

DISTRIBUTION AND CONTAMINATION STATUS OF HEAVY METALS IN ESTUARINE SEDIMENTS NEAR CUA ONG HARBOR, HA LONG BAY, VIETNAM

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(4 figures and 7 tables)

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ABSTRACT. The distribution, controlling geochemical factors and contamination status of heavy metals in estuarine sediments near Cua Ong Harbor, Ha Long Bay (Vietnam) were investigated. 36 surface sediment samples were collected and analyzed for major elements (Al, Ca, Fe, K, Mg, S), heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn), organic matter, loss on ignition (LOI), grain size composition and pH. Spatial distribution patterns of heavy metals as well as their controlling factors were elucidated based on geochemical mapping and statistical methods such as the Pearson Product-Moment linear correlation and Factor Analysis. The results illustrated that the distribution patterns of As, Cd, Cr, Cu, Ni, Pb and Zn are mainly controlled by organic matter and clay minerals and determined by the distribution of the fine-grained fraction ($\Phi < 63 \mu\text{m}$) in the sediments. In contrast, Fe and Mn compounds seem to exert some control on the distribution of Co. Carbonates partly control the distribution of Mn, but are not important with respect to the other studied heavy metals. The contamination status by heavy metals was assessed based on comparison with Canadian, Wisconsin-United States and Flemish numerical Sediment Quality Guidelines, and calculation of Geo-accumulation Index (I_{geo}) and Enrichment Factor (EF). The results indicated that natural processes such as weathering and erosion of bedrock are the main supply sources of heavy metals in sediments near Cua Ong Harbor. Among the studied heavy metals, only As is of concern whereas Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn seem to reflect their background concentrations in sediments of Ha Long Bay.

KEYWORDS: heavy metal, sediment, distribution, controlling factor, contamination status

1. Introduction

Studies on heavy metal pollution especially in coastal zones increased over the last few decades at global scale. However, in tropical and subtropical regions such as Vietnam and other Southeast Asian countries, only limited information about this topic is available, particularly in estuaries, where, in addition to natural inputs, concomitant activities such as harbor activities within the estuary, and industrial, agricultural and residential activities around the estuary can release heavy metals to the environment.

Sediments are considered to be an important carrier as well as a sink of heavy metals in the hydrological cycle (Celo et al., 1999). The majority of heavy metal emissions from anthropogenic activities accumulates in river and ocean sediments, where they are absorbed onto clays and other fine-grained materials. However, the sediments can release heavy metals to the overlying water via natural or anthropogenic processes, causing potential adverse effects to the ecosystems. Moreover, benthic organisms can take up metals directly from the sediments, which in turn enhance the potential of some metals entering into the food chain (Adamo et al., 2005; Chen et al., 2007).

In sediments, very little of the total metal content is present in free ionic or chelated form in the interstitial solution. Most of the metal content occurs in complex form with insoluble inorganic and organic ligands. Particularly, heavy metals can be absorbed on negatively charged surfaces of clay minerals, organic matter or iron and manganese hydrous oxides from which they can be removed by ion-exchange with hydrogen ions and other cation species. This labile or exchangeable fraction of heavy metals is largely bioavailable. Heavy metals are also occluded in precipitated iron and manganese hydrous oxides or present as carbonates or sulfides. In addition, metal atoms may also be present in the lattices of primary and secondary minerals. In the latter forms, metals are largely unavailable to organisms, therefore bioavailability is low (Thornton, 1995).

The assessment of heavy metal pollution in estuarine sediments is a complex process in which physical, chemical and biological data are required. Since in many areas the necessary biological data are not available, in environmental geochemistry, the assessment of contamination status is normally based on Sediment Quality Guidelines (SQGs) or quantitative indexes such

as Geo-accumulation Index (I_{geo}) and Enrichment Factor (EF), etc. ... with respect to reference values such as regional/local background values or average concentrations of shale, continental crust or upper continental crust, etc. ... (Aksu et al., 1997; Rubio et al., 2000; Woitke et al., 2003; Samir et al., 2006; Chen et al., 2007).

The objectives of this paper are to elucidate the distribution of a number of heavy metals (i.e. As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) in estuarine sediments near Cua Ong Harbor and to evaluate the geochemical factors that control the distribution pattern of the studied heavy metals. Moreover, based on the assessment of contamination status of the sediments, which heavy metals are enriched by anthropogenic input and/or which heavy metals reflect natural backgrounds will also be recognized.

2. Materials and methods

2.1 Study area

The study area is situated in an estuary where fresh waters from the Voi Lon River and its tributaries in the North enter the Ha Long Bay - a famous landscape of Vietnam approved by UNESCO as World Natural Heritage (Fig. 1). According to geological reconnaissance studies, the bedrocks consist of dolomitized limestone and biogenic limestone in the South (e.g. Luoi, Da Ba, Moi and Cay Khe Dong islands), and conglomerate, sandstone, siltstone, claystone and shale interbedded by thick coal layers in the hinterland and Cap Tien Trong and Cap Tien Ngoai islands. In addition, Quaternary unconsolidated sediments are distributed in the beaches and sand bars.

Since the estuary is subject to the inputs from rivers and runoff in nearby land areas, the study area is typically influenced by open-cast coal mining activities in the hinterland that promote the weathering of heavy metal-rich sulfidic minerals in coal and rock formations (Tiwary, 2001; Virendra et al., 2008). In addition, many harbor activities such as coal shipment, ship traffic, and ship maintenance may dispose metal-bearing chemicals such as exhausted fume, oil, grease, paint, antirust, etc. ... Moreover, the activities of habitant's motor boats around the harbor or at the wharfs as well as discharges of sewage and rubbish from residential areas through runoff and rivulet outlets along the coast are also possibly contributing to the contamination of the study area.

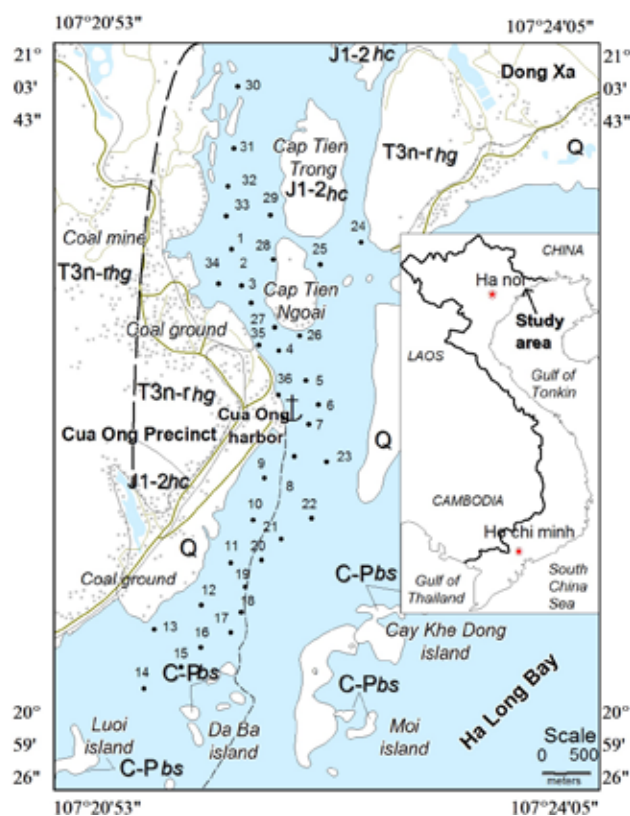


Figure 1. Study area and sampling locations

Note: C-Pbs - Carboniferous and Permian Bac Son Formation: dolomitized limestone and biogenic limestone; T3n-rhg - Triassic Hon Gai Formation: sandstone, siltstone interbedded by conglomerate, claystone, shale and thick coal layers; J1-2hc - Jurassic Ha Coi Formation: sandstone, siltstone, claystone and conglomerate; Q - Quaternary unconsolidated sediments: sand, silt, clay, and little of pebble, cobble and shell of organisms.

2.2. Sampling and sample pretreatment

The sampling campaign was carried out in February 2007. Surface sediment samples were collected with a grab from 36 locations near the Cua Ong Harbor. The sampling locations were distributed evenly around the harbor at an interval of approximately 500 meters between two contiguous locations. During sampling, precautions were taken to minimize any disturbance in the grain size distribution of the original sediment. For example, the sample was taken only when the grab was firmly closed upon arrival to the boat, so that any leakage of fine material withdrawn by seawater was avoided. In addition, to minimize metal contamination from the grab's wall, the outer part of the sediment sample was removed and only

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Measured (ppm)	26.2	8.8	48.3	46.6	7984.6	16.7	3404.3	3219.4
Certified (ppm)	28.2	11.6	59.6	65.4	9700	24.2	2700	3800
% recovery	93	76	81	71	82	69	126	85

Table 1. Comparison between the measured concentrations with the certified data in the standard reference material GBW07411 (n=1).

the inner part was further processed, and all materials used for treatment and storage of sediment samples were non-metallic (plastic or wood). After collection, the samples were placed in tightly sealed plastic containers, and then transported to the Vietnam Institute of Geosciences and Mineral Resources. Here, the samples were kept in dark condition and cool temperature (4°C) until they were transported to the Department of Earth and Environmental Sciences, Catholic University of Leuven (K.U. Leuven, Belgium) for further analyses. At the laboratory in Leuven, the sediment samples were dried at 40°C for 3 days, and then disaggregated in an agate mortar, homogenized and sieved over a 2mm-interval net. Only the < 2 mm fraction was used for chemical analysis.

2.3 Sample analyses and quality control

The organic matter content was determined by the Walkley-Black manual titration method (Brian, 2002). Grain size composition was determined by means of laser diffraction spectrophotometry (Malvern Mastersizer S long bed, Malvern, Worcestershire, UK). The total sulfur content was determined by incineration and titration with a Strohleim apparatus. Loss on ignition (LOI) was determined by heating sediment at 1000°C for 2 hours.

Sediment pH was measured in a suspension of 1/5 sediment to CaCl₂·2H₂O 0.01M solution after shaking for 2 hours.

The total elemental concentrations (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, K, Ni, Pb and Zn) were determined with the so-called 3 acid-digestion method. One gram of each sample was dissolved in a 3-acid mixture (4ml HCl [37%], 2ml HNO₃ [65%] and 2ml HF [48%]) in a Teflon beaker. The mixture was gently heated on a hot place until almost dryness, and subsequently re-attacked with the same amount of these three acids and heated to complete dryness at about 220°C. The residue was re-dissolved by gently heating with 20ml of 2.5M HCl, and filtered by a Whatman 0.4 µm membrane. Finally, this solution was diluted to 50ml with distilled water. These solutions were measured by F-AAS for Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn, and by ICP-MS for Al, As, Cd and Co.

All reagents were of extra pure quality, and all labwares used were either new or thoroughly cleaned before utilization. All the samples were repeatedly measured (n = 3) to control the precision of analytical instruments. Analytical precision was less than 5% for all elements. The efficiency of the digestion procedure and the analytical quality were controlled by the use of the standard reference material GBW07411 (soil). The comparison between the

Variable	Measured conc. in samples						Average conc. in reference material		
	Unit	Mean	Median	Min.	Max.	Std. Dev.	Sedimentary rock (clay and claystone)*	Upper continental crust**	Average continental crust**
Al	%	4.47	4.01	0.97	8.73	2.27	9.53	8.03	8.42
Ca	%	1.33	0.97	0.08	6.46	1.20	2.50	2.99	5.29
Mg	%	0.44	0.34	0.10	1.10	0.27	1.38	1.32	3.18
Fe	%	1.30	1.19	0.48	3.72	0.64	3.33	3.49	7.08
K	%	0.91	0.83	0.20	1.65	0.45	2.28	2.81	1.08
As	µg/g	26	25	13	62	9	6.6	1.5	1.0
Cd	µg/g	0.09	0.08	0.02	0.20	0.05	0.3	0.098	0.1
Co	µg/g	6	6	1	13	2	20	17	29
Cr	µg/g	27	26	10	49	11	100	85	185
Cu	µg/g	20	19	13	30	4	57	25	75
Mn	µg/g	108	101	18	318	59	700	500	1400
Ni	µg/g	8	8	3	20	4	95	44	105
Pb	µg/g	16	16	4	41	8	20	17	8.0
Zn	µg/g	40	40	12	93	17	80	71	80
S	%	0.12	0.10	0.09	0.18	0.04			
OM	%	1.65	1.39	0.27	3.44	0.90			
LOI	%	9.90	9.08	2.28	18.18	4.55			
Clay (<2µm)	%	18.38	19.41	2.31	30.20	6.97			
Fine fraction (<63µm)	%	53.24	50.63	5.64	84.84	21.06			
pH		7.68	7.79	7.01	8.21	0.40			

Table 2. Statistical parameters for heavy metals and other characteristics of the sediment

Note: * According to Vinogradov (1966); ** According to Taylor and McLennan (1985 and 1995)

measured concentrations with the certified data displays a relatively good agreement (Table 1).

2.4 Data processing

Spatial distribution patterns of heavy metals were demonstrated by means of software MAPINFO version 9.0. Different modules of the statistical software STATISTICA version 7.0 such as the Pearson Product-Moment linear correlation method and the Factor Analysis were used to elucidate the relationships between heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) and geochemical characteristics (Al, Ca, Mg, Fe, K, S, organic matter and LOI). Since for the above-mentioned parametric statistical treatments, an obligatory condition of input data was the "normality of variables", a normality testing was carried out based on histograms, probability plots and the Shapiro-Wilks test. In nature, many major and trace elements usually have a close to logarithmic distribution (Batista et al., 2006). Therefore, for Ca and Mg, a logarithmic transformation was performed to obtain a population distribution as close as possible to normality. The final data set was a combination between raw data for the normally distributed variables and log-transformed data for Ca and Mg in an attempt to satisfy the normality condition.

Contamination status of heavy metals in sediments of the study area was assessed by Sediment Quality Guidelines as well as by the Enrichment Factor (EF) and Geo-accumulation Index (I_{geo}) as suggested by MacDonald et al. (2003), Management Unit of the North Sea Mathematical Models (MUMM)- Royal Belgian Institute of Natural Sciences (2007), Rubio et al. (2000), Samir et al. (2006) and Chen et al. (2007).

3. Results and discussion

3.1 Sediment characterization

Statistical parameters (minimum, maximum, mean, median and standard deviation) for heavy metals and other geochemical characteristics of the sediments in the study area are presented in Table 2. Grain size composition strongly varies between sampling locations. The fine-grained fraction ($\Phi < 63 \mu\text{m}$) ranges from 5.64% in some samples located within the river's current (i.e. sample 1, 2, 3, 4 and 5) to 84.84% in quiet areas (i.e. sample 8, 9, 22, 23, 25, 35 and 36). Organic matter content as well as total sulfur content was low in the sediments (mean: 1.65% and 0.12% respectively). In addition, major elements such as Al, Ca, Mg, Fe and K are quite low in comparison to that of reference materials, i.e. average sedimentary rock, upper continental crust and average continental crust.

Variable	Al	Ca	Mg	Fe	K	As	Cd	Mn	Co	Cr	Cu	Ni	Pb	Zn	OM	LOI	Fine Fract.
Al	1,00	-0,24	-0,37*	0,46*	0,83*	0,61*	0,63*	-0,35*	0,10	0,79*	0,69*	0,65*	0,80*	0,60*	0,62*	0,59*	0,79*
Ca		1,00	0,70*	0,21	-0,36*	0,12	-0,09	0,64*	0,46*	-0,20	-0,11	0,07	-0,13	0,08	-0,09	0,02	-0,19
Mg			1,00	-0,14	-0,43*	-0,14	-0,22	0,39*	0,10	-0,40*	-0,28	-0,23	-0,31	-0,16	-0,35*	-0,23	-0,38*
Fe				1,00	0,43*	0,89*	0,51*	0,35*	0,80*	0,65*	0,62*	0,83*	0,71*	0,84*	0,51*	0,46*	0,46*
K					1,00	0,65*	0,78*	-0,44*	0,05	0,90*	0,74*	0,70*	0,87*	0,63*	0,69*	0,63*	0,88*
As						1,00	0,59*	0,13	0,58*	0,76*	0,65*	0,84*	0,84*	0,80*	0,56*	0,54*	0,63*
Cd							1,00	-0,20	0,26	0,81*	0,72*	0,74*	0,80*	0,71*	0,68*	0,63*	0,76*
Mn								1,00	0,71*	-0,21	-0,12	0,08	-0,18	0,13	-0,11	-0,03	-0,34*
Co									1,00	0,38*	0,40*	0,67*	0,37*	0,71*	0,40*	0,41*	0,14
Cr										1,00	0,91*	0,92*	0,95*	0,87*	0,86*	0,79*	0,90*
Cu											1,00	0,90*	0,88*	0,89*	0,90*	0,83*	0,81*
Ni												1,00	0,89*	0,98*	0,85*	0,79*	0,76*
Pb													1,00	0,87*	0,77*	0,73*	0,88*
Zn														1,00	0,81*	0,76*	0,70*
OM															1,00	0,92*	0,75*
LOI																1,00	0,71*
Fine fract.																	1,00

	Al	Ca	Mg	Fe	K	As	Cd	Mn	Co	Cr	Cu	Ni	Pb	Zn	OM	LOI	Fine fract.
S	0,42	-0,25	-0,30	0,50	0,52	0,53	-0,03	-0,23	0,58	0,51	0,60	0,55	0,43	0,57	0,97*	0,89*	0,42

Table 3a. Correlation matrix between heavy metals and geochemical characteristics of the sediment. Number of valid samples = 35; **b.** Correlation matrix between sulfur and other variables. Number of valid samples = 6. **Note:** * Correlation coefficient is significant with p -value < 0.05 ; **Bold:** very strong correlation (> 0.8); **Bold & Italic:** strong correlation (between 0.6 and 0.8); *Italic:* good correlation (between 0.4 and 0.6); and Regular: weak correlation (< 0.4)

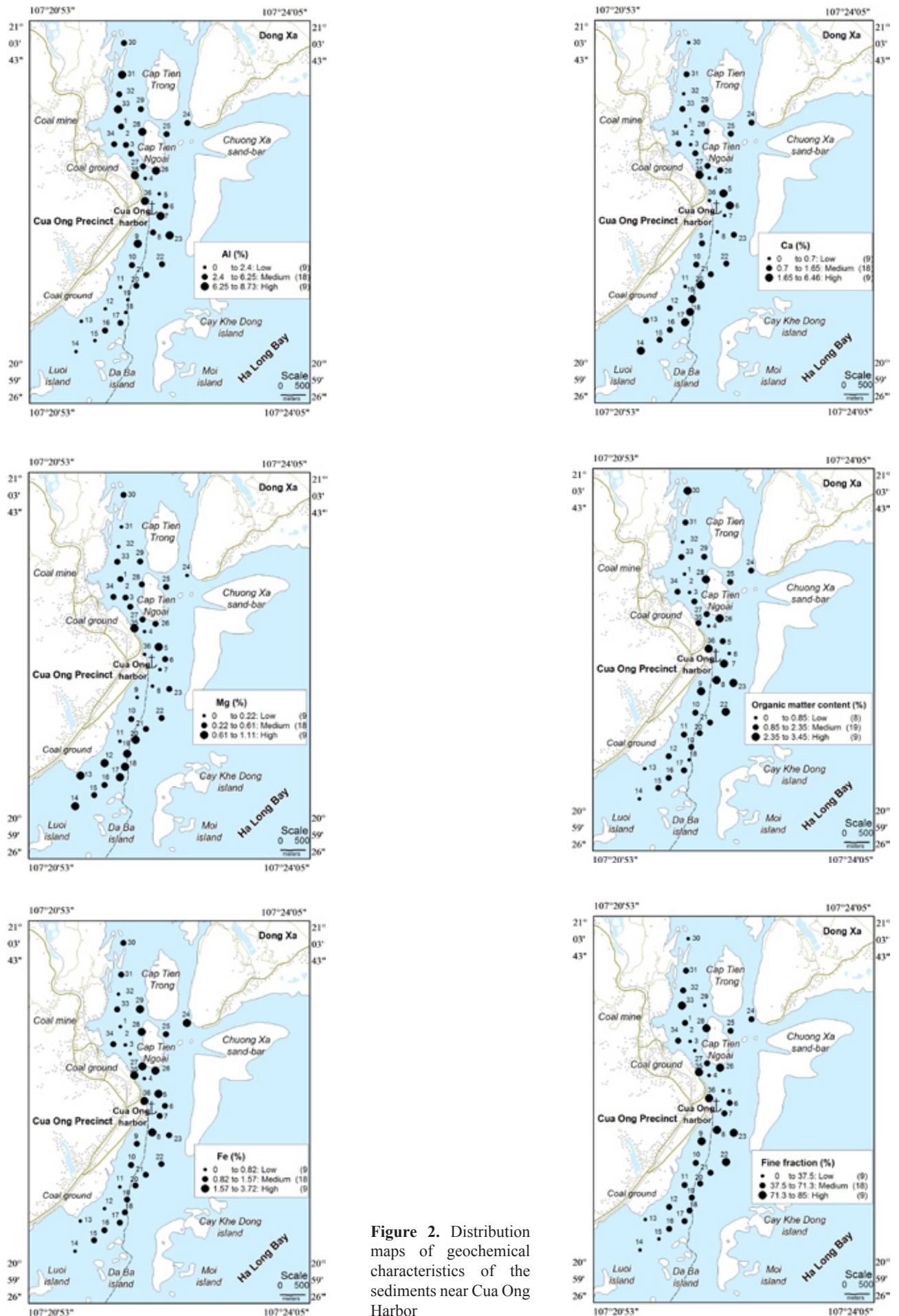


Figure 2. Distribution maps of geochemical characteristics of the sediments near Cua Ong Harbor

Sediment pH values, ranging from 7.01 to 8.21 (mean: 7.68), indicate that the medium is neutral to lightly basic.

3.2 Spatial distribution of heavy metals and their controlling factors

The spatial distribution patterns of geochemical characteristics and heavy metals are illustrated in different figures for the purpose of comparison (Figs 2a and 2b). For the sake of uniformity, and as a necessary simplification in descriptions, the following classification was used:

- Low concentration: corresponding to the range from the minimum value up to the 25th percentile concentration according to the probability distribution.
- Medium concentration: corresponding to the range from the 25th to the 75th percentile.
- High concentration: corresponding to the range of values from the 75th percentile up to the maximum.

In addition, a correlation matrix between heavy metals and other characteristics of the sediments is shown in Table 3a. The correlation coefficients of sulfur with other variables are separately calculated and given in Table 3b since only a limited set of samples was analysed for sulfur.

On the map, the distribution patterns of Ca and Mg are quite similar. The strong correlation between Ca and Mg ($r = 0.70$) indicates a common origin (Valdes et al., 2005). Since dolomite is a constituent of carbonate bedrocks in the study area, this likely explains the origin of Ca and Mg from the weathering of carbonate rocks. Their concentrations tend to be higher near the areas of carbonate bedrocks such as Cay Khe Dong and Da Ba islands (e.g. samples 12, 13, 14, 17, 18, 19, 20). However, an additional source of Ca is from biogenic materials, e.g. shells of organisms that were observed during the field survey. This explains the high concentrations of Ca at some sampling locations (sample 5, 6, 29 and 35) that occur far from the areas of carbonate bedrocks.

The distribution patterns of Al, K and organic matter are quite similar to that of the fine-grained fraction. Their concentrations are normally high near the banks or quiet areas (samples 24, 26, 27, 28, 35, 36) where hydrodynamic energy of the river and sea currents is weak, i.e. where the depositional conditions of fine grains are high. Strong to very strong correlations between Al, K and the fine-grained fraction ($r = 0.79$ and 0.88 respectively) can be explained by the fact that these elements are main constituents of clay minerals in the fine-grained fraction. The strong correlation between organic matter and the fine-grained fraction ($r = 0.75$) is noteworthy. It shows that organic matter is an important component in the fine-grained fraction and possibly demonstrates that the organic matter may form coatings on the surface of clay particles as reported by Wang and Chen (2000) and Chen et al. (2007). The correlations of Fe with Al, K, organic matter and fine-grained fraction are not too strong ($r = 0.46$, 0.43 , 0.51 and 0.46 , respectively), suggesting that apart from being a constituent of clay minerals and as coatings on the surface of clay particles, the distribution of Fe is also controlled by other factors.

The distribution patterns of As, Cd, Cr, Cu, Ni, Pb and Zn are almost similar to Al, K, organic matter and the fine-grained fraction. Strong to very strong correlations between them (r from 0.60 to 0.90) imply that these heavy metals can be (i) related to clay minerals that sorb heavy metals directly or (ii) related to organic matter, which is coated on the clay surface and hence interrelated with the fine-grained fraction (Chen et al., 2007). Differently from the above heavy metals, Co can be mainly bound to the compounds of Fe and Mn (e.g. iron and manganese hydrous oxides or possibly iron and manganese sulfides) ($r = 0.80$ and 0.71 , respectively). Moreover, Fe also has very strong correlations with As, Ni and Zn ($r = 0.89$, 0.83 and 0.84 , respectively) suggesting that Fe compounds are also important in explaining the distribution of these heavy metals. The strong correlation of Ca with Mn ($r = 0.64$) suggests the co-existence of Ca and Mn. As postulated by Rubio et al. (2000), Mn can form rhodochrosite (MnCO_3) inside calcite under co-precipitation of a calcite-manganese phase, but an alternative interpretation is the presence of dolomitic constituents rich in Mn. However, carbonates are not an important binding phase for other heavy metals since their correlations with Ca and Mg are weak. In addition, these negative correlations although they are not significant, also illustrate the inverse relationships between carbonates and heavy metals. In other words, as reported in literature the carbonates may act as a diluent of metal contents in the sediment (Aloupi and Angelidis, 2001).

Variable	Factor1	Factor2	Factor3
Al	0,82	-0,02	0,22
Ca	-0,09	0,36	-0,86
Mg	-0,22	-0,02	-0,91
Fe	0,50	0,80	0,05
K	0,90	-0,08	0,29
As	0,68	0,55	0,04
Cd	0,84	0,08	0,02
Mn	-0,32	0,75	-0,41
Co	0,20	0,94	-0,18
Cr	0,94	0,23	0,22
Cu	0,88	0,27	0,10
Ni	0,83	0,53	0,04
Pb	0,92	0,25	0,15
Zn	0,78	0,57	0,01
OM	0,83	0,24	0,11
LOI	0,80	0,23	-0,03
Fine-grained fraction	0,94	-0,03	0,16
Eigen value	11,11	3,30	1,01
% total variance	61,70	18,33	5,61

Table 4. Factor loadings of geochemical variables in Factor Analysis

Note: **Bold:** high to very high loading (>0.6); **Bold & Italic:** moderate loading (between 0.4 and 0.6); and Regular: low loading (<0.4)

Sulfur has very strong correlations with organic matter and LOI, suggesting the presence of sulfur in organic matter. The correlations with other variables such as heavy metals are not significant. Thus, it can be concluded that sulfur compounds (e.g. acid volatile sulfides) are not so important phases in binding heavy metals in the study area.

3.2.1 Factor Analysis (FA)

A Factor Analysis was carried out in an attempt to further clarify the major controlling factors that determine the distribution of heavy metals in the sediment. The Factor Analysis was performed on the entire data set (except for S due to the non-availability of values for many samples). We however acknowledge that the data set is rather limited, but the rather homogeneous sedimentary characteristics of all analysed samples supports this reconnaissance analysis of the data. But obviously the results should not be overinterpreted.

This analysis gave three principal factors that explain a high percentage (around 86%) of the total data variation in all samples, and also group the variables in a geochemically reasonable and interpretable manner. The loadings between principal factors and geochemical variables, as well as the positions of variables in the coordinates of the principal factors are given in Table 4 and Fig. 3. The three factors representing three different groups of variables can be described as follows:

Factor 1 accounting for 61.7% of the total variance is characterized by high loadings for the fine-grained fraction, organic matter, LOI, Al, K, As, Cd, Cr, Cu, Ni, Pb and Zn, and moderate loading for Fe. This factor reflects the binding of heavy metals (As, Cd, Cr, Cu, Ni, Pb and Zn) to organic matter and clay minerals, and as such their distribution patterns are controlled by the fine-grained fraction. Since Al and K represent the terrigenous

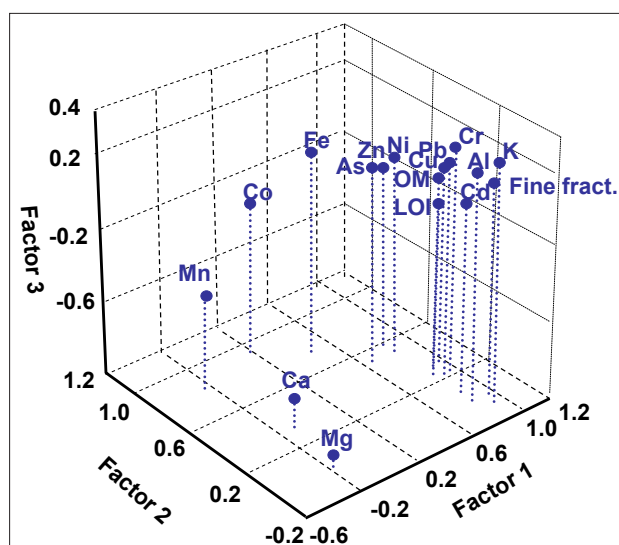


Figure 3. Variables in the coordinates of principal factors (Factor 1 vs. 2 vs. 3)

siliciclastic materials and are not influenced by anthropogenic activities in the study area, this factor can be considered to reflect the natural origin of major elements and heavy metals from weathering and erosion (Valdes, 2005).

Factor 2 accounting for 18.3% of the total variance is characterized by high loadings for Fe, Mn and Co, and moderate loadings for As, Ni and Zn. This factor likely represents iron and manganese compounds that seem to be the main binding phases for Co, and minor binding phases for As, Ni and Zn.

Factor 3 accounting for 5.6% of the total variance is characterized by high negative loadings of Ca and Mg, and a moderate negative loading of Mn. This factor stands

			As	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Sediment Quality Guidelines	Canadian	TEL	7.2	0.7	52.3	18.7		15.9	30.2	124
		PEL	41.6	4.2	160	108			112	271
	Wisconsin	TEL	9.8	0.99	43	32	460	23	36	120
		PEL	33	5.0	110	150	1100	49	130	460
	Flemish	Target value	20	2,5	60	20		70	70	160
		Limit value	100	7	220	100		280	350	500
Mean concentration (ppm)			26	0.09	27	20	108	8	16	40
Measured values in this study	Compared with the Canadian	%samples <TEL	0	100	100	43		97	97	100
		%samples between TEL-PEL	97	0	0	57		3	3	0
		%samples >PEL	3	0	0	0			0	0
	Compared with the Wisconsin	%samples <TEL	0	100	91	100	100	100	97	100
		%samples between TEL-PEL	83	0	9	0	0	0	3	0
		%samples >PEL	17	0	0	0	0	0	0	0
	Compared with the Flemish	%samples <Target	28	100	100	60		100	100	100
		%samples between Target-Limit	72	0	0	40		0	0	0
	%samples >Limit	0	0	0	0		0	0	0	

Table 5. Comparison between heavy metal concentrations and numerical Sediment Quality Guidelines

for the carbonates in the sediments, which play a minor role in binding heavy metals except for Mn.

Note that elements such as Fe, As, Ni, Zn and Mn that express moderate to high loadings with both factor 1 (or factor 3 in the case of Mn) and factor 2, are related to more than one geochemical process (Bailey et al., 2005).

3.3 Assessment on contamination status of heavy metals

Since previous studies in the study area as well as contiguous areas were quite scarce, local or regional background values were unavailable. In an attempt to infer anthropogenic from geogenic input, two possible approaches including comparison with numerical Sediment Quality Guidelines and classification by quantitative indexes such as Geo-accumulation Index (I_{geo}) and Enrichment Factor (EF) with respect to reference materials were used (Since the bedrocks in the study area were terrigenous sedimentary and carbonate rocks, the average continental crust, upper continental crust and average sedimentary rock (clay and claystone) as mentioned in Table 2 were selected as reference materials). As reported by many authors, both approaches have their

own limitations, e.g. the Sediment Quality Guidelines do not account for the physico-chemical attributes of the sediments such as grain size, organic matter content, sulfides, chemical species and complexes that may increase or decrease the potential for toxic effects at a specific area (Ingersoll et al., 2000); and the classification by quantitative indexes depends on the index and reference material used (Rubio et al., 2000). Therefore, a combination of these approaches can be a good option to give a more comprehensive and accurate assessment on the contamination status of heavy metals.

3.3.1 Sediment Quality Guidelines (SQGs)

Three sets of Canadian, Wisconsin- United States and Flemish numerical Sediment Quality Guidelines were selected as a result of their popularity in the world as well as granular composition and organic matter content in standard sediments (i.e. 50% fine-grained fraction in the case of Canadian and Wisconsin SQGs, or 10% clays and 2% organic matter in the case of Flemish SQGs) which are more or less equivalent to that of the studied sediments (as represented in Table 2). Therefore, these three sets of numerical SQGs were directly applied (without normalization) in assessing possible heavy metal contamination in sediments of the study area.

		As	Cd	Co	Cr	Cu	Ni	Mn	Pb	Zn
I_{geo} with respect to Average Sedimentary Rock	Max	2.7	-1.2	-1.2	-1.6	-1.5	-2.9	-1.7	0.4	-0.4
	Min	0.4	-4.4	-5.2	-3.9	-2.7	-5.7	-5.9	-2.8	-3.3
	Average	1.3	-2.6	-2.5	-2.6	-2.2	-4.2	-3.5	-1.0	-1.7
	STDV	0.5	0.8	0.8	0.6	0.3	0.7	0.9	0.8	0.7
I_{geo} with respect to Upper Continental Crust	Max	4.8	0.4	-1.0	-1.4	-0.3	-1.8	-1.2	0.7	-0.2
	Min	2.6	-2.8	-5.0	-3.7	-1.5	-4.6	-5.4	-2.5	-3.1
	Average	3.4	-1.0	-2.3	-2.4	-1.0	-3.1	-3.0	-0.8	-1.5
	STDV	0.5	0.8	0.8	0.6	0.3	0.7	0.9	0.8	0.7
I_{geo} with respect to Average Continental Crust	Max	5.4	0.4	-1.8	-2.5	-1.9	-3.0	-2.7	1.8	-0.4
	Min	3.2	-2.8	-5.8	-4.8	-3.1	-5.8	-6.9	-1.5	-3.3
	Average	4.0	-1.0	-3.1	-3.5	-2.5	-4.4	-4.5	0.3	-1.7
	STDV	0.5	0.8	0.8	0.6	0.3	0.7	0.9	0.8	0.7
EF with respect to Average Sedimentary Rock	Max	25.2	1.7	1.9	1.0	2.4	0.4	1.3	2.9	2.5
	Min	4.7	0.2	0.1	0.3	0.4	0.1	0.0	0.7	0.3
	Average	10.0	0.7	0.8	0.6	0.9	0.2	0.5	1.9	1.2
	STDV	4.9	0.3	0.5	0.2	0.4	0.1	0.4	0.6	0.5
EF with respect to Upper Continental Crust	Max	93.4	4.5	1.8	1.0	4.7	0.7	1.5	2.9	2.4
	Min	17.3	0.6	0.1	0.3	0.7	0.1	0.0	0.7	0.3
	Average	37.0	1.7	0.8	0.6	1.7	0.4	0.5	1.9	1.2
	STDV	18.0	0.8	0.5	0.2	0.8	0.2	0.4	0.6	0.5
EF with respect to Average Continental Crust	Max	146.9	4.6	1.1	0.5	1.6	0.3	0.6	6.4	2.2
	Min	27.2	0.6	0.0	0.1	0.2	0.0	0.0	1.5	0.3
	Average	58.1	1.7	0.5	0.3	0.6	0.2	0.2	4.2	1.1
	STDV	28.3	0.8	0.3	0.1	0.3	0.1	0.2	1.3	0.5

Table 6. Geo-accumulation Index and Enrichment Factor with respect to different reference materials

With respect to Canadian and Wisconsin SQGs, a site is determined as contaminated if at least 10% sample values exceed TEL (threshold effect level). Three ranges of chemical concentrations are defined by TEL and PEL (probable effect level) as follows: 1) concentrations of chemicals in sediments below TEL that are not associated with adverse biological effects; 2) concentrations between TEL and PEL that may occasionally be associated with adverse biological effects; and 3) concentrations above PEL that are expected to be frequently associated with adverse biological effects (MacDonald et al., 2003). With respect to Flemish SQGs for dredged material, the guidance of the Royal Belgian Institute of Natural Sciences is as follows (MUMM, 2007): 1) if the measured concentrations are below the target value, the dredged sediments may be dumped at sea; 2) if the concentrations lie between the target and the limit value, further investigations have to be conducted; and 3) if the concentrations exceed the limit value, the dredged sediments must not be dumped at sea. The comparison results were given in Table 5.

If compared to the Canadian SQGs, As has a mean concentration above TEL with 100% of samples exceeding TEL, in which 97% of samples fall in the range between TEL and PEL, and 3% of samples exceed PEL. Cu has a mean concentration higher than TEL and 57% of the samples fall in the range between TEL and PEL. In contrast, other heavy metals such as Cd, Cr, Mn, Ni, Pb and Zn have mean concentrations significantly lower than TELs, and only in few cases, i.e. for Ni and Pb, some of the samples exceed TEL values.

If compared to the Wisconsin SQGs, only As has a mean concentration above TEL and 100% of the samples exceed TEL, in which 83% of samples fall in the range between TEL and PEL, and 17% of samples exceed PEL. On the contrary, other heavy metals have mean concentrations much lower than TELs and more than 90% of the samples possess concentrations lower than TEL.

If compared to the Flemish SQGs, As has a mean concentration higher than the target value and 72% of samples lying between the target and the limit value; Cu has a mean concentration equal to the target value and 40% of samples between the target and the limit value, whereas other heavy metal concentrations in all samples are below the target value.

Although there is a small difference between the results obtained with three used SQGs, the above results lead to the conclusion that only As possibly is of concern that it may occasionally be associated with adverse biological effects. Based on the used criteria, the risk of Cu is unclear and needs to be examined by other approaches, and Cd, Cr, Mn, Ni, Pb and Zn are in principle not associated with adverse biological effects.

These results are comparable with the findings by Nguyen Thi Thuc Anh (2005) in other areas of Ha Long Bay. The author reported on As values which exceed the TEL of Canadian SQGs by 2-7 times in Tuan Chau, Cao Xanh, Ha Coi and Mong Cai areas. However, the mean concentrations of other heavy metals (Cd, Cu, Cr, Mn, Ni,

Pb and Zn) in this study are often lower than that of the reported findings in which heavy metal concentrations were one to two times higher than TELs.

3.3.2 Quantitative indexes

The Geo-accumulation Index (I_{geo}) and the Enrichment Factor (EF) are defined as follows:

$$1) \quad I_{geo} = \log_2 [C_m / 1.5 C_o]$$

Where C_m is the measured concentration of the heavy metal in the sediment samples; and C_o is the concentration of the heavy metal in the reference material; the factor 1.5 is used to compensate for possible variations of the reference data due to lithogenic effects (Aksu et al., 1997). Based on the I_{geo} value, the degree of heavy metal contamination is classified as follows: 1) $I_{geo} < 0$: unpolluted; 2) $0 \leq I_{geo} < 1$: unpolluted to moderately polluted; 3) $1 \leq I_{geo} < 2$: moderately polluted; 4) $2 \leq I_{geo} < 3$: moderately to strongly polluted; 5) $3 \leq I_{geo} < 4$: strongly polluted; 6) $4 \leq I_{geo} < 5$: strongly to very strongly polluted; 7) $I_{geo} \geq 5$: very strongly polluted.

$$2) \quad EF = [C_{metal}/C_{norm}]_{Sediment} / [C_{metal}/C_{norm}]_{Reference}$$

Where C_{metal} and C_{norm} are the concentrations of heavy metal and normalizer in the sediment samples and the reference material, respectively. In this approach, the normalizer is used to compensate for the differences in grain size and mineralogical composition between the sediment and the reference material. This requires that the normalizer must be an element of natural origin, and must have good correlations with heavy metals and the fine-grained fraction. Like many other authors (i.e. Aksu et al., 1997; Rubio et al., 2000; Woiitke et al., 2003), in this paper Al was selected as the normalizer because it had a strong correlation with fine-grained fraction and many heavy metals as mentioned above. Based on the Enrichment Factor (EF), the heavy metal contamination can be classified into the following levels: 1) $EF \leq 1$: no enrichment; 2) $1 < EF \leq 3$: minor enrichment; 3) $3 < EF \leq 5$: moderate enrichment; 4) $5 < EF \leq 10$: moderately severe enrichment; 5) $10 < EF \leq 25$: severe enrichment; 6) $25 < EF \leq 50$: very severe enrichment; 7) $EF > 50$: extremely severe enrichment.

The I_{geo} and EF were calculated for individual samples, and these results were averaged for the entire set of samples (Table 6).

The calculated Geo-accumulation Index (I_{geo}) values indicate that only As has high positive I_{geo} values with respect to all three reference materials ($I_{geo} = 1.3, 3.4$ and 4.0 respectively) which are ranked from "moderately polluted" to "strongly polluted". Pb is evaluated as "unpolluted to moderately polluted" with respect to average continental crust ($I_{geo} = 0.3$), and "unpolluted" with respect to average sedimentary rock and upper continental crust ($I_{geo} < 0$). Other heavy metals (Cd, Co, Cr, Cu, Ni, and Zn) have negative I_{geo} values for all three reference materials, which are evaluated as "unpolluted".

The Enrichment Factor (EF) values are quite variable for heavy metals. As is characterized by high EF values, i.e. 10.0, 37.0 and 58.1 with respect to average sedimentary

rock, upper continental crust and average continental crust, respectively. As a result, As is ranked in the classes from “severe enrichment” to “extremely severe enrichment”. Pb shows “minor enrichment” with respect to average sedimentary rock and upper continental crust (EF = 1.9 for both these reference materials), and “moderate enrichment” with respect to average continental crust (EF = 4.2). Zn shows “minor enrichment” with respect to all three reference materials (EF = 1.2, 1.2 and 1.1 respectively). Cd shows “minor enrichment” with respect to upper continental crust and average continental crust (EF = 1.7 for both these reference materials), and “no enrichment” with respect to average sedimentary rock (EF = 0.7). Cu shows “minor enrichment” with respect to upper continental crust (EF = 1.7) and “no enrichment” with respect to two other reference materials (EFs < 1). Other heavy metals (Co, Cr, Ni, and Mn) show “no enrichment” with respect to all three reference materials (EFs < 1).

Although there are some differences in the results of assessment and classification of heavy metal contamination levels depending on the reference material and the quantitative index used, the above results lead to the conclusion that As is of concern, the contamination of Cd, Pb, Cu and Zn is unclear, whereas other heavy metals (Co, Cr, Ni and Mn) can be classified as not polluted.

4. Conclusion

The bottom sediments near Cua Ong Harbor are characterized by low concentrations of fine-grained fraction (53.2%), organic matter (1.65%), sulfides (0.12%) as well as major elements such as Al (4.47%), Ca (1.33%), Mg (0.44%), Fe (1.30%) and K (0.91%). Sediment pH values, ranging from 7.01 to 8.21 (mean: 7.68), reflect a neutral to lightly basic medium. The distribution patterns of As, Cd, Cr, Cu, Ni, Pb and Zn are controlled by organic matter and clay minerals and determined by the distribution of the fine-grained fraction in the sediments. In contrast, iron and manganese compounds seem to exert some control on the distribution of Co. Carbonates partly control the distribution of Mn, but are not important with respect to the other studied heavy metals. In this case the carbonates act as a diluting agent of the heavy metal concentration. Natural processes such as weathering and erosion of bedrocks are main supply sources of heavy metals in sediments near Cua Ong Harbor. Among the studied heavy metals only As is of concern, which occasionally may be associated with adverse biological effects based on the comparison with SQGs. Furthermore, with respect to the reference materials and quantitative indexes, the sediments are considered to be moderately to strongly polluted by As. In contrast, the sediments are almost not polluted by other heavy metals (Cd, Co, Cr, Cu, Ni, Mn, Pb and Zn), and they seem to reflect background concentrations in the study area. In the future, biological and ecological studies need to be carried out to elucidate the influence of As to the ecosystems.

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