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# Fractionation and mobility of cadmium, lead and zinc in some contaminated and non-contaminated soils of Japan

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**We investigated the forms and mobility of cadmium (Cd), lead (Pb) and zinc (Zn) in four contaminated and four non-contaminated surface soils, collected from different localities of Japan using a sequential extraction procedure. The total metal concentration in soils ranged from 0.69 to 12.5 for Cd, 19 to 359 for Pb and 90 to 704 mg kg<sup>-1</sup> for Zn. The metal concentration in the contaminated soils was higher by 5 to 18 fold than in non-contaminated soils. Cadmium in the contaminated soils was dominantly associated with the exchangeable fraction (28 to 48%), while in non-contaminated soils; the residual fraction was the dominant one (29 to 32%). The major proportion of Pb (34 to 53%) and Zn (41 to 64%) was associated in the residual fraction. The mobility factor (MF = (F1 to F3/F1 to F6) × 100) among the metals was the highest for Cd (43%), and the lowest for Pb (11%). For all metals, the MF was several fold higher (Cd and Zn was 5 fold, and Pb was 2 fold) in the contaminated soils than in the non-contaminated soils. Higher mobility of metals in the contaminated soils may create a health risk by increasing their accumulation in the field crops.**

**Key words:** Heavy metals, mobility, source, mining industries.

## INTRODUCTION

Heavy metal contamination of arable soils through anthropogenic activities is a widespread and more serious problem at some locations in Japan. Rice fields in Japan have suffered from serious soil pollution by Cd and other heavy metals caused by rapid growing industrial activities during 1960s (Kitagishi and Yamane, 1981), where Cd pollution of rice fields led to renal impairment and bone disease in exposed populations (Kondo, 1996). Asami et al. (1994) investigated some Japanese soils and found that the total Cd, Pb and Zn concentrations were in the range of 0.7 to 8.8, 31 to 237 and 118 to 738

mg kg<sup>-1</sup>, respectively, which indicated large anthropogenic contribution of metals in soils. Makino et al. (2006) reported that the number of polluted paddy fields in Japan had expanded to 66 sites, with a total area of some 62.6 km<sup>2</sup>, as of 1996. Total Cd concentration in some top soils of Japan ranged from 0.03 to 19.7 mg kg<sup>-1</sup> (Geochemmap, 2004) which indicates that soils are highly contaminated with Cd. Since half of the Cd intake in Japanese people comes from rice (Toyoda et al., 1998), as a main food, it is urgently needed to understand the mobility of this element in soils to reduce Cd content in rice. Thus, it has become a priority to develop cost effective and environmentally sound technologies for the remediation of Cd contaminated paddy soils. A variety of *in-situ* (in-site) and *ex-situ* remedial methods have been used/proposed for the

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restoration of soils contaminated with heavy metals, which warrant investigation of the chemical forms of heavy metals in soils. Total metal concentration in soils is not enough to assess environmental impact of metal contaminants (Jeng and Singh, 1993; Kim and McBride, 2006).

The chemical forms of a trace element determine its behavior in the environment and its remobilization capacity (Ma and Rao, 1997). The use of extract solutions with a gradual increase from least aggressive to most aggressive provides additional information about trace element fractions that may be released from soil phase associations and become available for plant uptake when environmental factors change in the soil. Many of the methods used in the later years are based on the procedure developed by Tessier et al. (1979) to determine the amounts of metals associated with several phases in soils and sediments (Chlopecka et al., 1996; Kaasalainen and Yli-Halla, 2003). Heavy metals are associated with various soil components in different ways and these associations indicate their mobility and availability in soils (Ahumada et al., 1999; Singh, 1996). The chemical forms of heavy metals depend on their origin and physico-chemical properties of soils. The main factors, which affect metal mobility are pH, organic matter content, cation exchange capacity, texture and redox conditions (Kashem and Singh, 2004; Rieuwerts et al., 2006). A large number of sequential extraction procedures have been used to extract trace elements in soils, sediments, sewage sludge and dissolved solids in waters (Kennedy et al., 1997). The methods vary depending on the number of fractions extracted, nature of individual metals, the order of extraction and kind of reagents used. Reagent selectivity and the extent of trace element distribution have been examined and some studies showed poor selectivity (Kheboian and Bauer, 1987) or extensive redistribution (Rendell et al., 1980; Li and Shuman, 1996; Bunzl et al., 1999), while others showed good selectivity and limited redistribution (Kim and Fergusson, 1991). In spite of the limitations in reagent specificity and difficulties of overlap between phases, sequential extraction methods are now widely used to study changes in both soil and sediment pollutant phase associations, because these procedures provide information for both short-term biological uptake and longer-term bioavailability of trace elements (predicting release of elements from non-labile forms into labile forms).

The sequential extraction procedure used here is based on operationally defined mobile (F1 to F3) and immobile (F4 to F6) fractions, employed previously by Kashem and Singh (2001). Information on solid phase speciation of metals in soils and their distribution in contaminated and non-contaminated soils is essential (Davison et al., 2007; Amezcua-Allieri and Rodríguez-Vázquez, 2008). Therefore, this study was undertaken to investigate the chemical fractionation and mobility of Cd, Pb and Zn in selected contaminated and

non-contaminated surface soils of Japan, which may help with the remediation process of heavy metals in contaminated soils.

## MATERIALS AND METHODS

### Soil sampling

Four contaminated (Miyagi-1 and 2, Akita and Gumma) and four non-contaminated (Takizawa, Rokuhara, Hachirogata and Isawa) composite soil samples (0 to 15 cm) were collected from different locations of Japan. The Miyagi-1 and 2, and Akita soils were contaminated by surface water passing through mines after different types of industrial operations. The sources of Gumma soil contamination was the Annaka Zn mining industry, located at the Gumma Prefecture of Kanto district. Other seven soils were from different Prefectures of Thohoku district (Table 1). Rice and vegetables are the common agricultural crops. A part of each sample was air-dried, ground and passed through a 2 mm stainless steel screen before use. Some important characteristics of the soils used in this study are presented in Table 1. All analytical work of this study was performed at the Laboratory of Plant Physiology and Nutrition, Iwate University, Japan.

### Soil properties and heavy metals fractionation

Soil pH was measured in a 1:2 soil/water suspension. Soil organic carbon (OC) was determined by wet oxidation method of Walkley and Black (1934). Cation exchange capacity (CEC) was determined by extraction with 1 M  $\text{NH}_4\text{OAc}$  (pH 7.0) (Soil Surv. Lab. Staff, 1992). The hydrometer method (Bouyoucos, 1962) was used for the particle size distribution. Total metal concentrations (Cd, Pb and Zn) in the soils were determined by flame atomic absorption spectrophotometry (FAAS) after digestion with nitric-perchloric acid mixture (3:1). The chemical fractionation technique of Kashem and Singh (2001) modified from Tessier et al. (1979) was used. The procedure separates metals into six different fractions nominally described as: water-soluble (F1), exchangeable (F2), carbonate-bound (F3), iron and manganese oxides-bound (F4), organic matter-bound, and residual (F6). The experimental details of this procedure are presented in Table 2. Two-gram soil samples were used throughout the experiment. Duplicates analysis was performed for each sample. Heavy metals concentrations in extracts were determined by HITACHI 170-30 flame atomic absorption spectrophotometry (FAAS). The detection limit of Cd, Pb and Zn was  $<0.03 \text{ mg L}^{-1}$ .

### Calculations and statistical analysis

The results on metal content and distribution are expressed on oven dry weight basis. The relative index was calculated as a mobility factor (MF) (Salbu et al., 1998; Kabala and Singh, 2001) as:  $\text{MF} = (F1 + F2 + F3)/(F1 + F2 + F3 + F4 + F5 + F6) \times 100$ . Excel Inc (2003) was used to evaluate the results graphically as percentage of the total metal content and Pearson correlations coefficient by Minitab Inc (1992).

## RESULTS AND DISCUSSION

### Soil characteristics

Soil pH was between 4.7 in the Miyagi-2 soil to 6.5 in the Isawa soil. Relatively lower pH values in some of these

**Table 1.** Characteristics of the soils used.

Soils	Prefecture (location)	District	Textural class	pH	OC (%)	CEC (cmol kg <sup>-1</sup> )
Miyagi-1 (C)	Miyagi	Thohoku	Sandy loam	5.6	3.3	25.5
Miyagi-2 (C)	Miyagi	Thohoku	Sandy clay loam	4.7	2.4	22.4
Akita (C)	Akita	Thohoku	Sandy loam	5.0	5.3	19.4
Gumma (C)	Gumma	Kanto	Loamy sand	4.8	2.9	9.3
Takizawa (Nc)	Iwate	Thohoku	Loamy sand	4.9	10.3	31.4
Rokuhara (Nc)	Iwate	Thohoku	Sandy loam	5.2	11.0	45.0
Hachirogata (Nc)	Akita	Thohoku	Sandy clay loam	5.8	4.1	37.1
Isawa (Nc)	Iwate	Thohoku	Sand	6.5	0.3	8.6

C- denotes contaminated soil; Nc- denotes non-contaminated soil; OC - denotes organic carbon; CEC - denotes cation exchange capacity.

**Table 2.** Sequential fractionation procedure for heavy metals in soil.

Step	Fraction	Solution	Reaction time (h) / temperature (°C)	Device	Centrifuge (rpm)/ filtrate (min)
1	Water-soluble (F1)	20 mL of deionized water	1/20	Rolling table	10,000/ 30
2	Exchangeable (F2)	20 mL 1 M NH <sub>4</sub> OAc, pH 7	2 h at 20°C	Rolling table	10,000 rpm, 30 min
3	Carbonate bound (F3)	20 mL 1 M NH <sub>4</sub> OAc, pH 5	2 h at 20°C	Rolling table	10,000 rpm, 30 min
4	Fe and Mn oxide bound (F4)	20 mL of 0.04 M. NH <sub>2</sub> OH.HCl in 25% (v/v). Ac, pH 3	6 h at 80°C	Water bath Occasional manual shaking	10,000 rpm, 30 min
5	Organic matter bound (F5)	(i) 15 mL 30% H <sub>2</sub> O <sub>2</sub> (adj. pH 2), (ii) 5 mL of 3.2 M NH <sub>4</sub> OAc in 20% (v/v) HNO <sub>3</sub>	(i) 5.5 h at 80°C (ii) 0.5 h at 20°C	(i) Occasional manual shaking (ii) Rolling table	(i) - (ii) 10,000 rpm, 30 min
6	Residual (F6)	7 M HNO <sub>3</sub>		Water bath Occasional manual shaking	Filtrate

soils may be assigned to acid effluent coming from near by industrial operations as well as high humus content (Table 1). Soil textural class varied from sand to sandy clay loam. The organic matter (OM) content and cation exchange capacity (CEC) varied in these soils. The Rokuhara soil had 11.0%, while Isawa soil had only 0.3% of OM. Cation exchange capacity varied from 9 to 45 cmol kg<sup>-1</sup> (Table 1). The total metal concentration in soils ranged from 0.69 to 12.5 for Cd, 19 to 359 for Pb and 90 to 704 mg kg<sup>-1</sup> for Zn. Generally, the concentrations of most metals were several folds (5 to 18) higher in the contaminated soils than the non-contaminated soils (Table 1 and 3). The highest level of Cd was observed in the Gumma, Pb in the Miyagi-1 and Zn in the Miyagi-2

soils, indicating that the sources of contamination vary for the different soils tested. The source of contamination at the Miyagi location was the contaminated flood waters coming from different industries that elevated metals concentrations in this soil, while for Gumma soil that was the lead and zinc mining industry.

## Fractionation and distribution of metals

### Cadmium

There was a large variation in the Cd concentrations extracted from individual fractions and among soils

**Table 3.** Concentrations of Cd, Pb and Zn in individual fractions of soil and the total of soil ( $\text{mg kg}^{-1}$ ).

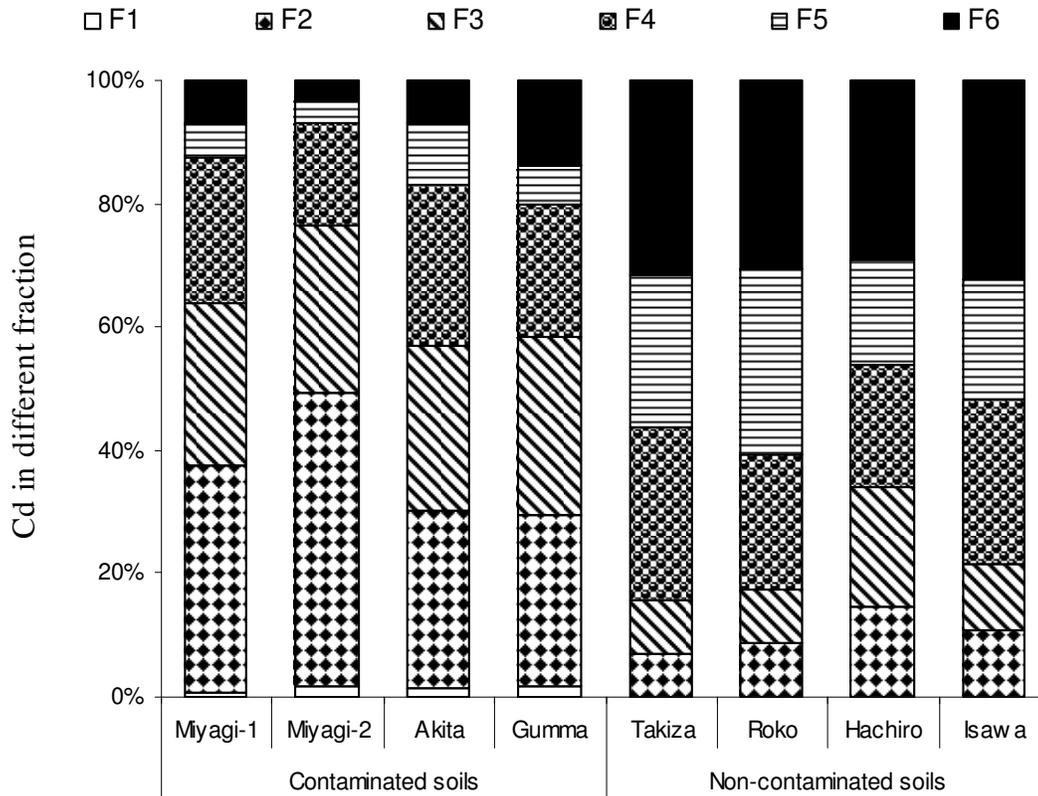
Soils	F1	F2	F3	F4	F5	F6	Sum <sup>K</sup>	TM <sup>L</sup>	Recovery (%)	MF <sup>M</sup> (%)
<b>Cd</b>										
Miyagi-1 (C)	0.03	2.12	1.50	1.36	0.31	0.40	5.72	5.4	105	64
Miyagi-2 (C)	0.14	3.81	2.19	1.31	0.29	0.28	8.02	7.2	111	77
Akita (C)	0.07	1.43	1.34	1.29	0.50	0.35	4.97	4.5	110	57
Gumma (C)	0.24	3.60	3.81	2.81	0.83	1.81	13.10	12.5	104	58
Takizawa (Nc)	ND	0.07	0.09	0.28	0.24	0.31	0.98	1.0	98	16
Rokuhara (Nc)	ND	0.07	0.07	0.17	0.24	0.24	0.79	0.9	88	17
Hachirogata (Nc)	ND	0.10	0.14	0.14	0.12	0.21	0.71	0.7	101	34
Isawa (Nc)	ND	0.07	0.07	0.17	0.12	0.20	0.64	0.7	91	22
<b>Pb</b>										
Miyagi-1 (C)	ND	7	41	161	28	99	335	359	93	14
Miyagi-2 (C)	ND	3	22	88	17	74	204	238	86	12
Akita (C)	ND	3	11	58	17	96	185	194	95	8
Gumma (C)	ND	14	33	77	18	39	180	193	93	26
Takizawa (Nc)	ND	1	<1	4	3	10	18	19	95	10
Rokuhara (Nc)	ND	1	<1	6	4	18	31	38	82	6
Hachirogata (Nc)	ND	<1	<1	6	2	9	19	22	86	9
Isawa (Nc)	ND	<1	<1	8	3	15	27	34	79	5
<b>Zn</b>										
Miyagi-1 (C)	1	41	98	144	30	168	481	508	95	29
Miyagi-2 (C)	10	60	110	132	30	276	619	704	88	29
Akita (C)	1	7	21	177	46	201	454	470	97	6
Gumma (C)	18	51	106	129	44	255	603	671	90	29
Takizawa (Nc)	ND	<1	1	21	7	55	85	90	94	2
Rokuhara (Nc)	ND	1	7	25	15	64	113	138	82	8
Hachirogata (Nc)	ND	1	3	17	5	66	92	106	87	4
Isawa (Nc)	ND	<1	2	29	9	71	112	123	91	2

C- Contaminated soil; Nc- Non-contaminated soil; ND-not detected. <sup>K</sup> Sum of F1 to F6; <sup>L</sup>Total metal concentration (nitric –perchloric extractable); <sup>M</sup> Mobility factor = ((F1 to F3/F1 to F6)×100).

(Table 3). In the contaminated soils, the highest amount of Cd (28 to 48%) was in the exchangeable (F2) form and lowest in the residual (F6) form (3 to 14%), while in non-contaminated soils, the distribution was just opposite of the contaminated soils implying that the residual fraction was the highest (29 to 32%) and the exchangeable was the lowest (7 to 15%) (Figure 1). Water soluble Cd was below detection limit in the non-contaminated soils. Water (F1) plus  $\text{NH}_4\text{OAc}$  extractable (F2 + F3) metals are defined as mobile fractions. Mobile fractions of Cd (57 to 77%) in contaminated soils was higher than those (17 to 34%) in non-contaminated soils. These results agree with those of Kashem and Singh (2001) and Chlopecka et al. (1996). They reported that heavy metals added to the soils from anthropogenic sources are relatively more mobile than those derived from parent material. From our results, it may be explained that Cd in the contaminated soils may be easily taken up by the crop and it also may constitute potential health and phytotoxicity problems (Udom et al., 2004). The mean proportion of Cd in the

mobile fractions (F1 + F2 + F3), oxide (F4), organic (F5) and residual (F6) fractions were 64, 22, 6 and 8%, respectively in the contaminated soils. The corresponding values in the non-contaminated soils were 22, 24, 23, and 31%. These results indicate that contamination increased the values of Cd in mobile fractions with a concomitant decrease in the organic and residual fractions, while opposite was the case with the non-contaminated soils. The proportion of Cd in the F4 bound fractions appeared to be similar in both types of soils (Figure 1). However, the value of Cd association in the oxide bound fraction was fairly low as compared to that reported by other investigators working on contaminated soils (Kashem and Singh, 2001; Chlopecka et al., 1996), where they mentioned that the anthropogenic inputs of Cd appeared to be in an oxide form, which was not the case in the Japanese soils.

Small amount of Cd in the organic matter fraction in contaminated soils is consistent with the low ion adsorption constant of Cd to the organic matter (Baron et



**Figure 1.** Distribution of Cd in various fractions of soils based on total concentration. F1-water soluble, F2-exchangeable, F3-carbonate bound, F4-oxide bound, F5- organic bound, F6-residual.

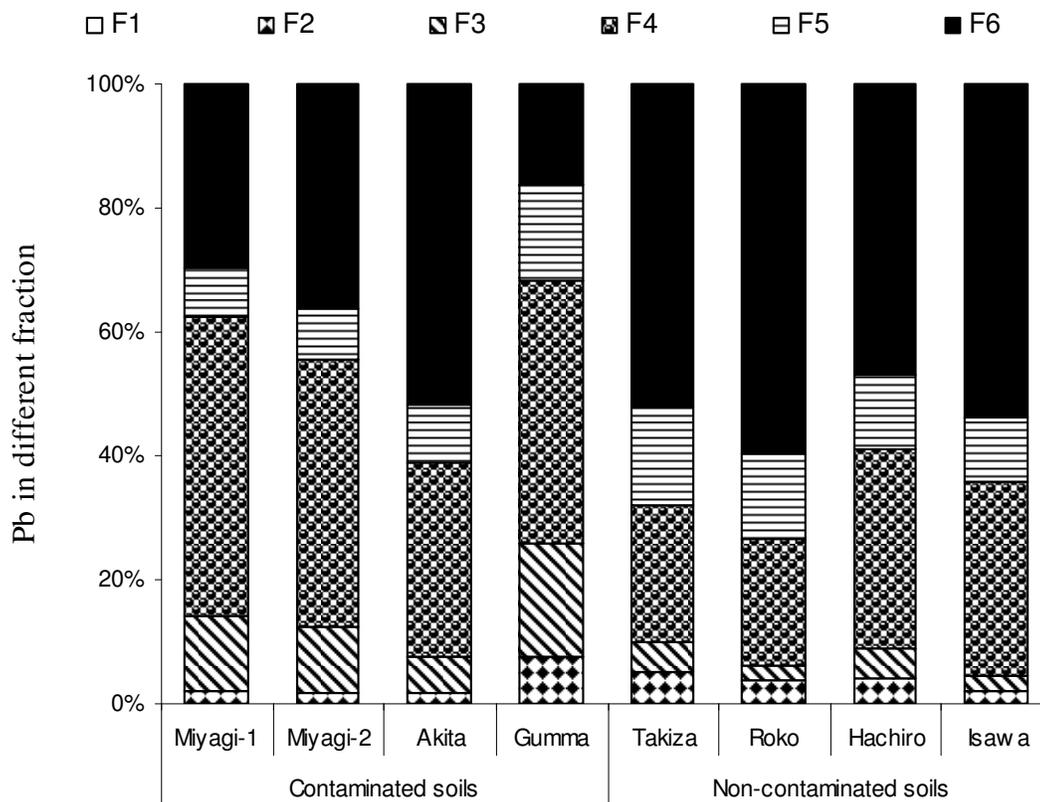
al., 1990) and with evidence that Cd does not appear to form strong complex with organic carbon (Sposito et al., 1982; Keefer et al., 1984). Relatively, a large amount of Cd in the mobile fraction in the contaminated soils may constitute potential health and phytotoxicity problems because plants do not provide food-chain protection for Cd (McLaughlin et al., 1996).

### Lead

Lead was not detected in the water soluble extract. The sum of Pb in the mobile form (F2 + F3) was 8 to 26% in the contaminated soils, and in the non-contaminated soils, it was 5 to 10% indicating higher mobility of Pb in the contaminated soils (Figure 2). In the contaminated soils, Pb was dominantly associated with the oxide fraction (31 to 48%), while in non-contaminated soils the residual fraction was dominant (52 to 60%) (Figure 2). The dominance of an oxide bound Pb in contaminated soils had been reported by several investigators (Kabala and Singh, 2001; Ahumada et al., 1999; Karczewska, 1996). A study conducted by Chlopeck et al. (1996) on contaminated soils observed that the mean percentage of Pb in the oxide bound fraction was estimated to be 41% while organically bound Pb was accounted for only 10%

of total Pb. Despite the fact that Pb has higher affinity to form complex with soil organic matter (Kabata-Pendias and Pendias, 1992), in our study soil, organic matter did not appear to play significant role. Only two soil samples (Takizawa and Rokuhara) (Table 1) with relatively high organic carbon (6%) have proportionately more Pb concentration with the organic fraction (15%) compared with those of lower ( $\leq 3\%$ ) organic carbon ( $<10\%$  of total Pb) (Figure 2). This result indicates that the proportion of Pb concentration with organic matter did not seem to increase with the extent of Pb contamination. Similar results were also reported by other investigators (Chlopecka et al., 1996; Kabala and Singh, 2001). Lead distribution in different fractions of soil between Akita and Gumma contaminated soils was found quite different though total Pb concentration was similar in both soils (Table 1). For example, mobile Pb in Gumma soil was 26% while in Akita soil; it was only 8% of total Pb. This might be due to the variation in soil properties, Akita soil has higher content of clay (2.5 times), OC and pH than those in Gumma soil, resulting in high adsorption capacity for Pb and hence resulted less mobile Pb in the Akita soil (Tables 1 and 3).

On the average, the amount of total Pb concentration associated with different fractions in the contaminated soils was in the order: oxide (41%)> residual (35%)>



**Figure 2.** Distribution of Pb in various fractions of soils based on total concentration. F1-water soluble, F2-exchangeable, F3-carbonate bound, F4-oxide bound, F5- organic bound, F6-residual.

mobile (15%) > organic (9%) while in the non-contaminated soils was: residual (54%) > oxide (26%) > organic (13%) > mobile (7%).

### Zinc

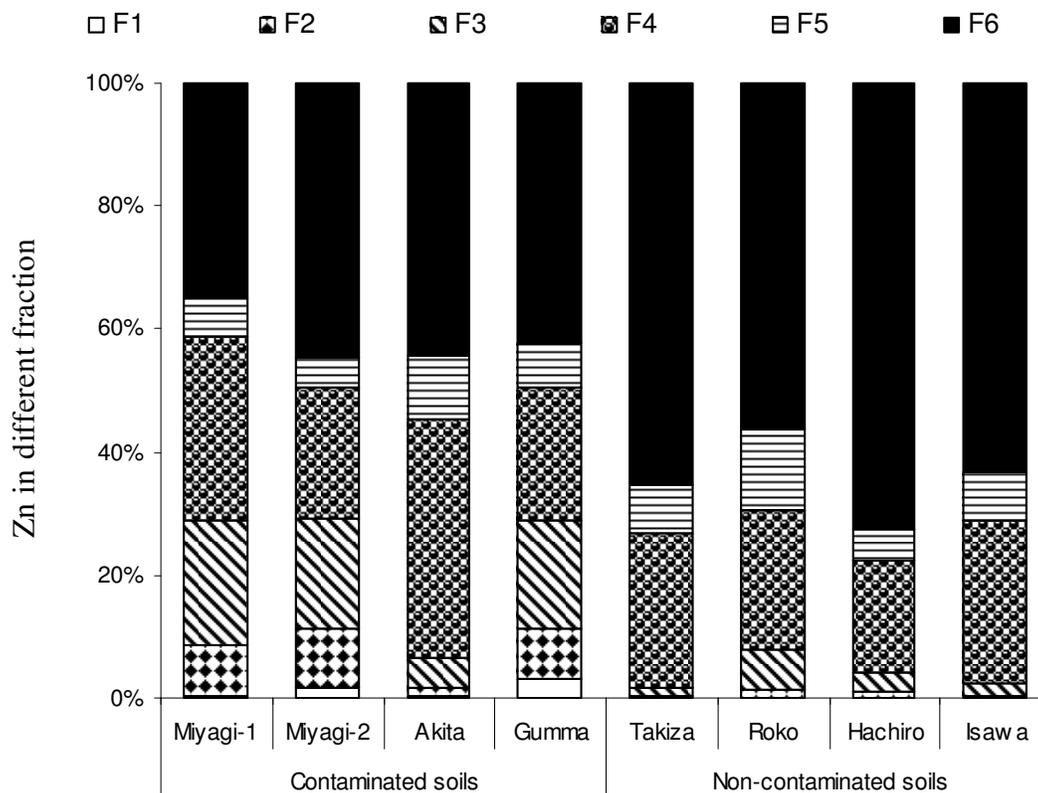
Zinc was present in all fractions in the contaminated soils like those for Cd. Among the fractions, Zn was mostly concentrated in the residual and in the oxide fractions. In the contaminated soils, the amount of Zn present in the residual and in the oxide fractions varied from 35 to 45% and 21 to 39%, respectively, while in the non-contaminated soils the corresponding values were 56 to 72% and 18 to 27% of total Zn. Zinc bound with organic matter was fairly small (<9%) and the difference among the contaminated and non-contaminated soils were negligible. However, the biggest difference was obtained with Zn present in the mobile (F1 + F2 + F3) fractions between contaminated (6 to 29%) and non-contaminated soils (<2 to 8%) in this study (Figure 3). Akita had lower proportion of mobile Zn (6%), which was similar to non-contaminated soils. On average, the association of Zn in the contaminated soils was 42, 28 and 23% in the residual, oxide and in the mobile fractions, respectively; however, the corresponding values in non-contaminated

soils were 64, 23 and 4% of total Zn. Among the non-residual fractions, the oxides (F4) fraction contained the greatest proportion of Zn in all soils (up to 39% in the Akita soil). This may be partially due to the high stability constants of Zn oxides (Ma and Rao, 1997). Several other investigators have also reported Zn to be associated with Fe-Mn oxides (Kuo et al., 1983; Ma and Rao, 1997; Ramos et al., 1994).

A relatively higher percentage of Zn in the mobile fraction of the contaminated soils as compared to the non-contaminated soils indicates that the anthropogenically added metals remained in the mobile fraction. It seems that when total metal load increase to the soil through human activities, it always increase the mobile fraction and hence increase their potential mobility and bioavailability. Xian (1989) found that mobile fraction of Zn (exchangeable plus carbonate) were strongly correlated with Zn uptake by cabbage plants (*Brassica oleracea*).

### Mobility of Cd, Pb and Zn in soil

The mobility factor (MF) varied in individual soils and among metals. In general, the MF values were highest for Cd (43%), and lowest for Pb (<11%), while intermediate



**Figure 3.** Distribution of Zn in various fractions of soils based on total concentration. F1-water soluble, F2-exchangeable, F3-carbonate bound, F4-oxide bound, F5- organic bound, F6-residual.

for Zn (14%). In the contaminated soils, the MF values were 37, 15 and 23% for Cd, Pb and Zn, respectively; the corresponding values in the non-contaminated soils were 10, 8 and 4%. Among the contaminated soils, the MF values were quite low for Pb of 8% and Zn of 6% in the Akita soil whereas in Gumma soil, MF for Pb and Zn increased up to 29% (Table 3). Many investigators studied the adsorption of heavy metals on soil components such as clay minerals, metal oxides and humic substances. The selectivity with which the cation-exchange sites of different clay minerals adsorb heavy metals cations was in the order  $Cd < Zn < Pb$  (Abd-Elfattah and Wada, 1981). The selectivity in adsorption of Cd, Zn and Pb on the hydrated oxides and oxides of iron and aluminum was almost same as that on clay minerals (McKenzie, 1980; Benjamin and Leckie, 1981). These results supported well the order of heavy metals in the mobile fractions found in our study. It is also confirmed that Cd will be more mobile than the other two metals. Therefore, Cd is likely to be easily taken up by vegetation grown in contaminated soils.

#### Relationships between total and mobility factor (MF) of metals with soil properties

The relationship between soil parameters, and the results

of sequential extraction was investigated (Table 4). Soil pH was inversely correlated with total and MF of all three metals, however, significant ( $p \leq 0.05$ ) results were obtained only with total Cd and Zn, and with MF-Pb. Soil pH was generally found to be an important inverse predictor of metal extractability (Rieuwertts et al., 2006), adsorption and movement in soils (Matos et al., 2001; Udom et al., 2004). Cation exchange capacity (CEC) also showed similar relationships like those of pH with total metals, but CEC resulted in stronger negative relationship with MF-Cd and Zn than soil pH did (Table 4). It can be inferred from the results that CEC is related to heavy metals mobility in soils. Organic carbon also plays significant negative relationship with MF-Cd in this study. Udom et al. (2004) and Robertson et al. (1982) reported that the CEC and organic matter (OM) contents can be used as good predictors of heavy metals mobility in soils. As the amount of OM increases, there is a tendency for more Cd and Zn to be absorbed on the soil complex and hence reduce their mobility and phytotoxicity levels in soils.

#### Conclusions

Different geochemical forms of metals are operationally defined by an extraction sequence that follows the order

**Table 4.** Correlation relationship between total concentration and MF (mobility factor) of Cd, Pd and Zn with soil properties.

Fraction/Factor	pH	Organic carbon	CEC
Total Cd	-0.55*	-0.39	-0.70**
Total Pb	-0.32 ns	-0.41 ns	-0.46 ns
Total Zn	-0.55*	-0.45 ns	-0.64*
MF Cd	-0.40 ns	-0.56*	-0.51*
MF Pb	-0.50*	-0.24 ns	-0.54*
MF Zn	-0.43 ns	-0.40 ns	-0.44 ns

\*, \*\* significant at  $p \leq 0.05$ ,  $p \leq 0.01$  probability levels, respectively; ns – non significant.

of decreasing solubility and hence bioavailability. A significant amount of Cd was associated in the mobile fraction while Pb and Zn in the immobile fractions indicating Cd were potentially more bioavailable than other metals. Soil contamination increased the proportion of heavy metals in the mobile fraction by a concomitant decrease in the residual fraction. Therefore, distribution and relative mobility of metals in this study indicates that metals added through industrial activities are more easily mobile and potentially phytoavailable than metals from geological origin.

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