Effect of calcined eggshell on fractional distribution and plant uptake of Cd, Pb and Zn in contaminated soils near mine

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Abstract
The fractional distribution of Cd, Pb and Zn in a soil contaminated by mine tailings and their uptake to lettuce (*Lactuca sativa var. longifolia)* were investigated after application of varying amounts of calcined eggshell (0, 1, 3, and 5 %). The experiments were conducted under greenhouse conditions during a 30-d period. A sequential extraction method was used to determine the binding forms of these metals in soils. The application of calcined eggshell decreased particularly the mobile fraction of these metals: from 43.3 to 0.2 % for Cd, from 4.8 to 1.4 % for Pb and from 5.4 to 0.4 % for Zn. Instead, the easily exchangeable fraction of Cd and the organically bound fraction of Pb and Zn were increased. This alteration of binding forms resulted in a diminished uptake of Cd, Pb and Zn by lettuce. The ratios of Cd, Pb and Zn uptake from soils to roots (total contents) decreased from 0.25 to < 0.01 for Cd, from 0.01 to < 0.001 for Pb and from 0.27 to 0.16 for Zn. The results suggested that the calcined eggshell can be used as an effective immobilization agent for the remediation of Cd, Pb and Zn contaminated soils.

Key Words
Heavy metals, contamination, stabilisation, transfer factor, waste material.

Introduction
Agricultural soils surrounding mining sites in South Korea are often contaminated with multiple metals such as Cd, Pb and Zn. It poses potential risks to plants, groundwater, and eventually human health. The contents of heavy metals in plants grown on those soils often exceeded the safe limits of Codex standards (1995; 0.2 and 0.3 mg/kg for Cd and Pb, respectively). For the remediation of those contaminated soils, the reuse of waste materials such as calcined eggshell can represent an environmentally-friendly and cost-effective alternative. Therefore, the objective of this study was to evaluate the effectiveness of calcined eggshell on the immobilization of Cd, Pb and Zn in soils using the sequential extraction method, because binding forms of heavy metals determine the plant availability and the potential for environmental contamination.

Materials and Methods
Greenhouse experiments
Soils were collected from a contaminated agricultural field (0 - 30 cm) near the closed mine Seosung, located in Seosan, the western South Korea. The soil samples showed a pH(H_2O; 1: 5) of 5.9, a OC content of 14.9 g/kg and a CEC of 11.4 $cmol_c$/kg. Total contents of Cd, Pb and Zn were 8.04, 1590 and 645 mg/kg (aqua regia digestion). The soil texture was clay loam. Four levels of calcined eggshell (ES 0, 1, 3, 5 %), which was prepared by calcination of raw eggshell at 900 °C ($CaCO_3 \rightarrow CaO + CO_2$ (g); Ok unpublished), were thoroughly mixed with soil samples. The mixed soil samples were placed in each pot (500-600 g a pot) in the greenhouse, brought to field capacity and incubated for three days. Each treatment was replicated twice. Seedlings of lettuce (4 weeks after germination) were transplanted into each pot and the plants were grown for 30 days in the greenhouse at 25 ± 2 °C. At harvest, leaves, roots and the soils were separated.

Soil and plant analyses
The leaves and roots dried at 85 °C were finely ground and portions (ca. 0.5 g) were digested with HNO_3 + H_2SO_4 + $HClO_4$ (10: 1: 4; 200 °C). Soil samples were air-dried and subjected to sequential extraction according to Zeien and Bruemmer (1989): (I) mobile fraction (NH_4NO_3), (II) easily mobilizable fraction (NH_4OAc), (III) in Mn-oxides occluded fraction (NH_2OH-HCl + NH_4OAc), (IV) organically bound fraction (NH_4-EDTA), (V) in poorly crystalline Fe-oxides occluded fraction (NH_4 oxalate buffer), (VI) in well crystalline Fe-oxides occluded fraction (ascorbic acid in 0.2 M NH_4 oxalate) and (VII) residual fraction (conc. HNO_3/conc. $HClO_4$). The extraction was carried out in three replicates. All metals in extracts were determined using a GBC Integra XL Dual ICP-OES.

Results

Fractional distribution of Cd, Pb and Zn in soils

Figure 1 showed that the dominant fraction of Cd was the mobile fraction (43.3 %) in soils without application of calcined eggshell (ES 0 %), whereas Pb was found mainly in the organically bound fraction (31.7 %) and Zn in the residual fraction (59.5 %). Increasing the application of calcined eggshell from 0 to 5 % decreased particularly the mobile fraction of all metals: from 43.3 to 0.2 % for Cd, from 4.8 to 1.4 % for Pb and from 5.4 to 0.4 % for Zn. Instead, the easily exchangeable fraction of Cd (up to 63.8 %) and the organically bound fraction of Pb (up to 52.5 %) and Zn (up to 6.4 %) were increased.

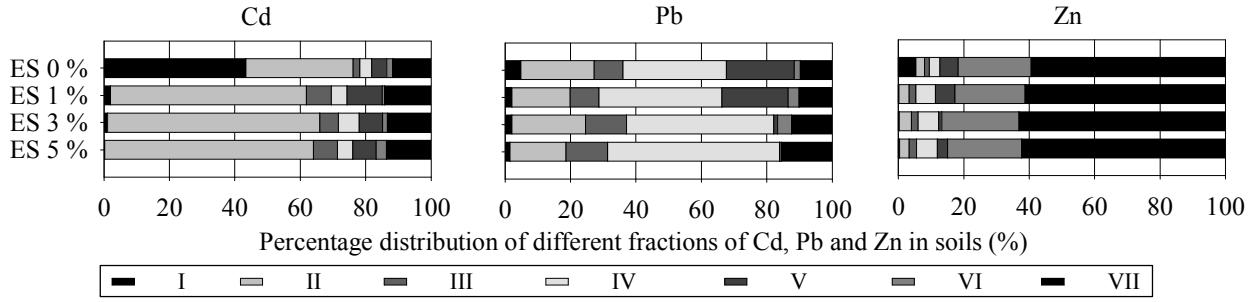

Figure 1. Percentage distribution of Cd, Pb and Zn fractions in contaminated soils with and without application of calcined eggshell (ES: calcined eggshell; I: mobile, II: easily mobilizable, III: in Mn-oxides occluded, IV: organically bound, V: in poorly crystalline Fe-oxides occluded, VI: in well crystalline Fe-oxides occluded, VII: residual fraction)

Plant uptake

Figure 2 presents the total contents of Cd, Pb and Zn in leaves and roots of lettuce. The Cd, Pb and Zn contents without application of calcined eggshell (ES 0 %) were 4.19, 0.78 and 133 mg/kg in leaves and 2.08, 12.9 and 180 mg/kg in roots, respectively. Increasing the amount of calcined eggshell from 0 to 5 % lowered the contents of all metals both in leaves and roots. The ratios of Cd, Pb and Zn uptake from soils to roots decreased from 0.25 to < 0.01 for Cd, from 0.01 to < 0.001 for Pb and from 0.27 to 0.16 for Zn. The translocation factors from roots to leaves revealed that Cd (2.0) was mainly accumulated in leaves, whereas Pb (< 0.1) and Zn (0.7) were mainly accumulated in roots.

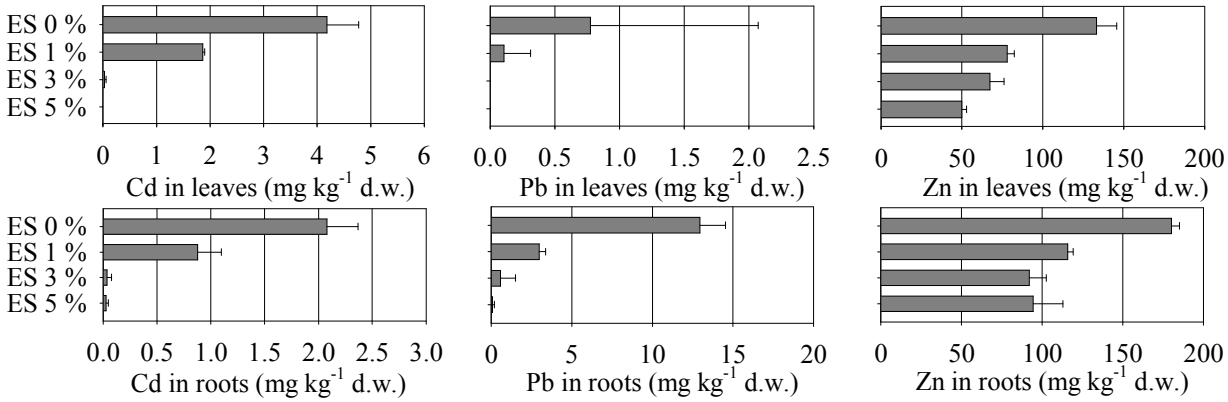

Figure 2. Cd, Pb and Zn uptake in leaves and roots of lettuce from contaminated soils with and without application of calcined eggshell (ES: calcined eggshell)

Conclusion

The application of calcined eggshell altered the mobile fraction of Cd, Pb and Zn to less mobile or immobile fraction in soils by increasing the soil pH. This resulted in a diminished uptake of Cd, Pb and Zn to lettuce. The calcined eggshell can be considered as an effective immobilization agent for remediation of Cd, Pb and Zn contaminated soils.

References

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