연구보문

Cadmium and Zinc Uptake Characteristics of Corn Plant in Arable Soil Contaminated by Smelting Factory Source

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ABSTRACT: The cadmium (Cd) and zinc (Zn) contamination of soils and cultivated crop plants by zinc smelting activities was studied. In the study area of the vicinity of △△ zinc smelting factory in Korea, soils and corn plants were sampled at corn harvesting stage and analyzed Cd and Zn concentration, as well as Cd and Zn fraction and chemical properties in soils. At 600 m radius of studied area, Cd and Zn were highly accumulated in the surface soils (0 - 20 cm) showed greater than the Korean warning criteria (Cd 1.5, Zn 300 mg kg^{-1}) with corresponding values 1.7 and 407 mg kg^{-1}, respectively. The leaf part gave higher Cd concentration with the corresponding value of 9.5 mg kg^{-1} as compared to the stem and grains parts (1.6 and 0.18 mg kg^{-1}), respectively. Higher Zn concentration was also obtained from the leaf part of the corn plant which gave the value of 1,733 mg kg^{-1}. The stem and grain part gave corresponding values of 547 and 61 mg kg^{-1}. The order of the mean Cd concentration in fractions is F3 (oxidizable fraction) > F2 (reducible fraction) > F4 (residual fraction) > F1 (exchangeable + acidic fraction). A highly positive correlation is observed between F2 and concentration of Cd and Zn in both plant parts, leaf and grain. Highly positive correlations are shown in the pH, exchangeable Ca and Mg, and CEC when correlated with Cd and Zn bound to F4 fractions. To reduce Cd and Zn uptake by corn plant in an arable land heavily contaminated with Cd and Zn as affected by smelting factory, an efficient and effective soil management to increase soil pH and CEC is thus recommended.

Key Words: Zinc smelting factory, cadmium, zinc, fraction

INTRODUCTION

△△ zinc factory (129°03′48″N and 37°02′E) located in the southeastern part of the Korean peninsula is the third largest zinc smelting factory in the world. This factory was founded in 1970s and now produces 450,000 tons of sulfuric acid (H_2SO_4), 280,000 tons of zinc, 1,700 tons of cupric sulfate and 900 tons of cadmium per year. However, there were issues previously reported about its ill-health effects to the heavy metal exposed workers, its living communities and in the environment. Crop plants growing on heavy metal contaminated medium can accumulate high concentrations of trace elements to cause serious health risk to consumers[1)]. Around 20 hectares of cultivated lands nearby the factory are planted mainly into corn, then some minor land area into radish, red pepper, and sesame plant. As grains of corn plant are consumed by human beings while fresh corn stover is utilized as feeding materials for ruminants, this was used as the sole test crop.

Cadmium is a toxic element and Zn in high concentrations, and numerous investigations showed that the pronounced amount of Cd and Zn were often found in arable soil adjacent to a non-ferrous metal

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production bases[2-4]. The processing and subsequent release of zinc to the environment is normally accompanied by cadmium environmental pollution because of zinc ores (ZnS) generally containing 0.1 - 5% and sometimes even higher cadmium[5]. Cadmium, unessential to plants, and zinc, essential to plants, are elements having similar geochemical and environmental properties. These two metals are exchangeable and somewhat mobile elements in soils[6]. Heavy metal uptake by roots depends on both soil and crop plant factors (e.g. source and chemical form of elements in soil, pH, CEC, organic material, plant species, plant age, etc,). Heavy metals present in various forms in soil. Different forms of heavy metals have different mobility and phytovavailability[7]. Knowledge of the heavy metal speciation in soil amended with sewage sludge is important for the understanding of the bioavailability and mobility of heavy metals in soils. Generally, the plant uptake of heavy metals is correlated to extractable forms of the metals rather than to the total metal contents in the soil[8]. The distribution of heavy metals among the water soluble, exchangeable + acidic, reducible, organic and residual fractions using sequential extraction analysis could assess the potential phytoavailability of heavy metals in soil.

Accumulation of Cd and Zn in plant parts in solution culture or in pot experiment had been reported[3,9-13]. However to our knowledge, there is little information about the fate and behaviors of the metals in crop tissues in fields. Therefore, the present investigation was undertaken to examine the metal distribution of Cd and Zn in the corn plant and their phytoavailability. The objectives of this study are mainly to; (1) investigate the degree of trace element contamination of soils located nearby the smelting factory; (2) show the metal distribution of Cd and Zn in different parts of the corn plant; (3) assess phytoavailability of Cd and Zn in soil through sequential fractionation; and (4) determine the relationship between the soil properties and phytoavailability of Cd and Zn.

2. Materials and methods

2.1 Soils

Sampling of soils was carried out on 7 August, 2006 to examine concentration of heavy metals. The sampling locations and topography of the study area are shown in Fig. 1. Soils (0 - 20 cm, 40 - 60 cm, and 60 - 80 cm in depth) were sampled by hand auger (2.5 cm in diameter) in the arable lands nearby the smelting factory with an estimated land area at 20 hectares. Twenty samples were randomly collected from these sites. The concentration of Cd and Zn were analyzed following the standard method which was established by the Korean Soil Environmental Conservation Act[14]. For analysis of Cd concentrations sieved soil samples (< 2 mm) were extracted by 0.1 N HCl solution, for Zn (finely milled soil samples, < 180 ㎛) were digested in 3:1 concentrated HCl and HNO_3 (aqua regia). The extracted solutions were analyzed for Cd and Zn concentrations through AAS (atomic adsorption spectrophotometer GBC Model AVANTA PM, Melbourne Australia). The sieved soils (< 2 mm) were analyzed for chemical properties as follows : pH (1 : 5 with H_2O), organic matter content[15]. The available P content was determined using the Lancaster method (5 g soil were

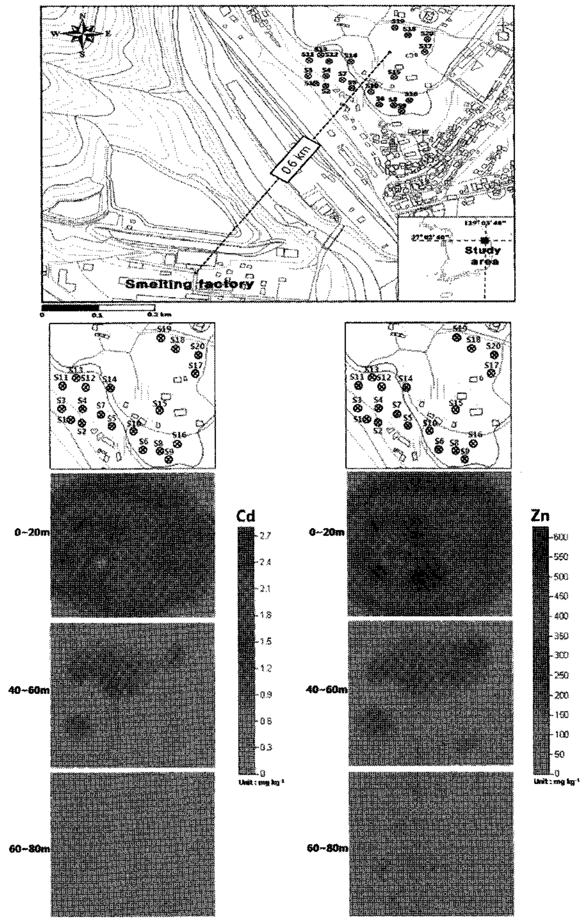

Fig. 1. Distribution of Cd and Zn concentration in soil sampled by depth in the vicinity of the △△ smelting factory.

extracted with 20 ml of 0.33 M CH_3CHOOH, 0.15 M lactic acid, 0.03 M NH_4F, 0.05 M $(NH_4)_2SO_4$ and 0.2 M NaOH at pH 4.25)[16]. Exchangeable Ca^{2+}, Mg^{2+}, and K^+ were extracted with 1 M NH_4OAc (pH 7.0) at a soil : solution ratio of 1 : 5 for 1 h. The solutions were analyzed by ICP-OES (inductively coupled plasma optical emission spectrophotometer Perkin Elmer Model OPTIMA 4300 DV, Shelton USA). Cation exchange capacity of soil was measured using 0.1 M NaCl following the ion retention method of Schofield[17]. Cadmium and Zn was fractionated by a modified sequential extraction procedure of BCR (the community Bureau of Reference now the European Union "Measurement and Testing Program") to water soluble, exchangeable + acidic, reducible, oxidizable, and residual fraction[18]. Extractions were conducted in 50 ml polypropylene centrifuge tubes. The supernatant was centrifuged at 6000 rpm for 15 min, and filtered between each successive extraction.

2.2. Crop plants

The vegetation of arable land nearby smelting factory consists of various crop plant mainly planted into corn, then a small portion of radish, red pepper, and sesame plant. The corn plant was selected as the main test crop as it is the major crop cultivated in the affected area and was divided into three main parts, namely, stem, leaf and grain plant tissue samples. The samples were thoroughly washed in deionized water, oven-dried at 70℃ for 72 h, ground, and digested using a solution of HNO_3 : H_2SO_4 : $HClO_4$ (10 : 1 : 4 volume/volume) for Cd and Zn. Cadmium and Zn were determined by using AAS.

3. Results and Discussions

3.1. Contamination of Cd and Zn in arable soil

Cd and Zn were highly accumulated more than the Korean warning criteria (Cd 1.5, Zn 300 mg kg^{-1}) with mean values 1.7 and 407 mg kg^{-1}, respectively, at the surface soils (0 - 20 cm). Higher concentration of Cd and Zn were found at the sample surface soil collected at 0 - 20 cm than in the other layers of its soil profile (Fig. 1). In addition for Cd, concentration decreased significantly at the increasing soil depth at 40 - 60 cm and 60 - 80 cm. The same distribution can be observed too in Zn which also decreased significantly at increasing soil depths. A higher Cd and Zn concentration at the surface soil than in the subsoil horizons may mean that the heavy metal sources doesn't come from the parent materials but from its external environment.

3.2. Distribution of Cd and Zn in corn plant

Table 1 shows the narrow variation in the Cd and Zn metal distribution in the stem, leaf and grain of the corn plant from all sampling sites. The leaf part gave higher Cd concentration with the corresponding value of 9.5 mg kg^{-1} as compared to the stem and grains parts (1.6 and 0.18 mg kg^{-1}), respectively. Higher Zn concentration was also obtained from the leaf part of the corn plant which gave the value of 1,733 mg kg^{-1}. The stem and grain part gave corresponding values of 547 and 61 mg kg^{-1}. Concentrations of Cd and Zn concerned in plant parts showed that the highest concentrations in the corn plant occurred in leaf, the lowest in grain. Corn leaf contained 26 - 105 times the content found in grains for Cd, and 17 - 46 times for Zn. Corn stem contained 3 - 24 times the level discovered in grains for Cd, and 2 - 14 times for Zn (Table 1). These results similar with the previous pot reports of Dudka *et al.*[3], who found that the concentrations of Cd and Zn in spring wheat plant were higher in straw than in grain by factors 1.5 - 2 and 3 - 7 for Cd and Zn, respectively and the field experiment of Granato *et al.*[19] who reported that the leaf part gave higher Cd concentration with the corresponding value of 10 mg kg^{-1} as compared to the grains

Table. 1. Cd and Zn concentration in corn plant cultivated in target soil sampling site

Corn plant	Cd (mg kg^{-1})		Zn (mg kg^{-1})	
	AM ± SD[1)]	Range	AM ± SD	Range
Stem	1.6 ± 0.5	0.5 - 2.6	547 ± 206	105 - 943
Leaf	9.5 ± 1.7	7.0 - 12.3	1,733 ± 498	1,043 - 2,803
Grain	0.18 ± 0.08	0.1 - 0.4	61 ± 22	34 - 123

[1)] AM ± SD means arithmetic mean ± standard deviation parts (0.2 mg kg^{-1}). Hong *et al.*[20] reported that Cd was more concentrated (4.1 - 5.9 times) in shoots than in roots under field experiment. Cadmium and Zn concentrations in the stems and leaves were higher compared to the grains. 80% (16 out of 20) and 85% (17 out of 20) of the grain samples yielded higher concentration of Cd and Zn than the maximum safe intake level for Cd (0.1 mg kg^{-1}) and Zn (40 mg kg^{-1}) established by FAO/WHO (Food and Agriculture Organization/World Health Organization) and Bowen[21], respectively. In Korea, only maximum permit limits of Cd and Pb in rice plant are established but still none for other crops. Moreover as grains are consumed by human beings, leaf and stems are consumed by animals as feeding stuff. Leaf parts of corn plant sampled in arable land near by smelting factory contained high amount of Zn (mean 1,733 mg kg^{-1}). High concentration of Cd and Zn in leaf and stem parts can cause serious health problem to animals. Just like, the grazing animal can ingest the metals either by consuming herbage that is internally or externally contaminated[22]. Of particular concern is Cd, because of the relatively low threshold toxicity on the part of the animal to the presence of relatively low concentration of this element in the body.

3.3. Fractionation of Cd and Zn in soil

In Table 2, the concentrations of Cd and Zn fractions in the soil samples are shown. The order of the mean Cd concentration in fractions is F3 (oxidizable fraction) > F2 (reducible fraction) > F4 (residual fraction) > F1 (exchangeable + acidic fraction). Highest mean concentration in Cd was obtained from F3 with a value of 1.0 mg kg^{-1} (38.5% of total Cd concentration). Other fractions gave corresponding values of 0.8 (30.7 %), 0.5 (19.2%) and 0.2 (7.7%) mg kg^{-1} for F2, F4 and F1, respectively. In zinc concentrations, F3 also gave highest value of 191 mg kg^{-1} followed by values of 86 (21.1%), 81 (19.9%) and 50 (12.3%) mg kg^{-1} for F4, F2, and F1, respectively showing the trend F3 > F4 > F2 > F1.

Table 3 shows the correlation of concentrations between the soil Cd, Zn fractions and the plant. Cd concentration in F1 showed a positive correlation with

Table 2. Concentration of Cd and Zn fractions in soil samples collected in the targeted sites

Fraction[1)]	Cd (mg kg^{-1})		Zn (mg kg^{-1})	
	AM ± SD[2)]	Range	AM ± SD	Range
F1	0.2 ± 0.1 (7.7%)[3)]	0.1 - 0.5	50 ± 25 (12.3%)	13 - 130
F2	0.8 ± 0.4 (30.7%)	0.3 - 1.9	81 ± 41 (19.9%)	21 - 217
F3	1.0 ± 0.4 (38.5%)	0.3 - 1.9	191 ± 68 (46.9%)	60 - 302
F4	0.5 ± 0.5 (19.2%)	0.01 - 2.3	86 ± 65 (21.1%)	4 - 280
F5	2.6 ± 0.9 (100%)	0.8 - 4.1	407 ± 142 (100%)	105 - 641

1)Fraction : F1 : Exchangeable + acidic fraction, F2 : Reducible fraction, F3 : Oxidizable fraction, F4 : Residual fraction, F5 : Total concentration
2)AM ± SD means arithmetic mean ± standard deviation
3)( ) means the proportion of each fraction (%) to total concentration

Table 3. Correlation between plant heavy metal concentration and soil heavy metal concentration

Fraction[1)]	Cd (mg kg^{-1})			Zn (mg kg^{-1})		
	Stem	Leaf	Grain	Stem	Leaf	Grain
F1	0.278	0.506*	0.502*	0.214	0.610**	0.698***
F2	0.196	0.578**	0.557**	0.277	0.701***	0.754***
F3	-0.087	0.238	0.315	-0.334	0.297	0.304
F4	-0.237	-0.176	-0.241	-0.535*	-0.338	-0.445*
F5	-0.057	0.282	0.251	-0.317	0.261	0.222

1)Fraction : F1 : Exchangeable + acidic fraction, F2 : Reducible fraction, F3 : Oxidizable fraction, F4 : Residual fraction, F5 : Total concentration
2) *, **, and *** denote significance at 95, 99, and 99.9% level, respectively

the Cd leaf and grain contents with corresponding values of 0.506* and 0.502*, respectively. Between F2 and Cd in leaf and grain, both parts show high correlation (0.578** and 0.557**). F3 showed a low positive correlation with the Cd leaf and grain contents with corresponding values of 0.238 and 0.315, respectively. High positive correlation is observed between Fland Zn leaf (0.610**) and grain (0.698***). A high positive correlation too is observed between F2 in both plant parts, leaf and grain with values 0.701*** and 0.754***, respectively. The F3 showed a low positive correlation in leaf and grain (0.297 and 0.304). However, F4 showed neagtive correlation with the Zn leaf and grain contents. Even though, highest mean concentrations in Cd and Zn in soil were obtained from F3, between F2 and Cd and Zn in leaf and grain, both parts show the highest correlation which means that F1 and F2 among the Cd and Zn fractions are easily absorbed by corn plant, but scarcely in F4. Metals confined in the exchangeable and bound to carbonates are likely to affect sorption-desorption process in soil. And metals bound to iron and manganese oxides are thermodynamically unstable under anoxic conditions (i.e., low Eh) in soils[23]. Metal confined in the residual fractions are usually not expected to be released over short period of time under the conditions usually encountered in nature[7,23].

3.4. Relationship between the soil properties and phytoavailability of Cd and Zn

Uptake of heavy metals by plants are not only influenced by their concentrations in soil, but also by their chemical forms and physicochemical properties of soil[5,7]. Table 4 shows the soil physical and chemical properties. A narrow pH variation was shown in the results with a corresponding mean value of

Table 4. Chemical properties of soils sampled in the arable land near △△ zinc smelting factory.

Data	pH	T-C	Av. P	Ex. Cation ($cmol^+ kg^{-1}$)			CEC
	(H_2O,1 : 5)	($g\ kg^{-1}$)	($mg\ kg^{-1}$)	K	Ca	Mg	($cmol^+ kg^{-1}$)
AM ± SD	5.3 ± 0.8	27 ± 6	345 ± 135	1.0 ± 0.4	4.4 ± 2.8	0.5 ± 0.5	8.2 ± 2.8
Range	4.4 - 7.9	19 - 42	40 - 573	0.4 - 2.1	1.3 - 13	0.03 - 1.7	5.3 - 9.2

Av. P : available phosphorus, T-C : total carbon, Ex. cation: exchangeable cation, CEC : cation exchange capacity

Table 5. Correlation between heavy metal fractions and soil properties

Heavy metal	Soil property	Heavy metal fraction[1)] F1	F2	F3	F4	F5
Cd	pH	-0.152	-0.083	0.608**	0.609**	0.550*
	Av. P_2O_5	-0.165	-0.302	0.122	0.484*	0.202
	OM	0.358	0.480*	0.140	0.139	0.374
	Ex. K	-0.072	-0.186	0.167	0.150	0.077
	Ex. Ca	-0.340	-0.302	0.457*	0.737***	0.458*
	Ex. Mg	-0.436	-0.350	0.461*	0.660**	0.382
	CEC	-0.365	-0.292	0.462*	0.655**	0.408
Zn	pH	-0.246	-0.045	0.794***	0.777***	0.672**
	Av. PsO_5	-0.221	-0.165	0.396	0.434	0.298
	OM	0.350	0.470*	0.163	0.076	0.310
	Ex. K	-0.068	-0.109	0.274	0.267	0.208
	Ex. Ca	-0.393	-0.253	0.700***	0.825***	0.563**
	Ex. Mg	-0.455*	-0.306	0.679***	0.750***	0.493*
	CEC	-0.347	-0.213	0.629**	0.766***	0.523*

[1)]Heavy metal fraction : F1 : Exchangeable + acidic fraction, F2 : Reducible fraction, F3 : Oxidizable fraction, F4 : Residual fraction, F5 : Total concentration

[2)] *, **, and *** denote significance at 95, 99, and 99.9 % level, respectively

5.3. Mean total carbon content is 27 mg kg^{-1}. Average available phosphorus corresponds to a value of 345 mg kg^{-1}. Mean values for exchangeable cations such as K, Ca and Mg are 1.0, 4.4 and 0.5 $cmol^{+}/kg$. The average CEC is 8.2 $cmol^{+}/kg$.

Table 5 shows the correlation between the heavy metal fractions and soil properties. A highly positive correlation is shown between the soil pH and Cd in F3 and F4 with values 0.608** and 0.609**, respectively. Cadmium concentrations in F4 correlated with exchangeable Ca and Mg gave highly positive results. Cadmium concentrations in F4 also yield a positive correlation with CEC in the soil. Meanwhile, a similar trend was shown between the soil pH and Zn in F3 and F4 with values 0.794*** and 0.777***, respectively. Cadmium concentrations in F3 and F4 yielded a highly positive correlation when correlated with exchangeable Ca and Mg. Zinc concentrations in F3 and F4 also yield a positive correlation with CEC in the soil. Cadmium and Zn in F4 which is scarcely absorbed by corn plant correlated with pH, exchangeable Ca, Mg and CEC gave highly positive results. Increases in CEC (negative charge) of soil can cause immobilization of metals[24]. Calcium addition in the form of lime also causes an inhibition of the uptake and translocation of metal from root to shoot. It is well documented that the availability of Zn depends on soil pH[5]. Soil management to increase pH, CEC, exchangeable Ca and Mg is recommended in reducing Cd and Zn uptake by corn plant cultivated in arable land heavily contaminated with Cd and Zn.

Conclusion

The present study has examined extent of contamination of arable soils in the vicinity of △△ zinc smelting factory and investigated distribution of Cd and Zn in different parts of the corn plant and determines the relationship between soil properties and phytoavailability of Cd and Zn. The arable soils were heavily contaminated with Cd and Zn. Cadmium and zinc concentrations with the corresponding mean values of 1.7 and 407 mg kg^{-1} in the soil surface were greater than the warning criteria. The leaf part gave higher Cd and Zn concentration compare with stem and grain parts. The order of the mean concentration of Cd and Zn fraction in soil is F3 > F2 > F4 > F1. Positive correlation is observed between F1, F2, and F3 and concentration of Cd and Zn in both plant parts, leaf and grain. F1, F2, and F3 could be accumulated in the leaf and grain parts of corn plant, but not F4. Highly positive correlations are shown in the pH, CEC, Ex. Ca, and Ex. Mg when correlated with Cd and Zn bound to F4 fraction. To reduce Cd and Zn uptake by corn plant in arable land affected by smelting factory, soil management to increase pH, CEC, exchangeable Ca and Mg is recommended.

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