



## Assessment of Cadmium and Zinc Contamination in the Soils Around Pha Te Village, Mae Sot District, Tak Province, Thailand

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### Abstract

In this study sequential extraction was used to fractionate cadmium (Cd) and zinc (Zn) from soils into six operationally defined groups; water soluble, buffer-exchangeable, carbonate, FeMn oxide, organic, and residual. Soil samples from agricultural areas surrounding Pha Te village, Mae Sot District, Tak Province, Thailand, were classified into four categories; forest soil, upland soil, upper-paddy soil and lower-paddy soil. Total soil Cd and Zn concentrations ranged from 0.63 to 30.4 mg kg<sup>-1</sup> and 14.4 to 594 mg kg<sup>-1</sup>, respectively. Cd and Zn concentrations were higher in the upper- and lower-paddy soil (5.93 to 30.4 mg kg<sup>-1</sup> for Cd and 286 to 594 mg kg<sup>-1</sup> for Zn). These soils are considered as polluted. Cd in the polluted soil was dominantly associated with the buffer-exchangeable and carbonate-bound (40 to 70 % of total Cd), while in non-polluted soils; the residual fraction was dominant (50 to 80 % of the total Cd). The major proportion of Zn (37 to 46 % of total Zn) in the non-polluted soil and the upper-paddy soil occurred in the residual fraction. On the other hand, the major proportion of total Zn in the lower-paddy soil was associated with FeMn oxides (36 % of total Zn). The results show that mobility and potential bioavailability of Cd and Zn (61 and 25 %) in polluted soil were higher than in non-polluted soils (15 and 19 % in Cd and Zn, respectively). Metal distribution in different chemical fractions in these soils depended on the respective total metal concentrations.

**Keywords:** Cadmium; Zinc; Soil; Fractions; Mae Sot

## Introduction

Cadmium (Cd) is a widespread pollutant and one of the most toxic heavy metals in the environment due to its high mobility and toxicity at low concentration. Cadmium accumulation in soils and cereal crops can enter the human food supply and is a widespread problem around the world. As a consequence of increasing levels of industrial and agricultural activities, soil accumulation of Cd is a major and growing environmental and food safety problem. Excessive Cd loads in humans may lead to impairment of kidney function and other chronic health effects [1].

Heavy metals in soils exist in various solid-phase forms, which can be operationally categorized into the following fractions: easily soluble (water soluble), exchangeable, carbonate bound, oxide bound (Fe and Mn oxides), organic bound, and silicate bound (residual). Heavy metal exists in soils in a number of physicochemical forms, each with different levels of bioavailability [2]. Thus, the forms of a heavy metal in soil provide useful information on the mechanism of metal stabilization [3]. To characterize the behavior of metals in soil, total soil concentration is not enough to assess the potential environmental impact of metal contaminants. Therefore, in order to measure heavy metal behavior in soil and especially to determine how readily metals are taken up by plant roots, it is necessary to evaluate the chemical speciation as well as the total content, as the former determines the metal's mobility and bioavailability. The use of extract solutions with a gradual increase from the least aggressive to the most aggressive ones provides additional information about how easily the element is released from soil particles and is made available to plants. Sequential extraction methods for soil and sediments have been developed predominantly to determine the amounts and proportions of metal elements present in different forms [4, 5].

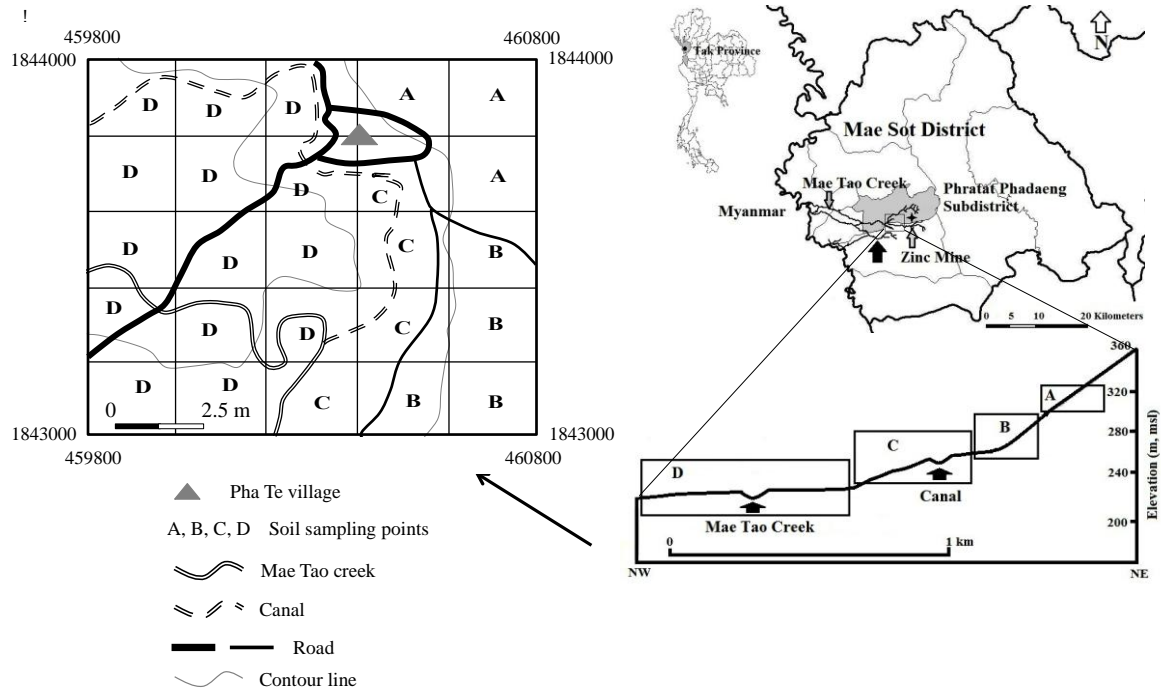
In 2002, the International Water Management Institute reported Cd contamination in soils downstream of the Mae Tao creek in the Mae Sot District, Tak Province in Thailand [6–9]. The report concluded that Cd levels in home-consumed rice would likely lead to Cd toxicity for the exposed population. Based on this report, we studied the characterization of Cd and zinc (Zn) in selected Cd-contaminated surface soils taken from different locations and land use types in the Mae Sot District, Tak Province, Thailand. The objectives of this study are therefore (1) to determine the distribution and chemical forms of Cd and Zn using a sequential extraction procedure for soils in the contaminated area; (2) investigate the relationship between forms of Cd and Zn, and certain soil properties; and (3) assess the potential mobility of Cd and Zn in soils.

## Material and methods

### 1) Soil sampling

The study area was previously described by Sriprachote [10]. Soils analyzed in this study were obtained from agricultural areas around Pha Te village (latitude  $93^{\circ} 37' 59.7''$ , longitude  $16^{\circ} 40' 34.4''$ ), which differed in both elevation and land use (Figure 1). They were classified into four categories; forest soil (A); upland or hill slope soil (B); lower-paddy soil (D); and upper-paddy soil (C), covering an area of about  $1 \text{ km}^2$ . The upper-paddy fields receive irrigation water through a small canal from the Mae Tao creek, and the outflow drains into the lower-elevation paddy fields. In the sampled area, the lower-paddy fields also receive irrigation water directly from the Mae Tao creek. Reference soil samples were collected from paddy fields located in the Hua Fai village 15 km north of the Pha Te village and located close to Mae Sot reservoir. At each sampling point, soil samples were collected from the surface soil (0–20 cm) using a soil tube 2.5 cm in diameter. Each soil sample comprised a composite sample of 10 sub-

samples taken from an area of 200 m × 200 m. Soil samples were air-dried, gently ground and passed through a 2-mm sieve homogenized and stored for subsequent analysis.



**Figure 1** Location of the study area; the Pha Te village. The black block indicates the areas where soil samples were collected. The categories of soil sampling sites include: forest (A), upland (B), upper-paddy (C) and lower-paddy (D).

**2) Soil analyses**

Particle size distribution was determined by the pipette method for silt and clay, and by dry-sieving for sand [11]. Soil pH was measured in a 1:5 (w/v) suspension of soil and distilled water [12]. Cation exchange capacity (CEC) was determined after saturation with a 1 M ammonium acetate (NH<sub>4</sub>OAc) solution according to the method of Rhoades [13]. Soil organic matter content was determined by using the Walkley and Black wet dichromate oxidation method [14]. Bioavailable Cd and Zn were extracted by 0.005 M diethylenetriamene-pentaacetic acid (DTPA) in a 1:2 (w/v) suspension of soil and extractant [15]. Total Cd and Zn were determined by digesting the soil in a mixture of HNO<sub>3</sub>, HClO<sub>4</sub> (60%) and H<sub>2</sub>SO<sub>4</sub> (5:2:1 by volume, 1 g of soil in 20 mL of the mixture) heated to 200°C for 2 hr [16]. The digestion was adjusted to 50 mL with distilled

water. The solution was filtered through No. 5C filter paper before analysis.

**3) Sequential extraction of soil Cd and Zn**

Particulate-bound Cd species of the soil samples were determined following the method of Salbu [17], which is a modified version of Tessier [4]. It is designed to separate heavy metals into six fractions: water-soluble (F1); buffer-exchangeable (F2); carbonate-bound (F3); iron and manganese (FeMn) oxide-bound (F4); organic-bound (F5); and residual (F6). The extractants are summarized in Table 1.

Batches of 2 g soil were each weighed into a 50 mL centrifuge tube. Following each extraction, the mixture was centrifuged for 30 min at 10000 x g, and the supernatant filtered through filter paper No. 42. All solid materials (with exception of F6) were washed with 10 ml of

distilled water before proceeding to the next extraction steps. The washes were collected with supernatant from the previous fraction. Cd and Zn in all extracts were analyzed using an atomic

absorption spectrophotometer (Shimadzu AA-6300) equipped with a graphite atomizer (Detection limit of  $0.0015 \text{ mg L}^{-1}$ ).

**Table 1** Extractants used for sequential extraction

Species	Reagent per 2 g soil	Shaking time and temperature
Water-soluble	20 mL distilled water	2 hr at 25 °C
Buffer-exchangeable	20 mL of 1 M $\text{NH}_4\text{OAc}$ pH 7.0	2 hr at 25 °C
Carbonate-bound	20 mL of 1 M $\text{NH}_4\text{OAc}$ pH 5.0	2 hr at 25 °C
FeMn oxide-bound	20 mL of 0.04 M $\text{OHNH}_2\text{HCl}$ in 25% HOAc	intermittently stirred 6 hr at 96 °C
Organic-bound	3 mL of 0.02 M $\text{HNO}_3$ + 5 mL of 30% $\text{H}_2\text{O}_2$ ; then add 20 mL of 0.8 M $\text{NH}_4\text{OAc}$ containing 0.0075 M $\text{HNO}_3$	intermittently stirred 2 hr at 80 °C, then shaken 1 hr
Residual	$\text{HNO}_3\text{-HClO}_4\text{-H}_2\text{SO}_4$	

## Results and discussion

### 1) Soil properties

The properties of the soil samples from the five sites are shown in Table 2. Forest soil, upland soil and upper-paddy soil were high in sand fraction (52 to 69 %) and low in silt fraction (9 to 20 %); therefore the soil texture was classified as sandy clay loam. Lower-paddy soil was classified as clay loam soil, with equal proportions of sand, silt and clay fractions (30 to 35 %). Soil pH was neutral pH (6.57 to 7.16) and the soils contained relatively high levels of organic matter (3.17 to 3.79 %) in upland soils, lower-paddy soils and upper-paddy soils. However, the forest soil sample showed a slightly acidic pH (5.39) and had only moderate organic matter content (1.53 %) [18]. The cation exchange capacity (CEC) ranged from 9.27 to 15.53  $\text{cmol kg}^{-1}$  soil. The reference soil was classified as loamy soil, with a high silt fraction (47 %). The soil was slightly acidic (pH 5.40) with a high organic matter content of 3.09 %. The cation exchange capacity was 17.9  $\text{cmol kg}^{-1}$  soil.

### 2) Total Cd and Zn in soil

Total Cd and Zn concentrations are summarized in Table 2. The average Cd concentration levels in the forest, upland and the reference soils were 0.77, 1.38 and 0.63  $\text{mg kg}^{-1}$ , respectively. On the other hand, higher levels of Cd were detected in the lower-paddy soil (30.4  $\text{mg kg}^{-1}$ ) and the upper-paddy soil (5.93  $\text{mg kg}^{-1}$ ). The maximum permissible total soil Cd concentration for sludge-amended soil is 3.0  $\text{mg kg}^{-1}$  [19]; therefore, only the paddy soils are categorized as polluted. Total Zn concentrations also varied; the forest, upland and reference soils had low Zn (6.57 to 40.3  $\text{mg kg}^{-1}$ ), which is within the normal range for total Zn in soil, and the Zn concentration may reflect the influence of parent materials. Soil total Zn in Thailand ranges from 5 to 158  $\text{mg kg}^{-1}$  with a mean value of 45  $\text{mg kg}^{-1}$  [20]. However, soil Zn levels in the lower-paddy and the upper-paddy soils were measured at 594 and 286  $\text{mg kg}^{-1}$ , respectively, with the highest levels of Zn (1,480  $\text{mg kg}^{-1}$ ) detected in the lower-paddy soil. These findings indicate that these soils are contaminated with Zn of an anthropogenic source.

### 3) DTPA-extractable Cd and Zn in soil

DTPA-extractable Cd ranged from 0.07 to 0.98 mg kg<sup>-1</sup> and 0.57 to 32.5 mg kg<sup>-1</sup> in the non-polluted and polluted soils, respectively (Table 2). DTPA-extractable Zn ranged from 0.38 to 10 mg kg<sup>-1</sup> in the non-polluted soil, and 22.8 to 346 mg kg<sup>-1</sup> in the polluted soil. On the other hand, DTPA-extractable Cd and Zn in the reference soil could not be detected and ranged from 1.46 to 2.93 mg kg<sup>-1</sup>, respectively. The highest concentrations of the DTPA-extractable Cd and Zn were detected in the lower-paddy soil (Cd 12.4 mg kg<sup>-1</sup> and Zn 112 mg kg<sup>-1</sup>). The results suggest that the soil solution must have higher lability of Cd and Zn in the lower-paddy soil.

A number of factors have been suggested to contribute to Cd and Zn accumulation in

soils with the highest organic matter content. Cd and Zn may be retained in this strongly adsorptive soil environment after reaching it as a result of cycling through vegetation, from application of Cd and Zn from contaminated fertilizers and manure, from wet deposition from the atmosphere, or from mining activities [21]. Table 3 gives simple correlation coefficients between the content of Cd and Zn, and soil properties. Cd and Zn had significant positive correlation with soil pH, organic matter and soil clay content. In contrast, there was no correlation between the content of Cd and Zn, and CEC. It would appear that for a wide range of soil pH, high levels of organic matter and clay content provided sufficient charge points for incremental Cd and Zn retention.

**Table 2** Physicochemical properties of the studied soils

Soil properties	Reference	Forest	Upland	Upper-paddy	Lower-paddy
Soil texture					
Sand (%)	29	69	58	52	35
Silt (%)	47	9	18	20	35
Clay (%)	24	22	24	28	30
pH (1:5)	5.40	5.39	6.57	7.16	7.08
OM (%)	3.09	1.53	3.17	3.79	3.40
CEC (cmol kg <sup>-1</sup> )	17.9	9.27	13.2	15.3	15.3
Total Cd (mg kg <sup>-1</sup> )	0.63±0.25 <sup>a</sup> (0.34–0.79) <sup>b</sup>	0.77±0.26 (0.58–1.06)	1.38±0.68 (0.50–1.92)	5.93±4.10 (2.56–11.7)	30.4±32.1 (2.28–78.9)
Total Zn (mg kg <sup>-1</sup> )	34.2±7.45 (25.9–40.3)	14.4±12.1 (6.57–28.3)	26.8±15.8 (8.99–36.2)	286±156 (165–512)	594±523 (122–1480)
DTPA-extractable Cd (mg kg <sup>-1</sup> )	nd <sup>c</sup> -	0.26±0.31 (0.07–0.62)	0.41±0.35 (0.12–0.98)	3.31±2.67 (0.57–6.77)	12.4±12.3 (0.61–32.5)
DTPA-extractable Zn (mg kg <sup>-1</sup> )	2.01±0.76 (1.46–2.93)	2.08±2.48 (0.38–4.93)	6.01±0.32 (2.66–10.6)	43.8±17.1 (24.9–60.9)	112±102 (22.8–346)
Sample Number	3	3	5	4	13

<sup>a</sup> Mean ± SD

<sup>b</sup> Values in the brackets denote the concentration range (minimum-maximum)

<sup>c</sup> Not be detected

**Table 3** Correlation coefficients between soil total and DTPA-extractable concentration of Cd and Zn with soil properties

Element	Clay	pH	OM	CEC
DTPA-Cd	.466*	.754**	.488**	.322
Total-Cd	.431*	.738**	.529**	.287
DTPA-Zn	.366	.733**	.411*	.161
Total-Zn	.531**	.774**	.585**	.309

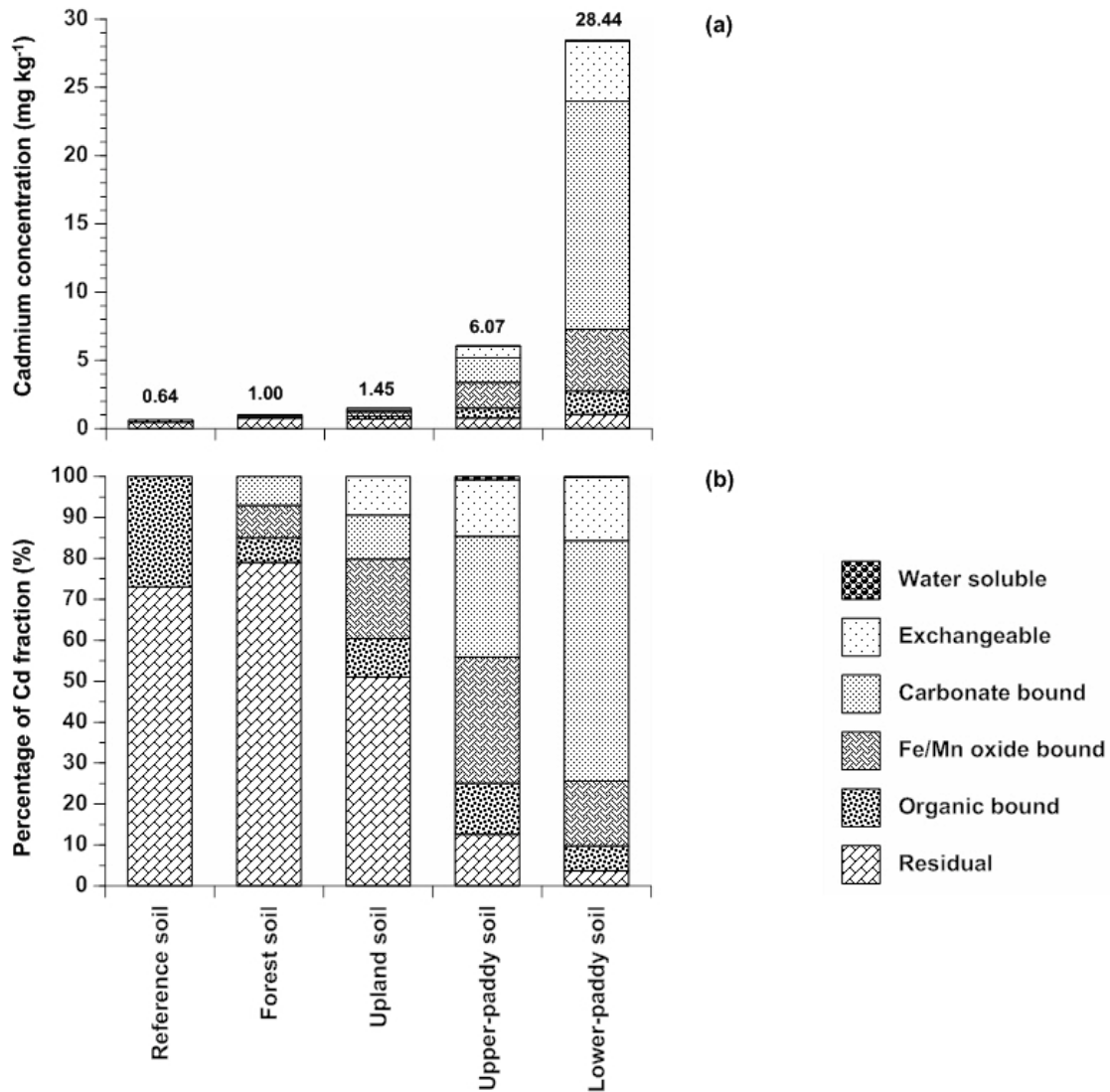
\*, \*\* Significant at  $p < 0.05$  and  $p < 0.01$  probability levels.

#### 4) Cd and Zn in fractionations based on solubility

The most significant difference in distribution of Cd at the sequential extraction was the significant contribution to the residual fraction (F6; Figure 2a, b). In the reference soil, Cd was distributed mainly in the residual fraction (73 % of total Cd) and the organic fraction (F5; 23 % of total Cd). Cd did not appear in other four fractions (F1 to F4). In the forest soil and the upland soil, the residual fraction dominated up to 80 % and 50 % of total Cd, respectively. The bulk of total soil Cd is found in the residual fraction, which is relatively unavailable to plants since it is held within the crystal structure of primary and secondary minerals. On the other hand, the contribution of the residual fraction (F6) was less than 5 % and 15 % of total Cd concentrations in the lower-paddy and upper-paddy soils, respectively. It has been suggested that metal concentrations in the residual fraction of soils or sediments may be indicative of background metal levels [4]. In all likelihood, heavy metals in the residual fraction are associated with silicate minerals.

The outstanding feature of the paddy soils is a particularly high Cd level which was extracted with 1 M  $\text{NH}_4\text{OAc}$  (F2 and F3). Depending on the pH (pH 7.0 or 5.0), this fraction may include Cd held by electrostatic adsorption (buffer-exchangeable) and that

is specifically absorbed [22]. Up to 70 % of total Cd in the lower-paddy soil and 40 % of the total Cd in the upper-paddy soil were detected in these two fractions. Chen [23] reported similar results identifying these fractions as the major chemical forms of Cd in polluted soils in Taiwan. The fraction extracted at pH 5.0 (F3) was higher than that extracted at pH 7.0 (F2) in all soil types, and was threefold higher in the lower-paddy soil than in non-polluted soil. Rajaie [24] have been reported that the Cd carbonate is the most dominant form of Cd in calcareous clay loam soil and sandy loam soil after incubation with Cd-contaminated compost. Khaokaew [25] also suggested that cadmium carbonate is the major species in the Mae Sot soils under flooding periods. Akkajit [26] reported that an exchangeable form of Cd (extracted with 0.1 M acetic acid) contributes the most to the soil total Cd in this area. The metals found in this fraction may become available to plants upon solubilization. Relative solubility of Cd in the buffer-exchangeable fraction is the highest and highly bioavailable; however, Cd associated with the carbonate fraction may be released in the soil solution when the soil pH is sufficiently low [27]. The water-soluble Cd fraction (F1) was detected in all soil samples, but at a very low contribution (< 1 %) even in polluted soils.



**Figure 2** Distribution of Cd in various fractions of soils (a) and its relative distribution (b).

Upper-paddy soil contained significant amounts of hydroxylamine-extracted Cd (F4) at levels up to 30 % of the total Cd, while it was relatively low in the forest soils (8 % of total Cd). The percentages of this fraction were equal to those in the lower-paddy soil and upland soil (16 to 19 % of total Cd). Iron and manganese oxides possess specific adsorption sites for divalent cations, which is one of the reasons for the remarkable ability of these oxides to adsorb Cd ions [22]. This fraction could be considered relatively stable, but this could be affected by changes in redox condition [28]. The relatively high percentage of the organically-complexed Cd (F5) was detected in the upper-

paddy soil (12 % of total Cd). However, Cd in this fraction was less than 10 % of total Cd both in the lower-paddy soil and non-polluted soil. The relatively low percentage of Cd in the organic fraction of polluted soils was also reported by Ma [29] and Chlopecka [30]. Organic matter is considered to play an important role in reducing plant uptake of Cd from soils due to its high CEC and influence on soil pH [31]. The minor role for the organic fraction in the speciation of Cd noted in the present study is consistent with the low adsorption constant of Cd to organic matter and with evidence that Cd does not appear to form strong organic complexes [30].

In case of Zn, fractional distribution between soils was similar to Cd. Generally speaking, the residual Zn (F6) occupied the largest fraction (Figure 3a, b). The percentage of this fraction was similar (37 % to 46 % of total Zn) in the upper-paddy soil and non-polluted soil, and contributed 29 % of total Zn in the lower-paddy soil. This is similar to observations reported by Ramos [32], Hseu [33], Margui [34], and Chirwa [35]. Higher Zn concentrations in this stable fraction indicate its importance as the storage fractions of Zn in soil. The result suggests that a relatively high percentage of residual Zn fractions in these soils are of lithogeneous origin and could not be mobilized.

The Zn extracted with hydroxylamine (F4, 16 to 36 % of the total Zn) followed the residual Zn. The FeMn oxide-bound Zn was considerably high, up to 36 % of the total Zn in the lower-paddy soils. In agreement with this result, other investigators also report the dominance of Zn bound to Fe and Mn oxides [29, 35–38]. The highest amount of organic-bound Zn (F5) was found in the non-polluted soil (12 to 14 % of total Zn). On the other hand, in the polluted soil less than 10% of the total Zn was found in this fraction. However, differences among the non-polluted and polluted soils were negligible. Zn is adsorbed more strongly in alkaline than in acidic soils, which is partly attributed to decreased competition from protons for adsorption sites. However, solubilization of organic matter in soils with high pH may also reduce Zn adsorption due to the formation of Zn-organic complexes.

### 5) Mobility of cadmium and zinc in soil

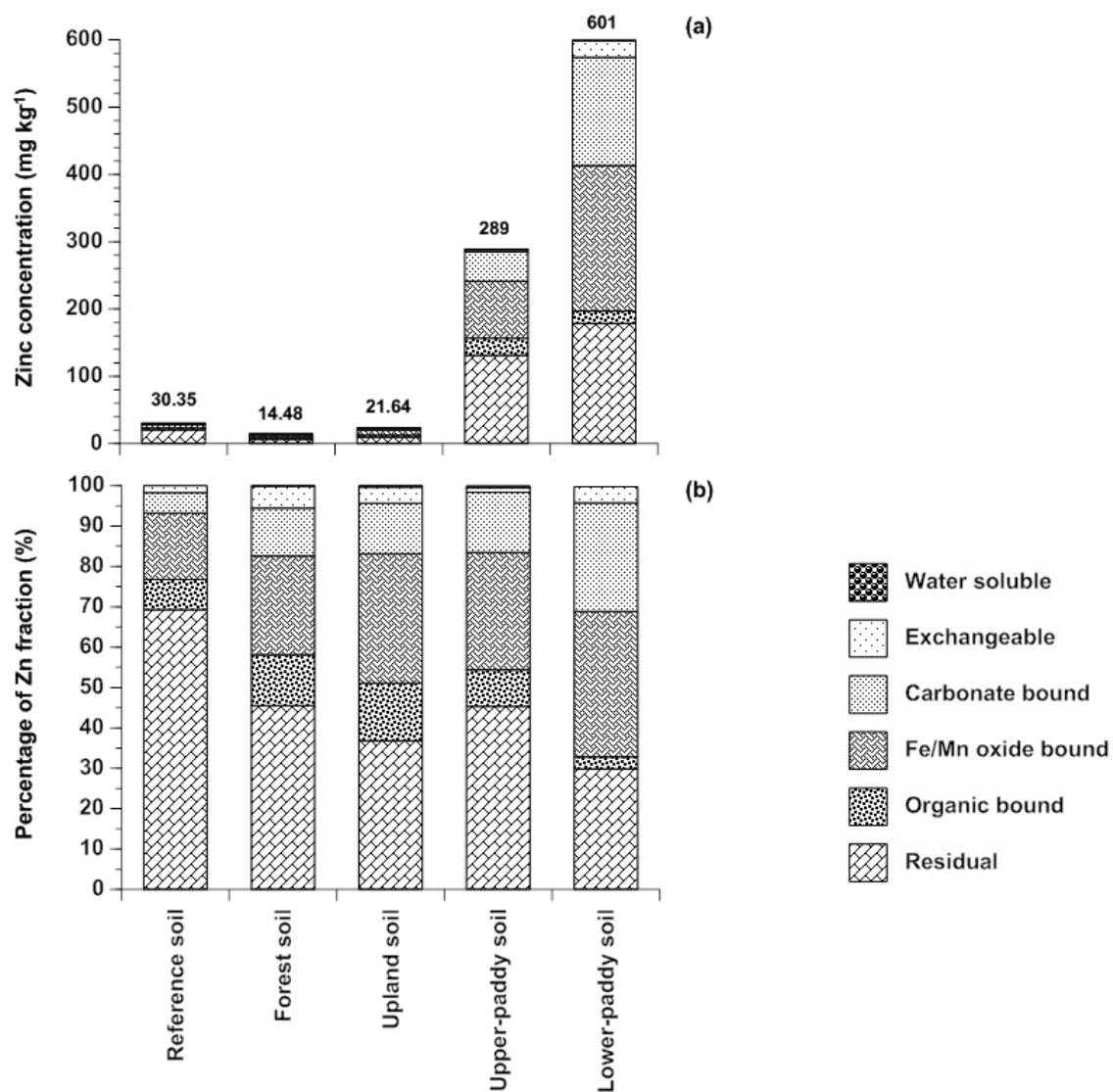
The mobility of metals in soils may be assessed on the basis of absolute and relative content of fractions weakly bound to soil components. The relative index was calculated as a mobility factor (MF) [17] as:  $MF = (F1+F2+F3) / (F1+F2+F3+F4+F5+F6) \times 100$ .

Since some metal forms (extracted in F3) are relatively less mobile (more strongly bound to soil components than those extracted in F1 and F2). The MF varied in individual soils and among metals. In general, the MF values were high for Cd (42 %) and low for Zn (22 %). In the polluted soil, the MF values were 61 and 25 % for Cd and Zn, respectively, the corresponding in the non-polluted soil were 15 and 19 %. These results confirmed the important finding that Cd will be more mobile and more easily taken up by vegetation grown in polluted soils than Zn.

The results of a single extraction DTPA showed significantly higher amounts of labile Cd and Zn than those released with water and  $NH_4OAc$  pH 7.0 (Table 4), but the amounts were considerably lower than that extracted with  $NH_4OAc$  pH 5.0. The amount of metals extracted with  $NH_4OAc$  (at different pH) has been reported to correlate with plant uptake and are used as indicators of potential bioavailability [27]. Change in pH, organic matter content, and redox status of the contaminated soils may alter bioavailability of weakly bound heavy metals.

The relationship between soil parameters, and the results of sequential extraction was investigated (Table 5). Soil pH was significantly correlated with all fractions of Cd and Zn. Soil pH was generally found to be an important predictor of metal extractability, retention, adsorption and movement in soils. Organic matter also plays a significant role related to Cd and Zn fractions, excepted water soluble and exchangeable fractions. However, CEC showed no significant correlated with Cd and Zn fractions. Udom et al [39] reported that organic matter contents and CEC could be used as good predictors of heavy metals mobility in soils. As the amount of organic matter increases, there is a tendency for more Cd and Zn to be adsorbed on the soil complex, reducing their mobility and phytotoxicity in soils.





**Figure 3** The distribution of Zn in various fractions of soils (a) and its relative distribution (b).

**Table 4** DTPA-extractable, water soluble, 1 M NH<sub>4</sub>OAc pH 5.0 and 7.0 extractable fractions of Cd and Zn (mean values) in studied soils

Element	Fractions extracted with:			
	DTPA	Water soluble	1 M NH <sub>4</sub> OAc pH 7.0	1 M NH <sub>4</sub> OAc pH 5.0
	----- mg kg <sup>-1</sup> -----			
Cd	6.34	0.059	2.18	8.05
Zn	60.11	0.94	12.01	82.13

**Table 5** Correlation coefficients between soil Cd and Zn fractions, and the properties of studied soils

Fraction	Clay	pH	OM	CEC
<b>Cadmium</b>				
Water soluble	0.596**	0.644**	0.363	0.355
Exchangeable	0.237	0.690**	0.327	0.130
Carbonate bound	0.424*	0.739**	0.502**	0.278
FeMn oxide bound	0.411*	0.769**	0.522**	0.247
Organic bound	0.549**	0.574**	0.639**	0.417*
Residual	0.358	0.380*	0.434*	0.182
<b>Zinc</b>				
Water soluble	0.464*	0.663**	0.279	0.158
Exchangeable	0.343	0.630**	0.314	0.191
Carbonate bound	0.432*	0.727**	0.527**	0.250
FeMn oxide bound	0.504**	0.767**	0.563**	0.275
Organic bound	0.470*	0.662**	0.533**	0.268
Residual	0.672**	0.772**	0.666**	0.420*

\*, \*\* Significant at  $p < 0.05$  and  $p < 0.01$  probability levels.

A relatively high percentage of Cd bound to the carbonate fraction in the lower-paddy soil may be due to precipitation of suspended materials from the Mae Tao creek in the paddy fields. A preliminary survey (results not shown) demonstrated that the sediments from the Mae Tao creek had a high pH (8.08). Moolthongnoi [40] revealed that the surface water of the Mae Tao creek, which passed through a zinc mining area, had high pH (6.94 to 8.62) and high concentration of  $\text{CaCO}_3$  (174 to 194  $\text{mg L}^{-1}$ ). The presence of heavy metals in the carbonate fraction might indicate a pH suitable for metal precipitation. Shiowatana [37] concluded that soil pH significantly determined the adsorption and sorption of metals and that its reduction increased the concentration of metal ions in the soil solution. Correlation analysis showed that  $\text{CO}_3$ -Cd increased with soil pH and organic matter (Table 5). Calcium carbonate tends to adsorb Cd form complexes such as  $\text{CaCdCO}_3$ , a double salt, under favorably high pH values [36].

A relatively higher percentage of Cd and Zn in the mobile fractions of the polluted soils indicate that anthropogenically added metals remained in the weak fraction and are more mobile than those derived from the parent material [30, 38]. It has been suggested that the mobility and the bioavailability of the metals in soils decreases in the order of the sequential extraction [29]. The operationally defined extraction sequence follows the order of decreasing solubility of the geochemical forms of the metals, hence metals in the buffer-exchangeable fraction and carbonate fraction are more available for plant uptake. By these criteria, Cd is considerably more mobile and biologically available in the lower-paddy soil.

Cd and Zn, closely linked to carbonates, are sensitive to pH changes and they can be mobilized when the pH becomes lower. Metals associated with oxides and organic fractions are not dangerous for the environment because the fractions are less extractable. But when the environment turns into an oxidized state,

they can be mobilized. The mechanism of metal retention in the soil is coprecipitation due to the pH of the soil solution. The residual fraction can be mobilized as a result of weathering, which means that this is only associated with long-term effects.

From the preliminary survey, the highest concentrations of Cd ( $73.1 \text{ mg kg}^{-1}$ ) and Zn ( $1,330 \text{ mg kg}^{-1}$ ) were detected in the creek sediment collected from the Mae Tao creek. Thailand's Department of Pollution Control [41] also reported that the Cd concentration of the sediments along the Mae Tao creek ranged from 44 to 63  $\text{mg kg}^{-1}$ , and the Cd concentration in the sediment samples collected from the zinc mining area ranges from 82 to 326  $\text{mg kg}^{-1}$ . Moonthongnoi [40] reported that Cd and Zn concentrations in surface water of the Mae Tao creek, which passed through the zinc mining area, was higher in the rainy season (0.028 to 0.032  $\text{mg L}^{-1}$  and 0.049 to 0.378  $\text{mg L}^{-1}$  for Cd and Zn, respectively) than in the dry season (Cd; 0.005 to 0.006  $\text{mg L}^{-1}$  and Zn; 0.049 to 0.091  $\text{mg L}^{-1}$ ). These results suggest that the paddy fields receive Cd via suspended sediments transported from the Mae Tao creek.

### Conclusion

Different geochemical forms of metal are operationally defined by an extraction sequence that follows the order of decreasing solubility and hence bioavailability. A significant amount of Cd was associated in the mobile fraction, while Zn dominated in immobile fractions, indicating that Cd is potentially more bioavailable than Zn. Soil pollution increased the proportion of heavy metals in the mobile fraction through a concomitant decrease in the residual fraction. Therefore, distribution and relative mobility of metals in this study indicates that metals added through anthropogenic sources are more easily mobile and potentially phytoavailable than metals from geological origin.

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