



## Necessity of normalization to aluminum to assess the contamination by heavy metals and arsenic in sediments near Haiphong Harbor, Vietnam

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### ABSTRACT

While assessing many different aspects of contamination by heavy metals and arsenic in sediments, the natural variability in element contents which depends on the grain-size and mineralogical composition of sediments, needs to be taken into account. In previous studies, the normalization of element contents to a reference element such as Al was commonly applied to compensate for granulometric and mineralogical effects. In the present study, through the investigation on the contamination of heavy metals and arsenic in sediments near Haiphong Harbor, the necessity of the normalization towards Al is assessed. The results indicate that before Al-normalization, the occurrences on the source and historical trend of contamination by heavy metals and arsenic can be masked by the distribution of clay ( $\Phi < 2 \mu\text{m}$ ) or fine ( $\Phi < 63 \mu\text{m}$ ) fractions as well as Al, Fe and organic matter. In contrast, after Al-normalization, spatial distribution of elements illustrates that Cr, Ni, Pb and Mn are enriched by the anthropogenic activities in the Haiphong industrial and harbor zone while As, Cd and Cu come from upstream sources, and Co and Zn indicate only locally-elevated contaminations. The vertical profile of elements in core sediments illustrates that the anthropogenic input of heavy metals and arsenic increased in recent years. Moreover, the assessment of the degree of contamination based on the Enrichment Factor (EF) and obtained local background values indicates a minor enrichment of all heavy metals and arsenic. This is not in line with the assessment based on the sediment quality guidelines or reference values from upper-continental or average-continental crust which states the “serious” contamination of Cd, Pb, Cu, Zn and especially As. Therefore, the normalization to Al is necessary in interpreting the source, historical trend and degree of contamination by heavy metals and arsenic in sediments of the study area.

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### 1. Introduction

Most of previous studies on metal contamination in sediments in Vietnam and particularly in Haiphong coastal zone have not taken into account the natural variability of metal contents in sediments. For instance, Thuc Anh (2006) has assessed the contamination status by heavy metals and arsenic in sediments mainly based on the comparisons of the total metal contents with the sediment quality guidelines of the United States and Canada. Since site-specific sediment quality criteria are not available, this may lead to over/underestimations of the contamination status of the area. In addition, spatial and temporal variations in grain size and mineralogical composition of the sediments did not allow her to recognize the source as well as historical trend of metal contamination in Haiphong coastal zone.

Since metals, originating from natural (bedrocks and mineralized deposits) and anthropogenic sources, accumulate together in sediments, it is difficult to determine what proportion of the sedimentary metal load is natural and what proportion is anthropogenic. This is because natural sedimentary metal loads can vary by several orders of magnitude, depending on the nature, grain size distribution and provenance of metal-rich/metal-poor minerals/compounds in the sediments (UNEP, 1995). In order to overcome this problem, a normalization procedure should be used to compensate for granulometric and mineralogical effects on metal contents and enable differentiation between inputs derived from anthropogenic activities and those from natural (bio)geochemical processes (UNEP, 1995; Summers et al., 1996; Covelli and Fontolan, 1997; Grant and Middleton, 1998; Aloupi and Angelidis, 2001b; Yau and Gray, 2005).

Generally, there are two types of normalization techniques when studying metal contamination in river-mouth and coastal sediments, namely (1) methods based on granulometric approaches and (2) methods using geochemical approaches.

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With regard to the granulometric approach, two procedures can be followed. The first simply relies on the separation of a specific fraction, e.g.  $\Phi < 63 \mu\text{m}$  or  $\Phi < 20 \mu\text{m}$  prior to chemical analyses (Grant and Middleton, 1998). The other procedure is based on the fact that metals tend to concentrate in the fine-grained fraction ( $\Phi < 63 \mu\text{m}$ ) of sediments, and linear relationships between their total contents and the percentage of this fraction are commonly found in sediments. Therefore, it is then possible to normalize metal contents by the percentage of the fine fraction (UNEP, 1995). However, granulometric normalization cannot fully compensate for metal variability, because natural metal contents and their variability in sediments are determined not only by grain size distribution, but also by the composition of primary and secondary minerals (UNEP, 1995).

To overcome this drawback, the geochemical approach is more commonly used. This comprises the normalization of metal data by the contents of a conservative element such as Al, Fe, Li, Rb, Sc, and organic carbon, etc. which represents one or more of major metal carriers of sediments (e.g. clay minerals, iron and manganese hydr/oxides and organic matter, etc.) (Covelli and Fontolan, 1997; Schiff and Weisberg, 1999; Aloupi and Angelidis, 2001b; Boszke et al., 2004). According to literature, the use of a conservative element as a normalizer necessitates that a number of assumptions are fulfilled: firstly, the normalizer should co-vary proportionally to the naturally-occurring contents of the metal of interest; secondly, the normalizer is insensitive to inputs from anthropogenic sources; and thirdly the normalizer is stable and is not subject to environmental influences such as reduction/oxidation, adsorption/desorption, and other diagenetic processes such as leaching that may alter its contents in the sediments (Schiff and Weisberg, 1999). Whenever a possible anthropogenic input of a conservative element is suspected, a preliminary investigation is recommended. By means of a data correlation matrix, the element can be chosen as a normalizer if it has significant relationships with the fine ( $<63 \mu\text{m}$ ) fraction and heavy metals of interest (Covelli and Fontolan, 1997).

Aluminum, which is one of the most important constituents of the aluminosilicate mineral fraction, is often used as a normalizer for several reasons: it is the most abundant naturally-occurring metal; it is highly immobile, so it is not affected significantly by diagenetic processes and strong redox effects in sediments; and finally its content is generally not influenced by anthropogenic sources (Schropp and Windom, 1988; Charlesworth and Service, 2000). Because naturally-occurring Al and other metals are tightly bound within the crystalline structure of the sediment minerals, the methods for elemental analyses must include complete sediment digestion. If Al is not completely released by a thorough digestion, the heavy metal to Al ratios may appear to be unusually high (Schropp and Windom, 1988).

Besides Al, Fe and Li are also common normalizers used in many studies (Schiff and Weisberg, 1999). However, likely limitations of using Fe as a normalizer is that the speciation and thus the mobility of Fe is redox sensitive, so it is affected by diagenetic processes, and additionally a small fraction of Fe in sediments may represent anthropogenically-induced Fe sulfides and oxides (Summers et al., 1996). The use of Li as a normalizer is better than Al in some cases, particularly for high-latitude coastal sediments (UNEP, 1995; Covelli and Fontolan, 1997; Aloupi and Angelidis, 2001a). For low-latitude countries such as Vietnam and other Southeast Asian countries, the advantages of Li have not yet been proven. Moreover, some authors also used organic carbon and trace elements (Cs, Eu, Rb, Sc, Sm, and Th, etc.) as normalizers. Unfortunately, with regard to organic carbon it is not easy to analyze and it is also a bulk analysis. In addition, organic carbon itself is subject to considerable augmentation by human activity, it can be degraded by (micro)-organisms and is often a contaminant (Voravit and San

Diego-McGlone, 1997). With regard to trace elements such as Cs, Eu, Rb, Sc, Sm, and Th, etc. they often occur in very low contents, which may lead to considerable errors in calculation.

Generally, the relative proportion of heavy metals and the normalizer in a natural sediment source are fairly constant. Therefore, the simplest approach in the geochemical normalization of heavy metals in sediments is to express the ratio of the content of a given heavy metal to that of the normalizer. An increase in the heavy-metal/normalizer ratios possibly indicates an enrichment of the heavy metal (Schropp and Windom, 1988). For example, some authors used the heavy-metal/normalizer ratios to evaluate contamination history recorded in sediments from the estuaries (O'Reilly Wiese et al., 1997), or to track contaminant sources (Cortesao and Vale, 1995; Kamau, 2002), or to assess the degree of enrichment by heavy metals in sediments (Covelli and Fontolan, 1997; Aloupi and Angelidis, 2001b; Abraham and Parker, 2008).

In the present study, through the evaluation of the spatial distribution in river-bed sediments and historical trends in vertical sediment sections as well as degree of enrichment of heavy metals and arsenic in sediments near Haiphong Harbor, we want to illustrate the importance of normalization to Al in the studies on environmental pollution in Vietnam.

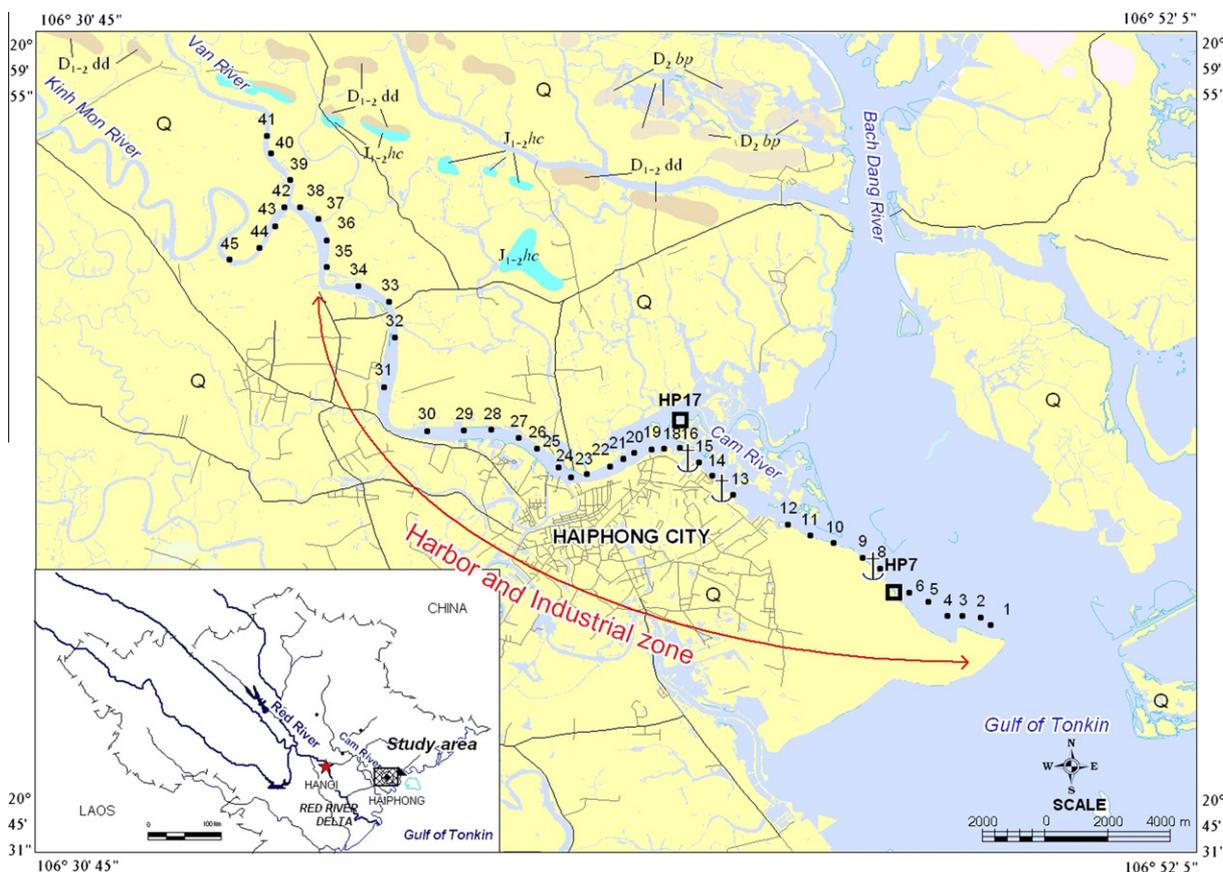
## 2. Materials and methods

### 2.1. Study area

The Cam River is formed by the mergence of Kinh Mon and Van Tributary Rivers in the northwest of the study area. It flows through Haiphong City and finally meets the Bach Dang River before reaching the sea in the east (Fig. 1). These rivers belong to the Red River system, whose catchment comprises several provinces in Northern Vietnam. Therefore, the Cam River is currently influenced not only by anthropogenic activities in Haiphong City, but also by anthropogenic activities in other provinces in Northern Vietnam.

Haiphong Harbor, situated over a 20 km length along the Cam River, is one of the most important harbors for international and national trade in Northern Vietnam. Historically, the harbor was established in 1876. Initially, in this area there were only harbor facilities for storing and transporting goods and passengers. The industry just started in 1954 when Northern Vietnam was liberated from the French rule. During the period 1965 – 1972, this area also suffered many bombing campaigns of the U.S. Army to prevent weapon importation into Vietnam. Since the late 1980s, together with the socio-economic reform in Vietnam, the industrialization and urbanization processes rapidly developed in Haiphong City. At present, the Cam River is receiving the discharges directly from a series of steel, glass, wood-processing, food-processing and ship-building factories, goods and petrol stores, and residential areas, etc. that are densely situated along the river banks. Every year, an estimated amount of 52.6 tons Cu, 20.2 tons Pb, 382 tons Zn, 2.9 tons Hg, 27.9 tons As and 2.0 tons Cd, etc. from human activities in Haiphong City is discharged into the Cam River (Phuong Hoa and Van Dieu, 2004).

Most of the study area is covered by Quaternary unconsolidated sediments including cobble, pebble, sand, silt, clay and remains of organic material. Bedrocks are mainly conglomerates, sandstones, siltstones, shales and limestones. Their presence reflects a "remaining paleotopography". According to Thuc Anh (2006), the mineralogical composition of intertidal sediments near the river-mouth consists of 48.2% quartz, 11% feldspar, 6% chlorites, 4.5% goethite, 10.2% kaolinite, 19.5% illite, <1% montmorillonite, and minor amounts of amphibole, tourmaline, titanite, zircon, micas, etc. The water of the Cam river is characterized by the following



**Fig. 1.** Study area and sampling locations. D<sub>1-2</sub>dd Devonian Duong Dong Formation: quartz sandstone, siltstone, claystone, cherty shale and marl; D<sub>2</sub>bp Devonian Ban Pap Formation: grey limestone, cherty limestone and clay-rich limestone; J<sub>1-2</sub>hc Jurassic Ha Coi Formation: conglomerate, gridstone, sandstone, siltstone interbedded with thin layers of coaly shale; Q Quaternary unconsolidated sediments: cobble, pebble, sand, silt, clay and remains of plant; ● river-bed sediment sample; and □ core-sediment sample.

physico-chemical parameters: pH: 7.1–7.4, salinity: 0.16–2.6‰, turbidity: 68–413 mg/l, and dissolved oxygen content (DO): 2.3–3.88 mg/l (Thuc Anh, 2006).

## 2.2. Sampling and sample pretreatment

The sampling campaign was carried out in January 2008. Forty-five river-bed sediment samples were collected from a boat by a grab at approximately 600 m-intervals along the Cam River. These sampling points can be divided into two zones, i.e. a locally harbor and industrial zone (0–25 km from the sea) and a locally-unindustrialized zone upstream of the former zone (25–35 km from the sea). In addition, two 65 cm-long sediment cores were also collected by inserting PVC tubes ( $\phi = 80$  mm) into the sediments. Both cores are located in the harbor and industrial zone area: core HP 17 is situated at an alluvial spit near a river-junction and core HP 7 at a mangrove forest near the sea (Fig. 1).

During sampling, precaution was taken to minimize any disturbance in the grain size distribution of the original sediment. For example, the river-bed sediment sample was taken only when the grab was firmly closed upon arrival to the boat, so that any leakage of fine material withdrawn by river-water was avoided. Moreover, to minimize metal contamination from the grab or the PVC tube, the outer part of the sediment sample was removed and only the inner part was further processed, and all materials used for treatment and storage of the samples were non-metallic (plastic or wood).

After collection, the sediment cores were extruded and sectioned over 3–4 cm intervals. Finally, the river bed-sediment and core-sediment samples were placed in tightly sealed plastic containers, and transported to the Vietnam Institute of Geosciences and Mineral Resources. Here, the samples were dried at 40 °C for 5 days, and then disaggregated in an agate mortar, homogenized and sieved over a 1 mm-interval net. Almost all sediment constituents were smaller than 1 mm in size except for some quartz particles, shells and remains of plant. Since these big-size materials nearly do not contain heavy metals and arsenic, the < 1 mm-sieved material can be considered sufficiently representative for the sediments in the study area and this was used for further analyses (Adamo et al., 2005).

## 2.3. Analyses and quality control

Analyses were carried out at the Department of Earth and Environmental Sciences, Catholic University of Leuven (K.U. Leuven, Belgium). The organic matter content was determined by the Walkley–Black manual titration method (Schumacher, 2002). Grain size composition was determined by means of laser diffraction spectrophotometry (Malvern Mastersizer S long bed, Malvern, Worcestershire, UK). Sediment pH was measured in a suspension of 1/5 sediment to CaCl<sub>2</sub>·2H<sub>2</sub>O 0.01 M solution after shaking for 2 h.

The total elemental contents of Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, K, Ni, Pb and Zn in sediments were determined according to the so-called 4 acid-digestion method. One gram of dry sediment was put in a Teflon beaker. After adding 20 ml HNO<sub>3conc</sub>, the beaker

**Table 1**  
Comparison between the measured concentrations with certified data of BCSS-1 (marine sediment) and GBW07311 (stream sediment) in the total elemental analysis ( $n = 2$ ).

		Major element (%)					Heavy metal ( $\mu\text{g/g}$ )								
		Al	Ca	Fe	K	Mg	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
BCSS_1 (marine sediment)	Measured	6.10	0.57	3.24	1.82	1.45	10.9	0.34	10.8	88.3	19.8	215	53.2	21.4	130
	Certified	6.26	0.54	3.29	1.80	1.46	11	0.25	11	123	19	229	55	23	119
	Recovery (%)	97	106	99	101	99	99	136	95	72	107	94	96	94	109
GBW 07311 (stream sediment)	Measured	5.27	0.35	3.07	2.61	0.37	173	2.50	7.8	24.9	81.0	2736	15.0	614	404
	Certified	5.49	0.34	3.07	2.73	0.37	188	2.30	8.5	40	79	2490	14.3	636	373
	Recovery (%)	96	104	100	96	100	92	109	91	62	103	110	105	97	108

was gently shaken and put on a hot plate at 200 °C until almost dry. Next, 20 ml  $\text{HClO}_{4\text{conc}}$  were added to the beaker (covered with a loose cap) and heated at 240 °C until almost dry. Next, 20 ml  $\text{HF}_{\text{conc}}$  were added to the beaker and heated at 240 °C until completely dry. Subsequently, the mixture was digested again in 5 ml  $\text{HClO}_{4\text{conc}}$  at 240 °C until almost dry. Finally, the mixture was dissolved by adding 20 ml 2.5 M HCl and put on a hot plate until the solid particles were entirely dissolved in the acid solution. The solution was filtered by a Whatman membrane and diluted to 50 ml with Milli-Q water. Finally, within two week the obtained solutions were measured by ICP–OES (Varian 720ES).

All reagents were of ultra-pure quality (Chem-Lab NV, Belgium), and all labwares used were either new or thoroughly cleaned before utilization. All the samples were measured three times by ICP–OES to control the analytical precision, in which the standard deviation was less than 5% for all elements. The efficiency of the digestion procedure and the analytical quality were controlled by the use of standard reference material BCSS-1 (marine sediment) and GBW07311 (stream sediment) ( $n = 2$ ). The comparison between the measured concentrations with the certified data illustrates a good agreement for almost all the elements (Table 1).

#### 2.4. Data processing

The potential normalizing elements available in our database are Al, Fe and organic carbon (OC). A Pearson Product–Moment correlation matrix between these potential normalizers with other characteristics (i.e. K, Ca, Mg, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, clay ( $\phi < 2 \mu\text{m}$ ) and fine fractions ( $\phi < 63 \mu\text{m}$ )) in surficial river-bed sediments was established for the purpose of defining the normalizer. Since for such 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, several major and trace elements often possess a close to logarithmic distribution (Batista et al., 2006). This was however not really the case in our limited dataset, except for Ca, where a logarithmic transformation was performed to obtain a population distribution as close as possible to normality.

Al, Fe and OC significantly (at  $p$ -value  $< 0.05$ ,  $n = 45$ ) correlate with each other ( $r = 0.48$ – $0.89$ ) and also with Ca, K, Mg, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, clay and fine fractions ( $r = 0.36$ – $0.88$ ), except for an insignificant correlation of OC with Ca ( $n = 0.10$ ). This suggests that Al, Fe and OC can be all chosen as the normalizer. However, Al is a major constituent of different sedimentary minerals (i.e. feldspar, chlorites, kaolinite, illite, montmorillonite and mica, etc.) in the studied sediments and completely released by the sample-digestion technique including hydrofluoric acid (HF). In addition, Fe and OC may be subject to the contamination by anthropogenic activities in the study area, e.g. Fe may come from previous American bombing campaigns or from current steel-rolling and ship-building factories, and OC from residential areas of Haiphong City. Therefore, in the present paper, Al was considered

as the most suitable normalizer. The vertical and horizontal distributions as well as the assessment of contamination degree were established based on the raw data (without normalization) and the Al-normalized data to illustrate the importance of the normalization approach towards Al in studying the contamination by heavy metals and arsenic in the Cam River–mouth.

### 3. Results and discussion

#### 3.1. Sediment characterization

Statistical parameters (mean, median, minimum, maximum and standard deviation) for major elements, heavy metals and arsenic, organic matter, pH and percentage of clay and fine fractions of the river-bed sediments are presented in Table 2. Generally, the contents of major elements such as Al, K, Ca, Mg and Fe are low if compared to those of upper continental crust and average continental crust. However, the sediments are characterized by a high percentage of the fine fraction (mean:  $83.27 \pm 8.33\%$ ) and low organic matter content (mean:  $1.30 \pm 0.28\%$ ). In addition, sediment pH values, ranging from 7.20 to 7.99, indicate a slightly alkaline nature. If compared to the Canadian Interim Marine Sediment Quality Guidelines, almost all heavy metals such as Cr, Cu, Ni, Pb and Zn exceed the Threshold Effect Levels (TELS) and especially As exceeds the Probable Effect Level (PEL).

#### 3.2. Spatial distribution

Spatial variations in contents of clay and fine fractions, Al, K, Ca, Mg, Fe, organic matter, and pH as well as in contents before and after Al-normalization of heavy metals (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) and As are illustrated in Fig. 2. The Al-normalized contents of these elements were multiplied by a factor 8 for a better visualization.

The fine fraction is generally high in the upstream area and near the river–mouth while clay fraction slightly increases towards the river–mouth. Similarly to the fine fraction, the contents of Al, Fe and organic matter slightly increase towards the upstream area or the river–mouth. K and Mg contents do not show any clear trends along the river while Ca contents increase towards the upstream area. The pH varies between 7 and 8 and does not show a systematic variation in the Cam River’s sediments.

Before normalizing to Al, the contents of Co, Cr, Mn, Ni, Pb and Zn do not show any difference between the harbor and industrial zone (0–25 km from the sea) and the unindustrialized zone (25–35 km from the sea) while in the unindustrialized zone, the contents of As, Cd and Cu slightly increase towards the upstream. In contrast, after normalizing to Al, the contents of Cr, Ni, Pb and Mn are higher in the harbor and industrial zone if compared to the unindustrialized zone while As, Cd and Cu show an increasing trend towards the upstream area in the unindustrialized zone, and Co and Zn contents do not show any clear trends except for some unusual peaks along the river–mouth.

**Table 2**

Statistical parameters for geochemical characteristics of the surficial river-bed sediments along the Cam River.

	Concentration in the studied samples						Concentration in reference material		Canadian marine sediment quality guidelines <sup>b</sup>	
	Unit	Mean	Median	Min.	Max.	Std. Dev.	Upper continental crust <sup>a</sup>	Average continental crust <sup>a</sup>	Threshold effect level (TEL)	Probable effect level (PEL)
Al	%	5.36	5.42	3.27	7.21	0.87	8.03	8.42		
K	%	1.85	1.83	1.52	2.06	0.11	2.81	1.08		
Ca	%	0.71	0.62	0.28	1.21	0.28	2.99	5.29		
Mg	%	0.48	0.48	0.34	0.65	0.07	1.32	3.18		
Fe	%	3.62	3.62	2.78	4.37	0.35	3.49	7.08		
As	µg/g	42	41	17	68	10	1.5	1.0	7.24	41.6
Cd	µg/g	0.48	0.45	0.28	0.78	0.12	0.098	0.1	0.7	4.2
Co	µg/g	17	18	13	23	2	17	29		
Cr	µg/g	90	90	56	110	11	85	185	52.3	160
Cu	µg/g	82	80	38	123	16	25	75	18.7	108
Mn	µg/g	827	841	533	1012	94	500	1400		
Ni	µg/g	55	55	44	69	6	44	105	15.9	
Pb	µg/g	92	91	56	132	15	17	8.0	30.2	112
Zn	µg/g	178	174	107	272	31	71	80	124	271
OM	%	1.30	1.27	0.82	2.05	0.28				
pH		7.75	7.76	7.20	7.99	0.20				
Clay ( $\Phi < 2 \mu\text{m}$ )	%	14.80	14.64	7.77	20.28	2.80				
Fines ( $\Phi < 63 \mu\text{m}$ )	%	83.27	85.20	63.86	98.36	8.33				

<sup>a</sup> According to Taylor and McLennan, 1995.<sup>b</sup> According to Canadian Council of Ministers of the Environment, 2001.

High percentages of clay ( $\Phi < 2 \mu\text{m}$ ) and fine ( $\Phi < 63 \mu\text{m}$ ) fractions towards the upstream area or the river-mouth are supposed to relate to the decreased flow velocity because of expansion of the river at these areas. Since Al and Fe are major constituents of aluminosilicate minerals that contribute to the the clay ( $\Phi < 2 \mu\text{m}$ ) and fine ( $\Phi < 63 \mu\text{m}$ ) fractions, and organic matter can form an armoring cover on clay particles, this also leads to high contents of Al, Fe and organic matter at these areas. The increase in Ca contents towards the upstream area indicates that this element may come from natural weathering and erosion of carbonate rocks in upstream areas.

As mentioned above, Al, Fe and OM have significant correlations with heavy metals and arsenic, so spatial distribution patterns of heavy metals and arsenic before Al-normalization are generally controlled by the distribution of these major elements as well as the clay and fine fractions. This partly masks the manifestation of the possible contamination of heavy metals and arsenic. However, those effects are eliminated to a major degree after normalizing the element data towards Al contents. The higher Al-normalized contents of Cr, Ni, Pb and Mn in the harbor and industrial zone suggest that they are likely enriched as a result of harbor and industrial activities in this zone. Since the Kinh Mon River flows through some industrial zones of Hanoi, Bacninh and Haiduong provinces before entering Haiphong City, the increase in the Al-normalized contents of As, Cd and Cu towards upstream area of this river may indicate that they come from these upstream pollution sources. Co and Zn did not show any clear trends, but their unusual peak values in the harbor and industrial zone may indicate local contributions from steel-rolling, wood-processing, food-processing, and ship-building factories, goods and petrol stores that are situated along the river banks.

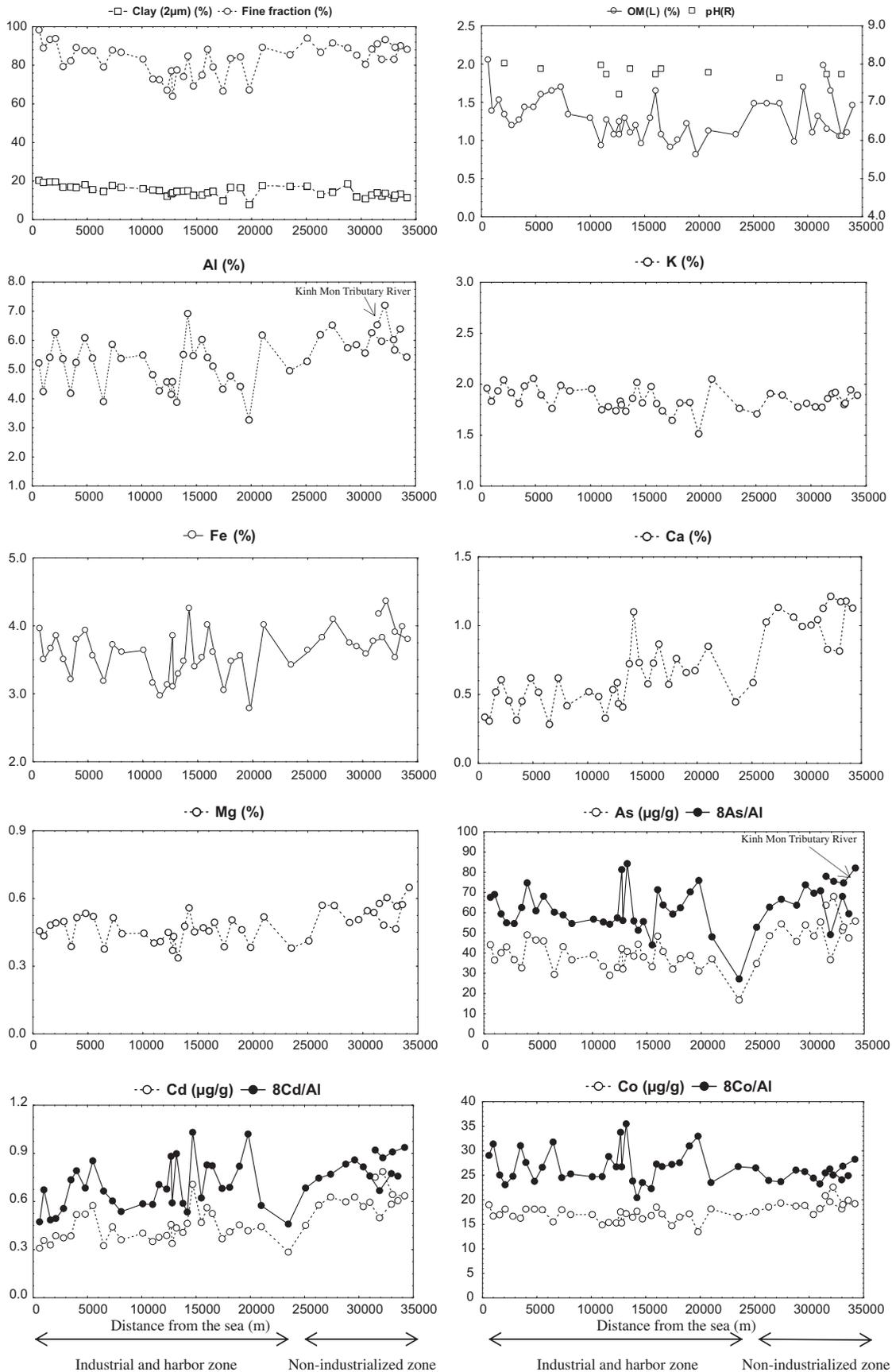
### 3.3. Vertical profiles

Investigations of vertical variations of heavy metals and arsenic in sediment cores allow to reconstruct the history of contamination within an aquatic environment, as well as to assess local background levels (Mora and Demeke, 1990; Swennen and Van der Sluys, 1998). Vertical profiles of the contents of Al, K, Ca, Mg, Fe, organic matter, pH, clay and fine fractions, as well as the contents of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn before and after Al-normalization in the cores

HP7 and HP17 are illustrated in Figs. 3 and 4 respectively. For a better visualization, Al-normalized data of elements were multiplied by a factor of 5.

The sediment core HP7 is divided into three intervals according to the Folk (1980) classification system in combination with the color and organic matter content of sediments. The upper interval from 0 to 6 cm deep consists of reddish brown colored silt, the middle interval from 6 to 15 cm deep is composed of light yellow colored organic matter-poor silt while the lower interval below 15 cm is made up of grey brown colored sandy silt. The pH values, ranging from 7.65 to 7.83, reflect a slightly alkaline nature through the sediment core. The clay ( $\Phi < 2 \mu\text{m}$ ) and fine ( $\Phi < 63 \mu\text{m}$ ) fractions do not change much along the core. Organic matter content is rather low in the middle section (6–15 cm) if compared with that in the two other sections. Similarly to the fine fraction, the contents of Al and K do not change much and Ca do not show any clear trend, whereas Fe and Mg show slightly-increasing trends from bottom to top. The vertical profiles of heavy metals and arsenic display rather similar trends before and after Al-normalization. Overall, the Al-normalized contents of Co, Cr and Ni do not change much along the core, whereas the Al-normalized contents of As, Cd, Cu, Mn, Pb and Zn increase by a factor of approximately 2 between the uppermost and the lowermost layers. Generally, for most heavy metals, the lowest Al-normalized contents were recorded either in the bottom sediments (>57 cm) or in the organic-poor interval (6–15 cm deep).

Core HP17 is also divided into three intervals, which consist (from top to bottom) of brown colored sandy silt (from 0 to 22 cm depth), gray colored organic matter-rich silt (from 22 to 40 cm depth), and gray colored organic matter-poor silt (from 40 to 65 cm depth). Generally, the fine fraction slightly decreases from bottom to top while clay content is rather constant along the core. The vertical profile of organic matter content indicates an organic matter-rich zone in the middle interval, and lowest values are recorded at the bottom of the core. The pH does not change much through the core, ranging from 7.20 to 7.59, which indicates a slightly alkaline medium through the core. Similarly to the fine fraction, the contents of Al, K, Ca and Mg decrease from bottom to top while the contents of Fe remain nearly constant. Before Al-normalization, the contents of As, Cd and Cr decrease, and the contents of Co and Ni do not change much while Cu, Mn, Pb and Zn



**Fig. 2.** Longitudinal trends of grain size, organic matter, pH, major elements (Al, K, Fe, Ca and Mg), heavy metals and arsenic in the river-bed sediment of Cam River. Open symbols and dashed lines indicate the original contents; solid symbols and solid lines represent the Al-normalized contents.

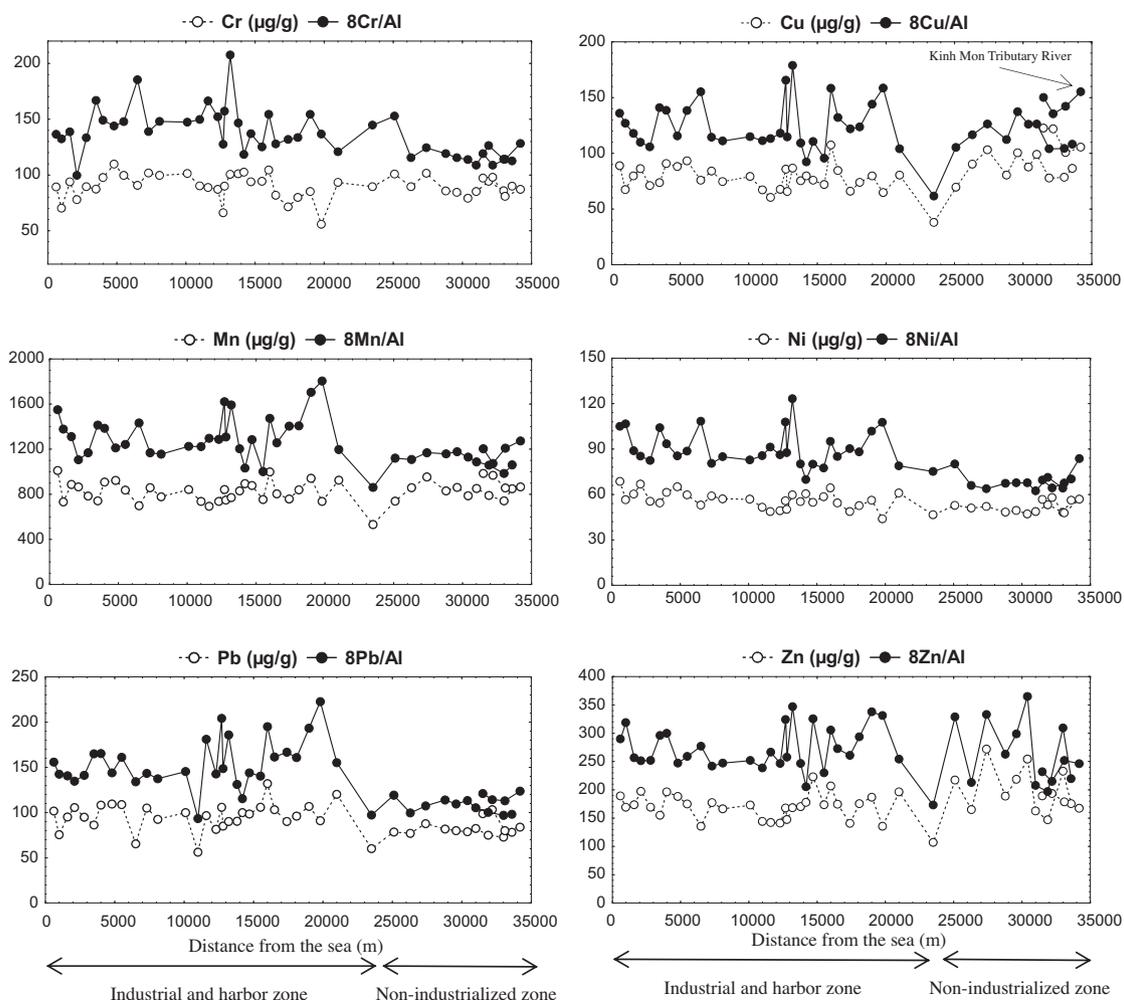


Fig. 2 (continued)

slightly increase from bottom to top. In contrast, the Al-normalized contents of As, Cd and Cr slightly increase, whereas the Al-normalized contents of Co, Cu, Mn, Ni, Pb and Zn increase by a factor of approximately 2 between the lowermost to the uppermost layers. The lowest Al-normalized contents of heavy metals and arsenic are recorded in the lower interval (>40 cm deep).

Basically, after normalizing to Al, the overall increases in the heavy-metal/Al ratios are comparable between the two cores. However, the As/Al and Cd/Al ratios in core HP7 increase more strongly compared to core HP17, whereas the Co/Al, Ni/Al and Zn/Al ratios increase more strongly in core HP17. In addition, these Al-normalized contents of heavy metals and arsenic in surficial layers are slightly different between the two cores. This may be explained by differences in sediment sources in which the core HP17 is formed by only sediments from the Cam River while core HP7 is also receiving sediments from the Bach Dang River and the sea with different heavy-metal/Al ratios. Moreover, different proximities of two cores to local pollution sources can also be the reason (Glasby et al., 2004). In summary, the overall increasing trends of Al-normalized contents of heavy metals and arsenic through the sediment cores (from bottom to top) illustrate that anthropogenic inputs have increased with time in the study area. This concurs with the socio-economic development of Hai Phong City in particular and Northern Vietnam in general over the past 50 years.

Moreover, as illustrated in the case of the sediment core HP17, the increasing trends (from bottom to top) in the contents of As, Cd, Co, Cr and Ni were not observed before Al-normalization, but

were clearly shown after Al-normalization. This means that the normalization procedure towards Al helps to clarify historical trends of these heavy metals and arsenic in the studied sediment core. In particular, it eliminates the effects of granulometric and mineralogical variability along the core which lead to underestimation of the contamination status of surficial sediment layers.

Absolute datings are not available to provide time series for our sediment cores. However, some authors (Swennen and Van der Sluys, 1998; Abraham and Parker, 2008) have suggested that the Al-normalized contents of heavy metals and arsenic generally become nearly constant when they reach local background levels. Considering the vertical distribution patterns of heavy metals and arsenic in our sediment cores, we assume that the sections from 0 to 57 cm in core HP7 and from 0 to 43 cm in core HP17 may represent the industrialization period from 1954 to 2008 while the sections deeper than 57 cm in core HP7 and 43 cm in core HP17 may represent the pre-industrialization period before 1954.

### 3.4. Assessment on the degree of enrichment

The degree of enrichment by heavy metals and arsenic in surficial sediments near Haiphong Harbor is assessed based on the Enrichment Factor (EF) that is widely used in environmental geochemistry (Rubio et al., 2000; Woitke et al., 2003; Abraham and Parker, 2008; Ho et al., 2010). The Enrichment Factor is defined as follows:

$$EF = [C_{\text{metal}}/C_{\text{Al}}]_{\text{Sediment}} / [C_{\text{metal}}/C_{\text{Al}}]_{\text{Reference}} \quad (1)$$

where  $C_{\text{metal}}$  and  $C_{\text{Al}}$  are the contents of metal and aluminum in the studied sediment and the reference (or background) values, respectively.

Based on the Enrichment Factor (EF), the 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;

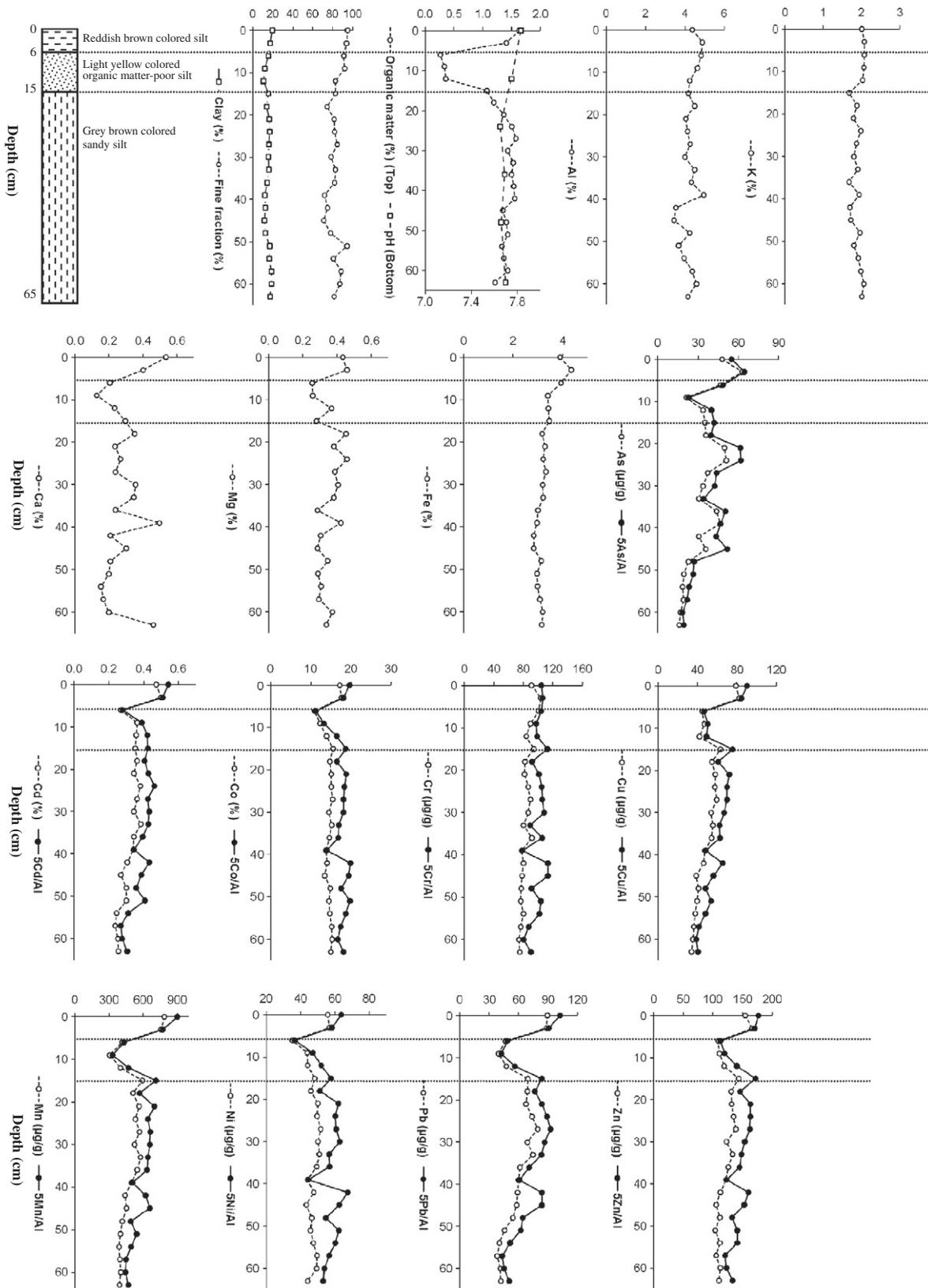
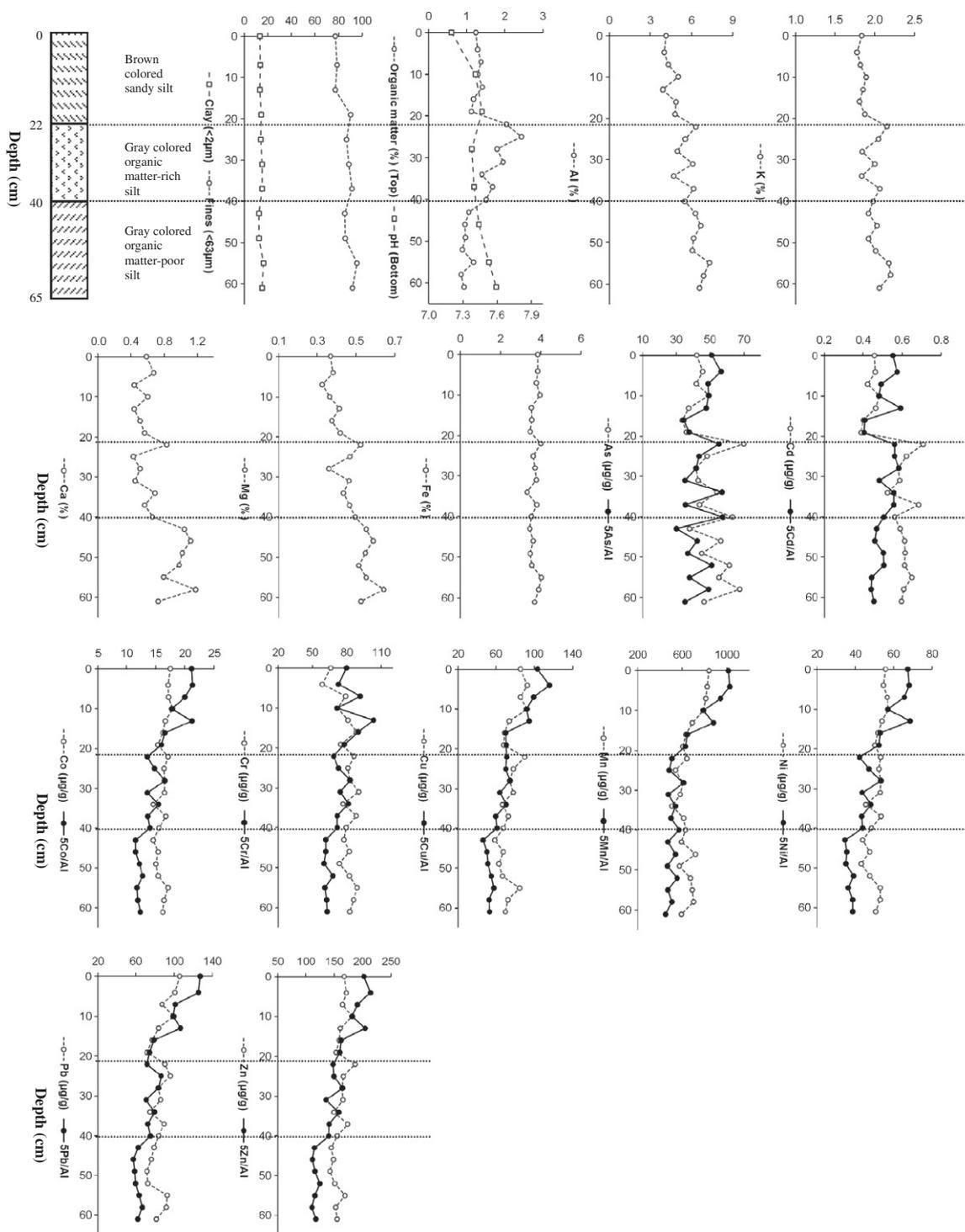


Fig. 3. Vertical profiles of major elements, clay, fine fraction, pH, organic matter content, heavy metals and arsenic in core HP7. Open symbols and dashed lines indicate the original contents; solid symbols and solid lines represent the Al-normalized contents.



**Fig. 4.** Vertical profiles of major elements, clay, fine fraction, pH, organic matter content, heavy metals and arsenic in core HP17. Open symbols and dashed lines indicate the original contents; solid symbols and solid lines represent the Al-normalized contents.

(5)  $10 < EF \leq 25$ : severe enrichment; (6)  $25 < EF \leq 50$ : very severe enrichment; (7)  $EF > 50$ : extremely severe enrichment (Rubio et al., 2000).

Under assumption that local background levels are reached in the studied cores, as discussed above, local background values are separately determined for the 57–65 cm interval in core HP7 and for the 43–65 cm interval in core HP17 (Table 3) based on the fact that lowest values which display a uniform pattern were recorded in these intervals. As suggested by some authors (e.g. Abraham and Parker, 2008), the establishment of local background

**Table 3**

Local background values after Al-normalization of heavy metals and arsenic near Haiphong Harbor.

Core	As/ Al	Cd/ Al	Co/ Al	Cr/ Al	Cu/ Al	Mn/ Al	Ni/ Al	Pb/ Al	Zn/ Al
HP7	4.00	0.06	3.48	17	8	91	11	9	25
HP17	8.06	0.09	2.40	13	11	99	7	12	23

levels is necessary to compare contents of the target heavy metals and arsenic in contaminated sediments with uncontaminated

**Table 4**  
EF values with respect to reference materials and local background values.

		As	Cd	Co	Cr	Cu	Ni	Mn	Pb	Zn
EF with respect to upper continental crust	Max	56.4	10.6	2.1	2.4	7.2	2.8	3.6	13.2	4.9
	Min	18.2	4.7	1.2	1.2	2.5	1.5	1.7	5.5	2.4
	Average	40.5	7.0	1.6	1.7	4.9	2.0	2.6	8.8	3.9
	STDV	7.2	1.5	0.2	0.2	0.9	0.3	0.4	1.8	0.6
EF with respect to average continental crust	Max	88.7	10.9	1.3	1.2	2.5	1.2	1.4	29.3	4.6
	Min	28.5	4.8	0.7	0.6	0.9	0.6	0.6	12.3	2.3
	Average	63.7	7.2	1.0	0.8	1.7	0.9	1.0	19.6	3.6
	STDV	11.3	1.6	0.1	0.1	0.3	0.1	0.2	3.9	0.6
EF with respect to local background values	Max	2.4	2.0	1.9	2.2	2.5	2.2	2.4	2.4	2.0
	Min	0.8	0.8	0.9	0.8	1.1	0.9	1.1	1.0	1.0
	Average	1.5	1.4	1.4	1.5	1.8	1.5	1.9	1.9	1.6
	STDV	0.5	0.3	0.3	0.3	0.3	0.3	0.3	0.4	0.2

sediments that are mineralogically and texturally similar or identical. Therefore, in the industrial and harbor zone of Haiphong City, the EF values of the river-bed sediment samples from No. 13 to No. 34 were calculated with reference to local background values derived from core HP17 because these sampling locations received sediments of the Cam River only, while the EF values of the samples from No. 1 to No. 12 were calculated with local background values derived from core HP7, which was also influenced by the sediment source of the Bach Dang River and the sea. All the EF values are then averaged for representing the degree of enrichment in the industrial and harbor zone of Haiphong City (Table 4).

For the purposes of comparison, the degree of enrichment by heavy metals and arsenic for 34 above-mentioned river-bed sediment samples is also assessed with respect to the reference values from the upper continental crust and the average continental crust as shown in Table 2.

As indicated in Table 4, with respect to the reference values from the upper continental crust and the average continental crust, As is ranked as very severely to extreme severely enriched (EF = 40.5 and 63.7), Cd and Pb as moderate severely to severely enriched (EFs = 7.0–19.6), Cu and Zn as minor to moderately enriched (EFs = 1.7–4.9), while Co, Cr, Ni and Mn are classified from no enrichment to minor enrichment (EFs < 3). However, with respect to local background values obtained from the sediment cores, the averaged EF values for As, Cd, Co, Cr, Cu, Ni, Mn, Pb and Zn range from 1.4 to 1.9 which all are classified as minor enriched.

Generally, there are remarkable differences in the degree of enrichment between the assessment based on the local background values and the assessment based on the upper continental crust and the average continental crust. The degrees of enrichment of heavy metals and arsenic with respect to the reference materials (continental crust) are much higher than those with respect to local background values, especially for As, Cd, Pb and Zn. This means the naturally-occurring (background) contents of these elements in the study area are high if compared to those in the reference materials. Moreover, as mentioned above, if compared to the Canadian Interim Marine Sediment Quality Guidelines, Cr, Cu, Ni, Pb, Zn and especially As can be considered to be “seriously polluted” (as assessed by Thuc Anh (2006)). Therefore, unless normalization procedures and local background values are taken into consideration, the contamination status for a specific area such as Haiphong Harbor may be misinterpreted.

#### 4. Conclusion

Through the investigation on the contamination by heavy metals and arsenic in sediments near Haiphong Harbor (Vietnam), the normalization approach towards Al has been proven to be necessary in many different studied aspects. Particularly, it helps to

determine the contamination sources when studying the spatial distribution of heavy metals and arsenic in surficial river-bed sediments or to clarify their historical trends when studying the vertical distribution in the core sediments. Moreover, when assessing the contamination status, the Al-normalization procedure as well as the local background levels should be taken into account to avoid misinterpretation on the degree of contamination by heavy metals and arsenic in sediments.

In future, this approach needs to be widely applied in the studies on environmental pollution by heavy metals and arsenic in sediments in the coastal zone of Vietnam.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jseaes.2012.05.015>. These data include Google maps of the most important areas described in this article.

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