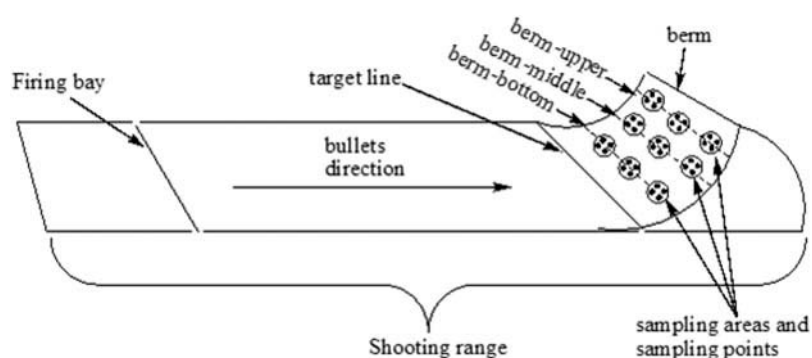




ENVIRONMENTAL CHEMISTRY, POLLUTION & WASTE MANAGEMENT | RESEARCH ARTICLE

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Pollution status of shooting range soils from Cd, Cu, Mn, Ni and Zn found in ammunition

Pogisego Dinake^{1*}, Onneetse Maphane¹, Karabo Sebogisi² and Obed Kamwi³

Abstract: Evaluation of concentration of heavy metals found in shooting range soil is important in assessing the pollution risk posed to biota. Soil samples from five shooting ranges found in Botswana were used in this study. All the five shooting ranges accumulated high concentration of Cu ranging from 67.4 ± 0.05 mg/kg to 1569 ± 13 mg/kg followed by Mn (25.9 ± 0.1 – 953.8 ± 2.8 mg/kg). Pollution risk indices were used to quantify the environmental pollution risk posed by the different heavy metals studied. It was established that even though all the five shooting ranges recorded low concentrations of Cd, this metal still posed the highest pollution risk than any other metal with S/P shooting range recording the highest potential ecological risk index (*peri*) of 8141 ($C_{Cd} \sim 3.6 \pm 0.03$ mg/kg) and TAB at *PERI* of 3507 ($C_{Cd} \sim 4.9 \pm 0.02$ mg/kg). Similarly, contamination factor (*CF*) value of 271 for Cd was measured at S/P shooting range indicating high contamination from Cd. Pollution risk indices were able to establish that even though concentration of Cd accumulated in the soil was low this heavy metal still posed highest pollution risk to biota. Continuous assessment of the pollution status of these shooting ranges should be carried out in order to establish appropriate best shooting range management practices and remedial strategies.

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Pogisego Dinake works as a lecturer in the department of Chemical and Forensic Sciences, Botswana International University of Science & Technology (BIUST), Botswana. He obtained his PhD in Chemistry in 2012 at Howard University in the United States of America (USA). His research interests are in Environmental Analytical Chemistry. He investigates environmental pollution of air, soil, water and living organisms from trace metals and organic pollutants. He also studies; chemical speciation of heavy metals in water, soil and biological systems and chemical remediation of toxic trace metal contaminated water and soil. He also applies supramolecular chemistry in the design, synthesis and application of macro ligands for environmental pollution monitoring such as molecular sieves for waste water purification. He has collaboration with researchers in Botswana, South Africa and USA. He has published in international journals. Recently he has established his own research laboratory and working on various environmental pollution projects.

PUBLIC INTEREST STATEMENT

This study is the first in Botswana in assessing pollution in shooting range soils from ammunition. Shooting ranges are a source of environmental pollution since toxic heavy metals are major constituents of bullets. Concentrations of toxic metals in the five military shooting ranges that have been in operation for over 30 years exceeded the world health organization (WHO) set limits. These toxic metals can be absorbed by plants endangering humans and animals that consume them. Adverse health effects such as respiratory and kidney problems can result from exposure to these hazardous metals. Most of the shooting ranges studied are not fenced making them accessible as grazing fields. Surface and underground water pollution is possible resulting in these toxic metals finding their way into the food chain. Therefore remedial measures such as cleaning of contaminated soils and fencing of shooting ranges should be carried out as soon as possible.

Subjects: Environment & agriculture; Earth sciences; Environmental studies & management; Physical sciences

Keywords: ammunition; shooting range; pollution risk index; environmental pollution; Botswana

1. Introduction

Heavy metals such as arsenic (As), antimony (Sb), cadmium (Cd) and zinc (Zn) present multi-element detrimental effects to biota (Seshadri et al., 2017). Shooting ranges have been found to be among the main sources of heavy metal pollution of the environment. Shooting ranges are the main source of environmental lead (Pb) pollution after the battery industry (Sehube et al., 2017) and most if not all heavy metal pollution of shooting range soil has focused on Pb (Mariussen, Johnsen, & Strømseng, 2017). This is due, in part, to the fact that ammunition contains an excess of 80% Pb slug and small traces of As, Sb, Cd, Cu, Ni, Mn and Zn whose environmental impact is rarely studied (Hockmann et al., 2015). Ammunition shots and bullets have been found to contain 95–97% metallic Pb by weight, 0.4–2.0% Sb, 0.2–0.8% As and mean concentrations of Sn, Se, Mn, Cd, Cr, Cu and Ni greater than 30 mg/kg (Fayiga & Saha, 2016). Pb is mainly found in the core of bullets and shots while Cu, Zn and Sb are constituents of bullet ore heads and cartridges (Mariussen et al., 2017; Urrutia-Goyes, Argyraki, & Ornelas-Soto, 2017).

Copper, zinc and nickel are essential elements in plants. Copper is a constituent of enzymes and plays a significant role in photosynthesis (Lange et al., 2017). Zinc Nickel is a component of the enzyme urease which plays an important function in seed germination (de Queiroz Barcelo et al., 2017). However, increased concentrations of these biologically important trace elements can have detrimental effects to biota. Accumulation of Zn in plants inhibits the uptake of iron and copper leading to pale yellow interveinal chlorosis on the leaves (Broadley, White, Hammond, Zelko, & Lux, 2007). Exposure to antimony causes respiratory problems such as chronic bronchitis, chronic emphysema, inactive tuberculosis, pleural adhesions and respiratory irritation characterized by chronic coughing, wheezing and upper airway inflammation (Sundar & Chakravarty, 2010). The adverse health effects associated with exposure to As include replacing other elements in plant enzymes leading to plant stunted growth and eventual death (Nagajyoti, Lee, & Sreekanth, 2010). Adverse health effects associated with exposure to arsenic (As) also include cardiovascular, diabetes and cancer as usually reaches the blood stream through ingestion, inhalation and skin contact (Alexander, Gulledge, & Han, 2016). Cardiovascular effects due to exposure to Sb in humans include increased blood pressure and alteration of electrocardiography (ECG). Abdominal pain, diarrhoea, vomiting, and ulcers are some of the gastrointestinal effects associated with exposure to Sb (Okkenhaug et al., 2013). High level of Cd causes decrease in seed germination, stunted growth in plants, disrupt enzyme activities and makes plants prone to fungal invasion (Laghlami, Baghdad, El Hadi, & Bouabdli, 2015). Its compounds relatively have high solubility in the soil making Cd more mobile and bioavailable (Sharma & Sachdeva, 2015).

Copper (Cu) is an essential element to plants, however, high levels of copper can lead to disruption of plant photosynthesis and reproduction processes (Laghlami et al., 2015). High concentrations of Cu have adverse health effects to the gastrointestinal tract and the liver. Pulmonary fibrosis and increased vascularity have also been reported in people exposed to high levels of copper (Laghlami et al., 2015). Low concentration of Cu has been reported to cause brain damage in animals (Department of Water Affairs and Forestry, 1996). Nickel is a known epigenetic carcinogen and can cause genetic modifications (Brocato & Costa, 2017). Physicochemical processes in the soil such as physical weathering, oxidation, sulfonation, dissolution and precipitation transform these heavy metals into the mobile and bioavailable forms that are detrimental to the biota (Kelebemang et al., 2017). Antimony is the second largest shooting range pollutant after Pb comprising 7% of bullet shot and bullet (Rooney, McLaren, & Cresswell, 1999). Sb concentration of 13,800 mg/kg has been found in a Swiss shooting range (Johnson, Moench, Wersin, Kugler, &

Wenger, 2005). Elevated concentrations of 5200 mg/kg, 1100 mg/kg and 830 mg/kg corresponding to Cu, Zn and Sb have been established at a Norwegian shooting range (Mariussen et al., 2017). These high concentrations of heavy metals were able to find their way into the water sources with concentrations of Zn, Cu and Sb in surface water measuring 1.6, 0.9 and 0.15 mg/l respectively (Mariussen et al., 2017). Other such high pollution from heavy metals such as Cu, Cd, Zn, Sb, As and Ni other than Pb emanating from ammunition have been found in Canada (Lafond, Blais, Martel, & Mercier, 2013), Spain (Rodríguez-Seijo, Alfaya, Andrade, & Vega, 2016), Switzerland (Evangelou, Hockmann, Pokharel, Jakob, & Schulin, 2012), South Korea (Lee et al., 2002) and the United States of America (Sehube et al., 2017). Most of these shooting range soils accumulated heavy metals concentrations far exceeding the USEPA critical limits. Heavy metal contamination of shooting range soils also poses risk of surface and underground water pollution (Wersin, Johnson, & Furrer, 2002). Concentrations of Sb as high as 1.59 mg/L have been reported in water found in close proximity to a shooting range (Okkenhaug et al., 2013). The accumulation of heavy metals into the soil which in turn may bind to the soil organic matter and eventual dissolution thereof has the potential to negatively affect the soil carbon sequestration process exacerbating the climate change phenomena (Jastrow, Amonette, & Bailey, 2007).

Heavy metals uptake by plants has also been reported leading to heavy metals finding their way into the food chain (Mozafar et al., 2002; Robinson et al., 2008). Elevated heavy metal concentrations of 25 mg/kg and 50 mg/kg for Cu and Ni respectively, have been found in plant species, which are a source of food for livestock (Robinson et al., 2008). Nine plant species in two decommissioned shooting ranges have been evaluated for their Cu, Zn, Sb and Cd concentrations and the potential health risk to animals made to graze in such shooting ranges (Evangelou et al., 2012). At a clay pigeon shooting range in Tuscany (central Italy) high concentrations of Sb, Ni, Zn, Mn and Cu were found in arthropod communities inhabiting shooting range soils (Migliorinia, Pigino, Bianchi, Bernini, & Leonzio, 2004). A reduction in soil enzymatic activity has also been reported in soils contaminated with heavy metals such as cadmium can have a negative effect in the soil chemistry due to its harmful effect to the microorganisms found in the soil which are important to soil fertility (Vig, Megharaj, Sethunathan, & Naidu, 2003). The mobility, bioavailability and bioaccessibility of heavy metals in shooting range soils is dependent on the physicochemical properties of the soil such as soil pH, cation exchange capacity (CEC), soil organic matter and moisture (Kelebemang et al., 2017). Under favourable conditions of soil properties the chemical weathering, solubility, mobility and bioavailability of heavy metals in shooting range soils can be enhanced (Ma, Hardison, Harris, Cao, & Zhou, 2007).

To the best of our knowledge no research has been carried out on heavy metal pollution of shooting range soils in Botswana except Pb, a study that was carried out by our research group. Botswana has shooting ranges all over the country that are used for shooting practices by the military, police services, prisons services and department of wild life national parks. This study follows our pioneering study that looked into pollution of shooting range soils from Pb which is the main constituent of ammunition (Sehube et al., 2017). Our pioneering study found elevated Pb pollution in shooting range soils with highs of up to 38 406.87 mg/kg far exceeding the set USEPA critical limit of 400 mg/kg Pb in soil (Sehube et al., 2017). Evaluation of the extent of shooting range soil pollution from heavy metals can help strengthen best management practices of shooting ranges. Soil remedial processes can also be employed for soil cleaning and reclamation. Based on the extent of heavy metal pollution, soil remediation methods and techniques such as chemical immobilization, physical soil excavation, phytoremediation and chemical washing techniques have been utilized in fighting shooting range soil heavy metal pollution (Sorvari, Antikainen, & Pyy, 2006). The objectives of this study include (1) quantitative evaluation of heavy metal pollution of shooting range soils found in Botswana (2) environmental pollution risk assessment of such pollution based on such methods as potential ecological risk index (PERI), heavy metal pollution load index (RI) and contamination factor (CF). The findings of this study will provide a baseline data for heavy metal pollution of shooting range soils in Botswana and will also provide a basic measure on the extent of heavy metal pollution emanating from similar ammunition used elsewhere

around in world. Appropriate remedial strategies and methods may also be suggested based on the extent of pollution encountered in the studied shooting ranges and shooting ranges using same type of ammunition around the world. In addition best shooting range management practices for future shooting range users will be suggested.

2. Materials and methods

2.1. Location and description of shooting ranges

Five military shooting ranges scattered across Botswana were used in this study. These shooting ranges are mostly used for small arms shooting practices using rifles of calibres 0.50", 5.56 mm, 7.62 mm, 7.65 mm and 9 mm. It is important to note that small arms ammunition contain predominantly the heavy metals under study. The five shooting ranges were Thebephatshwa (TAB) located in the southern part of the country (GPS coordinates: 24° 14' 42.79" South, 25° 19' 55.84" East), Shoshong (SHO) in central Botswana (GPS coordinates: 23° 2' 8.28" South, 26° 30' 7.12" East), Selibe Phikwe (S/P) in eastern Botswana (GPS Coordinates: 27° 50' 14.39" East, 21° 57' 58.55" South), Matsiloje, (MAT) with GPS coordinates: 21° 22' 12.00" South, 27° 52' 12.00" East in north eastern Botswana and lastly Pandamatenga (PANDA) located in northern Botswana (GPS coordinates 18° 31' 57.01" South, 25° 39' 14.22" East). The five shooting ranges and their year of establishment are shown in Figure 1(a) below. It is important to note that all these shooting ranges have been in operation for the past 16–32 years and that there has never been a single study carried out on possible pollution risk from heavy metal accumulation in these shooting ranges. Two of the shooting ranges studied are located in fenced military camps while the other three occur in open areas acting as grazing fields for livestock and small stock.

2.2. Soil sampling procedure and techniques

Berm soil samples were collected to a depth of 20 cm using a soil recovery probe in all the five the shooting ranges. This soil represents the surface layer (0–5 cm), the subsurface layer (5–10 cm) and the deeper soil layer (10–20 cm). The berm accumulates the highest proportion of bullets and shots since it acts as a barrier for bullets and shots after they have hit the target. The berm section of the shooting range was divided into three segments being; berm-upper, berm-middle and berm-bottom (Figure 2). The berm was divided into three sections because some bullets and shots can land at the bottom, or middle or upper section of the berm. Three circular sampling areas of radius 150 cm were made at the upper, middle and bottom of the berm along a central transect. In addition, four samples were collected from the three sampling points within the sampling area to make three composite samples representative of the upper, middle and bottom berm soils (Figure 2). This sampling technique was preferable because it covers a large area making the sample a true representation of the study site. Control soil samples which served as background samples were collected at a distance of 200 m away from the five shooting ranges. The collected samples were

Figure 1. (a) Location of shooting ranges sampled on the map of Botswana. (b) Map of Africa showing location of Botswana.

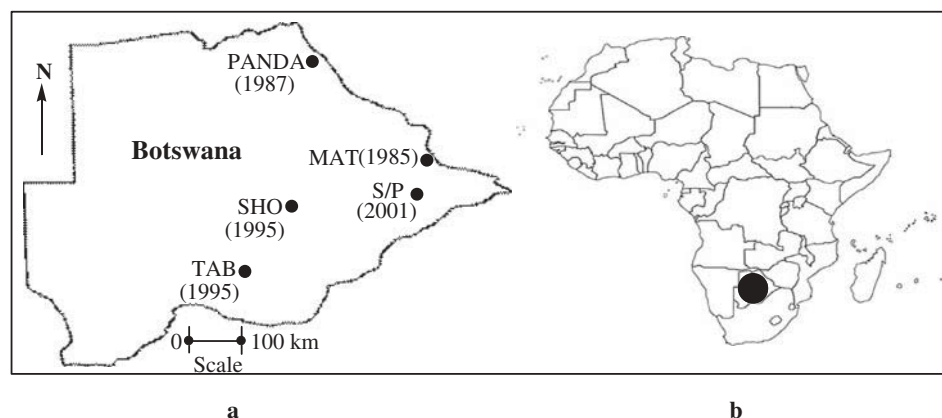
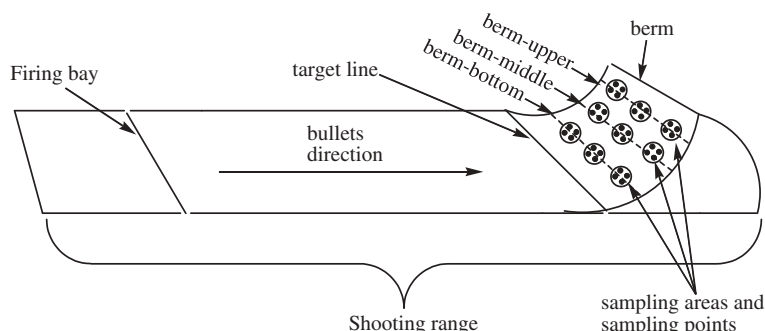


Figure 2. Schematic of sampling points in the berm of the shooting range.



then stored in butyrated zip-lock plastic bags for transportation to Botswana University of Agriculture and Natural Resources (BUAN) for further sample treatment and analysis.

2.3. Soil sample preparation and chemical analysis

The three quadruplicate samples from sampling points in three sampling areas of berm-upper, berm-middle and berm-bottom were mixed together to obtain three composite samples corresponding to each berm section. A total of nine berm soil samples were obtained from each range making a grand total of forty-five soil samples. The soil samples were air dried for a day after which a 2 mm stainless steel sieve was used to remove spent bullets, stones and rock pebbles, dry tree leaves and small tree barks. Soil sample digestion was achieved using the dry heating-block digestion procedure (USEPA Method 3050) by taking a 0.500 g of soil samples in 100 mL of 1:3 HNO₃/HCl mixture for two hours. After sample digestion total Cd, Cu, Ni, As, Sb and Zn concentrations were analysed using inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer, Optima 2100 DV). Quality check and control was done using certified reference material (CRM) of soil, NCS DC 73,320, obtained from the Botswana Geoscience Institute (BGI).

2.4. Physicochemical properties of shooting range soils

The physicochemical properties of the soil such as pH, electrical conductivity (EC), organic matter (OM) and cation exchange capacity (CEC) were determined using standard methods. A mixture of 0.01 M CaCl₂ solution and 40 mL of deionized water were added to 20 g of soil sample and pH measurements were taken using a calibrated crimson basic 20 pH meter at 25°C. The Walkley-Black procedure was used for the determination of the organic matter (OM) content as reported in the literature (Nelson & Sommers, 1982). The soil electrical conductivity (EC) was carried out in the ratio of 1:2 soil to water using the HACH SenseIon EC7 electrical conductivity meter (Tchoumou, Kami-Ouako, Mbilou, & Ossebi, 2017).

2.5. Environmental risk assessment of pollution from heavy metals

2.5.1. Potential ecological risk index

Potential ecological risk index (PERI) method was first used by Hakanson in 1980 (Hakanson, 1980). This method provides a powerful tool for estimating environmental pollution by combining the ecological and environmental impacts with toxicology (Ke et al., 2017). The potential ecological risk index of a single heavy metal (E_R^i) is given by Equation (1) below while Equation (2) evaluates the ecological risk (RI) emanating from contributions by all the toxic heavy metals present in the soil. The T_R^i signifies the biological toxic response factor of an individual metal while C_i and C_0 are concentrations of individual heavy metal and its background concentration respectively. The T_R^i values of the heavy metals under study are Cd = 30, Cu = Ni = 5 and Mn = Zn = 1 (Ke et al., 2017; Soliman, Nasr, & Okbah, 2015). Table 1 below categorises the potential ecological risk indices with corresponding pollution risk level.

$$E_R^i = T_R^i \times C_i/C_0 \quad (1)$$

Table 1. Categories of *PERI* and *RI* indicating the pollution risk level of heavy metals to the soil (Ke et al., 2017)

Pollution indicator	Pollution risk level				
	Low	Moderate	Considerable	High	Very high
E_R^i	<40	$40 < E_R \leq 80$	$80 < E_R \leq 160$	$160 < E_R \leq 320$	$E_R \geq 320$
<i>RI</i>	<150	$150 < RI \leq 300$	$300 < RI \leq 600$	$RI \geq 600$	

Table 2. Classification of contamination factor and corresponding level of soil contaminate on from heavy metal accumulation (Ke et al., 2017)

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

$$RI = \sum_{i=1}^m E_R^Q \quad (2)$$

2.5.2. Contamination factor

Assessment of pollution level can also be carried out using other pollution indicators such as the contamination factor (*CF*), given in Equation (3) below, where C_i and C_b are the mean concentrations of the heavy metal under investigation and its background concentration respectively. This represents the contamination level of an individual target heavy metal. Contamination factor, *CF*, correlates the background concentration of heavy metals in the soil with contributions from anthropogenic activities. The classification for contamination factor values and the corresponding degree of pollution are shown on Table 2 below.

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

The resultant overall integrated contamination given by the different target metals in the soil is evaluated using the pollution load index (PLI), given by Equation (4) below. It is determined by calculating the *n*th root of the *n* contamination factors (CF_n) multiplied together (Cao et al., 2015)

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots CF_n)^{\frac{1}{n}} \quad (4)$$

The $PLI > 1$ denotes polluted soil while $PLI < 1$ indicates no heavy metal pollution (Cao et al., 2015)

2.6. Statistical analysis of data

A statistical analysis technique such as the Pearson correlation coefficient (*r*) was used to evaluate the concomitant contributions towards heavy metal pollution from the soil physical and chemical properties as shown on Table 3 below. Pearson correlation coefficient can also help ascertain if the heavy metal pollutants under investigation have common anthropogenic source.

3. Results and discussion

3.1. Physicochemical properties of shooting range soils

The soils in the all the five shooting ranges studied experienced neutral to slightly alkaline pH. Shooting ranges such as S/P and SHO experienced neutral pH values of 6.7 and 6.9 respectively

Table 3. Pearson correlation coefficient range indicating the possible correlation between the properties of the soil and degree of pollution (Pejman, Bidhendi, Ardestani, Saeedi, & Baghvand, 2017)

Pearson correlation coefficient range	Correlation effect
0.5 to 1.0 or -0.5 to -1.0*	High correlation
0.3 to 0.5 or -0.3 to -0.5	Medium correlation
0.1 to 0.3 or -0.1 to -0.3	Low correlation

*A high negative Pearson correlation coefficient signifies direct negative correlation between two variables.

(Table 4). On the other hand, PANDA, MAT and TAB soils were slightly alkaline recording pH values of 8.3, 8.5 and 8.6 respectively. The soil pH values found in the five shooting ranges are consistent with the soil pH for the respective areas in which the shooting ranges are found (Ekosse & Anyangwe, 2012; Joshua, 1991). For example, in PANDA, the soil type is mainly dark clay vertisols with a pH range of 6.5 to 9.0 (Almendros et al. 2003; Moganane, Van Waveren, & Remmelzwaal, 1991). The alkaline soil pH of 8.3 found at the MAT shooting range is consistent with the alkaline soil pH of the soils found in the Matsiloje area which can reach pH values of 9.0 (Mitchell, 1976). The organic matter (OM) found in the five shooting ranges was in the range 0.54–1.88% with S/P soils experiencing the highest OM relative to the other four shooting ranges. The soil organic matter found at the five shooting ranges studied is consistent with average organic matter content of (0.5–1.9%) for the soils found in the study sites (Almendros et al. 2003; Joshua, 1991; Pardo, Ristori, D'acqui, & Almendros, 2003). For example, at the PANDA shooting range, organic matter of 0.54% was measured and previous studies found similar organic matter content in the Pandamatenga area in which the PANDA shooting range is located (Moganane et al., 1991). The soils electrical conductivity (EC) were in the range 33.9 ± 3.3 to 208.9 ± 8.8 $\mu\text{S/cm}$ and the highest electrical conductivity was recorded at S/P shooting range soil (Table 4). The organic matter and pH measurements at the five shooting ranges are within range of our preliminary studies on Pb pollution in the same shooting ranges (Kelebemang et al., 2017; Sehuba et al., 2017).

3.2. Total heavy metal concentration in shooting range berm soils

The berm soils of all the five shooting ranges accumulated highest concentrations of Cu in the range 67.4 ± 0.05 mg/kg to 1569 ± 13 mg/kg followed by Mn (25.9 ± 0.1 – 953.8 ± 2.8 mg/kg) as shown on Figure 3(a–c) below. On average, the berm soil of TAB shooting range collected the highest concentration of Cu (1190.7 mg/kg) compared to the other shooting ranges. On the other hand, all the shooting ranges investigated experienced lower concentrations of Cd of the range 0.2 ± 0.08 – 5.0 ± 0.064 mg/kg. The lowest concentration of Cd (0.2 ± 0.08 mg/kg) was recorded at MAT shooting range. The degree of pollution at a shooting range correlates to a larger extent with the frequency of shooting range use than the duration period the shooting range has been in use. TAB shooting range, even though started operation in 1995, accumulated the highest concentra-

Table 4. Physical and chemical properties of shooting range soils

Shooting Range	pH(H ₂ O) $\pm \delta^a$	OM ^b $\pm \delta(\%)$	EC ^c $\pm \delta$ ($\mu\text{S/cm}$)
TAB	8.6 ± 0.2^d	1.26 ± 0.13	170.8 ± 8.4
SHO	6.9 ± 0.2	0.73 ± 0.06	92.5 ± 8.0
S/P	6.7 ± 0.03	1.88 ± 0.42	208.9 ± 8.8
MAT	8.5 ± 0.1	0.73 ± 0.05	52.0 ± 23.8
PANDA	8.3 ± 0.1	0.54 ± 0.01	33.9 ± 3.3

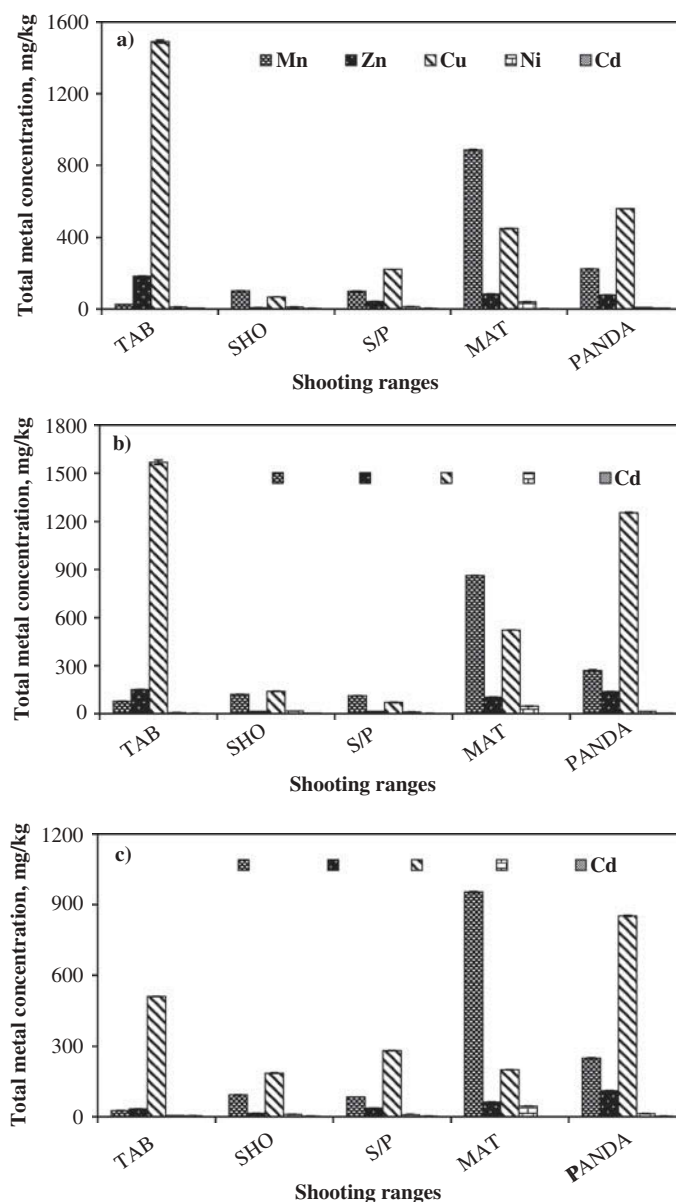
^a δ = Standard deviation.

^bOrganic matter.

^cElectrical conductivity.

^dMean $\pm$ standard deviation ($n = 3$).

Figure 3. Total concentration of five heavy metals in shooting range berm soils found in Botswana. (a) Upper-berm; (b) Middle-berm and (c) Lower-berm. Mean of $n = 3$; Standard error of the mean, $\delta x = \delta/\sqrt{n}$, where δ = standard deviation.



tion of Cu compared to the other shooting ranges studied that were established some years earlier such as MAT (1985) and PANDA (1987) with measured concentrations of Cu of 390.8 ± 0.6 mg/kg and 888.5 ± 2.3 mg/kg respectively. As shown in our earlier studies (Sehube et al., 2017), TAB shooting range accumulated the highest concentration of Pb ($38\,386 \pm 10\,197$ mg/kg) due to its frequent use by the Special Forces commando squadron based at the Thebephatshwa air base. The results from our previous studies correlate well with our current study. The middle of the berm accumulated the highest concentration of heavy metals compared to the upper and bottom sections of the impact berm. For an example, TAB shooting range experienced concentrations of 1569 ± 13 , 1490.7 ± 9.1 and 512.3 ± 0.5 mg/kg of Cu at the middle, upper and lower part of the impact berm respectively. One of the reasons for this observation is that when shooting at the targets, most of bullets and shots accumulate in the middle of the impact berm making this section of the berm have the highest density of bullets and shots resulting in higher concentrations of heavy metals around the same area. MAT shooting range acquired the highest average concentration of all the five studied heavy metals. Previous studies have discovered elevated

concentrations of heavy metals in berm soils of shooting ranges. A study by Islam, Nguyen, Jung, and Park (2016) found elevated concentrations of Cu at four times higher than the allowed Korean maximum contaminant level (MCL) of 150 mg/kg and Cd was found to be two times higher than the Korean warning level (Islam et al., 2016). Similar studies found that concentrations of Cu and Ni in shooting range berm soils far exceeded the Dutch Intervention Values (DIV) of 190 mg/kg and 210 mg/kg respectively (Robinson et al., 2008). It is important to note that this study is the first of its kind in Botswana and that there is no local information in the literature for heavy metals pollution in shooting range soils that could be used for comparisons. As a result, the findings obtained in this study were therefore used to investigate the extent of shooting range soils pollution from heavy metals Cd, Cu, Mn, Ni and Zn. A previous study by Mmolawa, Likuku, and Gaboutloeloe (2011) in the Matsiloje area where the MAT shooting range is found was able to measure soil background concentrations of 0.97 mg/kg Mn; 0.50 mg/kg Ni; 0.11 mg/kg Cu and 0.34 mg/kg Zn. In comparison, the concentrations of Cu, Mn, Ni and Zn found at MAT shooting range soil are much higher than these background concentrations, an indication that heavy metals from ammunition contributed to these high amounts of heavy metals deposit into shooting range soils. For example, the average concentration of Cu in the berm soils of MAT (390.8 ± 0.6 mg/kg) shooting range is 3500 times higher than the background concentration while the Ni concentration (44.7 ± 0.2 mg/kg) at the same shooting range was 90 times higher than the background concentrations. Quality control was performed using a soil certified reference material, NCS DC 73,320. A percentage recovery of over 90% was obtained for all the five heavy metals studied with accuracy of measurements within <3% RSD.

3.3. Effect of pH, organic matter and electrical conductivity on the distribution of heavy metals in shooting range soils

The soil properties such as pH, organic matter (OM) and electrical conductivity (EC) may have had an effect on such elevated levels of heavy metals at MAT shooting range. The alkaline soils (pH 8.6) at TAB shooting range provided for a suitable environment for the corrosion of the elemental heavy metals under study (Table 4 above). Concentrations of heavy metals Cu and Mn of up to 1569 ± 23 mg/kg and 184 ± 0.9 mg/kg respectively were recorded at TAB shooting range. At elevated pH, oxides, hydroxides, carbonates, sulphates and phosphates of the heavy metals under study become insoluble, thereby increasing their retention time in the soil. Their mobility become greatly reduced at elevated pH levels (Sporting Arms and Ammunition Manufacturers' Institute [SAAMI] 1996). Previous studies have found that soils with pH values of ≥ 7.0 experience restricted mobility of heavy metals whereas soils with pH values of ≤ 6.5 undergo enhanced metal mobility (SAAMI 1996). Our findings corroborate our previous studies where it was found that alkaline soils increased the stability of heavy metal oxides such as Pb oxides and carbonates (Sehube et al., 2017). A study by Ma et al. (2007) found out that as soil pH increased the weathering processes of Pb shot was greatly reduced leading to a decrease in mobility of Pb. The amount of organic matter (OM) present in the soil has been found to provide a suitable environment for the weathering of bullets and shots. Organic matter helps in the transformation of heavy metals present in shots and bullets into soluble complexes and thereby increasing the bioavailability and mobility of such heavy metals in the soil (Kelebemang et al., 2017; Sehube et al., 2017). S/P shooting range recorded the highest amount of organic matter ($1.88 \pm 0.42\%$ OM) while the lowest amount of organic matter ($0.54 \pm 0.01\%$ OM) was measured at PANDA shooting range.

The electrical conductivity evaluates the concentration of soluble salts present in the soil (Carmo, Lima, & Silva, 2016). Higher electrical conductivity (EC) in the soil implies higher concentrations of heavy metals in the soil are present in soluble form. S/P and TAB shooting range soils recorded the highest electrical conductivity values of 208.9 ± 8.8 μ S/cm and 170.8 ± 8.4 μ S/cm respectively. Consequently, TAB and S/P shooting ranges accumulated the highest concentrations of heavy metals in the berm soils. Concentrations reaching highs of 1569 ± 23 mg/kg and 282 ± 2 mg/kg Cu were recorded at TAB and S/P shooting range soils respectively. There is a direct relationship between the amount of organic matter in the soil and its electrical conductivity. Organic matter leads to production of organic and inorganic acids that are capable of dissolving

heavy metal complexes in the soil registering high values of electrical conductivity giving rise to increased bioavailability and mobility of heavy metals in the soil (Verma, Sharma, & Paramanick, 2015). To the best of our knowledge, no study has been conducted in Botswana shooting ranges that assessed the environmental impact of heavy metals such as Cd, Cu, Mn, Ni and Zn making it difficult to compare our findings with the similar data found elsewhere in Botswana.

3.4. Environmental risk assessment of pollution from heavy metals

3.4.1. Potential ecological risk index and RI

All the five shooting ranges experienced between moderate to very-high ecological pollution risk from Cd. The ecological risk index level due to Cd was in the range 52–8141 as shown on Table 5 below. The ecological risk index (*PERI*) for Cd was highest for S/P (8140.9) followed by TAB (3507.4) and lowest for PANDA (51.9) shooting ranges. It is worth noting that even though all the five shooting ranges accumulated the lowest amounts of Cd compared to the other four heavy metals (Mn, Zn, Cu and Ni), these small amounts of Cd pose the highest ecological risk compared to the other four heavy metals due to its high toxicity effect. Cd has lower USEPA critical limit (7.1×10^1 mg/kg) implying accumulation of smaller amounts of Cd into the soil pose a pollution risk. On the other hand the other heavy metals studied have much higher critical limits in the soil in which Cu = 3.1×10^3 mg/kg, Ni = 8.2×10^2 mg/kg, Zn = 2.3×10^4 mg/kg and Mn = 1.8×10^3 mg/kg. Most of the shooting ranges such as MAT and PANDA showed very low ecological risk from Mn with risk indices of 0.07 and 0.04 respectively even though the two shooting ranges accumulated higher concentrations of Mn (Table 5). This means that even though the shooting ranges may have experienced elevated levels of Mn, such high concentrations do not pose an ecological risk to the environment due in part to the high critical limit of Mn in the soil. The sum of the ecological risk indices (*RI*) of all the heavy metals studied indicates very high ecological risk with *RI* values greater than 600 for the three ranges TAB, SHO and S/P as shown in Table 5 below. The high *PERI* and *RI* indices quantify the potential risk posed by heavy metals to the living organisms inhabiting the shooting range soils and immediate environment. High potential ecological risk index of 1158 for Cd has been reported before in literature implying ecological hazard to biota (Shen et al., 2017). The high *PERI* and *RI* indices indicate that drastic remedial measures need to be taken to arrest the ecological contamination risk posed by these heavy metals to shooting range soils.

3.4.2. Contamination factor

The contamination factors (*CF*) corroborate the *PERI* and *RI* results. Cadmium (Cd) displayed the highest contamination factor than any other heavy metal studied in the five shooting range soils. *CF* for Cd was determined in the range 2–271 in all the five shooting ranges, indicating moderate to very high contamination of the soil from Cd (Table 6). As seen from the *PERI* results, the *CF* for S/P indicate that this shooting range experienced the highest contamination from Cd than any other shooting range under study. Contamination factor has been used as a good estimate of pollution risk of heavy metals in the soil (Matong, Nyaba, & Nomngongo, 2016; Mmolawa et al., 2011).

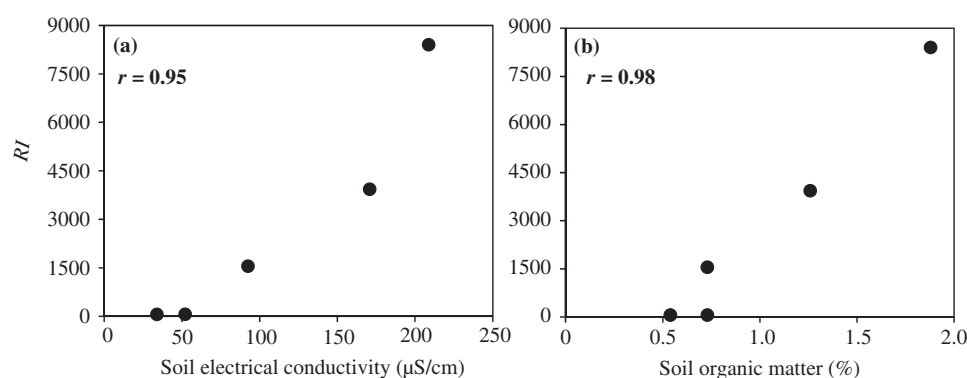
Table 5. *PERI* and *RI* indicating the pollution risk level of heavy metals to five shooting range soils under study

Shooting Range	<i>PERI</i>					<i>RI</i>
	Mn	Zn	Cu	Ni	Cd	
TAB	1.4	7.5	18.0	396.2	3507.4	3930.5
SHO	1.4	3.8	11.3	49.3	1484.6	1550.4
S/P	9.0	6.3	46.5	197.3	8140.9	8399.9
MAT	0.007	0.2	1.2	3.2	54.8	59.4
PANDA	0.04	0.4	1.0	0.7	51.9	54.0

Table 6. Contamination factor of the five shooting ranges showing level of contamination of shooting range soils from the five heavy metals investigated

Shooting Range	Contamination Factor (CF)				
	Mn	Zn	Cu	Ni	Cd
TAB	1.4	7.5	3.6	79.2	116.9
SHO	1.4	3.8	2.3	9.9	49.5
S/P	9.0	6.3	9.3	39.5	271.4
MAT	0.007	0.2	0.2	0.6	1.8
PANDA	0.04	0.4	0.2	0.1	1.7

Figure 4. Pearson correlation between; (a) soil EC and (b) soil organic matter to total ecological risk index (RI) of five heavy metals found in five shooting ranges found in Botswana. Mean of $n = 3$; Standard error of the mean, $\delta x = \delta/\sqrt{n}$, where δ = standard deviation.



3.5. Statistical assessment of pollution using the Pearson correlation coefficient

The effects of physicochemical properties of the soils such as organic matter (OM) and electrical conductivity (EC) on the pollution risk of heavy metals in shooting range soils were determined using the person correlation coefficient (r). There is direct correlation between the ecological pollution risk from heavy metals and the soil organic matter and electrical conductivity as indicated by the high Pearson correlation coefficients. Pearson correlation coefficient (r) of 0.95 depicted high ecological risk from heavy metals at high electrical conductivities of the soil (Figure 4). Similarly, correlation coefficient (r) of 0.98 suggested positive relationship between the ecological pollution risk of heavy metals and the soil organic matter (Figure 4). Our previous have shown that high organic matter stabilizes heavy metal complexes and salts in the soil enhancing the accumulation of such heavy metals in the soil (Kelebemang et al., 2017; Sehuba et al., 2017)

4. Conclusions

This study is the first in Botswana to assess the environmental pollution risk associated with heavy metal deposition in shooting range soils arising from ammunition. The findings from this study will provide a baseline data in Botswana for subsequent studies on heavy metal contamination of shooting range soils. High concentrations of Cu (1569 ± 13 mg/kg) and Mn (953.8 ± 2.8 mg/kg) were found in shooting range soils. However, the high concentration of heavy metal in the soil does not give a true picture of the environmental impact and risk from such heavy metal. Potential ecological risk (PERI) and contamination factor (CF) were able to establish that Cd, even though had lower concentrations measured in shooting range soils, posed greater environmental pollution risk than the other four heavy metals studied. The ecological risk (RI) emanating from contributions by all the five heavy metals present in the soil indicated very high pollution in three shooting ranges TAB, SHO and S/P. The environmental pollution risk posed by these heavy metals call for remedial actions and best shooting range management practices to be taken to arrest the situation before it spirals out of control. Remedial control measures such as chemical and phytoremediation processes can be employed to

control soil pollution of shooting range soils. Chemical remediation processes involving use of chemicals such as phosphate salts and lime have been found to immobilize heavy metals in the soil, reducing their mobility and bioavailability. Future studies into the best soil cleaning and soil reclamation strategies and methods should be conducted in order to come up with remedies and measures to control and manage pollution in shooting range soils.

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Competing Interests

The authors declare no competing interests.

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