EXAFS analysis of Pb speciation in bullet-contaminated range soils

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Abstract

This study was a lab-based investigation of range soils contaminated by 500 high velocity 7.62 mm jacketed Swedish military rounds. The 0.06 mm fraction of soil was analyzed using EXAFS to determine the speciation of Pb in the soil both before and after a simulated springtime snow melt. Contrary to previously published material, in both cases PbO and not hydrocerrusite was found to be the dominant lead species, which was attributed to the low organic content and pH of the soil when compared to previous studies.

Key Words

EXAFS, Pb speciation, shooting range.

Introduction

Civilian and military shooting ranges concentrate spent bullets in relatively small areas. The United States (U.S.) Environmental Protection Agency (EPA) estimates that 7.26 x 10^7 kg of Pb shot and bullets enter the U.S. environment each year at approximately 9000 non-military shooting ranges. In Denmark, annual deposition rates of bullets and Pb shot have been estimated at 800 tons (Joergensen and Willems 1987). One serious difficulty with in-situ research approaches when dealing with ranges is that a great deal of uncertainty exists concerning what ammunition has been fired during the lifetime of the range. Such records are usually difficult to come by and, when available, are usually not detailed enough to indicate accurately what shooting activities have taken place on a given firing point. These uncertainties make it difficult to establish a quantitative link between shooting activity and the eventual fate and distribution of the resulting metals. For example, it is plausible that unjacketed, subsonic, low caliber ammunition will produce different heavy metal loads in the berm sand than jacketed, high velocity, large caliber munitions. Differentiating the influence of the two munitions on an existing range without accurate records is nearly impossible.

Another factor which will influence the fate of metals in sand is the local climate (Dermatas *et al.* 2004). In northern latitudes, up to 70% of the annual groundwater recharge occurs in the three or four week period when the snow pack melts in springtime. At this time of year, evapotranspiration losses are minimal due to the lack of photosynthesis and the low temperatures, so most of the infiltrate eventually reaches the water table and ultimately surface water bodies. This snowmelt has been shown to have a lower pH than the average annual precipitation in northern Sweden (Laudon *et al.* 1999), and low pH has been cited as one factor which could increase the dissolution (Dermatas *et al.* 2004) or colloidal mobility of metals (Klitzke *et al.* 2008). The objective of this study was to use EXAFS (extended X-ray absorption fine structure) spectroscopy to identify the Pb minerals which exist in a bullet- contaminated soil before and after exposure to a simulated snowmelt.

Materials and methods

Bullet impacted sand

To produce the source term for the experiment, 500 rounds of 7.62 mm jacketed military ammunition were fired into an uncontaminated range sand obtained from an existing military range in Umeå, northern Sweden.

Lysimeter construction

Impact berm samples were used to construct two column-type lysimeters 0.4 m in diameter and 0.4 m deep. A 4 cm thick layer of bullet-impacted sand was then placed on the surface of the lysimeters. Based on historical water table fluctuation data, precipitation data and temperature data for the springtime snowmelt in northern Sweden, the infiltration rate for each lysimeter was calculated to be 0.48 liters/day or 1.00 mL/min for 8 hours daily. 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). The pH of the infiltrate was adjusted to a value of 4.8, which is an 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.

EXAFS analyses

Only the finest fraction of sand (< 0.06 mm) was investigated by EXAFS analysis. This fraction of bullet-impacted sand was analyzed both before and after the infiltration protocol. In addition, a 1 cm layer of initially uncontaminated sand taken from a depth 1 cm below the bottom of the bullet impacted sand was analyzed to determine the chemical speciation of Pb reaching this depth as a consequence of mobilization during infiltration. EXAFS data were collected in fluorescent mode using a Lytle detector filled with Kr, at the Pb L_{III}-edge at the super conducting multi-pole wiggler beamline i811 at MAX-Lab, Lund University, Sweden. The machine conditions were 1.5 GeV energy and 100–200 mA electron current. Spectra were recorded at room temperature at ambient atmospheric pressure using a double crystal monochromator (Si [111]). The energy was calibrated by a Pb foil, and the first maximum of the first derivative of the Pb L_{III}-edge set at 13.035 keV. Samples were positioned at 45° to the incident beam and a Ga filter was placed between the sample and the detector. The monochromator was detuned 15–25% to remove higher order harmonics. EXAFS data were collected at an exposure time of 2–4 s for each data point with 5 eV steps from 200 eV before the edge and 1 eV steps from the edge and up to 800 eV after the edge. Each EXAFS spectrum represents the average of 2-3 scans, each scan taking about 60 min to collect. For reduction and analysis of EXAFS data, the program WinXAS97 (Ressler, 1998) was used. From each averaged spectrum a polynomial pre-edge function was subtracted and the data were normalized. Above the absorption edge a cubic spline fit was used to remove the background. Data were k3-weighted, normalized and the edge-energy was set as the first maximum of the first-derivative. Transmission EXAFS data were obtained for a selection of model compounds diluted in boron nitride; hydrocerrucite [$Pb_3(CO_3)_2(OH)_2$); cerrucite ($PbCO_3$); litharge (PbO, tetragonal); and Pb bound to soil organic matter (SOM). These model compounds were used to reproduce the experimental curves of contaminated sand by a least-square, linear combination fitting (LCF) procedure. The fitting interval was performed over the k-range 1.0 – 8.7 $Å^{-1}$.The model compound for Pb bound to SOM was prepared by adding an aqueous solution of Pb(II) nitrate to an organic, fen peat soil (54% organic C content by mass), resulting in a final concentration of 4,000 µg Pb(II) g^{-1}. pH was adjusted to 5.0 by NaOH. Iron k-edge X-ray absorption near-edge spectroscopy (XANES) analyses revealed no detectable goethite in the organic soil (unpublished data).

Results

The EXAFS analyses and model fitting are shown in Figure 1. A simple visual comparison of EXAFS spectra reveals a similarity between the contaminated sand (before and after leaching) and the model compound litharge, indicating PbO(s) to be the most dominant Pb species in the first 30 cm. Also, the layer of soil 1 cm below the contaminated sand indicated that PbO(s) was present as the predominant Pb species, even if data were not fitted (because of a lower signal-to-noise ratio). The PbO(s) model compound showed a distinctive secondary peak in the normalized EXAFS spectrum at 3 $Å^{-1}$, which was shared by all experimental sands. In contrast, cerrusite had a trough at 3 $Å^{-1}$ and hydrocerrusite had a distinctive double peak. The best model for the experimental spectra of the contaminated sand was a linear combination of 25% Pb bound to organic matter and 75% PbO, and 30% Pb bound to organic matter and 70% PbO in the leached, contaminated sand. Given that the error sum of squares was decreased by 48% by adding organically bound Pb to the model only including PbO, the contribution from organic Pb complexes were highly significant.

Discussion

Based on our EXAFS analysis, a relatively small quantity of organic matter in the <0.06 mm fraction of the contaminated sand (0.65 mass-% organic C) would be enough to account for the complexation of 25% of total Pb. Given that natural organic matter on average contains one carboxyl group per six organic carbon atoms (Stevenson, 1994), a soil content of 0.65% organic C corresponds to a concentration of 45 mmol kg^{-1} carboxyls, which is more than enough to complex 25% of the total concentration of 110 mmol Pb kg^{-1} found in the contaminated soil. In a similar EXAFS study, Hashimoto and co-workers (2009) found that 38% of total Pb (at a concentration of 18,000 mg kg^{-1}or 87 mmol Pb kg^{-1}) was organically complexed in a shooting range soil containing 8.6% organic matter.

Most of the literature concerning field observations of Pb species on active firing ranges reports that hydrocerrusite ($Pb_3(CO_3)_2(OH)_2$) and cerrusite ($PbCO_3$) are the dominant solid species of Pb to be found (Johnson *et al.* 2005). In other studies, PbO(s) has been determined to be a minor component of the weathering products of bullets (Dermatas *et al.* 2004; Hardison *et al.* 2004). However, Hashimoto *et al.* (2009) recently determined that between 22% and 46% of the total lead in an amended shooting range soil was in the form of PbO.

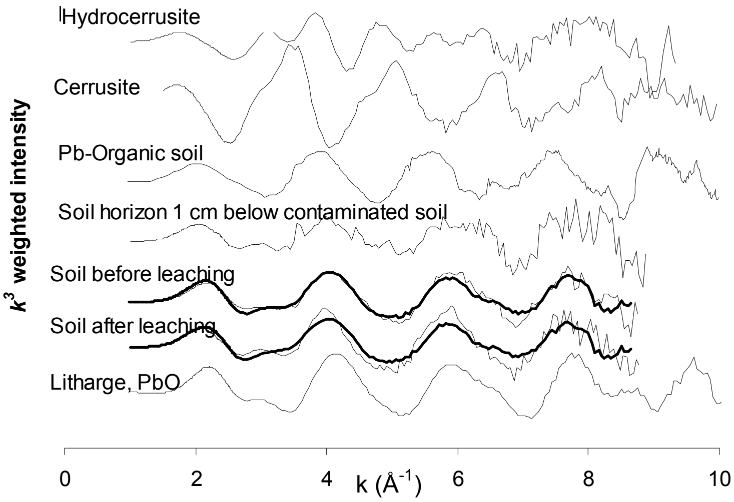

Figure 1. EXAFS spectra of model compounds and experimental samples

The formation of cerrusite and hydrocerrusite are predicated on the availability of the carbonate ion (Basta *et al.* 1993). Microbial activity in sands with significant amounts of organic matter may raise pore concentrations of CO_2 and it has been shown that an elevated partial pressure of CO_2 relative to the atmosphere favours the formation of Pb carbonates (Lindsay, 1979). The sand and gravel mixture used on Swedish ranges is quite low in organic material. Together with the low pH of 4.8 (shifting the equilibrium to carbonic acid and degassing of CO_2), this suggests a lack of available carbonate anions, which will favour the formation of PbO(s) over Pb carbonates.

Lead oxide exists in two forms; orthorhombic β-PbO (massicot) and tetragonal α-PbO (litharge). In most previous spectroscopic studies (Hashimoto *et al.* 2009; Scheckel, 2004), only massicot has been investigated, while Ma *et al.* (2007) only investigated litharge. Vantelon *et al.* (2005) considered both massicot and litharge but concluded that the signal of PbO was too weak to allow a non-ambiguous assignment to either litharge or massicot. In the current study, we only used litharge as model compound for PbO. However, given the similarity of EXAFS spectra for litharge and massicot, we cannot exclude possible contribution from massicot in our samples. Therefore, we have chosen to refer only to PbO throughout this article rather than to specify either litharge or massicot.

Based on their experimental observations, Ma *et al.* (2007) have proposed a three step model for the weathering of Pb in sand in which the first step is the oxidation of metallic Pb to PbO. Vantelon *et al.* (2005) have shown that in the weathered crust of bullets, PbO is the mineral which is found closest to the metal surface, indicating that it is the first product of weathering. Our results are in agreement with these observations and suggest that PbO is in fact the first product of weathering when a bullet is exposed to the environment, and that the kinetics of carbonate formation are significantly slower. The study reported by Hardison *et al.* (2004) is especially interesting in the context of our results because the sand used was the type used in children's play areas, which implies an organic content that is presumably at least as low as that in the current experiment. One possible explanation for these differences is that the kinetics of reaction between the various Pb minerals is different at 4°C than it is at 20°C. The effect of temperature on Pb speciation in sands has not been discussed in the literature.

Conclusions

The majority of the Pb in the sands was found to be in the form of PbO both before and after infiltration. This was explained by the low organic content and pH of the soil compared to previous studies which prevented the formation of carbonates, the rapid kinetics of reaction of PbO as compared to the Pb carbonates, and the higher ambient redox potential used in this experiment.

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