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Anthropogenic Input of Selected Heavy Metals (Cu, Cr, Pb, Zn and Cd) in the Aquatic Sediments of Hochiminh City, Vietnam

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Abstract The aquatic system of Hochiminh City comprises two main rivers: the Sai Gon and Nha Be rivers. Five canals discharge into these two rivers: NhieuLoc-ThiNghe, TauHu-BenNghe, TanHoa-LoGom, ThamLuong-BenCat and Doi-Te. The rivers and these canals collect effluent water from domestic and industrial sources. Most of these flows are not treated or at most are only primarily treated. A total of 33 sediment cores were taken from these rivers and canals. Chemical composition of these aquatic sediments has very high concentrations of several "urban" metals such as Cd, Cr, Cu and Zn. Most of the samples have exceeded the US EPA's toxicity reference values for Cu, Zn and Cr (82, 82 and 70%, respectively). The highest concentrations of these metals appear to be associated with the uncontrolled and untreated industrial runoff to the discharge canals. These concentrations in fluvial sediment are relatively low, which indicates the dilution process of the contaminants. This finding indicates that the anthropogenic inputs play an important role in the elevation of heavy metals in the aquatic system and organic matter seems to exert a strong geochemical control on the amount of heavy metals. The Pearson correlation coefficients calculated for Cd, Cr, Cu and Zn, are 0.89; 0.72; 0.93 and 0.87, respectively.

Keywords anthropogenic input · aquatic sediment · heavy metal · urban area · pollution

1 Introduction

The need to gain a better understanding of the behavior of urban environments and the consequences of living within or close to a city's boundaries is clearly justified by the fact that nearly all the population growth in the next 30 years will be concentrated in the urban areas of the world (U.N. Population Division (UNPD), 2001).

Presently, one of the most concerning pollutants around the world is heavy metals. With the growing interest in the rules that govern the fate of these metallic pollutants in urban environments, the aquatic sediments pose a particularly challenging scientific problem (De Miguel, Charlesworth, Ordóñez, & Seijas, 2005). In a natural environment, urban aquatic sediments have a high potential for storage of trace elements. Unlike natural rivers, however, a large proportion of the trace element load contained in urban sediments is not associated with the original geologic parent material, but with the steady supply

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of trace elements, both dissolved and in particulate form, carried by treated and untreated urban wastewaters. Especially in developing countries like Vietnam, the urban wastewaters also include wastewater from industries, hospitals and agricultural activities. Thus, these trace elements are released and accumulated in the aquatic sediment over long periods of time (Thuy, Tobschall, & An, 2000). The linkage between the concentration of toxic elements in the sediment and ecosystem health explain the growing interest and the consequent rapid increase in scientific publications dealing with metals in fluvial sediments (Sutherland, 2000).

The fast economic and industrial growth has caused a negative impact on the environmental quality of the Hochiminh city. The urban river systems in Hochiminh City are Sai Gon and Nha Be rivers. Five canal tributaries, NhieuLoc-ThiNghe, TauHu-BenNghe, TanHoa-LoGom, Doi-Te, ThamLuong-BenCat drain into these rivers. The aquatic system extends over very densely populated areas and is subject to intensive exploitation. Such activities result in the introduction of potentially hazardous levels of heavy metals into the riverine ecosystem. The discharge volume per day is estimated at 600.000 m^3 for domestic and 43.300 m^3 for industrial wastewaters, respectively (Triet, 2000). There are more than 700 medium and 22,000 small enterprises. The pollutants are released from different industries such as: knitting, paper production, rubber production, electroplating and other activities (Anh et al., 2003). The main pollutant sources of each river/canal could be summarized as follow:

- *Sai Gon River*: This river receives domestic wastewater from the city and surrounding area. This is also the source for the water supply for the city. Recently the river has been contaminated especially by the untreated industrial wastewater.
- *Nha Be River*: Wastewater from the canals of the Nha Be and Binh Chanh districts drain in to this river. There is an industrial zone of 18 enterprises located in the Nha Be district.
- *Doi-Te canal*: the pollutant sources are domestic and industrial wastewaters from residential area of District 8, small enterprises and ship repairing workshops. In addition, the wastewater from the different hospitals located in the District 5 is also a pollutant source.
- *Nhieu Loc-ThiNghe canal* is polluted mainly by domestic wastewater.
- *TauHu-BenNghe canal* is polluted by both domestic and industrial wastewater from small enterprises and the cottage handicraft industries.
- *TanHoa-LoGom canal* is one of the most polluted canals with the wastewater from an industrial zone of 34 factories. Small enterprises densely locate along the canal.
- *ThamLuong-BenCat canal* receives the discharge water from Tan Binh industrial zone and other factories. The domestic wastewater is also the source of contamination of these canal.

The present study is the first stage of a program to study an on-site phytoremediation procedure for the treatment of the contaminated aquatic system in Hochiminh city. An overall evaluation of sediment quality for the metallic contaminants was investigated. The distribution of heavy metals and the correlation with the geochemical parameters are also discussed with respect to their environmental significance and implications.

2 Materials and Methods

According to the previous study (Maqsud, 2004; Triet, 2000), 33 sediment samples were collected from most polluted sites of Nha be, Saigon rivers and their tributaries. The sampling of the rivers and channel was carried out in April and October 2005, respectively (Fig. 1). Surface core samples (0–30 cm) were taken with hand augers. To avoid contamination, all of the equipment used was plastic. The samples were stored and kept at 4°C until analysis. The geochemical parameters such as pH, redox-pontential (Eh), electricity conductivity (EC), dissolved oxygen (DO) and temperature were measured in situ. In the laboratory, grain size distribution of the representative sediment was studied to assess the clay content.

For trace metal studies, size fraction <63 μm is the most commonly recommended size because trace metals are often found mainly in clay/silt particles. In addition numerous metal studies were done in the <63 μm fraction, allowing better comparison of results. (Salomons & Förstner, 1984). Therefore, the samples were separated by wet sieving for the present

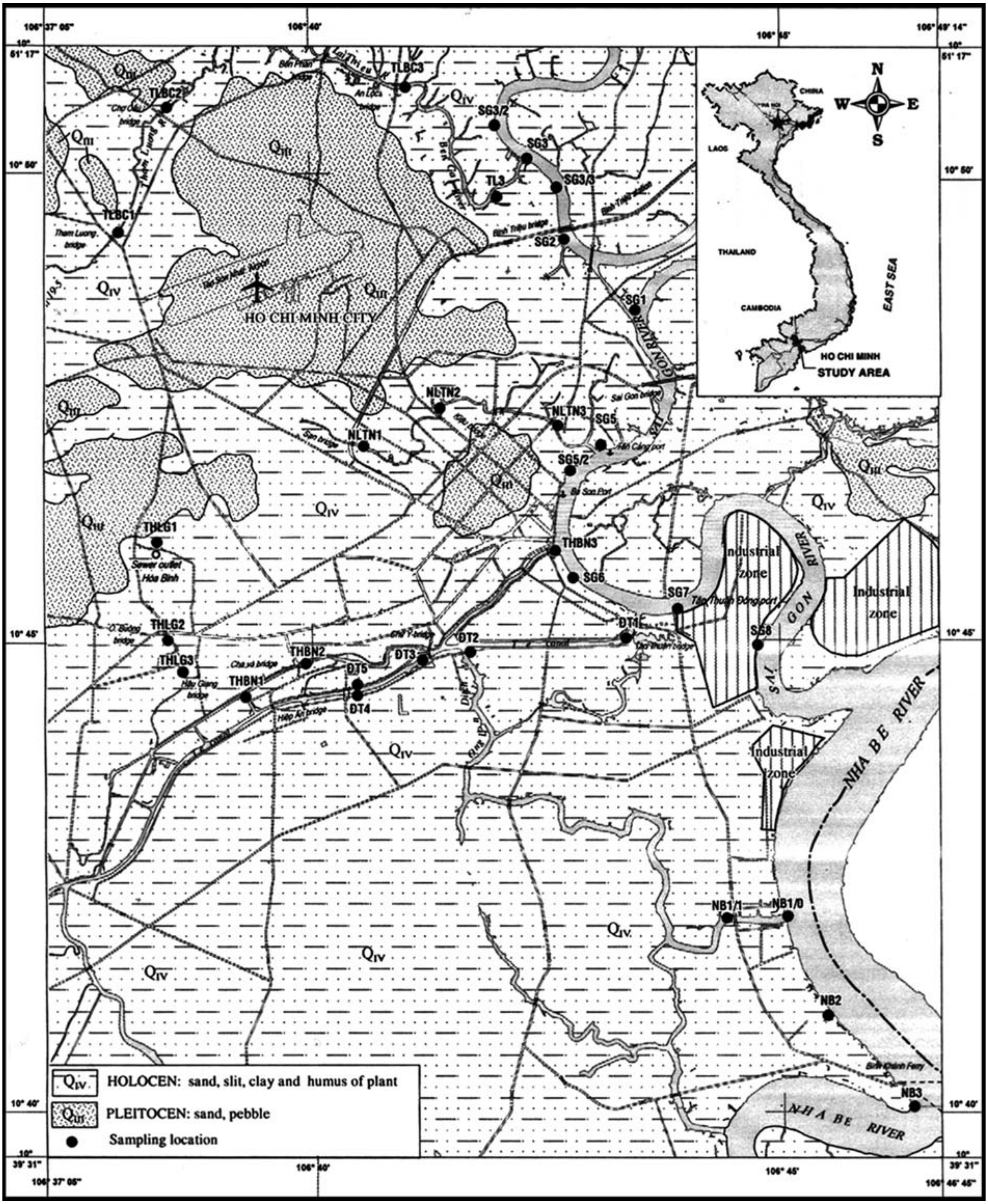

Fig. 1 The study area

study since sieving does not alter metal concentrations. The <63 μm fraction was extracted for further chemical analyses.

For chemical analysis, sediment samples were dried at 45°C. For total digestions, c.a. 5 g of sample material was heated with 15 ml HCl and 5 ml HNO_3 in the glass flask for 2 h. All trace metals were determined by flame atomic absorption spectrophotometer (AAS), model Analyst—300 PERKIN ELMER—USA. The organic matter content of the sediment was determined using the Tiurin method.

3 Results and Discussion

The geochemical parameters and analytical results are summarized in Tables 1 and 2. The concentrations for major elements are given in percentages, whereas for the heavy metals they are in mg/kg.

3.1 Geochemical Parameters

The rivers and their tributaries are characterized by the similar pH of nearly neutral. The average pH ranges between 6.68 (Sai Gon river) and 7.00 (Nha Be river). The other parameters such as DO, Eh, EC, TDS showed the variety between the studied locations, which indicate the wide range of the geochemical condition. The lower values of dissolved oxygen (DO) are observed in the canals, whereas the Sai Gon and Nha Be rivers have normal levels (Table 1). In particular, the TanHoa-LoGom has the lowest concentration of dissolved oxygen (0.06–0.16 mg/l), which indicates the highest pollution environment.

3.2 Organic Matter

The organic matter contents varied between the rivers and canals. In general, the sediments collected from the tributaries are enriched in OM as compared with fluvial sediment. The maximum value of 17.2 mg/kg is observed at TanHoa-LoGom canal (site TH-LG3), whereas the minimum value is measured at Nha Be river. According to the average mean, sediments collected from NhieuLoc-ThiNghe and TanHoa-LoGom contain elevated levels of organic matter as compared to other canals.

3.3 Chemical Composition

Similar to organic matter content, the heavy metals are also highest in canal sediments. The reason is the dilution of the contaminants in the Sai Gon and Nha Be rivers. Among the canals, TanHoa-LoGom canal is characterized by the elevated concentrations for Zn, Cr and Cu. The highest concentrations of Zn (4.026 mg/kg); Cr (2.290 mg/kg) and Cu (1.033 mg/kg) were found at the site TH-LG 3. Cd is also highest at that site (11.47 mg/kg). This elemental association is characteristic of urban particulate materials (soil and street dust), but also of discharges from several small electroplating factories. The TauHu-BenNghe canal (TH-BN2) is marked by high concentrations of Cu (217 mg/kg); Zn (854 mg/kg) and Cr (1.800 mg/kg). This is a sewer outlet, where the contaminants accumulate preferentially.

Although direct comparisons of the results of different investigations are complicated by the disparity in sampling locations, digestion procedures of the samples and the intensity of industrial discharges into

Table 1 In situ measured geochemical parameters

River/canal	pH	DO (mgO2/l)	Eh (mV)	Ec (mS/cm)
Nha Be river	(6.93–7.06)[a] 7.00[b]	(7.06–7.66) 7.31	((−8.0)–10) 2.75	(7.47–14.7) 11.9
Sai Gon river	(6.50–6.99) 6.68	(3.21–6.41) 4.05	((−12.0)–(−8.0)) −8.50	(6.26–12.7) 7.82
Doi-Te canal	(6.72–6.86) 6.82	(0.22–2.64) 1.89	(1.0–9.0) 3.25	(1.48–13.2) 9.40
NhieuLoc-ThiNghe canal	(6.55–6.69) 6.64	(0.07–4.42) 1.53	(10.0–19.0) 13.67	(0.60–8.47) 3.22
TauHu-BenNghe canal	(6.82–6.92) 6.86	(0.11–5.61) 1.96	((−3.0)–3.0) 0.67	(0.70–8.10) 3.44
TanHoa-LoGom canal	(6.64–6.85) 6.71	(0.06–0.16) 0.10	(0.0–16.0) 10.33	(0.86–1.14) 0.95
ThamLuong-BenCat canal	(6.48–7.05) 6.90	(0.05–3.47) 1.40	((−40)–2.0) −17.33	(0.50–6.21) 2.89

[a] minimum–maximum values

[b] arithmetic mean

Table 2 The chemical composition of aquatic sediments, compared with previous studies

River/canal	OM	Al	Fe	Mn	Cu	Pb	Zn	Cr	Cd
Nha Be river	(2.65–4.11)[b]	(14.8–19.8)	(5.21–7.75)	(0.01–0.07)	(11.9–25.1)	(2.59–28.6)	(68.5–256)	(18.9–32.6)	(0.07–0.09)
	3.25[c]	18.0	6.41	0.04	16.8	14.5	137	26.6	0.08
Sai Gon river	(3.12–5.26)	(17.4–20.1)	(3.14–8.30)	(0.01–0.12)	(14.3–58.8)	(3.31–63.1)	(79.8–237)	(19.5–41.5)	(0.03–0.24)
	3.96	19.0	6.13	0.06	31.6	23.8	157	28.0	0.10
Doi-Te canal	(2.55–4.09)	(17.0–21.0)	(5.90–9.34)	(0.04–0.08)	(23.3–57.2)	(5.55–33.9)	(128–243)	(24.1–41.5)	(0.04–0.08)
	3.50	19.2	6.92	0.06	42.2	18.0	195	28.6	0.06
NhieuLoc-ThiNghe canal	(3.46–10.48)	(14.9–20.2)	(4.49–6.46)	(0.04–0.06)	(30.7–304)	(19.9–117)	(349–1.453)	(25.1–85.9)	(0.04–2.10)
	7.78	17.5	5.48	0.05	188	52.3	761	53.2	1.35
TauHu-BenNghe canal	(5.24–6.67)	(18.9–19.4)	(5.35–5.98)	(0.04–0.07)	(98.8–218)	(7.16–20.8)	(405–854)	(82.6–1.800)	(0.03–0.14)
	6.00	19.1	5.67	0.06	154	12.8	627	710	0.07
TanHoa-LoGom canal	(4.70–17.2)	(10.2–18.1)	(4.11–5.89)	(0.02–0.04)	(37.1–1.300)	(5.95–30.2)	(423–4.026)	(30.8–2.290)	(0.04–11.47)
	9.63	13.3	5.00	0.03	404	16.5	2183	805	4.31
ThamLuong-BenCat canal	(3.97–5.57)	(18.0–20.0)	(3.55–7.90)	(0.02–0.12)	(21.7–81.5)	(1.78–29.9)	(83.9–943)	(24.9–35.7)	(0.07–0.24)
	4.65	19.1	5.72	0.06	37.2	10.4	291	30.0	0.14
Previous studies[a]									
NhieuLoc-ThiNghe canal					(30–150)	(25–210)	(91–205)	(65–100)	(0.4–3.0)
TanHoa- LoGom canal					(80–512)	(95–210)	(110–685)	(120–295)	(1.8–5.0)
Kinh Doi-Kinh Te-Tau Hu-Ben Nghe canal					(90–300)	(25–195)	(85–490)	(65–150)	(1.5–2.8)

The concentration of major elements and organic matter (OM) are given in %, whereas the trace elements in mg/kg;

[a] Maqsud (2004)

[b] minimum–maximum values

[c] arithmetic mean

the river, the concentrations of heavy metals in NhieuLoc-ThiNghe and TanHoa-LoGom seem to fall into the range reported by the previous study of Maqsud (2004). The exception is for an elevated content of Zn. The reason is the additional anthropogenic sources of Zn. In contrast, the measured level of Pb was relative low.

Since no national standard is available, international reference values were used to assess the ecotoxicological risk of the studied metals (Table 3). The measured concentrations of Cu and Zn (82% of the total samples) as well as Cr (70% of the total samples) are higher than the US EPA's toxicity reference values (US Environmental Protection Agency, 1999), with some exceptions in the Nha Be and Sai Gon rivers. According to the mean concentrations, all of the rivers and canals are polluted with Cu, Cr and Zn. In contrast, the concentration of Pb and Cd are relatively low, but the maximum values also exceeded the corresponding value. Similarly, most of the Canadian Sediment Quality Guidelines are exceeded for Zn and Cu (Environment Canada, 2002). The number of samples that have higher concentration than the respective Probable Effect Levels (PELs) are Cu, at 12% and Zn, at 30%. Particularly, all of the samples from TanHoa-LoGom are even higher than the respective PELs. The mean Cu, Zn and Cr concentrations in the TauHu-BenNghe canal are elevated compared to PEL.

According to the sample location, the elevated levels of "urban" elements Cu, Cr, Cd and Zn are associated with the direct supply of untreated urban and industrial runoff. Thus, it could be concluded that the anthropogenic inputs have caused the elevation of Cu, Cr and Zn in the aquatic sediment of Hochiminh City.

The correlation matrix of heavy metals, organic matter and major elements has shown that the heavy metals are well correlated (Cu–Cd: 0.97, Cr–Cd: 0.75, Zn–Cd: 0.89, Cr–Cu: 0.83, etc.). This indicates that these contaminants are released from the same sources. The organic matter contents and heavy metals (Cu (r=0.93), Cr (r=0.72), Cd (r=0.90) and Zn (r=0.87)) have shown the significant correlation coefficient (Table 4). Thus, the organic matter plays an important role in the distribution of heavy metals in the aquatic system.

In order to describe and interpret the results of multiple chemical variables better, a number of multivariate statistical techniques were employed, i.e. Hierarchical Cluster Analysis and K-means Cluster Analysis. Since the metal concentrations show strongly asymmetrical distribution, the data was transformed to the natural logarithms except for pH, before performing statistical calculations.

Hierarchical Cluster Analysis brings together similar sampling points in terms of natural or anthropogenic sources of elements. The pH and the contents of major, trace elements and organic matter of aquatic sediments

Table 3 Comparative present study with toxicological reference values

River/canal	Cu	Pb	Zn (mg/kg)	Cr	Cd
Nha Be river	(11.9–25.1) *16.8*	(2.59–28.6) *14.5*	(68.5–256) *137*	(18.9–32.6) *26.6*	(0.07–0.09) *0.08*
Sai Gon river	(14.3–58.8) *31.6*	(3.31–63.1) *23.8*	(79.8–237) *157*	(19.5–41.5) *28.0*	(0.03–0.24) *0.10*
Doi-Te canal	(23.3–57.2) *42.2*	(5.55–33.9) *18.0*	(128–243) *195*	(24.1–41.5) *28.6*	(0.04–0.08) *0.06*
NhieuLoc-ThiNghe canal	(30.7–304) *188*	(19.9–117) *52.3*	(349–1.453) *761*	(25.1–85.9) *53.2*	(0.04–2.10) *1.35*
TauHu-BenNghe canal	(98.8–218) *154*	(7.16–20.8) *12.8*	(405–854) *627*	(82.6–1.800) *710*	(0.03–0.14) *0.07*
TanHoa-LoGom canal	(37.1–1.300) *404*	(5.95–30.2) *16.5*	(423–4.026) *2183*	(30.8–2.290) *805*	(0.04–11.47) *4.31*
ThamLuong-BenCat canal	(21.7–81.5) *37.2*	(1.78–29.9) *10.4*	(83.9–943) *291*	(24.9–35.7) *30.0*	(0.07–0.24) *0.14*
Reference values					
Canadian EQG[a]					
Interim sediment quality guideline	35.5	35	123	37.3	0.6
Probable effect level	197	91.3	315	90	3.5
US EPA[b]					
Toxicity reference value	16	31	110	26	0.6

In brackets: minimum–maximum values; In italic: arithmetic mean

[a] Environment Canada (2002);

[b] US Environmental Protection Agency (1999)

Table 4 The Pearson correlation matrix for the aquatic sediments

N=33	Cd	Cr	Cu	Fe_2O_3	MnO	OM	Pb	Zn
Cd	1.00							
Cr	0.75[a]	1.00						
Cu	0.97[a]	0.83[a]	1.00					
Fe_2O_3	−0.09	−0.08	−0.12	1.00				
MnO	−0.13	−0.11	−0.14	0.70[a]	1.00			
OM	0.90[a]	0.72[a]	0.93[a]	−0.20	−0.22	1.00		
Pb	0.07	0.05	0.04	0.09	0.05	0.01	1.00	
Zn	0.89[a]	0.74[a]	0.92[a]	−0.26	−0.28	0.87[a]	0.06	1.00

N number of samples

[a] Correlation is significant at the 0.01 level (two-tailed)

from Hochiminh city are taken for Hierarchical Cluster Analysis. The aquatic sediments of Hochiminh city showed three main groups of samples including one completely separate from site TH-LG3 (Fig. 1). Two distinct clusters A and B are at about 60% of distance linkage distances. The three groups of samples are divided base on the concentration of heavy metals. The site TH-LG3 is characterized by the highest concentration, followed up by samples of Cluster A and Cluster B. The site TH-LG 3 is collected from TanHoa-LoGom canal, which is strongly affected by the wastewater from small-scale electroplating and mechanical activities.

The cluster A composes the sample sites taken from TauHu-BenNghe and most samples from Tan-Hoa-LoGom, ThamLuong-BenCat and NhieuLoc-ThiNghe canals. All of the samples of the Saigon and Nhabe rivers as well as Doi-Te canals are grouped together (Cluster B), with some exceptions of NhieuLoc-ThiNghe, TanHoa-LoGom and ThamLuong-BenCat canals (Fig. 2).

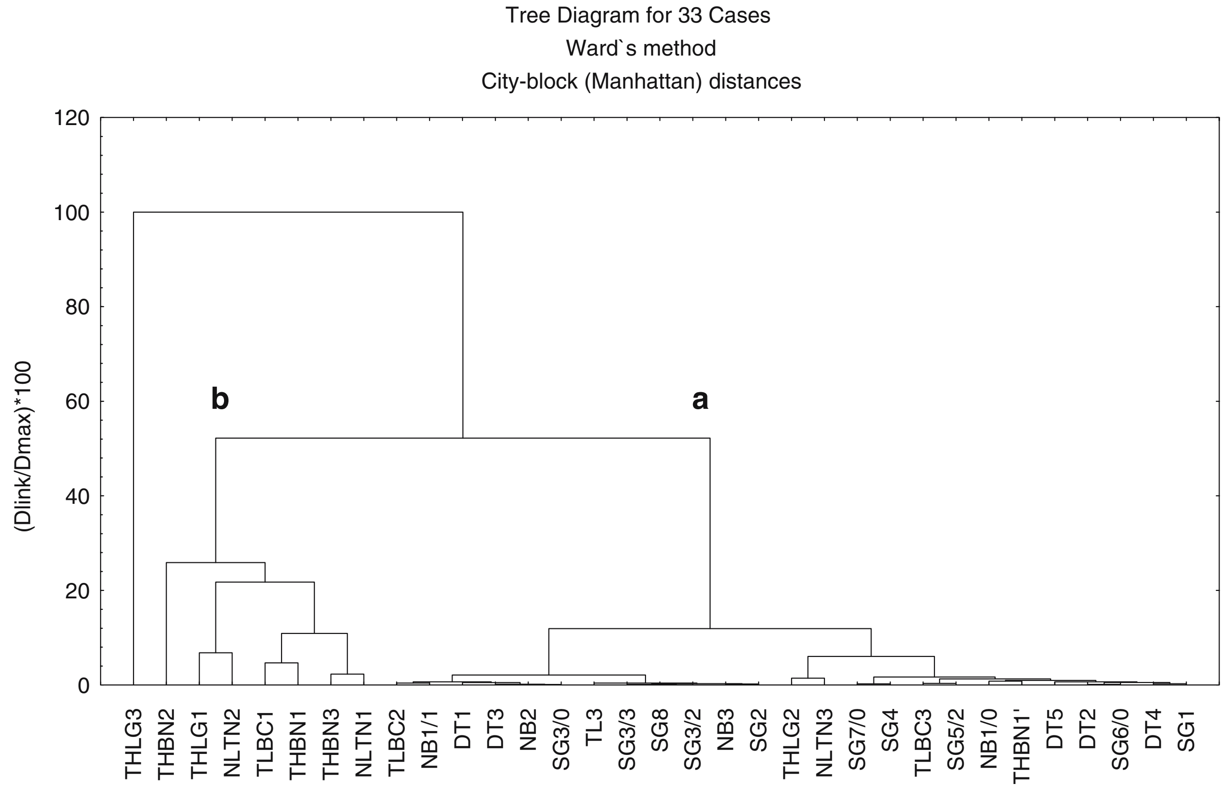

Fig. 2 Results of Hierarchical Cluster analysis for aquatic system. The variables are Al, Fe, Mn, Cd, Cr, Cu, Pb, Zn, OM and pH. Scale tree to dlink/dmax × 100

Geologically, according to Fig. 1, the samples are taken from Holocene sediments (Q_{IV}). Thus, the elevation in heavy metal contents in site TH-LG3 and Cluster A are due to anthropogenic inputs. This statement is confirmed by the pollutant sources of wastewater containing heavy metals from electroplating factories, mechanic works and other activities. In contrast, the sediment of Saigon and Nhabe rivers and Doi-Te canal illustrates the "natural" or "geologic background."

In addition, K-mean Cluster analysis for aquatic sediment systems are further analysed to quantify the difference between anthropogenic and natural groups. The result of K-mean Cluster analysis for major and trace elements and organic matter in three groups are given in Table 5. The "anthropogenic" group is composed of Cluster 1 and 2. The "heavily polluted" sample (TH-LG3) forms a group – Cluster 1 – of its own, while the less polluted samples of TanHoa-LoGom, TauHu-BenNghe and NhieuLoc-ThiNghe are reunited in Cluster 2. The Cluster 3 composed of remaining "natural" samples. The dissimilar nature of the sediments in the "natural" and "anthropogenic" reaches is manifested in the wide range of average concentrations of anthropogenic elements for all groups. For example, enrichment factors between "polluted" and "natural" (Cluster 2 vs. Cluster 3) is 4, 6, 12 and 7 for Cu, Zn, Cr, and Cd, respectively. The average content of organic matter is also elevated in the "polluted" Cluster. Especially, the "heavily polluted" Cluster showed maximum enrichment factor in comparison with "natural" Cluster (Cu: 22; Pb: 1.5; Zn: 19; Cr: 57 and Cd: 98). In contrast, the concentrations of "geogenic" or "natural" elements (Pb, Fe, Mn and Al) were fairly uniform in all clusters.

This primary study has showed the elevated concentration of Cu, Cr and Zn in the aquatic sediment of Hochiminh city. The second phase of this project aims to evaluate the metal bioavailability and mobility in the aquatic sediment i.e. to assess the percentage of metal that can be absorbed by plants (biological uptake). It is expected that this project will provide valuable information relating to the phytoremediation of the contaminated aquatic system, which will be useful in the design of full-scale treatment technology for the discharge canals.

4 Conclusion

The canal systems of Hochiminh city is polluted with toxic heavy metals (Cu, Cr and Zn), especially in the case of TanHoa-LoGom, TauHu-BenNghe and NhieuLoc-ThiNghe canals. Heavy metal distribution in the aquatic sediments shows a superimposition of anthropogenic inputs, in the form of untreated urban and industrial wastewaters. The anthropogenic inputs caused an enrichment of "urban" elements like Cu, Cr, Zn and to a lesser extent of Cd, individual elements of which show maximum enrichment factors from 19 to 98. Hence, toxicological threshold levels of those "urban" elements are exceeded and raise concerns about latent adverse effects on aquatic ecosystems and public health. Thus, a treatment protocol is required and the application of "the green technology" like phytoremediation is anticipated. Therefore, the second phase of the present study will aim at the mobility and phytoavailability of selected metals in the aquatic sediment. Such information is valuable to design the full scale phytoremediation

Table 5 Arithmetic means, of three clusters resulting from a K-mean cluster analysis

Element	Cluster no. 1	Cluster no. 2	Cluster no. 3	Enrichment factor cluster 1/3	Enrichment factor cluster 2/3
Al	12	16	19		
Fe	5.9	4.4	6.2		
Mn	0.040	0.025	0.057		
Cu	1,033	187	46	22	4
Pb	30	16	21	1	1
Zn	4,026	1,338	214	19	6
Cr	2,290	495	40	57	12
Cd	11	0.929	0.128	90	7

Values are given as percentages (%) for major elements and mg/kg for trace elements system to reclaim the heavy metals polluted aquatic sediment.

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