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Pollution assessment of antimony in shooting range soils

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ABSTRACT

Soil samples collected from the berm at Thebephatshwa (TAB) shooting range found in Botswana 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 (36 mg/kg) and the United States Protection Agency (31 mg/kg). The upper berm showed 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) indicated all four sections of the berm posed high risk to the environment. The upper berm exhibited extreme pollution from antimony (I_{geo} ~9), very high contamination (CF ~744) and extreme antimony enrichment (EF ~506) compared to 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.

KEYWORDS

Botswana, geoaccumulation index, mobility factor, risk assessment code, shooting range

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INTRODUCTION

Pollution in shooting range soils has focused mainly on Pb for many years.[1-7] This is due in part to the fact that Pb constitutes more than 90% of bullets and shots followed by Sb (7%) and trace amounts of As (<2%) and Ni (<0.5%).[8] On the other hand, antimony has been used in ammunition for quite some time as a hardening agent in bullets and shots.[9] It occurs naturally at concentrations of 0.15–2.0 mg/kg, < 1 mg/mL and 0.3–8.6 mg/kg in rocks, water and soil respectively.[10] This metalloid, being the second largest constituent of bullets and shots, has captured the attention of researchers and the few studies that have assessed its pollution status alongside Pb have documented significant amounts of this toxic trace element deposited in shooting range soils.[11] In Switzerland alone, 10 tons of Sb have been found in 2000 shooting range soils used by the military and for sports activities.[12] In the United States of America, there are about 3000 military and 9000 non-military shooting ranges with an estimated 1900 tons annual deposition of Sb into the soils.[13] In 2006, approximately 12 tons of Sb were deposited into small arms shooting range soils in Norway.[14] Due to its toxicity and widespread occurrence, Sb has been listed as a priority pollutant by the United States Environment Protection Agency (USEPA) since 1979.[15] Previous studies have shown that the mobility, bioavailability and bioaccessibility of toxic trace metals in shooting range soils are a consequence of weathering and oxidation of bullets and shots.[9] The environmental pollution risk posed by Sb is largely dependent on the chemical form in which it exists. The fate of the solubilized Sb metalloid depends to a large extent, on its chemical partitioning and speciation within shooting range soil matrix. In nature, the most common species of Sb are the neutral Sb(III) ($Sb(OH)_3$) and the anionic Sb(V) ($Sb(OH)^{6-}$).[16] Sb (V) has been found to be the most stable and abundant species and much more soluble than Sb (III).[12] Sb (V) poses a greater pollution risk to the environment than Sb (III) due to its high solubility even at pH close to neutral.[11] In addition, inorganic Sb species have been found to be more toxic than organic Sb compounds and as such Sb (III) is regarded as being more toxic than Sb(V).[17] Organic Sb species have been indicated to be less hazardous in comparison to the inorganic Sb species.[18] The most common organic Sb species include the mono-methylated (methylstibonic acid, $(CH_3)SbO(OH)_2$), di-methylated dimethylstibonic acid, $(CH_3)_2Sb(O)OH$) and tri-methylated (trimethylantimony dichloride, $(CH_3)_3SbCl_2$) chemical compounds which have been reported in soils contaminated with Sb.[18] Therefore, the toxicity of Sb species varies in the order organo-Sb < Sb(V) < Sb(III).[18]

In general, the widespread occurrence of Sb has caught the attention of scientists and researchers due to its carcinogenic effect to humans.[17] Exposure to Sb can induce irritation of the digestive system, slow growth of mammals and cause fertility problems in women.[17] Past research indicates that small concentrations of Sb absorbed and retained in the lungs may have a prolonged biological half-life.[19] Subsequent to acute Sb exposure, the highest concentrations of Sb are normally found in the kidney, adrenals, thyroid and liver and long term exposure gives rise to pneumoconiosis and fatal effects on the heart.[19] The lethal toxicity of Sb to humans has been reported to be 20 mg/kg body weight/day.[20] The presence of Sb in shooting range soils poses risk of Sb being transferred into the food chain through as they can be absorbed by plants and many of the areas studied have also served as grazing fields for domestic animals.[11] Elevated concentrations of Sb have been reported in vegetation growing on soils contaminated with Sb.[21] In addition, concentrations of Sb higher than background levels have also been detected in both surface and underground water sources near shooting ranges.[14] Soil conditions such as soil pH, organic matter (OM), cation exchange capacity (CEC), electrical conductivity (EC) and soil moisture have a significant impact on the speciation, weathering, mobility and fate of metalloid in the soil such as Sb.[14] The acidic pH of the soil has been found to significantly increase the sorption of Sb by Fe (oxy)hydroxides and thereby limiting Sb mobility.[22] Sb (III) has been shown to form a neutral complex $Sb(OH)_3$, in the pH range of 2 to 11, whereas Sb(V) exists predominantly as an oxyanion $Sb(OH)_6^-$ under the same soil pH conditions.[23] Previous studies have also shown that Sb(III) binds strongly to humic acids, making it more

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soluble and thereby accelerating its mobility and bioavailability in the soil.[24] In the presence of moisture and good soil aeration, Sb bound to Fe and Mn (hydr)oxide species can be released into the soil through reductive dissolution whereby the Sb(V) gets reduced to Sb(III) coupled with the oxidation of Fe(II) in the ferrous oxide to Fe(III).[25] The weathering and corrosion of Sb bullets and shots occurs through the oxidation and reduction processes involving aerobic (oxic) and anaerobic (anoxic) conditions.[22] As a result, it is imperative that speciation and redox transformation of Sb are extensively evaluated in order to establish the environmental pollution risk and toxicological effects to the environment of this hazardous element.

Botswana as a developing country needs to be proactive in pollution and waste management at shooting ranges so as to conserve and preserve her precious environment. To the best of our 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. Therefore, the objectives of this study include 1) determination of the concentration of Sb in the soils collected from a shooting range in Botswana, 2) assessment of the mobility and leaching of Sb in the soil 3) establishment of the environmental pollution risk posed by deposition of Sb into shooting range soils by applying pollution risk indices. The extent of Sb contamination of shooting range soils will give an idea on the potential management and control measures for Sb pollution of shooting range soils that can help restrict the migration and mobility of Sb in the soil.

EXPERIMENTAL

Descriptions of the shooting range studied

TAB shooting range is located in the southern part of Botswana with GPS coordinates: 24°14′42.79″ S, 25°19′55.84″ E (Figure 1a). Of particular interest is that TAB shooting range is located in a fenced military camp where military personnel and their families live (Figure 1b). 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.[7]

Soil sampling

Soil sampling was carried out at the berm and target line areas of the shooting range (Figure 2). 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 together 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 from the shooting range.

Analysis of total Sb at TAB shooting range soils

Total Sb concentration was determined using inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer, Optima7300DV). Samples were prepared by acid digestion using USEPA Method 3050. About 0.5 g of soil sample was combined with 25 ml of 1.1 v/v nitric acid in a 50 ml Teflon vial. The content was digested in a dry block digester for 16 hrs. Digested solution was cooled, filtered (Whatman No. 52) and diluted to 50 mL in a volumetric flask. Quality check and assurance was carried out using a certified reference material (CRM) for soil, NCS DC 73320, obtained from the Botswana University of Agriculture and Natural Resource (BUAN). The CRM contained a known concentration of 20 mg/kg of Sb. About 0.1 g of the CRM was taken through the same sample preparation procedure performed on shooting range soils. A percent recovery of 95% was achieved and the precision of measurements was <3% RSD, an indication of good accuracy of the analytical method.

Physical and chemical analysis of soil samples

Soil physicochemical properties such as pH, organic matter (OM) and cation exchange capacity (CEC) were all determined using standard methods. Briefly, pH measurements were carried out by taking 20 g of the homogenized soil sample into 40 ml of deionized water and 0.01 M $CaCl_2$ solution. The resulting soil solution was stirred vigorously and pH measurements were taken using a calibrated crimson basic 20 pH meter after allowing the slurry to settle for 30 minutes. The Walkley-Black procedure was used to determine the soil organic matter (OM).6 Soil cation exchange capacity was assessed using the USEPA Method 9081.

Fractionation studies and mineralogical studies

The migration and mobility of Sb in TAB shooting range soil was established using fractions obtained after the Tessier sequential extraction procedure.[26] This method determines partitioning of Sb in the different soil compartments; water-soluble and exchangeable (WE); carbonate bound (CB); Fe-Mn oxides (FM); organic matter bound (OM) and the residual (RS) fractions.[26] The WE and CB fractions are the most labile whilst the OM and RS fractions are considered inert. The TAB shooting range soil was evaluated using X-ray diffraction (X'pert Philips Electronic Instruments, Inc). The soils were pulverized from which an XRD suitable pellet was prepared. The XRD spectrum was recorded from 10° to 90° 2θ at 30 mA and tension of 45 kV. Minerals were identified using X'pert data high score software.[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.[27] 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.

Figure 1: a) Map of Botswana. b) Satellite map of TAB military camp. c) Expanded view of TAB shooting range inside military camp (Sources: Google Maps)

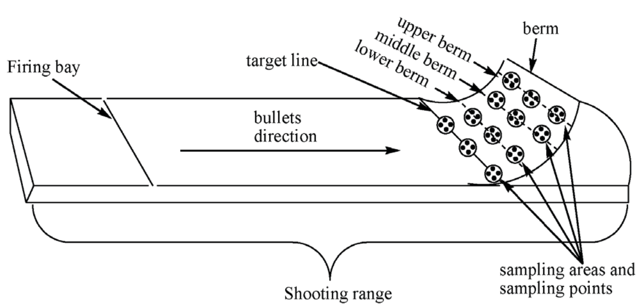

Figure 2: Schematic of sampling points in the berm and target line of TAB shooting range

RESULTS AND DISCUSSION

Analysis of total Sb at TAB shooting range soils

Total antimony concentrations in the range of 38.8–283.5 mg/kg were measured at TAB shooting range (Figure 3). 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 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 trace elements in a specific site and the deposition of spent bullets and shots in the soil found in that particular area.[28,29]

It is important to note that total Sb concentrations measured at TAB shooting range are higher than maximum contaminant limits of 31 mg/kg Sb in soil as set by the United States Environmental Protection Agency (USEPA) and 36 mg/kg as set by the World Health Organization (WHO).[30] Contrastingly, the low concentration of total Sb at the target is evident due to the fact that this section of the berm is furthest away from the point bullets and shots deposition. The occurrence of Sb at the target line is mainly attributed to processes such as friction as the bullet pierced through the target producing Sb powder. The target line is situated at the foot of the berm and, therefore, provides a favourable spot for the deposition of weathered Sb in the upper berm that was mobilised and migrated down the berm slope under gravity. Soil physicochemical properties play a pivotal role in the solubility and mobility of Sb in shooting range soils. The soils at the four sampling points were found to be slightly alkaline with pH range 7.6–8.0 (Table 1). The alkaline soils favour the dissolution of Sb minerals.[31] Conesa et al. (2010), observed enhanced solubility of Sb in shooting range soil with alkaline pH of 8.2.[31] Under alkaline conditions, Sb occurs in the form of an antimonite ($Sb(OH)^{6-}$) in the soil solution and the adsorption of this oxyanion by solid sorbents in the soil is normally not favoured at low pH.[32] 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.[33] 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. Quality control and quality assurance were carried out using the NCS DC 73320 certified reference material (CRM) for soil with recoveries of over 95% and accuracy within <3% RSD.

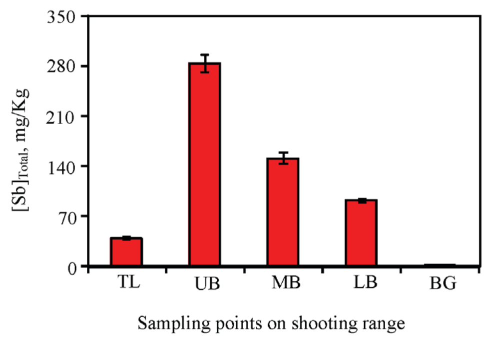

Figure 3: Concentrations of Sb in soils taken from four different points at TAB shooting range found in Botswana. Mean of n = 3; Standard error of the mean, $\delta_{\bar{x}} = \delta/\sqrt{n}$, where δ = standard deviation; TL = target line; UB = upper berm; MB = middle berm; LB = lower berm, and BG = background soil

Table 1. Physicochemical properties of TAB shooting range soils

Location on shooting range	pH_w±SD	CEC±SD (cmol/kg)	Organic matter ± SD (%)
Upper berm	7.80 ± 0.21	5.84 ± 0.32	9.72 ± 0.79
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

SD = Standard deviation, CEC = Cation exchange capacity

Fractionation and mobility of Sb

Sb was largely bound to organic matter (up to 45%), Fe-Mn oxides (30%) and residual matter (35%). 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 (35.4±2.5%) followed by FM (30.3±2.0) and OB (21.0±2.4). The relatively low concentrations of Sb in the labile WE and CB fractions compared to the other fractions is supported by the soil chemical properties of high pH, CEC and organic matter (Table 1). The high pH provides a suitable environment for the dissolution of Sb minerals such as ($Sb(OH)^{6-}$ anions.[17,34] 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 4). The high concentration of Sb in the WE and CB fractions in the upper berm corroborates the claim that the occurrence of Sb at this section comes mainly from Sb released from the weathering and corrosion of the high density of spent bullets and shots in this area. In a similar study by Van Vleek et al. (2011), highest concentration of Sb was found in the WE whereby the majority of spent projectiles were located.[9] The high concentration of Sb in the WE and CB fractions at the lower section of the berm could be a result of the downward migration of soluble Sb minerals.

The mobility of Sb in shooting range soil was estimated using a method suggested by Kabala and Singh (2001) as shown in equation (1).[35]

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

where
F_{WE} = water soluble fraction
F_{CB} = carbonate-bound fraction
F_{FM} = Fe-Mn oxides fraction
FOM = organic-bound fraction
FRS = 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 describes the potential mobility of Sb at TAB shooting range soil. The potential mobility of Sb is given in Figure 5 and show that there is high mobility of Sb at TAB shooting range (mobility factor

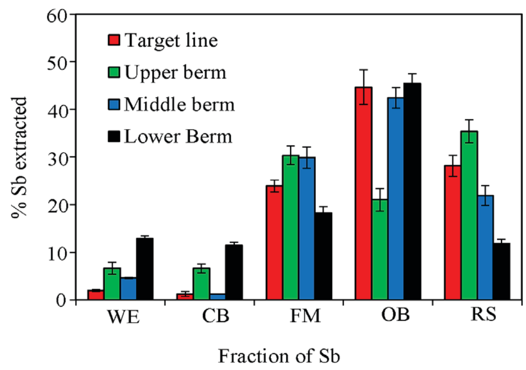

Figure 4: Sequential extraction procedure for Sb at four sampling points of TAB shooting range. Mean of n = 3; Standard error of the mean, $\delta_{\bar{x}} = \delta/\sqrt{n}$, where δ = standard deviation; WE = water exchangeable; CB = carbonate bound; Fe-Mn = iron and manganese oxide bound; OB = organic bound; RS = residual

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, the high soil pH accelerate the dissolution of Sb species such as $Sb(OH)^{6-}$.[17]

X-ray diffraction studies of the soil at TAB reveal the apparent prevalence of iron oxide minerals, such as goethite (α-FeOOH) which are known to form complexes with Sb (Figure 6).[17,24] In a study by Ackermann et al. (2009), amorphous iron oxides such as goethite were found to absorb Sb into their crystalline structure forming inner-sphere complexes.[17] In addition, soil physicochemical properties such as elevated levels of organic matter play a crucial role in the sorption of Sb.[17] The soils found at TAB shooting range 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.[17] The binding of Sb by humic acids in organic matter has been proposed to involve cation exchange process between free Sb ions and the carboxylic acid functional groups.[9] It has also been established that soils rich in organic matter can result in the formation of organo-complexes with concomitant lowering of pH of the formed complexes. Subsequently, the dissolution of the Sb-Fe oxides amorphous structures would take place leading to the release of the sorbed Sb.

Pollution risk assessment of Sb accumulation into the soil

Risk assessment code (RAC)

Risk assessment code (RAC) considers the percentage of Sb present in the mobile and labile fractions.[36] The ecological pollution risk depicted by the RAC codes are as follows; RAC <1% (code 1 and no risk) indicate no risk, 1%< RAC ≤10% (code 2 and low risk), 11%< RAC ≤30% (code 3 and medium risk), 31%< RAC ≤50% (code 4 and high risk) and RAC ≥51% (code 5 and very high risk).[37] This method has been widely applied towards assessment of environmental pollution risk from metalloids and heavy metals such as Sb, Pb, Cu and Cd found in shooting range soils.[27,38,39] 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.

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 ≤25%) compared to the middle and target line sections (4%< RAC ≤6%) as shown in Figure 7. 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 ~32 and medium risk at Cho-Do shooting range (RAC ~26).[38]

Geoaccumulation Index (I_{geo})

Geoaccumulation index (I_{geo}) describes the current contamination of soils with inorganic and organic contaminants relative to pre-industrial levels.[40,41] Risk assessment of pollution from trace element such as Sb can be classified into seven I_{geo} grades where Grade 1 indicates I_{geo} <0 and no pollution from the metalloid, 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). As depicted in Figure 8, 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 7) and total Sb concentrations

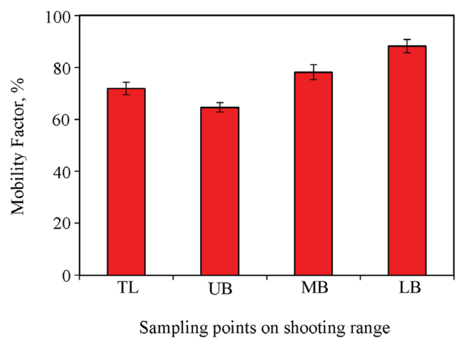

Figure 5: Mobility factor for Sb indicating the migration and fate of Sb at TAB shooting range. Mean of n = 3; Standard error of the mean, $\delta_{\bar{x}} = \delta/\sqrt{n}$, where δ = standard deviation. TL = target line; UB = upper berm; MB = middle berm and LB = lower berm

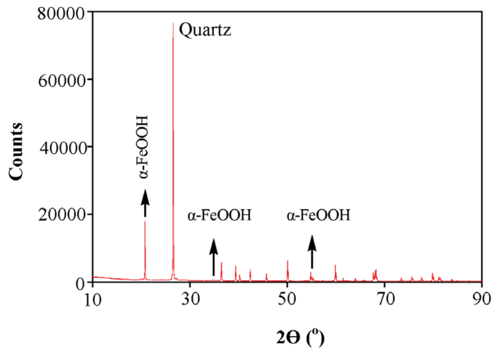

Figure 6: X-ray diffraction analysis patterns indicating the prevalence of α-FeOOH in TAB shooting range soil

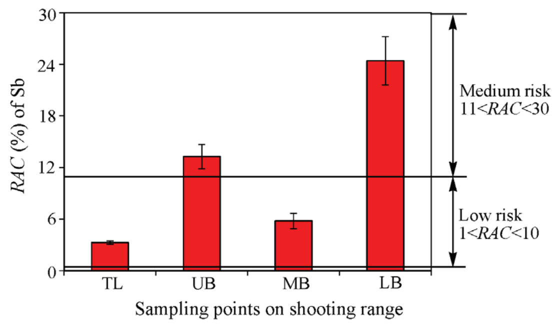

Figure 7: RAC of four different sampling points at TAB shooting range. Mean of n = 3; Standard error of the mean, $\delta_{\bar{x}} = \delta/\sqrt{n}$, where δ = standard deviation. TL = target line; UB = upper berm; MB = middle berm and LB = lower berm

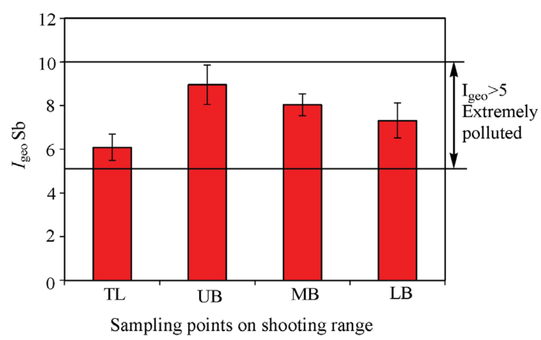

Figure 8: Geoaccumulation index (Igeo) for Sb at four different sampling points at TAB shooting range. Mean of n = 3; Standard error of the mean, $\delta_{\bar{x}} = \delta/\sqrt{n}$, where δ = standard deviation. TL = target line; UB = upper berm; MB = middle berm and LB = lower berm

results (Figure 3). 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)[42] 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.[42] Total concentration of Sb in the berm soils collected at the two shooting ranges were in the range 40.1–93.4 mg/kg.[42]

Contamination Factor (CF)

Contamination factor assesses soil contamination through comparison of geochemical background concentrations with contaminant concentrations in studied sites.[27] 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.[43] It also depicts the input of heavy metals into the environment arising from anthropogenic activities. CF <1 indicates low contamination, 1≤ CF <3 reflects moderate contamination while 3≤ CF ≤6 shows considerable contamination and lastly CF >6 represents very high contamination. In agreement with the results for RAC and I_{geo}, the upper berm (UB) at TAB shooting range experienced very high contamination at a CF ~750 (Figure 9). The very high contamination 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 provide 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 ~11.6.[44] 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.[30] This indicates that total concentration of Sb alone cannot be used to establish the pollution risk from Sb to the environment.

Enrichment Factor (EF)

The impact of human activities on the environment such as shooting exercises can be assessed using enrichment factor [EF].[27] EF relates concentration of a particular element arising from anthropogenic activities to the native undisturbed condition of the soil.[27] 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 such as Sb in the environment.

The degree of soil enrichment from a particular metal falls into seven categories. EF<1 represents no enrichment; 1≤ EF <3 show minor enrichment; 3≤ EF <5 (moderate enrichment); 5≤ EF <10 (moderate to severe enrichment); 10≤ EF <25 (severe enrichment) and EF ≥50 indicates extreme enrichment.[45] High enrichment factors of 69–506 have been determined at TAB shooting range indicating extreme Sb enrichment (Figure 10). 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 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.

IMPLICATIONS OF ANTIMONY POLLUTION FOR SHOOTING RANGE BEST MANAGEMENT PRACTICES

Even though amendment Sb polluted soils is beyond the scope of this study, it is however, important to highlight some of the potential soil amendment techniques that are available. The accumulation of Sb into TAB shooting range soils calls for pollution management and control procedures and protocols as suggested in manuals by the World Health Organisation (WHO)[30] and the United States Environmental Protection Agency (USEPA).[46] The USEPA has set out four main soil pollution management strategies at shooting ranges which include; (i) handling and confinement of spent projectiles, (ii) restriction of migration of contaminants, (iii) extraction and recycling of spent bullets and shots and (iv) recording and evaluation of environmental management plans (USEPA 2005).[46] Traps can be set up at shooting ranges to confine spent projectiles and prevents their contact with the soil and thereby preventing leaching of Sb into the soil. The collected spent projectiles can then be safely disposed.[47] Restriction of migration of weathered Sb chemical species can involve use of chemical amendments such as phosphate addition and liming.[49] Chemical amendments immobilise and reduce the solubility, mobility and leaching of Sb in shooting range soils.[50] Phytoremediation is an environmentally friendly method that involves the use of vegetation for the extraction of contaminants from polluted shooting range soils resulting in reduced mobility and migration of Sb chemical species in soil.[51]However, the physicochemical properties of shooting range soils should be considered for a successful remediation and soil reclamation effort.

CONCLUSIONS

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

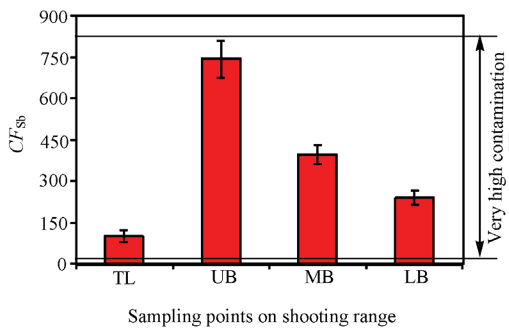

Figure 9: Contamination factor (CF) for Sb at four different sampling points at TAB shooting range. Mean of n = 3; Standard error of the mean, $\delta_{\bar{x}} = \delta/\sqrt{n}$, where δ = standard deviation. TL = target line; UB = upper berm; MB = middle berm and LB = lower berm

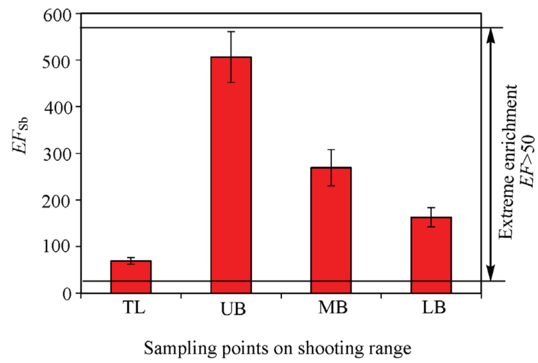

Figure 10: Enrichment factor (EF) for Sb at four different sampling points at TAB shooting range. Mean of n = 3; Standard error of the mean, $\delta_{\bar{x}} = \delta/\sqrt{n}$, where δ = standard deviation. TL = target line; UB = upper berm;MB = middle berm and LB = lower berm

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. As such 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. Other cost effective methods that are also environmentally friendly include 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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