# Fractionation and distribution of risk elements in soil profiles at a Czech shooting range

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## ABSTRACT

The fractionation and vertical distribution of risk elements in soil profiles at a shooting range characterized by alkaline soil were studied. High loading rates of lead (Pb) and antimony (Sb) were observed in the upper 30 cm of soil. Copper (Cu) contents are elevated compared to control soil but do not exceed guideline limits for agricultural soil. Zinc (Zn) and nickel (Ni) did not occur in excessive levels; however, easily mobilizable Zn fraction was higher in surface samples, whereas Ni appears to be relatively immobile. Pb and Cu loading in surface soils can be identified as fraction distributions are easily distinguished from those of non-polluted soils. At the firing line Cu, Sb and Zn are most abundant whereas Ni and Pb are concentrated at the target zone. Sequential extraction procedures proved effective for the monitoring of shooting range soils. However, data should be backed by other scenario dependent analyses to confirm the environmental fate of shooting range contaminants.

**Keywords**: lead; inorganic contaminants; BCR sequential extraction; soil probe; alkaline soil

Shooting ranges (SR) are the second largest source of Pb contamination, with annual depositions ranging from 10 to 60 000 tons in different countries (Ahmad et al. 2012). In addition to lead, SR soils are burdened with a range of risk elements (RE) present in excessive concentrations. Bullet lead exists as an alloy consisting of 90% Pb or more (Sorvari et al. 2006), which can contain variable quantities of Cu, Ni, Sb, Sn, As, Bi, Ag (Dufosse and Touron 1998, Randich et al. 2002). Jackets and casings contain Cu and Zn in varying proportions (Ackermann et al. 2009).

Bound RE can be observed in the environment by using simple extraction methods (Rauret 1998, Ettler et al. 2007) or by applying sequential extraction (SE) methods (Ettler et al. 2005, Bacon and Davidson 2008) which can provide information about the mode of occurrence (natural vs. anthropogenic), potential availability, mobilization and transport of trace metals (Filgueiras et al. 2002).

The aim of the study is to clarify the mobility of selected RE (Cu, Ni, Pb, Sb, Zn) being released from bullets at various soil depths. We assess the effectiveness of SE analyses for tracking the

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Supported by the Ministry of Education, Youth and Sports of the Czech Republic, Grant S.

Table 1. Basic soil properties in target area profiles

| Profile layer (cm) | CEC (mmol/100 mL) | $pH_{H_2O}$ | $pH_{KCl}$ | TOC | TIC |
|---|---|---|---|---|---|
| | | | | (%) | |
| SP 1 (0–12) | 12.50 | 8.48 | 7.65 | 4.89 | 1.48 |
| SP 1 (12–31) | 9.13 | 8.27 | 7.59 | 2.57 | 3.20 |
| SP 1 (31–x) | 5.75 | 6.56 | 5.91 | 1.24 | 0.00 |
| SP 2 (0–14) | 11.75 | 7.95 | 7.17 | 2.70 | 0.40 |
| SP 2 (14–29) | 9.63 | 7.96 | 7.26 | 1.32 | 6.15 |
| SP 2 (29–60) | 7.25 | 7.78 | 7.25 | 0.60 | 9.85 |
| SP 2 (60–90) | 6.25 | 7.85 | 7.39 | 0.26 | 9.80 |
| SP 3 (6–12) | 11.00 | 7.80 | 7.03 | 2.55 | 0.43 |
| SP 3 (12–37) | 9.75 | 7.87 | 7.02 | 2.23 | 0.58 |
| SP 3 (37–x) | 13.13 | 7.78 | 7.20 | 0.97 | 3.20 |
| Control (0–5) | 8.67 | 7.79 | 7.05 | 1.80 | 0.94 |

SP – soil pit; CEC – cation exchange capacity; TOC – total organic carbon; TIC – total inorganic carbon

mobility and binding of individual elements in a contaminated alkaline soil.

**Scientific hypothesis**. (i) In areas of concentrated shooting, a dissolution of ammunition and migration of RE in soil will be observed. (ii) Mobility and bonding of RE can be effectively monitored by a combination of single extraction methods and SE procedures.

## MATERIAL AND METHODS

**Sampling**. Samples were taken from an outdoor SR in eastern Czech Republic which is characterized by alkaline soil (Table 1). The range is principally an unregulated open grass strip, with no barriers between it and surrounding fields. At the target zone there is a banked soil backstop, leading up to a thicket of trees and a field used for growing crops. The SR has been in use for over 40 years with irregular operating intensity.

Figure 1 shows the sampling plan. Pits were dug to expose horizons at the target area (soil pits 1, 2, 3), and samples were taken from each layer. Surface samples were collected from topsoil 0–5 cm at the firing line, half way and in front of the target area. Control soil was taken from the top 5 cm of a nearby field (100 m from the study area, not influenced by activities of the SR).

**Sample treatment**. Samples were air dried, sieved < 2 mm and bullet fragments were seperated. The following basic soil properties were determined: pH ($pH_{H_2O}$, $pH_{KCl}$), cation exchange capacity, total organic carbon (TOC) and total inorganic carbon (TIC) content and soil texture classification (Pospíšil 1964, Carter and Gregorich 2008). Simple extractions were made using 2 mol/L $HNO_3$ (releasable) and total content determined by microwave digestion in a mixture of concentrated acids; $HF/HNO_3/HClO_4$ (Vaněk et al. 2010). The three step BCR SE was applied to detect binding of contaminants in soils. Contents of Pb, Ni and Zn in individual fractions were determined using Varian Spectra AA280 FS (fast sequence, Mulgrave, Australia) FAAS under standard analytical conditions. Calibration was matrix-matched with

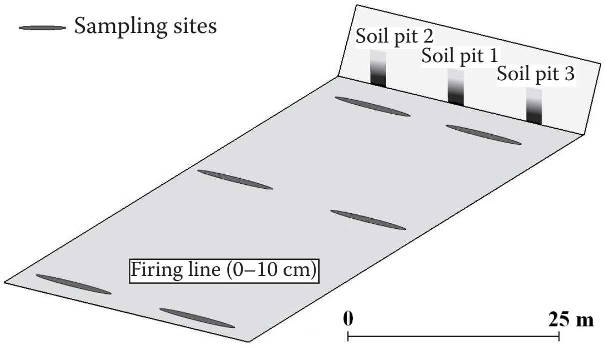

Figure 1. Shooting range sampling map

Table 2. EDX (energy – dispersive X-ray spectroscopy) analysis of bullet projectile from target area

| Localization | Element | Jacketed bullets | Non-jacketed bullets | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| | | composition (%) | | |
| Bullet core | Pb | 94.5 | 96.7 | 95.2 |
| | Al | 0.24 | 3.26 | 2.02 |
| | Sb | 3.78 | – | 2.78 |
| | Fe | 1.44 | – | – |
| Mantel[a] | Fe | 66.6 | – | – |
| | O | 33.4 | – | – |
| Mantel[b] | Cu | 83.2 | – | – |
| | Fe | 4.02 | – | – |
| | Pb | 4.3 | – | – |
| | Zn | 8.32 | – | – |

[a]bulk mantle; [b]thin layer between mantle and core

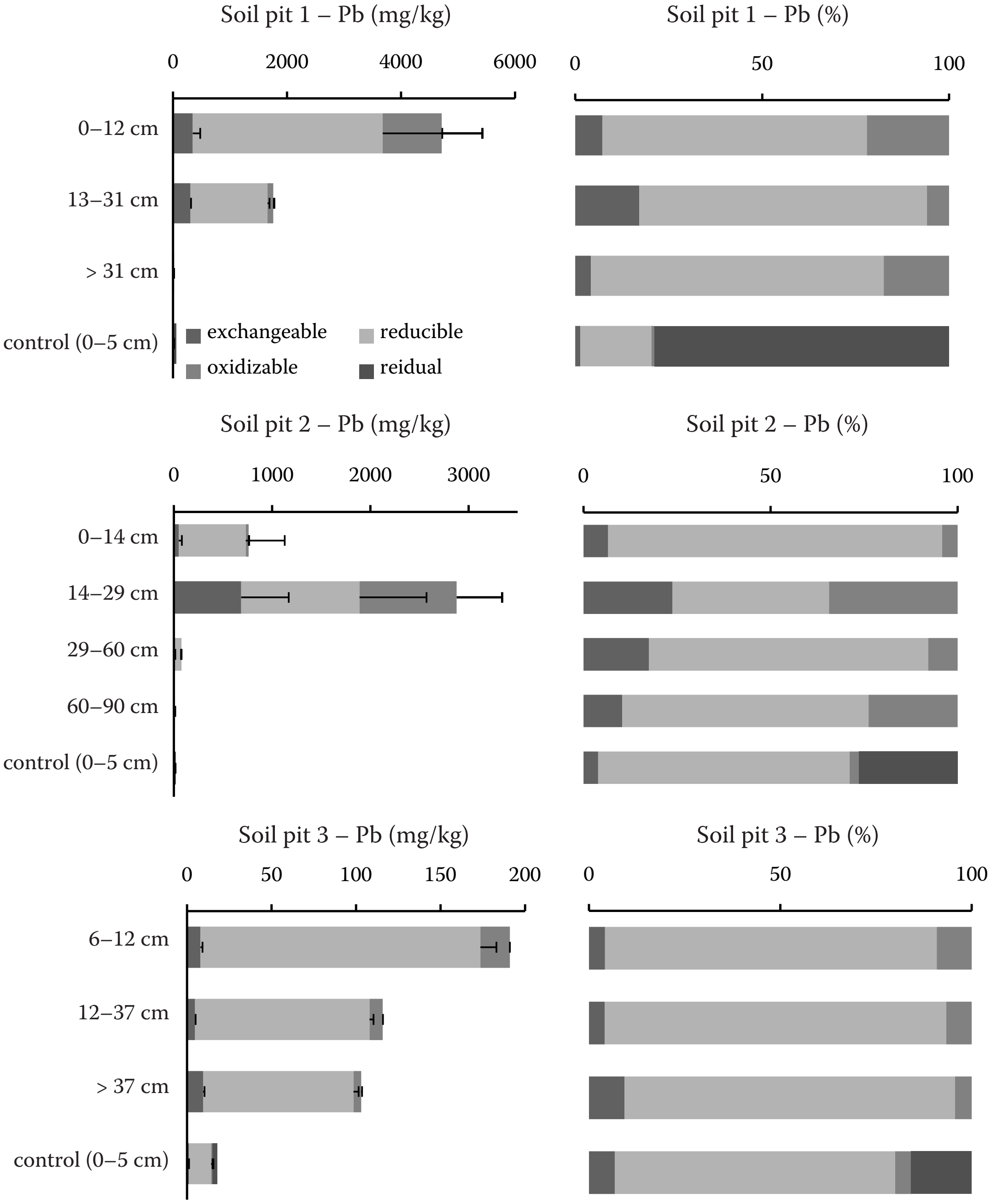

Figure 2. Sum of all Pb fractions

standards from Analytika s.r.o. (Prague, Czech Republic) Cu and Sb were determined by ICP-OES (Thermo Scientific iCAP 6500 Radial ICP, Cambridge, UK). A procedural blank was run for each extraction step, samples were analyzed in triplicates. A combination of energy – dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) was used to identify composition and mineralogy of projectile remains in soil samples using SEM PHILIPS XL 30 CP (Amsterdam, the Netherlands) equipped with EDX detector and PANalytical X'Pert Pro diffractometer (Almelo, the Netherlands), respectively.

## RESULTS AND DISCUSSION

**Basic soil parameters**. The study area is characterized by alkaline soil, texture is classed as silt loam. Mineralogical composition was identified for control samples and soil pit samples from the target area. Quartz was detected as the prevailing mineral, less

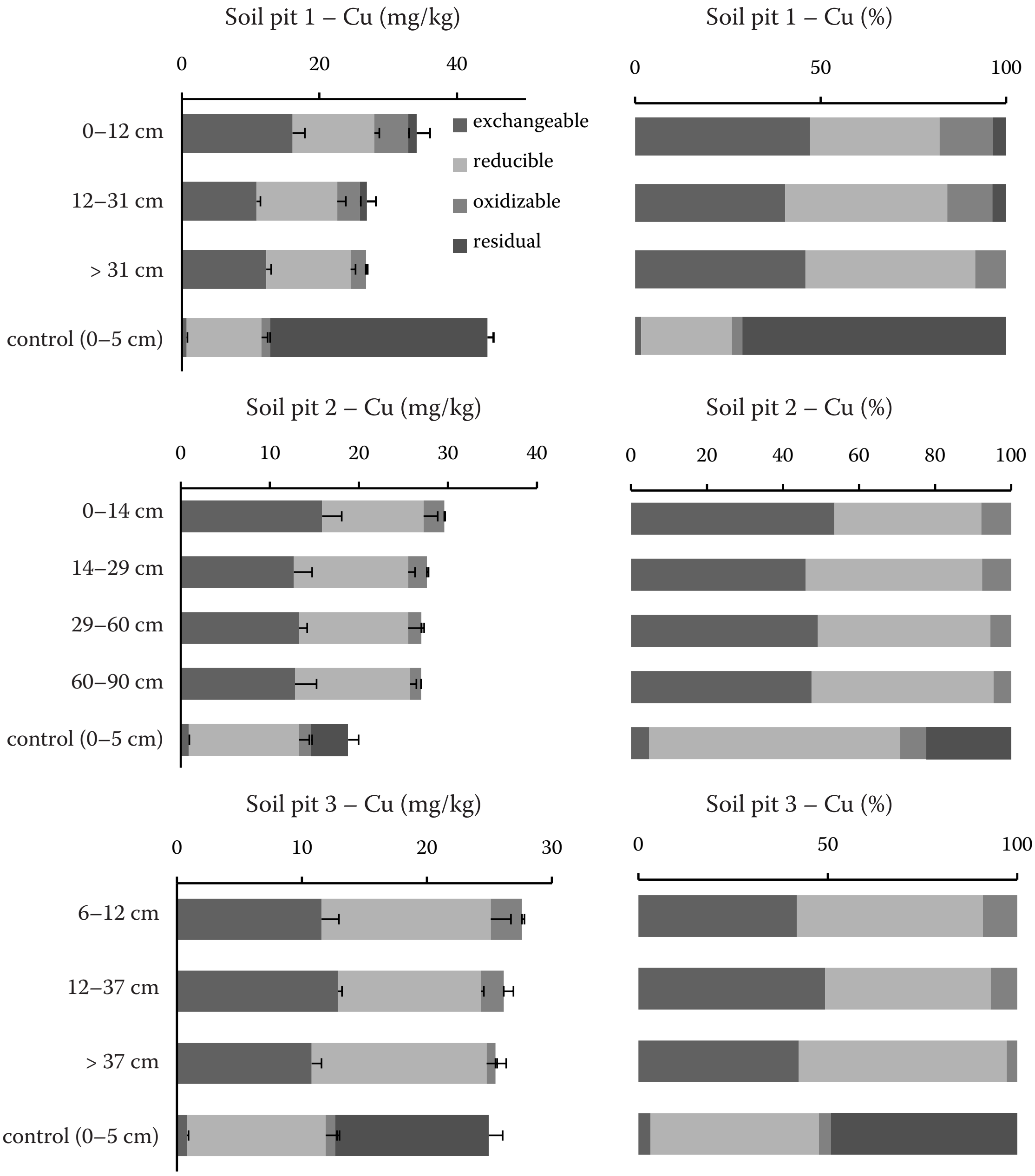

Figure 3. Sum of all Cu fractions

abundant was – albite, calcite and muscovite/illite and occasioning – dolomite, titanite, K-feldspar.

**Bullet composition**. Approximately 80% of bullets recovered were non-jacketed all lead alloy, most likely fired from pistols. The lesser proportion of recovered projectiles was either full metal jacket bullets most often fired from rifles, or semi-jacket type bullets.

An increased sorption of RE (mainly Pb) was observed at the bullet surface by newly formed minerals in the weathering crust: Lepidocrocite $\gamma$-$Fe^{3+}O(OH)$, goethite $\alpha$-$Fe^{3+}O(OH)$, akaganeite $\beta$-$Fe^{3+}(O.OH.Cl)$ and whewellite. In agreement with other findings (Lin et al. 1995, Cao et al. 2003) Pb secondary minerals present at the projectile surface occurred mainly in the form of cerussite $PbCO_3$ and hydrocerussite $Pb_3(CO_3)_2(OH)_2$. Table 2 lists elemental percentages of the major bullet components.

**Target area**. In soil pits 1 and 2, compared to control soil a significant enrichment of RE was observed, particularly for Sb and Pb. Surface enrichment of Cu, Ni and Zn was not so pronounced. Compared to guideline limits (GL) for agricultural

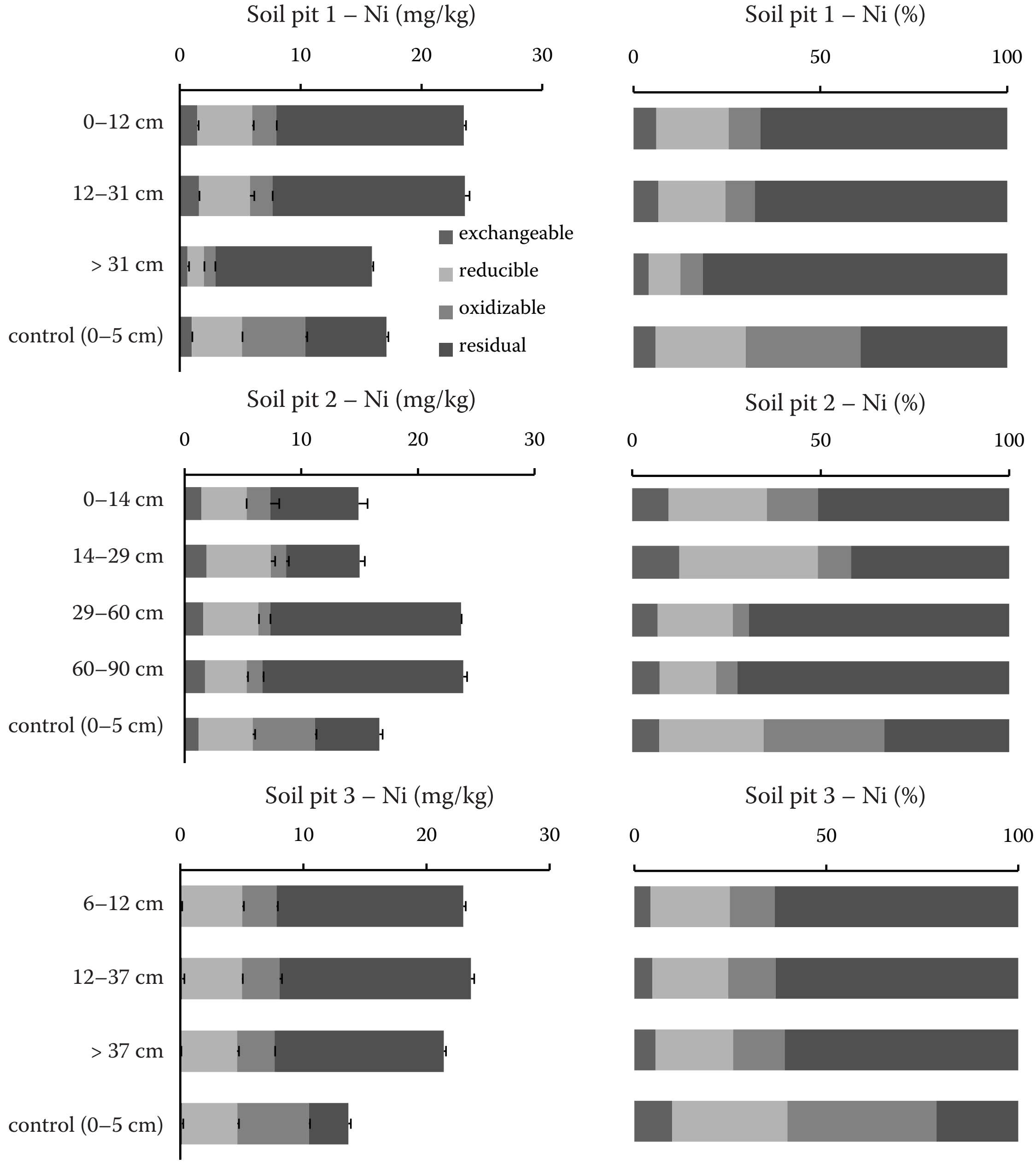

Figure 4. Sum of all Ni fractions

soils (Beneš 1993) the 2 mol/L $HNO_3$ extraction shows concentrations of Pb to be highly excessive.

**Sequential extraction**. Figures 2–5 illustrate the RE contents within each sampled horizon and percentage distribution of fractions: exchangeable, reducible, oxidizable and residual.

There is a well defined enrichment of Pb in the upper 30 cm of soil, after which Pb concentrations are within the GL. Speculations can be made as to reason why the underlying horizon in soil pit 2 is more highly enriched in Pb than the other soil pits. Cao et al. (2003) observed a substantial amount of downward migrating Pb in the subsurface soil which was linked to possible enhanced solubilization of organic complexes at alkaline pH and Knechtenhoffer et al. (2003) determined that it is not uncommon for preferential flow to mobilize significant amounts of Pb to subsurface horizons. The time frame of bullet decomposition in soil was observed by Jorgensen and Willems (1987) whereby 5–17% transformation from metallic Pb pellet to free ionic Pb had taken place within 6–13 years.

The residual Pb content was found to be negligible and fractions follow the order (red. > ox. > exch.

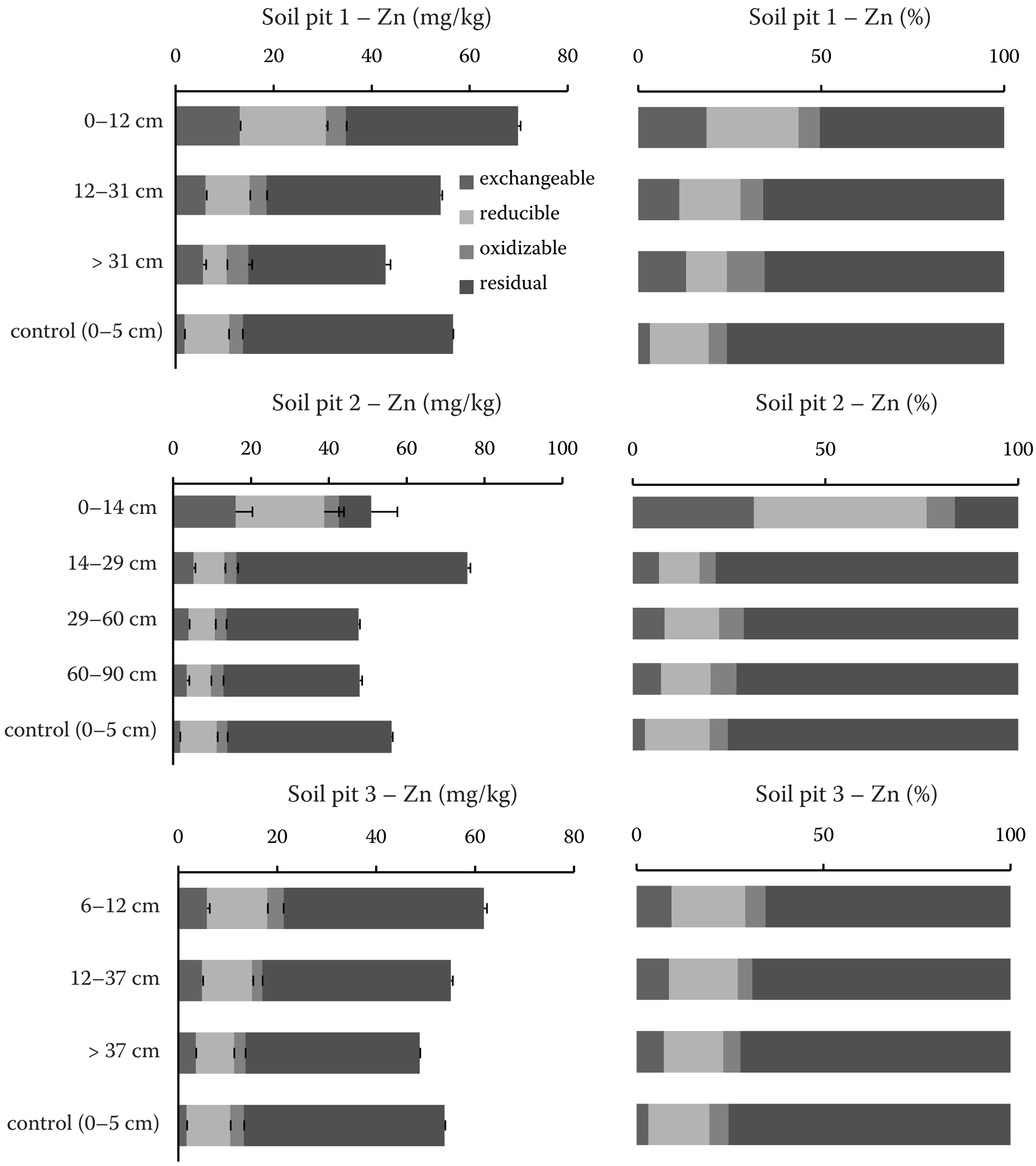

Figure 5. Sum of all Zn fractions

> res.). This fraction order was also observed by Conesa et al. (2010) and is common among many long term polltued soils regardless of the source of Pb as shown by other investigations (Takáč et al. 2009, Chrastný et al. 2010). Exchangeable Pb percentage in surface samples forms a weak negative correlation with $pH_{H_2O}$ and TOC ($R$ = 0.415 and 0.475, respectively). Leaching studies and long-term extraction experimentation could be applied to samples to aid prediction of Pb mobility.

An even distribution of Cu throughout the soil profile may be due to downward migration with soluble complexes (EPA 1992). Exchangeable Cu accounts for almost half of the total content in the alkaline soil whereas in the control sample < 5% Cu is easily exchanged, with the majority being bound to Fe/Mn oxides (Figure 3). Organically bound Cu is firmly coupled with the presence of TOC ($R$ = 0.932).

Nickel fraction percentages in target area soil are in agreement with those commonly observed

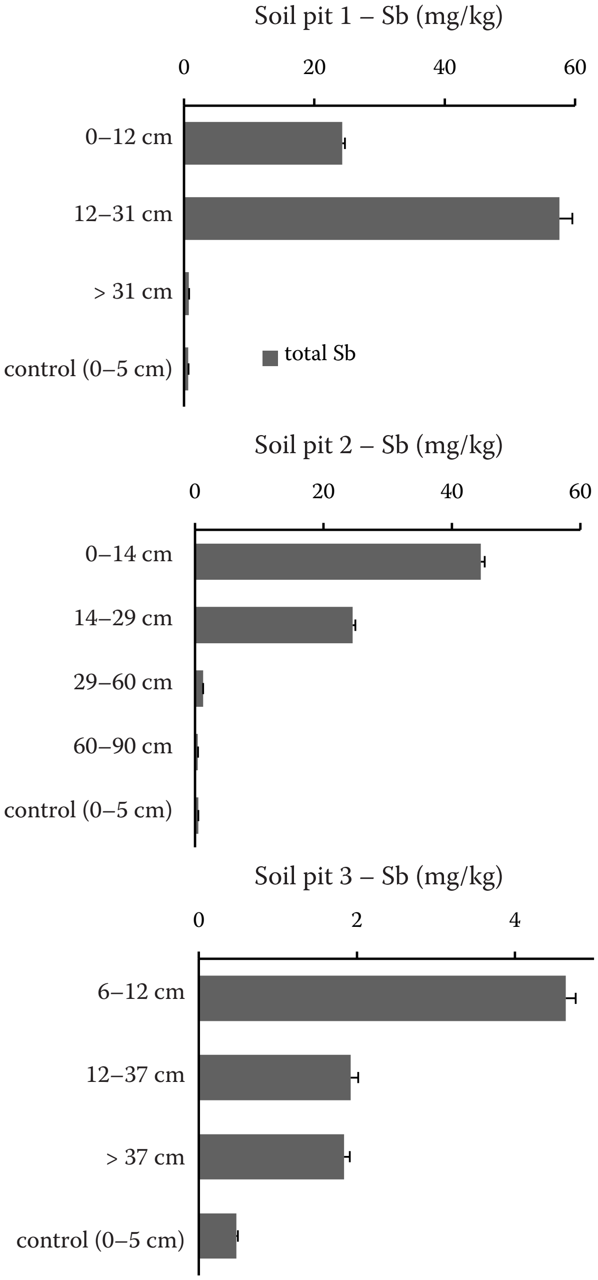

Figure 6. Content of Sb extracted by 2 mol/L $HNO_3$

in normal soils, predominantly in residual and Fe/Mn-bound fractions (Kabata-Pendias and Mukherjee 2007). Results of SE performed on two SR soils by Conesa et al. (2010) matched the analysis of our SR whereby more than 90% of Ni resides in the last three steps (Figure 4). Nickel does not form insoluble precipitates in unpolluted soils and therefore retention of Ni is exclusively through adsorption mechanisms (EPA 1992) as evident in the control soil.

Zinc concentrations in SR soils typically surpass background levels but are seldom excessive (Knechtenhofer et al. 2003, Migliorini et al. 2004). Total Zn content did not exceed 50% of the GL even at the surface, implying that this is not a highly problematic element. Tessier et al. (1980) found the majority of Zn in polluted soils to be associated with Fe/Mn oxides and Pustišek et al. (2001) observed that the exchangeable Zn portion also increases in samples which are increasingly contaminated. Despite low overall values, in the case of soil pits 1 and 2, a distinction can be made between fraction distributions of control soil and SR surface layers (Figure 5).

Individual fractions of Sb occurred below detection; therefore 2 mol/L $HNO_3$ extraction results are given (Figure 6). With the exception of soil pit 1 surface layer, there is a trend of decreasing Sb with depth, which becomes more pronounced after 30 cm. The results matched those of Vleek et al. (2011), whereby SR soil Sb concentrations are excessive in the upper 30 cm of a soil core after which the content decreases.

Two apparent trends exist with respect to RE distributions along the bullets path (Figure 7). (i) Soil contains elevated concentrations of Cu, Sb and Zn at the firing line and concentrations generally decrease with distance away from this point. (ii) Target area soil contains elevated concentrations of Ni and Pb and concentrations generally decrease with distance from the target mound. The observed distribution is consistent with the amounts that would be expected due to the composition of either bullet or casing.

Trends identified by SE and analysis of basic soil properties suggest that Pb retention in upper horizons is enhanced by alkaline soil conditions and sufficient organic carbon contents. Excessive concentrations in subsurface horizons may be due to enhanced formation of soluble organic ligand-Pb complexes at alkaline pH or preferential flow. SR soils can be identified primarily by a greater share of reducible Pb fractions. Despite low total values of Cu, there is a marked difference in fraction distribution between non-polluted soils and those affected by SR activities. Compared to background concentrations, Ni does not appear to be a problematic element. Zinc concentratiions are also not excessive but Zn is increasingly bioavailable in surface layers. Antimony is highly enriched in the upper 30 cm of soil. High concentrations observed at the firing line suggest that bullet casings or barrel discharges are the greatest

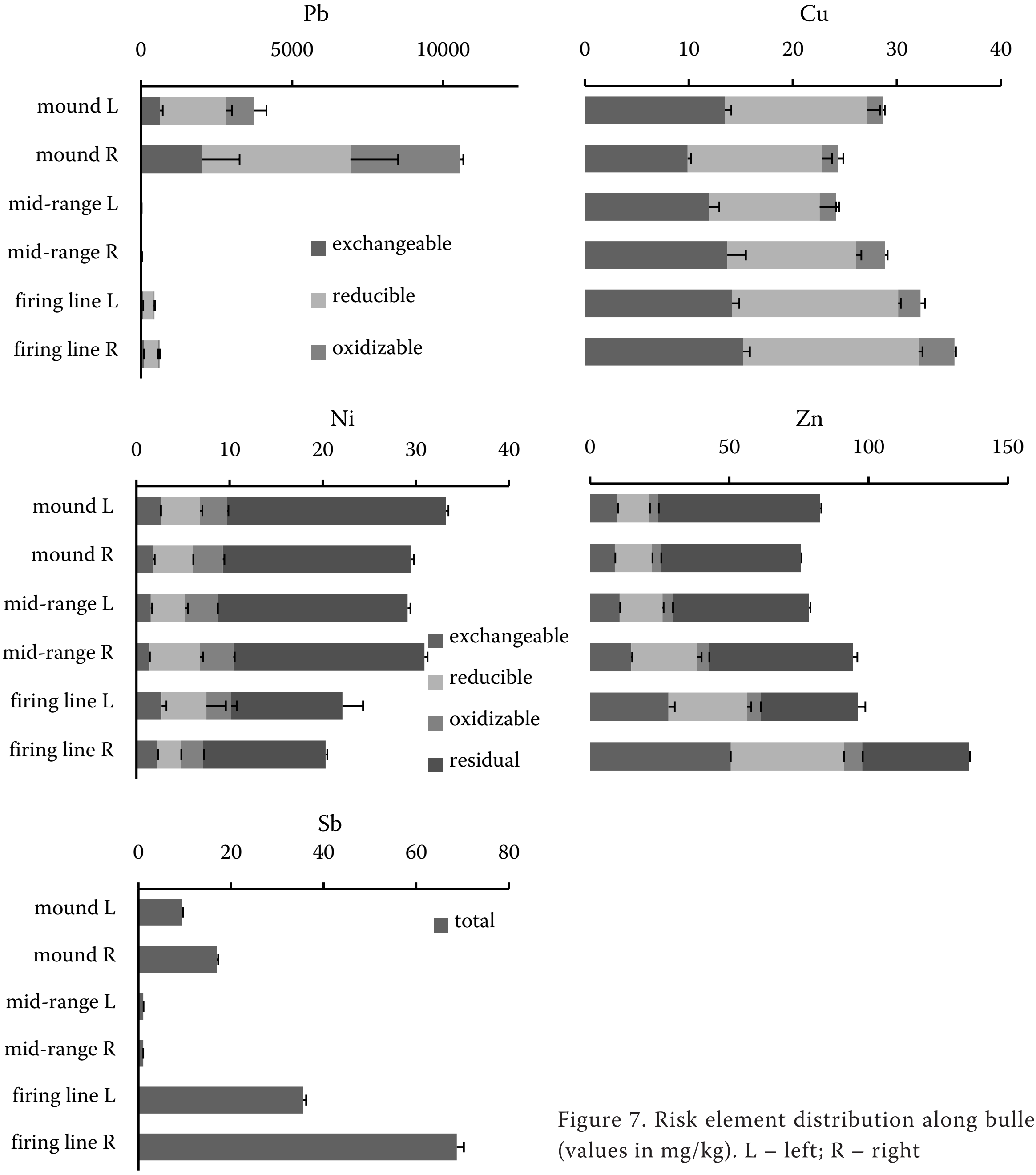

Figure 7. Risk element distribution along bullet path (values in mg/kg). L – left; R – right

source of Sb. In areas of concentrated shooting dissolution of ammunition and vertical migration of risk elements (Pb, Ni, Sb) was observed in the soil profile. Sequential extraction procedures are effective for monitoring shooting range soils. However, SE observations should be supported by other analysis tools specific to the aims of the user in order to confirm the environmental fate of SR contaminants. Anthropogenic inputs to a soil can be identified by the pattern of fraction distribution, irrespective of total concentrations. Single extraction procedures are suitable only for comparison of REs to guideline values and/or between study sites.

## REFERENCES

Ackermann S., Gieré R., Newville M., Majzlan J. (2009): Antimony sinks in the weathering crust of bullets from Swiss shooting ranges. Science of the Total Environment, *407*: 1669–1682.

Ahmad M., Hashimoto Y., Moon D.H., Lee S.S., Ok Y.S. (2012): Immobilization of lead in a Korean military shooting range soil using eggshell waste: An integrated mechanistic approach. Journal of Hazardous Materials, *209–210*: 392–401.

Bacon J.R., Davidson C.M. (2008): Is there a future for sequential chemical extraction? Analyst, *133*: 25–46.

Beneš S. (1993): Content and Balance of Elements in Spheres of the Environment. Ministry of Agriculture of the Czech Republic, Prague. (In Czech)

Cao X., Ma L.Q., Chen M., Hardison D.W., Harris W.G. (2003): Lead transformation and distribution in the soils of shooting ranges in Florida, USA. Science of the Total Environment, *307*: 179–189.

Carter M.R., Gregorich E.G. (2008): Soil Sampling and Methods of Analysis. 2nd Edition. Canadian Society of Soil Science, CRC Press, Boca Raton.

Chrastný V., Komárek M., Hájek T. (2010): Lead contamination of an agricultural soil in the vicinity of a shooting range. Environmental Monitoring and Assessment, *162*: 37–46.

Conesa H.M., Wieser M., Gasser M., Hockmann K., Evangelou M.W.H., Studer B., Schulin R. (2010): Effects of three amendments on extractability and fractionation of Pb, Cu, Ni and Sb in two shooting range soils. Journal of Hazardous Materials, *181*: 845–850.

Dufosse T., Touron P. (1998): Comparison of bullet alloys by chemical analysis: Use of ICP-MS method. Forensic Science International, *91*: 197–206.

EPA (Environmental Protection Agency (1992): Behavior of metals in soils. Technology Innovation Office, Office of Solid Waste and Emergency Response, Minnesota. Available at http://www.epa.gov/tio/tsp/download/issue14.pdf

Ettler V., Mihaljevič M., Šebek O., Nechutný Z. (2007): Antimony availability in highly polluted soils and sediments – A comparison of single extractions. Chemosphere, *68*: 455–463.

Ettler V., Vaněk A., Mihaljevič M., Bezdička P. (2005): Contrasting lead speciation in forest and tilled soils heavily polluted by lead metallurgy. Chemosphere, *58*: 1449–1459.

Filgueiras A.V., Lavilla I., Bendicho C. (2002): Chemical sequential extraction for metal partitioning in environmental solid samples. Journal of Environmental Monitoring, *4*: 823–857.

Jorgensen S.S., Willems M. (1987): The fate of lead in soils: The transformation of lead pellets in shooting-range soils. Ambio, *16*: 11–15.

Kabata-Pendias A., Mukherjee A.B. (2007): Trace Elements from Soil to Human. Springer-Verlag, Berlin.

Knechtenhofer L.A., Xifra I.O., Scheinost A.C., Flühler H., Kretzschmar R. (2003): Fate of heavy metals in a strongly acidic shooting-range soil: Small-scale metal distribution and its relation to preferential water flow. Journal of Plant Nutrition and Soil Science, *166*: 84–92.

Lin Z.X., Comet B., Qvarfort U., Herbert R. (1995): The chemical and mineralogical behaviour of Pb in shooting range soils from central Sweden. Environmental Pollution, *89*: 303–309.

Migliorini M., Pigino G., Bianchi N., Bernini F., Leonzio C. (2004): The effects of heavy metal contamination on the soil arthropod community of a shooting range. Environmental Pollution, *129*: 331–340.

Pospíšil F. (1964): Fractionation of humus substances of several soil types in Czechoslovakia. Rostlinná Výroba, *10*: 567–580. (In Czech)

Pustišek N., Milačič R., Veber M. (2001): Use of the BCR three-step sequential extraction procedure for the study of the partitioning of Cd, Pb and Zn in various soil samples. Journal of Soils and Sediments, *1*: 25–29.

Randich E., Duerfeldt W., McLendon W., Tobin W. (2002): A metallurgic review of the interpretation of bullet lead compositional analysis. Forensic Science International, *127*: 174–191.

Rauret G. (1998): Extraction procedures for the determination of heavy metals in contaminated soil and sediment. Talanta, *46*: 449–455.

Sorvari J., Antikainen R., Pyy O. (2006): Environmental contamination at Finnish shooting ranges – the scope of the problem and management options. Science of the Total Environment, *366*: 21–31.

Takáč P., Szabová T., Kozáková Ľ., Benková M. (2009): Heavy metals and their bioavailability from soils in the long-term polluted Central Spiš region of SR. Plant, Soil and Environment, *55*: 167–172.

Tessier A., Campbell P., Bisson M. (1980): Trace metal speciation in the Yamaoka and St. Francois Rivers (Quebec). Canadian Journal of Life Sciences, *17*: 90–105.

Vaněk A., Chrastný V., Komárek M., Galušková I., Drahota P., Grygar T., Tejnecký V., Drábek O. (2010): Thallium dynamics in contrasting light sandy soils – soil vulnerability assessment to anthropogenic contamination. Journal of Hazardous Materials, *173*: 717–723.

Vleek B.V., Amarasiriwardena D., Xing B.S. (2011): Investigation of distribution of soil antimony using sequential extraction and antimony complexed to soil-derived humic acids molar mass fractions extracted from various depths in a shooting range soil. Microchemical Journal, *97*: 68–73.

Received on October 18, 2012
Accepted on January 3, 2013

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