Dispersion, Speciation, and Pollution Assessment of Heavy Metals Pb and Zn in Surface Sediment from Disturbed Ecosystem of Jeneberang Waters

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Abstract Surface sediments were collected from seventeen stations in Jeneberang waters (riverine, estuarine, and marine). Lead (Pb) and zinc (Zn) concentrations were determined by atomic absorption spectrometry, and the speciation of metals was obtained by a sequential extraction procedure. Dispersion of Pb and Zn were found higher in the riverine and marine samples than the estuarine samples. Following speciation, the metals were found similar composition of fraction in the riverine and estuarine samples but any different in the marine samples. The results indicated that there is a change of dispersion pattern and speciation composition of metals due to the presence of the dam that lies at the boundary between the estuary and the river. The toxicity unit was indicated low toxicity level; pollution level was in weakly to moderately polluted while the aquatic environment risk attributed were no risky to light risk.

1. Introduction

The aquatic environmental contamination by heavy metals is a serious and worldwide problem due to their high toxicity, persistence, and bioaccumulation [1]; [2]. Despite the advances in sewage treatment technologies, water pollution caused by sewage discharge has still been a serious problem in many developing countries due to the high operating cost of sewage treatment facilities as well as lack of effective management and enforcement (e.g. [3]; [4]; [5].

Aquatic environment particularly estuarine and coastal is important zone due to its close relationship with human activities. These locations, the ultimate destination of terrestrial runoff, have become increasingly contaminated by the heavy metals in recent decades. The toxic effects of metals preserved in sediments seriously threaten the coastal ecosystems. Accordingly, determination of concentration and distribution of heavy metals deposited on the seabed is of important [6].

Sediments in the aquatic environment are sensitive indicators for assessment and monitoring heavy metal contaminant. Sediments not only serve as reservoirs for deleterious chemical species which cause negative effects on aquatic system and human health but also act as a source of metals for aquatic organisms via several pathways, including disposal of liquid effluents, terrestrial runoff, and leachates carrying chemicals originating from numerous urban, industrial and agricultural activities, as

well as atmospheric deposition. Therefore, sediments reflect the current quality of the aquatic environment as well as provide information on the impact of pollution sources [1].

Concentration and speciation assessments of heavy metals in sediment are useful to study the pollution level in the aquatic environment and to provide basic information for determination of aquatic environmental health risks [1]. Consequently, the concentrations of heavy metals in sediment are often monitored to provide basic information for the environmental risk assessment [7]. Determination of the speciation of heavy metals in sediments is important to assess their potential toxicity, a threat to the ecosystem, and source (natural processes or anthropogenic sources) [8].

The number of studies on dispersion, speciation, and pollution assessment of heavy metals in sediment have been published [9]; [10]; [11]; [12]; [13] however, all the studies carried out at naturally (normally) ecosystem and none information is available at disturbed ecosystem. The change of ecosystem will drive the change physic-chemical parameters within the environment and they could influence process and dynamics of heavy metal caused by the change of interaction pattern of metals and environment. A seasonal variable can stimulate the change of distribution and geochemical fractionation of heavy metals [14]. Following this research, analyze the effect of ecosystem changes due to the presence of the dam in an estuary on dispersion and speciation of heavy metals lead (Pb) and zinc (Zn).

2. Materials and Methods

2.1. Study area
Makassar, as the largest city in eastern Indonesia, is undergoing rapid economic growth and industrialization. The Jeneberang River flows through Makassar City, including the upstream area in the Bawakaraeng Mountains, Gowa district and the downstream area in the Makassar Strait. The Jeneberang River flows through village and city regions and therefore has the potential for contamination by various metals from agricultural, domestic, and transportation sources. There is also potential intake of metals from marine sources such as the Makassar international seaport, ship docking and manufacturing, hospital, and industrial sectors [14].

Jeneberang estuary is a disturbed ecosystem where around 3 km before the estuary there is a dam utilized by local water company for the material source. The dam changed flows pattern and mixing between fresh water and seawater in the estuary zone. The change will influence the physic-chemical parameters within the environment such as pH, temperature, and redox potential (Eh), could influence metal release from the solid to liquid phases that transformed sediments from the main metal sink to the sources for the overlying waters [2]. Moreover, there is a transport reduction of some suspended particles because of low water flow. Consequently, the flow of disposal and suspended particle from the rivers would be deposited along the dam.

2.2. Sediment sampling and pretreatment
A total of 17 surface sediment samples were collected from riverine, estuarine, and marine waters. The riverine water zone contained sampling stations R1–R3, the estuarine zone contained sampling stations E1–E7, and the coastal (marine) zone contained sampling stations CS1–CS7. Sample locations were determined by a global positioning system (Fig. 1).

The surface sediments were sampled using an Ekman grab sampler. At each sampling site, the top 0–10 cm of sediment were collected using a plastic spatula, and each sample was packed in a new polyethylene zipper bag. After collection, the samples were stored and transported to the laboratory in a cooler box with ice packs and then stored in a fridge at 4 °C before analysis. In the laboratory, samples were first sieved through a 2 mm nylon sieve to remove coarse debris and shell fragments, ground using an agate mortar and pestle in a fume cupboard, and then sieved through a 0.5 mm sieve to remove large particles and homogenize the mixture.

2.3. Analysis of sediment properties and suspended particulate matter

The texture of dry sediment samples was analyzed using a pipet procedure (after passing through a 63 μm sieve). Grain sizes from 2000 μm to 62.5 μm were classified as sand, those from 62.5 μm to 3.9 μm as silt, and those <3.9 μm as clay. The organic carbon (OC) content was analyzed using the Walkley-Black procedure and expressed as a weight percentage following sample combustion in a Loss on Ignition test. The suspended particulate matter (SPM) was measured using a gravimetric procedure, and the redox potential (Eh) of the sediment was measured using a portable Eh meter.
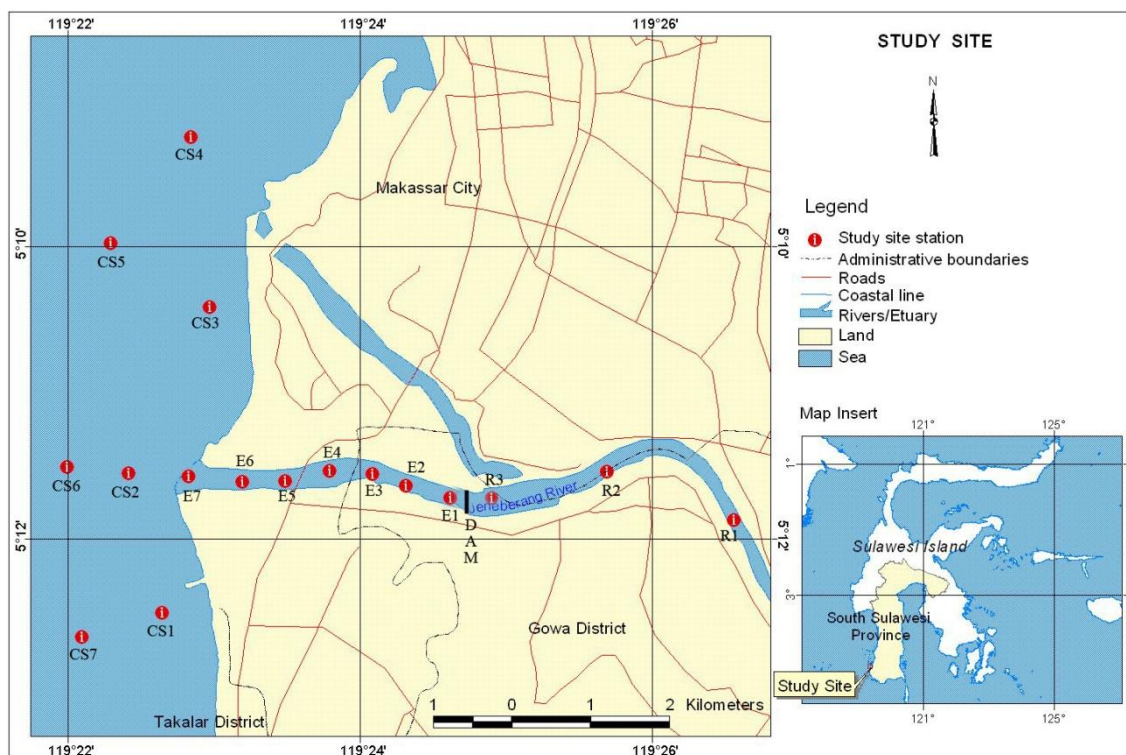
Figure 1. Location of sample sites

2.4. Heavy metals analysis and geochemical fractionation

The geochemical fraction of heavy metals was determined using sequential extraction procedure [15]. This method provides the exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residual fractions with the following procedures;

1. Exchangeable (F1). The sediment was extracted at room temperature for one h with 8 mL of either magnesium chloride solution (1 M $MgCl_2$, pH 7.0) or sodium acetate solution (1 M NaOAc, pH 8.2) with continuous agitation.

2. Bound to carbonates (F2). The residue from (i) was leached at room temperature with 8 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained and the time necessary for complete extraction was evaluated.

3. Bound to Fe-Mn oxides (F3). The residue from (ii) was extracted with 20 mL of either 0.3 M $Na_2S_2O_4$ + 0.175 M Na-citrate + 0.025 M H-citrate or 0.04 M NH_2OH-HCl in 25% (v/v) HOAc. The latter experiments were performed at 96 ± 3 °C with occasional agitation and the time needed for complete dissolution of the free iron oxides was evaluated.

4. Bound to organic matter (F4). The residues from (iii) were added 3 mL of 0.02 M HNO3 and 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3, and the mixture was heated to 85 ± 2 °C for 2 h

with occasional agitation. A second 3 mL aliquot of 30% H_2O_2 (pH 2 with HNO_3) was then added, and the sample was heated again to 85 ± 2 °C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added, and the sample was diluted to 20 mL and agitated continuously for 30 min. The addition of NH_4OAc is designed to prevent adsorption of extracted metals onto the oxidized sediment.

5. Residual (F5). The residue from (iv) was digested with a HF-$HClO_4$ mixture according to the procedure described below for total metal analysis.

The "selective" extractions were conducted in centrifuge tubes (polypropylene, 50 mL) to minimize losses of solid material. Between each successive extraction, the separation was effected by centrifuging at 10,000 rpm (12,000 g) for 30 min. The supernatant was removed with a pipet and analyzed for trace metals, whereas the residue was washed with 8 mL of deionized water; after centrifugation for 30 min, this second supernatant was discarded. The volume of rinse water used was kept to a minimum to avoid excessive solubilization of solid material, particularly organic matter. Deionized water used in preparing stock solutions and in each step of the leaching procedure was obtained from a Millipore Milli-Q3RO/Milli-Q2 system. All glassware used for the experiments was previously soaked in 14% HNO_3 (v/v) and rinsed with deionized water.

For total or residual metal analysis, the solid was digested with a 5:1 mixture of hydrofluoric and perchloric acids. For a 1 g (dry weight) sample, the sediment was first digested in a platinum crucible with a solution of concentrated $HClO_4$ (2 mL) and HF (10 mL) to near dryness; subsequently the second addition of $HClO_4$ (1 mL) and HF (10 mL) was made and again the mixture was evaporated to near dryness. Finally, $HClO_4$ (1 mL) alone was added, and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 12 N HCl and diluted to 25 mL. All of the above metal-containing solutions were subsequently analyzed by graphite furnace atomic absorption spectrometry (Shimudzu-AA 7000).

2.5. Quality control and assurance

To guarantee the analytical data quality, laboratory quality control and quality assurance were implemented by utilizing standard operating procedures, calibration with standards, analysis of reagent blanks, recovery of spiked samples and analysis of replicates. The precision and accuracy of the analytical procedures were checked by recovery tests on spiked sediment samples. Adopted analytical procedures indicated 91% to 110% recoveries of the spiked metals and marine sediment reference material (NMIJ CRM 7302-a) were achieved from the tested samples, which agreed with certified values. The average differences between the certified and measured results were within 11% variability. Background correction and matrix interference were monitored through the analysis calibration checks. All analyses were duplicated to ensure the representativeness of the quantitative results, and the ultimate results were expressed as the mean and standard deviation. All reagents used in the experiment were an analytical-reagent grade or better. All glassware and plastic were pre-cleaned by soaking in 10% HNO_3 (v/v) for overnight.

2.6. Data analysis

Toxicity unit (TU), defined as the ratio of heavy metal concentration to probable effect level (PEL), was calculated to evaluate the toxicity of each heavy metals [16]. The potential acute toxicity of heavy metals was estimated by the sum of individual TU. Assessment of heavy metals pollution was analyzed by geoaccumulation index and risk assessment code. The geoaccumulation index (Igeo) is expressed as the following equation [17]:

$$Igeo = \log 2 \, [C_n/(1,5 \, Bn)]$$

where Cn is the measured concentration of metal n in the sediment, and Bn is the geochemical background value of the metal n. Factor 1.5 compensates for possible fluctuations in the background

values for a given substance in the environment, as well as very small anthropogenic influences. Müller defined seven classes in the geoaccumulation index:

Igeo ≤ 0 is class 0 (unpolluted);
0 < Igeo ≤ 1 is class 1 (weakly polluted);
1 < Igeo ≤ 2 is class 2 (moderately polluted);
2 < Igeo ≤ 3 is class 3 (moderately to strongly polluted);
3 < Igeo ≤ 4 is class 4 (strongly polluted);
4 < Igeo ≤ 5 is class 5 (strongly to extremely polluted);
Igeo > 5 is class 6 and extremely polluted.

Risk Assessment Code (RAC) is an assessment index of the risk of heavy metal existence on the aquatic environment based on the geochemical fraction of heavy metal interaction with sediment particle which is potentially absorbed by the organisms. Risk assessment index was obtained by calculating the percentage of exchangeable and carbonate fraction in sediment [18]; [19]. The index can be defined in five classes:

RAC<1 (not risky);
1<RAC≤10 (light risk);
11<RAC≤30 (medium risk);
31<RAC≤50 (high risk),
RAC>50 (very high risk).

3. Results and Discussion

3.1. Sediment properties and dispersion of heavy metals

Sediment texture was dominated by sand in the river and estuary zone, but in the marine zone, it was dominated by clay. There was a high water flow in the river and estuary from the upstream region which led to turbulence in the estuary, where larger particles (e.g., sand) deposited on the bottom. The increasing concentration of SPM in the water column was influenced by the high levels of erosion and water runoff. SPM binds to organic matter, and with greater levels of erosion, the OC concentration in sediments increases. A seaward decrease in Eh was caused by an increase in pH and the weak flow of the water mass. The decrease in Eh caused the number of electrons in sediment to decrease. The number of electrons was directly proportional to the Eh. This is following [20], who reported a strong correlation between pH and Eh. Based on the Eh, the study area was determined to be a reducing zone (anaerobic conditions). The sediment texture (clay, silt, and sand), OC, Eh, and SPM properties are shown in Table 1.

The dispersion of Pb and Zn were the highest concentrations found in the riverine and marine zones, while lowest concentrations were found in the estuarine zone The concentrations of Pb and Zn in sediment around the estuary of the Jeneberang waters are shown in Table 1. Higher Pb and Zn concentration of riverine and marine sediment indicated that the pollutant source of sediment was derived from mainland and marine. Pollutant source of elements derived from the mainland was in the particulate forms entering river basin and it settled and accumulated as sediment in water bottom.

Higher Pb and Zn concentration in the riverine zone were presumably due to a higher concentration of the particulates derived from soil erosion entering the river basin. The particulate that characteristically concentrates the heavy metals retained at the dam deposited to the water bottom, and, due to lower water flow, accumulated in the sediment. Beside rivers, the pollutant source of Pb and Zn can be found in the coastal area as indicated by a higher Pb and Zn concentration in the coastal zone compared to the estuary. The main source of Pb and Zn was

presumably originated from the seaport activities and traffic transportation in the shore of northern Jeneberang Estuary [21]; [22]; [23].

Heavy metal dispersion of sediment was found higher in estuary than that in riverine. Estuary commonly plays a role as natural pollutant filtration since there is smaller solubility change of heavy metals entering estuary waters. The reduced solubility was attributed to enhanced salinity and pH level leading heavy metals easily absorbed by particle then settled as sediment in water bottom [24]; [25]. However, the heavy metal concentration of sediment found in this study was at low concentration.

As different pattern found in this study that the heavy metal concentration was lower in estuary was presumably attributed to two factors; 1) the dam restricted the riverine flow leading to a reduction of water mass flow, therefore most particulate heavy metals were deposited along the dam, and there were only small amount entering the estuary; 2) there was a strong turbulence of water flow in the estuary thus it decreased the deposition rate of particle.

Table 1. Pb and Zn concentration from surface sediment and sediment properties in Jeneberang waters.

Sampling points	Sites group	Pb (mg.kg^{-1})	Zn (mg.kg^{-1})	Clay (%)	Silt (%)	Sand (%)	OC (%)	Eh (mV)	SPM (mg/L)
R1	Riverine	3.330	65.926	17	24	59	2.155	-23.970	88.0
R2	Riverine	3.114	73.102	23	15	62	2.170	-28.065	84.0
R3	Riverine	3.263	79.275	13	13	74	2.140	-35.305	78.5
E1	Estuarine	0.449	48.287	26	15	59	2.475	-10.520	153.5
E2	Estuarine	0.573	53.737	25	16	59	1.680	-12.075	137.0
E3	Estuarine	0.995	50.647	15	6	79	1.795	-9.360	108.5
E4	Estuarine	0.973	55.176	17	6	77	1.920	-25.685	72.5
E5	Estuarine	1.400	55.047	14	5	81	1.630	-20.565	109.3
E6	Estuarine	1.488	52.021	13	6	81	1.755	-12.825	134.5
E7	Estuarine	1.596	55.093	23	5	72	1.970	-25.590	101.3
CS1	Marine	1.733	55.363	23	14	63	1.660	-34.700	60.0
CS2	Marine	2.001	52.495	18	13	69	1.885	-35.300	84.8
CS3	Marine	2.316	59.935	22	35	43	2.820	-47.200	81.3
CS4	Marine	3.130	72.326	23	56	21	3.250	-55.035	37.3
CS5	Marine	2.729	65.289	68	8	24	2.755	-47.190	22.8
CS6	Marine	2.435	59.634	68	9	23	2.540	-52.980	22.3
CS7	Marine	2.252	57.410	66	9	25	2.110	-52.430	21.3

The existence of a dam at the boundary between river and estuary though does not change the amount of water volume into the estuary as the concept of Continuity Law but the dam affects the pattern of mixing of river water and sea water in estuary. The water flowing to estuary falls from the surface of the dam into the estuary system and then mixed evenly because of the dominance of sea water mass and without plume of river water flow in the estuary to the coastal waters.

The dam causes a change in the mass velocity of the water at the upper boundary of the dam to be small enough that the particle deposition becomes high. As a result, the transport and flux of the heavy particulate metal into the estuary reduced due to deposit with the particles. This indication is seen in data obtained from heavy particulate metal of Pb and Zn that high enough in the particles [26]. The change in the distribution of heavy metals showed a significant decrease in the concentration of particulate heavy metals. This is consistent with [27] which states that the behavior of heavy metals in waters is strongly influenced by the interaction between dissolved and particulate phases as well as

metals inputs. The same is revealed by [28] that the temporal and spatial distribution of heavy metal strongly determined by local hydrodynamics plays a role in the dispersion of metals.

Table 2. Pearson's correlation coefficient between Pb, Zn, clay, silt, sand, OC, Eh, and SPM in Jeneberang waters.

	Pb	Zn	Clay	Silt	Sand	OC	Eh	SPM
Pb	1							
Zn	.873[**]	1						
Clay	.209	.053	1					
Silt	.431	.441	-.144	1				
Sand	-.445	-.313	-.803[**]	-.475	1			
OC	.508[*]	.479	.390	.706[**]	-.772[**]	1		
Eh	-.659[**]	-.493[*]	-.618[**]	-.428	.807[**]	-.659[**]	1	
SPM	-.627[**]	-.465	-.689[**]	-.198	.732[**]	-.481	.909[**]	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

The turbulence led to sediment resuspension resulting metal desorption from the sediment to the water column. Consequently, there was an increased element concentration dissolved in the zone as compared to riverine. Sediment resuspension caused desorption or release of heavy metals from the particle surface to the water column [29]; [30].

The sediment resuspension effect depends on the condition of the water bottom. As an example, there was an increase of nitrogen level that abruptly emerged as a reaction of the trapped water in the sediment (interstitial water) with the water column. However, the amount released depended on the diffusion gradient of long-term period. Sediment resuspension with clay character can increase the oxidation in the sediment increasing the potential redox level and reduce the organic materials, however it does not expose to an increased nutrient and oxygen consumption significantly in the water column [29].

The pattern of Pb and Zn dispersion in the sediment was similar to that in the particulate form. The results showed that heavy metals in the sediment where the deposition results of a particulate element that was further accumulated on the sediment [21]. The higher Zn concentration compared with Pb was attributed to a naturally increased intake of sediment particles from soil erosion and rock weathering on the mainland as a consequence of Zn concentration higher in soil and rock naturally. The heavy metal dispersion concentration was influenced by the sediment characteristics and concentration of suspended particulate matter (SPM). This was demonstrated by a correlation analysis of metal concentrations in the sediment, sediment characteristics, and the SPM. A strong correlation was found, as shown in Table 2. Heavy metal concentrations in the sediment were not only dependent on rock weathering but were also influenced by sediment deposition, the redox status, the OC concentration, and sediment texture. The results showed that the levels of SPM had the strongest correlation with heavy metals dispersion concentrations than in order sand and Eh.

Pb and Zn concentrations in this study area were approximately lower than several locations of Indonesian waters as reported by [31]; [32]; [9]. However, the results found in this study were by that reported by [23] and the other studies [33]; [34]; [35]; [36]; [8]; and [37]. The comparison of heavy metal concentration in this study with other reports is shown in Table 3.

Table 3. Comparison of Pb and Zn concentration (mg.kg^{-1}) of surficial sediments from different locations in Indonesia and some part of the world.

References	Locations	Pb	Zn
The present study	**Jeneberang Estuary**	**0.24-4.33**	**38.73-113,19**
[23]	Coastal of Makassar City	0,38-2,58	0-107,49
[31]	Tallo Estuary	13.25-83,01	40.02-294,76
[9]	Kendary Bay	0.84-17.02	-
[32]	Coastal of Semarang	37.80	161
[42]	Bangka Island	5,79	16,70
[43]	Coastal of Gresik	1,74-12,70	77,3-405,0
[44]	Kelabat Bay	11,46	13,64
[45]	Angke Estuary of Jakarta	18,64-29,57	56,58-69,30
[33]	Coast of Bohai Bay	16- 49	75- 288
[34]	Guadalquivir River Estuary	30–54	69–190
[11]	Caspian Sea, Iran	7.13-13.00	26.95-28.00
[12]	Changjiang River	13.5–35.5	47.2–124
[35]	Yellow Sea	4.31–21.9	18.8–96.2
[36]	Quintero Bay Chile	17–36	65–167
[10]	Coastal of Abu Dhabi	1.9	8.2
[8]	Yangtze River Estuary	28	70
[37]	Near-shore, north Shandong Peninsula	11.0–26.3	40.5–89.8

3.2.   Speciation of heavy metals Pb and Zn

Speciation of heavy metals in sediment is very important to analyze as geochemically sediment condition expresses the process occurred in water column. The speciation of element could also be used as a basis to identify the source of element in aquatic environment. The speciation of heavy metals Pb and Zn from surface sediments of Jeneberang waters expressed as mean percentage is shown in Fig. 2.
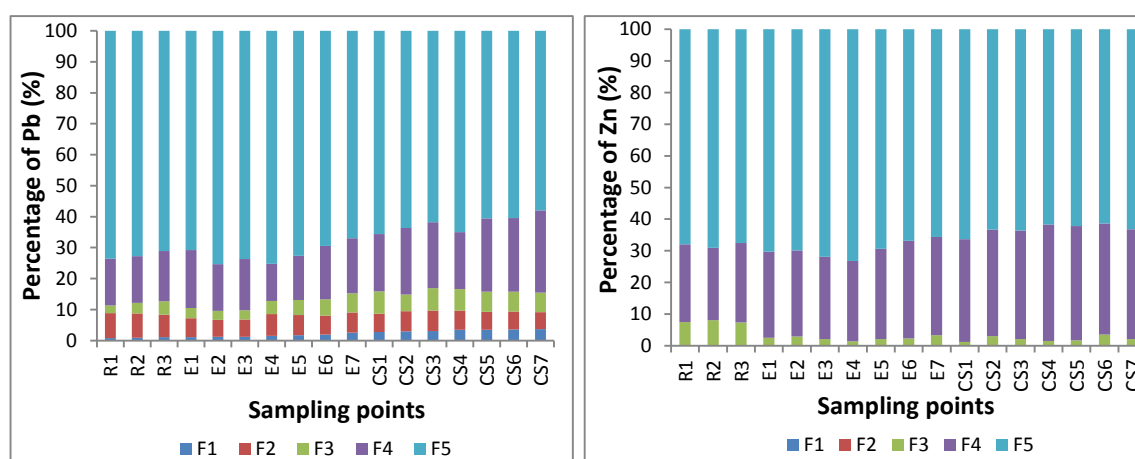
F1 (exchangeable), F2 (bound to carbonate), F3 (bound to Fe–Mn oxides), F4 (bound to organic), and F5 (residual)

Figure. 2 Percentage of speciation of Pb and Zn at Jeneberang waters

Measurement of total metal concentration is a fundamental aspect of sediment quality assessment. However, the metal fractionation in geochemical form is of crucial important that it had distinct mobility, migration ability, and chemical behavior. Therefore, sequential extraction procedure was proposed to study the strength and metal association with sediments [2]. The labile fraction of

exchangeable are weak structures and could be easily broken down by ion exchange so that it is high reactivity and mobility leading to high bioavailability. The fractions of organic are medium to high mobility, while the fractions of carbonate and Mn-Fe oxides are medium mobility that the structure could be broken down as the alteration of redox and decomposition. The resistant components comprise the non-labile fraction that can only be disrupted by strong acids.

Most of the Pb and Zn in surface sediments was strongly retained in the residual fraction. Our results indicate that the metals were strongly bound to the crystal lattices of minerals and thus had relatively low mobility, bioavailability, and toxicity. Therefore, the existence of this fraction in sediments is not harmful to organisms. The heavy metal complexes can be broken down when the sediments are decomposed [38]; [2]. The resistant fractions of Pb and Zn were found to be dominant in the study area, indicating that the main sources of Pb and Zn were from natural processes, such as rock weathering or soil erosion on the mainland and runoff entering the waters. The resistant components comprise the non-labile fraction that can only be disrupted by strong acids [39].

The small percentage of labile materials in the carbonate and exchangeable fractions found in this study indicated that the pollutant intake derived from human activity (anthropogenic sources) was lower than that from natural sources. This is by [38] and [40], who reported that the labile fractions associated with sediments commonly originate from anthropogenic sources, while the non-labile fractions commonly originate from natural processes. Even though, in the study area found potential metal intake from anthropogenic sources (presumably originating from seaport activities, transportation, the hospital, and industrial sites along the northern shore of the Jeneberang River estuary), however the stronger currents around the coastal area, the metals also tended to be present in the water column rather than deposited on the water bottom. The metals were considered to have been desorbed from the surface of the particles, due to the strong water turbulence. This is following [29] and [30], who both reported that sediment resuspension leads to elemental desorption into the water column.
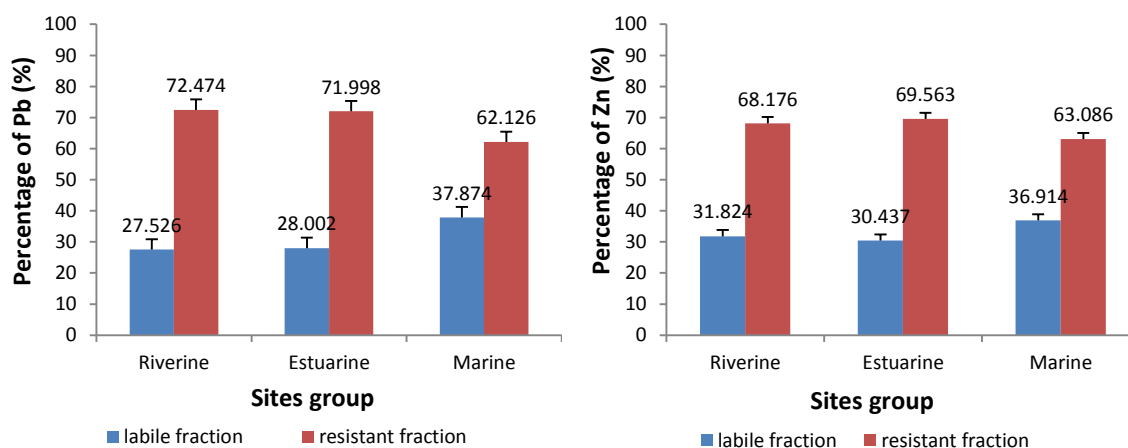
Figure. 3 The average percentage of geochemical fractionation (labile fraction and resistant fraction) of heavy metals Pb and Zn in based on sites group.

Most metals introduced by human activity are present in the exchangeable and carbonate fractions. The metals in the acid-soluble fraction are considered to be bound the weakest, and therefore the most mobile metals, in sediments and are defined as the exchangeable and carbonate fractions. Metals in these fractions have greater bioavailability. This situation poses a higher risk to the environment. The reducible (Fe-Mn oxide) and oxidizable (organic) phases act as a metal sink. The metals bound to these fractions can be mobilized by increasing/reducing oxidizing conditions in the environment [2].

Compare to the speciation in the natural ecosystem such as [23] classified the geochemical fractionation of samples around the Makassar coast as either acid soluble (exchangeable and carbonate fractions), reducible (Mn-Fe oxide fraction), or oxidizable (organic fraction). In their report, the mean percentages of Pb in the acid soluble, reducible, and oxidizable phases were 0–7, 64–78, and 16–33%, respectively. The mean percentages of the Zn fraction in the acid soluble, reducible, and oxidizable phases were 0–55, 39–100, and 0–25%, respectively. [46] reported that the Pb labile fraction from Jakarta Bay was dominated by the oxidizable (8.55–93.77), reducible (0.17–25.99%), and easily leachable and exchangeable phases (0–8.16%). Moreover, the percentage of Pb in the non-labile fraction ranged from 0 to 92.66%.

Table 4. Pearson's correlation coefficient between geochemical fractionation of Pb and Zn with sediment properties in Jeneberang waters.

		F1	F2	F3	F4	F5	Clay	Silt	Sand	OC	Eh	SPM
Pb	F1	1										
	F2	-.536[*]	1									
	F3	.906[**]	-.371	1								
	F4	.814[**]	-.535[*]	.638[**]	1							
	F5	-.929[**]	.434	-.841[**]	-.944[**]	1						
	Clay	.652[**]	-.473	.422	.796[**]	-.721[**]	1					
	Silt	.220	.133	.247	.046	-.162	-.144	1				
	Sand	-.712[**]	.341	-.524[*]	-.735[**]	.738[**]	-.803[**]	-.475	1			
	OC	.459	.013	.405	.433	-.500[*]	.390	.706[**]	-.772[**]	1		
	Eh	-.812[**]	.103	-.761[**]	-.680[**]	.820[**]	-.618[**]	-.428	.807[**]	-.659[**]	1	
	SPM	-.720[**]	.109	-.623[**]	-.588[*]	.700[**]	-.689[**]	-.198	.732[**]	-.481	.909[**]	1
Zn	F1	1										
	F2	.943[**]	1									
	F3	-.376	-.300	1								
	F4	.847[**]	.767[**]	-.625[**]	1							
	F5	-.842[**]	-.789[**]	.172	-.877[**]	1						
	Clay	.779[**]	.698[**]	-.219	.574[*]	-.595[*]	1					
	Silt	.071	.033	.000	.299	-.372	-.144	1				
	Sand	-.735[**]	-.640[**]	.194	-.690[**]	.753[**]	-.803[**]	-.475	1			
	OC	.373	.267	-.048	.491[*]	-.587[*]	.390	.706[**]	-.772[**]	1		
	Eh	-.801[**]	-.747[**]	.122	-.721[**]	.837[**]	-.618[**]	-.428	.807[**]	-.659[**]	1	
	SPM	-.775[**]	-.686[**]	.110	-.583[*]	.672[**]	-.689[**]	-.198	.732[**]	-.481	.909[**]	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

The speciation composition of the Mn-Fe oxide fraction in rivers is smaller (only 20%) than in estuaries with a composition of 80% found in waters without ecosystem disturbance [41]. In this study was found different, where the composition of Mn-Fe oxide fraction in rivers and estuaries is equal to heavy metal Pb, but on heavy metals Zn, the percentage of Mn-Fe oxide composition in rivers is greater than in estuaries. The high fractionation of Mn-Fe oxide in estuaries rather than in rivers because the estuary area is a high water mixing that increases manganese and iron oxides in water. The

Mn-Fe oxide fraction is higher than the organic fraction in rivers and will experience changes in composition when entering estuarine and coastal waters due to the complexity of the dynamics of the water masses in estuaries and beaches. Different things found in this study, the organic fraction has a higher composition than the Mn-Fe oxide fraction in the three aquatic regions (rivers, estuaries, and beaches). The presence of Mn-Fe oxides in sediments plays a very important role as it enhances the ability of sediments inbound heavy metals and naturally their content in high sediment/particle so that it is important to be fundamental in understanding the heavy metal geochemical processes in the sediments.

The correlations between the geochemical fractionation of Pb and Zn and the sediment properties are shown in Tables 4. The results of the correlation analysis indicated strong correlations between all the speciation and the sediment properties. The strongest correlation between speciation and sediment properties occurs in the sand, Eh, and SPM parameters. Analyzed by fraction was found the strong correlations between fractions F1 and F2 with clay, sand, Eh, and SPM. These fractions are weakly bound to surface of the sediments and depend on the physic-chemical parameters. The fraction F3 was strongly correlated with the Eh and SPM because this fraction was formed under reducing conditions. The fraction F4 was similar with fraction F1 and F2. This explains why OC which has not played a role in the formation of this fraction was distributed relatively homogenously throughout the study area. Fraction F5 was strongly correlated with the sediment texture and SPM because this component represents a chemical complex of metals in the crystalline mineral matrices within sediment particles.

3.3.   Pollution assessment of heavy metals

Toxicity unit, geoaccumulation index (Igeo) and risk assessment code (RAC) were applied to assess the potential toxicity acute, pollution level and environmental health risk of heavy metals lead (Pb) and zinc (Zn). Compared to the guideline values in China (GB 18668-2002), heavy metals contamination of Pb dan Zn in Jeneberang waters still under by Grade I at all sampling points, and it was categorized no polluted. The calculation of toxicity unit was obtained $\Sigma TU < 5$ indicating low toxicity level as shown in Table 5.

The range of the Igoe of Pb was 0.007-0.053, which was classified as weak pollution. The range of the Igoe of Zn was 0.775-1.273, which was classified as weak to moderate pollution. The RAC of Pb was 6.707-9.664, which was classified as a light risk. The RAC of Zn was 0-0.223, which was classified as no risk. The higher RAC of Pb indicated that the anthropogenic source of this pollutant was larger than that of Zn. The RAC of Zn was not a threat to aquatic biota because the majority of the Zn was in non-labile or residual fractions.

Table 5. Toxicity, Geoaccumulation index (Igeo) and risk assessment code (RAC) of Pb and Zn from surface sediments at Jeneberang waters

Sampling points	Toxicity Unit (TU)		Geoaccumulation Index		Risk Assessment Code (RCA)	
	Pb	Zn	Pb	Zn	Pb	Zn
R1	0.030	0.243	0.053	1.058	8.872	0.000
R2	0.028	0.270	0.050	1.174	8.722	0.000
R3	0.029	0.293	0.052	1.273	8.390	0.000
E1	0.004	0.178	0.007	0.775	7.252	0.000
E2	0.005	0.198	0.009	0.863	6.707	0.000
E3	0.009	0.187	0.016	0.813	6.837	0.000
E4	0.009	0.204	0.016	0.886	8.574	0.000
E5	0.013	0.203	0.022	0.884	8.285	0.000
E6	0.013	0.192	0.024	0.835	8.016	0.000

E7	0.014	0.203	0.026	0.885	9.115	0.114
CS1	0.015	0.204	0.028	0.889	8.664	0.115
CS2	0.018	0.194	0.032	0.843	9.439	0.143
CS3	0.021	0.221	0.037	0.962	9.664	0.085
CS4	0.028	0.267	0.050	1.161	9.661	0.106
CS5	0.024	0.241	0.044	1.048	9.284	0.136
CS6	0.022	0.220	0.039	0.957	9.348	0.209
CS7	0.020	0.212	0.036	0.922	9.136	0.223
∑	0.302	3.730				

4. Conclusions

Dispersion of metals was found higher in the riverine and marine samples than the estuarine samples. Following speciation, the metals were found similar composition of fraction in the riverine and estuarine samples but any different in the marine samples. These were indicated that the change of environment causes a change of dispersion pattern and speciation composition of metals due to the presence of the dam that lies at the boundary between the estuary and the river. There are potential hazards to environmental damage and marine biota caused by Pb due to the increased levels of this pollutant in the labile fraction in sediments along the coast of the Jeneberang waters, and this is a potential focus for future research and monitoring. This provides a strong indication that the source of anthropogenic heavy metal pollutants was mainly of the coastal waters and the potential level of pollutants of heavy metals Pb greater than heavy metals Zn.

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