Faculty of Resource Science and Technology

Assessment of trace elements bioavailability in soils around Kuala Lumpur

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Bachelor of Science with Honours
(Resource Chemistry)
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Assessment of trace elements bioavailability in soils around Kuala Lumpur

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A thesis submitted in partial fulfilment of the requirements for the Degree of Bachelor of Science with honours

Bachelor of Science with Honours
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2016

UNIVERSITI MALAYSIA SARAWAK

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List of Abbreviations:

Abbreviation	Full Name	Abbreviation	Full Name
As	Arsenic	B	Boron
Cd	Cadmium	Co	Cobalt
Cu	Copper	Cr	Chromium
Fe	Iron	Hg	Mercury
K	Potassium	Mg	Magnesium
Mn	Manganese	Na	Sodium
Ni	Nickel	Pb	Lead
Se	Selenium	Sn	Tin
Zn	Zinc	$CaCl_2$	Calcium chloride
HCl	Hydrochloric acid	H_2O_2	Hydrogen peroxide
HNO_3	Nitric acid	NH_4NO_3	Ammonium nitrate
EDTA	Ethylene diaminetetraacetic acid	AAS	Atomic Absorption Spectrometer
ICP-MS	Inductively Coupled Plasma Mass Spectrometry	ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
US EPA	United States Environmental Protection Agency	DTPA	Diethylenetriaminepentaacetic acid
$NaNO_3$	Sodium nitrate		

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Assessment of bioavailability of trace metals in soil around Kuala Lumpur.

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Resource Chemistry Programme

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ABSTRACT

Eleven sample locations around Kuala Lumpur were selected for this study which consists of a residential and commercial area, educational centre and area near lake side. In this study, total concentration and bioavailability of trace elements were investigated. Samples were analysed using Atomic Absorption Spectroscopy (AAS) for four elements, zinc (Zn), copper (Cu), nickel (Ni) and lead (Pb). pH and soil organic matter (LOI) were also determined. Acid digestion technique was carried out to approximate the total concentration of trace elements in soil. First estimation of the bioavailability of trace metals in soil was determined by single extraction with EDTA, NH_4NO_3 and $CaCl_2$ extraction. Station 4, Station 3, Station 7 and Station 2 were found to have high concentrations of Pb, Zn, Cu and Ni respectively by acid digestion. EDTA extraction showed better results for bioavailability of trace metals compared to NH_4NO_3 and $CaCl_2$ extraction. Trace metals extractable by EDTA extraction decrease in following order: Pb > Zn > Cu > Ni. Most of the investigated trace metals concentration in NH_4NO_3 extraction were below the detection limit.

Keywords: Kuala Lumpur, Trace metals, Bioavailability

ABSTRAK

Sebelas lokasi sampel sekitar Kuala Lumpur telah dipilih untuk kajian ini yang terdiri daripada kawasan perumahan dan komersil, pusat pendidikan dan kawasan berhampiran tepi tasik. Dalam kajian ini, jumlah kepekatan dan bioavailabiliti unsur surih telah disiasat. Sampel dianalisis menggunakan Spektroskopi Serapan Atom (AAS) selama empat elemen, zink (Zn), tembaga (Cu), nikel (Ni) dan plumbum (Pb). pH dan bahan organik tanah (LOI) juga ditentukan. Teknik penghadaman asid telah dijalankan untuk mendapat lebih kurang jumlah kepekatan unsur surih dalam tanah. Anggaran pertama bioavailabiliti logam surih dalam tanah ditentukan oleh pengekstrakan tunggal dengan EDTA, NH_4NO_3 *dan pengekstrakan* $CaCl_2$*. Station 4, Stesen 3, Stesen 7 dan Stesen 2 didapati mempunyai kepekatan tinggi bagi Pb, Zn, Cu dan Ni masing-masing oleh penghadaman asid. Pengekstrakan EDTA menunjukkan keputusan yang lebih baik untuk bioavailabiliti logam surih berbanding* NH_4NO_3 *dan* $CaCl_2$ *pengekstrakan. Logam surih yang ekstrak daripada pengekstrakan EDTA penurunan dalam perintah berikut: Pb > Zn > Cu > Ni. Kebanyakan kepekatan logam surih yang dikaji dalam pengekstrakan* NH_4NO_3 *adalah di bawah had pengesanan.*

Kata kunci: Kuala Lumpur, Logam surih, Bioavailabiliti

1.0 Introduction

The soil is a dynamic system made up of solid, liquid, and gaseous phases, which is subject to short term fluctuations such as variations in temperature, moisture status, redox reaction and pH. Examples of the longer term changes in soil properties including the organic matter content decrease with increasing cultivation or increasing temperatures. Besides, decreasing of pH soil due to acid precipitation or lack of regular liming in areas of high precipitation relative to evaporation. All of these changes in soil properties can each have remarkable effects on the form and trace elements bioavailability (Alloway, 2005).

Bioavailability of the trace elements is the amount of a contaminant or chemical that is available to living biota. Trace elements are the elements available in natural materials at concentration of less than 1000mg/kg. Elements of the periodic table are mostly trace elements (Basta *et al.,* 2005). Trace metal can be found in the soil system by the weathering of rocks or they are mostly introduced into the urban environment by man's activities. Most of these elements results from waste generated by residences and they are disposed of on land and in water bodies without proper treatment. It can be transferred and pass along the food chain. This will cause the bioaccumulation of toxin in organism and cause serious environmental concern to the local population (Giuseppe *et al.*, 2014). However, the bioavailability of trace elements is not only dependent upon their total concentration but also upon their soil and their ability to transfer into the soil solution from the solid phase (Zhao *et al.*, 2010).

Kuala Lumpur (KL) is the capital of Malaysia. There is huge amount of almost over eight million people live within the greater KL area. There was huge and vast amount of traffic that goes into or leaves the city every day. Former industries, land and buildings used for example residential, purposes, have contribute a lot of sources of various trace elements into the soil. The concentration of many trace elements in KL is enhanced by the atmospheric and terrestrial contamination (Thums, 2008). According to Fordyce *et al.* (2005), they stated that the potential hazards posed by hazardous material depend on a concentration, bioavailability and chemical form. Thus the contribution of trace metals into urban soils in KL has been maximized by human activities through urbanisation and industrialisation. The population in KL nowadays has been gradually increasing. Due to the high population density and intensive anthropogenic activities, the concentration of trace metals in soil may be different as before. In addition, there are lack of studies about the bioavailability of trace elements around the KL area.

This study is conducted to determine the concentration and bioavailability of Pb, Cu, Zn and Ni in soil samples from KL. It is important to investigate bioavailability of trace elements in soil in order to determine the risk involved in urban environments especially of their direct and indirect effects on human health and the steps that should be taken to minimize the effect.

2.0 Objectives

1. To determine the amount of trace elements contain in soil around KL.

2. To study the bioavailability of trace elements in soil around KL using chemical extraction method.

3.0 Literature review

3.1 Trace elements in soil

The soil in urban areas whether from domestic gardens or parks, cities or small towns are contaminated with a wide range of trace elements. Elements that generally contain in urban soils are B, Cd, Co, Cu, Pb, Hg, Ni and Zn. In Siu *et al.* research (2006), the mean concentration of Pb exceeded the target values recommended by the Netherlands Soil Contamination Guidelines (85mg/kg) and the mean Zn concentration was nearly exceed the standard value in urban soil in Hong Kong. Pb concentration is high in urban areas was because the uses of lead-based paint and fallout of engine exhaust from vehicles burning leaded gasoline (Hodel & Chang, n.d.). In Madejon *et al.* research (2008), the trace metals found in the Domingo Rubio tidal channel in Spain which is highly contaminated areas were As, Cd, Cu, Pb and Zn. From Sim *et al.* (2014) research, the distribution of heavy metals like Se, Sn, As in water of Batang Ai Reservoir was higher than other heavy metal such as Na, K, Mn, Cr, Ni Zn, Mg and Fe. It was due to the input of boating, fish feed and construction activities.

3.2 Properties of soil

3.2.1 Soil organic matter (SOM)

Soil organic matter is important in soil components to determine most of soil quality (Carter, 2002). However, soil dynamics is strongly affect the soil organic matter due to its highly sensitive. Soil health can be affected by how the soil is being used (Wander, 2004). Land degradation can be reversing by an increase in soil organic matter (Weil & Magdoff, 2004). Soil organic matter is made up of biota, insoluble humic substances and soluble biochemical likes amino acids, proteins, polysaccharides, carbohydrates and etc. Phenolic, carboxylic, alcoholic and amino groups can be found on humic substance and biochemical for metal sorption (USEPA, 1992). Soil organic matter will affect the bioavailability of trace metal in soils.

There are two types of methods that can be used to test the SOM in soil. In Gelma *et al.* report (2011), they stated that the Walkley-Black (WB) titration method revealed as rapid methods for organic carbon (OC) analysis in soils and sediments. In this method, potassium dichromate ($K_2Cr_2O_7$) was mixed with sulphuric acid to oxidise the organic matter. Then followed by remove of the excessive dichromate by ferrous ammonium sulphate ($Fe(NH_4)_2(SO_4)_2*6H_2O$) using back titration method. The other method that stated in Storer report (1984) was loss of weight on ignition. The soil sample was weighed before and after the heating of soil samples at 450°C. The weight loss indicated the soil organic matter contain in the soil.

3.2.2 Soil pH

Soil pH is a property that described the relative acidity or alkalinity of the soil. The pH scale is ranged from 1 to 14. Higher the soil pH typically means greater the alkalinity. Strongest acid is classified from pH 1 to 5 whereas values of 5 to 6.8 are considered moderately and weak acid. Soil pH ranged from 6.8 to 7.2 is considered neutral, and strong alkaline has pH value more than 8.3.

The sorption of trace metal decrease in low pH and this account in increase in the bioavailability and mobility of most trace metal forms (Rieuwerts, 2007). According to Gnandi and Tobschall (2002), Cd, Ni and Zn were easily mobilised under low pH and oxidising conditions of soils from a mining area in Togo. Another studies from King (1988) found that, for all horizons, most of the variation in exchangeable Cd, Co, Cu, Ni and Zn was explained by pH from the south eastern United States. Soil pH is important in regulation for microbial activity (Haynes, 1986) and the composition of the microbial population (Paul

& Clark, 1996). Negative effects of soil acidity is the plant growth will be affected (Silveira, 2013).

The effect of pH in the solubility of metals has been shown in many studies. Decrease in pH from 7 to 4.55 can increase solubility of trace element such as Pb, Cd and Zn (Riuwert *et al*, 1998). Similar study are reported by Eriksson (1989), he stated that the solubility of cadmium will be decreased in calcium chloride and ammonium acetate extraction if soil pH increase. Xiong and Lu (1993) concluded that solubility of Zn decreased as pH increased.

From United States Department of Agriculture (n. d.), there are two ways to test the pH in soil, first one was using 1:1 ratio of water to soil sample and the second one was using 1:2 ratio of 0.01M of $CaCl_2$ to soil sample. Both of them were tested with pH electrode.

3.3 Toxicity of various trace elements in soils

In Fraga study (2005), Cu is necessary for the development of connective tissue, nerve coverings and bone. However, the metal is considered to be highly toxic. The processes induced by an excess of Cu ion are damage of tissue of plant, elongation of root cells, alteration of membrane permeability, causing root leakage of ions and solutes and damage to DNA, in consequence, inhibition of photosynthetic processes (Woolhouse *et al.*, 1981).

For nickel, the most common symptom of Ni phytotoxicity is chlorosis. In plants under Ni stress, the absorption of nutrients, root development and metabolism are strongly retarded. Normally, the range of excessive of toxic amount of Ni in most plant species varies from 10 to 1000mg/kg. Decreased in growth, photosynthesis and cation absorption by mung bean cultivars of plants will be affected by the accumulation of Ni in soil (Fraga, 2005).

Zn is considered as phytotoxic and the toxic effect are likely to be similar with other trace elements. The common symptoms of Zn toxicity is chlorosis and retard the plant growth (Fraga, 2005).

For Pb, it is considered as highly phytotoxic because it may interfere some vital plant processes even in low concentration. Toxic effects are related mainly to disruption of fundamental biological processes of plants such as photosynthesis, growth and mitosis. The toxicity of organic Pb not only exceeds by far the toxicity of its inorganic forms, the effect caused by both type of Pb also not same in quantity (Kabata, 2014).

3.5 Methods to study bioavailability

In Babatunde *et al.* studies (2014), 4-step sequential extraction procedure proposed by the Standard Measurements and Testing Programme of the European Union was employed to analyse for the trace elements in soil. The digest of soil samples were analysed by Flame Atomic Absorption Spectrometer for the concentrations of Cu, Pb, Cr, Cd and Zn.

According to Houba *et al.* (2008), $CaCl_2$ is neutral salt solution and it is the most suitable for the extraction of bioavailability of trace metals in soil. The samples was determined by AAS. Karczewska (2002) stated that 0.02 M EDTA-Na, 1 M HCl, and 0.1 M HCl can extract high proportions of trace metals.

In Ivezic *et al.* research (2013), they were indicated few method to extract the trace metal in soil. First method is aqua regia extraction. The soil samples was digested with aqua regia (1/3 HNO_3 + 2/3 HCl) and the concentration was determined by ICP-OES. Second method is water extraction. The air-dried soil and ultra-pure water was added and shaken in high density polyethylene centrifugation tubes. The water trace metal concentrations were determined by ICP-MS for Cd and ICP-OES for Cu, Fe, Mn and Zn. Last method stated in his studies are ultra-pure HNO_3 extraction. This method is used to test the total metal concentration in soil by digest the soil in ultra-pure HNO_3 and analysed by ICP-OES.

There are some single extraction method to determine the bioavailability of trace elements in soil. In Zhu *et al.* (2012), DTPA, EDTA, $CaCl_2$, $NaNO_3$ and NH_4NO_3 extraction method were used to determine immobilization effect of trace metals.

4.0 Materials and methods

4.1 Study area and sampling locations

Kuala Lumpur, capital of Malaysia has been chosen to be the study area. This area has highest population in Malaysia. The anthropogenic activities through rapid urbanization and industrialization in KL has contribute a lot of changes of trace metals concentration in soils.

4.2 Sample collection

The soil samples were collected between the depths of 0-20 cm on the top soil. A total of 11 soil samples with three replicates each were analysed.

Table 1: The coordinates and site details of all the sampling site

Sampling site	Coordinate	Site details
1-University Malaya (A)	N 03°07.219' E 101°39.280'	It is situated at the road side with moderate traffic flow.
2- University Malaya (B)	N 03°07.176' E 101°39.285'	Garden in front of library which facing the road side with heavy traffic flow.
3- University Malaya (C)	N 03°07.185' E 101°39.388'	Lake side.
4- SK Sri Petaling	N 03°06.601' E 101°38.349'	It is at primary school with moderate traffic flow.
5- Stadium MPPJ	N 03°05.931' E 101°35.685'	It is used mostly for football matches.
6- UITM Shah Alam	N 03°04.097' E 101°29.906'	Educational centre.
7- Taman Sri Rampai	N 03°11.657' E 101°43.639'	It is located around residential and commercial area.
8- Tasik Titiwangsa (A)	N 03°10.561' E 101°42.460'	Lake side. Previously is for tin mining activities.
9- Tasik Titiwangsa (B)	N 03°10.595' E 101°42.518'	Lake side. Previously is for tin mining activities.
10- UTM (KL Campus) (A)	N 03°10.488' E 101°43.282'	Educational centre.
11- UTM (KL Campus) (B)	N 03°10.455' E 101°43.265'	Educational centre.

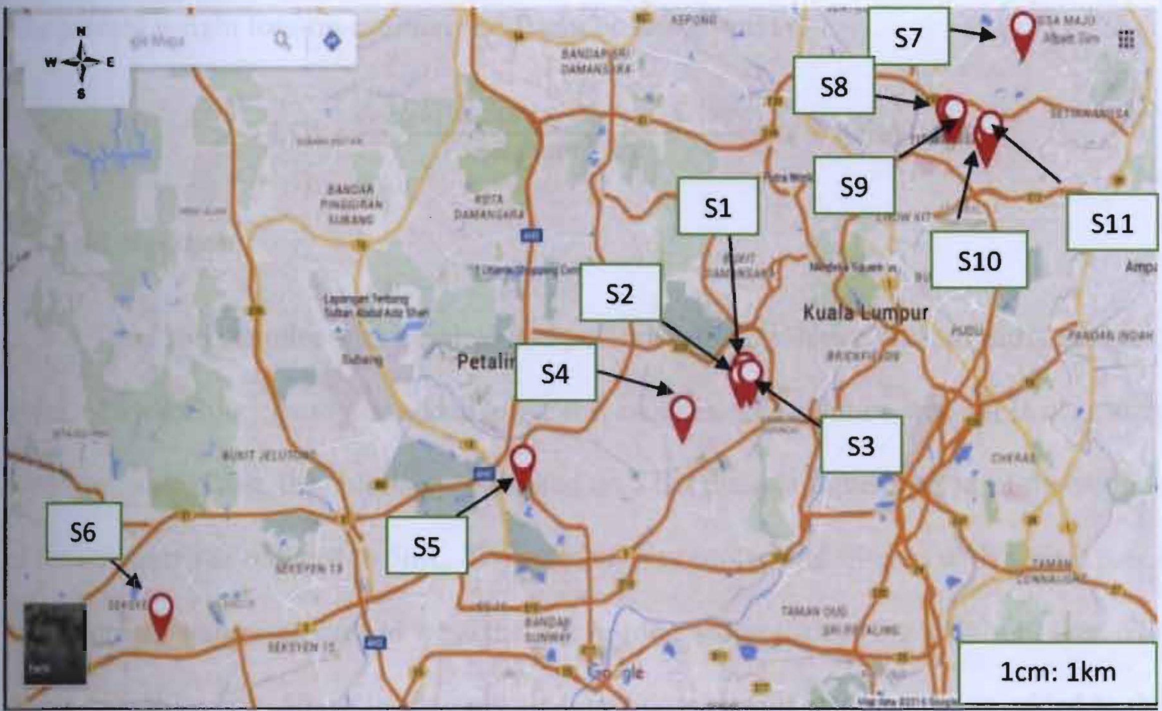

Figure 1: Sample location showed on google map.

4.3 Soil preparation

Stone, leaves or twigs were removed from the soil samples. Then the soil samples were dried in room temperature. The samples were grinded using mortal and sieve to obtain homogenized powder (Chen *et al.*, 2010).

4.4 Determination of soil pH

5g of soil was mixed with 25mL of distilled water to make a 1:5 soil solution. The solution was stirred for 30 minutes. After stirring, the pH meter was used for determination of soil pH. This process was repeated for 2 times to get the average results (Nelson & Su, 2010).

4.5 Determination of soil organic matter

1g of soil was put in a crucible. It was dried at 110°C for 4 hours followed by 5 hours in a 500°C furnace. The sample weight lost was recorded to determine the soil organic matter. 2 replicates were performed for each soil sample (Palmer *et al.*, 2013).

The percent weight loss-on-ignition (LOI) can be calculated as:

$$\text{LOI} = \frac{(weight\ at\ 110°C) - (weight\ at\ 500°C)}{weight\ at\ 110°C} \times 100\%$$

4.6 Acid digestion

1g of soil samples was weighed and put into a beaker. Next, 4mL of nitric acid and 10mL of hydrochloric acid was added to the soil samples. The solution was put in ultrasonic for 20 minutes. Then, the solution was heated on a hot plate in fume hood until the volume of the solution was reduced to 5mL. The solution was cooled and filtered with a filter paper and deionised water was used to wash the soil residue which stick at the wall of beaker. The filtrate was diluted to 50mL in the polyethylene bottle. 1% of nitric acid was added to the mixture. After this, the sample was sent to the AAS for analysis. 3 replicates were performed for each soil sample (EPA method 200.2, 1996).

4.7 Chemical extraction

0.05M EDTA, 0.1M NH_4NO_3 and 0.01M $CaCl_2$ was used to study the bioavailability of Zn, Cu, Ni and Pb respectively. 3g of soil sample was dissolved in 30mL of EDTA with pH 7.0. Then the solution was put in ultrasonic for 25 minutes. The solution was cooled and filtered with a filter paper. The filtrate was diluted to 50mL in the polyethylene bottle. 1% of nitric acid was added to the mixture. After this, the sample was sent to the AAS for analysis. 3 replicates were performed for each soil sample. Same procedure was repeated for NH_4NO_3 test and $CaCl_2$ test (Quevauviller, 2002). After this, the sample was sent to the AAS for analysis. 3 replicates were performed for each soil sample.

4.8 Trace element concentration determination by AAS

The model of AAS is iCE 3000 Series AA. Limit of detection (LOD) of AAS measurements of the elements of interest were calculated as three times the standard deviation for reagent blank measurements. Each sample was minus with procedure blank concentration to obtain the corrected concentration. All results obtained are reported as dry weight basis (mg/kg).

Table 2: Wavelength of trace elements detected by AAS.

Element	Wavelength (nm)
Copper	324.8
Nickel	232
Zinc	213.9
Lead	217

5.0 Results

5.1 Soil properties

5.1.1 Soil pH

Soil pH of the samples from Kuala Lumpur was ranged from 5.38 to 7.82 with a median value of 6.03. Soil in Station 1, 2 and 8 showed slightly alkaline as the result of pH value were 7.82, 7.32 and 7.24 respectively while the other stations tends to have slightly acidic soil.

Table 3: Soil pH of the sample (n=3)

Station	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
pH	7.82	7.32	6.03	6.07	5.93	6.19	5.67	7.24	5.38	5.57	5.53
SD	0.02	0.05	0.02	0.02	0.01	0.02	0.006	0.03	0.01	0.02	0.03

5.1.2 Soil organic matter (SOM)

Loss on ignition is calculated to interpret the percentage of organic matter content in soil. The organic content of Kuala Lumpur soil is between 2.00% and 12.6% with a median value of 3.95%.

Table 4: LOI of the soil (n=2)

Station	Weight lost after 500°C (g)	SD	sample weight (g) after 110°C	LOI (%)
1	0.044	0.002	0.983	4.48
2	0.04	0.001	0.987	4.05
3	0.038	0.003	0.989	3.84
4	0.121	0	0.964	12.6
5	0.045	0.005	0.993	4.53
6	0.04	0.001	0.986	4.06
7	0.024	0	0.998	2.40
8	0.02	0.001	0.999	2.00
9	0.039	0.003	0.993	3.93
10	0.039	0.003	0.987	3.95
11	0.037	0.013	0.983	3.76