Leachability of arsenic and heavy metals from blasted copper slag and contamination of marine sediment and soil in Ninh Hoa district, south central of Vietnam

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ABSTRACT

In recent years, shipping activities developed in Ninh Hoa district (south-central Vietnam), have raised an urgent environmental concern related to the use of copper slag as abrasive material for removing rust from the surface of the ships. This study was conducted to investigate the characteristics of the blasted copper slag (BCS). Enrichment Factors (EF) were used to assess the contamination status of sediments and soils in the surroundings of the BCS dump site. The potential release of As and heavy metals (HMs) from BCS was examined through pH_{stat} and cascade leaching tests in combination with XRD analysis. From the results, As, Cr, Ni, Pb and Zn were characterized as moderate severely enriched to severely enriched while Cu showed extremely severe enrichment in the sediments. Regarding the soil collected at the dump site, it was strongly contaminated with As, Cu and Zn (extremely severe enrichment) whereas Cr, Ni and Pb were ranked as severely enriched. This study also demonstrates that it is important to use local background values of As and HMs in soils and sediments for a correct estimation of the degree of As or HM contamination. The cascade leaching test results from the BCS showed that the concentrations of the regulated HMs leached were lower than the EU limit for non-hazardous waste; except for Cu. Results from pH_{stat} leaching tests at pH 4 with BCS indicated that upon acidification, HM release from the <1 mm fraction is higher compared to the bulk sample. A significant release of Cu from BCS was also observed for both fractions (<1 mm fraction and bulk sample) in pH_{stat} leaching tests. In view of the elevated Cu concentrations found in the slag, the potential recovery of Cu from BCS should be investigated.

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1. Introduction

Assessment of heavy metal (HM) contamination is a complex process because of the natural occurrence of HMs in the environment. In general, sediment/soil quality guidelines (SQGs) and some sediment/soil indices such as the geo-accumulation index (Müller, 1969), enrichment factor (Duce et al., 1975), pollution load index (Tomlinson et al., 1980) and marine sediment pollution index (Shin and Lam, 2001) are used to assess the contamination status of sediment/soil. Using SQGs to assess HM contamination in sediment/soil shows some limitations because it does not take into account the background level of HMs and do not include a correction for differences in matrix characteristics (e.g., particle size, organic matter, and mineral composition of the examined soil/sediment). The geo-accumulation index, pollution load index and marine sediment pollution index take into account site specific background concentrations of HMs but do not include a correction for differences in matrix characteristics. The enrichment factor (EF), which uses a normalizer to correct for the differences in particle size and clay mineral content, is widely used in environmental geochemistry to assess the contamination status of HMs in sediment/soil (e.g., Rubio et al., 2000; Woitke et al., 2003; Ho et al., 2012).

The present study was performed in Ninh Hoa, a town located in Khanh Hoa province, south central Vietnam. In recent years, with the development of the shipping industry, there is an urgent environmental concern relating to the use of copper slag as abrasive material for removing rust and marine deposits from ships. A shipyard located at the beach in Ninh Hoa (south of Van Phong bay,
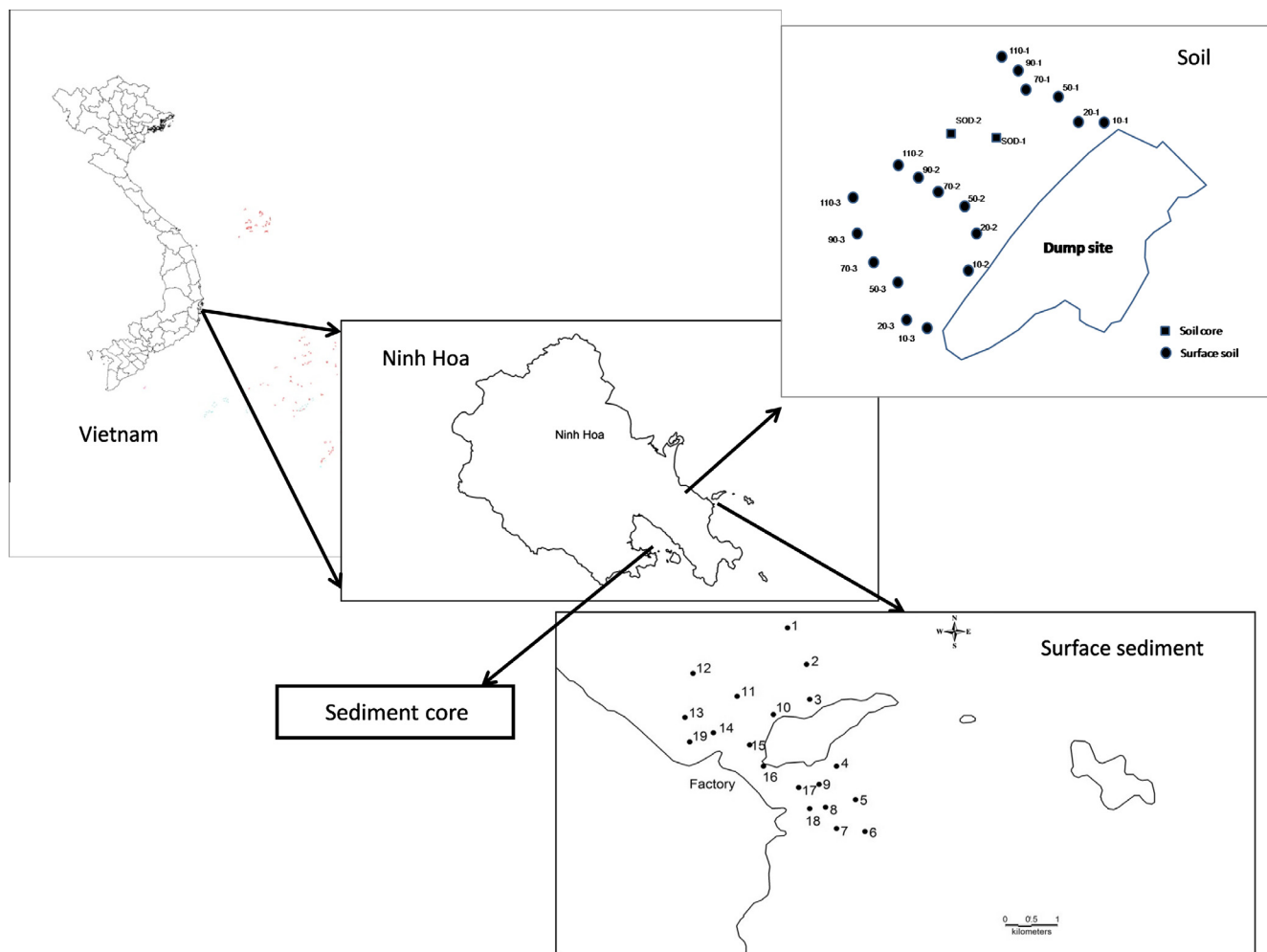
Fig. 1. Location of the sampling sites.

Khanh Hoa province, Fig. 1) has used copper slag as a blasting agent until 2011. Since the year 2000, blasted copper slag (BCS) has been dumped without any treatment in a dump site which is about 3 km from the shipyard. The composition of the BCS and the leachability of As and HMs from BCS has never been studied before, even though it likely is the most important anthropogenic source of HMs in the study area. Moreover, studies on metal contamination in soils and sediments of this area, and in Vietnam in general, are rather limited. Additionally, most of the studies were based on Canadian SQGs and did not take into account the regional background values for HMs (Le, 2003; Nguyen, 2009). Copper slag can be either dumped or recycled as a secondary material (Gorai et al., 2003). Therefore, an environmental study, taking into account the potential release of HMs from BCS, should be carried out in order to provide essential information to select the most "environmentally friendly" management options of these slags: reuse (using BCS without any treatment), recycling (using after some treatment) or controlled disposal. In this work, the actual and long term release of As and HMs from BCS was examined by using a cascade leaching test (NEN 7349). A pH$_{stat}$ leaching test (CEN/TS 14429 test) was carried out to assess As and HM release of BCS under the influence of acidification. Particle size was a variable in the studied BCS (Table 1). To investigate the influence of particle size on the release of As and HMs in BCS, the leaching tests were performed in different particle size fractions (<1 mm and bulk with pH$_{stat}$ leaching test, <1 mm and <125 μm with cascade leaching test). This study also provides a first characterization of As and HM contamination of sediments and soils nearby the BCS dump site.

Although a lot of controversy exists about the use of the term 'heavy metals' (e.g., Batley, 2012; Chapman, 2012), the term 'heavy metals' is used in this study to indicate particularly the elements Cd, Cr, Co, Cu, Ni, Pb and Zn. Arsenic, which is actually a metalloid, will be mentioned separately.

2. Methodology/materials and methods

2.1. Sampling and sample pretreatment

The study area is located in Ninh Hoa, Khanh Hoa province, Vietnam. The geological substrate in this area mainly consists of alternative distribution of Jura–Kreta magmatic rocks, sediments and Quaternary sediments (Nguyen, 2006). Two sampling campaigns were undertaken in December 2010 and in December 2011. Nineteen marine surface sediment samples (approximately 1 kg each) were collected adjacent to the shipyard at 500 m intervals, located near the beach of Ninh Hoa (Fig. 1). The samples were taken from a boat by a grab and the exact coordinates of the sampling locations were recorded by GPS (Garmin – GPS12). Additionally, to infer background concentrations, one sediment core (150 cm in length with a diameter of 7 cm) was collected at a mangrove in an alluvial spit connected to the sea which is located at a distance of 12 km from the shipyard. The geological setting of the cored area is comparable to the study area near the shipyard. After collection, the sediment core was sectioned over 10 cm intervals.

Soil samples were collected at the dump site. At the dump site, surface soil samples were taken approximately 10 m, 20 m, 50 m,

Table 1
Total element concentrations in BCS compared to other studies.

	Factory	This study ($n = 4$) Average ± SD	Gorai et al. (2003)	Alter (2005)	Lim and Chu (2006)	Das et al. (2010)	Vítková et al. (2011)	Najimi et al. (2011)	Schmukat et al. (2011)
Al_2O_3 (%)	3.69	3.77 ± 0.17	N/A	3.5	3.90	2.3	6.11	4.43	5
CaO (%)	2.80	3.02 ± 0.25	0.7–17.42	3.0	1.00	3.95	10.8	22.25	3
K_2O (%)	0.30	0.42 ± 0.23	N/A	N/A	4.14	N/A	2.13	N/A	N/A
MgO (%)	1.28	1.37 ± 0.13	1.00–3.51	2.0	0.81	2.82	2.64	1.56	N/A
SiO_2 (%)	ND	2.93	24.7–40.97	35.0	33.21	30.91	38.1	9.57	30
P_2O_5 (%)	0.12	0.11 ± 0.02	N/A	N/A	N/A	N/A	0.35	N/A	N/A
MnO (%)	0.17	0.17 ± 0.02	0.04–0.49	N/A	N/A	0.44	0.07	N/A	N/A
Total Fe (%)	40.32	41.02 ± 1.54	39.65–47.7	N/A	37.9	N/A	31.68	57.42	35
Total S (%)	0.19	0.21 ± 0.06	0.11–1.51	1	N/A	1.24	0.66	N/A	N/A
Cu (%)	0.84	0.85 ± 0.04	0.6–2.1	1.50	0.80	1.53	1.8	0.99	0.81
As (mg/kg)	847	798 ± 88	N/A	1000	N/A	N/A	92	N/A	565
Cd (mg/kg)	24	23 ± 1	N/A	<100	<1	N/A	N/A	N/A	5
Co (mg/kg)	227	228 ± 12	1040–4000	900	N/A	400	12263	N/A	277
Cr (mg/kg)	651	566 ± 71	N/A	1589	280	N/A	337	N/A	N/A
Mo (mg/kg)	ND	2054	N/A	N/A	N/A	N/A	44	N/A	1340
Ni (mg/kg)	139	113 ± 37	14–600	N/A	100	200	36	472	N/A
Pb (mg/kg)	854	853 ± 61	N/A	N/A	710	N/A	N/A	4734	N/A
Zn (mg/kg)	0.92	0.84 ± 0.18	500–7220	14000	6060	N/A	211	7543	15040
pH	8.08	8.22 ± 0.12	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Particle size (%)									
>1 mm	40.02	36.0 ± 3.7	N/A	N/A	N/A	N/A	76.4	N/A	N/A
1 mm to 125 µm	49.8	49.7 ± 6.1					18.5		
<125 µm	10.0	14.2 ± 6.9					5.1		

ND: not detected.
N/A: not available.

70 m, 90 m and 110 m away from the dump site. To increase the representativeness, at each sampling position, a sample was composed of 3 sub-samples. Two core soil samples were collected at a distance of 60 m (0–60 cm depth) (SOD1) and 100 m (0–160 cm depth) (SOD2) from the dump site in order to evaluate the extent of contamination with depth and with distance from the site. The soil cores were sectioned over 5 cm intervals (upper 0–40 cm) and 10 cm (from 40 cm depth to bottom of the cores). After collection, the samples were placed in sealed plastic bags, and transported to University of Science (Ho Chi Minh City, Vietnam). Here, the samples were air dried, homogenized in a porcelain mortar and sieved over a 2 mm mesh sieve. In addition, three representative samples of BCS in the dump sites and one BCS sample from inside the factory were collected. All BCS samples were air dried. Part of each BCS sample was crushed in a porcelain mortar for physico-chemical analysis whereas another part of each sample was used for leaching tests, without crushing.

2.2. Characterization of samples

Immediately after sampling, pH and redox potential (Eh) of the sediments were measured at the sampling sites with a Hanah pH/Eh meter (HI 8424). Soil pH was measured with a $CaCl_2$ 0.01 M solution with a liquid/solid (L/S) ratio of 10 (l/kg). All soil, sediment and BCS samples were transported to the University of Leuven (KU Leuven, Belgium) for further analysis. Total elemental (Al, Ca, Fe, K, Mg, P, S, As, Cd, Co, Cr, Cu, Mn, Ni and Zn) content of samples were determined with ICP-OES (Varian 720ES, Varian Inc., Walnut Creek, CA, USA) after being digested by the so-called 3 acids digestion method (HNO_3, $HClO_4$, HF) in a Teflon beaker on a hot plate.

Mo was not measured in soil and sediment samples, because the focus of the study was initially on As, Cr, Cu, Ni, Pb and Zn. In the BCS samples, Mo was measured and because of the high concentrations found in the BCS, special attention will be paid to Mo in the leaching studies. All glassware was rinsed with HNO_3 0.5 M before usage and all reagents were of analytical grade. In order to evaluate the quality of the analytical method, a certified reference material (GBW 07311, sediment) was analyzed. In addition, blank and duplicate samples (10% of the total amount of samples) were also included in the analytical procedure at random.

The analytical results of the certified reference material show a good agreement with certified values for almost all the elements except for Cr. The comparison between the measured concentrations with the certified data in the certified reference material is given in Table 2.

Particle size was determined by laser diffraction spectrophotometry (Malvern Mastersizer S long bed, Malvern, Worcestershire, UK) after removing carbonates (0.1 M HCl, 24 h), iron oxides (0.5% oxalic acid, boiling for 20 min) and organic carbon (35% H_2O_2, 60^0C until no reaction observed anymore) and applying a peptizing solution (10 g/l sodium polyphosphate, boiling) to sediments and soils. The content of oxidizable substances (OS: organic matter + sulfides content) was determined by the Walkley and Black manual titration method (Nelson and Sommers, 1982). A mineralogical sample characterization was conducted by X-ray diffraction (Philips PW1830 diffractometer with Bragg/Brentano θ–2θ setup, CuK radiation, 45 kV and 30 mA, graphite monochromator). On selected surface marine sediment/soil (high concentration of HMs) an XRD analysis was performed. The carbonate components in the

Table 2
Comparison between the measured concentrations with the certified data in the certified reference materials (average ± standard deviation).

GBW 07311	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Certified	188 ± 20	2.3 ± 0.2	40 ± 4	79 ± 4	2490 ± 130	14.3 ± 1.5	636 ± 34	373 ± 21
Measured $n = 5$	162 ± 1	2.2 ± 0.4	30 ± 4	75.3 ± 0.4	2537 ± 30	13.9 ± 0.4	577 ± 13	356 ± 5
Recovery rate (%)	83 ± 1	96 ± 20	70 ± 11	95 ± 1	102 ± 1	96 ± 3	89 ± 2	94 ± 2

sediment samples were eliminated by a HCl 1 N treatment before XRD analysis.

2.3. Leaching tests

2.3.1. Cascade leaching test (CLT)

The investigation of leaching as a function of the L/S ratio was performed with the CLT (NEN 7349). This is a serial batch test in which the material is successively extracted five times, resulting in L/S ratios of 20, 40, 60, 80 and 100 (l/kg). In the present study, a CLT was performed on two particle size fractions: the <1 mm and <125 μm fractions of the BCS to investigate the different release of As and HMs in these fractions. The particle size distribution of bulk sample is given in Table 1. The extractions were carried out in duplicate in acid rinsed 50 ml polyethylene centrifuge tubes with screw caps. 30 ml of Milli-Q water, acidified to pH 4 with HNO_3 (ultrapure) was added to 1.5 g of dry sample, shaken (24 h), centrifuged (3000 rpm, 10 min), and filtered (0.45 μm, Chromafil® PET-45/25, Macherey). This test was performed with distilled water acidified to pH 4 and without any pH adjustment during the test.

2.3.2. pH$_{stat}$ leaching test

The pH$_{stat}$ leaching test (CEN/TS 14429) at pH 4 was performed with two particle size fractions of BCS, namely the bulk sample (not sieved) and the fraction <1 mm. This leaching test was carried out to assess the influence of acid conditions on the release of HMs and As from the BCS. An automatic multititration system (Titro-WicoMultititrator, Wittenfield and Cornelius, Bochum, Germany) was used for the pH$_{stat}$ experiments. 80 g of sample was put in an erlenmeyer flask together with 800 ml of Milli-Q water (L/S ratio = 10 l/kg). The pH was continually monitored and adjusted by automatic addition of a 1 M HNO_3 solution. The first batch of pH$_{stat}$ was performed during 168 h. This experiment demonstrated that no additional HM release was observed between 120 h and 168 h. Therefore, the subsequent pH$_{stat}$ leaching test was performed during 120 h. A sample of 10 ml of the suspension was taken over a filter (0.45 μm, Chromafil® PET-45/25, Macherey–Nagel GmbH & Co. KG, Germany) by means of a syringe attached to

a flexible tube at regular time intervals (0; 1; 3; 6; 12; 24; 48; 72; 96 and 120 h/168 h). When the pH$_{stat}$ leaching test was finished, the residue was dried to perform a XRD analysis in order to investigate possible changes in the mineralogical composition of the solid phase during the leaching test.

2.4. As and HM contamination assessment

The degree of As and HM contamination is based on classification of enrichment factors (EF). EFs were calculated by the following equation:

$$EF = \frac{\frac{[Metal]_s}{[Normalizer]_s}}{\frac{[Metal]_B}{[Normalizer]_B}}$$

where EF = Enrichment factor; $[Metal]_s$ and $[Normalizer]_s$ are the concentrations of HM and normalizer in the sample; $[Metal]_B$ and $[Normalizer]_B$ are the concentrations of HM and normalizer in the reference material.

A factor used as normalizer must covary in proportion to the naturally occurring concentrations of the metal of interest and must be insensitive to inputs from anthropogenic sources and stable to environmental influences (Loring, 1990; Schiff and Weisberg, 1999). Aluminum, Fe and organic matter can be a proxy to normalize As and HM data in sediment (Herut and Sandler, 2006). However, Fe and organic matter may be influenced by anthropogenic activities in this area, e.g., Fe may come from the BCS, and organic

matter from domestic waste of residential areas. Therefore, the present study used Al as normalizer because Al was observed to correlate to the fine fraction (⩽63 μm) and As, HMs and Al was completely released by the sample digestion technique used (Ho et al., 2012).

Because the compositions of soils and sediments are site specific and are influenced by several factors such as the geological substrate, Blaser et al. (2000) suggested the use of local background values (e.g., from a deep soil layer not affected by pollution) as reference material. In the present study, local background concentrations for sediment and soil were determined, respectively based on the analysis of a sediment core taken in a mangrove far away from the shipyard and based on the analysis from a soil core taken at a distance of 100 m from the dump site.

3. Results and discussion

3.1. General sample characteristics

3.1.1. Blasted copper slag

XRD analysis of BCS samples revealed the dominance of amorphous phases (>90%) and the occurrence of fayalite, magnetite, maghemite and elemental copper. Average chemical composition, particle size and pH of the BCS analyzed are presented in Table 1 and compared to the composition of (other) copper slag published in literature. The <1 mm fraction of BCS in this study showed a higher value compared to Vítková et al. (2011), which might be due to blasting effect on copper slag in this study. The pH value of BCS (8.22) indicated a weak alkalinity. The BCS samples were mainly composed of Fe, Ca, Al and Si (percentage levels). Among the HMs, Cu and Zn appeared to be the predominant contaminants present followed by Mo, Pb, As, Cr (Table 1). It can be seen from Table 1 that the BCS in the present study have a lower SiO_2 and higher Mo content compared to other studies. According to Gorai et al. (2003), typical copper slag usually contains impure iron silicate glass with small inclusions of copper and copper sulfide. Moreover, the variation in chemical properties of copper slag depends on the types of furnace or treatment process used. However, the result of XRD analysis suggest that fayalite and sulfide phases exist in the present BCS but are not the major phases because of the low content of SiO_2 and S found in the samples.

3.1.2. Sediment–soil
3.1.2.1. Sediment.
XRD results indicated that the main components in the analyzed sediments after carbonate removal were quartz, albite, oligoclase, orthoclase, muscovite and some amorphous phases. The average and range for the fine fraction (⩽ 63 μm, silt and clay), OS, pH and elemental concentrations in the surface sediment and sediment core are presented in Table 3.

In surface sediment, generally the fine-grained fraction shows higher values in the quite areas which are far from the harbor (i.e., samples 1, 3, 6, 8, 9, 18). The contents of OS as well as total S content in surface sediments were low (average: 0.34% and 0.19% respectively). In addition, concentrations of major elements such as Al, Fe and K are low compared to those reported for Cua Luc estuary (northern Vietnam) (Ho, 2012) while the contents of Ca, Mg and pH values were higher than found in the Cua Luc estuary (Ho, 2012) (Table 3). HMs and As showed high concentrations in samples which contain high Al concentrations (samples 1, 2, 3, 12, 13, 14 and 18) or samples collected near the harbor (samples 16, 19) (Fig. 1). If compared to data from the Cua Luc estuary (Ho, 2012), the average concentrations of As, Cu, Pb and Zn were higher while those of Cr and Ni were lower. Depth profiles of major elements, OS and pH of the sediment core are given in Fig. 2. From

Table 3
Average and range of fine fraction (⩽63 μm), OS, pH and element concentrations in the surface sediment, sediment core, surface soil and soil core.

	Unit	Surface sediment		Cua Luc estuary (northern Vietnam) (Ho, 2012)	Sediment core		Surface soil		Soil core	
		Average	Range		Average	Range	Average	Range	Average	Range
Al	%	1.009	0.12–3.28	3.04	7.39	5.18–9.52	5.53	2.68–7.98	7.27	5.09–10.33
Ca	%	21.991	10.82–27.65	0.23	2.47	0.35–12.76	0.97	0.1–2.95	0.15	0.07–0.52
Fe	%	1.3	0.06–9.14	1.89	3.58	2.46–4.88	9.8	0.58–34.47	3.49	2.85–4.48
K	%	0.54	0.06–1.44	0.99	1.68	1.23–2	2.25	0.03–4.29	0.03	0.02–0.13
Mg	%	0.94	0.58–1.74	0.6	0.53	0.41–0.73	1.63	0.03–8.07	1.05	0.44–8.07
P	%	0.02	0.02–0.03	N/A	0.03	0.02–0.05	0.02	0.01–0.04	0.02	0.01–0.02
S	%	0.19	0.16–0.3	N/A	0.93	0.05–2.47	0.07	0 003–0.24	0.005	0.002–0.02
As	mg/kg	19	1–168	14	18	14–24	283	5–940	16	1–220
Cd	mg/kg	N/A	N/A	N/A	0.2	0.08–0.37	16	3–37	0.83	0.03–8.26
Co	mg/kg	N/A	N/A	7	13	9–18	40	1–127	2.93	0.24–30.26
Cr	mg/kg	35	8–135	44	37	24–44	142	5–415	24	16–110
Cu	mg/kg	332	1–3321	14	12	8–15	2797	18–8978	111	2–1688
Mn	mg/kg	148	34–365	110	448	231–714	640	253–1072	561	173–1030
Ni	mg/kg	11	3–35	19	14	9–20	16	2–41	2.16	0.76–9.14
Pb	mg/kg	22	1–170	18	34	23–43	241	25–715	31	17–182
Zn	mg/kg	187	3–1733	65	79	56–101	2357	40–6709	169	24–2222
OS	%	0.34	0.18–0.7	2.94	2.01	0.66–4.57	0.83	0.16–3.63	0.2	0.04–0.53
pH		9.88	7.78–11.77	5.56	6.54	3.54–8.36	7.05	5.18–8.43	5.69	4.37–7.26
⩽63 μm	%	33.73	1.59–93.37	75	90.91	75.06–98.49	40.71	23.38–71	50.31	21.54–72.06
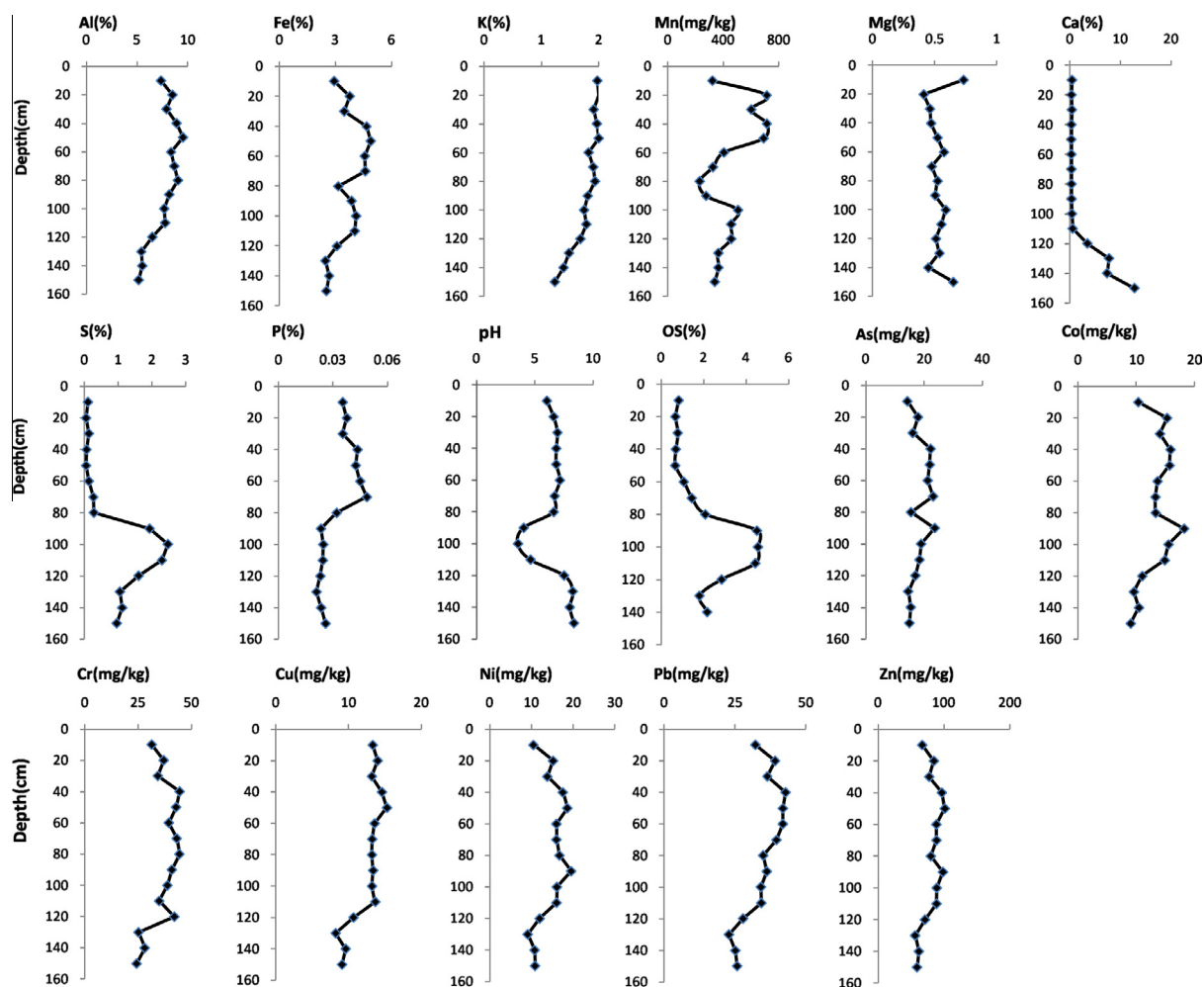
Fig. 2. Variation in major element content, HM and As concentrations, OS and pH with depth in the sediment core.

top to bottom, three layers can be distinguished based on color differences. The upper layer (0–70 cm) was characterized as a brown–reddish mud, the second layer (70–110 cm) consisted of gray mud with a few of black stripes and the lowest layer (110–150 cm) was characterized by light gray colors with some shell fragments at the bottom of the core. Results from the particle size analysis indicated

Table 4
Correlation matrix between major elements, As and HMs, OS and fine fraction (⩽63 μm) in sediment core.

Variables	Al	Ca	Fe	K	Mg	P	S	As	Co	Cr	Cu	Mn	Ni	Pb	Zn	OS	⩽63 μm
Al	**1**	**−0.88**	**0.82**	**0.91**	−0.26	**0.70**	−0.38	**0.66**	**0.78**	**0.84**	**0.94**	0.37	**0.86**	**0.93**	**0.88**	−0.16	**0.66**
Ca	**−0.88**	**1**	**−0.71**	**−0.94**	0.20	**−0.51**	0.17	**−0.54**	**−0.75**	**−0.77**	**−0.90**	−0.30	**−0.70**	**−0.80**	**−0.78**	−0.03	**−0.84**
Fe	**0.82**	**−0.71**	**1**	**0.67**	−0.26	**0.69**	−0.17	**0.88**	**0.77**	**0.73**	**0.83**	0.49	**0.83**	**0.91**	**0.93**	−0.05	**0.54**
K	**0.91**	**−0.94**	**0.67**	**1**	−0.19	**0.65**	−0.43	0.46	**0.66**	**0.73**	**0.91**	0.41	**0.64**	**0.83**	**0.71**	−0.25	**0.71**
Mg	−0.26	0.20	−0.26	−0.19	**1**	−0.15	0.13	−0.33	−0.42	−0.35	−0.14	−0.42	−0.33	−0.26	−0.30	0.08	−0.01
P	**0.70**	**−0.51**	**0.69**	**0.65**	−0.15	**1**	**−0.78**	0.51	0.27	0.51	**0.64**	0.37	0.42	**0.81**	0.51	**−0.68**	0.23
S	−0.38	0.17	−0.17	−0.43	0.13	**−0.78**	**1**	0.00	0.12	−0.14	−0.27	−0.27	0.00	−0.43	−0.03	**0.95**	0.06
As	**0.66**	**−0.54**	**0.88**	0.46	−0.33	0.51	0.00	**1**	**0.771**	**0.70**	**0.63**	0.26	**0.83**	**0.76**	**0.88**	0.13	0.46
Co	**0.78**	**−0.75**	**0.77**	**0.66**	−0.42	0.27	0.12	**0.77**	**1**	**0.72**	**0.80**	0.42	**0.93**	**0.76**	**0.94**	0.29	**0.66**
Cr	**0.84**	**−0.77**	**0.73**	**0.73**	−0.35	0.51	−0.14	**0.70**	**0.72**	**1**	**0.77**	0.25	**0.80**	**0.76**	**0.81**	0.05	**0.72**
Cu	**0.94**	**−0.90**	**0.83**	**0.91**	−0.14	**0.64**	−0.27	**0.63**	**0.80**	**0.77**	**1**	0.47	**0.81**	**0.92**	**0.88**	−0.09	**0.73**
Mn	0.37	−0.30	0.49	0.41	−0.42	0.37	−0.27	0.26	0.42	0.25	0.47	**1**	0.28	0.49	0.42	−0.36	0.12
Ni	**0.86**	**−0.70**	**0.83**	**0.64**	−0.33	0.42	0.00	**0.83**	**0.93**	**0.80**	**0.81**	0.28	**1**	**0.83**	**0.97**	0.21	**0.61**
Pb	**0.93**	**−0.80**	**0.91**	**0.83**	−0.26	**0.81**	−0.43	**0.76**	**0.76**	**0.76**	**0.92**	0.49	**0.83**	**1**	**0.89**	−0.26	**0.59**
Zn	**0.88**	**−0.78**	**0.93**	**0.71**	−0.30	0.51	−0.03	**0.88**	**0.94**	**0.81**	**0.88**	0.42	**0.97**	**0.89**	**1**	0.14	**0.66**
OS	−0.16	−0.03	−0.05	−0.25	0.08	**−0.68**	**0.95**	0.13	0.29	0.05	−0.09	−0.36	0.21	−0.26	0.14	**1**	0.24
<63	**0.66**	**−0.84**	**0.54**	**0.71**	−0.01	0.23	0.06	0.46	**0.66**	**0.72**	**0.73**	0.12	**0.61**	**0.59**	**0.66**	0.24	**1**

Values in bold are significant with $p < 0.05$.

Table 5
Average of Al and HM concentrations in sediment core in this study compared to other studies.

Site	Al (%)	As (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Length of the cores	Digestion method
Ninh Hoa district central of Vietnam – this study	7.39	18	0.2	13	37	12	14	34	79	150 cm	HNO_3 + HF + $HClO_4$
Sediment core in mangrove forest in Nha Phu lagoon – central Vietnam (Nguyen, 2006)	5.18	N/A	N/A	N/A	19	N/A	7	26	43	100 cm	[a]
Background values from Cam river mouth – northern Vietnam (Ho et al., 2012)	6.78	15	N/A	14	85	40	33	34	105	190 cm	HNO_3 + HF + $HClO_4$

[a] X-ray fluorescence (XRF) technique, N/A: not available.

relatively uniform distribution of fine-grained material along the sediment core. Total P content slightly decreased at higher depth and displayed a small variation. Total S content showed little variation from the surface till 80 cm depth and then it increased significantly at a depth of 90 cm of the core. High contents of total S and low pH values in the lower interval (90–120 cm) may indicate sulphidic conditions in the mangrove forest. The content of OS in the sediment core showed a similar trend to the total S content which can be explained by the accumulation of sulfides and organic matter near dead roots in the mangrove forest (Marchand et al., 2006). Generally, K and Mg contents did not change much with depth while Al and Fe contents slightly varied. The contents of Al and Fe appeared to be slightly higher in the interval from 40 to 110 cm depth (highest at 50 cm depth for both Al and Fe), and then gradually decreased in the subsequent interval (120–150 cm) (Fig. 2). Variation in contents of Fe was reflected in the color of the sediment core, since high contents of Fe occurred in the reddish colored parts. Ca content showed little variation from the surface till 110 cm depth and then it increased significantly at a depth of 120 cm until the bottom of the core. This increase could be explained by the carbonate accumulated at the bottom of the sediment core in the form of shell fragments. This also could explain for the slightly higher pH values (8.00–8.36) between 120 cm and 150 cm depth. The lowest pH values were found in the interval from 90 to 120 cm (4.06 and 4.09), where also was found the highest value for oxidizable components (sulfides and organic matter).

As, Cr, Cu, Ni, Pb and Zn concentrations showed a similar trend along the sediment core. They displayed relative small variations with depth, as their distribution was stable at the top (0–30 cm) and bottom (120–150 cm) interval and only changed slightly in the interval between 40 and 110 cm depth. Correlation analysis indicated strong to very strong positive correlations between Al and As, Cr, Cu, Ni, Pb and Zn (R from 0.66 to 0.94) (Table 4), implying the enrichment of these elements and adsorption to Al-containing components (clay minerals, phyllosilicates).

A comparison of sediment composition in this study with other studies performed in Vietnam is given in Table 5.

3.1.2.2. Soil. The soils from the study area are mainly Ferrasols which originated from in situ weathering of granite (NIAPP, 2004). Heterogeneous occurrence of dust BCS was observed in the top layer soil (0–5 cm) during sampling. Results from XRD analysis on the surface soil showed that the main mineral phases identified in the soil sample were quartz, anorthite, microline, orthoclase and amorphous phases. The average and range for the fine fraction (⩽63 μm), OS, pH and elemental concentrations in soil samples are presented in Table 3. Concentrations of major elements (Al, Fe), As and HMs, S and OS of surface soil samples as a function of the distance to the dump site are given in Fig. 4. Total Fe content decreased with distance away from the dump site, while Al content did not change so much. Concentrations of As and HMs in surface soil samples decreased significantly with increasing distance from the BCS dump site. High concentrations of these elements were recorded close to the dump site which is most likely due to the deposition of fine BCS particles (dust) on the soil surface close to the dump site. Because As and HM contamination was related to particulate contaminants, a heterogeneous distribution of contamination can be expected. Although two soil cores were collected, the SOD1 (60 cm) was likely too short to deduce background values. Therefore, only the longer soil core SOD2 (160 cm) was described in the present paper.
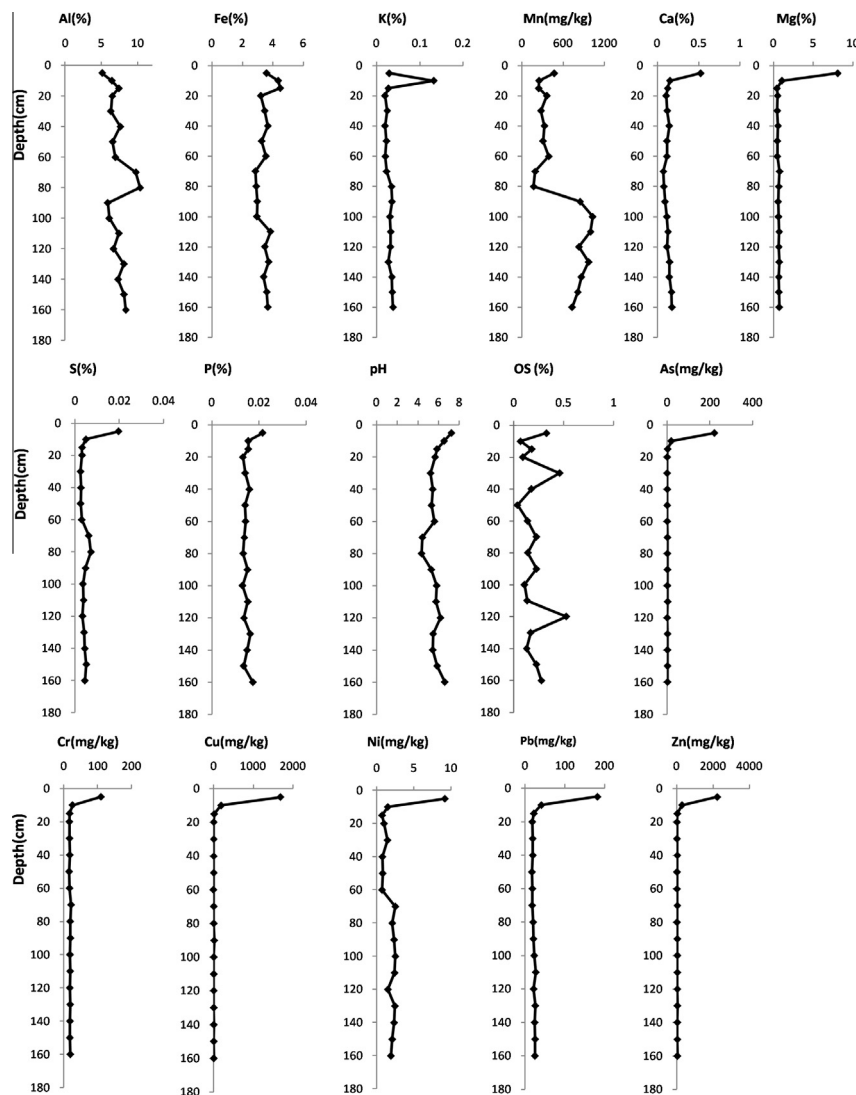
Fig. 3. Variation in major element, HMs, As and pH in the soil core (SOD2).

Profiles of major elements, OS and pH of the soil core (SOD2) are given in Fig. 3. Along the soil core, Fe content did not change much with depth while Al content increased significantly at 70–80 cm. Mn content experienced little variation from top till 80 cm and increased significantly at 90 cm and remains stable until 150 cm. Concentration of As, HMs and total S rapidly declined downward in these profiles. Elevated levels of As and HMs were observed in the top layer (0–10 cm) which may be explained by the presence of BCS dust particles that have been spread by wind and rain. BCS dust can be transported by wind during transportation of the waste from the factory to the dump site and it can also be dispersed by wind and run-off water from the dump site to surrounding area. It should be noted that the dump site went into operation in 2000; but it was only covered by plastic material in 2001. Furthermore, the shipping repairing activities produced about 90,000 tons of BCS/year from 1999 to 2010.

3.2. Assessment of local background values and HM contamination

3.2.1. Sediment

Arsenic and HMs only showed minor variation in the sediment core with lowest concentrations reached at the interval of 100–

150 cm depth (Fig. 2). As suggested by some authors (Swennen and Van der Sluys, 1998; Baize and Sterckeman, 2001), the vertical profile of As and HM concentrations generally becomes flattened when reaching background values. The relatively low As and HM concentrations and the small variation with depth indicate that contamination by atmospheric deposition is not likely to be important in this core. Consequently, background values of As and HMs can be deduced from the average concentrations of HMs in the interval at 100–150 cm depth. Therefore, these values will be used for the calculation of enrichment factors (EFs). It is worth noting that shipyard industry started in 1999. Furthermore, fishing activity was the main anthropogenic influence in this area before 1999, supporting the absence of no enrichment of As and HMs from industrial activities before this year. Absolute dating was not available in this study; however Nguyen (2006) and Schimanski and Stattegger (2005) studied the geochemical and mineralogical alteration processes in sediments in Khanh Hoa province and reported that the average vertical sedimentation rate of this area is approximately 0.05–0.1 cm/year. Under the assumption that sedimentation rates are comparable in our study area, we can assume that bottom layers in the profiles are not affected by contamination in the past and therefore they can be considered representative for actual background values.

Average, minimum and maximum EF with respect to different reference materials are given in Table 6. As can be seen from Table 6, there are remarkable differences in the degree of enrich-ment for As, Cr, Cu, Ni and Pb calculated using the local background values and the calculation of the enrichment factor based on the composition of the upper continental crust and the average
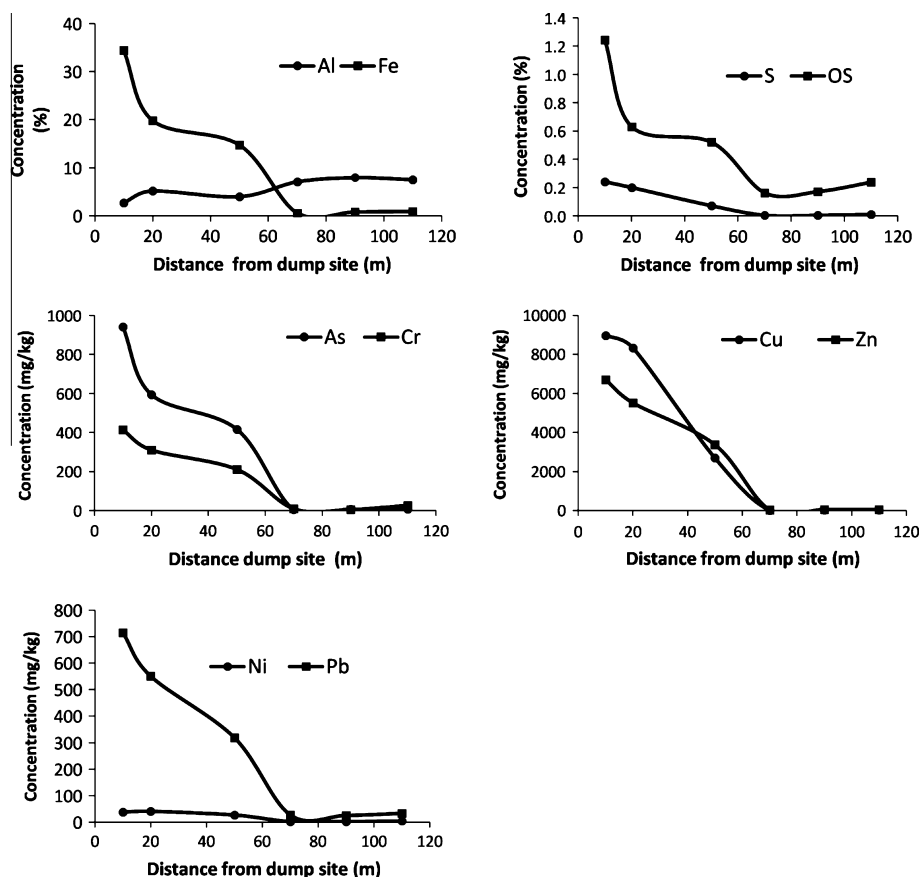

Fig. 4. Concentrations of major elements (Al, Fe), As and HMs (Cr, Cu, Ni, Pb and Zn), S and OS of surface soil samples as a function of the distance to the dump site.

Table 6
EF values in sediment/soil with respect to different reference materials and local background values.

		As	Cr	Cu	Ni	Pb	Zn
Sediment							
EF with respect to upper continental crust	Min	11	1	1	1	2	1
	Max	676	13	804	12	63	150
	Average	101	5	86	4	10	18
EF with respect to average continental crust	Min	18	1	0	0	5	1
	Max	1063	6	281	5	139	140
	Average	159	2	30	2	22	16
EF with respect to background values in Cam river mouth, Hai Phong province, Vietnam (Ho et al., 2012)	Min	1	1	0	1	1	0
	Max	57	11	424	13	26	86
	Average	11	5	68	5	6	15
EF with respect to local background values	Min	1	2	1	2	1	1
	Max	47	27	1,447	34	30	119
	Average	7	11	155	10	5	14
Soil							
EF with respect to upper continental crust	Min	4	0	1	0	1	1
	Max	1877	15	1075	3	126	283
	Average	356	4	220	1	27	65
EF with respect to average continental crust	Min	6	0	0	0	3	1
	Max	2953	7	376	1	281	263
	Average	559	2	77	0	61	61
EF with respect to local background values	Min	2	0	3	1	1	1
	Max	951	64	3894	53	92	559
	Average	180	19	797	19	20	129

Classification of EF (Rubio et al., 2000): EF ⩽ 1: no enrichment; 1 < EF ⩽ 3: minor enrichment; 3 < EF ⩽ 5: moderate enrichment; 5 < EF ⩽ 10: moderately severe enrichment; 10 < EF ⩽ 25: severe enrichment; 25 < EF ⩽ 50: very severe enrichment; EF > 50: extremely severe enrichment.

continental crust. With respect to the reference values from the upper continental crust and the average continental crust, As is characterized by an extremely severe enrichment, Cu by extremely severe to very severe enrichment, Pb by a moderately severe to severe enrichment, while Cr and Ni have a moderate to minor enrichment. With respect to background values in the sediment of Cam river mouth and local background values obtained from this study, As showed severe to moderately severe enrichment, Cr, Ni, Pb by moderate to moderately severe enrichment while Cu is characterized by an extremely severe enrichment. However, there is no difference in the assessment of Zn with respect to different reference materials and local background value; all EFs for Zn indicate as severe enrichment. Generally, the degree of enrichment of As and Pb with respect to the other reference materials are much higher than those with respect to local background values. These results are in the line with the conclusion from Ho et al. (2012) who found that As, Cd, Pb and Zn contamination in Vietnam is overestimated if normalization procedure and local background values are not taken into consideration. Furthermore, the degrees of enrichment of Cr, Cu and Ni with respect to the other reference materials were found to be lower than those calculated with local background values. This might cause an underestimation of the contamination status of these elements. Thus it can be concluded that the contamination status for a specific area such as Ninh Hoa district may be misinterpreted (under-or overestimation) if local background values are not taken into account. Although using general background values as conservative approach is also useful in some cases in terms of environment and human health protection. However, local background values play an important role in contamination assessment; they could help in tracing the origin of contamination.

3.2.2. Soil

Results from the soil core taken at 100 m from the dump site (SOD2) indicated homogeneous concentrations of elements investigated in the interval at 50–160 cm depth (Fig. 3). Therefore, to assess contamination of surface soil, local background values were derived from the average concentrations of elements in the interval of 50–160 cm depth in this core. EFs were calculated with respect to the upper continental crust, the average continental crust and local background as discussed above (Table 6). The averaged EF values showed that there was no difference in contamination degree for As, Cu and Zn with respect to different reference materials; they all were characterized by an extreme severe enrichment. However, remarkable differences were observed in the magnitude of EF values themselves: EF values of As and Pb with respect to local background concentrations were much lower compared to those calculated with respect to upper continental crust and average continental crust as a reference. The opposite phenomenon was observed for Cu, Cr and Ni where EF values with respect to local background concentrations were much higher compared to of the values calculated with respect to crust values. For all HMs and As, EF values decreased with increasing distance from the dump site (Fig. 4). This again may relate to the dispersion of fine BCS dust by wind, with a more pronounced accumulation of BCS particles close to the dump site.

Result from enrichment assessment demonstrated the importance of using local background in As and HM contamination assessment. It is clear from this result that if local background was not taken into consideration, As exhibited a higher enrichment than Cu (both in sediment and in soil). In contrast, when local background was taken into account, the enrichment of Cu was much higher compared to As (both in sediment and soil) (Table 6). This may illustrate that the origin of As and HM contamination in sediment and soil in this area and is related to the industrial activity.

3.3. Arsenic and HM release during leaching of BCS

3.3.1. Cascade leaching test (CLT)

Cumulative leached concentrations of major elements, As, HMs and pH from BCS in CLT are given in Fig. 5. During the CLT, the initial pH (=4) mostly increased up to a value of 7.9 (<125 μm fraction) and 6.4 (<1 mm fraction). However, pH values changed slightly between the subsequent steps (from 7.9 to 7.6 for the <125 μm fraction, from 6.4 to 5.2 for the <1 mm fraction). The extent of pH-change mainly depends on the acid neutralizing capacity (ANC) of the samples (Cappuyns and Swennen, 2008). The BCS sample with the smaller particle size (<125 μm fraction) was characterized by a higher ANC than the coarser particle size fraction (<1 mm fraction), most likely because of higher reactivity of the smaller particles.

Generally, two groups of elements could be distinguished based on their release during CLT. The first group included Ca, K, S, As, Pb and Mo showing higher releases in the <125 μm fraction compared to those in the <1 mm fraction whereas the second group including Al (except L/S = 20), Fe, Si, Cd, Cu, and Zn showing an opposite behavior. The amount of Al and Fe released during CLT was very low (cumulative mass leached 34 mg/kg and 92 mg/kg in the <1 mm fraction for Al and Fe, respectively), suggesting that no significant dissolution of Al/Fe-containing minerals occurred. This agrees with the mineralogy of the solid phases with the occurrence of fayalite, magnetite and maghemite, which are known as stable phases in copper slag. Cr and Ni concentrations in the leachates were below detection limit (DL = 0.005 mg/l) while Cd and Pb were only released in the first L/S fraction in both two particle size fractions. The leached concentrations were 0.04 mg/kg and 0.23 mg/kg for Cd in the <125 μm fraction and in the <1 mm fraction respectively. The leachable concentration of Pb in the <1 mm fraction (0.2 mg/kg) was lower than in the <125 μm fraction (0.4 mg/kg). Arsenic and Mo were not detectable in the <1 mm fraction. In the <125 μm fraction they were released in the first extraction (L/S = 20) while concentrations decreased in the subsequent extractions (L/S = 40 and 60) and not detectable any more at L/S = 80 and 100. Zn displayed the highest concentration at L/S 20 for both particle size fractions and decreased in the subsequent L/S fractions. Cu was mainly released from the <125 μm fraction at L/S 20 (11 mg/kg) and then smaller amounts of Cu (between 1 and 5 mg/kg) were released during the subsequent extraction. In the <1 mm sample, the maximum leachable concentration of Cu was observed at L/S 40 (26 mg/kg), followed by a much lower release in the following extractions.

The cumulative mass of As and HMs leached in the 5 extractions was compared to EU limits for non-hazardous waste (DIN38414-S4 leaching test). This test implies a 24 h leaching at L/S ratio of 10, without any pH adjustment. Although the operational conditions from the CLT differ from the specifications of the DIN38414-S4 leaching test, the limit values are used as a reference, and not to verify compliance with environmental legislation. The results showed that the cumulative masses of all elements leached were below the EU limit for non-hazardous waste except for Cu. The results suggest a low cumulative leachability (<1.0% total concentration) of metals from BCS in this study except for Cu and Cd (1.0% from total concentration for both Cu and Cd). However, special attention should be paid to Cu because the high total amount of Cu (average 0.85%) in the BCS and the high amounts of this element that are released.

3.3.2. pH_{stat} leaching test

pH_{stat} leaching test at pH 4 were performed for two particle size fractions of BCS, namely the bulk sample (not sieved) and the fraction <1 mm to examine whether the release of HMs is influenced by particle size. ANC at pH 4 of the bulk BCS was lower than in
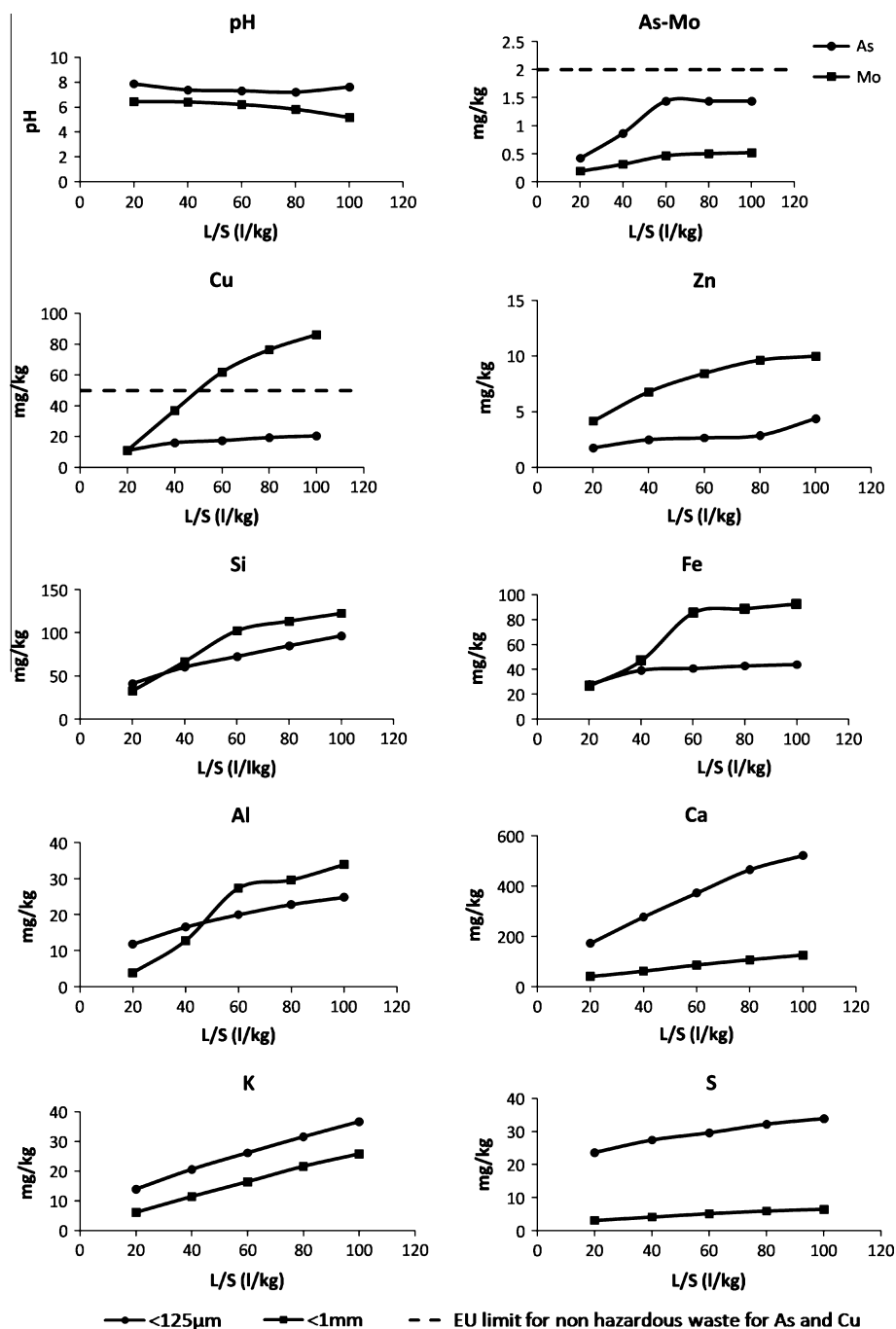
Fig. 5. Cumulative leached concentrations of As, Mo (only from the <125 μm fraction as the values from the <1 mm fraction were below detection limit), Cu and Zn, major elements (Ca, K, S, Al and Fe) and pH from BCS in the cascade leaching test.

the fraction <1 mm (42 mmol/kg and 33 mmol/kg respectively). The CLT also showed that ANC is higher for the smaller particle fractions. The release of major elements, As and HMs from BCS in pH_{stat} leaching test are given in Fig. 6. Co was not detected in the leachate. In general, the amount of major elements (Al, Ca, Fe, Mg, Mn and S), HMs (Cr, Mo, Ni, Pb and Zn) and As released after 120 h were relatively low (<1% total content) except for some elements such as Cd, Cu, K and Si (>1% of total content). Generally, elements in the fraction <1 mm showed a higher release compared to those in the bulk sample (Al, Fe, K, Mg, Si, As, Cr, Cu, Mo, Ni and Zn), except for Ca, Mn, Cd, Pb and S which showed small difference between the two fractions. This is explained by the fact that smaller particle have higher specific surface areas (Karius and Hamer,

2001). The particle size of waste materials (in addition to their composition) strongly influences the contaminant leachability (Ettler et al., 2009).

Release patterns of Al, Fe, Si, As and Mo were quite similar and were characterized by an initial slow release which increased dramatically at 120 h. As and Mo were detected after 1 h of leaching in the fraction <1 mm while they were not released, at least at detectable concentrations (DL = 0.02 and 0.001 mg/l for As and Mo, respectively) from the bulk sample. Cr was also detected in the leachate of the <1 mm sample after 72 h (0.07 mg/kg), whereas it was not detected from the bulk sample. However, Cd exhibited a similar leaching trend in both fractions (<1 mm and bulk), it was only detected (DL = 0.001 mg/l) after 1 h of leaching and released
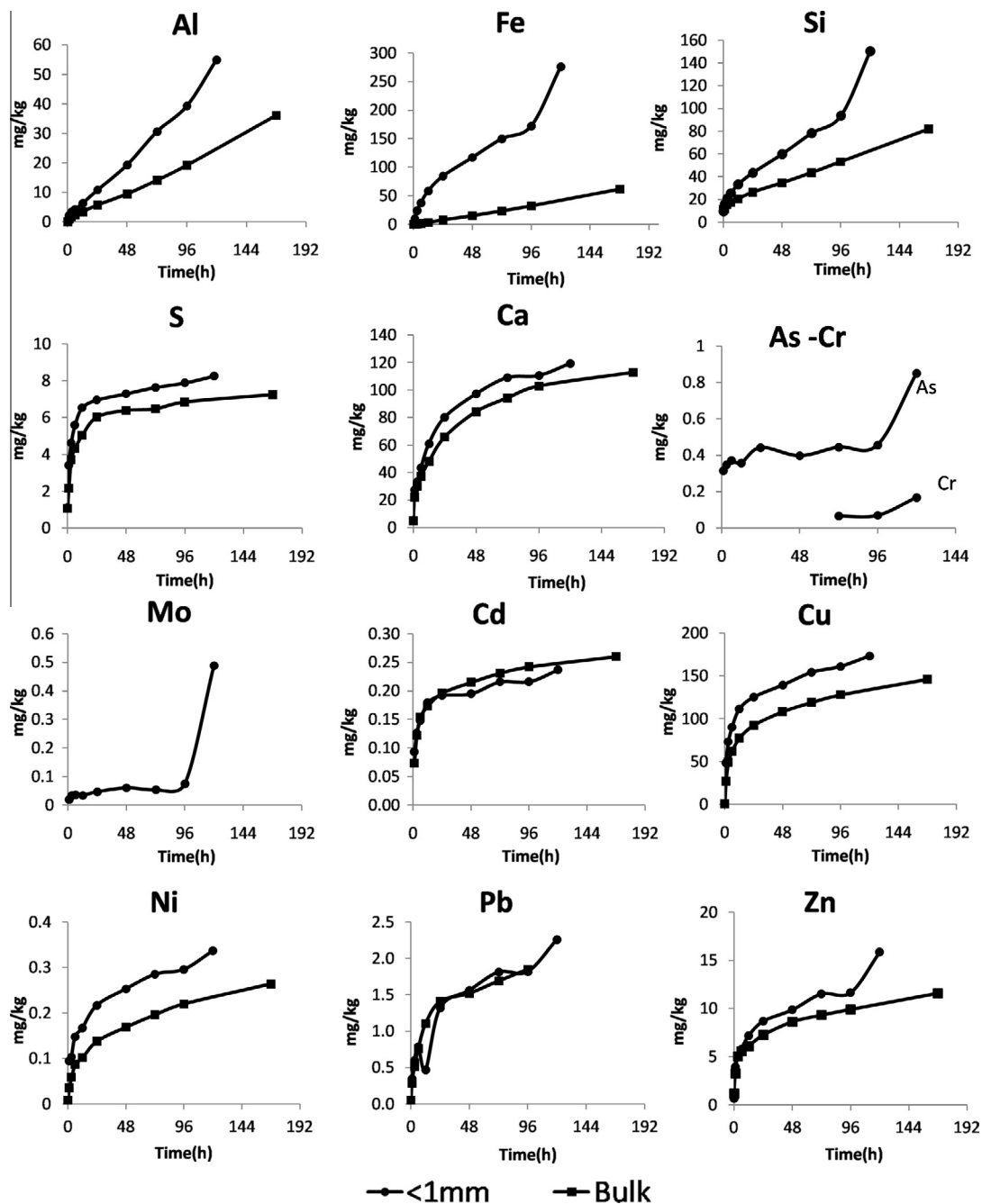
Fig. 6. Release of major elements, As and HMs from BCS in pH$_{stat}$ leaching test at pH 4. For As and Mo, the values were below detection limit for the bulk sample.

slowly in similar concentrations. The maximal release of Cu and Zn from the <1 mm fraction (173 mg/kg and 16 mg/kg respectively) was higher than the amount released from the bulk sample (146 mg/kg and 12 mg/kg respectively). This indicates that particle size is a key factor in determining HM release from the BCS in pH$_{stat}$ leaching test.

It is clear from the results that, although Cu and Zn have similar total concentrations in BCS, the leached amount of Zn was much lower than for Cu (leachability of Cu and Zn respectively 2.0% and 0.2% of total content). Similar trends were observed for Cd compared with As, Cr, Ni, Mo and Pb: Cd has a very low total concentration in the BCS compared to As, Cr, Co, Ni, Mo and Pb, but its leachability (1.0% of total content) was higher compared to the leachability of As, Cr, Ni and Pb (0.1%, 0.1%, 0.3% and 0.3% of total

content, respectively). Cu and Cd are usually characterized by a medium to high mobility under influence of acidification in solid samples (e.g., sediments/soils) (Förstner et al., 1986; Sahuquillo, 2003). Moreover, Cu usually exhibits the highest release among HMs in copper slag during leaching tests (Lim and Chu, 2006; Vít-ková et al., 2011). Therefore, the higher leachabilities of Cu and Cd in comparison with other HMs in BCS in this study correspond well with previous studies.

It is clear that the leached percentage of an element is not affected by its total content in BCS and leached amounts do not correlate with total content (cfr. van der Sloot and Dijkstra (2004)).

XRD results on the residue after pH$_{stat}$ leaching test did not show any significant compositional differences. The major phases in the BCS are glass phases, typically being compact and

homogeneous (Tossavainen, 2005). The relatively low release of As and HMs from BCS in this study suggests that As and HMs are (partly) immobilized in glass phases.

A low release of As and HMs from copper slag was also observed with other leaching tests, such as US EPA's Toxicity Characteristic Leaching Procedure (TCLP) (Lim and Chu, 2006; Shanmuganathan et al., (2008)).

In general, relatively higher As and HM concentrations were released during pH_{stat} leaching test compared to the CLT. The difference between the amount of As and HMs leached in the pH_{stat} and the CLT is likely caused by the pH difference between the leachates in these tests. Leaching of HMs usually increases as pH decreases (van der Sloot and Dijkstra, 2004) and the pH is kept at a constant value of 4 during pH_{stat} leaching, whereas pH was neutral to weakly alkaline during CLT.

Arsenic can occur in anionic form (as arsenate or arsenite) which explains its release at more alkaline pH values. Dissolution of arsenic minerals and As-binding species such as Fe and Al oxy-compounds can occur at lower pH (O'Neill, 1995). Amorphous and crystalline oxide phases of Al and Fe are ubiquitous in many alkaline wastes (Warren and Dudas, 1985) which can adsorb oxyanions such as arsenate, arsenite and molybdate (Cornelis et al., 2008). Therefore, the similar release pattern of As and Mo with Al and Fe in this study might be explained by dissolution of Al/Fe (hydr) oxides containing As and Mo.

The results of the leaching test indicate that a smaller particle size and acidification accelerated the release of examined elements in BCS. In the present study, mainly the release of Cu from BCS was significant.

Consequently, the spreading of fine BCS particles is of major concern and measures to prevent the further wind dispersion of fine BCS particles should urgently been taken. As a first management measure, covering the dump site to avoid dispersal of fine particles by wind should be envisaged, because these particles can easily release Cu into the environment. In view of the elevated Cu concentrations found in the slag, the potential recovery of Cu from the BCS should be investigated.

4. Conclusion

Through the investigation of sediment and soil in Ninh Hoa district, Khanh Hoa province, south central Vietnam, As and HM contamination of surface soil and surface marine sediment collected near the dump site and shipyard was recorded. The presence of fine dust of BCS was also visually recognized and its presence explained the high values of As and HM in the surface soil/sediment. Local background values were used to assess the degree of contamination with As and HMs. It can be deduced from this study that, the contamination status can be underestimated (for Cu, Cr, Ni and Zn) or overestimated (As and Pb) if local background values are not taken into account. The pH $_{stat}$ leaching test of BCS collected at the dump site provided information on the leachability of As and HMs in BCS under influence of acidification and indicate that the BCS has a low ANC and low leachabilities of As and HMs. However, mainly Cu was released in significant amounts upon acidification. According to the results of the leaching test, even though BCS particles were recorded in the surface sediment/soil, the risk for environmental release of As and most HMs from the soil and sediment was relatively low, except for Cu. Nevertheless, the leaching of Cu from the BCS exceeds the EU regulatory limit for non–hazardous waste. If recycling of this slag is considered, attention should be paid to the release of Cu under acidifying conditions. Additionally, spreading of BCS dust particles is of major concern and measures to prevent the further wind dispersion of fine BCS particles should been taken.

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