



Use of soil amendments to immobilize antimony and lead in moderately contaminated shooting range soils



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HIGHLIGHTS

- Chemical stabilization of shooting range soil with various amendments was trialed.
- Reducing agent FeSO₄ reduced Sb^V to Sb^{III} and decreased Sb leaching.
- However it greatly increased Pb and heavy metal leaching.
- FeSO₄ + ViroSoil™ was best overall treatment at reducing leaching of Sb and Pb.

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ABSTRACT

Shooting ranges are a source of environmental concern around the world as they are a source of toxic antimony (Sb) and lead (Pb). In-situ chemical stabilization is a strategy to reduce metal(loid) leaching and bioavailability. However it is difficult to find the right treatment due to the fact that Pb is a cation and Sb an anion, under oxidised conditions and they often show the opposite mobility in soil, on the application of amendments. A batch experiment was set up with two soils (slightly acidic and alkaline), two red mud based amendments (ViroSoil™ 1 and 2) alone and in combination with two reducing agents (zero valent iron and iron sulphate), to assess the effect of the treatments on metal(loid) leaching and compare it to unamended soil and soil amended with goethite, a known Sb adsorbent. Iron sulphate was effective at reducing Sb leaching due to the reduction of Sb^V to Sb^{III} which bound more strongly to iron (hydr)oxides in soil. However it had an adverse effect on the leaching of Pb due to its acidifying effect and reductive dissolution of manganese (hydr)oxides. Combining ViroSoil™ amendments with FeSO₄ still reduced Sb leaching but also Pb leaching and proved a suitable treatment.

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1. Introduction

Shooting ranges are a source of environmental concern around the world [1] especially in countries where they are prevalent such as the USA, Canada, Scandinavia and Switzerland [1,2]. Lead based bullets enter the soil and are weathered over time, mobilising metal(loids) such as lead (Pb) and antimony (Sb) which are components of the bullets (93.1% Pb, 1.9% Sb) [1,3]. In Switzerland 400 t Pb and up to 25 t Sb enter the soil in shooting ranges every year while in larger countries such as the USA deposits are up to 72,600 t Pb and 1900 t Sb [1,4]. Both Pb and Sb are toxic and as such, pollutants of primary concern [5,6]. Shooting range soils have been

shown to have reduced soil enzyme activity and invertebrates with high Pb concentrations, while Pb has been shown to reduce litter decomposers in soil, showing that the pollution in shooting range soils can damage soil health [7]. High levels of Pb can also be found in plants growing in shooting range soils [7,8] and this may cause problems for grazing animals, as in Switzerland it is common to use shooting ranges for grazing when not in use or decommissioned. The elevated levels of metal(loid)s in shooting ranges can lead to elevated concentrations in the aquatic environment surrounding them [9–12]. Even though Pb is found in much higher concentrations in bullets and shooting range soil than Sb, it has been found that Sb can be much higher than Pb in leachate from shooting range material [13] reaching over the Swiss regulatory value of eluent from polluted sites (Sb 10 µg l⁻¹, Pb 50 µg l⁻¹) [2,14]. This is due to the fact that Sb is more soluble than Pb in the near neutral pH range [15]. At neutral pH Pb²⁺ is bound strongly to clays, organic matter and iron (Fe) (hydr)oxides while the binding to Fe (hydr)oxides by Sb in its oxidised form (Sb^V) starts to become weaker due to its

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anionic nature ($\text{Sb}(\text{OH})_6^-$) [16–19]. Therefore it could be necessary to remediate shooting ranges to prevent the leaching of these toxic elements and reduce their bioavailability.

One method of doing this, is in-situ chemical stabilisation, where amendments are added to the soil to reduce the mobility of the contaminants [20]. This may be difficult when trying to remediate both cationic (Pb^{2+}) and anionic ($\text{Sb}(\text{OH})_6^-$), pollutants as often amendments have the opposite effect on them. The addition of biochar has been shown to reduce the concentration of exchangeable Pb and Pb leaching, due to an increase in pH, phosphorous and organic matter content [21–23]. However this treatment gave mixed results for Sb, with no decrease found for leaching and either a decrease or no change found for exchangeable Sb [22,23]. This may be due to the increased dissolved organic carbon (DOC) and phosphate competing with Sb for Fe (hydr)oxide binding sites, or the increase in pH causing weaker binding of Sb^{V} to Fe (hydr)oxides [19,24]. The addition of phosphorus is often a good stabilization strategy for Pb, as highly insoluble minerals are formed [25], but Sb may become more mobile due to competitive adsorption of phosphate on iron (Fe) (hydr)oxides [1,24,26]. Also liming or addition of other materials that raise soil pH may reduce soluble Pb [21,27] but increase soluble Sb due to the reduction in binding of Sb^{V} to iron (hydr)oxides at pH's over 6 [1,19].

One type of amendment that might allow the immobilisation of both Pb and Sb is based on 'red mud' a waste product from aluminium refining. Although originally very alkaline (pH 11.5) it can be 'neutralised' to give it a less extreme pH and have various additives incorporated to modify its properties [28,29]. Containing large quantities of Fe and aluminium (Al) (hydr)oxides as well as other minerals (sodalite, crancrinite, quartz, brucite, calcium carbonate, para-aluminohydrocalite, portlandite, hydrocalumite, hydrotalcite) it would provide a large number of binding sites for Sb and Pb. Furthermore the alkaline pH may lead to precipitation reactions immobilising Pb [28]. Moreover the bonds formed between the contaminants and red mud minerals are thought to strengthen over time due to occlusion within minerals, isomorphic substitution and diffusion into oxide lattices or mineral micro-pores [30–32]. On the other hand, it is also possible that the alkaline pH of these amendments may enhance Sb leaching. One way of remedying this could be the reduction of Sb^{V} (normally found under oxidised conditions) to its reduced form Sb^{III} which binds to Fe (hydr)oxides with fairly equal strength over a wide range of pH [19,24].

In this study we investigated two red mud based soil amendments alone and in combination with two reducing agents on two soils of differing properties but similar metal(loid) concentrations. This combination of red mud amendments and reducing agents has to our knowledge, not been applied before to soils contaminated with both lead and antimony and if successful would be a huge advance for the remediation of shooting range soils. We compared them to goethite, an Fe (hydr)oxide known to strongly bind Sb and to unamended soil. Leaching of the soil amendment mixtures was followed over time.

We expected increased immobilization of Sb and Pb in the red mud and goethite treatments due to the increased number of Fe (hydr)oxide binding sites, an additional immobilization of Pb in treatments with increased alkalinity and increased immobilization of Sb in treatments with reducing agents due to the conversion of antimonate to the stronger binding antimonite.

2. Materials and methods

2.1. Soils

The two soils used in this experiment were taken from two shooting range sites in Switzerland. One soil was taken from an

Table 1

Soil characterization parameters. Mean \pm standard deviation ($n=5$) [33].

| Parameter | Chur | Losone |
|---|------------------|------------------|
| pH H_2O | 8.2 \pm 0.1 | 6.1 \pm <0.1 |
| Electrical Conductivity (mS cm^{-1}) | 0.12 \pm <0.01 | 0.18 \pm <0.01 |
| Organic Carbon (%) | 0.81 \pm 0.02 | 5.43 \pm 0.90 |
| Cation Exchange Capacity ($\text{cmol}(+)\text{kg}^{-1}$) | 10.3 \pm 1.3 | 17.9 \pm 0.2 |
| Calcium carbonate (%) | 15.2 \pm 2 | <2 |
| Total Sb (mg kg^{-1}) | 21 \pm 1 | 17 \pm 2 |
| Total Pb (mg kg^{-1}) | 500 \pm 25 | 620 \pm 5 |
| Total Cu (mg kg^{-1}) | 66 \pm 13 | 63 \pm 3 |
| Total Ni (mg kg^{-1}) | 55 \pm 3 | 61 \pm 3 |
| Total Zn (mg kg^{-1}) | 110 \pm 3 | 100 \pm 1 |
| Total Mn (mg kg^{-1}) | 860 \pm 10 | 480 \pm 6 |
| Total Fe (%) | 3 \pm 0.04 | 3 \pm 0.05 |
| Soil texture classification | Silty loam | Silty loam |

Table 2

Amendment characterization.

| Parameter | VS1 | VS2 |
|---|------|-------|
| pH $\text{H}_2\text{O}^{\text{a}}$ | 8.7 | 11.8 |
| Organic Carbon (%) ^b | 0.44 | 0.40 |
| Inorganic Carbon (%) ^c | 0.50 | 0.45 |
| Sb (mg kg^{-1}) ^d | 6.8 | 5.5 |
| Pb (mg kg^{-1}) ^d | 75.5 | 82.5 |
| Cu (mg kg^{-1}) ^d | 27.6 | 29.0 |
| Ni (mg kg^{-1}) ^d | <1 | <1 |
| Zn (mg kg^{-1}) ^d | 42.3 | 42.8 |
| Mn (mg kg^{-1}) ^d | 339 | 336 |
| S (mg kg^{-1}) ^d | 1065 | 1065 |
| Cl (mg kg^{-1}) ^d | 8041 | 7964 |
| Fe (%) ^d | 30.6 | 29.6 |
| Al (%) ^d | 6.8 | 6.4 |
| Na (%) ^d | 3.58 | 2.97 |
| Si (%) ^d | 2.09 | 1.99 |
| Ca (%) ^d | 2.78 | 2.64 |
| Mg (%) ^d | 0.49 | 10.95 |

^a 1:2.5 amendment:water shaken for 24 h and settled for 30 min.

^b Difference between Total C (Combustion 900 °C, Solid sample module, SSM-5000A, Shimadzu and TOC-L Shimadzu) and inorganic C.

^c Addition of HCl plus heating to 200 °C with the same instrument as above.

^d XRF (Spectro Xepos, Amtek).

alluvial site along the Rhine river next to the city of Chur (Eastern Switzerland); the other from a site surrounded by forest in a side valley of the Melezza river at Losone (Southern Switzerland). Both sites have high average annual precipitation (1000–1200 mm) and temperatures between 23 °C in summer and 1 °C in winter. Samples were taken from the upper soil layer (0–30 cm), the sod and rooty materials were removed. All samples were mixed in-situ and again in the lab, to give one homogenized sample per site. The samples were air dried, sieved to less than 2 mm grain size and stored in plastic bags prior to laboratory analysis. Soil characterization has been carried out by Conesa et al. [33] and can be found in Table 1. They are classified as moderately contaminated soils.

2.2. Amendments

Iron^{II} sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, analytical grade) and zero valent iron (Fe^0 , $\text{Fe} < 10 \mu\text{m}$, analytical grade) were used as reducing agents. Two different formulations of the commercially available reagent ViroSoilTM a red mud derivative (Virotec Europe, Newcastle, UK), consisting mainly of iron and aluminium oxides and calcium and magnesium minerals were used as binding agents [28]. Characteristics of the two VirosoilTM amendments can be seen in Table 2. Goethite synthesized by the alkaline method [34] was used as reference binding agent.

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