Relationship Between The Bioavailability of Sediment-Bound Metals and Their Concentrations in Benthic Invertebrates

by Shinta Kristanto

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ABSTRACT

This study aimed to analyze the concentrations of Cu and Zn in the bioavailable fractions of sediments and its relation to the concentration of metals in benthic biotas and environmental parameters in coastal sediments of Makassar. It was conducted on the coastal waters of Makassar, from estuary of Jeneberang River to estuary of Tallo River. All metals analysis were conducted with dry, <63 µm grain size sediment samples. Metal speciation in sediments was determined using the BCR (Community Bureau of Reference) three steps sequential that extract exchangeable and acid soluble fraction, reducible, and oxidisable fraction. Benthic organisms sampled were polychaeta (worms) representing the deposit feeder, and bivalves (clams) representing the filter feeder. Total metal concentration in soft tissue was extracted by wet destruction. Cu and Zn accumulation in worms (deposit feeder) associates with fraction 2 (reducible) and fraction 3 (oxidisable) due to higher content of TOC and BOT in sediments, while the accumulation of metals in shellfish (filter feeder) is related to metal concentrations in water colomn.

Keywords: metals, sediment, speciation, bentic invertebrates

INTRODUCTION

Marine sediments known as a contaminants sink, including metals derived from land and atmosphere. There have been many studies that prove organisms, both plants and animals, can accumulate metals with different concentrations in different environments, and are not always influenced by the total concentration in the sediment or water column (Louma, 1989).

Metal can be associated with various phases of the sediment such as: a) adsorption on surface particles (clay, humic acid, metal oxyhydroxydes); b) bound to carbonates; c) occluded in Fe and Mn oxides; d) bound on living or detrital organic materials; e) bound in the crystal matrix sediments (Tessier and Campbell, 1987). Association of metals in sediment fractions produces various metal species that have the potential of different bioavailability on biotas. The most easily exchangeable fraction is the fraction that has a high bioavailability, namely Fe and Mn oxides, carbonates, organic matters and clay minerals (Neff, 2002). In oxic sediment, Fe/Mn oxides and organic materials are important in controlling metals in estuaries (Thomas and Bendell-Young, 1998).

Benthic organisms with different feeding behavior such as filter feeders and deposit feeders, will accumulate metals from sediment matrixes with different concentrations. Important factors that affect the absorption of metals from sediments by benthic biota are the concentration in sediments, differences in feeding behavior, as well as geochemical phases in associated sediments.

Copper (Cu) and Zinc (Zn) are essential metals for the metabolism of biota, but increasing concentrations above the standard minimum requirement will have deleterious effects on biotas. The use of Cu and Zn as a raw material in antifouling paints (TBT) is one of the main sources of these metals entering the sea (Srinivasan and Swain, 2007; Bao et al., 2008). With the increasing development of coastal areas of Makassar, anthropogenic inputs of these metals will also affect sediments and biotas living on it.

This study aimed to analyze the concentrations of Cu and Zn in the bioavailable fractions in sediments and its relation to the concentration of metals in benthic biota and environmental parameters in coastal sediments of Makassar

MATERIALS AND METHODS

Sampling was conducted on January 2011, at 20 points along the estuary of Jeneberang River to Tallo River (Figure 1). Sediment samples were taken only on the surface (1-3 mm depth), which is part of oxic layer, using a Van Veen Grab Sampler and were put into plastic containers and stored in a cool box for transportation. Before the extraction process samples were stored in plastics bags and frozen in a freezer at a temperature of - 20°C to prevent biochemical process that can damage the sample. Sediment samples were filtered using dry sieving method to get the grain size of <63μm.

Metal speciation in sediments was determined using the BCR (Community Bureau of Reference) three steps sequential (Table 1) that extract exchangeable and acid soluble fraction, reducible, and oxidisable, used by Ure et al., (1993) in Davidson et al., (1994), Yuan et al., (2004) and Zhou et al., (2010) .

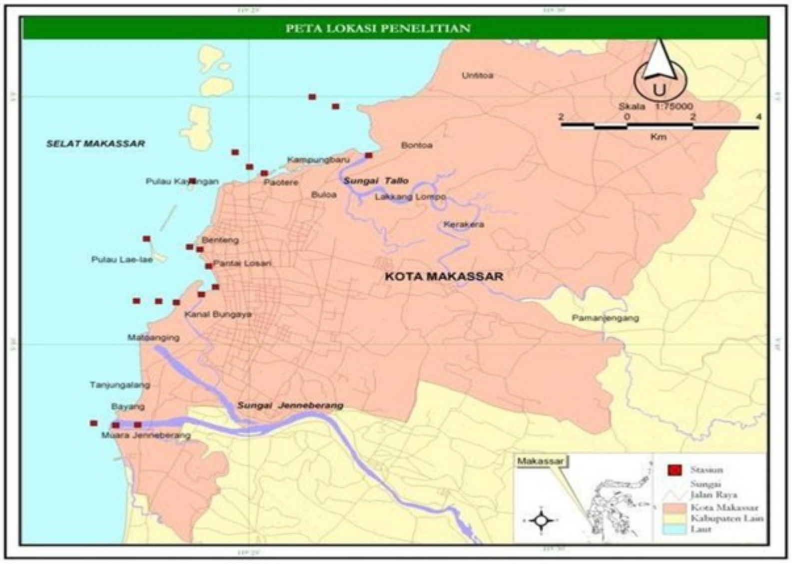


Figure 1. Map of the area, showing sampling locations.

Benthic organisms sampled were polychaeta (worms) representing the deposit feeder, and bivalves (clams) representing the filter feeder. Total metal concentration in pooled soft tissue was extracted by wet destruction using HNO_3 (nitric acid) dan $HClO_4$ (perchlorate acid) (Japanese Ministry of Environment, 2004).

Table 1. The BCR Three-Steps Sequential Procedures

Phase	Fraction	Extracted components	Procedures
1	Acid Soluble	exchangeable ions and carbonates	40 ml CH_3COOH added on 1 gram dry sediments (<63 um)., shake for 16 hours
2	Reducible	Fe-Mn oxides	40 ml $NH_2OH.HCl$ (pH 2 , HNO3), shake for 16 hours
3	Oxidizible	Organic matters dan sulfites	10 ml H_2O_2, 1 hr disgestion , 1 hr water bath, add 10 ml H_2O_2, 1 hr water bath, add 50 ml CH_3COONH_4 (pH 2, HNO_3)

Analysis of sediment parameters, pH and redox potential were carried out in situ, while the analysis of organic ingredients, DOM (dissolved organic matter) and TOC (total organic carbon) and sediment particle size were conducted in the Laboratory of Chemical Oceanography, Department of Marine Science, Faculty of Marine Science and Fisheries, UNHAS. Sediment samples analysis for Pb and Cd fraction in sediment were analyzed in Laboratory of Center for Environmental Health (BTKL), Ministry of Health, Jakarta. Metals concentrations in organisms and sediments were analyzed using *Atomic*

Absorption Spectrophotometer (Hitachi- Z 2000 Tandem Flame/Furnace AAS) with Limit of Detection (LOD) for each metals are Cu (0,006 ppm), and Zn (0,031 ppm). Analysis for Cu and Zn concentrations using flame detector.

Data analysis was performed by grouping all the stations into seven (7) locations and differences in metal concentrations at each site were tested using Analysis of Varience (one way ANOVA). Pearson Correlation was carried out to analize the relationship between metals in organisms and metal fractions in sediments with sedimen parameters.

RESULT AND DISCUSSION

Sediment characteristics and water parameters

Sediment charecteristics of each studied sites is presented in Table 2. All parameters analyzed was choosen because its relationship to metal accumulation in sediments. Silt and Clay fractions of sediments and total organic materials are increasing towards the north coast of Makassar. These parameters supported metal association in sediment. It is also interesting to note that through the north coast of Makassar, the sedimets are more reduced by having decreasing redox potential (Eh). Reducing environments will hold metals tightly in sediments.

Tabel 2. Sediment parameters in each site

Sites	**Eh (mV)**	**TOM (%)**	**TOC (%)**	**GS < 63µm (%)**	**Silt + Clay (%)**	**Sand (%)**
M S Jeneberang (Jene)	133.78	2.84	1.82	0.52	48.7	51.3
Tanjung Merdeka (TM)	16.33	6.84	2.18	1.56	33.0	67.0
Losari	-161.18	6.58	1.86	0.81	54.3	45.7
Kanal Benteng	-136.92	7.62	2.27	4.28	68.3	31.8
Kanal Paotere	-239.78	17.46	1.87	1.92	76.3	23.7
M S Tallo	-53.44	13.42	2.06	0.42	95.7	4.3
P Bonetambung	45.67	41.15	1.46	0.21	84.0	16.0

Water parameters are ilustrated in Table 3. Temperature and pH are homogen throughout the studied sites. Lowest salinity is found highest in estuary of Tallo River. Dissolved Organic Materials (DOM) is one water parameters that has high relationship with metal accumulation in water colomn, and highest DOM concentrations is found in Kanal Paotere. This study site is an area of public port and located in a populous area.

Tabel 3. Water parameters

Sites	Salinity (ppt)	DO (mg/L)	pH	Temp (°C)	DOM* (mg/L)	Cu* (mg/L)	Zn* (mg/L)
M S Jeneberang (Jene)	30.0	4.6	7.2	30.5	22.91	0.13	0.08
Tanjung Merdeka (TM)	29.9	5.7	7.3	30.9	21.07	0.14	0.07
Losari	29.7	6.5	7.3	32.8	8.84	0.14	0.09
Kanal Benteng	29.8	4.5	7.3	30.6	19.70	0.09	0.05
Kanal Paotere	29.3	4.6	7.2	31.1	25.07	0.08	0.08
M S Tallo	19.2	4.0	7.0	30.4	16.60	0.06	0.06
P Bonetambung	30.3	4.6	7.3	30.9	12.33	0.14	0.11

* Source : Werorilangi, et.al., 2012

Cu concentrations are increasing through the north coast of Makassar, whereas Zn concentrations are mostly homogen in all sites. It is interesting to note that both Cu and Zn concentrations is high in control site, Bonetambung Island.

Metals Concentrations in Sediments

Although total metal content does not provide significant information on the impacts of metals on organisms, but the information is very important to identify the source of metals entering the waters. There are no significant differences of total concentrations of Cu and Zn in all studied sites based on statistics ANOVA (Fig. 2).

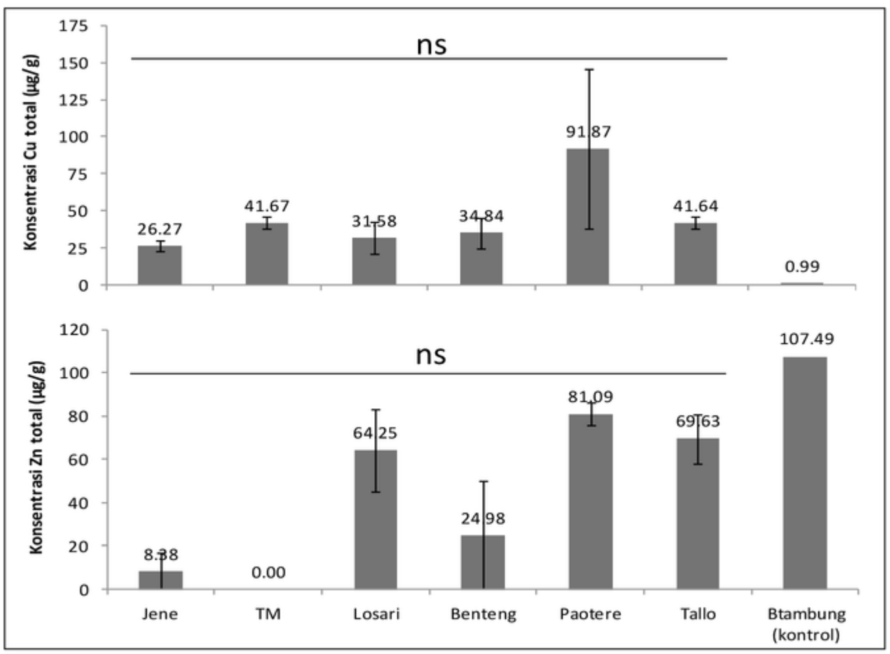


Figure 2. Total metal concentration in sediments

Concentration of Cu and Zn are highest on Kanal Paotere, which is where most of the waste entering the coast of Makassar city and a public port location. Cu concentrations are also high in Losari Beach and estuary of Tallo River. Highest Cu and Zn concentrations found in some sites is assumed to correlate with the usage of antifouling paint in ships, aside from city wastes.

Suprisingly, Zn is found highest in control site, Bonetambung Islad, where the location is far from the mainland. Sediment in Bonetambung Island is the only studied sites which has lighter color of sediment. According to Libes (2009), coastal sediments (pelagic) which has lighter color is a type of biogenic sediments that are composed of hard and soft parts of dead organisms, such as shells, bones, and fecal. This is also in conjuction with highest percentage of organic materials (TOM) found in Bonetambung Island (Table 2).

Metal Fractions Concentrations

This study used a speciation method by the Community Bureau of Reference (BCR) three steps sequential that extract exchangeable and acid soluble fraction (fraction 1), reducible (associated with Fe/Mn oxides, fraction 2), and oxidisable (associated with organic materials and sufides, fraction 3). Metals in fractions 1, 2, and 3 are labile metals, where the movement is strongly influenced by environmental conditions. Metal on fraction 1 has the highest mobility (most available form) being the most easily exchangeable and has a very weak bounding in the sediment matrix (Zimmerman and Weindorf, 2010). Bioavailability of metals for biotas is in conjuction with the most high to low mobility fractions, that is the fraction 1> fraksi 2 > fraction 3.

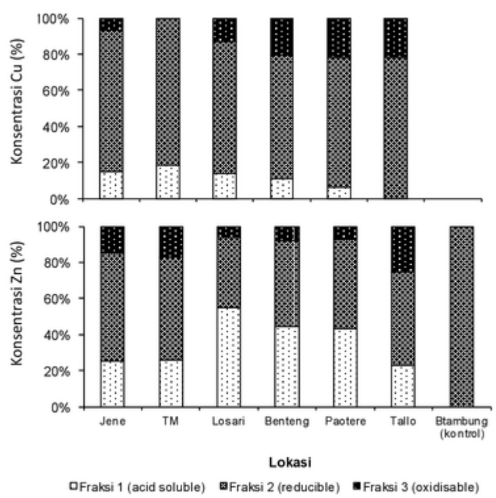


Figure 3. Percentage of metal fractions in sediments of sampling site (Jene = Jeneberang; TM = Tanjung Merdeka; Btambung = Bonetambung)

Distribution of metal fractions in sediment are presented in Fig 3. Percentages of Cu and Zn in fraction 1 are 0-18% and 0-55%; fractions 2 are 69-82% and 39-100%; while in fraction 3 are 0-22% and 0-25%. Zn are mostly found in fraction 1, whereas Cu mostly in fraction 2 and 3. This indicates that Zn is more bioavailable to biotas than Cu.

Metals concentrations in biotas and its relationship with bioavailable fractions of metal in sediments

Polychaetes

Polychaetes live in sediments by swallowing particles (deposit feeder), thus causing organism is constantly exposed to contaminants in the sediment. Substrate characteristics where they live is mud clay mud with a high organic carbon content (Junardi and Ward, 2008).

Concentrations of Cu and Zn in a pooled samples at each sites are shown in Figure 3. Range oncentration of each metal is 0-3.91µg / g for Cu, and 0-168.42 mg /g for Zn. Accumulation of both metals highest on estuary of Tallo River and for Zn, concentrations is also high in Kanal Benteng. There were no polychaetes found in Kanal Paotere, assuming that this sites is the most polluted.

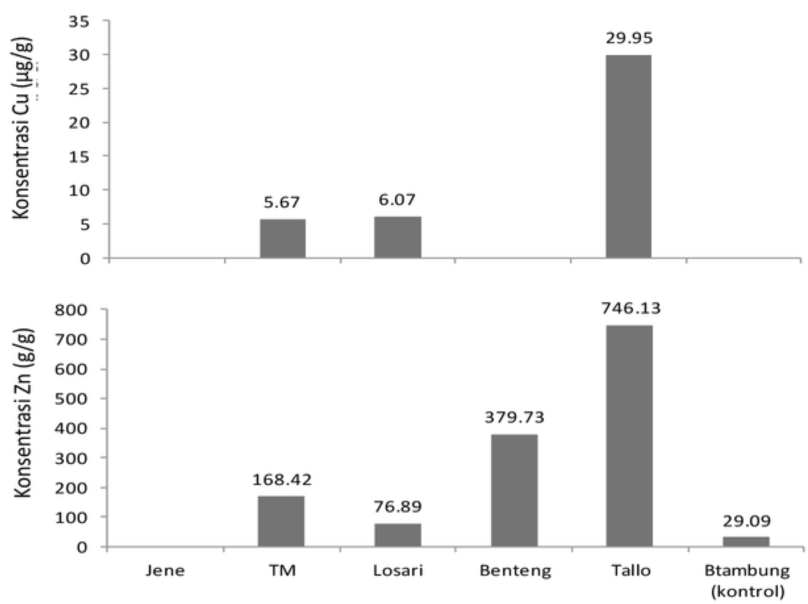
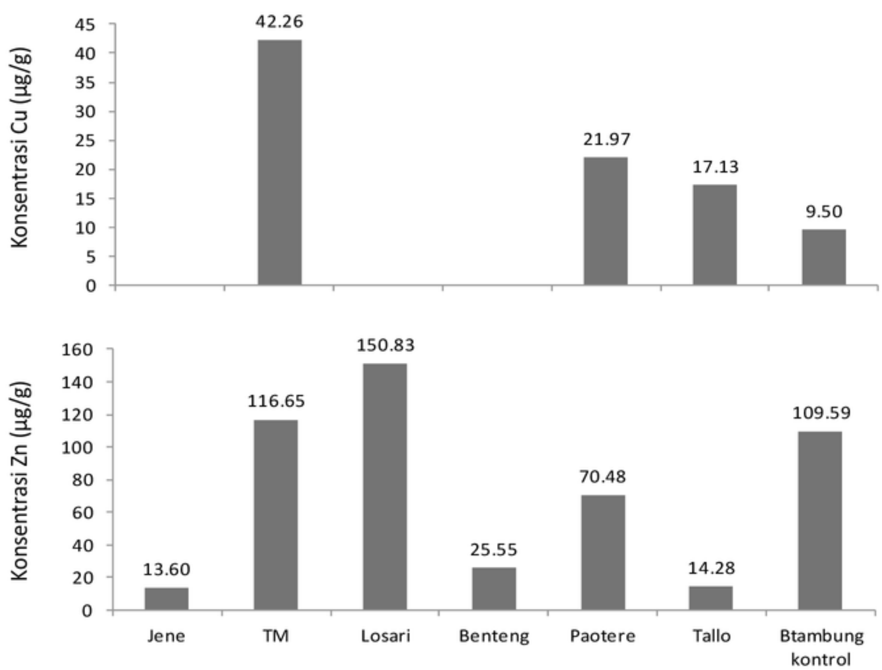


Figure 3. Metal concentrations in polychaetes (worm) in sampling location (Jene = Jeneberang; TM = Tanjung Merdeka; Btambung = Bonetambung)

Bivalves

Bivalves are filter feeders, taking food by filtering water through the gills, the same way used to remove oxygen from the water column. This feeding behaviour and as a benthic organism making them prone to accumulate metals from water column and from sediments.

Metal concentrations in bivalves are 0–42.26 µg/g for Cu dan 13.60–150.83 µg/g for Zn (Figure 4). It interesting to note that accumulation pattern in bivalves is different than in polychaetes, in which, highest accumulation by polychaetes for both metals in the north coast of Makassar (estuary of Tallo River and Kanal Benteng), whereas, bivalves from the south coast of Makassar Tanjung Merdeka and Losari Beach) accumulates more metals.



Jene = Jeneberang; TM = Tanjung Merdeka; Btambung = Bonetambung

Figure 4. Metal concentrations in bivalves

Relationship with Metal Fractions in Sediments and Environmental Factors

Copper (Cu)

There is a positive correlation between the concentration of metals in polychaetes with Cu concentrations in sediment and negative correlation and highly significant with concentrations of Cu in the water column. Theses indicates the source of Cu in the worms do not come from the water column but rather from sediment. While in bivalves, although not significant, both correlated positively, which implies that shellfish absorb Cu from both media but is more dominant in the water column. There are also strong and positives correlation between Cu in polychaetes and Cu in fraction 2 and 3, and also with TOM in sediments. These imply that polychaetes accumulates metal associated with organic materials in sediments. pH is also have a strong correlation ($r = -0.825$, $p>0.05$) with concentration in the worms. As the water become acidic, many more metal is the form of free ion, therefore are more bioavaillable to the biotas.

The value of a strong correlation and significant between Cu fraction and environmental factors are more common in worms than in shells, it also suggests that the accumulation of Cu in worms is strongly influenced by the dynamics of sediments.

Table 4. Pearson correlation value of Cu and Zn concentrations in biotas with metals and environmentals factors in sediments

	Metal Concentrations			
	Polychaetes		Bivalves	
Parameters	Cu	Zn	Cu	Zn
Sediments	0.882	-0.104	0.073	0.258
Fraction 1	-0.962	0.459	0.275	-0.137
Fraction 2	0.997*	0.909*	-0.007	-0.323
Fraction 3	0.981*	0.978**	-0.121	-0.544
Waters	-1**	-0.735	0.284	0.609
TOC	0.129	0.525	0.786	-0.32
GS < 0.63 um	-0.772	0.119	0.678	-0.234
TOM sediments	0.999*	-0.311	-0.793	0.251
pH	-0.825	-0.68	-0.096	0.363
Eh	0.108	-0.179	0.036	-0.193
DOM	0.139	0.411	0.594	-0.562

* significant at $\alpha < 0.05$ (2-tailed)
** very significant at $\alpha < 0.01$ (2-tailed)

Zinc (Zn)

There is a negative correlation between the concentration of Zn in polychaetes with Zn concentrations in the sediment (Table 4), indicating that the increase in the concentration of Zn in the worms are not affected by the concentration in the sediment. However, there are a significant strong positive correlation with fractions 2 ($r = 0909$, $p <0.05$) and 3 ($r = 0.978$, $p <0.01$) in sediments. This indicates that although the concentration of metals in the sediment did not correlate with the concentration in the worm, but the association of Zn in the sediment matrix may influences absorption in the worms.

The source of Zn accumulation in shellfish may have came from the water column , indicated by quite a good positive correlation between the concentration of Zn in water with a concentration in bivalves.

CONCLUSIONS

Concentration of total metals in benthic organisms found higher in the group of Polychaeta (worms) in comparison with bivalves (clams). Metal concentrations in the worms are found high on the north coast (estuary of Tallo River and Kanal Benteng); while in bivalves are found high in the south coast (Tanjung Merdeka and Losari Beach). Cu and Zn accumulation in polychaetes (deposit feeder) associated with fraction 3 and fraction 2 because the content of TOC and BOT high in sediments; whereas the accumulation of Cu and Zn in bivalves (filter feeders) are more related to the total concentrations in water colomn.

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