

Original Paper

GEOCHEMICAL FRACTIONATION OF TOXIC TRACE HEAVY METALS (CR, CU, PB, AND ZN) FROM THE ESTUARINE SEDIMENTS OF 5 RIVER MOUTHS AT JAKARTA BAY, INDONESIA

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ABSTRACT

Jakarta Bay is located at the north coast of Jakarta bordered by 106 03'00" Longitude and 6 10'30" Latitude. Administratively bordered by Bekasi Regency on the east and Tangerang Regency on the west. There are 13 -19 rivers flow to the bay with 2050 industries that produce hazardous waste, including heavy metals. Metal concentrations in surface sediments and their spatial distributions have increased, recently. Concentration of Pb during 10 years period increase from 23.3 mg kg⁻¹ to 118.2 mg kg⁻¹. The objectives of this study is to know the distribution of Chromium (Cr), Copper (Cu), Lead (Pb), and Zinc (Zn) of Jakarta Bay, Indonesia and their geochemical partition in marine sediments that are bound to "Exchangeable Fraction", "Reducible Fraction", "Fe-Mn Oxide Fraction", "Oxidize able Fraction", and "Residual Fraction". The result showed that the concentration of heavy metals in the sediments in most locations were above the Canadian Standard for Contaminated sediments. Concentration of Cr ranged from 48.68—292.09 ppm, Cu ranged between 18.62—151.82 ppm, Pb ranged from 39.7—303.42 ppm, and Zn ranged between 165.83—487.69 ppm. Standard for Cr, Cu, Pb, and Zn are 22 ppm, 30 ppm, 25 ppm, and 60 ppm, respectively. Percent fraction of Cr in labile fraction (F1, F2, and F3) ranged from 30-60 %, while for Cu, its percent fraction mostly bound to lithogenic fraction as much as 38–78%. Percent of labile fraction of Pb ranged from 22-54 %, while for Zn as much as 15-72%. These meant that not only Cr but also Pb and Zn were possible to be easily released in the environment as bioavailable metals for biota, especially, benthic invertebrates.

Keywords: geochemical fractionation, heavy metals, estuary, sediments, Jakarta Bay

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INTRODUCTION

Heavy metal pollution of riverine and coastal environments has been reported throughout the region of Southeast Asia (Hungspreugs, 1988). Release of heavy metals to the marine environment is increasing as industrial development continues in areas where

monitoring and enforcement of environmental regulations is difficult due to a lack of laboratory facilities and enforcement mechanisms (World Bank, 1994). In Indonesia, information on the heavy metal content of marine sediments is limited to areas

of high economic importance such as Jakarta Bay and the Strait of Malacca (World Bank, 1994; Edinger and Browne, 2000).

Sediment plays a crucial role in water quality due to its role as a sink and a potential later release of these contaminants to the water column under various changes of physicochemical conditions (Salomons and Forstner, 1984). Studies of the trace metal contamination of sediments often rely on the analysis of total metal content; however, information on total concentration is not sufficient for an understanding of the environmental behaviour of trace metals as only a fraction of the total metal is available for biological or diagenetic processes (Groot et al., 1982; Martin et al., 1987; Tack and Verloo, 1995). Assessment of heavy metal contamination of the coastal environment based solely on total metal content also possesses the difficult problems to regulators of how to distinguish between background lithogenic trace metal that is relatively unavailable to marine biota and labile trace metal.

A previous study (Takarina, 1996) of the surficial sediments of two rivers that flow through the city of Semarang identified priority heavy metal pollutants in each river. High levels of Cr (75–1651 ug/g) were found in riverine sediment from sample sites immediately downstream of tanneries situated along the Babon River. The West Flood Canal had high levels of Zn and Ni (161–573 and 37–581 ug/g respectively) in sediments collected downstream of the wastewater outfall of electroplating industries. Moreover, based on its geochemical fractionation, the Semarang coastal area also already contaminated with those metals (Takarina, 2004). This study assessed the extent to which the observed contamination of river sediments is accumulating in the coastal marine environment and establishes a baseline for heavy metal speciation in the coastal sediments of Central Java, Indonesia.

Like Semarang, Jakarta bay is also quite productive with mangrove system along the coast of the bay. However, in the last few decades mangrove area has been converted into settlement areas, fishing and shipping industries. Remaining mangrove forest was estimated about 172.36 ha in 1995, which showed sharp decline when compare to that in 1960s (1,334.62 ha) (Aboejoewono, 2000),

Because functions of mangrove forest as a pollutant trap in coastal region has been greatly reduced and practices of sustainable development were lacking, the amount of waste reached into the bay area has sharply risen in the past 10 years. Estimated 21,000 industries such as port facility, ship building, galvanized/metal electroplating contributed 460.3 m³ of waste per month with approximately 10% of it as heavy metals. Most of those industries do not have a proper waste treatment facility (Anonymous, 2000). Consequently, heavy metal contaminants can be found in sediments and benthic organisms within the bay.

Metal concentrations in surface sediments of Jakarta Bay and their spatial distributions have been studied by Hutagalung (1994, 1995), Rochyatun (1995) and Williams *et al.* (1997) in Arifin (2005). Concentration of Pb during 10 years period varies between 23.3 mg kg⁻¹ and 118.2 mg kg⁻¹. Based on Takarina (2009), concentration of Pb tends to increase, ranges from 30.0 mg kg⁻¹ - 350.0 mg kg⁻¹. This study is aimed to know the increasing trend of heavy metals content in Jakarta Bay.

MATERIALS AND METHODS

Sediment sampling

In this study, a total of 15 sediment samples were collected from the coastal area of Jakarta Bay. The samples were taken from the 5 river-mouths, namely Karang (Mkr), Baru (Mb),

Sunda Kelapa (Msk), Tawar (Mtw) and Tiram (Mtr). From each river mouth, there were 3

sub samples collected from left side, right side and the middle part of river mouth (**Fig 1**).



Fig 1. Map of Location (Source: <http://geology.com/world-cities/Jakarta-Indonesia.shtml>)

Two comparison samples were also collected from upstream of Ciliwung River (Ch1 and Ch2) to see the possible anthropogenic effects to the estuaries and two from Penjaliran Island (Pj1 and Pj2) located at National Park of Kepulauan Seribu, one of Marine Protected Areas (MPAs) in Indonesia (it is about 100 km up North of Jakarta Bay).

Sediment samples were collected using a 3.5 L Ekman grab sampler. The top 2–3 cm of the sediment layer was collected using a plastic spatula, and subsequently placed in the acid-washed plastic-bags and stored at 4° C during transportation to Affiliation Laboratory, Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Indonesia, Depok.

Analysis of heavy metals (Cr, Cu, Pb, and Zn) in the sediment

The geochemical fractionation of Cr, Cu, Pb, and Zn was determined on a 1 g aliquot of

bulk sediment using a series of three sequential leaches, a residual digestion and a separate oxidizing leach (Buckley and Winters, 1992). The first sequential leach, denoted F1, was adjusted to pH 2 with weak 5 mL acetic acid glacial (25%) for 16h at room temperature as described in Chester and Hughes (1967). This acidification extracted metals predominantly from carbonates, hydrated sulfides, and weakly bound metals adsorbed on mineral surfaces.

The second leach, denoted F2, was carried out by addition 20 mL 1M hydroxylamine hydrochloride (NH₂OH HCl) at room temperature for 16h at pH 5–6. This leach extracted potentially reducible metals (Chester and Hughes, 1967). The third leach, denoted F3, was performed with 20 mL 0.04M NH₂-OH HCl at pH 2 heated to 80° C. This leach extracted predominantly strongly-adsorbed metals at mineral surfaces (Tessier et al., 1979). The sum of metal extracted by these three leaches is defined as labile metal. A 0.5g

aliquot of the residue from the first three leaches was analyzed for total metal content by a four acid digestion ($\text{HClO}_4/\text{HNO}_3/\text{HCl}/\text{HF}$) at 200°C . This residual digestion, denoted F5, extracted metals bound within lithogenic material and complexed with organic matter. To account for metals bound to organic matter, the F5 fraction is presented as the total metal content of the residual fraction minus the metal content of the organic fraction. The organic fraction leach, denoted F4, was performed on a separate 1g aliquot of sediment, treated with an oxidizing leach of 2 mL hydrogen peroxide 10% and 3 mL nitric acid 25% at pH 2 for 24h. This leach will extract metals associated with organic matter and oxidisable sulfides. Leachates from the labile, organic fractions, and residue from total destruction were analyzed using Atomic Absorption Spectrophotometer (AAS) Perkin Elmer 3100.

Statistical Analysis

Two-way ANOVA was performed for each metal to test for differences in metal concentration (Cr, Cu, Pb, and Zn) between geochemical fractions (F1-F5) and locations.

RESULTS AND DISCUSSION

Heavy metals (Cr, Cu, Pb, and Zn) content in the sediment

Certified Reference Material (CRM) MESS1 for method verification, and gain the % (percentage) recovery for Cr: 106.67 ppm, Cu: 83.36 ppm, Pb: 34.64 ppm, and Zn: 181.74 ppm. Based on the result of metals analysis using Atomic Absorption Spectrophotometry, the content of heavy metals is explained below:

Chromium (Cr)

Chromium content in the sediments at the study areas ranged from 48.68-292.09 ppm. Based on the Canadian Standard for Contaminated Sediments showing a Cr threshold of 22 ppm, the high concentration of Cr indicated these metal-polluted areas if compared with those observed (6.63 ppm and 7.65 ppm) in Penjaliran Island considered as the background values. Correspondingly, Cr concentration was higher in the Muara Baru (292.09 ppm) (**Fig. 2**). This due to waste disposal from PLTU moorings and ships loading and unloading of finished goods industry (Rochyatun & Rozak, 2007). Cr metal naturally is a matter that can be found in the earth's crust. However, pollution resulted from industry activities in the location have exceeded the threshold level. Those industries are textiles, paint, pharmaceutical, wood and leather.

Percentage of Cr on the labile fraction (fraction 1, 2, and 3) were ranged between 25-50% ($F = 2.5$, $P = 0.00$), whereas in the lithogenic material ranged 30-60% (Figure 3). This indicates that the Cr metal in the location ($F = 2.4$, $P = 0.00$) were already contained in the sediments and will be potentially released to marine environment, then it became available for organisms.

Copper (Cu)

Regarding to the Cu threshold value of 30 ppm from the Canadian Standard for Contaminated Sediments, some of the locations, apparently, were considered as a polluted areas indicated by the variation of Cu content from 18.62-151.82 ppm (**Fig 4**).

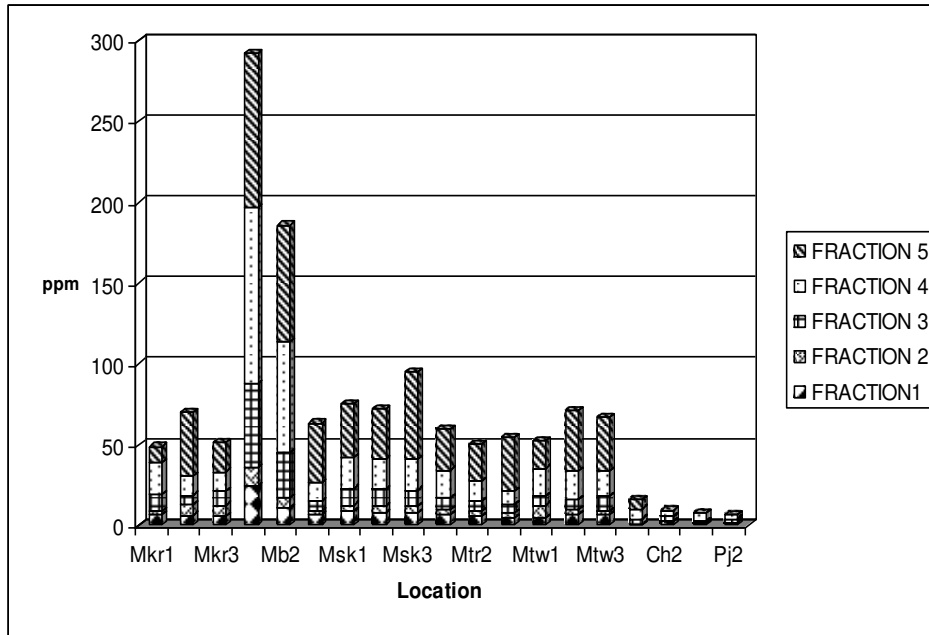


Fig 2. Concentration of Cr (ppm) in each geochemical fraction by site/location

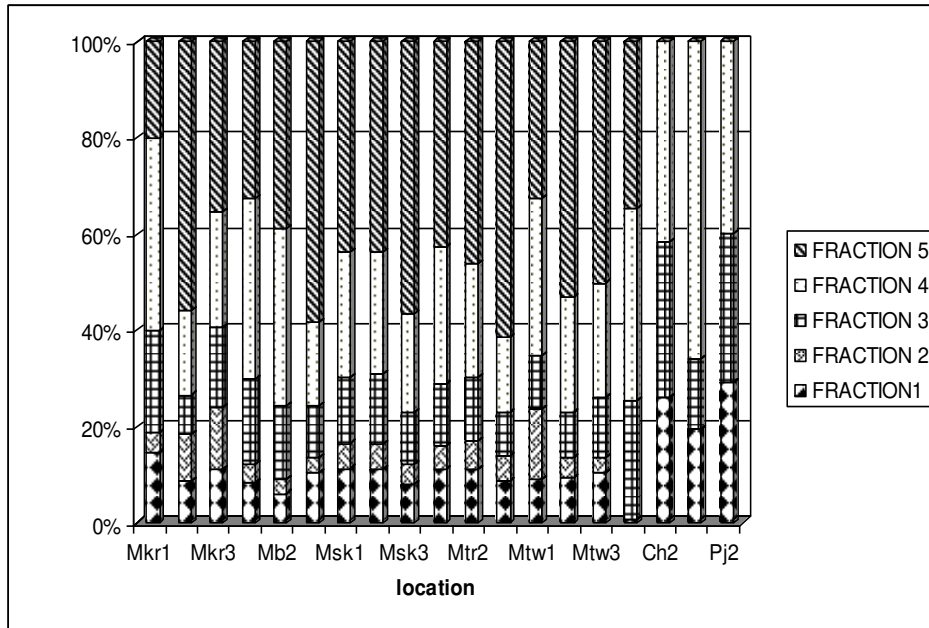


Fig 3. Percent contribution of Cr on each geochemical fraction to total metal concentration at each sampling area/location

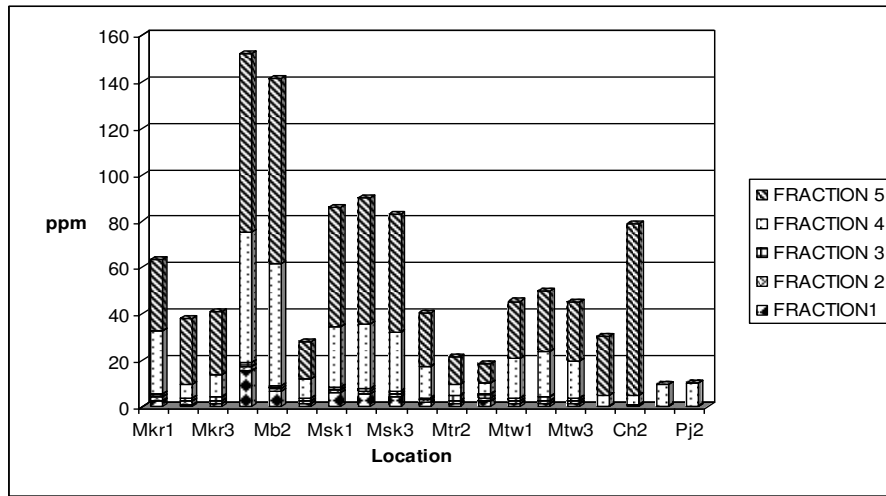


Fig 4. Concentration of Cu (ppm) in each geochemical fraction by site/location

Cu content exceed the threshold in some locations were probably due to as the impact of waste industrial inputs, while the values observed in Penjaliran Island (Pj1 and Pj2) showed relatively lower Cu content (9.82 and 10.29 ppm). This is because, this Island is away from pollutant sources and human settlement.

(Indonesia Ministry of Environment, 1995). However, not all locations contained high Cu concentration because only small numbers of industries (the paint industry and electroplating) yielded Cu and those plants were not spread evenly across the research sites (State Ministry of Development Supervision and the Environment, 1981).

Cu commonly is used in electroplating industries along with Ni, Cr, and Zn

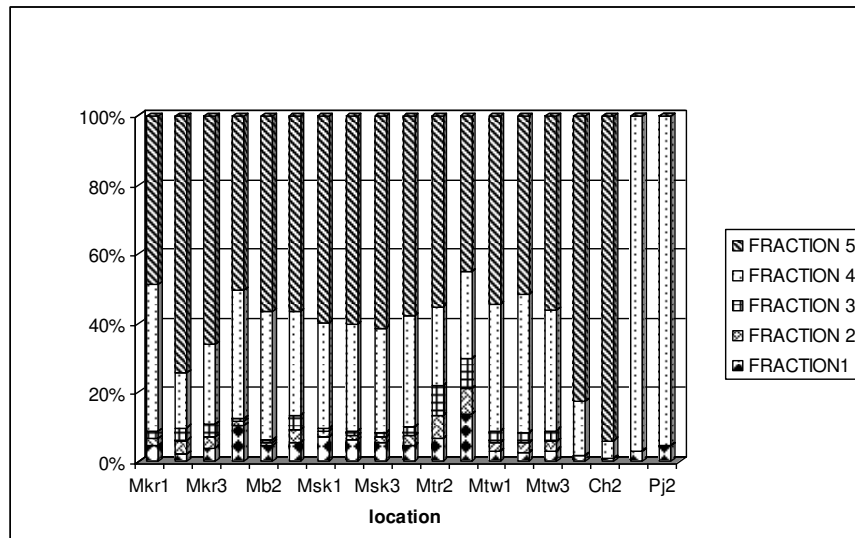


Fig 5. Percent contribution of Cu on each geochemical fraction to total metal concentration at each sampling area/location

Percentage of Cu on the labile fraction (fraction 1, 2, and 3) were ranged between 5-25% ($F = 2.5$, $P = 0.00$) (Figure 5), whereas in the lithogenic material ranged 50-65%. The high concentration of Cu ($F = 2.4$, $P = 0.00$) on lithogenic material also indicates high concentration on sediments. Therefore, this condition is relatively safe as long as the changes (for example very low pH) do not occur and the metal remained bound to the sediment and do not enter the environment.

Pb (Lead)

Pb content in the study areas was ranged from 39.7-303.42 ppm (Fig. 5). Based on the Canadian Standard for Contaminated Sediments, threshold limit value for Pb is 25 ppm. This indicates that the location of all the areas of research have Pb content exceed the threshold value. At all locations, Pb content was higher compared to the value from Penjaliran (2.34 and 4.47 ppm), especially at

Sunda Kelapa Harbour, where a lot of ships, boats and industries are docked.

Percentage of Pb on the labile fraction (fraction 1, 2, and 3) were ranged between 22-55% ($F = 2.5$, $P = 0.00$), whereas in the lithogenic material ranged 25-55% (Figure 7). This indicates that the Pb metal in the location ($F = 2.4$, $P = 0.00$) were already contained in the sediments and will be available for marine benthic organisms when extreme condition (such as very low pH) occur.

Zinc (Zn)

Zn concentration ranged between 165.83-487.69 ppm and background value on the Penjaliran Island ranged 31.67-32.87 ppm (Fig. 7), while Canadian Standard for Contaminated Sediment's threshold value is 60 ppm. This indicates that the Zn content at each location of the research exceed the threshold value and background value.

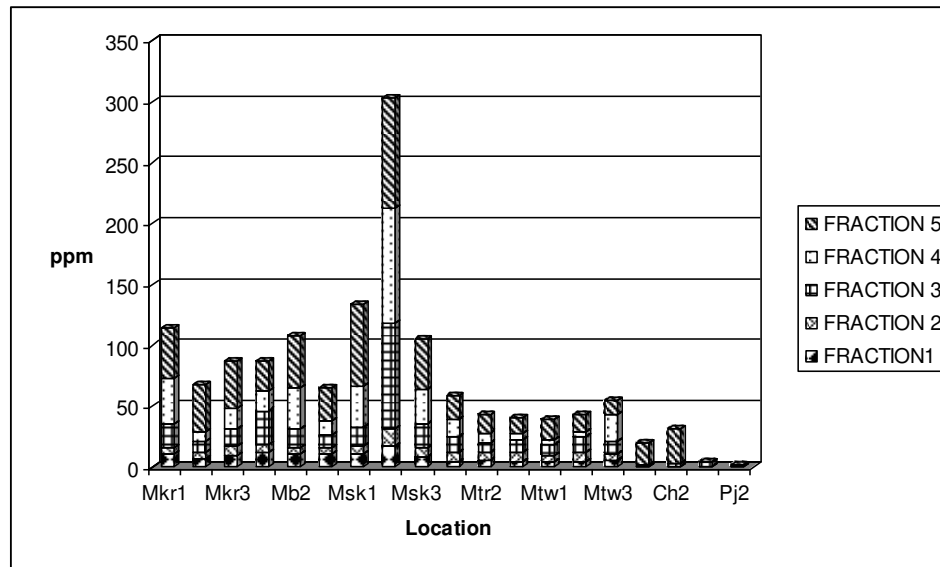


Fig 6. Concentration of Pb (ppm) in each geochemical fraction by site/locations

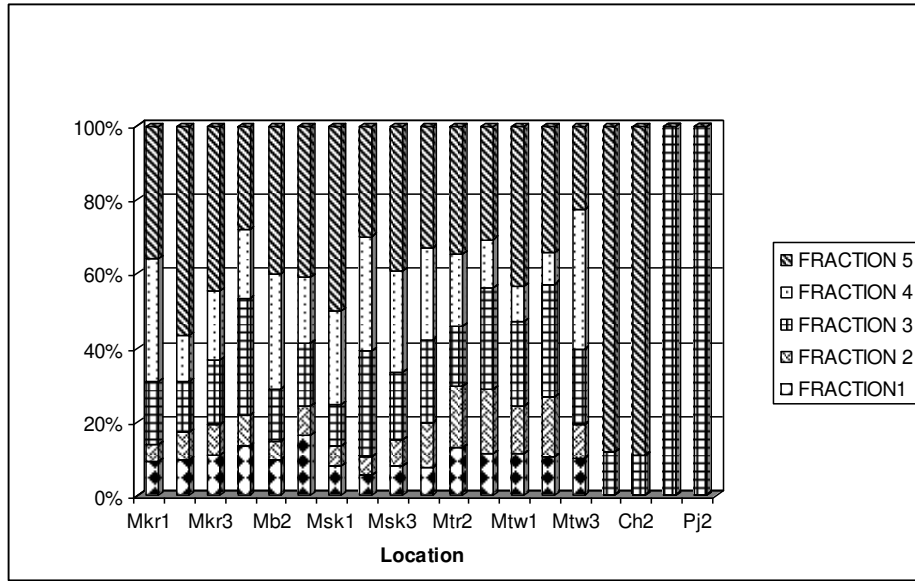


Fig 7. Percent contribution of Pb on each geochemical fraction to total metal concentration at each sampling area/location

Zn is generally used in paint making industry, oil refining, rubber, agrochemical, pharmaceutical, electronics, etc. Zn has the highest rate compared to other three metals (Cr, Cu, and Pb). Percentage of Zn metal

labile fraction ranged between 22-75% ($F = 2.5, P = 0.00$), and in lithogenic material was 18-43%. The high percentage of Zn in labile fraction indicates its potential to pollute the marine ecosystems.

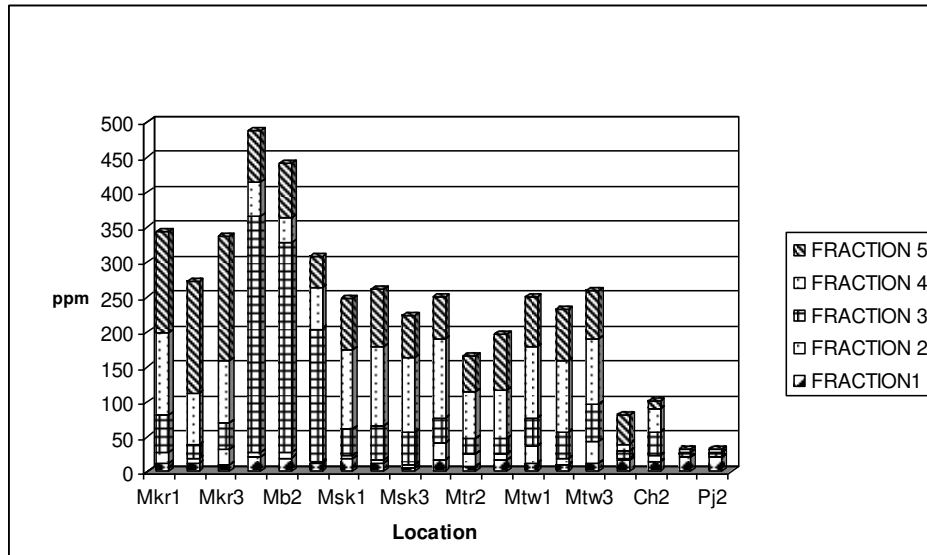


Fig 8. Concentration of Zn (ppm) in each geochemical fraction by site/location

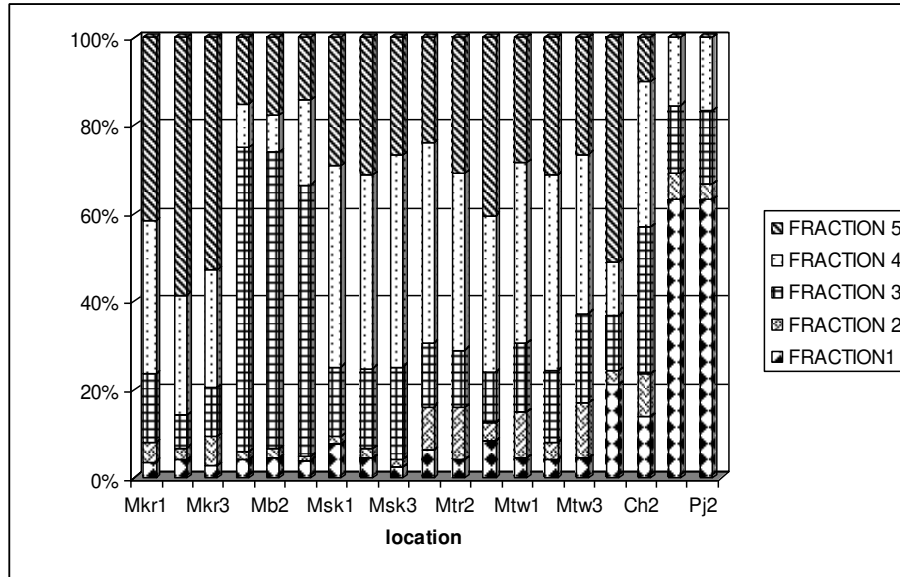


Fig 9. Percent contribution of Zn on each geochemical fraction to total metal concentration at each sampling area/location

Table 2. Two-Way Analysis : differences of Cr, Zn, Cu, Pb in sediments between locations and geochemical fractions

	Cr		Zn		Cu		Pb	
	F	P	F	P	F	P	F	P
Location	2.4	0.00*	2.4	0.00*	2.4	0.03*	2.4	0.00*
Fraction and Total	2.5	0.00*	2.5	0.00*	2.5	0.00*	2.5	0.00*
Interaction	1.7	0.65	1.7	0.00	1.7	0.89	1.7	0.19

*Statistically significant : for a given locations and geochemical fractions, metal concentrations are significantly different ($p < 0.05$).

Compare to heavy metals content that have been previously analyzed in eight river sediments that flow into Jakarta Bay (Takarina, 2007), the heavy metals content in this study (5 river mouths) are higher. The highest Chromium (Cr) content in this study was 285 ppm compare to 72 ppm in the previous study, Pb was 300 ppm compare to 270 ppm, and Cu was 156 ppm compare to 96 ppm (Takarina, 2009).

CONCLUSION

Based on the data obtained during the research, it was known that the assay Cr, Zn, and Cu were the highest in Muara Baru, while the Pb assay was the highest in Sunda Kelapa river mouth (estuary). This is due to Muara Baru and Muara Sunda Kelapa are the region with high level of industrial activity and near the loading-unloading vessels. Most of heavy metals found were higher than Canadian

Standard for Contaminated Sediments or the previous research that have already done by some scientist in the same area.

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