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Assessing lead mobility rate from spent corroded and non-corroded bullets fragments on different soil types of tropical ecosystems

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Abstract. Lead ions mobility from spent metallic Pb bullets is under increasing scrutiny as a potential significant source of soil contamination. This study investigates effect of soil-properties types on Pb(II) mobility from spent corroded and non-corroded bullets and associated environmental risk using water, toxicity characteristic leaching procedure and synthetic precipitation leaching procedure as leaching techniques. From results, loamy soil properties (pH and organic matter-specific) apparently favored high mobility rate of Pb(II) (0.004 - 1.166 % Pb contamination) from spent bullets compared to sandy and clay soil types. Consequently, Pb(II) mobility from corroded bullet (0.035 - 1.166 %) was significant ($p < 0.05$) compared to non-corroded bullet (0.004 - 0.873 %) due largely to surface area differences. Percentage Pb contamination increased proportionally with bullet retention time in the different soils types. The experiment reported average decomposition rate of 6.9 g Pb/kg within a 28 weeks retention time. Leaching potential of Pb from spent bullet arising from water, toxicity characteristic leaching procedure and synthetic precipitation leaching procedure was quite significant ($p < 0.05$) in order of over 100 mg/L. Both toxicity characteristic leaching procedure-Pb and synthetic precipitation leaching procedure-Pb exceeded the 5 mg/L and 15 µg/L critical levels suggested by United State Environmental Protection Agency for Pb (II) mobility and hazardous classification. A significant positive correlation existed between corroded and non-corroded Pb (II) levels within each leaching solutions. Continued dissolution of metallic Pb (II) from spent Pb-bullets may be a mechanism for natural attenuation of Pb in soils. An important result of this study is the clear influence of soil properties on Pb mobility.

Keywords: mobility rate; lead; percentage contamination; soil; bullet; leaching.

1. Introduction

Lead contamination of shooting ranges soils has overtime been of environmental concern due to constant impact and build-up of spent bullet fragment in soils [1-5]. Large amount of spent ammunitions in forms of corroded and non-corroded bullets are often found around impact berm of most shooting range soils [6]. These bullets pellets are mainly composed of 90-95% metallic lead and other trace metals [7]. Spent bullets arising from firing activities undergo fragmentation, as a result of constant impact with soil surfaces and other existing deposited bullet pellets [8]. In soil, the metallic lead core begins an oxidation process facilitated by chemical reaction with soil components to form carbonates, oxides, and sulfates [3, 9]. The bullet age, soil type and conditions place a vital role on lead mobility from the fragmented bullets into the environment [1]. This may constitute environmental problems: runoff contamination of soils and water bodies, significant risk to groundwater pollution and may pose challenge to remediation techniques [10, 11].

Spent bullet pellets collected from shooting range soils have been shown to be visibly corroded and covered with crust materials [9, 12]. A significant portion of these crust materials composes of hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), cerussite ($PbCO_3$) and anglesite ($PbSO_4$) [13]. It takes an estimated 100 - 300 years for complete transformation of bullet pellet in soil [9], significant percentage of which will disintegrate into particulate lead over a few years of deposition in soil raising environmental concern. Many studies have reported total metal concentration in shooting range soils and the use of leaching tests like toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP) to assess environmental risk of lead in shooting range soils [2, 13-17]. However, few of these studies have reported on actual leaching rate of lead from spent bullets and effect of soil types on leachability of lead from spent bullets [2, 11, 18-20].

Dissolution of Pb species from corroding metallic Pb bullets is known to pose great risk to shooting range soil environment [21]. Therefore, important to evaluate contamination rate of Pb from bullets which will not only help in determining soil-Pb levels, but also potential toxicity and remediation methods. Since the oxidation rate of lead and the resulting weathering product is highly variable and site specific [10, 21], an understanding of the behavior and rate of disintegration of bullets fragments of different ages in different soil types and conditions will help to design appropriate remediation techniques. Tropical terrestrial ecosystems may have a significant impact on the behavior and disintegration rate of bullets fragments in soils which is a prerequisite for designing appropriate remediation techniques.

In view of this, this study investigates the effect of tropical soil properties on lead mobility rate from spent

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metallic corroded and non-corroded bullet pellets. Secondly, an additional aim of the current study is the assessment of the environmental risk of Pb from corroded and non-corroded metallic bullet using TCLP and SPLP leaching tests and water.

2. Experimental

2.1. Sample collection, processing and characterization

Corroded and non–corroded bullet fragments were obtained from an impact berm (100 m long, 18 m wide and 20 m high) of a major military shooting range soil in Ibadan. The range and soil sampling points were located within the 7°29’25” N and 3°56’45” E tropical humid ecosystem of southwestern Nigeria. The region has approximately six to eight months of rainfall with average annual intensity of 100 to 350 mm/h and temperature range of 22 to 45 °C.

Three soil sample types (sandy, clay and loamy) from similar geological formation of the Precambrian basement complex igneous and metamorphic rocks were sampled for the experiment. The soils (about 25 kg each) were collected from locations with minimal pollution sources, using stainless steel hand shovel. Drying of the soils was done at ambient temperature in the laboratory, after which ground and sieve through a 4 mm mesh sieve and stored for further analysis.

Spent 6.5 mm caliber metallic Pb-bullet fragments were collected from impact berm of an active military shooting range and classified “corroded”. Similarly, whole non-corroded metallic Pb bullets of same caliber were obtained. The spent bullets crusts were rinse-off using deionized water and dried at ambient temperature. The three soils types were then used to evaluate effects of soil properties and conditions on lead mobility from the corroded and non-corroded bullet fragments to derive percentage Pb contamination in soils.

The soils and bullets were characterized (in triplicates) as follows: soil pH determined in a soil-water ratio of 1:1 (w/v) using Hanna pH meter (Hanna Instrument, Kehl, Germany) and particle size analysis carried out using hydrometric method [22]. Soil organic carbon content determine by Walkley and Black method [23] and phosphate by Bray No. 1 method [24]. Soil nitrate content determination is by distillation method following extraction with 2 M KCl solution [25]. For total Pb determination, about 5.0 g of dried soil was digested with 50 mL of HCl : HNO_3 acid mixtures at 3:1 ratio (v/v) in a covered 100 mL beaker and heated on a hot plate for 3 h [26]. After cooling the extracts were filtered through Whatman (Cat No. 1001, 110 mm) filter paper and made to a 50 mL standard volumetric flask and stored for Pb analysis. Similarly, about 1.0 g of corroded and non-corroded spent bullet was digested for total lead analysis.

Total Pb in the extracts was analyzed using Varian SpectrAA 600 flame atomic absorption spectrophotometer. Sequential extraction of the soils before experiment and at various stages (8, 16 and 28 weeks) of experiment was carried out to identify the different fractions of Pb using Tessier method [27].

2.2. Laboratory soil - Pb mobility experiment

To evaluate effects of soil types and conditions on mobility rate of Pb from spent corroded and non-corroded metallic bullet, sandy, clay and loamy soils were used for the laboratory experimental set-up.

For sandy soil, 100 g portions of soil were each weight into 24 high density polyethylene bottles (250 mL) followed by addition of two spent corroded bullet pellet (about same weights) and 10 mL deionized water. The bottles were placed in dark and maintained at 20 - 32 °C and 2 - 5% humidity. The temperature and moisture content of the soil samples were conditioned to simulate average environmental conditions of tropical climates below earth surface. Total lead concentrations were determined in the soil samples after thorough mixing on weekly bases for 28 weeks (1 - 17 & 22 - 28 weeks). This was repeated for clay and loamy soil types.

2.3. Laboratory batch leaching experiment

Batch toxicity characteristic leaching procedure and synthetic precipitation leaching procedure described by the USEPA Methods 1311 and 1312 [14] with minor modifications (replacing 30 rpm 18 h mixing configuration with mechanical shaking for 1 - 28 weeks), and deionized water were adopted to investigate leaching rate Pb(II) from spent corroded and non-corroded bullet. Considering TCLP leaching procedure, three (about 12.5 g) corroded bullets were each placed into 24 high density polyethylene bottles (in triplicate). A 250 mL glacial acetic acid leaching solution adjusted using 1 M NaOH solution to pH 4.93±0.05 was added to each bottle. A specific liquid-to-solid ratio of 20:1 was employed and the solution was intermittently mixed and allowed to stand for 1 week and filtered through 0.45 µm membrane. The filtrate was then acidified with 2 mL HNO_3 and concentrated to 50 mL extract prior to Pb determination using FAAS. This procedure was repeated weekly for 28 weeks (1 - 17 & 22 - 28 weeks).

The same procedure was similarly conducted on the non-corroded bullet pellets.

For batch SPLP procedure, the extracting fluid at pH of 4.22±0.05 is made of two inorganic acids (HNO_3 and H_2SO_4) to simulate acidic rainwater percolating the soil. Deionized water leaching on the other hand was to simulate neutral environment in which soil is a dominant factor in determining the pH of extract. The SPLP and deionized water extractions are similar to those described above for the TCLP procedure.

All chemical analysis and experiment were performed following strict quality control/quality assurance (QC/QA) including use of reagent grade water and Analar grade chemicals (BDH Limited Poole, England), blank and replicates. Satisfactory precision within ±6% were obtained.

$$Percentage\ Pb\ contamination = \frac{C_F - C_I}{C_B} \times 100$$

where C_F is the final Pb concentration in soil. C_I is the initial Pb concentration in soil and C_B is the Pb concentration in bullets (corroded or non-corroded).

2.4. Statistical analysis

Analysis of variance ($p < 0.05$) was performed on the data-set to assess Pb mobility/leachability potentials among different soils and leaching solutions. Similarly, T-testing ($p < 0.05$) was used to establish Pb mobility relationship between corroded and non-corroded bullet pellets for the soil types and leaching solutions. Spearmen correlation [17] was carried out to evaluate Pb leachability among leaching solutions with respect to time. Microsoft Excel (2010 version) was used for statistical data evaluation.

3. Results and discussion

3.1. Lead dissolution rate from bullets

Table 1 shows percentage Pb contamination rate from spent corroded and non-corroded metallic bullet on three different soil types. Averagely, percentage Pb contamination rate of loamy soils (0.43±0.30; 0.25±0.24) were slightly higher, comparatively to sandy (0.28±0.23; 0.14±0.14) and clay (0.27±0.20; 0.16±0.14) soils arising from both corroded and non-corroded bullets respectively. These is evidence in cumulative contamination rate of loamy - 10.3% > sandy - 6.73% > clay - 6.56% for corroded bullets and loamy - 5.93% > clay - 3.90% > sandy - 3.40% for non-corroded bullets over the 28 weeks period. The high surface areas of the abrasive corroded bullets appeared to impact higher levels of Pb in soils compared to non-corroded bullets. Soils with large quantity of spent corroded bullets are therefore of environmental concern due to increase levels of bullet-borne contaminants [28].

Table 1. Percentage lead contamination in soils.

Time interval (weeks)	Corroded bullet (Pb%)			Non corroded bullet (Pb%)		
	Sandy	Loamy	Clay	Sandy	Loamy	Clay
1	0.013	0.035	0.018	0.001	0.004	0.018
2	0.011	0.067	0.030	0.007	0.030	0.024
3	0.033	0.052	0.031	0.014	0.048	0.023
4	0.048	0.091	0.045	0.020	0.048	0.030
5	0.053	0.127	0.071	0.022	0.051	0.043
6	0.055	0.176	0.071	0.035	0.051	0.045
7	0.055	0.230	0.076	0.035	0.051	0.045
8	0.055	0.282	0.135	0.035	0.051	0.045
9	0.066	0.259	0.162	0.035	0.102	0.046
10	0.203	0.263	0.191	0.035	0.117	0.046
11	0.206	0.360	0.181	0.032	0.132	0.100
12	0.211	0.378	0.207	0.117	0.150	0.111
13	0.229	0.419	0.245	0.139	0.250	0.114
14	0.256	0.433	0.308	0.145	0.256	0.146
15	0.411	0.465	0.341	0.148	0.286	0.161
16	0.420	0.478	0.363	0.160	0.292	0.197
17	0.466	0.624	0.391	0.168	0.312	0.265
22	0.475	0.565	0.464	0.177	0.336	0.276
23	0.507	0.667	0.459	0.260	0.327	0.303
24	0.530	0.702	0.478	0.298	0.342	0.309
25	0.544	0.709	0.501	0.331	0.380	0.309
26	0.553	0.830	0.558	0.340	0.684	0.353
27	0.612	0.911	0.610	0.396	0.755	0.394
28	0.713	1.178	0.628	0.453	0.873	0.497

Loamy soils with low pH (4.72±1.12) value, high organic matter content (11.1±1.54%), nitrate (78.6±4.55 mg/kg)) and phosphate (23.7±2.13 mg/kg) levels (Table 2), around berms of shooting range are potential sinks for Pb and enhances mobility. Organic matter and pH have generally been found important factor in weathering and transformation of metallic Pb bullets into oxides and carbonate [12].

Table 2. Initial soil-bullet pellet characterization (n = 3).

Parameter	Sandy	Loamy	Clay	Corroded bullet pellet	Less corroded bullet pellet
pH	4.76±1.43	4.72±1.12	5.85±1.22	-	-
Sand content (%)	94.7±1.63	69.2±1.21	62.7±0.67	-	-
Silt content (%)	3.96±1.32	23.6±1.13	6.86±0.21	-	-
Clay content (%)	1.34±0.33	7.20±0.25	30.5±2.43	-	-
Organic carbon (%)	1.80±0.13	11.1±1.54	3.09±0.44	-	-
Nitrate (mg/kg)	46.5±12	78.6±4.55	50.6±3.54	-	-
Phosphate (mg/kg)	10.3±2.71	23.7±2.13	10.4±2.43	-	-
Lead (mg/kg)	300±35	433±38	386±52	547,235	846,223

n - number of samples analyzed (mean ± SD)

Furthermore, bioavailable fractions of Pb were shown to slightly increase for the soils after the experiment (Table 3), which explain the relative increases in percentage contamination of Pb with time. Analysis of variance ($p < 0.05$) showed significant difference in percentage Pb contamination among the three soils types for corroded bullets. Here soil properties and the corroding potential of the bullets may account for the difference. However, no significant differences were observed among the soil types for non-corroding bullets which could be attributed to low corroding potentials of the bullets. Statistical T-testing between corroded and non-corroded bullets for each soil types indicated a mark significant difference owning to the differences in bullets nature.

Table 3. Different fractions of lead (% geochemical phases) in soils ($n = 3$).

Parameter	Before experiment			After experiment		
	Sandy	**Loamy**	**Clay**	**Sandy**	**Loamy**	**Clay**
Exchangeable metal	7.09	17.6	7.75	14.1	22.5	12.4
Metals bound to carbonates	10.6	12.2	6.75	10.1	10.7	8.44
Metals bound to Fe-Mn oxides	12.1	6.87	14.5	11.4	8.69	15.9
Metals bound to organic matter	7.09	26.9	17.4	5.13	28.9	21.1
Residual metals	63.1	36.4	53.6	59.3	29.2	42.2

n - number of samples analyzed.

The age of bullets which corresponds to its corroding potential is a positive indicator of soil Pb contamination in shooting range soils. Retention time of bullets in soils greatly influenced Pb mobility from spent bullets as shown in Figure 1.

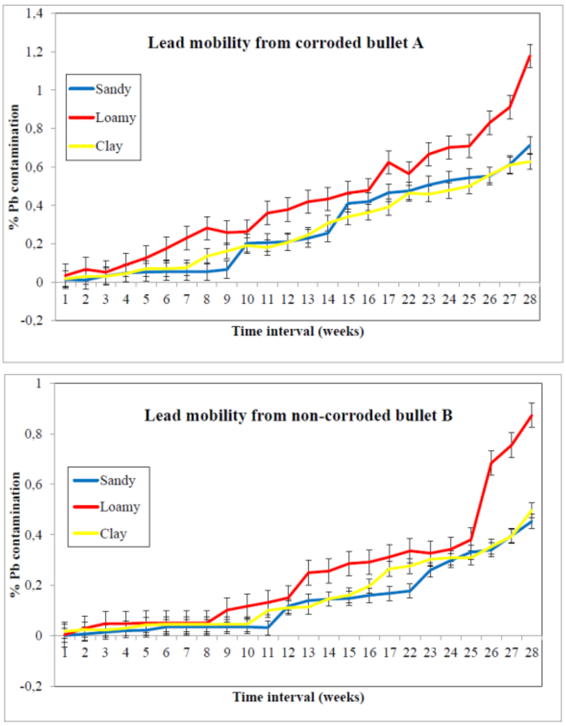


Figure 1. Lead mobility in soils: A - corroded bullet, B - non-corroded bullet.

Percentage Pb contamination increased proportionally with retention time of bullets in soils. The rate of soil Pb contamination from corroded bullets is much rapid (from 3 weeks) while non-corroded bullets from week-8, due to high surface area of the corroded bullets. The loamy soils were more prone to contamination than other soil types. From the experiment, after contacting soil, metallic Pb in bullets becomes oxidized and transformed into dissolved and particulate Pb species at a decomposition rate of 6.4 g Pb/kg/28 weeks for corroded bullets and 7.4 g Pb /kg/28 weeks for non-corroded bullets. The average of 6.9 g Pb/kg/28 weeks appears to agree with Manninen and Tanskanen [29] figure of 10 g Pb/kg/yr decomposition rate. Contaminated loamy soils from shooting range may leach sufficient Pb to pose significant environmental risk.

3.2. Lead leaching potential from bullets

Although leaching tests have widely been applied to extractable Pb in soils, this study evaluates the leaching potentials of Pb from spent corroded and non-corroded bullets by simulating various environmental conditions. Distilled water leaching method was meant to simulate natural reaction of water to lead bullet in soil, SPLP for acid rain simulation and TCLP for toxicity testing potentials. Apparently, concentration of leached Pb from spent corroded bullets is more than non-corroded bullet, which could be attributed to surface area phenomenon (Table 4).

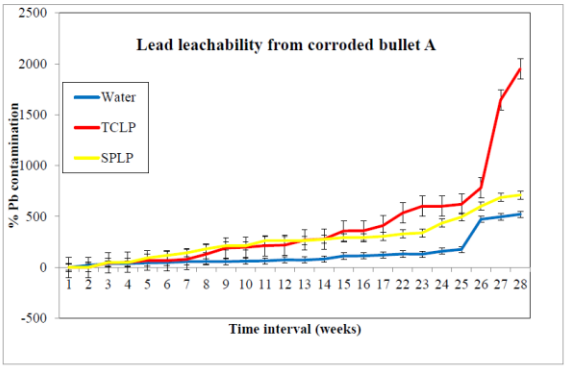
Table 4. Lead levels (mg/L) in leaching solutions.

Time interval (weeks)	Corroded bullet			Non corroded bullet		
	Water	**TCLP**	**SPLP**	**Water**	**TCLP**	**SPLP**
1	0.00	0.00	0.00	0.00	9.75±0.21	0.00
2	19.7±0.15	0.00	0.00	0.00	59.5±0.11	0.00
3	36.6±0.18	45.4±2.1	49.0±1.1	27.2±1.12	62.3±0.19	9.33±1.31
4	37.3±0.11	49.0±1.5	48.9±2.1	32.2±1.05	99.0±0.14	11.4±0.11
5	43.4±0.24	67.3±1.3	93.0±1.7	32.4±0.85	141±.1.4	65.7±1.4
6	48.1±0.18	67.1±1.7	117±2.7	32.3±0.77	145±2.2	75.6±1.2
7	56.8±0.33	78.6±2.2	143±3.9	46.5±1.42	159±1.8	81.2±1.4
8	57.4±1.43	130±4.1	182±3.8	50.3±1.66	160±3.7	90.6±1.7
9	56.6±1.32	190±3.4	213±4.2	50.3±1.43	158±4.1	113±2.1

Time interval (weeks)	Corroded bullet			Non corroded bullet		
	Water	TCLP	SPLP	Water	TCLP	SPLP
10	60.5±1.56	198±3.3	213±4.3	55.7±1.12	165±3.2	142±2.1
11	64.0±1.32	213±3.6	263±7.4	58.6±2.14	165±3.4	153±1.8
12	73.5±3.28	219±2.9	262±7.2	61.7±1.52	176±2.9	154±3.4
13	72.1±2.10	268±2.4	262±8.3	62.4±1.22	207±4.7	160±3.3
14	82.5±2.15	278±4.1	275±9.3	66.1±2.43	235±2.3	167±2.8
15	111±3.4	358±3.7	293±11	67.5±1.90	263±10	170±4.6
16	113±2.1	360±8.2	293±16	119±3.5	279±11	175±7.3
17	122±3.5	410±10	304±12	104±2.1	280±10	177±5.8
22	131±4.3	535±24	328±11	127±2.3	368±14	272±11
23	130±5.1	600±18	338±14	129±1.8	405±12	292±10
24	158±4.6	600±11	435±14	152±10	393±11	294±14
25	177±5.5	621±25	495±11	153±6.3	413±13	368±32
26	473±4.5	783±23	600±18	157±3.5	425±21	690±29
27	496±8.8	1645±34	686±12	181±2.7	428±13	798±30
28	522±7.6	1951±19	711±12	194±2.8	698±11	933±34

(Mean ± SD)

Corroded bullet had higher surface area due to corrosion than the non-corroded bullet. TCLP leachates showed significant levels of Pb compared to others. The following leaching order TCLP > SPLP > water was observed. Irrespective of bullet surface area (corroded-high and non-corrode-low), distilled water at pH of 7.00 showed least leaching potential for Pb.



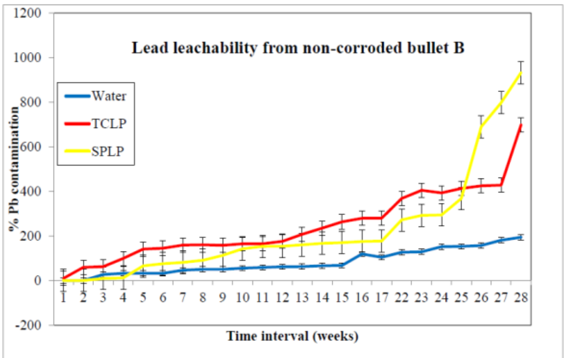


Figure 2. Lead levels in leaching solutions: A - corroded bullet, B - non-corroded bullet.

Water leaching models are less appropriate as they tend not to reflect real estimates of acidity encountered in the environment, and also do not mimic buffered water systems found in soils. In acid rainfall instance (SPLP with pH of 4.22), Pb leaching rate increases from 0 - 711 mg/L for corroded and 0 - 933 mg/L for non-corroded over time, resulting in possible soil-Pb contamination. Although the buffering capacity of soil would course pH of influx rainfall to rapidly approach neutral, acid rain may not enhance Pb peculation but enhance contaminated soil-Pb runoffs.

The TCLP leaching method which simulates landfill condition shows that Pb from both bullets fragments are potential hazards to the environment with values corroded 0-1951 mg/L and non-corroded 0-698 mg/L within 28 weeks leaching period. Important to note, spent corroded and non-corroded metallic-Pb bullets fragments can be classified hazardous under the Resources Conservation and Recovery Act (RCRA), thereby, requiring remediation for disposal soils [30].

Analysis of variance ($p < 0.05$) showed significant difference in Pb concentration among water, TCLP and SPLP leachates for corroded and non-corroded bullets. These further suggest that the different Pb leaching potentials among leaching solutions is a function of pH. Statistical T-testing similarly showed significance differences ($p < 0.05$) in Pb levels between corroded and non-corroded bullets for water, TCLP and SPLP, which confirms leaching potential is strongly dependent on bullet surface area, age and pH. Furthermore, a strong positive correlation water - 0.842; TCLP - 0.901; SPLP - 0.948 was observed between both bullets types for the various leaching time. Figure 2 shows proportional increase in Pb leachability from both bullets with time, with TCLP having highest leachability rate. Extensive and prolong immersion of bullets in leaching solutions will enhance complete dissolution of Pb.

4. Conclusions

The effect of three different soil types on mobility rate of Pb from spent corroded and non-corroded metallic bullets obtained within a tropical active military shooting range was studied. Consequently, environmental risk of bullets was also examined using water, TCLP and SPLP leaching techniques. The bullets collected contain high concentration of Pb matrix as expected. Corroded bullet impacted higher levels of Pb particularly on loamy soil-Pb which was a function of soil property. Retention time of bullet in soil greatly influence the degree of contamination. An average 6.9 g Pb/kg/28 week was reported during the period of study. The leaching potential of TCLP-Pb, SPLP-Pb from bullets proof hazardous exceeding comparative limits in soils of 5 mg/L and 15 µg/L respectively. An important result of this study is the clear influence of soil properties on Pb mobility in soil. This work confirms specific literature that explains how Pb migrates from bullets in soils and the time dependent nature and weathering of Pb bullet in soils.

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Conflict of interest

The author declares no conflict of interest.

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