# DETERMINATION OF HEAVY METAL CONCENTRATION IN SURFACE AND SUB SURFACE SOIL AROUND ULU TUALANG NEWLY-CLOSED LANDFILL, TEMERLOH, PAHANG

HAIRUL ISHYAM BIN HUSSEIN

UNIVERSITI MALAYSIA PAHANG

# UNIVERSITI MALAYSIA PAHANG

## BORANG PENGESAHAN STATUS TESIS♦

JUDUL    **: DETERMINATION OF HEAVY METAL CONCENTRATION IN SURFACE AND SUB-SURFACE SOIL AROUND ULU TUALANG NEWLY-CLOSED LANDFILL, TEMERLOH, PAHANG**

SESI PENGAJIAN    :    **2010/2011**

Saya         **HAIRUL ISHYAM BIN HUSSEIN**

**(HURUF BESAR)**

mengaku membenarkan tesis (PSM/~~Sarjana~~/~~Doktor Falsafah~~)* ini disimpan di Perpustakaan Universiti Malaysia Pahang dengan syarat-syarat kegunaan seperti berikut :

1. Tesis adalah hakmilik Universiti Malaysia Pahang
2. Perpustakaan Universiti Malaysia Pahang dibenarkan membuat salinan untuk tujuan pengajian sahaja.
3. Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. **Sila tandakan ( √ )

    ☐ SULIT     (Mengandungi maklumat yang berdarjah keselamatan    atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972)

    ☐ TERHAD     (Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)

    ☑ TIDAK TERHAD

                            Disahkan oleh

_____     _____
(TANDATANGAN PENULIS)     (TANDATANGAN PENYELIA)

Alamat Tetap  **Peti Surat 269,**     **En.Azizan Ramli**

               **Kg. Dasar Baharu, 91207,**     Nama Penyelia

               **Kunak, SABAH.**

Tarikh :   **2 DECEMBER 2010**     Tarikh:    **2 DECEMBER 2010**

CATATAN:     *     Potong yang tidak berkenaan.
          **     Jika tesis ini **SULIT** atau **TERHAD**, sila lampirkan surat daripada pihak berkuasa/organisasiberkenaan dengan menyatakan sekali sebab dan tempoh tesis ini perlu dikelaskan sebagai **SULIT** atau **TERHAD**.

          ♦     Tesis dimaksudkan sebagai tesis bagi Ijazah Doktor Falsafah dan Sarjana secara penyelidikan, atau disertasi bagi pengajian secara kerja kursus dan penyelidikan, atau Lapuran Projek Sarjana Muda (PSM).

# DETERMINATION OF HEAVY METAL CONCENTRATION IN SURFACE AND SUB-SURFACE SOIL AROUND ULU TUALANG NEWLY-CLOSED LANDFILL, TEMERLOH, PAHANG

**HAIRUL ISHYAM BIN HUSSEIN**

**A thesis submitted in fulfillment
of the requirements for the award of the Degree of
Bachelor of Chemical Engineering**

**Faculty of Chemical & Natural Resources Engineering
University of Malaysia Pahang**

**NOVEMBER 2010**

"I hereby declare that I have read this thesis and in my/our opinion this thesis has fulfilled the qualities and requirements for the award of Degree of Bachelor of Chemical Engineering"

Signature            :        …………………………

Name of Supervisor  :       Mr. Azizan Ramli

Date                :        2 December 2010

I declare that this thesis entitled *"Determination of Heavy Metal Concentration in Surface and Sub Surface Soil around Ulu Tualang Newly-Closed Landfill, Temerloh, Pahang"* is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

Signature        :………………………………

Name           : Hairul Ishyam Bin Hussein

Date            :  2 December 2010

*Dedication to*

> *My beloved mother & father*
> *My dearest brother & sister*
> *My inspiring friends*

> *Thank you...*

# ACKNOWLEDGEMENT

With the name of the Almighty, Alhamdulillah Praise Allah S.W.T. for His helps and guidance that I finally able to complete this Projek Sarjana Muda (PSM).

First of all, I would like to take this opportunity to convey my gratitude towards my parents, En. Hussein Pisang and Pn. Halifah Bacho, for their prayers, supports and love that can make my dreams to become a successful person become reality. I appreciate their sacrifice, patient and morale support throughout my research and my studies.

I would like to thank my supervisor Mr. Azizan Ramli for his supervision and unflinching support almost over a year. I am deeply grateful for his inspiration and guidance in helping me to understand the concepts of environmental research. I thank him for his patience in reviewing my work that helped me to improve my research contributions. I appreciate his help in guiding me to overcome my research and other problems.

I grateful acknowledge the Faculty of Chemical and Natural Resources Engineering for the supports which enabled this work to be carried out. Thank all the technicians and staff in the Chemical and Natural Resources Engineering Laboratory for their help in completing my research.

I sincerely thanks to my dear friends for their helps and moral supports, and encouragement.

# ABSTRACT

European community had been stated 13 types of heavy metals that have the highest concern. There were including As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sn, and Tl. Some of these heavy metals such as Cu and Ni are actually necessary to our human body but mostly are very dangerous to our health for example Cu can cause cardiovascular disease while can cause cytotoxic role in plant if in excessive amount. This heavy metal pollution in soil is usually occurring in landfill that near the industrial estate. This situation become worst when there is no proper dumping system in that particular area. So, this research will be conducted to determine the presence and distribution of copper and nickel in surface and sub-surface soils around Ulu Tualang Newly-Closed Landfill, Temerloh, Pahang. This research data will become reference for the landfill management and reconstruction. Samples obtained by digging at different point and two samples for each point, one for surface and one for sub-surface soil. The sample heated using oven, pulverized and sieve to get homogeneity. After that the sample digested using SCL (South California Laboratory) method that used HCl and $HNO_3$ as the digester. After dilution and vacuum filtered the sample analyzed using Atomic Absorption Spectrophotometry (AAS). For the result, after the sample spiked Cu was detected at 19.2-70.35 mg/kg while Ni was detected around 51.25-99.65 mg/kg. As a conclusion, for the depth differences, the distribution of the heavy metal seems did not have pattern and Ni concentration are higher than copper for both soil layers.

# ABSTRAK

Masyarakat Eropah telah menyatakan 13 jenis logam berat yang memiliki kepedulian yang tertinggi. Ini termasuklah As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sn, dan Tl. Beberapa logam berat seperti Cu dan Ni sebernarnya diperlukan untuk tubuh manusia kita tetapi sebahagian besar sangat berbahaya untuk kesihatan kita misalnya Cu boleh menyebabkan penyakit jantung sementara boleh menyebabkan peranan sitotoksik dalam tanaman jika dalam jumlah berlebihan. Pencemaran logam berat dalam tanah biasanya terjadi pada tapak pelupusan yang berdekatan dengan kawasan industri. Situasi ini menjadi lebih buruk apabila tidak ada sistem pelupusan yang sewajarnya di kawasan tersebut. Oleh itu, kajian ini akan dilakukan untuk menentukan kewujudan dan taburan tembaga dan nikel dalam permukaan tanah dan sub-permukaan sekitar tapak pelupusan Ulu Tualang yang telah ditutup, Temerloh, Pahang. Data kajian ini akan menjadi panduan bagi pengurusan tapak pelupusan dan rekonstruksi. Sampel diperolehi dengan menggali pada titik yang berbeza dan dua sampel untuk setiap titik, yang pertama untuk permukaan dan satu untuk sub-permukaan tanah. Sampel dipanaskan menggunakan ketuhar, dihaluskan dan ditapis untuk mendapatkan aduan sempurna. Setelah itu sampel dicerna menggunakan kaedah SCL (South California Laboratory) yang mengunakan HCL dan $HNO_3$ sebagai pencerna. Setelah dicairkan dan ditapis, sampel dianalisis menggunakan Spektrofotometri Serapan Atom (SSA). Keputusannya, Cu dikesan pada 19.2-70.35 mg/kg sedangkan Ni dikesan sekitar 51.25-99.65 mg/kg. Sebagai kesimpulan, atas perbezaan kedalaman, taburan logam berat nampaknya tidak mempunyai pola dan kepekatan nikel lebih tinggi dari tembaga untuk kedua-dua lapisan tanah.

# TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# LIST OF APPENDICES

# LIST OF ABBREVIATION

| | | |
|---|---|---|
| Ni | - | Nickel |
| Cu | - | Copper |
| US EPA | - | United State Environmental Protection Agency |
| SCL | - | Southern California Labratory |
| ASTM | - | American Society Of Testing And Materials |
| MSW | - | Municipal Solid Waste |
| GCL | - | Geomembrane Clay Liner |
| PVC | - | Polyvinyl Chloride |
| CPE | - | Chlorinated Polyethylene |
| CSPE | - | Chlorosulphonated Polyethylene |
| EPDM | - | Ethylene Propylene Rubber |
| PP | - | Polypropylene |
| LLDPE | - | Linear Low-Density Polyethylene |
| MDPE | - | Medium-Density Polyethylene |
| HDPE | - | High- Density Polyethylene |
| $CH_4$ | - | Methane |
| $CO_2$ | - | Carbon Dioxide |
| $HNO_3$ | - | Nitric Acid |
| $H_2O_2$ | - | Hydrogen Peroxide |
| AAS | - | Atomic Absorption Spectroscopy |
| XRF | - | X-Ray Fluorescence Radioisotope |
| Ca | - | Calcium |

| | | |
|---|---|---|
| EDTA | - | Ethylene-Diamine-Tetra-Acetic |
| $NO_2$ | - | Nitrogen Dioxide |
| FLAA | - | Flame Atomic Absorption Spectrometry |
| GFAA | - | Graphite Furnace Atomic Absorption |
| ICP-AES | - | Inductively Coupled Plasma Atomic Emission Spectrometry |
| ICP-MS | - | Inductively Coupled Plasma Atomic Emission Spectrometry |
| ppm | - | Part Per Million |
| Df | - | Dilution Factor |
| HCl | - | Hydrochloric Acid |
| PEL | - | Permissible Exposure Limit |

# CHAPTER 1

# INTRODUCTION

## 1.1    Research background

As we know Malaysia is a country that has a high industrial technology in manufacturing and production process. Therefore, this country is very dependent in using a large amount of metals especially in construction site; processing plant and mining industry. All of these activities are producing massive amount of waste than contain very high concentration of heavy metal. These heavy metal wastes are usually thrown away by some industrial companies to the landfill area without treating them. In a couple of years, the concentration of these heavy metals will increase rapidly and will start to affect the surrounding area. This heavy metal pollution did not just stop bring harms to human, but also to animal, plant and the ecosystem.

## 1.2    Problem statement

Most of people did not concern about heavy metal pollution especially at the landfill. They just think a landfill is an area that used for dispose their factory and domestic waste. Most landfill sites are open dump without a proper leachate or gas collecting and treating system (Roongtanakiat *et al.,* 2003).  An unlined landfill cannot prevent leacheate flowing to the area around the landfill sites and underground water beneath it. The leacheate are usually containing high concentration of heavy metal (Roongtanakiat *et al.,* 2003).

When the heavy metal contaminated the water bodies and the water used by human or animal, they will suffer serious damages to their vital organ due to the toxicity (Yadav, 2009). While the land that contaminated with this heavy metal cannot be use for plantation or farming because the soil will have very high acidity level. So the purpose of this study is to determine the heavy metal concentration at Ulu Tualang closed landfill in order to make sure the level of the heavy metal concentration is in safe condition.

## 1.3    Objectives

i.   To determine the presence and distribution of heavy metals (Ni and Cu) concentration in soil taken from the newly-closed Ulu Tualang landfill.

ii.  To determine the differences of heavy metal concentration between surface and sub-surface soil.

## 1.4    Scope of Research

### 1.4.1   Type of Heavy Metal

In this study, there are two types of metal that will be focus. The first one is nickel and the second one is copper. Nickel is a silvery-white lustrous metal, belongs to transition metal element category and has a high melting point (1453°C). It is hard, ductile and can be used for anti-corrosion purpose due to its properties. Nickel and its compound are mainly used in construction, automobile manufacturing and battery production.

Copper is a transition metal that belongs to Group 11 of the periodic table. Its melting point is around 1084°C and has a good thermal conductivity around 401

W.m$^{-1}$.K$^{-1}$. Copper are usually used as electrical conductor and become important material in building construction. Cu concentration in landfill is quite high when clothing and wood industries waste founded while high Ni values might be contributed to metal processing or municipal waste including batteries (Kasassi *et al.,* 2007).

### 1.4.2   Area Description & Layer of Soil

There are 5 layers in soil structure including O-horizon (0-2 inch), A-horizon (2-10 inch), B-horizon (10-30 inch), C-horizon (30-48 inch) and R-horizon. In this research, the heavy metal concentration analysis will conducted only for A and B-horizon layer. Surface soil (A-horizon) is the layer that below the O-horizon layer and contain a lot of organic matter. Sub-Soil (B-horizon) is a zone of accumulation to occur and consist of mineral layers.

The Ulu Tualang closed landfill is located at Mukim Mentkab, Temerloh, Pahang state of Malaysia. The landfill is near the Temerloh Industrial Estate and Mentakab Industrial Park that focusing in stainless steel fabrication and wood base industry. As additional information, there are 15 landfills are located in Pahang state. 13 of them are operated by Alam Flora including the Ulu Tualang Landfill. The landfill had been closed in 30$^{th}$ June 2010 and handed over to Cypark Resource Sdn. Bhd.
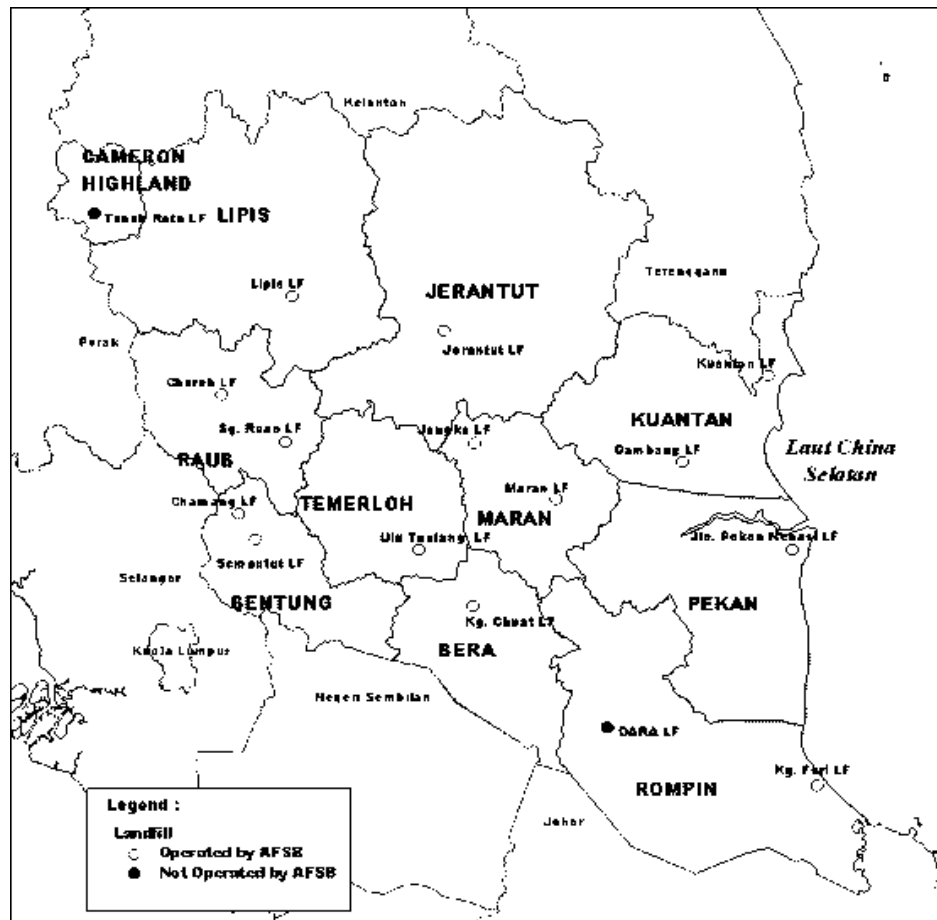
**Figure 1.1** Location map of Ulu Tualang closed landfill

The company list  that probably using the landfill ;

   i.     Megaply Industries (M) Sdn Bhd (Plywood & Veneers).

   ii.    Intan Suria Sdn Bhd (Frames - Picture,Wood Products).

   iii.   SQ Wooden Picture Frame Moulding Sdn Bhd (Picture Frames - Wholesaler & Manufacturers).

   iv.   LCS Precast Sdn Bhd (Piling).

   v.    Mentakab Stainless Steel Works (Stainless Steel Fabricators).

   vi.   Syarikat Perniagaan Boon Wee (Biscuits - Wholesaler & Manufacturers,Food Products).

   vii.  Mentakab Agricultural Machinery Sdn Bhd (Agricultural Equipment & Supplies, Tractor Distributors & Manufacturers).

### 1.4.3   Acid Digestion Method

There are several types of acid digestion method that can be used for heavy metal extraction such as US EPA (Eniromental Protection Agency) method 3050, SCL (Southern California Labratory) method, ASTM (American Society of Testing and Materials) method and US EPA method 6020. For this research, the method that will focused is the SCL method. The detail methodolgy will be explained at the next chapter.

### 1.5      Rational and Significance

The purpose of this experimental research conducted is to get the mean value of copper and nickel concentration in Ulu Tualang newly-closed landfill. With this mean value, it can be compared to US EPA soil standard to make sure either the area have in the safe level. Besides that, statistical data that obtained will be very useful for this landfills management for treatment and soil remediation purpose.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1    Overview

This chapter wills reviews the types of landfills such as landfill for commingled MSW, landfill for shredded solid waste and monofills landfills. It also will review the element of landfill closure plan, part of sanitary landfill, Ni and Cu toxicology, an overview of sampling processing and analysis, Ni and Cu alternative removal and a brief of in-situ measurement. Besides that, a previous research also will be reviewed.

## 2.2    Types of Landfills

### 2.2.1   Landfills for Commingled MSW

Municipal solid waste (MSW) usually comes from household waste and industrial waste. So major of the landfills in this world are designated for commingled MSW. This type of landfill also accept limited amount of nonhazardous industrial wastes and sludge wastewater treatment plants. Demand for this type of landfill is very high even abandoned or closed landfills in some locations are being reused by excavating the composed material and some cases, the composed material stockpiled, and a liner is installed before the landfill is reactivated for landfilling purpose (Tchobanoglous *et. al*., 1993).

### 2.2.2 Landfills for Shredded Solid Waste

This type of landfill is an alternatives ways to solid waste disposal where it involving shredding steps for the solid wastes before places them in a landfill. With this new method, the shredded solid waste can be placed at up to 35 percent greater density than the common method. On the other hand, it also had disadvantages including needs of highly cost shredding facility. But it can save a lot of money in areas where landfill capacity is very expensive and can produce compost that can be used as intermediate cover material (Tchobanoglous *et. al*., 1993).

### 2.2.3 Landfills for Individual Waste Constituents

Known as monofills, these landfills typically accept combustion ash, asbestos, and other similar waste. The designated wastes usually isolated from common solid waste. This type of waste are nonhazardous but may release constituents in concentration that exceed applicable water quality and sometimes contains small amounts of unburned organic material that will causing odors problems. Gas recovery system usually recommended for solving this problems (Tchobanoglous *et. al*., 1993).

### 2.3 Element of Landfill Closure Plan

### 2.3.1 Final Cover Design

For the first element of the closure plan is the final cover design. The surface that placed over a landfill that wanted to be closed called final cover. It is very important to design this final cover following the parameters to make sure it can functional to control the emissions of the landfill and can support the growth of vegetation process. Vegetation is the favorite method that used for covering the closed landfill site. So, when planning the landfill closure, the planners should select

the best plant that can survive for this purpose. Besides that, the planner also must plan the type, density, permeability and thickness of soil that will be used for covering the landfill (Tchobanoglous *et. al.*, 1993).

### 2.3.2    Surface Water Control Design

The second element is the drainage control design. Drainage control system is very important to prevent and controlling the surface water from penetrate the final cover. The worst case scenario of a landfill is when the surface water penetrates the cover soil and leach the heavy metal to the underground water. There are several features that should be consider when design the drainage control system including (Tchobanoglous *et. al.*, 1993);

1. The shortest distance of collecting and routing of surface water off from the landfill.
2. Selection of channel and drainage ways
3. Calculating the slope to maximize the removal of surface water.
4. Specification of material that used for the drainage for easier maintenance.

### 2.3.3    Landfill Gases Control Design

The third element is the landfill gases control design. A landfill gas control system is very important for an active landfill or a closed landfill. This is important because, gases such as methane are continuously generated from the landfill. The crucial steps for designing a gas control system are selection of material and the placement of wellheads, valves, and collection pipes in the final cover. The material should be flexible and strong enough for various conditions. It is also important to consider the quantity of methane gas production for combustion process (Tchobanoglous *et. al.*, 1993).

### 2.3.4   Leachate Treatment & Control Design

The forth element is the leachate treatment and control design. Besides contaminating the sub surface soil, leachate also can mobilize the contaminant further to the underground water. To minimize the problem, the planner should reconsider the final cover design, the types of waste placed in the landfill, the climate and precipitation of the area (Tchobanoglous *et. al*., 1993). Some of modern countries start using green technology to control the leachate such as using Vitever grass to absorb the leachate content in the soil (Roongtanakiat *et. al*., 2003).

### 2.3.5   Environmental Monitoring Facilities Design

The final part of the plan is designing the environmental monitoring facilities. These facilities are very important to make sure that the integrity of the landfill is maintained. The plan usually follows the guidelines of the regulatory agency. Monitoring facilities that usually installed are groundwater monitoring wells, vadose zone lysimeters, gas vents, leachate treatment facilities and storm water holding basins (Tchobanoglous *et. al*., 1993).

### 2.4   Part of Sanitary Landfill

### 2.4.1   Bottom Liner System

Function of a bottom liner is to prevent the trash from coming in contact with the outside soil, particularly the groundwater. There 3 types of liner that usually used such as clay liner, plastic liner and composite liner. Geomembrane clay liner or GCLs are comprised of a thin layer of sodium or calcium bentonite bonded to a layer or layers of geosynthetic (Bouazza,2001). The geosynthetics are either geotextiles or a geomembrane.

For plastic liner, the liner are from synthetic material such as polyvinyl chloride (PVC), chlorinated polyethylene (CPE), chlorosulphonated polyethylene (CSPE), ethylene propylene rubber (EPDM), polypropylene (PP), linear low-density polyethylene (LLDPE), medium-density polyethylene (MDPE) and, more recently, the bituminous geomembrane. A research by Rowe and Sangam (2002) stated that High-density polyethylene (HDPE) geomembranes have been used exclusively in landfill applications, especially for bottom liners, because of their relatively high resistance. While a composite liner is a liner of two component, a geomembrane and a layer of permeability soil (Giroud and Bonarpate, 1989).

### 2.4.2   Water Drainage and Leachate Collecting System

The purpose of a leachate collection and removal system is to remove contaminated water from the base of a landfill waste containment cell for the purpose of minimizing the hydraulic head on the liner system or subgrade of the landfill cell (Warith *et. al*., 2004). A leachate collection and removal system should consist of a granular soil layer or geocomposite drainage layer of adequate long-term hydraulic conductivity so as to collect the leachate being transmitted through the waste mass (Koerner and Soong, 2000).

### 2.4.3   Methane Collection System

When solid waste is buried in a landfill, the biodegradable fractions of the solid waste will be decompose via a complex series of microbial and abiotic reactions. Methane ($CH_4$), one of the terminal products, is formed by methanogenic microorganisms under anoxic conditions, either through the direct cleavage of acetate into $CH_4$ and carbon dioxide ($CO_2$) or the reduction of $CO_2$ with hydrogen (Spokas *et. al*., 2006).

Methane that produce from the landfill can be used to fuel industrial or commercial boilers, to generate electricity using internal combustion engines or gas turbines, and to produce a substitute natural gas suitable for compression or pipeline

transport. Beside supplying the energy, recovery of methane from the landfill also can reduce global warming because methane is second most important greenhouse gas.

## 2.5    Heavy Metal Toxicology

### 2.5.1    Copper Toxicology

Copper plays important role in ecosystem including $CO_2$ assimilation, ATP synthesis and considered as a micronutrient for plants (Yadav, 2009). On the other hand, when it in excess amount, it can bring harms to human, animal and plant. The increasing of Cu can be enhancing by many factors. There are including industrial and mining activities. High concentration of Cu in soil can plays cytotoxic role, induces stress and cause injury to plant that leads to plant retardation and leaf chlorosis (Lewis *et al.*, 2001). For human, excess amount of Cu can cause cardiovascular disease and diabetes while acute Cu toxicity can result in liver disease and neurological defects (Uriu-Adams and Keen, 2005).

### 2.5.2    Nickel Toxicology

Nickel is also can bring many negatives effects to our health and the ecosystem if in excessive amount. Similar with the Cu, the Ni level in soil can be enhancing by mining activity, industrial waste and open burning of coal. Plant grown in high Ni containing soil showed impairment of nutrient of nutrient balance and resulted in disorder of cell membrane functions (Yadav, 2009). Human that lives in that polluted area will have percentage to get lung cancer due to its carcinogenic properties (Kasprzak *et al.*, 2003).

**2.6     Sample Processing & Analysis**

To determine the concentration of the heavy metal compound in the landfill soil, a suitable method must be chosen in order to get the accurate value. There were several method had been used by other researchers to processing the sample. The first step is the sample collecting. The common method is using a driller. Drilling depth sometimes had to be extending to find the maternal rock and to get a varied depth of the wells (2.3-17.5m) because the thickness of waste in the landfill is varied (Kasassi *et al.,* 2007). The sampling point can be chosen randomly or systematically using gridding method.

For the second step is sample digestion. The sample that obtained from the first step must be digesting to extract the heavy metal compound from the soil. The best method needed to make sure the heavy metal is fully extracted and give the real concentration level when conduct the analysis stage. For pollutant inputs are not silicate-bound, a 'pseudo total' analysis of strong acid digest such as aqua-regia digestion method is sufficient (Sabienë *et al.*, 2004). The alternative way is digesting the sample with $HNO_3$ and $H_2O_2$ using the Method 3050B suggested by USEPA (Chen *et al.,* 2004).

Besides using chromatographic separation and spectroscopic techniques such as Atomic Absorption Spectroscopy (AAS), in situ analysis method can be used to reduce time and effort that needed to extract the sample before can analysis it. The capability to perform direct, in situ analysis of solid soil sample, without the need for digestion as is potentially available through portable XRF instruments would be a major step forward (Radu and Diamond, 2008). A fast method for sure gives a lot of advantages especially when it comes to human health issues. This will be discussing further in the next subtopic.

## 2.7    Ni and Cu Alternative Removal Techniques

Different from Method 3050B and aqua-regia digestion method, removing copper, Cu from contaminated landfill soil using flushing method is quite challenging. Flushing Cu from the soil with 0.1M aqueous solution of ethylene-diamine-tetra-acetic (EDTA) reported can be maximize the extraction efficiency about 60% (Palma and Medici, 2002) can give a reason why this study still get a place for further research. Beside ex-situ method, in-situ removal techniques are a very important due to its potential to become the main rapid treating method for heavy metal pollution. One of the most popular is the electro-kinetic removal technique. It relies on the application of low-density direct current between electrode placed in the soil and works due to the presence of enough moisture in the soil particle to have an inherent electrical conductivity (Ravera *et al.,* 2005).

On the other side, nickel removal from soil also becomes the main title for many researches. As a fact, not all of the heavy metal can be easily flush from the soil including Ni and Cu. Therefore, most of this intellectual person starts to think to prevent the metals to transport into the soil (Imperato *et. al.*, 2003). And the result, the come with a solution that is using calcium (Ca) as the factor to increase the Ni desorption level into the soil. Ca can compete strongly with other metals to get adsorption sites on the mineral surface (Wang *et al*., 1996) and automatically can prevent other hazardous metal to pollute the soil. As we know, Ca is a not hazardous element even taken in a high concentration.

## 2.8     In-situ versus Ex-situ Measurements

### 2.8.1  Differential Pulse Anodic Stripping Voltammeter

In-situ measurement means the soil analysis conducted at the field area. It differs with the ex-situ measurement. With this new type of measurement, researcher did not need to collect a large of number of samples, transport them to the laboratory, pre-treatment them according the detection method that will be used to determine the composition such as AAS or ICP-MS (Tieje *et al*., 2003). The major advantages of this method is it can detect and identify metals in multi-metal mixtures while the well-known AAS method just only can detect one heavy metal for each testing.

### 2.8.2  Portable XRF Techniques

XRF or X-ray Fluorescence Radioisotope had many advantages than the conventional method because it faster and provide simultaneous analysis of up to 25 elements (Radu and Diamond, 2009). Even though the AAS analysis method is widely used and very precise, but this method is very slow and expensive. Besides that, this portable XRF instruments are highly correlated with AAS and it do not need any digestion of samples (Radu and Diamond, 2009).

**2.9     Heavy Metal Distribution in Landfill Soil**

Previous research by Kasassi *et. al.* (2008) had been done at a closed unlined landfill located near Thessaloniki, in northern Greece. From Figure 2.1, his research data shows that Cu concentration is around 8.13-356.25 mg/kg while Ni concentration detected around 5.63-63.75 mg/kg. For this research Aqua Regia extraction method had been used and 40 samples had been taken.

| Drilling | Metals | Mean values | Std. dev. | Range |
|---|---|---|---|---|
| 1 | Cd | 2.50 | 1.50 | 0.75–3.88 |
|   | Cr | 74.69 | 55.30 | 37.50–156.25 |
|   | Cu | 18.75 | 5.30 | 15.00–26.25 |
|   | Ni | 40.00 | 16.04 | 20.00–58.75 |
|   | Pb | 10.62 | 5.25 | 3.75–16.25 |
|   | Zn | 24.84 | 3.83 | 20.00–29.38 |
| 2 | Cd | 2.33 | 1.31 | 0.63–4.00 |
|   | Cr | 18.83 | 12.41 | 6.25–38.13 |
|   | Cu | 27.88 | 12.82 | 17.50–42.50 |
|   | Ni | 30.50 | 11.93 | 18.13–45.00 |
|   | Pb | 9.38 | 5.18 | 3.75–14.38 |
|   | Zn | 38.38 | 6.13 | 30.00–46.88 |
| 3 | Cd | 1.19 | 0.80 | 0.63–1.75 |
|   | Cr | 39.69 | 11.05 | 31.88–47.50 |
|   | Cu | 27.81 | 6.63 | 23.13–32.50 |
|   | Ni | 35.63 | 29.17 | 15.00–56.25 |
|   | Pb | 7.50 | 1.77 | 6.25–8.75 |
|   | Zn | 25.94 | 3.09 | 23.75–28.13 |
| 4 | Cd | 6.84 | 8.09 | 0.75–18.75 |
|   | Cr | 15.88 | 10.85 | 3.88–25.00 |
|   | Cu | 18.28 | 5.98 | 10.00–23.75 |
|   | Ni | 34.38 | 29.07 | 5.63–63.75 |
|   | Pb | 10.00 | 6.96 | 2.50–16.25 |
|   | Zn | 29.69 | 12.08 | 14.38–41.88 |
| 5 | Cd | 2.66 | 1.85 | 0.50–7.50 |
|   | Cr | 43.52 | 17.28 | 24.38–73.13 |
|   | Cu | 26.31 | 8.62 | 14.38–40.63 |
|   | Ni | 40.27 | 17.81 | 13.13–59.38 |
|   | Pb | 13.67 | 6.04 | 7.50–26.25 |
|   | Zn | 49.63 | 30.21 | 23.13–100.00 |
| 6 | Cd | 3.15 | 2.59 | 0.75–9.38 |
|   | Cr | 49.43 | 48.24 | 10.00–171.88 |
|   | Cu | 68.58 | 97.39 | 8.13–356.25 |
|   | Ni | 23.05 | 13.94 | 6.00–46.88 |
|   | Pb | 29.43 | 25.99 | 11.25–92.50 |
|   | Zn | 78.72 | 108.12 | 6.38–343.75 |

**Figure 2.1** Heavy metal distributions in soil at Thessaloniki closed unlined landfill

Source: Kasassi *et. al.* (2008)

A research that conducted by Esssaku et. al. (2003) at Chennai landfill, India founded that Cu content is ranged from 75-217 mg.kg while Ni concentration ranged from 21-112 mg/kg. For this research, Aqua Regia method also had been used and 12 samples had been taken.

| S.No | Particulars | Hg | As | Cd | Ni | Pb | Cu | Cr | Zn |
|------|-------------|------|------|------|------|------|------|------|------|
| 1 | Minimum | 0.039 | 0.077 | 0.820 | 21.0 | 53.0 | 75.0 | 110.0 | 167.0 |
| 2 | Maximum | 0.78 | 1.561 | 1.77 | 50.0 | 112.0 | 217.0 | 261.0 | 503.0 |
| 3 | Median | 0.21 | 0.451 | 1.28 | 33 | 85 | 105 | 129.5 | 230.5 |
| 4 | Mean ± SD | 0.29±0.22 | 0.57±0.38 | 1.29±0.31 | 32±8 | 86±16 | 113±42 | 140±40 | 284±111 |
| 5 | Indian Compost Standards * | 0.15 | 10.0 | 5.0 | 50 | 100 | 300 | 50 | 1000 |
| 6 | USEPA Compost Standards ** | 17.0 | 41.0 | 39.0 | 420 | 300 | 1500 | 1200 | 2800 |

All the values are in mg/kg.　No. of samples: 12
\*　MSW (Management and Handling) Rules, 2000.
\*\* US Composting Council, 1997.

**Figure 2.2** Statistic of heavy metal concentration in soil containing MSW fine fraction at Chennai landfill

Source: Esssaku *et. al.* (2003)

# CHAPTER 3

# METHODOLOGY

## 3.1    Overview

This chapter will discuss about the methodology of this research. There are 7 stage of work flow for this research, starting with identifying problem and ended with analyzing result data. Rather than in-situ method, ex-situ had been chosen because limitation of equipment and the precision of the method itself. Apparatus, reagents and equipment also listed in this chapter for future references.

## 3.2    Research Activities
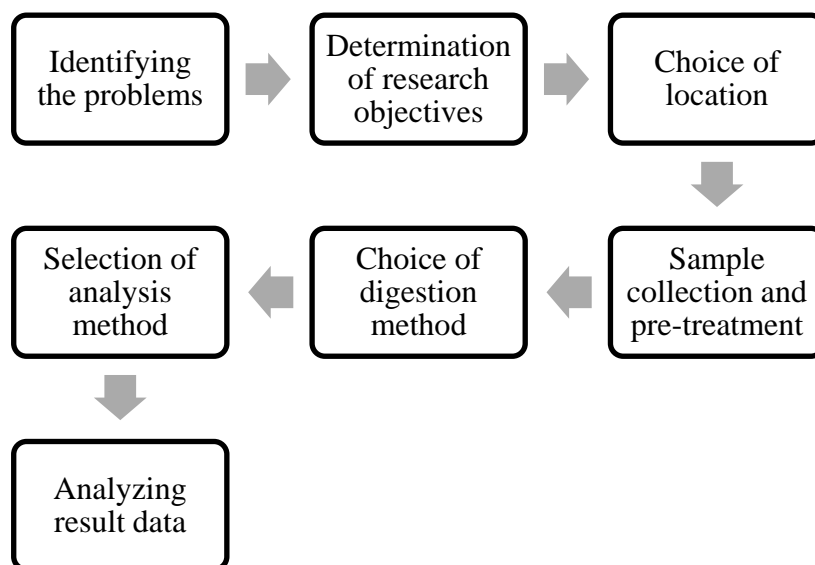


**Figure 3.1** Research activities work flow

### 3.2.1   Identifying the Problem

Before research's title confirmed, first of all, field of the research must be determined and selected. For this research environmental case study had been chosen. Then, selection of problem usually based on problem that our country faced. After further reading, landfilling problem had been selected and discussed for title selection.

### 3.2.2   Determination of Research Objectives

Before conducting the experimental works, the objectives of this research must be clearly stated. This objective will guide the research to achieve the main purpose of this research and prevent unnecessary works that can interrupt the quality of the collected data.

### 3.2.3   Choice of Location

To conduct an environmental case study research, the first thing that must be considered is the case scenario and a research target area. So, for this research, choice of location was very critical. The first criteria that should be filled are the target area must a closed landfill.

### 3.2.4   Sample Collection and Pre-treatment

50m x 50m area had been chosen to represent the landfill area. The area gridded systematically (10m x 10m) uses measuring tape and rope. That will give 25 sampling points. For each sampling point, 2 samples had been taken, first sample taken at 2-10 inch depth for the top soil and second sample taken at 10-30 inch depth for the sub-surface soil. Mini shovel had been used for the digging works a steel rules used for determine the depth. The samples kept in plastic bag, numbered 1 to

25 and labeled 'A' for the top soil while 'B' for the sub surface soil. The raw samples then transported to laboratory.

Pre-treatment of the sample start with drying the raw sample using microwave or drying oven around 30°C - 40°C for 15 minutes. The samples allowed cooling before pulverized using mortar and pestle. After that, the samples sieved and mix thoroughly to achieve homogeneity. Then the treated sample sealed to prevent contamination before it proceeds to the next step.

**3.2.5   Digestion Process**

There are several acid digestion methods that can be chosen for extracting the heavy metal content in the soil samples such as US EPA method 3050, ASTM method 9.3.4, SCL method and US EPA draft method 6020. The purpose of the acid digestion is to solubilize all elements of interest. To achieve the purpose this acid digestion method must perform two distinct tasks, the first one it must decompose the sample matrix to expose the entire mass to the acid cocktail and second is it must react with the elements of interest to form water-soluble compound (Kimbrough and Wakakuwa, 1992). Each of this method has different extraction capability. For this research, From Figure 3.1, SCL method had been chosen due its high capability extraction of Cu and Ni and this method also faster than other method (Kimbrough and Wakakuwa, 1992).

| sample | elem | method |  |  |  |
|---|---|---|---|---|---|
|  |  | 3050 | SCL | 6020 | ASTM 9.3.4 |
| A | V | 31000 | 31000 | 29000 | 19000 |
| B | Ni | 270 | 310 | 210 | 230 |
|  | V | 28000 | 32000 | 28000 | 19000 |
| C | Ba | 340 | 510 | <200 | 220 |
|  | Cu | 1200 | 1100 | 1600 | 930 |
|  | Pb | 340000 | 110000 | 140000 | 880000 |
|  | Zn | 140 | 93 | <200 | 88 |
| D | As | 280 | 400 | <200 | 120 |
|  | Ba | 210 | 310 | <200 | 97 |
|  | Cr | 300 | 260 | <200 | 290 |
|  | Cu | 1300 | 1200 | 1600 | 670 |
|  | Pb | 280000 | 140000 | 150000 | 430000 |
|  | Sb | 1200 | 1300 | 510 | <50 |
|  | Zn | 1200 | 1100 | 620 | 940 |
| E | Pb | 130000 | 140000 | 150000 | 380000 |
|  | Sb | 2600 | 5300 | 2400 | <50 |
| F | As | 330 | 330 | <200 | <50 |
|  | Cu | 800 | 730 | 1300 | 970 |
|  | Pb | 220000 | 110000 | 90000 | 800000 |
|  | Sb | 23000 | 97,000 | 13,000 | 690 |
| G | Ag | <50 | 230 | <200 | <50 |
|  | Cd | 1600 | 2000 | 1800 | 1600 |
|  | Cu | 5000 | 6600 | 5500 | 4400 |
|  | Ni | 290 | 370 | 390 | 390 |
|  | Pb | 280000 | 110000 | 99000 | 230000 |
|  | Zn | 1400 | 1500 | 1600 | 1200 |
| H | Co | 610 | 460 | 690 | 91 |
|  | Cr | 6000 | 9000 | 8000 | 9100 |
|  | Cu | 470 | 680 | 670 |  |
|  | Mo | 2300 | 3200 | 2400 | 3200 |
|  | Ni | 13000 | 16000 | 13000 | 16000 |
|  | Pb | 190 | 350 | 450 | 280 |

**Figure 3.2** Heavy metal extractions using various methods

Source: Kimbrough and Wakakuwa (1992)

This method required 1.00-4.00 g of dried sample to be digested in a mixture of 9 mL of concentrated hydrochloric acid and 3 mL of concentrated acid at ambient air in a 50 mL digestion vessel. This mixture must be prepared in a fume hood due to the volatility of the acids. The sample and reaction mixture were slowly heated to 95°C to prevent an overly vigorous reaction. For the vapor recovery, a watch glass had been used. The digestion was continued until the disappearance of $NO_2$ (reddish brown) fumes and no more changes in appearance (Kimbrough and Wakakuwa, 1992).

In addition, the sample must be brought to near dryness and if necessary 10 ml of deionized water added to enhance the solubility of the metal chloride and metal nitrate. The times taken for the fumes disappear vary due to the type of soil. Most of

the samples take 30 minutes to 2 hours to achieve the condition. The digestate is the filtered using AAS grade filter paper (Whatman 41 or equivalent) and collected in a 100 mL volumetric flask. To enhance the filtration rate, a vacuum filter had been used for replacing the conventional filtration method. Then, the filter paper is washed with no more than 5 mL of hot (95 °C) concentrated hydrochloric acid and then 20 mL of hot deionized water (Kimbrough and Wakakuwa, 1992).

### 3.2.6   Analysis Using AAS

There are many type of analysis equipment that can be use for heavy metal determination in slurry mixture such as flame atomic absorption spectrometry (FLAA), graphite furnace atomic absorption (GFAA), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma atomic emission spectrometry (ICP-MS) (Kimbrough and Wakakuwa, 1992). For this research, FLAA had been used due to the equipment availability.

For preparing the standard solution, stock solution of Cu and Ni at 1000 ppm used. The stock solution diluted using ultra pure water to 1 ppm, 5 ppm, 30 ppm and 50 ppm using 100 mL volumetric flask for both heavy metal. For accurate dilution, micropipette had been used. Ultra pure water used to prevent contamination in the standard solution that can affect the standard curve. When dilution the stock solution, his equation had been used;

$$m_1 V_1 = m_1 V_2 \hspace{3cm} (3.1)$$

Where m1 is the stock solution concentration (in ppm), $m_2$ is the prepared standard solution concentration, $V_1$ is the volume that needed for the dilution, $V_2$ is the volume of the volumetric flask.

Before analyzing the samples, a calibration test must be conducted first. This test ran with dilute a 1000 ppm of stock solution to prepare 10 ppm, 20 ppm & 40 ppm standard solution for both heavy metal. With this calibration, the efficiency of

the spectrometer can determine. So, an accurate reading can be obtained. The spectrometer re-calibrated after each group of 10 successive measurements (Kasassi *et. al.*, 2008).

### 3.2.7   Analyzing Result Data

The data that obtained from the AAS is in part per million. So, when convert it to concentration unit, it will become µg/L. If the sample spiked, the value must be multiply with the Df (Dilution Factor). Df equation is shown below;

$$Df = \frac{\text{volume of dilution}}{volume\ of\ sample\ used}$$

(3.2)

Before the data taken, the value of the correlation coefficient must be determined first. The acceptable value is 0.9-0.99. If the values lower than 0.9 that means that the standard solutions have contamination and the data can not be taken. For this research the correlation coefficient for copper is 0.9906 and 0.9815. So, there is no problem with the standard curve and the data is valid for become the result.

This calculation will show the example of calculation for sample 1A for copper;

$$8.84\ ppm = \frac{8.84\ \mu g}{L}\ x\ \frac{dilution\ volume}{sample\ weight}\ x\ \frac{1000\ g}{1\ kg}\ x\ Df$$

$$= \frac{8.84\ \mu g}{L}\ x\ \frac{100\ mL}{1\ g}\ x\ \frac{1000\ g}{1\ kg}\ x\ 50$$

$$= 44.2\ \text{mg/kg}$$

Other samples calculation shown at the appendix A. After the value obtained, the value used to plot a graph.

### 3.3    Apparatus and Materials

i.      Shovel.

ii.     Measuring tape.

iii.    Rope.

iv.     Point pointer.

v.      Steel ruler.

vi.     Poly bag.

vii.    Drying ovens – able to maintain $30°C \pm 4°C$.

viii.   Mortar & pestle.

ix.     Sieve.

x.      Analytical balance.

xi.     Digestion vessels – 50ml

xii.    Filter paper.

xiii.   Vacuum filter.

xiv.    Funnel or equivalent.

xv.     Graduated cylinder.

xvi.    Heating source – adjustable and able to maintain a temperature of 90-95C.

xvii.   Temperature measurement device – capable of measuring to at least $125°C$.

xviii.  Vapor recovery device (ribbed watch glasses, appropriate refluxing device, and appropriate solvent handling system).

xix.    Volumetric flask – 100ml.

### 3.4    Reagent

i.      Ultra pure water.

ii.     Nitric acid (concentrated), $HNO_3$, 65 %. CAS no. 7697-37-2, Fisher Scientific.

iii.    Hydrochloric acid (concentrated), HCL, 37%. CAS no. 2315-95-7, Fisher Scientific.

**3.5    Analytical Equipment**

i.    Hitachi's Polarized Zeeman Atomic Adsorption Spectrometry (Flame Version)

**3.6    Precaution**

There are several precautions that should be concerned when conducting this research. It is very important to ensure the data that obtained from this research are accurate and valid for future reference. The things that we need to consider are;

i.    Plastic equipment must be used for handling, storing and analyzing the sample to prevent metal-contamination in the sample.

ii.   All equipment should be cleaned before treating the next sample to minimize the potential of cross-contamination.

iii.  Make sure heat the slurry mixture (sample + digester) not exceed 95°C to prevent an overly vigorous reaction.

iv.   Only used ultra pure water when using the AAS equipment to ensure the AAS reading did not interurpted by outside contamination.

v.    When handling the concentrated HCl and $HNO_3$, used glove, mask and do the wwork inside the fume hood.

### 3.7　Summary of Procedures
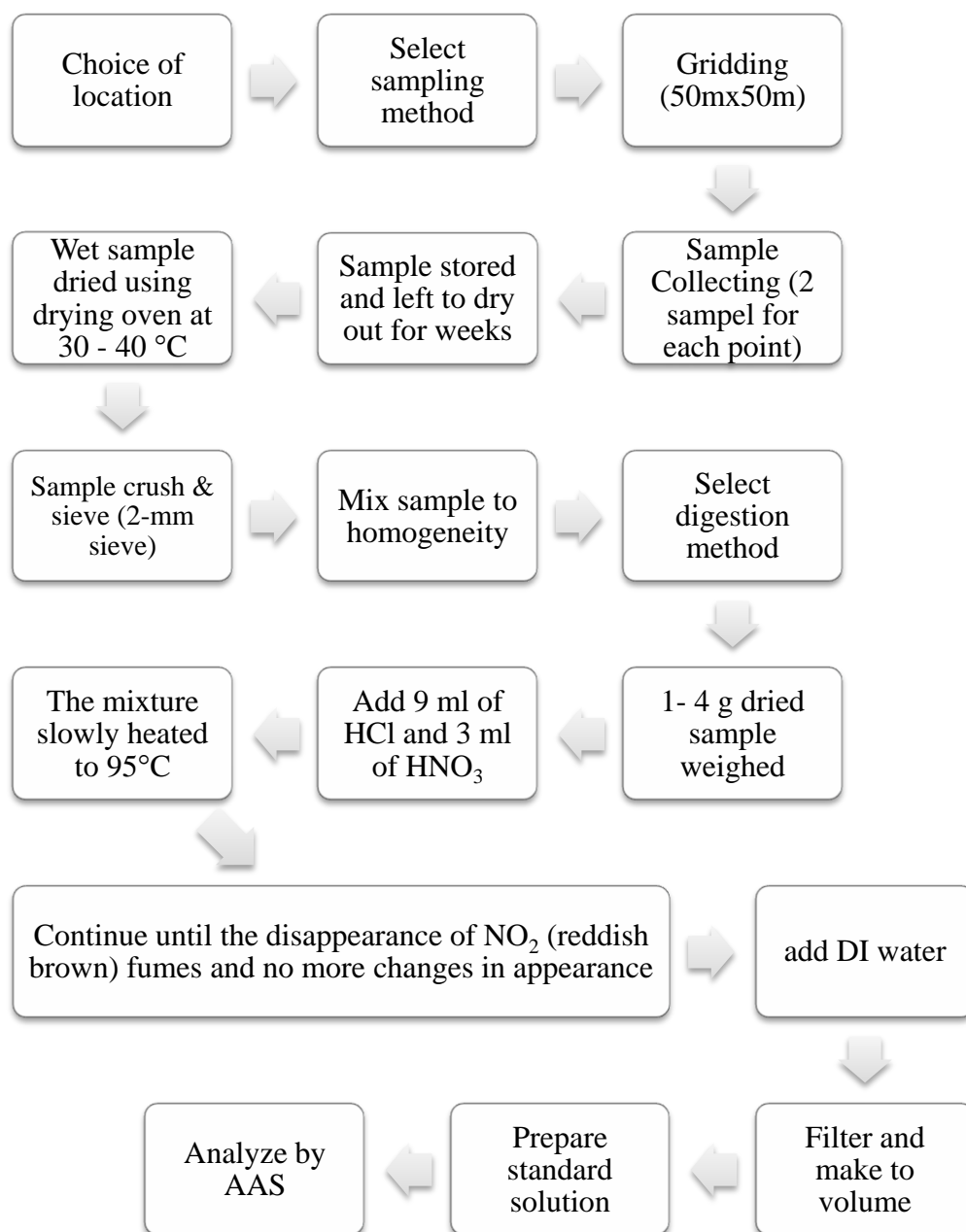


**Figure 3.3** Summary of procedures

# CHAPTER 4

# RESULT & DISCUSSION

## 4.1    Overview

SCL method digestion method and atomic adsorption spectrometry analysis is one of accurate combination method for analyzing heavy metal concentration in contaminated soil (Kimbrough and Wakakuwa, 1992). This method had been practiced and proved by many researcher and environmental engineer for environmental assessment. Even though there are many in-situ method had been developed recently, this combination method still become favorite and bench mark method due to its precision data. At the end, the data that obtained from this research will very useful for future references for this landfills treatment and soil remediation purpose.

## 4.2    Heavy Metal Distribution for Different Depth

For the first parameter, heavy metal concentration will be determined for different layers of soil. So, for the first run, 50 samples digested and analyzed using the combination method. 25 samples had been tested for the top soil and other 25 samples tested for sub-surface soil. After finished the analysis step, data that obtained were in negative value. The negative value also proved by Cristidis *et. al.* (2007). The negatives values were obtained for both heavy metals. So, 10 samples had been selected and spiked to get the actual concentration value. Figure 4.1, 4.2, 4.3 and 4.3 shows the distribution of the heavy metal in grid view.
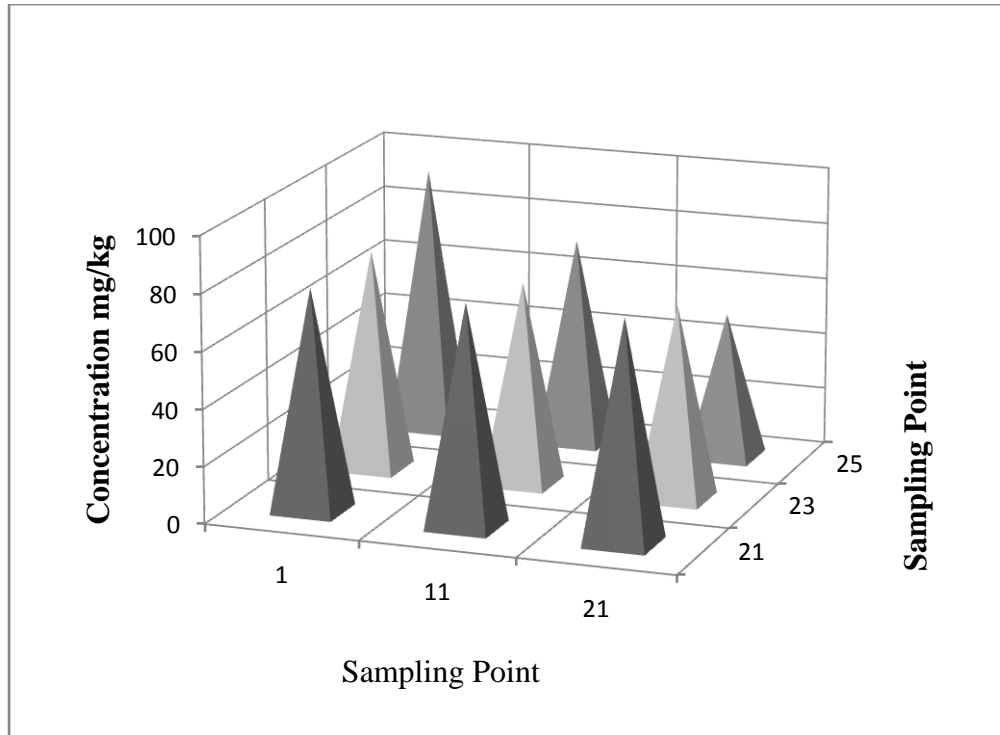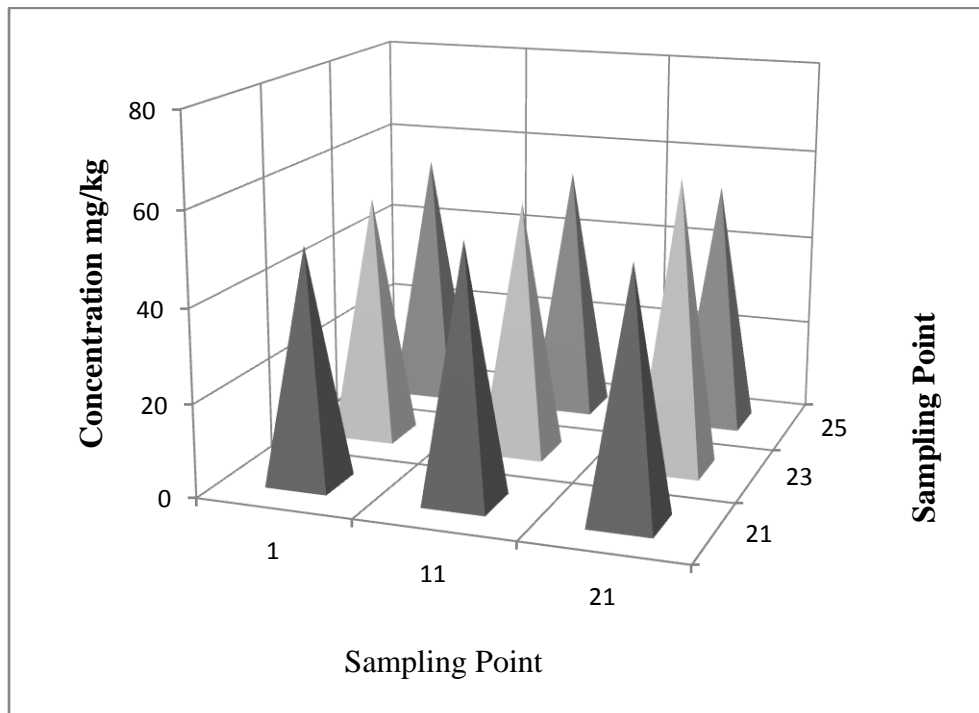
**Figure 4.1** Distribution graph for nickel in top soil
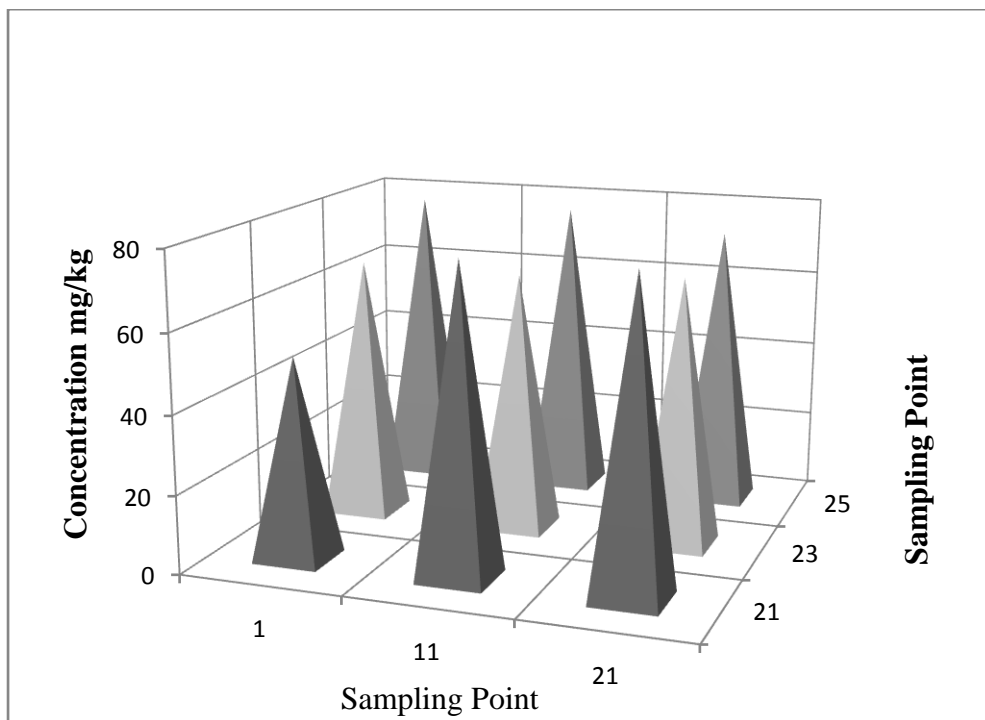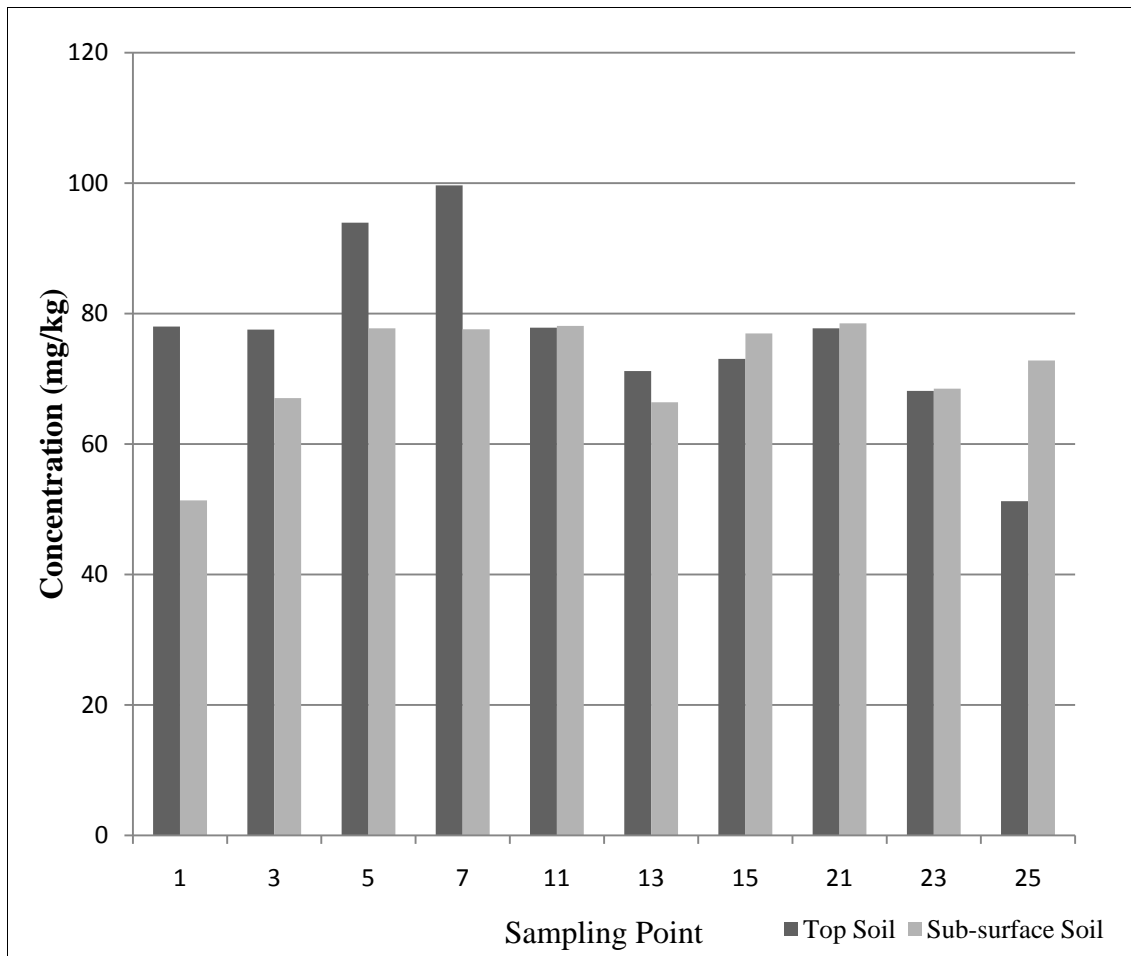


**Figure 4.2** Distribution graph for nickel in sub surface soil
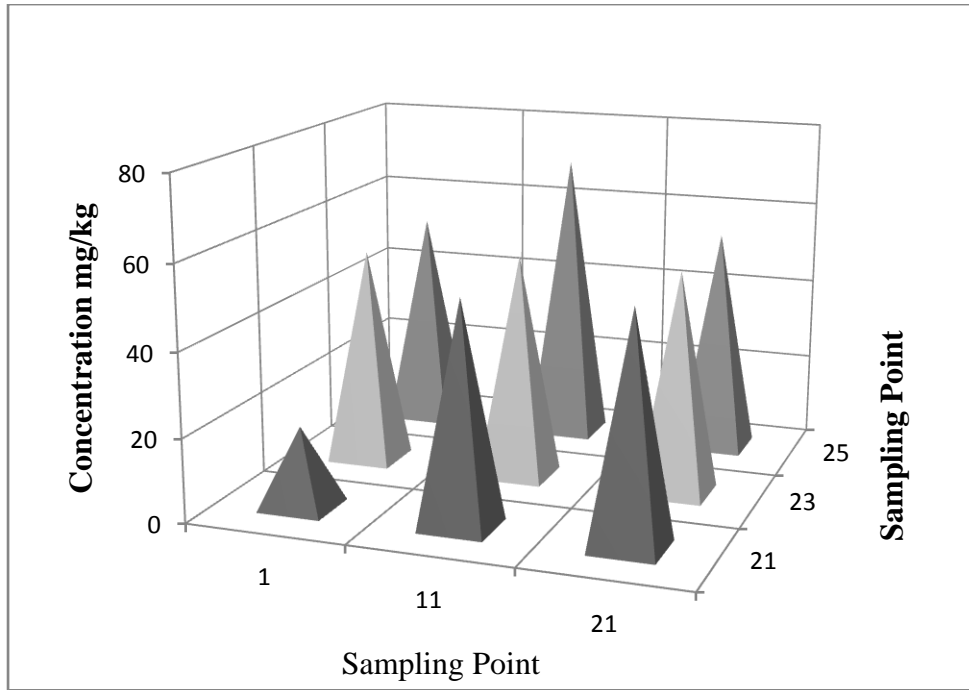
**Figure 4.3** Distribution graph for copper in top soil



**Figure 4.4** Distribution graph for copper in sub surface soil

**Figure 4.5** Graph of nickel concentration versus sampling point

From Figure 4.5, sampling point 1,3,5,7 and 13 shows that nickel concentration in top-soil is higher than the sub-surface soil while sampling point 11,15,21,23 and 25 shows differently. Average nickel concentration for top soil is 76.84 mg kg$^{-1}$ while average concentration for the sub-surface soil is 71.5 mg kg$^{-1}$. Since Malaysia has not yet to come with her own maximum allowable limit, the comparison had been done according to the limit values published by European community. For EU, Permissible Exposure Limit (PEL) for nickel in soil is 30-75 mg kg$^{-1}$. That means 60% of top soil samples and 50% of the subsurface soil samples had been exceeded the PEL value.
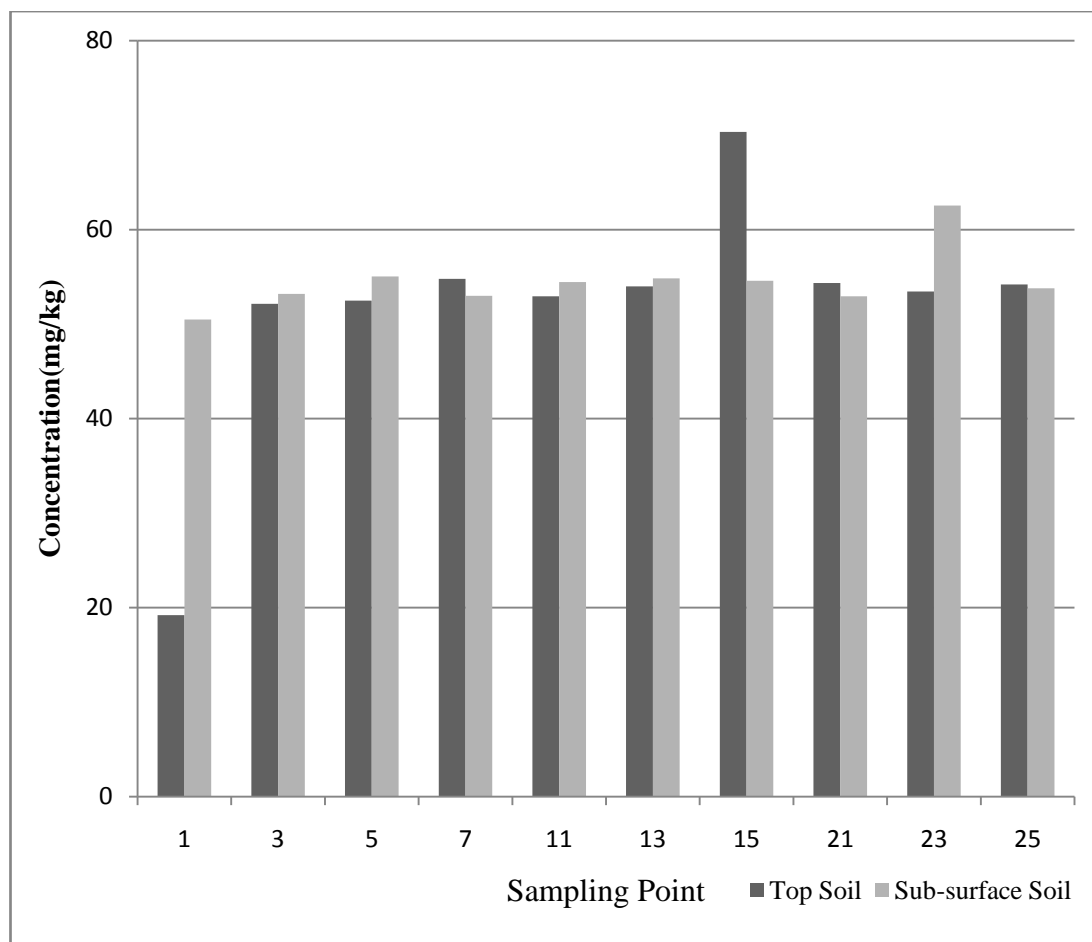
**Figure 4.6** Graph of copper concentration versus sampling point

From Figure 4.6, sampling point 1,3,5,11,13 and 23 shows that copper concentration in sub-surface soil is higher than the sub-surface soil while four other sampling point shows differently. Average copper concentration for top soil is 51.8 mg kg$^{-1}$ while average concentration for the sub-surface soil is 54.5 mg kg$^{-1}$. For sampling point 1, top-soil Cu concentration very low can be explained by phytoextraction of metals by natural vegetation (Esakku *et. al*., 2003). PEL for Cu concentration in soil according to the EU is 50-140 mg kg$^{-1}$. So, there are no Cu-contamination problem is determined for this landfill as the EU limit value is 140 mg/kg.

## 4.3    Ni and Cu Concentration Comparison
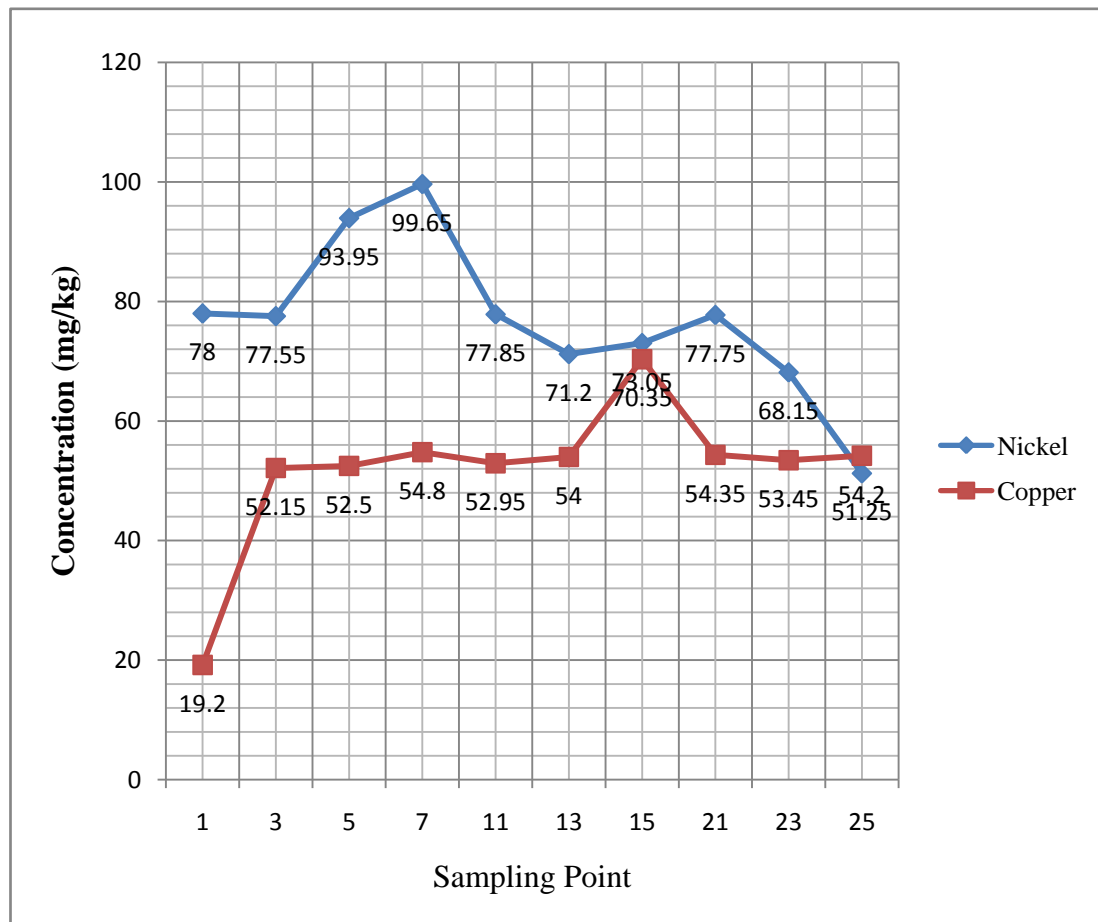


**Figure 4.7** Graph of heavy metal concentration versus sampling point for sub surface soil

Figure 4.7 shows that Ni concentration in the soil is higher than Cu for all sampling points for top soil. Difference of mean value for both heavy metals is around 25.04 mg/kg. The largest difference is at sampling no. 1 and the lowest is at sampling point no. 15. High concentration of Ni might be contributed to metal-processing waste and municipal wastes such as batteries, electric and electronic equipment waste (Kasassi *et. al*., 2008).
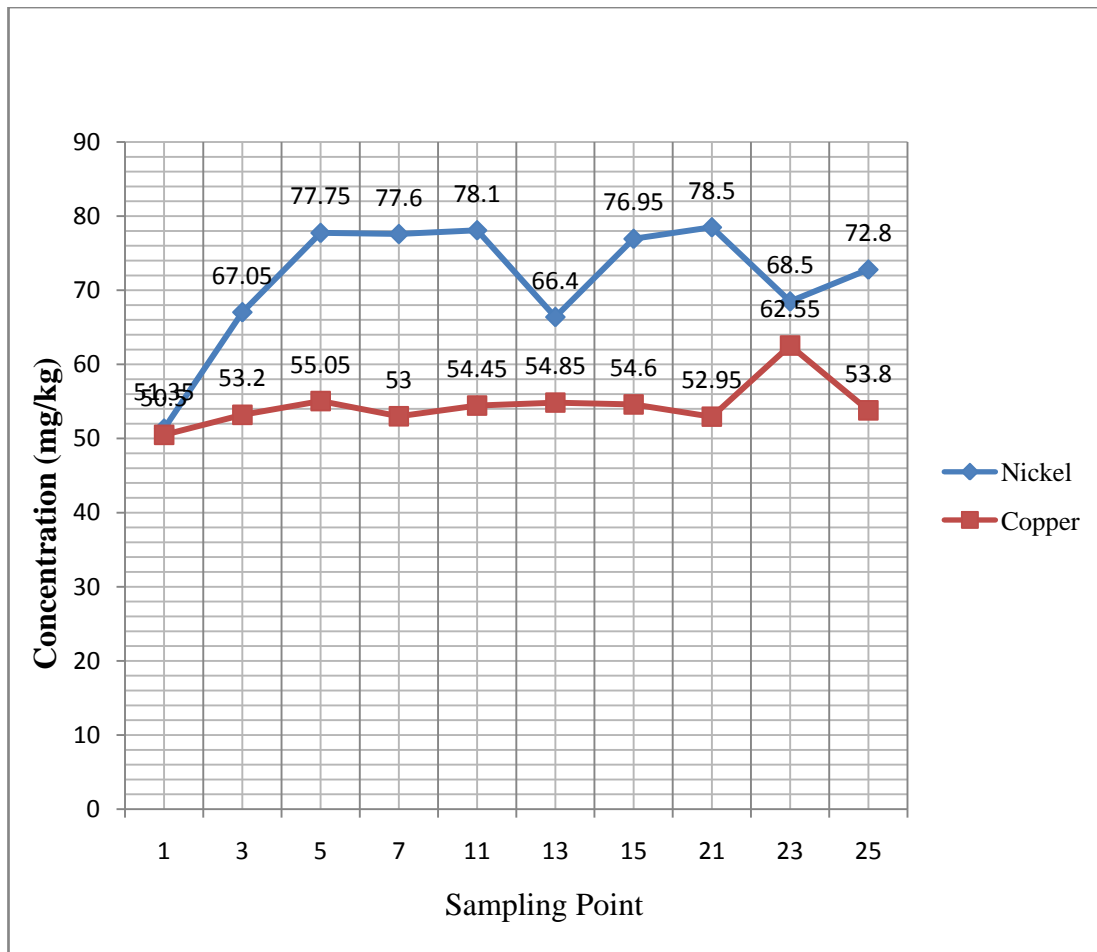
**Figure 4.8** Graph of heavy metal concentration versus sampling point for sub surface soil

Figure 4.8 shows that Ni concentration in the sub-surface is also higher than Cu for all sampling point. Difference of mean value for both heavy metals is around 17 mg/kg. The largest difference is at sampling no. 21 and lowest is at sampling point no. 1. Figure also shows that the Cu distribution of concentration in the sub-surface soil is constant. Constant concentration of copper might be issued from clothing or wood industries or pipeline sections waste (Kasassi *et. al.*, 2008).

## 4.4    Metal Chloride and Metal Nitrate

In this research, the acid digestion method had been used. This can be explained using chemical reaction of copper and nickel with the concentrated acid. The chemical reaction for both heavy metals had shown below;

$$Cu^{2+} + 2HCl \rightarrow CuCl + H_2 \qquad\qquad (4.1)$$
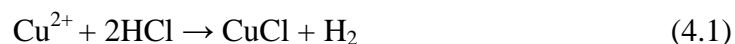
This equation shows that copper ion will react with the hydrochloride acid to form water soluble copper (II) chloride.

$$Cu^{2+} + 4\ HNO_3 \rightarrow Cu\ (NO_3)_2 + 2\ H_2O + 2\ NO_2 \qquad\qquad (4.2)$$
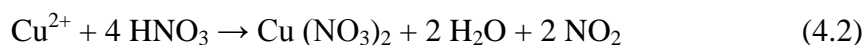
Equation above shows that copper ion will form copper (II) nitrate that also soluble in water when reacted with nitric acid.

$$Ni^{2+} + 2HCl \rightarrow NiCl + H_2 \qquad\qquad (4.3)$$

For nickel, reaction with hydrochloric acid will form nickel (II) nitrate that quite high solubility in water (254 g/100 mL).

$$Ni^{2+} + 4\ HNO_3 \rightarrow Ni\ (NO_3)_2 + 2\ H_2O + 2\ NO_2 \qquad\qquad (4.4)$$
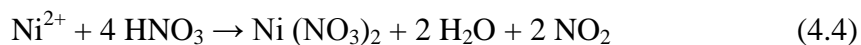
While, when nickel reacts with nitric acid, it will form low solubility salt, nickel (II) nitrate that have solubility in water around 94.2 g/100 mL. From this chemical reaction, adding water after digestion the sample will help increase the heavy metal extraction (Chuangcham et. al., 2008).

**4.5     Soil Properties**

According to data in table 4.1, the type of soil samples are various such as clay, coarse sand, peat and laterite. From the observation also, there are no significance differences in type of the soil for both layers. 40% of the samples are clay soil, 30% are peat soil and other 30% are laterite soil. From table 4.2, the pH value was generally neutral and sub acidic for both soil layers. Only few samples from the landfill showed pH value lower than 6.3. The pH value ranged from 5.11-7.20 for the top soil while for sub surface soil, it ranged from 5.68-6.90.

**Table 4.1** pH values for top soil and sub surface soil

| Sampling Point | Top Soil (pH) | Sub-surface Soil (pH) |
|:---:|:---:|:---:|
| 1 | 5.11 | 5.68 |
| 3 | 6.70 | 5.65 |
| 5 | 6.33 | 6.33 |
| 7 | 6.29 | 6.11 |
| 11 | 6.86 | 6.90 |
| 13 | 6.59 | 6.89 |
| 15 | 6.55 | 6.62 |
| 21 | 6.78 | 6.69 |
| 23 | 7.20 | 6.72 |
| 25 | 6.60 | 6.81 |

From table 4.1 and 4.2, the data also showed that clay type soil have lower pH than other type of soil. For peat soil, the pH value ranged 6.55-6.62 while laterite soil pH value ranged from 6.60-7.20.

**Table 4.2** Type of soil

| Sampling Point | Top Soil | Sub-surface Soil |
|---|---|---|
| 1 | Clay, Coarse sand, white-brown | Clay, Coarse sand, white-brown |
| 3 | Clay, Coarse sand, white-brown | Clay, Coarse sand, white-brown |
| 5 | Clay, white-brown | Clay, white-brown |
| 7 | Clay, Coarse sand, white-brown | Clay, Coarse sand, white-brown |
| 11 | Peat, dark-brown | Peat, dark-brown |
| 13 | Peat, dark-brown | Peat, dark-brown |
| 15 | Peat, dark-brown | Peat, dark-brown |
| 21 | Laterite, red-brown | Laterite, red-brown |
| 23 | Laterite, red-brown | Laterite, red-brown |
| 25 | Laterite, red-brown | Laterite, red-brown |

## 4.6     Summary

Table 4.3 showed the maximum, minimum, mean value for Ni and Cu concentration in top soil and sub surface soil. Only Ni mean values in the top soil exceed the EU and US EPA permissible exposure limit. For Cu content, it is far below the limit value and maybe it can determine higher at the lower layer.

**Table 4.3** Heavy metal content of the Ulu Tualang closed landfill

| | Nickel | | Copper | |
|---|---|---|---|---|
| | Top Soil | Sub surface | Top Soil | Sub surface |
| Minimum | 51.25 | 51.35 | 19.2 | 50.5 |
| Maximum | 99.65 | 78.50 | 70.35 | 62.55 |
| Median | 77.65 | 74.87 | 53.72 | 54.12 |
| Mean | 76.84 | 71.5 | 51.8 | 54.5 |
| EU PEL (*Langenkamp et. al., 2001) | 75 | | 140 | |
| US PEL (*Adapted from U.S. EPA, 1993) | 75 | | 4300 | |

# CHAPTER 5

# CONCLUSION

## 5.1 Conclusion

This determination of soil samples from Ulu Tualang newly-closed landfill clearly revealed the presence of copper and nickel in the top and sub surface soil. With acid digestion method and analysis using AAS, Ni concentration had been detected higher than the Cu for both layer of soil. Higher concentration of Ni maybe contributed by metal-processing waste that operated around the landfill and municipal wastes such as batteries, electric and electronic equipment. Even though the heavy metal had been detected in all samples, but there are no significance difference in concentration for both top and sub surface soil. From the result also, this landfill soil can be classify as sub acidic due to the pH value ranged from 5.11 to 7.20. From observation, the samples that taken can be categorized into three type of soil; clay type, peat and laterite. Different types of soil have differences in heavy metals adsorption and this statement can be added as the new parameter for the future research.

## 5.2    Recommendation

After finished this research, there are several improvement that can be done for the future work. With this, the data that will be obtained from the future research will more accurate and help to gain further understanding in determination of heavy metal in soil. To realize it, the research should;

i.   Compare the used acid digestion method with other digestion method such as Aqua Regia method or US EPA method.

ii.  Conduct this research for other layer of soil such as C-horizon (30-48 inch depth) and R-horizon (>48 inch depth).

iii. Determine heavy metal concentration not only for soil but also conduct it for the landfill leachate and plant.

# REFERENCES

Bouazza A., 2002. Geosynthetic clay liners. Geotextiles and Geomembranes, 20; 3-17.

Chen, T.B., Zheng, Y.M., Lei, M., Huang, Z.C., Wu, H.T., Chen, H., Fan, K.K, Yu, K., Wu, X., Tian, Q.Z., 2004. Asessment of heavy metal pollution in surface soils of urban parks in Beijing, China. Chemosphere, 60;542-551.

Chuangcham, U., Charusiri, P., Milne-Home, W., Lertsirivorakul, R., Boonsener, M., 2008. Adsorption of heavy metal from landfill leachate in soil: A case study of Kham Bon Landfill, Khon Kaen province, NE Thailand. GREAT International Symposium.

Christidis, K., Robertson, P., Gow, K., Pollard, P., 2007. Voltamemetric in situ measurement of heavy metals in soil using a portable electrochemical instrument. Measurement, 40; 960-967.

Donahue, S. & Auburn, 2000. Heavy metal soil contamination. Soil Quality-Uraban Technical Note.

Esakku, S., Palanivelu, K., Joseph, K., 2003. Assesment of Heavy Metals in a Municipal Solid Waste Dumpsite. Workshop on Sustainable Landfill Management, pp. 139-145.

Giroud, J.P., Khatami, A., Badu-Tweneboah, K., 1989. Evaluation of the rate of leakage throgh composite liners.Geotextiles and Geomembrane, 8; 337-340.

Imperato, M., Adamo, P,. Naimo, D., Arienzo, M., Stanzione, D., Violante, P., 2003. Spatial distribution of heavy metals in urban soils of Naples city (Italy). Enviromental Pollution, 124; 247-256.

Kasassi, A., Rakimbei, P., Karagiannidis, A., Zabaniotou, A., Tsiouvaras, K., Nastis, A., Tzafeiropolou, K., 2007. Soil Contamination by heavy metal: Measurement from a closed unlined landfill. Biosource Technology, 22; 8578-8584.

Kasprzak, K.S., Sunderman Jr.F.W., Salnikow, K., 2003. Nickel carcinogenesis. Mutation Research, 533; 67-97.

Kimbrough, D.E. and Wakakuwaa, J., 1992. A study of the linear ranges of several acid digestion procedures. Enviro. Sci. Technol.,Vol. 26.

Koerner, R.M. and Soong, T.Y., 2000. Leachate in landfills: the stability issues. Geotextiles and Geomembrane, 18;293-309.

Langenkamp, H., Duwel, O., Utermann, J., 2001. Trace element and organic matter contents of European soils. A progress report.

Lewis, S., Donkin, M.E., Depledge, M.H., 2001. Hsp70 expression in Enteromorpha intestinalis (Chlorophyta) exposed to environmental stressors. Aquatic Toxicology, 51; 277–291.

Palma, L.D. & Medici, F., 2002. Recovery of copper from contaminated soil by flushing. Waste Management, 22; 883-886.

Radu, T. & Diamond, D., 2008. Comparison of soil pollution concentrations determined using AAS and portable XRF techniques. Hazardous Materials, 171; 1168-1171.

Ravera, R., Ciccarelli, C., Gastaldi, D., Rinaudo, C., Castelli, C., Osella, D., 2005. An experiment in the electrokinetic removal of copper from soil contaminated by the brass industry. Chemosphere, 63; 950-955.

Roongtanakiat, N., Nirunrach, T., Chanyotha, S., Hengchaovanich, D., 2003. Uptake of heavy metal in landfill leachate by vertiver grass. Nat. Sci., 37; 168-175.

Rowe, R.K. & Sangam, H.P., 2002. Durability of HDPE geomembranes. Geotextiles and Geomembrane, 20; 77-95.

Sabienë, N., Brauzaukienë, D.M., Rimmer, D., 2004. Determination of heavy metal mobile forms by different extraction methods. Ekologija, 1;36-41.

Spokas, K., Bogner, J., Chanton, J.P., Morcet, M., Aran, C., Graff, C., Golvan, Y.M., Hebe, I., 2006. Methane mass balance at three sites: What is the efficiency of capture by gas collection system? Waste Managemennt, 26;516-525.

Tchobangolous, G., Theisen, H., Vigil, S.A., 1993. Intergrated solid waste management. Engineerin Principle and Management Issues. McGraw-Hill, Inc.

Tietje, O., 2003. Explorative data analysis of heavy metal contaminated soil using multidimensional spatial regression, Environmental Geology, 44;893-904.

Uriu-Adams, J.Y, Keen, C.L., 2005. Copper, oxidative stress, and human health. Molecular Aspects of Medicine, 26; 268-298

Wang, W.Z., Brusseau, M.L., Artiola, J.F., 1996. The use of calcium to facilitate desorption and removal of cadmium and nickel in subsurface soils. Contaminant Hydrology, 25; 325-336.

Warith, M.A., Evgin, E., Benson, P.A.S, 2004. Suitability of shredded tires for use in landfill leachate collection system. Waste Managmenet, 24;967-979.

Yadav, S.K., 2009. Heavy metals toxicity in plants: An overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants. South African Journal of Botany.

**Table A.1** Cu and Ni concentration values for 10 selected sampling points

| Sampling Point | Cu | | Ni | |
|---|---|---|---|---|
| | Top soil (mg/kg) | Sub surface soil (mg/kg) | Top soil (mg/kg) | Sub surface soil (mg/kg) |
| 1 | 19.2 | 50.5 | 78 | 51.35 |
| 3 | 52.15 | 53.2 | 77.55 | 67.05 |
| 5 | 52.5 | 55.05 | 93.95 | 77.75 |
| 7 | 54.8 | 53 | 99.65 | 77.6 |
| 11 | 52.95 | 54.45 | 77.85 | 78.1 |
| 13 | 54 | 54.85 | 71.2 | 66.4 |
| 15 | 70.35 | 54.6 | 73.05 | 76.95 |
| 21 | 54.35 | 52.95 | 77.75 | 78.5 |
| 23 | 53.45 | 62.55 | 68.15 | 68.5 |
| 25 | 54.2 | 53.8 | 51.25 | 72.8 |

**Table A.2** EU limit values for concentration of heavy metal in soil

| Elements | Limit values (mg/kg dm) | | | |
|---|---|---|---|---|
| | Directive 86/278/EEC 6<pH<7 | 5≤pH<6 | 6≤pH<7 | pH≥7 |
| Cd | 1 – 3 | 0.5 | 1 | 1.5 |
| Cr | - | 50 | 75 | 100 |
| Cu | 50 – 140 | 30 | 50 | 100 |
| Hg | 1 – 1.5 | 0.1 | 0.5 | 1 |
| Ni | 30 – 75 | 30 | 50 | 70 |
| Pb | 50 – 300 | 70 | 70 | 100 |
| Zn | 150 – 300 | 100 | 150 | 200 |

Source: Langenkemp *et. al*., 2001

**Table 1. Regulatory limits on heavy metals applied to soils (Adapted from U.S. EPA, 1993).**

| Heavy metal | Maximum concentration in sludge (mg/kg or ppm) | Annual pollutant loading rates | | Cumulative pollutant loading rates | |
|---|---|---|---|---|---|
| | | (kg/ha/yr) | (lb/A/yr) | (kg/ha) | (lb/A) |
| Arsenic | 75 | 2 | 1.8 | 41 | 36.6 |
| Cadmium | 85 | 1.9 | 1.7 | 39 | 34.8 |
| Chromium | 3000 | 150 | 134 | 3000 | 2,679 |
| Copper | 4300 | 75 | 67 | 1500 | 1,340 |
| Lead | 420 | 21 | 14 | 420 | 375 |
| Mercury | 840 | 15 | 13.4 | 300 | 268 |
| Molybdenum | 57 | 0.85 | 0.80 | 17 | 15 |
| Nickel | 75 | 0.90 | 0.80 | 18 | 16 |
| Selenium | 100 | 5 | 4 | 100 | 89 |
| Zinc | 7500 | 140 | 125 | 2800 | 2500 |

**Figure A.1** US EPA regulatory limits on heavy metals applied to soils

Source: Donahue, S. & Auburn, 2000

| | Average concentrations in soil [a, b, c] | B value (threshold limit value) [d] | Extent of anomalies of natural origin [a, b, c] | Maximal available amount in the percentage of total concentration [c] |
|---|---|---|---|---|
| Cr | 50-200 | 75 | 3500 | 5 |
| Co | 10-15 | 30 | 300 | 30 |
| Ni | 15-30 | 40 | 5000 | 20 |
| Cu | 15-40 | 75 | 250 | 20 |
| Zn | 50-100 | 200 | 900 | 20 |
| As | 0,1-15 | 15 | No data | 38 |
| Se | 0,1-3 | 1 | 120 | 7 |
| Mo | 1-2 | 7 | 101 | 27 |
| Cd | 0,01-2 | 1 | No data | 20 |
| Sn | 1-5 | 30 | 50 | No data |
| Ba | 100-500 | 250 | 3000 | No data |
| Hg | 0,01-5 | 0,5 | No data | 11 |
| Pb | 15-30 | 100 | 1200 | 12 |
| Ag | 1-2 | 2 | 30 | No data |

Table 1.: Trace metal contents of soils. References: a) Aubert and Pinta (1978); b) Kabata-Pendias and Pendias (1984); c) Adriano (1986); d) Hungarian Governmental regulation number 10/2000 (2000).

**Figure A.2** Average concentration of heavy metal in soil and Hungarian Threshold limit value (TLV)

Source: Sipos, P. & Poka, T., 2001

| Parameter | Fee per kg of contaminant discharged |
|---|---|
| (i) BOD$_5$ at 20°C | RM 0.50 |
| (ii) Ammoniacal Nitrogen | RM 500.00 |
| (iii) Mercury | RM 2500.00 |
| (iv) Cadmium | RM 2500.00 |
| (v) Chromium, Hexavalent | RM 2500.00 |
| (vi) Chromium, Trivalent | RM 2500.00 |
| (vii) Arsenic | RM 2500.00 |
| (viii) Cyanide | RM 2500.00 |
| (ix) Lead | RM 2500.00 |
| (x) Copper | RM 2500.00 |
| (xi) Manganese | RM 2500.00 |
| (xii) Nickel | RM 2500.00 |
| (xiii) Tin | RM 2500.00 |
| (xiv) Silver | RM 2500.00 |
| (xv) Selenium | RM 2500.00 |
| (xvi) Barium | RM 2500.00 |
| (xvii) Fluoride | RM 2500.00 |
| (xviii) Formaldehyde | RM 2500.00 |
| (xix) Zinc | RM 500.00 |
| (xx) Boron | RM 500.00 |
| (xxi) Iron | RM 500.00 |
| (xxii) Phenol | RM 500.00 |
| (xxiii) Sulfide | RM 500.00 |
| (xxiv) Oil and Grease | RM 500.00 |

**Figure A.3** Method of computing leachate-related license fee

Source: Malaysia Environmental Quality Act: Fifth Schedule (Regulation 27)

**APPENDIX B**



**Figure B.1** Ulu Tualang closed landfill



**Figure B.2** Gridding process

**Figure B.3** Sample collecting



**Figure B.4** Sample pulverized and sieved
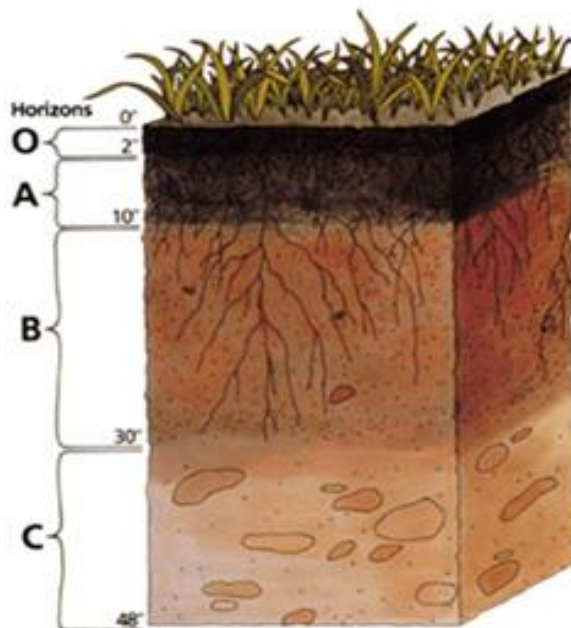
**Figure B.5** Sample digestion



**Figure B.6** Diluted samples and ready for AAS analysis

**Figure B.7** Hitachi's AAS equipment



**Figure B.8** Layers of Soil; O-horizon, A-horizon, B-horizon, C-horizon