Contamination and Potential Ecological Risk Factors of Potentially Toxic Elements Present in the Soil of Shooting Range: Comparison with the Global Soils

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Received: November 29, 2019      Accepted: January 21, 2020      Online Published: March 31, 2020
doi:10.5539/ep.v9n1p37                  URL: https://doi.org/10.5539/ep.v9n1p37

Abstract

This study was carried out to determine potentially toxic element (PTE) contamination and their potential ecological risk factors in shooting range soil. For this purpose soil samples were collected from different locations (left side, right side, shooting point, middle, and stop-butt) from the shooting range of Frontier Corps Training Centre (FCTC) present in Warsak, Peshawar. The soil samples were analyzed for pH, electrical conductivity (EC) and potentially toxic elements including Cd, Cr, Ni, Pb, and Zn. The strong acids digested extracts were analyzed using atomic absorption spectrophotometry to determine the concentrations of selected PTEs. The concentration of Pb was found to be maximum at stop-butt i.e. 2049 mg/kg and exceeded the United States Environmental Protection Agency (US-EPA) critical value of 400 mg/kg, while its concentrations at left, right, shooting point and middle were 14.0 mg/kg, 18.8 mg/kg, 47.4 mg/kg, and 18.2 mg/kg, respectively and exceeded the background level of normal soils which is 10 mg/kg for Pb. This study revealed that the shooting range soil was highly contaminated with Pb, and very high contamination factor and potential ecological risk for Pb was observed at stop-butt, very high contamination factor and potential ecological risk for Cd, while moderate contamination factor for Zn was observed at all locations of the shooting range. In Pakistan, the environmental perspective of shooting range soils is overlooked and there is a need to take steps to avoid such contamination of soils with Pb and other PTEs that can enter into food chains and can also leach to contaminate the aquifer. Replacement of vegetation of shooting range with PTE tolerant species, addition of soil conditioners and uncontaminated soil would reduce the mobility of these contaminants into aerial portions of plants and protect the groundwater contamination.

Keywords: lead contamination, contamination factor, potentially toxic elements, ammunition pellets, shooting range

1. Introduction

The contamination of shooting range soils is an issue of global concern, because of the accumulation of potentially toxic elements (PTE) in soil which are derived from ammunition pellets (Dinake et al., 2019; Rodríguez-Seijo et al., 2017). The pellets used in ammunition are mainly composed of PTEs such as lead (Pb), zinc (Zn), antimony (Sb), arsenic (As), copper (Cu) and nickel (Ni) (Migliorini et al., 2004; Sanderson et al., 2014). When the spent ammunition pellets come into contact with water or soil, their weathering causes oxidation of metals to secondary forms such as oxides and carbonates, which are soluble hence serving as a source of PTE contamination into the soil. Many recent studies have shown that the soils of shooting ranges are highly contaminated with Pb due to abrasion of Pb bullets passing through the soil (Dinake et al., 2019; Islam and Park, 2017; Mariussen et al., 2017; Rodríguez-Seijo et al., 2017; Sehube et al., 2017).

The Pb contamination of shooting range soils has gained significant attention by the scientific community due to elevated concentrations of it present in the soils of shooting ranges and possible adverse effects to human health associated with exposure to Pb (Dinake et al., 2019; Sanderson et al., 2014; Sehube et al., 2017). The other components of bullets such as Cu (casing of the bullet), Ni and Zn (alloys with copper), Sb (hardening agent) and As (lead impurity) have also been identified in significant amounts in addition to Pb (Johnsen and Aaneby, 2019;
Peddicord and LaKind, 2000). There is 97% of Pb in Pb-shots, while the Pb-bullets encompass 90% of metallic Pb (Fayiga and Saha, 2016). Despite the presence of these metals in the Pb-based bullets in smaller amounts, they can accumulate at elevated levels in the soils (Hardison et al., 2004; Johnsen and Aaneby, 2019) and can contaminate the groundwater as well (Islam and Park, 2017; Sanderson et al., 2014). Pb is preferred metal to be used in manufacture of ammunition pellets (Dinake et al., 2019; Fayiga and Saha, 2016; Johnsen and Aaneby, 2019) because of its high density (11.34 g/cm³), low melting point (327.4°C), high malleability and high resistance to corrosion (Rodriguez-Seijo et al., 2017; Sehube et al., 2017).

Pb has harmful effects to animals, humans and all ecological resources (Islam and Park, 2017). In humans, deleterious health effects are more prominent in children. Even lower concentrations of Pb up to 10 µg/dl, can instigate damage to the brain and nervous system, behavioral problems, hearing problems, slowed growth, headaches and impairment of vision in children (Sehube et al., 2017). In adults, complications during pregnancy, reproductive problems (like birth defects, low birth weight and decreased fertility), digestive problems, high blood pressure, neurological disorders, concentration and memory problems, kidney dysfunction and muscle/joint pain are associated with Pb exposure (Hardison et al., 2004; Sehube et al., 2017).

Pb contamination in the environment is of significant concern, because of having injurious effects on organ systems, particularly the neurological system, the kidneys and the blood (Dinake et al., 2019; Hardison et al., 2004; Tong et al., 2000). The issue of contamination of the shooting range soils requires special attention in order to continue the necessary operation of these ranges and ongoing use of the land without destroying the environment (Johnsen and Aaneby, 2019; Sanderson et al., 2014; Sorvari, 2011).

The purpose of this study was to determine PTE contamination particularly Pb and evaluate the contamination factor and ecological risk factor of PTEs in shooting range soil, Peshawar, Pakistan. According to authors’ knowledge no one has conducted a systematic scientific study on the selected study area.

2. Materials and Methods

2.1 The Study Area

This study was carried out at Frontier Corps Training Centre (FCTC) Warsak, which lies on the north western boundary of Peshawar. Peshawar is the capital city of Khyber Pakhtunkhwa Province and lies between 33° 44’ and 34° 15’ north latitudes, 71° 22’ and 71° 42’ east longitude (Khan et al., 2016) (Fig.1). The FCTC shooting range was established in 1985, and was used by Swat scouts since 1996.

![Figure 1. Location map of study area](image-url)
2.2 Soil Sampling

Five locations were selected in the shooting range i.e.; 1) shooting point, 2) middle, 3) stop-butt (also known as berm and back stop), 4) left, and 5) right. Three points were identified in each location on the basis of their distance from the middle point of the shooting range. The first point selected of each location was 200 m apart, second was 300 m apart and third was 400 m apart from the middle point. So three samples from left, right, stop-butt, and shooting point and one from the middle were taken. Total thirteen soil samples were collected at the depth of 0-15 cm with help of an auger and kept in polythene bags and properly marked.

The soil samples were air dried and then pulverized to 200-mesh size. The sieved and pulverized soil samples were kept in oven over night at 110°C to remove moisture. The samples were then cooled by placing in a desiccator and used for further analyses.

2.3 Laboratory Analysis

For determination of pH and electrical conductance (EC), soil was mixed with deionized water (1:5, weight: volume) in a glass beaker. The content was thoroughly mixed and allowed to stand for 30 min (Khan et al., 2016). The pH of soil solution was then recorded using pH meter (Melter Delta 320) after standardizing the instrument with standard buffer solutions. The EC of soil solution was then recorded using Conductometer (JENWAY 4060) after calibrating the instrument with freshly prepared standard of KCl solution.

For determination of PTEs, dried and pulverized soil samples (1 g) were taken in teflon beakers and 15 ml of aqua regia (HNO₃:HCl at 1:3 ratio) was added and the samples were kept overnight following the method adopted by Khan et al. (2010). The subsequent morning, soil samples were steadily heated on hot plate in a fume hood until they were nearly dried up. The samples were slowly heated again till near to dryness after adding 5 ml of HClO₄. Then deionized water was added to the beakers and aliquot was filtered through watt-man filter paper No. 42 and diluted to 50 ml with deionized water into volumetric flasks. The concentrations of selected PTEs such as Pb, Cd, Zn, Cr and Ni in the extracts were determined using Atomic Absorption Spectrophotometer (Perkin Elmer 700) (Al-Khashman and Shawabkeh, 2006; Galal and Shehata, 2015; Rehman et al., 2017; Tüzen, 2003).

2.4 Contamination Factor

The contamination factor (Cif) is defined as the ratio between elemental concentration between focus and the background areas. The following formula is used to determine contamination factor.

\[ C_{if} = \frac{C_i}{C_{ri}} \]  

Where ‘C_i’ is the elemental concentration in focus area and ‘C_{ri}’ is the elemental concentration in the background area (Hakanson, 1980). The degrees of contamination factor and standard values are given in Table 2.

2.5 Ecological Risk Factor

The ecological risk factor (Er_f) is used to express the potential ecological risk of a given contaminant, and it is determined through the following formula (Hakanson, 1980).

\[ E_{r_f} = T_{r_f} \times C_{if} \]  

Where ‘Tr_f’ is the toxic-response factor for a given substance, and ‘C_{if}’ is the contamination factor. The terminologies used to express the degrees of ecological risk factor are given in Table 2.
Table 1. Soil basic properties, PTE concentrations and descriptive statistics of shooting range soil

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Locations of shooting range</th>
<th></th>
<th></th>
<th></th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Standard deviation</th>
<th>Background Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>Left Right Shooting point Middle Stop-butt</td>
<td>6.5</td>
<td>6.9</td>
<td>7.1</td>
<td>6.9</td>
<td>7.0</td>
<td>6.5</td>
<td>7.1</td>
<td>6.88</td>
</tr>
<tr>
<td>EC (µS/cm)</td>
<td></td>
<td></td>
<td>0.2</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Pb (mg/kg)</td>
<td></td>
<td></td>
<td>14.0</td>
<td>18.8</td>
<td>47.4</td>
<td>18.2</td>
<td>2049</td>
<td>14.0</td>
<td>2049</td>
<td>430</td>
</tr>
<tr>
<td>Cd (mg/kg)</td>
<td></td>
<td></td>
<td>1.40</td>
<td>1.44</td>
<td>1.91</td>
<td>2.37</td>
<td>2.57</td>
<td>1.4</td>
<td>2.6</td>
<td>1.9</td>
</tr>
<tr>
<td>Zn (mg/kg)</td>
<td></td>
<td></td>
<td>67.2</td>
<td>77.3</td>
<td>63.8</td>
<td>71.0</td>
<td>75.0</td>
<td>63.8</td>
<td>77.3</td>
<td>70.9</td>
</tr>
<tr>
<td>Cr (mg/kg)</td>
<td></td>
<td></td>
<td>9.15</td>
<td>8.30</td>
<td>11.0</td>
<td>12.6</td>
<td>12.5</td>
<td>8.3</td>
<td>12.6</td>
<td>10.8</td>
</tr>
<tr>
<td>Ni (mg/kg)</td>
<td></td>
<td></td>
<td>21.8</td>
<td>17.5</td>
<td>22.5</td>
<td>25.1</td>
<td>27.7</td>
<td>17.5</td>
<td>27.7</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Table 2. Standard values of contamination factor and ecological risk factor

<table>
<thead>
<tr>
<th>Contamination factor</th>
<th>Values</th>
<th>Degrees</th>
<th>Ecological risk factor</th>
<th>Values</th>
<th>Degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cif &lt; 1</td>
<td>Low contamination factor</td>
<td>Er i &lt; 40</td>
<td>low potential ecological risk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 ≤ Cif &lt; 3</td>
<td>Moderate contamination factor</td>
<td>40 ≤ Er i &lt; 80</td>
<td>moderate potential ecological risk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 ≤ Cif &lt; 6</td>
<td>Considerable contamination factor</td>
<td>80 ≤ Er i &lt; 160</td>
<td>considerable potential ecological risk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cif ≥ 6</td>
<td>Very high contamination factor</td>
<td>160 ≤ Er i &lt; 320</td>
<td>high potential ecological risk</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1 Soil Basic Properties

Soil pH is the extremely significant factor that controls PTE speciation and their mobility in the soil solution (Han, 2007). The pH of soil samples ranged from 6.5 (slightly acidic) to 7.1 (near neutral) (Table 1). The EC of soil is an important parameter which measures the amounts of salts present in soil (USDA, 2014). No significant variation in EC values of different soil samples of shooting range was observed. The values of EC ranged from 0.2 µS/cm to 0.4 µS/cm (Table 1). The physical properties of soil influence the bioavailability and mobility of PTEs. The mobility of PTEs increases with decreasing pH and they become more bioavailable at low pH and vice versa (Khan et al., 2016).

3.2 PTEs in Soil

Table 1 summarizes the concentrations of selected PTEs in the soil samples collected from different locations of the shooting range, significant variation was observed in their concentrations. The concentrations of PTEs were compared with their respective background levels in the normal soils universally given by Bohn et al. (2002) and Pb concentration was also compared with the critical value of Pb given by United States Environmental Protection Agency (US-EPA). The PTE concentrations were found to be highest at stop-butt that could be linked with falling of ammunition pellets at stop-butt. Among the selected PTE concentrations (Pb, Cd, Zn, Cr and Ni), Pb concentration was found highest at stop-butt, which was 2049 mg/kg far exceeding the USEPA critical value of 400 mg/kg (Sehube et al., 2017) and its concentrations at left, right, shooting points and middle were 14.0 mg/kg, 18.8 mg/kg, 47.4 mg/kg, and 18.2 mg/kg, respectively, hence exceeded the background levels in normal soils (10 mg/kg). The higher Pb concentration at shooting point was possibly due to the discharge of Pb powder at the time of shooting of bullets, shots and projectiles. Whereas the possible reason of higher Pb concentration at the left, right and middle of shooting range was that some of the weathered Pb might have been mobilized and migrated to the other locations of shooting range.

These results were in agreement with those reported in previous studies like Sehube et al. (2017) because they have also observed higher concentration of Pb at soils of stop-butt and shooting line of different shooting ranges (maximum concentration of Pb was found at berm soil of Bephatshwa (TAB) shooting range (Botswana) i.e. 38,386 mg/kg), due to the discharge of Pb powder. Fayiga and Saha (2016) have also reported the similar trend of Pb concentration in Florida shooting ranges, Pb concentration ranged from 10,068 mg/kg to 70,350 mg/kg in
mid-berm (stop-but) soils.

Table 3. Contamination factor and ecological risk factor of shooting range soil

<table>
<thead>
<tr>
<th>Locations</th>
<th>Contamination factor (C\text{f})</th>
<th>Ecological risk factor (E\text{r})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb</td>
<td>Cd</td>
</tr>
<tr>
<td>Left</td>
<td>1.40</td>
<td>23.33</td>
</tr>
<tr>
<td>Right</td>
<td>1.88</td>
<td>24.00</td>
</tr>
<tr>
<td>Shooting point</td>
<td>4.74</td>
<td>31.83</td>
</tr>
<tr>
<td>Middle</td>
<td>1.82</td>
<td>39.67</td>
</tr>
<tr>
<td>Stop-butt</td>
<td>204.95</td>
<td>42.83</td>
</tr>
</tbody>
</table>

The pollution extent in the study area is determined through contamination factor. The values of contamination factor of Pb, Cd, Zn, Cr and Ni at different locations of shooting range are given in Table 3.

At stop-butt, very high contamination factor (C\text{f} 204.95) for Pb was observed due to elevated Pb concentration found at this location and considerable Pb contamination was observed at shooting point with C\text{f} 4.74.

The concentration of Cd at left, right, shooting point, middle and stop-butt of shooting range was 1.40 mg/kg, 1.44 mg/kg, 1.91 mg/kg, 2.38 mg/kg, and 2.57 mg/kg, respectively, hence all the soil samples contain Cd higher than the background level i.e. 0.06 mg/kg. Lee et al. (2002) also reported Cd concentration (0.35 mg/kg) exceeding the background level in the soil of Korean shooting range, and observed that the metal concentrations become higher when heavy continuous shooting is practiced in the range.

Very high contamination factor for Cd was observed at all locations of shooting range possibly due to low background level (0.06 mg/kg) of Cd in normal soils.

The concentration of Zn at left, right, shooting point, middle and stop-butt was 67.2 mg/kg, 77.3 mg/kg, 63.8 mg/kg, 71.0 mg/kg, and 75.0 mg/kg, respectively, hence exceeding background level (50 mg/kg). Sorvari (2011) reported similar kind of results in the shooting range of Finland, where he has observed 90 mg/kg Zn concentration at shotgun range and 76 mg/kg Zn concentration at rifle range. Lee et al. (2002) documented that in the soil of Korean shooting range the highest level of metal contaminant was found to be of Zn which was 90 mg/kg. The contamination factor values given in Table 3 indicate moderate Zn contamination at all five locations of the shooting range.

According to Bohn et al. (2002) the concentration of Ni and Cr in normal soil is 40 mg/kg and 20 mg/kg, respectively. The Ni and Cr concentrations at left, right, shooting point, middle and stop-butt of shooting range were 12.5 mg/kg and 21.8 mg/kg, 17.5 mg/kg, 22.5 mg/kg, 25.1 mg/kg and 27.7 mg/kg, respectively, and 9.15 mg/kg, 8.30 mg/kg, 11.0 mg/kg, 12.6 mg/kg and 12.5 mg/kg, respectively. The contamination factor values of Ni and Cr reveal their low contamination in soil of shooting range. The Cr concentration at all locations of shooting range was found within the background level of Cr in normal soils due to the fact that Cr is not found in the ammunition pellets as a constituent. The concentration of Ni was within the background concentration level found in normal soils probably due to the fact that this element is not present in the ammunition pellets in higher amounts. Sanderson et al. (2012) on the contrary, affirmed Ni concentration slightly higher than the background concentration level in the soil of four shooting ranges around Australia. The overall distribution of PTEs at different locations of shooting range is given in Fig. 2.
Figure 2. Concentrations (mg/kg) of PTEs at different locations of shooting range, whereas A, B, C, D, and E represent Pb, Cd, Zn, Cr and Ni, respectively. Error bars represent standard deviation.

One way ANOVA using SPSS (version 21) was conducted to compare PTEs contamination at left, right, shooting point, middle and stop-butt. The PTEs (Pb, Cd, Zn, Cr and Ni) at stop-butt showed significant difference from left, right, middle and shooting point at p < 0.05 level. Similarly, significant difference was also recorded between all the locations for the PTE contamination at p < 0.05 level.

The values of potential ecological risk factor for Pb, Cd, Zn, Cr and Ni at different locations of shooting range are given in Table 3. The stop-butt of the shooting range indicated very high ecological risk of Pb (Er > 320 i.e. 1024.75), whereas, at the other locations of shooting range, low potential ecological risk of Pb was observed. There was very high potential ecological risk of Cd in all locations of the shooting range due to the fact that Cd has a high toxic response (i.e. TR 30). The Er values for Zn, Cr and Ni were less than 40 at different locations of shooting range hence revealing low potential ecological risk of Zn, Cr and Ni in the shooting range.

Warsak dam exists in the proximity of the study area due to which there is shallow water table upto 5 ft in the study area, and about 48 tube wells are operational in the locality (Bilal and Sarwar, 2008). The Pb and Cd contamination in shooting range can be a serious hazard of ground water contamination in the study area. The contaminated ground water if used for irrigation can set off Pb contamination in plants also hence causing risk to biota and human health. The withdrawal from the aquifer in the vicinity of shooting range for drinking and domestic purposes may pose a serious risk to human health.

The ammunition pellets become disintegrated and pulverized upon impact with the soils of stop-butt, the disintegration causes change in the grain size distribution of shooting range soils and ultimately Pb contamination of environment is instigated as a result of weathering of bullet fragments (Fayiga and Saha, 2016; Johnsen and Aaneby, 2019). The primary issues associated with contaminated shooting ranges are mainly ecological risks. The adverse impacts on ecosystem include vegetation destruction, poisoning in several animal classes (including predatory birds, terrestrial birds, amphibians and small mammals) and major health risk to wildlife like mortality of birds due to accidental ingestion of Pb-bullets (Johnsen and Aaneby, 2019; Sorvari, 2011).
There are many shooting ranges in Pakistan where shooting practices are carried out which suggests that Pb is being deposited at elevated rates on the soils of such areas consequently disrupting ecosystems and posing risk to human health. The remediation of soils of shooting ranges can be done by several methods based on phytoremediation, stabilization, physical separation and chemical treatment like extraction (Dinake et al., 2019; Sorvari et al., 2006).

4. Conclusion
The results of the study showed that the soil of Frontier Corps training centre Warsak, Peshawar is highly contaminated with Pb. The Pb concentration was found to be highest at the stop-butt because ammunition pellets fall at the stop-butt. The Pb concentration was also higher at the shooting point probably due to the discharge of Pb powder during shooting. There was very high contamination factor and potential ecological risk of Pb at stop-butt and very high contamination factor and potential ecological risk factor for Cd was also observed at all locations of the shooting range. The contaminated shooting range soils should be remediated with phytoremediation particularly phytoextraction, in this way the threat of ground water contamination can be eliminated. The shooting range vegetation should be replaced with the PTE tolerant plant species.

Acknowledgements
The authors greatly acknowledge the guidance and cooperation provided by Major Jawad Ahmed Bukhari, Frontier Corps. We are thankful to FC for permitting us to collect soil samples from the shooting range.

References


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