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Spatial Distribution and Mobility Factor of Heavy Metals in Agricultural Soil in the Vicinity of Abandoned Lead Ore Dressing Plant, Klity Village, Thailand

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Abstract

The concentration and mobility spatial distribution of heavy metals (lead, zinc, cadmium and chromium) including potential ecological risk have been evaluated for the polluted surface soil from mining activities in Upper Klity village, Thailand. Soil samples were collected from the residential and agricultural areas and the area of ore dressing plant. Heavy metals content presented higher in the ore dressing plant area than those found in residential and agricultural areas. Lead was the predominant polluted metal with two hot spots surrounding the ore dressing plant and open pit mine. Mobility distribution of these metals was followed closely with their concentration. Vertical soil profiles proved that mobility factors were only high at the top soil layer and became lower at deeper soil layers for all metals, and the quantities of lead, zinc, cadmium and chromium in both soil profiles can be ordered from large to small as: Reducible, Residual, Oxidizable, Acid extraction and Exchangeable fractions. These results indicated that the contamination was caused by anthropogenic mining activities. Potential Ecological Risk (PER) exhibited a low potential ecological risk with the averages of 3.79 and 81.3 in agricultural and ore dressing plant areas, respectively. However, most individual potential ecological risk values were small and classified as low for all heavy metals. This study recommends that heavy metals were unlikely to cause additional adverse health risk effects in residential and agricultural area. On the other hand, the risk of heavy metals pollution in the ore dressing plant area should be of primary concern.

Keywords: zinc; cadmium; chromium; exchangeable; acid extraction; ore dressing plant; vertical distribution

1. Introduction

Metalliferous mining and processing, including dumping of wastes, often produce severe heavy metal pollution (Baker *et al*., 1994). Open pits mining activities have caused serious environmental impacts on soil and water streams and generated millions of tons of ore tailings (Bhattacharya *et al*., 2005). The mobility and bioavailability of heavy elements in soil lead to the accumulation of these contaminants by vegetation and animals (Nannoni *et al*., 2011), especially in agricultural zone in the neighborhood of mining area as it could lead to a long-term health effect. The mobile fraction of heavy metals in soil can be determined in forms which are available for uptake by plants (Ettler *et al*., 2005). Exchangeable fraction is considered to be bioavailable, carbonate bound, Fe-Mn oxides bound and organic bound may be potentially bioavailable, while the residual fraction is mainly not available to either plants or animals (He *et al*., 2005). Sequential extraction procedure developed by Tessier *et al*. (1979) has been widely used to identify heavy metal forms and species presented in soil and is among the operationally defined methodologies widely applied for assessing heavy metal mobility in sediments, soils and waste materials (Guevara-Riba *et al*., 2004).

Bo Ngam lead mine is located in Klity village, Cha Lea Sub district, Thong Pha Phum district, Kanchanaburi, Thailand, which is approximately 450 km northwest of Bangkok. The mine was an important lead producer during 1960s to 1980s. The area of this open pits mine is 47.84 km^2. Lead in this area is in the form of cerussite ($PbCO_3$) (Rotkittikhun *et al*., 2006). Crude ore was transported to ore dressing plant located 6 km south from Bo Ngam mine. Production of lead came from an extract by flotation process to the 60% mineral ore and ore tailings. There was no smelting process in this area. Mining activities ended and ore dressing plant was closed in 1999 following the incident of leak of tailing from sediments pond into Klity canal, resulting in the termination of these mining activities by the injunction of Thailand Department of Mineral Resources and Pollution Control Department. Previous studies reported lead concentration of soil samples in Upper Klity with the average of as high as 598.7 mg/kg (Pusapukdepob *et al*., 2007), 142,400 mg/kg for the surface soil in ore dressing plant area (Rotkittikhun *et al*., 2006), whereby in the Upper Klity agricultural and residential soils, the contaminated level ranged from 226-2,785 mg/kg (PCD, 2004). Study by Rotkittikhun *et al*. (2006) indicated a high level of lead bioavailability when 26 plant species surrounding mining area were found to be contaminated with lead at the level of more than 1,000 mg/kg in their shoots where 3 species showed extremely high lead concentrations in their shoots (12,200-28,370 mg/kg) and roots (14,580-128,830 mg/kg).

Although the studies of lead contamination in Klity area have been reported by many researchers, none have investigated the various forms of lead species, the relation of bioavailable fractions and behavior of heavy metals in this area. In this paper, we report the comprehensive study on spatial distribution, source identification and potential ecological risks of heavy metals in agricultural and residential soils from Upper Klity village. The objectives of this research are: (i) to establish the spatial distribution of heavy metals concentration in agricultural surface soils around abandoned ore dressing plant; (ii) to determine the mobility speciation of metals using the sequential extraction procedure and (iii) to assess the potential of vertical metals mobility in soil profiles and bioavailability in soils. This will facilitate the usage management of the land to avoid the risk caused by the heavy metal contamination.

2. Materials and Methods

2.1. Study area

Klity ore dressing plant is located in Upper Klity village close to Klity canal. The stream flows southward past Upper Klity Village, Klity ore dressing plant area, Lower Klity Village and finally reaches Srinakarin reservoir. Annual temperature of Thong Pha Phum district, Kanchanaburi is 26.9 °C , with average maximum and average minimum temperature of 33.6 during the summer months and 21.5 °C during winter season, respectively. Annual rainfall is 1,485 mm (the highest in July to August and lowest in November to January).

This area is surrounded by residential and agricultural zones in the north, west and southwest and forest in the east and southeast. Agriculture has been exercised along the canal, and the major crops are maize, rice, cabbages and seasonal vegetables. Ore dressing plant area is located in the central part of the upper Klity village. This study covers an area of 22 km^2, defined by the WGS 1984 UTM zone 47N coordinates: longitude 488667-492639 (E) and latitude 1656024-1651595 (N). The land use can be separated to residential and agricultural (55%), forest (40%) and ore dressing plant area (5%).

2.2. Soil sampling

A total of 35 soil samples was collected from agricultural and residential area surrounding the abandoned ore dressing plant from Upper Klity village (Fig. 1). Sampling sites were selected considering the distribution of metals concentrations in cultivation area, spare lands in residential area and roadside surrounding the dressing plant. The analysis of total heavy metals was applied to surface soils which were collected at 0-20 cm depth randomly taken from the cultivation area. Vertical soil profiles were sampled close to the ore dressing plant area and cultivated area at four depth layers, surface soil 0-20 cm, subsurface soil 20-40 cm, and 40-60 cm, 60-80 cm for most annual crops and shrub root could reach in these layer. One kilogram of each soil sample was collected and stored in self-sealing plastic bags. Geographical coordinates of sampling locations were recorded at each sampling point with a global positioning system (GPS).

2.3. Laboratory analyses

2.3.1. Total heavy metals concentration

The samples were digested with mixed acid digestion and determined for heavy metals by Inductively Coupled Plasma Spectrometry (Agilent Technologies model 700 series). In laboratory, soil samples were air-dried at ambient temperature for 4 days. Dried soil was homogenized by grinding and mixing then sieved through 2 mm mesh. Sieved soil was dried in hot-air oven at 80 °C to constant weight and stored in closed plastic bags until analysis. In order to determine the total Pb, Zn, Cd, and Cr concentrations, soil samples were solubilized by mixed acid digestion. The digesting solution (HNO_3, 70% and HCl, 70%) was added to 1 g of powdered soil. The solutions were then heated using hot-plate at 90 °C for 1 hour. After cooling, the digested samples were brought to a 50 ml final volume with DI water and then filtered using 0.45 μm Whatman filter. The solutions were stored in polyethylene bottles.

2.3.2. Physio-chemical properties

The samples were sent to test for their physio-chemical properties at the Office of Science for Land Development, Land Development Department, Ministry of Agriculture and Cooperatives. In this study, two samples of surface soil were selected as representatives, i.e. agricultural area and ore dressing plant area.

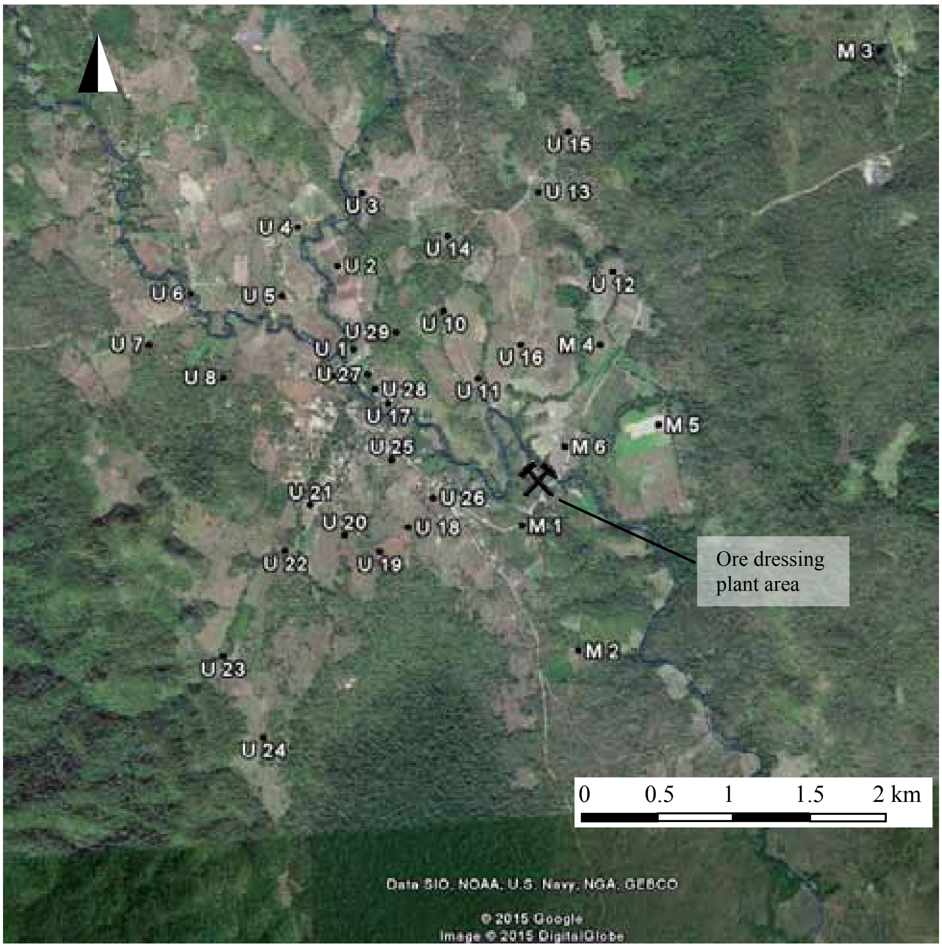


Figure 1. Location map and collected samples of the studied area

Cation Exchange Capacity (CEC) was measured by determining calcium, magnesium, sodium and potassium concentration in a mixture obtained by the reaction of soil with a 1 M NH_4OAc solution. Soil pH was measured in a 1:1 (w/w) soil: 1 M KCl. Organic Matter (OM) was determined according to procedure of Walkley-Black (Walkley and Black, 1934).

2.3.3. Sequential extraction

The sequential extraction procedure is employed to partition the metals into exchangeable (F_{exc}), acid extraction (F_{aci}), reducible (F_{red}), oxidizable (F_{oxi}) and residual (F_{res}) soil fractions. The sequential extraction followed the procedure reported by Tessier. Each chemical fraction was defined in order of extraction procedure as follows: (1) *Exchangeable*: 1 M $MgCl_2$ extraction at pH 7; (2) *Acid extraction*: 1 M NaOAc extraction at pH 5 adjusted by HOAc; (3) *Reducible*: 0.04M $NH_2OH{\cdot}HCl$ at pH 2 in 25% HOAc; (4) *Oxidable*: 30% H_2O_2/0.02M HNO_3, and (5) *Residual*: mixture of HNO_3 and HCl. This procedure required 1 g of powdered soil sample in 125 ml flask. After the reaction, the mixture was centrifuged in order to separate the supernatant and the residual, where the supernatant was used for analytical determination. Bulk concentration in soil samples as well as soil fractions were determined by inductive coupled plasma-optical emission spectrometry (ICP-OES) using the Agilent Technology 700 series.

In this study, the optimized sequential extraction procedure was applied to assess mobility factor (MF) of heavy metal in the samples. The mobility of heavy metals in soil may be assessed by comparing the exchangeable and acid extraction fractions with the total heavy metal concentration as follows (Kabala and Singh, 2001).

$$\mathrm{MF} = \frac{\mathrm{F_{exc}} + \mathrm{F_{aci}}}{\text{Total concentration}} \times 100 \qquad (1)$$

2.4. Spatial analysis

Geographic Information System (GIS) was used to analyze the spatial distribution pattern of heavy metals in the study area. The inverse distance weighted (IDW) technique was used to interpolate the different soil attributes to produce the geo-spatial distribution maps. IDW employs a specific number of nearest points that are then weighted according to their distance from the point being interpolated. In this study, the power of 2 and the number of neighboring samples of 12 were chosen to clearly show both spatial variation and spatial patterns of the heavy metals.

2.5. Potential ecological risk (PER)

The potential ecological risk index method is an approach to evaluate the heavy metal contamination from the perspective of sedimentology. It does not only consider heavy metal level in the soil, but does also associate ecological and environmental effects with toxicology (Haiyuan, 2010). Potential ecological risk index was originally proposed by Hakanson (1980) and widely used (Guo *et al.*, 2010; Suresh *et al.*, 2012; Li *et al.*, 2013). The equations for calculating the PER were proposed by Guo *et al.* (2010) as follows:

$$C_f^i = \frac{C^i}{C_n^i} \tag{2}$$

$$C_d = \sum_{i=1}^{n} C_f^i \tag{3}$$

$$E_r^i = T_r^i \times C_f^i \tag{4}$$

$$PER = \sum_{i=1}^{m} E_r^i \tag{5}$$

where C_f^i is individual pollution factor, C^i is practically observed value of heavy metals in soil samples, C_n^i is the reference value of the metal, which comes from background values of soil heavy metals in study area, E_r^i is potential ecological risk index of an individual metal, T_r^i is toxicity response coefficient of a certain kind of metal toxicity using standard heavy metal toxicity coefficient, which are defined for Cr=2, Cu and Pb=5, Zn=1, Cd=30 and Ni=6 (Guo *et al.*, 2010; Fu *et al.*, 2009), and PER is the summation of E_r^i.

2.6. Statistical analysis

Correlations between the total heavy metals concentration in soils were determined by means of Pearson product-moment correlation (*r*). The statistical significant of correlation was determined by *t* test.

3. Results and Discussion

3.1. Physio-chemical properties

Selected physico-chemical properties of surface soils, i.e. pH, CEC, extracable and OM are reported in Table 1. Two soil sample sites represented agricultural soil and ore dressing plant soil, respectively. Agricultural soil pH was 7.0, but this became rather acidic in the ore dressing plant soil (5.6). Soil texture was classified by USDA triangle as loam component with loam and clay loam in agricultural and ore dressing plant soils, respectively. Soil CEC and OM content were high, which were 12.83 cmol/kg, 3.63 % and 15.43 cmol/kg, 2.88 % in agricultural and ore dressing plant soils, respectively. CEC value increased with the percentage of clay fraction and organic matter. Calcium was the highest extractable ion in all soil samples.

3.2. Heavy metals in soil

3.2.1. Lead

The studied soil samples were grouped into two categories; agricultural and residential area (U), and area surrounding abandoned ore dressing plant (M). Total concentrations of lead in soils ranged widely from 22.9-4,264 mg/kg (Table 2). For agricultural and residential area, this was 22.9-215 mg/kg with the average of 90.6 mg/kg. This represents the background level in this area which is lower than the Thailand Standard of lead for residential and agricultural purposes (400 mg/kg). For the ore dressing plant abandoned area, this was 51.38-4,264 mg/kg with the average of 987 mg/kg. Around the ore dressing plant area which represented the contaminated area, the average value was 10 times higher than the level found in residential and agricultural area, and three samples (M1, M4 and M6) were found to have a greater lead level than Thailand standard. The highest concentration was measured in soil sample collected from the area close to the ore tailing pond (M1), which indicated that a certain extent of lead spreading from the ore dressing

Table 1. Physiochemical properties of studied soil

Sample Site	pH	CEC (Cmol/kg)	Extractable (mg/kg)				OM (%)	Particle size distribution (%)			Texture class
			P	K	Ca	Mg		Sand	Silt	Clay	
Agricultural soil	7.0	12.8	22	41	4383	102	3.63	29.8	49.8	20.4	Loam
Ore dressing plant soil	5.6	15.4	7	55	1468	250	2.88	41.2	28.6	28.6	Clay Loam

activity. Literature demonstrated that the highest lead concentration in the surface soil in the ore dressing plant area could be as high as 124,400 mg/kg (Rotkittikhun *et al.*, 2006), and 1,243-93,900 mg/kg in lead-zinc mine tailing area in Spain (Rodriguez *et al.*, 2009), or could be as low as 53.4-5,536 mg/kg in northern Kosovo (Nannoni *et al.*, 2011), and 65.0-130 mg/kg in the vicinity of copper smelter (Szerszen *et al.*, 1993; Kabala and Singh, 2001).

The mobility of lead in studied soils was assessed by a comparison of the weakly bound fractions with the total lead content. Mobility factor values (Table 2) ranged from 2.66-45.76% (average: 10.27%), with the highest found in the contaminated soil sample M1. The ore dressing plant area exhibited a higher lead mobility than that agricultural and residential area. Acid extraction fraction was mainly associated with weakly bound fractions with concentrations ranging from 2.37-1,669 mg/kg. Note that the average mobility factor in agricultural and residential area and ore dressing plant area were 7.76% and 22.4%, respectively.

3.2.2. Zinc

Total concentrations of zinc in agricultural and residential area and ore dressing plant area ranged from 19.7-172 mg/kg (average 46.7 mg/kg) and 22.6-131 mg/kg (average 54 mg/kg), respectively. Within the ore dressing plant area, the highest value was found in the M1 sample, which was the same point as that with the highest value of lead. The highest concentration was found in agricultural and residential area near roadside (U7) in the West of map. In most cases, statistics showed that areas with high lead contamination would also be contaminated with zinc.

The mobile fractions of zinc ranged from 0.15-19.2 % (4.96% on average) and the highest was found in M1 sample. The weakly bound fraction was mainly associated with the acid extraction fraction which ranged from 0.03-21.01 mg/kg and accounted for 3.04% of total concentration. The average mobility factor in the ore dressing plant area, and the agricultural and residential area were 6.9% and 4.5%, respectively.

3.2.3. Cadmium

Cadmium content in soils ranged from 0.33-1.48 mg/kg, with the highest below 1 mg/kg (Table 2), and the average concentration was 0.61 mg/kg, while standard of cadmium in Thailand residential and agricultural soil is not over 37 mg/kg. The results demonstrated that the average cadmium content in the agricultural and residential area was higher than that of in the ore dressing plant area. The mobile fractions of cadmium ranged from 5.36-37.4 % with the average of 15.5%. The weakly bound fraction was mainly associated with the exchangeable fraction, which accounted for 10.4% of the total concentration.

3.2.4. Chromium

Total chromium contents in agricultural and residential area, and ore dressing plant area ranged from 14.3-74.0 mg/kg (average 32.1 mg/kg) and 5.56-30.9 mg/kg (average 15.0 mg/kg), respectively. Mobility factors of chromium in soils were below 1% (average: 0.46%), with the highest of 0.97% in the vicinity of the ore dressing plant (M5).

There was a positive correlation between the total lead and zinc with statistical significant of $r = 0.44$, $p < 0.01$, but not between the total cadmium and chromium ($p > 0.01$). The total zinc concentration seemed to have a good correlation with cadmium ($r = 0.48$, $p < 0.01$). The most statistically significant correlation was between cadmium and chromium ($r = 0.67$, $p < 0.01$).

3.3. Spatial distribution of heavy metals

Spatial distribution patterns of total heavy metals concentration (lead, zinc, cadmium and chromium) and mobility factor were used by GIS software to produce contour maps and identify the potential sources of heavy metals in study area. The distribution of heavy metals was interpolated by IDW technique. These maps illustrated the distinct contaminated zones and mobility potential in the Upper Klity village.

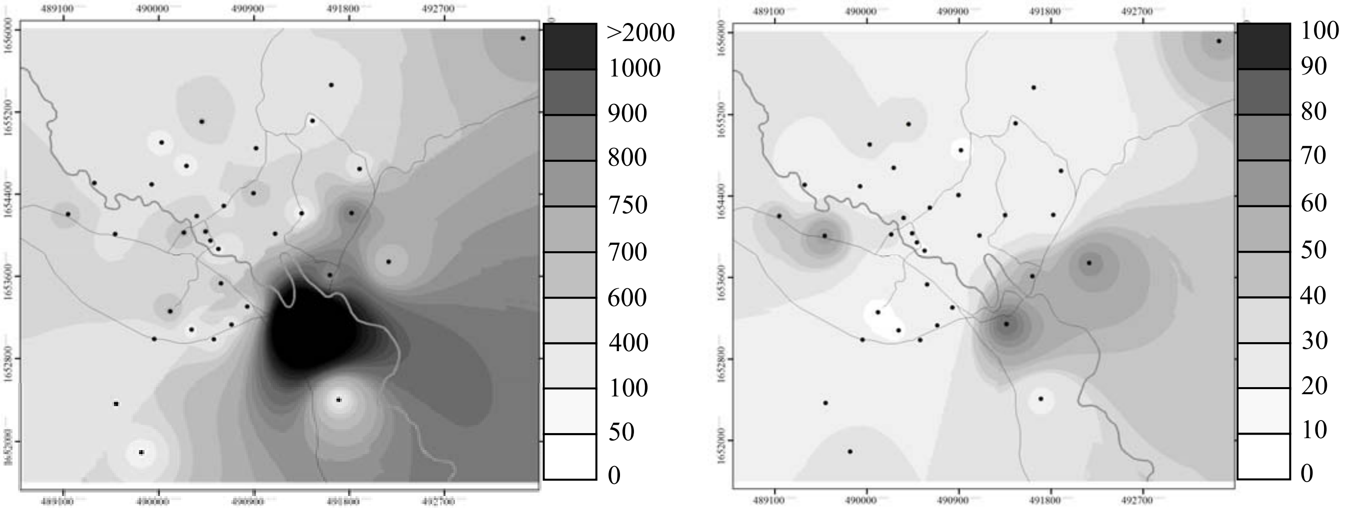
The spatial distribution of heavy metals in the Upper Klity agricultural and ore dressing plant areas are shown in Figs. 2 to 5. The results indicated that the total lead concentration in surface soils are predominant in the ore dressing plant and its vicinity with the total lead concentration of more than 4,200 mg/kg (Fig. 2(a)). In contrast, samples from the agricultural and residential areas had a lower level of contamination, i.e. in the range of 28.3 to 215 mg/kg. Based on Thailand standard of lead for agricultural and residential purposes, there is no sample collected from agricultural zone exceeded this standard. The two hot spots with high mobility factor were found in the vicinity of the ore dressing plant and near the open pit mine in the northeast of map with value of more than 40% and 20% of total lead, respectively (Fig. 2(b)). It was noted that there were no clear relationships between the distance from ore dressing plant and the lead contamination level which suggested that the contamination might also be induced by other mining activities such as transportation of the ore.

Table 2. Total concentrations, weakly bound fractions (mg/kg), and mobility factors (MF, %) of Pb, Zn, Cd and Cr from upper Klity village

Soil sample	Pb				Zn			
	F_{exc}	F_{aci}	Total Pb	MF	F_{exc}	F_{aci}	Total Zn	MF
Residential and agricultural area								
U1	1.15	10.4	105	11.0	2.23	11.1	90.2	14.7
U2	1.40	1.13	28.1	8.99	0.59	0.04	28.3	2.24
U3	9.78	8.76	153	12.1	1.52	0.08	32.8	4.86
U4	2.45	1.48	33.4	11.8	0.71	0.21	20.9	4.42
U5	1.06	1.43	58.0	4.28	1.11	0.34	46.9	3.10
U6	0.82	3.04	77.3	4.99	1.63	2.44	69.4	5.86
U7	16.1	10.8	169	15.9	1.69	0.18	172	1.08
U8	13.6	6.43	73.3	27.3	0.26	0.30	89.4	0.62
U9	13.5	15.5	215	13.5	0.94	0.22	39.1	2.98
U10	8.91	11.4	200	10.2	1.47	0.41	29.6	6.32
U11	3.84	5.50	117	7.95	1.53	0.11	24.6	6.71
U12	1.12	2.42	60.7	5.82	1.01	0.20	31.4	3.86
U13	0.53	1.44	45.2	4.35	0.23	0.19	33.6	1.25
U14	0.70	1.15	66.5	2.77	0.47	0.05	35.1	1.48
U15	1.95	2.91	82.9	5.87	1.46	0.61	78.6	2.64
U16	0.51	0.55	23.9	4.41	0.01	0.03	24.3	0.15
U17	0.52	0.49	28.6	3.53	2.80	1.24	47.6	8.49
U18	0.40	1.08	41.9	3.51	0.50	0.40	34.9	2.56
U19	1.80	1.96	38.7	9.71	1.48	0.16	38.2	4.29
U20	0.44	0.52	34.1	2.82	1.13	0.52	27.5	6.02
U21	0.23	5.38	211	2.66	0.51	0.82	27.6	4.82
U22	0.35	1.80	53.5	4.02	1.03	0.17	47.1	2.54
U23	0.73	2.68	85.4	4.00	1.19	0.90	36.6	5.72
U24	1.91	1.29	22.9	14.0	1.61	0.05	25.9	6.43
U25	1.61	11.9	184	7.39	0.47	0.74	51.7	2.34
U26	2.25	4.02	87.3	7.19	3.03	2.01	84.4	5.98
U27	2.06	10.1	164	7.39	1.40	0.58	27.8	7.12
U28	0.23	2.46	93.1	2.88	0.25	1.25	38.3	3.94
U29	0.45	3.16	74.4	4.85	1.19	0.67	19.7	9.48
Vicinity ore dressing plant area								
M1	283	1669	4264	45.8	4.03	21.0	131	19.2
M2	2.27	2.37	51.4	9.03	1.29	0.24	24.0	6.36
M3	1.54	70.5	348	20.7	0.54	0.92	52.1	2.81
M4	0.34	27.1	540	5.08	0.29	0.11	25.2	1.61
M5	33.7	33.9	204	33.1	0.72	1.21	22.6	8.53
M6	0.80	106	515	20.8	0.56	1.58	69.3	3.10

Table 2. Total concentration, weakly bound fractions (mg/kg), and mobility factors (MF, %) of Pb, Zn, Cd and Cr from upper Klity village (cont.)

Soil sample	Cd				Cr			
	F_{exc}	F_{aci}	Total Cd	MF	F_{exc}	F_{aci}	Total Cr	MF
Residential and agricultural area								
U1	0.05	0.03	0.46	18.5	0.03	0.07	34.1	0.28
U2	0.03	0.04	0.46	15.5	0.09	0.11	45.6	0.44
U3	0.06	0.02	0.49	15.9	0.05	0.06	26.2	0.45
U4	0.04	0.03	0.36	18.2	0.08	0.03	17.0	0.63
U5	0.06	0.01	0.49	14.2	0.06	0.04	29.9	0.31
U6	0.25	0.07	0.86	37.4	0.05	0.01	14.3	0.42
U7	0.06	0.02	1.14	7.02	0.09	0.12	51.7	0.40
U8	0.08	0.02	0.81	12.4	0.10	0.18	42.9	0.66
U9	0.05	0.04	0.52	16.9	0.07	0.03	26.8	0.40
U10	0.02	0.03	0.54	9.8	0.11	0.02	28.9	0.45
U11	0.04	0.01	0.33	17.9	0.06	0.02	17.7	0.50
U12	0.09	0.01	0.61	16.2	0.06	0.03	16.3	0.55
U13	0.05	0.02	0.47	14.9	0.07	0.02	25.7	0.37
U14	0.05	0.03	0.57	15.2	0.06	0.03	22.1	0.41
U15	0.08	0.02	0.64	14.8	0.05	0.02	15.7	0.43
U16	0.02	0.00	0.52	5.36	0.05	0.07	33.6	0.36
U17	0.12	0.03	0.63	24.8	0.07	0.11	27.8	0.64
U18	0.05	0.02	0.72	9.03	0.05	0.01	53.9	0.10
U19	0.06	0.03	0.78	11.5	0.07	0.04	33.9	0.33
U20	0.04	0.02	0.71	9.59	0.06	0.06	41.9	0.28
U21	0.02	0.03	0.56	10.5	0.05	0.15	31.4	0.65
U22	0.09	0.04	1.48	8.21	0.06	0.04	74.0	0.13
U23	0.08	0.04	0.64	19.6	0.07	0.05	34.4	0.36
U24	0.05	0.00	0.61	8.70	0.05	0.16	47.4	0.46
U25	0.06	0.03	0.66	13.9	0.04	0.03	24.4	0.30
U26	0.08	0.03	0.65	17.4	0.04	0.02	25.6	0.24
U27	0.07	0.02	0.47	18.6	0.12	0.03	22.9	0.63
U28	0.02	0.02	0.61	6.43	0.01	0.04	35.1	0.14
U29	0.08	0.03	0.45	25.0	0.05	0.04	29.4	0.33
Vicinity ore dressing plant area								
M1	0.11	0.03	0.62	23.4	0.04	0.07	15.4	0.71
M2	0.11	0.03	0.40	33.7	0.06	0.03	10.5	0.91
M3	0.05	0.03	0.73	11.8	0.08	0.06	30.9	0.45
M4	0.02	0.03	0.37	15.1	0.03	0.02	5.56	0.78
M5	0.01	0.03	0.36	11.3	0.06	0.06	12.0	0.97
M6	0.07	0.10	0.64	25.7	0.03	0.06	15.5	0.53



(a) Total Pb (mg/kg)

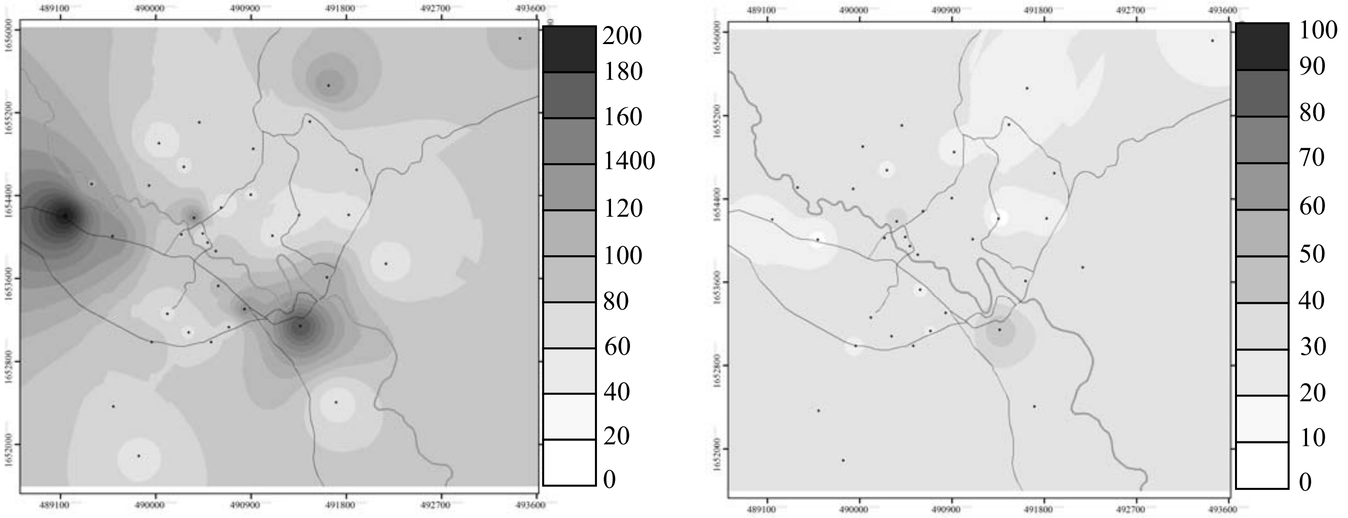
(b) Mobility factor Pb (%)

Figure 2. Spatial distribution of lead: (a) total concentration and (b) mobility factor

Fig. 3 indicates a lesser spatial variability of zinc in the surface soil when compared to lead. There are two hot spots, (i) near roadside and (ii) ore dressing plant (Fig. 3(a)) with concentration of 172 and 131 mg/kg, respectively. This distribution pattern followed closely with the pattern of lead where the low zinc zone was found in agricultural area. Lower mobility factors were exhibited in most of the area in this work (lower than 20%), where the highest mobility factor was found in the ore dressing plant area with the value of 19.18% (Fig. 3(b)).

For cadmium, the spatial distribution shown in Fig. 4 indicates a low concentration in the surface soil of Upper Klity village, with the high levels observed in the west and southwest of the map (Fig. 4(a)). The results reveal that 94.3% of samples contained total concentration lower than 1 mg/kg, and all samples were found to contain cadmium within the concentration range of 0.33 to 1.48 mg/kg, which are lower than Thailand agricultural and residential soil standard. Specifically, it was proven that the studied areas were only slightly contaminated with cadmium. However, the mobility distribution pattern was rather high with the value ranged from 5.36 to 37.4%, the high levels were unselectively found both in agricultural and ore dressing plant areas (Fig. 4(b)).

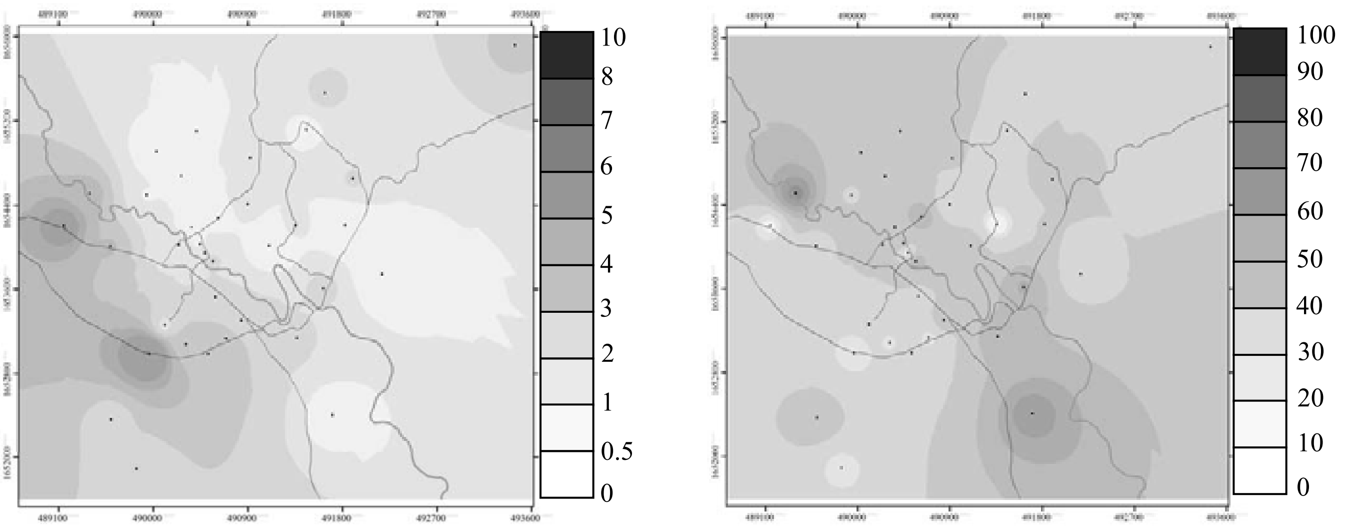
The spatial distribution of total chromium in the surface soils is shown in Fig. 5(a), which demonstrated that the distribution of chromium followed a similar pattern to that of cadmium. High contamination was found in the west and southwest sections with the value ranged from 5.36 to 74.0 mg/kg. All samples exhibited



(a) Total Zn (mg/kg)

(b) Mobility factor Zn (%)

Figure 3. Spatial distribution of zinc: (a) total concentration and (b) mobility factor



(a) Total Cd (mg/kg)

(b) Mobility factor Cd (%)

Figure 4. Spatial distribution of cadmium: (a) total concentration and (b) mobility factor

the mobility factor of lower than 1% (0.10 to 0.97%) where the hot spots were exhibited in the southeast section on the map which are the agricultural area near ore dressing plant zone (Fig. 5(b)).

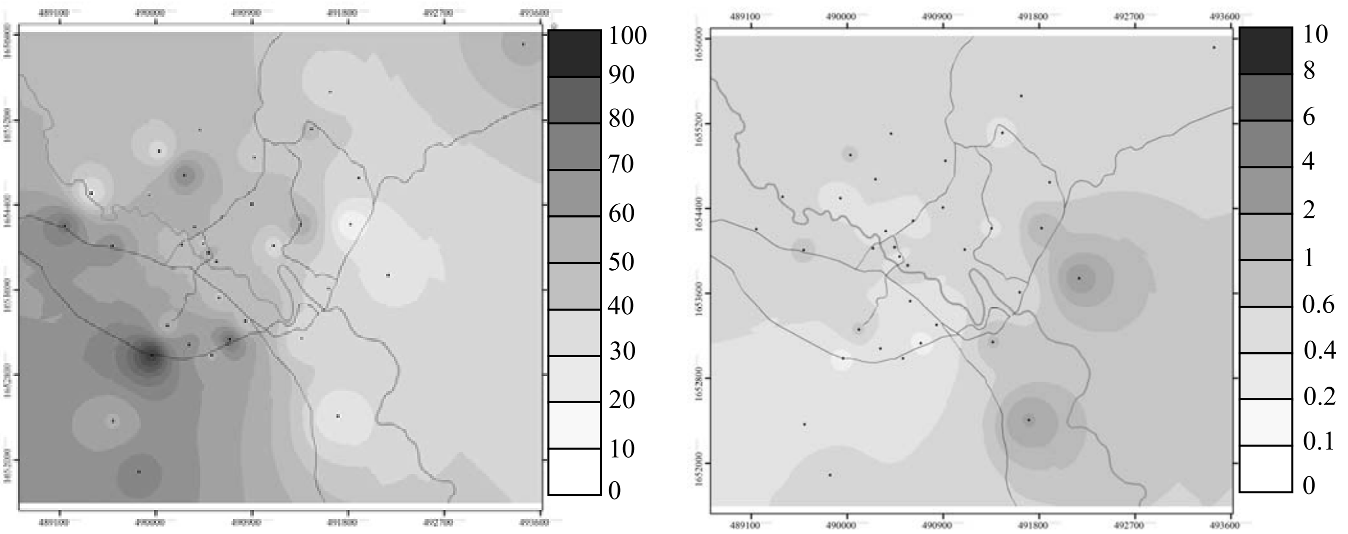
In this study, the spatial distribution of heavy metals is illustrated that the contaminations are restricted in ore dressing zone and the mobility distribution patterns are slightly proportion in agricultural zone. These findings indicated that the mining activities input the lead in ore dressing plant area remained in weakly bound forms, consequently increasing their mobility and bioavailability in this area.

3.4. Vertical distribution of heavy metals

A vertical distribution of the various heavy metal compounds in soil profiles is useful for the determination of the degree of contamination and potential transfer or mobility of heavy metals to soil. Agricultural and ore dressing plant soil samples were collected at 4 different depths. Fig. 6 exhibited the fraction percentage on the distribution of lead, zinc, cadmium and chromium into the soil samples and this is discussed below.

3.4.1. Lead

The total concentration of lead was the highest in the soil top layer and decreased towards deeper layer both in agricultural and ore dressing plant soils (Table 2). Lead in all layers of agricultural and ore dressing



(a) Total Cr (mg/kg)

(b) Mobility factor Cr (%)

Figure 5. Spatial distribution of chromium: (a) total concentration and (b) mobility factor

plant soils were mainly bound in the reducible fraction with 31.2 to 36.9% and 36.9 to 55.0%, respectively. The percentage of exchangeable fraction in ore dressing plant soil profiles was rather small (0.63 to 10.0%). The acid extraction fraction ranged from 25.4 to 27.8% in agricultural soil and 15.9 to 38.6% in ore dressing plant soils. This finding is similar to the report from lead smelters where only 6% of exchangeable fraction and 13% of acid extraction fraction were found in the contaminated soil (Chlopecka *et al*., 1996). According to study of surface layer soil (Szopka *et al*., 2013) higher organic matter was contained high Oxidizable fraction in agricultural soil. The surface enrichment may be due to the accumulation from the degradation by plants, which also indicates that the pollution is of recent years. This is because the pollutants are always absorbed into top soil first, and then sinks into deeper positions by chemical exchange (Nemati *et al*., 2011).

Fig. 6 demonstrates that there was only a slight difference in the vertical distribution of the various lead fractions particularly at the deeper soil layer. The mobility factor for the agricultural soil ranged from 28.7 to 31.8%, and remained unaltered with soil depth. On the other hand, vertical variation of lead fractions became more apparent at the ore dressing plant, i.e. the exchangeable and acid extraction fractions appeared to exist in a larger content in the surface layer (0-40 cm depth). This resulted in a high mobility factor in the top soil layer (46.7%) when compared to the lower layer (16.5%).

3.4.2. Zinc

In both soil samples, the main fractions were reducible fraction followed by residual and oxidizeable fractions (Table 3). The reducible fraction in ore dressing plant soil profiles slightly increased with depth, while this variation was not observed in agricultural soil profiles. The exchangeable fraction was only present at low level, i.e. 2.34 to 6.86 % and 3.79 to 6.49 % in agricultural and ore dressing soils, respectively.

The mobility factor of zinc in agricultural surface and subsurface soils was relatively low throughout the depth of the soil layer. On the other hand, the mobility factor of zinc in all ore dressing plant soil profiles were higher than agricultural soil, while in ore dressing plant soil the mobility factor decreased with depth (Fig. 6). Similar to lead, the vertical distribution in agricultural soil did not vary significantly with soil depth.

3.4.3. Cadmium

The cadmium content in soil was relatively low where the concentration varied in the range from 0.16 to 1.16 mg/kg (agricultural threshold = 37 mg/kg). Fig. 6 demonstrates that there was no linear trend for the vertical variation of cadmium fraction in the ore dressing plant soil. On the other hand, the mobility factor in agricultural soil profiles slightly decreased with depth, i.e. the percentage dropped from 29.4% at top soil to 23.3% at deeper layer. Cadmium was mainly associated with residual and reducible fractions (Table 3) whereas the exchangeable fraction was the major mobile component for both agricultural soil (11.0-18.3%) and ore dressing plant soil (6.9-17.5%).

3.4.4. Chromium

The exchangeable and acid extraction fractions were only slightly present in all soil profiles (< 1%). Reducible is the main fraction with the value varied from 11.7 to 45.5% in agricultural soil and 28.5 to 41.3 % in ore dressing plant soil (Fig. 6). This reducible fraction significantly decreased with soil depth, while the opposite was observed for the residual fraction. Due to its low exchangeable and acid extraction fractions, the mobility factor of chromium was only quite small (< 1 %) at all soil depths.

In shorts, based on the results found in this work, the quantities of lead, zinc, cadmium and chromium in both soil profiles can be ordered from large to small as: Reducible > Residual > Oxidizable > Acid extraction and Exchangeable fractions. The reducible fraction of lead in soil profiles was in a higher proportion than the other metals, this result according to study by Rodriguez *et al*. (2009) as had been reported large amount of metals mainly associated with the reducible form for pasture land and mine tailings areas. The mobility factor was only high at the top soil layer and became lower at deeper soil layers for all metals. This is because the extraction and degradation mechanisms of heavy metal are transformed in to forms that weakly bound by plant. Lead and cadmium indicated high mobility, whereas zinc and chromium exhibited low mobility. The mobility was derived from the acid extraction fraction for lead and zinc, while exchangeable was the mobile fraction for cadmium.

3.5. Potential ecological risk (PER)

The grading standard of heavy metal potential ecological risk index is listed in Table 4 (Guo *et al*., 2010). The potential ecological risk index is the summation of an individual metal risk E_r^i and the comprehensive PER index is shown in Tables 5 and 6. Most individual E_r^i values were small and classified as low grade. However, there was one exception at the vicinity of the ore dressing plant (M1) where E_r^i of lead was classified in a serious level with the highest of 235. It is noted that cadmium was classified in

Table 3. Sequential extraction of heavy metals in soil profiles (%wt)

Element	Location	Depth (cm)	Exchangeable	Acid extraction	Reducible	Oxidizable	Residual	MF	Total concentration (mg/kg)
Pb	Agricultural area	0 - 20	4.21	27.4	39.1	19.2	10.2	31.6	831
		20 - 40	2.74	26.4	36.2	20.5	14.2	29.2	590
		40 - 60	3.32	25.4	34.8	12.2	24.3	28.7	265
		60 - 80	3.98	27.9	31.8	13.3	23.1	31.8	213
	Ore dressing plant	0 - 20	9.86	36.8	45.2	4.78	3.32	46.7	4087
		20 - 40	10.0	28.4	36.9	9.64	15.1	38.4	3269
		40 - 60	1.71	27.7	54.9	6.98	8.65	29.4	1118
		60 - 80	0.63	15.9	42.5	15.4	25.6	16.5	317
Zn	Agricultural area	0 - 20	4.79	3.76	47.6	18.0	25.8	8.55	117
		20 - 40	6.86	6.70	35.5	20.1	30.9	13.6	61.2
		40 - 60	4.66	3.73	39.4	34.5	17.7	8.39	32.2
		60 - 80	2.34	0.92	37.6	22.0	37.1	3.26	21.8
	Ore dressing plant	0 - 20	6.49	13.4	37.2	8.78	34.1	19.9	157
		20 - 40	6.30	10.6	38.9	12.2	32.0	16.7	156
		40 - 60	5.19	3.10	43.2	18.9	29.7	8.29	29.7
		60 - 80	3.79	3.83	36.4	24.0	31.9	7.62	26.6
Cd	Agricultural area	0 - 20	17.7	11.8	17.7	23.5	29.4	29.4	0.34
		20 - 40	18.3	12.2	20.7	12.2	36.6	30.5	0.16
		40 - 60	13.3	13.3	26.7	20.0	26.7	26.7	0.15
		60 - 80	11.8	11.8	23.5	23.5	29.7	23.5	0.17
	Ore dressing plant	0 - 20	10.3	8.62	30.1	34.5	16.4	18.9	1.16
		20 - 40	13.6	12.1	22.7	6.06	45.5	25.8	0.66
		40 - 60	17.5	4.76	36.5	9.52	31.8	22.2	0.63
		60 - 80	6.90	6.90	37.9	17.2	31.0	13.8	0.29
Cr	Agricultural area	0 - 20	0.16	0.25	45.5	18.0	36.1	0.41	53.0
		20 - 40	0.20	0.16	38.1	31.4	30.2	0.37	49.1
		40 - 60	0.32	0.43	33.6	23.1	42.6	0.76	27.7
		60 - 80	0.39	0.29	11.7	40.9	46.8	0.68	20.5
	Ore dressing plant	0 - 20	0.37	0.33	41.3	26.6	31.4	0.70	51.6
		20 - 40	0.42	0.40	39.3	27.3	32.7	0.82	42.6
		40 - 60	0.74	0.69	31.9	19.4	47.2	1.43	21.6
		60 - 80	0.14	0.29	28.5	23.4	47.7	0.43	20.7

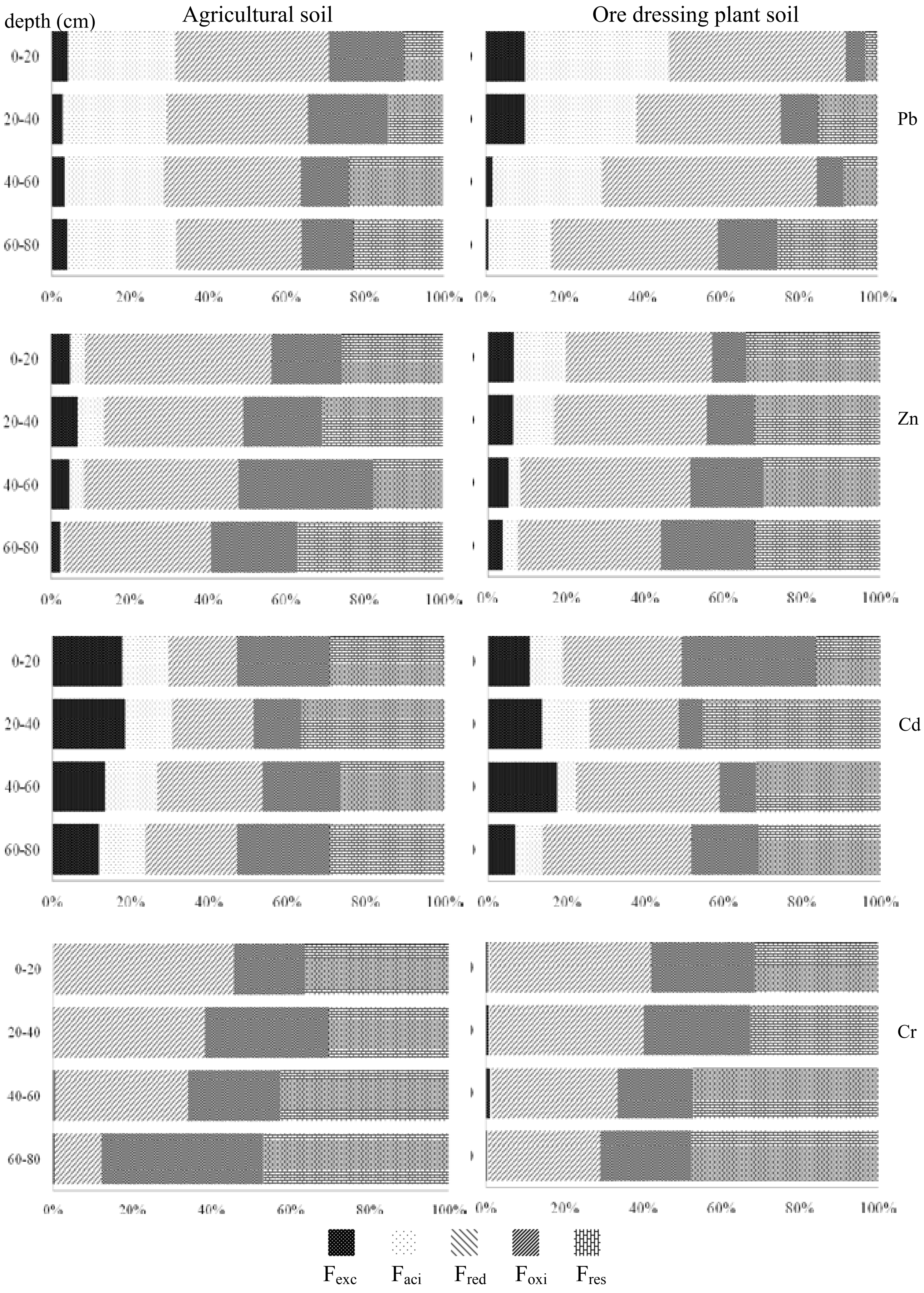


Figure 6. Distribution of Pb, Zn, Cd and Cr in soil profiles

Table 4. Grade standard of E_r^i and PER

Potential ecological risk index of an individual metal, E_r^i	Pollution ecological risk index, PER	Grades of potential ecological risk
< 40	< 150	Low - grade
40 - 79	150 - 299	Moderate
80 - 159	300 - 600	Severe
160 - 320	> 600	Serious
> 320		

Table 5. Individual potential ecological risk E_r^i of heavy metals in surface soil

Soil sample	E_r^i			
	Pb	Zn	Cd	Cr
Residential and Agricultural area				
U1	5.79	1.93	21.9	2.13
U2	1.55	0.61	21.9	2.84
U3	8.46	0.70	23.3	1.63
U4	1.84	0.45	17.1	1.06
U5	3.20	1.01	23.3	1.87
U6	4.27	1.49	40.9	0.89
U7	9.30	3.68	54.3	3.22
U8	4.05	1.92	38.6	2.67
U9	11.9	0.84	24.8	1.67
U10	11.1	0.63	25.7	1.80
U11	6.48	0.53	15.7	1.10
U12	3.35	0.67	29.1	1.02
U13	2.49	0.72	22.4	1.60
U14	3.67	0.75	27.1	1.38
U15	4.58	1.69	30.5	0.98
U16	1.32	0.52	24.8	2.09
U17	1.58	1.02	30.0	1.73
U18	2.31	0.75	34.3	3.36
U19	2.13	0.82	37.1	2.11
U20	1.88	0.59	33.8	2.62
U21	11.7	0.59	26.7	1.96
U22	2.95	1.01	70.5	4.61
U23	4.71	0.78	30.5	2.15
U24	1.26	0.55	29.1	2.96
U25	10.1	1.11	31.4	1.52
U26	4.82	1.81	30.9	1.60
U27	9.04	0.60	22.4	1.43
U28	5.14	0.82	29.1	2.19
U29	4.10	0.42	21.4	1.83
Vicinity Ore dressing plant area				
M1	235	2.80	29.5	0.96
M2	2.83	0.51	19.1	0.65
M3	19.2	1.12	34.8	1.93
M4	29.8	0.54	17.6	0.35
M5	11.3	0.48	17.1	0.75
M6	28.4	1.48	30.5	0.97

Table 6. Calculation of potential ecological risk (PER) of surface soils

	E_r^i , Agricultural area				PER	E_r^i , Ore dressing plant area				PER
	Pb	Zn	Cd	Cr		Pb	Zn	Cd	Cr	
Average	5.00	1.00	29.9	2.00	37.9	54.5	1.16	24.8	0.93	81.4
Maximum	11.9	3.68	70.5	4.61	90.7	253	2.80	34.8	1.93	293
Minimum	1.26	0.42	15.7	0.89	18.3	2.83	0.48	17.1	0.35	20.8

moderate grade in U6, U7 and U22 soil samples which could be due to its high toxicity.

Table 6 presents the average level of potential ecological risk indices of an individual metal E_r^i with grade classifications. The results showed that, in the surface soil of ore dressing plant area, lead content exhibited a moderate potential ecological risk (average of 54.5) whereas all other metals posed low potential ecological risk. PER for heavy metals in agricultural and ore dressing plant area could be ordered from high to low as: Cd > Pb > Cr > Zn and Pb > Cd > Zn > Cr, respectively. The calculated PER values were ranged from 18.3 to 90.7 with an average of 37.9 for agricultural area and 20.8 to 293 with average of 81.3 for ore dressing plant area. Based on the classification proposed by Guo *et al*., 2010 (Table 4), soils in the area of concern for this study were classified in the low grade degree of potential ecological risk (PER < 150).

4. Conclusions

Spatial distribution of total concentration and mobility of heavy metals (lead, zinc, cadmium and chromium) in agricultural and lead ore dressing plant surface soils from Upper Klity village were investigated. Results indicated that lead was a predominant element in this area, which was primarily restricted to the vicinity of the ore dressing plant. This study clearly showed that high concentrations of lead came from intensive smelting and mining processes and the values are higher than the corresponding concentrations found worldwide in natural soils (Zhao *et al*., 2007; Wei *et al*., 2009). In addition, the mobility of lead was higher than the other heavy metals, and the mobility factor of lead in the area near the abandoned ore dressing plant was clearly higher than that in the agricultural area. The calculated mobility factors in soil profiles were high near the surface layer and became lower at the deeper layers. PER index suggested that each individual metal pollution level in surface layer had a low-grade of potential ecological risk, except that of lead which exhibited a moderate potential ecological risk in the ore dressing plant area. The average comprehensive PER index indicated a low-grade degree in both soils. Based on this finding for the whole Upper Klity village, the contents and risk assessment of heavy metals are classified as low level in the agricultural area, and are unlikely to cause additional adverse health risk to the associated ecosystem. However, the risk of heavy metals pollution in the ore dressing plant area should be of primary concern. Therefore, the zoning declaration for cultivation and heavy metal polluted area are recommended for the future land use.

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