Trace element distributions in aquatic sediments of Danang – Hoian area, Vietnam

H.T.T. Thuy · H.J. Tobschall · P.V. An

Abstract Distribution of the trace elements Cr, Cu, Ni, Pb and Zn in surficial sediments of the river/sea environment in Danang – Hoian area (Vietnam) was investigated to examine the degree of metal pollution caused by anthropogenic activities. Point sources from domestic and industrial wastes are identified as dominant contributors of trace element accumulation. Surficial sediments of Hoian River show extremely high total concentrations of Cu (Average Concentration 295 μg/g), Ni (AC 112 μg/g), Pb (AC 396 μg/g) and Zn (AC 429 μg/g) that exceed assigned safety levels ER-M. Similarly, the sediments of Han River show high Pb (AC 188 μg/g) and Zn (AC 282 μg/g) contents. In marine sediments of Thanhbinh beach Pb is also enriched (138 μg/g) above guideline levels. In contrast the sediments of the Cude River are dominated by trace element concentrations close to background values.

Key words Trace element · River sediment · Marine sediment · Anthropogenic impact · Vietnam

Introduction

In urban areas industrial and domestic wastewater introduces various types of pollutants such as toxic metals which often cause serious damage to aquatic and other environmental systems. The Danang – Hoian region is a developed urban area in central Vietnam that is densely populated (about 4000 people per km^2 in Danang city and 400–3800 people per km^2 in Hoian – Dienban). Some of the large industrial zones of the region such as Hoakhanh and Kimlien are located in the Danang city. Chemical, metal processing factories and cement factories are the major industries, and they are found in these industrial zones. In addition, Hoian is one of the attractive tourist cities of Vietnam. Recently, along with the development of the urban area, special attention has been paid to waste disposal problems in Danang – Hoian area (Binh 1995; Lien and others 1992). Due to the lack of treatment plants and the rather old sewage system, the domestic and industrial wastewater is normally discharged directly into soils and surface waters and this causes environmental pollution. Figure 1 shows selected sewage outfalls in the Danang – Hoian area. High levels of trace elements detected in the aquatic system have raised serious concerns regarding public health. However, little has been published about the distribution of trace elements in surficial sediments in relation to anthropogenic sources in the Danang – Hoian region. The present work addresses the distribution of trace elements in the surface sediments of the Danang – Hoian region (Vietnam) and examines the impact of anthropogenic sources introduced into this region. This information will be useful in management and suitable development of the area.

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Methodology

Aquatic sediment samples (0–30 cm) were collected from Cude, Han and Hoian Rivers as well as Thanhbinh Beach (Fig. 1). The samples were taken from discharge canals and allied receiving water bodies. About 0.5 kg of sediment samples were collected from each sampling station and transferred into polyethylene bags. They were dried at ambient room temperature and stored in the dark. Subsequently, the sediment samples were transported to Germany for further analysis. Thereafter, the samples were oven dried at a temperature of 40 °C until a stable weight for analyses was reached. The samples were sieved through a 63-μm, nylon sieve to prevent possible stripping of trace elements from sediments. The silt and clay fractions of selected samples were further separated by sedimentation (Atterberg method). The content of total organic carbon (TOC) was determined using the titration method of Gaudette and others (1974) in order to find out the presence of absorbing organic ligands, which can

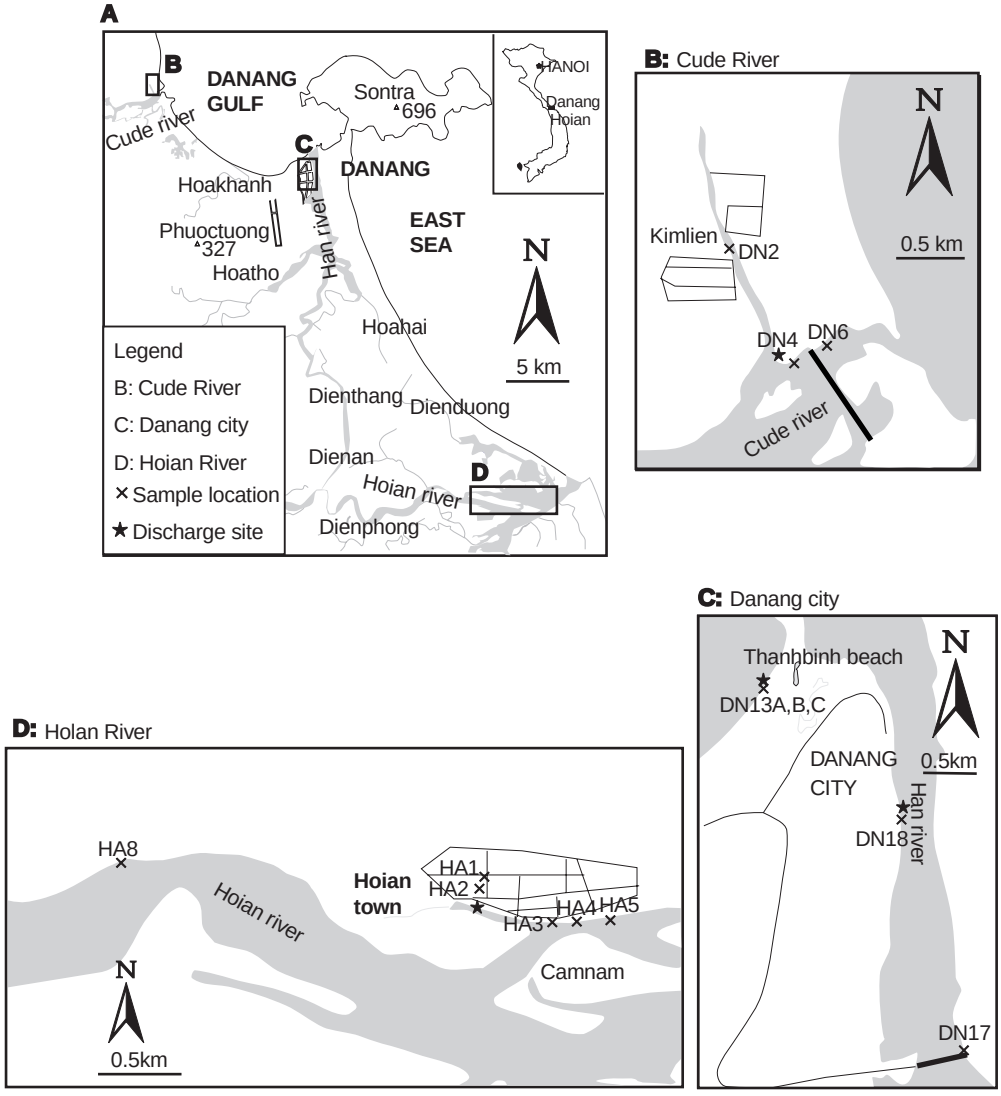


Fig. 1
Sample locations in Danang – Hoian area (Vietnam). Map **A** shows the regional setting of sampling area. Maps **B**-**D** are zoomed views of sampling sites. In Cude, Han Rivers and Thanhbinh Beach water and sediments were collected from the same locations. For Hoian River, water samples were collected from sites *HA1*, *HA2* and *HA4*

bind trace elements to sediment particles. For the metal analysis, about 0.1 g of sediment sample was digested using a combination of concentrated acids of HF–HNO_3–$HClO_4$ (Heinrichs and Herrmann 1990). Metal concentrations (Cr, Cu, Ni, Zn, Pb, Al, Fe and Mn) were determined by ICP-OES. The accuracy of the data lies within ±10% for all elements. The precision (Relative Standard Deviation, RSD in %) of the digestion method used for metal determination in sediments was calculated by the analysis of reference sample SARM 51 digested ten times. The RSD for all elements lies within ±10%. The precision of instrumental techniques ICP-AES and AAS lies within ±10% for all of elements.

Results and discussions

Grain size distribution

Figure 2 illustrates the grain size distribution of river and sea sediments of the Danang- Hoian area. Fine grains dominate the sediment of Hoian River as compared to other fluvial and marine sediments. The marine sediment from the Thanhbinh Beach exhibits a coarse texture, which contains more than 99% of sand. The domination of the coarse texture of Han River can be explained by the influence of marine activities. Because of its drainage pattern (south–north direction) the river is strongly effected by activities of the East Sea as compared to Cude and Hoian River (west–east direction). The fine grains are carried by sea waves to the East sea, and the sediments of Han River therefore are characterized by a coarse texture.

Description of metal distributions in river and marine sediments of Danang- Hoian area

The activities of rivers are strongly affected by marine processes, as illustrated by the increasing salt concentration of waters in the estuarine area. Higher salt levels are observed in Cude (20 g/l) and Hoian (25 g/l) estuaries, whereas the lower levels (0.1–0.5 g/l) are observed in the inland part of the rivers (Binh 1995). Similarly, as a result

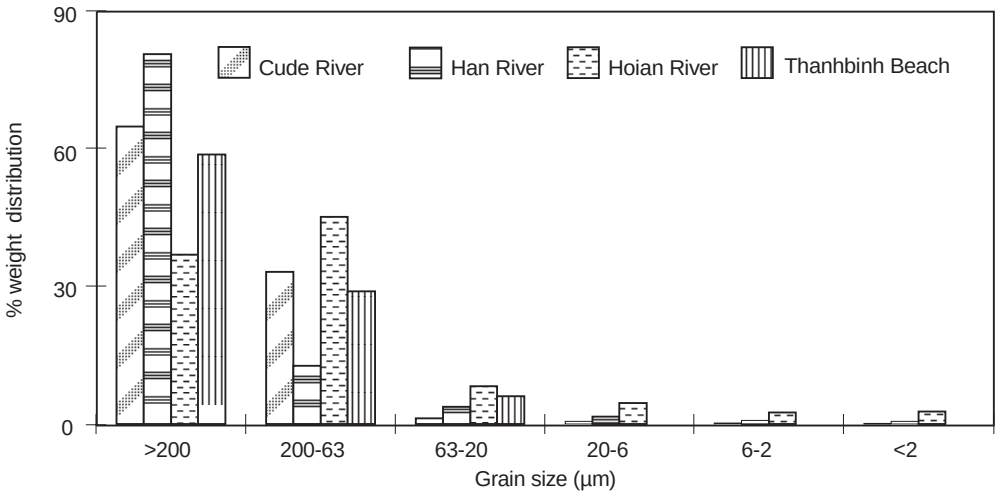


Fig. 2
The percent weight distribution of different grain sizes in Cude, Han, Hoian Rivers and Thanhbinh Beach

of tidal activities, the waters are characterized by the Cl-Na type, which contains 1700–2600 mg/l Cl^-. Otherwise, the less affected waters show the Cl-HCO_3 type. Sediment metal and TOC concentrations of Cude, Han and Hoian Rivers and Thanhbinh Beach are summarized in Table 1.

Cude River is located in the northern of part of Danang City with a catchment area of 1200 km^2. The river originates from the western mountain then flows through Kimlien industrial zone before falling into Danang Gulf. The main tributaries of Cude River are the North and South Rivers. Cude River serves as an irrigation water supply and for transport facilities. The river section in Kimlien domain was selected for the present study since the waste from local industries influences the surface water quality. The catchment area of the study section is characterized by quaternary clastic rocks, which consist primarily of fluvial, marine and mixture of both facies. The water of Cude River is alkaline with a pH of 7.6 (Fig. 3). The increase of pH in river water is probably due to the mixing of seawater from the Danang gulf. The Eh strongly decreases in the river water (Eh –37.8 mV) as compared to canal water (Eh 27.1 mV). Theoretically, the Eh determines the distribution of all redox equilibria but unfortunately the Eh cannot be measured unambiguously in most natural waters. There are two reasons for the

Table 1
Concentrations of metals and TOC in sediments (fraction <63 μm) of the rivers and a beach of Danang – Hoian area (Vietnam)

Element		Study area				ER-M[b]
		Cude River	Han River	Thanhbinh Beach	Hoian River	
Cr	Range (μg/g)	62–95	50–98	78–1005	111–251	–
	Mean	75	74	484	160	
Cu	Range (μg/g)	66–106	107–299	62–344	91–983	390
	Mean	75	203	166	295	
Zn	Range (μg/g)	38–85	184–380	43–266	<1.1[a]–914	260
	Mean	61	282	177	429	
Pb	Range (μg/g)	<4.8[a]–103	47–330	<4.8[a]–133	114–832	110
	Mean	n.d	188	n.d	396	
Ni	Range (μg/g)	<1.0[a]–62	<1.0[a]–49	<1.0[a]	22–154	50
	Mean	n.d	n.d	n.d	112	
Al_2O_3	Range (μg/g)	6.3–8.0	0.3–6.6	3.2–7.2	2.4–8.5	–
	Mean	7.0	3.5	5.3	6.0	
Fe_2O_3	Range (μg/g)	3.4–5.0	0.7–6.2	3.8–18	0.7–13	–
	Mean	4.2	3.5	9.7	6.2	
MnO	Range (μg/g)	0.04–0.10	0.01–0.13	0.04–0.71	0.01–0.12	–
	Mean	0.06	0.07	0.34	0.70	
TOC	Range (μg/g)	1.4–5.3	1.0–1.5	0.2–1.0	1.6–9.1	–
	Mean	3.0	1.2	1.2	3.8	

[a] detection limit
[b] Effects Range-medium, a value above which effects are frequently, or always observed as predicted amongst most species (Long and Morgan 1990)

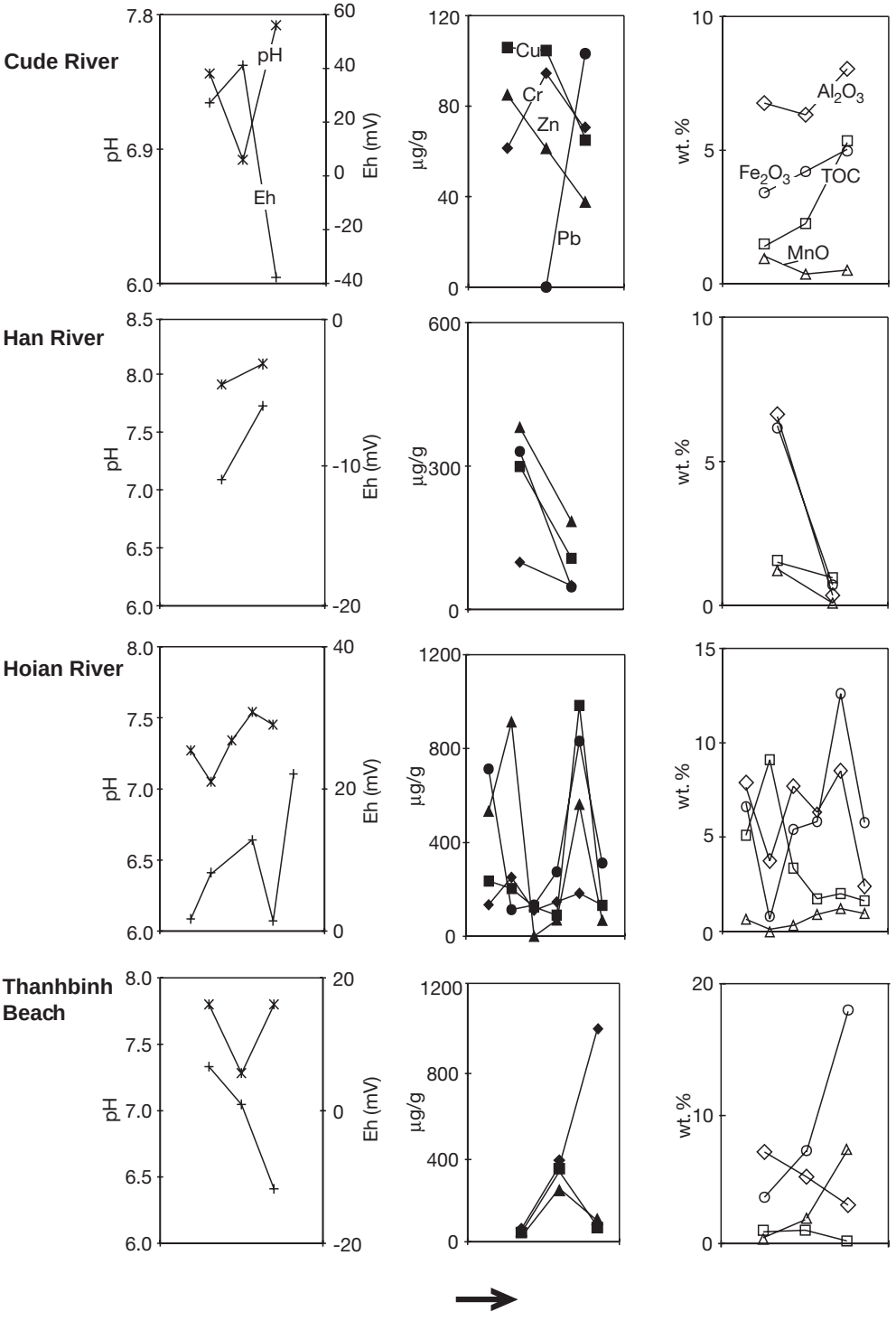


Fig. 3
Variation of pH, Eh, TOC and trace metals in rivers and beach of Danang – Hoian area (Vietnam). TOC and trace metal analyses were done on sediments (fraction < 63 µm). Refer to Methodology and Fig. 1 for detail of sampling locations. *Arrow* indicates the water flow direction

large discrepancies: lack of equilibrium between different redox couples in the same water sample and analytical difficulties in measuring with Pt-electrode. However, the Eh measurements provide reproducible results when the redox conditions are controlled mainly by Fe^{2+}/Fe^{3+} (Singer and Stumm 1970). For trace elements Cu, Zn and Mn show similar distribution patterns, which are enriched in the sediment of the discharge canal. It suggests anthropogenic inputs of these metals. On the contrary, Ni, Al, Fe and TOC are increased in fluvial sediments reflecting a geological origin. Cr shows elevation (95 µg/g) at the channel outlet.

The Han River has been formed from various tributaries as Tuyloan, Vinhdien, Yen and Ainghia. The Han's course runs through whole urban area of the Danang-Hoian region. The catchment of the river is characterized by the presence of recent sediments (quaternary sediments). The river is intensively exploited for water supply (drinking and irrigation) and transport. The water levels of river are largely dependent on tidal levels. Water of

Han River is alkaline (pH 8.0) and Eh ranges between –6.2 (DN17) and –11.3 mV (DN 18). The mixing with sea water causes the increase of pH in Han River as compared to Cude River and the metal concentrations show a longitudinal decrease (Fig. 3). Although DN18 is a site for domestic waste disposal, the concentrations of metals and TOC are lower than those at site DN17. It is related with the coarse texture, which is also evidenced by the reduction of Al_2O_3 levels (3.5 wt. %) in marine sediment. The concentration of Ni in sediments of Han River is below the detection limit.

Danang city has a sewer system of total length 72 km discharging both industrial and domestic waters including storm water. Due to the lack of treatment facilities, the waste waters are discharged directly in to sea at the Thanhbinh Beach. This famous beach located in the center of Danang city, is highly contaminated and no longer suitable for swimming (Binh 1995). A pH of 7.8 was measured in the discharging canal of Thanhbinh Beach (Fig. 3). The pH decreases slightly at the canal sea confluence to a level of pH 7.3. Further seawards the pH increases to 7.8 and the Eh shows a decreasing trend in the seaward direction: canal (6.6 mV) > canal sea confluence (0.6 mV) > seawater (–11.8 mV). In the sewer canal, an exceptional enrichment of Pb is observed (133 μg/g), whereas at other sites the Pb concentrations are lower than the detection limit. Similarly when compared to other sites, the concentration of Al_2O_3 is also relatively high (7.2 wt. %). At the canal outlet (site DN13B) the concentrations of most metals (Cr 370 μg/g, Cu 344 μg/g and Zn 265 μg/g) show an increasing trend reflecting anthropogenic contribution to pollution. The concentration of TOC is also slightly increased (1.0 wt. %). Further at site 13C trace elements such as Cr (1000 μg/g), Fe (18 wt. %) and Mn (7.0 wt. %) are enriched in sediments as compared to canal sediments.

Thubon (locally called Hoian) is the largest river in middle Vietnam. The river has annual sediment discharge is about 15 ! 10^6 tons. The river originates from a mountain area (Ngoclinh, Tramy and Bana) in the western part of the Danang-Hoian region. The Thubon's course runs through various rocks from basement rocks (Avuong complex B-O_{av}) to recent sediment. The river section in Hoian town was selected for the present study. The study catchment area features subordinates of quaternary clastic sediments. The contamination of river water is attributed to various sewer outfalls (Pagoda Bridge or Central market) and additionally, agricultural waste has also a significant impact on water quality. In the Hoian River, the pH values range from 7.3 to 7.5 (Fig. 3). The Eh ranges between 1.4 and 22.1 mV. The sewer sediment (HA2) is characterized by the enrichment of Cr (251 μg/g), Zn (913 μg/g) and TOC (9.1 wt. %) as compared to river sediments. Reduced concentrations of Al_2O_3, Fe_2O_3 and MnO in river sediment reflect a lithogenic origin of these elements. The enrichments of Cu, Zn, Pb, Al_2O_3 and Fe_2O_3 are observed at the sewer outlet (HA1) as compared to upstream site HA8. This is due to the receiving urban runoff. At the site HA4, the concentrations of Cr (117 μg/g), Ni (154 μg/g) and Pb (274 μg/g) have increased due to the influence of domestic wastes from the Central Market.

Comparison of trace element concentrations between discharge canals and their allied receiving water bodies

The dilution factor, F_{dil} (i.e., the relationship between metal concentrations in discharge canals and their receiving water bodies) was calculated to assess the impact of waste waters of the Danang – Hoian area. The F_{dil} for trace elements of the Cude River, Hoian River and Thanhbinh Beach of the study area is defined by

$$F_{dil} = [M_{rec}]/[M_{can}]$$

where $[M_{can}]$ is concentration of trace elements in sediment of discharging canal, $[M_{rec}]$ is concentration of trace elements in sediment of receiving water bodies.

As summarized in Table 2, F_{dil}s for Cr in Hoian River shows a decrease of metal concentrations when compared to the discharge canal ($F_{dil} = 0.4–0.7$). This information indicates that waste water is a potential pollutant source for the Hoian River. However, Cr shows enrichment in sediments of the Cude River and Thanhbinh Beach as compared with discharge canals. It is probably due to the fact that the Cr originates from other contributors as well. Copper shows a "dilution" effect in fluvial sediments of Cude River. However, the marine sediments of Thanhbinh Beach exhibit enrichment in Cu as compared with sewer sediments ($F_{dil} = 1.5–5.6$). In Hoian River F_{dil}s for Cu show wide variation, which ranges between 0.4 and 4.8. The increase of F_{dil} is observed for Ni in the Cude River as well as in the Hoian River (Table 2). Hence the Ni levels of marine sediments of Thanhbinh Beach are below the detection limit. F_{dil}s for Zn are decreased in Cude River ($F_{dil} = 0.4–0.7$) and Hoian River

Table 2
Calculated dilution factors of trace metals in sediment (fraction < 63 μm) of rivers and a beach of Danang – Hoian area (Vietnam)

	Dilution factor (F_{dil})				
Sample	Cr	Cu	Ni	Zn	Pb
Cude River					
DN 4	1.5	1.0	2.5	0.7	< 4.8[a]
DN 6/1	1.1	0.6	< 1.0[a]	0.4	< 4.8[a]
Thanhbinh Beach					
DN 13B	4.7	5.6	< 1.0[a]	6.2	< 4.8[a]
DN 13 C	12.9	1.5	< 1.0[a]	2.7	< 4.8[a]
Hoian River					
HA 8	0.5	0.6	1.3	0.1	2.7
HA 1	0.5	1.2	1.0	0.6	6.3
HA 3	0.4	0.6	0.2	< 1.1[a]	1.2
HA 4	0.6	0.4	1.2	0.1	2.4
HA 5	0.7	4.8	0.5	0.6	7.3

[a] detection limit

(F_{dil} = 0.1–0.6) indicating that Zn originates from waste waters. However, marine sediments of Thanhbinh Beach show enrichment of Zn (F_{dil} = 2.7–6.2). Pb shows enrichment in fluvial sediments of Hoian River (F_{dil} = 1.2–7.3) and this can be explained by the fact that Pb is also released not only from the sewer but also from other sources such as shipping, traffic, etc.

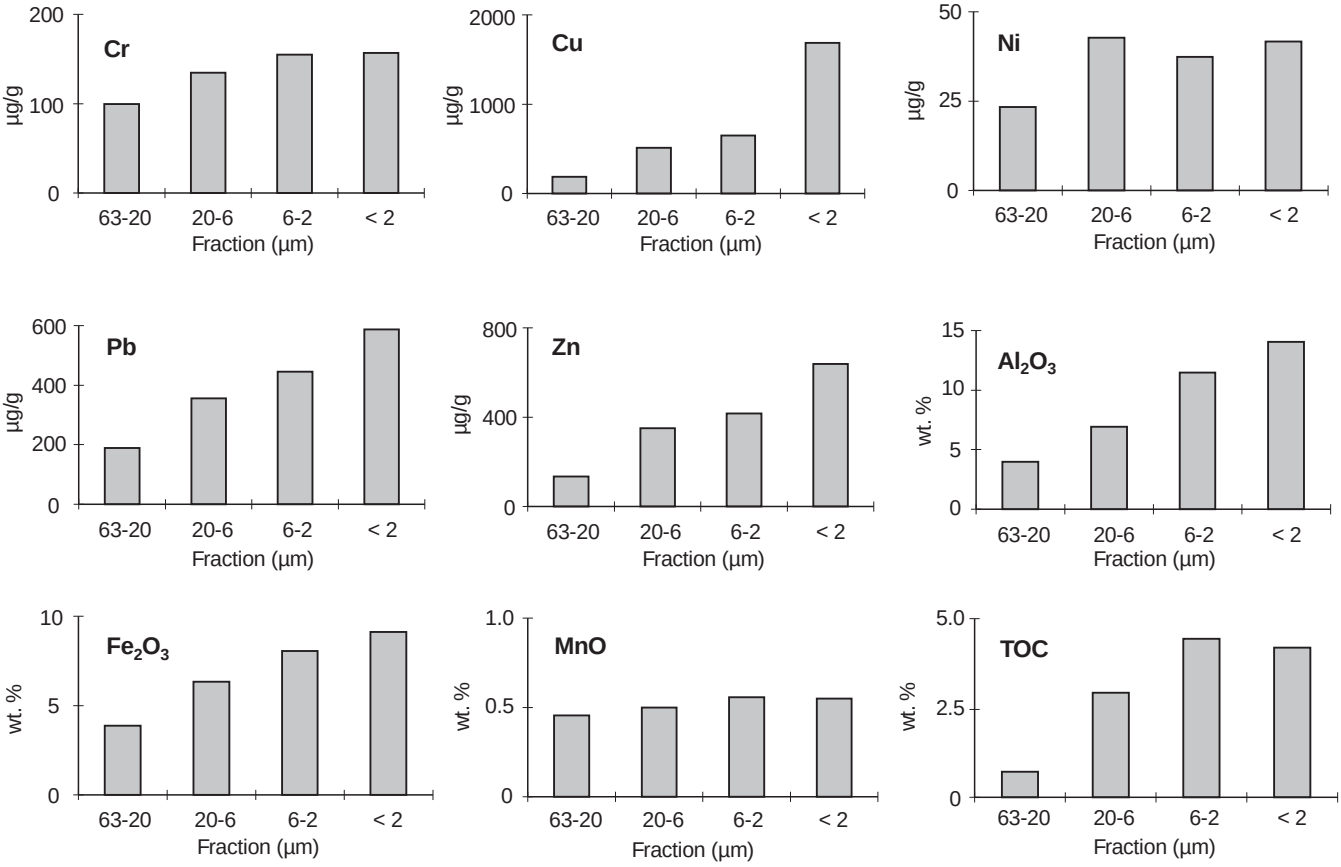
Metal distribution in the different grain size fractions

The distribution of trace elements in grain size fractions is illustrated in Fig. 4. Most of the trace elements such as Cr, Cu, Pb and Zn are enriched in the clay fraction (< 2 μm). The concentrations of elements increase with decreasing grain size, due to the fact that the trace elements tend to concentrate both within and on surfaces of sediment particles. The finer fractions have a larger contact surface area (specific surface area) and therefore the intensity of metal sorption by the fine particles is higher than in coarser particles (Förstner and Wittmann 1981). Mineralogically, the clays have also larger specific surface areas as compared to quartz rich coarse fractions. On the other hand, Cr which has a coordination number of 6, may fit into the octahedral position of the clay minerals and sequioxides, substituting for elements normally found there. The distribution of Ni among the fractions is not clear. Among the major elements, Al and Fe are dominant in the clay fraction. Aluminum, which has coordination numbers of 6 and 4, is one of the major components of the weathering products including clay minerals and secondary Al-oxides (Gibbsite). Iron fits into octahedral positions and can form silicates and/or hydrated oxides. The distribution of Mn is relatively homogeneous among grain size fractions. TOC concentrations are also enriched in fine silt (6–2 μm) and clay fraction (< 2 μm). The enrichment of TOC in finer fractions is associated with the elevated heavy metal concentrations, which indicates the great influence of organic matter on metal sorption.

Comparison of Cu and Zn in waters and sediments

The partitioning of Cu and Zn in water and sediments to assess located pockets of pollution in Danang – Hoian area (Vietnam) was also examined. Fig. 5 illustrates the distribution of Cu and Zn in sediments (fraction < 63 μm) and water from rivers and sea in the Danang – Hoian area. The distribution of Cu and Zn exhibit similar patterns in sediment and water of Cude River. Much of wastewaters that flow into the river are from the vicinity. There is a similar tendency of Cu distribution in sediment and water of Han River, whereas Zn shows a contrasting distribution. The decrease in Cu and Zn towards

Fig. 4
Relative distribution of metals and TOC in various grain size fractions (average concentration) in sediments of Danang – Hoian area (Vietnam)



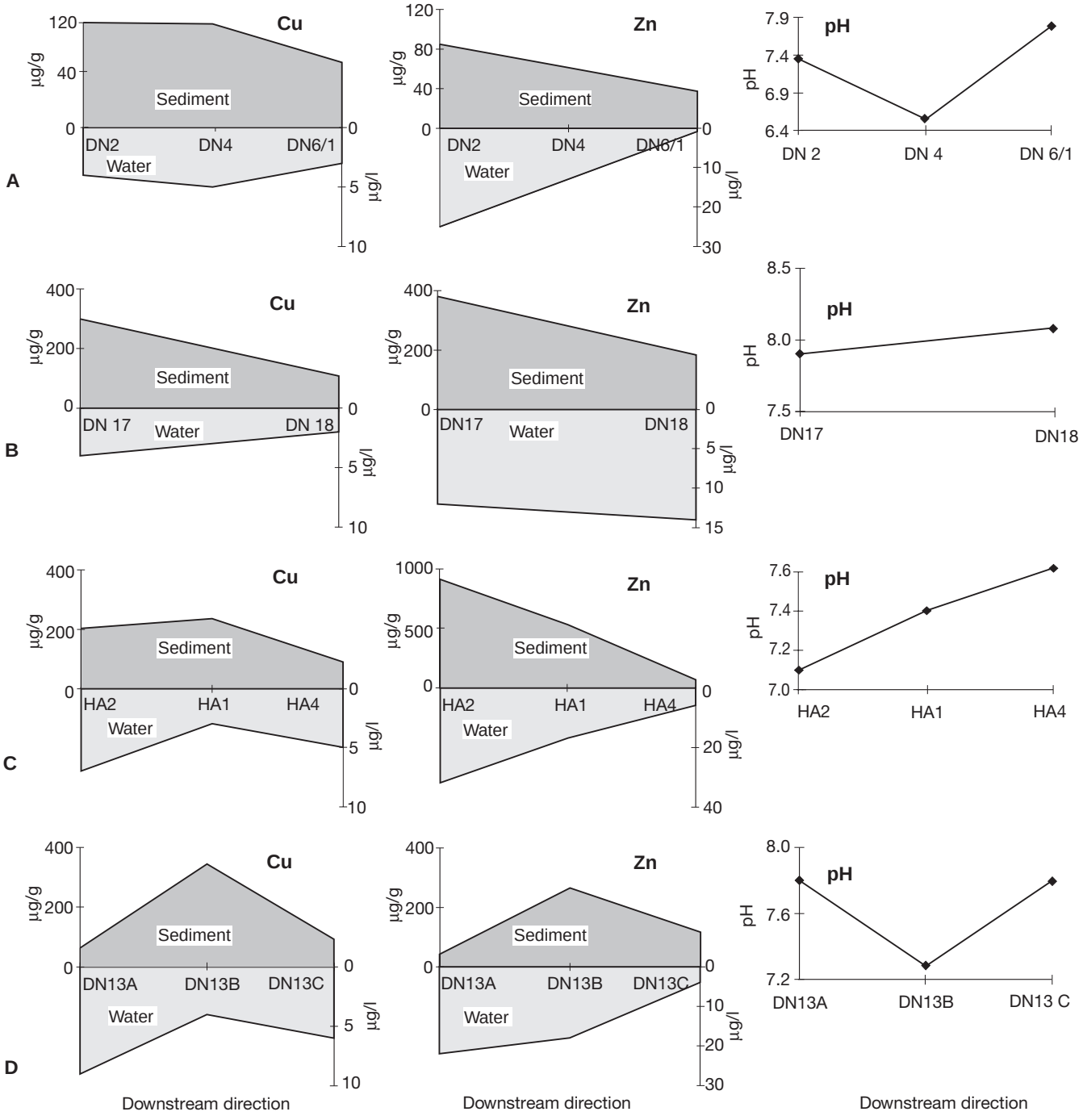


Fig. 5
Distribution of Cu and Zn in sediments (fraction < 63 μm) and waters from different locations of Danang – Hoian area (Vietnam). Variations of pH in water at the same locations are given in third column. **A** Cude River, **B** Han River, **C** Hoian River and **D** Thanhbinh Beach. *Arrow* indicates the water flow direction

downstream is in accordance with the depletion of Fe_2O_3 and TOC (see also Fig. 3). For Hoian River, Cu and Zn increases at site sewer canal HA2 (Fig. 5) and this clearly indicates the influence from waste water. Further decrease of metal concentrations towards downstream is explained largely due to the "dilution effect" with seawater. The contrasting behavior of Cu in sediment and water may be explained in accordance with the distribution pattern of Fe_2O_3. The distribution of Zn and TOC in sediments exhibits similar patterns. It is clear that organic matter plays an important role in the mobility of Zn. The distribution of Cu and Zn exhibit opposition patterns in sea sediment and water in the Thanhbinh Beach. This is largely ascribed to pH changes.

Evaluation of sediment quality

With no national accepted guidelines for sediment quality, it is difficult to determine the significance of metal

loading documented in the Danang – Hoian area (Vietnam) in term of public health. Therefore, the effects-based criteria [Effects range-medium (ER-M)] of Long and Morgan (1990) was employed to sediment pollution by trace elements. ER-M is a value for the "concentrations (of metals) above which effects are frequently observed, or predicted amongst most species". Using these data as a guide, it is argued that the concentrations of Cude River are below guideline levels for Cu, Zn and Pb and to a lesser extent for Ni (Table 1). The concentrations of Cu, Ni and Zn of Thanhbinh Beach are both within guidelines of safety regulations. However, the maximum value of Pb in the Thanhbinh Beach exceeds the guideline level. Similar observations were made for the Han River. Some local enrichments of Cu, Ni, Zn and Pb are observed in the Hoian River, which are above guideline levels.

Conclusions

Diffuse sources (domestic and industrial waste disposal) are major contributors in the elevation of metal content, especially Cr, Cu, Zn and Pb of sediments of the Danang – Hoian area (Vietnam). Distribution of trace elements in dissolved and particulate phases are largely influenced by water pH, distribution pattern of organic carbon and Fe oxides. In terms of public health, it is evident that the Hoian River is polluted with respect to Cu, Ni, Pb and Zn. However, the degree of pollution is comparably low in Han River and Thanhbinh Beach. When compared to other water bodies, sediments of the Cude River are dominated by trace element concentrations close to background values.

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