Environmental Geochemistry of Heavy Metals and Plagioclase Background Enrichment Factor in Coastal Sediments at Lumpue - Parepare, South Sulawesi, Indonesia

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Abstract. Lumpue Beach is an urban area in Parepare Bay with a harbour, tourism, and a landfill site. The purpose of this research was to determine the provenance, level and distribution of heavy metals in coastal sediments. Surface sediment samples were analysed for grain size, mineragraphy, petrography and total heavy metal content (Cu, Zn, Pb, Co, Ni, Fe). The minimum-maximum background enrichment factor (EF) range was calculated from the plagioclase mineral content of trachyte porphyry and andesite. Weathering alteration was quite high in trachyte porphyry rocks; andesite mineragraphy produced predominantly sedimentary plagioclase (25-45%), hornblende (10-40%), and rock fragments (40-45%). The grab sampling method produced samples dominated by plagioclase (30-50%), hornblende (15-40%) and alkali chemical conditions were important in Fe, Ni, Pb, Cd, Cr, and Cu enrichment. Enrichment of heavy metals was supported by the mesokurtic-very leptokurtic dynamic sorting characteristics of Lumpue beach, becoming very leptokurtic - platykurtic to the north (Parepare Bay). The enrichment factor (EF) of Pb > 1 was calculated from the concentration of various non-earth sources. The order of heavy metal concentration based on EF 0.5 ≤ EF ≤ 1.5 was Pb> Zn> Cr> Fe> Cu> Ni, with Cu ≤ 0.5, indicating heterogeneous heavy metal sources correlated with urban area, river and ultrabasic regional lithology, with Trachyte-andesite alteration, especially enrichment in heavy metals Ni, Cr, Cu. Index of geoaccumulation (Igeo) was in the ranges: uncontaminated to heavily contaminated for Fe; uncontaminated to moderately contaminated for Cu, Zn, Ni, Cr and Cd; and uncontaminated for Pb. The intensity of heavy metal contamination followed the direction of sedimentation from various sources. Euclidian Cluster distance showed heavy metal distribution patterns correlated with rivers passing through urban areas and with regional geological lithology.

1. Introduction

As an urban area produces change in geochemical composition of coastal sediments, all activity has an impact on driving accumulation of non-organic as complex particles [1]. Parepare on the Makassar Strait coast of South Sulawesi, Indonesia, is a rapidly growing town situated in a bay which has long served as a harbour for fishing and trade. As this urban centre grows, the functions of coastal areas in and around Parepare Bay include human settlement, fishing, landfill and tourism. One impact from the anthropogenic activities in the area could be a degradation of the environmental geochemistry, as heavy metals released to the environment can react with seawater to
produce toxic compounds in both the water column and the sediment along the coast. Concentrations of pollutants, including toxic metals originating from both natural geological and anthropogenic sources, are deposited in sediments, where toxic materials will tend to accumulate [1,2]; when disturbed, clay sediments as well as coarse-fine sand can release heavy metals before resettling. Lumpue Beach in Parepare Bay directly faces the Makassar Strait, and is an area at potential risk of heavy metal contamination.

The purpose of this research was to determine the provenance, level and distribution of heavy metals in coastal sediments along Lumpue Beach in Parepare Bay. The approach used included the use of polarization microscopy to determine the provenance of heavy metal deposits trapped in clay sediment [3], as identified from the morphology of heavy metal mineral grains during precipitation. The heavy metals studied were Fe, Cu, Zn, Pb-Ni, Cr, Cd, selected based on their solubility and hydrochemistry [4].

2. Methodology

2.1. Study site
Parepare Bay is a small bay around 1.3 km long with an embayment depth of 296 m, on the western coast of South Sulawesi, Indonesia. Lumpue Beach is adjacent to the township of Parepare to the north and mangrove forests as well as urban areas to the south. This site (Figure 1) was chosen because it is in a catchment area for sand, clay, heavy metal, urban areas and is part of the Parepare volcanic arc with lithology comprising fine (ash) to lapilli tuffs, trachytic, basalt, and andesitic volcanic breccias [5], and Upper Miocene age rocks [6].

![Geological Map of Sulawesi](Image)

**Figure 1.** Geological Map of Sulawesi [6] showing the study area.

2.2. Sampling and sample preparation
Samples were collected using a PVC tube (diameter 60 mm) which was pressed into the coastal sediment as far as it could go (i.e. until a hardpan or solid substrate was encountered) to obtain samples of each sedimentary layer. This core was used for chemical analysis. A trench was then dug to
enable a visual observation and qualitative description of each layer. From the trench profile, structure and sediment direction could be determined. Sampling was carried out at four points (AT1, AT2, AT3, AT4) with two vertical samples (tube core and trench profiles) at each sample point (AT1 = H1A-H1B; AT2 = H2A-H2B; AT3 = H3A-H3B; AT4 = H4A-H4B), with a spacing of 350 m between stations. A further three samples of surface sediment (sand) were collected in the shallow offshore waters using a grab (AT5, AT6, AT7).

The wet weight of sand samples (150 g/station) was measured using a GF-200 digital balance. Each sample was then dried for several hours at 50°C. A dry sample of 100 g/station was spread out and separated based on particle size through sieving using an Automatic Sieve and Shaker CONTROLS Type D411. Sediment fractions of 2,000 µm, 1,000 µm, 500 µm, 250 µm, 125 µm, 62.5 µm and 2 µm diameter were obtained through sieving with mesh numbers 10, 18, 35, 60, 120, 230 and Pannin Concentrate (PAN). Particles within the sand size range (0.5 - 0.125 mm) were used to smear the slides. Dry weight was determined by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) with teflon tube digestive acid solution. All heavy metal concentrations were measured in units of ppm.

2.3. Sample analysis

Petrography was analysed descriptively base on visual observation and magnified photographs (Nicol //50x). Mineralogy was examined using an Eclipse Ci-L (Ci-L BF-BP) binocular microscope.

Grain size analysis was conducted at the Sedimentology Laboratory, Department of Geological Engineering, Faculty of Engineering, Hasanuddin University. A 50 g wet sample was dried directly under the sun (9 to 3 pm) at ambient temperature (20°C to 23°C) to separate the sand, silt and clay fractions. Semi-logarithmic grain size distribution curves were fitted to each sample, to determine the grain-size distribution type in term of kurtosis (KG) and described based on the classification of [7]. The texture of sediment components was analysed using ternary diagrams [8].

Interpretation of heavy metal concentrations followed the Enrichment Factor (EF) classification method described in [9]. This classification method divides heavy metal concentrations into 6 EF classes: (1) ≤ 1, background concentration (2) 1-2, Minimal enrichment (3) 2-5, Moderate enrichment (3) 5-20, Significant enrichment (4) 20-40, High enrichment (5)> 40 Very high enrichment. For each element and station, EF was calculated using the equation in [9]:

\[
EF = \left( \frac{C_x}{C_{ref}} \right)_{sample} \cdot \left( \frac{C_x}{C_{ref}} \right)_{background}^{-1}
\]

where

\[
C_x = \text{total concentration of trace elements}
\]

\[
C_{ref} = \text{element of reference contamination (Fe, Cu, Zn, Pb, Ni, Cr, Cd) originating from the coastal sediment layer}
\]

To complement EF, the geoaccumulation Index approach [9,10] to evaluating metal contamination levels was also used. The Igeo value for each element (metal) was determined using the equation:

\[
Igeo = \log_2 \left( \frac{C_n}{1.5x B_n} \right)
\]

where

\[
C_n = \text{concentration of the examined element (metal) in the sediment sample}
\]

\[
B_n = \text{background level of this element in the combined earth and crust geochemical reference (Table 1)}
\]

The geoaccumulation index distinguishes 7 classes of quality for sediments: Igeo ≤ 0 uncontaminated (class 1); 0 <Igeo ≤ 1 uncontaminated to moderate contamination (class 2); 1 <Igeo ≤ 2 moderate contamination (class 3); 2 <Igeo ≤ 3 moderate to heavy contamination (class 4); 3 <Igeo ≤ 4 heavy contamination(class 5); 4 <Igeo ≤ 5 heavy to very heavy contamination (class 6); Igeo ≥ 5 very heavy contamination (class 7). Igeo values were analysed to produce maps of contamination levels along the Lumpue Beach coastline.
Table 1. Igeo range values with geochemical background values based on multi-data earth crust, paleovulcanic and surface anthropogenic influences

| Layers | Fe (ppm) | Cu (ppm) | Zn (ppm) | Pb (ppm) | Ni (ppm) | Cr (ppm) | Cd (ppm) |
|--------|---------|---------|---------|---------|---------|---------|---------|
| H1A    | 0.596   | 2.027   | 0.981   | -0.816  | -1.217  | 0.504   | 0.662   |
| H1B    | 0.626   | 1.675   | 0.995   | -0.590  | -0.330  | 0.767   | 1.264   |
| H2A    | 0.716   | 0.770   | 1.009   | -0.700  | -0.171  | 0.782   | 1.398   |
| H2B    | 0.686   | 1.605   | 0.968   | -0.741  | -0.377  | 0.904   | 0.954   |
| H3A    | 0.730   | 1.605   | 1.038   | -0.700  | -0.421  | 0.767   | 1.264   |
| H3B    | 0.742   | 1.750   | 1.009   | -0.636  | -0.280  | 0.871   | 1.750   |
| H4A    | 0.651   | 1.814   | 0.954   | -0.700  | -0.543  | 0.700   | 1.264   |
| H4B    | 0.649   | 1.674   | 0.995   | -0.590  | -0.504  | 0.525   | 0.954   |

Cluster analysis was performed based on an Euclidean distance dissimilarity matrix for the eight sample sites in software Statistica v.10 and SPSS IBM v.25. The results were presented in tabular and graphic form.

3. Results

3.1. Petrography
Volcanic breccia was exposed on the surface and was covered by alluvial deposits which were composed of unconsolidated boulders, clay, silt, sand and gravel. The petrography of the volcanic breccia fragment consisted of basalt porphyry and porphyry trachyte, while the matrix was composed of volcanic material in the form of plagioclase, orthoclase, biotite, and pyroxene (Figure 2).

Figure 2. Coastal sediments sampled from Lumpue Beach in Parepare Bay: (A) Basalt Porphyry (B) Trachyte Porphyry. Pl = plagioclase; Bt = Biotite; Hbl = Hornblende (Nicol //50x)

3.2. Mineragraphy
The mineral composition of the eight sediment samples taken from Lumpue Beach (Table 2) was predominantly comprised of plagioclase, hornblende and rock fragments. Other components included biotite and opaque minerals. The source of these minerals was traced to the weathering of porphyry trachyte rock and porphyry basalt at sampling stations AT05 and AT07.
Table 2. Main components of the coastal sediment samples taken from Lumpue Beach, Parepare Bay

| Sample | Minerala (%) | Pl  | Hbl | Bt  | Op  | RkFrag |
|--------|--------------|-----|-----|-----|-----|--------|
| AT-01  |              | 45  | 10  | 5   | 0   | 40     |
| AT-02  |              | 30  | 40  | 0   | 5   | 45     |
| AT-03  |              | 30  | 25  | 0   | 0   | 45     |
| AT-04  |              | 25  | 30  | 0   | 0   | 45     |
| AT-05  |              | 40  | 30  | 5   | 15  | 10     |
| AT-06  |              | 30  | 40  | 0   | 5   | 25     |
| AT-07  |              | 50  | 15  | 5   | 5   | 25     |

a Pl = plagioclase; Hbl = hornblende; Bt = biotite; Op = opaque materials; RkFrag = rock fragments

3.3. Grain Analysis
The semi logarithmic grain size distribution curves (Figure 3) show a similar weight percentage of grain passing and grain size at stations AT1 to AT3, whereas at AT4 there is a 20% difference. The grain size distribution of sediments at stations AT5, AT6 and AT7 was relatively similar to that at station AT4, with a dominant grain size ± 0.51 mm, and was directly related to the sedimentation at the AT4 station. Sediment tended to accumulate around station AT4 then disperse towards the other stations.

The grain size shows continuity of kurtosis (KG). The mesokurtic-very leptokurtic and very leptokurtic-platykurtic types are characteristic of the western coast of South Sulawesi including Parepare Bay (Table 3). The dominant texture types at the sampling stations were very fine sand, sand mixed with sedimentary material and sand-sized sediment components.
Table 3. Sediment grain size distribution type at eight stations along Lumpue Beach based on the classification in [7].

| Station | Dominant type | Sorting (σ)               | Skewness (Sk)              | Kurtosis (KG)     |
|---------|---------------|---------------------------|---------------------------|------------------|
| AT1     | Coarse sand   | Moderately well sorted    | Very fine skewed          | Mesokurtic       |
| AT2     | Coarse sand   | Moderately well sorted    | Very fine skewed          | Leptokurtic      |
| AT3     | Coarse sand   | Moderately sorted         | Very fine skewed          | Very leptokurtic |
| AT4     | Coarse sand   | Moderately well sorted    | Fine skewed               | Mesokurtic       |
| AT5     | Fine Sand     | Very well sorted          | Very fine skewed          | Platykurtic      |
| AT6     | Fine Sand     | Very well sorted          | Very fine skewed          | Very leptokurtic |
| AT7     | Fine Sand     | Very well sorted          | Very fine skewed          | Platykurtic      |

There were differences in the content of sand, silt and clay at AT2, AT6 and AT7. The similarity in grain size for stations AT1 to AT3 was high: 76.34 - 79.63% passed the 1 mm sieve; 57.38 - 60.29% the 0.5 mm sieve; 40.75 - 46.50% the 0.25 mm sieve; 7.41 - 11.41% the 0.125 mm sieve; 5.35 - 10.39% the 0.063 mm sieve and 5.14 - 10.18% the 0.002 mm sieve. The percentage by weight of certain fractions passing the sieve increased at AT3 and AT4 (1 mm, 79.84%; 0.5 mm, 58.67%; 0.25 mm, 45.56%; 0.125 mm, 21.37%; 0.063 mm, 20.36%, 0.002 mm, 210.16%). The percentage of grain size 0.5 mm passing the sieves at stations AT5 to AT7 was on average 1.0%.

3.4. Enrichment Factor (EF)
Interpretation of heavy metals following the 6 class Enrichment Factor classification [9] was normalised using the Aluminium (Al) set of EF background values for several reasons: (1) Al is part of the plagioclase composition (2) Al is associated with solid earth (3) Al is generally mixed with trace metals (4) the Al set is appropriate when metal sources are quite diverse. Table 5 shows that the enrichment factor (EF) value > 1 for Pb is interpreted as a non earth crust concentration with various sources. The order of concentrations of heavy metals in the range EF 0.5 ≤ EF ≤ 1.5 was Pb > Zn > Cr > Fe > Cu > Ni, while for Cu EF ≤ 0.5. This order indicated changes in heavy metal concentrations correlated with rock weathering (Table 3).

Table 4. Heavy metal enrichment factors (EF) at Lumpue Beach in Parepare Bay

| Cu     | Zn     | Pb     | Cr     | Ni     | Fe     | Cd     |
|--------|--------|--------|--------|--------|--------|--------|
| Kurtosis | 6.985  | -0.744 | 0.955  | -0.390 | -0.436 | -2.063 | 0.415  |
| Minimum | 0.138  | 0.821  | 2.903  | 0.501  | 0.191  | 0.509  | 0.191  |
| Maximum | 0.591  | 0.899  | 3.654  | 0.832  | 0.297  | 0.602  | 0.667  |
| Skewness | 2.551  | 0.158  | 0.872  | 0.893  | 0.093  | 0.215  | 0.736  |

3.5. Geo accumulation Index (I geo)
The metal contamination levels based on the Index of geoaccumulation [9,10] are shown in Figure 4. The results show that the Index of geoaccumulation (Igeo) for the various elements varied considerably between sites (Figure 4). Geochemical background values (Table 1) indicate multiple sources, including natural weathering of earth crust, paleovulcanic and surface anthropogenic influences. The Igeo values for iron (Fe) ranged from uncontaminated to heavily contaminated, while for most elements the range was uncontaminated to moderately contaminated. For the element Pb, contamination above the (relatively high) background levels was not detected. Figure 4 also shows that the intensity of heavy metal contamination is related to the distribution of sedimentation arising from various sources.
Figure 4. Heavy metal contamination levels along Lumpue Beach in Parepare Bay based on index of geoaccumulation (Igeo) values: A. chrome, Cr; B: cadmium, Cd; C: lead, Pb; D: Nickel, Ni; E: iron, Fe; F: copper, Cu (Blue = class 1; green = class 2; yellow = class 3; orange = class 4; red = class 5)

3.6. Cluster analysis

Clusters of heavy metal distribution in the bottom layer (A) and the top layer (B) of coastal sediments show the Euclidian distance for each sample (Table 5). Contribution The horizontal distribution of AT1A, AT4A, AT4B located around layers 2B, AT2B, AT3B, shows different sources and layers of abrasion in the sedimentary layer. While the vertical distribution in the lower layer occurs at AT2B, AT1B, AT4B and correlates with the upper layer AT3A. The effect of heavy metal distribution along the coast reinforces the effect of heavy metal precipitation following the sedimentation pattern (Table 5).

Table 5. Heavy metal content dissimilarity matrix of Euclidian distances between the lower (A) and upper (B) layers of coastal sediments taken at four sites.

| Site  | 1:AT1A | 2:AT1B | 3:AT2A | 4:AT2B | 5:AT3A | 6:AT3B | 7:AT4A | 8:AT4B |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|
| 1:AT1A| 0      | 20.279 | 32.751 | 13.980 | 24.108 | 32.448 | 15.204 | 20.513 |
| 2:AT1B| 20.279 | 0      | 15.161 | 10.080 | 8.978  | 7.870  | 11.154 | 8.432  |
| 3:AT2A| 32.751 | 15.161 | 0      | 14.677 | 12.447 | 10.312 | 23.010 | 29.472 |
| 4:AT2B| 13.980 | 10.080 | 14.677 | 0      | 11.183 | 10.085 | 5.829  | 21.229 |
| 5:AT3A| 24.108 | 8.978  | 12.447 | 11.183 | 0      | 5.079  | 15.572 | 14.013 |
| 6:AT3B| 32.448 | 7.870  | 10.312 | 10.085 | 5.079  | 0      | 15.777 | 22.307 |
| 7:AT4A| 15.204 | 11.154 | 23.010 | 5.829  | 15.572 | 15.777 | 0      | 16.053 |
| 8:AT4B| 20.513 | 8.432  | 29.472 | 21.229 | 14.013 | 22.307 | 16.053 | 0      |

The cluster distribution diagram (Figure 5) shows the effect of wave-driven distribution of heavy metals. This diagram indicates that heavy metals which appear to originate from sources upstream from river estuaries are directly related to the lithogenic composition of the watersheds. Distribution cluster patterns follow the patterns of tidal rise and fall, with material originating around AT4A then from AT4B the contaminants seem to spread north with heavy metal concentrations occurring at AT2 and AT3.
Figure 5. Cluster distribution of heavy metals at the eight sediment sampling sites along Lumpue Beach, Parepare Bay

4. Discussion and Conclusion

Mineragraphy of the sediment samples was dominated by plagioclase (25-45%), hornblende (10-40%), rock fragments (40-45%) and for the grab samples by plagioclase (30-50%) and hornblende (15-40%). These mineragraphic characteristics show weathering and alteration in porphyry trachyte; andesite is quite valuable and can play an important role in Fe, Ni, Pb, Cd, Cr and Cu enrichment under alkaline chemical conditions. Enrichment in heavy metals is supported by the dynamic sorting characteristics of the mesokurtic-very leptokurtic Lumpue Beach sediment types which become very leptokurtic-platykurtic to the north of Parepare Bay.

The enrichment factor (EF) value of Pb > 1 was calculated from the concentration of various non-earth sources. The order of heavy metal concentrations based on EF (Pb > Zn > Cr > Fe > Cu > Ni > Cu) indicates the heterogeneity of heavy metal sources correlated with urban areas, rivers and regional lithology comprising ultramafic rocks and dacite alteration, specifically heavy metal enrichment in Cu [11], Ni and Cr [12].

The index of geoaccumulation (Igeo) shows the intensity of heavy metals following the direction of sedimentation from various sources. The range of Igeo classes was highest for Fe (uncontaminated to heavily contaminated), while apart from Pb (no detected contamination), the other heavy metal Igeo categories ranged from uncontaminated to moderately contaminated. The distribution of higher levels of contaminants appear to be related to the potential sources present as well as the sedimentation patterns. These sources include ports, urban centres, waste material (garbage) reaching the shore from the urban conglomeration as well as garbage brought to the area by water movements (waves and currents). Furthermore, there are several rivers that pass through urban areas flowing into Parepare Bay which contribute to an increase in the concentration of heavy metals that settle on the lower (A) and upper (B) layers of coastal sediments.
The Euclidian distance cluster shows that heavy metal concentrations are dominated by material transport from AT4 to AT2 and AT3. Heavy metal concentrations in AT4 correlate with several rivers that pass through urban areas but also relate to the regional and geological lithology. These results highlight the importance of obtaining data on natural background levels of elements (in this case heavy metals) in pollution studies, so that anthropogenic inputs can be distinguished from concentrations due to the natural environmental geochemistry, such as the relatively high background levels of lead (Pb) in the study area.

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