

REMEDIATION OF SOIL CONTAMINATED WITH INORGANIC POLLUTANTS

J. Kumpiene¹, C. Maurice²

*Div. of Waste Science & Technology, Luleå University of Technology, Sweden,
¹juku@sb.luth.se, ²chma@sb.luth.se.*

Abstract

Development of onsite (*in situ*) soil treatment methods e.g. stabilization using soil amendments is gaining popularity as techniques less disruptive to the natural ecosystems and less expensive compared with conventional soil remediation methods. The study aimed at estimating the changes in the metal mobility resulting from the addition of the industrial rest products (coal fly ash, blast furnace slag) as amendments to the heavy metal contaminated soil. Soil samples contaminated with Cu, Cr, As, Pb were mixed either with 5% blast furnace slag (HS) + 4.6% peat or 5% coal fly ash (FA) + 4.6% peat. The chemical sequential extraction was applied to determine the redistribution of metal fractions in stabilized soil. The addition of the coal fly ash reduced the mobility of Pb by increasing pH of soil and by reducing the exchangeable fraction. Organic matter (peat) facilitated the stabilisation of Cu through the increase of the metal fraction bound to OM. Blast furnace slag was inefficient to increase the fraction bound to Fe-Mn oxides. On the contrary, the oxide fraction of Cu, Cr, and As decreased significantly after the addition of slag, probably due to the changes in redox conditions during the aging of the samples.

1. Introduction

The high costs associated with the removal of pollutants from soil have been encouraging to apply more innovative soil remediation technologies. Development of onsite (*in situ*) soil treatment methods e.g. stabilization using natural and synthetic soil amendments is gaining popularity as techniques less disruptive to the natural ecosystems and less expensive compared with conventional soil remediation methods. Also, it contributes to the reduction of landfilled amount of waste. Soil additives, e.g. organic matter, aluminosilicates, Fe and Mn (hydro)oxides, etc., could facilitate the stabilization of metals and diminish their bioavailability as well as prevent their transport to the surface and groundwater through the formation of insoluble contaminant species and without drastically altering the physical or chemical properties of the soil (Berti and Cunningham, 2000).

The aim of this study was to estimate the changes in the metal mobility resulting from the addition of the amendments to the heavy metal contaminated soil. The work also aimed at studying the potential of using industrial rest products as soil additives in stabilisation of heavy metal contaminated soil.

2. Materials & Methods

Soil

Soil samples collected from a wood impregnation industrial site and from a copper ore transshipment station (thereafter respectively called soil R and soil S) in Northern Sweden were used in the laboratory stabilisation experiment.

Amendments

The soil amendments tested were natural organic matter (peat), coal fly ash, and blast furnace slag. The last two are classified as waste products. Soil samples were mixed either with 5% blast furnace slag (HS)

+ 4.6% peat or 5% coal fly ash (FA) + 4.6% peat. Mixtures were left for two weeks to age in closed polypropylene containers at room temperature.

Sequential extraction

The chemical extraction method developed by Tessier (1979) was adopted for the determination of the four operationally defined metal fractions of the soil samples. The quantities indicated below refer to 1 g soil samples (dry weight).

(I) *Exchangeable*. The soil was extracted at room temperature for 1 h with 8 mL of magnesium chloride solution (1 M MgCl₂, pH 7.0) with continuous agitation.

(II) *Bound to carbonates*. The residue from (I) was leached at room temperature with 8 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc) continuously agitating for 5 h.

(III) *Bound to Fe-Mn oxides*. The residue from (II) was extracted with 20 mL of 0.04 M NH₂OH-HCl in 25% (v/v) HOAc (pH ~ 2) at 96 ± 3°C with occasional agitation for 6 h.

(IV) *Bound to organic matter*. To the residue from (III) were added 3 mL of 0.02 M HNO₃ and 5 mL of 30% H₂O₂ adjusted to pH 2 with HNO₃, and the mixture was heated to 85 ± 2°C for 2 h with occasional agitation. A second 3 mL aliquot of 30% H₂O₂ (pH 2 with HNO₃) was then added and the sample was heated again to 65 ± 2°C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M NH₄OAc in 20% (v/v) HNO₃ was added and the sample was diluted to 20 mL and agitated continuously for 30 min. The addition of NH₄OAc is done to prevent adsorption of extracted metals onto the oxidized sediment.

The extractions were conducted in centrifuge tubes (polypropylene, 50 mL) to minimize losses of solid material. Between each extraction, separation was achieved by centrifuging at 10 000 rpm for 30 min. The supernatant was removed with a pipette, filtrated through a 0.45 µm nitrocellulose membrane filter and analyzed for metals with inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer). The residue was rinsed between each extraction step with 8 ml of double distilled water. The total metal content of the initial soil samples was measured with X-ray fluorescence (XRF) spectrum multi-element analyser (Niton 700).

A multiple sample comparison Fisher's least significant difference (LSD) procedure ($p < 0.05$) (Montgomery, 2001) was applied to discriminate among the sample means using a software *Statgraphics Plus 5.0*. A principle component analysis (PLS) was performed by use of a software *Simca-P 9.0* (Umetrics).

3. Results

The soil samples collected from the wood impregnation industrial site (R) contained very high concentrations of Cr, Cu and As that 40 to 660 times exceeded the generic guideline values for the contaminated soils in Sweden (SNV, 1994). The metals in soil arise from the chemical substance chromated copper arsenate (CCA) that is widely used to preserve wood. The soil from the copper ore transshipment station (S) was mostly contaminated with lead and copper. The total metal concentrations of the initial soil samples are summarised in Table 1.

Table 1 The total metal concentrations of the initial soil samples

Soil	Cu	As	Zn	Ni	Cr	Pb
mg/kg						
R	3709 ± 160	9958 ± 170	339 ± 69	540 ± 140	4618 ± 320	66 ± 19
S	198 ± 60	<68	<47	351 ± 87	<180	1680 ± 59

R - soil from a wood impregnation industrial site; S - soil from a copper ore transshipment station.

The addition of the amendments notably increased the pH as well as the salinity of soil samples (Figure 1).

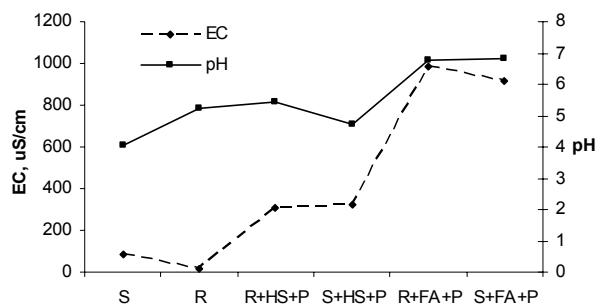


Figure 1 Changes in soil pH and electrical conductivity (EC) in response to the used amendments. R – soil from a wood impregnation industrial site; S – soil from a copper ore transshipment station; HS – blast furnace slag; FA – coal fly ash; P – peat.

In the PLS plot (Figure 2), the observations representing the total metal content (T) of the samples had the strongest load on the components (most distant from the origin), while the load of the observations representing the amended soil samples was reduced. It indicates the reduction of the total metal concentration in the soil samples amended with the additives. The dominating metal fraction determined in the samples was bound to Fe-Mn oxides. The metal fraction bound to organic matter was detected in lesser extent, followed by exchangeable and the fraction bound to carbonates. Only in the S sample the exchangeable Pb fraction dominated.

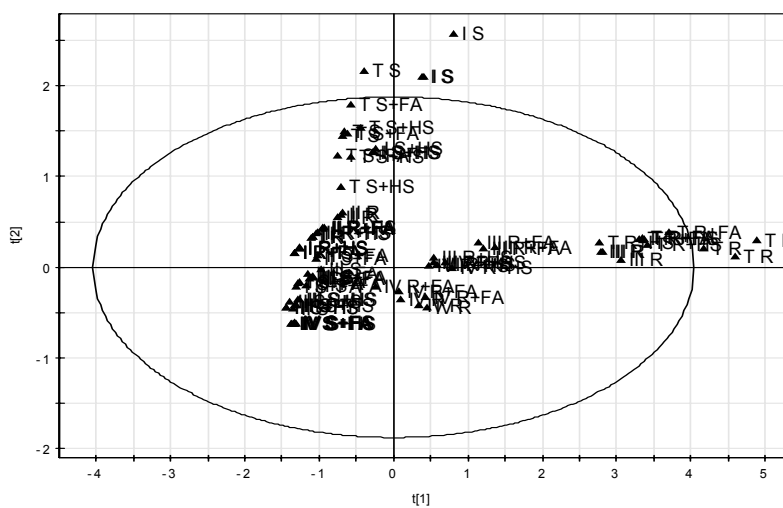


Figure 2 Principle component analysis (PLS) for the metal fractionation in the soil samples. The first component (t[1]) represents As, Cr and Cu, while the second one (t[2]) - Pb. R – soil from the wood impregnation industrial site; S – soil from the copper ore transshipment station; HS – blast furnace slag; FA – coal fly ash; P – peat. Roman numbers represent the fractions extracted; T – total metal content.

The largest effect on metal redistribution in both soil samples was observed for Cu, i.e. the addition of the blast furnace slag and peat significantly increased the Cu fraction bound to organic matter while reducing the fraction bound to Fe-Mn oxides (Figure 3). In the case of As and Cr, the comparison of mean fraction redistribution indicated that the fraction bound to Fe-Mn oxides was significantly reduced at 95.0% confidence level, while no statistically significant changes were observed in the other fractions.

The metal fraction redistribution was considerable in the soil S amended with coal fly ash (FA), i.e. FA had a significant effect on the reduction of exchangeable Pb and increased the fraction bound to carbonates, while the blast furnace slag to a lesser extent reduced exchangeable and the fraction bound to Fe-Mn oxides.

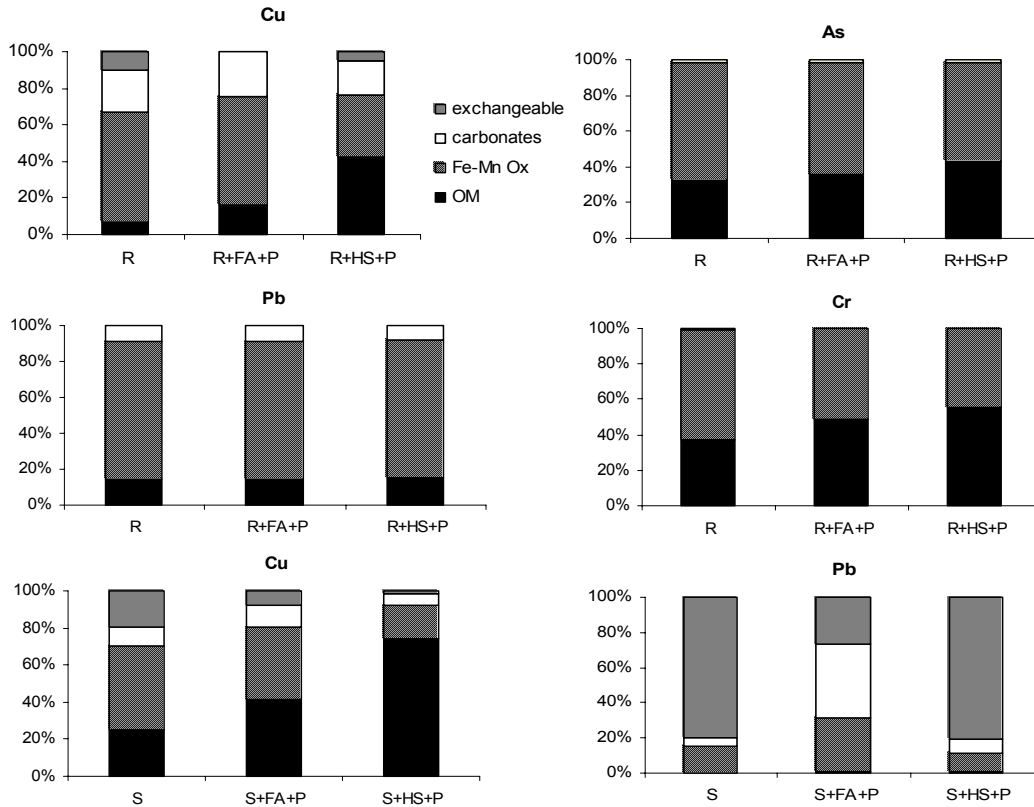


Figure 3 Metal distribution among operationally defined fractions. R – soil from the wood impregnation industrial site; S – soil from the copper ore transshipment station; HS – blast furnace slag; FA – coal fly ash; P – peat.

4. Discussion

Theoretically, the role of the soil amendments is to reduce the bioavailability of toxic elements and to prevent the translocation of metals into trophic chain (Mench, 2000). Applying industrial rest products as soil amendments for the stabilization of heavy metal contaminated soil is an attempt to reduce the amount of landfilled residues.

In this study soil amendments had little or no effect on the redistribution of As and Cr fractions. For Pb and Cu, amendments positively affected the exchangeable fraction that was significantly reduced (Figure 3). A longer aging time though might change the redistribution of the metal fractions. The lower total metal concentration determined in the soil samples amended with additives was most likely due to the dilution effect.

The metal fraction bound to Fe-Mn oxides was expected to increase in the soil samples amended with blast furnace slag. Blast furnace slag is an iron bearing material, which can be reactive for many trace metals. However, in all studied cases the opposite effect was observed, i.e. the metal fraction bound to Fe-Mn oxides decreased after the addition of the slag. Fe-Mn oxides are unstable under anoxic conditions; hence storage of the soil in closed containers, particularly amended with peat, could lead to the redox variations. Consequently, the release of metals already present in the complexes with oxides instead of the hold of the additional metals might occur.

Coal fly ash resembles closely the clay minerals having large active surface area. Fly ashes usually contain large fraction of carbonates that explains the increased Pb bound to this particular fraction. This fraction is susceptible to pH variations; thus reduction of soil pH may lead to the release of Pb or transfer back to the exchangeable fraction.

Organic matter (OM) is an essential soil component providing the soil with a strong buffer capacity for resisting severe chemical changes (Stevenson, 1994). Adsorption and/or ion exchange by particulate media such as peat might be a proper option for removal of colloidal and dissolved metals and can provide long-term storage for contaminants (Jones and Chapman, 1995). Also it would facilitate the vegetation establishment, which in turn would reduce migration of contaminants, prevent deflation and direct exposure of contaminated soil to humans. However, natural organic matter such as peat is acidic and may negatively affect the mobilization of metals that have low affinity for OM (e.g. Mn, Zn). Also, it may affect the metal fraction bound to carbonates. The addition of fly ashes with high pH would neutralize the soil. The neutralization effect of FA was observed in our study. The carbonation of ashes may lead in a long time span to the decrease in pH; hence the decrease in soil acidity might not be a long term result.

5. Conclusions

The addition of the coal fly ash to the soil contaminated with Pb can reduce the mobility of the metal first by increasing pH of soil and also by significantly reducing the exchangeable metal fraction. Organic matter in the form of peat facilitated the stabilisation of Cu, that has a high affinity for OM, through the increase of the metal fraction bound to OM. Blast furnace slag was inefficient to increase the metal fraction bound to Fe-Mn oxides. On the contrary, the oxide fraction of Cu, Cr, and As decreased significantly after the addition of slag, probably due to the changes in redox conditions during the aging of the samples.

The multi-elemental contamination of soil may require an appropriate combination of the stabilising amendments specific for the target metals. The aging of the amended soil along with the variations of temperature, freezing, acid rain, drying, etc. may affect significantly the metal fraction redistribution in a long time perspective and should also be studied.

Acknowledgements

This work was financially supported by European Union Structural Funds and New Objective 1, North Sweden Soil Remediation Centre, contract no 113-12534-00.

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