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The Predicting Environmental Fate of Cd, Cu, and Pb by Sequential Fractionation in Mine Tailings and Agricultural Soils

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ABSTRACT

토양내에 있어 중금속의 총량 분석만으로는 오염 토양에 대한 환경 평가를 위한 충분한 자료가 되지 못한다. 또한 중금속의 토양내 위해성은 중금속과 토양과의 화학적 상호작용에 의해 결정되기 때문에 중금속의 화학적 형태를 규명하는 것은 토양 환경에 있어서 그들의 이동성과 거동 특성을 평가하는데 중요한 자료가 된다. 연속 추출법은 구봉 광산의 광미로부터 Cd, Cu, Pb을 화학적 형태에 따라 분리하고, 인위적으로 중금속을 포화시킨 광미와 두 밭토양에 있어 중금속의 토양내 거동 특성을 예측하기 위하여 이용되었다. 광미중 Pb의 대부분은 Fe-Mn oxide, carbonate의 결합 형태로 존재하였으며, Cu와 Cd은 각각 71.8%와 42.9%가 유기물, carbonate의 결합형태로 존재하였다. 상당량의 Cd(94.9%), Cu(95.1%), 그리고 Pb(85.8%)은 토양내 잠재적으로 이동 가능한 형태로 존재하였다. 유성과 논산의 밭토양에 가해진 Cd는 대부분 이동성이 가장 높은 치환태로 존재하였으며, 유성과 논산 토양에서 각각 67.9%와 93.2%가 치환태로 존재하였다. 토양에 가해진 Cd, Cu, Pb은 대부분 이동이 용이한 형태로 존재하였으며, 토양과의 결합세기는 Pb > Cu > Cd 순으로 감소하였다.

Ⅰ. Introduction

In the last decades, human activity has continuously increased the levels of heavy metals circulating in the environment. Contamination of heavy metals in the environment is of major concern because of their toxicity and threat to human life and the environment. Much research has been conduced on heavy metal contamination in soils from various anthropogenic sources such as industrial wastes, automobile emissions, mining activity, and agricultural practice.

Based on primary accumulation mechanisms in soil, heavy metals can be classified into five categories: (i) adsorptive and exchangeable, (ii) bound to carbonate phases,

(iii) bound to reducible phase (Fe and Mn oxides), (iv) bound to organic matter and sulfides, and (v) detrital or lattice metals (residual). Heavy metals present in these categories have different remobilization behaviors under changing environmental conditions. Geochemical forms of heavy metals in soil affect their solubilities, which directly influence their bioavailability. Therefore, determining total content of heavy metals may give information concentration concerning possible enrichment of the soil with heavy metals, but generally and for most element, there is not sufficient criteria for estimating their biological effects. this is because it is the chemical form of a metal in the soil and sediment that determines its mobilization capacity and behavior in the environment.

The primary objectives of this study were to investigate the chemical partitioning of Cd, Cu, and Pb in mine tailings, to evaluate the effect of physical and chemical properties of soils on metal partition in to different fractions, and to predict the fate related to adsorption and mobility of heavy metals added in soil environment.

Ⅱ. Materials and Methods

Mine tailings and two plowland soils, saturated with Cd, Cu, and Pb, were used in this study. The individual soil was saturated using concentrated Cd, Cu and Pb solutions and washed with deionized water to remove most of the excess salt until the conductivity of the rinse stabilized <2.0 μS/cm. These soils reflect various form of heavy metal for metal adsorption and movement in soil environment. The procedure of Tessier et al. (1979) selected for the study, was designed to separate heavy metals into six operationally designed fractions: water soluble, exchangeable, carbonate bound, Fe-Mn oxide bound, organic bound and residual fractions.

1g of each soil sample was weighed into 50 ml polycarbonate centrifuge tube and the following fractions were obtained.

(1) Water soluble

Soil sample extracted with 15 ml of deionized water for 2 h.

(2) Exchangeable

The residue from water-soluble fraction was extracted with 8 ml of 1 M $MgCl_2$ (pH 7.0) for 1 h.

(3) Carbonate Bound

The residue from water-soluble fraction was extracted with 8 ml of 1 M NaOAc (adjusted to pH 5.0 with HOAc) for 5 h.

(4) Fe-Mn Oxides-Bound

The residue from carbonate fraction was extracted with 20 ml of 0.044 M $NH_2OH \cdot HCl$ in 25% (v/v) HOAc at 96℃ with occasional agitation for 6 h.

(5) Organic-Bound

The residue from Fe-Mn oxide fraction was extracted with 3 mL of 0.02 M HNO_3

and 5 ml of 30% H_2O_2 (adjusted to pH 2 with HNO_3). The mixture was heated to 85℃ for 2h, with occasional agitation. A second 3mL solution of 30% H_2O_2 (pH 2 with HNO_3) was added and the mixture heated again to 85℃ for 3h with intermittent agitation. After cooling, 5 ml of 3.2 M NH_4OAc in 20% (v/v) HNO3 was added and the samples diluted to 20 ml and agitated continuously for 30 min.

(6) Residual

The residues from organic fraction were digested using a mixture of HF-HCl/HNO_3 dissolution procedure in the digestion Bomb. The residues were washed with 15mL of deionized water followed by vigorous hand shaking and then followed by 30min of centrifugation before each successive extraction, separation was done by centrifuging at 3,000 rpm for 30 min. The supernatants were filtered through 0.2 ㎛ cellulose acetate membrane. The metal concentrations of solution were analyzed with Atomic Absorption Spectrophotometer (AAS).

Ⅲ. Results and discussion

Soil has long been regarded as a repository for society's waste. Gradually mobilized by biological process, soil contaminants can pollute water supplies and impact food chains. Heavy metals such as Cd, Cu, and Pb are all potential soil pollutants. Soils consist of heterogeneous mixtures of organic and solid components as well as a variety of soluble substances. Therefore, metal distribution among specific forms varies widely based on the metal's chemical properties and soil characteristics. Thus it is important to evaluate the availability and mobility of heavy metals to establish environmental guidelines for potential toxic hazards and to understand chemical behavior and fate of heavy metal contaminants in soils.

1. Sequential Fractions

The sequential extraction used in this study is useful to indirectly assess the potential mobility of heavy metals in the soils. The six chemical fractions are operationally defined by an extraction sequence that follows the order of decreasing solubility. Assuming that bioavailability decreases in the order: water soluble > exchangeable > carbonate > Fe-Mn oxide > organic > residual. This order is just a generalization and offers only qualitative information about metal bioavailability.

All of the metals examined in the Gubong mine tailings, Pb was the highest (2.082 $cmol_c/kg$), followed by Cu (0.284 $cmol_c/kg$), and Cd (0.0437 $cmol_c/kg$). Pb was mostly concentrated in the Fe-Mn oxide and carbonate fractions, although it was also present in other fractions. The Percentage of total Pb in the Fe-Mn Oxide and carbonate fraction were 48.3% and 26.8%, repletively. The greater percentage of Pb in the Fe-Mn oxide and carbonate fractions than that in residual fraction probably reflects the great tendency for Pb availability and mobility in soils. The distribution patterns of Cd and

Cu in various chemical fractions were similar to the Pb distribution, but the percentage of total Cu in the organic fraction was the highest (71.8 %) and the percentage of total Cd in the carbonate fraction was the highest (42.9 %). The potential mobility and bioavailability of heavy metals in Gubong mine tailings would be in the order: Cd > Pb > Cu.

2. Association pattern

In order to investigate the association pattern of heavy metals in various chemical fractions, heavy metals were sequentially fractionated in Gubong mine tailings and two plowland soils saturated with Cd, Cu, and Pb. The total association amounts of heavy metals in various chemical fraction were in the order: Pb > Cu > Cd. In Yusung soil, The contents of Pb in exchangeable, carbonate, Fe-Mn oxide, organic and residual fraction were 0.387, 0.326, 0.375, 0.043, and 0.066 $cmol_c$/kg, respectively. The percentage of total Pb in the exchangeable, carbonate, and Fe-Mn Oxide fraction, which have relatively weak binding force was 91 %. The association patterns of Cu and Cd were similar to the Pb association, but the Cu assocaiation was the highest in the Fe-Mn oxide fraction (30.4 %) and the Cd association was the highest in the exchangeable fraction (67.9 %). In Nonsan soil, associated Cd was mostly concentrated in the exchangeable fraction and the percentage of total Cd in the exchangeable fraction was 93.2 %. Pb and Cu were concentrated in the exchangeable, carbonate, and Fe-Mn oxide fraction. In Gubong mine tailings saturated with heavy metals, the contents of Pb in carbonate and Fe-Mn oxide fraction were 1.206 and 1.251 $cmol_c$/kg, respectively and the percentage of total Pb in carbonate and Fe-Mn oxide fraction were 39.2 and 40.7 %, respectively. The association patterns of Cd in various fractions was similar to the Pb association, but the association of Cu in organic fraction was higher than that in exchangeable fraction. Adding heavy metals to the soil, Cd, Cu, and Pb may mostly be associated on exchangeable, carbonate, and Fe-Mn oxide bounds.

Ⅳ. Conclusion

A sequential extraction procedure was used to fractionate Cd, Cu, and Pb present in Gubong mine tailings and to predict the fate of heavy metals added in soils.

Different geochemical fractions are operationally defined by an extraction sequence that generally follows the order of decreasing solubility. The carbonate and Fe-Mn oxide fractions were the most abundant pool for all the metals in soils studied. Therefore, they should be evaluated when studying the pollution levels of heavy metals in soils

Of all the heavy metals added in soil, the affinity of Pb was the highest in the binding sites of the soil and heavy metals were bound mostly on exchangeable, carbonate, and Fe-Mn oxide bounds. Therefore, the heavy metals added in soil may have potential mobility and bioavailability as toxic pollution sources, although these have a low solubility, directly.

References

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Table 1. Physical and chemical properties of two plowland soils (Nonsan, Yousung) and Gubong mine tailings.

Sample	pH	CEC	OM	Texture	*P.S.D(%)		
	H_2O	$cmol_c/kg$	(%)		Clay	Silt	Sand
Yusung	4.55	9.5	2.87	CL	30	38	33
Nonsan	4.94	7.0	1.94	SCL	24	54	23
Gubong	8.75	1.0	1.12	L	16	36	48

* P.S.D : Particle size distribution

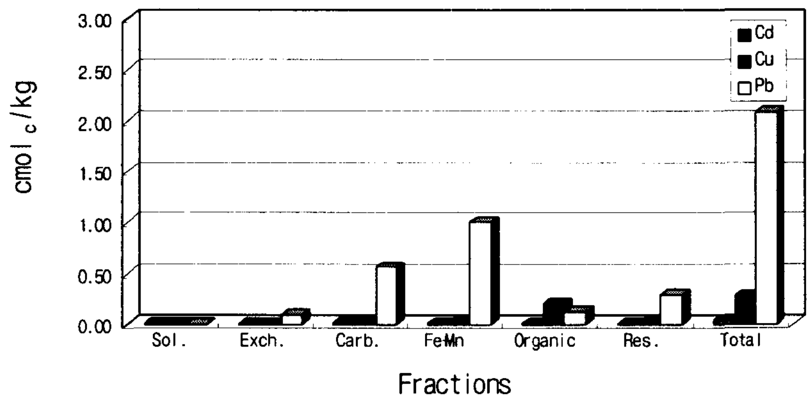

Figure 1. Distribution of heavy metals in various chemical fractions in Gubong mine tailings.

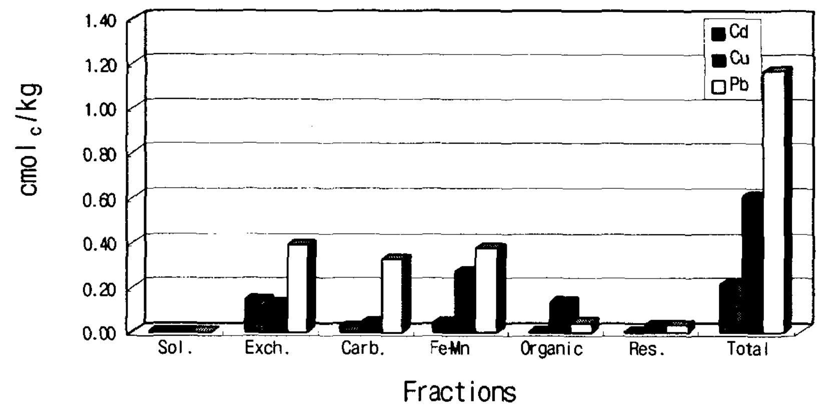

Figure 2. Distribution of heavy metals in various chemical fractions in Yusung plowland soil saturated with Cd, Cu, and Pb.

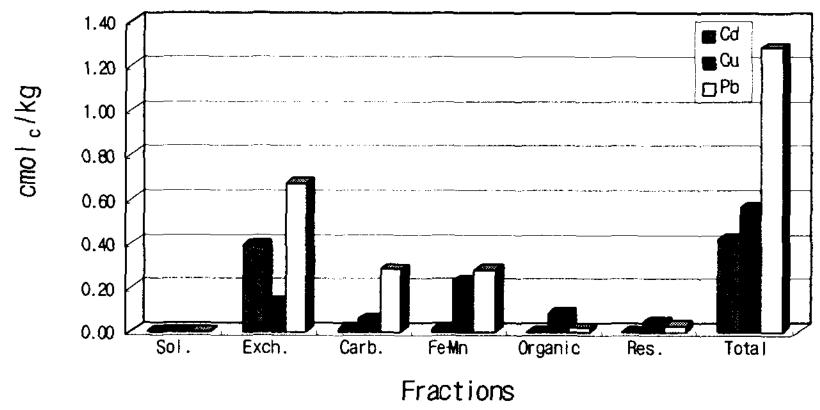

Figure 3. Distribution of heavy metals in various chemical fractions in Nonsan plowland soil saturated with Cd, Cu, and Pb.

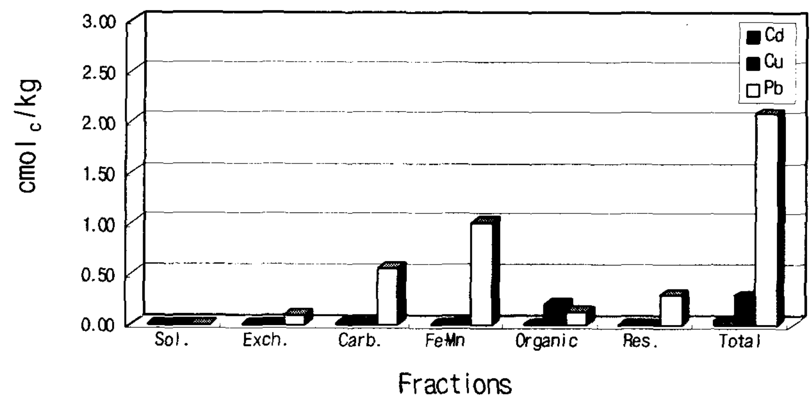

Figure 4. Distribution of heavy metals in various chemical fractions in Gubong mine tailings saturated with Cd, Cu, and Pb.