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Fractionation of Metals in Soil Surrounded Gold Mine at Phichit Province Using a Continuous-flow Sequential Extraction

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Abstract

Fractionation of metals is the important information to predict the mobility and bioavailability of metals in the environment. These data is used to estimate the degree of metals contamination. The main purpose of this study is to investigate the fractionation of Aluminium (Al), Cadmium (Cd), Copper (Cu), Iron (Fe), and Zinc (Zn) in soil surrounded gold mine at Phichit province using a continuous-flow sequential extraction. A five-stage sequential extraction procedure was performed to compare various fractions of these metals in different soil sample. These results showed that mostly metals at different direction and distance were from natural source except Cu, Fe, and Zn in soil at the route of L1-L3-L10. Their enrichment factor was higher than 1 indicating the anthropogenic source from human activity. Furthermore the fractionation of five metals except Zn could be divided into two groups affecting by transportation of gold mine. Considering Cu and Fe distribution, Cu fractionation at L1, L3, and L10 was contributed in water soluble and exchangeable phase whereas it was mostly occurred in oxidizable phase at R1, R3, R10, and C100. Therefore Cu at L1, L3, and L10 was more potentially labile into environment than others. However Fe fraction of both groups was mainly associated in residue phase indicating immobile or very stable.

Keywords: Fractionation, Metals, Soil, Gold mine, Continuous-flow sequential extraction

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1. Introduction

Fractionation of metals in soil is the important issue for metals contamination. Metals in soil as the natural or anthropogenic form can be transported to environment depending on their chemical speciation and solubility. For example Lusilao-Makiese and co-worker [1] showed that 91 -95% of Hg species in soil at gold mine creek, Gauteng, South Africa was nonsoluble indicating less transport Hg was found to affect in the site. Yin and his group [2] presented that Pb, Zn and Cu was predominant found in residue fraction while Cd existed in various fractions followed by: well-crystallized iron oxyhydroxides-associated > residual > reducible > exchangeable > organic-associated in soil around the mining area, Guangdong province, China. Therefore the order of mobility of these metal in the site was Cd > Pb > Zn > Cu. Moreover the toxicity of metals in soil is affected by their chemical formation rather than their total amount. For example Huang and co-worker [3] showed that Cd content in soil around mining area, Beijing, China highly exhibited in acid soluble indicating easily mobile Cd was promoted the water quality problem at Miyun Lake, which is located approximately 80 km northeast of Beijing. Carvalho and his group [4] presented that the proportion of As in oxy-hydroxide fraction was more than of Sb for soil contaminated by old Sb-Au and As-Au mines, Portugal. It was demonstrated that the toxicity of As was higher than Sb in all soil studied. Generally a continuous-flow sequential extraction procedure using a series of chemicals with increasing strength is a widely used method to study metal fractionation because of its speed, ease of operation, high extraction efficiency, free from contamination, and also less degree of readsorption of metals in soil [5, 6]. This procedure is realized as a useful way to provide the occurrence, bioavailability, potential mobility and transport of metals. In this research this method was applied to study five metals including Al, Cd, Cu, Fe, and Zn fraction in soil surrounded gold mine at Phichit province. These metals such as Cu and Zn are known as non-biodegradable and accumulate in plant and animal tissues [7].

The purpose of this study was described 1) the Enrichment Factor (EF) for Al, Cd, Cu, Fe, and Zn content in soil surrounded gold mine at Phichit province and 2) the fractionation of metals in soil surrounded gold mine at Phichit province using a continuous-flow sequential extraction. These results will give the information of the origin of metals as natural or anthropogenic source and their potential mobility in soil surrounded gold mine at different direction and distance.

2. Materials and Experiment

2.1 Soil samples

Six sites surface soil surrounded gold mine and one control surface soil was collected using hoe and spade. Each two of these six sites were far from gold mine 1, 3, and 10 km, respectively whereas one control surface soil was far from gold mine 100 km as uncontaminated soil. Details of all samples were described as followed:

L1: far from gold mine 1 km (left)

L3: far from gold mine 3 km (left)
L10: far from gold mine 10 km (left)
R1: far from gold mine 1 km (right)
R3: far from gold mine 3 km (right)
R10: far from gold mine 10 km (right)
C100: far from gold mine 100 km

All samples were placed in labeled polyethylene bags for transport to the laboratory. Soil samples were dried using oven at 100°C, overnight, ground, and sieved before extraction.

2.2 Extraction reagents

A five-stage sequential extraction procedure (modified Tessier extraction scheme) [8] was performed using a continuous-flow system as the following solutions:

Step I (Water soluble): Deionized water
Step II (Exchangeable): 0.01 M magnesium nitrate ($Mg(NO_3)_2$)
Step III (Acid soluble): 0.11 M acetic acid (CH_3COOH)
Step IV (Reducible): 0.1 M hydroxylamine hydrochloride ($NH_2OH.HCl$) adjusted to pH 2 with nitric acid (HNO_3), 85°C
Step V (Oxidizable): 8.8 M hydrogen peroxide (H_2O_2) adjusted to pH 2 with nitric acid (HNO_3), 75°C

2.3 A continuous-flow sequential extraction procedure

0.25xx g of soil sample was transferred to a clean extraction chamber together with magnetic bar. A glass fiber filter was then placed on the outlet followed by a rubber gasket, and the chamber cover was securely clamped in position. The chamber was connected to the extractant reservoir, peristaltic pump, and the collector vial using tygon tubing and placed on magnetic stirrer. The magnetic stirrer and peristaltic pump were switched on to start the extraction. Heating of the extractant in steps IV and V was carried out by passing the extractant through a glass heating coil approximately 120 cm in length, placed in a water bath, which was set up between peristaltic pump and extraction chamber. Extracts from the extraction chamber was collected in plastic vials at required volume intervals.

2.4 Digestion of soil residues and soil samples

1.xxxx g of soil samples and 0.1xxx g of dried soil residues from extraction chamber were transferred to the vessels together with 1 ml H_2O_2 and 9 ml of HNO_3. The samples were heated to 220 $^{\circ}$C within 25 min. and digested using microwave digestion (Microwave 3000, Anton Paar). After cooling, the digested solutions were filled up to an appropriate volume with deionized water by volumetric flasks.

2.5 Analysis of metals in extracts and digests

All of the extracts obtained from extraction procedure and digested solution from soil samples and dried soil residues were subjected to Atomic Absorption Spectrometer (PinAAcle 900T, PerkinElmer). Metals concentration was obtained by the standard matrix-matching calibration method in which working standard solutions were prepared in the same extracting reagent as the sample solutions to be measured.

2.6 Statistics

The enrichment factor, the degree of metals contamination to indicate the contaminated origin as natural or anthropogenic source, is expressed as follow

$$EF = \frac{\left(C_{metal} / C_{normalizer} \right)_{sample}}{\left(C_{metal} / C_{normalizer} \right)_{background}}$$

where EF is the enrichment factor

C_{metal} is metal content (mg.kg^{-1} soil)

$C_{normalizer}$ is Al content (mg.kg^{-1} soil)

$\left(C_{metal} / C_{normalizer} \right)_{sample}$

is concentration of metal after normalization

$\left(C_{metal} / C_{normalizer} \right)_{background}$

is concentration of metal in natural after normalization

Furthermore total amount of five metals obtained from microwave digestion and their content obtained from a continuous-flow sequential extraction were statistically compared the difference using t-test. A probability of $p > 0.05$ was considered statistically significant.

3. Results and Discussion

3.1 Enrichment factor

Enrichment factor (EF) is the value indicating the degree of contamination of metals as natural and anthropogenic source. It is calculated using the average amount of crustal material. Al is applied as the crustal reference metal [9, 10]. Values of EF lower than 1 is suggested that the amount of metal is from the origin or natural. Whereas values of EF higher than 1 is indicated that the metal concentration is from the anthropogenic source.

The enrichment factor of metals (Al, Cd, Cu, Fe, and Zn) in soil surrounded gold mine at different direction and distance shows in Figure 1. Cu, Fe, and Zn in soil at L1, L3, and L10 were found higher than EF = 1 indicating these metals was from human activity. Considering the transportation system of gold mine, the vehicles usually use the route from L1-L3-L10 in order to transport from gold mine to other place. The highest amount of Cu and Zn were found at L1, L3, and L10 because the transportation is the important source for Cu [11] and Zn [12, 13]. In addition to Cu, Fe, and Zn were found with higher level in soil surrounded other gold mines as contaminated metals [14, 15].

However higher amount of Cu and Zn in soil surrounded gold mine at L1, L3, and L10 were lower than the standard amount of Cu (45 mg.kg^{-1}) and Zn (70 mg.kg^{-1}) in soil [16].

3.2 The fractionation of metals in soil

Using t-test, there is no significant difference ($p > 0.05$) between the total amount of five metals obtained from microwave digestion and their content obtained from a continuous-flow sequential extraction (Table 1). It is indicated that a continuous-flow sequential extraction system can be used to study the fractionation of metals in soil surrounded gold mine at Phichit province. These results were corresponded with other research [17].

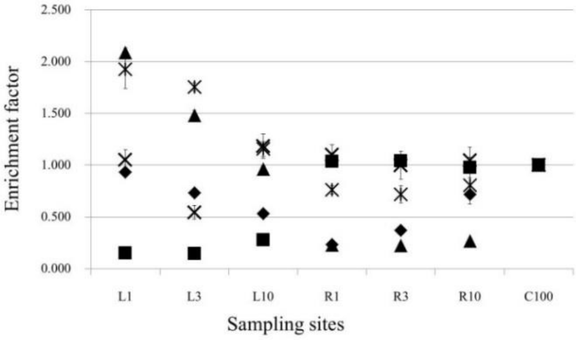

Figure 1 Enrichment factors of metals: (♦) Al (■) Cd (▲) Cu (x) Fe (*) Zn in soil at L1: far from gold mine 1 km (left), L3: far from gold mine 3 km (left), L10: far from gold mine 10 km (left), R1: far from gold mine. 1 km (right), R3: far from gold mine 3 km (right), R10: far from gold mine 10 km (right), and C100: far from gold mine 100 km

Table 1 Total amount of five metals obtained from microwave digestion and a continuous-flow sequential extraction

Sampling sites	Total amount of metals (mg.kg^{-1} soil)									
	Al^a	**Al^b**	**Cd^a**	**Cd^b**	**Cu^a**	**Cu^b**	**Fe^a**	**Fe^b**	**Zn^a**	**Zn^b**
L1	117.668	116.052	0.074	0.072	1.007	1.364	20.766	20.146	10.001	9.549
	± 1.071	± 1.914	± 0.006	± 0.003	± 0.013	± 0.202	± 0.491	± 0.518	± 0.884	± 0.418
L3	92.225	91.735	0.070	0.069	0.714	0.970	10.577	10.904	9.114	9.300
	± 1.729	± 2.453	± 0.006	± 0.006	± 0.016	± 0.421	± 2.108	± 2.465	± 0.113	± 1.081
L10	66.918	67.253	0.134	0.134	0.464	0.468	23.004	24.932	6.017	6.097
	± 1.415	± 2.888	± 0.005	± 0.003	± 0.008	± 0.008	± 0.871	± 6.150	± 0.378	± 0.126
R1	29.705	29.949	0.503	0.502	0.110	0.113	21.407	20.927	3.967	3.856
	± 1.582	± 1.646	± 0.007	± 0.007	± 0.011	± 0.006	± 2.343	± 1.912	± 0.169	± 0.256
R3	46.369	47.580	0.505	0.508	0.108	0.105	19.456	24.746	3.731	3.738
	± 1.189	± 2.500	± 0.006	± 0.013	± 0.008	± 0.006	± 3.012	± 5.752	± 0.473	± 0.567
R10	90.260	89.130	0.474	0.472	0.129	0.123	20.370	21.564	4.195	3.963
	± 1.229	± 1.774	± 0.036	± 0.055	± 0.007	± 0.006	± 1.942	± 5.037	± 1.005	± 1.028
C100	125.720	125.699	0.485	0.474	0.482	0.494	19.474	18.520	5.195	5.224
	± 1.204	± 1.533	± 0.012	± 0.012	± 0.008	± 0.008	± 4.645	± 3.599	± 0.070	± 0.652
t-value^c	0.581		1.225		1.554		1.162		0.866	

All data was calculated in triplicate.

a = Total amount of five metals obtained from microwave digestion

b = Total amount of five metals obtained from a continuous-flow sequential extraction

c = t-value from t-test ($p > 0.05$, t-critical = 1.943)

L1: far from gold mine 1 km (left), L3: far from gold mine 3 km (left), L10: far from gold mine 10 km (left), R1: far from gold mine 1 km (right), R3: far from gold mine 3 km (right), R10: far from gold mine 10 km (right), and C100: far from gold mine 100 km

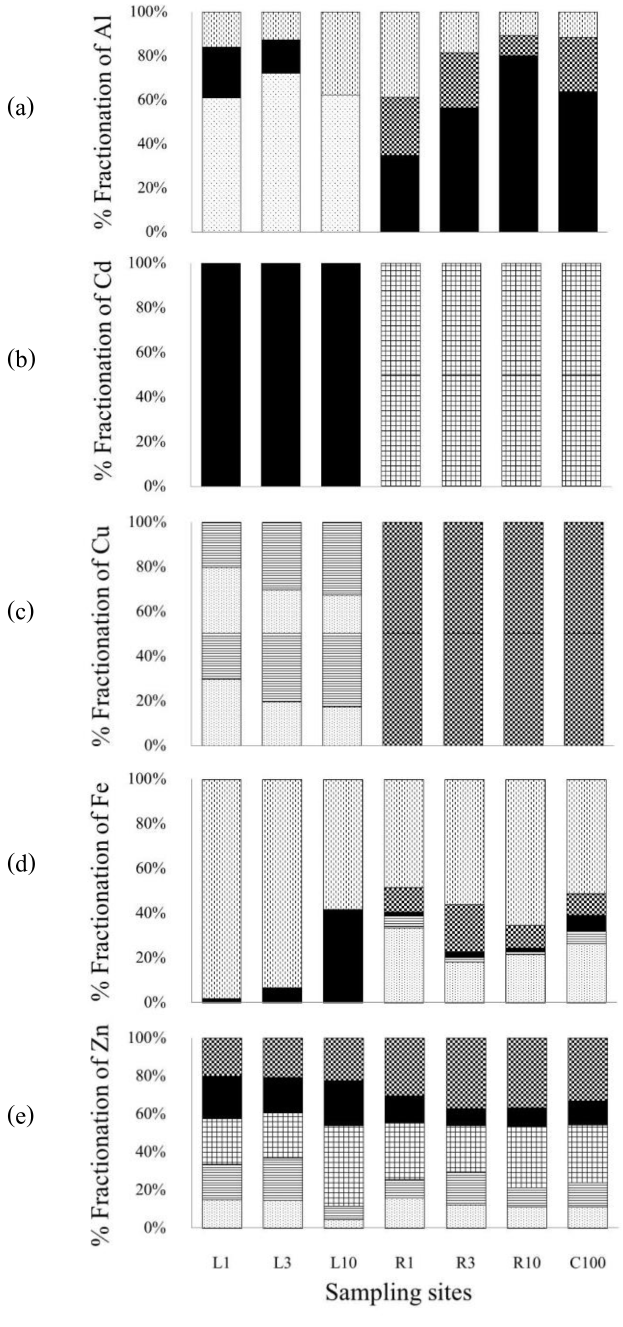

Figure 2 Fractional distribution of metals expressed as a percentage of total metals content: (a) Al (b) Cd (c) Cu (d) Fe (e) Zn in soil at L1: far from gold mine 1 km (left), L3: far from gold mine 3 km (left), L10: far from gold mine 10 km (left), R1: far from gold mine 1 km (right), R3: far from gold mine 3 km (right), R10: far from gold mine 10 km (right), and C100: far from gold mine 100 km obtained from a continuous-flow sequential extraction: ⊡ Water soluble phase, ⊟ Exchangeable phase, ◫ Acid soluble phase, ■ Reducible phase, ▩ Oxidizable phase, and ⧈ Residue phase

The fractional distribution of Aluminium (Al), Cadmium (Cd), Copper (Cu), Iron (Fe), and Zinc (Zn) expressed as a percentage of their content in soil surrounded gold mine at Phichit province using a continuous-flow sequential extraction presents in Figure 2a – 2e, respectively.

The result showed that it could be divided into two groups of sampling sites including group A: L1, L3, L10 and group B: R1, R3, R10, C100. The different pattern of five metals fractionation could be affected by the human activity. The route of L1-L3-L10 is always used to transport from gold mine to other place therefore their metals fractionation at these sites except Zn were dissimilar with others. The fractionation of metals at R1, R3, and R10 was the same pattern as their fraction at C100 or uncontaminated soil.

The fraction of Al for group A was distributed in water soluble phase > reducible phase ~ residue phase while Al fractionation in group B was presented in reducible phase > oxidizable phase ~ residue phase. These results replied that Al at L1, L3, and L10 was more easily labile than Al at R1, R3, R10, and C100.

The fractionation of Cd for group A and B was mostly bounded in reducible and acid soluble phase, respectively. These results replied that all sites of Cd was moderate mobilize under normal environmental condition.

Cu fractionation for group A was contributed in water soluble and exchangeable phase whereas it was mostly occurred in oxidizable phase for group B. These results indicated that Cu at L1, L3, and L10 was more potentially transport than Cu at R1, R3, R10, and C100. It was indicated that transportation changed the Cu fractionation in soil.

The fraction of Fe for group A was mainly associated in residue phase and slightly bounded in reducible phase. In contrast Fe fractionation for group B was appeared in residue phase > water soluble phase > oxidizable phase > reducible phase > exchangeable phase. It was indicated that Fe was immobilized metal in soil.

The fractionation of Zn for group A was similar to another group. Its distribution was predominantly found in acid soluble and oxidizable phase. Moreover it was slightly performed in water soluble, exchangeable, and reducible phase. This Zn fraction pattern was similar to another work [18].

4. Conclusions

The fractionation of Al, Cd, Cu, Fe, and Zn in soil surrounded gold mine at different direction and distance (Phichit province) was observed using a continuous-flow sequential extraction. Cu, Fe, and Zn were presented as contaminated metals surrounded gold mine because of gold mine's transportation. Moreover their fractionation was indicated that Cu in soil affected with transportation was more potentially mobile into environment than others. Fe distribution both contaminated and uncontaminated soil was mainly occurred in residue phase indicating that Fe mobility was limited whereas their fractionation of Zn was showed similar pattern.

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