Faculty of Resource Science and Technology

# DETERMINATION OF COPPER IN SOIL OF KUCHING CITY

Chan Yean Kwan

(35676)

**Bachelor of Science with Honours**
**(Resource Chemistry)**
**2015**

# DETERMINATION OF COPPER IN SOIL OF KUCHING CITY

Chan Yean Kwan (35676)

A thesis submitted in partial fulfillment of the requirements for the Degree of Bachelor of
Science with Honours
(Resource Chemistry)

Bachelor of Science with Honours
( Resource Chemistry)
2015

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# List of Abbrevations

| | | |
|---|---|---|
| AAS | : | Atomic Absorption Spectroscopy |
| AdsDPCSV | : | Adsorptive Differential-Pulse Cathodic Stripping Voltametry |
| DPASV | : | Differential-Pulse Anodic Stripping Voltametry |
| ICP-AES | : | Inductively-Coupled Plasma Atomic Emission Spectroscopy |
| ICP-OES | : | Inductively-Coupled Plasma Optical Emission Spectroscopy |
| ICP-MS | : | Inductively-Coupled Plasma Mass Spectroscopy |
| FPXRF | : | Field-Portable X-ray Fluorescence |
| XAFS | : | X-ray Absorption Fine Structure Spectroscopy |
| LOI | : | Loss on-ignition |
| As | : | Arsenic |
| C | : | Carbon |
| Cd | : | Cadmium |
| Cr | : | Chromium |
| Cu | : | Copper |
| Hg | : | Mercury |

Ni            :    Nickel

Pb            :    Lead

USEPA         :    United States Environmental Protection Agency

$HNO_3$       :    Nitric acid

$H_2O_2$      :    Hydrogen peroxide

$Na(PO_3)_6$  :    Sodium hexametaphosphate

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# Determination of Copper in soil of Kuching city

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## ABSTRACT

Heavy metals pollution is currently of major environmental concern. The present study was conducted to determine copper concentration in soil of Kuching city and to assess the level of copper pollution in soil. A total of 20 surface soil samples (0 - 10 cm depth) were collected from different locations in Taman BDC and Samajaya. The collected samples were analyzed by Atomic Absorption Spectroscopy (AAS) following the acid digestion of the soil samples. These copper concentrations of Taman BDC and Samajaya ranged from 4.42 mg/kg to 69.1 mg/kg and 0.968 mg/kg to 17.6 mg/kg. The results indicate that soils in Kuching have normal concentrations of Cu. Cu concentrations were not correlated with soil parameters such as pH (1: 5 soil-water ratio), soil organic matter (using loss on-ignition method) and clay content (using pipette method). Geoaccumulation index was also used to assess the level of copper contamination in soil.

Keywords: Copper, soil, pH, SOM, clay

## ABSTRAK

*Pencermaran logam berat kini menjadi perhatian utama berkaitan alam sekitar. Kajian ini telah dijalankan untuk menilai tahap pencemaran kuprum di tanah untuk kota Kuching. Sebanyak 20 sampel di permukaan tanah (0 - 10 cm) telah dikumpulkan dari Taman BDC dan Samajaya. Sampel-sampel dianalisis dengan menggunakan Spektroskopi Serapan Atom selepas menjalankan pencernaan acid sampel tanah. Sampel- sampel tanah yang dikumpul dari Taman BDC dan Samajaya mengandungi kuprum antara 4.42 mg/kg hingga 69.1 mg/kg dan 0.968 mg/kg hingga 17.6 mg/kg. Hasil kajian menunjukkan tanah kota Kuching mengandungi kuprum dalam kandungan yang normal. Kandungan kuprum tidak dikaitkan dengan parameter tanah seperti pH (nisbah tanah-air 1 : 5), bahan organik tanah (kaedah loss on-ignition) dan kandungan tanah liat (kaedah pipet). Indeks geoaccumulation juga digunakan untuk mengkaji tahap pencemaran kuprum tidak berlaku di kawasan kajian.*

*Kata kunci: Kuprum, tanah, pH, bahan organik tanah, kandungan tanah liat*

## 1.0 Introduction

Soil acts as a source and sink for many heavy metals, preventing them from reaching other parts of the environment. Extensive human activities such as agriculture, mining, industry, smelting, and burning fossil fuels together with the disposal of materials containing heavy metals, a long list which all contribute to the high content of heavy metals in soils (University of the West of England, 2013).

Heavy metals are highly persistent and may lead to geoaccumulation, bioaccumulation and biomagnification. High contents of heavy metals in urban soils pose an ecosystem and health risk as the metals may migrate to groundwater and rivers either in solution or as particulate material. Hence, heavy metal elements present in the soil is one of the most important signs of environmental pollution (Mmolawa *et al.*, 2011). Metals in urban soils have been shown to be very useful tracers of environmental pollution. They may come from various anthropogenic activities, such as mining, agriculture, construction, waste disposal, industrial and energy production, vehicle exhaust, as well as coal fossil fuel combustion. The anthropogenic activities produces airborne metals, which are deposited into urban soil as the metal-containing dust falls (Odat & Alshammari, 2011). Some studies show that the potential mobility and associated risk of heavy metal pollutants may be higher in urban soils compared to rural and agricultural soils (Li *et al.*, 2014).

Like all other metals, Cu is highly persistent in the environment and remain biologically active after its use has ceased (Ahmed & Zannat, 2012). The released Cu in the soil may attached strongly to the organic matter and other components such as clay in the top soil layers. Hence, the released Cu may not move very far but some water-soluble

copper compounds can enter groundwater (Beni *et al.*, 2005; Yin *et al.*, 2011).

Elevated emissions and their deposition over time can lead to soil surface contamination which threaten human health because of the close proximity to large populations via ingestion, inhalation, and dermal contact (Luo *et al.*, 2011). According to Reddy and Sekhar (2013), traces of Cu promote rancidity and off-flavors in foods and beverages. In humans, it acts as specific enzyme cofactors, and aids in the formation of haemoglobin. On the contrary, excess Cu causes diarrhea, anemia, kidney and liver damage. Excess copper concentration is also detrimental to plants as it impairs root growth and morphology (Ippolito *et al.*, 2011).

Measures of air and water quality and their impacts have been well documented but the impacts of soil pollution on our health have had a much lower profile. Its variable physical, chemical, biological characteristics and mineral composition lead to analytical complexity (Shirdam *et al.*, 2008; University of the West of England, 2013).

The economic development of Kuching and the increase in population imply a further increase in the generation of wastes from the residential, commercial and industrial sectors. Therefore, the present study has been undertaken to determine the copper in soil of Kuching city and to assess its pollution level. Besides that, the correlation between pH, organic matter and clay content to copper distribution were also determined.

## 2.0 Literature

Heavy metals are commonly defined as those having a specific density of ranging from 3.5 to 7g/cm$^3$. Heavy metals frequently reported in literature with regards to potential hazards are zinc (Zn), nickel (Ni), lead (Pb), chromium (Cr), mercury (Hg), arsenic (As), copper (Cu), and cadmium (Cd) (Mmolawa et al., 2011; Wuana & Okieimen, 2011).

The presence of Cd, Cu, Pb and Zn in gasoline, oil lubricants, car components, industrial and incinerator emissions make them as good indicators of soil contamination (Li et al., 2001). The contaminant concentration in soil mainly depends on the adsorption properties of soil matter. Organic matter may influence the concentration of heavy metals in soil by different processes such as release of heavy metals containing organic matter into the soil, extraction of heavy metals by organic matter in the soil forming organic complexes and so on (Deka & Sarma, 2012). Furthermore, environmental factors such as land use, temperature and rainfall can artificially change organic matter content as well heavy metals concentration in soil. The heavy metal ions solubility in soil is mainly influenced by pH, conductivity and other factors (Deka & Sarma, 2012).

## 2.1 Potential harm/ benefit of heavy metals

Heavy metals pollutants in soils can impair important biochemical processes, threatening human health, animal life and plant growth. They cause serious health problems when they enter directly into human bodies by dermal contact, dust ingestion or breathing. Besides that, metals in polluted soil are more mobile compared with those in unpolluted ones. As a result, groundwater contamination may occurs. These metals may migrate to groundwater and rivers either in the form of solution or as particulate material.

However, the mobility or leachability is often not very high due to relatively strong bonding (Li *et al.*, 2014).

For example, lead is health-endangering metal for human and its effects include nerve damage to the sense organs and nerves controlling the body in adults, brain damage and mental retardation in young children. Low concentration of cadmium is extremely toxic, and the major effects of this metal poisoning are diarrhoea, stomach pains, bone fracture, possibly even infertility and so on (Bakirdere & Yaman, 2008; Es'haghi *et al.*, 2011). According to Es'haghi *et al.* (2011), the range of its biological half-life in the human body is from 10 to 33 years. Therefore, it is important to understand the content, distribution, mobility and possible sources of soil heavy metals.

**2.2 Sources of heavy metals**

a.   **The geochemical background**

Heavy metals exist primarily: from mineralogical composition of the rock whether originally-formed (from extrusive and igneous rocks) or initially deposited (from marine sediments, moraines, and alluvium), which have sometimes been modified by subsequent mineralization (Baize, 2010).

b.   **The soil processes leading to natural pedogeochemical concentration**

The inheritance in upper soil horizons can markedly change by:

- Translocation of clay particles leading, over the long-term, to the formation of upper soil horizons which have markedly lower trace elements content than deeper soil horizons.

- Direct and total weathering of clay minerals giving rise to upper soil horizons which are very poor in trace and major elements.

- Podzolisation, where iron, aluminium and most trace metals form organometallic complexes, which are able to move down from the upper A and E layers and accumulate at depth in spodic B horizons (Baize, 2010).

c. **The contamination induced by man**

According to Baize (2010), diverse anthropogenic additions have much more recently been added to the pre-existing natural stocks:

i) atmospheric fallout from origins both far or near;

ii) trace elements brought unwittingly by fertilizer, sewage sludge or waste spreading.

Routes from soils to human intake

* **Ingestion- Eating soil (geophagia)**

The most important pathway for human exposure to soil contamination is ingestion especially children as they crawl on the floor, put things in their mouths, and spend more time outdoors. In fact, consumption of vegetables with some soil still attached may leads to accidental ingestion in adults (University of the West of England, 2013). Regular consumption of mollusks would increase the daily intake of copper by 5.7 - 136 mg/day (Agency for Toxic Substances and Disease Registry, n.d.).

* **Inhalation**

Workers who are working with soil (for example, in agriculture) and others nearby inhale particles released into the air, which may lodge in the lungs or absorbed into the bloodstream (University of the West of England, 2013).

* **Skin contact**

Skin absorption (also known as dermal or transcutaneous absorption) is the least

possible pathway for heavy metals as it only tends to favour more volatile, organic compounds (University of the West of England, 2013).

- **Indirect contact**

Vehicles emit heavy metals through lubricating oil consumption (cadmium) and tire wear (cadmium, zinc), fuel combustion, road abrasion, and brake wear (copper and lead) and so on release heavy metals into the soil. Lead also comes from worn metal alloys in the engine and exhaust gas. The transportation of heavy metal emissions can be absorbed by the roadside grasses through their roots (Yan *et al.*, 2012).

They enter the human food chain when they are consumed either by agricultural livestock or by humans. Soil contaminants in turn, move into ground water, contaminating drinking water and subsequent undesirable effects. Overloaded body's own detoxification systems result in a toxic contaminant in the human body (Yan *et al.*, 2012; University of the West of England, 2013).

Accelerated industrialization and urbanization has resulted in an increased pollution of soil and its concentration in soil is frequently reported as an indicator of urban environmental quality as urban soils are the "recipients" of various pollutants. Continuous released of trace metals into the natural environment through the weathering of soils and bedrocks, combustion of fossil fuels, mining activities, atmospheric emission, domestic emissions, agricultural activities, and industrial activities resulting in a biotics or abiotic cyclic process. As a result, trace metals are converted into toxic substances (Ali & Shakrani, 2014; Suleiman *et al.*, 2007; Wei & Yang, 2010; Wuana, & Okieimen, 2011).

## 2.3 Sources of copper

Global soil Cu contents from 1 to 140 mg/kg. Its content depends on the geology of the soil parent material, primary and secondary minerals as well as mineral deposit types (Romić *et al.*, 2014). Cu in soils may exist in the following forms: (i) organically bound, (ii) exchangeable, (iii) water soluble, (iv) associated with carbonates and hydrous oxides of Fe, Mn, and Al, and (v) residual.

Most Cu associates with sulfide, forming very soluble minerals such as CuS and $Cu_2S$. Chemical weathering of these primary copper sulphide minerals such as chalcopyrite ($CuFeS_2$), as well as chalcocite ($Cu_2S$), bornite ($Cu_5FeS_4$), and tetrahedrite (($CuFe)_{12}Sb_4S_{13}$) will form secondary minerals including the oxide mineral cuprite ($Cu_2O$), the carbonate minerals malachite ($Cu_2(CO_3)(OH)_2$) andazurite ($Cu_3(CO3)_2(OH)_2$), the sulphate minerals brochantite ($Cu_4SO_4(OH)_6$) and antlerite ($Cu_3SO_4(OH)_4$) (Canadian Council of Ministers of the Environment, 1999). According to Agency for Toxic Substances and Disease Registry (n.d.), the largest anthropogenic release of copper to the environment is by far to land.

Table 1. Mean copper concentrations from different sources (Agency for Toxic Substances and Disease Registry, n.d.).

|  |  | Sources of release | Mean copper concentrations | Maximum copper level |
|---|---|---|---|---|
| Air | Natural | - Wild forest fires<br>- Windborn soil particles | 5 to 200 ng/m$^3$ | 0.1 mg/m$^3$ as a fume |
|  | Anthropogenic | - Combustion<br>-Processing of copper containing materials |  | 1.0 mg/m$^3$* as a dust or mist |
| Water | Anthropogenic | - Natural soil weathering<br>- Atmospheric deposition<br>- Waste disposal | 4–10 ppb | 1300ppb* |
| Soil | Anthropogenic | - Municipal refuse<br>- Coal fly ash | 5 to 70 mg/kg |  |

* Agency for Toxic Substances and Disease Registry (2004)

The anthropogenic sources of Cu in the soil environment are from mining activities, waste emissions, sewage sludge applications, fertilizers, and fungicides in agricultural applications. According to Wuana, & Okieimen (2011), agriculture is the main human influence on the soil. In fact, pesticides used in agriculture such as fungicidal sprays containing copper such as Bordeaux mixture ($Ca(OH)_2+CuSO_4$) has lead to accumulation of Cu up to 200-500 mg/kg compared to 5-30 mg/kg in soils without fungicide due to its low solubility (Schwer, 2010).

Based on Schwer (2010), the application of sewage sludge to agricultural fields has also led to increased Cu concentrations, with some field soils exceeding 1600 mg $kg^{-1}$. Furthermore, soil Cu concentrations with extensive mining activities have been found as high as 2000 mg/kg, and higher values (4500 mg/kg) near to Cu processing facilities, which are much higher than normal Cu concentration range. An average person eats and drinks about 1 mg of Cu/day (U.S. Recommended Dietary Allowance is 0.6 - 2 mg/day). Based on the study of Richardson (2001), the mean natural emission rates for Cu are $5.0 \times 10^7$ kg/y for North America, $2.6 \times 10^6$ kg/y for Canada, and $2.0 \times 10^9$ kg/y globally.

Table 2. Ambient background soil concentrations for copper in different countries (Alloway, 2008).

| Country | Copper concentrations (mg/kg) |
|---|---|
| World | 13.0-34.0 |
| England and Wales | 15.6 |
| Germany | 22.0 |
| USA | 18.0 |

## 2.4 Speciation and bioavailability of copper

Copper is a high priority persistent, bio accumulative and toxic (PBT) chemical which does not degrade, and is not destroyed by combustion. It cycles between the surface ground water, soil, waters, and atmosphere. Copper occurs in three oxidation states in the environment as a solid metal $Cu^0$, as the cuprous ion $Cu^+$, and as the cupric ion $Cu^{2+}$. Soil Cu occurs in various forms: specifically sorbed; in organic residues and living organisms; in the soil solution; occluded in soil oxides; in the lattice structure of primary and secondary minerals and on soil exchange sites.

Bioavailable copper are usually water-soluble and exchangeable; carbonate, organic matter oxide, and complexes copper are potentially bioavailable fractions as the mineral fraction is considered the non-bioavailable (Ippolito et al., 2011). Its soil bioavailability depends on amount and nature of organic matter, soil pH, CEC, and redox potential, and soil minerals (Romić et al., 2014). According to Kiaune& Singhasemanon (2011), there are 50% of copper in contaminated soil was associated with organic matter, 28% formed $CuCO_3$, 11% $Cu_2O$ and 11% $CuO$.

### 2.4.1 Soil pH

Soil pH is a measure of the soil solution's acidity and alkalinity. By definition, pH is the 'negative logarithm of the hydrogen ion concentration, $H^+$ (pH = -log $H^+$). Soils are referred to as being acidic, neutral, or alkaline (Montana State University, n.d.) .
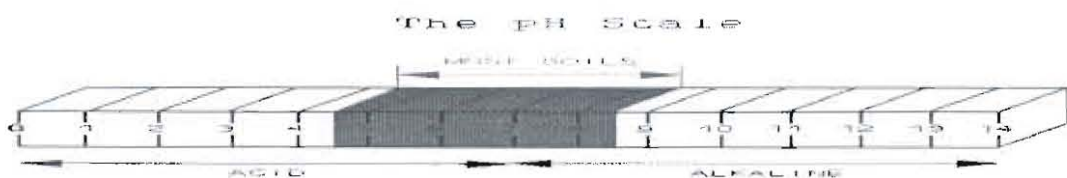


Figure 1. The soil pH scale (Montana State University, n.d.).

The Cu adsorption capacity increased with increasing pH. As a result, the number of negative pH dependent charges increases, which in turn increases the negative charge density at the colloid's surface. Soils with a higher pH, along with more organic matter contributes to higher CEC than soils with less organic matter. Therefore, it is important to know how the pH affects the soil Cu distribution (Nascimento *et al.*, 2003; US EPA, 1992). Alkaline soil conditions tend to favour precipitation of Cu, leading to the formation of $CuCO_3$, CuO, or mixed hydroxy-carbonate mineral species. This shows that copper mobility is greater under acidic than alkaline conditions (Canadian Council of Ministers of the Environment, 1999; Ippolito *et al.*, 2011 ).

## 2.4.2 Soil organic matter (SOM)

Soil organic matter such as organic litter may occur on the surface of the soil in various stages of deposition and decomposition, and roots may be present in the surface or subsurface soils an be observed in dark-colored soils and can retain a large number of chemicals, forming organometallic compounds. Besides, soil organic matter consists of living organisms, insoluble humic substances, and soluble biochemicals such as carbohydrates, polysaccharides, amino acids, organic acids, proteins, lignin and so on. The biochemicals and humic substances provide acidic functional groups such as such as phenolics, carboxylic, enolic-OH, alcoholic and amino groups for metal sorption (USEPA, 1992).

The stability in soil and relative abundance (up to 80% soil organic matter) of humic substances (humic and fulvic acids and humin) plays a significant role with respect to metal interactions. Humic substances have a selectivity for the alkali metal cations, serve