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Geochemistry of heavy metals (Pb, Cr and Cu) in sediments and benthic communities of Berau Delta, Indonesia

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Abstract—Surficial sediments were collected from 17 locations in the estuarine region of the Berau Delta, Indonesia in April and September of 2007. Sediments were characterized by a simultaneous extraction procedure that estimates the concentration of metal partitioned onto operationally defined geochemical components of the sediment. The results showed that total metals in sediments were as follows, Pb (3–19 $\mu g\, g^{-1}$ dry weight, dw), Cr (10–81 $\mu g\, g^{-1}$), and Cu (2–24 $\mu g\, g^{-1}$). These metal concentrations were higher in April than in September by a factor of 1.8. Most of these metals were also tightly bound in non-reactive component of sediments, and only a small fraction was associated with iron and manganese components (easily reducible and reducible fractions). The percentage of potentially bioavailable of each metal was 14.3% for Pb; 14.5% for Cr and 7.2% for Cu. We concluded that metal concentrations in sediment of Berau Delta were mostly not available to benthic biota.

Key words: Geochemistry, partition, metal bioavailability, Berau Delta

Introduction

Aquatic sediments are the ultimate sink for heavy metals of both natural and anthropogenic origin (NRC-Canada 1988). Once in the sediments these metals may be accumulated by benthic-dwelling organisms (e.g., mollusks and demersal fishes) which can then accumulate such metals from the sediments to the next trophic level. However, the availability of these metals to benthic organisms depends on various factors including the geochemical characteristics of the sediments and the partitioning of the metal among different sediment components (Bendell-Young et al. 1992). For instance, metal ions adsorbed on fine grain size suspended sediments are often considered to be bioavailable, whereas metals complexed with organic matter or included in amorphous metal oxides through precipitation or co-precipitation are likely to be less bioavailable; metals present in crystalline structure are generally unavailable (Amiard et al. 2007).

Studies of the heavy metals contamination of sediments often rely on the analysis of total metal content (Ergul et al. 2008, Mzimela et al. 2003, Rochyatun and Rozak 2008). Although such information is important, it is recently recognized that availability of metals is of more importance than its total concentration. Biovailability is usually studied by determining the speciation of metals within sediment components. Many studies have reported relationships between metal bioavailability and metal partitioning in different geochemical phase (Amiard et al. 2007, Bendell-Young et al. 1994, Fang and Wang 2006). In Southeast Asia, information on the heavy metal speciation is limited to polluted areas such as, the Strait of Malacca (Yap et al. 2003), the coast of Semarang City (Takarina et al. 2004) and the Jakarta Bay (Lestari 2008). Studies under natural background condition have not been done, hence, our study tried to fill the gap. The objective of our study was to determine heavy metal speciation among sediment fractions under natural condition, and to determine a possible accumulation of the metals in benthic biota.

Materials and Methods

Study Area

Berau Delta of East Kalimantan, located 350 km north of Balik Papan City, covers a total area of 34,127 km^2 (Fig. 1). The economy of the Berau regency is characterized by a heavy dependence on the extraction of mineral and natural resources, mainly coal mining and logging. Forestry accounts for about 30% of local gross domestic product (Keulartz and Zwart 2003). The coal reserve is estimated 121,380,288 t in Dec 2003 (Ishlah and Fujiono 2004). The mining product is exported to Asian nations and for national need.

Human activities at the terrestrial such as coal mining,

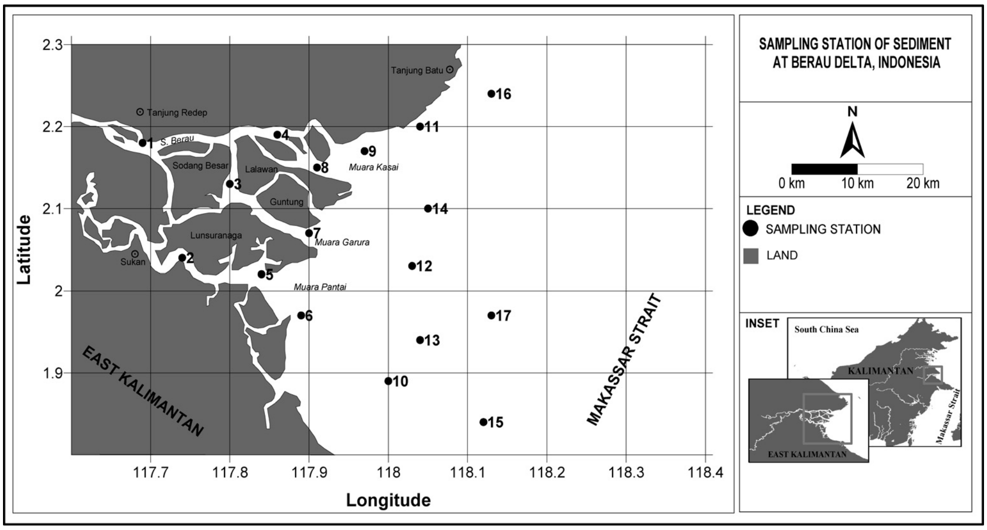

Fig. 1. Sampling station of sediments at Berau Delta, Indonesia

logging, tourism, agriculture and shrimp culture to some extent can influence the state of estuarine ecology. These activities may increase the flux of contaminants (heavy metals and pesticides), and lead to habitat degradation and changes of biota population. In effort to minimize negative impact of economic development, the local government has declared about 1,300,000 ha as marine conservation area that includes 66,000 ha coral reefs system and 49,000 ha mangrove forests. This conservation area will be used for sustainable use of fisheries, marine tourisms, development of social and economic communities, as well as research and development (Anonim 2005).

Sediment Geochemistry

Seventeen (17) stations were selected and divided into three zones, rivers (river body), river mouths and estuarine area in early April 2007 (representing 1st transition monsoon) and early September 2007 (representing 2nd transition monsoon). Four stations were in the river body, 5 stations within river mouth and 8 stations in estuarine area (Fig. 1). Three composite grabs of sediment samples from each station were retained. Only the upper portion (0.5–2 cm) of sediment was analyzed. These upper regions are directly involved in the exchange of metals between sediment and overlaying water plus provide the layer of sediment to which benthic biota are most exposed. The sediment samples were then placed in acid-washed polypropylene bottles and kept at 4°C for transport to the laboratory prior to wet extractions.

All samples were analyzed based on simultaneous extraction method (Bendell-Young et al. 1992). The procedure estimated the concentration of metals partitioned into operationally defined geochemical fractions of the sediments i.e., easily reducible (associated with manganese oxide phase, ERE), reducible (associated with manganese and iron oxide phase), organic (organically bound, ORG), and residual fractions. The easily reducible extract removed metals bound to manganese oxide and all easily extractable components including phosphates, carbonates and reactive iron. The reducible extract removed metals bound to manganese oxides (easily reducible metals) and metals bound to iron oxides (the reducible metals). The actual reducible metals (RED) were determined after analysis by subtracting easily reducible fractions (ERE) from the reducible fraction. Aqua-regia digestion (3 : 1 HCl : HNO_3) was considered 'near total' digest of the sediment and dissolve most of the heavy metals in the fine grained sediments. The amount of metal in the residual fraction (RES) was estimated as aqua-regia minus the other 3 phases (fractions).

The sediment sample (5.0 mg wet weight) was taken and digested with 0.1 NH_2OH HCl in 0.01 N HNO_3 for 0.5 h to get a fraction of ERE. The same amount of sediment sample was also digested with 0.1 N NH_2OH HCl in 25% CH_3COOH at 95°C for 6 h to obtain a reducible fraction (REC), while for organic fraction, the sediment sample was subjected to 1 N NH_4OH digestion for one week. To estimate residual fraction (RES), the amount of metal extracted with aqua-regia digestion at 70°C for 8 h was subtracted by three fractions of metal (RES = Total metal − ERE − RED − ORG). Concentrations of metal recovered from the simultaneous sediment extractions were converted to μg metal g^{-1} dry weight of sediment. Quality control measures included analysis of laboratory method blanks and duplicate certified reference material (CRM BCSS-1) from Institute for National Measurement Standards, National Research Council of Canada. Recoveries of Cu and Pb elements were 98.8 and 100% of the certified values, respectively; while Cr element was only 63% of the certified values.

Heavy Metal in Molluscs

Biota samples i.e., cockle (*Anadara antiquata*) and gastropod (*Telescopium telescopium*) were analyzed for Pb, Cr and Cu's tissue concentrations. The specimens were dissected and dried in an oven to a constant weight for 24 h at 60°C. The dried tissues (5.0 g) were cold digested with 10.0 ml HNO_3 for 24 h, and then heated in a digester at 100°C for 6 h. Finally, the sample was added with 2–3 ml H_2O_2 (CEM, 1991). All samples of sediments and biota were then analyzed by a flame atomic absorption spectrophotometer, FAAS (Spectra A-20 Plus, Varian, Inc.).

Results

Physical and chemical characteristics of Berau delta during two sampling campaigns were summarized in Table 1. Water quality parameters generally reflected a tropical estuarine system, i.e., water temperature (28.2–31.6ºC), pH (7.6–8.2), salinity (6–32 psu), dissolved oxygen (3.6–7.1 mg L^{-1}), and total suspended solid (TSS 5–230 mg L^{-1}). Concentration of Pb total in sediment varied from 3.4 to 18.5 $\mu g\,g^{-1}$ dry weight, while for Cr and Cu were 10.1 to 80.6 $\mu g\,g^{-1}$ and 1.6 to 24.5 $\mu g\,g^{-1}$, respectively. Spatial distribution of Pb, Cr and Cu concentration tended to decrease, but not significance, from river body to estuarine during 1st transition monsoon (April). However, during the 2nd transition monsoon (September), the average of the metals had a maximum concentration in river mouth (Fig. 2). Moreover, metal concentrations were generally higher in April than in September by a factor of 1.8 on average (range 1.1 for Pb to 3.2 for Cr).

Concentration of Pb, Cr and Cu were measured in each of the sediment fractions i.e., ERE, RED, ORG and RES. Concentration of Pb and Cu were mostly in the form of resid-

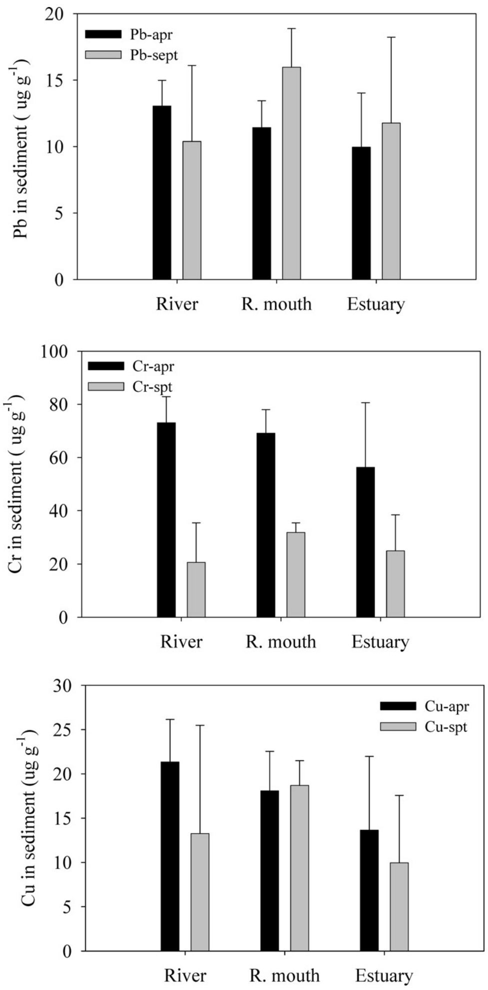

Fig. 2. Total concentrations of Pb, Cr and Cd in sediments across three zones (river, river mouth and estuary) in Berau Delta in April and September 2007

Table 1. Summary of water quality condition at Berau Delta. DO–dissolved oxygen, TSS-total suspended solid

St.	Position		Depth (m)	Salinity (psu)		Water Temp (°C)		pH		DO (mg L^{-1})		TSS (mg L^{-1})	
	East	North		Apr.	Sept.	Apr.	Sept.	Apr.	Sept.	Apr.	Sept.	Apr.	Sept.
1	117.69	2.18	2.0	6	—	30.2	—	7.4	—	4.30	—	4.8	—
2	117.74	2.05	12.0	24	24	29.4	29.7	7.7	7.7	4.34	3.64	11.3	—
3	117.79	2.13	5.0	10	22	30.5	29.5	7.7	7.8	3.90	6.68	14.8	19.5
4	117.86	2.20	3.0	12	18	31.0	28.9	7.9	7.6	5.19	3.99	10.1	133.8
5	117.84	2.02	7.0	—	28	—	30.0	7.8	7.8	—	4.01	7.3	—
6	117.89	1.97	4.5	—	30	—	30.6	8.1	7.9	—	3.97	13.5	—
7	117.90	2.08	4.0	18	—	30.8	—	8.0	—	4.82	—	19.3	231.7
8	117.91	2.15	3.0	15	24	31.6	29.2	8.2	7.9	6.50	4.45	12.7	—
9	117.97	2.17	2.0	20	28	32.1	28.5	8.2	7.7	7.11	3.93	21.1	55.6
10	118.00	1.89	4.0	25	31	31.1	29.7	8.0	8.0	6.33	5.24	8.5	13.3
11	118.04	2.20	4.0	29	32	31.0	28.7	8.2	8.2	5.10	5.66	11.1	31.4
12	118.03	2.03	3.5	21	—	30.2	—	8.1	—	6.19	—	23.6	—
13	118.04	1.94	20.0	25	—	30.4	—	8.0	—	6.37	—	7.4	—
14	118.04	2.10	12.0	26	30	30.2	28.7	8.2	8.1	5.57	5.44	14.5	22.2
15	118.12	1.84	15.5	29	32	30.0	28.9	8.0	8.2	6.10	6.13	9.0	10.5
16	118.13	2.24	9.0	30	32	29.7	28.2	8.2	8.1	4.90	5.59	9.3	10.5
17	118.13	1.97	27.5	29	32	30.4	28.2	8.1	8.1	6.18	5.46	9.0	15.8

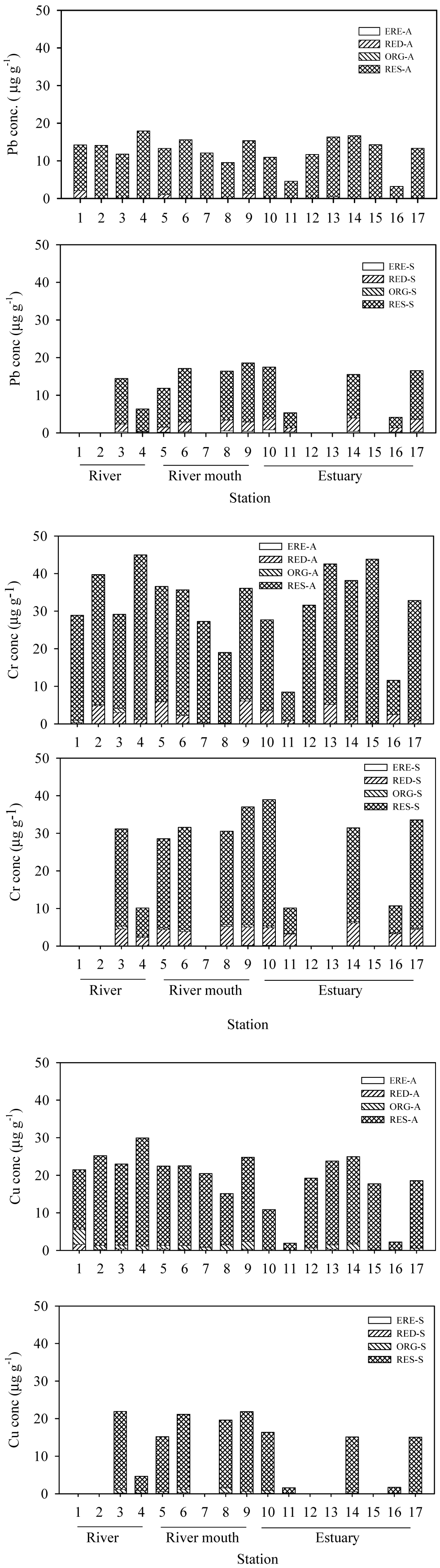

Fig. 3. Concentrations of Pb (a) , Cr (b) and Cu (c) in different sediment fractions in April and September, 2007

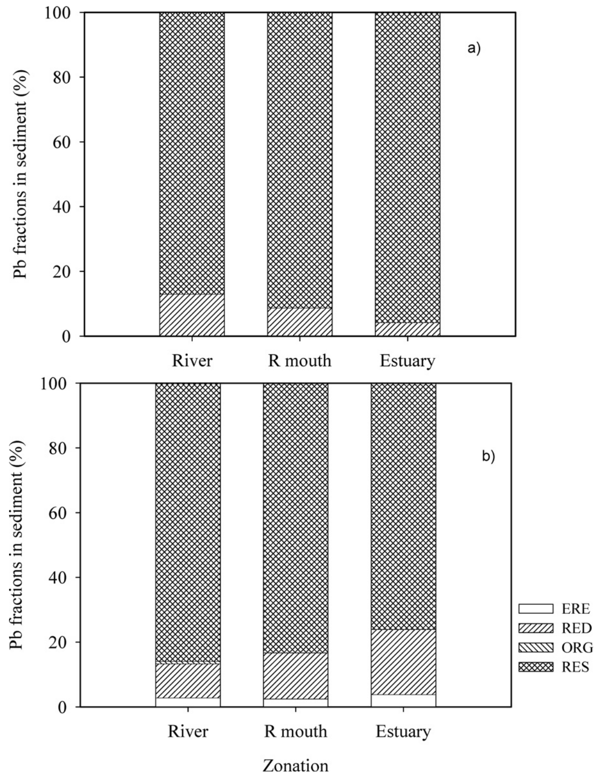

Fig. 4. Pb partitioning in different sediment fractions in April 2007 (a) and September 2007 (b)

ual (RES) fractions during both the 1st and 2nd transition monsoon (Fig. 3a, c). In contrast, concentration of Cr was largely in the form of residual (RES) and reducible (RED) fractions, respectively (Fig. 3b). High concentration of RES fraction of these three metals indicated that most metals fractions partitioned to non-reactive component of sediments.

By taking an average from each station and looking at percentage of each fraction of metals (Fig. 4), it was shown that Pb in sediment mostly existed in residual fraction (non-reactive component, 85–95%) and the remaining of fractions (RED) was small in percentage (14.3% in total) in the three zones in April. In September, Pb speciation among sediment fractions showed different trend, i.e., increasing reactive component toward estuarine zone.

Cr and Cu were also dominated by residual fractions, with the value of 85.7 and 88.3 percent, respectively. Only small percentage of reactive components (ERE and RED fraction) was available at sediments (Fig. 5, 6). The percentage of reactive component of Cr in three zones in September was double compared to that in April (Fig. 4b). In contrast, the percentage of reactive component of Cu across zone was relatively constant both in April and September (Fig. 6).

Pb in tissues of cockle (*A. antiquata*) and gastropod (*A. telescopium*) were $7.5\pm2.35\,\mu g\,g^{-1}$ and $4.5\pm0.11\,\mu g\,g^{-1}$; while for Cr: 1.4 ± 0.09 and $0.9\pm0.05\,\mu g\,g^{-1}$, respectively. Moreover, concentration of Cu in cockle's tissues was also low ($4.9\pm0.58\,\mu g\,g^{-1}$), but Cu in gastropod was relatively

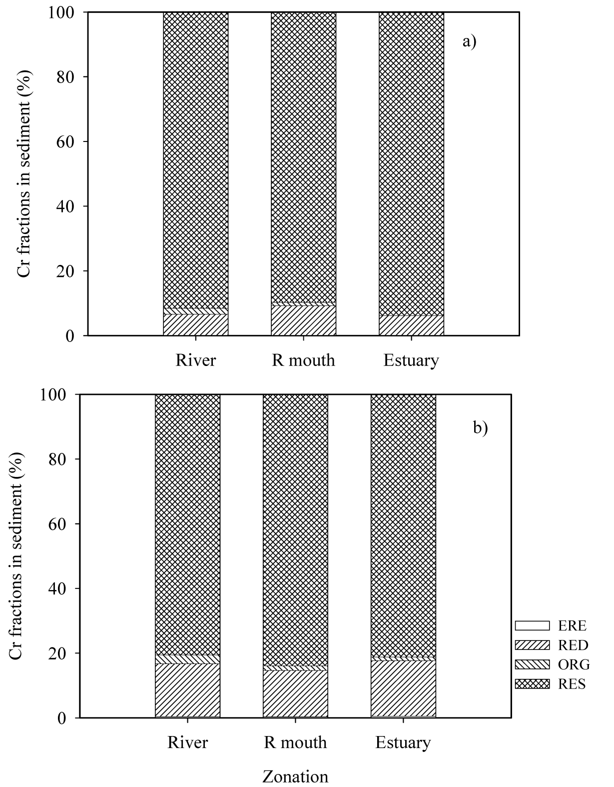

Fig. 5. Cr partitioning in different sediment fractions in April 2007 (a) and September 2007 (b)

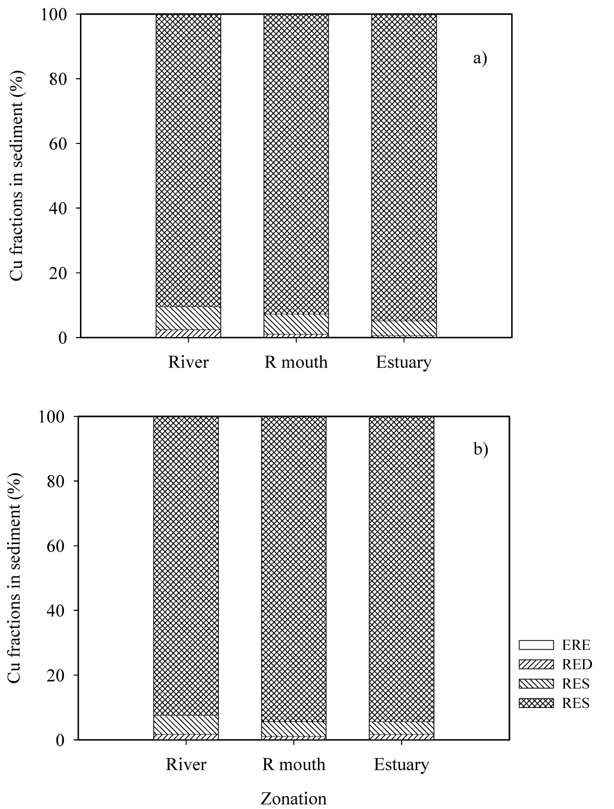

Fig. 6. Cu partitioning in different sediment fractions in April 2007 (a) and September 2007 (b)

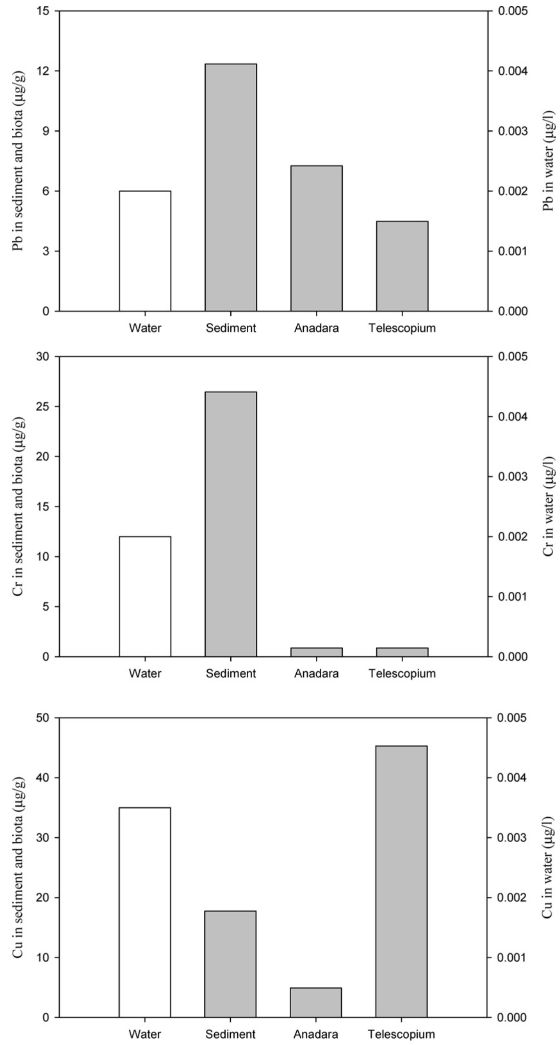

Fig. 7. Metal concentrations (Pb, Cr and Cu) in components of Berau Delta ecosystem (water, sediment and mollusks). The value of metals in water was taken from Arifin and Koesmawati, 2007), total metal in sediments was an average of metal concentrations from stations in river mouth and estuary zones.

high ($45.3 \pm 0.51\ \mu g\, g^{-1}$). It showed that there was lack of bioaccumulation of metals (Pb and Cr) for both species, but there was a potential accumulation of Cu by *T. telescopium* (Fig. 7).

Discussion

Metal bioavailability to organisms depends on various factors including geochemical and biological processes. Determination of metal concentration in organism provides information on the bioavailable fraction of metal. However, measurement of metal in tissues does not provide information regarding the process controlling metal uptake. Determining the geochemical association of metals to sediment fractions will provide useful information about the origin, ab-

Tabel 2. Average metal concentrations in surface sediments. Berau delta sediments (Avg–average, sd–standard deviation) compared with other Indonesian bay sediments

Ecosystem	Pb (μg g^{-1})		Cr (μg g^{-1})		Cu (μg g^{-1})	
	Avg	sd	Avg	sd	Avg	sd
Berau Delta, Kalimantan[1]	11	3	44	25	16	7
Kau Bay, Halmahera[2]	—	—	315	34	43	5
Jakarta Bay, Java[3]	26	16	36	14	23	19
Banten Bay, Java[4]	19	4	23	9	10	3
Dumai Bay, Sumatera[5]	32	9	—	—	6	2

[1] present study, [2] Middelburg et al. (1989),[3] Williams et al. (2000), near shore stations (i.e., excluding stations 45–52), [4] Booij et al. (2001), [5] Amin et al. (2009)

solute levels, lability of metals and mode of occurrence of a metal. By combining these two approaches, it allows us in understanding the processes influencing bioavailability of metals.

Pb, Cr and Cu concentrations did not reflect significantly decreasing toward estuarine zone during 1st transition monsoon (April) and the 2nd transition monsoon (September), (Fig. 2). Temporal variation showed that the concentration of metals was generally higher in April than in September by a factor of 1.8 on average. This might relate to seasonal fluctuation of sediment load from upland after rainy season where the highest precipitation occurred in March (Arifin et al. 2006).

Spatial distribution of the metals was relatively uniform across the zones, except at station station 11 and 16 where sediments were composed of large grain size particles (sand). Compared to other coastal ecosystems in Indonesia, the observed Pb concentration was lower than those observed in sediments collected in the Banten Bay (Java), the near-shore locations of Jakarta Bay (Java) and Dumai Bay (Sumatera) (Williams et al. 2000, Booij et al. 2001, Amin et al. 2009) (Table 2). Moreover, the present metal concentrations of Cu and Cr were similar (Cu) or lower (Cr) than those measured in Kau Bay (Middelburg et al. 1989) (Table 2). The absence of metal concentration gradients and the similarity to other Indonesian ecosystems suggest that metal concentrations in the Berau Delta are representative of the natural background.

Speciation of Pb, Cr and Cu in the surficial sediment followed a similar pattern. The residual (RES) and reducible (RED) fractions accounted for the majority of the metal sorption, with the RES fraction accounting for highest in all zone. Non-reactive component (RES fraction) of Pb was 92% in river sediment, 90% in river mouth sediment and 87% in estuarine sediment (Fig. 4). Similar trend was also reflected for Cr and Cu, that these two metals were bounded to non-reactive component of sediment (Fig. 5, 6). On the other hand, the speciation of Pb and Cr in reactive components was almost double in September compared to that in April (Fig. 4, 5). These increases of reactive component at river mouth and estuary might relate to the increasing microbial activities and increasing concentration of iron in these two zones. An important implication of this sediment geochemistry is its possible role in influencing metal availability to benthic organisms. Several studies have shown that the speciation of a heavy metal among sediment fractions affects the transfer of the metal from sediment particles to biota. For example, Luoma and Bryan (1982) found a strong correlation between lead (Pb) tissue of *Scrobicularia plana* and the ERE fraction ($r=0.78$). Similarly, Cd bioaccumulation in ragworm (*Nerreis diversicolor*) strongly increased with increasing concentration of labile Cd in sediment (ERE), (Amiard et al. 2007). Moreover, the study by Yap et al. (2002) at tropical coastal ecosystem also showed that significant correlation (0.76–0.79) was observed between Cd and Cu in green-lipped mussel (*Perna viridis*) and Cd and Cu of sediment (ERE fractions).

Based on trace metals in water (Arifin and Koesmawati 2007) and our data on metals in sediment and biota, it showed that concentrations of Pb, Cr and Cu did not reflect any significant accumulation by *A. antiquata* and *T. telescopium* from sediments (Fig. 7). This was supported by geochemistry of metals in sediments where most of Pb, Cr and Cu were associated with non-reactive or non-labile component of sediments. Therefore, these three metals in Berau estuarine did not potentially available to be accumulated by benthic dwelling organisms.

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