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Trace Elements in Suspended Particulate Matter and Sediments of the Cai River: Nha Trang Bay Estuarine System (South China Sea)

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Abstract

The distribution of particulate form of organic carbon (POC), Al, Fe, Ti, Li, Zn, Pb, U, Sc, Sn, Bi, Zr, Ba, As, Sr, W, V, Co, Cu, Ni, Mo, Cr, Mn, Ba, Sn, Sb, Hg, and Ag in the Cai river and Nha Trang Bay generally followed the distribution of total suspended matter (SPM) and was characterized by the most significant loss in the frontal zone of the estuary with highest horizontal gradients within the salinity interval of 8–20‰. The most part of these elements are supplied to the estuary with the Cai river discharge. Sedimentary Al, Fe, Ti, Li, Sc, Co, Cs, Zr, Cr, Zn, Co, Ni, Cu, Pb, Sn, and V are most likely controlled by the accumulation of their most fine-grained host minerals in sea floor depression of the bay. Sedimentary Bi, W, As, U, and Mo are mainly deposited with the coarse river material near the river mouth. The distribution of Ca, Sr, Mn, and Ba is largely controlled by the total inorganic carbon (TIC) content in the sediments. Metal form study revealed the highest percent contents of the labile forms for Mn, Co, and Pb in the sediments. The high levels of weak acid-soluble Pb and Co (30% and 43% of the total content in sediment, on average, respectively) contributes to a contamination problem in the Nha Trang Bay which arises from the Cai River discharge.

Keywords: Vietnam, tropical estuary, trace elements, selective extraction, bioavailable metal forms

1. Introduction

Southeast Asia has experienced a rapid and colossal economic growth with Vietnam being one of the fastest growing countries. Most development activities (e.g., industry, agriculture,

human settlement, tourism, and transport) take place in coastal zones [1–4]. This hazard is increased by the high vulnerability of these areas to environmental changes. The Cai River and the Nha Trang Bay of the South China Sea are inhabited by unique biota. This region is now exposed to the multiple anthropogenic stressors such as human settlement, agriculture and aquaculture, tourism and transport [5].

Over the past two decades, comprehensive studies of the organic geochemistry patterns and contamination levels and trends in the Nha Trang Bay have been undertaken [6–14]. The most recent research of the abundance, distribution and speciation of the major and trace elements in the sediments allowed to track the fate of potential contaminants in the Cai River–Nha Trang Bay estuarine system along the salinity gradient [5, 15]. It was shown that most trace element contents were at natural levels and are derived from the composition of rocks and soils in the watershed. A severe enrichment of Ag was most likely derived from metal-rich detrital heavy minerals. Geochemical fractionation of the riverine material generally determined the metal enrichment in surface sediments along the salinity gradient. The parts of actually and potentially bioavailable forms were most elevated for Mn and Pb (up to 36 and 32% of total content, respectively). Overall, the most bioavailable parts of trace elements were associated with easily soluble amorphous Fe and Mn oxyhydroxides.

In estuarine region, suspended particulate matter (SPM) acts as a major carrier as trace elements get adsorbed on to major elements like Fe and Mn oxyhydroxides and organic matter and get precipitated, where coarse material may settle into the estuarine system as sediments and finer materials get transported into the ocean [16–18]. It is important to study major and trace elements, as excess input of these metals may settle into the estuary due to salinity gradient [19–22]. The present study summarises the data on the abundance, distribution, partition, speciation and bioavailability of major and trace elements in the suspended particulate matter (SPM) and surface sediments of the Cai River estuary under multiple stresses.

2. Materials and methods

2.1. Environmental setting

The Cai River, its estuary and the adjacent part of the Nha Trang Bay belong to the Central Southern Coastal Region of Vietnam (Khanh Hoa Province). The fresh river water ($S < 0.1\text{‰}$) and saline South China Sea water ($S \approx 36\text{‰}$) form a major water-mixing zone. The fill dam built 8 km upstream from the river mouth limits the water exchange and marks the riverine boundary of the water-mixing zone (**Figure 1**). The Cai River estuary and Nha Trang Bay can be divided into three sub-zones: (1) river ($S < 0.1\text{‰}$), (2) transitional waters (estuary) ($0.1\text{‰} > S > 32\text{‰}$) and (3) sea (bay) ($S > 32\text{‰}$). In the transitional waters, the salinity (S) increases from the river to the sea and from the surface to the bottom. The water column is

highly stratified with the pronounced horizontal and vertical salinity gradients [5]. The climate seasonality and human activities (such as urbanisation, land use, damming, tourism, coastal construction, transportation, aquaculture and fisheries) expose the Nha Trang Bay to multiple pressures [14, 23–26].

2.2. Field work

The water and sediment samples were collected in the Cai River estuary and Nha Trang Bay in July 2013 along the salinity gradient at five locations for surface water layer (sts. 1, 3, 4, 7, 8, **Figure 1**) and at seven locations for surface sediments (sts. 2–8, **Figure 1**). The sampling stations were located in the riverine (st. 1), transitional (sts. 2–4) and marine (sts. 5–8) sub-zones of the dry season.

The surface water samples were obtained using a plastic Niskin bottle. The temperature, alkalinity and salinity of the water samples were measured on-board immediately after collection using portable conductivity apparatuses HI 98129 Combo and HI 98302 DIST 2 (Hanna Instruments, Germany). The suspended particulate matter was collected by filtering of water samples in an all-glass filtering system, on pre-weighted filters: 0.45 μm polycarbonate filters (Millipore-Isopore) for total suspended matter (TSM); combusted and pre-weighted glass fibre filters (Whatman GF/F) for particulate organic carbon (POC) and acid-clean cellulose filters (Millipore HA) for geochemical analyses. In the laboratory, all filters were rinsed with 250 ml Milli-Q water to remove salts and dried to constant weight at 60°C.

The surface sediment sampling, transportation and preparation procedures were performed using standard clean techniques that were described elsewhere [5].

2.3. Analytical methods

The surface sediment samples were subjected to grain size and mineral composition analyses. The grain size analysis was performed by wet sieving [27, 28].

The dissolved organic carbon in water samples was determined by high-temperature (at 680°C) thermocatalytic oxidation with dispersion-free IP detection. The total carbon (TC) contents in suspended particulate matter (SPM) and sediment samples were determined by dry burning at 900°C in oxygen flow and the total inorganic carbon (TIC) contents were determined by dry burning at 200°C with H_3PO_4 . The DOC, TC and TIC analyses were performed with the analyser TOC 5000-V-CPH (Shimudzu Co., Japan). The total organic carbon (TOC) contents were determined as a difference between TC and TIC contents in the samples [10].

For the total Al, Fe, Ti, Ca, Na, Mn, Li, V, Cr, Co, Ni, Cu, Zn, As, Sr., Zr, Mo, Cd, Ag, Sn, Sb, Cs, Ba, Pb, Bi and U content analysis, the samples were subjected to the total acidic dissolution in $\text{HNO}_3 + \text{HF} + \text{HClO}_4$ in an open system with further determination of element contents using

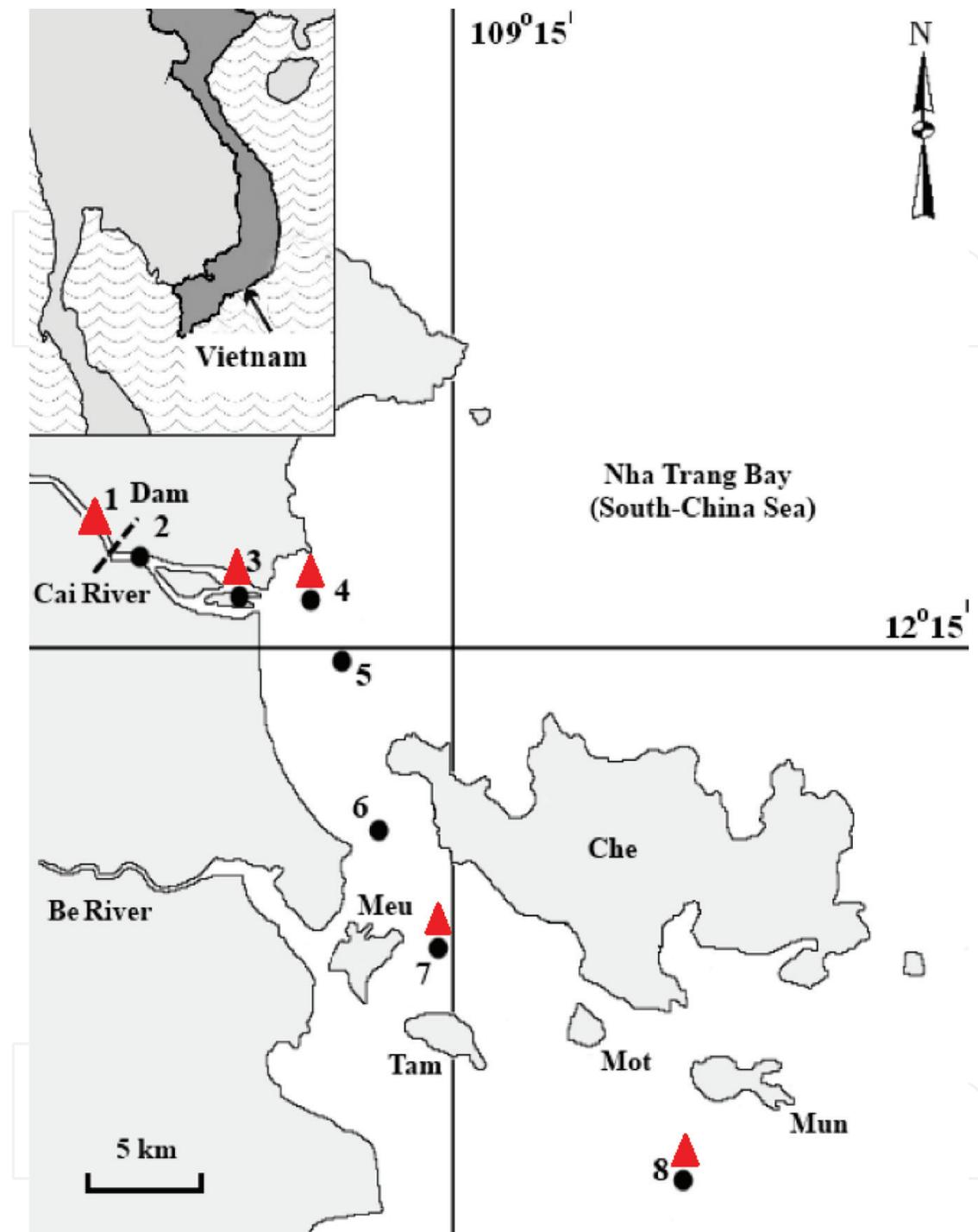


Figure 1. Location of study sites.

the ICP method on the X-7 ICP-MS spectrometer (Thermo Scientific, USA) [29]. The detailed sample decomposition and analytical procedures are described elsewhere [16]. The Hg content was determined in the dry samples using a pyrolyse method on the RA-915+ spectrometer with background correction and a two-chamber atomiser PYRO-915+ (Lumex, Russia) [9, 14].

To assess the chemical form of selected metals (Fe, Mn, Cr, Zn, Cu, Pb, Ni and Co) in the sediments, the samples were subjected to single chemical reagent (single-step) extraction procedures. The weak-acid-soluble (labile) metals were extracted using 25% acetic acid, the oxalate-soluble metals were extracted using ammonium oxalate-oxalic acid buffered solution at pH 3.2 (Tamm extraction), the pyrophosphate-soluble metals were extracted by 0.1 M sodium pyrophosphate. To isolate the weak acid-soluble metals, 15 ml of 25% acetic acid was added to 1.1 g of dry sample in polypropylene vials and shaken in a mechanical shaker for 6 h with acetic acid. Then, each extract with the sediment was filtrated into a 25 ml glass volumetric flask. The sediment on the filter was washed with 10 ml of distilled water and the wash water was added to the flask [27]. To isolate the amorphous iron oxides and their associated microelements, 50 ml of ammonium oxalate-oxalic acid buffered (Tamm) solution was added to 1.1 g of dry sample in the 250 ml flat bottom flask, shaken for 1 h and filtrated to a 250 ml glass volumetric flask. The sediment on the filter was washed with 10 ml of distilled water that was mixed with a small amount of oxalic acid and the wash water was added to the flask. Then, the filter with sediment was added to the sediment in the flat-bottom flask and subjected to one more repeated extraction and the extract was added to the 250 ml volumetric flask [30]. To isolate the organically bound metals, 15 ml of 0.1 M sodium pyrophosphate was added to 1.1 g of dry sample in polypropylene vials and shaken in a mechanical shaker for 15 min, left for 24 h and then filtrated to a 250 ml glass volumetric flask. The sediment on the filter was washed with 10 ml of 0.1 M sodium pyrophosphate and the wash water was added to the flask [31]. The metal contents in the extracts were further determined using an atomic absorption spectrometer (AAS) Hitachi 180-8 (Hitachi Co., Japan) in the Analytical Centre of Moscow State Lomonosov University.

The relative accuracy of the analytical determinations was within the standard deviations that were established by the certified reference materials (CRM) SDO-1 (Russia) (for SiO_2 , TOC and TIC), SRM 521-84P (Russia) (for Na_2O , Al_2O_3 , S_{total} , K_2O , CaO , MnO , Fe_2O_3 , Li, V, Cr, Zn, As, Sr., Zr, Mo, Ag, Sn, Ba, Pb), AGV-2 (USA) (for MgO , P_2O_5 , TiO_2 , Co, Ni, Cu, Sr., Sb, Cs, U) and Mess-3 (Canada) (for Hg).

3. Results and discussion

3.1. Abundance and distribution of major and trace elements in surface SPM

The hydrology of the riverine sub-zone of the studied part of the Cai River—Nha Trang Bay estuarine system is strongly influenced by the fill dam. The surface fresh water layer flows seaward over the dam, while the upstream penetration of the near-bottom saline water lenses is blocked [5]. In July 2013, the salinity of the surface fresh-water layer varied from 0‰ to 36‰. The frontal zone of the contact of fresh and saline waters occurred downstream from the fill dam (sts. 2–3, **Figure 1**), where the horizontal salinity gradient was 3.5‰ per 1 km distance. The temperature (T) of the water column varied in narrow ranges and decreased from

the river to the sea from 30 to 29°C in the surface water layer. The pH of the water column increased from neutral in the riverine waters (pH 7) to low-alkaline in the transitional and sea waters (pH 8–9). The dissolved organic carbon (DOC) concentration in the surface water layer varied within the ranges 1.1–2.5 mg l⁻¹ and was distributed uniformly (2.3–2.5 mg l⁻¹) in the frontal zone and transitional waters and exhibited a minimum of 1.1 mg l⁻¹ in the marine part of the transect at salinity >30‰ (**Figure 2**).

The suspended particulate matter (SPM) showed a concentration maximum of 50 mg l⁻¹ near the river mouth (sts. 1) at salinity 0‰ and then a decrease seaward to the values of around 1 mg l⁻¹ at salinities 32–36‰, following from the sedimentation of the coarsest fluvial material in the frontal zone of the estuary at the sharp decrease in the river flow velocity enhanced by the dam influence (**Figure 2**). The distribution pattern of particulate organic carbon (POC) was close to the SPM distribution. The maximal POC concentration (1–1.25 mg l⁻¹) was found in the fluvial part of the estuary (sts. 1–3) at salinities 0–8‰ because of an intensive sedimentation of the organically enriched suspended river material in the frontal zone of the estuary. In the transitional waters, the POC concentration lowers seaward to 0.94 mg l⁻¹ at salinities around 20‰ and further to 0.18–0.21 mg l⁻¹ at salinities 32–36‰ (**Figure 2**). The organic carbon content in the SPM (POC, % of dry SPM weight) varied within the range 2–17%. The higher organic carbon content >10% was found in SPM of the marine waters at the salinity >30‰ (**Table 1**).

The distribution of particulate form of Al, Fe, Ti, Li, Zn, Pb, U, Sc, Sn, Bi, Zr, Ba, As, Sr., W, V and Ag followed the distribution of total suspended matter and was characterised by a maximum in the river water and then a sharp decrease seaward of element relative concentration (in µg l⁻¹) with highest horizontal gradients within the salinity interval of 8–20‰ (**Figure 3**). The absolute concentration of these elements (in µg g⁻¹ of the dry SPM weight) followed the same trend of decreasing seaward but was elevated in the both riverine and transitional waters (0–20‰) (**Table 1, Figure 3**). The most significant losses of suspended elements occurred in the frontal to transitional zone of the estuary (0–20‰) by an intensive sedimentation of dissolved and suspended river material. The most part of these elements must be supplied to the estuary with the Cai River discharge. In estuaries, the flocculation and coagulation of riverine microcolloids are initiated when the salinity increases. These processes are accompanied by a rapid scavenging of dissolved trace elements from the water column. Further deposition of newly-formed aggregates contributes to the enrichment of sediments in trace elements [32].

The distribution of particulate form of Co, Cu, Ni, Mo and Cr and, in some lesser extent, Mn, Ba, Sn, Sb and Hg is characterised by the most significant loss in the frontal zone of the estuary where the coarsest river material enriched in detrital minerals is deposited at the sharp decrease of the river flow velocity enhanced by the dam (**Table 1, Figure 3**). Both relative (in µg l⁻¹) and absolute (in µg g⁻¹ of the dry SPM weight) concentrations of these elements sharply decrease with the highest horizontal gradients at the initial salinity rise (0–8‰). The depletion in these elements in the transitional waters (at salinities 8–32‰) was followed by negligible increase of their relative concentrations and significant increase of

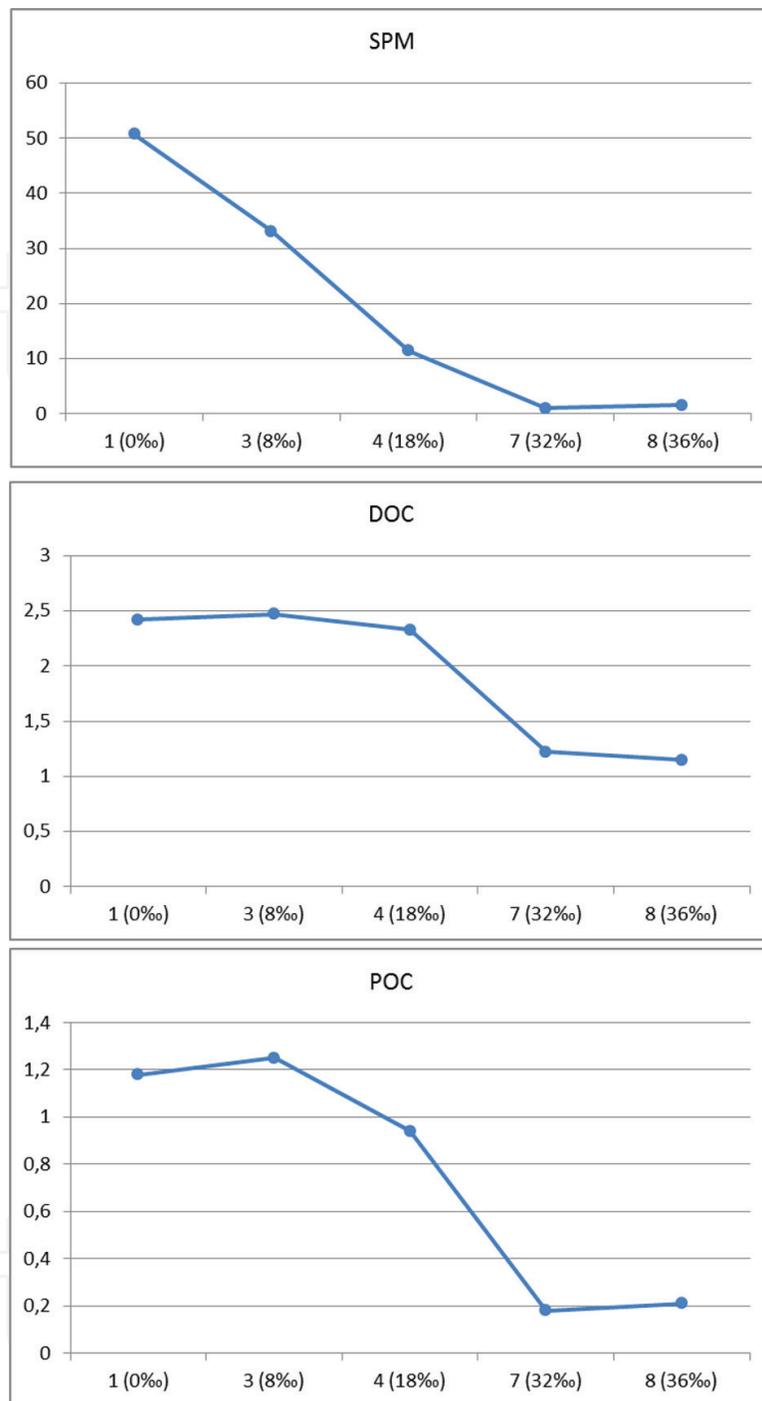


Figure 2. SPM, DOC and POC concentrations in surface water layer (in mg l⁻¹).

absolute concentrations of Co, Cu, Ni, Mo, and Cr at salinities 32–36‰ (**Table 1, Figure 3**). In the stratified Cai River estuary, the significant part of the particulate trace elements may be carried out seaward with the surface water layer. In the marine part of the estuary, with a homogenisation of the water column, most of the fine-grained material of surface water layer enriched in clay minerals, carbonates and trace metals is deposited [5]. Since SPM in

Station (S %)	1 (0%)	3 (8%)	4 (18%)	7 (32%)	8 (36%)
Li	57.09	60.32	57.37	9.50	8.67
Al	15.11	15.41	14.61	1.30	0.78
Ca	0.31	0.16	0.16	0.83	0.82
Sc	15.85	15.42	16.17	5.65	3.52
Ti	0.18	0.15	0.12	0.03	0.02
V	94.07	109.59	127.60	63.59	17.39
Cr	187.21	57.34	72.09	66.18	91.86
Mn	737.05	410.08	342.46	461.65	479.05
Fe	4.67	4.77	5.31	0.45	0.25
Co	175.41	13.66	12.24	60.91	116.96
Ni	384.24	52.48	61.56	119.56	171.20
Cu	201.66	31.60	34.25	119.16	201.11
Zn	116.07	119.56	103.54	28.00	35.7
As	42.42	34.88	39.85	6.61	89.64
Sr	45.32	46.63	61.39	201.82	201.40
Zr	27.46	22.74	22.62	4.25	2.52
Mo	51.58	9.13	9.45	10.97	13.57
Ag	0.22	0.18	0.22	0.25	0.13
Sn	9.19	8.56	6.57	2.53	1.77
Sb	0.97	0.93	0.94	0.22	0.20
Cs	16.30	15.12	11.80	0.97	0.77
Ba	286.38	205.25	248.46	28.48	157.93
W	12.01	5.63	5.43	1.64	1.06
Hg	0.89	0.49	1.11	2.28	0.91
Pb	65.17	63.05	75.28	44.76	26.88
Bi	9.66	9.84	14.59	1.14	0.42
U	9.08	10.33	8.77	0.49	0.43
POC	3.68	3.85	9.39	7.87	7.29

Table 1. Major and trace elements contents in SPM (in $\mu\text{g g}^{-1}$, except for Al, Fe, Ti, Mn, Ca and POC in % of dry weight).

transitional and marine waters were enriched in organic carbon, the particulate organic matter of terrigenous and/or planktonogenous origin most probably contributed to trace element accumulation in SPM in the bay.

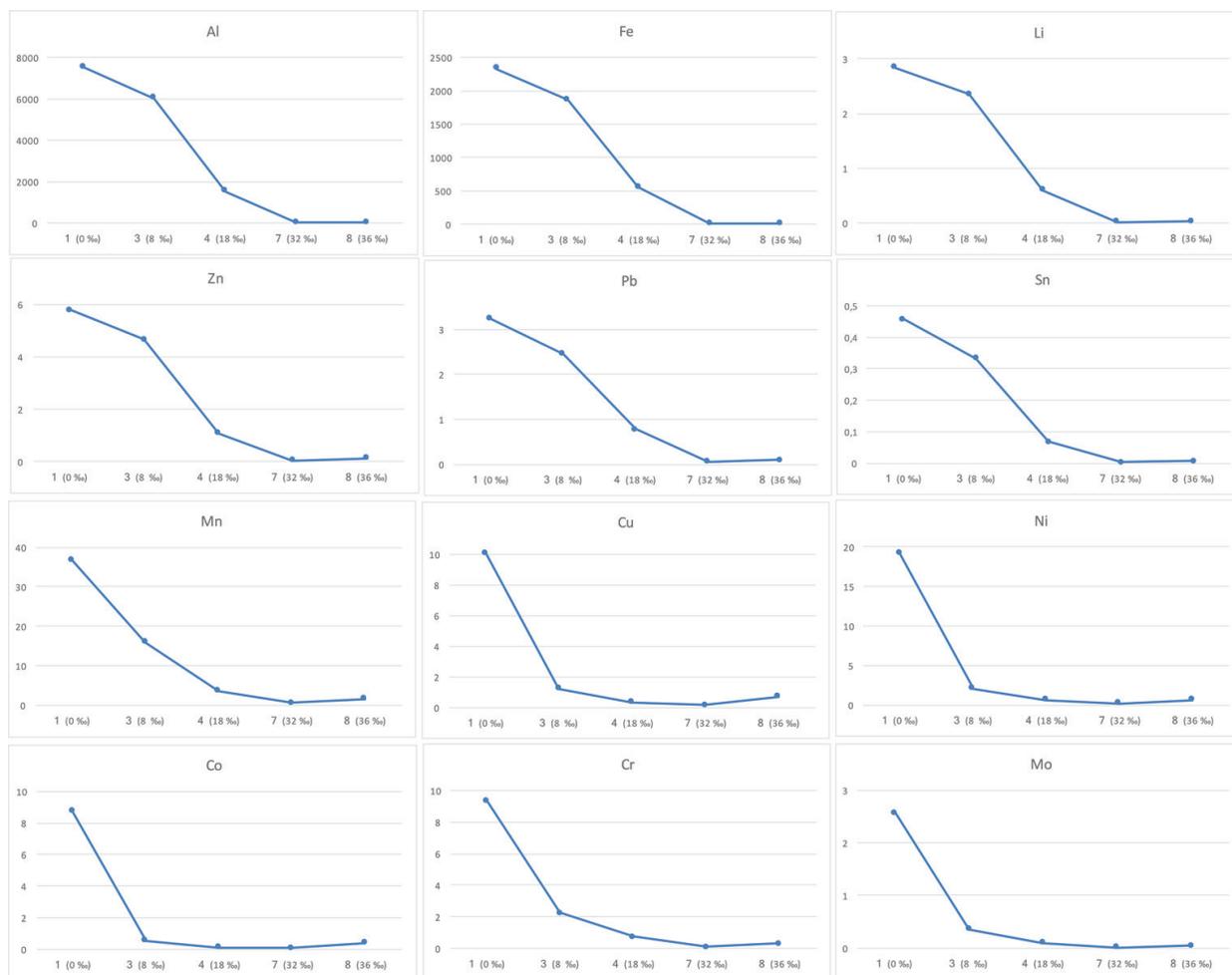


Figure 3. Major and trace elements contents in SPM (in $\mu\text{g l}^{-1}$).

3.2. Abundance and distribution of major and trace elements in surface sediments

The percent of the content of sand- ($63\ \mu\text{m}$ – $2\ \text{mm}$), silt- (2 – $63\ \mu\text{m}$) and clay- ($<2\ \mu\text{m}$) sized material in the studied sediments is shown in **Table 2**. The sediments near the river mouth were mostly sandy, while the coarsest sediment is from station 4. Downstream, in the transitional sub-zone, the sediment contains less sand and more silt and clay. The most fine-grained sediment, with the highest clay content, is from marine stations 7–8.

The total contents of Al, Fe, Ca, Mn, Ti, TOC and TIC are reported in **Table 3**. The mean contents of the major elements are within the range of the Clark contents in shale, pelagic clays and average world riverbed sediments [33–37]. The distribution of Fe and Ti in the river-sea transect is similar to that of Al. The observed distribution of major elements in the sediments illustrates the grain size and mineral fractionation processes. Al, Fe, Ti and Mn (to a lesser extent) increase seaward in the sediments with the clay-sized materials.

The distribution of the inorganic carbon (TIC) content in the sediments along the river-sea transect is characterised by only two significant values in the marine part (2,1 % at st. 7 and

Stations	Sand (63 μm –2 mm)	Silt (2–63 μm)	Clay (<2 μm)	TOC	TIC
2	49.58	23.96	26.46	1.77	0
3	47.81	28.28	23.91	1.49	0
4	71.03	19.23	9.74	0.89	0
5	28.47	47.48	24.05	1.55	0
6	49.31	37.6	13.09	1.76	0
7	3.26	42.69	54.05	0.61	2.11
8	2.37	28.96	68.67	1.02	0.88

Table 2. Sand, silt, clay, TOC and TIC contents in sediments (in % of dry weight).

0.88% at st. 8). Sedimentary organic carbon (TOC) varied within the range of 0.6–1.8% and showed no affinity to the other major or trace elements that were studied. This may be due to the intensive microbial decomposition of particulate organic matter, which occurs in the water column during estuarine sedimentation processes [38, 39]. The post-depositional diagenetic reactions, which are enhanced by resuspension processes at sediment disturbance events (such as tides, storms and upwelling), may also contribute to a destruction of sedimentary organic matter and the formation of organic-poor sediments [40].

The mean content of the major part of the studied trace elements (Li, V, Cr, Co, Ni, Cu, Zn, As, Sr, Zr, Mo, Cd, Sn, Sb, Cs, Ba, Hg and Pb) in the sediments from the Cai River estuary and Nha Trang Bay is lower or corresponds to the reference values for shale, pelagic clays and the average world riverbed sediments (**Table 3**). The Ag content was negligible or below the detection limit at all locations along the salinity gradient. Thus, natural enrichment of Ag reported in the previous study [19] had a temporary/impact character [33–37]. However, relative sediment enrichment with Bi, W and, at some sites, with Sr. needs special study.

To normalise the obtained geochemical data for the grain-size effects and identify the enrichment zones along the salinity gradient, the metal/Al ratios were calculated [27, 41, 42]. The distribution of metal/Al ratios along the Cai River—Nha Trang Bay transect is provided in **Figure 4**. The results revealed associations of elements that are characterised by a similar geochemical behaviour in the sediments along the salinity gradient. Sedimentary Fe, Ti, Li, Sc, Co, Cs, Zr, Cr, Zn, Co, Ni, Cu, Pb, Sn, V, As, U and Mo varied in relatively narrow ranges. Major part of these elements tended to increase seaward with an elevation at station 7 at heightened carbonate content. The observed distribution of the normalised trace element contents reflects the association with and/or inclusion of Fe, Ti, Li and trace elements in the lattices of clay minerals that constitute the bulk of the fine-grained sedimentary material accumulated in the sea floor depression in the bay [42]. Sedimentary Bi and W decreased significantly from river to the sea. These elements may be associated with the coarsest river material enriched in detrital minerals which is mostly deposited in the riverine part of the estuary. The distribution of Sr. and Ca and, in a lesser extent, of Mn and Ba is largely controlled by the total inorganic carbon (TIC) content in the sediments. These elements form low-soluble carbonates in aquatic environments [36]. The distribution of trace elements in

Element	Mean	SD	Range	Shale ^a	Pelagic clay ^a	River sed ^b
Al	10.8	2.05	7.67–12.23	8.8	8.4	4.3
Fe	3.98	0.64	2.46–4.51	4.72	6.5	2.5
Ti	0.36	0.05	0.25–0.40	0.46	0.46	0.31
Mn	0.04	0.01	0.03–0.06	0.085	0.67	0.05
Ca	1.26	1.93	0.36–6.16	1.6	1.0	1.7
Li	47.9	8.2	34.7–62.7	66	57	20
V	89.3	12.0	61.4–100	130	120	50
Cr	45.8	9.9	27.9–66.7	90	90	50
Co	8.5	1.8	4.9–12.2	19	74	15
Ni	23.2	6.12	14.2–38.1	50	230	25
Cu	18.5	4.12	12.1–26.9	45	250	20
Zn	104.6	16.17	69.8–121	95	170	60
As	22.2	6.3	12.2–30.9	13	20	6
Sr	145	166	61.3–605	170	180	150
Zr	85.2	10.4	61.7–104	160	150	250
Mo	3.0	1.5	0.6–5.1	2.6	27	1.5
Ag	0.1	0.01	0.07–0.1	0.07	0.11	0.1
Sn	5.9	1.3	3.7–7.9	3.0	4.0	4.0
Sb	1.2	0.2	0.9–1.4	1.5	1.0	2.0
Cs	11.1	1.6	7.9–13.1	5.0	6.0	4.0
Ba	274	18	256–323	580	2300	290
Hg	0.03	0.01	0.02–0.05	0.18	0.10	0.05
Pb	54.4	11.0	35.1–61.6	20	80	15
Bi	9.5	9.0	0.9–27.6	0.43	0.53	0.2
U	6.6	1.5	3.9–8.0	2.7	2.6	3
W	10.4	7.2	2.4–24.6	0.3	0.42	0.4
TOC	1.36	0.39	0.61–1.77	—	—	1.4
TIC	1.49	0.69	<0.01–2.10	—	—	0.4

^aCited from [24].

^bCited from [46].

Table 3. Major and trace elements contents in sediments (in $\mu\text{g g}^{-1}$, except for Al, Fe, Ti, Mn, Ca, TOC and TIC in % of dry weight).

sediments is strongly influenced by the water column stratification because of the natural fractionation and deposition of materials of different grain sizes at sites, which are determined by hydrodynamic conditions [5, 13, 43, 44].

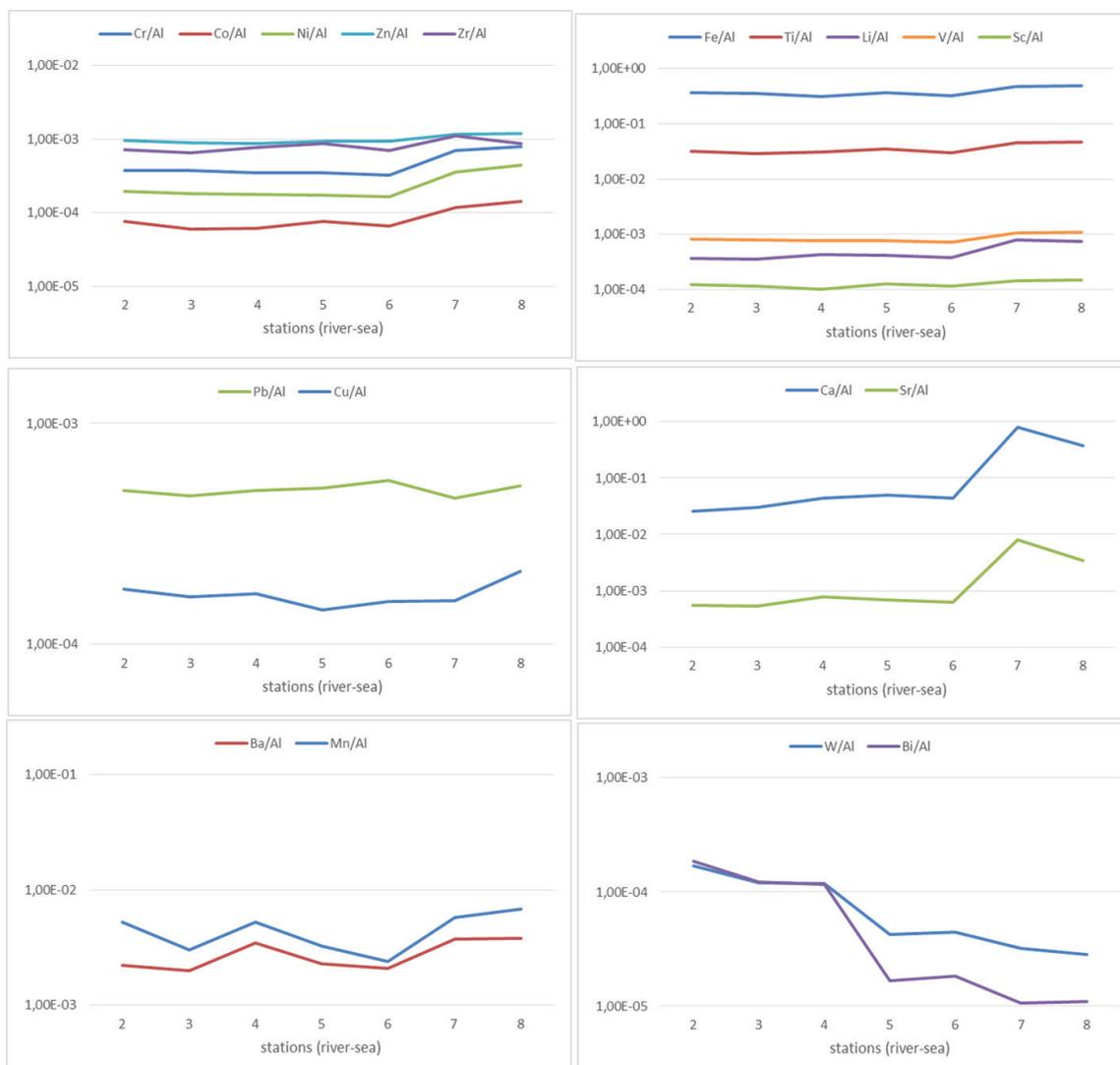


Figure 4. Element/Al ratio in sediments.

3.3. Speciation of major and trace elements in surface sediments

Major and trace elements are bound to a variety of sediment fractions that range from easily extractable (and bioavailable) to resistant residual mineral phases [45–49]. The total contents of the oxalate-soluble, pyrophosphate-soluble and weak-acid-soluble forms of Fe, Mn, Cr, Zn, Cu, Pb, Ni and Co are provided in **Table 4**. In this work, ammonium oxalate (pH 3.2–3.3) served to mobilise the easily soluble amorphous Fe-oxyhydroxides and acid-soluble fulvates [30, 31, 50]. Sodium pyrophosphate (pH 10) was used to remove organically bound metals from the sediments. This extract also mobilised part of easily soluble amorphous Fe-oxyhydroxides [13]. Acetic acid removed the labile metals in ion exchange positions, the easily soluble amorphous compounds of iron and manganese, the carbonates and the metals that are weakly held in organic matter [27].

The total content of the oxalate-soluble (amorphous) Fe increased from the river to the sea, whereas its percent content varied insignificantly (18–24% of the total content) and is the

highest in sediments in the frontal zone (sts. 2–3). The percent content of the weak-acid-soluble Fe, which is mostly comprised of easily soluble amorphous oxides, was constant in the transitional zone (10–11% of the total content), reached the maximum of 18% in the coarsest sediment from station 4 and lowered to 7–8% in the bay sediments. The percent content of the pyrophosphate-soluble Fe was low and decreased from 6–1% of the total Fe along the salinity gradient. The total and percent contents of oxalate-soluble Mn (18–58%), weak-acid-soluble Mn (13–54%) and pyrophosphate-soluble Mn (9–28%) were the highest in the coarse sediments of the frontal zone (sts. 2–3). Seaward, the contents of the studied forms of Mn decreased in the sediments in the transitional sub-zone (sts. 4–6) and increased again in the bay (sts. 7–8).

The oxalate-soluble form comprised 9–14% (12% on average) of the total content for Cr, 3–11% (8%) for Pb, 5–11% (7%) for Zn, 3–23% (15%) for Cu, 5–12% (9%) for Ni and 13–22% (17%) for Co. The weak-acid-soluble form comprised 8–12% (9% on average) of the total content for Cr, 23–34% (30%) for Pb, 4–19% (12%) for Zn, 1–8% (2%) for Cu, 8–24% (17%) for Ni and 20–66% (44%) for Co. The contents of pyrophosphate-soluble form were below the detection limit for Ni and Co. This form comprised 0.3–3% (2% on average) of the total content for Cr, 5–17% (11%) for Pb, 1–16% (10%) for Zn and 1–26% (12%) for Cu. According to the comparative extractability from sediments, Ni, Zn, Cr and Cu are low-labile and mainly occur in the residual phase. These metals were mainly extracted in the detrital fraction, which emphasises the importance of natural weathering and erosion in drainage basins. Fe and Zn are moderately labile and occur in the less resistant phases such as crystallised Fe/Mn oxides and organic compounds that may be a threat in the long term. Mn, Co and Pb are labile, held in ion exchange positions, bound to easily soluble amorphous Fe/Mn compounds and weakly held in organic matter. The high levels of acid-soluble Pb and Co (30 and 43% of the total content on average, respectively) compared to previously studied estuarine and coastal sediments contributes to a contamination problem in the Nha Trang Bay, which arises from the Cai River discharges, while the elevated level of easily reducible and organically bound Pb fractions (8 and 11% of the total content on average, respectively) also contributes to the anthropogenic input of Pb [5, 13].

The contents of oxalate-soluble (amorphous) forms were higher than the contents of pyrophosphate-soluble (organically bound) forms at all sites for Fe, Mn, Ni, Co and Cr (**Table 4**). Therefore, the most bioavailable parts of Ni, Co and Cr are bound to amorphous Fe and Mn oxyhydroxides and acid-soluble organic compounds. The contents of pyrophosphate-soluble forms were higher than the contents of oxalate-soluble forms at most of the sites for Pb, Zn and at some sites for Cu. Among the elements studied, most of the bioavailable Pb, Zn and Cu was most likely bound to organic substances. According to the mean determined amounts of the oxalate-soluble, pyrophosphate-soluble and weak-acid-soluble forms, the studied elements can be arranged in the following increasing order of average potential bioavailability: Cr < Ni < Cu < Zn < Fe < Pb < Co < Mn. The most bioavailable trace elements in sediments that were studied were scavenged by amorphous iron oxyhydroxides in the course of estuarine sedimentation. This result supports the fact that Fe and Mn oxyhydroxides largely control the bioavailability in sediments [7, 19, 32].

Figure 5 illustrates the distribution of the ecologically most significant weak-acid-soluble (labile) fraction along the river-sea transect. Mn, Co and Pb have the highest percent contents of the labile form but exhibit different spatial distributions showing some sporadic enrichments

Stations	Cu	Zn	Ni	Co	Pb	Cr	Fe	Mn
Weak acid-soluble								
2	0.4	18	5.6	4	16.4	3.4	4540	344
3	0.4	14	4.8	4.6	14	4.8	5620	144
4	0.2	13.2	3.4	2.2	13.4	3.2	2840	36
5	0.2	14	3	6	16	4.8	7640	58
6	≤0.2	4	2.4	1.8	12	5.2	2660	164
7	0.2	15.8	3	3.4	20	3.4	3440	52
8	≤0.2	7.6	5	2.6	15.6	5.6	2920	264
Mean	0.525	12.9	3.82	3.6	15.84	4.22	4244	133.6
Mean	2.8	12.3	16.5	42.4	29.1	9.2	10.6	32.0
(% of total content)								
Pyrophosphate-soluble								
2	5.6	18.6	≤0.2	≤0.2	4.8	1	2580	180
3	2	10.4	≤0.2	≤0.2	7	0.8	2940	82
4	2.6	9	≤0.2	≤0.2	7	≤0.2	1300	30
5	0.8	14.8	≤0.2	≤0.2	5.4	0.4	1480	32
6	0.4	1.2	≤0.2	≤0.2	5	0.8	420	50
7	1	13.4	≤0.2	≤0.2	9.6	1.6	1360	42
8	0.2	2	≤0.2	≤0.2	7.6	≤0.2	600	90
Mean	2.24	10.84	≤0.2	≤0.2	5.74	1	1652	65.9
Mean	12.1	10.4	—	—	10.6	2.2	4.1	15.8
(% of total content)								
Oxalate-soluble								
2	3	5.6	1.4	1.6	5.4	5.3	11,300	375
3	3.7	7	2.2	1	6.8	5.2	10,550	172
4	2.5	8	1.6	0.6	3.4	4	5480	75
5	2.1	6.8	1.3	2.2	5.4	6	8250	87
6	0.4	6.5	2.2	1.2	1.1	7	7500	158
7	4.4	8.7	2.6	1.5	4.1	5	7550	90
8	0.5	8.1	2	1.9	1.2	6.2	8430	255
Mean	2.93	7.42	2	1.44	4.56	5.57	8572	152.1
Mean	15.8	7.1	8.6	16.9	8.4	12.2	21.5	36.4
(% of total content)								

Table 4. Major and trace element form contents in sediments (in $\mu\text{g g}^{-1}$).

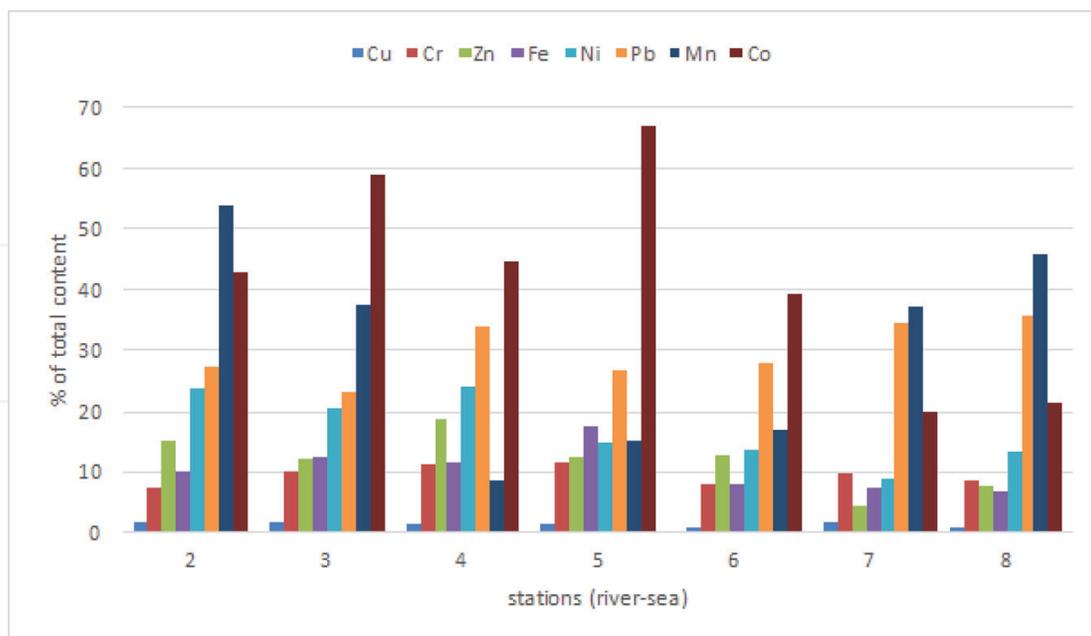


Figure 5. Weak acid-soluble (labile) metal form in sediments.

along the salinity gradient. Thus, the distribution of the most abundant labile Co is complicated by a pronounced maximum of 67% in the sediment at station 5. The sediments are mostly enriched with labile Fe, Zn, Cr and Ni in the frontal and transitional sub-zones (sts. 2–5). Cu exhibit the lowest contents of the labile form. Therefore, in the studied sediments, Cu is most likely bound to the residual mineral phase that is comprised of detrital heavy minerals.

4. Conclusions

The suspended particulate matter (SPM) showed a concentration maximum (50 mg l^{-1}) near the river mouth and then a decrease seaward to the values of around 1 mg l^{-1} at salinities 32–36‰, following from the sedimentation of the coarsest fluvial material in the frontal zone of the estuary at the sharp decrease in the river flow velocity enhanced by the dam influence. The distribution pattern of particulate organic carbon (POC) was close to the SPM distribution and varied within the range $0.18\text{--}1.25 \text{ mg l}^{-1}$. The organic carbon content in the SPM (POC, % of dry SPM weight) varied within the range 2–17%. The higher organic carbon content >10% was found in SPM of the marine waters at the salinity >30‰.

The distribution of particulate form of Al, Fe, Ti, Li, Zn, Pb, U, Sc, Sn, Bi, Zr, Ba, As, Sr., W, V and Ag followed the distribution of total suspended matter and was characterised by a maximum in the river water and then a sharp decrease seaward of element relative concentration (in $\mu\text{g l}^{-1}$) with highest horizontal gradients within the salinity interval of 8–20‰. The most part of these elements must be supplied to the estuary with the Cai River discharge. The distribution of particulate form of Co, Cu, Ni, Mo and Cr and, in a lesser extent, Mn, Ba, Sn, Sb and Hg is characterised by the most significant loss in the frontal zone of the estuary where the coarsest river material enriched in detrital minerals and pronounced increase of their absolute concentrations

at salinities 32–36‰. In the stratified Cai River estuary, the significant part of the particulate trace elements may be carried out seaward with the surface water layer. In the marine part of the estuary, with a homogenisation of the water column, most of the fine-grained material of surface water layer enriched in organic matter and trace metals is deposited.

Sedimentary Fe, Ti, Li, Sc, Co, Cs, Zr, Cr, Zn, Co, Ni, Cu, Pb, Sn, V, As, U and Mo varied in relatively narrow ranges along the salinity gradient and tend to increase seaward. These elements are most likely controlled by the accumulation of their most fine-grained aluminosilicate host minerals and materials in the sea floor depression of the marine sub-zone. Sedimentary Bi and W, are generally uniformly low but tend to decrease seaward. These elements may be associated with the coarsest river material enriched in detrital minerals which is mostly deposited in the riverine part of the estuary. The distribution of Sr and Ca and, in a lesser extent, of Mn and Ba is largely controlled by the total inorganic carbon (TIC) content in the sediments.

The distribution of trace elements in SPM and sediments of Cai River—Nha Trang Bay estuarine system is strongly influenced by the water column stratification because of the natural fractionation and deposition of materials of different grain sizes at sites, which are determined by hydrodynamic conditions.

Assuming that the mean determined amounts of the oxalate-soluble, pyrophosphate-soluble and weak-acid-soluble forms are a measure of the potential metal bioavailability in sediments of the Cai River—Nha Trang Bay estuarine system, the studied elements can be arranged in the following increasing order of average potential bioavailability: $Cr < Ni < Cu < Zn < Fe < Pb < Co < Mn$. This sequence is true for sediments in different sub-zones of the water-mixing zone: estuary (transitional waters) and sea (bay). Metal form study revealed the highest percent contents of the labile (weak acid-soluble) form for Mn, Co and Pb in the sediments. The high levels of labile Pb and Co (30 and 43% of the total content in sediment, on average, respectively) contribute to a heavy metal contamination problem in the Nha Trang Bay, which arises from the Cai River discharge. The elevated level of amorphous (oxalate-soluble) and organically bound (pyrophosphate-soluble) Pb fractions (8 and 11% of the total content in sediment, on average, respectively) also contribute to the anthropogenic input of Pb. The most bioavailable parts of the studied trace metals are associated with easily soluble amorphous Fe and Mn oxyhydroxides.

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