Original Research Article

EVALUATION OF ENVIROMENTAL GEOCHEMISTRY OF TRACE METAL POLLUTANT IN SEDIMENTS OF OUTLET JENEBERANG RIVER MAKASSAR SOUTH SULAWESI

Abstract

The Jeneberang river flows between settlements, rice fields and traditional harbors located in the southernmost city of Makassar. Heavy metal data were obtained from seven points of sediment depth near the river, Cr,Mn,Cd,Cu,Zn,Pb were analyzed by using ICP-OES. The average concentration of the seven points is (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 Sand fractions dominate the concentrations of Mn>Zn>Cr>Pb=Cu and Mn>Cr>Zn>Cu>Pb and percentage change of silt clay illustrate migration, exchangable phases and enrichment of heavy metals from anthropogenic. The order of average Igeo value is: Cd>Cr=Pb>Mn>Cu>Zn which generally enters as class 1 i.e. $0 < Igeo < 1$ = unpolluted to moderated polluted. 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 Pb and Zn is strengthened by statistical analysis of correlation factors of the two elements and multiple scatter shows minimal enrichment that also groups equal to Igeo value from unpolluted to moderated polluted.

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 (Najamuddin et al,2016), composition sediments of river sediments always been influenced by natural (geologic) and unnatural (pollution) factors (Karbassi and Pazoki,2015). Then trapped in the sediment of the river which is a collection of materials from the water media transportation. (Miller *et al.*, 2003) The main carrier of heavy metals due to its chemical-physical properties (Fukue et al., 2006; Rath et al., 2009; Mur et al., 2017). Heavy metal contamination is a primary environmental concern in sediments (Nemati et al, 2011). The component of river sediments (Huang et al, 2020) as loose material serves as a trap (Huang et al, 2019) for dissolved and main particulate elements in octahedral structure of clay minerals. However, a small amount of metal content in the form of free ions such as iron, manganese hydrous oxide (Costa et al, 2016) and most of it forms complex metals. The exchange of ions with hydrogen ions and cation species, then enriched (Chappaz et al, 2008) by the influence of river system which is environmental pollutants (Dassenakis et al., 1998). Accumulation of heavy metals in sediment poses a long-term threat to the water environment (Duodu et al, 2016).

This research used geo-accumulation sediment quality indicator (Igeo) which is considered to determine and compare the concentration of heavy metals in sediments (Muller,1969 and Enrichment Factor (EF)) to distinguish between metals derived from anthropogenic and metal from natural procedures and to assess the level of anthropogenic influence (Huu et al., 2010). Based on chemical fractions and multivariate analysis, the main purpose of this research 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 (Farmer et al,1983).

2. Lithology

Regional geology of rocks exposed in the upstream of the Jeneberang River is a group of Lompobattang volcanic rocks, alluvium and coastal deposits (Sukamto and Supriatna, 1982). Consists of lithic tuff, Vitric tuff, basalt and andesite porphyry. It is dominated by plagioclase, pyroxene, opaque, quartz, volcanic glass, biotite and hornblende (Tonggiroh and Syam, 2019). The primary source of elements are igneous rocks of which silicates and aluminosilicates are the dominant compounds (Bowie and Thornton, 1985).

3. Materials AND Methods

The data collection was conducted in August, 2019 which was included in the eastern season, the dry season (BMKG) in the Jeneberang River (Jnb) of Makassar City. The sediment data collection of test well (0.3 x 0.3) with a maximum depth of 0.50 m, with a total of 7 sample stations at different distances (Figure 1). Samples were dried at a temperature of 80^{o}C by using an oven with the aim of (1) trace elements with Inductive Coupled Plasma-Osiloscope Emision Spectroscopy (ICP–OES) (2) grain size analysis. Samples were quartered and weighed 100 grams per station.

Grain sorting was carried out using the sieve analyze method for 15 minutes, the grains were divided into class hoses limited by the size of the sieve hole opening which are 2.36 mm, 1.18 mm, 0.6 mm, 0.425 mm, 0.3 mm, 0.15 mm, and from 0.15 mm (Pan).

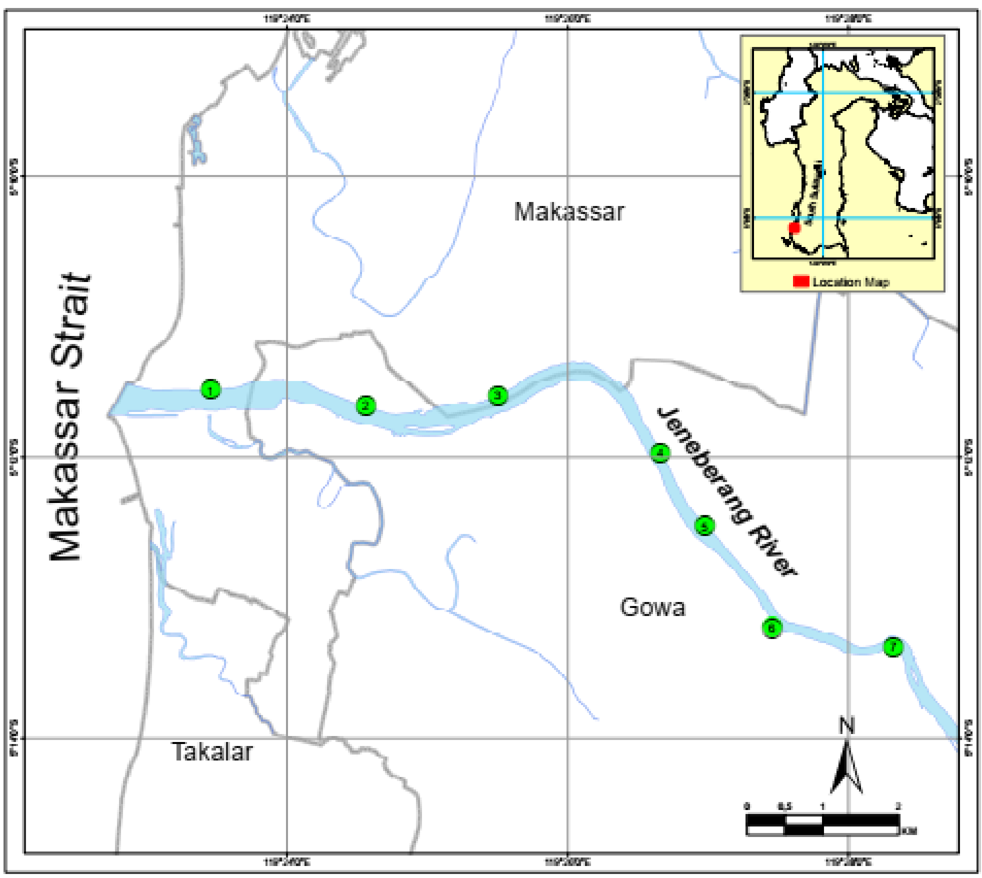

Figure 1. Map of the Research Area and location of Sampling Points

3.1 Statistical Analysis

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

4. Results and Discussion

4.1 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 by using SPSS v.25 for linear regression iteration on Cr,Mn,Cd,Cu,Zn,Pb is defined as heavy metals which only has correlation of Cd, Pb, Cr with dependent variables of Cd and Equations; $Y = 0.734 + 0.025 X1 + 0.034X2$. 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 R^2 <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 (Najamuddin et al, 2016). 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 [mk kg^{-1}] and their ranges of metals in sediment samples compared with other areas.

Stasion	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
Minimum	747.00	0.6	37.00	79.00	55.00	20.00
Maximum	1810.00	0.8	72.00	203.00	284.0	46.00
Det.Limit	2	2	2	2	2	2
Average earth crust	770		39 50	67 75		14
Average Shale	850		45 33	95 95		19

4.2 Grain Size

Using multiple scatter statistics for the order of concentration marks the accumulation of heavy metal transport at each station. The composition at station 1 of sand (95.23%), silt (4.43%), clay (0.34%) and Mn> Zn> Cr> Cu> Pb. The composition at station 2 of sand (64.96%), silt (32.26%), clay (2.78%) and Mn> Zn> Cr> Pb = Cu. The composition at station 3 of sand (78.56%), silt (19.63%), clay (1.81%); Mn> Cr> Zn> Cu> Pb. Figure 2A. The characteristics of station 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. The only exception to station 2 is the similarity of Cu, dominant in the exchange phase (exchangeable) of Pb and Cr, Zn at station 3 significantly attached to the reducible silt.

The unstable fraction was strengthened by the dominance of silt at station 4, sand (26.84%), silt (50.74%), clay (22.42%) where Mn> Zn> Cr> Cu> Pb, as a transition station 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. Station 5; sand (62.26%), silt (33.46%), clay (4.28%); Mn> Cr> Zn> Cu> Pb; station 6; sand (74.27%), silt (24.36%), clay (1.37%); Mn> Cr> Zn> Cu> Pb; station 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 (Farmer, 1991) . 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).

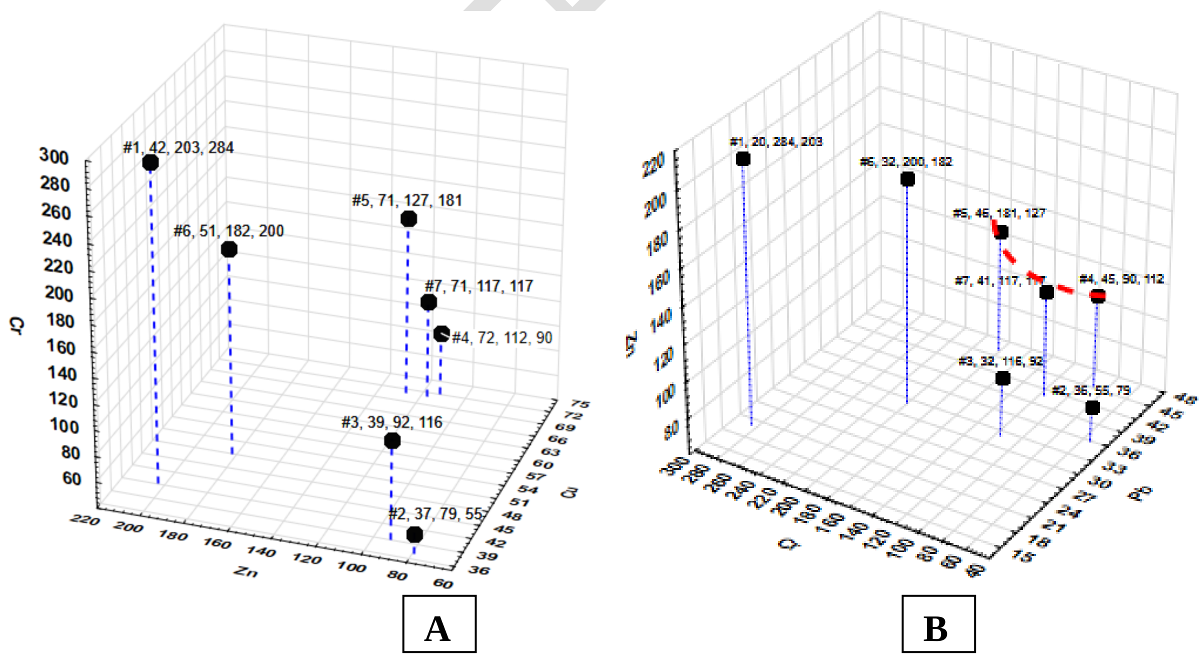

Figure 2. (A) Irregular grouping of Cr, Zn, Cu (B) Distribution of Zn, Cr, Pb linearity

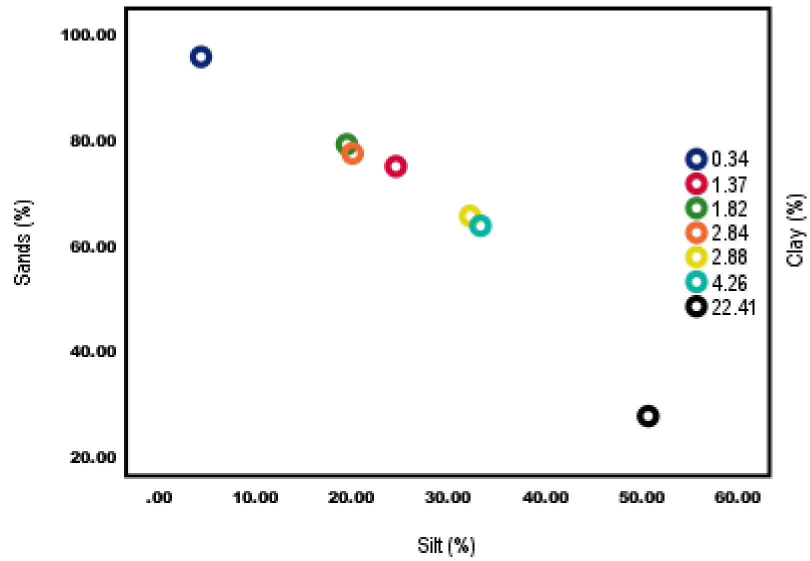

Figure 3. The sediment fraction undergoes an inverse

4.3 Level of Metal Contamination

The general assessment of river sediments using the geoaccumulation (Igeo) index (Muler, 1969) 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: (Muller, 1969):

$$\text{I-geo} = \log 2\ (Cn/1.5Bn)$$

Where Cn is a measured concentration of metal (n) in sediment, Bn is the geochemical background value of the element n in the surrounding rock, but is not available then used the average value of shale (Turekian and Wedepohl, 1961) and 1.5 is the background matrix correction factor due to lithogenic effects (Lin et al, 2008; Lu et al, 2009). The background values used in this research 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 g_{ao} 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 Igeo values is: Cd> Cr = Pb> Mn> Cu> Zn which is generally included as class 1, i.e 0 <Igeo <1 = unpolluted to moderated polluted.

Using EF as an approximate approach to metal concentrations in sediments which involves uncontaminated background values (Huu et al, 2010), normalizes the measured heavy metal levels (Cd, Mn, Pb, Zn, Cd, Cr) linked to sample reference such as Fe, Al or Zn (Mendiola et al., 2008). EF of a heavy metal in sediment can be calculated by the following formula :
EF=(Cmetal/Cnormaliser)/(Cmetal/Cnormaliser)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 Igeo value from unpoltaminated 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.

5. Conclusions

1. All the heavy metals researched 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 exchangable phase, heavy metal enrichment, weakens Cr immigration and Mn flocculates so that the potential of Pb , Zn is getting stronger from anthhopogenic 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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