DETERMINATION OF CADMIUM (Cd) AND CHROMIUM (Cr) CONCENTRATION AT SURFACE AND SUB SURAFCE SOIL AROUND NEWLY-CLOSED LANDFILL IN ULU TUALANG, TEMERLOH

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JUDUL : DETERMINATION OF CADMIUM (Cd) AND CROMIUM (Cr) CONCENTRATION AT SURFACE AND SUB SURFACE SOIL AROUND NEWLY-CLOSED LANDFILL IN ULU TUALANG, TEMERLOH.

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A report submitted in partial fulfillment of the
requirement for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical Engineering
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DECEMBER 2010

I declare that this thesis entitled "Determination of Cadmium (cd) and Chromium (cr) Concentration at Surface and Sub Surafce Soil Around Newly-Closed Landfill in Ulu Tualang, Temerloh" 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."

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Name : Jashiratulain Bt Ahmad Jailani

Date : 3rd December 2010

To my late father;
Ahmad Jailani Bin Hj Othman
To my beloved mother;
Nazariah Bt Nasir
My sisters and brother
&
All my friends

For all their encouragements, guidance and understanding
Thank you for everything

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"In the name of God, the most gracious, the most compassionate"

I would like to express my sincere gratitude and love to my beloved mother and the entire family for the consistent of love, support and guidance shown to me all the time.

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ABSTRACT

Heavy metal contamination in landfill is one of the major concerns in order to avoid harmful effects towards health living and environment. The aim of this study is to come out with the distribution of the concentration of Cadmium (Cd) and Chromium (Cr) contaminated in soil of closed landfill, to compare it with the United States Environmental Protection Agency (USEPA) soil standard. The 200 grams (g) of 25 soil samples were taken at 25 points from a newly closed landfill in Ulu Tualang, Temerloh at two (2) parts of soil partition which are in surface (0-2 inch) and subsoil (2-10 inch), respectively. The sample was processed using acid digestion method of SCL (Southern California Laboratory) and was analyzed using Flame Atomic Absorption Spectrometry (FLAA). The range of Cd concentration that had been analyzed is from 49.4 to 66.15 mg/kg, while for Cr concentration determination, the result showed that the range is between 5.35 to 71 mg/kg. Available results from the landfill indicated that all concentration of Cd is exceeded the USEPA soil standard while the data for Cr is under the control value. The result can be used in future for reference and if possible, it may be needed for soil treatment if there are any future plans or activities for the landfill.

ABSTRAK

Pencemaran logam berat di sekitar tapak pelupusan sampah adalah salah satu masalah yang harus di ambil berat untul mengelakkan kesan yang merbahaya terhadap kesihatan hidupan dan alam sekitar. Objektif kajian ini adalah untuk mendapatkan taburan kepekatan Kadmium (Cd) dan Kromium (Cr) yang tercemar di dalam tanah pada tapak pelupusan sampah, untuk membandingkannya dengan nilai United States Protection Agency (USEPA) Soil Standard. 25 sampel tanah yang mempunyai berat 200 gram (g) setiap satu di ambil dari 25 titik kajian di tapak pelupusan sampah yang baru ditutup di Ulu Tualang, Temerloh pada dua bahagian tanah iaitu pada permukaan (0-2 inci) dan sub permukaan (2-10 inci) tanah. Sampel-sampel itu telah diproses berdasarkan kaedah penghadaman asid dan dianalisis menggunakan Flame Atomic Absorption Spectrometry (FLAA). Kepekatan kadmium di dalam tanah adalah di antara 49.4 hingga 66.15 mg/kg, manakala kepekatan kromium pula adalah di antara 5.35 hingga 71 mg/kg. Data dari kajian menunjukkan semua nilai kepekatan kromium bagi sampel yang dikaji adalah melebihi USEPA Soil Standard, manakala bagi kromium pula semua data adalah masih di bawah nilai kawalan. Data dari kajian boleh digunakan sebagai panduan untuk masa hadapan dan jika berkemungkinan ianya boleh diperlukan bagi rawatan tanah jika terdapat rancangan atau sebarang aktiviti yang ingin dijalankan di tapak pelupusan sampah berkenaan.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

BOD	-	Biological Oxygen Demand
Cd	-	Cadmium
COD	-	Chemical Oxygen Demand
Cr	-	Chromium
FLAA	-	Flame Atomic Absorption Spectrometry
GFAA	-	Graphite Furnace Atomic Absorption Spectrometry
ICP-AES	-	Inductively Coupled Plasma Mass Spectrometry
ICP-MS	-	Inductively Coupled Plasma Atomic Emission Spectrometry
MSW	-	Municipal Solid Waste
Ni-Cd	-	Nickel-Cadmium
NTP	-	National Toxicology Program
SWM	-	Solid Waste Management
USEPA	-	United States of Environmental Protection Agency

LIST OF SYMBOLS

%	-	percentage
±	-	plus minus
°C	-	degree celcius
cm	-	centimeter
g	-	gram
kg	-	kilogram
m	-	meter
mg/kg	-	milligram per kilogram
mg/L	-	milligram per liter
mL	-	mililiter
mm	-	milimeter
ppm	-	part per million

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

An experimental method of research was performed to assess the presence or absence of heavy metals in newly closed landfill in Ulu Tualang; and the concentration of each heavy metal when present. With the location of the landfill that is located around an industrial and residential area, the chance of contamination of heavy metal is high there.

After a long time, waste that decomposed at the landfill will make the soil become polluted and may contain large amount of heavy metal. There are some of heavy metal can react with rain rich oxygen to form sulphur and then produces macromolecule of sulphides (P.J. *et al*., 2006). These hazardous molecules will influences the quality of atmosphere thus may affect health and life of animal and human being that closed to the landfill. Usually after the landfill is closed, that placed is usually reconstructed as recreational places or residential area. A lot of problems will occur if the soil becomes porous and not stable because of the presence of heavy metal in the soil. Even though there are some heavy metal that may good for the soil, but most of heavy metal that come from industrial waste are toxic and dangerous to human. This issues then will make the reconstructed area are not safe and not suitable for human lives. (G.M. Greenway & Q. J. Song, 2002)

1.2 Problem Statement

Modern life today is unexceptional from contacting with heavy metals directly or non directly. Most common example for heavy metals enter human body is via food, drinking water and air. If it is not due to the daily requirements, it may also occur unnoticeable which if exist in high concentration, may lead to poisonous. Simply define, heavy metals are metal and metal compounds that may harm human health when absorbed or inhaled. Undeniable, heavy metals do needs in life but just in a small amount, it becomes toxic when have it in an exceed amount. Heavy metals cannot be degraded or destroyed, and what make it worse is that they tend to bioaccumulate which means the concentration of heavy metals may increase in biological organism over time.

Heavy metals are example of wastes that are not allowed to dispose off to landfill due to its potential hazardous impact on public health and the surrounding environmental. Heavy metals that appears in disposal site comes from variety of sources such as batteries, consumer electronics, ceramics, light bulbs, house dust and many more. This type of waste has to dispose off at a place especially designated for such purposes. It is impossible to ensure that all the disposal waste received by disposal landfill are hundred percent free from heavy metals and as the landfill is located in an open area, heavy metals may exist there naturally whereby acidic rain will be one of the source.

Main purpose of this research is to ensure the existence of Cadmium (Cd) and Chromium (Cr) for surface soil and subsoil in 25 points of drilling at closed landfill located in Kampung Ulu Tualang, Mukim, Temerloh, Pahang. Used to be the second largest landfill in Pahang, it received hundred tones of waste per day whereby heavy metals are also included as the component of waste. The soil sample is taken somewhere around this landfill with gridding measurements of 50m X 50m. 25 soil samples are taken in every points of 10m X 10m for surface soil and subsoil. Advance for the main purpose is to determine either Cd or Cr is the higher concentration in surface soil and subsoil for each drilling.

1.3 Objective of Study

i. To ensure the existence of Cd and Cr in surface soil and subsoil follow by the determination of the concentration of each of the heavy metals.
ii. To make a comparison of the value of the concentration of Cd and Cr with USEPA soil standard.

iii. To develop a distribution model of the concentration of Cd and Cr at each point as well as at the part of soil (surface and subsurface soil).

1.4 Scope of Research

1.4.1 Methodology

For this purpose, collection, preparation and analysis of sample was done in determining the heavy metal concentration. The concern part of determining the result is the preparation of the samples where an acid digestion method was involved. The purpose of this method is to solubilize all the elements of interest. To do this, a digestion procedure must perform two distinct tasks; (D. E. Kimbrough & J. Wakakuwa, 1992).

1. It must decompose the sample matrix to expose the entire mass to the acid cocktail.
2. It must react with the elements of interest to form water soluble compounds.

To complete the process, dilution medium is added to form a solution that is suitable for analysis by a variety of analytical instruments (typically Flame Atomic Absorption Spectrometry (FLAA), Inductively Coupled Plasma Mass Spectrometry (ICP-AES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Graphite Furnace Atomic Absorption Spectrometry (GFAA). Dilution medium that may be used are like distilled water, deionized water and ultra pure water.

1.4.2 Area description

A landfill, also known as a dump or rubbish dump is a site for the disposal of waste materials by burial and is the oldest form of waste treatment. Historically, landfills have been the most common methods of organized waste disposal and remain so in many places around the world.

Ulu Tualang closed land fill located in Temerloh Pahang with an area of approximately 20 acres, used to be the second largest landfill in Pahang, it had operated many years before it had been closed recently. It had no longer available to accommodate the waste and need to use landfill in Bera for the purpose. Located around an industrial area and residential area which was the major sources of waste in the disposal landfill of Ulu Tualang. 60% of waste in the landfill was distributed by the factories from the nearby industrial area. The remaining is from the residential area waste. The list below are some of the factories that are operate around Ulu Tualang landfill :

i. Megaply Industries (M) Sdn Bhd (Piling)

ii. Intan Suria Sdn Bhd (Frame-picture wood products)

iii. SQ Wooden Picture Frame Moulding Sdn Bhd (Picture frame-wholesaler & manifacture)

iv. LCS Precast Sdn Bhd (Piling)

v. Mentakab Stainless Steel Works (Stainless Steel Fabricators)

vi. Syarikat Perniagaan Boon Wee (Biscuits-Wholesaler & manufacturer, food products)

vii. Mentakab Agricultural Machinary Sdn Bhd (Agricultural equipment & supplies, tractor distributors & manufacturers)

What can be concluded is that most of the factories around the closed landfill are operating with wood and steel base product.

Figure 1.1: Map location of closed landfill in Ulu Tualang

The soil sample examined was taken from Ulu Tualang newly closed landfill. Generally, parts of soil are divided to 4 partitions. Each represents as 0 A, B, C where the partition is categorized according to their depth as in Figure 1.2.

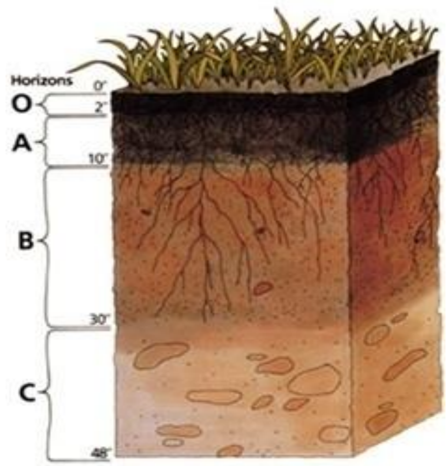

Figure 1.2: Partitions of soil

O : 0-2 inch = 0 – 5.08 cm

A : 2-10 inch = 5.08 – 25.4 cm

B : 10-30 inch = 25.4 – 76.2 cm

C : 30-40 inch = 76.2 – 121.92 cm

For this research, part A and B only that was covered throughout the experiment where A and B represent surface and sub surface soil partitions. Gridding was done at the closed landfill with measurement of 100mX100m, where 25 points will be measured in the grid with measurement of 10mX10m. The location of gridding was chosen as advised by the representative of the Temerloh Municipal Council. At each point, 2 samples of 200 g were taken as part of surface soil and subsoil.

1.5 Rationale & Significance of Study

This study was done on the significance of the closed landfill in Malaysia. In the future, mostly the closed landfill will be developed to something that provides benefit to human. Currently, there is a residential area had been developed from the closed landfill and surely this development need details study also soil remediation to avoid unnecessary incident coming later. Apart from this significance, the closed landfill may give a bad effect towards human health and environment if it is not properly closed. Now, local authorities simply wash their hands off dumps once these are no longer useable since there is no legal document spelling out their responsibilities to ensure closed landfills do not pollute. *(www.thestar.com.my,* 2010). So, the data presented on this study might be needed for future soil remediation.

This study is to determine the existence and the concentration of Cd and Cr in surface soil and subsoil for closed landfill. The result obtained will be compared to the standard United States Environmental Protection Agency (USEPA) Soil Standard. From the comparison, the closed landfill can be predicted as having the potential to do any activity or not. Also, the data might use as a guide for further research of the landfill or for soil treatment as example.

CHAPTER 2

LITERATURE REVIEW

2.1 Municipal Solid Waste (MSW)

There has been a significant increase in the generation of municipal solid wastes (MSW) in Malaysia over the last few decades. This is largely a result of rapid population growth in the country. Currently, the generation of municipal solid waste in Malaysia is about 8 million tones per annum. This solid waste volume is still increasing at the rate of 1.5% every year (*Professional Training Program on Integral Solid Waste Management in Southeast Asian Cities*, 2005). The reasons for this trend could be due o the changing of lifestyles, food habits and changes in the standard of living (*Sanitary landfill: Toward Sustainable Development, LUMES* 2000-2001). MSW in cities is collected by the municipalities and transported to designated disposal sites normally at low lying area on the outskirts of the city for disposal. The choice of a disposal site is more a matter of what is available than what is suitable.

A research done by Chai Xiaoli *et al.*, (2007), it shows that more than 90% waste are disposed in landfill at China but this developing country has recently closed more than 1000 landfills because of environmental concern. An example from Chai Xiaoli *et al.*, (2007) research, they stated that after the largest landfill in China, Shanghai Laogang Landfill that constructed in 1985 along the shore of the East China Sea was closed after handling and treats about 30 million tones of refused up to 2005, they preferred MSW landfill to replaced previous landfill because of its offers potential economic benefits by creates additional disposal capacity for the placement of fresh refuse, and recycles the stabilized, valuable resource.

In a study done by A.F Al-Yaqout *et al.*, (2003), they compared the soil contamination at the leachate landfill from developed country which is USA, Germany and Italy in term of amount of pH, bio-oxygen demand (BOD), chemical oxygen demand (COD) and distribution of heavy metal with their country. The data below shown the result obtained from the study.

Table 2.1: Comparison of leachate quality of Kuwait with other leachates reported for developed countries

Parameter (mg/l)	**Kuwait**	**USA**	**Italy**	**Germany**
Alkalinity (as CaCO3)	250–6340	240– 8965	4250– 8250	-
pH	6.9– 8.2	5.1–6.9	6.0–8.5	5.7– 8.1
BOD	30– 600	13,400	2125– 10,400	400–45,900
COD	157.9–9440	1340– 18,100	7750– 38,520	1630–63,700
Sulfate	55– 3650	0.01– 1280	219–1860	1– 121
Zn	0.0– 4.8	18.8– 67	5 – 7	-
Pb	0– 0.2	0 –4.46	–	–
Cu	0– 0.2	0 –0.1	–	–
Fe	0.3– 54.1	4.2–1185	47–330	8– 79
Ca	5.6– 122	254.1– 2300	0 – 175	70– 290
Mg	5.2– 268	233– 410	827–1469	100–270

2.2 Type of Municipal Solid Waste (MSW

2.2.1 Nonhazardous MSW (A.Y. Abubakar, 2008)

These are type of wastes if it is discarded does not pose much danger to human health and environment as compared to hazardous municipal solid waste. Some examples of nonhazardous MSW are as follows:

- Packaging waste
- Food and organic waste
- Garden waste
- Plastics
- Bulky waste
- Construction and demolition wastes
- Paper wastes

2.2.2 Hazardous MSW (A.Y. Abubakar, 2008)

Sources of hazardous waste include those from industrial processes, mining extraction, tailings from pesticide based agricultural practices, etc. Industrial operations lead to considerable generation of hazardous waste and in a rapidly industrializing country such as India the contribution to hazardous waste from industries is largest. Hazardous waste generation from industries is also critical due to their large geographical spread in the country, leading to region wide impacts. The annual growth in hazardous waste generation can be directly linked to industrial growth in the country. State such as Malaysia, a developing country which is relatively more industrialized, face problems of toxic and hazardous waste disposal far more acutely than less developed states. The major hazardous waste-generating industries in Malaysia include:

- Petrochemicals
- Pharmaceuticals
- Pesticides
- Paint and dye
- Petroleum
- Fertilizers
- Asbestos
- Inorganic chemicals
- General engineering industries.

During the last 20 years, the industrial sector in Malaysia has increased in size. Hazardous wastes from the industrial sectors also contain heavy metals, cyanides, pesticides, complex aromatic compounds, and other chemicals which are toxic, flammable, reactive, and corrosive or have explosive properties.

2.3 Solid Waste Management (SWM)

In order to have a satisfactory, efficient, and a sustainable system of solid waste management, proper planning, implementation, and management systems must be incorporated in framing the national policy for solid waste management for the country. Present and future ways to manage solid waste stream need consideration of the following aspects. Setting targets for waste reduction. Reduction at source can be accomplished in three ways;

- fees and tax incentives to promote market mechanisms to effect source reduction
- mandatory standards and regulation,
- education and voluntary compliance with policies by business and consumers, (Marcin *et al.,* 1994).

However, these strategies need to be sensitive to the concerns of possible loss of business and jobs in affected industries. Reduction in the quantity of municipal solid waste could affect employment, taxes/revenues, and economic activity in unpredictable ways (Marcin *et al.,* 1994). In particular, there are six elements of solid waste management :

- ✓ Generation
- ✓ Storage
- ✓ Collection
- ✓ Transportation and transfer
- ✓ Processing and treatment
- ✓ Disposal

Among all the technical components, collection, transportation, treatment and disposal of waste need urgent attention.

2.4 Heavy metal

Nowadays, the usage of heavy metals is wide and can be found anywhere. Sooner or later, everything becomes waste including the heavy metals. At the end, all the waste will go to the landfill site for disposal purpose. If the disposal waste is not meet the standard of the heavy metal waste, this may contribute to the heavy metal pollution.

Heavy metal pollution not only affects the production and quality of crops, but also influences the quality of the atmosphere and water bodies, and threatens the health and life of animals and human being (A. Kasassi *et al.,* 2008). In order to avoid any unnecessary incident regarding to heavy metals, guideline of disposing heavy metals needed to practice correctly. The environmental problem with heavy metals is that they are unaffected during degradation of organic waste and have toxic effects on living organisms when exceeding a certain concentration (S. Esakku *et al.*, 2003).

Heavy metal pollution of the environment, even at low levels, and their resulting long-term cumulative health effects are among the leading health concerns all over the world. For example, bioaccumulation of Pb in human body interferes with the functioning of mitochondria, thereby impairing respiration, and also causes constipation, swelling of the brain, paralysis and eventual death (E. A. Oluyemi *et al.,* 2008).

2.5 Cadmium (Cd)

2.5.1 Background of Cd

Cadmium is a lustrous, silver-white, ductile, very malleable metal. Its surface has a bluish tinge and the metal is soft enough to be cut with a knife, but it tarnishes in air. It is soluble in acids but not in alkalis. It is similar in many respects to zinc but it forms more complex compounds.

About three-fourths of cadmium is used in Nickel-Cadmium (Ni-Cd) batteries, most of the remaining one-fourth is used mainly for pigments, coatings and plating, and as stabilizers for plastics. Cadmium has been used particularly to electroplate steel where a film of cadmium only 0.05 mm thick will provide complete protection against the sea. Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission. Cadmium can mainly be found in the earth's crust. It always occurs in combination with zinc. Cadmium also consists in the industries as an inevitable by-product of zinc, lead and copper extraction. After being applied it enters the environment mainly through the ground, because it is found in manures and pesticides.

Naturally a very large amount of cadmium is released into the environment, about 25,000 tons a year. About half of this cadmium is released into rivers through weathering of rocks and some cadmium is released into air through forest fires and volcanoes. The rest of the cadmium is released through human activities, such as manufacturing. Consequently, the main mining areas are those associated with zinc. World production is around 14.000 tonnes per year, the main producing country is Canada, with the United States of America (USA), Australia, Mexico, Japan and Peru also being the major suppliers.

2.5.2 Health effects of Cd

Human uptake of cadmium takes place mainly through food. Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed. An exposure to significantly higher cadmium levels occurs when people smoke. Tobacco smoke transports cadmium into the lungs. Blood will transport it through the rest of the body where it can increase effects by potentiating cadmium that is already present from cadmium-rich food.

Other high exposures can occur with people who live near hazardous waste sites or factories that release cadmium into the air and people that work in the metal refinery industry. When people breathe in cadmium it can severely damage the lungs. This may even cause death. Cadmium is first transported to the liver through the blood. There, it is bond to proteins to form complexes that are transported to the kidneys. Cadmium accumulates in kidneys, where it damages filtering mechanisms. This causes the excretion of essential proteins and sugars from the body and further kidney damage. It takes a very long time before cadmium that has accumulated in kidneys is excreted from a human body. Other health effects that can be caused by cadmium are:

- Diarrhoea, stomach pains and severe vomiting
- Bone fracture
- Reproductive failure and possibly even infertility
- Damage to the central nervous system
- Damage to the immune system
- Psychological disorders
- Possibly DNA damage or cancer development

2.5.3 Environmental effects of Cadmium (Cd)

Cadmium waste streams from the industries mainly end up in soils. The causes of these waste streams are for instance zinc production, phosphate ore implication and bio industrial manure. Cadmium waste streams may also enter the air through (household) waste combustion and burning of fossil fuels. Because of regulations only little cadmium now enters the water through disposal of wastewater from households or industries.

Another important source of cadmium emission is the production of artificial phosphate fertilizers. Part of the cadmium ends up in the soil after the fertilizer is applied on farmland and the rest of the cadmium ends up in surface waters when waste from fertilizer productions is dumped by production companies. Cadmium can be transported over great distances when it is absorbed by sludge. This cadmium-rich sludge can pollute surface waters as well as soils.

Cadmium strongly adsorbs to organic matter in soils. When cadmium is present in soils it can be extremely dangerous, as the uptake through food will increase. Soils that are acidified enhance the cadmium uptake by plants. This is a potential danger to the animals that are dependent upon the plants for survival. Cadmium can accumulate in their bodies, especially when they eat multiple plants. Cows may have large amounts of cadmium in their kidneys due to this. Earthworms and other essential soil organisms are extremely susceptive to cadmium poisoning. They can die at very low concentrations and this has consequences for the soil structure. When cadmium concentrations in soils are high they can influence soil processes of microorganisms and threat the whole soil ecosystem.

In aquatic ecosystems cadmium can bio accumulate in mussels, oysters, shrimps, lobsters and fish. The susceptibility to cadmium can vary greatly between aquatic organisms. Salt-water organisms are known to be more resistant to cadmium poisoning than freshwater organisms. Animals eating or drinking cadmium sometimes get high blood-pressures, liver disease and nerve or brain damage.

2.6 Chromium (Cr)

2.6.1 Background of Cr

Chromium is a lustrous, brittle, hard metal. Its colour is silver-gray and it can be highly polished. It does not tarnish in air, when heated it borns and forms the green chromic oxide. Chromium is unstable in oxygen, it immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal below. Chromium main uses are in alloys such as stainless steel, in chrome plating and in metal ceramics. Chromium plating was once widely used to give steel a polished silvery mirror coating.

Chromium is used in metallurgy to impart corrosion resistance and a shiny finish; as dyes and paints, its salts colour glass an emerald green and it is used to produce synthetic rubies; as a catalyst in dyeing and in the tanning of leather; to make molds for the firing of bricks. Chromium (IV) oxide (CrO_2) is used to manufacture magnetic tape. Chromium is mined as chromite ($FeCr_2O_4$) ore. Chromium ores are mined today in

South Africa, Zimbabwe, Finland, India, Kazakhstan and the Philippines. A total of 14 million tonnes of chromite ore is extracted. Reserves are hestimated to be of the order of 1 billion tonnes with unexploited deposits in Greenland, Canada and USA.

2.6.2 Health effects of Cd

People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium(IV); hexavalent chromium.

For most people eating food that contains chromium (III) is the main route of chromium uptake, as chromium (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the chromium contents of food. When food in stores in steel tanks or cans chromium concentrations may rise. Chromium (III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium (III) can cause health effects as well, for instance skin rashes.

Chromium (VI) is a danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium. Chromium (VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. After breathing it in chromium (VI) can cause nose irritations and nosebleeds.

Other health problems that are caused by chromium (VI) are:

- Skin rashes
- Upset stomachs and ulcers
- Respiratory problems
- Weakened immune systems
- Kidney and liver damage
- Alteration of genetic material
- Lung cancer
- Death

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema.

Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch. Carcinogenicity- Chromium and most trivalent chromium compounds have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals. According to NTP, there is sufficient evidence for carcinogenicity in experimental animals for the following hexavalent chromium compounds; calcium chromate, chromium trioxide, lead chromate, strontium chromate,and zinc chromate.

2.6.3 Environmental effects of Cr

There are several different kinds of chromium that differ in their effects upon organisms. Chromium enters the air, water and soil in the chromium (III) and chromium (VI) form through natural processes and human activities. The main human activities that increase the concentrations of chromium (III) are steal, leather and textile manufacturing. The main human activities that increase chromium (VI) concentrations are chemical, leather and textile manufacturing, electro painting and other chromium (VI) applications in the industry. These applications will mainly increase concentrations of chromium in water. Through coal combustion chromium will also end up in air and through waste disposal chromium will end up in soils. Most of the chromium in air will eventually settle and end up in waters or soils. Chromium in soils strongly attaches to soil particles and as a result it will not move towards groundwater.

In water chromium will absorb on sediment and become immobile. Only a small part of the chromium that ends up in water will eventually dissolve. Chromium (III) is an essential element for organisms that can disrupt the sugar metabolism and cause heart conditions, when the daily dose is too low. Chromium (VI) is mainly toxic to organisms. It can alter genetic materials and cause cancer. Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops.

Acidification of soil can also influence chromium uptake by crops. Plants usually absorb only chromium (III). This may be the essential kind of chromium, but when concentrations exceed a certain value, negative effects can still occur. Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal. In animals chromium can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation.

2.7 Landfill

Landfill is the most widely use method to dispose waste. Most of the countries in the world are practicing this method. Landfill as refuse disposal is a widely accepted technology, especially in developing countries, because of its low investment and operational costs (C. Xiaoli *et al.*, 2007). The household waste disposed of in municipal solid waste (MSW) landfills contains a mixture of many chemical compounds originating from the various discarded products. A number of these chemicals are released during the lifetime of the landfill and result in released of heavy metals to the environment receptors (U. Chuangcham *et al.*, 2008).

The other problem that is significant to landfill is gas emission such as methane (CH_4), carbon dioxide (CO_2), hydrogen sulfide (H_2S) and other type of greenhouse gas that is produce due to the decomposition process occurs in landfill. Landfill gas effected plant growth (Leone *et al.*, 1983) but the main concern of landfill gas emission is methane, which is highly flammable that causes fire hazards in landfills (Abdullah *et al.*, 1999).

The leachate from landfills usually has high content of pollutants, especially heavy metals and other harmful substances which became contamination in the area around the landfill sites and in ground water (N. Roongtanakiat *et al*., 2003).

CHAPTER 3

METHODOLOGY

In order to run this research project, the method used is divided to three main phases;

i. Collection of soil samples

ii. Preparation of samples

iii. Flame Atomic Absorption Spectrometry (FLAA) Analysis

3.1 Apparatus

All the glassware and machinery equipment used in the process of the experimental procedure from first phase to the third phase were borrowed and booked from FKKSA laboratory and some of them are personal belonging. Below is the list of equipment used throughout the project base on the phase methodology;

- Sample collecting
    - Shovel
    - Plastic bag
    - Ruler
    - Rope

    - Weighing machine

- Sample preparing
    - Oven
    - Mortar stone
    - Sieve
    - Spatula
    - Weighing boat
    - Weighing machine
    - 100 ml beaker
    - Heater
    - Watch glass
    - Glass rod
    - Thermometer
    - 10 ml measurement cylinder
    - Pipette
    - Vacuum filter
    - Filter paper
    - 100 ml volumetric flask
    - 50 ml volumetric flask

- Sample analysis
    - Flame Atomic Absorption Spectrometry (FLAA)

3.2 Reagent

All reagent used for the project were provided by FKKSA Laboratory. Of all three phases involved, only the second and third phases involved the use of acid and/or dilution medium.

- Sample preparing
  - Hydrocloric acid (HCl)
  - Nitric acid (HNO_3)
  - Ultra pure water

- Sample analysis
  - Ultra pure water

(Note that ultra pure water was used for all dilution purposes)

3.3 Procedure

3.3.1 Collection of Soil Samples

The total of 50 soil samples were taken in Ulu Tualang newly closed landfill within an area of 10 000 m^2. The gridding of the landfill was measured and the location of the gridding was as advised by the representative of Temerloh Municipal Council in the measurement of 100 m X 100 m where each point is in the point of 10m X 10m. At each point, 2 soil samples were taken each at surface (0-2 inch) and subsurface soil(2-10 inch). This gave the total number of the soil samples are 25 from the surface and another 25 from the surface soil. All the samples taken were in 200g in weight. Figure 3.1 below is an illustration of the gridding that were made where the number in each box represented the sampling points.

1	**2**	**3**	**4**	**5**
6	**7**	**8**	**9**	**10**
11	**12**	**13**	**14**	**15**
16	**17**	**18**	**19**	**20**
21	**22**	**23**	**24**	**25**

Figure 3.1: Grid of sampling points

For each soil sample, it was labeled according to the sampling point and partition where alphabet A represented the soil sample from the surface while alphabet B represented the sample form the subsurface partition. For example 15B is the sample taken from the sampling point of 15 and at subsurface soil. Then, all the collected samples was stored in the plastic bag before bring it to the next phase.

3.3.2 Preparation of Samples

Generally, heavy metal in the sample is digested using acid digestion method process. Before proceed to the next process, there is the need to prepare the sample in a dry powder form. The soil sample was first dried using an oven until it had fully dry. Then the sample was crushed using mortar stone to lose the clump form of the sample. Finally the sample was sieved using a <2 mm sieve to produce the dry powder sample.

Proceeded with an acid digestion method, this method was performed to determine the concentration of an element (heavy metal) from the solid matrices (soil) (D. E. Kimbrough & J. Wakakuwa, 1992). There is a lot of method that can be use in order to digest the sample. For this purpose, the SCL (Southern California Laboratory) method had been chosen due to the time needed to finish the digestion is short, also the reagents requires are available in FKKSA Laboratory. Below is a step by step of the SCL method;

1. 1g of dry sample was weighted using weighing machine.
2. The sample was digested with the mixture of 9 ml of HCl and 3ml in a 100 ml beaker and covered it with a watch glass.
3. The sample and the reaction mixture were heated slowly using heater to ±95°C (to prevent overly vigorous reaction). The digestion was continued until the disappearance of NO_2 (reddish brown) fumes and there was no more change in appearance.
4. The digestate was filtered using a vacuum pump and a filter paper (Whatman 41) and collected it in a 100 ml volumetric flask.
5. The sample was diluted using ultra pure water.

3.3.3 FLAA Analysis

Analysis of the heavy metal contents in the soil samples was done with the use of FLAA. The FLAA not only detects the presence of heavy metals, but if present, it is also designed to provide the concentrations in part per million (ppm) (C. C. Gian et al., 2009).

FLAA relies heavily on the Beer-Lambert Law. The electrons of the atoms in the atomizer can be promoted to higher orbital for a short amount of time by absorbing a set quantity of energy such as light of a given wavelength. This amount of energy or wavelength is specific to a particular electron transition in a particular element, and in general, each wavelength corresponds to only one element. This gives the technique its elemental selectivity. As the quantity of energy put into the flame is known, and the quantity remaining at the other side (at the detector) can be measured, it is possible, for Beer-Lambert law, to calculate how many of these transitions took place, and thus get a signal that is proportional to the concentration of the element being measured (C. C. Gian et al., 2009).

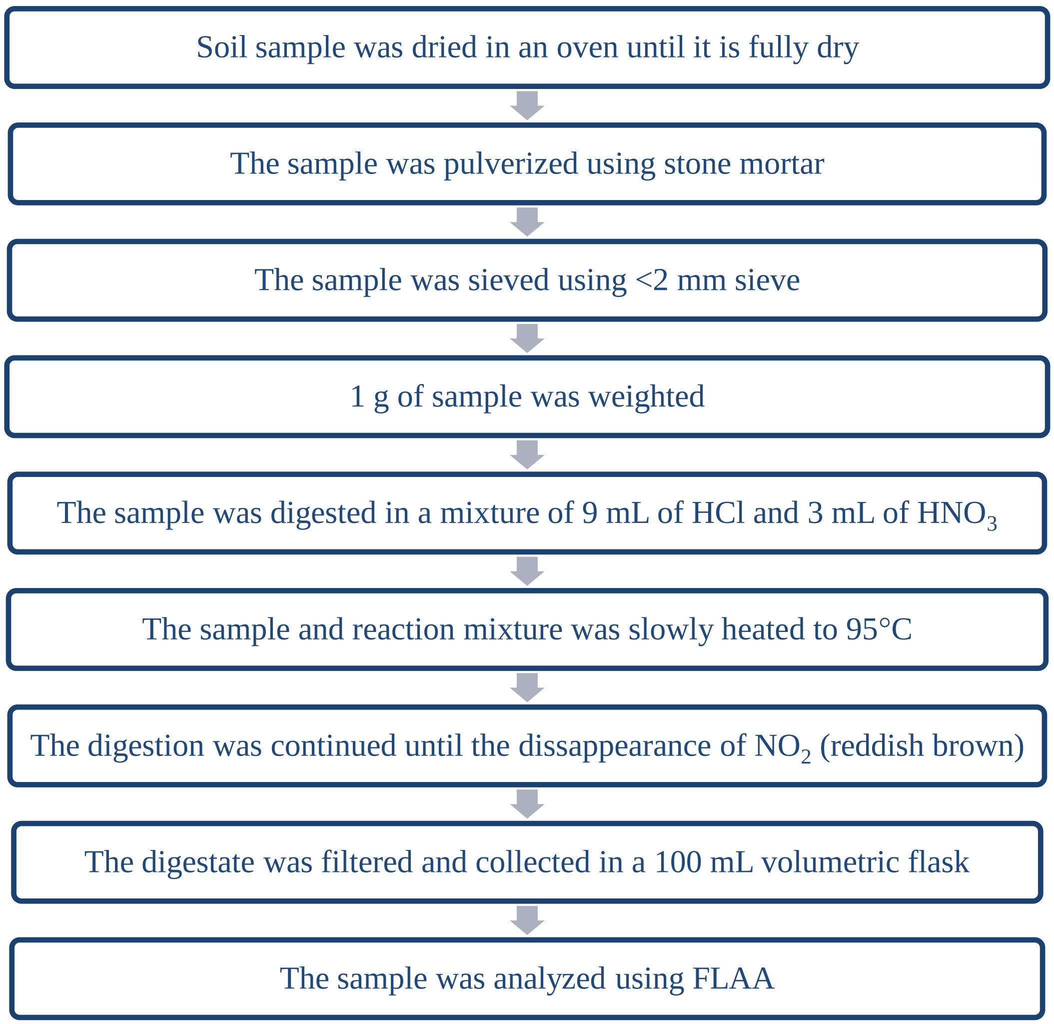

Figure 3.2: Schematic diagram of research methodology

3.4 Preparation of Standard Calibration Curve

The selected heavy metals were Cd and Cr. For each of the selected metals, 4 standards were set for calibration of the FLAA. For Cd, the standards are as follows, 1 ppm, 5 ppm, 10 ppm and 20 ppm while for Cr, the standards prepared are 1 ppm, 10 ppm, 30 ppm and 100 ppm. The calibration curve of well prepared standards and an accurate FLAA should present as a linear curve. All the standards was prepared as dilution formula below;

$$M_1V_1 = M_2V_2$$

where;

M = contentration in ppm

V = volume in mL

Subscript 1 = ultra pure water

Subscript 2 = stock solution of heavy metal (Cd, Cr)

CHAPTER 4

RESULT & DISCUSSION

4.1Introduction

All the result obtained after analyzing by FLAA was all in negative value. This was a situation when spiking the sample is needed. At low metal concentration, spiking the sample is a better alternative (P. Petra, 2007). The sampling points chosen was covered almost an area of the gridding with the blue box color at surface and sub surface soil as in Figure 4.1 below;

1	2	3	4	5
6	7	8	9	10
11	12	13	14	15
16	17	18	19	20
21	22	23	24	25

Figure 4.1: Grid of chosen sampling points for spike samples

4.2 Sample Spiking

The validation of the sample procedure was assessed by using spiking method to obtain the exact value. Below is the procedure for ppm spiking experiment for both Cd and Cr;

- 1 ml of filtered sample was mixed with 250 µL of 1000 ppm heavy metal stock solution (Cd and Cr) in a 50 mL volumetric flask. The mixture was diluted using ultra pure water.
- The sample was analyzed using FLAA.

Samples are spiked for several reasons. One reason is to tune the analysis device, a second reason is to calibrate responses of the device, and a third reason is to provide internal standards and surrogate compounds (*www.freepatentsonline.com*, 2010).

Formulation below is for preparation of 5 ppm spiking method for both Cd and Cr;

$$(A\ \text{ppm}) = \frac{A\ \text{mg}}{1000\ \text{L}} \times \frac{\text{volumetric flask vol}}{\text{weight of sample}} \times \frac{1000\ \text{g}}{1\ \text{kg}} \times \text{dilution factor}$$

$$\text{Dilution factor} = \frac{\text{volumetric flask volume}}{\text{weight of sample}}$$

A = detected value – 5 ppm

4.3 Data Assessment

Data was gathered from all analyzing and organized in table. The concentration is in ppm, of soil samples after spiking the samples were converted into mg/kg as shown in previous sub chapter, and then compared to USEPA Soil Standard. Appendix A shows the data for the USEPA soil standard of heavy metals. Table 4.1 and 4.2 show the pH and physical properties of the chosen samples respectively. Full data for Cd and Cr concentration is show in Table 4.3. The distribution of Cd and Cr are show in Figure 4.2 to 4.5.

Table 4.1 : pH of soil samples

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

Table 4.2 : Physical properties of soil samples

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

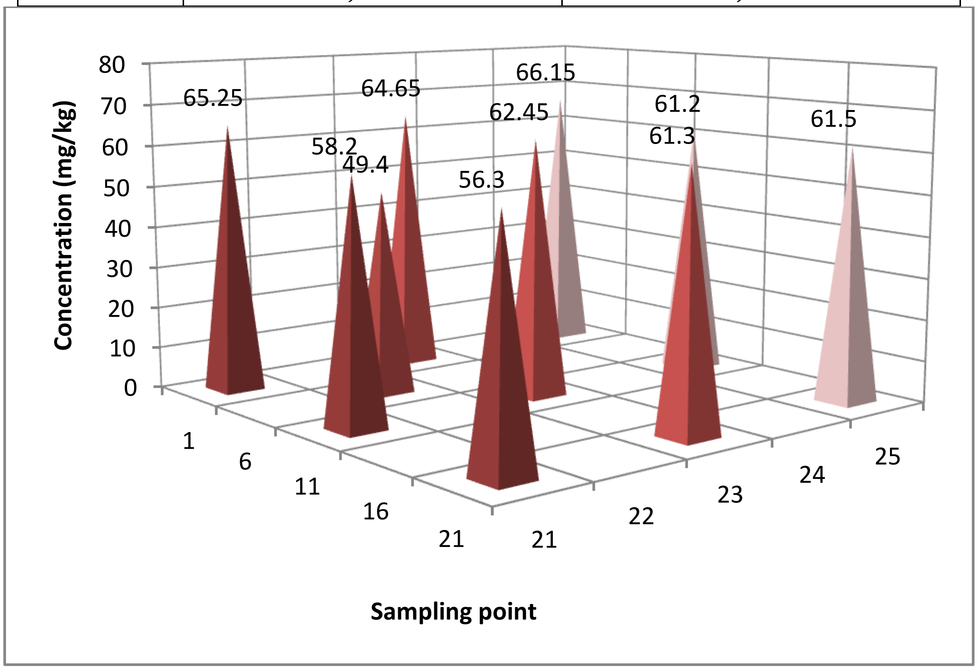

Figure 4.2: Distribution of Cd concentration at surface soil

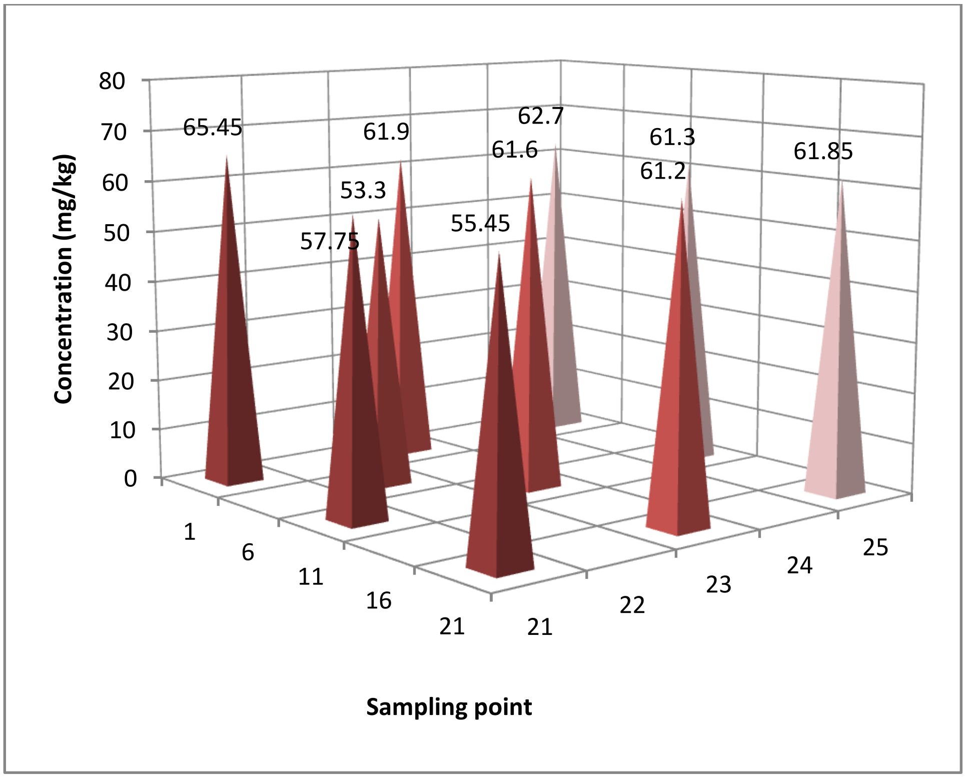

Figure 4.3: Distribution of Cd concentration at sub surface soil

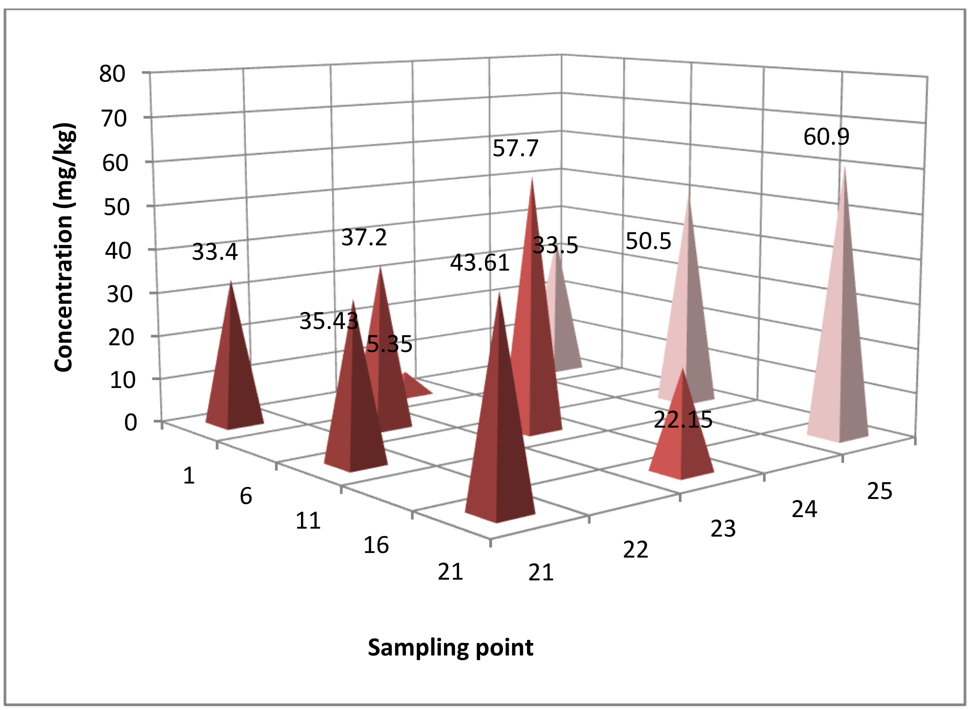

Figure 4.4: Distribution of Cr concentration at surface soil

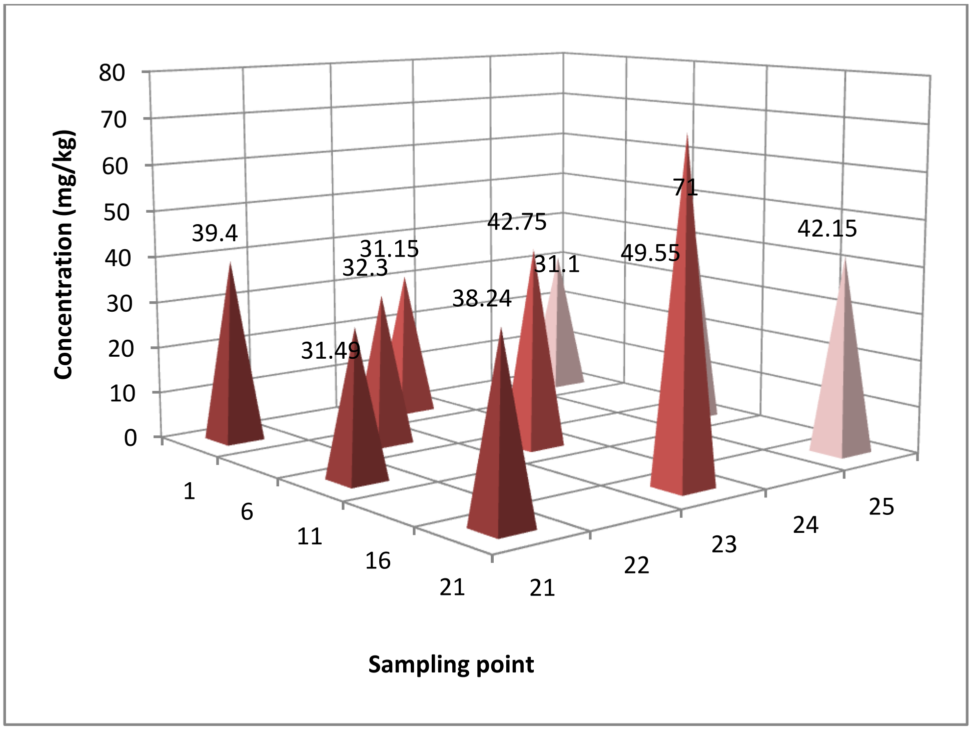

Figure 4.5: Distribution of Cr concentration at sub surface soil

From the distribution of Cd and Cr concentration in surface and sub surface soil in Figure 4.2 to 4.5, it can be summarize that all the concentration of Cd and Cr are differ at every points. For distribution of Cd at surface soil, the concentration is between 49.4 to 66.15 mg/kg and at sub surface soil; the concentration is between 55.45 to 65.45 mg/kg. All the data are showing not much difference between sampling points. For Cr concentration, at surface soil, the data is between 5.35 to 60.9 mg/kg while at sub surface soil the range is between 31.1 to 71 mg/kg.

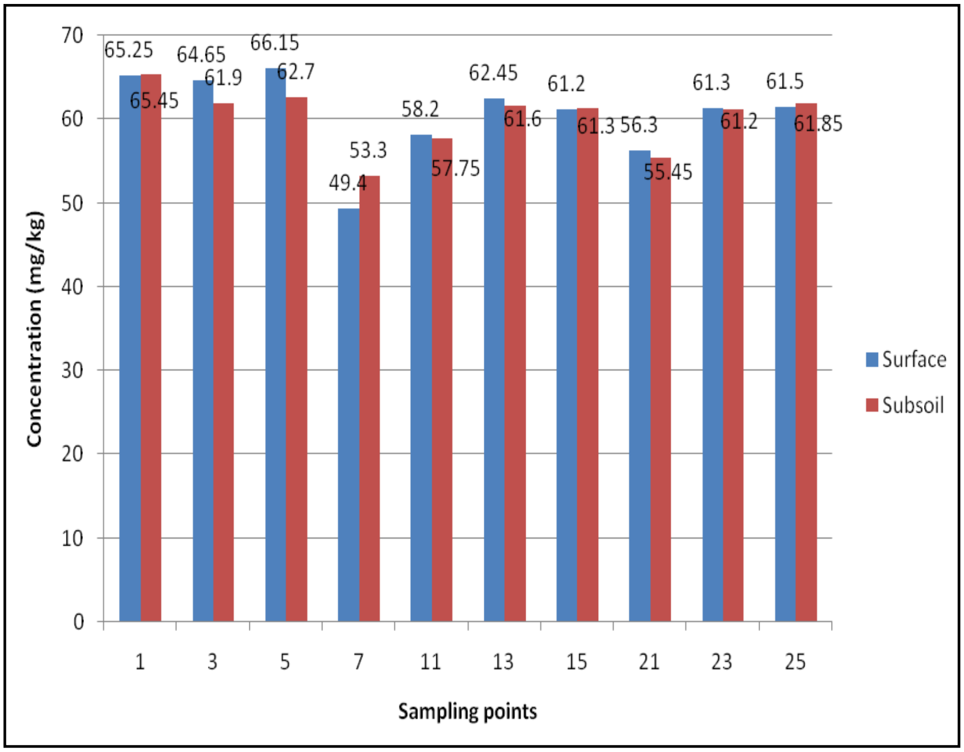

Figure 4.6: Distribution of Cd at surface and sub surface soil

Figure 4.6 is the distribution of Cd concentration at surface and sub surface soil at 10 chosen sampling points. At every point, the result shown is fluctuated, which means at some points, the concentration is higher at surface compare to the subsurface and at some other point, the result is vice versa.

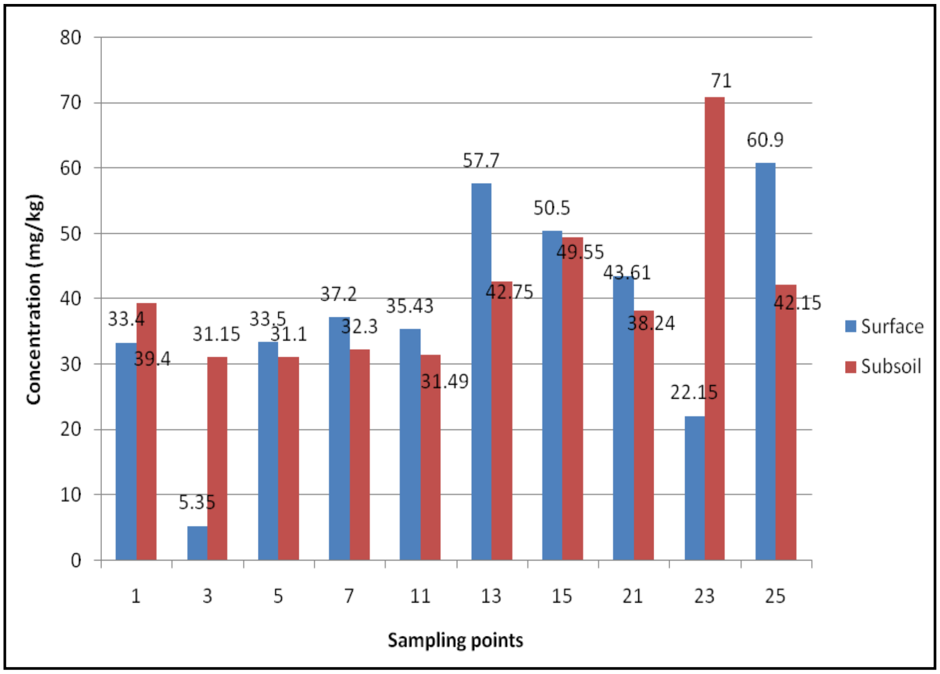

Figure 4.7: Distribution of Cr at surface and sub surface soil

Figure 4.7 is the distribution of Cd concentration at surface and sub surface soil at 10 chosen sampling points. At every point, the result shown is fluctuated, which means at some points, the concentration is higher at surface compare to the subsurface and at some other point, the result is vice versa.

Table 4.3: Concentration of Cd and Cr at surface and subsurface soil

Sampling points	Surface soil		Sub surface soil	
	Cd	Cr	Cd	Cr
	(mg/kg)			
1	65.25	33.4	65.45	39.4
3	64.65	5.35	61.9	31.15
5	66.15	33.5	62.7	31.1
7	49.4	37.2	53.3	32.3
11	58.2	35.43	57.75	31.49
13	62.45	57.7	61.6	42.75
15	61.2	50.5	61.3	49.55
21	56.3	43.61	55.45	43.61
23	61.3	22.15	61.2	22.15
25	61.5	60.9	61.85	42.15

From the comparison charts above, the concentration Cd and Cr are fluctuated against the partitions of soil. Also, at every sampling points and partitions, the value of Cd is highest than Cr. This might due to the sources of waste from household and industrial which are the major contributors of Cd. Even the landfill had already closed and no longer accommodate anymore waste, the smoke release from nearby industrial activity might settle at the landfill as dust. The major activities of industrialization that is located close to the landfill is mostly operated base on wood and metal base that will release Cd dust. If it not because of the external sources, the soil itself do contains Cd as a natural occurrence. All the values were compared to the USEPA soil standard. For all samples, the concentration of Cd is higher than the limited value of 39 mg/kg. USEPA standard for Cr is 1200 mg/kg and the entire sample examined is under the control value. The range value of pH for the sample is between 5.11 to 6.9 which means the soil at the landfill is low acidic.

After some time, this data might change due to the climate change. For example, during a rainy day, the rainwater that settles in the surface of the soil may migrate to the deepest soil and groundwater, that it may change the contents of the soil. This may give the value of the current concentration of the heavy metal change. The data represents in this study is hopefully to give some benefits for future reference or soil remediation.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

All the concentration of Cd at every points and partitions are highest compared to Cr. At every points of sampling the distribution of heavy metals at surface and sub surface soil is fluctuated. For each heavy metals (Cd and Cr), some point of sampling have highest value for the surface sample, while at another point, the concentration of heavy metal is highest at sub surface soil. At every points and partitions, the concentration of Cd is exceeded the USEPA standard (39 mg/kg), however the concentration of Cr is under the control value (1200 mg/kg).

5.2 Recommendation

At the end of the study, there are some improvements are needed and can be done in order to improve the current result;

1. Increase the number of sampling points and ensure that it covers almost the whole landfill.
2. Take the samples from the various depth. This study was only covered the surface (0-20 inch) and sub surface (2-10 inch) soil. After some short time, the

current result obtained may differ due to the migration of the heavy metal that can happen because of rainwater. Since the depth from 0 to 10 inch is almost expose to an air, the rainwater contacted to the surface may easily flow to the ground within the range of the taken depth and change the heavy metal contents of the soil. Also, after some time the current surface may undergo the change of level due to the natural occurrence such as air and wind.

3. The study comes with an analysis of leachate. Landfill leachate is liquid that moves through or drains from a landfill. Since the leachate is in a liquid form, it must be easier to flow and transfer the pollutant in it to the surrounding. Do study the other parameter too such as Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) for the landfill leachate. The study of contamination of heavy metals is a very minor scope for landfill study. To get the details data of the landfill study, other than just heavy metal contamination is important too including the landfill leachate.

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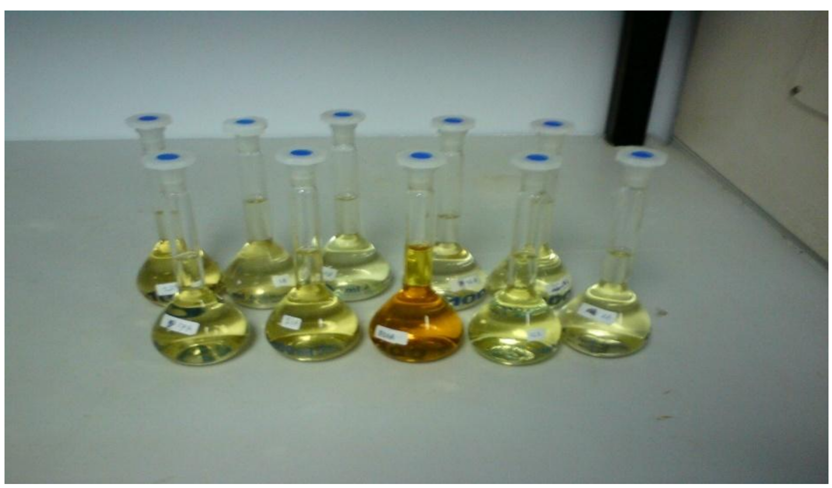
APPENDIX A

Table of USEPA Soil Standard (503 Standard)

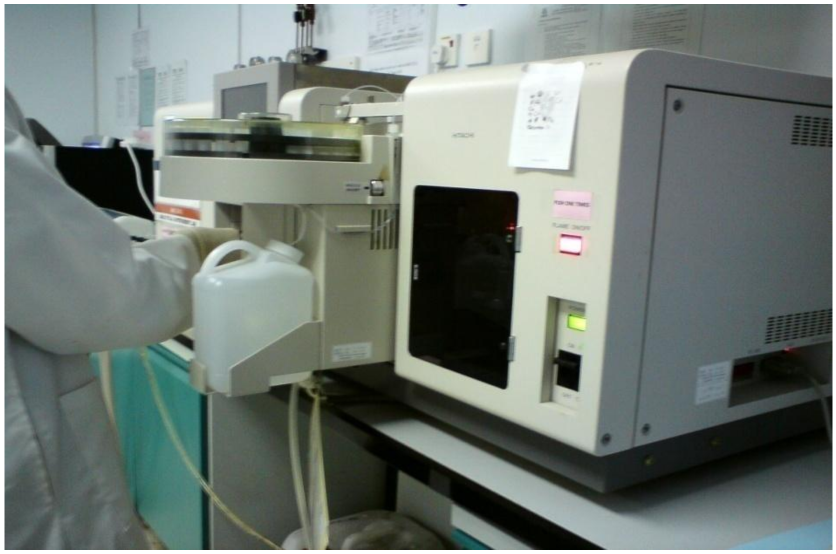
Chemical	Lowest Exposure Limit[a]	99th Percentile Concentration[b]	503 Standard[c]	Grade 1 End-Product Standard[d]
As	1	10	41	10
Cd	27	16	39	16
Cr (total)	3,000	180	1,200	180
Cu	1,500	1,020	1,500	1,020
Pb	270	1,030	300	300
Hg	12	11	17	11
Mo	280	NA[e]	75[f]	75
Ni	420	160	420	160
Se	72	NA	36	36
Zn	2,800	2,190	2,800	2,190

APPENDIX B

Weighing the sample



Samples for analysis by FLAA



FLAA

Data reading