Enviromental Geochemistry of Bawakaraeng Mountain Soil:
Implication for Anthropogenic Impact Gowa South Sulawesi Indonesia

Adi Tonggiroh 1) Rafiuddin Syam 2)
1 Engineering Chemistry Lab, LBE Environment, Geochemistry, Engineering Faculty of Hasanuddin University, Indonesia
2 Mechanical Dept. Engineering Faculty of Hasanuddin University, Indonesia

the corresponding author’s e-mail: adi_unhas@yahoo.com

Abstract. Determination of heavy metal are done on Mount Bawakaraeng soil to find out the impact of anthropogenic, using range proximity matrix independent variables on camps, fired, garbage. There are two concentrated heavy metal zone and two particular zone (sample point 29, zone I; sample point 3 and 5, zone II) as concentrated heavy metal on rocks fractures, lavene statistic probability show the source of heavy metal Cr are different. Surface soil samples are taken on mapping variable, forest fires, especially for top and bottom of soil only garbage variable are taken. Furthermore, using Inductively Coupled Plasma Oscilloscope Emission Spectrometer (ICP-OES), X-Ray Fluorescence (XRF). Rock Samples analysis are done using thin section method on polarized microscope to find out the composition of volcanic minerals.

EF range are higher and lower than 2 are showing the enrichment of heavy metal are naturally formed and EF relatively moderate by human activities. (Igeo) camp are Cr (0.606), Cu (0,529), Mn (0.383), Zn (0.590) Cd (-0.779), Pb (0.440); fired are Cr (0.586), Cu (0.514), Mn (0.383), Zn (0.590), Cd (-0.770), Pb (0.447); garbage is Cr (0.584), Cu (0.461), Mn (0.343), Zn (0.579), Cd (-1.110), Pb (0.458). the difference of EF and Igeo value are affected by sample point 3,5,29 and indexes value 1.5 on volcanic rocks soil. Friedman test are showing relatively small differences between human activities and nature factor, which indicating that Bawakaraeng Mount morphology are easily affected by exogenic and endogenic factors.

Key Words : Bawakaraeng mountain, anthropogenic, heavy metals, proximity matrix.

1. Introduction
Heavy metal contamination are happened caused by anthropogenic interaction, precipitation of surface water [5], which accumulated on soil [12]. These factors are important on research location which composed by soil from parent materials [3] [14] [31]. Vulcanic having permeability properties, same porosity and different fractures quantity. The difference on fractures are caused by resistances of trachyte, andesite and volcanic breccia along with fault zone.

On volcanic rocks environment, heavy metal transported on surface following soil particles [2] [4] [9] [19] [24] [29] [32] [22], permeabilities, rock fragment size and concentrated. The metal content in soil is a sum of metals originating from natural processes and human activity. It is estimated that the contribution of metals from anthropogenic sources in soil is higher than the contribution from natural ones [13].
Study area located in south part of Sulawesi island on S $5^\circ16'30''$, E$119^\circ55'48''$; S$18^\circ18'7.2''$, E$119^\circ57'21.6''$; S$5^\circ19'15.6''$, E$119^\circ56'56.4''$; S$5^\circ19'15.6''$, E$119^\circ56'2.4''$; S$5^\circ17'9.6''$, E$119^\circ54'57.6''$ (see figure 1).

![Figure 1. Area of Research](image)

Mount Bawakaraeng are dominated by volcanic rocks, fault structures, fractures, and the mount becomes important as Jeneberang River upstream (current area of Jeneberang river). As tropical wet forest are having yearly average rainfall (1991 to 2000) 380.85 mm/yr, (2001 to 2010) 267.66 mm/yr and 270.80 mm/yr (2011 to 2017) (calculation of raw data from Meteorological Climatology and Geophysical Agency Pagentungan Unit Gowa Regency, South Sulawesi Indonesia), temperature range from 2$\degree$C to 6$\degree$C (before period of 2000 year) and 8$\degree$C to 14$\degree$C (after period of 2000 year) (fig 2).

Note from Tribunnews (2015), human activities are increase to thousands people per year, this causing the land clearing for camping, losses of soils layer, garbage and forest fires (figure 3).

This research is funded by Research and Community Services of Hasanuddin University. The samples are taken on March to May 2017 using methods of geochemist mapping, enrichment factors, ige and multivariate statistic as heavy metal concentrate determination on soils.

2. Regional Geology

Mount Bawakaraeng are part of south regional geology of mandala West Sulawesi, two mountain alignment which elongated relatively north to south, Mount Bone and Mount Lompobattang landscape. The two mountains are separated by Walanae Fault (Jaya, 2013) and Mount Bawakaraeng (2284 m asl)
as Pleistocene volcanic mountain with its cone called Mount Lompobattang (2874 m asl). In western side laid Mount Baturape with its height 1124 m asl and in northern lain Mount Cindako with its height reaching 1500 m asl.

![Figure 2. Rainfall data the Periods from 1991 to 2017](image)

3. Material and Methods
Using 31 soil samples which taken from camp sites, waste disposal and fires area, there are difficulties to determine distribution boundary location because the changes of soil surfaces by human activities. Sampling are done vertically on top layer and bottom layer 10 cm to 40 cm. Soil samples are dried and sieved to separate size < 0.062 mm using sieved machine in chemical engineering laboratory of Unhas Engineering Faculty, afterward packed in sample plastic bags then analyzed using ICP-OES, XRF.

The rocks which going to be analyzed are sliced and polished to 0.03 mm and 0.05 mm thick, placed on top of preparation glass to observe under polarized microscope in mineral optic laboratory of Geology department, Faculty Engineer, Hasanuddin University.

Geochemical data is consisting of major and minor element processed using hierarchy cluster proximity matrix statistic method and factor analyze on software SPSS IB v.22, Statistica v.10.

4. Geology Local
4.1. Geomorphology and drainage pattern
Geomorphology are grouped into 2 unit (fig 4).

- **Very Steeply Mountain Morphology**
  This morphology having percentage of slope 62.66% - 104.44% Scattering in southern and north northeastern of Bulu Bawkaraeng, Moncong Lompobattang, Bulu Porong, Bulu Baria, Bulu Ganting and Bulu Asumpolong.

- **Steep Mountain Morphology**
  This morphology having percentage of slope 25.86% - 38%. Scattering in northern of Jeneberang river area. Tanralili Lake and its Surrounding and on the western of Bulu Porong alongated to south.

  The slope are affecting rocks resistance, the increases of rainfall on layer of soil surface and human feet trace as early forming of rill erosion, gully erosion which irregularly formed on volcanic rocks morphology.
4.2. Lithology

**Vulcanic breccia.** Lithology of volcanic breccia fragment are consisting of phenocryst (plagioclase, peroxin, hornblende, biotite, opaque minerals) and base mass in form of microcrystalline plagioclase, **andesite porphyry.** Lithology of volcanic breccia matrix are consisting of (rock fragment, plagioclase, orthoclase, muscovite, biotite, volcanic glass, opaque mineral), **Crystal tuff.** Petrography of thin section (pyroxene, plagioclase, opaque mineral, crystallite plagioclase, and base mass glass), **Basalt Porphyry** (Travis, 1955). Petrography analysis on thin section (pyroxene, biotite, hornblende, orthoclase, plagioclase, opaque mineral, crystallite plagioclase and base mass glass), **Andesite Porphyry** and petrography analysis on thin section (plagioclase, pyroxene, orthoclase, biotite, opaque mineral, crystallite plagioclase and base mass glass, **Trachyte** (fig. 3).

Weathering processes modify the mineralogy, petrography (microfabric) and geochemistry of rock materials [26] (fig 5). Rocks fragment microscopic identification on volcanic breccia showing phenocry plagioclase minerals, pyroxene, hornblende, biotite ace equigranularity (A,B,C,E). Plagioclase crystallite (E) pyroxene crystallite (F), bad sortation on tuff (D) are showing this kind of rocks are easily affected by weathering. Increases of weathering degree are influenced by altitude [26]. Autochthonous of tuff type are easily weathered by climate changes from hot to cold, groundwater circulation and effect of some cynabacterial [17], the weathering residues forming silt and clay as association with Pb, Zn, Cr and Cu [1].
4.3 Structure Geology
Systematic joint in lithology of trachyte are analyzed using fan diagram which resulting greatest principal stress ($\sigma_1$) are relatively west north west – east southeast ($N285^\circ E$) and least principal stress ($\sigma_3$) relatively north northeast – south southwest ($N15^\circ E$) (fig. 6) which is impact of Walanae Fault to south [10].

**Bawakaraeng Strike Slip Fault.** The fault structure relatively elongated from Northeast to Southwest and cut across by Lompobattang Strike Slip Fault, which formed by pressure on volcanic rocks which relatively west northwest – east southeast with shifting relatively righting (dextral).

**Lompobattang Strike Slip Fault.** The fault structure relatively elongated from northwest to southeast. The fault structure and volcanic rocks fractures directly correlated on slope forming and landslide. Indirect correlation as tracking route, decreases of vegetation and surface erosion.
Figure 5. Micrograph photo of thinsection magnified 50x: (A) porhyry fragmen (B) porphyry basalt (C) trachyte porphyry fragmen (D) vulcanic breccia matrix (E) porphyry basalt (F) porphyry andesite (G) trachyte

5. Geochemistry

5.1 Index Geoaccumulation

Effect of metal concentration and contamination soil level are using Boxplot statistic and Geoaccumulation index and (Igeo) was originally stated by [16]. I geo is calculated as follows:

\[ I_{geo} = \log_2 \left( \frac{C_n}{1.5B_n} \right) \]

Where: 
- \( C_n \): Element concentration from soil samples (0.04 mm to 0.06mm), 
- \( B_n \): background value 1.5 (Muller, 1969).

Classification: Class 0 (\( I_{geo} \leq 0 \)) Practical Uncontaminated; Class 1 (0 < \( I_{geo} \leq 1 \)) Uncontaminated to Moderately Contaminated; Class 2 (1 < \( I_{geo} \leq 2 \)); Class 3 (2 < \( I_{geo} \leq 3 \)) Moderately to Heavily Contaminated; Class 4 (3 < \( I_{geo} \leq 4 \)) Heavily Contaminated; Class 5 (4 < \( I_{geo} \leq 5 \)) Heavily to Extremely Contaminated; Class 6 (\( I_{geo} > 5 \)) Extremely Contaminated.

Geo-accumulation Index (Igeo) Value for camp sample point are Cr (0.606), Cu (0.529), Mn (0.383), Zn (0.590) Cd (-0.779), Pb (0.440); fired are Cr (0.586), Cu (0.514), Mn (0.383), Zn (0.590), Cd (-0.770), Pb (0.447); garbage are Cr (0.584), Cu (0.461), Mn (0.343), Zn (0.579), Cd (-1.110), Pb (0.458).
Negative value results from Cd (-0.779; -0.770); (-1.110) indicated there are some soils yet Uncontaminated to Contaminated by heavy metal.

5.2 Enrichment Factor

Simplification to find out environment contamination, using Enrichment Factor (EF), such as are used to review contamination on various environment media [6] [8] [18] [33] [20].

\[
EF = \frac{C_x}{C_{ref}} \text{ sample} / \frac{C_x}{C_{ref}} \text{ background}
\]

Where \(C_x\) is the concentration total of trace element, \(C_{ref}\) is element reference contamination (Cr,Cu,Mn,Zn,Cd,Pb) from soil variable on sample point of garbage, fired, and camp site without anthropogenic references (Table 1).

Table 1. Enrichment Factor for heavy metals in three variables

| Variable | Cr(ppm)      | Cu(ppm)     | Mn(ppm)     | Zn(ppm)     | Cd(ppm)     | Pb(ppm)     |
|----------|--------------|-------------|-------------|-------------|-------------|-------------|
| Camp SD  | 0.377±1.2655 | 0.340±1.275 | 0.700±1.143 | 0.810±1.134 | 0.394±1.197 | 0.731±1.308 |
| Skewness | -1.294       | -1.651      | 0.134       | -0.261      | -2.052      | 0.282       |
| Kurtosis | 1.897        | 3.370       | 1.157       | -1.774      | 5.060       | 2.569       |
| Fired SD | 0.214±1.933  | 0.144±1.677 | 0.338±1.897 | 0.492±1.337 | 0.342±1.514 | 0.765±1.297 |
| Skewness | 0.04         | -0.292      | 0.204       | -0.680      | -0.590      | -0.171      |
| Kurtosis | -1.682       | -1.959      | -1.244      | -1.317      | -1.592      | 0.631       |
| Garbage SD | 0.375±2.660 | 0.299±2.657 | 0.622±1.779 | 0.869±1.195 | 0.521±2.065 | 0.709±1.384 |
| Skewness | 1.572        | 1.446       | 0.420       | 0.729       | 1.324       | 0.937       |
| Kurtosis | 1.603        | 1.702       | -1.205      | 1.826       | 0.684       | 0.297       |

There are average enrichment value on all variable which dominated by garbage>fired>camp where EF>2 states deficiency to minimal enrichment and EF 2-5 moderate enrichment.

5.3 Ranking

Chain model from 112 respondent on exogenous factor (human activities) and endogenous (weathering, water, climate, rock, slope, geology structure, vegetation). That square factor (R²) exogeneous value 92.1% and endogenous is 7.9% (Tabel 2).

Table 2. Variable effect on metal sources, Model Summary\(^b\)

| Model | R   | R Square | Adjusted R Square | Std. Error of the Estimate | Durbin-Watson |
|-------|-----|----------|-------------------|---------------------------|---------------|
| 1     | .959\(^a\) | .921     | .905              | 18.973                    | 1.474         |

\(^a\) Predictors: (Constant), water infiltration, properties structure, slope quantity, weathering intensity, resistence of rock; \(^b\) Dependent Variable: influence human

Table 3. Hypotesis on human activities

| Variable             | Mean Rank |
|----------------------|-----------|
| Human Activities     | 0.377±1.2655 |
| Properties Rock      | 19.54     |
| Structure Geology    | -1.294    |
| Slope Degree         | 1.897     |
| Climate Change       | 0.214±1.933 |

| Statistics Test      |    |
|----------------------|----|
| N                    | 25 |
| Chi-Square           | 65.787 |
| df                   | 4  |
| Asymp.Sig.           | .000 |
5.4 Distribution

Zona I. The lowest range proximity matrix (0.131) and the highest (0.967) are heavy metal concentration on the peak of Mount Bawakaraeng distributed to north of Bulu Sarongan. Particular sample 3 and 5, does not have effect on proximity matrix as distribution indication and heavy metal concentration on rocks fractures. Zone II (Fig.6).

![Figure 6. Zone of heavy metals distribution](image)

The lowest range proximity matrix (0.191) and the highest (0.886) indicated on sample 21, 19, 27 heavy metal concentration distributed to north of Bulu Sarongan, Bulu Sarobaia (Fig. 7).
Figure 7. Zonation distribution of heavy metal

Analysis One Way Anova are showing the average of heavy metal increases: Mn (629.42 ppm)>Cr (106.35 ppm)>Zn (74.13 ppm)> Cu (49.23) > Pb (49.80) > Cd (0.65 ppm). Minimum rate of Mn (213.0 ppm); Cr (22.0 ppm); Zn (38.0 ppm); Cu (7.0 ppm); Pb (33.0 ppm); Cd (0.19 ppm), and maximum are Mn (1210.0 ppm); Cr (198.0 ppm); Zn (103.0 ppm); Cu (86.0 ppm); Pb (80.0 ppm); Cd (1.06 ppm). Lavene Statistic probabilities value (0.00 < 0.05) are considered the heavy metal variants aren’t same and F value (1.34) are showing the source of heavy metal are significantly different especially Cr and Cd (Table 4).

Table 4. One Way Anova Analysis

| Element | Cr Ppm | Cu ppm | Mn ppm | Zn ppm | Cd ppm | Pb ppm |
|---------|--------|--------|--------|--------|--------|--------|
| Average | 106.35 | 49.22  | 629.41 | 74.12  | 0.64   | 49.80  |
| Max     | 198    | 86     | 1210   | 103    | 1.06   | 80     |
| Min     | 122    | 7      | 213    | 38     | 0.19   | 33     |
| Mean    | 106.35 | 49.23  | 629.42 | 74.13  | 0.65   | 49.80  |

Test of Homogeneity of Variances

| Statistic | df1 | df2 | Sig. |
|-----------|-----|-----|------|
| Lavene    | 75.346 | 5 | 0.00 |
| Multiple Comparison |
| Cr | Cd | 0.007 |
| Cu | Mn | 0.000 |
| Cr | Cu | 0.398 |
| Zn | Cr | 0.889 |
Squared Euclidean Distance garbage variable there are similarity on heavy metal distribution on sample 1, 6 and 8 with distance average (0.437) and on sample 2 (3.602). Fig 8a, show the forming of three cluster which are: (1, 2, 3, 7, 9, 12, 14); II (18.25) and III (5). On camp variable heavy metal distribution are showed on sample 22, 31, 29 (1.820) on sample 14 (2.470) with four cluster, which are: I (9); II (14, 18, 23, 24, 25); III (22, 29, 31) and IV (30), figure 8b. Fired variable are indicated by increasing of distance average value on sample 17, 20, 21 (2.280) and sample 4, 6, 17 (6.250) with four cluster, which are: I (4, 11, 12); II (6, 16); III (17, 20) and IV (2, 27, 28) on fig 8c.

Figure 8. Heavy metal distribution on (a) garbage (b) camp (c) fired

6. Conclusion
Increases of heavy metal Mn>Cr>Zn>Cu>Pb>Cd, that heavy metal source actually heterogonous enough on soil mainly heavy metal Cr (laven probabilistic = 0.00 < 0.05), this is could be caused by Cr having relatively constant mobilities. The difference value of range proximity matrix is showing that heavy metal distribution heterogeneously divided into two zone, indicated by changes of homogeneity to two zone heterogeneities that almost all camp, fired and garbage variable as soil sampling point are contaminated by human activities. The differences on EF and Igeo value, could be affected by homogeneity of sample point 3 and 5 (zone I), sample point 29 (zone II), and uses of background value on soils from weathered volcanic rocks. Friedman Test showing there are small differences between human activities and natural factor, showing that geomorphology of Bawakaraeng Mountain unstable enough towards the changes from exogeneous and endogenous.

References
[1] Adamo P.,Denaix L.,Teribile F, Zampell M.,2003.Characterization of Heavy Metas in Contaminated Volcanic Soils of the Solofrana river valley (southern Italy).Geoderma 117.346-366
[2] Adams, M., Zhao, F., McGrath, S., Nicholson, F., Chambers, B., 2004. Predicting cadmium concentrations in wheat and barley grain using soil properties. J. Environ. Qual. 33,532–541
[3] Alloway, B.J., 2012. Heavy Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability Springer
[4] Baize, D., Bellanger, L., Tomassone, R., 2009. Relationships between concentrations of trace metals in wheat grains and soil. Argon. Sustain. Dev. 29, 297–312
[5] Botte SE.,Freije,RH.,Marcovecchio,J.E.,2007.Dissolved Heavy Metal (Cd,Pb,Cr,Ni) Concentration in Surface Water and Pore Water From Bahia Blanca Estuary Tidal Flats.Bull.Environ.Contam.Toxicol.79,415-421
[6] Chester, R., Stoner, J.H., 1973. Pb in particulates from the lower atmosphere of the eastern Atlantic. Nature 245, 27–28.

[7] Flores V, L.M., Ducaroir, J., Jaunet, A.M., Robert, M., 1996. Study of the distribution of copper in an acid sandy vineyard soil by three different methods. Eur. J. Soil Sci.47

[8] Hernandez, L., Probst, A., Probst, J.L., Ulrich, E., 2003. Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. Science of the Total Environment 312, 195–219.

[9] Huang, M., Zhou, S., Sun, B., Zhao, Q., 2008. Heavy metals in wheat grain: assessment of potential health risk for inhabitants in Kunshan, China. Sci. Total Environ. 405, 54–61

[10] Jaya A,Nishikawa.2013.Paleostress reconstruction from calcite twin and fault-slip data using the multiple inverse method in the East Walanue fault zone:Implication for the Neogene contraction in South Sulawesi,Indonesia.Journal of Structural Geology.55.p.34-49

[11] Jimenez MS.,Osuna FP.,Fernandez ACR.,2003.Geochemical evidences of the Anthropogenic alteration of trace metal composition of the sediments of Chiricahueto marsh (SE Gulf of California), Environmental Pollution 125. 423–432

[12] Karimi A.,Haghnia GH.,Safari T.,Hadadian,2017.Lithogenic and anthropogenic pollution assessment of Ni, Zn and Pb in surface soils of Mashhad plain, northeastern Iran. Catena 157,151–162

[13] Loska K, Wiechula, Irena Korus,2004, Metal contamination of farming soils affected by industry, Elsevier

[14] Luo, L., Ma, Y., Zhang, S., Wei, D., Zhu, Y.-G., 2009. An inventory of trace element inputs to agricultural soils in China. J. Environ. Manag. 90, 2524–2530.

[15] Muller, G.,1969. Index of geoaccumulation in sediments of the Rhine River. Geo. J., 2, (3): 108-118.

[16] Nash DJ.,Laren SJ.,2007. Geochemical Sediments & Landscape,Blacwell Publ.1.173-199

[17] N’guessan, Y.M., Probst, J.L., Bur, T., Probst, A., 2009. Trace elements in stream bed sediments from agricultural catchments (Gascogne region, S-W France): where do they come from? Science of the Total Environment 407, 2939–2952.

[18] Oliver, D.P., Hannam, R., Tiller, K.G., Wilhelm, N.S., Merry, R.H., Cozens, G.D., 1994. The effects of zinc fertilization on cadmium concentration in wheat grain. J. Environ. Qual. 23, 705–711.

[19] Preston W, Silva Y J.A.B, Nascimento C WA, Cunha Karina PV,

[20] Silva DJ, Ferreira HA,2016, Soil contamination by heavy metals in vineyard of a semiarid region:An approach using multivariate analysis, Elsevier

[21] Tonggiroh.A , 2013.Application of Principal Analysis Component and Mobility of Heavy Metals in Mine Setting Ponds Nickel Laterite , Konawe North, Southeast Sulawesi. Advances in Environmental Biology, 8(22) , p. 461-467

[22] Tribunnews.com,17 Agustus 2015.

[23] Wang, C., Ji, J., Yang, Z., Chen, L., Browne, P., Yu, R., 2012. Effects of soil properties on the transfer of cadmium from soil to wheat in the Yangtze River Delta region, China—a typical industry—agriculture transition area. Biol. Trace Elem. Res. 148, 264–274.
[30] Wang, C., Wang, J., Yang, Z., Mao, C., Ji, J., 2013. Characteristics of lead geochemistry and the mobility of Pb isotopes in the system of pedogenic rock–pedosphere–irrigated riverwater–cereal–atmosphere from the Yangtze River delta region, China. Chemosphere 93, 1927–1935.

[31] Wei, B., Yang, L., 2010. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchem. J. 94, 99–107.

[32] Wu, J., Norvell, W., Hopkins, D., Welch, R., 2002. Spatial variability of grain cadmium and soil characteristics in a durum wheat field. Soil Sci. Soc. Am. J. 66, 268–275.

[33] Redon PO., Bur Thomas., Guiresse M., Probst JL., Toiser A., Revel JC., Jolivet C., Probst .A. 2013. Modelling trace metal background to evaluate anthropogenic contamination in arable soils of south-western France Geoderma, vol. 206 . pp. 112-122

Acknowledgments
We would like to appreciate any support by NVJT Foundation,Kosmik Unhas, BEM Economic Unhas, Mapala-PNUP-Kompas Sospol-Equilibrium-Panditas-Nobel-PAL;KPA-Reichas-Celebes-Kriyaw-Lontara-Wirpala, Primpungan Ana’Gowa.