016;162:315–323.

180. Ahmad M, Lee SS, Lim JE, Lee SE, Cho JS, Moon DH, Hashimoto Y, Ok YS. Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions. *Chemosphere* 2014;95:433–441.

181. Ahmad M, Ok YS, Rajapaksha AU, Lim JE, Kim BY, Ahn JH, Lee YH, Al-Wabel MI, Lee SE, Lee SS. Lead and copper immobilization in a shooting range soil using soybean stover- and pine needle-derived biochars: chemical, microbial and spectroscopic assessments. *J. Hazard. Mater.* 2016;301:179–186.

182. Vithanage M, Herath I, Almaroai YA, Rajapaksha AU, Huang L, Sung JK, Lee SS, Ok YS. Effects of carbon nanotube and biochar on bioavailability of Pb, Cu and Sb in multi-metal contaminated soil. *Environ. Geochem. Health* 2017;39:1409–1420.

183. Rajapaksha AU, Ahmad M, Vithanage M, Kim KR, Chang JY, Lee SS, Ok YS. The role of biochar, natural iron oxides, and nanomaterials as soil amendments for immobilizing metals in shooting range soil. *Environ. Geochem. Health* 2015;37:931–942.

184. Seshadri B, Bolan NS, Choppala G, Kunhikrishnan A, Sanderson P, Wang H, Currie LD, Tsang DCW, Ok YS, Kim G. Potential value of phosphate compounds in enhancing immobilization and reducing bioavailability of mixed heavy metal contaminants in shooting range soil. *Chemosphere* 2017;184:197–206.

185. Wawra A, Friesl-Hanl W, Puschenreiter M, Soja G, Reichenauer T, Roithner C, Watzinger A. Degradation of polycyclic aromatic hydrocarbons in a mixed contaminated soil supported by phytostabilisation, organic and inorganic soil additive. *Sci. Total Environ.* 2018;628–629:1287–1295.

186. Chrysochoou M, Dermatas D, Grubb DG. Phosphate application to firing range soils for Pb immobilization: The unclear role of phosphate. *J. Hazard. Mater.* 2007;144:1–14.

187. Deem LM, Crow SE. Department of Natural Resources and Environmental Management; Reference module in earth systems and environmental sciences, University of Hawaii Manoa, Honolulu, HI, United States, Elsevier Inc. 2017.p. 1.

188. Sanderson P, Naidu R, Bolan N. Application of a biodegradable chelate to enhance subsequent chemical stabilisation of Pb in shooting range soils. *J. Soils Sediments* 2017;17:1696–1705.

189. Nriagu JO. Lead orthophosphates-IV formation and stability in the environment. *Geochim. Cosmochim. Acta.* 1974:38:887–898.

190. Dermatas D, Chrysochoou M, Grubb DG, Xu X. Phosphate treatment of firing range soils: Lead fixation or phosphorus release? *J. Environ. Qual.* 2008;37:47–56.

191. Shi Z, Erickson LE. Mathematical model development and simulation of in situ stabilization in lead-contaminated soils. *J. Hazard. Mater.* 2001;87:99–116.

192. Kumarathilaka P, Ahmad M, Herath I, Mahatantila K, Athapattu BCL, Rinklebe J, Ok YS, Usman A, Al-Wabel MI, Abduljabbar A, Vithanage M. Influence of bioenergy waste biochar on proton- and ligand-promoted release of Pb and Cu in a shooting range soil. *Sci. Total Environ*. 2018;625:547–554.

193. Hashimoto Y, Sato T. Removal of aqueous lead by poorly-crystalline hydroxyapatites. *Chemosphere* 2007;69:1775–1782.

194. Hashimoto Y, Yoshida T, Sato, T. Phosphorus-induced lead immobilization in a shooting range soil using poorly-crystalline hydroxyapatite and incinerated poultry waste. ASA-CSSA-SSSA International Annual Meetings, NewOrleans, USA, 2007.

195. Chen S, Xu M, Ma Y, Yang J. Evaluation of different phosphate amendments on availability of metals in contaminated soil. *Ecotox. Environ. Safe.* 2007;67:278–285.

196. Yoon JK, Cao X, Ma LQ. Application methods affect phosphorus-induced lead immobilization from a contaminated soil. *J. Environ. Qual.* 2007;36:373–378.

197. Uchimiya M, Bannon DI, Wartelle LH. Retention of heavy metals by carboxyl functional groups of biochars in small arms range soil. *J. Agric. Food Chem.* 2012;60:1798–1809.

198. Uchimiya M, Klasson KT, Wartelle LH, Lima IM. Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorptionisotherms and the release of cations. *Chemosphere* 2011;82:1431–1437.

199. Qiu Y, Zheng Z, Zhou Z, Sheng GD. Effectiveness and mechanisms of dye adsorption on a straw-based biochar. *Bioresour. Technol.* 2009;100:5348–5351.

200. Sporting Arms and Ammunition Manufacturers' Institute, SAAMI. Lead Mobility at Shooting Ranges. Project No. 13081.01, Flintlock Ridge Office Center, 11 Mile Hill Road, Newtown, CT 06470. 1996. 22–24.

201. Fayiga AO. Remediation of inorganic and organic contaminants in military ranges. *Environ. Chem.* 2019;16:81–91.

202. Johnson CA, Moench H, Wersin P, Kugler P, Wenger C. Solubility of antimony and other elements in samples taken from shooting ranges. *J. Environ. Qual.* 2005;34:248–254.

203. Sneddon J. Clemente R. Riby P. Lepp NW. Source-pathway-receptor investigation of the fate of trace elements derived from shotgun pellets discharged in terrestrial ecosystems managed for game shooting. *Environ. Pollut.* 2009;157:2663–2669.

204. Knigge T, Kohler HR. Lead impact on nutrition, energy reserves, respiration and stress protein (hps 70) level in Porcellio scaber (Isopoda) population differently preconditioned in their habitats. *Environ. Pollut.* 2000;108:209–217.

205. Heier LS, Lien IB, Strømseng AE, Ljønes M, Rosseland BO, Tollefsen KE, Salbu B. Speciation of lead, copper, zinc and antimony in water draining a shooting range—Time dependant metal accumulation and biomarkerresponses in brown trout (Salmo trutta L.). *Sci. Total Environ.* 2009;407:4047–4055.

206. Liu R, Gress J, Gao J, Ma LQ. Impacts of two best management practices on Pb weathering and leachability in shooting range soils. *Environ. Monit. Assess.* 2013;185:6477–6484.

207. Technisches Datenblatt contrAA®700, Analytik Jena AG, Jena, Germany, 2007.

208. US Environmental Protection Agency (USEPA), *Test Methods for Evaluation of Solid Waste*, vol. IA, Laboratory Manual Physical/Chemical Methods,SW846, 40CFRParts 403 and 503. 3rd Ed. US Government Printing Office, Washington, DC, 1995.

209. Gelman F, Binstock R, Haliez L. Application of the Walkely-Black titration for the organic carbon quantification in organic rich sedimentary rocks. *Fuel*. 2012;96:608–610.

210. Matong JM, Nyaba L, Nomngongo PN. Fractionation of trace elements in agricultural soils using ultrasound assisted sequential extraction prior to inductivelycoupled plasma mass spectrometric determination. *Chemosphere* 2016;154:249–257.

211. Cheng S, Liu G, Zhou C, Sun R. Chemical speciation and risk assessment of cadmium in soils around a typical coal mining area of China. *Ecotoxicol. Environ. Saf*. 2018;160:67–74.

212. Dinake P, Kelebemang R. Critical Assessment of Mechanistic Pathways for Chemical Remediation Techniques Applied to Pb Impacted Soils at Shooting Ranges – A review. *Chem. Pollut. Bioavailab.* 2019; 31:282–305.

213. Beiyuan J, Awad YM, Beckers F, Tsang DC, Ok YS, Rinklebe J. Mobility and phytoavailability of As and Pb in a contaminated soil using pine sawdust biochar under systematic change of redox conditions. *Chemosphere* 2017;178:110–118.