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LEAD LEACHABILITY FROM SHOOTING RANGE SOILS

BADANIA WYMYWALNOŚCI OŁOWIU Z GLEBY NA TERENIE STRZELNIC

Abstract: Lead contamination of soil in shooting ranges creates an environmental problem. Samples of soil were analyzed for total lead (T-[Pb]) and extracted lead (TCLP-[Pb]) using toxicity characteristic leaching procedure (TCLP). Total content of lead in soil samples varied from 640 to 4600 ppm. The TCLP test indicated that lead in most of soil samples exceeded the 5 ppm, a critical level of EPA regulation for solid and hazardous waste. The ratios of leaching lead (TCLP-[Pb]) to total lead (T-[Pb]) in soil samples ranged from 1.9 % to 5.2 %. The TCLP extracts from soil samples indicated lead concentration levels of 5 to 45 times over the US EPA regulatory level of 5 ppm and this was characterized as a toxic waste.

Keywords: soil, lead soil contamination, shooting range, total lead, extracted lead, TCLP

Heavy metals particularly damage groundwater and their movement through soil is of considerable concern. Soil contamination usually originates from industrial and human activities but can also be done due to a variety of natural phenomena. The eight toxic metals such as arsenic, cadmium, lead, selenium, barium, chromium, silver and mercury are considered relevant in terms of potential toxicity to biological life and human health. Lead is recognized in all countries as a potentially toxic metal for humans [1].

Firing range activities become a potentially significant source of soil contamination with lead because lead is used in ammunition production. New shotgun pellets contain 97 % lead, 2 % antimony, 0.5 % arsenic and 0.5 % nickel. The annual consumption of lead used for shotgun ammunition in some European countries (Denmark, Finland,

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Sweden, United Kingdom) is about 500–1000 Mg [2]. Shooting range soil contamination has been investigated in many countries [3–10].

Lead being an amphoteric metal is soluble over a wide range of pH, but is more soluble under acidic than alkaline conditions [11]. The oxidation and dissolution of metallic lead result in various compounds, predominantly: oxide, carbonate, sulfate, chloride, phosphate and sulfide.

Study on reuse of lead contaminating urban soils was done in the Netherlands [12]. The soil samples contained from 3 ppm to over 3000 ppm of lead. The leachability, based on test NVN 2508, was higher in sandy soils (4 % to 13 %) than in clay soils (1 % to 4 %). An increase of humic substances in soil up to 20 % reduced the leachability of lead to about 10 %. The lead mobility in soils was determined to be low. The study recommended the reuse of moderately lead-contaminated urban soils by overlaying the contaminated soil with a layer of clean soil.

Toxicity characteristics leaching procedure (TCLP) was carried out for determination of lead leachability. The determination of total lead content is not sufficient to assess the environmental impact on polluted soils. The TCLP simulates leaching of toxic lead in landfill environments, and the test could be important in evaluation of toxicity of wastes [6, 13]. Leaching tests are valuable as a supplementary tool to chemical analysis for the assessment of the mobility of inorganic compounds in soil. Depending on the kind of contaminated soil it may be satisfactory to leave the contamination as it is, as long as the mobility is low and predictable and does not present an unacceptable risk of harm to the environment or to the health [14].

Existing leaching procedures

A number of selected leaching procedures commonly used in various countries are summarized in Table 1 [14].

Table 1

The most common leaching procedures for granular waste and industrial sludges

Type of test	Test procedure (duration; leachant pH; liquid/solid ratio)	Country/region
Column leaching test	NEN 7343 column test (21 d; 4.0 with HNO ₃ ; 0.1 to 10)	The Netherlands
	Nordtest-column test (24 h; 4.0 with HNO ₃ ; 1 to 2)	Nordic Countries
	Combined column + batch leaching (24 h; 4.0 with HNO ₃ ; 24)	Denmark
Batch leaching test	DIN 38414 S4 (24 h; pH water; 10)	Germany, Austria
	AFNOR X31-210 (24 h; pH water; 10)	France
	JST-13 (6 h; pH water; 10)	Japan
	EN 12457 (6 h, 18 or 24 h; pH water; 2 to 10)	European Union
	Nordest (6 h, 18 h or 24 h; 4.0 with HNO ₃ ; 2 to 10)	Nordic Countries
	NEN 7349 serial (23 h; 4.0 with HNO ₃ ; 20)	The Netherlands
	ENA Skaktest (24 h; 4.0 with H ₂ SO ₄ ; 4)	Sweden
TVA Eluattest (24 h; pH water 5 to 6; 10)	Switzerland	

Table 1 contd.

Type of test	Test procedure (duration; leachant pH; liquid/solid ratio)	Country/region
	WRU Bach Extraction (2–80 h; 5.0 buffer NaOAc; 1)	United Kingdom
	EP Tox Method 1310 (24 h; 5.0 buffer NaOAc; 20)	USA
	TCLP Method 1311 (24 h; pH 2.9 HOAc, or pH 5.0 buffer HOAc/NaOAc; 20)	USA

To establish the parameters controlling leaching of element in the laboratory tests, two different types of leaching tests are used, those carried out in batches and those carried out in columns. In batch tests only solubility is considered as relevant in controlling the release process, whereas in column tests percolation and diffusion are considered to dominate. For batch experiments the most relevant controlling parameters are pH, temperature, time, ratio liquid/soil (L/S), shaking and type intensity, concentration and nature of the leachant, ionic strength, liquid/solid separation procedure, atmosphere (air or inert) and the volume of air in the shaking container. For column experiments the most relevant parameters are pH, elution rate, temperature, time filling procedure, particle separation, ionic strength, column material, column design and column dimensions [14].

The purpose of present study was to examine: 1) total lead concentration distributions in shooting range soils contaminated by lead pellets; and 2) using TCLP test for correlation between total lead and leaching characteristics of lead in these soils.

Experimental part

Samples of soil were collected from two rifle/pistol military shooting ranges. For each shooting range samples of surface soil (0–10 cm depth) were collected from the front, the middle and the end of the berm shooting range. Samples of soil were digested with nitric(V) acid and peroxide using the hot block digestion procedure and method 3050A [15] for determination of total metal concentrations. The toxicological characteristics leaching procedure (TCLP) method 1311 [16] is a test used to determine the heavy metal toxicity of contaminated soil. In this study, the soil samples were extracted with fluid solution no. 1 ($\text{pH} = 4.93 \pm 0.05$), which was prepared by adding 11.4 cm^3 glacial acetic acid to 0.5 dm^3 D.I. water, and then adding 128.6 cm^3 1.0 M NaOH solution and diluting to a volume of 2.0 dm^3 .

The concentrations of total lead in soils and in TCLP extract were determined by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) using PerkinElmer Optima instrument. Calibration standards were prepared from multi-element standard. Three standards and blank were used for calibration. The standards were prepared in nitric(V) acid/hydrochloric acid matrix, as specified in method 6010 [17].

The performance of the instrument, during the analysis, was evaluated by determining the method detection limit (MDL) and several quality control (QC) parameters. The method reported level (MRL) value for lead is 0.3 ppm.

Several QC checks were performed to ensure that the ICP was operating properly. The calibration was initially checked using a standard at the midpoint of the calibration range. The standard was recovered within the $\pm 5\%$ guidelines specified in the standard procedure. The interference check sample was run to ensure that the wavelengths chosen are proper. The interference check sample contained high concentrations of Al, Na, Ca, and Mg, with low levels of the analytes of interest. A laboratory continuing check standard (CSTD) was run to verify the performance of instrument and method. The values of the CSTD were recorded within $\pm 10\%$ required limits. A duplicate sample was analyzed and the analyte recorded within $\pm 15\%$ of the original sample. The samples were spiked before digestion with (2 mgPb/dm^3). The spike recoveries for the samples were 94 % to 106 %. The laboratory spike blank (LSB) and laboratory spike duplicate blank (LSDB) were run with average recovery (or accuracy) 96 % to 107 %, the precision for data set was evaluated by calculating the difference between the results found for the LSB and LSDB, and then dividing the difference by the average of the two results. The relative percent difference (% D) or precision was 4 % to 8 %.

Quality assurance (QA)/quality control (QC)

Calibration standards were prepared from multi-element standard. Three standards and one blank were used for calibration. The standard samples were prepared in nitric(V) acid/hydrochloric acid matrix, as specified method 6010 [17]. To assure the accuracy and precision of a method, a series of QA/QC procedures were performed to validate the data from EPA methods (see summary Table 1 and 2) to ensure that the ICP was operating properly. The calibration was initially checked using a continuing check standard (CSTD) at the midpoint of calibration range. The CSTD was recovered within the range of acceptance ($\pm 5\%$) guidelines specified in the method, and during run the recovery was within the acceptance ($\pm 10\%$). An interference check sample was run to ensure that the wavelengths chosen for the method did not have any undetected spectra interference. The check sample contained high concentrations of Al, Na, Ca and Mg, with low levels of the analytes of interest. The samples were spiked before digestion (1 ppm for Ag, Ba, and 2 ppm for Cr, Cd, As, Pb, and Se). During the TCLP extraction, blank and duplicate samples, and standard reference materials (SRM) were processed along with the samples. Blank extraction samples were run used to detect contamination introduced in the sample processing and analysis procedure. Additionally, sample duplicates were also extracted to assure reproducibility of the method. The reported concentration could not deviate more than 20 % between the duplicates, and reference materials. An extraction blank was processed and analyzed with each extraction sample set (10 samples). In addition, laboratory spike blank (LSB) and laboratory spike blank duplicate (LSBD) were analyzed with each extraction set samples of (10 samples). The performance of instrument was evaluated by determining the method detection limit (MDL) for each analyte using EPA protocol (US EPA, 1984). Method reported limits (MRLs) are given in experimental part.

Results and discussion

Total lead concentration

Samples of soil were collected from two firing ranges. For each range samples were analyzed for total lead and extracted lead, the results are presented in Table 2. Range no. 1 had the highest pH (8.3 to 8.6) whereas range no. 2 (samples G to L) results were of the lowest pH (6.5 to 7.4) (Table 2).

Table 2

Lead leachability from soil contaminated with lead bullets pellets

Sample no. and range: (1) and (2); (sample: front, middle, berm)	pH in water	pH ^a (in water) and (HCl added)	Total [Pb] ^c [ppm]	TCLP [Pb] ^c [ppm]	Extraction ^b [%]
Range no. (1)					
A (1) front	8.3	1.1	1070	25.7	2.4
B (1) front	8.3	1.1	1240	32.2	2.6
C (1) middle	8.3	1.0	1680	36.9	2.2
D (1) middle	8.5	1.1	1740	33.1	1.9
E (1) berm	8.4	1.0	4400	206.8	4.7
F (1) berm	8.6	1.1	4600	225.4	4.9
Range no. (2)					
G (2) front	6.6	1.0	1080	45.4	4.2
H (2) front	6.5	1.1	1140	45.6	4.0
I (2) middle	6.9	1.0	640	20.5	3.2
J (2) middle	7.0	1.1	650	24.1	3.7
K (2) berm	7.3	1.1	2650	135.2	5.1
L (2) berm	7.4	0.9	2740	142.5	5.2

^a pH (5 g solids [not "dry solids"] + 96.5 cm³ D.I. water); if pH is < 5.0, use extraction fluid no. 1 and go to extraction. If pH is > 5.0, then 3.5 cm³ 1 M HCl was added to determine extraction fluid, if pH is < 5.0, use extraction fluid no. 1, if pH is > 5.0 use extraction fluid no. 2. Extraction fluid no.1 (11.4 cm³ HOAc + 128.6 cm³ 1.0 M NaOH for 2.0 dm³) pH = 4.93 ± 0.05. Extraction fluid no. 2 (11.4 cm³ HOAc for 2.0 dm³) pH = 2.88 ± 0.05.

^b Ratio of TCLP [Pb] to total [Pb] × 100 %.

^c Quality control (QC) parameters: Reference standard material, SRM (94–105 % recovery), Continuing check standard, CSTD (95–104 %), Lab spike blank, LSB (96–107 %), Lab spike blank duplicate, LSBD (95–104 %), Lab spike matrix, LSM (94–106 %), Lab spike matrix duplicate, LSMD (96–104 %).

Accuracy and precision of metals analysis: Accuracy was determined as a ratio of LSB and LSBD (96 to 103 %), or a LSM and a LSMD (96 to 105 %); the precision was determined by calculating the difference between the results found for the LSB and LSBD, and then dividing the difference by the average of the two results (4 to 8 %).

Lead concentrations in five samples (A to F, range no. 1) were exceptionally high (1070 ppm to 4600 ppm), and the other six samples (G to L, range no. 2) exhibited high concentration of Pb (from 640 ppm to 2740 ppm), exceeding US EPA critical levels of 400 ppm. The higher concentrations measured were probably obtained due to the

the presence of large lead particles in those soil samples. The solids appear fine enough to pass through a 9.5 mm sieve. This indicates that substantial accumulation of lead was primarily due to large lead particles. Lead distribution in surface soils was related to the number of lead bullets (ie, the more bullets, the greater lead concentration in the soil). Total lead concentration in surface soils in the area in front of the berm ranged from 1070 to 1240 ppm (range 1) with the highest concentration in middle 1740 ppm (range 1) and the lowest in middle 640 ppm (range 2) from the shooting stands (Table 2). The highest lead concentration (4600 ppm, range 1; and 2740 ppm, range 2) was in the backstop berm which includes lead associated with metallic bullet fragments. Most soils are considered contaminated with lead if they contain more than 200 ppm, the upper limit for a common soil [18].

Elemental lead can be readily dissolved in acid solutions. The lead pellets in the presence of oxygen, water and carbon dioxide could form: PbO , PbCO_3 , $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$. Formation of these compounds produces an increase in soil pH and reduces the migration of lead [3].

Toxicity characteristic leaching procedure (TCLP)

The leaching procedure uses a buffered acetic aqueous solution at a liquid to solid ratio (L/S) of 20:1 [16]. In this study, TCLP of lead in the shooting range soils was performed with solution no. 1 (pH 4.93 ± 0.05). The extraction procedure requires the preliminary evaluation of the soil pH to determine the proper extraction solution necessary for the experiment. All samples in the study were calcareous. When concentrations of lead in soil samples exceed 400 ppm, the TCLP test is recommended [17]. The leachates from twelve soil samples indicated higher lead concentration which was of 5–45 times over the US EPA regulatory critical level of (5 ppm) and would be characterized as hazardous waste [19]. The ratios of TCLP lead values to total lead values from soil samples from range no. 1 varied from 2.2 % to 4.9 % and for range no. 2 from 3.2 % to 5.2 %. The variation in these data suggests that lead retention was site dependent.

Prediction of extractable components based on the total contents is very uncertain and a laboratory extraction can not reflect the chemistry of a waste placed in the environment. There are many variables that affect leaching behavior including redox properties, reduction by metal not being hazardous eg, iron, additives present, sorption processes, precipitation of hydroxides and acid-base changes. In some cases when iron metal, hydrous ferric oxide, zinc metal, phosphate and lime are present in waste, such a mixture passes the TCLP test. It is difficult to predict result of a sample that can be very specific for a waste sample. Even with a large number of tests done for waste samples it is hard to assess if they meet regulations based on total-metal (T-Me) concentrations but only on leached amounts in the TCLP test. Even if the content of total metals is very high, a leached fraction can pass the TCLP test.

To understand what really happens in the field and TCLP test, the process of oxidation and reduction should be considered [20]. The standard potentials of the reduction of divalent ions to metals are as follows: copper, 0.34 V; lead, -0.13 V; iron,

-0.45 V, and zinc, -0.76 V. This means that iron can reduce Pb(II) as follows: $\text{Fe} + \text{Pb}^{+2} \rightarrow \text{Fe}^{+2} + \text{Pb}$. Lead(II) cations in solution will be reduced by iron, so that the lead concentration will remain very low if metallic iron is present and accessible in solution.

Conclusions

Soil of firing range has been characterized for total and leached lead content. Concentration levels of lead were found in the range of 640 to 4600 ppm (twelve samples). TCLP was carried out on size-fractionated homogeneous soil. The TCLP tests indicated a high leaching possibility of lead in firing ranges that exceeded critical level (5 ppm). The leachates from all soil samples indicated high lead concentration which were of 5 to 45 times over the US EPA regulatory critical level (5 ppm) and would be considered as hazardous waste [19].

References

- [1] Research Triangle Institute. Toxicological Profile for Lead. Prepared for US Department of Health and Human Services, 1999.
- [2] Lin Z., Commet B., Qvarfort U. and Herbert R.: *The chemical and mineralogical behavior of Pb in shooting range soils from central Sweden*. Environ. Pollut., 1995, **89**, 303–309.
- [3] Astrup T., Boddum J.K. and Christensen T.H.: *Lead distribution and mobility in a soil embankment used as a bullet stop at shooting range*. J. Soil Contam., 1999, **8**, 653–665.
- [4] Basunia S. and Landsberger S.: *Contents of lechability of heavy metals (Pb, Cu, Sb, Zn, As) in soil at the Pantex Firing Range, Amarillo, Texas*. J. Air & Waste Manage. Assoc., 2001, **51**, 1428–1435.
- [5] Bruell R., Nikolaidis N.P. and Long R.P.: *Mobility and remediation of lead from shooting range soils*. Hazard. Ind. Wastes, 1998, **30**, 155–162.
- [6] Bruell R., Nikolaidis N.P. and Long R.P.: *Evaluation of remedial alternatives of lead from shooting range soil*. Environ. Eng. Sci., 1999, **16**, 403–414.
- [7] Chen M. and Daroub S.H.: *Characterization of lead in soils of a rifle/pistol shooting range in central Florida, USA*. Soil Sedim. Contam., 2002, **11**, 1–17.
- [8] Sever C.W.: *Lead in outdoor ranges*. [In:] National Shooting Range Symposium Proceedings, October 17–19, 1993, Salt Lake City. North American Hunting Club, Minnetonka, MN, 1993, pp. 87–94.
- [9] Stansley W., Widjeskog L. and Roscoe D.E.: *Lead contamination and mobility in surface water at trap and skeet ranges*. Bull. Environ. Contamin. Toxicol., 1992, **49**, 640–647.
- [10] Cao X., Ma L.Q., Chen M., Hardison D.W., Jr. and Harris W.G.: *Lead transformation and distribution in the soils of shooting ranges in Florida, USA*. Sci. Total Environ., 2003, **307**(1–3), 179–189.
- [11] Stumm W. and Morgan J.J.: *Aquatic Chemistry*. John Willey & Sons, Inc., New York 1996 (3rd Edition).
- [12] Van der Sloot H.A., Wijkstra J. and Leeuwen J.: *Potential for reuse of lead-contaminated urban soils*. [In:] Goumans, J.J.G., Van der Sloot, H.A., Aalbers, Th.G. (Eds.), *Waste Materials in Construction*. Elsevier, Amsterdam 1991.
- [13] Cao X., Ma L.Q., Cheng M., Hardison D.W. Jr. and Harris W.G.: *Weathering of lead bullets and their environmental effects at outdoor shooting ranges*. J. Environ. Qual., 2003, **32**, 526–534.
- [14] Van der Sloot H.A. and Heasman L., Quevauviller Ph.: *Harmonization of Leaching/Extraction Tests*. Elsevier, Amsterdam 1997.
- [15] US EPA Method 3050A., 1990. Acid Digestion of Sediments, Sludges, and Soils.
- [16] US EPA Method 1311, 1990. Toxicity Characteristic Leaching Procedure (TCLP).
- [17] US EPA Method 6010, 1986. Inductively Coupled Plasma Atomic Emission Spectroscopy.
- [18] Lindsay W.L.: *Chemical Equilibria in Soils*. John Wiley & Sons, New York 1979.
- [19] US EPA, 1995 (SW-846). Test Methods for Evaluating Solid Waste. Vol. IA: Laboratory Manual Physical/Chemical Methods. Washington, DC 20460.

- [20] Kendall D.S.: *Toxicity characteristic leaching procedure and iron treatment of brass foundry waste*. Environ. Sci. Technol., 2003, **37**, 367–371.

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Abstrakt: Problem środowiskowy stanowi zanieczyszczenie na terenie strzelnic gleby ołowiem. Analizowano próbki gleby na zawartość ołowiu ogółem i ekstrahowanego, wykorzystując metodę ługowania TCLP. Ogólna zawartość ołowiu w próbkach glebowych wahała się od 640 do 4600 ppm. Test TCLP wskazał, że ołów w większości próbek glebowych przewyższył 5 ppm, co dla stałych/trwałych niebezpiecznych odpadów oznacza poziom krytyczny według regulacji EPA. W próbkach gleby stosunek ługowanego ołowiu do ołowiu ogółem waha się od 1,9 % do 5,2 %. Ekstrakty TCLP z próbek glebowych wykazały poziom stężeń ołowiu od 5 do 45 razy przewyższający poziom 5 ppm, określony przez amerykańską regulację EPA i gleby z terenu strzelnic oceniono jako toksyczne.

Słowa kluczowe: gleba, zanieczyszczenie gleby ołowiem, teren strzelnic, ołów ogółem, ekstrahowany ołów, TCLP