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The mobility of heavy metals in the sediment of the To–Lich River and the Kim–Nguu River in Hanoi City has been assessed based on selective sequential extraction procedure and the relationship between heavy metal concentration and organic matter content in the sediment has been examined. The heavy metal concentration of the sediment samples varied to a great extent by the difference of the sampling site and metal type. The heavy metals were bound with sediment particles through the phases such as exchangeable, carbonate, oxide, organic matter, and residual. The percentage of each phase was different according to the metal type; the organic matter and the oxide were predominant for the group of Cu, Pb, and Ni and the group of Zn and Cd, respectively, and each phase was almost equal for Cr. The total heavy metal concentration in the sediment was correlated with organic matter content for Cu, Pb, and Ni while no correlations were found for Cd, Zn, and Cr.

INTRODUCTION

Over a long period, heavy metals along with other metals and minerals have been released from chemical compounds through industrial activities. The level of heavy metals in aquatic environment has been of much concern during the last decades due to the adverse effects of some metals on living organisms in food chains and human health.

The analysis of bottom sediments has been used to determine the extent and source of trace metal contamination in aquatic environment. Sediments have the capacity for accumulating trace metals and other contaminants over time and serve to time integrated assessment of contamination that has occurred in water body (Mark *et al.*, 1982). Yousel *et al.* (1994) indicated that the transport of metals through sediments is a very slow process since the sediments possess high metal retaining capacity.

Due to rapid expansion of Hanoi City, more waste products have been discharged from municipalities and factories and spilled into waterways. Some pollutants in the waste products are adsorbed onto the surface of fine–grained particles, which settle and form polluted sediments at the bottom of waterways. The polluted sediments pose the risk of recontamination of overlying water through the release of pollutants from the sediments. In Hanoi City, the To–Lich River and the Kim–Nguu River are the main source of irrigation water

for suburban agricultural land. The discharge of industrial wastewater into the rivers has adversely affected the quality of stream and sediments in the river system (Environmental Information Office, 2001). Hence it is of importance to assess the interaction of heavy metals with components of river sediments.

Heavy metals in sediment exist in different chemical forms or different particle–binding phases. Heavy metals are complexed with organic compounds, adsorbed or occluded in carbonates and oxide minerals, and in the structure of primary and secondary minerals. In environmental studies, the determination of these gives more insight into the mobility, availability, and toxicity for trace metals. For these determinations, various approaches based on metal adsorption and desorption have been designed and extraction procedures are most widely used in soil science.

In the present study, the retention mechanisms of heavy metals in the sediment of the To–Lich River and the Kim–Nguu River in Hanoi City has been assessed based on selective sequential extraction (SSE) procedure, and the correlations of heavy metals with organic matter in the sediment have been examined.

MATERIALS AND METHODS

Study areas and materials

The To–Lich River and the Kim–Nguu River in Hanoi City are the main source of irrigation water for suburban agricultural land. The urban and industrial wastewater of 429,000 m^3 per day is being discharged to these rivers.

Sediment samples were collected from the surface zone (20 cm) of the sediment at the 12 sites submerged with water on December 3 to 6 of 2005, The core samples of 90 cm depth were also taken at 3 sites where

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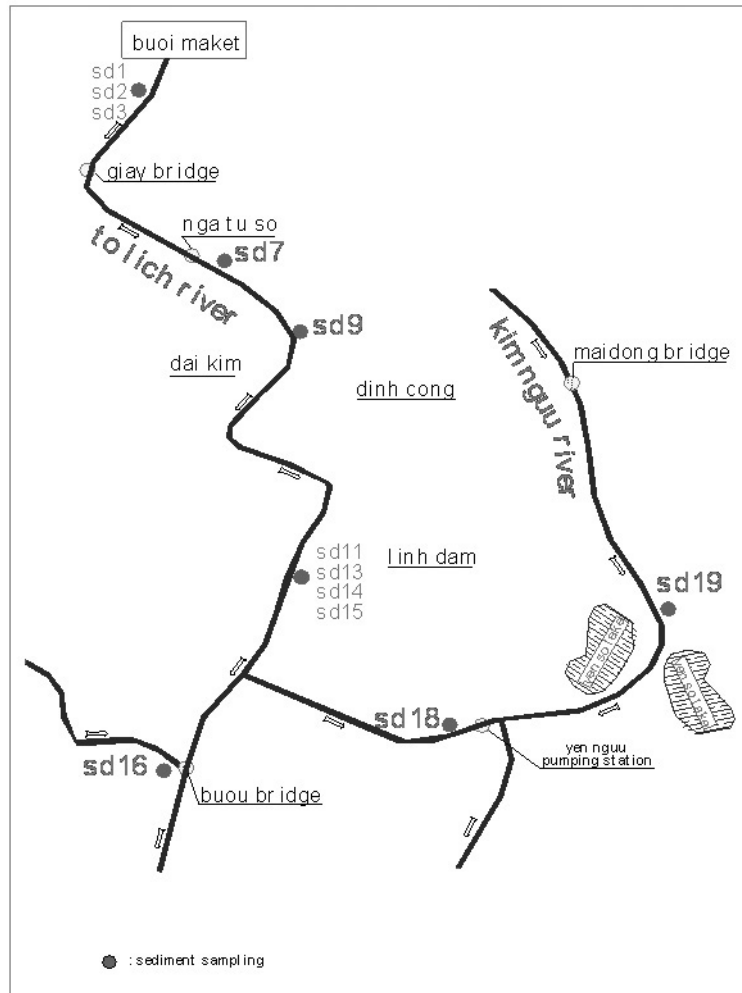
Fig. 1. Location of the sampling sites.

Table 1. Location of the sampling sites

Sediment sample		Location
No	Depth (cm)	
SD 1	0–30	
SD 2	30–60	Buoi market
SD 3	60–90	
SD 7	0–20	Nga Tu So
SD 9	0–20	Dai Kim
SD 11	0–20	
SD 13	0–30	
SD 14	30–60	Linh Dam
SD 15	60–90	
SD 16	0–20	Cau Buou
SD 18	0–20	Yen Nguu pump station
SD 19	0–20	Yen So lake

sediment surface is exposed to the air (Fig. 1 and Table 1).

Methods

The pH was measured using soil suspended with soil/water ratio of 1/25. Organic matter: Organic carbon was determined by the Tyurin method, and multiplying the organic carbon by 1.724 gives the organic matter content (Committee of Soil standards for Analyses and Measurement, 1986). Particle size distribution was determined by the Tyurin method (Khoa, *et al.*, 1996).

Selected sequential extraction (SSE): The basic utility of SSE is its use of appropriate reagents to release different heavy metal fractions from soil solids by destroying the binding agents between the metals and the soil solids and permitting the metal species to be detected.

Total metal concentration, heavy metals in the sediment was digested with $1 M$ HNO_3 at $96°C$ for an hour and centrifuged, and the dissolved metals in the supernatant were analyzed by atomic absorption spectrophotometer (Committee of Soil standard methods for Analyses and Measurement, 1986).

RESULTS AND DISCUSSION

Chemical and physical properties of sediment

The chemical and physical properties of the sediment samples are shown in Table 2. The pH was in a range of 7.10 to 7.83. The organic matter content varied 3.36 to 7.97%. The highest organic matter content in SD 19 suggests the inflow of organic wastes from the factories such as Huu–Nghi food, Hai–Chau candy, Dong–Nam–A beer, open markets, and residence (Fig. 1).

Table 2. Chemical and physical properties of sediment

No	pH (H₂0)	Organic matter (%)	Particle size distribution (%)				Total heavy metal concentration (mg kg⁻¹)					
			Clay (2 μm)	Silt (2–20 μm)	Fine sand (20–200 μm)	Coarse sand (200–1000 μm)	Cu	Pb	Zn	Cd	Cr	Ni
SD 1	7.58	4.13	4.33	24.33	30.54	40.65	260	368	250	4.4	540	65
SD 2	7.71	4.28	4.00	24.00	49.43	22.57	320	395	441	5.3	550	63
SD 3	7.83	4.45	4.33	24.33	48.65	22.69	345	425	345	5.2	525	48
SD 7	7.56	6.55	3.33	25.00	44.42	27.25	472	490	478	20.0	505	165
SD 9	7.45	5.60	4.00	35.30	55.47	5.23	445	450	490	40.0	517	108
SD 11	7.80	3.54	7.33	57.33	30.34	5.23	357	348	422	2.7	638	57
SD 13	7.26	3.54	7.33	53.33	36.08	3.26	340	280	395	2.5	637	52
SD 14	7.10	3.36	8.51	54.23	30.12	7.44	220	260	370	3.7	615	58
SD 15	7.25	3.84	10.3	59.00	25.45	4.77	240	370	325	2.7	605	50
SD 16	7.45	4.54	5.67	25.33	54.10	14.90	401	435	324	8.5	560	64
SD 18	7.14	4.94	4.33	19.76	58.21	17.46	415	430	535	17.0	655	142
SD 19	7.17	7.97	5.00	19.33	64.78	11.35	475	665	520	3.5	585	151
ML*							*200*	*300*	*450*	*3*	*400*	*110*

* Maximum permissible concentrations of potentially toxic heavy metal for crops after application of sewage sludge (Steve, 1994).

All the sediment samples have relatively low clay content, ranging between 3.33 and 10.3%. For SD 11, 13, 14, and 15 the predominant fraction was silt and fine sand while was coarse sand, find sand, and silt for the other samples.

Heavy metal concentrations in sediment

Total heavy metal

Table 2 shows the total heavy metal concentrations of the sediment samples, along with the maximum permissible level for crop growth. The metal concentrations varied to a great extent among the samples: 220 to 475 mg/kg for Cu, 260 to 664 mg/kg for Pb, 324 to 550 mg/kg for Zn, 2.5 to 40 mg/kg for Cd, 505 to 655 mg/kg for Cr and 48 to 165 mg/kg for Ni. In comparison with the maximum permissible level for crop growth, Cr and Cu exhibited the highest pollution where the metal concentrations exceeded the permissible level in all the samples. The Pb and Cd exceeded the permissible level in nine to ten samples while Zn and Ni were below the permissible level in seven to eight samples.

Distribution of partitioned heavy metal on sediment fractions

The mobility and availability of heavy metals in sediments depend on how the metals are associated with the components of the sediment, and the measure of the mobility and availability of metals serves to predict the behavior of heavy metals in the sediment. The metals are bound to the solid component of the sediment through phases such as exchangeable, carbonate, oxides and hydroxides, and organics. The selective sequential extraction of heavy metals provides the detailed insight on how the metals are associated with the components of the sediment.

Tables 3 to 8 presents sequentially fractionated metal concentrations in sediments, and the heavy metal percentage for each fraction calculated from above results is shown in Fig. 2. For Cu (Table 3 and Fig. 2), the metal associated with organic matter exhibited the highest percentage with a range of 65 to 88%. Tessier *et al.*, (1979) indicated that Cu exhibits the highest stability constants for most ligands among the heavy metals

Table 3. Concentration of sequentially fractionated Cu in sediments (mg kg⁻¹)

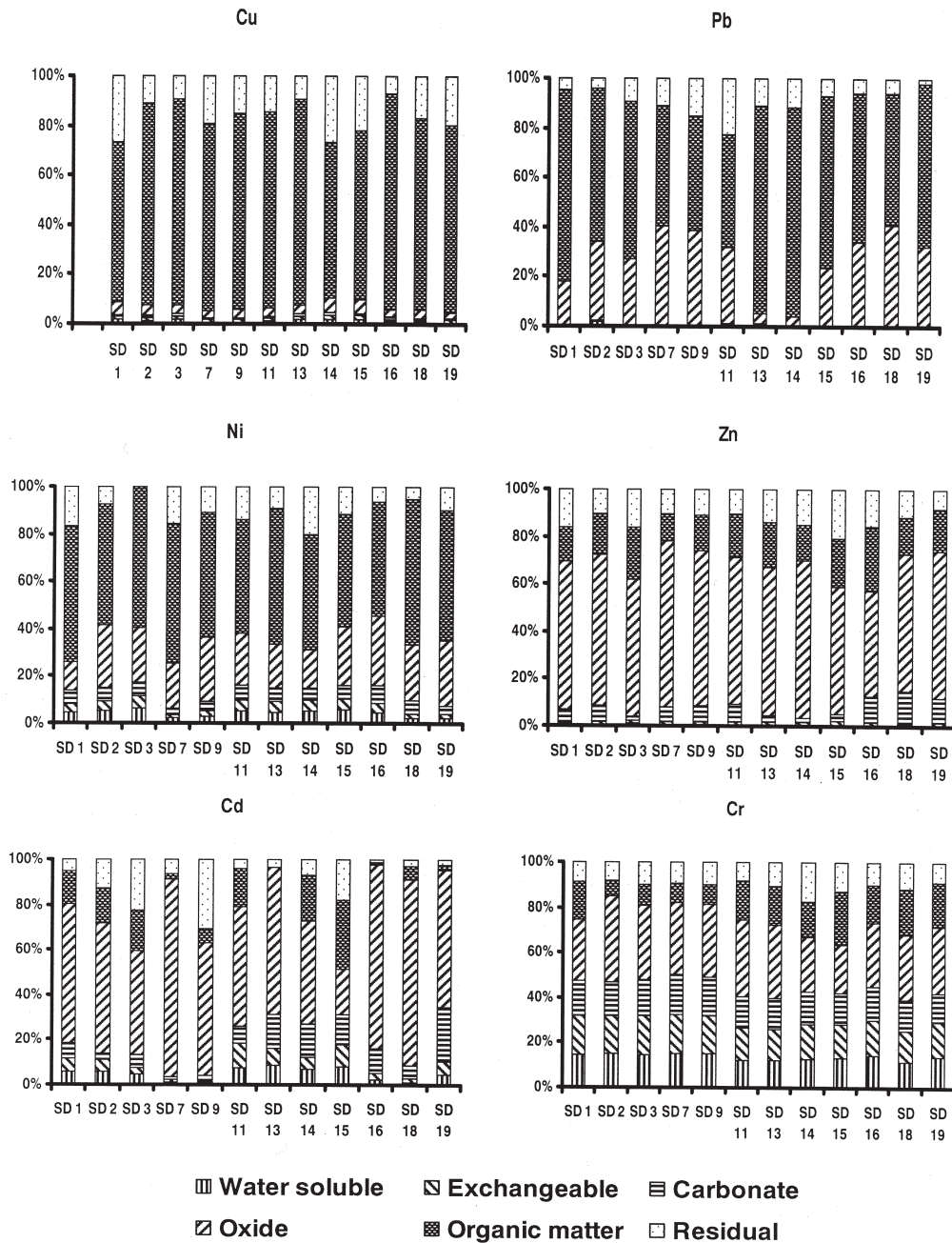| No	Water soluble fraction	Exchangeable fraction	Carbonates fraction	Oxide fraction	Organic matter fraction	Residual fraction	Total
SD 1	3.9	3.9	1.8	13.6	171.6	70.2	265.0
SD 2	3.8	4.2	2.4	14.8	265.5	35.2	325.9
SD 3	5.1	4.4	5.1	12.2	289.6	33.2	349.6
SD 7	3.9	3.4	4.3	13.8	359.9	89.2	474.5
SD 9	3.8	4.0	3.2	14.4	356.2	67.9	449.5
SD 11	4.2	3.8	3.4	12.4	286.5	52.1	362.4
SD 13	5.1	4.4	5.1	12.2	289.6	33.3	349.6
SD 14	4.1	3.8	1.9	12.9	142.3	59.2	224.3
SD 15	3.8	4.3	2.1	13.5	167.6	53.3	244.4
SD 16	4.0	4.2	3.5	12.5	356.1	28.1	408.4
SD 18	4.1	3.8	2.6	13.2	326.5	69.5	419.5
SD 19	4.0	3.8	2.8	10.9	365.2	95.3	481.9

Fig. 2. Distribution of heavy metal in various chemical forms in sediment.

Table 4. Concentration of sequentially fractionated Pb in sediments (mg kg⁻¹)

No	Water soluble fraction	Exchangeable fraction	Carbonates fraction	Oxide fraction	Organic matter fraction	Residual fraction	Total
SD 1	0.0	0.4	0.5	65.1	287.5	17.8	371.3
SD 2	7.0	3.0	0.2	125.4	246.9	15.6	398.1
SD 3	0.0	0.8	0.2	115.2	273.8	38.5	428.5
SD 7	0.0	1.0	0.2	198.5	237.7	55.2	492.6
SD 9	0.4	0.6	0.0	173.9	206.7	68.7	450.3
SD 11	1.9	0.5	0.8	107.2	161.1	78.7	350.2
SD 13	2.6	0.0	0.9	11.3	235.7	30.6	281.2
SD 14	0.0	0.0	1.0	10.3	219.6	29.8	260.7
SD 15	0.5	0.0	1.2	85.6	256.6	26.4	370.2
SD 16	1.2	0.8	1.4	145.6	258.5	25.6	432.5
SD 18	0.5	0.0	2.2	175.3	229.3	25.5	432.7
SD 19	0.2	0.0	1.0	215.3	434.3	12.5	663.3

Table 5. Concentration of sequentially fractionated Ni in sediments   (mg kg^{-1})

No	Water soluble fraction	Exchangeable fraction	Carbonates fraction	Oxide fraction	Organic matter fraction	Residual fraction	Total
SD 1	3.1	2.6	3.9	8.6	38.8	11.2	67.9
SD 2	3.5	2.4	4.1	17.6	33.4	5.1	66.1
SD 3	3.1	2.6	3.0	12.0	30.1	0.1	50.9
SD 7	3.4	2.7	4.7	32.1	98.2	26.5	167.7
SD 9	3.1	2.6	4.8	31.2	59.6	12.5	113.7
SD 11	3.2	2.8	3.9	13.1	29.5	8.3	60.8
SD 13	2.5	2.6	3.3	10.4	32.5	5.3	56.6
SD 14	3.2	2.7	3.0	9.8	28.6	12.0	59.3
SD 15	3.2	2.4	3.2	13.4	25.8	6.2	54.3
SD 16	3.2	2.8	5.4	20.4	33.5	4.2	69.4
SD 18	3.5	2.7	8.2	35.0	91.5	7.5	148.4
SD 19	3.6	2.8	5.4	42.9	85.6	15.3	155.6

Table 6. Concentration of sequentially fractionated Zn in sediments (mg kg^{-1})

No	Water soluble fraction	Exchangeable fraction	Carbonates fraction	Oxide fraction	Organic matter fraction	Residual fraction	Total
SD 1	1.5	4.6	33.4	346.2	81.2	89.6	556.5
SD 2	2.5	4.5	31.9	282.0	78.2	46.2	445.4
SD 3	3.2	4.6	6.9	198.2	75.1	56.2	344.3
SD 7	3.2	4.2	31.9	334.8	56.2	50.1	480.5
SD 9	3.0	4.6	34.9	320.8	75.2	53.3	491.8
SD 11	2.1	4.6	32.9	263.0	78.6	44.7	425.9
SD 13	2.0	4.3	12.2	248.1	75.2	56.2	398.1
SD 14	3.1	2.5	8.0	250.1	56.2	56.9	376.8
SD 15	2.8	4.5	9.7	175.6	66.1	68.3	327.0
SD 16	1.6	4.6	35.3	146.2	89.2	52.1	329.1
SD 18	1.8	5.3	74.8	310.0	82.3	63.2	537.4
SD 19	4.1	5.1	55.0	324.1	95.3	42.1	525.7

Table 7. Concentration of sequentially fractionated Cd in river sediments (mg kg^{-1})

No	Water soluble fraction	Exchangeable fraction	Carbonates fraction	Oxide fraction	Organic matter fraction	Residual fraction	Total
SD 1	0.3	0.3	0.3	2.9	0.7	0.3	4.8
SD 2	0.3	0.3	0.2	3.1	0.9	0.7	5.4
SD 3	0.2	0.2	0.3	2.6	1.0	1.3	5.6
SD 7	0.2	0.2	0.3	17.8	0.5	1.3	20.3
SD 9	0.3	0.2	1.1	23.9	2.6	12.6	407
SD 11	0.2	0.3	0.2	1.6	0.5	0.1	2.9
SD 13	0.3	0.2	0.5	2.0	0.0	0.1	3.0
SD 14	0.3	0.2	0.6	2.0	0.9	0.3	4.3
SD 15	0.3	0.3	0.4	0.6	1.0	0.6	3.2
SD 16	0.2	0.3	1.0	7.8	0.1	0.1	9.5
SD 18	0.3	0.3	1.0	14.7	1.0	0.6	17.9
SD 19	0.2	0.3	1.1	2.8	0.1	0.1	4.6

Table 8. Concentration of sequentially fractionated Cr in sediments   (mg kg^{-1})

No	Water soluble fraction	Exchangeable fraction	Carbonates fraction	Oxide fraction	Organic matter fraction	Residual fraction	Total
SD 1	91.9	112.8	100.7	174.0	105.5	57.6	642.9
SD 2	95.7	108.7	99.4	246.9	45.2	52.8	648.6
SD 3	92.2	107.9	100.0	206.9	56.2	63.2	626.4
SD 7	93.5	107.1	109.6	199.8	53.2	56.2	619.4
SD 9	93.1	106.4	109.4	199.9	55.2	61.2	625.3
SD 11	91.5	104.4	104.4	251.1	127.1	61.0	739.5
SD 13	90.5	99.9	100.7	241.3	126.3	76.2	735.1
SD 14	92.0	111.7	105.0	175.0	114.2	125.6	723.6
SD 15	94.4	106.2	98.3	149.0	168.6	89.5	706.0
SD 16	95.7	103.1	102.9	189.1	110.2	65.2	666.2
SD 18	90.2	102.5	104.7	221.3	156.3	86.5	761.6
SD 19	92.7	104.6	85.7	197.5	135.7	56.5	672.6

considered. Based on this, Ho (2000) suggested that the high affinity of organic ligands with heavy metals makes Cu in river sediments more stable, leading to the suppression of diffusion and dispersion of Cu. In addition, organic compounds under the reduced condition may be more active to bind with Cu. Thus the organic matter plays an important role in the immobilization of Cu. Following the organic matter, the fraction associated with heavy metals was in the order of residual, oxide, exchangeable, carbonate, and water soluble. Similar results were obtained by Ho (2000).

The Pb and Ni, in similar to Cu, were concentrated in the organic matter fraction (Tables 4 and 5, Fig. 2), ranging from 45 to 84% for Pb and from 51 to 32% for Ni. The oxide fraction was second in proportion ranging from 4 to 40% for Pb and 13 to 32% for Ni, followed by the residual carbonates, exchangeable and water soluble. Ho (2000) indicated that Pb and Ni in the sediment of To–Lich and Kim Nguu River were mostly present in oxide fractions. Behnar and Catherine (2006) showed that Ni in the sediment of Lachine Canal, Canada was concentrated in residual fractions.

The highest percentage for Zn was found in the oxide fractions, ranging between 45 and 70% (Table 6 and Fig. 2). The association of Zn with each fraction decreased in the order of oxides (45–70%), organic matter (12–27%), residual (8–21%), carbonates (2–8%), exchangeable (0.6–1.3%), and water soluble (0.2–1%). These results agree with those observed by Ho (2000). Ho (2000) also indicated that mobilized Zn is adsorbed on Mn, Fe, and Al hydroxides. Dahrazma and Mulligan (2006) showed that more than 60% of Zn in the sediment was sorbed as oxides fractions.

The average percentage of Cd associated with each fraction in the sediment (Table 7 and Fig. 2) was 60% for oxides, 10% for organic matter, 9.6% for carbonate, 9.4% for residual, 5.6% for exchangeable and 5.4% for water soluble. Brigden and Santillo (2004) indicated that Cd in the sediment is potentially biovailability, because metals present in the exchangeable is usually thought to be ready available for plant uptake.

For Cr (Table 8 and Fig. 2), the oxide fraction exhibited the highest percentage (25–45%) followed by the organic matter (8–28%), exchangeable and carbonate (15–21%), water soluble (14–18%) and residual (10–20%).

Correlation between the organic matter content and total heavy metal concentration

Some heavy metals are predominantly bound with organic matter fraction (Tables 3 to 8 and Fig. 3), which could be related to the organic matter present in high amount in the sediment (Table 2). Figure 3 shows the relationship between heavy metal concentration and organic matter content in the sediment. Positive correlations exist between the two parameters for Cu, Pb, and Ni while no correlations were found for Cd, Zn, and Cr (not shown here). Similar results have been reported by others. Dilek et al. (2001) indicated that heavy metal concentration in sediment was correlated with organic
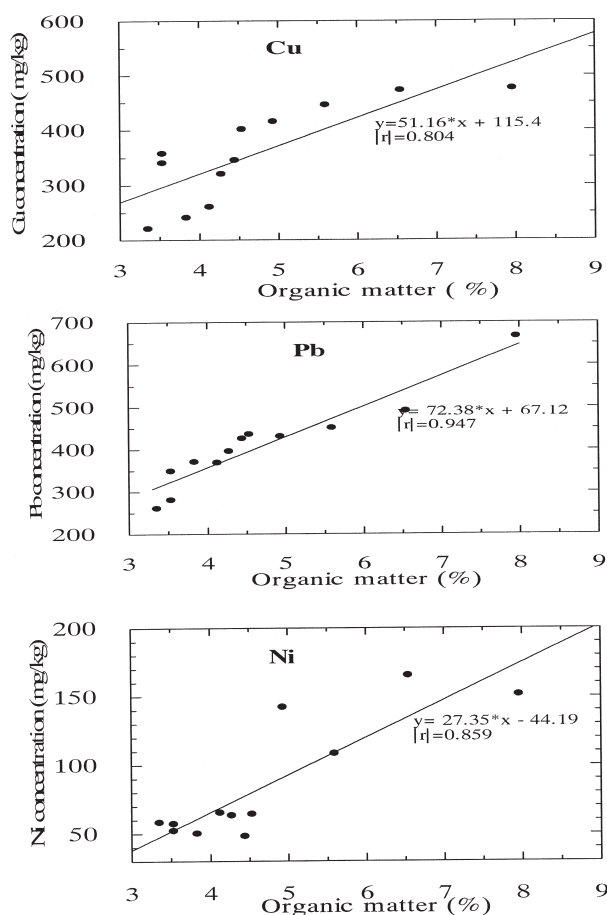
Fig. 3. Correlation between organic matter and heavy metal concentration (The correlations are significant at 1% level).

carbon content of samples rather than with the depth of samples. Senastien et al. (2000) asserted that the organic matter is the most important factors affecting both dissolved and total heavy metals in sediment.

The mechanisms proposed for the immobilization and consequent reduction in the phytoavailability of metals by organic matter include the enhanced metal adsorption through increased surface charge, increase in the formation of organic and inorganic metal complexes, the precipitation of metals, and the reduction of metals from mobile form with higher valence to immobile form with lower valence (Bolan and Duraisamy, 2003). There is an evidence to suggest that the major functional group of the humic acid with which the metal cations interact is carboxyl group. Humic substances have high affinity with copper, resulting in the formation of stable complexes (Dahrazma and Mulligan, 2006). Fukue et al. (2006) improved that high concentration of heavy metal in sediments are probably due to the high organic content resulting from humus. Kamon et al. (2006) showed that heavy metal solubility in marine sediment is increased as dissolved organic carbon increases. The complexation of metals with organic legands is one of the mechanisms that control the availability and mobility of metals. The formation of soluble organo–metal complexes increases the availability and mobility of trace

metals. On the other hand, the formation of metal complexes with solid–phase organics may increase the partitioning of metal toward the solid–phase. Thus the organic matter is an important factor that controls the retention of trace metals by soil (Sudan *et al.*, 1997).

CONCLUSIONS

The heavy metal concentration of sediment samples varied to a great extent by the difference of the sampling sites and metal type.

The percentage of heavy metal retained by each fraction in the sediment was different according to the metal type; he group of Cu, Pb, and Ni and that of Zn, Cd were retained predominatly by the organic matter and the oxide, respectively, while Cr was retained almost equally by all fractions.

The total heavy metal concentration in the sediment was correlated with organic matter content for Cu, Pb and Ni while no correlations were found for Cd, Zn and Cr.

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