

MIGRATION AND CHANGE IN CHEMICAL SPECIATION OF CONTAMINANT RARE METALS (AG, IN, SN, SB, AND BI) IN SOILS

H. Hou^A, T. Takamatsu^B, M.K. Kosikawa^B and M. Hosomi^C

^A Graduate School of Technology, Tokyo University of Agriculture & Technology, Tokyo, Japan.

^B Soil Science Section, National Institute for Environmental Studies, Tsukuba, Japan.

^C Faculty of Technology, Tokyo University of Agriculture & Technology, Tokyo, Japan.

Abstract

Vertical distributions of Ag, In, Sn, Sb, and Bi, and their chemical speciation, were analyzed in four soils (Andosol, Cambisol, Fluvisol, and Regosol) one and half years after contamination. Total concentrations of metals were determined by ICP-MS using acid-digested soil samples, and chemical speciation was determined using an eight-step sequential extraction procedure. Most of the contaminant metals remained in the top layers of the soils, but small portions had moved to the sub-layers. Silver was present mainly in the metal-organic complex-bound, H₂O₂-extractable organic bound, and residual forms. Indium was found mainly in the carbonate-bound, metal-organic complex-bound, and H₂O₂ extractable organic bound forms. The dominant forms of Bi, Sn, and Sb were similar, i.e. the metal-organic complex-bound and amorphous metal oxide-bound forms. Metal migration in soils was associated with the exchangeable, carbonate-bound, and metal-organic complex-bound forms. The capacities of soils to adsorb and retain the metals were in the order: Andosol > Regosol > Fluvisol > Cambisol. Among the five metals, In and Bi were relatively mobile, Sn and Ag were immobile, and Sb had an intermediate mobility.

Additional Keywords: Pb-free solder, column experiment, sequential extraction

Introduction

Lead is harmful to human health, and Pb poisoning of children is a serious pediatric problem. For this reason, various efforts are made to reduce the use of Pb. For example, the European Union (EU) is planning to ban the use of Pb-containing materials (eg. Pb solders) in electrical and electronic products by July 2006 (Turbini *et al.*, 2001), and thus substitutive materials (eg. Pb-free solders) are being developed in the related industries (especially in the EU and Japan). However, these Pb-free materials contain some rare metals (Ag, In, Sb, Bi, etc.), in addition to several familiar metals (Zn, Cu, and Ni). Although the Pb-free materials are called “environment-conscious materials”, several studies have demonstrated that such rare metals are often toxic to animals and humans (Ratte, 1999; Winship, 1987; Nakajima *et al.*, 2000; Dipalma, 1988). In addition, Ag and Sb have been specified as priority contaminants by the U.S. EPA. In the future, extensive use of Pb-free materials will increase the environmental loads of these metals and may cause new pollution problems. Therefore, knowledge about the behavior and effects of these metals in the environment is essential. This knowledge is, however, extremely limited at present. Therefore, we investigated the behavior (migration, accumulation, and change in chemical forms) of Ag, In, Sn, Sb, and Bi in 4 representative soils of Japan.

Materials and Methods

Plastic columns (6.5 cm internal diameter × 35 cm height) were filled (up to 30 cm) with air-dried and sieved (2 mm mesh) soils (Andosol, Cambisol, Fluvisol, or Regosol which are typical soil types in Japan), and glass-fibre filters were laid on the soil surface. The prepared soil columns were installed at an appropriate depth in a lawn field to expose them to precipitation (in Tsukuba, Japan). After the soils had been naturalized for 3 months, metal solutions containing Ag, Bi, Sb, In, and Sn were added to the soil surface on May 11, 2001 (Table 1). The amounts

Table 1. Amounts of metal added to the soils in columns

| Metal | Reagent | Background, ppm | Amounts of metals added | Expected Conc ⁿ *, ppm |
|-------|--|-----------------|---------------------------------|-----------------------------------|
| Bi | Bi(NO ₃) ₃ · 5H ₂ O | 0.3 | 0.498 mg-Bi (1.16 g as reagent) | 3 |
| In | InCl ₃ · 4H ₂ O | 0.09 | 0.299 mg-In (0.763 mg) | 1.8 |
| Sb | C ₈ H ₄ K ₂ O ₁₂ Sb ₂ · 3H ₂ O | 0.8 | 1.33 mg-Sb (3.64 mg) | 8 |
| Ag | AgNO ₃ | 0.15 | 0.498 mg-Ag (0.783 mg) | 3 |
| Sn | SnCl ₄ · 5H ₂ O | 2.5 | 4.15 mg-Sn (12.3 mg) | 25 |

*: Metal concentrations in the upper 5-cm soil layers, which are expected in the case that the additional metals distribute homogeneously in those layers (apparent specific gravity of soil was assumed to be 1.0).

of metals added (Table 1) were 10-20 times higher than the background levels (in Andosol). The soil columns were retrieved on November 19, 2002 (ca. 1.5 years after contamination), and the soils were divided into 2 cm sections (depth-wise). Soil samples were freeze-dried and gently ground to less than 200 mesh. They were then digested with HNO₃/HClO₄/HF in high-pressure bombs, and analyzed for the metals using ICP-MS (Yokogawa Analytical Systems HP 4500). To analyze the chemical speciation of the metals, the sequential extraction methods of Krishnamurti *et al.* (1995) were employed, with some modification. Detailed procedures are shown in Table 2. The extracts obtained were filtered and then analyzed for the metals using ICP-MS.

Table 2. Eight-step sequential extraction procedure for analyzing chemical forms of metals.

| Step | Chemical form | Extractant* | Condition |
|------|---|---|---|
| 1 | Exchangeable | 10ml of NH ₄ NO ₃ (pH 7) | 4h at 25°C |
| 2 | Carbonate-bound | 25ml of 1M CH ₃ CO ₂ NH ₄ (pH 5) | 6h at 25°C |
| 3 | Metal-organic complex-bound | 30ml of 0.1M Na ₄ P ₂ O ₇ ·10H ₂ O (pH 10) | 20h at 25°C |
| 4 | Easily reducible metal oxide-bound | 20ml of 0.1M NH ₂ OH in 0.01M HNO ₃ | 30min at 25°C |
| 5 | H ₂ O ₂ extractable organic bound | 5ml of 30% H ₂ O ₂ (pH 2), 3ml of 0.02M HNO ₃ ; then 3ml of 30% H ₂ O ₂ (pH 2); cool, 10ml of 2M NH ₄ NO ₃ in 20% HNO ₃ | 2h at 85°C 2h at 85°C 30min at 25°C |
| 6 | Amorphous metal oxide-bound | 10ml of 0.2M (NH ₄) ₂ C ₂ O ₄ (pH 3) | 4h at 25°C (dark) |
| 7 | Crystalline Fe oxide-bound | 25ml of 0.2M (NH ₄) ₂ C ₂ O ₄ (pH 3) in 0.1M Ascorbic acid | 30min at 95°C |
| 8 | Residual | Residue in step 7 was digested with HF-HClO ₄ | 6h at 140°C |

* One gram of soil was used for extracting sequentially. After extraction, the extract was collected by centrifugation (3,000 rpm, 10 min). The residue was washed once with 10 ml of distilled water, and the washing was combined with the extract. The residue from the step 4 extraction was washed exceptionally well several times, and the washings from the second and subsequent washes were discarded.

Results and Discussion

Vertical distribution of contaminant metals in soils

In all four soils types, the contents of Ag, In, Sn, Sb, and Bi (concentration × soil weight) were very high in the top soil layers (0–2 cm layers plus filters), and decreased drastically in the sublayers, approaching the background levels with increasing depth (Figure 1). Similar accumulation of metals has been observed at the surface of many polluted soils (eg. McBride *et al.*, 1999). However, the abilities of soils to adsorb metals, and thus the penetration depths of metals, differed slightly according to the soil species. Andosol was the strongest adsorbent for most metals (only 0 - 4% of the metals transferred to depth of below 2 cm), except for In, ca. 36% of which was transferred to below 2 cm and its penetration front reached a depth of ca. 25 cm, with a peak at ca. 18 cm. This high adsorption ability of Andosol is probably due to its abundant allophane, large surface area, and high organic matter content. The high transfer rate of In in Andosol may be explained by significant negative relationships between the percent of In held in the top soil layer and C contents and Allophyne contents ($r = -0.838$, $p = 0.2$; $r = -0.872$, $p = 0.2$, respectively). In Cambisol, all contaminant metals moved partially from the top layer of soil to sublayers, and the transfer rates were in the order: Bi (42.4%) > Sn (16%) > In (14.3%) > Ag (13.9%) > Sb (13.5%). Bismuth moved the most rapidly, by far. Although In and Sb had the lowest transfer rates, their recoveries (total amounts in columns) were not quantitative, indicating that some In and Sb migrated deeper than 30 cm (out of the columns) (rapid migration as inert organic complexes is a possible mechanism). In Fluvisol, all metals moved into subsoil layers, and the transfer rates were: Sb (27%) > Bi (22%) > Sn (14%) > Ag (11%) > In (5%). Once again, the recoveries of In were not quantitative. The transfer rates in Regosol were: Sb (29%) > In (10%) > Sn (8.9%) > Ag (8.4%) > Bi (5%). The relatively high mobility of Sb may have resulted from the low organic matter content in Regosol, because a good correlation was observed between the percentages of Sb held in the top soil layers and the carbon contents of soils ($r = 0.985$, $p = 0.01$). In Regosol, portions of all metals other than Ag migrated deeper than 30 cm.

Speciation of metals in soils

Chemical forms of the contaminant metals in the upper 10 cm of soil layers are shown in Figure 2. Silver was mainly present in the metal-organic complex-bound (Me-Org), H₂O₂-extractable organic bound (H₂O₂-Org), and residual forms. Similar abundance of organic Ag has been observed previously (Jin Zhou *et al.*, 1998). The residual forms were more abundant than those of the other metals, probably due to the production of insoluble oxides and salts (Ag₂O, AgCl, and Ag₂SO₄). In the top (most contaminated) soil layers, In was found predominantly in the carbonate-bound, Me-Org, and H₂O₂-Org forms, and Cambisol and Fluvisol were relatively rich in the Me-Org

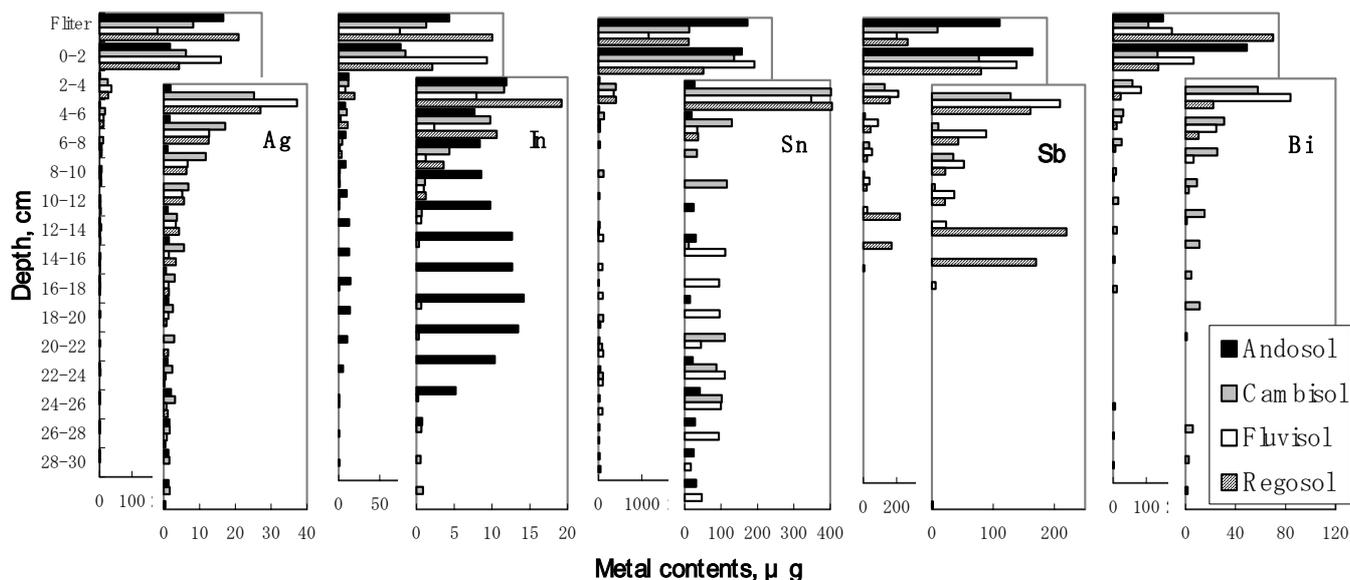


Figure 1. Vertical distribution of metals in column soils after weathering for one and half years. Values have been corrected for background concentrations.

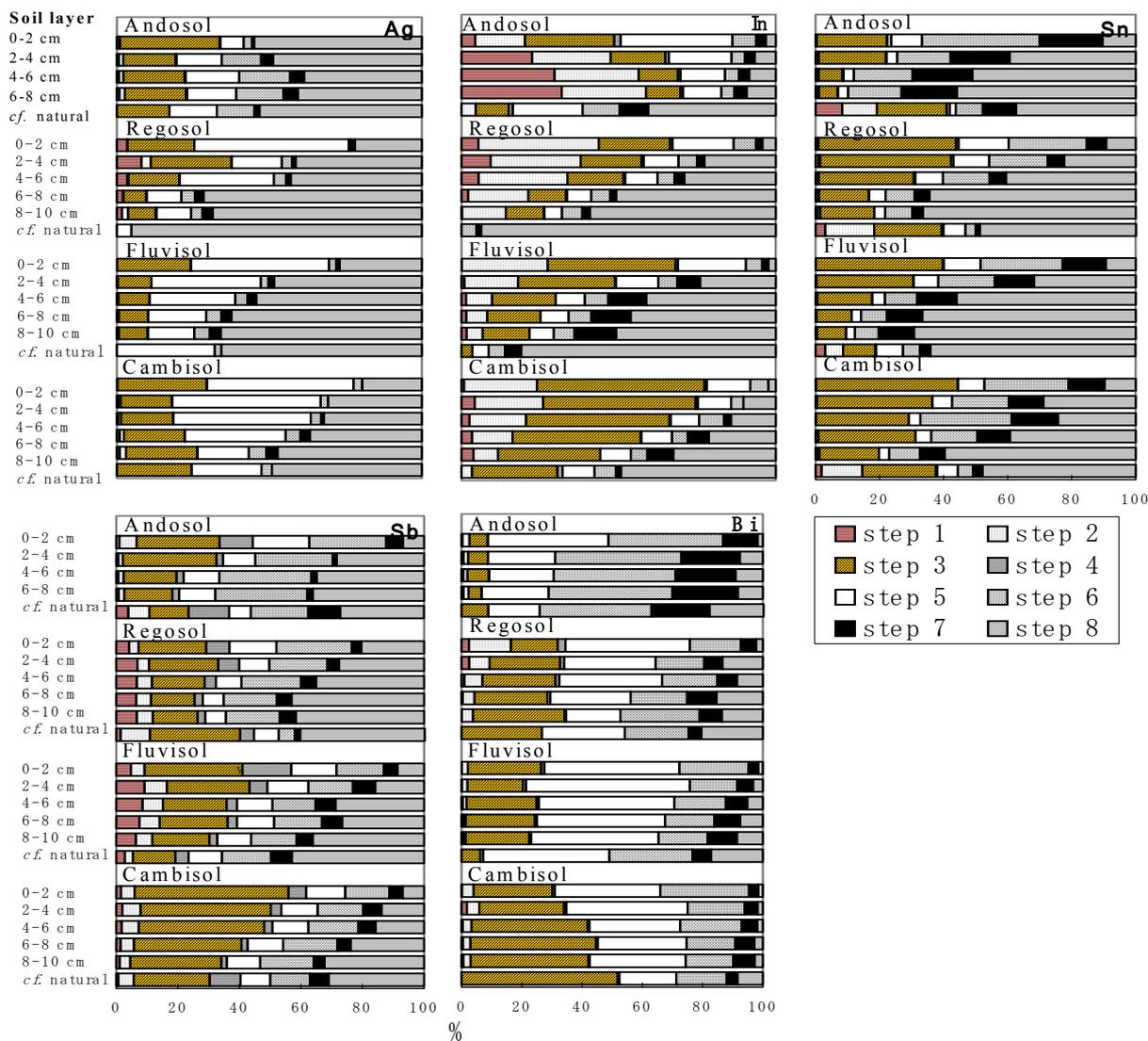


Figure 2. Percent distribution of chemical forms of rare metals in the upper 10 cm of soil layers.

Step 1: Exchangeable; Step 2: Carbonate-bound; Step 3: Metal-organic complex-bound; Step 4: Easily reducible metal oxide bound; Step 5: H₂O₂ extractable organic bound; Step 6: Amorphous metal oxide-bound; Step 7: Crystalline Fe oxide-bound; Step 8: Residual.

form, whereas Regosol was relatively rich in the carbonate-bound form. Jinzhou *et al.* (1998) have reported that carbonic acid and organic matter participate in the retention of In in soil. In the Andosol, only a small portion of In was present in the exchangeable (EXC) form in the top soil layer, but this form became dominant in the sub-layers. This must have been responsible for the high mobility of In in Andosol. Tin was found predominantly in the Me-Org and amorphous metal oxide-bound (Am-MeOx) forms, and also partly in the H₂O₂-Org and crystalline Fe oxide-bound (Cr-FeOx) forms. Tin was rich in both the Am-MeOx and Cr-FeOx forms, compared to Ag and In. Tin is known to substitute for Fe in minerals, because of its similar radius, and thus becomes embedded in Fe-containing minerals (Yi *et al.*, 1995). Antimony, like Sn, occurred mainly as the Me-Org, H₂O₂-Org, Am-MeOx, and Cr-FeOx forms, and the Me-Org form was relatively rich in Cambisol and Fluvisol, whereas the Me-Org and Am-MeOx forms were almost equivalent in Andosol and Regosol. This is in agreement partial with the results by Lintschinger *et al.* (1998), in which Sb was shown to exist mainly in the organic form. In addition, incorporation of Sb into Fe/Al-oxides has been shown by sequential extraction analysis of sediments (Brannon and Patrick, 1985). Bismuth in Andosol was found predominantly in the Am-MeOx, H₂O₂-Org, and Cr-FeOx forms. Cambisol was relatively rich in Me-Org-Bi, whereas Regosol and Fluvisol were rich in H₂O₂-Org-Bi. The relatively large mobility of Bi observed in Cambisol may have resulted from the abundance of the Me-Org form.

Conclusions

The capacities of soils to adsorb and retain the metals investigated under our experimental conditions were in the order: Andosol > Regosol > Fluvisol > Cambisol. Among the 5 metals, In and Bi were relatively mobile, whereas Sn and Ag were immobile, and Sb showed intermediate mobility. The metals seem to have migrated through the soil by two processes: 1) slow stepwise (chromatographic) movement by repeated adsorption–desorption cycles; 2) rapid migration as inert metal-organic complexes. In soils with low binding abilities, the latter process is relatively important, and thus some of the contaminant metals may reach deep soil layers and/or groundwater within a short period, even though the contamination may appear to be restricted to the soil surface. Metal migration in soil was associated with the EXC, Carbonate-bound, and Me-Org forms. In particular, the Me-Org form may be the key, because it is the most probable source of metal-organic complexes that dissolve in soil solution.

Acknowledgements

We would like to thank Mrs. K. Takada of the National Institute for Environmental Studies (abbreviated as NIES) and Dr. T. Tanaka of the Chemistry Behavior Laboratory (NIES) for assistance with ICP-MS analysis.

References

- Dipalma, J.R. (1988). Bismuth toxicity. *AFP Clinical Pharmacol.* 38, 244-246.
- Jinzhou, D., Xiongxing, D., Xiangke, W. and Zuyi, T. (1998). A multitracer study on the adsorption of 47 elements on a calcareous solid components. *J. Radioanal. Nucl. Chem.* 230, 129-134.
- Krishnamurti, G.S.R., Huang, P.M., van Rees, K.C.J., Kozak, L.M. and Rostad, H.P.W. (1995). Speciation of particulate-bound cadmium of soils and its bioavailability. *Analyst* 120, 659-665.
- Lintschinger, J., Michalke, B., Hostede, S.S. and Schramel, P. (1998). Studies on speciation of antimony in soil contaminated by industrial activity. *Intern. J. Environ. Anal. Chem.* 72, 11-25.
- McBride, M.B., Richard, B.K. Steenhuis, T. and Spiers, G. (1999). Long-term leaching of trace elements in a heavily sludge-amended silty clay loam soil. *Soil Sci.* 164, 613-623.
- Nakajima, M., Takahashi, H., Sasaki, M., Kobayashi, Y., Ohno, Y. and Usami, M. (2000). Comparative developmental toxicity study of indium in rats and mice. *Teratogenesis, Carcinogenesis, and Mutagenesis* 20, 219-227.
- Ratte, H.T. (1999). Bioaccumulation and toxicity of silver compounds. A review. *Environ. Toxicol. Chem.* 18, 89-108.
- Turbini, L.J., Munie, G.C., Bernier, D., Gamalaki, J. and Bergamn, D.W. (2001). Examining the environmental impact of lead-free soldering alternatives. *IEEE Trans. Electron. Pack. Manuf.* 24, 4-9.
- Winship, K.W. (1987). Toxicity of antimony and its compounds. *Adv. Drug React. Ac. Pois. Rev.* 2, 67-90.
- Yi, W., Halliday, A.N., Lee, D.C. and Christensen, J.N. (1995). Indium and tin in basalts, sulfides, and the mantle. *Geochim. Cosmochim. Acta*, 59, 5081-5090.