Transfer factor as indicator of heavy metal content in plants around adipala steam power plant

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Abstract. The purpose of this research is to identify and characterize the main and trace metals in plant (cassava leaves and grass) and soil. Results of the characterization was used to determine the transfer factor (TF) of metal absorption from soil to plant around Adipala power plant located in Cilacap Regency. Measurement of metal concentrations were carried out using instrumental neutron activation analysis techniques. Samples were irradiated in Rabbit and Lazy Susan system facility at the Kartini research reactor located in Centre for Accelerator Science and Technology. Irradiated samples then counted using HPGe detector. Concentration values for heavy metals were below the maximum recommended value stated by WHO and FAO. Transfer factor (TF) is used to assess the concentration of metals in cassava leaves and grass taken from soil. The TF value calculated in this research were below 1, this implied that cassava leaves and grass were safe from the risk of heavy metals. The highest transfer factor value is Sb, it showed that is Sb was more mobile compare to other metals.

1. Introduction

Human activities sometimes contribute impacts to the environment in order to meet their needs. These impacts can be either positive or negative. One negative impact due to human activities is the decline of environment quality, such as the soil quality degradation due to waste pollution produced by household, industrial, and agricultural activities. One of the most impactful pollution or contaminants for soil is heavy metal. This contaminants infiltrate into soil and increase the toxicological effect because soil is closely related to agriculture [1].

Combustion of coal in thermal power plant can result in escalation of certain element concentration in fly ash, which are defined as enriched elements, such as Cd, Cr, Pb, and Zn. These elements have greater tendency to get out of the solid phase (fly ash). These toxic trace elements indicate subsequent enrichment of concentrations from coal to bottom ash and fly ash [2].

Since September 2016, Adipala 2 Steam Power Plant, located in Bunton Village, Adipala District, Cilacap Regency has begun its operation. This power plant can produce up to 660 MW of electricity, while the Adipala 1 Steam Power Plant located in Winong Village produce 2 x 300 MW electricity and began to operate in 2006, it is also generated from coal burning to produce steam. The power plant produces gas and solid waste in the form of fly ash which is 80-90% of the total ash and the rest is bottom ash. In general, fly ash contains heavy metals such as Fe, Ni, Zn, Cu, Mn, Pb and Cd [1] and radionuclides Ra-226, Th-232, Th-234 and K-40 [3].
The effect of fly ash on environment is unavoidable because of its fine texture so it can easily be carried by wind. Fly ash contains toxic heavy metals that can penetrate and accumulate into plant resulting in poisoning plants and animals. However, fly ash also contains micro and macro nutrients that are useful for plant growth [1, 4]. Metals accumulate in some parts of plants that have secondary metabolites, which are responsible for certain pharmacological activities. Because of its toxicity level, heavy metal on plant is one of major environmental issue that should not be ignored [4].

Accumulation of heavy metals in agricultural land is related to human activities, e.g. mining, smelting, cement plant, fuel production, power transmission, traffic, and intensive agriculture. It also depends on environmental conditions such as pH, temperature, humidity, and organic materials, [1, 5-7]. Heavy metal content in soil is generally used to indicate the level of soil contamination. The accumulation of heavy metals in the soil depends on various factors such as chemical elements, pH, organic matter content, texture, and cation exchange capacity of the soil [5]. Plants obtain nutrients including metals from the soil for growth. Plants absorb heavy metals from the soil through ionic exchange, redox reactions, or dissolution-precipitation [5, 6, 8]. If the concentration is high enough, trace metals can accumulate in plants. Then if contaminated plants consumed by human, it will be a threat for human health [9].

At low dose, some heavy metals are important micronutrients for plants, but in higher doses, they can cause metabolic disorders and interrupt population growth. It also applies to humans, Cu is one of trace metals which is important for human health, but in high doses Cu can cause health problems such as anemia, liver damage, kidney damage, and irritation [10].

The purpose of this study is to identify and characterize the main and trace metals in soil and plants (cassava leaves and grass). The data is used to calculate transfer factor (TF) of metal absorption from soil to plants and to evaluate possible health risks to the human body through food chain transfer. Samples for this study were taken around Adipala Steam Power Plant.

2. Methodology
In order to identify trace metals on soil and plants (especially cassava leaves and grass), instrumental neutron activation analysis was used (INAA). The data obtained from the analysis was then processed for estimating metal content and examining transfer factors. INAA is a highly representative analytical technique for analysing trace metals because of its high sensitivity, high accuracy, and lower limit detection [11]. Transfer factor (TF) of heavy metals from soil to plants is one simple way to explain human exposure to metals through the food chain [12]. Metal uptake from soil to plants measured by transfer factor (TF) is an index used to assess metal mobility from soil to plants. The TF for each particular metal can vary greatly depending on the type of plant, as well as from one environment to another. The main parameters that modify TF are; physical and chemical characteristics of soils, behaviour of trace metals in soils and plants, and environmental changes [13]. Transfer factor from soil to plants is calculated as the ratio of metal concentration in plants and metal concentration in soil as stated in equation (1) [5, 13-15].

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TF = \frac{\text{metal concentration in plant}}{\text{metal concentration in soil}}
\]  

(1)

2.1. Tools and Materials
Kartini research reactor with power of 100 kW was used to irradiate samples. Lazy Suzan facility at Kartini research reactor was used to irradiate samples with long half-time of decay, while pneumatic facility was used for samples with short half-time of decay. A set of gamma spectrometer consists of HPGe Ortec detector, MCA Spectrum Master ORTEC 92X, and Maestro software, was used to count and analyze samples. Sampling equipment, e.g. GPS, sample container, small shovel, rustproof pulverizer, drying tray, 100 mesh sieve, homogenizer, heating chamber, ovens, polyethylene vials were used to prepare samples prior to analysis.
Materials used for this study were soil, cassava leaves, and grass samples taken around Adipala Steam Power Plant, primary standards, secondary standards and aquabidest. Reference materials used for primary standards were SRM 2711a Montana II Soil and SRM 1573a Tomato Leaves.

2.2. Sampling Location
Samples used in this study were soil, grass, and cassava leaves and taken from 3 different location around Adipala Cilacap steam power plant. Location 1 (L1) was 2.8 km away from power plant chimney, located in Cibolang, Gombong Harjo (7°41'07.3" S and 109°08'15.2"E). Location 2 (L2) was 2 km away from power plant chimney, located in Silang Sur, Wlahar Village (7°40'11"S and 109°8'5.5"E). While location 3 (L3) was 2.1 km away from power plant chimney, located in Bauton, Sawangan Village (7°41'6"S and 109°9'22.9"E). All sampling locations were located at Adipala District, Cilacap Regency, Central Java.

2.3. Sample Preparation
Grass and cassava leaves were washed using aquadest, then samples were dried and pounded into 100 mesh of particles. Next, samples were inserted into vials as much as 100 mg and labelled. This preparation steps were also applied to soil sample, however soil sample did not need to be washed and only 50 mg of sample was inserted into vials.

2.4. Sample Irradiation and Counting
Plant samples of 100 mg and soil of 50 mg in vials, were irradiated in the research reactor for 5 minutes for short half-life and a total of 18 hours in 3 days for middle and long half-lives. Gamma-ray measurements were performed with a high purity germanium detector (HPGe p-type). The counting was carried out after a 5 minutes delay and samples was counted for 5 minutes. This applied for identify short half-life elements. Whereas samples with middle half-life were counted 3 days after irradiation. Samples with long half-life were counted 3 weeks after irradiation.

3. Results and Discussion
The main metals in soil are Al, Si, Ba, K, Ca, Mg, Ti, Na and Fe and toxic metals in soil are Sc, V, Cr, Cu, Zn, As, Mn, Co, Se, and Cd [9, 11, 16]. All metals mentioned before other than Si were identified using INAA method. The metal concentrations were varied from 811.33 mg/kg of Ba to 4.201% of Fe. All identified metals are shown in Figure 1 and Table 1 on appendix.

There are references for metal concentration in soil around the world, for example, Ti content in soil varies between 0.1 – 0.9%, Na content in soil is ranging from 0.07 – 0.74%, and Al content in soil varies between 1.0 – 6.4% [11]. In this study, we identified those metals (Ti, Na, and Al) and concentration of mentioned metals were still between those references. Concentration of Ti varied between 0.437 – 0.743%, while Na concentration was ranging from 0.491 – 0.679%, and Al concentration varied between 1.560 – 3.906%.

![Figure 1. Main (minor and major) metals histogram identified in soil](image-url)
Trace metals in soil were identified and analysed in this research. The specific value of each metals was presented in Table 2 on appendix and histogram of trace metals was shown on Figure 2. UK had been issued regulation regarding maximum metal concentration in soil at pH 6. According to UK regulation, maximum concentration of Zn in soil is 250 mg/kg, then 100 mg/kg for Cu, 400 mg/kg for Cr, and 3 mg/kg for Cd [5]. Whereas in Germany, maximum Zn content in soil is 200 mg/kg, maximum Cu content is 60 mg/kg, 100 mg/kg is maximum Cr content, then maximum Cd content is 1.5 mg/kg [5]. Concentration of Zn, Cu and Cr around Adipala power plant were below maximum values issued by UK and Germany. However, Cd content in soil had exceeded maximum concentration allowed in UK and Germany, Cd content in soil reached 3.38 mg/kg. Nevertheless, few European countries stated that Cd content in agricultural land can be at 5 mg/kg maximum [7]. The results showed that average level of metals identified in soil around Adipala power plant was at background level.

![Figure 2. Histogram of trace metals in soil](image)

Metal concentrations in cassava leaves are displayed in the form of histograms on Figures 3 and 4 while the specific values were presented in full appendix. On Figure 3, the graph shows concentration of 9 metals (Fe, Zn, Ba, Rb, Cr, Cu, K, Mn, and Ce) which are ranging from 0.60 mg/kg to 48.0 mg/kg. Whereas on Figure 4, concentration of 12 metals (Co, Mg, La, Sc, Cd, Cs, Se, Sm, As, Na, Sb, and Al) varies between 0.017 mg/kg until 1.24 mg/kg. Of all 21 detected metals, some which need more concern are Cr, Zn, Cu, Cd, As and Sb, because they are included in heavy and toxic metals [6, 15, 16].

WHO and FAO had been issued regulation about recommended values for Cu, Cr, Cd, and As content in vegetable. Concentration of Cu and Cr in vegetables should not exceed 30 mg/kg. While for Cd, concentration should be 0.3 mg/kg maximum and As concentration should be below 1.0 mg/kg [15, 18]. According to Environmental Protecting Administration of China (EPAC), maximum concentration of Cu, As, and Cd in vegetables are 50 mg/kg, 30 mg/kg, and 0.3 mg/kg respectively [20]. Based on this study, concentration of Cu, Cr, Cd, and As detected in cassava leaves were below maximum values that are issued by WHO and FAO. Average concentration of Sb detected in cassava leaves around Adipala power plant was 0.42 mg/kg, which is below maximum values issued by WHO and FAO [19]. As comparison, area located 1 km away from cement plant in Nigeria had detected 0.02 mg/kg of Cd, 0.93 mg/kg of Cu, and 0.05 mg/kg of Zn [21]. Those are lower than detected metal concentration around Adipala power plant.

According to Regulation of Directorate General of Drug and Food Control Number 03725/B/SK/VII/89 about Maximum Limits of Metal Contamination in Foods for Fresh Vegetables, safe limit of Cu is 30 mg/kg and Zn is 40 mg/kg [22]. Copper and zinc which are rich of micronutrients are important for human health. Enzymatic elements are important for plant growth, but at excessive level, they can be toxic and harmful to human health [18].
The metal concentrations in grass shown in Figures 5 and 6 and specific values are presented on appendix. All metals analysed in grass presented in this study are trace metals. Figure 5 is a histogram of metal concentrations from 1.0 mg/kg to 97 mg/kg and Figure 6 is a histogram of trace elements in grass with concentration between 0.02 mg/kg to 0.78 mg/kg. As cassava leaves absorb heavy metals and become toxic, so does the grass. Grass absorbs important metals and heavy metals through its root or leaf system in various forms. In general, soil contains many elements, but only a very small percentage of this elements is useful for plant growth [23].

Grass is direct path of metals into the animal's body and then into humans through meat and milk. Trace metals that are included in toxic metals are Zn, Cu, and Cr. Concentration of those toxic metal are shown on Figure 5. Actually, Zn and Cr are needed for grass nutrient, but Cr is not needed by grass. The concentrations of these three elements are maximum recommended values issued by WHO and FAO. Maximum limit of Zn content is 60 mg/kg [15]. Concentration of Cu based on WHO regulation should not exceed 30 mg/kg [17], but EPAC has higher limit of Cu content which is 50 mg/kg [20]. While maximum concentration of Cr is 30 mg/kg [18].
Figure 5. Histogram of trace metals in grass (1.0 mg/kg until 97 mg/kg of concentration)

Figure 6 shows a histogram of trace elements in grass for concentrations of 0.02 mg/kg to 0.78 mg/kg. Cd, As and Sb metals are not needed by grass and are toxic heavy metals. Concentration of As was detected around 0.055 mg/kg to 0.233 mg/kg with average concentration of 0.161 mg/kg. Sb ranged between 0.026 mg/kg and 0.060 mg/kg with an average of 0.042 mg/kg, and Cd ranged from 0.023 mg/kg up to 0.045 mg/kg with an average Cd concentration of 0.033 mg/kg. Those three metals are still below the maximum limit based on WHO / FAO recommendations [17, 18]. Low concentrations of some heavy metals (Cu, Cr, Mo, Ni, Se, and Zn) at low concentration are highly important for health and reproductive functions of plant and animal. However, if these metals exceed the maximum limit, they can cause toxicity to plants and animals [6].

TF is one of key components to assess human exposure to metals through food chain. Plant species (cassava leaves and grass) have capacities whether to remove or accumulate heavy metals. The results of TF calculation are shown on Figure 7, there are 6 heavy metals (Sb, Cu, Zn, Sd, Cr and As) which are used for transfer factor reference [6, 10, 15]. Those six metals are toxic metals which are not important for either grass or animal growth and can be harmful to human health [15]. TF were calculated using equation (1) and it gave results of TF ranging from 0.011 to 0.067. The lowest TF was hold by As, while the highest TF was hold by Sb. Graph on Figure 7 shows almost all average TF value in grass is greater than TF value on cassava leaves, except Sb.

The TF value calculated in this research is below 1, thus cassava leaves and grass are safe from the risk of heavy metals. Higher TF values (≥1) indicate higher metal absorption from the soil by plants that can cause harm to human health. On the contrary, a TF value below 1 indicates a poor plant response to metal absorption and plants is safe for human consumption [5]. However, if TF value is higher than 1, it can not be concluded that soil is the only source of heavy metal contamination in plants. Source of heavy metals in plants can be from deposition of air or other unknown sources [10].
The TF value for Sb is the highest among those six metals. It is 6 times higher than TF value of As in cassava leaves and 4.3 times higher than TF value of As in grass. As highest TF value, it indicates that Sb is more mobile than other metals. The sequence of more mobile metal to less mobile metal is Sb, Cu, Zn, Cd, Cr, and As. These results also support the finding that As accumulation in plants is relatively low [6].

![Figure 7. Histogram of transfer factor from soil to plants](image)

4. Conclusion
By using instrumental neutron activation analysis (INAA), toxic metals such as Sb, Cu, Zn, Cd, Cr and As could be detected in soil and cassava leaves which are taken around Adipala power plant. Other metals such as Sm, Mn, Co, Sc, Al, Na, Cs, Fe, Ba, Rb, La, K, Mg Ti, Se and Ce were also identified. Characterization of concentrations of toxic metals (Sb, Cu, Zn, Cd, Cr and As) in soils and plants (cassava leaves and grass) was found below the recommended maximum limit issued by WHO and FAO. Transfer factor (TF) is one of key components of human and animal exposure to heavy metals. In this study, TF value was found between 0.01 and 0.07. The TF value of Sb was the highest among all, so it can be concluded that Sb was more mobile than other toxic metals.

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## Appendix

**Table 1. Concentration of metals in cassava leaves and grass**

| Metals | Concentration, mg/kg | Limit |
|--------|----------------------|-------|
|        | Cassava leaves       | Grass |
|        | L1          | L2          | L3 | Average | L1          | L2          | L3 | Average |
| Fe     | 20,314      | 28,184      | 47,68 | 32,059 | 56,272 | 43,967 | 24,699 | 41,646 |
| Ba     | 2,565       | 9,933       | 21,482 | 11,327 | 13,811 | 5,797 | 19,229 | 12,946 |
| Cr     | 7,358       | 4,067       | 3,387 | 4,937 | 3,672 | 1,489 | 0,090 | 1,750 |
| Cu     | 3,320       | 6,674       | 2,870 | 4,288 | 4,781 | 2,594 | 3,008 | 3,461 |
| Zn     | 4,947       | 3,85        | 2,302 | 3,700 | 6,215 | 4,832 | 2,845 | 4,631 |
| K      | 2,769       | 3,679       | 2,338 | 2,929 | 5,452 | 4,913 | 1,880 | 4,082 |
| Rb     | 2,951       | 3,826       | 0,768 | 2,515 | 1,914 | 1,554 | 1,370 | 1,613 |
| Mn     | 1,441       | 0,753       | 1,307 | 1,167 | 0,274 | 0,520 | 0,548 | 0,447 |
| Ce     | 1,025       | 0,595       | 0,814 | 0,811 | 2,269 | 0,927 | 1,608 | 1,601 |
| Co     | 1,239       | 0,238       | 0,204 | 0,56 | 0,350 | 0,523 | 0,440 | 0,438 |
| Mg     | 0,416       | 0,463       | 0,627 | 0,502 | 1,534 | 1,393 | 2,024 | 1,650 |
| La     | 0,475       | 0,306       | 0,640 | 0,474 | 2,215 | 1,868 | 2,199 | 2,094 |
| Se     | 0,811       | 0,093       | 0,116 | 0,34 | 0,154 | 0,228 | 0,191 | 0,191 |
| Cd     | 0,261       | 0,144       | 0,264 | 0,223 | 0,023 | 0,031 | 0,045 | 0,033 |
| Cs     | 0,109       | 0,08        | 0,038 | 0,076 | 0,047 | 0,018 | 0,026 | 0,030 |
| Se     | 0,038       | 0,084       | 0,099 | 0,074 | 0,032 | 0,191 | 0,076 | 0,100 |
| Sm     | 0,057       | 0,044       | 0,078 | 0,06 | 0,776 | 0,399 | 0,221 | 0,465 |
| As     | 0,017       | 0,100       | 0,035 | 0,051 | 0,055 | 0,134 | 0,033 | 0,074 |
| Na     | 0,042       | 0,048       | 0,039 | 0,043 | 0,037 | 0,077 | 0,054 | 0,056 |
| Sb     | 0,036       | 0,038       | 0,014 | 0,029 | 0,026 | 0,039 | 0,060 | 0,042 |
| Al     | 0,038       | 0,004       | 0,015 | 0,019 | 0,048 | 0,077 | 0,085 | 0,070 |
Table 2. Concentration of trace metals in soil, mg/kg

| Metals | Concentration, mg/kg | L1 | L2 | L3 | Average |
|--------|----------------------|----|----|----|---------|
| Ce     | 23,729±2,38          | 39,678±3,87 | 24,872±1,297 | 29,426 |
| Se     | 0,972±0,07           | 2,264±0,179 | 0,636±0,052 | 1,291  |
| Cr     | 74,519±0,11          | 64,171±2,29 | 671,536±4,87 | 68,614 |
| Ba     | 468,364±31,42        | 277,901±24,69 | 73,062±15,65 | 275,109 |
| Cs     | 3,755±0,07           | 4,022±0,48  | 0,576±0,016 | 2,784  |
| Sc     | 28,131±0,34          | 22,849±1,73 | 75,034±0,374 | 32,005 |
| Rb     | 53,19±0,93           | 54,353±2,62 | 21,246±1,484 | 42,93  |
| Zn     | 83,117±6,07          | 55,098±13,126 | 113,343±9,05 | 83,853 |
| Co     | 25,471±0,12          | 18,153±1,23 | 85,541±4,85 | 29,722 |
| Sb     | 0,403±0,06           | 0,276±0,06  | 0,636±0,11  | 0,438  |
| Mn     | 17,033±6,66          | 6,713±0,52  | 34,128±0,27 | 19,291 |
| Cu     | 112,960±6,41         | 62,436±4,17 | 76,934±9,30 | 67,443 |
| Sm     | 4,156±0,12           | 4,436±0,96  | 3,717±0,16  | 4,103  |
| Cd     | 71,390±5,96          | 54,964±3,23 | 87,794±4,09 | 71,383 |
| As     | 5,301±0,81           | 6,558±1,78  | 2,386±0,27  | 4,748  |
| La     | 20,640±0,89          | 24,976±6,13 | 15,106±1,27 | 20,241 |

Table 3. Concentration of minor and major metals in soil

| Metals | Concentration, % | L1 | L2 | L3 | Average |
|--------|------------------|----|----|----|---------|
| Ti     | 0,543±0,04       | 0,437±0,13 | 1,743±0,05 | 0,571 |
| Na     | 0,542±0,542      | 0,679±0,14 | 0,491±0,02 | 2,652 |
| K      | 6,451±3,451      | 5,945±0,42 | 7,684±0,36 | 2,629 |
| Al     | 2,431±2,431      | 3,906±1,97 | 1,560±0,05 | 1,835 |
| Mg     | 1,550±1,550      | 1,622±0,28 | 2,333±0,16 | 4,201 |
| Fe     | 5,838±5,838      | 4,276±4,1 | 2,489±0,20 | 0,574 |