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Assessment of Heavy Metal Pollution in River Water of Hanoi, Vietnam Using Multivariate Analyses

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Abstract Concentrations of heavy metals in water of the Nhue River (a suburban/rural river) and one of its tributaries, the To Lich River (an urban river), in Hanoi, Vietnam had been monitored, and spatial and seasonal variations in their composition were evaluated by means of principal component analysis and cluster analysis. Heavy metal concentrations in water of the two rivers were generally lower than the surface water quality standard in Vietnam, except for manganese in several sites, although they were higher than the median values in freshwater of the world by 0.42–43 times in Nhue and 0.13–32 times in To Lich. The two multivariate analyses represented that the composition of heavy metals in river water of To Lich was distinctly different from that of Nhue. It was also suggested that metal concentrations and their composition in Nhue river water would be affected by inflowing water of To Lich and wastewater discharged from the up- and middle-stream basin, and that they gradually recovered along the direction of water flow in the downstream area in rainy season.

Keywords Hanoi · Heavy metals · Multivariate analysis and River water

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In Vietnam, the rapid domestic growth and industrialization since the introduction of the renovation policy in 1986 have caused serious environmental pollution by wastes, wastewater and exhausted gases because of the delay in improvement of environmental measures (Ishigaki and Chieu 2003). Water pollution in urban rivers and channels of Hanoi, the capital city of Vietnam, caused by untreated domestic and industrial wastewater has been in serious condition, and the pollutants discharged into the rivers have damaged aquaculture in the downstream area (JICA 2000a; Ishigaki and Chieu 2003; VEPA (Vietnam Environment Protection Agency) 2006). High concentrations of several toxic heavy metals, e.g., Cr, Hg, are also frequently detected in the effluents from factories of paper industry and metal processing (Ishigaki and Chieu 2003).

A series of field survey in the Nhue and To Lich Rivers, both of which run through western part of Hanoi City and its downstream area, had been conducted in the period from 2005 to 2006 in order to evaluate the current situation of pollution in these rivers, with a special focus on heavy metal pollution. In this report, seasonal and spatial variations in heavy metal concentrations and composition in water of the two rivers were assessed by means of multivariate analyses (principal component analysis (PCA) and cluster analysis).

Materials and Methods

The Nhue–To Lich River Basin and locations of sampling stations are illustrated in Fig. 1. The Nhue River originates from the Hong River (Red River) at Nh 1. This river is a main irrigation system for totally 49,247 ha of agricultural lands in this basin, although it is also used for aquaculture, domestic use, industrial and craft productions and waste and rain water drainage (VEPA (Vietnam Environment

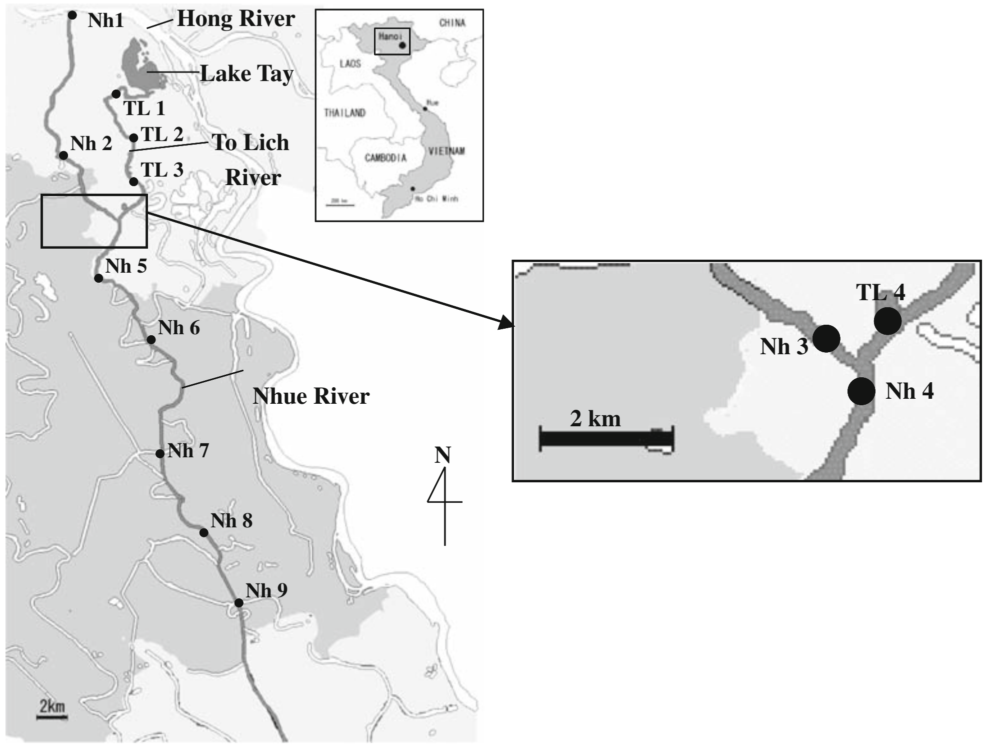

Fig. 1 The Nhue—To Lich River Basin and locations of sampling stations

Protection Agency) 2006). Nhue runs through two urbanized areas, namely Cau Dien which locates between Nh 1 and Nh 2 and Ha Dong between Nh 2 and Nh 3. Small production establishments in craft villages are also located along this river, and the wastewater from them is usually discharged into the river without prior treatments (VEPA (Vietnam Environment Protection Agency) 2006). Furthermore, there are four confluences with discharge channels from the inner part of Hanoi City between Nh 1 and Nh 3 (JICA 2000b). On the other hand, the To Lich River originates in northern edge of the city center of Hanoi, receives water from Lake Tay, runs through the residential area in western part of the inner city and finally flows into Nhue between Nh 3 and Nh 4. Industrial and domestic wastewater discharging into this river amounts to 290,000 m^3 day^{-1}, which accounts for two-thirds of the total volume of wastewater generated in Hanoi City (Nguyen et al. 2007). There is a complex of factories of mechanical engineering, rubber, soap and tobacco in Thuong Dinh between TL 2 and TL 3, and factories of leather and paint industries are located near TL 1 and TL 4, respectively (Ho and Egashira 2000; Nguyen et al. 2007). Severe pollution in river water and sediment of this river by organic matter and heavy metals (Cd, Cr, Cu, Pb and Zn) at the sites near from industrial wastewater discharges has been reported (JICA 2000b; Nguyen et al. 2007).

Samples of river water were taken at 9 (Nh 1–Nh 9) and 4 (TL 1–TL 4) stations from Nhue and To Lich, respectively (Fig. 1). Samples were taken in three occasions: October 2005 (the end of rainy season) and January (dry season) and June (the beginning of rainy season) 2006, except for TL 3 and Nh 1 where the samples were collected only in June 2006. Samples were taken in plastic bottles, brought back to laboratory with keeping them at 4°C and stored at the same temperature in a refrigerator until analysis.

The pH of the sample was measured using a portable pH meter at the sampling site. Suspended solid (SS) content was determined following the general method in laboratory. Total organic carbon (TOC) was determined using a TOC analyzer (TOC-V_{CPH}, Shimadzu, Kyoto, Japan). In order to determine total concentrations of heavy metals, 50 mL of the sample was taken in a Teflon beaker and digested with 5 mL of HNO_3 (60% (v/v)) on a hot plate at 95°C for 4 h. After digestion, the sample was transferred into a plastic volumetric flask and adjusted to 50 mL with Milli-Q water. The sample was finally filtered through a membrane filter (PTFE with a 0.45 μm pore size, Whatman, Florham Park, NJ) and analyzed for heavy metals (As, Cr, Cu, Mn, Ni, Pb and Zn) using an ICP-MS (7500c, Agilent Technologies, Santa Clara, CA). Recoveries of the analyzed metals in a certified reference material NMIJ CRM 7202-a 'River Water' (National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan) in this study were 74.1 ± 1.7%, 83.3 ± 0.7%, 89.5 ± 1.4%, 89.9 ± 1.2%, 114.4 ± 27.6%, 108.3 ± 7.9% and 70.1 ± 19.2% for As, Cr, Cu, Mn, Ni, Pb and Zn, respectively (mean values for triplicate analyses). Method detection limits calculated according to EPA 200.8 requirement of the equipment analogous to that used in the present study (7500ce, Agilent Technologies) were reported to be several ten ng L^{-1} for all the elements analyzed in this study (Wilbur et al. 2004).

In order to characterize the studied river basin according to the types of heavy metal contaminants in river water, two multivariate analyses, PCA and cluster analysis, were applied for the data set of SS, TOC and heavy metal concentrations in river water at all the stations collected in each time of sampling. In cluster analysis, normalized Euclidean squared distances between each sampling station were 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) for Microsoft Excel (Hayakari 2006).

Results and Discussion

The pH, SS, TOC and concentrations of heavy metals in water of the Nhue and To Lich Rivers are summarized in Tables 1 and 2, respectively. Concentrations of heavy metals in river water at all the stations in the two rivers were lower than the surface water quality standard in Vietnam A (TCVN 5492-1995) which is applied to water sources for domestic supply, except for Mn in several stations. However, the metal concentrations were generally higher than the median values for freshwater in the world (Bowen, 1979) by 0.42 (Zn at Nh 2 in January 2006)–43 (Ni at Nh 5 in January 2006) times in Nhue and 0.13 (Pb at TL 4 in January 2006)–32 (Ni at TL 1 in January 2006) times in To Lich.

The results of PCA for SS, TOC and heavy metal concentrations in river water of the studied river basin in each time of sampling are summarized in Tables 3 and 4. The dominant factors whose cumulative variances amounted up to 90% of the total variance were listed. Similarity between the stations with regard to the composition of heavy metals, SS and TOC in river water in each season is illustrated as a dendrogram in Fig. 2. Different features in the types of the pollutants at each station and similarity linkages between the stations were observed between seasons.

In June 2006 (the beginning of rainy season), upstream stations in Nhue, i.e. Nh 1 and Nh 2, were characterized by high scores in factor 2 which were attributed to high

Table 1 Total concentrations of heavy metals (μg L^{-1}), pH, SS and TOC (mg L^{-1}) in water of the Nhue River

	As	Cr	Cu	Mn	Ni	Pb	Zn	pH	SS	TOC
October 2005										
n	8	8	8	8	8	8	8	8	8	8
Mean	4.80	3.81	4.04	143	4.73	2.26	30.5	7.3	27	18.3
SD	1.28	1.20	2.59	35	1.20	0.91	15.5	0.1	4	9.6
Min.	2.87	1.85	2.13	83.9	2.60	1.41	11.5	7.1	17	8.29
Max.	6.11	5.40	10.2	207	6.54	4.19	61.9	7.4	31	32.8
January 2006										
n	8	8	8	8	8	8	8	8	8	8
Mean	3.81	7.13	4.44	84.3	7.10	3.90	11.0	7.3	40	13.8
SD	0.67	5.56	2.75	38.2	6.09	3.22	5.8	0.2	25	3.4
Min.	3.03	1.79	2.34	43.9	3.36	1.30	6.24	7.0	14	10.3
Max.	4.62	18.8	11.1	161	21.5	11.5	23.6	7.6	97	18.8
June 2006										
n	9	9	9	9	9	9	9	9	9	9
Mean	5.74	3.76	7.38	82.7	2.95	6.43	15.9	7.4	70	3.70
SD	0.69	3.18	3.94	24.4	1.51	4.10	7.8	0.2	30	1.22
Min.	4.86	1.35	3.18	52.2	1.54	2.41	9.66	7.2	24	2.42
Max.	7.13	10.3	14.6	119	6.28	14.2	33.6	7.7	134	50
TCVN 5492-1995 A[a]	50	50 (100)	100	100	100	50	1000	6–8.5	20	–
Freshwater (world)[b]	0.5	1	3	8	0.5	3	15	–	–	–

[a] Surface water quality standard in Vietnam for water sources of domestic supply. Cr: hexavalent (trivalent)

[b] Median value for freshwater in the world (Bowen 1979)

Table 2 Total concentrations of heavy metals (μg L^{-1}), pH, SS and TOC (mg L^{-1}) in water of the To Lich River

	As	Cr	Cu	Mn	Ni	Pb	Zn	pH	SS	TOC
October 2005										
n	3	3	3	3	3	3	3	3	3	3
Mean	5.60	8.37	4.57	114	6.00	1.89	31.6	7.3	35	21.2
SD	2.14	2.97	2.03	69	2.89	0.44	14.1	0.1	7	1.2
Min.	4.10	6.54	2.39	34.0	3.21	1.48	15.4	7.3	29	20.0
Max.	8.05	11.8	6.40	156	8.98	2.36	40.7	7.4	42	22.3
January 2006										
n	3	3	3	3	3	3	3	3	3	3
Mean	4.70	3.15	5.98	149	7.33	0.55	17.8	7.3	38	48.5
SD	1.96	1.83	6.20	5	7.60	0.21	3.3	0.1	6	3.0
Min.	3.54	1.18	1.82	144	2.66	0.39	15.5	7.2	32	45.1
Max.	6.96	4.80	13.1	153	16.1	0.79	21.5	7.4	42	50.9
June 2006										
n	4	4	4	4	4	4	4	4	4	4
Mean	10.3	11.2	8.38	116	3.36	2.84	36.1	7.6	42	10.7
SD	4.1	10.8	6.02	43	1.01	1.07	15.5	0.3	8	4.9
Min.	6.67	2.74	4.50	71.8	2.60	1.83	23.1	7.3	35	5.06
Max.	15.1	26.0	17.3	167	4.83	4.09	58.5	7.9	54	16.9
TCVN 5492-1995 A[a]	50	50 (100)	100	100	100	50	1000	6–8.5	20	–
Freshwater (world)[b]	0.5	1	3	8	0.5	3	15	–	–	–

[a] Surface water quality standard in Vietnam for water sources of domestic supply. Cr: hexavalent (trivalent)

[b] Median value for freshwater in the world (Bowen 1979)

concentrations of SS and Pb. The SS and Pb are considered to be derived from the Hong River. Nh 5 showed high scores in both factors 1 and 2 which were ascribed to high Cr, Cu, Ni, Pb, Zn and SS concentrations. Their sources would be resuspension of the surface sediment or discharge of wastewater nearby. On the other hand, stations in To Lich were characterized by high negative scores in factor 2 which were explained by high TOC. A high concentration of Cr was also detected at TL 1 and TL 4, which was reflected in high scores in factor 1. As mentioned above, wastewater discharges from the neighboring factories of leather and paint industries could be considered as ones of the pollution sources. In addition, Cr in river water of To Lich was significantly correlated with As ($r = 0.972$, $p < 0.05$) in this period, which suggests that As is discharged from the common sources to Cr. Arsenate and Arsenite are utilized in production of dyestuffs and as a preservative of leather products (Japan Environmental Sanitation Center 2005). In cluster analysis, the stations in To Lich (TL 1, TL 3 and TL 4) formed a distinct cluster which showed the highest concentrations of As, Cr, Mn, Zn and TOC among the three main clusters. Nh 5 alone formed another cluster which was explained by the highest Cu, Ni, Pb and SS contents. The other stations in Nhue were divided into two clusters: one consisted of the upstream stations (Nh 1–Nh 3) and another of the middle- and down-stream ones.

In October 2005 (the end of rainy season), Nh 4, the station just after the confluence with To Lich, had high positive and negative scores in factors 1 and 2, respectively, which was attributed to high concentrations of Cu and Zn (factor 1) and Pb (factor 2). This implies a significant contribution of the inflow of To Lich river water to the rises in concentrations of these metals in Nhue river water around the confluence point, although the concentrations of these elements at TL 4, the adjacent upstream station in To Lich from the confluence, were lower than those at Nh 4. Cluster analysis also showed that Nh 4 and the stations in To Lich (TL 2 and TL 4) formed a cluster which had the highest concentrations of the contaminants included in factor 1 as well as Pb. Scores in factor 2, for which TOC had a high loading, at Nh 5 and Nh 6 were higher than those at stations in To Lich, implying the existence of discharges of domestic wastewater and/or effluents from craft villages around these stations. The middle- and down-stream stations in Nhue, i.e., Nh 5–Nh 9, formed another cluster which was characterized by the highest concentrations of Mn and TOC. The similarity between stations in this cluster decreased in the following order: (Nh 5 = Nh 6) > Nh 7 > (Nh 8 = Nh 9).

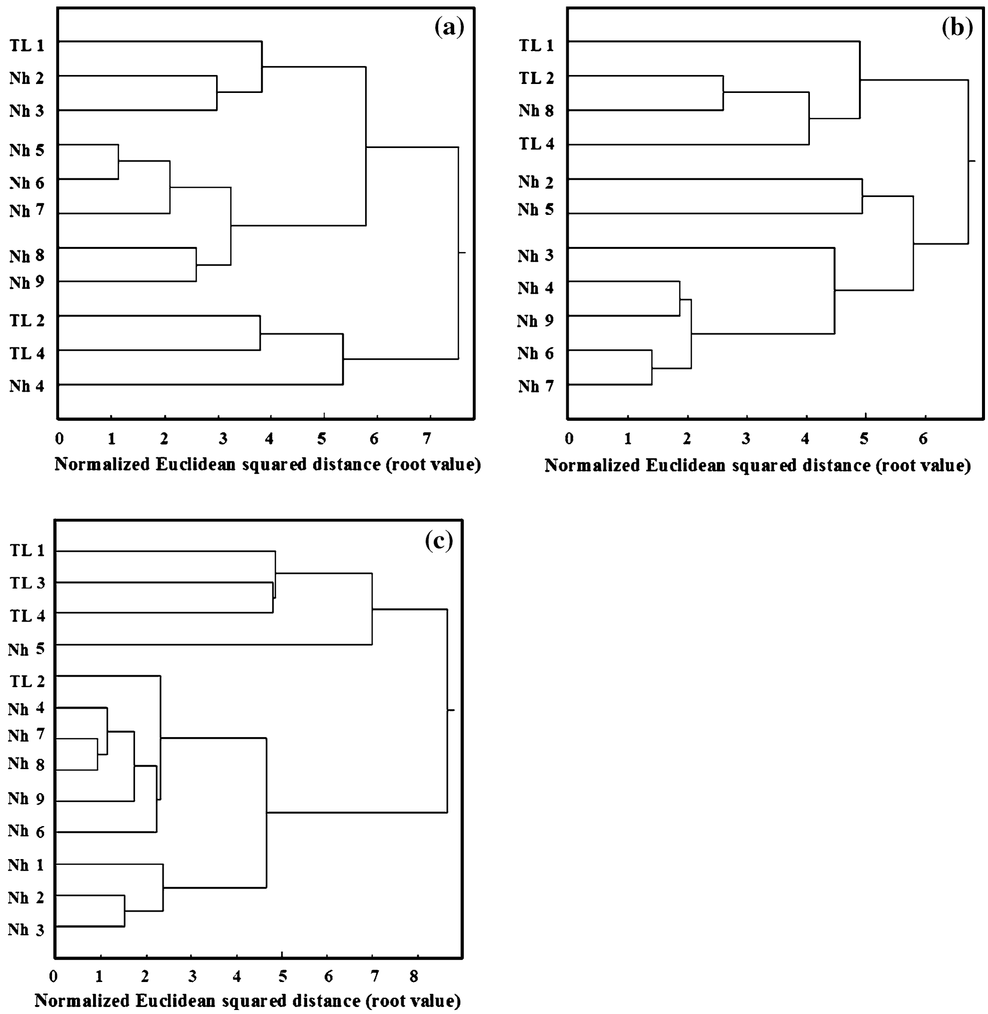

Fig. 2 Dendrograms for SS, TOC and concentrations of heavy metals in river water of the Nhue and To Lich Rivers collected in October 2005 (**a**), January 2006 (**b**) and June 2006 (**c**)

This tendency suggests that the concentrations of pollutants in river water of Nhue in the corresponding area would decrease along the direction of water flow due to the natural purification function of this river, and it was true of As, Cr, Cu and TOC.

In January 2006 (dry season), the river water of To Lich did not flow into Nhue because the water gate at TL 4 is closed during the corresponding season, and thus the contribution of To Lich river water to the water quality of Nhue can be negligible. High scores in factor 1, for which Cr, Ni and Pb had high loadings, and factor 2, which was characterized by high loadings of Cu and Zn, were characteristic of Nh 2. Nh 5 also got a high score in factor 1. In cluster analysis, these two stations formed a cluster which showed the highest concentrations of Cr, Cu, Ni, Pb and Zn. These stations could be considered to be affected by the wastewater discharged from the urbanized areas and craft villages around these stations. On the other hand, stations in To Lich in this period were characterized by high negative and positive scores in factors 1 and 2, respectively, which were ascribed to high concentrations of Mn and TOC, respectively. Cluster analysis also showed that the cluster of all the stations in To Lich and Nh 8 was characterized by the highest concentrations of As, Mn and TOC. Dissolved oxygen in river water of To Lich measured at every station in this period (an approximate value) was apparently lower than that of Nhue (data not shown). Dissolved Mn is considered to change into suspended form by forming Mn oxide with an increase of DO concentration (Saeki and Okazaki 1993), and it is thus suggested that poor DO in river water of To Lich would have kept a large portion of Mn in the water in dissolved form.

The mean water flow rate of Nhue at Nh 4 (34.6 $m^3\ s^{-1}$) was about 3 times as high as that of To Lich at TL 4 (10.7 $m^3\ s^{-1}$) in rainy season (July–October) of 1999 (JICA 2000b). In Nhue, about 70–80% of the annual total

Table 3 Factor loadings of heavy metals, SS and TOC in river water in principal component analysis (PCA)

Variable	Factor 1	Factor 2	Factor 3	Factor 4
October 2005 (the end of rainy season)				
As	**0.724**	0.483	*−0.071*	0.419
Cr	**0.637**	0.190	*−0.598*	*−0.110*
Cu	**0.692**	*−0.666*	*−0.153*	0.191
Mn	0.365	0.349	**0.804**	0.149
Ni	**0.731**	0.181	0.337	*−0.383*
Pb	0.268	***−0.923***	0.18	0.069
Zn	**0.788**	*−0.485*	0.025	0.172
SS	**0.678**	0.226	*−0.049*	*−0.550*
TOC	0.265	**0.781**	*-0.136*	0.301
Variance	3.30	2.62	1.20	0.821
Proportion to the total variance	0.366	0.291	0.133	0.091
January 2006 (dry season)				
As	*−0.303*	0.363	*−0.449*	**0.660**
Cr	**0.880**	0.131	*−0.372*	*−0.095*
Cu	0.396	**0.662**	0.559	*−0.030*
Mn	***−0.640***	0.605	0.009	*−0.078*
Ni	**0.655**	0.401	*−0.184*	*−0.571*
Pb	**0.747**	0.039	0.244	0.567
Zn	0.237	**0.895**	0.188	0.231
SS	*−0.139*	*−0.370*	**0.790**	0.000
TOC	*−0.620*	**0.704**	0.035	*−0.227*
Variance	2.88	2.55	1.41	1.20
Proportion to the total variance	0.320	0.283	0.156	0.134
June 2006 (the beginning of rainy season)				
As	**0.716**	*−0.578*	0.383	
Cr	**0.712**	*−0.352*	0.568	
Cu	**0.750**	0.404	*−0.034*	
Mn	**0.842**	*−0.081*	*−0.409*	
Ni	**0.835**	0.482	*−0.082*	
Pb	0.288	**0.867**	0.227	
Zn	**0.575**	*−0.131*	*−0.451*	
SS	0.344	**0.861**	0.107	
TOC	0.622	***−0.713***	*−0.131*	
Variance	3.91	2.88	0.928	
Proportion to the total variance	0.434	0.320	0.103	

The largest absolute value for each variable in each season and negative values are shown in bold and italic letters, respectively

water flow results from that in rainy season (VEPA (Vietnam Environment Protection Agency) 2006). On the other hand, the wastewater was proven to comprise 65.5%, 72.3% and 34.4% of the total water flow in the up-, middle- and down-stream of To Lich, respectively, in December (dry season) 1993 (JICA (Japan International Cooperation Agency) 2000a). These observations suggests that the concentrations and composition of heavy metals in river water of Nhue would be largely governed by the water flow from the Hong River, the headwater of Nhue, especially in rainy season, while those of To Lich would be greatly affected by those of inflowing domestic and industrial wastewater. This estimation would be supported by the result of cluster analysis in which the stations in To Lich tended to form a different cluster from those of the stations in Nhue in each time of sampling. Heavy metal concentrations and their composition in Nhue river water, however, would be also affected by inflowing river water of To Lich and wastewater from the urbanized areas and craft villages in the up- and middle-stream basin, and they tended to gradually recover along the direction of water flow in the downstream area in rainy season.

Table 4 Factor scores for heavy metal concentration in river water in principal component analysis (PCA)

Station	Factor 1	Factor 2	Factor 3	Factor 4
October 2005 (the end of rainy season)				
Nh 2	−2.41	−1.14	0.430	−0.189
Nh 3	−1.95	−2.24	−0.289	−0.233
Nh 4	2.32	−3.69	−0.065	0.966
Nh 5	0.168	1.86	0.273	0.629
Nh 6	−0.355	1.59	0.323	1.52
Nh 7	−1.20	1.05	−0.028	0.061
Nh 8	0.529	0.182	0.734	−0.072
Nh 9	−0.770	0.500	1.89	−0.187
TL 1	−1.85	0.476	−2.48	−0.713
TL 2	2.43	0.356	0.654	−2.15
TL 4	3.09	1.06	−1.44	0.374
January 2006 (dry season)				
Nh 2	2.58	1.56	1.35	2.34
Nh 3	−0.046	−2.70	2.08	−0.033
Nh 4	0.281	−1.81	0.070	0.009
Nh 5	3.22	0.064	−1.53	−1.48
Nh 6	0.096	−0.659	−0.671	0.169
Nh 7	0.891	−0.189	−1.21	0.138
Nh 8	−1.44	−0.843	0.498	−0.736
Nh 9	−0.842	−0.931	−0.873	0.370
TL 1	−0.050	3.20	1.34	−1.62
TL 2	−2.20	0.920	0.400	−0.545
TL 4	−2.48	1.38	−1.45	1.39
June 2006 (the beginning of rainy season)				
Nh 1	−1.17	1.39	0.625	
Nh 2	0.762	2.05	0.334	
Nh 3	−0.217	0.875	0.089	
Nh 4	−1.16	0.011	0.207	
Nh 5	3.05	3.81	0.340	
Nh 6	−2.57	−0.592	0.315	
Nh 7	−1.98	−0.550	−0.070	
Nh 8	−1.87	−0.044	0.042	
Nh 9	−1.16	0.002	−0.524	
TL 1	1.97	−3.21	2.20	
TL 2	−0.923	−0.835	−0.667	
TL 3	1.20	−1.18	−2.330	
TL 4	4.08	−1.74	−0.567	

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