The impact of phlogopite-rich mine tailings on the speciation of water-soluble Pb in contaminated boreal shooting range soil

Salla Venäläinen

Faculty of Agriculture and Forestry, University of Helsinki, Helsinki, Finland, Email salla.venalainen@helsinki.fi

Abstract
Changes in the water-solubility and the speciation of bullet-derived lead (Pb) in a contaminated shooting range soil were investigated in a pot experiment. Samples from the uppermost organic soil were incubated for 21 months with different particle-size fractions of untreated and artificially weathered (i.e. acid-treated) tailings from apatite ore beneficiation. Soil samples were subjected to water extraction. To estimate the proportion of the less toxic, non-cationic and organic Pb compounds in the total water-soluble Pb, the extracts were passed through cation exchange columns and analysed for Pb and dissolved organic carbon (DOC) before and after the cation exchange. Addition of untreated tailings to the organic soil decreased the water soluble Pb and increased the relative abundance of water-soluble and non-cationic Pb. On the contrary, incubation with the unsieved or the small particle-size fraction of the acid-treated tailings increased the water-solubility of Pb as well as the relative abundance of the most toxic Pb^{2+} and $PbOH^+$ species. The results indicated that the untreated and the large-sized acid-treated tailings might be suitable to the remediation of Pb-contaminated soils, whereas the unsieved and the small-sized acid-treated tailings may enhance leaching of Pb and, thus, cannot be considered as amendments.

Introduction
Lead (Pb) is toxic to living organisms and, if dissolved to the soil water, may end up in food chain and harm the ecosystem and human health. Due to its excellent ballistic properties, Pb is a commonly used element in shotgun pellets. Thus, shooting range soils are often subjected to Pb contamination.

The speciation and the mobility of Pb are strongly dictated by soil organic matter (SOM), soil pH and the nature of the mineral material present. In Finland, shooting ranges are typically located in boreal forest areas, where the topsoil is peaty and rich in humic substances, primarily humic and fulvic acids (HA and FA). In contact with such compounds, Pb is likely to form chelates and other organic complexes (Stevenson 1982). These compounds are more mobile and less toxic than the free Pb cation (Pb^{2+}) or the Pb hydroxycomplex ($PbOH^+$). The formation of organic Pb complexes is promoted by elevated soil pH, which contributes to the dissociation of H^+ from carboxyl and other organic functional groups and to the formation of negatively charged surfaces. Furthermore, high pH increases the stability of organometallic complexes but, on the other hand, increases the solubility of HAs (Klucakova & Pekar 2008) and, thus, the mobility of organically bound Pb. On the contrary, acid conditions promote the dissolution of Pb from pellets and increase the abundance of free Pb^{2+}.

If leached to the mineral soil horizons, Pb may be retained by hydrated Al and Fe oxides or amorphous silica emerging from the edges of weathered silicate minerals (Aualiitia and Pickering 1987; Elzinga and Sparks 2002). Such retention is specific in nature and favoured by low pH. Pb is also known to form various compounds with apatite and, in calcareous soils, with carbonate minerals. In certain conditions, the reaction between apatite and Pb may result in the formation of sparingly soluble pyromorphites [$Pb_{10}(PO_4)6(OH, F, Cl)_2$] (Cao et al. 2004). It can also be adsorbed through cation exchange with apatitic Ca^{2+} (Chen et al. 1997) or be specifically sorbed by functional surface groups of apatite (Mavropoulos et al. 2002). The free Pb^{2+} may also be adsorbed by calcite surfaces (Fulghum et al. 1988) through a specific mechanism (Rouff et al. 2002). Precipitation of Pb as carbonates also occurs (Taylor and Lopata 1984; Al-Degs et al. 2006).

Apatite ore mining at the Siilinjärvi carbonatite complex (described in detail by Puustinen 1971) produces mine tailings that mainly consist of a trioctahedral silicate mineral, phlogopite [$KMg_3(Si_3Al)O_{10}(OH)_2$)], accompanied by carbonate minerals, mostly calcite ($CaCO_3$), and fluorapatite [$Ca_5(PO_4)_3F$]. The chemical composition of the tailings in relation to Pb immobilisation may enable the material to act as an *in situ* remediation media on contaminated shooting ranges.

The aim of the study was to investigate the tailings-induced changes in the water-solubility, i.e. potential bioavailability, and in the speciation of water-soluble Pb (Pb_{ws}) in contaminated shooting range soil. For this purpose, an incubation experiment was carried out by amending contaminated soil with mine tailings of various particle sizes differing in the mineralogical composition (Hartikainen and Hartikainen 2008). A portion of the material was artificially weathered with strong acid, since acid-treatment has been shown to increase the abundance of reactive Al and Fe oxyhydroxides in the tailings (Hartikainen and Hartikainen 2008). The beneficial utilisation of the mine tailings aims to the reduction of bioavailability of Pb and, thus, protection of ecosystem and the groundwater, as well as to the decrease in the amount of waste produced by the mining industry.

Materials and methods
Soil samples
The soil samples originated from the organic horizon of Hälvälä shooting range (61°00.644' N, 025°28.406' E) located in Hollolla, southern Finland (area described in detail by Hartikainen and Kerko (2009)). The soil in the area is sandy with a moss layer on the top. In the laboratory, the shotgun pellets were picked out of the soil by hand and the pellet-free material was homogenized.

Tailings materials
The tailings provided by Kemira GrowHow Oyj originated in Siilinjärvi apatite ore, eastern Finland (63°6.893' N, 27°43.994' E). To investigate the impact of artificial weathering on the Pb immobilizing effect of the tailings, the material was treated with strong sulphuric acid. A portion of both untreated (UT) and acid-treated (AT) tailings was passed through a 2-mm sieve. Unsieved material was also included in the experiment.

Design of the incubation experiment
For the incubation experiment, 50-g samples of the homogenized peaty soil were amended with each of the tailings materials in four replicates. Four soil samples without tailings treatments served as controls. All the experimental units were moistened with 25 mL of mQ-H_2O (30% of water holding capacity) and incubated at 20°C for 21 months. During the incubation, the evaporated water was replaced by watering the samples according to weight loss.

Pb speciation
Following the incubation, water-extractable Pb was extracted at a soil:solution ratio of 1:200 (dw:V, 2h shaking, 250 rpm). A portion of the suspensions were filtered through a coarse (12-25-µm) filter paper (Pb_{tot}) and the rest of the solutions through a 0.2-µm membrane filter (Pb_{ws}). The membrane filtrates were subjected to cation exchange (CE) by passing them through solid phase extraction (SPE) tubes that were preconditioned with 0.4 M KH_2PO_4 (pH 5). The solutions were analysed for Pb with ICP-OES before and after the CE. The abundance of cationic Pb in various treatments was calculated as the difference between soluble Pb before and after the CE. To differentiate between the inorganic cationic Pb species (Pb^{2+} and $PbOH^+$) from the less toxic, organic cationic Pb species the solutions were also analysed for dissolved organic carbon (DOC) before and after the CE. The proportion of organic cationic Pb species in each solution was estimated as the difference between DOC before and after the CE. Finally, to determine the total Pb (Pb_{tot}) in each sample, the paper filtrates were subjected to microwave digestion and analysed for Pb with ICP-OES.

Results and discussion
Figure 1 depicts the Pb_{tot} and the Pb_{ws} (mg/l) and the solution pH before the CE and Figure 2 Pb_{ws} after the CE (note the scales). All size fractions of the UT tailings as well as the large particles of the AT tailings elevated the solution pH, whereas the unsieved and the small particle-size fraction of the AT tailings had no effect on pH. All particle-size fractions of the UT tailings decreased Pb_{ws}, especially the unsieved material. The large particle-size fraction of the AT tailings had no effect on Pb_{ws}, while both the unsieved and the small particle-size fraction of this material increased this Pb pool notably. In the soil amended with the unsieved and the small particle-size fraction AT tailings, Pb_{ws} was equal to the Pb_{tot}, i.e. no Pb was bound by the large-molecular humic substances or by particulate organic matter. This was probably due to the low pH of the tailings that resulted in the disintegration of Pb from its compounds.

Passing the solutions through the CE columns decreased the Pb_{ws} substantially in all treatments (Figure 2). The proportion of non-cationic Pb to the total soluble Pb was substantially higher for the soil amended with the UT tailings (9–12%) than for the soil amended with the AT tailings (1–4%). In the control soil, the ratio was 5%. This suggests that the UT tailings increased the abundance of the less toxic, non-cationic Pb in the soil water at the expense of the more toxic, cationic Pb species. The phenomenon can be explained by the liming effect of the UT tailings that resulted in increased stability of organic Pb complexes. The proportion of non-cationic DOC to the total DOC ranged between 81–97%. The high ratios indicate that the CE did not affect the DOC notably and that nearly all of the Pb retained by the CE column was in inorganic form.
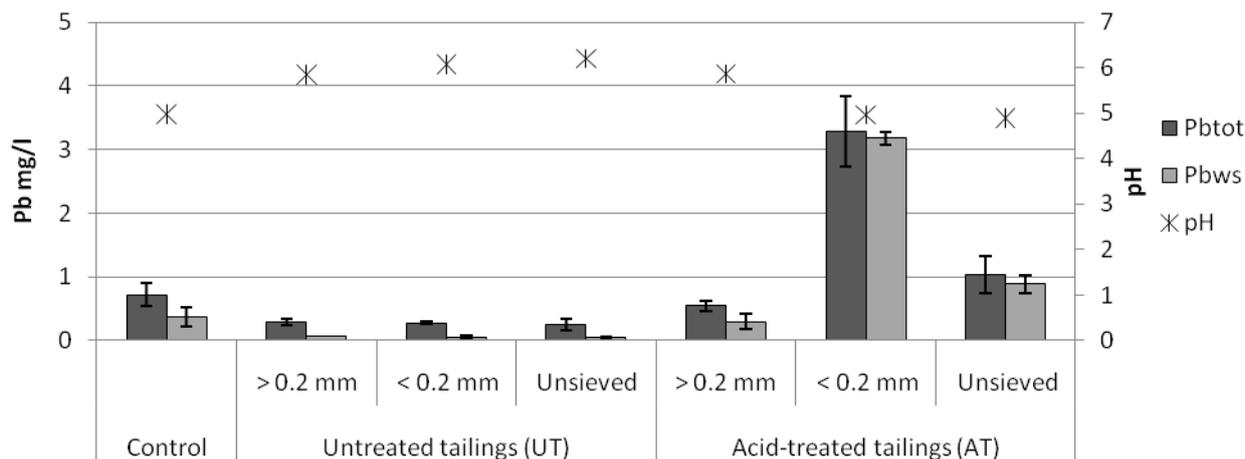

Figure 1. Total Pb in the samples (Pb$_{tot}$), soluble Pb (Pb$_{ws}$) and pH in the water extract before cation exchange. The error bars indicate the standard deviations of Pb.
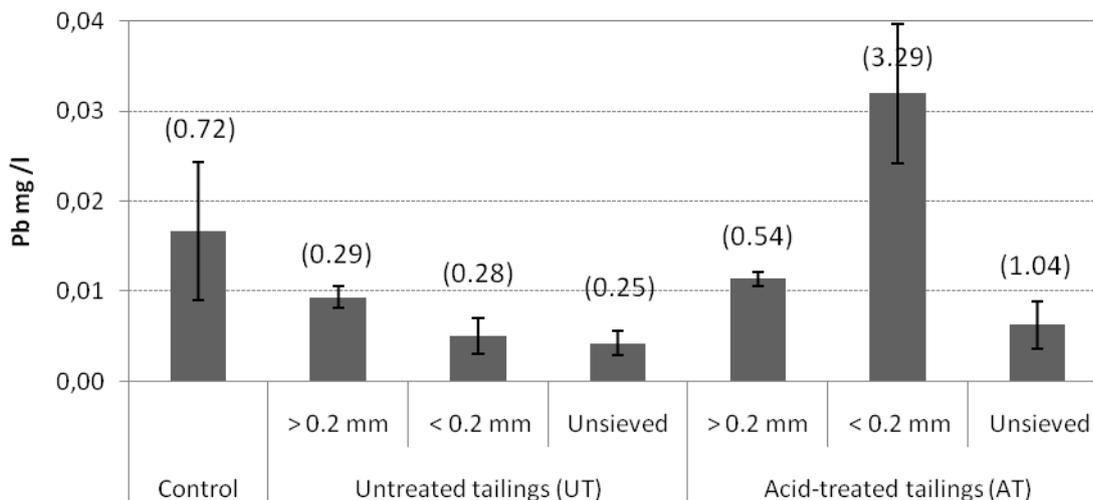

Figure 2. Non-cationic Pb in the water solution. The values in the brackets indicate Pb$_{tot}$ (mg/l) and the error bars indicate the standard deviations of Pb.

Conclusion

The results showed that amending Pb-contaminated, organic shooting range soil with untreated tailings from apatite ore beneficiation may reduce the water-solubility of Pb and increase the abundance of organic Pb complexes at the expense of the more toxic, inorganic cationic Pb species. The untreated tailings elevate soil pH thus resulting in increased stability of organic Pb-complexes. Since high pH increases the solubility of organic matter, the untreated tailings may induce increased leaching of Pb complexes deeper into the mineral soil horizons. However, it is likely that, in mineral soil, Pb is strongly retained by the hydrated Al and Fe oxides and other inorganic soil components present. Acid-treated tailings substantially increase the water-solubility of Pb and disintegrate Pb from its organic compounds increasing the abundance of the most toxic Pb^{2+} and $PbOH^{+}$ species. Thus, it cannot be considered to be utilized as a soil amendment.

References

Al-Degs YS, El-Barghouthi MI, Issa AA, Khraisheh MA, Walker GM (2006) Sorption of Zn(II), Pb(II), and Co(II) using natural sorbents: Equilibrium and kinetic studies. *Water Research* **40**, 2645–2658.

Aualiita TU, Pickering WF (1987) The specific sorption of trace amounts od Cu, Pb and Cd by inorganic aprticulates. *Water Air and Soil Pollution* **35**, 171–185.

Cao X, Ma LQ, Rhue DR, Appel CS (2004) Mechanisms of lead, copper, and zinc retention by phosphate rock. *Environmental Pollution* **131**, 435–444.

Chen X-B, Wright JV, Conca JL, Peurrung LM (1997) Effects of pH on heavy metal sorption on mineral apatite. *Environmental Science and Technology* **31**, 624–631.

Elzinga EJ, Sparks DL (2002) X-ray absorption spectroscopy study of the effects of pH and ionic strength on Pb(II) sorption to amorphous silica. *Environmental Science and Technololgy* **36**, 4352–4357.

Fulghum JE, Bryan SR, Linton RW, Bauer CF, Griffis DP (1988) Discrimination between adsorption and coprecipitation in aquatic particle standards by surface analysis techniques: lead distributions in calcium carbonates. *Environmental Science and Technology* **22**, 463–467.

Hartikainen H, Kerko E (2009) Lead in various chemical pools in soil depth profiles on two shooting ranges of different age. *Boreal Environtal Research* **14 (Suppl. A)**, 61–69.

Hartikainen SH, Hartikainen HH (2008) Phosphorus retention by phlogopite-rich mne tailings. *Applied Geochemistry* **23**, 2716–2723.

Klucakova M, Pekar M (2008) Behaviour of partially soluble humic acids in aqueous suspension. *Colloids and Surfaces A-Physicochemical and Engineering Aspects* **318**, 106–110.

Mavropoulos E, Rossi AM, Costa AM, Perez CAC, Moreira JC (2002) Studies on the mechanism of lead immobilization by hydroxyapatite. *Environmental Science and Technology* **36**, 1625–1629.

Puustinen K (1971) Tetraferriphlogopite from the Siilinjärvi carbonatite complex, Finland. *Bulletin of the Geological Society of Finland* **45**, 35–42.

Rouff AA, Reeder RJ, Fisher NS (2002) Pb (II) sorption with calcite: A radiotracer study. *Aquatic Geochemistry* **8**, 203–228.

Stevenson FJ (1982) Humus Chemistry. John Wiley & Sons, Inc., Canada.

Taylor P, Lopata VJ (1984) Stability and solubility relationships between some solids in the system lead oxide-carbon dioxide-water. *Canadian Journal of Chemistry* **62**, 395–402.