

The mobility of Pb and Sb originating from small arms ammunition in a coarse grained unsaturated surface sand

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Abstract

Uncontaminated soil obtained from two shooting ranges in Sweden was used to construct two bench scale lysimeters. These lysimeters were then used to quantify the transport of Pb and Sb leaching from bullet-contaminated sand placed on the surface of both lysimeters. The lysimeters were subjected to infiltration which reproduced the springtime snowmelt in northern Sweden, and the effluent was analyzed for dissolved Pb and Sb. The Pb concentrations in the effluent stayed at or near background levels for the duration of the experiment while the Sb concentrations showed a classic breakthrough curve.

Key Words

Shooting range, leaching, lysimeters.

Introduction

Several studies have been published which examine Pb concentrations and mineralization in shooting range sands but fewer papers exist which examine Sb (Cao *et al.* 2003; Dermatas *et al.* 2004; Knechtenhofer *et al.* 2003; Ma *et al.* 2007). The transport of Pb and other metals from shooting range soils has been experimentally examined in some detail (Johnson *et al.* 2005; Jorgensen and Willems, 1987). The mobility of Pb has been shown to be affected by the redox potential (Eh), pH, cation exchange capacity (CEC) and available anions – including carbonate, phosphate and sulfate (Basta *et al.* 1993). Factors which have been observed as influencing Pb chemistry in firing range sand include pH (Cao *et al.* 2003; Dermatas *et al.* 2004; Ma *et al.* 2007; Lin *et al.* 1995), mineralogy (Dermatas *et al.* 2004), natural organic matter and water content (Ma *et al.* 2007). There is very little experimental information in the literature about the effects of such basic attributes as temperature and Eh on Pb chemistry and conflicting reports exist concerning the relative solubility of Pb minerals (Lindsay, 1979, Knechthofer *et al.* 2003). Furthermore, there are no studies concerning the kinetics of reaction of various Pb minerals existing on firing ranges. The complexity of the chemistry and the significant gaps in the current state of knowledge necessitates a site-specific approach to deal with the potential fate and transport of metals on various firing ranges (Dermatas *et al.* 2004; Cao *et al.* 2003). Little information is available in the literature concerning the transport and environmental fate of any of the non-Pb heavy metal alloying agents in metal bullets, particularly Sb (Johnson *et al.* 2005, Scheinost *et al.* 2006). While little is known about the speciation and geochemical fate of Sb in sands and sediments (Krupka and Serne 2002), is that the toxicity of Sb is thought to be similar to that of arsenic (Scheinost *et al.* 2006) and standardized tests have shown Sb to be toxic to invertebrates (Kuperman *et al.* 2005). Therefore, the evidence indicates that if Sb is mobilized from a shooting range, it could pose a significant environmental concern.

The purpose of this experiment was to quantify the transport of Pb and Sb through the standardized soil used in the berms of Swedish military ranges. All military range berms in Sweden are constructed using a standardized mixture of sand and pea gravel, making experimental observations at one site cautiously relevant to other sites. Unfortunately, such a mixture of sand and gravel is also highly permeable, allowing the rapid movement of water through its pores. Furthermore, it is very low in both clay and natural organic matter (NOM), which are the soil components which typically contribute the most to the retardation of dissolved contaminants (Boulding and Ginn 2004).

Materials and methods

Bullet impacted sand

Uncontaminated range sand was obtained from an existing military range in Umeå, northern Sweden, where a new impact berm had been installed. The sampling was performed on the side of the berm facing away from the firing point to minimize the potential of pre-existing heavy metal contamination. X-Ray fluorescence (XRF) analysis confirmed that the sand did not have prior heavy metal contamination. A total

of 500 rounds of 7.62 mm jacketed military ammunition were then fired into the soil in a controlled fashion on an indoor range.

Lysimeter construction

Uncontaminated range sand was used in the construction of two lysimeters measuring 40 cm in diameter and 40 cm in depth. Sand samples were obtained from two Swedish military shooting ranges, from the back side of the berm facing away from the firing points. X-Ray fluorescence (XRF) analysis confirmed that the sand did not have prior heavy metal contamination. The sand columns were built up gradually by compacting 2 cm thick layers of sand sequentially to ensure maximal density. Following the compaction of each layer, the sand surface was scarified with a nylon comb. This was done both to ensure complete hydraulic connectivity with the subsequent sand layer and to minimize the potential for horizontal preferential flow. A 4 cm thick layer of bullet-impacted sand was then placed on the surface of each of the two lysimeters.

A 40 cm diameter 1-bar ceramic pressure plate cell (Soilmoisture Ceramic-B0.5M2) was installed at the base of each lysimeter. This pressure plate has an effective pore size of 6.0 μm . The negative head was created with a hanging column of effluent in the outflow hose from the pressure plate. The negative head determined the degree of saturation of the sand column. Time domain reflectometer (TDR) probes were installed at depths of 5 cm, 20 cm and 35 cm below the surface of the lysimeter to ensure that the sand moisture was maintained within an acceptable range. The TDR probes automatically read sand moisture content and sent the information to a datalogger every 30 seconds. The head was adjusted by trial and error to produce a sand moisture content of $0.20 + 0.05$ (mass ratio) throughout the lysimeter, which is consistent with surface conditions of the sand at the shooting range. Saturated conditions occurred at a moisture content of 0.37.

Infiltration protocol

The infiltration rate for a sand during the springtime snowmelt in northern Sweden was determined by integrating historical water table fluctuation data, precipitation data and temperature data from SGU, Geological Survey of Sweden; SMHI, the Swedish meteorological society and from BALTEX, the Baltic Sea Experiment (unpublished data). A 15 year period from 1985 – 2000 was used to calculate the average time for complete snowmelt (31 days) and the average total infiltration caused by the snowmelt (115 mm). Historical hourly temperature data was not available, so it was assumed that melting and therefore infiltration occurred between 10 am and 6 pm. Given the surface area of the lysimeters (0.126 m²), the infiltration rate for each lysimeter was calculated to be 0.48 liters day⁻¹ or 1.00 ml min⁻¹ for 8 hours daily.

Infiltrate chemistry and ambient temperature

The chemical composition of the snowmelt was determined using rainfall chemistry from Svartbergets Research Station (Swedish University of Agricultural Sciences) in Vindeln (Lat./Long. 67°11' N; 19°38' E). Aqueous concentrations are shown in Table 1. The pH of the infiltrate was adjusted to a value of 4.8, which is a historical average value of the springtime snowmelt runoff in the area of interest (Laudon *et al.* 1999). The lysimeters were placed in an environmental chamber and the ambient temperature was held at a constant value of 4° C, again to simulate environmental conditions during the period of snowmelt as closely as possible.

Results

The leachate from the lysimeters was chemically analyzed for Pb and Sb for the duration of the experiment. The pH of the leachate remained stable throughout the period of analysis at 4.8 ± 0.1 and while the redox potential was not monitored, ambient conditions and temperature were not changed for the duration of the experiment. The water samples were not filtered, but the use of the ceramic pressure plate removed all particles greater than the pore size of 6.0 μm . The data are shown in Figure 1. Lead concentrations generally remained stable or decreased slightly over time throughout the experiment in both lysimeters. The concentration remained under 2 $\mu\text{g/L}$, which is lower than the Swedish Environmental Protection Agency (EPA) limit of 10 $\mu\text{g/L}$ set for drinking water (Naturvårdsverket 1999, Annex 4). Thus, the origin of the Pb observed in the leachate is likely to be background and not originate from the bullet fragments. This implies that the Pb from the bullet impacted sand is relatively immobile, even in sands which have no clay fraction and little organic matter to retard the contaminants in the lysimeter effluent.

In contrast, the Sb in the effluent from both lysimeters showed a classic breakthrough curve. At the peak concentration, the Sb in the effluent was over two orders of magnitude higher than the Pb concentrations,

despite Sb being a minor alloying agent in the bullets. Figure 1 shows that peak concentrations of Sb in the lysimeter containing the sand from Umeå reached 124 µg/L and this occurred after 29 days of infiltration. This effluent would be considered “very seriously” contaminated according to the Swedish EPA guidelines for groundwater (Naturvårdsverket 1999, Annex 4). The transport of Sb in the lysimeter containing the sand from the first range is retarded by approximately 10 – 15 days relative to that of the second range and peak concentrations of Sb were not achieved before the snowmelt infiltration protocol ended. The area under the right hand curves of figure 1 provides the total mass of Sb which was mobilized. 1.7 mg and 0.6 mg of Sb were captured in the effluent of the two lysimeters. Given the standardized berm sand used by the Swedish military, the results should be applicable to military ranges throughout Sweden assuming a similar bullet distribution and infiltration pattern.

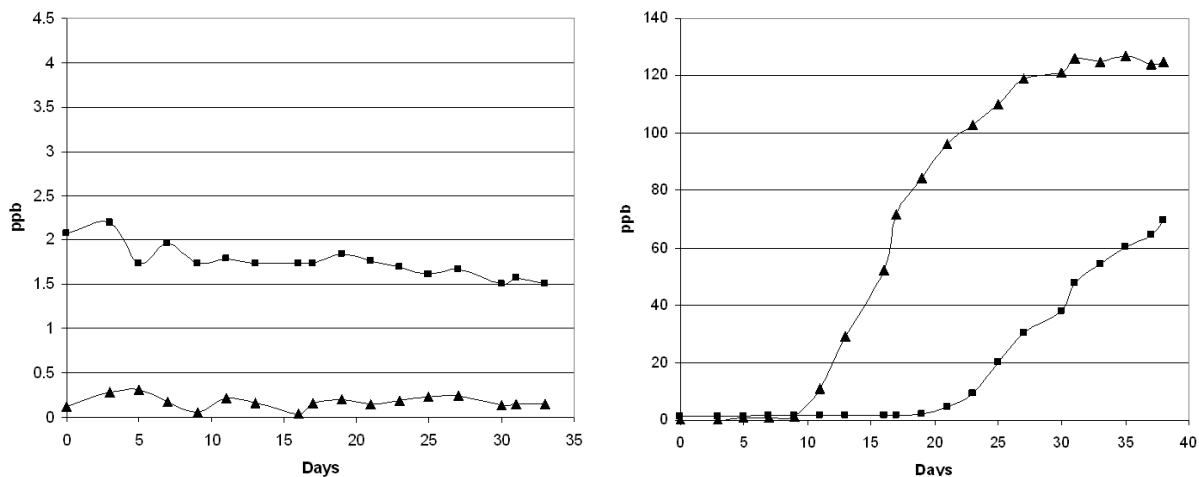


Figure 1. Pb (left) and Sb (right) concentrations in lysimeter effluent. Triangle and square symbols show results from the two different lysimeters

Discussion

As was pointed out in the introduction, there are significant knowledge gaps in the state of the art concerning the environmental impacts of Sb. Our observations indicate that Sb is highly mobile both in speed of transport and mass of transport in the vadose zone of Swedish berm sands. This contrasts with the findings of Knechtenhofer *et al.* (2003) who showed that within 40 cm sand depth Sb concentrations on a shooting range approached background concentrations. However, the sands investigated by Knechtenhofer *et al.* (2003) had a very low pH of 3.6 and contained 15% organic carbon, making comparisons with our results difficult. There is some evidence in the literature that complexation with organic ligands may stabilize Sb compounds (Brookins, 1972).

The difference in the rate of Sb transport between the two lysimeters may reasonably be attributed to slightly different concentrations of either Fe (hydro)xides or clays, either of which have been shown to have a considerable impact on the sorption of antimony (Tighe *et al.* 2005). However, our experimental observations are in general consistent with the observations of Johnson *et al.* (2005) who noted that the release of Sb from shooting range sands was significant and considerably higher than the release of Pb. Further work will have to be performed to determine the redox processes that control the oxidation of Sb in surface sands.

Conclusions

Transport of Pb in the Swedish range sands was found to be negligible, with no clear solute breakthrough curve and with aqueous concentrations remaining stable at below 2 ppb. However, Sb was found to be far more mobile, with solute breakthrough occurring between 5 and 14 days and concentrations rising to over 125 ppb within one month.

References

- Basta NT, Pantone DJ, Tabatai MA (1993) Path analysis of heavy metal adsorption. *Soil Agron. J.* **85**,1054-1057.
- Boulding JR, Ginn JS (2004) 'Practical handbook of soil, vadose zone, and ground water contamination.' 2nd Ed. (Lewis Publishers)
- Brookins DG (1972) Stability of stibnite, metastibnite and some probably dissolved antimony species at 278.1°K and 1 atm. *Econ. Geol.* **67**, 369-372.
- Cao RX, Ma LQ, Chen M, Hardison DW, Harris WG (2003) Weathering of lead bullets and their environmental effects at outdoor shooting ranges. *J. Environ. Qual.* **32**, 526-534
- Dermatas D, Dadachov M, Dutko P, Menounou N, Arienti P, Shen G (2004) Weathering of lead in Fort Irwin firing range soils. *Global Nest* **6(2)**, 167-175.
- Johnson CA, Moench H, Wersin P, Kugler P, Wenger C (2005) Solubility of antimony and other elements in samples taken from shooting ranges. *J Environ Qual.* **24**, 248-254
- Jorgensen SS, Willems M (1987) The fate of lead in soils: the transformation of lead pellets in shooting range soils. *Ambio* **16**, 11-15.
- Knechtenhofer LA, Xifra IO, Scheinost AC, Fluhler 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. *J. Plant Nutr. Sand Sci.* **166**, 84-92.
- Krupka KM, Serne RJ (2002) Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Sediments. *Pacific Northwest National Laboratory, Richland, Washington. PNNL-14126*
- Kuperman RG, Checkai RT, Simini M, Phillips CT, Speicher JA, Barclift D (2005) Toxicity benchmarks for antimony, barium and beryllium determined using reproduction endpoints for *Folsomia candida*, *Eisenia fetida* and *Enchytraeus crypticus*. *Env. Toxicol. and Chem.* 754-762.
- Laudon HS, Köhler S, Bishop KH (1999) Natural acidity or anthropogenic acidification in the spring flood of northern Sweden. *Sci. Tot. Environ.* **234**, 63-73.
- Lindsay WL (1979) 'Chemical equilibria in sands' (John Wiley Publishers, New York)
- Ma.LQ, Hardison DW, Harris WG, Cao X, Zhou Q. (2007) Effects of soil property and soil amendment on weathering of abraded metallic Pb in shooting ranges. *Water Air Soil Pollut.* **178**, 297-307.
- Naturvårdsverket (1999) 'Metodik för inventering av förorenade områden.'
- Scheinost AC, Rossberg A, Vantelon D, Xifra I, Kretzschmar R, Leuz AK, Funke H, Johnson A (2006) Quantitative antimony speciation in shooting-range sands by EXAFS spectroscopy. *Geo. Cosmo. Acta*, **70**,3299-3312.
- Tighe M, Lockwood P, Wilson S (2005) Adsorption of antimony (V) by floodplain soils, amorphous iron(III) hydroxide and humic acid. *J. Environ. Monit.* 1177 – 1185.