

Original Study Article
**EVALUATION OF ENVIROMENTAL GEOCHEMISTRY OF
TRACE METAL POLLUTANT IN SEDIMENTS OF OUTLET
JENEBERANG RIVER, INDONESIA**

Abstract

The Jeneberang River flows between settlements, rice fields, traditional ports which are located in the southernmost part of Makassar. Regional development and increasing population are anthropogenic as a source of heavy metal input to rivers, and require a sustainable geochemical study of the environment. Study objectives, concentration and spatial distribution, use of sediment samples for grain size and Coupled Plasma-Osiloscope Emission Spectroscopy (ICP-OES) method for trace elements. The average yield of the seven river sediment samples was (Cr)149 mg kg⁻¹ (Mn)1388.14 mg kg⁻¹, (Cd)0.74 mg kg⁻¹, (Cu)54.71 mg kg⁻¹, (Zn)130.28 mg kg⁻¹, (Pb)3675 mg kg⁻¹.

The conclusion on the grain size of the sand, it is known that the order is dominated by concentration: Mn>Zn>Cr>Pb=Cu then changes to the grain size of silt clay: Mn>Cr>Zn>Cu>Pb, showing indications of migration, exchange phase and heavy metal enrichment. The order of heavy metal contamination uses the Igeo average value: Cd>Cr=Pb>Mn>Cu>Zn is class 1, namely $0 < I_{geo} < 1$ = not polluted to moderately polluted, and the order of heavy metal enrichment uses EF: Cu (0.64), Mn (0.58), Pb (0.56), Zn (0.73), Cd (0.41), Cr (0.55), generally $EF < 2$ is deficiency to minimal enrichment. It seems that the heavy metals in the minimum contamination and enrichment criteria which are strengthened by statistical analysis of correlation factors and multiple scatter are Pb and Zn.

Keywords : *Jeneberang river, trace metal, enviromental geochemistry*

1. Introduction

The supply of trace elements from the weathering of Lompobattang volcanic rocks, rapid population development, socio-economic and urbanization increase the concentration of metal elements in Jeneberang river, the concentration of Pb and Zn in Jeneberang derived mainly from rivers and natural sources [1], composition sediments of river sediments always been influenced by natural (geologic) and unnatural (pollution) factors [2]. Then trapped in the sediment of the river which is a collection of materials from the water media transportation [3]. The main carrier of heavy metals due to its chemical-physical properties [4][5][6]. Heavy metal contamination is a primary environmental concern in sediments [7]. However, a small amount of metal content in the form of free ions such as iron, manganese hydrous oxide [8] and most of it forms complex metals. Accumulation of heavy metals in sediment poses a long-term threat to the water environment [9].

This study used geo-accumulation sediment quality indicator (I_{geo}) which is considered to determine and compare the concentration of heavy metals in sediments and Enrichment Factor (EF) to distinguish between metals derived from anthropogenic and metal from natural procedures and to assess the level of anthropogenic influence [10]. Based on chemical fractions and multivariate analysis, the main purpose of this study is to investigate the concentration and spatial distribution of heavy metals Cu, Pb, Zn, Cr, Mn in the Jeneberang watershed. An assessment of environmental transformation processes depend on knowledge of the chemical speciation and partitioning of trace elements [11].

2. Materials and Methods

Study data collection on the Jeneberang River (Jnb) sediment was carried out during August 2019, or during the rainy to dry season [12]. Sediment sampling was taken from 7 test wells at a depth of 0.50 m and different distances between points (Figure 1).

The samples were dried using an oven at 80°C for two purposes, namely: (1) trace elements with *Inductive Coupled Plasma-Osiloscope Emission Spectroscopy* (ICP-OES) (2) grain size analysis. Samples were quartered and weighed with a weight of 100 grams per sample. Then sorting the grains using the sieve analyze method for 15 minutes, the grains are divided into class intervals which are limited by the size of the sieve openings to get a grain size classification.

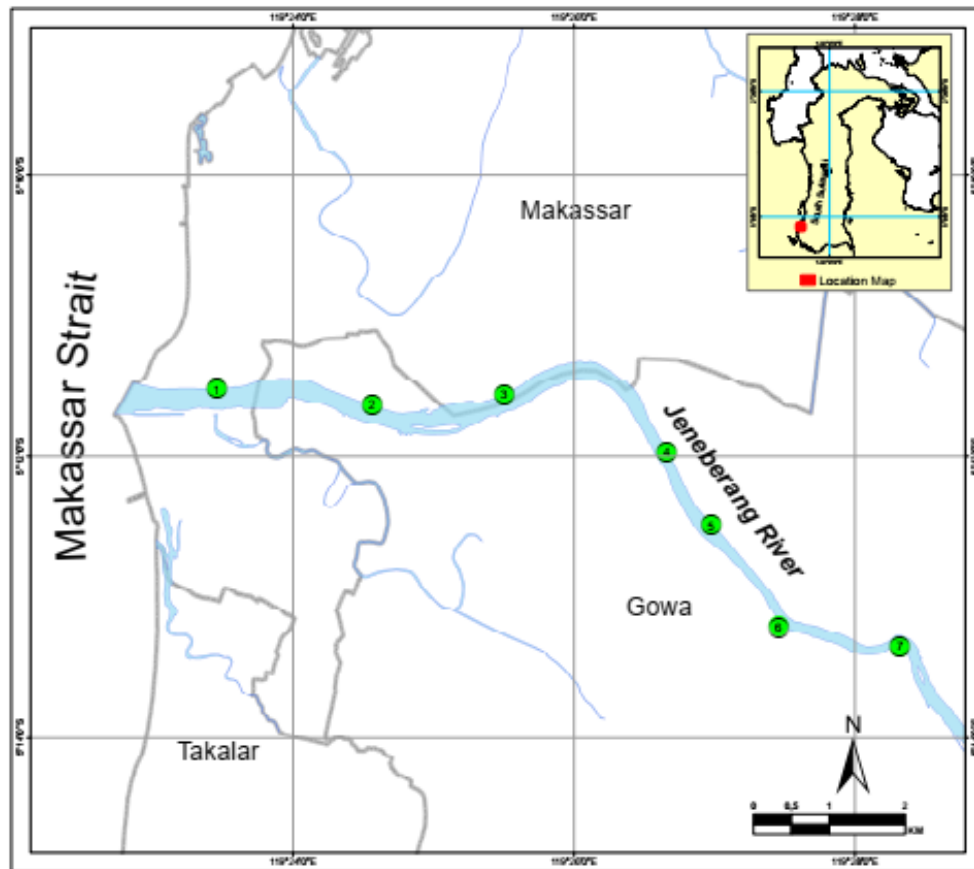


Figure 1. Map of the Study Area and location of Sampling Points

2.1 Statistical Analysis

To understand the geochemical study of the elements **Cr, Mn, Cd, Cu, Zn, Pb, in** sediment, it requires separation of data factor analysis and multiple scatter on statistical software SPSS IBM v.22 and STATISTICA v.10 for Windows.

3. Results and Discussion

3.1 Heavy Metal Concentration

Statistical description of heavy metals Cr,Mn,Cd,Cu,Zn,Pb at the same depth (between 0 and 0.50 m) are shown in table 1. Using SPSS v.25 for multiple regression on Cr, Mn, Cd, Cu, Zn, Pb. The correlation coefficient between Cd and Pb is 0.413, while the Cd and Cr variables are -0.499, Pb is bigger, Pb has an effect on Cd. Therefore it is defined as a heavy metal which only has a correlation of Cd, Pb, Cr with the dependent variable Cd and Equation ; $Y = 0.734 + 0.025 X_1 + 0.034 X_2$. Cd (average 0.7 mg kg⁻¹) may strengthen the influence of element Zn (average 130.28 mg kg⁻¹) which has similar chemical properties of transition metal. Although the predictors of Pb, Cr has a large effect on Cd but these three elements show a weak correlation (average R² <26%) caused by Pb can function as a predictor. The weak correlation of each element has different sources, Pb derived mainly from Jeneberang and natural sources [1]. The emergence of strong influence of Pb and similarity of Cr, Cd, Zn requires simplification of correlation between each element using analytical factors. To produce initial eigenvalues, there are two extraction factors of squared loadings, namely 2.17 and 1.73 with matrix components of Pb and Zn.

Table 1. Mean concentrations and their ranges of metals in sediment samples

Sampling Point	Metal Concentration [mk kg ⁻¹]					
	Mn	Cd	Cu	Zn	Cr	Pb
1	1810	0.61	42	203	284	20
2	747	0.73	37	79	55	36
3	1140	0.81	39	92	116	32
4	1400	0.81	72	112	90	45
5	1630	0.71	71	127	181	46
6	1590	0.83	51	182	200	32
7	1400	0.72	71	117	117	41
Median	1400	0.73	51	117	117	36
Average	1388.14	0.74	54.71	130.28	149	36
Min.	747.00	0.6	37.00	79.00	55.00	20.00
Max.	1810.00	0.8	72.00	203.00	284.00	46.00
Det.Lim	2	2	2	2	2	2
Average earth crust	770		39 50	67 75		14
Average Shale	850		45 33	95 95		19

3.2 Grain Size

Using multiple scatter statistics for the order of concentration marks the accumulation of heavy metal transport at each sampling point. The composition at sampling point 1 of sand (95.23%), silt (4.43%), clay (0.34%) and Mn> Zn> Cr> Cu> Pb. The composition at sampling point 2 of sand (64.96%), silt (32.26%), clay (2.78%) and Mn> Zn> Cr> Pb = Cu. The composition at sampling point 3 of sand (78.56%), silt (19.63%), clay (1.81%); Mn> Cr> Zn> Cu> Pb. The characteristics of sampling point 1, 2, 3 appear to be the dominance of the sand layer and the change in the percentage of silt clay illustrate the proportion of heavy metals on the migration ability which could have a more potential effect with

anthropogenic sources (Figure 2A). The only exception to sampling point 2 is the similarity of Cu, dominant in the exchange phase (exchangeable) of Pb and Cr, Zn at sampling point 3 significantly attached to the reducible silt.

The unstable fraction was strengthened by the dominance of silt at sampling point 4, sand (26.84%), silt (50.74%), clay (22.42%) where $Mn > Zn > Cr > Cu > Pb$, as a transition sampling point for heavy metal accumulation. The large proportion of heavy metals in silt, clay illustrates Cu, Pb and Cr, Zn gives a more potential effect due to its enrichment ability, immigrate to different fractions with stronger anthropogenic sources. Sampling point 5; sand (62.26%), silt (33.46%), clay (4.28%); $Mn > Cr > Zn > Cu > Pb$; sampling point 6; sand (74.27%), silt (24.36%), clay (1.37%); $Mn > Cr > Zn > Cu > Pb$; sampling point 7; sand (76.83%), silt (20.43%), clay (2.74%); $Mn > Cr = Zn > Cu > Pb$. The differences in the inverse properties of Cr, Zn shows a very low proportion weakly bound to the sediment, the enrichment transfer and reduction in the silt (Figure 2B). These elements are controlled by anthropogenic and Pb, Cu, Cr, Zn are reduceable elements thus dominating the silt in all sediment samples. The presence of Mn in sand, silt, clay is related to chemical properties that experience flocculation and deposition with other elements in aquatic conditions which can produce stable complex compounds, other redistributional processes and the early post-depositional diagenetic release and mobility of some elements [13]. The sand silt clay component illustrate that the influence of river sediment is more dominant by alluvial and coastal deposits than by the weathering of rocks (Figure 3).

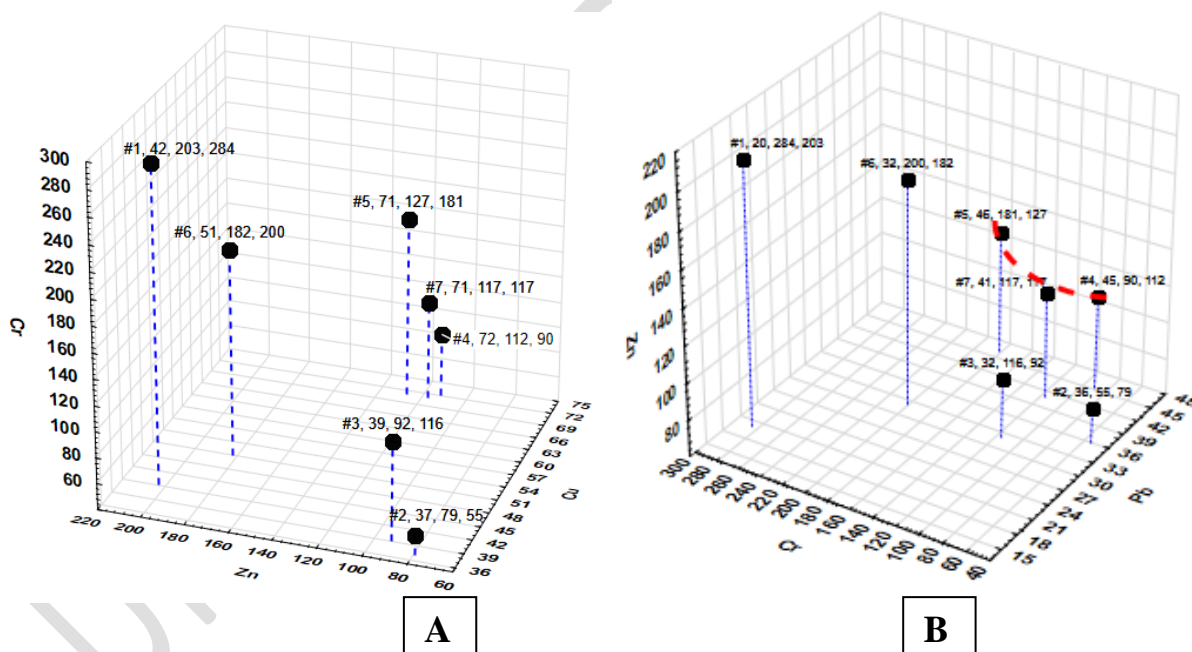


Figure 2. (A) Irregular grouping of Cr, Zn, Cu (B) Distribution of Zn, Cr, Pb linearity

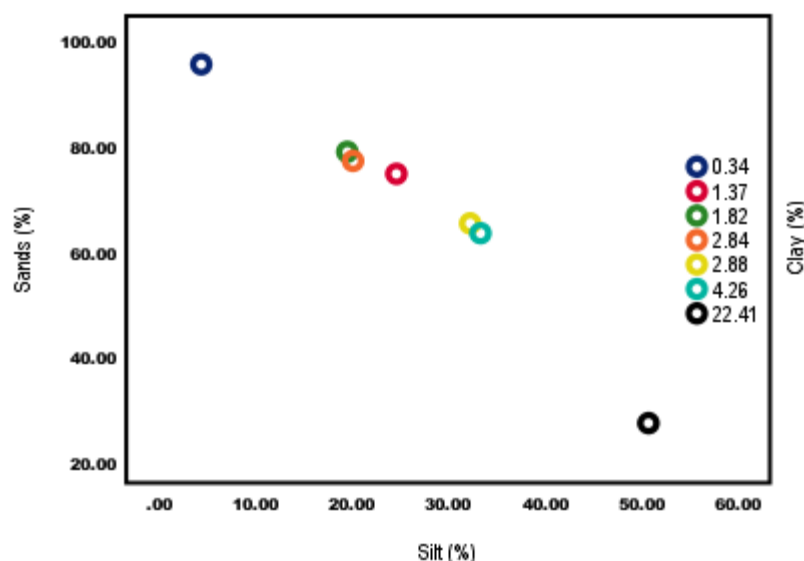


Figure 3. The sediment fraction undergoes an inverse

3.3 Level of Metal Contamination

The general assessment of river sediments using the geoaccumulation (Igeo) index and enrichment (EF) to assess the distribution and contamination of Mn, Cd, Cu, Zn, Cr, Pb. The geoaccumulation index of heavy metals by calculating the base 2 logarithm of the total metal concentration is calculated based on the background concentration using the following mathematical formula [14] :

$$I\text{-geo} = \log_2 (C_n/1.5B_n)$$

Where C_n is a measured concentration of metal (n) in sediment, B_n is the geochemical background value of the element n in the surrounding rock, but is not available then used the average value of shale [15] and 1.5 is the background matrix correction factor due to lithogenic effects [16][17]. The background values used in this study were in mg kg⁻¹: 82 for Cr, 810 for Mn, 35 for Cu, 95 for Zn, 0.3 for Cd and 20 for Pb. Based on I_{geo} data and Müller geoaccumulation ratings, the contamination levels for each metal are as follows: 0.32 for Cu, 0.35 for Mn, 0.38 for Pb, 0.26 for Zn, 0.51 for Cd, 0.38 for Cr. The order of average I_{geo} values is: Cd > Cr = Pb > Mn > Cu > Zn which is generally included as class 1, i.e $0 < I_{geo} < 1$ = unpolluted to moderately polluted.

Using EF as an approximate approach to metal concentrations in sediments which involves uncontaminated background values [10], normalizes the measured heavy metal levels (Cd, Mn, Pb, Zn, Cd, Cr) linked to sample reference such as Fe, Al or Zn [18]. EF of a heavy metal in sediment can be calculated by the following formula :

$$EF = (C_{\text{metal}}/C_{\text{normaliser}})/(C_{\text{metal}}/C_{\text{normaliser}})_{\text{background values}}$$

Where $(C_{\text{metal}}/C_{\text{normaliser}})_{\text{soil}}$ are the metal concentrations in the sediment sample and $(C_{\text{metal}}/C_{\text{normaliser}})_{\text{background values}}$ is the natural background of the heavy metals and normalising elements.

The Enrichment factors (EF) Cu (0.64), Mn (0.58), Pb (0.56), Zn (0.73), Cd (0.41), Cr (0.55) are generally $EF < 2$ is deficiency to minimal enrichment. Showing Zn's enrichment, Pb, indicates minimal enrichment that also groups equal to the I_{geo} value from unpolluted to moderately polluted. The concentration of all three elements in the sediments in the study area was not the only one affected by

weathering of volcanic lithology, alluvial sediments and coastal sediments. But other sources are more likely to be anthropogenic. Because the samples were taken near the activities of the people's port, the housing is quite dense, then Zn,Pb can be considered from the motor boat engine that burns leaded gasoline, residential waste residents.

4. Conclusions

1. All the heavy metals studied have accumulated significantly in sediments of Jeneberang River, the average concentrations of the seven points are Cr (149 mgkg⁻¹), Mn (1388.14 mg kg⁻¹), Cd (0.74 mg kg⁻¹), Cu (54.71 mg kg⁻¹), Zn (130.28 mg kg⁻¹), Pb (3675 mg kg⁻¹).
2. The sand fraction dominates the concentration of Mn> Zn> Cr> Pb = Cu and Mn> Cr> Zn> Cu> Pb and the percentage change in silt clay illustrates migration, the exchangeable phase, heavy metal enrichment, weakens Cr immigration and Mn flocculates so that the potential of Pb , Zn is getting stronger from anthhropogenic sources.
3. The Assessment of pollution level using geoaccumulation index shows Cd> Cr = Pb> Mn> Cu> Zn is a potential hazard to human activities. The enrichment factor (EF) Cu (0.64), Mn (0.58), Pb (0.56), Zn (0.73), Cd (0.41), Cr (0.55) generally EF <2 is deficiency to minimal enrichment. The enrichment of Zn, Pb which is strengthened by the statistical analysis of the correlation factor of the two elements and the multiple scatter statistic shows that the minimum enrichment is also equal to the Igeo value from unpolluted to moderate polluted.

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