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Chemical Form of Soluble Cadmium and Copper in Arable Soils and its Implication to their Mobility

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Abstract

To clarify the chemical form of soluble cadmium and copper in arable soils, the molecular weight distribution and ion composition of water-soluble cadmium and copper in soils were investigated. The solution extracted with water from soil was fractionated by ultrafiltration and then cadmium and copper in 4 molecular weight size classes were determined. About 50% of water-soluble cadmium was present in the fraction with a molecular weight of 500 or less, 12–25% in the fraction with a molecular weight of 500–300,000 and 25–37% in the fraction with a molecular weight of 300,000 or more. For copper, 4–19% was present in the fraction with a molecular weight of 500 or less and 40–75% was present in the fraction with a molecular weight of 10,000–300,000 and 300,000 or more. The water-soluble heavy metals were also fractionated with ion exchange resin. More than 90% of cadmium was detected in the cation fraction. Conversely, approximately 80% of copper was detected in the anion fraction. These results indicate that water-soluble cadmium in soil is present as divalent cations, and copper is dissolved in a form bonded with substances such as organic matter in soil. To understand the difference in the mobility of cadmium and copper in soils, a plastic container was filled with moist soil and the soil moisture was allowed to evaporate only from the upper part of the container. Water-soluble cadmium was concentrated to a level of 68.5 times the background concentration at the top of the soil and copper was concentrated to 6 times the background concentration. Such a difference in the mobility was discussed in relation to the chemical form of soluble cadmium and copper.

Discipline: Agricultural environment
Additional key words: heavy metal, ion exchange resin, ultrafiltration

Introduction

Heavy metals in soil are elements which affect human health through crops and the water system[18]. It is known that their interaction with organisms (e.g. toxicity to humans and absorbability in plants) varies markedly depending on differences in the chemical form of the heavy metal elements[12,27]. Heavy metals in soil are present in various chemical forms, but among those forms, water-soluble heavy metals have a large environmental impact due to processes such as absorption in plants, and moving into groundwater and river water. However, the chemical forms of heavy metals in soil solution have not been much investigated[7,16]. Analysis of the chemical forms of heavy metals in soil has been done with serial extraction methods using various extracting reagents[9,15,24,25], but with these methods, water-soluble heavy metals are included in the exchangeable fraction in the evaluation, and thus little knowledge[8,11] has been gained regarding the chemical forms and dynamics of water-soluble heavy metals.

It is possible to perform molecular size fractionation of soluble matter using ultrafiltration[19]. To determine the ion composition of soluble matter, the chemical forms of heavy metals in river water were investigated using the ion exchange resin method[6]. The dynamics of heavy metals in soil moving toward lower layers has been previously studied[10], but the dynamic behavior of heavy metals in soil moving from lower layers to the surface layer due to the evaporation of water is unclear.

Therefore, this research aimed to develop an experimental method for investigating the chemical form and

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dynamics of water-soluble heavy metals in soil. For the heavy metal elements cadmium and copper, the dissolved molecular weight distribution was determined using ultrafiltration, and the ion composition was determined using the ion exchange method. The concentration of water-soluble heavy metals in top soil due to evaporation of soil solution was also investigated using a container filled with soil.

Materials and methods

1. Molecular weight composition of water-soluble cadmium and copper using ultrafiltration

For the experiment, location-specific soils were collected from the surface at 6 continuous sites (Table 1: A–F) ranging from mountain forest to lowland (Yasato area, Ibaraki Prefecture, Japan) and soils from 3 layers (Table 1: G1, G2, G3) of different depths were collected from an upland field of light-colored Andosol (Sapporo, Japan). These samples were then used in a series of experiments. One-hundred mL of deionized water was added to 10 g of each air-dried soil sample, and after shaking for 1 hour at room temperature, each was filtered with a membrane filter (pore size 0.2 µm) and used for chemical forms analysis.

Filtrate was fractionated 20 mL at a time into 4 fractions (molecular weight (Mw): 500 or less, 500–10,000, 10,000–300,000, and 300,000 or more), thereby separating dissolved heavy metals in the filtrate by molecular weight. This was done using a nitrogen gas pressurization ultrafiltration cell (UHP-43K, ADVANTEC Co., Japan) and 3 types of ultrafiltration membranes (YM05, YM10 and XM300, Amicon Inc., USA). This filtration procedure was carried out under stirring and nitrogen gas pressures of 3–5 kg/cm^2 according to the molecular weight cut-off of the filter.

2. Ion composition of water-soluble heavy metals using the ion exchange resin method

Light-colored Andosol (G1) was used as the soil sample. Fifty mL of deionized water was added to each 10 g air-dried soil sample, and after shaking for 1 hour at room temperature, each solution was filtered using a membrane filter (pore diameter 0.2 µm) and used for analysis. The filtrate was divided into 3 parts of 10 mL each, and passed through a column filled with 5 mL each of cation exchange resin (Amberlite - IR120B), anion exchange resin (Amberlite - IRA400) or a mixed resin combining equal amounts of cation exchange resin and anion exchange resin, thereby fractionating the ion forms of the heavy metals in the solution. The fraction which passed through the mixed resin is the neutral fraction, and the composition of heavy metal ions in the soil extract was determined by subtracting the concentration of this neutral fraction from the fraction which passed through the cation exchange resin or the anion exchange resin.

3. Mobility of water-soluble heavy metals in soil due to water evaporation

A plastic container (width 5 cm × height 4 cm × length 20 cm) inclined at an angle of approximately 30º from level was filled with approximately 170 g of air-dried light-colored Andosol G1 (Table 1). Then water was added to comprise 70% of the maximum water holding capacity, and the system was left at room temperature (Fig. 1). Every 24 hours, the weight of the container was measured, and water was supplied at the bottom of the inclined surface in just the amount to compensate for water lost due to evaporation. After supplying approximately 1 L of water over 50 days, the soil was air-dried in the container, and approximately 1 g of soil was sampled from each of 10 points on the surface (Fig. 1 ①–⑩), and after shaking for 1 hour at room temperature with a soil : water ratio of 1 : 5, the solution was filtered with a membrane filter

Table 1. Properties of soils used

Site	Land Use	Soil Type	pH (H_2O)	Total C (g kg^{-1})	Total Cd* (mg kg^{-1})	Total Cu* (mg kg^{-1})	Water-soluble Cd (mg kg^{-1})	Water-soluble Cu (mg kg^{-1})
A	Forest	Brown forest	5.2	45.2	0.176	51.5	0.149	0.420
B	Orchard	Andosol	5.6	32.9	0.191	45.6	0.115	4.370
C	Upland field	Andosol	6.1	12.6	0.112	43.3	0.078	3.100
D	Paddy	Gray lowland	5.9	23.4	0.109	27.5	0.044	0.390
E	Paddy	Gray lowland	6.3	30.5	0.196	51.5	0.034	1.000
F	Cattle feces disposal field	Andosol	6.9	60.7	0.218	67.5	0.053	2.480
G1	Upland field (0–15 cm depth)	Light-colored Andosol	6.2	28.5	0.289	39.8	0.118	0.100
G2	Upland field (15–25 cm depth)	Light-colored Andosol	6.2	27.5	0.223	41.2	0.127	0.082
G3	Upland field (35–45 cm depth)	Light-colored Andosol	6.1	15.7	0.247	38.6	0.033	0.017

*: Digested with nitric acid and perchloric acid.

(pore size 0.2 μm), and the heavy metal concentration and ion composition in the solution were analyzed.

4. Determination of cadmium and copper

Concentrations of cadmium and copper of each solution in the experiments were determined with electrothermal atomic absorption spectrometry (AA-800 + GTA-100, Varian Inc., Australia) using a pyrolytically coated carbon tube at analytical wavelengths of 228.8 nm for cadmium and 324.8 nm for copper. The operating conditions for the determinations were optimized. The accuracy and precision of the analytical methods were tested with standard reference materials (Pond sediment, NIES, Japan). All experiments were performed in triplicate.

Results

1. Molecular weight composition of water-soluble cadmium and copper using ultrafiltration

Fig. 2 shows water-soluble heavy metals concentration and Figs. 3 and 4 do the molecular weight distribution of water-soluble cadmium and copper in different soils (A–F) and different depths of a soil (G1, G2, G3). The water-soluble heavy metal concentrations in these soils were 389–4,370 ng/g for copper and 3.4–14.9 ng/g for cadmium. In the subsoils of soil G (G2, G3), the water-soluble heavy metal concentrations were lower than those in the surface soil. The molecular weight distribution of cadmium in water-soluble form showed that the highest percentage occurred in the fraction with a low molecular weight (Mw 500 or less), and in all soils, this fraction accounted for approximately 50% of the total amount of soluble cadmium. The next highest percentage was 25–37% in the fraction with Mw of 300,000 or more. The percentage of the fraction with intermediate molecular weight (Mw 500–300,000) was 12–25%. This molecular weight distribution pattern was the same for all the soils. The molecular weight distribution of water-soluble species of copper differed from the distribution of cadmium. The fraction with a molecular weight of Mw 500 or less accounted for a small percentage of 4–19% of the total amount of water-soluble copper. The fractions with the highest percentage were the fraction with Mw 300,000 or more and the fraction with Mw 500–10,000, and these constituted 40–75%. Therefore, soluble cadmium in soil was shown to segregate in the low molecular weight fraction with Mw of 500 or less, while copper was distributed among the fraction with Mw of 500 or greater. The amount of water-soluble heavy metal contained in soil (by soil sampling site) is shown in Fig. 2, and the molecular weight distribution of water-soluble heavy metal in each soil is shown in Figs. 3 and 4.

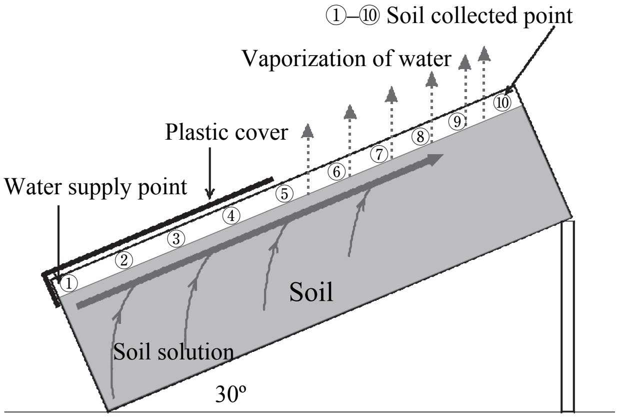

Fig. 1. Container used in the experiment to move water-soluble heavy metals to the soil surface by evaporation of water

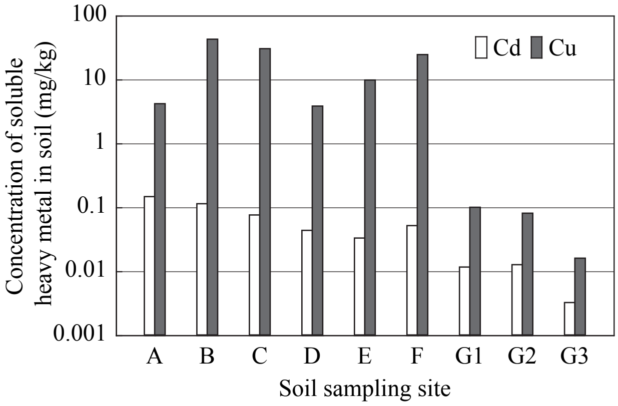

Fig. 2. Water-soluble heavy metals concentration in soil samples collected from sites with different land use (A–F) and at different soil depths (G1, G2, G3)

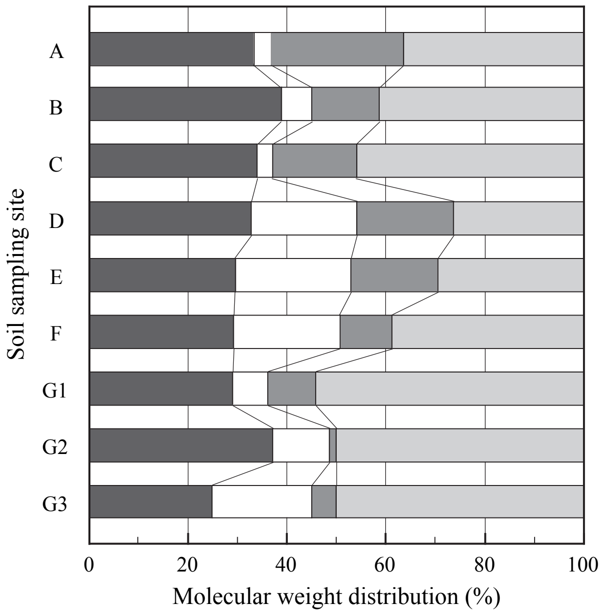

Fig. 3. Molecular weight distribution of water-soluble cadmium in each soil

■: Mw>300,000, □: 300,000>Mw>10,000,
▨: 10,000>Mw>500, ░: 500>Mw.

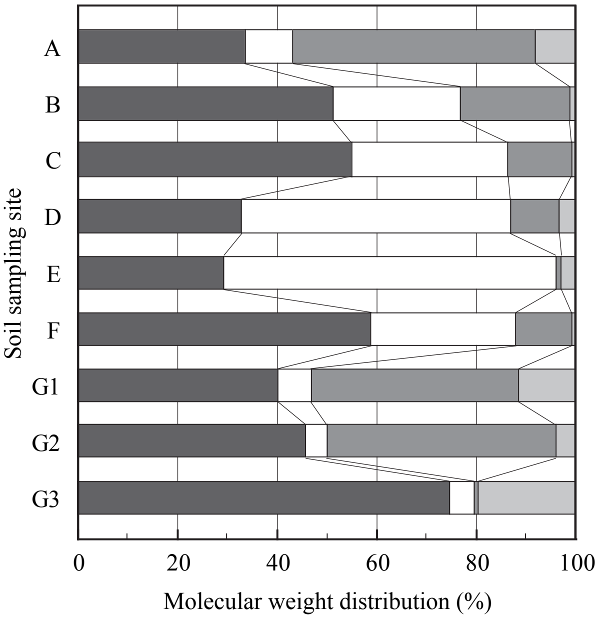

Fig. 4. Molecular weight distribution of water-soluble copper in each soil

■: Mw>300,000, □: 300,000>Mw>10,000,
▩: 10,000>Mw>500, ░: 500>Mw.

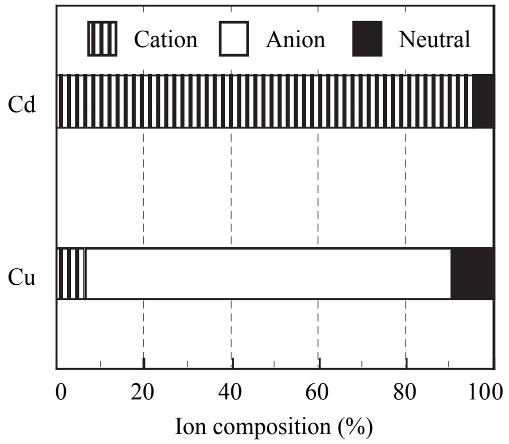

Fig. 5. Ion composition of soluble heavy metals in light-colored Andosol (G1)

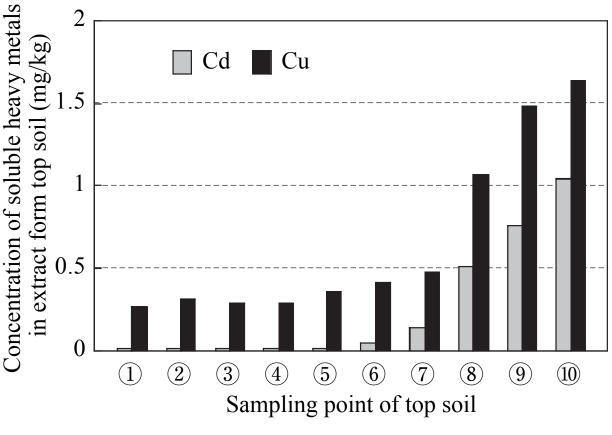

Fig. 6. Accumulation of soluble heavy metals to top soil with water evaporation from soil

2. Ion composition of water-soluble heavy metals using the ion exchange resin method

Fig. 5 shows the amount of each ion of cadmium and copper as a percentage of the total dissolved amount for soil G. Total concentrations in the extract were 0.027 ng/mL for cadmium and 1.57 ng/mL for copper. For cadmium, cations accounted for 95.6% and for copper, anions accounted for 83.5%. In the neutral fraction, cadmium accounted for 4.4%, and copper accounted for 9.9%. The tendency for the cation percentage to be high for water-soluble cadmium, and for the anion percentage to be high for water-soluble copper was the same even when other soils were analyzed.

3. Mobility of water-soluble heavy metals in soil due to water evaporation

Fig. 6 shows the water-soluble heavy metal concentration in solution extracted from surface layer soil at each sampling point (Fig. 1. ①–⑩) after water had evaporated. Water-soluble heavy metals in the surface layer soil accumulated markedly at the top of the inclined surface due to evaporation from the soil surface. Water-soluble cadmium concentration at the uppermost point ⑩ was 68.5 times that at ①, and similarly copper concentration at ⑩ was 6.0 times that at ①. The water-soluble heavy metal concentration in surface soil at the intermediate points ②–⑨ of the incline gradually increased from the bottom to the top of the incline. Fig. 7 shows the ion composition of water-soluble heavy metal at position ⑩ where water evaporation resulted in the greatest accumulation of water-soluble heavy metal. For cadmium, ion composition at accumulation point ⑩ was 99.1% cations, 0% anions and 0.9% neutral fraction, and for copper, ion composition was 13.9% cations, 63.1% anions and 23% neutral fraction.

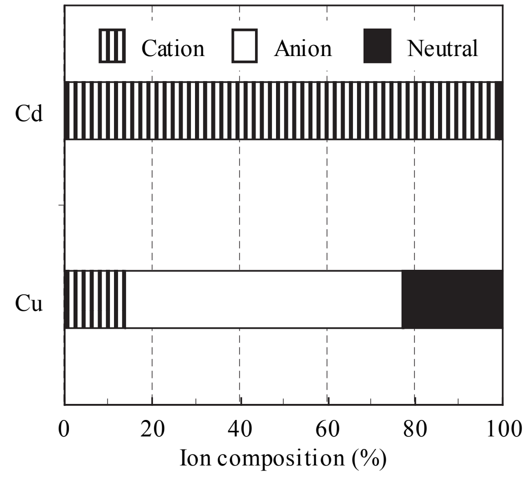

Fig. 7. Ion composition of soluble metals in the top soil at sampling point ⑩

Discussion

In the present study, we examined water-soluble cadmium and copper in soils and their chemical forms. The concentrations of cadmium and copper in the soils used in this experiment fall within the concentration ranges for unpolluted soil in Japan[2,13]. The contents of the heavy metals are different depending upon soil types. However, the soils (A to F) were collected from neighboring sites, so the concentration of heavy metals in the soils may be strongly affected by the materials added to the soil related to each land use, such as pesticides containing heavy metals in orchards, and cattle manure containing heavy metals. The higher concentration of water-soluble copper in soil B, C and F may be due to the above reasons.

Water-soluble cadmium in soil accounts for 20–90% of total cadmium in soil, but variation in this value is due to differences in soil pH. In soils with high pH, solubility is low (Table 1). Also, these values are similar to the exchangeable cadmium concentration in soil[3]. Compared with cadmium, water-soluble copper is 0.8–9.2% of total copper in soil, and it does not dissolve easily in water. This is due to the fact that, compared to cadmium, a greater proportion of copper is in a form contained within crystal structures[17]. In soil G, the amount of water-soluble cadmium and copper extracted with water from soil sampled was lower in deeper soil layers (Table 1). Total concentration of both elements in soil was almost equal, and thus it was evident that the percentage of water-soluble heavy metal relative to the total amount of heavy metal was higher in the upper layer of soil than in the lower layer of soil. There are a number of conceivable causes for this phenomenon. One is that the amount of organic matter (such as water-soluble fulvic acid) present in soil decreases in lower soil levels (Table 1). As a result, the amount of water-soluble copper which can dissolve by bonding with water-soluble fulvic acid decreases, because copper has a high bonding strength with organic matter[21] such as fulvic acid. The second potential cause is that the amount of hydrated oxides and oxides of iron and aluminum, which are clay minerals having high bonding strength with metals, varies with depth[17,22,23]. Clay minerals were not measured in these experiments, but since the amount of clay minerals increases with soil level depth, it is conceivable that a large amount of metal was adsorbed, resulting in a decrease in the eluted amount.

The molecular weight distribution for water-soluble cadmium (Fig. 3) shows the greatest percentage in the fraction with the smallest molecular weight, and this agrees with the result where cadmium was predicted to be present in the greatest quantity as divalent cations[26]. It was recognized that a large amount of cadmium is dissolved in the fraction with molecular weight of 300,000 or more in the upper layer of soil, and this may be a form adsorbed to humic substances or fine clay minerals with a high molecular weight, but the true nature was not clear from these experiments. On the other hand, the molecular weight distribution for water-soluble copper (Fig. 4) shows that the amount present in the fraction with molecular weight of 500 or less was extremely low, and the percentage dissolved with a large molecular weight was high. Copper is an element which bonds easily with organic matter, and this suggests that dissolved copper was present in a form bonded with water-soluble humic substances like fulvic acid. The molecular weight of fulvic acid in water (such as river water) was reported to be approximately 800[1]; it was reasonable to assume that copper in the fraction with molecular weight of 500 or greater was bound with organic compounds. The trend in molecular weight distribution of the heavy metals was found to be the same in all soils used. However, the molecular weight distribution of heavy metal elements might be affected through the ultrafiltration process, in which compressed soil colloids on the filter might modify the original chemical composition of the soil extract. Usually in the ultrafiltration method, the pore diameter of the filter may show considerable variation, so that a precise separation of trace elements might be difficult. To clarify the difference among soils in molecular weight distribution of water-soluble heavy metals, further consideration in greater detail will be necessary to minimize analytical artifacts.

The ion composition of soluble heavy metals (Fig. 5) showed high levels of cadmium cations and copper anions. This result was consistent with postulations based on the results that most of cadmium in soil solution was present in the dissolved fraction (< 1 KDa, molecular weight cut-off filter)[28] and that cadmium was a divalent cation[7], and copper bound with soluble organic compounds. It was assumed that, since copper was bound with soluble organic compounds, which dissolve as anions, the majority of copper was detected in the anion fraction.

The difference of chemical form of water-soluble cadmium and copper clearly was reflected in the difference in the mobility of these metals in the experiment (Figs. 1 & 6). Due to evaporation from the inclined soil surface, soluble heavy metals in soil accumulated on the upper part of the surface soil layer (Fig. 1 point ⑩). While the copper concentration in the water extracted soil solution was higher than that of cadmium (Fig. 2), the level of cadmium accumulation was higher than that of copper in this experiment with the inclined container. It may be possible that some reactions occurred, which lowered the copper concentration in the soil solution, such as copper in soil solution attaching to soil components during movement. Since copper tends to bind with organic compounds[14], it may be fixed by binding with insoluble organic substances in soil[20], such as humic acid. The ion compositions of the soluble cadmium and copper, which accumulated at the surface layer (Fig. 7 point ⑩), were almost consistent with those before accumulation (Fig. 5). Therefore, the chemical form of each element in soil solution was assumed to be retained in almost identical ionic composition percentages. Although accumulation of salts at the soil surface due to evaporation has been often observed and causes inhibition of crop growth[5], the accumulation of soluble heavy metals in soil due to evaporation was first measured in the present study. The results of the present study suggest a possibility of removal of water-soluble heavy metals from contaminated soil; water-soluble heavy metals may migrate to the soil surface by applying water to the soil followed by evaporation, and the surface soil containing the heavy metals that migrated from the whole soil may be removed. However, since the soluble fraction of most heavy metals other than cadmium in soil is generally less than 10%[4], it may be necessary to solubilize the heavy metals in soil for the above proposed method to be effective.

In conclusion, the present study clearly shows the difference in chemical form between water-soluble cadmium and copper in soils, and also shows that the difference affects the mobility of these heavy metals in soil due to evaporation from the soil surface. The molecular weight distribution of water-soluble cadmium and copper in soils was for the first time determined in the present study. The results obtained agreed with the findings found for aquatic humic substances and also with the prediction based on chemical equilibrium[21]. These results contribute to clarify behavior of the heavy metals in soil, which is needed to minimize the absorption of the metals by crops.

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