UNIVERSITI PUTRA MALAYSIA

HEALTH RISK ASSESSMENT OF HEAVY METALS IN THE ENVIRONMENT AT KG. JENJAROM, KUALA LANGAT, SELANGOR

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By

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Thesis submitted in fulfilment of the requirement for the degree of Bachelor Science (Environmental and Occupational Health) from the Faculty of Medicine and Health Sciences

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HEALTH RISK ASSESSMENT OF HEAVY METALS IN ENVIRONMENT AT KG JENJAROM, KUALA LANGAT, SELANGOR

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Introduction: Battery factory in Kg Jenjarom operated smelting process which leads to the release of lead (Pb) to the environment via air dispersion and discharging into the waterway. Other harmful heavy metals such as arsenic (As), nickel (Ni), cadmium (Cd) and chromium (Cr) also can coexist in the environment which might cause serious health problem to the community. **Objectives:** The aim of this study is to determine the heavy metals concentrations in air, soil and water and to predict the health risk from heavy metals exposure. **Methodology:** Environmental samples were taken at three different distances from the factory: 500 m, 1.0 km and 1.5 km. Air samples were collected by using personal air sampling pump, the topsoil samples were collected using scoop and High-Density Polyethylene (HDPE) bottles were used to collect the sample of surface water. The analyses were carried out in the laboratory using Inductive Coupled Plasma Mass Spectroscopy (ICPMS). **Results**: The results showed that the air Cr concentrations (1.627) were high in air and exceeded the Air Quality Standard by Agency for Toxic Substances and Disease (ATSDR). While for soil and water samples, Pb concentrations (0.17) were high in the topsoil and exceeded the Standard of Dutch Target for soil while the heavy metals in surface water did not exceed the National Water Quality Index for Malaysia Class iv (Irrigation). Based on Health Risk Assessment (HRA), Hazard Quotient (HQ) for Ni (8.82) and Cr (15.6) in air were more than one. Lifetime Cancer Risk (LCR) for air Cr was 2.34 x 10^{-2} and exceeded the acceptable lifetime cancer Risk (1 x 10^{-6} to 1 x 10^{-4}). However, for soil and water, all heavy metals had HQ of less than 1 and LCR in an acceptable range. **Conclusion:** These results, indicated that exposure to air Ni and Cr might result in non-carcinogenic acute and chronic health effects for the community, while exposure to air Cr could lead to cancer.

Keywords: Heavy metals, Environmental samples, Health risk assessment, Non-carcinogenic health risk, Carcinogenic health risk.

PENILAIAN RISIKO KESIHATAN LOGAM BERAT DALAM PERSEKITARAN DI KG JENJAROM, KUALA LANGAT SELANGOR.

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Pengenalan: Kilang bateri di Kg Jenjarom mengendalikan proses peleburan yang membawa kepada pelepasan logam berat seperti plumbum (Pb) ke persekitaran melalui penyebaran udara dan pembuangan di saluran air. Logam berat seperti arsenik (As), nikel (Ni), kadmium (Cd) dan kromium (Cr) boleh wujud bersama di persekitaran yang boleh menyebabkan masalah kesihatan yang serius kepada masyarakat. **Objektif:** Tujuan kajian ini adalah untuk menentukan bacaan logam berat di udara, tanah dan air dan untuk meramalkan risiko kesihatan dari pendedahan kepada logam berat. **Kaedah:** Sample persekitaran diambil pada jarak yang berbeza dari kilang (500m, 1.0 km and 1.5 km). Sampel udara dikumpulkan dengan menggunakan pam pensampelan udara peribadi, sampel tanah dikumpul dengan menggunakan scoop manakala botol High-Density Polyethylene (HDPE) digunakan untuk mengumpul sampel air. Analisis sampel dilakukan dengan menggunakan Inductive Coupled Plasma Mass Spectroscopy (ICPMS). **Keputusan**: Hasil kajian menunjukkan bahawa bacaan udara Cr (1.627) tinggi di udara dan melebihi piawaian kualiti udara oleh Agency for Toxic Substances and Disease (ATSDR). Sementara untuk sampel tanah dan air, bacaan Pb (0.17) tinggi di dalam dan melebihi piawaian Standard of Dutch Target tetapi tidak pada piawaian National Water Quality Index for Malaysia Class iv (Irrigation). Berdasarkan peniliaian risiko kesihatan (HRA), Hazard Quotient (HQ) untuk Ni (8.82) dan Cr (15.6) untuk pernafasan telah lebih dari nilai satu. Lifetime Cancer Risk (LCR) Cr dalam udara adalah 2.34×10^{-2} dan melebihi kadar selamat untuk risiko barah seumur hidup (1×10^{-6} to 1×10^{-4}). Namun kesemua logam berat dalam tanah dan air, mempunyai HQ kurang dari nilai satu dan LCR di dalam kadar yang selamat. **Conclusion:** Hasil ini menunjukkan bahawa pendedahan kepada Ni dan Cr mungkin mengakibatkan kesan kesihatan jangka pendek dan panjang kepada masyarakat, sementara pendedahan kepada Cr untuk jangka masa panjang boleh menyebabkan barah.

Keywords: Logam berat, Sampel persekitaran, Penilaian risiko kesihatan, Risiko kesihatan bukan karsinogenik, Risiko kesihatan karsinogenik.

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ABREVIATION

As	Arsenic
Ni	Nickel
Cd	Cadmium
Cr	Chromium
Pb	Lead
HRA	Health Risk Assessment
ADD	Average Daily Dose
LADD	Lifetime Average Daily Dose
RfD	Reference Dose
RfC	Reference Concentration
HQ	Hazard Quotient
LCR	Lifetime Cancer Risk
URF	Unit Risk Factor
CSF	Cancer Slope Factor
EC	Exposure Concentration
ATSDR	Agency for Toxic Substances and Disease
OEHHA	California Office of Environmental Health Hazard Assessment
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation
ICPMS	Inductive Coupled Mass Plasma Spectroscopy
$\mu g/m^3$	microgram per metre cubic
mg/Kg	milligram per kilogram
mg/L	milligram per litre

CHAPTER 1

INTRODUCTION

1.1 Research Background

Heavy metal is any metallic elements which has a relatively high density and can be toxic or poisonous even at low concentrations. Examples for heavy metals that common are Pb, As, Cd, Cr and Ni. Those heavy metals are natural components that can be found from earth's crust. It cannot be destroyed or degraded (Lenntech, 2019). Even though it can be found naturally in the environment, those heavy metals are widely used in industrial activities starting from early industrial revolution era. Heavy metals were act as raw materials or fuels for any activities. As for industry, heavy metals can bring benefits or profit as its price is quite cheap and can produce more thing. Unfortunately, heavy metals that released to the environment from those activities can lead to problem for environment itself such as metal pollution and degradation of atmosphere, water bodies and also food crops. Most concerning issue from heavy metals present in the environment is it can cause adverse health effects to human.

Activities such as factories and mining will produce lots of heavy metals to the environment either through air, water and soil. From the environmental exposure, human can expose to those heavy metals directly or indirectly. Those exposure can pass through into human body in many ways such inhalation, ingestion or through dermal (Cao et al., 2014). For inhalation, all free heavy metals in form of particulate released by industrial activities will be inhaled by human can bring negative impact to them. For example, exposure to heavy metals can cause acute and chronic health effect such as lung cancer and asthma.

While for ingestion, human might not ingest the heavy metals directly. It comes when hygienic issue from certain individual. Exposure from direct contact to metals by hand and not properly wash the hand before eating is one of the ways for heavy metals exposure. Not just that, exposure through dermal also might possible as most of our product contain those metals secretly. For example, Pb can present in cosmetics products as it applied on our skin and it can enter through it and cause further health effects (Bawa et al., 2015).

Exposure to high concentration of Cr may cause toxic effect such as liver, kidney problems and genotoxic carcinogen (ATSDR, 2012). While for lead (Pb), Pb is also a highly toxic and carcinogenic metal and may cause chronic health risks, including headache, irritability, abdominal pain, nerve damages, kidney damage, blood pressure, lung cancer, stomach cancer and gliomas. As the children are most susceptible to Pb toxicity, their exposure to high levels of Pb cause severe health complexities such as behavioural disturbances, memory deterioration and reduced ability to understand, while long-term Pb exposure may lead to anaemia (Järup, 2003).

According to Järup et al.,(1998), Cd also bring another health effect such as kidney damage, skeleton damage, and itai-itai disease if human expose to it for a long period. Another experimental studies in human and animals also highlighted that Cd may cause cancer to human (IARC, 1993). While for Ni and As, chronic bronchitis, reduced lung function and skin lesions, and cancer of the lung and skin (ATSDR, 2015; WHO, 2018). Among all level of the community, most vulnerable group for heavy metals exposure is children and also senior citizen as for children, their body system is still in development and not strong enough to expose all kind of dangerous exposure in the environment. While for senior citizen, their bodies and immunization already weak due to their age. So, if heavy metals around them it might cause worse health effect towards them.

By doing health risk assessment, the level of risk of heavy metals that being exposed to human can be determined through their hazard identification, route of exposure, dose response relationship and risk characterization. After that, further mitigation action can be done as we already determined the significant of effect of heavy metals towards human.

1.2 Research Problem

Heavy metals such as Cd, As and Cr are naturally occurring elements that have a high atomic weight and a density of at least five times greater than that of water (Tchounwou et al., 2012). Heavy metals have a wide range of applications covering industries, domestic, agriculture, medical and technological. This has led to their wide distribution in the environment; raising concerns over their potential effects on human health and the environment (Tchounwou et al., 2012). Heavy metals released through air, water and soil can exposed human with all kind of adverse health effect. Breathing in heavy metals particles, drinking polluted water from polluted water sources, and direct exposure to high heavy metals concentration in soil can lead to so many adverse health effects.

There is a lead acid battery factory in Kg Jenjarom, Kuala Langat, Selangor which operates daily. The factory is located near to the community housing area and the villagers were concerned on the fact that the factory’s activities released Pb residues into the environment. The smelting of old car batteries released Pb into the air in which indirectly, it would get deposited on the topsoil or Pb from the factory processes can be discharged into the waterway. Pb in the air will expose the community through inhalation which can pose acute or chronic health effects and exposed through accidental ingestion and dermal contact from soil and water during recreational activities.

Apart from that, presence of other heavy metals such as As and Cr also can be found in the soil as it can be coexisted naturally. But industrial activities such as battery factory at Kg Jenjarom already make the concentration keep increasing by time to time. Free particulate in the air will be deposited in the soil after so long present in the air.

Research Questions

1. What are the heavy metals such as arsenic, cadmium, chromium, nickel and lead concentration in the environment especially in air, water and soil in Kg Jenjarom?
2. Is there any association between of heavy metals such as arsenic, cadmium, chromium, nickel and lead concentration with regard to the distance?
3. Is the concentration of arsenic, cadmium, chromium, nickel and lead in the environment already exceed the limit?
4. Is there any significant health risk of the heavy metal like arsenic, cadmium, chromium, nickel and lead to the community?
5. Are there any differences of arsenic, cadmium, chromium, nickel and lead concentration in different distances from the source?

1.3 Study Justification

The purpose of the study is to determine the concentration of As, Cd, Cr, Ni and Pb in the environment in Kg Jenjarom and also to understand significant risk of heavy metals to the community surrounding. Apart from that, the reason why those heavy metals were chosen in this study because their toxicities especially to human health which might can lead to acute and chronic health effects. By doing Health Risk Assessment, potential impact of heavy metals to human can be estimated either it is safe or not and also can improve the awareness among communities about health risk posed by heavy metals which can cause acute and chronic health effect that their exposed in daily life (Li et al.,2014; Fasihah et al., 2017).

By doing this study, it also can help other future studies and become a baseline study which related with this issue as there is no related studies about heavy metals in Kg Jenjarom area especially the lead (Pb) levels in the environment. This study also can educate communities about the effect of heavy metals and they can do something to save their life and also to educate responsible people to aware about the health effect of heavy metals in human especially.

1.4 Objectives

1.4.1 General Objectives

To assess the concentration of arsenic, cadmium, chromium, nickel and lead in the environment and their relationship with health risk in Kg Jenjarom, Kuala Langat

1.4.2 Specific Objectives

i. To determine the concentration of As, Cd, Cr, Ni and Pb in the environment either air, soil and water.

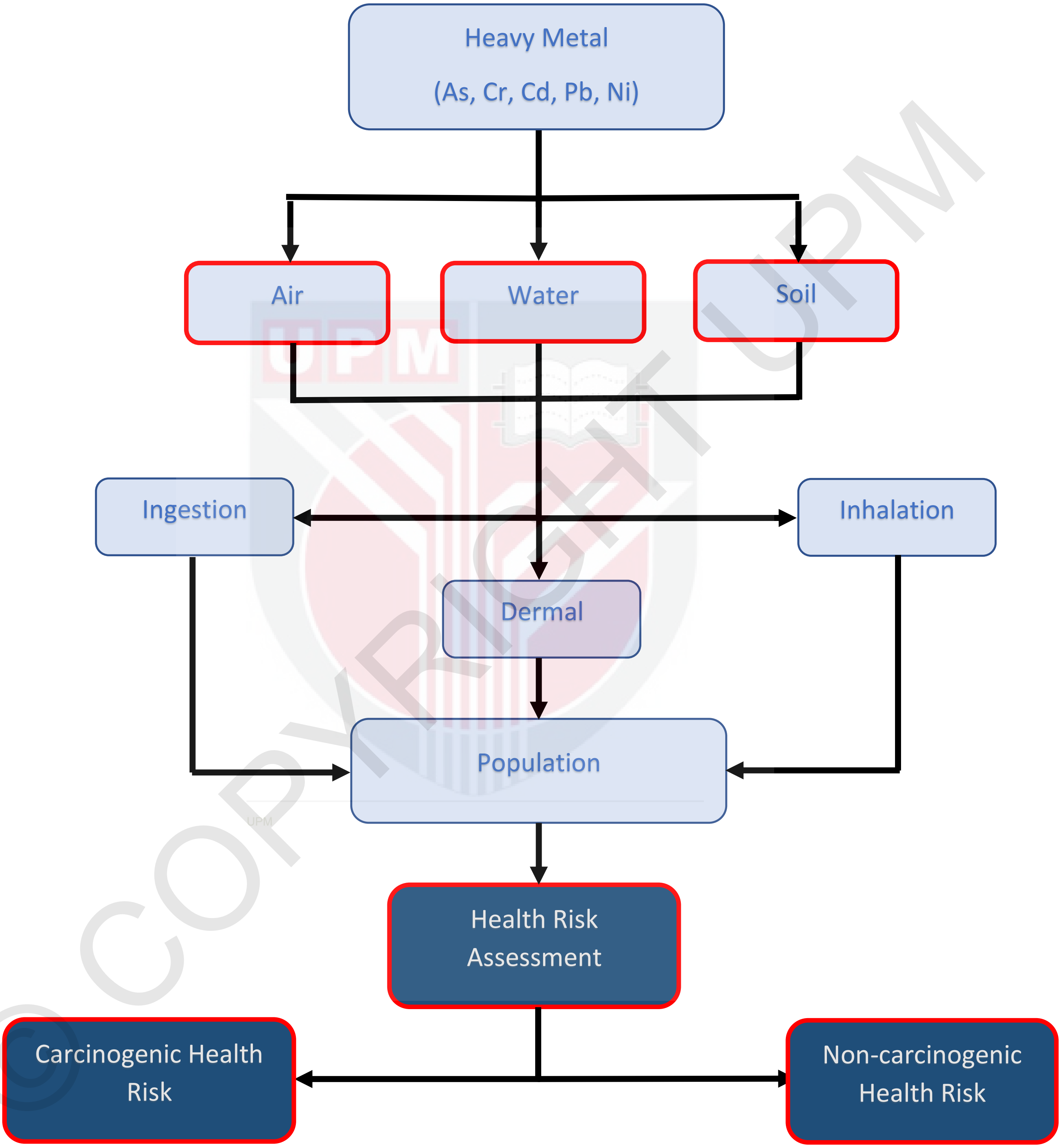
ii. To compare the As, Cd, Cr, Ni and Pb concentration in the environment with the standards in Malaysia or other countries

iii. To determine the relationship between the As, Cd, Cr, Ni and Pb concentration with the distance from the point source.

iv. To compare As, Cd, Cr, Ni and Pb concentration at different distances

v. To determine the health risk from As, Cd, Cr, Ni and Pb concentrations in the environment at various distance from the sources.

1.5 Conceptual Framework



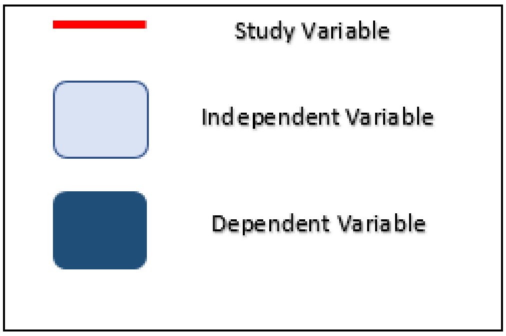


Figure 1.1: Study Conceptual Frameworks

1.6 Definition Terms

1.6.1 Conceptual Definition

I. Environment

Environment is everything around us. It includes all of the living and the nonliving things with which we interact. And it includes a complex web of relationships that connect us with one another and with the world we live in (Miller and Spoolman, 1979).

II. Heavy Metals

Heavy metal is any metallic elements which has a relatively high density and is toxic or poisonous at low concentrations. In this study, heavy metals that being focused are As, Ni, Cd, Cr and Pb. All these heavy metals might can lead to serious health effect to human. According to Knight et al., (1997), chromium is an essential element that needed by human body. But, excessive intake or exposure to chromium can lead to serious health issues such as toxic effect such as liver, kidney problems and genotoxic carcinogen. Apart from that, Cd may bring another health effect such as kidney damage, skeleton damage, and Itai-Itai disease (Jarup et.al.,2000).

Besides that, As also can cause skin lesion if being exposed in short-term and skin cancer if exposed for too long (WHO, 2018). While Pb, can Pb to severe health complexities such as behavioural disturbances, memory deterioration and reduced ability to understand, while long-term Pb exposure may lead to anaemia (Järup, 2003). Ni exposure also might bring negative impact to human as it leads to chronic bronchitis, reduced lung function, and cancer of the lung and nasal sinus (ATSDR, 2005)

III. Route of Exposure

According to Tchounwou (2012), the main route of exposure for heavy metals are inhalation, dermal contact and oral ingestion. This statement was being supported by (Baastrup et al., 2008). It occurs because most of industrial activities might release the heavy metals to the air and discharge through the water body. Heavy metals in the air also can deposited on topsoil after being in the air for a long time period. Human can accidentally expose to that through inhalation of contaminated air, drinking polluted water or oral ingestion and direct contact of dermal for soil particles.

IV. Health Risk Assessment (HRA)

Human health risk assessment is considered as the characterization of the potential adverse health effects of humans as a result of exposures to environmental hazards (USEPA, 2012). HRA also can classifies elements into carcinogenic and non-carcinogenic. Non-carcinogenic chemicals are assumed to have a threshold; a dose below which no adverse health effects will be observed where an essential part of the dose-response portion of a risk assessment includes the use of a reference dose (RfD). Also, carcinogens are assumed to have no effective threshold. This assumption implies that there is a risk of cancer developing with exposures at low doses and, therefore, there is no safe threshold for exposure to carcinogenic chemicals. Carcinogens are expressed by their Cancer Potency Factor (Lushenko, 2010).

V. Non-Carcinogenic Health Risk

Non-carcinogenic health risk is health effect arise due to exposure to any kind of pollutant for short-term period. It also might not lead to death. For example, exposure to nickel can lead to bronchitis (ATSDR, 2005).

VI. Carcinogenic Health Risk

For carcinogenic health risk is any health effect to human arise due to long-term effect to any pollutants. According to USEPA (2012), cancer is one of example of health effect and human expose to certain pollutants for 70 years.

1.6.2 Operational Definition

I. Heavy metals

The measurement of arsenic, cadmium, chromium, nickel and lead in ambient air will be conducted by using Gillian Personal Sampling Pump with filter paper. The sampling procedure for air sample will be based on NIOSH Method 0600 for free particles. While for water samples, it will be collected by using HDPE bottles (Fasihah et al., 2017). Meanwhile for soil samples, topsoil (0-15 cm) will be taken by using auger and placed in free-metal plastic bags (Onianwa & Fakayode, 2000). Then, samples will be analysed with ICPMS after digesting with concentrated HNO_3 (Dudka & Miller, 1999). Each sample will be taken 3 times for each sampling point based on the distance from the source.

II. Health Risk Assessment

Health risk assessment is an assessment to determine a significant risk for any kind of non-carcinogenic and carcinogenic hazardous materials which consists of 4 basic steps known as hazard identification, dose-response assessment, exposure assessment and risk characterization (USEPA, 2009).

III. Non-Carcinogenic Health Risk

Non-carcinogenic health risk can be predicted by Health Risk Assessment (USEPA, 2012). Average daily dose for any pollutant is calculated by considering duration exposure, exposure frequency and so on. By doing so, the health effect for exposed pollutant at any time period can be determined.

IV. Carcinogenic Health Risk

For carcinogenic health risk, lifetime average daily dose is calculated for determine the significant effect of any pollutants for 70 years of exposure (USEPA,2012). This method can determine any serious health effect to human such as cancer.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals in Air

Heavy metals may come from many different sources in urbanized areas, including vehicle emissions, industrial discharges and other activities (Harrison et al., 1981). Metal smelting is regarded as one of the most important anthropogenic heavy metal emission sources (Nriagu.and Pacyna, 1988). During smelting process, heavy metals in the ores are evaporated from the matrix, and eventually go into the atmosphere, if no pollution control technology is applied (Pacyna and Pacyna, 2002). Once it evaporated and dispersed to the atmosphere, it can fly away and affecting the environment and also human. Most concerning issue is when the industrial area is nearby the community area as there are so many people will expose directly and high in concentration. For example, Pb is widely used in mining and also manufacturing factories. It is because Pb price is quite cheap and also it can turn into new and good products. Mostly Pb will undergo smelting process and be in fumes form. Then, it will release to the atmosphere and will affect workers and also surrounding community health.

Instead of industrial activities, heavy metals also can be found in other sources such as combustion of vehicle fuel and paint that might contain Pb. So, from this kind of sources also can cause many health effects to human especially for the children and senior citizen. Those heavy metals exposure will be inhaled by human and lead to further health issues to human as it can cause chronic health risks, including headache, irritability, abdominal pain, nerve damages, kidney damage, blood pressure, lung cancer, stomach cancer and gliomas. As the children are most susceptible to Pb toxicity, their exposure to high levels of lead cause severe health complexities such as behavioural disturbances, memory deterioration and reduced ability to understand, while long-term Pb exposure may lead to anaemia (Järup, 2003). Imagine if exposure can come from human surrounding already can lead to serious health effect in long time period and added the exposure from nearby industrial activities that released heavy metals to the environment. The impact to human especially can become worse and make the effects appear in very short time period.

2.2 Heavy Metals in Water

Heavy metal can be found in water as it naturally occurrence or from anthropogenic activities (Khan et al., 2013). Heavy metals basically come from corroded pipeline, mining activities and also agriculture activities as some heavy metals such as arsenic, lead, and cadmium as it run off from the site of activities into the water sources due to improper waste water management (Karavoltsos et al., 2008). Corroded pipeline can contribute to heavy metals contamination to human as it will affecting human water sources for daily used. Due to industrial activities that keep increasing year by year, it can more bring an alarming situation especially for those who lived near that area as those activities might discharged some residual that contain chemicals and also heavy metals.

Human already exposed to the heavy metals in water due to natural occurrence and corroded pipelines. If their water sources contaminated with those discharged residues from industrial activities, the heavy metals concentration might increase and exceed the safe limit for human to expose. That situation can cause so many adverse health effects due to over exposure to heavy metals. For example, Cr is an essential element that needed by human body. But, excessive intake or over exposure to Cr can lead to serious health issues such as toxic effect such as liver, kidney problems and genotoxic carcinogen (Knight et al., 1997).

Same goes to As, as according to WHO (2018), As is commonly can be found in water sources as it comes from discharged residual from industrial activities. Exposure to arsenic may lead to skin lesions and also skin cancer if it exposed for a long time period. By doing a health risk assessment, we can determine what kind of exposure that human exposed and how bad is it from that kind of exposure.

2.3 Heavy Metals in Soil

Recently, industrial activities such as factories, fossil fuel burning and mining activities are keeping increasing. Most an alarming situation when all those activities being done nearby the community's areas which might can bring health effect to the community itself. It is because some heavy metals released to the environment and become deposited in the environment. According to Ripin et al, (2014), industrial activities been emitted the heavy metals into atmosphere as aerosols and distributed in soil and can be transported within a distance and up to several kilometres away from their sources and transferred to the soil through wet or dry deposition. Human can expose to the heavy metals either directly from inhalation of free particles in the air or even through soil by accidently ingestion. This situation might be worrying especially for the children.

Children exposure to heavy metals cannot be prevented well due to their normal behaviour and activity as a child to play outdoor. Unhygienic practices among them can lead to accidental ingestion of heavy metals after they playing at outdoor. For example, exposed to heavy metals such as lead can lead to blood lead level in children increase and caused neurobehavior effect (Herbert et al., 1990). Not just them that can expose to heavy metals through accidental ingestion from soil. Adult or other individual can expose to heavy metals from consumption of plant that contaminated with heavy metals. According to Mattina et al., (2003), plant can uptake and translocate the heavy metals and organic pollutants in soil. Based on their study, after the samples taken such as tomatoes, zucchini and lettuce and being analysed, there are presence of heavy metals such as Pb, As and Cr in plant samples. It shows that plants also can uptake the heavy metals in soil and can affect human health from accidental ingestion of contaminated plant. From that study, soil exposure also can bring impact to human especially for those who live nearby the industrial activities that released all kind of heavy metals to the environment.

A study from Ripin et al., (2014) for heavy metals assessment in soil in Perlis, Malaysia stated that concentration of heavy metals in industry area and heavy traffic area contained high concentration of heavy metals such as Cd, Pb, As and Cr. Those heavy metals were released into the atmosphere from industrial activities and also combustion in vehicles around there. Exposure to high Cd concentration might bring health impact to human as it can be in our food such as contaminated vegetation and water polluted with cadmium through run off from soil which can cause cancer, convulsions and kidney damage (NLM, 2017).

2.4 Standards for arsenic, nickel, cadmium, chromium and lead in environment

All the concentration of heavy metals produced from this study will be compared with the permissible limit standards to determine the safe level of exposure to human. As for the concentration of heavy metals in water will be compared with National Water Quality Index for Malaysia Class iv (Irrigation). While for concentration heavy metal in soil will be compared with Standard of Dutch Target and for concentration of heavy metal in air, it will be compared with standard limit from ATSDR Air Quality Guidelines.

2.5 Heavy Metals and Health Effects

Heavy metals exposure through inhalation, ingestion and also dermal exposure might lead to serious health effects. According to previous study by Saha et al., (2017), Hazard Quotient (HQ) for water Cr, As and Pb was more than one and signed of non-carcinogenic such as skin lesions and kidney failure from Cr exposure. Inhalation of heavy metals such as Pb might also lead health effects such as shortness of breath and reduced lung function (USEPA, 2018). But the effect might can be more worsen to children as it can cause neurobehavioral effects. Long term exposure to heavy metals can lead to carcinogenic health effect such as cancer and this issue can be calculated and determine by calculating the Lifetime Cancer Risk (LCR). Based on previous study by Goudarzi et al., (2018), long-term exposure from inhalation and ingestion of Cr and Pb already exceeded the acceptable range as it more than 1 x 10^{-4} which it indicates that there were significant carcinogenic health effects such as lung cancer and skin cancer.

2.6 Health Risk Assessment

Concentration of heavy metal are commonly being compared with international standards in order to determine the safe level of heavy metal exposure at study area. By comparing the concentration with standards, it will not indicate the whole criteria for health risk exposure as it maybe can show the potential health effect after long term exposure. So, by doing health risk assessment (HRA), all aspects of exposure will be obtained and can determined the exact possible health risk to human (Ab Razak et al., 2015).

EPA states that health risk assessment is contributing the calculation of Hazard Quotient (HQ) for non-carcinogenic health risk while for Lifetime Cancer Risk (LCR) for carcinogenic health risk which contain such variables like heavy metal concentration, ingestion rate, body weight, exposure duration and slope factor (Muhammad et al., 2015). HQ < 1 indicates that there is no significant health risk to human while for acceptable range for LCR are from 1 in 10000 to 1 in 1 million.

According to WHO (2018), heavy metal such as As can cause skin lesion to human as acute effect from exposure through water and also can cause skin cancer after long period exposure or chronic health effect. But there are some heavy metal that essential to our own body for body growth and function such as Cr. Exposure to it in large amount that exceed the limit can also lead to serious health effect (Khan et al., 2010). Heavy metal exposure for chronic exposure are depends on their species toxic, neurotoxic, carcinogenic or mutagenic (Sharma et al., 2008).

Spickett et al., (2012) state that, health risk assessment is important to understand the potential health risk for heavy metal exposure towards human. All those information from health risk assessment are very important as it can help decision makers to set up policies or regulations to protect human’s health (Sobus et al., 2011).

Table 2.1: Standard Value for Heavy Metals in the Environment for Various Standards

Heavy Metals	a. Standard value in air ($\mu g/m^3$)	b. Standard value in soil (mg/kg)	c. Standard value for surface water (mg/l)
Arsenic	0.01	29	0.1
Nickel	0.0022	35	0.2
Cadmium	0.005	0.8	0.01
Chromium	0.02	100	0.01
Lead	0.15	85	5

a. ATSDR Air Quality Guidelines; b. Standard of Dutch Target; c. National Water Quality Index for Malaysia Class iv (Irrigation).

CHAPTER 3

METHODOLOGY

3.1 Study Location

This study was conducted nearby the lead acid battery factory in Kg Jenjarom. That factory was discharging some residual chemicals that might contain heavy metals into the environment. That factory was releasing heavy metals through the air from smelting processes and discharged chemicals into the waterways. The distances for sampling which the environment samples taken were at 500 M, 1 KM and 1.5 KM away from the point source. Each environmental sample was taken at least 3 samples and have 3 sampling point based on the distance from the source. Each distance will have 3 samples for air, water and soil samples.

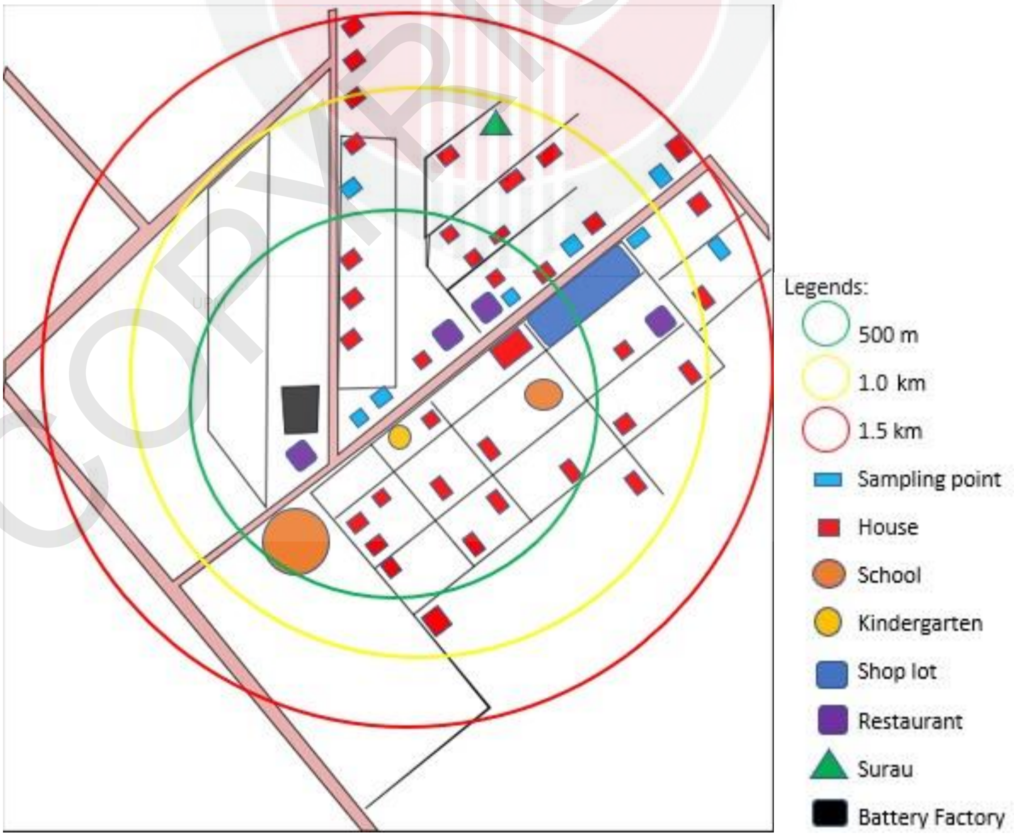


Figure 3.1: Maps of air and soil sampling point

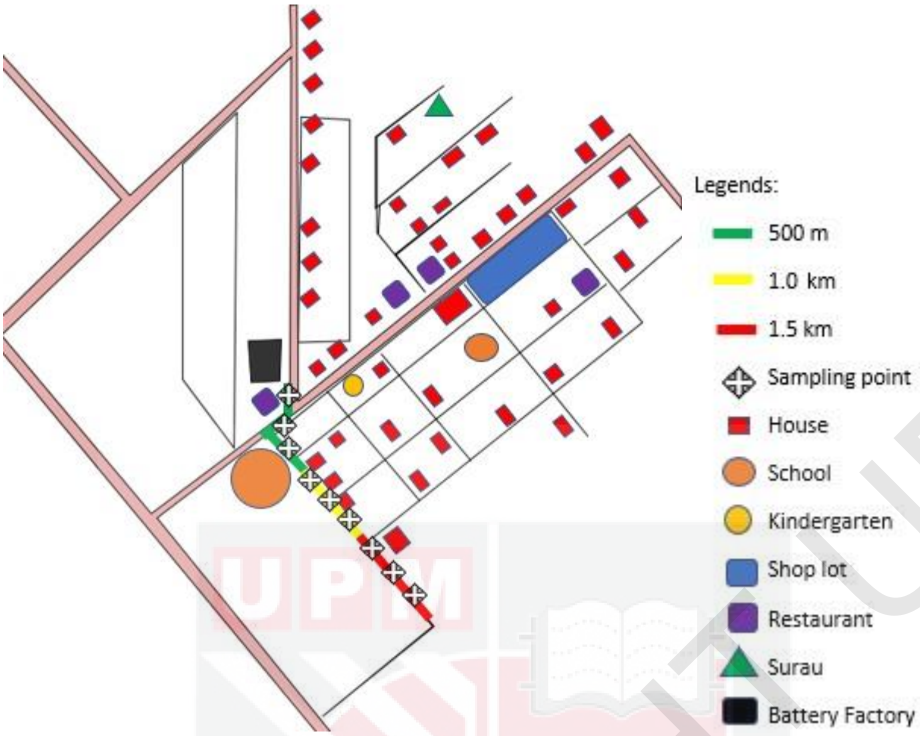


Figure 3.2: Maps of water sampling point

3.2 Study Design

This was a cross-sectional study which aimed to determine the heavy metals concentration in the environment. Health risk of heavy metals in Kg Jenjarom also being measured to predict the risk of the exposure towards human. No human samples needed as samples taken only from the environment which were air, water and soil samples.

3.3 Sample Collection

The environment samples taken were the ambient air, topsoil and also water samples. The samples were the nearby area of factory as a point source of exposure and the area that more distance from the factory. A study from Chen et al., (2012) mentioned that soil samples taken based on the distance from the point source. Each environment samples from air, soil and water taken at least 3 samples for each distance that being set which at 500 M, 1 km and 1.5 km away from the source. So, total samples from air, soil and water will be 27 samples.

3.4 Sampling Method

Methods for sampling for environmental samples such as air, soil and water were based on US EPA methods (Fasiha et.al, 2017; Onianwa & Fakayode 2000). and NIOSH method 0600 (Intan et al., 2016). Specific instruments to collect the samples were used such as personal sampling pump, scoop and HDPE bottles.

3.5 Data collection and Instrumentation

3.5.1 Ambient Air Samples

For determination of heavy metal in air, personal air sampling pump with a combination of filter paper and cyclone for separation of PM_{10} were used with a flow rate at 2,0 L/min based on NIOSH method 0600 for particulates in air. Sampling pumps were placed in house of the nearby community based on distance from the source. Sampling pumps were placed near the window about breathing zone height for at least 24-hour sample (Intan et al., 2016). Samples taken will be based on the distance that have been set. Further information on procedures for collection of ambient air samples will be discussed below.

Figure 3.3: Gillian Personal High-Volume Sampling Pump

3.5.1.1 Preparation before sampling

a) All the cassettes were washed with Decon detergent and rinsed with running water. Then, cassettes were soaked in 69% of Nitric Acid as for acid wash process for 24 hours. After that, soaked cassettes were rinsed again with distilled water and let it dried.

b) At the same time, Filter papers were wrapped with aluminum foils and dried in oven at 40 ^{0}C for half day to reduce moisture. Once it was done, dried filter papers were weighted with micro-scale device to get the initial weight (W_1). All those filter papers were placed in the cassettes along with the support pads and placed completed cassettes in desicator for 24 hours as final procedure to remove moisture.

3.5.1.2 During sampling

a) Each sampling pump was calibrated to the flow rate of 2.0 L/min.

b) Then those sampling pumps and completed with cassette were turned on and placed it in the house of community in Kg. Jenjarom. Sampling pumps were set up near the house windows about breathing zone height. The sampling pumps were running for 24 hours.

3.5.1.3 Post sampling

a) Final flow rate of each sampling pump was obtained.
b) Then, sampling pumps were turned off after 24 hours and all filled cassettes were placed in plastic bags prior for transportation to the laboratory
c) Filter paper was weighted again and recorded as final flow rate (W_2).

3.5.2 Water Samples

As for water samples, HDPE bottles were used for the collection of water samples at 15 cm depth from the surface water at nearby waterway which near with the source. Sample collection also based on the distance that being set early. The collected samples were acidified immediately with 3 ml nitric acid (69%) before it being sealed as this method was adopted from USEPA Method 3005A. Then, those samples stored in cooler box at 4^0C before transferring the samples to laboratory for analysis with ICP-MS. Total sample taken were 3 samples for each distance that being discussed early (Fasiha et.al, 2017).

3.5.3 Soil Samples

According to Onianwa & Fakayode (2000), top soil (0-20 cm) depth were taken by using scoop and place the sample in free-metal plastic bags then sent it to the laboratory for analysis. The soil samples were taken at least 3 for each distance that have been set.

Figure 3.4: Scoop

3.6 Laboratory Analysis

3.6.1 Ambient air samples

Based on hot digestion method by US EPA (2005), filter papers were cut into pieces and placed in 250 ml quartz beaker. Then 30 ml of 10% HNO_3 was added and refluxed for 30 minutes at 95 ^{0}C. After that, 10 ml of clean deionized water was also being added in order to cool down the solution for 30 minutes. Last but not least, that solution was filtered with Whatmann 541 Filter Paper and transferred the filtered solution into polypropylene bottle for analysis with ICP-MS.

Next, concentration of heavy metals in ambient air was determined by using following formula.

Equation 1

$$\boxed{C = \frac{(\text{*µg metal/L}) \times \text{Digestion Volume (L/filter)}}{\text{Vstd}}}$$

Therefore:

C = Total concentration of heavy metals (µg metal/m^3)

*µg metal/L = Concentration determined from analysis with ICP-MS

Digested Volume = Total sample extraction volume from extraction procedure

Vstd = Standard air volume pulled through the filter, m^3

Source: Office of Air Quality Planning and Standards US EPA (2005)

3.6.2 Soil samples

Samples of soil taken from study area was dried at 105 ^{0}C for 2 hours in order to remove moisture in soil samples. Then, dried soil was crushed with pestle mortar and sieved with 2 mm sieve. At the same time, aqua regia solution was prepared by adding 130 ml of HCI and diluted it with 120 ml of distilled water. 50 ml of HNO_3 also was added to complete the aqua regia solution preparation.

one gram of sieved soil samples was mixed with 15 ml of aqua regia solution in crucible and placed in fume cupboard overnight. Then, place the samples in oven at 120 ^{0}C and cooled for a few minutes before filtering the mixed solution with 0.45 µm filter membrane.

Next, concentration of heavy metals in soil was determined by using following formula.

Equation 2

$$\boxed{C = \left[\frac{(\text{*ppb metal}) \times \text{Dilution volume (mL)} \times \text{Mark-up volume (mL)}}{\text{Sample Weight (g)}}\right] \div 100000}$$

C = Total concentration of heavy metals (mg/kg)
*ppb metal = Concentration of heavy metals determined by ICP-MS
Dilution Volume = Total sample extraction from extraction procedures
Mark-up Volume = Aqua Regia Solution

Extracted samples in laboratory were sent to Instrumentation Lab at Faculty Science, University Kebangsaan Malaysia (UKM) for analyzing with Inductively Coupled Plasma-Mass Spectroscopy (ICPMS) model Elan 9000, Perkin Elmer, USA.

3.7 Health Risk Assessment

Health risk assessment divided into 2 categories which for non-carcinogenic health risk and carcinogenic risk. Those 2 health risks have different equations to determine the risk and that equations are adopted from US EPA (2009).

3.7.1 Non-Carcinogenic Health Risk

US EPA states that intake of heavy metals such as Cd and Cr can cause non-carcinogenic health effects to human (USEPA, 2011). Average Daily Dose (ADD) formula (Table 3.1) was used for ingestion and dermal exposure while Exposure air concentration (EC) was used for inhalation exposure.

Formula of ADD for ingestion and dermal were stated below:

Soil: (Ingestion) $$ADD = \frac{C \times IR \times EF \times ED}{BW \times AT}$$ Equation 3

(Dermal) $$ADD = \frac{C \times SA \times AF \times ABS \times EF \times ED \times CF}{BW \times AT}$$ Equation 4

Water: (Ingestion) $$ADD = \frac{C \times IR \times EF \times ED}{BW \times AT}$$ Equation 5

(Dermal) $$ADD = \frac{C \times Kp \times ET \times EF \times ED \times CF}{BW \times AT}$$ Equation 6

While for EC formula was stated below:

Air: $$EC = \frac{C \times ET \times EF \times ED}{AT}$$ Equation 7

For non-carcinogenic health risk, HQ > 1 indicates that there is a significant risk while HQ < 1 indicates that there is no significant risk. Formulas used for the calculation of HQ are as followed:

$$\text{Ingestion/Dermal: } HQ = \frac{ADD}{RfD} \qquad \text{Equation 8}$$

$$\text{Inhalation: } HQ = \frac{EC}{RfC} \qquad \text{Equation 9}$$

Reference Dose (RfD) and Reference Concentration (RfC) were used in this study as being mentioned by Integrated Risk Information System (2012) and California EPA were shown in Table 3.2.

Table 3.1: Parameters Values for Average Daily Dose (ADD) and Lifetime Average Daily Dose (LADD)

Variable	Value	Unit	Source
C = Average Concentration of Heavy Metal	Depends on results	$\mu g/m^3$, mg/kg, mg/l	Based on results
IR = Ingestion Rate (water)	2	l/day	USEPA (2002)
IR = Ingestion Rate (soil)	100	mg/day	US EPA (1997)
EF = Exposure Frequency	350	Days/year	US EPA (2002)
ED = Exposure Duration	7	Years	-
BW = Body Weight	65	Kg	USEPA (2002)
AT = Average period of exposure	365 x ED	Days	USEPA (2002)
SA = Surface Area	5700	cm^2/event	USEPA (2002)
AF = Adherence Factor	0.07	mg/cm2	USEPA (2002)

ABS = Dermal Absorption Factor	0.001	-	USEPA (2002)
CF = Conversion Factor (Soil)	1×10^{-6}	kg/day	USEPA (2002)
CF = Conversion Factor (Water)	0.001	l/cm^3	USEPA (2004)
Kp = Dermal Permeability Coefficient	As = 1×10^{-3} Ni = 2×10^{-4} Cd = 1×10^{-3} Cr = 2×10^{-3} Pb = 1×10^{-4}	-	USEPA (2004)
ET = Exposure Time (water)	0.58	Hr/event	USEPA (2004)
ET = Exposure Time (Air)	24	Hr/event	USEPA (2004)

Table 3.2: Reference Dose and Reference Concentration

Heavy Metals	**RfD (mg/kg/day) (Ingestion)**	**RfD (mg/kg/day) (Dermal)**	**RfC (mg/m^3)**
As	3×10^{-4}	1.23×10^{-1}	3.0×10^{-5}
Ni	2×10^{-2}	5.4×10^{-3}	5.0×10^{-5}
Cd	1.0×10^{-3}	5.0×10^{-6}	1.0×10^{-5}
Cr	3.0×10^{-3}	1.5×10^{-5}	1.0×10^{-4}
Pb	3.5×10^{-3}	4.2×10^{-4}	-

RfD by USEPA Integrated Risk Information System (2012); RfC by California EPA

3.7.2 Carcinogenic Health Risk

According to US EPA, intake of heavy metals such as Pb and As can cause carcinogenic health effect such as cancer to human. Lifetime Average Daily Dose (LADD) formula (Table 3,1) was used for ingestion and dermal exposure while Exposure air concentration (EC) was used for inhalation exposure. Exposure Duration for carcinogenic effect had being set for 70 years due to lifetime exposure.

While for Exposure air concentration (EC) in the unit of mg/m^3 also be determined from the result of the study. Risk which between 1×10^{-6} and 1×10^{-4} is considered as acceptable risk. But for the risk is a significant if exceed the 1×10^{-4}. The risk can be calculated as follow:

Ingestion: Risk = LADD x CSF Equation 10

Inhalation: Risk = EC x URF Equation 11

Cancer Slope Factor used in this study were shown in Table 3.4

Table 3.3 Cancer Slope Factor and Unit Risk Factor

Heavy Metal	CSF (mg/kg/day)	URF (µg/mg^3)$^{-1}$
As	1.5	3.3×10^{-3}
Ni	1.5×10^{1}	4.2×10^{-3}
Cd	4.2×10^{-1}	1.5×10^{-1}
Cr	9.1×10^{-1}	2.6×10^{-4}
Pb	8.5×10^{-3}	1.2×10^{-5}

Source: CSF and URF from OEHHA Cancer Potency Values (2019)

3.8 Data Analysis

Data that obtain from this study was analyzed by using software Statistical Package for Social Science (SPSS) version 22. In this study, samples taken were too small which is 27 samples. So, non-parametric tests were used to analyze the data. Sign-rank test was used to compare the heavy metals concentration with the standard values while Spearman’s rho correlation was used in order to determine the relationship between the heavy metals concentrations and distances from the point source. Lastly, Kruskal Wallis test also being used to determine the differences between the heavy metal concentration at different distances. Apart from that, health risk for heavy metals exposure at Kg Jenjarom were analyzed with health risk assessment (HRA). The HRA is a tool to measure or estimate the risk posed to human caused by any contaminants (USEPA, 2002).

CHAPTER 4

RESULTS

4.1 Heavy Metals Concentration in Environment

Table 4.1 shows the mean for heavy metals concentration that present in air. While for Table 4.2 and 4.3 show the mean for heavy metals concentration that present in soil and water respectively. Heavy metals that being studied are As, Ni, Cd, Cr and Pb. Those samples were taken at specific set of distances which at 500 m, 1.0 km and 1.5 km from battery factory in Kg Jenjarom.

As for mean for heavy metals concentration in air, the concentrations were listed in descending order with Cr>Ni>Pb>As>Cd and that order was applied for each distance. while for the average mean of concentration of heavy metals in soil at 500 m and 1.0 km from the battery factory was Pb>Cr>As>Ni>Cd. But for 1.5 km, there was slightly different in the mean of concentration as Cr>Pb>As>Ni>Cd. Besides that, mean concentration of heavy metals in water at 500 m were also listed in descending order with Pb>Ni>Cr>As>Cd. While for concentration at 1.0 km and 1.5 km, it had exact order of mean for both distances which were Ni>Pb>Cr>As>Cd. These sequences can be seen in Table 4.4.

Overall, concentration of Cr was high compared to other heavy metals in the air. But for soil and water, the concentration of Pb was high compared to other heavy metals.

Table 4.1: Concentration of Heavy Metals in Air at Different Distances (µg/m3)

Samples	Concentration of Heavy Metals in Air at different distances (µg/m3)				
	As	Ni	Cd	Cr	Pb
500 m					
1	0.003	0.440	0.001	1.594	0.223
2	0.006	0.530	0.002	1.824	0.305
3	0.002	0.480	0.002	1.727	0.185
Mean	0.004	0.484	0.002	1.715	0.238
Std. Dev	0.002	0.044	0.001	0.115	0.061
1.0 km					
1	0.001	0.436	0.001	1.545	0.116
2	0.002	0.429	0.001	1.522	0.070
3	0.003	0.422	0.001	1.523	0.387
Mean	0.002	0.429	0.001	1.530	0.191
Std. Dev	0.001	0.007	0.0002	0.013	0.171
1.5 km					
1	0.003	0.441	0.001	1.570	0.124
2	0.001	0.482	0.001	1.712	0.163
3	0.004	0.452	0.001	1.630	0.010
Mean	0.003	0.458	0.001	1.637	0.099
Std. Dev	0.002	0.021	0.0002	0.071	0.079

Table 4.2: Concentration of Heavy Metals in Soil at Different Distances (mg/kg)

Samples	Concentration of Heavy Metals in Soil at Different Distances (mg/kg)				
	As	Ni	Cd	Cr	Pb
500 m					
1	0.783 x 10^2	0.165 x 10^2	0.048 x 10	0.963 x 10^2	0.333 x 10^3
2	0.579 x 10^2	0.101 x 10^2	0.033 x 10	0.167 x 10^3	0.982 x 10^2
3	0.438 x 10^2	0.240 x 10^2	0.138 x 10	0.538 x 10^2	0.252 x 10^3
Mean	0.599 x 10^2	0.169 x 10^2	0.073 x 10	0.106 x 10^3	0.227 x 10^3
Std. Dev	0.175 x 10^2	0.694 x 10^2	0.057 x10	0.571 x 10^2	0.119 x 10^3
1.0 km					
1	0.140 x 10^3	0.487 x 10^2	0.259 x 10^2	0.965 x 10^2	0.446 x 10^3
2	0.115 x 10^3	0.253 x 10^2	0.107 x 10^1	0.520 x 10^2	0.130 x 10^3
3	0.692 x 10^2	0.941 x10^1	0.036 x 10^1	0.520 x 10^2	0.130 x 10^3
Mean	0.108 x 10^3	0.278 x 10^2	0.912 x 10^1	0.668 x 10^2	0.236 x 10^3
Std. Dev	0.359 x 10^2	0.198 x 10^2	1.456 x 10^1	0.257 x 10^2	0.182 x 10^3
1.5 km					
1	0.106 x 10^3	0.340 x10^2	0.119 x 10^1	0.966 x 10^2	0.165 x 10^3
2	0.409 x 10^2	0.528 x10^1	0.001 x 10^2	0.239 x 10^3	0.241 x 10^2
3	0.503 x 10^2	0.143 x 10^2	0.032 x 10^1	0.048 x 10^3	0.591 x 10^2
Mean	0.657 x 10^2	0.179 x 10^2	0.054 x 10^1	0.128 x 10^3	0.826 x 10^2
Std. Dev	0.351 x 10^2	0.147 x 10^2	0.058 x 10^1	0.996 x 10^2	0.731 x 10^2

Table 4.3: Concentration of Heavy Metals in Water at Different Distances (mg/L)

Samples	Concentration of Heavy Metals in Water at Different Distances (mg/L)				
	As	Ni	Cd	Cr	Pb
500 m					
1	0.002	0.004	0.002 x 10^{-2}	0.008	0.153
2	0.002	0.003	0.002 x 10^{-2}	0.001x10^{-1}	0.123
3	0.002	0.024	0.018 x 10^{-2}	0.009	0.018
Mean	0.002	0.010	0.073 x 10^{-3}	0.009	0.098
Std. Dev	0.003 x 10^{-1}	0.012	0.009 x 10^{-2}	0.009x10^{-1}	0.007x 10^{1}
1.0 Km					
1	0.002	0.024	0.016x10^{-2}	0.098	0.018
2	0.002	0.022	0.014x10^{-2}	0.009	0.015
3	0.002	0.023	0.014x10^{-2}	0.009	0.015
Mean	0.002	0.023	0.147x10^{-3}	0.039	0.016
Std. Dev	0.006x10^{-2}	0.009x10^{-1}	0.001x10^{-2}	0.051	0.002
1.5 Km					
1	0.002	0.023	0.148x10^{-3}	0.008	0.013
2	0.002	0.022	0.141x10^{-3}	0.009	0.013
3	0.002	0.022	0.141x10^{-3}	0.007	0.013
Mean	0.002	0.022	0.143x10^{-3}	0.008	0.013
Std. Dev	0.002x10^{-1}	0.006x10^{-1}	0.004x10^{-3}	0.006x10^{-1}	0.004x10^{-1}

Table 4.4: Sequence of Heavy Metals Concentration

Environmental samples	500 m	1.0 km	1.5 km	Overall
Air	Cr>Ni>Pb>As>Cd	Cr>Ni>Pb>As>Cd	Cr>Ni>Pb>As>Cd	Cr>Ni>Pb>As>Cd
Topsoil	Pb>Cr>As>Ni>Cd	Pb>Cr>As>Ni>Cd	Cr>Pb>As>Ni>Cd	Pb>Cr>As>Ni>Cd
Water	Pb>Ni>Cr>As>Cd	Ni>Pb>Cr>As>Cd	Ni>Pb>Cr>As>Cd	Pb>Ni>Cr>As>Cd

N = 27

4.2 Comparison with Standard Values

Based on the heavy metals concentration that present in the air, soil and water which already being analysed, that concentration value being compared with standards values either with Malaysian Standard or International Standard. Table 4.5 shows that the heavy metals concentration in air obtained were compared with air quality standard derived by U.S Department of Health and Human Services, (ATSDR). As for mean of heavy metals concentration in air, all studied heavy metals such as As and Cd were had low in concentration and not exceeded the standard limit. While for Ni, Cr and Pb already exceeded the standard limit.

While for heavy metals concentration in soil and water also shown in Table 4.5. Mean of heavy metals concentration was reported and being compared with Standard of Dutch Target. The heavy metals concentration in soil were low and not exceeded the standard limit except for As, Cd and Pb as both slightly exceeded the Intervention Value of Standard of Dutch Target. As for the mean of heavy metals concentration in water. Those mean concentrations were being compared with National Water Quality Index for Malaysia Class iv (Irrigation). All heavy metals concentrations were not exceeded the standard limits.

Table 4.5: Comparisons between Mean and Median Heavy Metals Concentration with Standard Values

Variables	Concentration in air			Concentration in soil			Concentration in water		
	Median (IQR) (µg/m³)	Mean (SD)	Standard[a] (µg/m³)	Median (IQR) (mg/kg)	Mean (SD)	Standard[b] (mg/kg)	Median (IQR) (mg/L)	Mean (SD)	Standard[c] (mg/L)
As	0.003(0.002)	0.003(0.002)	0.01	69.31(63.4)	*77.9(35)	29.0	0.019(5x10^{-4})	0.002(2.67x10^{-4})	0.1
Ni	0.443(0.048)	*0.457(0.342)	0.0022	16.49(19.91)	20.84(13.82)	35.0	0.022(0.0108)	0.018(0.008)	0.2
Cd	0.001(0.00007)	0.001(4.41x10-^{4})	0.005	0.48(0.96)	*3.461(8.434)	0.8	0.00014(7x10^{-5})	1.04x10^{-4}(6.4x10^{-5})	0.01
Cr	1.594 (0.186)	*1.627(0.105)	0.02	96.26(79.79)	99.187(64.68)	100.0	0.0089(0.0015)	0.009(9.71x10^{-4})	0.01
Pb	0.163 (0.171)	*0.176(0.117)	0.15	130.24(213.73)	*181.95(137.04)	85.0	0.015(0.0574)	0.042(0.055)	5

N=27

*Exceeded value

[a] Air Quality Standard derived by ATSDR
[b] Standard of Dutch Target for soil
[c] National Water Quality Index for Malaysia Class iv (Irrigation)

4.3 Relationship between Heavy Metals Concentration and Distances

Table 4.6 shows the correlation between heavy metals concentration in air and distances from the point source which were at 500 m, 1.0 km and 1.5 km. From that table, correlation between heavy metals concentration and distances in air were not significant ($p>0.01$). In the meantime, correlation between heavy metals concentration in soil and water with the distances also displayed in Table 4.6. As for soil, there was no correlation between the heavy metal concentration and the distances ($p>0.01$).

Meanwhile, the correlation between heavy metals concentration and distances in water were no significant correlation ($p>0.01$) except for Pb. It was significantly correlated ($p<0.01$) with the distance and had strong negative correlation coefficient ($r= -0.930$). The concentration was decreased as distance increases.

Table 4.6: Relationship between Heavy Metals Concentration and Distances

Variables	Distance (km)					
	Air (µg/m3)		Soil (mg/kg)		Water (mg/L)	
	r	p-value	r	p-value	r	p-value
As	-0.162	0.677	-0.053	0.893	-0.347	0.360
Ni	-0.158	0.685	-0.053	0.893	0.159	0.683
Cd	-0.622	0.074	-0.316	0.407	0.320	0.401
Cr	-0.264	0.493	0.000	1.0	-0.503	0.168
Pb	-0.580	0.102	-0.476	0.195	-0.930	*0.0003

N=27
Spearman's rho test
*significant at p<0.01

4.4 Differences of Heavy Metals Concentration between Distances

Table 4.7 shows the differences of concentration of studied heavy metals in air such as As, Ni, Cd, Cr and Pb in the air between their distances from the point source. Kruskal Wallis test was conducted in order to determine the significant differences of concentration of heavy metals between distances. There were no significant differences for all heavy metals since their p-value were above 0.05 while their Z values were listed in the table below.

As for the heavy metals concentration in soil and water, their concentrations were listed in Table 4.7 as well. For heavy metals in soil, there were no significant differences between the distances as their p-values were above 0.05 same as the concentration in air. But for concentration in water, there was slightly different because only Pb had the p-value was below than 0.05 which we can conclude that there was a significant different for Pb in water as near distance from the factory had higher concentration compared to further distances. However, for other heavy metals in water, there were no significant differences.

Table 4.7: Differences of Heavy Metals Concentration at Different Distances

Variables	Air (µg/m3)		Soil (mg/kg)		Water (mg/L)	
	Z	p-value	Z	p-value	Z	p-value
As	1.3	0.513	3.3	0.193	3.8	0.146
Ni	5.6	0.061	0.62	0.733	1.8	0.390
Cd	4.5	0.105	1.8	0.393	0.8	0.663
Cr	5.9	0.051	1.1	0.584	4.8	0.088
Pb	2.7	0.252	2.4	0.298	6.9	*0.031

N=27
Kruskal Wallis test
*Significant at $p<0.05$

4.5 Health Risk Assessment

In order to predict the health risk for exposure to heavy metals in the environment at Kg Jenjarom, all the parameters or information to calculate the Hazard Quotient (HQ) for non-carcinogenic health risk and Lifetime Cancer Risk (LCR) for carcinogenic health risk formula by US EPA were gathered from related previous studies and also from Risk Assessment Guidelines by US EPA. Based on Table 4.8, it shows the HQ and LCR for heavy metals in air. As for Ni and Cr, HQ for both heavy metals were more than one (Ni=8.82) and (Cr=15.6). It indicates that exposure to Ni and Cr from inhalation might can cause non-carcinogenic health risk such as respiratory problems. Other heavy metals had HQ below than one. For carcinogenic health risk, LCR for Cr only was above from the acceptable range of risk which LCR for Cr was 2.34 x 10^{-2}. Due to high chances of risk, exposure to chromium can lead to irritation to respiratory tract and breathing (Engwa et al., 2018). Apart from that, other heavy metals were within the acceptable range which at between 10^{-6} to 10^{-4} and less than 10^{-6}. Besides that, HQ and LCR for heavy metals that present in soil and water were shown in Table 4.8 as well. Exposure to heavy metals from soil can come across from accidental ingestion of soil itself and also skin contact directly to the soil (USEPA, 2002). HQ for every studied heavy metal was below than one which indicate that there was no significant non-carcinogenic health risk from the exposure to the soil. Same goes to carcinogenic risk where the LCR for every heavy metal was within the acceptable range. As for water. exposure to heavy metals in water also can happen from ingestion such as drinking and dermal contact during recreational activities. Same as soil, HQ for both ingestion and dermal were below than one and LCR also were within the acceptable range.

Table 4.8: Hazard Quotient and Lifetime Cancer Risk for Health Risk Assessment (HRA)

Variables	Air		Soil				Water			
	HQ	LCR	HQ		LCR		HQ		LCR	
			Ingestion	Dermal	Ingestion	Dermal	Ingestion	Dermal	Ingestion	Dermal
As	9.0×10^{-2}	8.86×10^{-7}	3.6×10^{-1}	4.26×10^{-7}	1.6×10^{-5}	6.37×10^{-8}	1.8×10^{-1}	2.33×10^{-6}	8.2×10^{-6}	4.29×10^{-8}
Ni	*8.82	1.15×10^{-5}	1.43×10^{-3}	5.68×10^{-6}	2.6×10^{-6}	1.02×10^{-8}	2.6×10^{-2}	1.0×10^{-4}	4.74×10^{-5}	4.9×10^{-8}
Cd	1.0×10^{-1}	4.43×10^{-7}	4.74×10^{-3}	1.89×10^{-8}	7.05×10^{-6}	2.83×10^{-8}	5.48×10^{-3}	2.86×10^{-3}	3.56×10^{-6}	2.15×10^{-8}
Cr	*15.6	**2.34×10^{-2}	4.6×10^{-2}	1.83×10^{-4}	5.77×10^{-6}	2.3×10^{-8}	1.7×10^{-1}	3.6×10^{-1}	2.19×10^{-5}	2.28×10^{-7}
Pb	N/A	2.03×10^{-7}	7.12×10^{-2}	9.95×10^{-7}	2.12×10^{-7}	8.46×10^{-10}	7.8×10^{-1}	1.36×10^{-3}	9.32×10^{-7}	4.85×10^{-10}

N/A = Not Available
*HQ > 1
** LCR > 1×10^{-4}
Key:

HQ<1 indicates no significant non-carcinogenic risk.

HQ>1 indicates significant non-carcinogenic risk.
LCR<10^{-6} indicates no significant lifetime cancer risk
LCR>10^{-6} indicates significant lifetime cancer risk

CHAPTER 5

DISCUSSION

5.1 Heavy Metals Concentration in Environment

Mean of heavy metals concentrations in ambient air, soil and water are shown in Table 4.1, 4.2 and 4.3 respectively. As for concentration in air for each distance that being set in this study which at 500 m, 1.0 km and 1.5 km from the factory, Cr had highest in concentration compared to other heavy metals. The results shown were quite identical from previous study by by Cao et al., (2015). Increasing of Cr and Pb concentration in air as lots of heavy metals released to the environment from the production of acid battery factory (Cherry et al., 2010). Apart from emission from the factory, heavy metals can come other sources such as vehicles, paint and also naturally (Njati & Maguta, 2019). Community in Kg Jenjarom also can expose through soil which by accidental ingestion and direct dermal contact (USEPA, 2002). This is happening because all particles of heavy metals in the atmosphere that released from human activities can distributed by atmosphere within the distance and transfer into soil by wet or dry deposition (Soriano et al., 2012).

In the meantime, the Pb concentration in soil was the highest same as from the previous study from (Jamal et al., 2019). As we can see in Table 4.2, for 500 m and 1.0 Km, Pb was higher in soil but Cr was higher at 1.5 Km from the point source. factor such as emission rates and meteorological factor such as wind speed might affecting the dispersion and raining factor might lead to varies deposition rates (Aelion et al., 2008). Besides that, mean of heavy metals concentration in water can be determined in table 4.3. Acid battery factory in Kg. Jenjarom also discharged some chemicals that might contained heavy metals along the waterways. Communities also did some complaint on that issue because they used that waterways as for recreational activities. So, they might expose to the heavy metals released by the factory through accidental ingestion and dermal contact.

Based on the Table 4.3, the mean of Pb concentration was high within 500 m radius from the factory. But after going through along the waterways, Pb concentration was decreased but Ni was increased. It is because heavy metals particles were reacting with other particles and deposited to the bottom of the waterways (Stirk & Van Staden, 2001)

5.2 Comparison with Standard Values

In order to determine the significant health effects to human as from certain exposures. The determined heavy metals concentrations were compared to standard values either with Malaysia's standards or International's standard. Those standard values are the numbers for the safe limit of exposure on certain chemicals towards human. By doing so, we can determine any significant health effects if the concentrations are higher than the standard values. Health effects on human from the exposure can be predicted. Apart from that, we also can plan any preventive measures to reduce the risks or effects after determining the differences of the numbers.

For the heavy metal's concentration in ambient air, it was shown in Table 4.5. Because the sample size was less than 30, non-parametric test was conducted and reported the median of concentration then compared with the standard values. As for the concentration in ambient air, mean concentration of Ni, Cr and Pb were higher than the air quality standard derived by U.S Department of Health and Human Services, (ATSDR). Inhalation of those heavy metals in air can possess such health effects such as neurobehavior effect among children, respiratory problems or even worse which is cancers (USEPA, 2008).

Apart from that, the mean of heavy metals concentration in soil and water also shown in table 4.5. Heavy metals concentration in soil was being compared with the Standard of Dutch Target as Malaysia do not have any standard for soil safe limit values. Regarding the deposited heavy metals on topsoil released by that factory, mean of heavy metals concentration were not exceeding the standard except for Pb, Cd and As which slightly higher. From that situation, exposure to As through dermal contact can cause skin lesions and long-term effect which is skin cancer (ATSDR, 2005).

Exposure from water also can cause further health effects as the factory might discharged the heavy metals through the waterway. Those concentrations were being compared to National Water Quality Index for Malaysia Class iv (Irrigation) as want to determine the significant health risk towards human from accidental ingestion exposure and also to determine the safe limit for the environment. From this study, all heavy metals concentration was not exceeding both standards values and it safe for human exposure but depends on duration and frequency.

5.3 Relationship between Heavy Metals Concentration and Distances

Based on this study, there was no correlation between the heavy metals concentration and distances. This result was applied for ambient air and soil except for water as their numbers can be determined in Table 4.6. Due to small sample size which is less than 30, non-parametric testing was conducted which is Spearman’s rho correlation. As for ambient air, emission rate of pollution factor, meteorological factor such as wind speed can affect the dispersion of pollutants (Dobra and Viman, 2006). Meteorological factor like wind speed can contribute to dispersion to the surrounding.

Theoretically, wind speed, wind direction and raining are keep changing every day and it can cause different places and different distance might have differences in spread-ness of pollutant. In the meantime, emission rates also keep changing depends on their production rates. Apart from that, other pollutant sources also might can contribute to different reading of concentration of heavy metal such as vehicles. So, there were condition that affecting the correlation of concentration in air and also distances.

Same goes to concentration of heavy metals in soil. There was no correlation between concentration and distances. It affected with the dispersion of heavy metals released by factory and deposition on the top soil. Once again, the meteorological factor can affect the reading as weak wind speed can depositing the heavy metals on short distance with the factory and vice versa (Dobra and Viman, 2006). Raining factor also can contribute to this situation as when raining the floating heavy metals automatically deposited throughout the dispersion. Apart from that, the reading of concentration also can affect with natural occurrence of heavy metals in soil (Aelion et al., 2008). Certain sampling point of topsoil might contain different natural concentration which can make the reading different between the distances.

Different story for heavy metals concentration in water as most of studied heavy metals were not had correlation with the distance except for Pb. The concentration was decreased as distance increases. It might cause by natural processes as water body is cleaning itself from pollutant and ion interaction occurred between heavy metals ion and other particles ion (Stirk & Van Staden, 2001). Raining also can contribute some factor for reducing the concentration with increasing distances. All-natural occurrence is might the factor which can contribute to such reading for the heavy metals concentration in water.

5.4 Differences of Heavy Metals Concentration between Distances

Table 4.7 was shown the significant difference values for heavy metals concentration in ambient air, soil and water between distances. Distances were set up at 500 m, 1.0 km and 1.5 km from the point source. Due to the sample size is lesser than 30, non-parametric testing was conducted which is Kruskal Wallis. From this study, there was no significant differences of concentration of heavy metals between distances especially for ambient air and soil. The nearest distance from the point source had variety concentration of studied heavy metals. Same goes too far distance from the point source, their concentration had variety in numbers. It is because concentration of heavy metals in ambient air were affected by some factors such as emission rates from the factory, meteorological factor such as wind speed and wind direction (Dobra and Viman, 2006). Apart from that other sources such as vehicles might contribute to the reading of concentrations.

This result can be applied to the differences of heavy metals concentration in soil which there was no significant differences. Same reason with ambient air factor which is meteorological factor as the heavy metals would deposit onto the top soil when factors such as wind speed and rain play a role for that situation. Besides that, natural occurrence for studied heavy metals in the soil at certain sampling point or distances may affecting the reading directly or indirectly (Aelion et al., 2008) But different situation for concentration in water, as Pb concentration had a significant different between distances. The nearest distance to the factory had higher concentration compared to the further distance. It occurred because natural processes within the water body and ion exchange between heavy metals particles and others.

5.5 Health Effects and Risk Assessment of Heavy Metals

Health risk assessment is a tool to predict any significant non-carcinogenic and carcinogenic health risk on certain exposure to pollutants (USEPA, 2009). By considering the duration and frequency of exposure, Hazard Quotient (HQ) and Lifetime Cancer Risk (LCR) values can be determined for non-carcinogenic and carcinogenic health risk respectively. If the value of HQ is below than one, it indicates that there is no significant non-carcinogenic health risk for certain pollutants and if HQ is more than one, non-carcinogenic health risk is significant Same goes to LCR value, 1×10^{-6} and 1×10^{-4} is considered as acceptable risk and mention there is no significant carcinogenic health risk towards human while if the LCR value is above 1×10^{-4}, it indicates that human can possess carcinogenic health risk.

In this study, certain factors were considered to calculate and predict the HQ such as duration frequency was seven year as the exposure from the factory was started seven years back. Apart from that, exposure frequency also taking into account because to determine the period of exposure within a year. So, average period of exposure was total days of exposure for 7 years. But different with LCR, average period of exposure was set to 70 years as to determine the lifetime exposure for the pollutants.

As for heavy metals in ambient air, human can expose to it through inhalation. (USEPA, 2002). Hazard Quotient for Ni and Cr were above than one which its values were 8.8 and 15.2 respectively. Based on previous study by Saha et al., (2017), HQ for Cr and Pb from the exposure at industrial area were more than one and it indicates than non-carcinogenic health effects such as shortness of breath and reduced lung function appeared. Apart from that, exposure to nickel and chromium by inhalation can cause other respiratory problems from inhaled nickel such as bronchitis and asthma (ATSDR, 2005) meanwhile chromium might lead to irritation of respiratory lining, shortness of breath and wheezing (USEPA, 2017; Engwa et al., 2012). Long-term exposure through inhalation might can possess carcinogenic health risk. This situation can be seen as LCR value for chromium (Cr) were above 1 x 10^{-4}. According to ATSDR (2012), long-term exposure to inhaled chromium can cause carcinogenic health effect such as lung cancer. This situation was quite similar from previous study by Goudarzi et al., (2018) as the LCR value for inhaled Cr was exceeded the acceptable range and it indicates carcinogenic health effects such as lung cancer.

Heavy metals concentration was also determined in soil. Therefore, human can expose to heavy metals in soil through accidental ingestion and direct dermal contact (USEPA, 2002). Both exposure pathway shown that there was no significant non-carcinogenic health risk as HQ for ingestion and dermal contact were below than one for all studied heavy metals. Carcinogenic health risk also not significant for all heavy metals as LCR was within the acceptable range. In the meantime, acid battery factory also discharged the heavy metals in the waterways and communities in Kg Jenjarom were used waterways as recreational activities. Therefore, communities can expose to discharged heavy metals through accidental ingestion and dermal contact during swimming (USEPA, 2002). After taking account the duration and exposure frequency, HQ values for all heavy metals were determined and there was no significant non-carcinogenic health risk as HQ values were below than one. Same goes to LCR, all have the values were within the acceptable range.

CHAPTER 6

CONCLUSION, STUDY LIMITATION, RECOMMENDATIONS

6.1 Conclusion

Overall, the results showed that concentration of Cr was high in air compared to other heavy metals. Meanwhile in soil and water, Pb concentration was higher compared to other heavy metals. At the same time, concentrations of Cr, Ni and Pb in air exceeded the air quality standard by ATSDR. As for soil, Pb and As concentrations were higher than the Standard for Dutch Target Intervention Values. However, in water, all heavy metals concentration did not exceed the National Water Quality Index for Malaysia Class IV (Irrigation). The relationship between heavy metals concentration and distances was not significant except for the Pb concentration in water. This situation also occurred for Pb concentration at different distances and its concentration in water showed significant differences with distance. Air Cr and Ni showed non-carcinogenic health risk, while, air Cr showed carcinogenic health risk to the nearby community. Strength of this study was the results can use as references for further study on heavy metals exposure at Kg Jenjarom as it showed there were present of heavy metals in the environment due to battery factory activities. This study also notifies the authority to aware on this serious health issue regarding the heavy metal exposure at Kg Jenjarom.

6.2 Study Limitation

This study was conducted as cross-sectional study where inferences might happen along the study process. Apart from that, insufficient fund for sampling processes and laboratory analysis might one of the limitations during this study. Small sample size occurred from that situation and it cannot represent the exact overall environmental situation at study area. Besides that, shortage and not appropriate equipment also occur during this study as proper equipment can bring more specific and accurate reading of concentration of heavy metals. The health issues or health symptoms among the community also can be considered in the study as it can show is there any correlation with the environmental situation and their symptoms. Apart from that, future study should improve in sampling size by increasing the sampling points where the results can be presented as real situation at study area. Improving equipment to more accurate such as changing to high-volume air sampler (HVAS) from personal air sampling pump because HVAS is more accurate for environmental sampling compared to personal air sampling pump. Besides that, to strengthen the study, identification of other sources of pollutant can be done in order to reduce the confounding. Moreover, questionnaire also can be included to gather the related health symptoms from the exposure among the community members. Through this, the correlation between predicted and current health issues among the communities can be obtained.

6.3 Recommendations

From this study, the Ni, Cr and Pb exceeded the air quality standard values and might influence the health symptoms among communities around acid battery factory at Kg Jenjarom. Exposure for a lifetime duration towards the heavy metals can lead to cancer risk for human as it being predicted it probability by determination of lifetime cancer risk during health risk assessment, therefore the environmental monitoring should carried out The acid battery factory should abide to the environmental law and control any emissions.in order to reduce the emissions and discharge of heavy metal into the air or water bodies. Local authorities should enforce laws and regulations and at the same time, monitor the industrial activities which emit pollutant to the environment to prevent and protect nearby communities.

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APPENDICES

Appendix 1: Niosh Method 0600

PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE 0600

DEFINITION: aerosol collected by sampler with 4-µm median cut point

CAS: None RTECS: None

METHOD: 0600, Issue 3 **EVALUATION: FULL** **Issue 1: 15 February 1984**

Issue 3: 15 January 1998

OSHA: 5 mg/m³

NIOSH: no REL

ACGIH: 3 mg/m³

PROPERTIES: contains no asbestos and quartz less than 1%; penetrates non-ciliated portions of respiratory system

SYNONYMS: nuisance dusts; particulates not otherwise classified

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm nylon cyclone, Higgins-Dewell [HD] cyclone, or aluminum cyclone + tared 5-µm PVC membrane)

FLOW RATE: nylon cyclone: 1.7 L/min
HD cyclone: 2.2 L/min
Al cyclone: 2.5 L/min

VOL-MIN: 20 L @ 5 mg/m³
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 10 mg/m³ (lab and field)

BIAS: dependent on dust size distribution [1]

OVERALL PRECISION ($\hat{S}_{rT}$): dependent on size distribution [1,2]

ACCURACY: dependent on size distribution [1]

MEASUREMENT

TECHNIQUE: GRAVIMETRIC (FILTER WEIGHT)

ANALYTE: mass of respirable dust fraction

BALANCE: 0.001 mg sensitivity; use same balance before and after sample collection

CALIBRATION: National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights

RANGE: 0.1 to 2 mg per sample

ESTIMATED LOD: 0.03 mg per sample

PRECISION: <10 µg with 0.001 mg sensitivity balance; <70 µg with 0.01 mg sensitivity balance [3]

APPLICABILITY: The working range is 0.5 to 10 mg/m³ for a 200-L air sample. The method measures the mass concentration of any non-volatile respirable dust. In addition to inert dusts [4], the method has been recommended for respirable coal dust. The method is biased in light of the recently adopted international definition of respirable dust, e.g., ≈ +7% bias for non-diesel, coal mine dust [5].

INTERFERENCES: Larger than respirable particles (over 10 µm) have been found in some cases by microscopic analysis of cyclone filters. Over-sized particles in samples are known to be caused by inverting the cyclone assembly. Heavy dust loadings, fibers, and water-saturated dusts also interfere with the cyclone's size-selective properties. The use of conductive samplers is recommended to minimize particle charge effects.

OTHER METHODS: This method is based on and replaces Sampling Data Sheet #29.02 [6].

EQUIPMENT:

1. Sampler:
   a. Filter: 5.0-µm pore size, polyvinyl chloride filter or equivalent hydrophobic membrane filter supported by a cassette filter holder (preferably conductive).
   b. Cyclone: 10-mm nylon (Mine Safety Appliance Co., Instrument Division, P.O. Box 427, Pittsburgh, PA 15230), Higgins-Dewell (BGI Inc., 58 Guinan St., Waltham, MA 02154) [7], aluminum cyclone (SKC Inc., 863 Valley View Road, Eighty Four, PA 15330), or equivalent.
2. Personal sampling pump, 1.7 L/min ± 5% for nylon cyclone, 2.2 L/min ± 5% for HD cyclone, or 2.5 L/min ± 5% for the Al cyclone with flexible connecting tubing.
   NOTE: Pulsation in the pump flow must be within ± 20% of the mean flow.
3. Balance, analytical, with sensitivity of 0.001 mg.
4. Weights, NIST Class S-1.1, or ASTM Class 1.
5. Static neutralizer, e.g., Po-210; replace nine months after the production date.
6. Forceps (preferably nylon).
7. Environmental chamber or room for balance, e.g., 20 °C ± 1 °C and 50% ± 5% RH.

SPECIAL PRECAUTIONS: **None.**

PREPARATION OF SAMPLERS BEFORE SAMPLING:

1. Equilibrate the filters in an environmentally controlled weighing area or chamber for at least 2 h.
2. Weigh the filters in an environmentally controlled area or chamber. Record the filter tare weight, W_1 (mg).
   a. Zero the balance before each weighing.
   b. Handle the filter with forceps (nylon forceps if further analyses will be done).
   c. Pass the filter over an anti-static radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
3. Assemble the filters in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette.
4. Remove the cyclone's grit cap before use and inspect the cyclone interior. If the inside is visibly scored, discard this cyclone since the dust separation characteristics of the cyclone may be altered. Clean the interior of the cyclone to prevent reentrainment of large particles.
5. Assemble the sampler head. Check alignment of filter holder and cyclone in the sampling head to prevent leakage.

SAMPLING:

6. Calibrate each personal sampling pump to the appropriate flow rate with a representative sampler in line.
   NOTE 1: Because of their inlet designs, nylon and aluminum cyclones are calibrated within a large vessel with inlet and outlet ports. The inlet is connected to a calibrator (e.g., a bubble meter). The cyclone outlet is connected to the outlet port within the vessel, and the vessel outlet is attached to the pump. See APPENDIX for alternate calibration procedure. (The calibrator can be connected directly to the HD cyclone.)
   NOTE 2: Even if the flow rate shifts by a known amount between calibration and use, the nominal flow rates are used for concentration calculation because of a self-correction feature of the cyclones.
7. Sample 45 min to 8 h. Do not exceed 2 mg dust loading on the filter. Take 2 to 4 replicate samples for each batch of field samples for quality assurance on the sampling procedure (see Step 10).

NOTE : Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

8. Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in an environmentally controlled area or chamber.

CALIBRATION AND QUALITY CONTROL:

9. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.
10. The set of replicate field samples should be exposed to the same dust environment, either in a laboratory dust chamber [8] or in the field [9]. The quality control samples must be taken with the same equipment, procedures, and personnel used in the routine field samples. Calculate precision from these replicates and record relative standard deviation (S_r) on control charts. Take corrective action when the precision is out of control [8].

MEASUREMENT:

11. Weigh each filter, including field blanks. Record this post-sampling weight, W_2 (mg), beside its corresponding tare weight. Record anything remarkable about a filter (e.g., visible particles, overloading, leakage, wet, torn, etc.).

CALCULATIONS:

12. Calculate the concentration of respirable particulate, C (mg/m³), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1)}{V} \times 10^3, \text{ mg/m}^3,$$

where: W_1 = tare weight of filter before sampling (mg),
W_2 = post-sampling weight of sample-containing filter (mg),
B_1 = mean tare weight of blank filters (mg),
B_2 = mean post-sampling weight of blank filters (mg),
V = volume as sampled at the nominal flow rate (i.e., 1.7 L/min or 2.2 L/min).

EVALUATION OF METHOD:

1. Bias: In respirable dust measurements, the bias in a sample is calculated relative to the appropriate respirable dust convention. The theory for calculating bias was developed by Bartley and Breuer [10]. For this method, the bias, therefore, depends on the international convention for respirable dust, the cyclones' penetration curves, and the size distribution of the ambient dust. Based on measured penetration curves for non-pulsating flow [1], the bias in this method is shown in Figure 1.

   For dust size distributions in the shaded region, the bias in this method lies within the ± 0.10 criterion established by NIOSH for method validation. Bias larger than ± 0.10 would, therefore, be expected for some workplace aerosols. However, bias within ± 0.20 would be expected for dusts with geometric standard deviations greater than 2.0, which is the case in most workplaces.

Bias can also be caused in a cyclone by the pulsation of the personal sampling pump. Bartley, et al. [12] showed that cyclone samples with pulsating flow can have negative bias as large as −0.22 relative to samples with steady flow. The magnitude of the bias depends on the amplitude of the pulsation at the cyclone aperture and the dust size distribution. For pumps with instantaneous flow rates within 20% of the mean, the pulsation bias magnitude is less than 0.02 for most dust size distributions encountered in the workplace.

Electric charges on the dust and the cyclone will also cause bias. Briant and Moss [13] have found electrostatic biases as large as −50%, and show that cyclones made with graphite-filled nylon eliminate the problem. Use of conductive samplers and filter cassettes (Omega Specialty Instrument Co., 4 Kidder Road, Chelmsford, MA 01824) is recommended.

2. Precision: The figure 0.068 mg quoted above for the precision is based on a study [3] of weighing procedures employed in the past by the Mine Safety and Health Administration (MSHA) in which filters are pre-weighed by the filter manufacturer and post-weighed by MSHA using balances readable to 0.010 mg. MSHA [14] has recently completed a study using a 0.001 mg balance for the post-weighing, indicating imprecision equal to 0.006 mg.

   Imprecision equal to 0.010 mg was used for estimating the LOD and is based on specific suggestions [8] regarding filter weighing using a single 0.001 mg balance. This value is consistent with another study [15] of repeat filter weighings, although the actual attainable precision may depend strongly on the specific environment to which the filters are exposed between the two weighings.

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[12] Bartley DL, Breuer GM, Baron PA, Bowman JD [1984]. Pump fluctuations and their effect on cyclone performance. Am Ind Hyg Assoc J *45*(1): 10–18.

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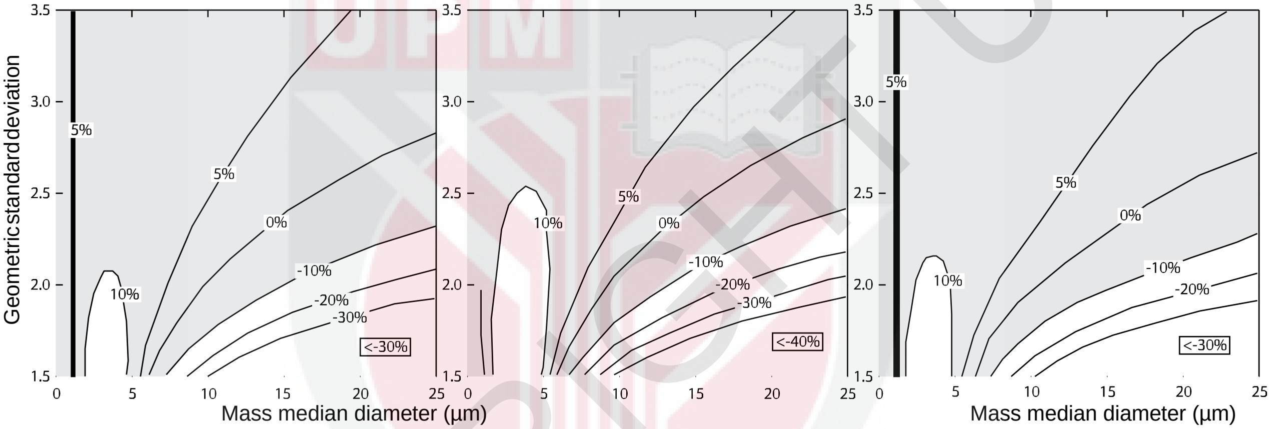
[14] Koqut J [1994]. Private Communication from MSHA, May 12, 1994.

[15] Vaughn NP, Chalmers CP, Botham [1990]. Field comparison of personal samplers for inhalable dust. Ann Occup Hyg *34*: 553–573.

METHOD REVISED BY:

David L. Bartley, Ph.D., NIOSH/DPSE/ARDB and Ray Feldman, OSHA.



10-mm Nylon cyclone at 1.7 L/min

Higgins-Dewell cyclone at 2.2 L/min

Figure 1. Bias of three cyclone types relative to the international respirable dust sampling convention.

APPENDIX: Jarless Method for Calibration of Cyclone Assemblies

This procedure may be used in the field to calibrate an air sampling pump and a cyclone assembly without using the one-liter "calibration jar".

1. Connect the pump to a pressure gauge or water manometer and a light load (adjustable valve or 5-µm filter) equal to 2" to 5" H_2O with a "TEE" connector and flexible tubing. Connect other end of valve to an electronic bubble meter or standard bubble tube with flexible tubing (See Fig. 2.1).
   NOTE: A light load can be a 5-µm filter and/or an adjustable valve. A heavy load can be several 0.8-µm filters and/or adjustable valve.
2. Adjust the pump to 1.7 L/min, as indicated on the bubble meter/tube, under the light load conditions (2" to 5" H_2O) as indicated on the pressure gauge or manometer.
3. Increase the load until the pressure gauge or water manometer indicates between 25" and 35" H_2O. Check the flow rate of the pump again. The flow rate should remain at 1.7 L/min ± 5%.
4. Replace the pressure gauge or water manometer and the electronic bubble meter or standard bubble tube with the cyclone having a clean filter installed (Fig. 2.2). If the loading caused by the cyclone assembly is between 2" and 5" H_2O, the calibration is complete and the pump and cyclone are ready for sampling.

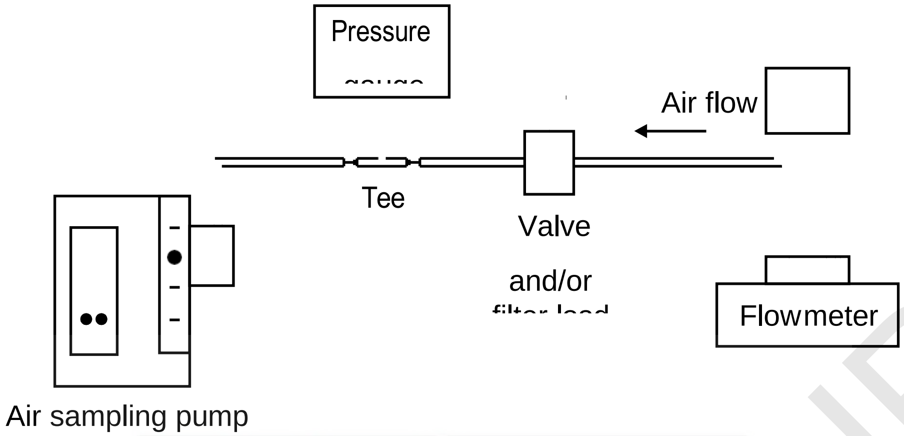


Figure 2.1. Block diagram of pump/load/flow meter set-up.

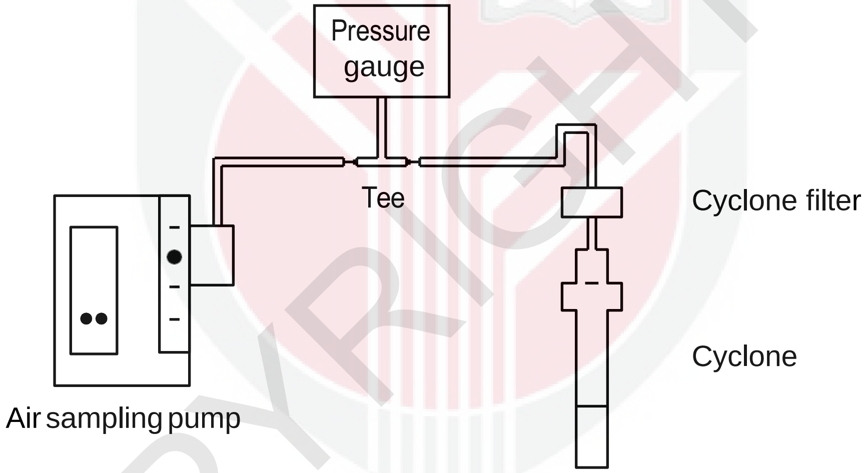


Figure 2.2. Block diagram with cyclone as the test load.

Appendix 2: Acidification and Filtration Method for Water Sample

METHOD 3010A

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA) or inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010 may be analyzed by FLAA or ICP for the following:

Aluminum
*Arsenic
Barium
Beryllium
Cadmium
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Magnesium
Manganese
Molybdenum
Nickel
Potassium
*Selenium
Sodium
Thallium
Vanadium
Zinc

* Analysis by ICP

NOTE: See Method 7760 for the digestion and FLAA analysis of Silver.

1.3 This digestion procedure is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization. Consult Method 3020A for samples requiring graphite furnace analysis.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL or equivalent.

4.2 Watch glasses - Ribbed and plain or equivalent.

4.3 Qualitative filter paper or centrifugation equipment.

4.4 Graduated cylinder or equivalent - 100mL.

4.5 Funnel or equivalent.

4.6 Hot plate or equivalent heating source - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (1:1), HCl. Prepared from water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beakerwith a ribbed watch glass or equivalent. Place the beaker on a hot plate or equivalent heating source and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result.
Should this occur, discard the sample and reprepare.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution), cover the beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned. Rinse the filter and filter apparatus with dilute nitric acid and discard the rinsate. Filter the sample and adjust the final volume to 100 mL with reagent water and the final acid concentration to 10%. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. A replicate sample should be processed with each analytical batch or every 20 samples, whichever is greater. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch of samples processed and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and delisting petitions (see Method 7000, Step 8.7). Although not required, use of the method of standard addition is recommended for any sample that is suspected of having an interference.

9.0 METHOD PERFORMANCE

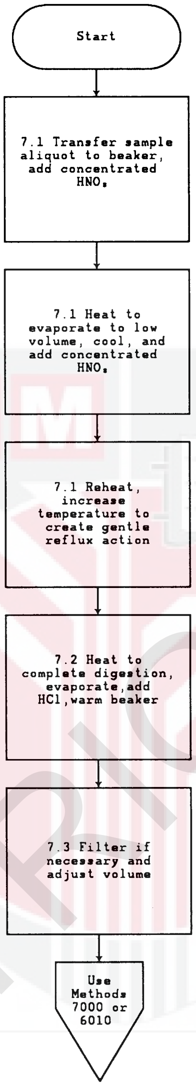
9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specificationfor Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 3010A
ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS ANALYSIS BY FLAA OR ICP SPECTROSCOPY



Appendix 3: Hot Acid Digestion Method by US EPA

METHOD 3005A

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface and ground water samples for analysis by flame atomic absorption spectroscopy (FLAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

Aluminum
Antimony**
Arsenic*
Barium
Beryllium
Cadmium
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Magnesium
Manganese
Molybdenum
Nickel
Potassium
Selenium*
Silver
Sodium
Thallium
Vanadium
Zinc

* ICP only
**May be analyzed by ICP, FLAA, or GFAA

1.2 When analyzing for total dissolved metals filter the sample, at the time of collection, prior to acidification with nitric acid.

2.0 SUMMARY OF METHOD

2.1 Total recoverable metals - The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals - The sample is filtered through a 0.45-µm filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards.

3.0 INTERFERENCES

3.1 The analyst should be cautioned that this digestion procedure maynot be sufficiently vigorous to destroy some metal complexes.

Precipitation will cause a lowering of the silver concentration and therefore an inaccurate analysis.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers of assorted sizes or equivalent.

4.2 Watch glasses or equivalent.

4.3 Qualitative filter paper and filter funnels.

4.4 Graduated cylinder or equivalent.

4.5 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95ºC.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Both plastic and glass containers are suitable.

6.3 Sampling

6.3.1 Total recoverable metals - All samples must be acidified at the time of collection with HNO_3 (5 mL/L).

6.3.2 Dissolved metals - All samples must be filtered through a 0.45-µm filter and then acidified at the time of collection with HNO_3 (5 mL/L).

7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed, add 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass or other suitable covers and heated on a steam bath, hot plate or other heating source at 90 to 95°C until the volume has been reduced to 15-20 mL.

<u>CAUTION</u>: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.

7.4 Adjust the final volume to 100 mL with reagent water.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch. Refer to Chapter One for the proper protocol when analyzing spikes.

9.0 METHOD PERFORMANCE

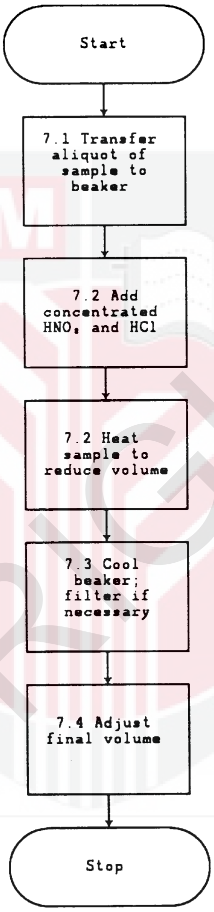
9.1 No data provided.

10.0 REFERENCES

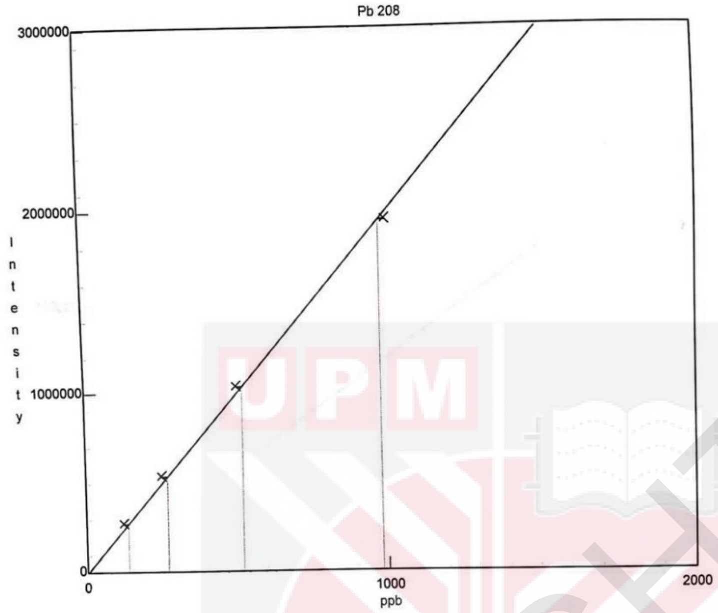
1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

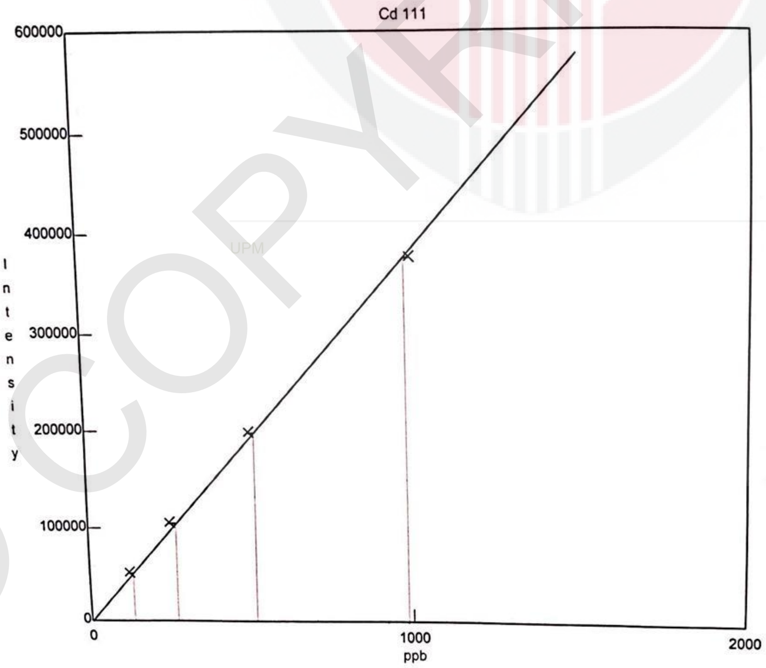
2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specificationfor Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 3005A
ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY



Appendix 4: Linearity of ICPMS





Appendix 5: Laboratory Work