



Faculty of Sciences

Department of Chemistry and Forensic Sciences

**ANTIMONY POLLUTION IN THEBEPHATSHWA SHOOTING
RANGE SOILS,**

by

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SUMMARY OF CONTENTS

The aim of the study was to assess pollution of antimony(Sb) in shooting range soils. Antimony in lead bullets is a serious environmental concern in shooting range soils. Thebephatshwa shooting range (TAB) in Botswana, was used for the study. The objectives of the study were to ;

- To investigate antimony concentration in shooting range soil of TAB.
- To make some recommendations on some remediation practices that should be carried out in the shooting ranges for the soil reclamation purpose.

Sb concentrations were determined using ICP-OES and in all the shooting range sampling sites that were first investigated. Soil samples collected at TAB shooting range berm showed variable total concentrations of antimony in the range 38 ± 1 to 283 ± 12 mg/kg. Total antimony concentrations found in the soils were higher than the set regulatory levels by the World Health Organization of 36 mg/kg and the United States Protection Agency of 31 mg/kg. Environmental pollution risk assessment based on geoaccumulation index (I_{geo}), contamination factor (CF) and enrichment factor (EF) indicated all the four sections of the berm posed high risk to the environment. The upper berm exhibited extreme pollution from antimony ($I_{geo} \sim 9$), very high contamination ($CF \sim 744$) and extreme antimony enrichment ($EF \sim 506$) than the other three sections studied. Elevated levels of antimony at TAB shooting range call for best shooting range management practices, soil remediation and reclamation methods to be carried out at this shooting range to minimize the mobility and bioavailability of antimony.

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The undersigned certifies that he has read and hereby recommends for acceptance by the College of Science a dissertation/thesis titled: **‘Pollution Assessment of Antimony in Shooting Range Soils’** in fulfilment of the requirements for the degree of Master of Science in Analytical Chemistry of the BIUST.



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DEDICATION

This work is dedicated to my good friends, and fellow chemists **Balimi Kgosi and Ouma Mosehla**. You will forever be missed!!

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ACRONYMS

BOBS: Botswana Bureau of Standards

BMP: Best Management Practices

CEC: Cation Exchange Capacity

CRM: Certified Reference Material

ICP-OES: Inductively Coupled Plasma- Optical Emission Spectrometer

TAB: Thebephatshwa Air Base

USEPA: United States Environmental Protection Agency

WHO: World Health Organisation

XRD: X-Ray Diffraction

Abstract

Shooting ranges are commonly contaminated with Antimony (Sb), which is released during weathering of bullets. Antimony in lead bullets is a serious environmental concern in shooting range soils and consequently its concentration must be measured in shooting ranges for this study. Thebephatshwa shooting range (TAB) in Botswana was used to determine Sb concentrations. The Sb concentrations were determined using ICP-OES and in all the sampling sites of the shooting range being investigated. Soil samples recorded at TAB shooting range berm showed variable total concentrations of antimony in the range 38 ± 1 to 283 ± 12 mg/kg. Total antimony concentrations found in the soils were higher than the set regulatory levels of 36mg/kg by the World Health Organization and the United States Protection Agency 31 mg/kg. The upper berm recorded elevated levels of antimony 283 ± 12 mg/kg due in part to the highest density of spent projectiles found in this part of the berm. Sequential extraction studies established that antimony was partitioned mostly in the organic and residual fractions of the soil. Environmental pollution risk assessment based on geoaccumulation index (I_{geo}), contamination factor (CF) and enrichment factor (EF) of Sb indicated that all the four sections of the berm posed high risk to the environment. The upper berm exhibited extreme pollution from antimony of $I_{geo} \sim 9$, very high contamination of $CF \sim 744$ and extreme antimony enrichment $EF \sim 506$ than the other three sections studied when compared to the set I_{geo} . Elevated levels of antimony at TAB shooting range call for best shooting range management practices, soil remediation and reclamation methods to be carried out at this shooting range to minimize the mobility and bioavailability of antimony.

CHAPTER 1

INTRODUCTION

Antimony (Sb) occurs naturally as the sulphide ore stibnite (Sb_2S_3) and valentinite (atomic number 51; atomic mass 121.75g/mol; density 6.64g/cm³; melting point 631°C) (Sb_2O_3) (Cooper & Harrison, 2009). It is a metalloid belonging to group 15 of the periodic table (He et al., 2011). Its symbol, Sb, is derived from the Latin word stibium. It also lends its name to stibnite the mineral containing antimony (Cooper & Harrison, 2009). Antimony, a metalloid rather than a genuine metal, exists as four allotropes, the most stable of which is the metallic and grey. The non-metallic yellow, the black, and the explosive white forms are also known. Metallic antimony often expands slightly when frozen, making it one of the just four elements known to do so (Cooper & Harrison, 2009). Antimony exists in four valence states 0, -3, +3, and +5 (Tylenda, et al., 2015). In its trivalent and Penta states, it usually forms compounds (Hansell, 2015) .

BACKGROUND STUDY OF ANTIMONY

1.1 Accumulation cause on environmental effects (Effects of Accumulation of Antimony into the Environment)

In the environment where antimony is found not only animals are affected by its contamination. People get exposed to Sb through the air and air dust, drinking water from tap or bottled water, food, and food containers (Belzile, et al., 2011). Abrasion of tires, brake linings, and motor bearings, wear of rails, wheels, as well as cables of operational trains, are main sources of Sb in high-traffic areas (Belzile, et al., 2011). Workers who are exposed to airborne dust containing Sb may develop respiratory issues. Antimony exposure was linked to lead intoxication in 1916 after workers who were exposed to antimony started having symptoms including headache, stomach discomfort, constipation, colic, disliking for food, lack of appetite, tiny mouth ulcers with salivation, dizziness, weight loss, albuminuria, and glycosuria (Cooper & Harrison, 2009). Although experimental and epidemiologic evidence are lacking, antimony is suspected to be carcinogenic (Hayes, 1997). A little quantity of Sb in the human body can induce disorders of the liver, skin, respiratory, and cardiovascular systems, as well as cancer (Zeng, et al., 2015). Chronic airborne antimony exposure at 9 mg/m³ levels may worsen eye, skin, and lung irritation (Hayes, 1997). Long-term antimony inhalation can exacerbate pneumoconiosis, abnormal electrocardiograms, stomach discomfort, diarrhea, vomiting, and stomach ulcers, according to laboratory animal studies (Hayes, 1997).

All mineral elements, whether essential or non-essential adversely affect an animal life if included in the diet at excessive levels (council, 1980). Plants are also affected by the contamination (Tylenda, et al., 2015). The concentration of Sb in the environment has been reported to have grown in recent decades as a result of industrial and other anthropogenic activities resulting in soil and vegetation pollution in both industrialized and non-industrialized regions (Roselli, et al., 2016). A lifetime studies with mice showed that 5ppm antimony as potassium antimonyl tartrate in drinking water reduced the mean life span of female slightly (council, n.d.). Birds are particularly significant bio-indicator creatures since they are constantly exposed to harmful substances and may bio accumulate them (Grove et al., 2009). Local pollution is reflected in resident birds, whereas migratory species transfer toxicants across great distances (Roselli, et al., 2016).

Antimony and its compound are considered priority environmental pollutants by the USEPA and European Union (Tylenda, et al., 2015). The uptake of antimony by plants has been found to be proportional to the soluble concentration in soil (Tylenda, et al., 2015). Antimony occurs in two oxidation states in the environment: antimonite Sb (III) and antimonate Sb (V). Antimonate is the predominate form under aerobic settings, whereas antimonite exists in reducing conditions, which occur when soils get waterlogged (Tylenda, et al., 2015). Understanding antimony speciation in plant tissue is critical for understanding antimony transport and transformation following absorption by plants (Wei, et al., 2016) . As antimony is absorbed by plant roots from soil, a potential human and animal Sb exposure pathway is through food and feed, respectively (Wei, et al., 2016). Despite the fact that Sb (III) and Sb (V) are not necessary plant elements, studies have shown that plants rapidly absorb and translocate these two Sb species from soil via roots to shoots (Wei, et al., 2016).

1.2 Shooting ranges

Ecosystem pollution caused by numerous anthropogenic activities, such as shooting practice, has become a worldwide challenge owing to the negative impacts on human health as well as flora and fauna (Anon., n.d.). Although many studies have been conducted to assess the environmental risks posed by other anthropogenic activities, the risks posed by shooting ranges have received little

attention, owing in part to the confidentiality of activities conducted at shooting ranges and the restricted access to such locations (Anon., n.d.). Any country's defense requires shooting ranges to train and maintain soldiers' marksmanship talents (Bandara & Vithanage, 2016). According to a recent inventory, Finland has a total of 2,000-2,500 outdoor shooting ranges (Sorvari, 2007). These shooting ranges are particularly constructed for weapon usage qualifications, training, practice, or competitions, such as the Olympics. Military or law enforcement agencies run shooting ranges; however, the vast majority of ranges are privately owned by civilians and athletic groups and cater mostly for recreational shooters (Anon., 2017). The quantity and extent of environmental pollution at these locations are determined by the type of shooting activity (Sorvari, 2007). Shooting ranges are designed such that shooters stand on one side of the range and shoot at targets on the other. As depicted in Figure 1, a typical shooting range comprises of a firing line, range floor, target, and impact berm.

- **Firing line**

The firing line is where the trainers/shooters are stationed. It is usually an open or built dwelling

- **Range floor**

The distance between the target and the shooting line is referred to as the range floor. The distance between the range floor and the ground is determined by the type of weapon practiced on the range.

- **Target**

Paper, plastic, or metals are commonly used to create moveable or stationary targets.

- **Impact berm**

The impact berm is behind the target. Traditionally, earthen berms of sand between 4.5 and 8 m high have been used. To reduce environmental pollution from Sb, earthen berms have lately been replaced by sand traps, steel traps, and rubber traps. Impact berms contain used bullets and their pieces (Bandara & Vithanage, 2016).

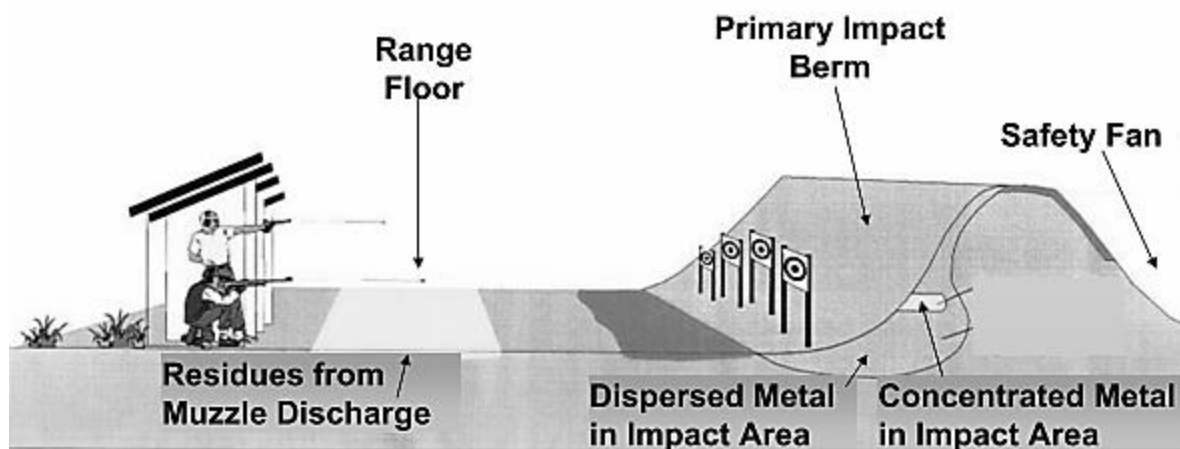


Figure 1. Shooting range layout (*council, n.d.*)

The berm, as seen in Figure 1, acts as a wall, trapping the fired bullets and preventing them from traveling any farther. As it is close behind the target line, the berm accumulates a significant concentration of antimony over time. Antimony is present in the soil as spent bullets, broken shards, microscopic particles, and lead stains on larger sand grains (Kelebemang, 2017).

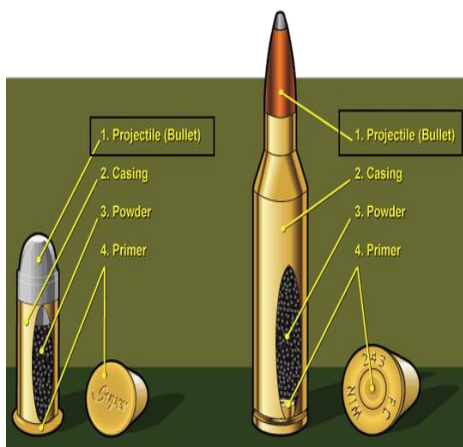


Figure 2: Structure of a bullet (*Firearms, 2015*)

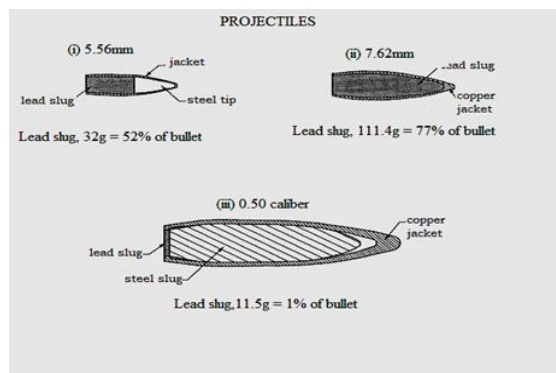


Figure 3. Lead Bullets Projectile Composition (*Bricka, 2000*)

The pristine bullets are composed of a Pb–Sb core (powder) Figure 2, a Fe mantle, and trace quantities of Cu, Ni, and Zn in an interlayer between the core and mantle (Anon., n.d.). The lead projectile Figure 3 is frequently wrapped in either a whole metal jacket encompassing the entire lead core or a full metal jacket containing the core but leaving the base unprotected; copper is a typical material utilized (Scott, et al., 2012). Bullets and shots are typically made of lead or lead–antimony alloys containing between 0.5 and 3 percent antimony to strengthen the lead (Lewis, et al., n.d.). Lead is the primary component, accounting for around 97 percent of the shot and approximately 90 percent of the rifle bullets, depending on the type (Sorvari, 2007). Since antimony may account for as much as 2–5% of a projectile's total mass (e.g., Swiss bullets comprise 95% Pb, 2% Sb, 3% Cu, and 0.5 percent Ni by weight), it must be considered as a potential pollutant of concern when considering the impact of shooting ranges on soil and soil water systems (Vleek, et al., 2011). New and emerging munitions are designed and tested, taking into consideration the ecological compatibility and range sustainability approach while using them due to the potential environmental impacts and human health risks associated with the use of lead–antimony alloys in small-arms ammunition. Consequent to this there has been an initiative to develop lead-free bullets (O'Connor, et al., 2009). Using non-lead-antimony ammunition is recommended and in California from 1 July 2019, non-lead-antimony ammunition started to be used when shooting wildlife (Marie Russell, et al., 2019).

1.5 Problem statement

No effort has ever been made in Botswana, to quantify the extent of pollution from antimony found in ammunition as well as the mobility, transformation, and bioavailability of antimony after deposition into the environment since the inception of the Botswana Defence Force (BDF) in

1977. The existence of elevated antimony in soils, sediments, surface/ground water and biological system have received considerable attention worldwide due to its adverse consequences in , drinking and irrigation water sources as well as agricultural crop production and its migration through the food chain (Herath, et al., 2017). Antimony has been recognised as one of the genotoxic elements, thus it is not considered as an essential element either in plants or animals (Boeck, et al., 2003). Exposure to Sb can induce irritation of the digestive system, slow growth of mammals and cause fertility problems in women (Govind & Madhuri, 2014). Long-term exposure to Sb can result in high concentrations of Sb in the kidneys, adrenals, thyroid and liver and rise to pneumoconiosis and fatal effects on the heart (Tylenda, et al., 2022). The presence of Sb in shooting range soils poses risk of Sb being transferred into the food chain as they can be absorbed by plants and many of the areas studied also served as grazing fields for domestic animals (Gall, et al., 2015). Thus, Botswana provides an unparalleled setting for this specific research . A preliminary study was carried out recently with lead and established that there are large concentrations of lead in shooting range soils, reaching concentrations of 38000mg/kg. This study is thus a vital step forward to help in policy formulation and implementation of optimal management practices for the impacted regions in the future (Kelebemang, 2017). To the best of my knowledge, no research study has been conducted in the past to establish and assess the extent of Sb pollution at military shooting ranges found in Botswana

There might be some traces of heavy metals including antimony in soils around the military shooting ranges. The aim of the project is to evaluate and ascertain the extent of antimony concentrations from ammunitions in soils near military shooting ranges found in Botswana

1.6 Objectives of this study include

- To investigate antimony concentration in shooting range soil of TAB in Botswana.
- Assessment of the mobility and leaching of Sb in the soil
- Establishment of the environmental pollution risk posed by deposition of Sb into shooting range soils by applying pollution risk indices

CHAPTER 2

2.1 Historical background and uses of Antimony

Antimony was first identified in different compounds as early as 4000BC, when the Chaldeans employed it for its exquisite casting characteristics (Cooper & Harrison, 2009). It was also employed in the colouring of glass (Tylenda, et al., 2015). Antimony sulphide was discovered in a 2500BC Egyptian cosmetic box intended for use as a lip rouge. (Cooper & Harrison, 2009). A black mineral containing antimony (III) sulphide was used as make-up to the eyelashes and around women's eyes during the Roman era to accentuate them (Cooper & Harrison, 2009). Antimony has been used medicinally from ancient times for its emetic and diaphoretic properties, and it was a popular therapy in the middle ages for a variety of diseases. In the 17th and 18th centuries, antimony cups were popular as a technique to include therapeutic sweating, vomiting, and purging (Tylenda, et al., 2015). Although antimony was recognized as a cosmetic and medicine, it was responsible for numerous deaths among patients who were given antimony-containing medications (Tylenda, et al., 2015).

2.2 Problem to the world

The lithosphere is rich in antimony (Sb), a non-essential harmful element for life (Zeng, et al., 2015). Antimony is frequently thought to act similarly to arsenic, which is not always justified (add reference). Antimony and its compounds are toxic to humans and may potentially be carcinogenic (Fei, et al., 2017). Despite not being a required element, this metalloid is easily absorbed by plant roots from soil. Many countries are concerned about antimony contamination (He, et al., 2011). Antimony enters the environment through both natural and anthropogenic methods. Mining and industry emissions appear to be the primary sources of antimony contamination (He, et al., 2011). However, due to its mobilization from minerals and related rocks, as well as human-induced activities such as mining, military training, smelting, and the use of pharmaceuticals and pesticides, Sb is present at elevated concentrations in various environmental, biological, and geological compartments (Anon., n.d.). Over the last few decades, there has been a surge in awareness about the presence and analysis of antimony in various geological, environmental, and biological systems (Anon., n.d.). A series of critical reviews on the occurrence of antimony, as well as its typical characteristics of solution chemistry, has been published. Furthermore, there has been increasing worldwide scientific interest in Sb contamination across many environmental, biological, and geological compartments (Anon., n.d.). Currently, antimony is used widely in a

number of industrial activities such as the creation of paint pigments, flame retardants, plastic, glassware, and ceramics, as well as alloys in ammunitions and battery manufacturing facilities (Anon., n.d.).

2.1 Antimony reservoirs, minning and production

Antimony is a metalloid that naturally exists in soils (Steely, et al., 2007). It is the ninth most exploited metal in the world, with more than 2 million mined per year (Scheinost, et al., 2006). Due to its favourable qualities, it is employed in non-metal goods as antimony trioxide (Sb_2O_3), particularly in flame retardants, alloys, and semiconductors, as well as a catalyst in plastics, for glassware fining, and as a pigment in paints and lacquers (Scheinost, et al., 2006). The background concentration of Sb in soils ranges from 0.2 to 0.5 mgkg^{-1} , with the notable exception of the Xikuangshan mining zone, where Sb concentrations of up to 35 mgkg^{-1} were recorded (Martin, et al., 2013). Global antimony output has increased dramatically, for example, from 55 kt in 1990 to 180 kt in 2012 (Kenneth, et al., 2015). Currently, China accounts for 84% worldwide Sb production, notwithstanding the closure of certain large-scale mines (Kenneth, et al., 2015). Sb production has expanded at least tenfold, and it has become a trace element metalloid of importance in the global economy, with an annual output of 150 000 t (Shtangeeva, et al., 2011). Only 165 000 t of the metalloid were produced worldwide in 2008 (Belzile, et al., 2011).

Table 1: Major Sb production by mines in the world from 2010-2015 (Anon., n.d.)

Country	Antimony mine production/metric tons					
	Year					
	2010	2011	2012	2013	2014	2015
China	120 000	150 000	145 000	120 000	120 000	115 000
Russia	3000	3300	3500	7000	9000	9000
Australia	-	-	-	-	5800	5500
Bolivia	3000	3900	4000	5000	5500	5000
Tajikistan	2000	2000	2000	4700	4700	4700
Turkey	-	-	-	-	4500	4500
Burma	-	-	-	9000	3300	3500
South Africa	3000	4700	3800	3100	1600	-

Natural sources account for 41 percent of antimony in the atmosphere, including wind-borne soil particles (32.5%), volcanoes (29.6%), sea salt spray (23.3%), forest fires (9 %), and biogenic sources (12.1%) (Tylenda, et al., 2015). Antimony exists in the earth's crust and is naturally discharged into the atmosphere as particulate matter or adsorbed to particulate matter (Tylenda, et al., 2015). The amounts of dissolved Sb in unpolluted surface water are far below $1\mu\text{g. L}^{-1}$, often in the tens to hundreds of ng range L^{-1} . Sb emissions into the atmosphere from various activities across the globe (e.g., smelting, combustion of fossils) and natural sources were estimated to 6.1 kty^{-1} in the 80's (Belzile, et al., 2011). Sb enrichments in air aerosols, plants, soils, sediments, water, and alpine areas also indicate widespread Sb pollution (Shtangeeva, et al., 2011). Acid mine drainage is a significant contributor, as Sb is found at places affected by mining activity with other pollutants (Anon., n.d.), Sb may also be discharged into the environment by copper smelters or copper conventional power stations that use coal or tire-derived fuels (Anon., n.d.). Antimony has also been also discovered in drinking water held in polyethylene bottles, when Sb_2O_3 was utilized as a catalyst in the bottle's manufacture (Anon., n.d.). The element is also present in brake dust and functions as a lubricant in friction material of brakes (Ackermann, et al., 2009).

2.2 Antimony in Shooting Range Soils

Antimony enters the environment either naturally or through anthropogenic ways (He, et al., 2011). The substantial input of Sb into the environment also occurs at shooting ranges since the majority of bullets fired contain significant concentrations of Sb (Ackermann, et al., 2009). Ammunition projectiles includes 2-5 percent metallic Sb employed as a hardener, and as such shooting practice is a significant source of Sb pollution in the soil (Kerstin, et al., 2014). The act of firing bullets into the berm soil also results in the anthropogenic introduction of Sb at a shooting range (Martin, et al., 2013). Sb migration in shooting ranges has been a great concern in several countries where studies have been conducted, including the United States, Canada, Norway, Sweden, Finland, China, and Switzerland (Martin, et al., 2013). It is estimated that 1900t of Sb is deposited in soils in the United States alone, whereas Swiss shooting ranges measure up to 13800 mgkg^{-1} , with typical background amounts of 8.6 mgkg^{-1} (Martin, et al., 2013) and the country currently has roughly 2170 shooting ranges (Ackermann, et al., 2009). Norway, small arms shooting ranges

alone deposit roughly 12 tons of Sb, whereas in the United Kingdom, clay pigeon shooting, and game contribute an estimated 100 tons of Sb in soils alone (Wan, et al., 2013).

Table 2: Some of the studies that have been carried out on antimony in shooting range soil across the world

No	Studies done	Year	Country	Reference
1	Quantitative antimony speciation in shooting range soils by EXAFS spectroscopy	2006	Switzerland	(Scheinost et al., 2006)
2	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	2011	USA	(Vleek et al., 2011)
3	Accumulation of Sb, Pb, Cu, Zn and Cd by various plants species on two different relocated military shooting range soils	2012	Switzerland	(Evangelou et al., 2012)
4	Antimony (Sb) contaminated shooting range soil: Sb Mobility and immobilization by soil amendments	2013	Norway	(Okkenhaug et al., 2013)
5	Antimony migration trends from a small arms range firing range compared to lead, copper, and zinc	2013	USA	(Martin et al., 2013)
6	Chemical leaching of antimony and other metals from small arms shooting range soil	2013	Canada	(Lafond et al., 2013)
7	Changes in Sb speciation with waterlogging of shooting range soils and impacts on plant uptake	2013	Switzerland	(Wan et al., 2013)

8	Release of antimony from contaminated soil induced by redox changes	2014	Switzerland	(Hockmann et al., 2014)
9	Antimony Retention and release from drained and waterlogged shooting range soil under field conditions	2015	Switzerland	(Hockmann et al., 2015)
11	Antimony (Sb) and lead (Pb) in contaminated shooting range soils: Sb and Pb mobility and immobilization by iron-based sorbents, a field study	2016	Norway	(Gudny Okkenhaug15 April 2016)
12	Use of soil amendments to immobilise antimony and lead in moderately contaminated shooting range soils	2017	Switzerland	(Tandy et al., 2017)
13	Recovery and leachability of antimony from mine and shooting range soils	2017	Poland	(Lewinska et al., 2017)
14	Antimony mobility during prolonged waterlogging and reoxidation of shooting range soil: A field experiment	2018	Switzerland	(Tandy et al., 2018)
15	Release and Biomethylation of Antimony in Shooting Range Soils upon Flooding	2018	Switzerland	(Grob et al., 2018)

Significant volumes of Pb- Sb based bullets are deposited into shooting range soils as a result of shooting range activity, with the deposited bullet prone to weathering over time (Sanderson, et al., 2012). Lead-antimony bullets deposition is generally more restricted to small regions on shooting ranges, yet metal loading can be exceedingly high (Olive, 2006). The deposition of metallic Sb in the form of shotgun ammunition has been reported in the Netherlands, Denmark, Finland, Sweden, Canada, and England (Cao, et al., 2003). At rifle and gun ranges, fixed targets are frequently placed right in front of a berm, which serves to limit projectiles from traveling further. Due to the fact that bullets can penetrate several decimetres into the soil and get shattered and deformed, facilitating bullet weathering, very high Sb concentrations have been documented in the soil of these berms (Olive, 2006). Table 3 shows soil Sb concentration of over 5.0mg/kg were measured at the upper 30cm depth of soil in Chesterfield, Massachusetts (Vleek, et al., 2011). Concentrations within 0-20 cm soil depth were 2.3 mg/kg Sb at 2cm from the shooting stand at Gossau (Switzerland), while topsoil (0-20 cm depth) 20 m behind the stop butt at the same shooting range had 402 mg/kg Sb (Olive, 2006).

Table 3: Depth of soil sampling of soil derived from humic acid (HA) mass fraction in Chesterfield, Massachusetts (*Vleek, et al., 2011*)

Soil core depth (cm)	Sb(mg/kg)
0-5	5.0
5-10	4.0
10-15	1.3
15-20	1.0
20-25	1.0

2.3 Chemical transformation and mobility of antimony in shooting range soils

Anthropogenic Sb in the shooting range occurs as a result of spent bullet weathering and corrosion, followed by being broken down by soil water, resulting in Sb mobilization (Okkenhaug, et al., 2016). Antimony (Sb) occurs in a variety of oxidation states (-III, 0, III, V), with oxidation states III and V being the most common inorganic species in nature, with antimonite ($\text{Sb}(\text{OH})_3$) and antimonate ($\text{Sb}(\text{OH})_6^-$) being the most common chemical species in aquatic settings (Okkenhaug, et al., 2016). Sb species undergo redox changes via oxidation and reduction processes in aerobic (oxic) and anaerobic (anoxic) conditions (Indika, et al., 2017). Sb may be found in sulphides and oxides minerals such as, Valentinite (Sb_2S_3), and Senarmontite (Sb_2O_3) as seen in Figure 4 below in a natural setting (Indika, et al., 2017). Naturally occurring minerals, iron, manganese, and aluminium oxyhydroxides have been found to have Sb affinity but having a stronger affinity for Fe and Mn (hydr) oxides (Indika, et al., 2017). The most stable species of antimony is the oxidized species Sb (V), which is sorbed by iron (hydr) oxide and calcium antimonate ($\text{Ca}(\text{Sb}(\text{OH})_6)_2$) (Ahmad, et al., 2014). The interaction of Sb (V) with surface (terminal) hydroxyl groups ($\equiv\text{FeO}^-$, $\equiv\text{FeOH}^\circ$, $\equiv\text{FeOH}^{2+}$) is responsible for the sorption effect (Okkenhaug, et al., 2016). Lin (1996) calculated that it takes roughly 200 years for pellets to completely dissolve and convert in shooting range soil, and established that the release of Sb by bullet weathering is equivalent to the release of Pb, provided such bullets contain between 2 and 5% Sb. The pH of the soil, the redox potential of the soil, the ionic composition of the soil solution and the nature of the soil's solid phase all influence Sb solubility (Olive, 2006). Sb (III) is more intensively sorbed in neutral and alkaline soils than anionic Sb (V) (Okkenhaug, et al., 2016). Concentrations much above background values have been discovered in shooting ranges, both in groundwater concentrations of up to 50 g Sb L^{-1} and 100 g Pb L^{-1} and in runoff water concentrations of 5–20 g Sb L^{-1} and 4–840 g Pb L^{-1} .

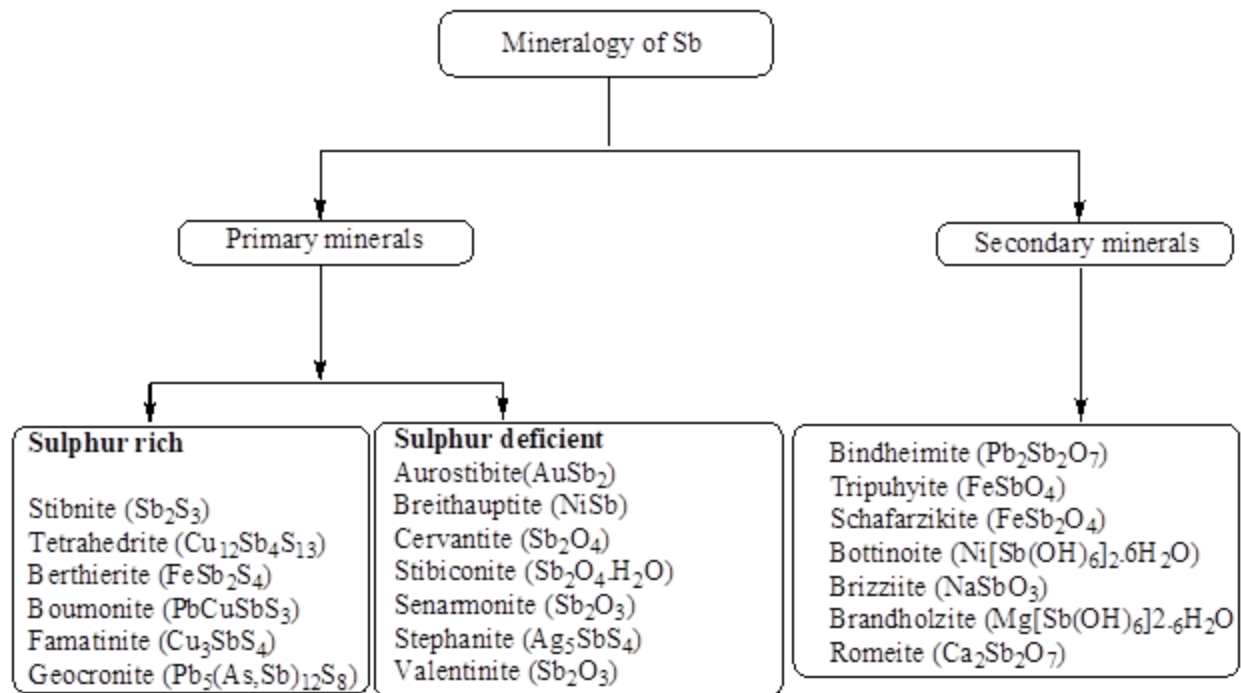
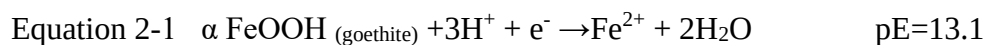
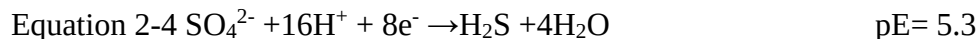
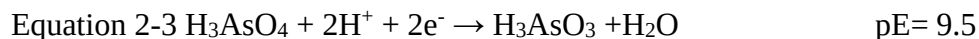


Figure 4. Showing primary and secondary Sb minerals (Indika, et al., 2017)

According to research, even though the concentration of Sb in bullets is lower than that of Pb, the concentration of Sb in the effluent from a Lysimeter filled with bullet-impacted sand was up to 125 g L⁻¹, whereas the concentration of Pb was less than 2 g L⁻¹ (Okkenhaug, et al., 2016). It was also discovered in shooting range soil that nearly half of the Sb in the 0.5mm fraction was adsorbed to minerals that are soluble at pH 2 (Wan, et al., 2013). (Kerstin, et al., 2014) discovered that there is increased Sb mobilization in competition for binding sites on ironhydroxides. Because of its positive charge below pH 7.8-8.1 and high specific surface area, ferrihydrite, a short-ordered Fe (III) oxyhydroxide and a widespread mineral found in terrestrial systems such as soil and sediment, operates as a particularly efficient sink for antimony (Mitsunobu, et al., 2006).

After Fe (III) is reduced to Fe(II) at a pE of 13.1, Sb (V) is reduced to Sb (III) at a pE of 12.9, followed by As (V) to As (III) at a pE of 9.5, but before sulphate is reduced to sulfide at a pE of 5.3; see Equations 2-1–2-4 (Martin, 2014).





In the environment, Sb (III) and Sb (V) form oxyanions due to their strong interaction with hydroxides [e.g., Sb (OH)₃ and Sb (OH)₆, respectively] that are predominantly observed in environmental reactions (Martin, 2014).

2.4. Bioavailability and Phytoavailability of Sb in Shooting range soils

Although research on environmental behaviour and bioavailability is limited, Sb metalloid often exist as oxyanions in environmental systems, with the +5 and +3 oxidations having biological and environmental significance (Wilson, et al., 2013). Through root and foliar absorption, the metalloid may pollute soils and accumulate in plants (Pierart, et al., 2015). The fate and transport of Sb in firing range soils have been widely reported to be related to the metal bioavailability according to the Korean Ministry of National Defense (Ahmad, et al., 2014). Although antimony is not a necessary element, it is easily taken up by plant roots from soils, and tests conducted in the Xikuangshan mine region in China revealed average Sb concentrations of up to 54.0 mg kg⁻¹ in radish leaves and 143.7 mg kg⁻¹ in 34 and 21 families of ferns, beyond the acceptable limit of 5mgkg⁻¹ (He, et al., 2011). Increased Sb concentrations in plant tissues may result in phytotoxicity consequences such as growth retardation, photosynthesis inhibition, and a reduction in the absorption of certain metabolites (Indika, et al., 2017). After 31 weeks of metal treatment, lettuce plants cultivated in soil spiked with Sb in the form of Sb₂O₃ revealed a 10% suppression of shoot biomass, according to one study (Indika, et al., 2017). Figure 5 shows Schematic diagram of suggested Sb uptake and transfer routes in the roots and shoots.

In Switzerland, it is normal practice to graze on military shooting ranges and herbivore Sb intake is determined by their food choices (Evangelou, et al., 2012). The study done on two different relocated military shooting ranges by Evangelou and team showed that the level of intake of Sb by grazing deer and other animals was very low as the planted *P. aviculare* and *R. acetosa* which had the highest concentration of Sb (310 µgkg⁻¹) are either consumed in small quantities or not consumed at all (Evangelou, et al., 2012). On shooting ranges in Grafenwohr, Germany, analysed metal concentrations in leaves from several species and they discovered that the concentrations of most metals were within the typical range for plants (Zellmer & Schneider, 1993). A shooting

range in Switzerland of all plants on calcareous soil collected 1.5-2.6-fold greater mean Sb concentrations ($195\text{--}275\text{ mg kg}^{-1}$ dry weight) than plants on acidic soils ($71\text{--}128\text{ mg kg}^{-1}$) (Evangelou, et al., 2012). Another study performed in Switzerland on four different plants namely *T. repens*, *L. perenne*, *P. lanceolata* and *R. obtusifolius*, Sb absorption varied greatly among the plant species studied, *L. perenne* had the lowest Sb concentration of 0.005 g g^{-1} , whereas *R. obtusifolius* had the highest quantities of 0.3 g g^{-1} (Hockmann, et al., 2018). Research performed in China by Cui indicated that when the concentration of Sb (III) or Sb (V) surpassed 20 mM , rice root elongation was decreased (Cui, et al., 2015).

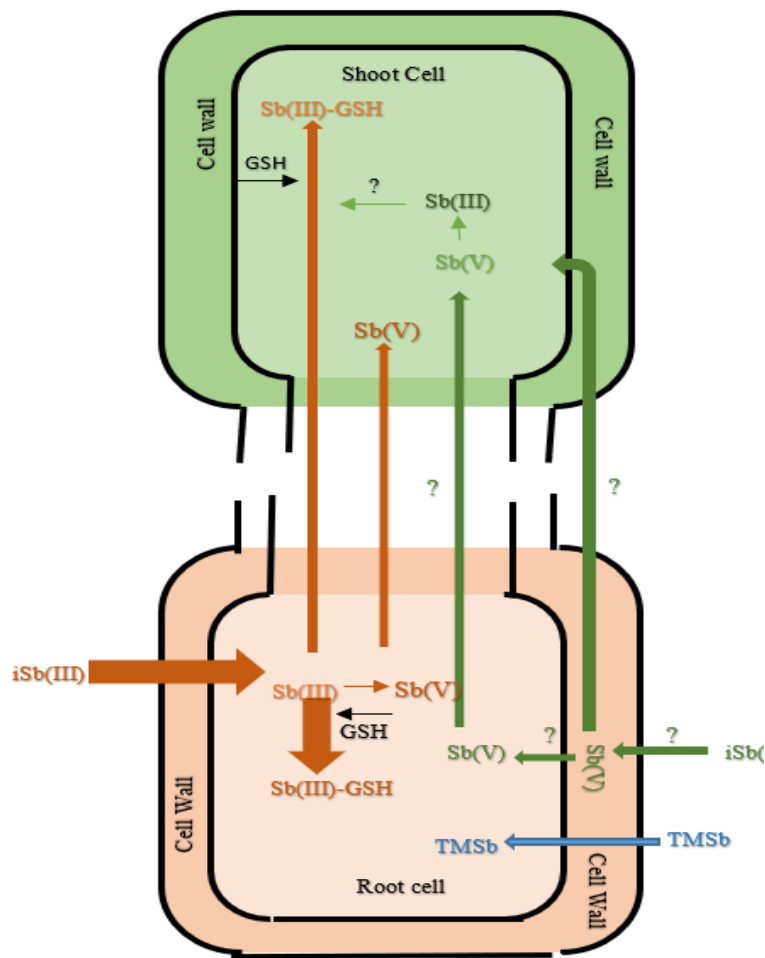


Figure 5. Schematic diagram showing Bs uptake and transfer routes in the roots and plants, Adapted from (Ji, et al., 2017)

2.5. Effect of soil chemical and physical properties on the transformation and fate of Sb in Shooting range soils

2.5.1. Effect of soil type

The effect of soil chemical and physical properties on the transformation and fate of Sb in shooting range soils has been proven to be influenced by soil structure, texture, depth and type. The shooting ranges are mostly made up of sandy dirt. The stop butts that capture bullets are mostly made of sand, with a little silt and clay (Sanderson, et al., 2012). To reduce weathering, sand is a preferred material for stop butt construction (Sanderson, et al., 2012). Soil texture is determined by the relative quantities of particles of various sizes, such as clay, silt, and sand, which comprise the mineral component of the soil (Dinake, et al., 2019). Antimony concentration decreases with increased soil depth and soils at shooting range pose a major hazard due to migration of antimony into ground water or as runoff (Tylenda, et al., 2015). Literature shows that naturally Sb is found in soil, and it's expected to be found in runoff, and studies performed in United States from 19 cities found 14% of runoff contaminated with antimony ranging from 2.6 to 23 $\mu\text{g/Kg}$, and in Switzerland 0.3-1.0 $\mu\text{g/Kg}$ (Tylenda, et al., 2015). Manganese (Mn) and Iron hydroxides are key constituents in most soils, and they are controlling the movement of Sb (Hockmann, et al., 2018). The phrase "iron oxides" refers to a combination of iron oxides, hydroxides, and oxyhydroxides, all of which are highly reactive mineral phases in nature (Indika, et al., 2017). Studies shows that Calcareous shooting range soil after being waterlogged attributed to reduction of Sb(V) to Sb (III) by being more sorption to the metal (hydr)oxide (Tandy, et al., 2018).

Studies performed on a clay pigeon shooting range located near Siena Tuscany Italy demonstrated high concentrations of Sb, which were detected throughout the shooting area and exceeded the natural soil value of 1 $\mu\text{g/g}$ (Migliorini, et al., 2004). The soil at the clay pigeon shooting range under investigation was significantly polluted by antimony and lead, the major components of spent ammunition (Migliorini, et al., 2004). The concentrations of the other two sites in study E and F exceeded the threshold values defined by Italian law of (10 $\mu\text{g/g}$ for private or public land) 16.3 $\mu\text{g/g}$ and 13.9 $\mu\text{g/g}$ respectively (Migliorini, et al., 2004). Another study conducted in Losone, Switzerland, revealed that bullet cores are composed of a few metallic Sb grains contained in a metallic Pb matrix rather than a Pb-Sb alloy (Olive, 2006). The study detected a homogeneous mix of Pb and Sb in Pb-rich grains in weathered portions of a bullet discovered in front of the stop butt, implying that Sb dissolution and re-precipitation occurred, and Sb was largely present as

anoxidized bullet core grains (Olive, 2006). Another shooting range in Switzerland, Sb was discovered mostly as elemental Sb grains in the Eischenbach shooting range's stop butt, but it was also identified in Fe- and Pb-rich crusts encircling soil particles and in Fe- and Pb-rich individual conglomeratic grains (Olive, 2006). According to Ackermann (2008), the results indicated that Sb accumulated in sections of the weathering crust where there was also a large concentration of Fe (Anon., n.d.).

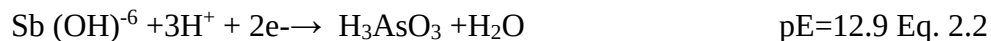
In Norway to avoid fires when using ammunition, the shooting ranges are located in peatlands (Okkenhaug, et al., 2018). The topsoil closest to the backstop berm has been found to contain the greatest Sb concentrations of $110 \pm 0 \text{ mg kg}^{-1}$ (Okkenhaug, et al., 2018). Antimony showed high mobility in all samples with leaching values exceeding the EU and Norwegian leaching limit for ordinary waste landfills (0.07 mg L^{-1}) (Okkenhaug, et al., 2018). These high concentrations could be attributed to bullet fragments or components adsorbing to the soil matrix (Okkenhaug, et al., 2018). The presence of coarse material in the backstop berm (large stones, gravel) increased the risk of ricochets and the dispersal of bullet fragments outside the backstop berm region (Okkenhaug, et al., 2018). In a Trainor's project that they undertook they built four separate, well-characterized shooting range test berms (Sand, Loamy sand, Silt loam and Sandy loam) and fired about 2,000 - 5.56 mm rounds into each berm (Trainor, 2017). Table 5 shows values of Sb metalloid in each soil type.

Table 4: Total metal concentrations of Trainor project at Greely Donnelly training Area in Alaska where in the 1 test berms analyzed by x-ray fluorescence (XRF). Pristine soil concentrations shown for comparison. LLD = lower limit of detection (Trainor, 2017).

Soil type	Status	Sb mg/kg	±
Sand (a)	fired	281	2.21
Sand (b)		275	2.21
Sandy loam (a)	fired	42.5	1.61
Sandy loam (b)		61.8	1.66
Loamy sand (a)	fired	25.7	1.57
Loamy sand (b)		32.5	1.60
Silt Loam (a)	fired	9.56	1.53
Silt Loam (b)		12.0	1.53
Silt loam	pristine	bld	/
Sand	pristine	6.37	1.57
Loamy sand	pristine	6.29	1.52
Sandy loam	pristine	6.56	1.52

2.5.2. Effect of Soil pH

Soil pH is one of the most important factors affecting the mobility and bioavailability of antimony(Sb). Despite the fact that metallic Sb is insoluble in water and rather inert when exposed to air, the soil system it is a significantly reactive (Olive, 2006). Sb's oxidation state has a substantial influence on its mobility in soils. Both Sb (III) and Sb (V) hydrolyze rapidly in aqueous solution (Olive, 2006). The most prevalent Sb (III) species in water, is Sb (OH)₃ or (HSbO₂) (Olive, 2006). Antimony pentoxide (Sb₂O₅) dissolves easily in aqueous solutions, forming [Sb (OH)₆], which may exist throughout a large pH range (2.7–10.4), whereas antimony trioxide (Sb₂O₃) is less soluble in aqueous solutions regardless of pH, forming insoluble antimony hydroxide [Sb (OH)₃] (Anon., n.d.). The Sb equilibrium is controlled by the following equation:



At pH 7 and pE 13.6, this equation yields a concentration ratio of 1018.4 of $\text{Sb}(\text{OH})_6$ to $\text{Sb}(\text{OH})_3$ in well-aerated oxic water (Eh 0.8V). According to Willems and Jorgensens (1987), Sb in crust material occurs as amphoteric hydrated antimony trioxide (Sb_2O_3 , aq.), which has weak solubility and is more soluble in bases than acids (Olive, 2006). Sb was reduced in soils with a pH of 7.4, but not in soils with a pH of 3.5 (Olive, 2006). These findings were reinforced by the solubility minimum of the presumably present Sb compound in the bullet crust at pH 4-5 (Olive, 2006). Willems and Jorgensens (1987) were unable to detect Sb compounds by XRD in the same study because Sb was present in an amorphous condition or in too small quantities to be recognized by XRD, they said (Olive, 2006).

The weathering and change of metallic Pb-Sb bullets to secondary minerals has been found to increase soil pH in shooting ranges (Hardison JR, 2003). Several investigations have confirmed Sb's affinity for Fe oxides. At low pH, Fe oxides adsorb this anionic hydrolysis species, but it becomes mobile beyond their point of zero charge, i.e., at neutral and basic pH values (Scheinost, et al., 2006). Under reducing circumstances, the trivalent neutral complex, $\text{Sb}(\text{OH})_3^0$, becomes most stable species, sorbing Fe oxides throughout a wide pH range and remaining relatively immobile in the process even in neutral soils (Scheinost, et al., 2006).

2.5.3. Effect of soil organic matter (SOM)

Soil properties (pH, organic matter, clay mineral and moisture content) and meteorological parameters (temperature, rainfall) can differ greatly between locations, which has important consequences for range management (Sanderson, et al., 2012). Organic matter (OM) in the soil is made up of living organisms, soluble biochemicals (amino acids, proteins, carbohydrates, and organic acids), and insoluble humic compounds (Kelebemang, 2017). The rate of OM creation is determined by three major factors: the amount of plant and animal matter that stays in the soil, the physical qualities of the environment, and the quality of the OM itself (Dinake, et al., 2019). The bio-chemicals serve as metal sorption sites, resulting in the formation of water-soluble complexes that promote metal mobility (Kelebemang, 2017). The Complexes with metals are formed through the exchange and adsorption processes of soil organic matter, both soluble and insoluble (Rooney, 2002). Due to the presence of negative charge across a wide pH range, soil organic components, mostly humic substances, play a key role in Sb sorption (Zhao, et al., 2014). Sb (III) associated

with natural organic matter, dissolved organic carbon (DOC), and humic acids is easily oxidized by photo-oxidants such as hydrogen peroxide (H_2O_2), and these processes can be beneficial in the transformation of high toxic Sb (III) species into less toxic Sb(V) species in contaminated aquatic and terrestrial areas (Indika, et al., 2017). Since both are negatively charged at ordinary soil pH, Sb (III) binding to humic acids has been confirmed, Sb (V) in solution is less likely to interact with soil organic matter (Olive, 2006). Antimony has also been shown to bind to organic matter in soil, such as humic acid (HA) (Vleek, et al., 2011). Soil humic acid is an essential component of soil organic matter because it supports the transfer of inorganic and organic pollutants to (Okkenhaug, et al., 2016). Shooting ranges in Norway have high Organic matter (OM) content, ranging from 30 to 90% of dry mass, with high concentrations of dissolved organic matter (DOM) in the pore water (Okkenhaug, et al., 2018). The shooting ranges are made of peat. Peat is created by organic material left over from the incomplete breakdown of stored plant organic matter as a result of more or less water-saturated circumstances (Okkenhaug, et al., 2018). Values of dissolved organic carbon (DOC) can reach 250 mg L^{-1} the carbon component, whereas peatland discharge concentrations range between 5 and 40 mg L^{-1} (Okkenhaug, et al., 2018). There was no adsorption on humic by Sb (V) supplied as $\text{KSb}(\text{OH})_6$ at concentrations of $10 \text{ }\mu\text{mol/L}$, but there was adsorption at Sb(V) concentrations of 50-70 $\mu\text{mol/L}$ (Olive, 2006).

2.5.4. Effect of cation exchange capacity

Soil CEC, is the most common parameter used to assess metal mobility. Cation Exchange Capacity (CEC) is a soil physicochemical parameter that reflects the soil's ability to bind and release cations in soil solution at a specific pH level (Champman, 1965). CEC represents the soil's capacity to retain cations accessible to plants (Aran, et al., 2008). CEC is used to discuss soil fertility, together with other soil metrics such as colloid and nutrient content (Kelebemang, 2017). Cation ion exchange is a process involving free metal cations and $-\text{COO}-\text{H}^+$ functional groups, as well as a mixture of bidentate chelation and metal bridging with carboxyl and hydroxyl groups. These are involved in Sb binding to the by HA (Vleek, et al., 2011). Due of the toxicity risks involved with Sb exposure, it is vital to have a complete understanding of the chemistry that occurs on Sb shots and bullets (Kelebemang, 2017). Under favourable soil conditions, s the bullets and shot will undergo oxidation, carbonation, and hydration processes, making Sb mobile and available to biota

(Dinake, et al., 2019). In a study performed Steinsjøen military shooting range in Østre Toten, Akershus County, south Norway, peatland were found to have high cation exchange capacity (CEC), and at near neutral pH, antimony was found to have a modest interaction with organic ligands. However, affinity rose significantly at higher pH (Okkenhaug, et al., 2017). For studies, that were performed at Losone showed high CEC (110 mmolc/kg) and base saturation (BS) 20% CEC, with Ca^{2+} being the dominant exchangeable cation (Olive, 2006). For the same peatland study at Zuchwil shooting range CEC was found to be 212 mmolc/kg with BS of 99% CEC. The soil CEC is largely dependent on the type of soil and the mineral content of the soil as shown in Figure 6 below.

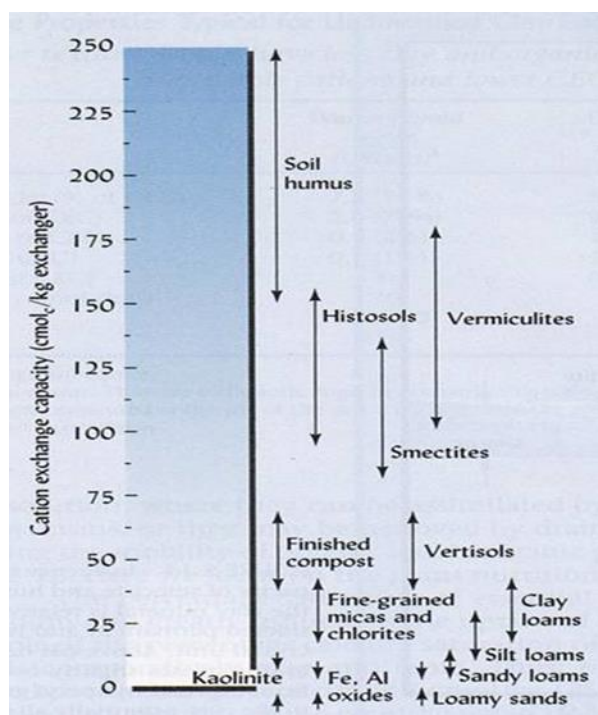


Figure 6. CEC values of different soil types, media, and minerals (Kelebemang, 2017).

2.5.5. Effect of Soil moisture

Soil moisture is a critical physical feature of soil that influences the rate of weathering, transformation, movement, and destiny of Sb (Dinake, et al., 2019). The soil's moisture level creates an ideal condition for the erosion and corrosion of Sb shots and bullets (Dinake, et al., 2019). It lubricates the Pb-Sb shots by forming a thin aqueous layer on the Pb-Sb shot surface, allowing reactive gases such as oxygen (O_2) and carbon dioxide (CO_2) from the atmosphere to

diffuse to the metal surface, resulting in the formation of Sb weathering compounds such as Sb carbonates, sulphates, oxides, and phosphates, as well as their subsequent solubilisation and dissolution products (Sehube, et al., 2017). Understanding metal transport at shooting ranges requires not only estimating the quantity of pollutants spread from bullet fragments due to interactions with the environment and pore water flow, but also identifying the speciation of the mobile species (Trainor, 2017). Furthermore, determining the speciation of dissolved metal(oids) (for example, Sb oxidation state) is critical for understanding the precise soil (bio)geochemical conditions that affect weathering and mobility routes, as well as possible bioavailability (Trainor, 2017). There are just a few papers on Sb speciation and mobility in soils or solid phase heterogeneous materials in the literature. Batch extractions using water or acidified water, as well as pore water examinations, are examples of study (Olive, 2006). According to Meima and Comans (1998), Sb leaching in cremated municipal bottom ashes was likely controlled by sorption to amorphous Fe/Al-hydr oxides at neutral pH levels. They also proved that by adding salts of Fe (III) or Al (III) to the bottom ash, Sb could be effectively extracted from solution (Olive, 2006). In another study the berm runoff's average Pb and Sb values were determined by inductively coupled plasma-mass spectrometer (ICP-MS). Results showed that there was very little variation in the aqueous concentrations of Pb among the soil types (with slight increases in the sandy loam and loamy sand) but Sb concentrations were elevated with respect to Pb, with average values exceeding 100 µg/L and also significant variation in the Sb concentrations among the soil types (Trainor, 2017).

The presence of Sb in water and sediment from a mining-contaminated river indicated that the vertical distribution of Sb in the sediment corresponded closely to that of Fe and Mn (Olive, 2006). Sb(V) leaching from sediments (with deionized water and stirring) was greatest at higher pH levels, and Sb(III) leaching was lowest at intermediate pH levels (Olive, 2006). Sb mobilization was more likely in sediments containing low quantities of iron oxides and Mn oxides (Olive, 2006).

2.6 Use of amendments to immobilize antimony in contaminated shooting range soils

Currently, shooting range management and clean-up rely heavily on written guidelines and guidance materials such as the United States Environmental Protection Agency's (USEPA) 'Best

management practices of lead outdoor ranges (Dinake, et al., 2019). To mitigate the environmental risk posed by contaminated shooting ranges, intervention is essential, where the quality of the groundwater resource must be maintained (Rooney, 2002). Excavation, transportation of polluted soils, and subsequent burial were the most typical restoration methods for such sites in recent decades (Lafond, et al., 2012). These methods, however, are neither permanent nor environmentally friendly (Lafond, et al., 2012). In Europe and North America, laws prohibit the dumping of significantly contaminated soils with Sb without first being treated (Lafond, et al., 2012).

The management of contamination of shooting range soils is based on four management strategies (Dinake, et al., 2019):

- I. bullet control and containment,
- II. avoidance of contaminant movement,
- III. bullet removal and recycling, and
- IV. recording and assessment of environmental management plans.

2.6.1 Phytoremediation method

Plants may be used to control contamination via surface run-off. The metalloid can pollute soils and accumulate in plants, through root and foliar uptake (Zeng, et al., 2015). Vegetation may also help to stabilize Sb. Planting grass is an important and easy erosion control method. However, Sb uptake by plants is typically at a minimum, and the highest concentrations of Sb typically remain in the roots. Yin et al. (2000) reported that Rye grass played an important role in the immobilization of Sb in a former shooting range soil (Ji, et al., 2017). In addition, some species of plants (rice) have even been reported to accumulate Sb(III) (Ji, et al., 2017). Sb (III) was found in greater concentrations in the roots of rye grass than in the Sb (V) and TMSb treatments. Because Sb (OH)₃ and As(OH)₃ have the identical tetrahedral molecular shape, Sb(III) is thought to be taken up by aquaporin channels in the same way as As(OH)₃ is As(III). However, Sb uptake by plants is typically at a minimum, and the highest concentrations of Sb typically remain in the roots. Many scientists have looked at phytoremediation research in their effort to identify ecologically acceptable ways and procedures for controlling and managing Pb pollution in shooting range soils (Dinake, et al., 2019). Furthermore, phytoremediation slows the movement of Sb and its erosion from shooting range soils.

2.6.2 Berm Soil Replacement

Replacing berm soils with sand is another possibility, since it has been demonstrated that sand is a superior choice because of its low organic matter, low moisture content, and high pH, which can discourage or at least reduce Sb mobility in soils at the ranges studied (Kelebemang, 2017). Yin et al., (2010) as well found replacing berm soils with sand as another possibility of reducing Sb mobility in the soil (Yin, et al., 2010).

2.6.3 Red mud treatment of soil contaminated with Sb in shooting range

The waste product of aluminium processing is called red mud. Although it is quite alkaline (pH 11.5), it may be neutralized to give it a less extreme pH and have other additives introduced to adjust its properties (Tandy, et al., 2017). It would provide a great number of binding sites for Sb and Pb due to its high concentration of Fe and Aluminium (Al) (hydr) oxides, as well as other minerals (sodalite, crancrinite, quartz, brucite, calcium carbonate, para-aluminohydrocalite, portlandite, hydrocalumite, hydocalcite) (Tandy, et al., 2017). Furthermore, the bonds established between pollutants and red mud minerals are anticipated to intensify with time due to blockage by mineral micro-pores. Experiment done by Tandy et al., (2017) on Losone, Switzerland, shooting range soil showed that leaching on soil treatments increased initially up to week 7 or 11, then decreased (Tandy, et al., 2017). Tandy et al., (2017) discovered that the hematite crystallinity of metal-laden red mud increased over 3 months, raising the possibility that metals, or in this case antimony, may be absorbed as impurities in the developing crystals and thus become less accessible over time than if it was simply adsorbed to the surface. By week 26, all treatments have decreased Sb leaching in Losone soil except zero valent iron, with the lowest treatments comprising iron sulphate (Tandy, et al., 2017). Iron sulphate was particularly successful in lowering Sb leaching from soil, most likely because of the conversion of Sb (V) to Sb (III) in its presence, which bound more firmly to Fe (hydro) oxides throughout a wide pH range (Tandy, et al., 2017).

CHAPTER 3

EXPERIMENTAL

3.1. Descriptions of the Shooting Range Studied

TAB shooting range is in the southern part of Botswana with GPS coordinates: 24° 14' 42.79'' South, 25° 19' 55.84'' East . Of particular interest is that TAB shooting range is in a fenced military camp where military personnel and their families live . This range has been in operation for more than 20 years and no study has been undertaken previously to ascertain the pollution risk posed by antimony contained ammunition

3.2. Soil sampling

Soil sampling was carried out at the berm and target line areas of the shooting range . Three sampling points with a radius of 150 cm were located at the upper, middle, lower berm, and target line. Four soil samples were obtained along central transect within each sampling point using a soil recovery probe to a depth of 20 cm from the earth surface. The four samples were then mixed to make a composite sample representative of each sampling point. A total of 12 composite samples were obtained. The soil samples were collected into airtight butyrated zip-lock plastic bags and transported to the laboratory for analysis. Background soil samples were collected at a distance of 200 m outside the shooting range in an area being windward from the center and having the same soil characteristics, for providing background reference concentrations of Sb.

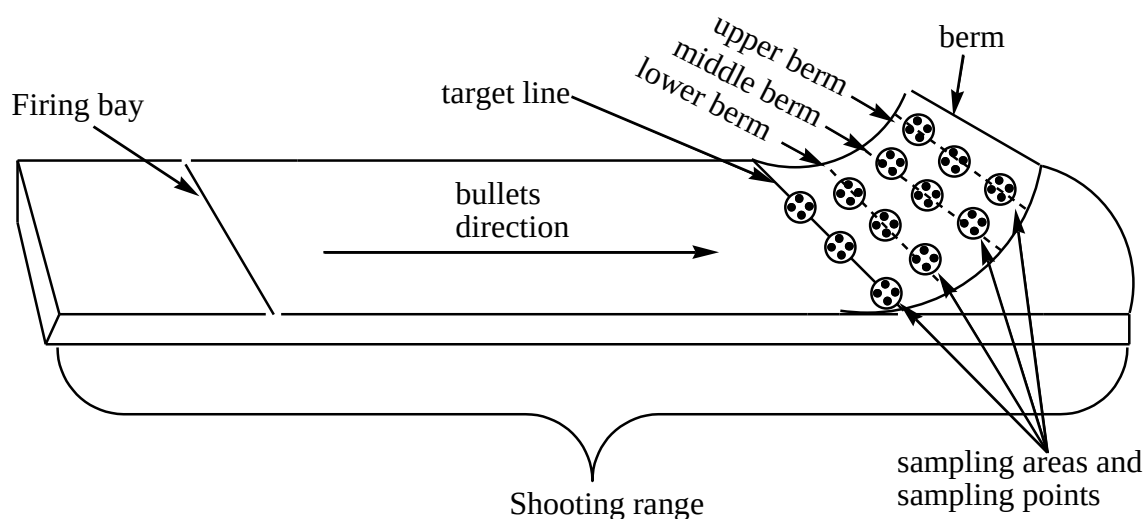


Figure 7. Schematic of sampling points in the berm and target line of TAB shooting range

3.3. Sample preparation and analysis of total Sb at TAB shooting range soils

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

Total Sb concentration was determined using inductively coupled plasma optical emission spectrometry (ICP-OES; Thermo Fisher ICAP 7400). Samples were prepared by acid digestion using USEPA Method 3050 with 1:1 v/v nitric acid. Quality check and assurance was carried out using a certified reference material (CRM) for soil, NCS DC 73320, was obtained from the Botswana University of Agriculture and Natural Resource (BUAN). Sample preparation for the CRM was the same as for the TAB shooting range soils.

3.4. Physical and chemical analysis of the soil samples

The soil physicochemical properties such as pH, electrical conductivity, organic matter (OM) and cation exchange capacity (CEC) were all determined using standard methods.

3.4.1 pH and Electrical Conductivity (Dikinya, 2011)

The Hanna pH/EC – meter was used to measure the pH and Electrical Conductivity. The meter was switched on to ‘stand-by’ position for warming up.

For each sample that has been passed through a 2mm sieve, three portions of 20g each was weighed into three separate 100ml plastic bottles. One bottle is labelled pH-1, other 2 and the last one 3.50ml of water was added to bottles and closed each bottle tightly, put on the shaker (Stuart orbital Shaker) and secure the bottles tightly. Shaken for two hours at a speed of about 300 rpm after which the samples were removed from the shaker and allowed to stand for one hour.

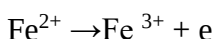
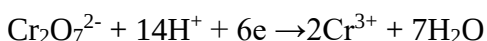
The pH/EC-meter was switched to measuring mode. The PH electrodes were calibrated in using the Rochelle buffer solutions pH 4, 7 and 10 buffer solutions and the EC electrode was also calibrated using conductivity standard solution. After calibration, the electrode was immersed in the upper part of the sample suspension, not stirring the suspension, and waited for a stable reading. Noted the value, rinse the electrodes, and repeated for each sample.

3.4.2 Cation Exchange Capacity Determination (Kelebemang, 2017)

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

3.4.3 Organic Matter (Dikinya, 2011)

The Walkley and Black method was used to determine the Organic Matter in all the berm soil. The Walkley-Black (WB) titration method is a method used for analysis of organic carbon in soils and sediments. The method is based on the oxidation of organic matter potassium dichromate ($K_2Cr_2O_7$), sulphuric acid mixture followed by back titration of the excessive dichromate by ferrous ammonium sulphate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$). The average oxidation number for organic carbon is considered as zero and the reactions involved in the WB titration method are as follows:



1 gram of soil was weighed into 500ml conical flask, 10 ml of 1N potassium dichromate was pipetted into the conical flask. Carefully 20ml of 80% sulphuric acid was added into the above 500ml conical flask. The procedure produced heat and spurting in some of the samples this was carried out in a fume hood and gloves were worn all times. The conical flask was swirled gently and allowed the mixture to stand in the fume hood for 30minutes. Some of the mixture developed greenish colour so further 10ml potassium dichromate and 20ml concentrated Sulphuric acid. Some samples did not develop green colour, approximately 200ml of deionised

water was added. 10 ml phosphoric acid was added. The mixture was titrated with 0.5N ferrous ammonium sulphate adding 5ml of the redox indicator when the solution has become greenish. The end point was reached when the solution become steadily bluer during the titration changes from a bluish purple to turquoise green.

The results were calculated using the following equation:

$$\%OC = \frac{0.396 \times [\text{vol of } K_2Cr_2O_7 \times \text{Normality}] - [\text{vol of } (Fe (NH_4)_2(SO_4)_2 \times \text{Normality}]}{\text{Mass of Soil}}$$

$$\% \text{organic matter} = 1.72 \times \% \text{organic carbon (OC)}$$

3.4.4 Fractionation studies

A sample is exposed to a wet chemistry sequence in the sequential extraction procedure. The sample is extracted in a solution intended to selectively remove or dissolve a specific form or solid component with which the metal in question is associated at each stage of the method. The extraction solution's parameters are regulated to restrict the extracted item's resorption and precipitation. The reagents get more aggressive as the sequence advances, and their specificity decreases. (Fine, 2010)

Sequential extraction was developed in the 1970. In general, the metal extraction procedures are performed in the following order: aqueous and/or electrolyte solutions are used to extract the soluble and/or exchangeable metal species; a weak acid for metals linked to carbonates; a weak reducing agent for metals dissolved in Mn oxhydroxides and amorphous iron oxyhydroxides; a weak oxidizing agent for characterizing metals in organic components; a strong reducing agent for characterizing metals in organic components; a strong reducing agent to characterize metals associated with well crystallized iron oxyhydroxides and a strong mineral acid(s) to dissolve the residue left after all method stages have been completed; mostly aluminosilicates. (Fine, 2010)

During the experimental (Tessier, et al., 1979) was followed as it was designed to characterize metals by their pollution potential. Tessier protocol was used as is:

A dry weight of 1gram of pulverised and homogenised sample was weighed using analytical balance (ae Adam Nimbus max 210g-0001g NBL ∞214e). This was done for all the chosen five Berms.

- i. *Exchangeable Sb*; The 1g of homogenised soil sample was extracted at room temperature for 1hour with 8ml of sodium acetate solution (1M NaOAc pH 8.2) with continuous agitation using BOECO Germany C-28A centrifuge.
- ii. *Sb Bound to Carbonates*; the residue from (i) was leached at room temperature with 8ml of 1M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained and the time necessary for complete extraction was evaluated at 4hours.
- iii. *Sb Bound to Fe-Mn oxide*; the residue from (ii) was extracted with 20ml 0.004M NH₂OH.HCL in 25% (V/V) HOAc. The experiment was performed at 96±3°C with occasional agitation and the time needed for completion of the free iron oxides was evaluated at 2hours.
- iv. *Sb Bound to Organic Matter*; To the residue from (iii) were added to 3ml of 0.02M HNO₃ and 5ml of 30% H₂O₂ adjusted to pH2 with HNO₃ and the mixture was heated to 85 ±2°c for 2hours with occasional agitation. A second 3ml aliquot of 30% H₂O₂ (pH 2 with HNO₃) was then added, and the sample was heated again to 85 ±2°c for 3hours with intermittent agitation. After cooling, 5ml of 3.2 NH₄OAc in 20% (v/v) HNO₃ was added, and the sample was diluted to 20ml and agitated continuously for 30mins.
- v. *The Residual Sb*; the residue from (IV) was digested with Aqua regia (HNO₃ + HCL) mixture according to the procedure described below. All the residues from steps i-v were analysed using ICP-OES.

3.4.5 Leaching test: Synthetic Precipitation Leaching Procedure (SPLP)

(Kelebemang, 2017)

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

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

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

3.5 Inductive coupled plasma Optical Emission Spectrometer(ICP-OES; Thermo Fisher ICAP 7400). (Mendham, et al., 2010)

Plasma spectroscopy is based on electronic transitions between electronic energy levels of atoms and ions of elements, and it includes both electromagnetic radiation absorption and emission. Because the electronic energy levels are widely separated, the transition may be seen in the visible, ultraviolet, and X-ray areas of the electromagnetic spectrum. The accompanying spectrum transitions are characterized by thin lines and substantial changes in dipole moment, the approach has a high sensitivity. Antimony was measured using the Thermo Icap dual inductive coupled plasma optical emission spectrometer. The ICP-OES apparatus is made up of a nebulizer, a torch, an auto sampler, a lens, and a data recorder. The nebulizer introduces the sample into the device as a solution. The peristaltic pump and argon gas flow push the sample into the mixing chamber. The sample is carried in the form of aerosol by the argon stream. The excitation is provided by two or three turns of metal induction tube through which flows a radio frequency current. The energized atoms then produce their distinctive radiation, which is sorted and supplied to the detector based on wavelength. The detected signals are subsequently translated into electrical signals, which are ultimately turned into concentration information for the analyzer (Kelebemang, 2017).

3.6 Characterization Studies

3.6.1 Mineralogical identification of berm soil (Kelebemang, 2017)

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

The radiation used was a cu-K α with a wavelength of 1.54056 Å within the values of 2θ between 5-90 degrees. The intensity of collected radiation at each angle, ($^{\circ}2\theta$) 5.00 – 90 degrees was measured. Each sample took about 10 minutes to run. The machine was run at 40 V and 40 mA. The interplanar spacing d, peak intensities, and position of peak ($2\theta^{\circ}$) were obtained directly

from the captured XRD data. Then Bruker software EVA, was used for data analysis, including phase identification, structure refinement and quantitative phase analysis

3.7. Pollution risk assessment

The environmental pollution risk due to deposition of Sb into TAB shooting range soils was assessed and quantified using pollution risk indices (Dinake, et al., 2018). Pollution risk indices such as risk assessment code (*RAC*), geoaccumulation index (I_{geo}), contamination factor (*CF*) and enrichment factor (*EF*) were used to give a quantitative measure of the ecological risk posed by Sb accumulation at TAB shooting range

3.7.1 Risk assessment code (RAC)

Risk assessment code (*RAC*) considers the percentage of Sb present in the mobile and labile fractions (Latosinska, et al., 2021). It was first coined by Perin and co-workers in 1985 and it ranks the hazard found at shooting ranges in terms of risk codes with code 1 representing the lowest risk level and code 5 the highest risk level (Perin et al. 1985). In more detail, the ecological pollution risk depicted by the *RAC* codes are as follows; $RAC < 1\%$ (code 1 and no risk) indicate no risk, $1\% < RAC \leq 10\%$ (code 2 and low risk), $11\% < RAC \leq 30\%$ (code 3 and medium risk), $31\% < RAC \leq 50\%$ (code 4 and high risk) and $RAC \geq 51\%$ (code 5 and very high risk). This method has been widely applied towards assessment of environmental pollution risk from heavy metals such as Sb, Pb, Cu and Cd found in shooting range soils (Islam et al. 2016; Islam and Park 2017; Dinake et al. 2018b). It is given by the ratio of Sb concentration in the exchangeable and labile fractions (bound to carbonates) to the concentration of Sb partitioned in all the five soil fractions as indicated in equation (1) (Dinake, et al., 2018).

$$RAC = \frac{C_1 + C_2}{C_t} \times 100 \quad (1)$$

Where C_1 and C_2 represent the respective concentrations of Sb in the exchangeable and carbonate fractions and C_t defines the total concentration of Sb in all the five soil compartments. *RAC* does not only give a quantitative assessment of the ecological risk from accumulation of Sb into shooting range soils, it also establishes the extent of Sb mobility and bioavailability.

3.7.2. Geoaccumulation Index (I_{geo})

Geoaccumulation index (I_{geo}) was first introduced by Muller (1969) in a study that determined heavy metal pollution in sediments through comparison of the current levels of heavy metal concentrations with heavy metal levels determined before the industrial revolution (Muller, 1969). It describes the current contamination of soils with inorganic and organic contaminants relative to pre-industrial levels.

It can be determined using the equation;

$$I_{geo} = \text{Log}_2[C_i/(1.5 \times C_b)] \quad (2)$$

Where C_i represents the concentration of the heavy metal i determined in the soil while C_b is the background concentration of heavy metal i in the area under study. The constant 1.5 is a factor that denotes the background value correlation factor, and it compensates for potential background variations resulting from lithogenic alterations ((Muller, 1969); (Rodriguez-Seijo, et al., 2016)). It multiplies geochemical background concentrations in order to permit fluctuations of amount of a given contaminant in the environment and the little influences from anthropogenic activities. Risk assessment of pollution from heavy metal such as Sb can be classified into seven I_{geo} grades where Grade 1 indicates $I_{geo} < 0$ and no pollution from the heavy metal, $0 < I_{geo} < 1$ (Grade 2 and shows unpolluted to moderately polluted soils), $1 < I_{geo} < 2$ (Grade 3, moderately polluted), $2 < I_{geo} < 3$ (Grade 4, moderately to heavily polluted), $3 < I_{geo} < 4$ (Grade 5, polluted soils), $4 < I_{geo} < 5$ (Grade 6, heavily to extremely polluted) and $I_{geo} > 5$ (Grade 7, extremely polluted soils).

3.7.3. Contamination Factor (CF)

Contamination factor assesses soil contamination through comparison of geochemical background concentrations with contaminant concentrations in studied sites (Dinake, et al., 2018). It describes the contribution of a given contaminant to the overall pollution of the environment by establishing the fraction of a given substance in the total pollution (Hakanson, 1980). It also depicts the input of heavy metals into the environment arising from anthropogenic activities. CF is determined using equation (3);

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

where C_i and C_b represent total concentrations of the analysed heavy metal in the soil and geochemical background respectively. $CF < 1$ indicates low contamination, $1 \leq CF < 3$ reflects moderate contamination while $3 \leq CF \leq 6$ shows considerable contamination and lastly $CF > 6$ represents very high contamination.

3.7.4. Enrichment Factor (EF)

The impact of human activities on the environment such as shooting exercises can be assessed using enrichment factor [EF] (Dinake, et al., 2018). EF relates concentration of a particular element arising from anthropogenic activities to the native undisturbed condition of the soil (Dinake, et al., 2018). It assesses the enrichment or depletion of a particular element in the studied site. In addition, EF helps address the ecotoxicological and chemoecological impact of a particular element in an environment. The evaluation of Sb enrichment in TAB shooting range soils was carried out using equation (4) (Mmolawa, et al., 2011).

$$EF = \frac{C_i}{[\text{Median } C_i \text{ Background} + (2 \times \text{MAD } C_i \text{ Background})]} \quad (4)$$

Where C_i represents the total concentration of heavy metal i such as Sb in shooting range soils; median C_i Background depicts the concentration of heavy metal i in unperturbed soils and MAD C_i Background indicates median absolute deviation from the median and has the following definition:

$$\text{MAD} = \text{median}(|C_i \text{ Background} - \text{median}(C_i \text{ Background})|)$$

which translates to determining the median of replicate concentrations background metal i in the soil; then subtract the median calculated above from each concentration of background heavy metal i ; then determine the absolute value of the differences between the individual background

concentration of heavy metal i and their median and eventually get the median of these absolute differences. The degree of soil enrichment from a particular metal fall into seven categories. $EF < 1$ represents no enrichment; $1 \leq EF < 3$ show minor enrichment; $3 \leq EF < 5$ (moderate enrichment); $5 \leq EF < 10$ (moderate to severe enrichment); $10 \leq EF < 25$ (severe enrichment) and $EF \geq 50$ indicates extreme enrichment (Mmolawa, et al., 2011).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Soil properties and Physical parameters

The TAB shooting range is more than 15 years, since it was established. The shooting range soils from TAB are predominantly sandy. The area is the Kalahari group, which dominates the sandveld, whereas surface sands and weathering residues dominate the hardveld (Popego, et al., 2019). The principal landforms in the hardveld include hills and escarpments, which are related with the dominant rock types and rock formations, as well as the river networks (Popego, et al., 2019). The stop butts that capture bullets are made of sand and to reduce weathering. Sand is a preferred material for stop butt construction (Sanderson, et al., 2012). The pH and electrical conductivity of the TAB soil samples were determined. The pH ranged between lowest of 7.6 and 8 highest at the upper berm. Target line and Middle berm recorded pH's of 7.8 and 7.9 respectively (Table 6). The soils at the four sampling points were found to be slightly alkaline and alkaline soils favour the dissolution of Sb minerals (Conesa, et al., 2010). The study showed that the dissolved concentration of Sb is strongly pH dependent, and Sb occurring as an oxyanion ($\text{Sb}(\text{OH})_6^-$) has increased solubility at increasing pH. The adsorption of this oxyanion by solid sorbents in the soil is normally not favoured at low pH's (Serna, 2002). The soil organic matter at the four sampling points at TAB shooting range was in the range 9.55–11.42% which is considered high and may support the formation of Sb (III) organic ligand complexes (Mariussen, et al., 2017). Sb weathering, transformation, mobility, and bioavailability were all shown to be influenced by soil cation exchange capacity (CEC). The binding capacity of metals such as antimony in soils is regulated by the soil's CEC, which is a measure of the quantity of exchangeable cations that a particular mass of soil can hold. The more the CEC, the greater the soil's binding capability, resulting in decreased Sb mobility and bioavailability. CEC ranged between 5.84 and 9.87 cmol/kg for the target line and the berms respectively.

Table 1: Physicochemical properties of TAB shooting range soils

Location on shooting range	pH _w ± δ^a	CEC ^b ± δ (cmol/kg)	Organic Matter ± δ (%)
Upper berm	7.80 ± 0.21	5.84 ± 0.32	9.72 ± 0.79 ^c
Middle berm	8.0 ± 0.93	8.13 ± 0.71	9.55 ± 0.25
Lower berm	7.9 ± 0.62	7.54 ± 0.66	11.42 ± 0.82
Target line	7.6 ± 0.18	9.87 ± 0.83	9.60 ± 0.41

a= Standard deviation (δ)

b = Cation exchange capacity(CEC)

c=Mean ± standard deviation ($n = 3$)

4.2. Concentration of total Sb at TAB shooting range soils

Total antimony concentrations of the range 38.8–283.5 mg/kg were determined at TAB shooting range. The upper portion of the berm area accumulated the highest concentration of Sb (283.5 mg/kg) whilst the target line collected the lowest concentration of Sb (38.8 mg/kg). The middle section of the berm also accumulated high concentration of Sb after the upper berm. The highest total concentration of Sb found on the upper berm could be attributed to the large density of spent bullets and shots that were found in this part of the berm. This implies that during the firing exercises, bullets pierce through the practice targets and collect in this section of the berm. Previous studies have established that there is direct correlation between elevated concentrations of heavy metal in a specific site and the deposition of spent bullets and shots in the soil found in that particular area (McCarteney, 1994); (Anon., n.d.). Background concentration of Sb was determined in the soil collected 200 m away from the shooting range and was found to be 0.381±0.002 mg/kg.

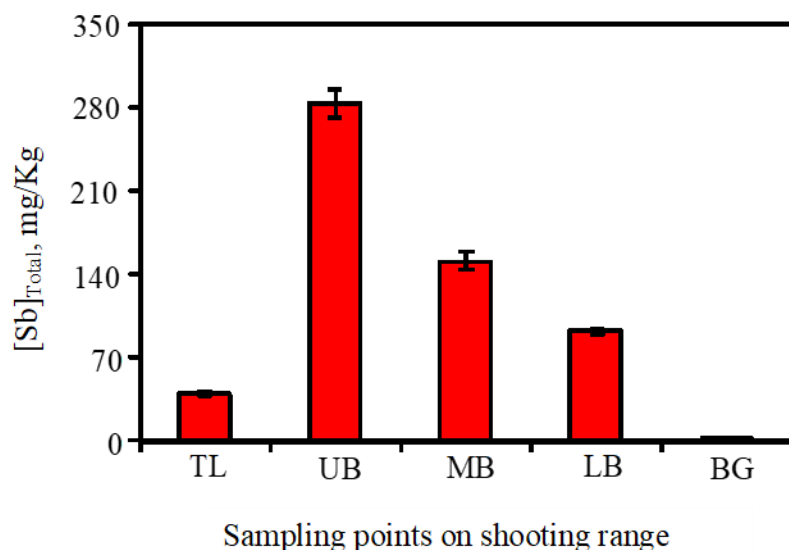


Figure 8. Concentration of Sb in the soils taken from four different points at TAB shooting range found in Botswana. Mean of n=3; standard error of mean, TL= target line; UB= upper berm; MB= middle berm, LB= lower berm and BG

4.3 Fractionation and mobility of Sb

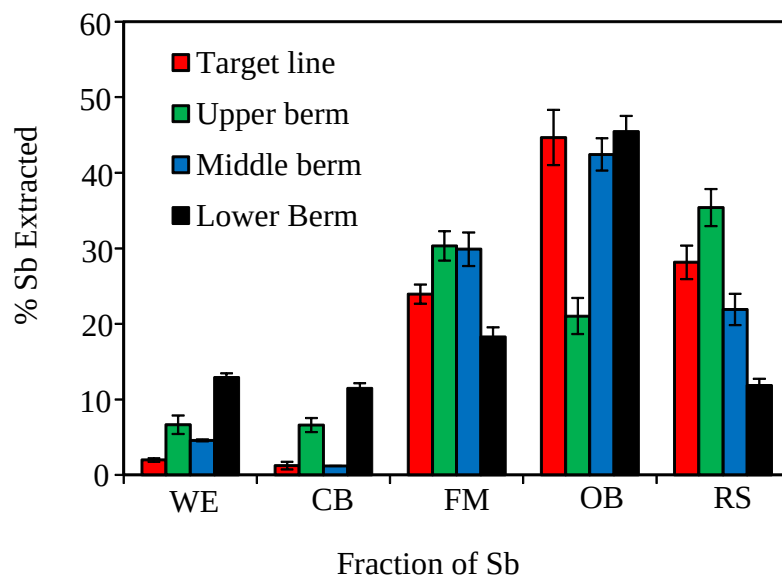


Figure 9. Sequential extraction procedure for Sb at four sampling points of TAB shooting range. Mean of n=3. WE= water exchangeable; CB= carbonate bound; Fe- Mn= Iron and Manganese oxide bound; OB = organic bound; RS= residual

The sequential extraction procedure (SEP) is commonly used to assess the distribution of heavy metals across the different soil compartments (Anon., n.d.). The SEP helps establish the occurrence of the different Sb mineralogical forms in the soil that may be chemically active or inert. Sb species that are chemically active are considered mobile and bioavailable while the inert species are not readily bioavailable and exist in the less soluble Sb mineral forms (Mariussen, et al., 2017). The application of SEP ascertains for the biochemical and physicochemical availability, migration, toxicity, and fate of Sb in shooting range soils (Conesa et al. 2010). The partitioning of Sb in the different soil compartments was determined in five different extractions including the water soluble and exchangeable (WE), carbonate-bound (CB), organic-bound (OB), Fe-Mn oxides bound (FM) and residual fraction (RS). Each fraction bore corresponding ecological toxicity and the extent of Sb bioavailability. The WE and CB fractions displayed direct toxicity and the heavy metals in these fractions were considered highly bioavailable (Li, et al., 2012). On the other hand, the FM and OB fractions were considered potentially toxic to biota and the heavy metals in this fraction are potentially bioavailable. However, the RS fraction did not possess any ecological toxicity and the metal mineralogical species were considered stable in this fraction and were not bioavailable ((Li, et al., 2012); (Dinake, et al., 2018)). It can be shown from Figure 9 that Sb was mostly restricted to the OB, FM, and RS fractions. Sb was mostly partitioned in the organic fraction (up to 45%) followed by the FM fraction and the little amount of Sb that was retained in the carbonate compartment (1-12%). The upper section of the berm, where the highest density of unspent bullets and shots was found, contained the highest amount of Sb partitioned in the residual fraction (35%) followed by FM and OB fractions partitioning, 30 and 21% of Sb respectively. The low concentrations of Sb in the labile WE and CB fractions compared to the other fractions was supported by the soil chemical properties of high pH, CEC, and organic matter (Table 1). The high pH provided a suitable environment for the dissolution of Sb minerals such as $(\text{Sb}(\text{OH})_6^-)$ anions (Anon., n.d.). Furthermore, the upper berm and lower berm sections of the berm experienced high concentration of Sb in the WE and CB fractions than the middle and target line sections of the berm (Figure 9). The high concentration of Sb in the WE and CB fractions in the upper berm corroborated the claim that the occurrence of Sb at this section came mainly from Sb released from the weathering and corrosion of the high density of spent bullets and shots in that area. In a similar study by Britton et al. (2011), the highest concentration of Sb was found in the WE whereby the majority of spent projectiles were located (Vleek, et al., 2011). On the other hand, the high

concentration of Sb in the WE and CB fractions at the lower section of the berm were thought to be a result of the migration of soluble Sb minerals down the berm due to gravity.

The mobility and fate of Sb in shooting range is strongly dependent on how a particular heavy metal is strongly or weakly bound to soil components. For this study, the mobility of Sb in shooting range soil was estimated using a method suggested by Kabala and Singh (2001) as shown in equation (1) (Kabala & Singh, 2001).

$$\text{Mobility Factor (MF)} = \frac{F_{WE} + F_{CB} + F_{FM} + F_{OM}}{F_{WE} + F_{CB} + F_{FM} + F_{OM} + F_{RS}} \quad (1)$$

where, F_{WE} = water soluble fraction
 F_{CB} = carbonate-bound fraction
 F_{FM} = Fe-Mn oxides fraction
 F_{OM} = organic-bound fraction
 F_{RS} = residual fraction

It is important to note that this is an estimate of the mobility of Sb since Sb in the fractions F_{FM} and F_{OM} is relatively less mobile. As a result, this would describe the potential mobility of Sb at TAB shooting range soil. The potential mobility of Sb is given in Figure 10. As shown on Figure 10, there is high mobility of Sb at TAB shooting range (mobility factor of 60-90%). The high mobility of Sb at TAB can be associated to a large extent with the soil physicochemical properties of high soil pH and high organic matter. As mentioned earlier, high soil pH accelerates the dissolution of Sb species such as $Sb(OH)_6^-$ (Anon., n.d.).

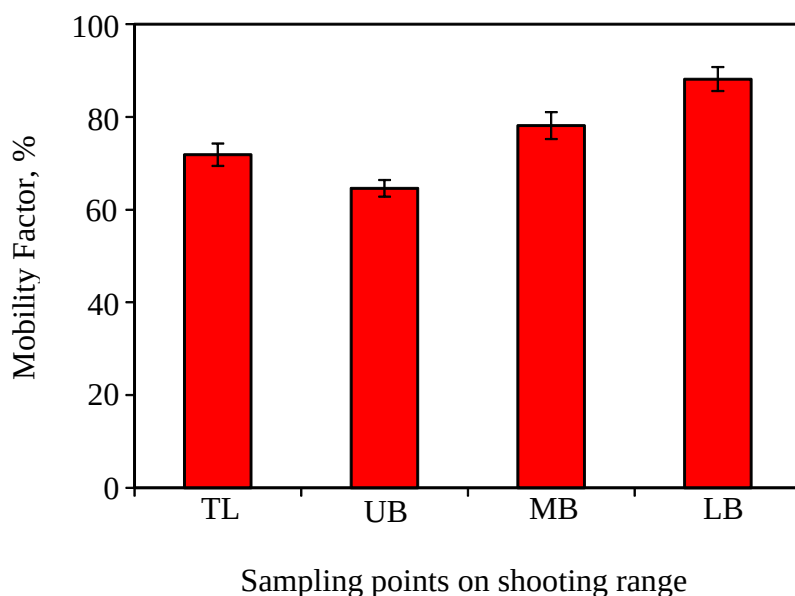


Figure 10. Mobility factor for Sb indicating the migration and fate of Sb at different sampling point at TAB shooting range. Mean of n=3, TL= target line; UB= upper berm; MB= middle berm; LB= lower berm

X-ray diffraction studies of the soil at TAB revealed the apparent prevalence of iron oxide minerals such as goethite (α -FeOOH) which formed complexes with Sb (Figure 11).

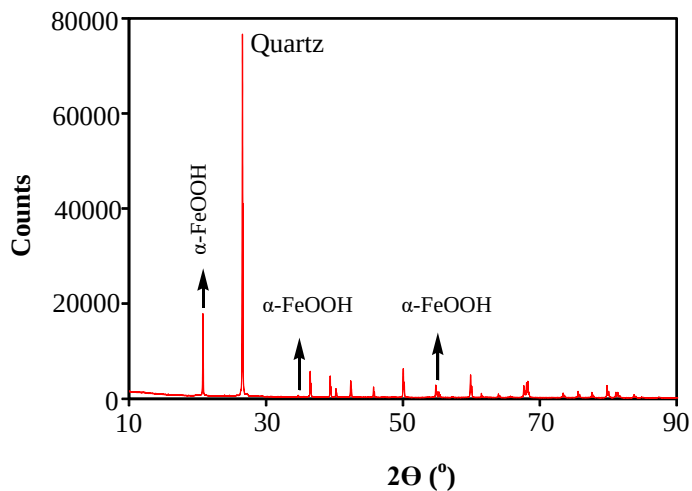


Figure 11. X-ray diffraction analysis patterns indicating the prevalence of α -FeOOH in TAB shooting range soil

In a similar study by Ackermann *et al.* (2009), the amorphous iron oxides such as goethite have been found to absorb Sb in their crystalline structure forming inner-sphere complexes (Anon., n.d.). Furthermore, soil physicochemical factors such as high quantities of organic matter have been found to have an important impact in Sb sorption (Anon., n.d.). The soils found at TAB shooting range were found to have high content of organic matter (9.55 – 11.42%). The prevalence of high organic matter in the form of such substances as humic acid is associated with high sorption rate for Sb (Anon., n.d.). The binding of Sb by humic acid in organic matter has been proposed to involve cation exchange process between free Sb ions and the carboxylic acid functional groups (Vleek, et al., 2011). It has also been demonstrated that soils rich in organic matter can result in the production of organo-complexes, with the resulting decrease of the pH of the produced complexes. Subsequently, the dissolution of the Sb-Fe oxides amorphous structures would take place leading to the release of the sorbed Sb.

4.4. Pollution risk assessment of Sb accumulation into the soil

The sequential extraction procedure helps in categorization of Sb in different chemical species indicating their chemical lability and inertness. This then provides a good measure of the mobility and bioavailability of Sb in the soil. However, sequential extraction procedure does not give a quantitative measure of the pollution risk posed by the highly mobile and bioavailable Sb. In order to give a good estimate of the environmental pollution risk from Sb accumulation into the soil, risk assessment code has been utilized (Dinake, et al., 2018).

4.4.1. Risk assessment code (RAC)

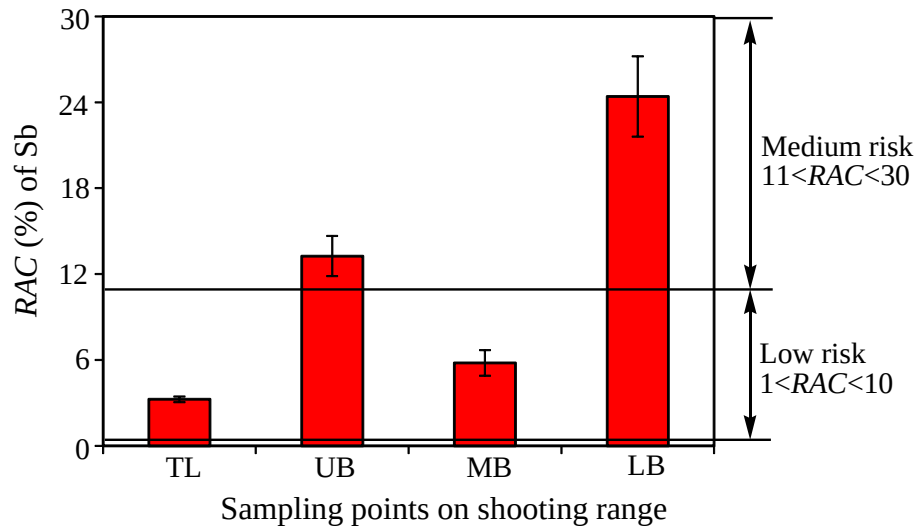


Figure 12. RAC of four different sampling points SB at TAB shooting range. Mean of $n=3$; TL= target line; UB= upper berm; MB= middle berm; LB= lower berm

The accumulation of Sb into TAB shooting range soils posed low to medium ecological risk. The lower section and upper sections of the berm displayed pronounced environmental pollution risk ($13\% < RAC \leq 25\%$) compared to the middle and target line sections ($4\% < RAC \leq 6\%$) as shown in Figure 12. These findings corroborate the results that the upper and lower sections of the berm accumulated the highest total Sb concentrations, due in part to the highest density of spent bullets and shots found in the upper berm. The findings in this study are consistent with those of a similar study carried out in South Korea that indicated high risk from Sb pollution at one shooting range, the We-rye shooting range, with an $RAC \sim 32$ and medium risk at Cho-Do shooting range ($RAC \sim 26$) (Islam & Park, 2016).

4.4.2. Geoaccumulation Index (I_{geo})

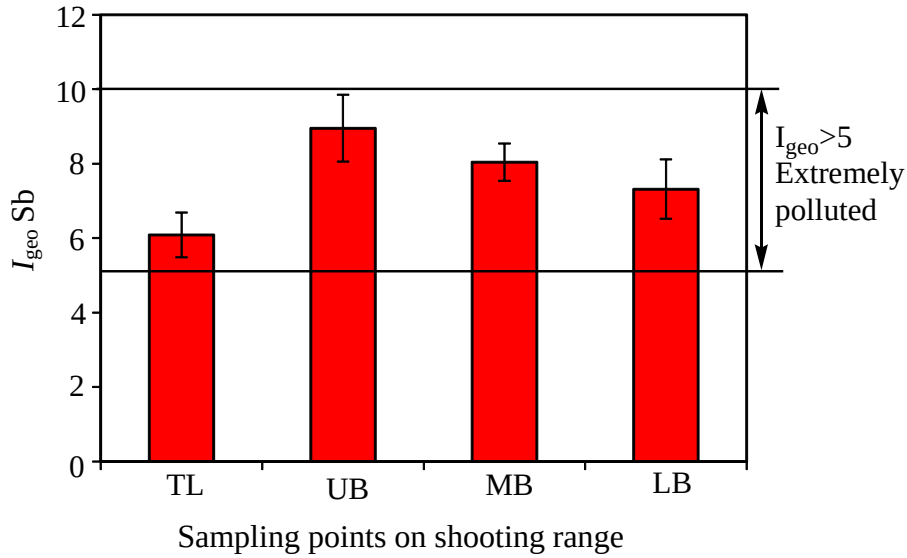


Figure 13; Geoaccumulation index (I_{geo}) for Sb four different sampling points at TAB shooting range. Mean of $n=3$; Standard error of mean, $\delta\bar{X} = \delta/\sqrt{n}$, where δ =standard deviation; TL= target line; UB=upper berm; MB=middle berm, LB=lower berm.

As depicted in Figure 13, TAB shooting range soils exhibited extreme pollution from Sb with I_{geo} of 6 to 9 (Grade 7). The highest I_{geo} of 9 was determined for the upper berm soils and these results agreed well with the RAC (Figure 12) and total Sb concentrations results (Figure 8). The high density of spent bullets and shots found in the upper berm section of the berm contributed significantly to the elevated levels of Sb. Corrosion and weathering processes on these spent bullets and shots resulted in the release of Sb. The I_{geo} results obtained in this study corroborate the findings by Lewinska and Karczewska (2019) in which two shooting ranges in Poland (Wroclaw and Olesnica shooting ranges) experienced I_{geo} values of 7.14–8.36 indicating extreme pollution from Sb (Lewinska & Karczewska, 2019). Total concentration of Sb in the berm soils collected at the two shooting ranges were in the range 40.1–93.4 mg/kg (Lewinska & Karczewska, 2019).

4.4.3. Contamination Factor (CF)

The results for RAC and I_{geo} , the upper berm (UB) at TAB shooting range experienced very high contamination at a $CF \sim 750$ See Figure 14.

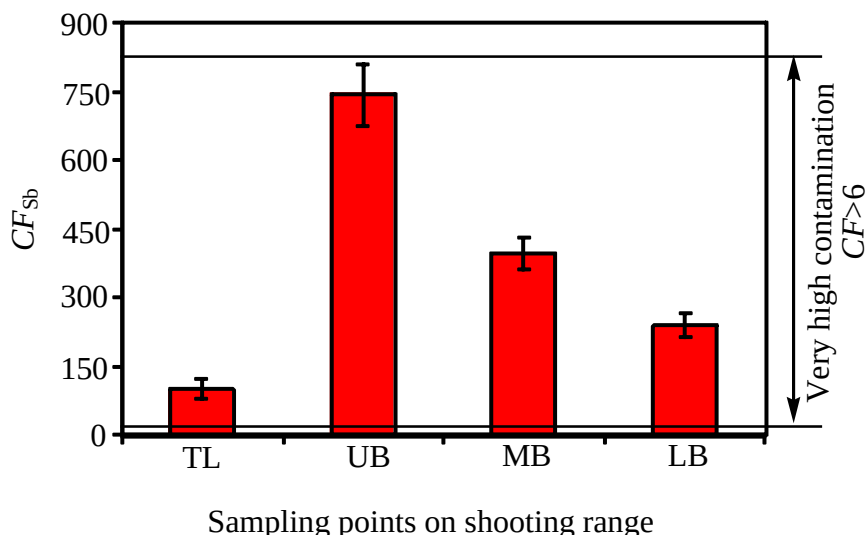


Figure 14. Contamination factor (CF) for Sb at four different sampling points at TAB shooting range. Mean of $n=3$; TL= target line; UB=upper berm; MB=middle berm, LB=lower berm

The very high contamination ($CF \sim 750$) at the upper berm corroborates the findings that a high density of Pb shots and bullets were found in this section of berm. In addition, all the other three sampled sections of TAB berm indicated very high contamination from Sb with contamination factor of the range 100-400. The favourable physicochemical properties of the soil such as the alkaline pH, high CEC and organic matter provided a suitable environment for weathering and dissolution of Sb minerals. In a similar study in China, very high contamination from Sb was established at a small arms shooting range with $CF \sim 11.6$ (Bai & Zhao, 2020). It is important to note that up to 14 mg/kg of Sb was found deposited in this shooting range soils, a concentration which is well below the WHO set maximum contaminant level of 36 mg/kg (Chang, et al., 2002). This indicated that total concentration of Sb alone cannot be used to establish the pollution risk from Sb to the environment.

4.4.4. Enrichment Factor (EF)

High enrichment factors of 69-506 have been determined at TAB shooting range indicating extreme Sb enrichment see Figure 15.

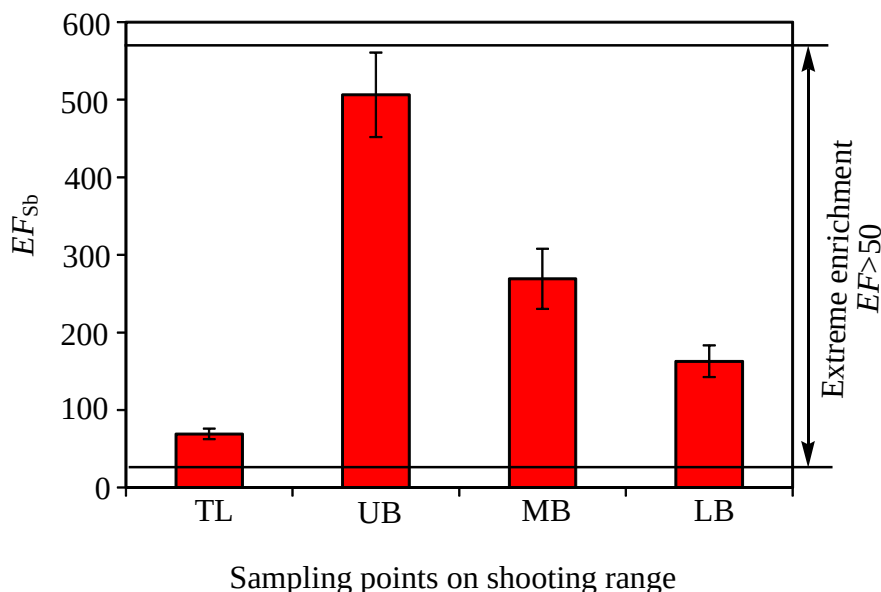


Figure 15. Enrichment factor (EF) for Sb at four different sampling points at TAB shooting range. Mean of $n=3$; TL= target line; UB=upper berm; MB=middle berm, LB=lower berm

All the four sections of the berm (TL, UB, MB and LB) showed extreme Sb enrichment. However, the UB section showed the largest EF of 506 compared to the other three sections with the TL bearing the lowest EF of 69. These results corroborate the results obtained for RAC , I_{geo} and CF which indicated high Sb content in the UB. In a similar study, extreme Sb enrichment of up to 98.61 was also determined at a military shooting range and training centre in El Teleno (Leon, Spain) with corresponding Sb total concentration of 96.10 mg/kg.

CONCLUSIONS AND RECOMMENDATIONS

This study has shown that pollution risk from Sb at shooting ranges cannot be ignored even though Sb is not a major component of shots and bullets. Being the first to be carried out in Botswana, it provides baseline data on Sb concentration in shooting range soils. It has been shown that different sections of shooting range berm pose distinct degree of environmental pollution risk. It has been shown further that the section where spent bullets and shots are collected such as the upper berm presents the highest pollution risk. Total Sb concentration determined in shooting range soils alone does not give a true picture of the environmental pollution risk. Total Sb concentration in TAB shooting range berm soils was found to be 3–7 times higher than the set maximum contaminant limit (MCL) by the World Health Organization (WHO). However, this only gives information about the amount of Sb stored in shooting range soils but does not provide a quantitative measure of the degree of hazard posed by such large amounts of Sb deposited into the soil. Thus environmental pollution risk assessment indices such as risk assessment code (*RAC*), geoaccumulation index (I_{geo}), contamination factor (*CF*) and Enrichment factor (*EF*) play a pivotal role in giving a quantitative measure of the pollution risk from exposure to Sb. Pollution risk assessment indices indicate a high environmental pollution risk at all sections of the berm at TAB shooting range with the upper berm posing the highest risk relative to other two sections: the middle berm and lower berm. The high environmental pollution risk posed by Sb deposition into TAB shooting range soils calls for expedited soil amendment and reclamation strategies. Soil remediation techniques that have been applied to polluted shooting range soils include such techniques as chemical amendments using phosphate and liming for immobilization of Sb to reduce its mobility and leaching into the soil. However, there is need for cost effective methods that are environmentally friendly such as phytoremediation. These methods have been found to be suitable because they do not involve removal of the soil which leads to loss of microorganism habitat.

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