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Chemical Bioavailability of Heavy Metals in Sediments from a Typical Tropical Estuary (South Vietnam)

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Abstract

The total contents of TOC, TIC, Fe, Mn, Cr, Ni, Zn, Cu, Pb and Co along with their chemically bioavailable forms were determined in surface sediments from the river Cai - Nha Trang Bay estuarine system of the South China Sea. Sedimentary Fe, Co, Cr, Zn, Ni, Cu and Pb varied in relatively narrow ranges along the salinity gradient and were within the reference background and Sediment Quality Guidelines (SQG) values.

Metal form study revealed the highest percent content 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) contributes to a 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 contributes to the anthropogenic input of Pb. The most bioavailable trace elements in sediments that were studied were scavenged by amorphous iron oxyhydroxides and organic microcolloids in the course of estuarine sedimentation. Analysis and speciation of metals in sediments in estuaries allow tracking the fate of pollutants. Specific metal forms are found to be useful environmental indicators.

Keywords: Bioavailable Metal Forms; Nha Trang Bay; South China Sea; Selective Extraction; Trace elements

Introduction

Heavy metals represent important environmental pollutants, particularly in lands with anthropogenic stress [1]. In estuarine region, sediments act as a major carrier as trace elements get adsorbed on to major elements like Fe and Mn oxyhydroxides and organic matter. It is important to study major and trace elements as excess input of these metals may settle into the estuary due to salinity gradient [2-5].

The biogeochemical functions of living matter are mainly accumulation functions whose occurrence may or may not be dependent on the environment. Living organisms accumulate pollutants when these are at large concentrations [6]. The actually and potentially bioavailable fractions can be, respectively, considered as the portions of the total amount of a chemical present in a specific environmental compartment that, within a given time span, is either available or can be made available for uptake by (micro)organisms or plants, from either the direct surrounding of the organism or the plant, or by ingestion of food [7]. Fractionation of total metal contents is applied for assessment of chemical bioavailability of the metals.

For the speciation of solid phase associated elements, either single or sequential extraction techniques are used. The application of sequential extraction is still subjected to much controversy. Non-selectivity of the extractants and trace element redistributions among phases during extraction are the main problems of sequential extraction procedure [8]. For surveying soil or sediment contamination, a partial, single step extraction that is not phase-selective but affects a variety of labile and relatively stable trace metal associations may be easier to apply and more suited to carry out when many samples are involved [9]. Such extractions may give indications about the origin of the metals. Thus, high levels in the exchangeable, acid soluble and easily reducible fractions may indicate pollution from anthropogenic sources [10, 11].

The Cai River and the Nha Trang Bay form one of the major estuarine systems in the South China Sea, which is inhabited by

unique biota. This area, which was wilderness not long ago, now experiences a significant anthropogenic load from the local people activities and particularly the quickly growing touristic industry. Moreover, aquaculture, which is currently one of the most rapidly developing production sectors in coastal Vietnam, contributes to the degradation of estuarine and coastal ecosystems [12]. In the recent decades, significant research efforts have been undertaken to evaluate the organic geochemistry patterns and contamination levels and trends in the Nha Trang Bay [13-16]. The first complex geochemical study of the Nha Trang Bay covered the distribution of Total Organic Carbon (TOC), *n*-alkanes and the bulk concentration of major and trace elements in the surface sediments [17-19]. Heavy metals were shown to be largely associated with a sediment fractions of amorphous Fe and Mn oxides [12].

Further analysis of speciation of heavy metals in the sediments of the Cai River estuary and Nha Trang Bay would allow to track the fate of potential contaminants. Therefore, the present study summarizes the data on the abundance, distribution, partition, speciation and bioavailability of Fe, Mn, Cr, Ni, Zn, Cu, Pb and Co in surface sediments of the Cai River estuary under multiple stresses.

Materials and Methods

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 (sts.1-8, Figure 1). The salinity of the water samples was measured on-board immediately after collection using portable conductivity apparatuses HI 98129 Combo and HI 98302 DIST 2 (Hanna Instruments, Germany). The surface sediment samples were obtained by scuba-divers with a manual plastic piston corer, which was designed at the Shirshov Institute of Oceanology (Russia). On the riverine station 1, the sediment sampling was not possible due to the weather conditions. Three samples were collected at each location. The upper layer (0-6 cm) of the samples was retrieved using stainless steel spatulas. Where present, the surface oxic yellowish layer (0-3 cm) was retrieved and collected separately. The sample was transferred into pre-cleaned polyethylene containers and frozen until arrival in the laboratory. One portion of the sample was kept frozen until the grain size and mineralogy analyses. One portion was dried to constant weight at 60°C until the major- and trace-element analyses. The sampling, sampling transportation and preparation procedures were performed using standard clean techniques that were described elsewhere [20].

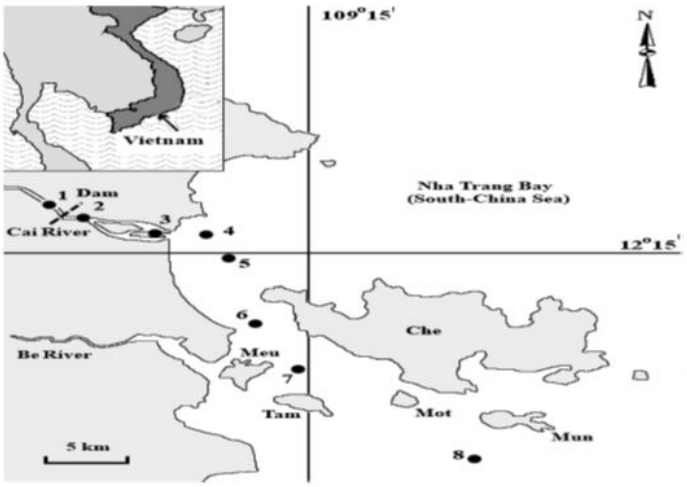

Figure 1: Location of Study Sites.

Analytical Methods

For the total Fe, Mn, Cr, Ni, Zn, Cu, Pb and Co content analysis, the samples were subjected to the total acidic dissolution in HNO_3+HF+$HClO_4$ in an open system with further determination of element contents using the ICP-AES and ICP-MS methods on the ICAP-61 (Thermo Jarrell Ash, USA) and X-7 (Thermo Scientific, USA) spectrometers, respectively. The detailed sample decomposition and analytical procedures are described elsewhere [21].

The Total Carbon (TC) contents in sediment samples were determined by dry burning at 900°C in air 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 [16,17]. The grain size analysis was performed by wet sieving.

To assess the chemical form of 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 hours 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 [20]. 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 hour 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. 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 [22]. 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) and SRM 521-84P (Russia) [12, 21].

Results and Discussion

Abundance and Distribution of Major and Trace Elements in Surface Sediments

In July 2013, the salinity of the surface 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 percent of the content of sand- (63 μm - 2 mm), silt- (2 - 63 μm) and clay- (<2 μm) sized material in the studied sediments is shown in Table 1. 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.

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

The total contents of Fe, Mn, TOC and TIC are reported in Table 2. The mean contents of the major elements are within the range of the Clark contents in shale, pelagic clays, average world riverbed sediments [23,24]. The observed distribution of major elements in the sediments illustrates the grain size and mineral fractionation processes. 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 0.88 % at st.8) (Table 2). 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 [25]. Fe and Mn (to a lesser extent) increase seaward in the sediments with the clay-sized materials.

Element	Range	Mean±SD	Shale[a]	Pelagic clay[a]	River sed[b]	ERL[c]	ERM[c]
Fe	2.46-4.51	3.98±0.64	4.72	6.5	2.5	-	-
Mn	0.03-0.06	0.04±0.01	0.085	0.67	0.05	-	-
Cr	27.9-66.7	45.8±9.9	90	90	50	81	370
Cu	12.1-26.9	18.5±4.1	45	250	20	34	270
Co	4.9-12.2	8.5±1.8	19	74	15	-	-
Ni	14.2-38.1	23.2±6.1	50	230	25	20.9	51.6
Pb	35.1-61.6	54.4±11.0	20	80	15	46.7	218
Zn	69.8-121	104.6±16.2	95	170	60	150	410

TOC	0.61-1.77	1.36±0.39	-	-	1.4	-	-
TIC	<0.01-2.10	1.49±0.69	-	-	0.4	-	-
[a] - cited from Li, 1991 [23]; [b] - cited from Savenko, 2006 [24]; [c] - cited from Long et al., 1995 [27].							

Table 2: Total metal contents in sediments and reference values (in μg g^{-1}, except for Fe, Mn, TOC and TIC in % of dry weight).

Metal toxicity limit is highest permissible content in soil (total or bioavailable concentration) that does not pose any phytotoxic effects or a metal in edible parts of plants do not exceed food hygiene norms [1]. For marine and estuarine ecosystems, sediment quality guidelines were empirically derived in order to assess the potential heavy metal toxicity and threshold levels [26]. The mean content of the studied trace elements (Cr, Ni, Zn, Cu, Pb and Co) 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 and Effects Range-Low (ERL) and Effects Range-Median (ERM) Sediment Quality Guidelines (SQG) (Table 2) [27]. Sedimentary Fe, Co, Cr, Zn, Co, Ni, Cu and Pb varied in relatively narrow ranges. Major part of these elements tended to increase seaward with an elevation at station 7 at heightened carbonate content. 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 [28]. The distribution Mn is largely controlled by the Total Inorganic Carbon (TIC) content in the sediments. Mn may form low-soluble carbonates in aquatic environments [24]. The distribution of trace elements in 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 [12,28-30].

Speciation of Major and Trace Elements in Surface Sediments

In soils the heavy metals can exist in different forms, being more or less accessible to plants. These forms are results of variety of organic and inorganic chemical combinations [6]. Freshly discharged or dissolved metals entering aquatic ecosystems can be present as free ions but tend to occur as ferro- or manganese oxyhydroxide, carbonate, or sulfide complexes. Metals are quickly scavenged by Fe and Mn oxyhydroxides [31], and when combined with the other potential ligands, metal bioavailability is quickly reduced. Therefore, major and trace elements are bound to a variety of sediment fractions that range from easily extractable (and bioavailable) to resistant residual mineral phases [7-11,32].

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 3. In this work, ammonium oxalate (pH 3.2-3.3) served to mobilise the easily soluble amorphous Fe-oxyhydroxides and acid-soluble fulvates [12,33,34]. 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 [22, 32]. 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 [12,20].

The percent 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 Figure 2 and Figure 3. 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 (Figure 2 and Figure 3). 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, 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 [12, 29, 32].

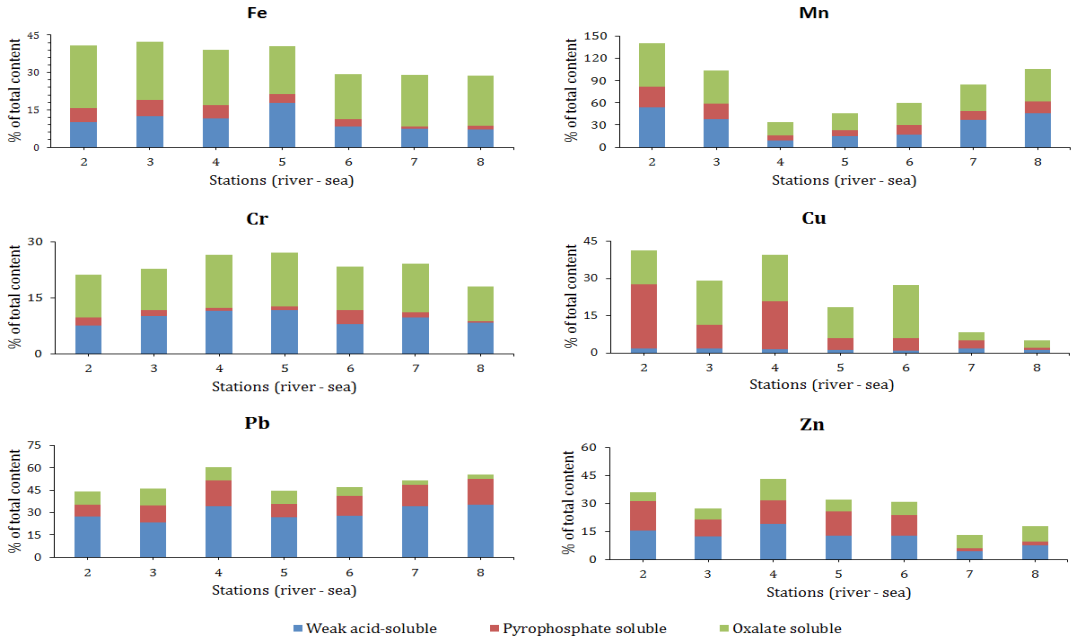

Figure 2: Fe, Mn, Cr, Cu, Pb and Zn form distribution along the salinity gradient.

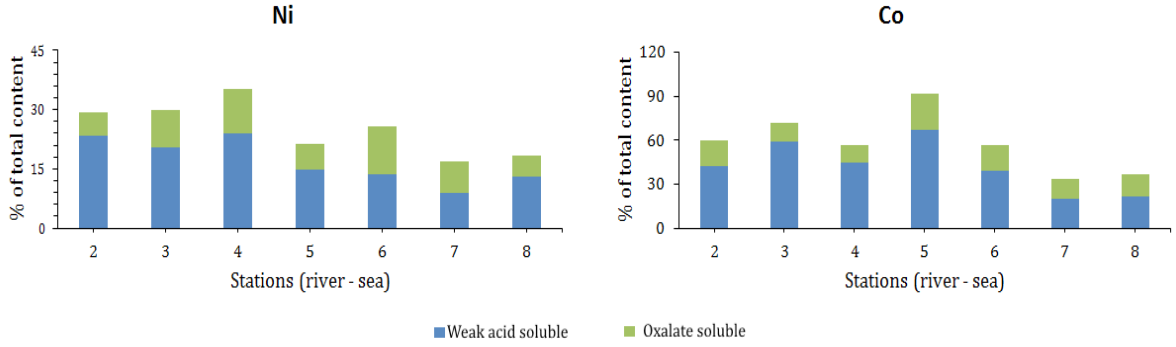

Figure 3: Ni and Co form distribution along the salinity gradient.

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 3), (Figure 2 and Figure 3). Therefore, the most bioavailable parts of Ni, Co and Cr are bound to amorphous Fe and Mn oxyhydroxides and acid-soluble organic compounds. The manganese and iron hydroxides represent the basic phase, where the heavy metals quantities are adsorbed, co-precipitated and integrated in the soil and sediment [35]. 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. The organic matter in the soil and sediment can retain a large amount of heavy metals or can release some of them due to microbiological activities [36].

Element	Station (river - sea)							Mean
	2	3	4	5	6	7	8	
				Weak acid-soluble				
Fe	4540	5620	2840	7640	3440	2660	2920	4237
Mn	344	144	36	58	52	164	264	152
Cr	3.4	4.8	3.2	4.8	3.4	5.2	5.6	4.34
Cu	0.4	0.4	0.2	0.2	0.2	≤0.2	≤0.2	0.28
Co	4.1	4.6	2.2	6.2	3.4	1.8	2.6	3.51
Ni	5.6	4.8	3.4	3.1	3.1	2.4	5.2	3.89
Pb	16.4	14.1	13.4	16.3	20.2	12.1	15.6	15.34
Zn	18.3	14.1	13.2	14.4	15.8	4.2	7.6	12.37
				Pyrophosphate-soluble				
Fe	2580	2940	1300	1480	1360	420	600	1526
Mn	180	82	30	32	42	50	90	72
Cr	0.1	0.8	≤0.2	0.4	1.6	0.8	≤0.2	0.74
Cu	5.6	2.2	2.6	0.8	1.1	0.4	0.2	1.84
Co	≤0.2	≤0.2	≤0.2	≤0.2	≤0.2	≤0.2	≤0.2	-
Ni	≤0.2	≤0.2	≤0.2	≤0.2	≤0.2	≤0.2	≤0.2	-
Pb	4.8	7.1	7.2	5.4	9.6	5.2	7.6	6.63
Zn	18.6	10.4	9.1	14.8	13.4	1.2	2.3	9.91
				Oxalate-soluble				
Fe	11300	10550	5480	8250	7550	7500	8430	8437
Mn	375	172	75	87	90	158	255	173
Cr	5.3	5.2	4.1	6.2	5.1	7.3	6.2	5.53
Cu	3.2	3.7	2.5	2.1	4.4	0.4	0.5	2.37
Co	1.6	1.1	0.6	2.2	1.5	1.2	1.9	1.43
Ni	1.4	2.2	1.6	1.3	2.6	2.2	2.1	1.91
Pb	5.4	6.8	3.4	5.4	4.1	1.1	1.2	3.91
Zn	5.6	7.1	8.2	6.8	8.7	6.5	8.1	7.24

Table 3: Metal form contents in sediments (in μg g^{-1}).

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, 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). The most bioavailable parts of the studied trace metals are associated with easily soluble amorphous Fe and Mn oxyhydroxides. This result supports the fact that Fe and Mn oxyhydroxides are readily complex trace metals in sediments [2,11,31].

Figure 2 and Figure 3 illustrates the distribution of the ecologically most significant weak-acid-soluble (labile) fraction along the river-sea transect. 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 maximum of 18 % in the sediment from station 5 and lowered to 7-8 % in the bay sediments. Mn, Co and Pb have the highest percent contents of the labile form but exhibit different spatial distributions showing some sporadic enrichments along the salinity gradient. Thus, total and percent contents of weak-acid-soluble Mn (13-54 %) 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 marine end-member of the transect (st.7-8). The distribution of the most abundant labile Co is complicated by a pronounced maximum of 67 % in the sediment at station 5 at the enhanced labile Fe content. The sediments are mostly enriched with labile Fe, Zn, Cr and Ni in the frontal and transitional sub-zones (sts.2-5). Cu exhibits the lowest contents of the labile form. Therefore, in the studied sediments, Cu is may be partially bound to the residual mineral phase that is comprised of detrital heavy minerals.

Figure 2 illustrates the distribution of the pyrophosphate-soluble fraction along the river-sea transect. The percent content of the pyrophosphate-soluble Fe was low and decreased from 6 to 1% of the total Fe along the salinity gradient. The percent content of pyrophosphate-soluble Mn (9-28%) was the highest in the coarse sediments of the frontal zone (sts.2-3) and in the bay (st.7-8). The percent content of pyrophosphate-soluble Pb was lowest in the frontal zone of the estuary (st.2) and tended to increase seaward, while organically bound Cr was constantly low along the salinity gradient. Organically bound Cu and, especially Zn is most significant in the riverine part of the estuary and decrease from river to the sea. In estuaries, flocculation and coagulation of riverine organic micro colloids (and Fe/Mn oxyhydroxides) are accompanied by a scavenging and co-precipitation of dissolved heavy metals. Further deposition of newly formed aggregates contributes to the enrichment of sediments in bioavailable pyrophosphate-soluble forms of metals which have a chemical affinity to organic matter.

Figure 2 and Figure 3 illustrates the distribution of the oxalate-soluble fraction along the river-sea transect. 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 amorphous form is most abundant for Fe and Cr in both estuarine and bay sediments. The amorphous Mn is enhanced in riverine (st.2-3) and marine (st.7-8) end-members of the transect, while percent content of amorphous form of Pb, Co and Ni is significant in all sediments studied but tends to decrease seawards. Iron and manganese oxyhydroxides (FeOOH and MnOOH) largely control bioavailability in estuarine sediments [11,12,36]. The role of oxyhydroxides in controlling metal bioavailability is tremendously important and requires further investigation.

Conclusions

In the Cai River - Nha Trang Bay estuarine system sedimentary Fe, Mn, Cr, Ni, Zn, Cu, Pb and Co varied in relatively narrow ranges along the salinity gradient and tend to increase seaward. Cr, Ni, Zn, Cu, Pb and Co are at natural levels and within the reference background and SQG values. The distribution of total contents of heavy metals in sediments of the estuarine system is strongly influenced by the deposition of materials of different grain sizes.

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) contributes to a 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 contributes to the anthropogenic input of Pb. The results showed that fractionation of total metal contents is essential for correct assessment of the contamination level and potential contaminant bioavailability.

Along the salinity gradient, the sediments are mostly enriched with the potentially bioavailable heavy metals in the frontal and transitional zones of the estuary. The most bioavailable parts of Co, Ni and Cr are associated with easily soluble amorphous Fe and Mn oxyhydroxides, while Pb, Zn and, especially Cu are weakly held in organic matter. Therefore, specific metal forms are found to be useful environmental indicators.

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