Immolization of Pb and Sb in Shooting Range Soil: Column experiment providing an Industrial waste Iron-based sorbent.

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Abstract.

Shooting ranges are sources of lead (Pb) and antimony (Sb) contamination to soil. In this study, we investigated if low cost industrial waste could be used as a sorbent to immobilize Pb and Sb. The sorbent contain oxides of iron (Fe, 26%), aluminum (Al, 5%) and calcium (Ca, 5%). Total concentrations of Pb and Sb in the soil test were 3600 mg/kg and 72 mg/kg, respectively. Total organic carbon (TOC) content was 5%. In the experiment, four different mixtures of this sorbent were tested, using 15 columns. The sorbent was either mixed into the soil or used as filter at the bottom of the column. The experiment was carried out over a five-week period. Drainage water was collected periodically and analyzed for Pb, Sb, dissolved organic carbon (DOC), Fe and pH. The retention effect of mixing 10% by volum of sorbent into the soil was shown to be approximately 60% for both Pb and Sb. When the sorbent was used as a filter at the bottom of the columns retention was about 90%. The results indicated that shifts in redox conditions during the test period, lead to increased mobilization of Sb. Such scenarios may take place in real treatment situations.

Introduction

Small-arms shooting ranges are recognized sources of heavy metal and -metalloid pollutants. The most common contaminates are lead (Pb), copper (Cu) and antimony (Sb). In Norway approximately 103 tons of Pb and 12 tons of Sb were deposited at small arms shooting ranges in 2006 [1]. Trace metals in soils are mostly partitioned in organic and inorganic fractions. The fraction of metals bound to solid solids react quickly to physicochemical changes in the soil. Such changes occur typically under shifts in pH and redox conditions, changes in DOC in pore water and even to changes in quality or quantity of solids such as iron oxides [2]. Study by Hockmann et. al [3] have shown strong seasonal fluctuation in Sb leaching from non-waterlogged calcareous soil, which seem to be driven by fluctuation in DOC and probably also bicarbonate concentrations. Another study from Hockmann et. al [4] provided evidence that transitioning from oxidative to anaerobic conditions in soils can lead to reduction of Sb(V) to Sb(III) within days to weeks. That means that Sb(V) is less stable in redox-variable soils than previously assumed. Given that Sb(III) is more toxic than Sb(V), redox condition is one of the key factors for estimating mobility, and thereby risk of leaching of Sb from soil. In landfills, there are two alternative methods by which to reduce the risk of Pb and Sb leaching from contaminated soil. The first is to collect all the seepage from the soil and purify the water. The second is amending the soil aiming at stabilizing the pollutants, thus reducing metal mobility. The second alternative may be a more cost-effective method than continuous water treatment, particularly at large scale. Both lime and phosphate amendments has successfully been used to stabilize Pb in shooting range soil [5]. In many case liming can increase soil pH, effecting a reduction of sorption capacity for the negatively charged Sb(V) oxyanion (Sb(OH)\textsubscript{5}) [5,6]. Liming also increases leaching of DOC in soils high in organic matter. Since humic acids are the major binding sites for antimony in such soils, a side effect of liming may lead to increased mobility of antimony. Phosphate competes for
sorption sites and increases mobility of antimony. When stabilizing shooting range soil it is important to immobilize both Pb and Sb. Ferric oxyhydroxides provide stable sorption sites for both Sb and heavy metals like Pb and Cu. Hence, ferric oxyhydroxides (co)precipitates both cationic and anionic substances. Both anions and cations may bind on the surface of iron oxides in two ways: specific and nonspecific adsorption [5,7]. Nonspecific adsorption is controlled by electrostatic interactions between the sorbent surface and the ions present in solution. In the case of specific adsorption, the migration of anions and cations from the solution result in inner-sphere adsorption where the hydroxyl groups coordinate with a single iron atom. Bonding of anions on the adsorbent surface is accompanied by the release of hydroxyl groups, which contribute to the alkalization of the soil environment [7]. The specific adsorption of anions is possible in an environment where pH is higher than the pH (pzc) of the sorbent, while the adsorption of cations can proceed in a slightly acidic environment, in which their solubility is the highest [8]. In this study, we aimed to investigate if an iron-based sorbent stemming from industrial waste could immobilize Pb and Sb from contaminated shooting-range soil. The study was performed over 5 weeks. Consecutive water extractions were taken to learn if the sorbent would immobilize the trace metals over time.

Materials and Methods

Soil material was collected from backstop berm located at Tittelsnes military shooting ranges in Sveio municipality, in Norway (UTM 59.7146301269531 N, 5.50814199447632 E). The shooting range was in use for 55 years. The climate is oceanic, with 1800 mm average annual precipitation. Mean temperature of the coolest month is 1°C and the warmest month is 14°C. The bedrock consists mostly of acidic gneiss.

Table 1, Content of TOC, Sb, Pb, Ca, Fe, Cu and pH in control soil from Tittelsnes (n=3).

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>TOC</th>
<th>Sb mg/kg</th>
<th>Pb mg/kg</th>
<th>Ca g/kg</th>
<th>Fe g/kg</th>
<th>Cu mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>7,7</td>
<td>5%</td>
<td>72,7 ± 2,1</td>
<td>3633 ± 57,7</td>
<td>21,5 ± 0,2</td>
<td>32,4 ± 0,5</td>
<td>180,0 ± 10</td>
</tr>
<tr>
<td>Sorbent</td>
<td>11,2</td>
<td>-</td>
<td>0,7± 0,1</td>
<td>4,4± 0,2</td>
<td>52± 0,3</td>
<td>277± 8,8</td>
<td>20,7± 0,6</td>
</tr>
</tbody>
</table>

All extractions were carried out in triplicate unless stated otherwise. Acid digestion of soil samples were carried out using a mixture of hydrogen fluoride (HF) and concentrated nitric acid (HNO₃) in a ratio1/5, with 0,25 g samples (oven-dried (105°C) in an ultrclave (260°C). Digestion of certified reference soils (2711a og 2710a) was conducted, and the recoveries were 96,5 and 100 % for Cu, 97,8 and 100% for Pb and 88% for Sb. Elemental analysis was conducted using inductive coupled plasma mass spectrometry (Agilent Technologies 8800 ICP-MS Triple Quad). The sorbent was derived from industrial waste, produced by Tinzir Titan & Iron AS based in Tyssedal, Norway. It is a byproduct of titanium and iron smelting, and consists mostly of oxides of iron, calcium, titanium, zinc, aluminum and sulfur. pH is approx. 11 and relative density is 1.5-1.86 g/cm³. The sorbent was manually sifted at 6.7 mm mesh. The columns were of stainless steel with diameter 10 cm. Columns of both 100 cm and 50 cm were used. Each soil type received 5 different treatments, with sorbent added per volume: 1) Untreated soil, 2) Soil with 5% sorbent, 3) soil with 10% sorbent, 4) soil with 5% sorbent as a filter at the bottom of the column, 5) soil with 10% sorbent as a filter in the bottom of the column. Each triplicate was made of one 100 cm column and two 50 cm columns. The soil was homogenized in a cement mixer before it was mixed with the sorbent. The sorbent was mixed into the homogenized soil by hand. The column bases had stainless steel screening (mesh size 0.5 mm) and a Weissband Rundfilter aschefrei 125 mm filter attached to facilitate gravity drainage. Whatmans 40 ashless 9,0 filter paper was placed on top of each column to spread the water evenly. Water was added manually to each column to field capacity. The columns were equilibrated in 24 hours before distilled water was carefully added in top to replace the exact volume of the equilibrium water.
samples were collected after approximately 2 hours. This procedure was repeated 5 times: days 1, 2, 3, 10 and 45. Water samples were filtered through 0.45 µm polyether sulfon membrane filters to analysis of total Pb and Sb. Element concentrations in the collected water were determined using the ICP-MS. pH was measured manually with an Orion SA 720 pH meter. DOC was measured with Shimadzu TOC-V CPN Carbon analyzer.

Results

The results show clear differences between treated and untreated soil. The concentrations of Pb and Sb in the leached water varied from 80-150 µg/l for Pb and from 200-450 µg/l for Sb (figure 1). Comparatively, concentration decreased to 50 µg/l for Pb and 120 µg/l for Sb with 5% sorbent mixed with the soil. The 10% sorbent-soil mix significantly increased adsorption (over 10% increase) compared to 5% sorbent-soil mix.

The leached concentrations of Pb and Sb were fairly stable during the first days of the experiment, but after 45 days, however, the concentration of leached Sb increased from all treatments. This may be connected to changing redox conditions. Hockmann et. al [3] reported that a transition from oxidative to anaerobic conditions can lead to reduction of Sb(V) to Sb(III) in soils within days to weeks, and that Sb(V) is sensitive to the redox environment. Figure 2 shows retention effects for both Pb and Sb. Interestingly, the retention efficiency remains almost unchanged even with increased leaching over the 45 days period. Effective retention in the 5% sorbent treated soil was approximately 50% for Pb and less than 50% for Sb. Increasing the sorbent additions to 10% had a greater effect for Sb than for Pb. Better retention was achieved when using the same amount of sorbent as a filter at the bottom of the columns, compared to mixing the sorbent with the soil. A sorbent filter volume corresponding to 5%
resulted in retention of approx 90% of lead and 75% of antimony. Comparatively, 10% sorbent filter volume added to the bottom of the column resulted in 95% retention of lead and 90% of antimony. The observed effect of the sorbent used as a filter compared to mixed in the soil may be incomplete contact of soil water with sorbent that the sorbent doesn't get contact with the majority of the water with less than 10% of sorbent added to the soil. All the water is forced through the sorbent when it is used as filter at the bottom. The total cumulative capacity of the sorbent filter to retain Pb and Sb remains to be determined.

Conclusions

This study shows that industrial waste with high iron oxide content may be used to retain lead and antimony contamination in soil from shooting ranges. Low sorbent cost makes it plausible to consider establishing a functional method, based on an industrial waste, to stabilize contamination in soil from shooting ranges, in landfill. There is a significant effect both when the sorbent is used as a filter at the bottom of the columns and also when the sorbent is mixed within the soil profile, although our results show that the sorbent is more effective when used as filter at the bottom of the soil. We found indications of shifts in redox condition during the test period. This might cause difficulties in landfill as the stabilization Sb and Pb should be permanent and effective in both oxic and anoxic conditions.

References