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Characterization of heavy metal pollution in river sediment of Hanoi City and its downstream area by multivariate analyses

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ABSTRACT

In order to get a grasp of the current situation and characteristics of heavy metal pollution in the river environment of Hanoi City and its surrounding area, river sediment was sampled from the To Lich River (urban river) and the Nhue River (suburban/rural river) for three times during the period of October 2005 to June 2006 and analyzed for heavy metals. Accumulations of heavy metals in river sediment of the Nhue (in the suburban area of Hanoi) and the To Lich were found to have been progressing in the last 8 years due to wastewater discharge from the central part of Hanoi and urbanized areas along the rivers. Concentrations of As, Cr, Cu, Mn, Ni and Zn the in sediment of the Nhue were higher in the dry season than in the rainy season. However, multivariate analyses (principal component analysis and cluster analysis) revealed that, regardless of seasons, there were two characteristic areas with regard to heavy metal composition in river sediment: (1) the To Lich with high levels of Cd, Zn and TOC from anthropogenic origins, and (2) up- and down-stream parts of the Nhue with high concentrations of As, Mn and Pb derived from the Hong River, the headwater of the Nhue.

Keywords: Cluster analysis; Hanoi; Heavy metal; Principal component analysis; River sediment; Seasonal variation

1. Introduction

A remarkable domestic socioeconomical development has been made in Vietnam since the introduction of the renovation policy in 1986. The industrial sector is growing especially impressively, achieving a 12.4–18.1% annual increase in the ratio to total gross domestic production in the period 2000–2004 [1]. On the other hand, environmental pollution by wastes, wastewater and exhausted gases has become a serious problem because environmental measures have not compensated for the rapid domestic growth and industrialization [2].

Most rain water together with wastewater from domestic and production activities in Hanoi, the capital city of Vietnam, is discharged without treatments to rivers and lakes, and it causes the increases in severe deterioration of the water quality and related problems [3]. The pollution of the water environment with toxic heavy metals and metalloids derived from wastewater discharge is of great concern as well as pollution from organic substances. Heavy metal-contaminated water and sediment can trigger pollution of arable soil if the river water containing suspended sediment is used for irrigation of

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the cultivated lands. Heavy metal toxicity can also cause ecological deterioration in aquatic ecosystems [4]. It is thus important to understand the condition of pollution by heavy metals and their behavior in the water environment of Hanoi and its downstream area.

The objectives of this study are (1) to get a grasp of the current situation of contamination in the river environment of Hanoi and its surrounding area with a special focus on heavy metals and (2) to evaluate the characteristics of heavy metal pollution in the rivers and the possible pollution sources by means of statistical analyses. For this purpose, an urban river, the To Lich River, and a suburban/rural river, the Nhue River, were selected, and river sediment was sampled three times from several locations along the rivers during a period from October 2005 to June 2006.

2. Materials and methods

2.1. Description of the studied area

The Nhue–To Lich river basin and sampling stations for the river sediments are described in Fig. 1 and Table 1.

The Nhue River receives water from the Hong River at Lien Mac Gate (Nh1), runs along western and southern edges of central Hanoi and finally meets the Day River at Phu Ly, Ha Nam Province. The total area of this watershed is about 107,530 ha, of which 20,030 ha belongs to Hanoi. The width of the watershed is about 20 km [5]. About 70–80% of the annual total water flow of the river results from that in rainy season (June–October). During the dry season (November–May of the following year), the water flow is mainly from the Hong River. This river serves as a main irrigation system for totally 49,247 ha of cultivated lands in the basin, although it is also used for aquaculture, domestic use, industrial production, craft production and waste- and rain water drainages [3]. Nhue also runs through two urbanized areas, Cau Dien in Tu Liem District which locates between Nh1 and Nh2 and Ha Dong, the capital city of Ha Tay Province which is located between Nh2 and Nh3. In Ha Dong, there are several craft villages from which the wastewater is directly discharged into the sewage system and then to the Nhue without treatment [3]. In addition, there are four confluences with discharge channels from the inner part of Hanoi City between Nh1 and Nh3 [6].

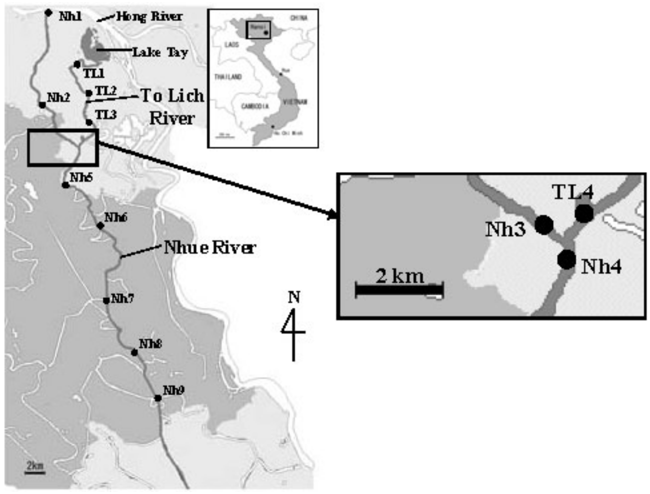

Fig. 1. Nhue–To Lich river basin and location of sampling stations.

Table 1
Description of sampling stations

River	Station	Location	GPS	
			Latitude (N)	Longitude (E)
Nhue	Nh1	Lien Mac Bridge No. 1, Tu Liem	21°05′21.8″	105°46′16.2″
	Nh2	Doi Bridge, Tu Lium	20°59′49.8″	105°45′47.0″
	Nh3	Before confluence with To Lich River, Thanh Tri	20°57′10.9″	105°48′24.0″
	Nh4	After confluence with To Lich River, Thanh Tri	20°57′07.9″	105°48′30.4″
	Nh5	Ta Thanh Oai, Thanh Tri	20°55′42.2″	105°49′09.0″
	Nh6	Chiec Bridge, Thuong Tin, Ha Tay Province	20°52′07.5″	105°49′50.4″
	Nh7	Dong Quan Bridge, Phu Xuyen, Ha Tay Province	20°47′39.5″	105°50′13.8″
	Nh8	Tan Dan Bridge, Phu Xuyen, Ha Tay Province	20°44′22.6″	105°52′12.6″
	Nh9	Coy Than Bridge, Phy Xyuen, Ha Tay Province	20°41′38.9″	105°53′29.9″
To Lich	TL1	Bridge on Dong Quan Street, Cau Giay	21°02′24.2″	105°48′23.1″
	TL2	Moi Bridge, Thanh Xuan	21°00′03.3″	105°49′07.5″
	TL3	Lu Bridge, Hoang Mai	20°58′47.9″	105°47′40.8″
	TL4	Thanh Liet Dam, Thang Tri	20°57′27.3″	105°48′36.9″

The To Lich River originates from northern edge of the city center of Hanoi, receives water from Lake Tay and runs through the residential area in western part of the inner city and finally flows into Nhue through Thanh Liet Dam at TL4. This dam started to operate in 2003. The gate of the dam is seldom open in dry season to maintain the water level in To Lich and prevent the polluted water of To Lich from discharging into Nhue. In rainy season, the gate is controlled according to the water level of Nhue. To Lich also irrigates 1,361 ha of agricultural land in Hanoi City [7]. Many manufacturing enterprises are located along the river, including a complex of factories of mechanical engineering, rubber, soap and tobacco in Thuong Dinh, Thanh Xuan District between TL2 and TL3; and leather and paint factories are located near TL1 and TL4, respectively [7,8]. A plastic company is located about 85 m upstream from TL3 in Kim Giang, Thanh Xuan District [7]. There are several confluents with rivers and discharge channels from the city center and the residential area in the city between TL1 and TL4 [6]. Industrial and domestic wastewater flowing into the To Lich amounts to 290,000 m^3/d, which accounts for two-thirds of the wastewater generated in Hanoi City [7].

2.2. Sample collection and storage

Samples of river sediments were taken at nine (Nh1–Nh9) and four (TL1–TL4) stations from the Nhue and To Lich, respectively (Fig. 1, Table 1). Samples were taken in October 2005 (end of rainy season), and January (dry season) and June (beginning of rainy season) 2006 from each sampling station except for TL3 and Nh1, where the samples were collected only in June 2006. Samples were collected using an Ekman–Birge grab and taken into plastic bottles to bring them back to the laboratory. Fresh sediment samples were stocked in a freezer, and the frozen samples were thawed and freeze-dried for chemical analysis.

2.3. Sample analysis

In order to determine heavy metal contents in the sediment sample, 0.1 g of the freeze-dried sample was taken in a Teflon beaker and successively digested with 5 mL of HNO_3 (60% (v/v)) at 120°C for 40 min, 1 mL of $HClO_4$ (60% (w/w)) and 3 mL of HF (50% (w/w)) at 160°C for 1 h, and 5 mL of HNO_3 (60% (v/v)) at 120°C for 40 min. After cooling, the digest was transferred into a plastic volumetric flask and adjusted to 50 mL with Milli-Q water. The sample was filtered through a 0.45-μm disk filter and analyzed for heavy metals and metalloids (As, Cd, Cr, Cu, Mn, Ni, Pb and Zn) using an ICP-MS (7500c, Agilent Technologies, Santa Clara, CA). Recoveries for the analyzed elements in a certified reference material NMIJ CRM 7303-a 'Lake Sediment' (National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan) by the applied method in this study ranged from 75% (Cr) to 135% (Cd) (mean values for triplicate analyses).

Total organic carbon content (TOC) in sediment was analyzed for the freeze-dried sample using a TOC analyzer (TOC-VCPH, Shimadzu, Kyoto, Japan) equipped with a solid sample module (SSM-5000A, Shimadzu).

Bottles, beakers and flasks used for sample storage and analysis of heavy metals were pre-cleaned with dilute nitric acid and then rinsed with Milli-Q water. Nitric and perchloric acids for analysis of poisonous metals (Wako, Osaka, Japan) were used for sample digestion and preparation of stock solution, whereas HF was of practical grade (Wako).

2.4. Statistical analysis

In order to characterize the studied river basin according to the types of heavy metal contaminants in river sediment, two kinds of multivariate analyses, principal component analysis (PCA) and cluster analysis, were applied for the data set of heavy metal concentrations and TOC in sediment samples collected at all the stations in each time of sampling. In cluster analysis, normalized Euclidean squared distance between each sampling station was calculated and the clusters of the stations were linked following Ward's method. The statistical treatments were performed using PCA97.xla Ver. 1.7 (for PCA) and Cluster97.xla Ver. 3.7 (for cluster analysis) with Microsoft Excel [9].

3. Results and discussion

3.1. Heavy metal concentrations in river sediment

Concentrations of heavy metals and TOC in sediments of the Nhue and To Lich Rivers are illustrated in Figs. 2 and 3, respectively. Concentrations of Cd, Cr, Cu, Pb and Zn in sediment of the Nhue and To Lich and those of As and Mn in the Nhue were generally higher than the average values for sediment in the world [10] and/or the mean values for unpolluted agricultural soils in Hanoi [11]. In addition, concentrations of all the metals measured, except for As and Mn, in the sediment samples collected at Nh2, Nh5 and TL3 in June 2006, are higher than those sampled at the corresponding sites in July 1998 [8] by 0.454–6.84 times (2.1 times in average), although those at Nh1 in June 2006 are consistent with or higher than those at the same site in July 1998 [8]. This finding suggests that accumulations of heavy metals in river sediment of the Nhue (in the suburban area of Hanoi) and the To Lich have been progressing in the last 8 years due

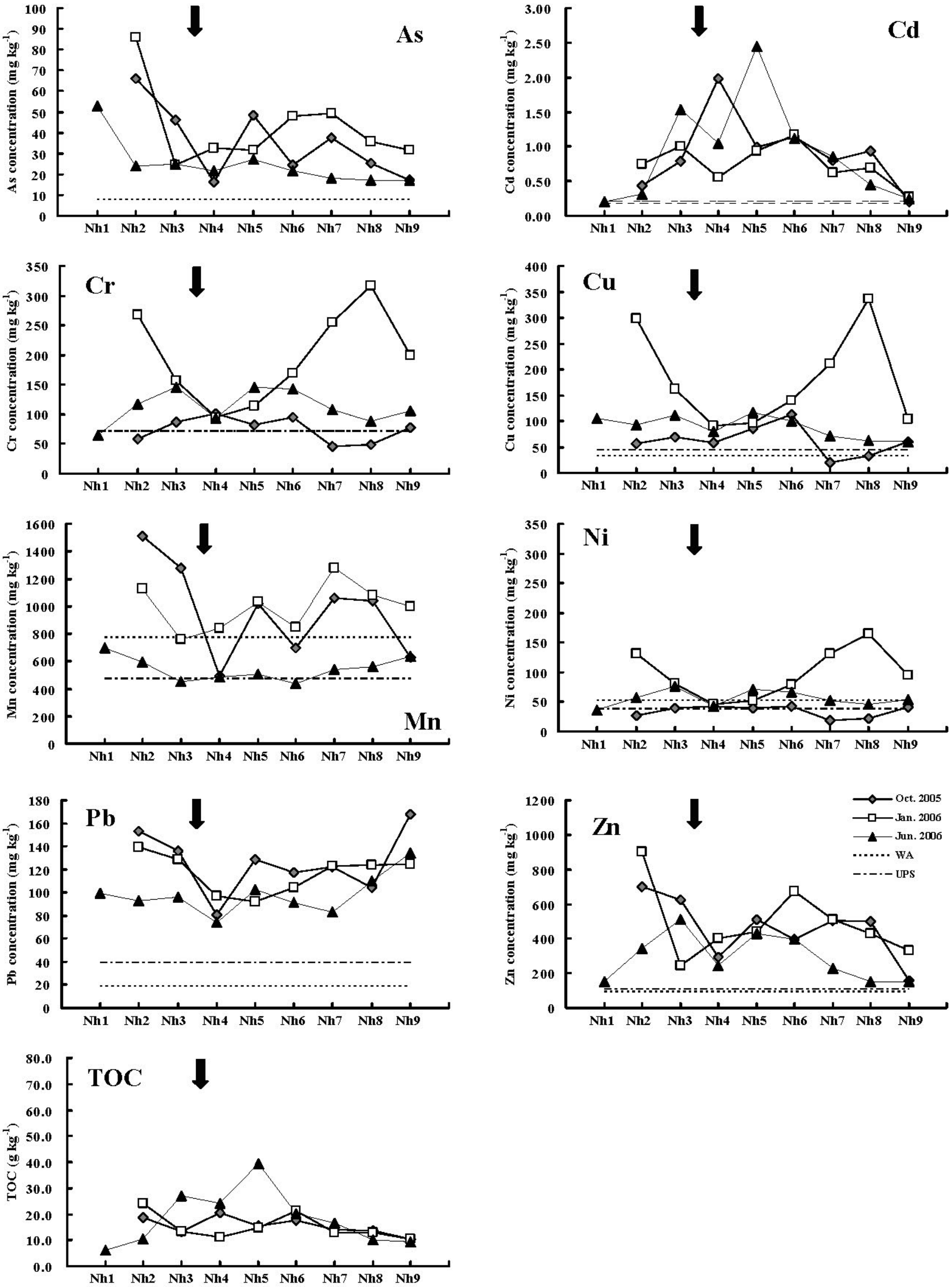

Fig. 2. Concentrations of heavy metals and TOC in sediment of the Nhue River. Lines WA and UPS represent the average value for sediment in the world [10] and the mean value for uncontaminated agricultural soils in Hanoi [11], respectively. Black arrows indicate the confluence of the To Lich River.

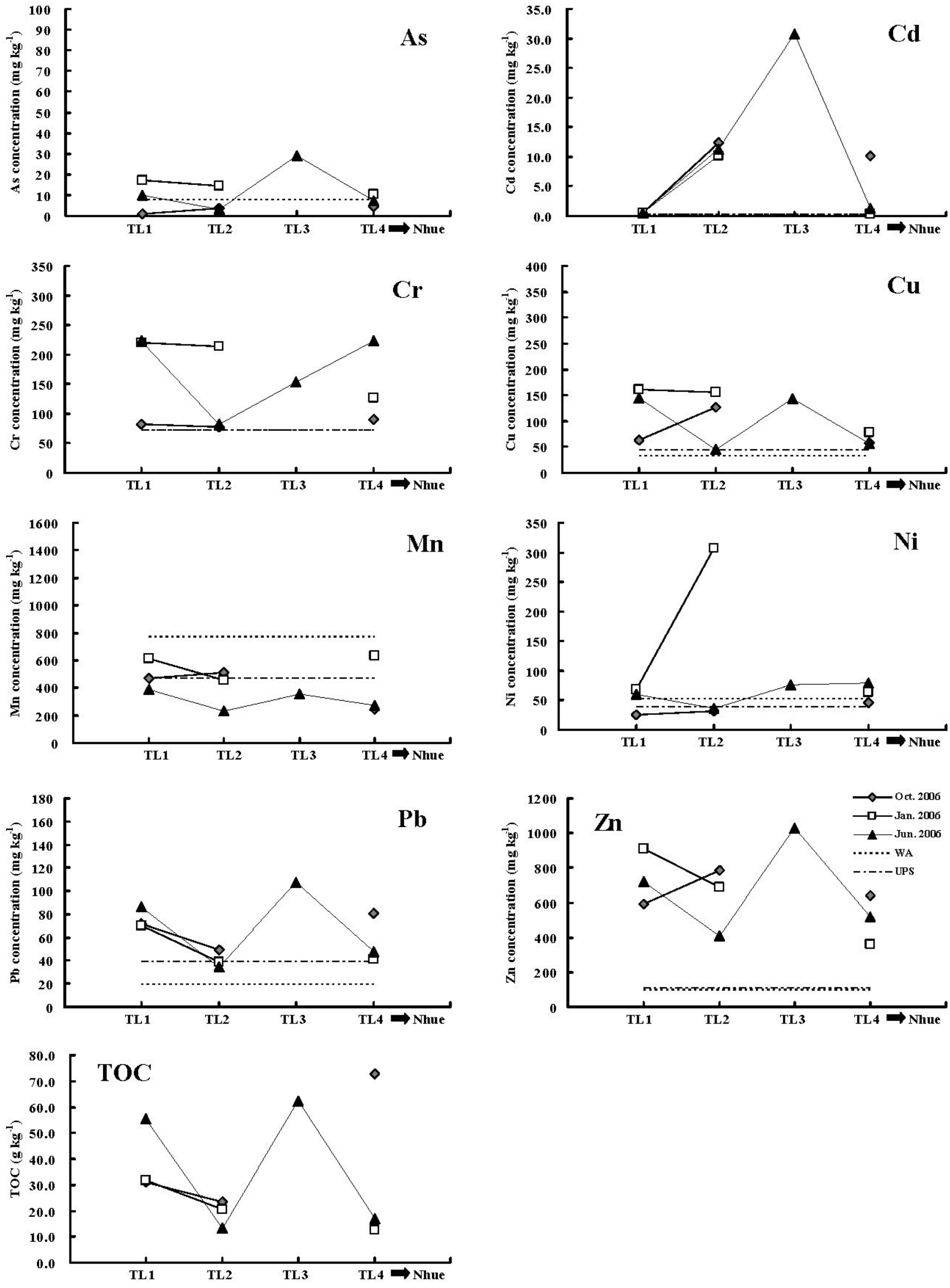

Fig. 3. Concentrations of heavy metals and TOC in sediment of the To Lich River. Lines WA and UPS represent the average value for sediment in the world [10] and the mean value for uncontaminated agricultural soils in Hanoi[11], respectively.

Table 2
Factor loadings of heavy metals and TOCin river sediment in principal component analysis(PCA). Largest absolute value for eachvariable and negative values are shown in bold and italic letters, respectively

Time of year	Variable	Factor 1	Factor 2	Factor 3
Oct 2005 (end of rainy season)	As	***–0.812***	0.060	0.489
	Cd	**0.777**	*–0.425*	0.224
	Cr	**0.670**	0.629	0.241
	Cu	0.528	0.193	**0.660**
	Mn	***–0.891***	*–0.126*	0.406
	Ni	0.539	**0.728**	0.265
	Pb	***–0.757***	0.466	0.118
	Zn	0.152	***–0.789***	0.547
	TOC	**0.703**	*–0.250*	*–0.088*
	Variance	4.17	2.06	1.34
	Proportion to total variance	0.463	0.229	0.149
Jan 2006 (dry season)	As	**0.862**	*–0.019*	*–0.184*
	Cd	*0.375*	**0.754**	0.420
	Cr	**0.731**	0.498	0.257
	Cu	**0.832**	0.368	0.206
	Mn	**0.813**	*–0.446*	0.128
	Ni	0.048	**0.785**	0.601
	Pb	**0.823**	*–0.419*	0.805
	Zn	0.296	**0.741**	*–0.576*
	TOC	0.112	**0.705**	*–0.676*
	Variance	3.55	2.99	1.49
	Proportion to total variance	0.395	0.332	0.166
June 2006 (beginning of rainy season)	As	*–0.264*	**0.823**	*–0.179*
	Cd	0.613	0.131	***–0.702***
	Cr	**0.787**	*–0.158*	0.554
	Cu	0.618	**0.694**	0.019
	Mn	***–0.689***	0.677	0.190
	Ni	**0.738**	0.108	0.480
	Pb	*–0.161*	**0.829**	0.215
	Zn	**0.972**	0.091	*–0.172*
	TOC	**0.884**	0.300	*–0.097*
	Variance	4.22	2.46	1.18
	Proportion to total variance	0.469	0.273	0.132

Table 3
Factor scores for heavy metalsand TOC in river sediment

Time of year	Station	Factor 1	Factor 2	Factor 3
Oct 2005 (end of rainy season)	Nh2	−2.92	−0.947	1.41
	Nh3	−1.17	0.649	1.46
	Nh4	1.30	1.64	−0.905
	Nh5	−0.793	0.894	1.19
	Nh6	0.784	1.78	0.784
	Nh7	−2.45	−1.50	−1.26
	Nh8	−1.74	−1.36	−1.25
	Nh9	−0.731	2.35	−1.21
	TL1	1.11	−0.863	−1.17
	TL2	2.90	−1.99	1.29
	TL4	3.71	−0.654	−0.342
Jan 2006 (dry season)	Nh2	3.70	1.26	−1.07
	Nh3	−0.508	−1.35	0.630
	Nh4	−1.24	−1.77	−0.254
	Nh5	−0.811	−1.46	−0.403
	Nh6	0.191	0.106	−1.19
	Nh7	1.99	−0.546	0.814
	Nh8	2.34	0.331	1.71
	Nh9	0.066	−1.59	0.763
	TL1	−0.657	1.86	−2.50
	TL2	−2.36	4.11	1.67
	TL4	−2.72	−0.958	−0.168
June 2006 (beginning of rainy season)	Nh2	−2.94	2.31	−0.874
	Nh3	−1.07	0.442	0.389
	Nh4	0.939	0.599	0.815
	Nh5	−1.21	−0.467	−0.651
	Nh6	0.863	1.24	0.672
	Nh7	0.287	0.001	0.631
	Nh8	−1.30	−0.481	0.038
	Nh9	−2.14	−0.092	0.035
	TL1	−2.11	6.618	0.751
	TL2	2.93	0.132	1.02
	TL4	−0.370	−3.42	−2.21
		4.43	1.96	−2.02
		1.69	−2.84	1.40

to wastewater discharges from the central part of Hanoi and urbanized areas along the rivers. Nguyen et al. [7] reported that the sediment samples collected at the sites affected by effluent discharges from factories around TL2 and TL3 contained high concentrations of heavy metals (especially Cd), which is consistent with the results obtained in the present study.

Seasonal variations in heavy metal contents and TOC in sediments were recognized in both Nhue and To Lich, but they appeared to be larger in Nhue than in To Lich. Concentrations of As, Cr, Cu, Mn, Ni and Zn in sediment of the Nhue collected in January 2006 (dry season) were higher than those in June 2006 (beginning of rainy season). It is generally recognized that heavy metals are concentrated in finer fractions of sediment [12]. It is thus speculated that concentrations of these metals in river sediment will decrease in the rainy season because of resuspension of fine surface sediment particles enriched with heavy metals under strong water flow but increase in the dry season due to promotion of sedimentation of the suspended metals under lower water flow rate.

3.2. Multivariate analyses for heavy metals in river sediment

The results of PCA for heavy metal concentrations and TOC in river sediments of the studied river basin in each time of sampling are summarized in Tables 2 and 3. The factors whose cumulative variances amounted up to 90% of the total variance are listed in Table 2. Similarity between the stations with regard to the composition of heavy metals and TOC in river sediment in each season is illustrated as a dendrogram in Fig. 4.

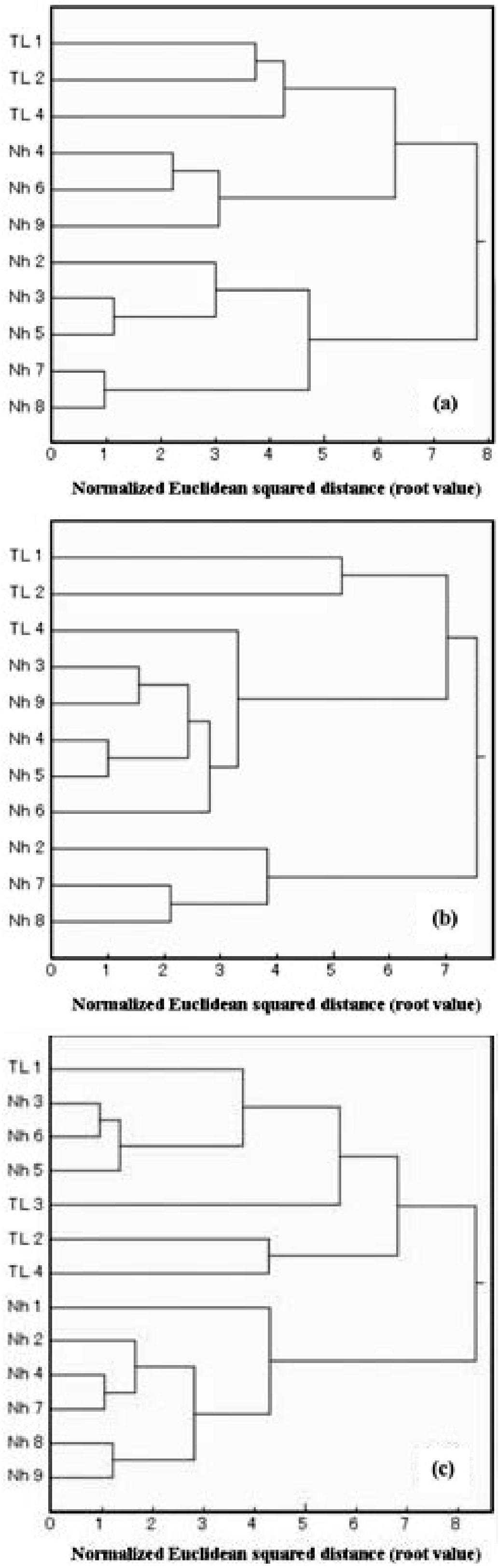

Fig. 4. Dendrogram for heavy metals and TOC in river sediment collected in October 2005 (a), January 2006 (b) and June 2006 (c).

In June 2006 (beginning of rainy season), TL1 and TL3 got high scores in factor 1 which were attributed to high concentrations of Zn and TOC, as well as Cr in TL1. On the other hand, a high negative value in factor 1 was characteristic of Nh1 which was explained by its relatively high Mn concentration. Nh1 also got a high score in factor 2 which was ascribed to high concentration of As. In addition, TL2 and TL3 were characterized by high negative scores in factor 3 which were attributed to extremely high Cd concentrations. Among the three main clusters in the dendrogram (Fig. 4(c)), except for TL3, the cluster which consisted of TL1, Nh3, Nh5 and Nh6 had the highest concentrations of Cr, Cu, Ni, Zn and TOC, whereas the cluster of Nh1, Nh2, Nh4, Nh7, Nh8 and Nh9 had the highest values of As, Mn and Pb. The cluster of TL2 and TL4 was characterized by the highest concentration of Cd. However, TL3 alone exhibited higher concentrations of metals analyzed, except for Cr and Mn, and TOC than other clusters, which implies that the river sediment around this station is heavily polluted with heavy metals and organic matter which would be derived via wastewater discharges from neighboring factories.

Similar characteristics in composition of heavy metals and TOC in river sediment of the studied area were recognized in the other seasons (October 2005 and January 2006). Sediment of the To Lich (TL1, TL2 and TL4) was characterized by high concentrations of Cd, Zn and TOC, which are discharged with domestic and industrial wastewater from the catchment area. On the other hand, sediment in up- and down-stream parts of the Nhue (especially Nh2, Nh7 and Nh8) contained high concentrations of As, Mn and Pb, which are derived from the Hong River, the headwater of the Nhue. Heavy metal composition in sediment in middle-stream of the Nhue is suggested to be disturbed by inflowing river water of the To Lich and wastewater from urbanized areas and craft villages in the region, and then to be gradually recovered toward downstream.

4. Conclusions

By comparing the data obtained in the present study with those in previous reports, accumulations of heavy metals in river sediment of the Nhue River (in the suburban area of Hanoi) and the To Lich River were found to have been progressing in the last 8 years due to wastewater discharge from the central part of Hanoi and urbanized areas along the rivers. Application of multivariate analyses (PCA and cluster analysis) was also found to be effective in identifying the polluted areas with heavy metals in the studied river basin as well as the types of heavy metal contaminants. To prevent the contamination with heavy metals of anthropogenic origins in the river environment from progressing, appropriate countermeasures at the pollution sources, e.g., introduction of suitable wastewater treatment systems in factories, should be immediately established.

References

[1] Tong Cuc Thong Ke (General Statistics Office), 2008, http://-www.gso. gov.vn/ (in Vietnamese) (accessed 22 September 2008).
[2] T. Ishigaki and L.V. Chieu, Current situation on the technology of wastewater treatment in Hanoi, Vietnam, J. Water Waste, 45 (2003) 975–979 (in Japanese).
[3] Vietnam Environment Protection Agency, Environment Report of Vietnam, The current state of water environment in 3 river basins of Cau, Nhue–Day and Dong Nai River System, 2006, http://www.nea.gov.vn/PDF_Soe2006_VN/HTMT_Tongquan06.htm (accessed 24 September 2008).
[4] M. He, Z. Wang and H. Tang, The chemical, toxicological and ecological studies in assessing the heavy metal pollution in Le An River, China, Water Res., 32 (1998) 510–518.
[5] Water Environment Partnership in Asia, Nhue–To Lich river basin, 2008, http://www.wepa-db.net/policies/cases/vietnam.htm (accessed 24 September 2008).
[6] Japan International Cooperation Agency, The study on environmental improvement for Hanoi City in the Socialist Republic of Vietnam, Technology Transfer Report, Tokyo, 2000.
[7] T.L.H. Nguyen, M. Ohtsubo, L.Y. Li and T. Higashi, Heavy metal pollution of the To-Lich and Kim-Nguu River in Hanoi City and the industrial source of the pollutants, J. Fac. Agr., Kyushu Univ., 52 (2007) 141–146.
[8] T.L.T. Ho and K. Egashira, Heavy metal characterization of river sediment in Hanoi, Vietnam, Commun. Soil Sci. Plant Anal., 31 (2000) 2901–2916.
[9] S. Hayakari, Excel Add-in Factory "Hayakari" (for offers of free soft wares for statistics and climate analysis), 2006, http://www.jomon.ne.jp/~hayakari/index.html (in Japanese) (accessed 25 September 2008).
[10] H.J.M. Bowen, Environmental Chemistry of the Elements, Academic Press, London, 1979.
[11] T.L.T. Ho and K. Egashira, Heavy metal status of agricultural soils in Tuliem and Thanhtri Districts of Hanoi City, Vietnam, J. Fac. Agr., Kyushu Univ., 43 (1999) 489–497.
[12] U. Förstner and G.T.W. Wittmann, Metal Pollution in the Aquatic Environment, 2nd rev. edn., Springer-Verlag, Berlin, 1981.