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Geochemical assesment of heavy metals in postmining laterite nickel, North Konawe Southeast Sulawesi

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Abstract. This study aims to determine the concentration and migration of various heavy metals in soil texture. A total of 21 soil samples from Block A (12 samples) and Block B (9 samples), were inductively combined with ICP-OES methodology to determine the concentration levels of Mn,Cr,Ni,Fe,Zn and ICP-MS for Co,Pb,Cd in soil samples as toxic contaminants. The results showed I-*geo* indicated contamination levels that ranged from practically uncontaminated for Cd, uncontaminated to moderately for Pb, uncontaminated to moderately contaminated soil for Fe, moderately contaminated for Co,Zn,moderately to heavily contaminated For Mn,Ni , heavily contaminated for Cr. I-geo relationship and heavy metal concentration. Although Block A and Block Igeo have the same category, which is of concern are Cd and Pb, the concentrations of these two heavy metals are very small. Generally, Cd and Pb react chemically under acidic conditions, whereas lateritic soil is an alkaline oxide soil. Heavy metals Cr and Mn function freely to control the mobility of Fe, Co, Ni. And Fe only controls Co and Ni. While Pb, Zn Cd are included in the low mobility group or zero contamination. Multidimensional scaling statistics (MDS) for two-dimensional mapping in blocks A Mn, Co, Ni, Cr shows active mobility following the soil depth where the chemical function of Fe controls the mobility of Mn so that the concentration of Mn increases, three-dimensional mapping shows that Cr and Fe function to control the mobility of Co, Mn,Ni so that the concentration increases. Two-dimensional mapping in Block B, Cr and Mn functions freely to control the mobility of Fe, Co, Ni. And Fe only controls Co and Ni. While Pb, Zn Cd are included in the low mobility group or zero contamination, three-dimensional mapping is known to have active concentrations of Cr and Mn and control the mobility of Ni, Co, Fe.

1. Introduction

Since 2004, the management of nickel mines in the Motui area has been started using the open pit mining method. Currently, some of the mines have stopped operating due to the reason that laterite nickel reserves are not economical, which is followed by reclamation. This anthropogenic effect leaves topographical changes which of course will have a disturbance in the physical and chemical properties of the lateritic soil. After nickel mining leaves vacant land or post-mining land, there are other disturbances [1] on the land and soil [2].

Laterite soil is a soil residual from ultramafic weathering, which is a type of soil found in tropical and subtropical climates [3]. These soils are formed by tropical weathering of ultramafic rocks that show iron enrichment [4]. In the post-mining area of laterite nickel, there is waste overburden material which is composed of irregular lateritic soil layers and ultramafic outcrops resulting from mining stripping. Waste soil layers experience changes in soil geochemical quality features, chemical reactions determine

the mobilization and redistribution of elements in the soil profile [5], and high sensitivity to interactions with metals [6].

From the observation step on post-mining land, it is known that the land in the reclamation topography becomes unproductive or difficult to grow by vegetation. Metal concentrations in soil associated with vegetation are influenced by the type and mineralogy properties of the source rock and the process by which the soil is formed in the solid phase [7]. Fe and Mn oxides, hydroxides and hydroxides play an important role in controlling the mobility of other elements in post-mining land [8]. Changes in metal chemistry in soil include metal affinity, soil components and soil matrix [9]. This study aims to assess the concentration of heavy metals Mn, Cr, Co, Ni, Pb, Zn, Cd, Fe in post-mining nickel laterite land which will later be used as an evaluation for remediation on unproductive soils.

2. Research Area
Geographically, the research location at the coordinates is located at 121º40'0'E; 3º10'16" S; 121º49'0" E, 3º10'16"S; 121º40'0" E, 3º20'4"S; 121º49'0", E and 3º20'40"S and are administratively located in North Konawe Regency Southeast Sulawesi Province.
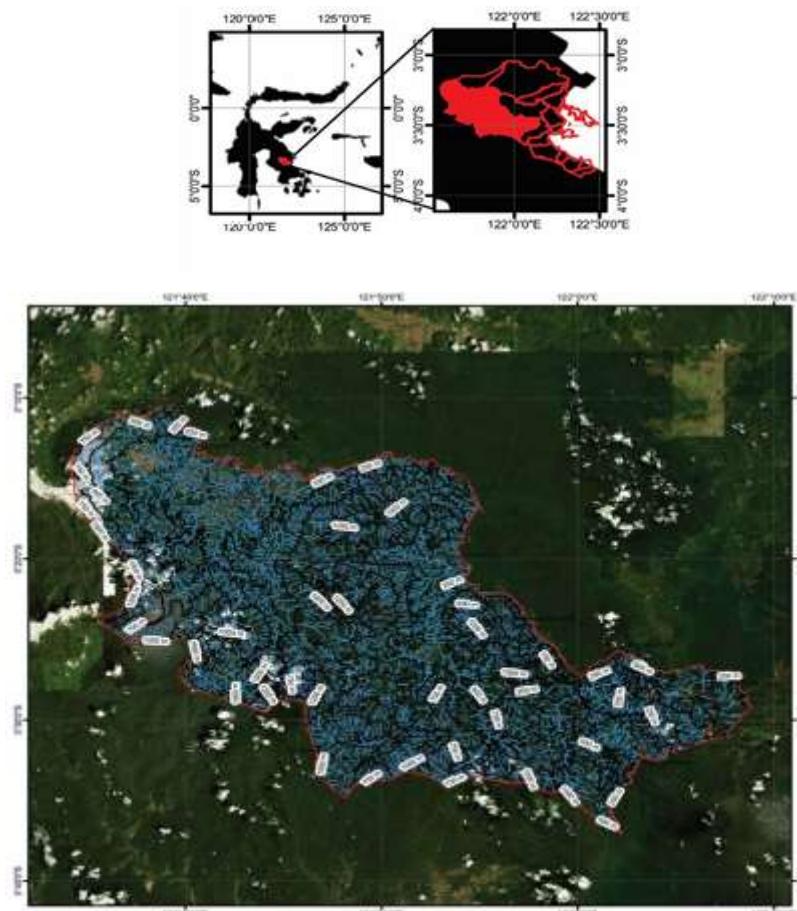
Figure 1. Research Area

3. Methods
Observations of the research site showed that ultramafic homogeneity was the source of nickel laterite, so a simple random sampling method was applied in area A (no vegetation) and area B (there is vegetation). Determination of sampling points selectively and strategically targeted to estimate the direction of heavy metal concentrations using the judgmental soil sampling method, soil samples were taken at a depth of (0 – 20cm), using a hand drill. Preparation of soil samples, starting with cleaning of

plant residues, then stirred until evenly distributed, put in a plastic bag and stored at 4ºC. Furthermore, the analysis of soil quality and heavy metal concentrations was carried out using ICP-OES (Inductively Coupled Plasma-Optically Emission Spectrometry), ICP-MS (Inductively coupled plasma mass spectrometry) and XRF (X-Ray fluorescence).

4. Results and Discussion
The geochemical characteristics of heavy metals in laterite soils depend on their mobility, immobility, acidity, stability, instability, ionic changes and the formation of toxic compounds. Although it requires a long time of interaction of heavy metals with oxygen, hydrogen is slightly accelerated by anthropogenic, changes in topography reclamation and changes in ground water table.

4.1 Soil Properties
Soil samples A01,A02,A03 are representative samples of heavy metals MM01,MM03,MM05 and B04, B05, B06 part of MM07; 09; 11 (Table 1). The lateritic soil texture in areas A and B, shows the same class but there is a difference in decreasing the sand content (37 to 7%) increasing clay soil (19 to 37%), while the silt content is increasing (29 to 73%). This indicates that the porosity and permeability of the soil are not good and will further affect the decline in soil fertility and productivity.

Table 1. Soil texture in area A (index A) and area B (index B)

No	Texture (%)			Class
	Sand	Silt	Clay	
A01	29	33	37	Clay-clay
A02	7	63	30	Dusty clay
A03	8	73	19	Dusty clay
B04	7	70	24	Dusty clay
B05	37	29	34	Clay-clay
B06	15	65	19	Dusty clay-clay

The entire research area has a pH value range with an acidic status (5.45 to 5.92), the low pH value indicates the level of soil acidity affects the solubility of soil nutrients. An increase in pH in acidic soils can increase the availability of macronutrients and reduce the solubility of Al and Mn elements, if the pH is lower, the amount of Fe and Mn will dissolve in large quantities.

In area A, the content of C-Organic A(0.66%), N-Total (0.05%) was lower than in area B (1.72%), N-Total (0.49%). This difference is that the penetration and leaching of rainwater affect the nature of the element nitrogen which is easily lost in the soil and the lowest base saturation value is 19% with very low to very high status with a value of 31% and has an average value of 26.24% so that the soil fertility of area A is lower than area B. It is indicated that leaching by rainwater involves a large number of cations of limonite mineral base on lateritic soils.

4.2 Total Metal Concentration
Table 2, is a statistical description of the heavy metals in the study area. Mn concentration, greater than the threshold value 250 – 4400 mg/l, nickel mining complex 3500 mg/kg [10], < 400 mg/kg [11]. Skewness and positive kurtosis indicate maximum concentration starting from the soil surface, increasing slowly in area A, in area B Mn actually decreases (Figure 2A).

The decrease in concentration is associated with Fe [12], possibly by soil solution disturbances which are limited by the slope of the topography Cr > threshold value 50 mg/kg,Australia,250 mg/kg, Canada, 150 – 300 mg/kg, China;500 mg/kg;Germany,100 mg/kg,Tanzania;180 mg/kg, Netherland; 290 mg /kg, New Zealand;11 mg/kg, USA [13-18]. Skewness and kurtosis showed the active mobility of Cr by rainwater or surface water run off then dissolved and precipitated. In Figure 2B, it is also seen that the trend of similar mobility in all areas is limited by the characteristics of soil absorption, where the

texture of dusty clay is more in area B. Soluble and unabsorbed chromium is in the form of Cr(VI) which then dissolves into groundwater. The leachability of Cr(VI) increases with increasing soil pH [19].

Table 2. Statistics of heavy metal concentration in the study (all elements in ppm   concentration, except Fe in %)

Elements	Min	Max	Mean	Skew	Kurt
Mn	2950.00	8130.00	4347.27	1.987	4.630
Cr	5310.00	17200.00	11070.00	-0.021	-1.529
Co	509.00	944.00	697.55	0.429	-1.063
Ni	6840.00	11900.00	8801.82	0.734	-0.462
Pb	1.00	12.00	3.82	2.069	4.497
Zn	233.00	385.00	290.91	0.799	-0.084
Cu	56.00	102.00	74.09	0.553	-0.430
Cd	.04	0.25	0.1200	0.624	0.223
Fe	22.60	39.10	29.0000	0.697	-0.774

Co > soil threshold value 1.6 – 16 mg/kg [13]. Figure 2C, the distribution of Co area A tends to increase controlled by Mn, and actually decreases in B, which is supported by skewness and kurtosis. Co has slightly more mobile chemical properties than Cr, Ni which reflects the absorption on the soil surface and organic matter in the soil texture.

Ni > the threshold value of regulatory standards of heavy metals in agricultural soil, namely Ni : 60 mg/kg, Australia; 100 mg/kg, Canada; 40 – 60 mg/kg, China; 200 mg/kg, Germany; 100 mg/kg, Tanzania; 100 mg/kg, Netherlands; 160 mg/kg, New Zealand; 230 mg, UK; 72 mg/kg, USA [13], [14], [15], [16], [17], [18]. The peak pattern of the graph (Figure 2D), that Ni is controlled by Mn, Cr, Co which is supported by skewness and kurtosis, but slightly different in the Ni area A pattern is controlled by Co.

Pb > lower than 300 mg/kg, Australia; 200 mg/kg, Canada; 80 mg/kg, China; 1000 mg/kg, Germany; 200 mg/kg, Tanzania; 530 mg/kg, Netherland; 160 mg/kg, New Zealand; 200 mg/kg, USA [13], [14], [15], [16], [17], [18]. The Pb mobility pattern resembles Mn, Co, Cr (Figure 2E) that the control between heavy metal mobility reflects the character of soil texture and the presence of plants. This mobility property is supported by positive skewness and kurtosis, heavy metal Pb has a stronger effect in area A compared to area B. Pb compounds are suppliers of heavy metals needed by plants, and the nature of these compounds increases significantly in soil [22]. The exact physiological function of Pb in soil is unknown and the addition of phosphate fertilizer has the potential to poison the soil [21].

Zn > threshold value 200 mg/kg, Australia; 500 mg/kg, Canada; 200 – 300 mg/kg ,China; 600 mg/kg,Germany;150 mg/kg,Tanzania;720 mg/kg,Netherland;1100 mg/kg, [13], [14], [15], [16], [17], [18]. Skewness and Zn kurtosis Normal distribution in all areas. Indicates that Zn mobility is controlled by all heavy metals, except in area B only controlled by Cr (Fig. 2F). Soil contamination increases through surface runoff, irregular soil accumulation and the addition of agricultural materials [20], the Zn content in fertilized soil only reduces nutrients for plants [21].

Cd is positive and normally distributed at values < 0.35 ppm. This indicates that Cd is maximally concentrated vertically (Figure 2G). The concentration of Cd increases in soils containing clay, silt associated with Fe and Mn [7]. Cd is a supplier of heavy metals needed by plants, and the nature of this compound increases significantly in the soil [22].

The exact physiological function of Cd in soil is unknown and the addition of phosphate fertilizer has the potential to poison the soil (Sumner, 2000). Heavy metal Fe < threshold value Fe: 5.6 – 50,147 mg/kg [13], its skewness and kurtosis showed that Fe had a positive value, normally distributed and had the same distribution pattern in all areas (Figure 2H).
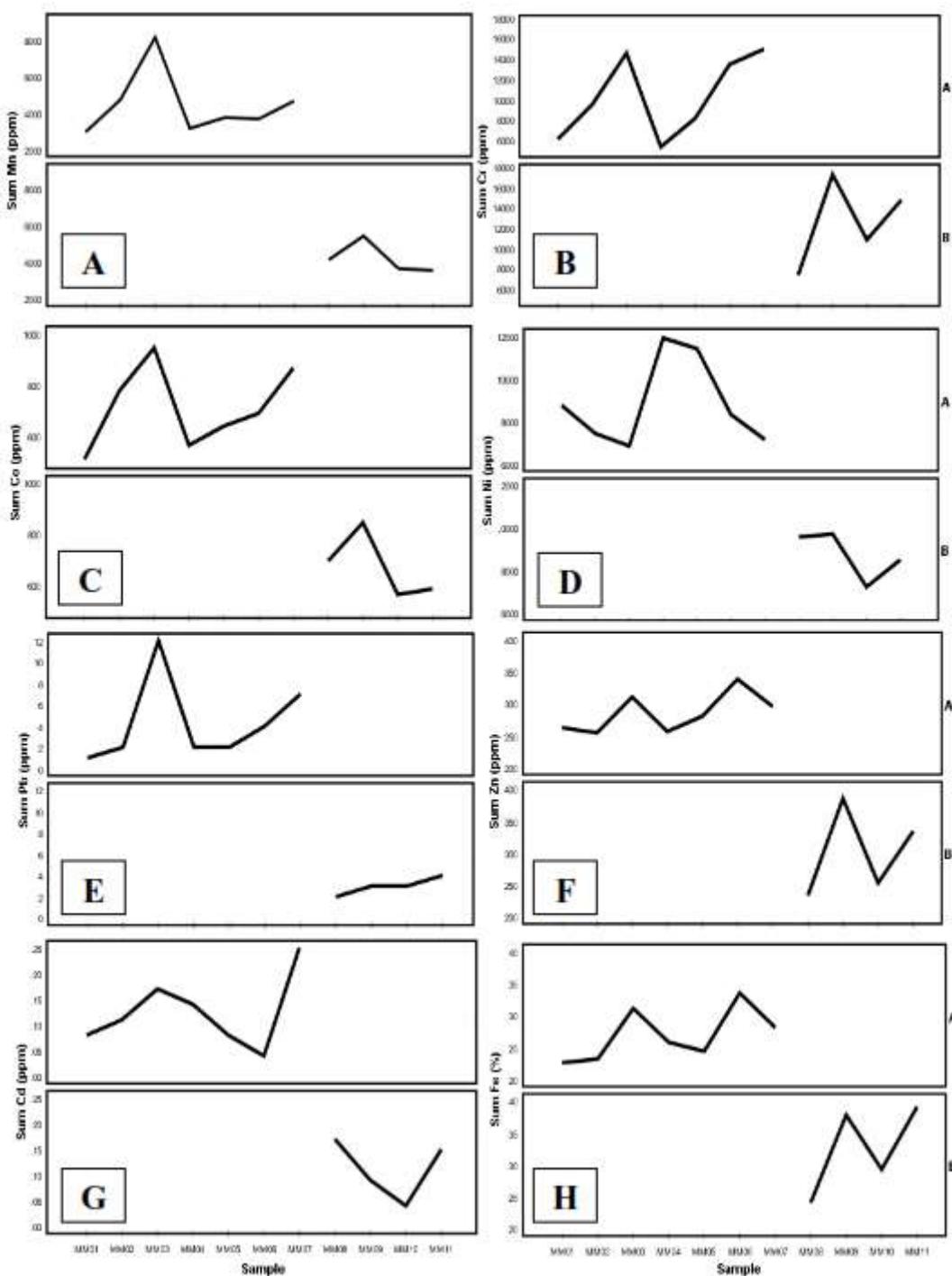
Figure 2. Line graph of I*geo* sum heavy metals vs sample in areas A and B

4.3 Principal Component Analysis

4.3.1 Igeo; The heavy metal index in the study area uses the value of the geo-accumulation index (Igeo) calculated for different metals using the Mullers equation, namely: Igeo = log2 (Cn/1.5Bn) Where: Cn = measured concentration of element n in the sediments, Bn = geochemical background for the element. Here are seven geoaccumulation index classes, as follows: Class 0 = Igeo <0 (practically uncontaminated); Class 1= 0 < Igeo < 1 (uncontaminated to moderately contaminated); Class 2 = 1 < Igeo < 2 (moderately contaminated); Class 3 = 2 < Igeo < 3 (moderately to heavily contaminated); Class

4 = 3 < Igeo < 4 (heavily contaminated); Class 5 = 4 < Igeo < 5 (heavily to extremely contaminated); Class 6 = 5 < Igeo (extremely contaminated).

The similarity of Igeo area A and B, that heavy metal contamination is in class 2 and 3, indicates the occurrence of physical degradation of the soil which accelerates the mobility of heavy metals. Except for Pb,Cd (practically uncontaminated), the mobility of these two heavy metals is hampered in an alkaline geochemical environment and the soil texture tends to be bound by Fe.

Table 3. Igeo statistics of heavy metals

	Igeo								
	Mnx	**Crx**	**Cox**	**Nix**	**Pbx**	**Znx**	**Cux**	**Cdx**	**Fex**
MM01	2.196	2.509	1.433	2.669	-1.096	1.321	0.658	-2.193	0.257
MM02	2.400	2.702	1.616	2.597	-0.795	1.307	0.673	-2.055	0.268
MM03	2.637	2.888	1.701	2.562	-0.017	1.394	0.852	-1.866	0.395
MM04	2.225	2.452	1.477	2.802	-0.795	1.311	0.748	-1.950	0.314
MM05	2.299	2.636	1.531	2.783	-0.795	1.350	0.741	-2.193	0.290
MM06	2.292	2.854	1.564	2.646	-0.494	1.432	0.795	-2.494	0.428
MM07	2.394	2.900	1.664	2.580	-0.251	1.372	0.748	-1.698	0.351
MM08	2.343	2.592	1.568	2.708	-0.795	1.270	0.651	-1.866	0.285
MM09	2.462	2.962	1.653	2.714	-0.619	1.488	0.911	-2.142	0.480
MM10	2.291	2.760	1.478	2.586	-0.619	1.306	0.778	-2.494	0.369
MM11	2.277	2.894	1.494	2.657	-0.494	1.426	0.857	-1.920	0.495
max	2.637	2.962	1.701	2.802	-0.017	1.488	0.911	-1.698	0.495
min	2.196	2.452	1.433	2.562	-1.096	1.270	0.651	-2.494	0.257
avg	2.347	2.741	1.562	2.664	-0.616	1.362	0.765	-2.079	0.357

4.3.2 Heavy Metals Factor; The correlation of heavy metals to contamination requires analysis of their associations, using factor analysis will provide some information about the distribution and strengthen the indication of the type of heavy metal pollution.

Factor analysis was carried out by evaluating the principal component analysis and calculating the eigenvalues, starting with 3 unrotated factors and apparently only producing 1 factor, namely Mn (0.819), Cr (0.934), Co (0.828), Pb (0.808), Zn (0.702), Cd (0,359), Fe (0,867), Mn I*geo* (0,09), Cr I*geo* (0,105), CoI*geo* (0,09), Pb I*geo* (0,101), Zn I*geo*(0,003), Cd I*geo* (0,03), Fe I*geo* (0.08) Then proceed to rotated 2 factors and the main with varimax at loading values> 0.7 for various metals is presented in Table 4.
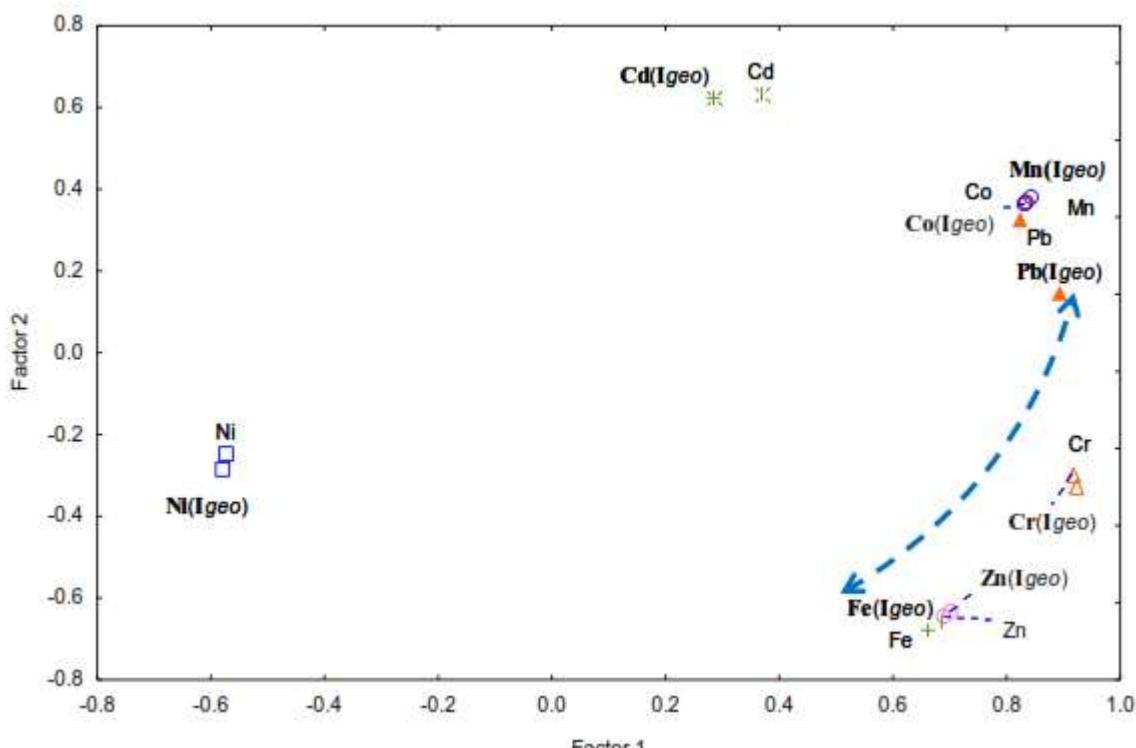
Table 4. Factor loadings for varimax rotated PCA of metal data in soil samples (bold loadings are statistically significant)

Parameters	Factor - 1	Factor - 2
Mn	**0.874335**	0.263601
Cr	0.485765	**0.849275**
Co	**0.888332**	0.262102
Ni	-0.595308	-0.188390
Pb	0.837410	0.286620
Zn	0.102018	**0.939738**
Cd	0.692177	-0.240028
Fe	0.059803	**0.946420**
Mn(I*geo*)	**0.874335**	0.263601
Cr(I*geo*)	0.501236	**0.821081**
Co(I*geo*)	**0.868408**	0.266830

Parameters	Factor - 1	Factor - 2
Ni($Igeo$)	-0.625804	-0.162702
Pb($Igeo$)	**0.771868**	0.470260
Zn($Igeo$)	0.117417	**0.937101**
Cd($Igeo$)	0.622891	-0.286019
Fe($Igeo$)	0.090015	**0.945857**

Factor 1 accounted for 54.481% of the total variance, had a high load on the elements Mn and Co paired with Mn(Igeo) and Co(Igeo), indicating a strong influence of heavy metal mobility on the texture of dusty clay. While factor 2 explained that about 21.994% of the total variance was composed of Cr, Zn, Fe and paired with their respective Igeos. This factor indicates the contribution of metals is a source of reduced C-organic content in the soil.

Figure 3, the distribution of heavy metal pairs in factor 1 and factor 2, shows two groups, namely: (1) Mn, Co and (2) Fe, Zn where Cr forms an exponential pattern (dotted blue line) which is a heavy metal whose mobility lies in in both groups. Except Ni and Cd are not part of the contamination.


Figure 3. Correlation of factor 1 and factor 2

5. Conclusion and Recommendation

The low content of organic C and acidic pH affects the ability of the soil to maintain soil fertility and productivity through the activity of soil microorganisms. The dusty clay fraction shows the slow formation of granulation in the soil and especially in the formation of stable soil aggregates. Low C-organic reduces the stimulation of root growth so that plants will be disturbed which reduces soil fertility.

The pattern of heavy metal data in this study shows that the concentration of heavy metals in soil can be used as a strong geochemical guide for remediation, especially post-mining land bioremediation. However, it should be noted that the geochemical background values used are guided by rock

homogeneity and soil texture. The soil quality test in the study area was classified as silty clay sand, which is a chemical property of hydro-hydroxy oxidized soil which is weathering of ultramafic rocks.

Soil texture properties have been influenced by anthropogenic activities, especially the reclamation stage in which the soil is piled up gradually or randomly. As a result, soil aggregates are low and the vertical distribution of metal concentrations increases which causes the accumulation of heavy metals to be higher than the threshold values set by several countries. The geochemical conditions of heavy metals Mn, Co, Fe, Zn, Cr were associated with variations in soil pH, which tended to be more acidic in soil samples.

Acknowledgments

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