## ASSESSMENT OF HEAVY METALS IN DUST FALL IN KAMPAR

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## ASSESSMENT OF HEAVY METALS IN DUST FALL IN KAMPAR

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A project report submitted in partial fulfillment of the requirements for the award of Bachelor of Engineering (Hons.) Environmental Engineering

> Faculty of Engineering and Science Universiti Tunku Abdul Rahman

> > September 2015

#### DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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#### APPROVAL FOR SUBMISSION

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#### ASSESSMENT OF HEAVY METALS IN DUST FALL IN KAMPAR

#### ABSTRACT

The aim of this study was to determine the concentration and composition of dust fall in Kampar, Malaysia as an abandoned tin mining area from mid-February to mid-June 2015. The dust fall samples were collected in the form of rainwater, which was a combination of dry and wet deposition, by using polyethylene bottles on a monthly basis so as to determine the concentration of undissolved solids, dissolved solids and total solids from eight monitoring stations. The concentration of heavy metals (B, Al, Cr, Mn, Fe, Ni, Zn, As, Cd, Sn, Hg and Pb) was analyzed using an inductively coupled plasmamass spectrometer (ICP-MS). The results showed that the average concentration of total solids around Kampar were 20.39  $\pm 2.60 \text{ mg/m}^2/\text{day}$ , which was below the value of 133  $mg/m^2/day$  as recommended by the Malaysian Department of the Environment. Zn, As and Al were recorded as the dominant heavy metals in rainwater followed by B, Fe, Cr, Pb, Ni, Mn, Hg, Sn and Cd. However, toxic heavy metals which include As, Hg and Pb were found to be exceeded the Drinking Water Quality Standard as recommended by Malaysia and USEPA. The enrichment factors (EF) revealed that the source of the heavy metals in the rainwater was anthropogenic, except for Mn and Fe. This study suggests that former mining activities and anthropogenic activities such as motor vehicles and construction activities were the main sources of dust fall in the study areas.

Keywords: Dust fall, heavy metals, tin mining, Kampar, Malaysia

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#### LIST OF SYMBOLS / ABBREVIATIONS

- UTAR Universiti Tunku Abdul Rahman
- DOE Department of Environment
- WHO World Health Organization
- USEPA United States Environment Protection Agency
- ICP-MS Inductively coupled plasma mass spectrometry
- r<sup>2</sup> r-squared value
- SD standard deviation
- Al Aluminium
- As Arsenic
- Cd Cadmium
- Cr Chromium
- Cu Copper
- Fe Iron
- Hg Mercury
- Mn Manganese
- Ni Nickel
- Pb Lead
- Sn Tin
- Zn Zinc
- PM Particulate matter

#### **CHAPTER 1**

#### INTRODUCTION

#### **1.1** Air Pollution

Air pollution and its impacts have become one of the most challenging global issues for public health and environmental quality (Naddafi *et al.*, 2006). In recent decades, air pollution has been much focused on atmospheric particles as a result of its potential adverse health effects and the subsequent need to have a better control or regulate these pollutants (Moreno-Grau *et al.*, 2002; Fang *et al.*, 2007). Particular attention has been focused on the large or settleable particles (> 10  $\mu$ m) called dust among many pollutants. These particulates with an aerodynamic size of above 10  $\mu$ m are the main component of dust fall (Sami *et al.*, 2006) which have the capability to absorb different metal and metalloid compounds mainly because of their structural features that contain soil coagulated clay and silt particles (Escudero *et al.*, 2007). From a toxicological prospective also, dust particles are well established to contain higher concentrations of potentially toxic heavy metals, such as As, Cu, Fe and Mn (Escudero *et al.*, 2007).

Over the past few years, air pollution has been a major issue in Malaysia. According to the Environmental Quality Report 2013 (Publish Year: 2014) by Department of Environment Malaysia, industries including power plants, motor vehicles and open burning activities are still the major sources of air pollution in Malaysia. Besides, active and former mining activities are also a major contributor of air pollution in Malaysia. Malaysia was once a great success in tin mining industries which contributed as a major economic pillar. However, contamination from former mining activities had been a major concern for a long time since commercial mining were introduced in the earlier days. Mining has been recognized as one of the human activities which may degrade the quality of the environment (Donkor *et al.*, 2005). Mining activities cause the destruction of natural ecosystems through removal of soil and vegetation, and also burial beneath waste disposal sites (Cooke & Johnson, 2002). Heavy metal contamination usually happens at mining sites. These heavy metals come mainly from the processing of ores, disposal of tailings and wastewaters around mines (Donkor *et al.*, 2005). These heavy metals can be released into the environmental media especially soil, sediment and water (Abdul-Wahab & Marikar, 2011). Most of these heavy metals exposed from the mining activities still exist and may not diminish over certain period (Mansor *et al.*, 2010).

#### 1.2 Background of Study Area

Kampar, founded in 1887, is a town in the state of Perak, Malaysia. Kampar also refers to Bandar Kampar and the surrounding area of 10-20 square miles. From a geographical and geological viewpoint, Kampar is located in the newly created Kampar District and lies within the radius of Lembah Kinta, its position resembling a crater at the foot-end of Gunung Bujang Melaka that is irrigated by Sungai Keranji and Sungai Kampar which comprises alluvial soil that is rich with tin metals. These rivers cause the soil and gravel that contains tin metal to settle at the river banks and base. This process happened millions of years ago, making this area abound with mounds of tin ore.

In earlier days, Kampar was popular with mining activities. The collapse of the tin industry in Malaysia in 1985 had ceased all the mining operations in state of Perak, most of the mining sites had to be shut down which include Kampar. However, Kampar has emerged from the tin mine tailings into a fast growing hub for tertiary education in Perak in just over two decades.

These mining activities in the earlier days make the town possibly exposed to bare and contaminated soil and rocks, then cause heavy metal pollution in the air. Besides the former mining activities, there are few general points which may also contribute to the heavy metal pollution in Kampar, which include emission from motor vehicles, construction activities, open burning and so on.

#### **1.3 Problem Statements**

Previous studies by Alshaebi *et al.* (2009), Mansor *et al.* (2010) and Abdul-Wahab & Marikar (2012) showed that mining is one of the most important sources of heavy metal contamination in the environment. Therefore, Kampar as a tin mining tail could be contaminated by heavy metals that causes deterioration of air quality. In addition, the potential of an increase of population growth in Kampar leads to increase in amount of traffics and also more construction activities can be seen, resulting in deterioration of air quality in Kampar. The concentration of air pollutants in the atmosphere could increase with respect to increment of these factors. So far there is no assessment has been done on Kampar yet. Therefore, this study was conducted to study on the level of air pollution (heavy metals) in Kampar. This, in effect, would indicate how influential mining tail and population growth were on the concentration and chemical composition of dust fall in the atmosphere.

Besides, there are only limited studies can be found that relate to the assessment of heavy metals in dust fall in Malaysia. Although there are quite a number of Air Quality Monitoring Stations in Malaysia, heavy metal is not the parameter for them to test on; and also the limited guidelines from DOE standards for heavy metals in the air. Thus, it is important to study on the heavy metals in the air in order to understand the level of air pollution in Kampar as these heavy metals are very harmful to human health and the environment.

### 1.4 Aims and Objectives

The aim of this study was to investigate the air quality was affected by tin mining tail in Kampar by capturing dust fall monthly at different sampling locations.

The objectives of this study are as following:

- To determine the concentration of dissolved solids and undissolved solids in dust fall collected in Kampar.
- To determine the concentration of heavy metals in dust fall collected in Kampar.
- iii) To determine the correlation coefficient and enrichment factor of heavy metals in dust fall in Kampar.

#### **CHAPTER 2**

#### LITERATURE REVIEW

#### 2.1 Dust Fall

Dust fall is the term used to describe atmospheric particles that settle down over a given area and time under the influence of gravity. These settleable particles usually have aerodynamic diameter of more than 10  $\mu$ m and are main component of dust fall. Atmospheric dust plays an important role in the fate and transport of air pollutants. Dust can act as a carrier for different types of pollutants, especially pesticides, by adsorbing them on the suspended particles and transporting them to remote areas (Al-Awadhi and AlShuaibi, 2013).

Monthly average dust fall composition (dissolved and undissolved solids) as well as total solids, should be lower than 133 mg/m<sup>2</sup>/day as recommended by the DOE Malaysia. Undissolved solids is termed as solid that cannot dissolve in water, which the undissolved solids will be separated by using filter paper in this research. While dissolved solids is termed as solids that can dissolve in water, which is used to determine the concentration of heavy metals by using ICP-MS. In this study, similar method was used as one of the researchers reviewed, Alahmr *et al.* (2012) to capture the dust fall (wet and dry deposition) from different sampling locations on monthly basis to determine the concentration of heavy metals in the atmosphere.

#### 2.1.1 Pathways

Dust fall is depleted continuously from the atmosphere through two main pathways: dry and/or wet deposition. Pollutants are deposited and derived upon the earth's surface by rainfall when the particulates and pollutants in the atmosphere are chemically reacted. (Afroz *et al.*, 2003).

Meteorological conditions such as wind direction and velocity, intensity and distribution of rainfall, humidity, pressure and temperature will influence the dust fall path (Mohamed *et al.*, 2013). Determination of the dust fall rate and its chemical compositions are important in order to understand dust pollution (Pandey *et al.*, 2008).

#### 2.1.2 Possible Sources of Dust Fall

Sources of atmospheric particulates can be natural or anthropogenic. These particles are naturally produced by volcanoes, grassland fires, sea spray, desert dust and by various kinds of biological sources such as bacteria, fungal spores, pollen, fragments of vegetable organisms and of animals (Kalbere *et al.*, 2010). Anthropogenic particles which originate from human activities, such as the fossil fuel combustion in vehicles, power plants, domestic heating and industrial processes (Kalbere *et al.*, 2010).

One of the studies from Alahmr *et al.* (2012) indicated that the possible source of dust fall are mainly from soil dust, fine particles from solid waste, emissions from industry, plant residue along with the main source, which is presumably derives from combustion of fossil fuel in vehicles that is strongly associated with the high traffic load. Besides, undissolved solids demonstrated a lower mean concentration compared to dissolved solids that can be indicated that the dust particles were mainly brought down from the atmosphere through wet deposition process. Particulates can enter human respiratory system by inhalation

that may as an aftermath of having great impacts on human health (Polizzi *et al.*, 2007).

#### 2.1.3 The Dust Fall Studies in Malaysia

As shown in Table 2.1, Norela *et al.* (2004) and Norela *et al.* (2009) concluded that the concentration of deposited particulates of both studies had exceeded the permissible limit (133 mg/m<sup>2</sup>/day) as stipulated by the DOE Malaysia. The concentration of deposited particulates in both areas may probably further exceed the limit due to rapid development of the industrial areas. It could be also concluded from the studies that high level of particulates in the air caused throat irritation and adverse health effects to the nearby communities. In the finding of Alahmr *et al.* (2012), the mean concentration of total solids in dust fall was under the permissible limit while in the studies of Latif and Rozali (1999) showed the concentration of total solids had slightly exceeded the permissible limit due to the studies were conducted at industrial area. Their studies concluded that high concentration of deposited solids in dust fall are mainly due to anthropogenic activities such as emissions from vehicles, industrial activities and power stations. The results from these studies will be used as a guidance and comparison to investigate the significant of dust fall between the regions of Kampar, Malaysia.

Area	Insoluble solids	Soluble solids	Total solids	References
Semi-urban area (Kajang and	53.08 ± 34.64	78.41 ±37.31	$131.50 \pm 71.95$	Alahmr et. al., 2012
Bangi, Malaysia)				
Residential Area (Nilai, Malaysia)	37.83 ±13.53	$216.11 \pm 35.45$	$253.95 \pm 7.54$	Norela et al., 2009
Power Station (Serdang,	213.86 ±114.81	$226.69 \pm 171.50$	$440.54 \pm 9.07$	Norela et al., 2004
Malaysia)				
Dust fall during haze Malaysia	58.38 ±34.04	59.07 ±34.05	$117.45 \pm 54.79$	Latif and Rozali, 2000
Industrial Area (Air Keroh,	$63.85 \pm 42.02$	$74.45 \pm 62.76$	139.39 ±87.88	Latif and Rozali, 1999
Malaysia)				
Industrial Area (Teluk Kalung,	69.84 ±48.53	80.12 ±64.53	$149.96 \pm 90.50$	Latif and Rozali, 1999
Malaysia)				

 Table 2.1: Summary of selected dust fall research results (mg/m²/day)

nd: no data

#### 2.2 Chemical Composition in Dust Fall

#### 2.2.1 Heavy metals

Heavy metals are defined as any metallic chemical element with relatively high density, or high relative atomic weight. Heavy metals in the environment cannot be destroyed and most of the heavy metals are toxic to living organisms when exceeding a certain concentration (Sherene, 2010). Heavy metals such as arsenic, cadmium, chromium and mercury are dangerous even at low concentration (Dinis & Fi úza, 2011).

Poisoning by exposure to heavy metals can affect central nervous system, damage lungs, liver, kidneys, blood composition and other vital organs. Long-term exposure to heavy metals can cause tardy effects on physical, muscular and neurological degenerative processes. Long term contact with some metals may also trigger allergies. Previous studies have found that human exposure to high concentration of heavy metals will lead to their accumulation in the human body. Heavy metals can be exposed to human through three major routes which include inhalation, ingestion and skin absorption. Heavy metals that pose a significant threat to human and animal health is due to their low mobility and also their long term persistence in the environment (Adelekan & Abegunde, 2011).

#### 2.2.2 Sources

Heavy metals have been utilized in many different field areas over decades. The natural source of heavy metals in the environment is mainly from crustal material that is either by weathering and eroding processes on the Earth's surface or injected by volcanic activity into the Earth's atmosphere (Callender, 2013). Both sources account for 80% of all the natural sources; while biogenic sources and forest fires account for 10% each (Callender, 2013). Eroded particles emerge in the atmosphere as windblown dust. Moreover, some particles are released by vegetation.

Intensive anthropogenic activities are caused by the high density in population, where population will produce a large number of heavy metal sources that have considerable influence on human health (Xi *et al.*, 2010). Generic sources of heavy metals include mining, industrial production (such as foundries, oil refineries, smelters), chemical industry, petrochemical plants and untreated sewage sludge; while disperse sources such as emissions from traffic, coal burning power plants and also metal piping (Xi *et al.*, 2010).

Atmospheric emissions are most likely to have a greater impact on human health and the environment due to either the large quantity involved, or their ability to widespread disperse which may originate from a wide range of exposure pathways. In particular, heavy metals such as Cd, Hg and Pb, are of great concern to human health and to the environment, mostly due to these heavy metals are capable to travel long distances in the atmosphere before deposition (Dinis & Fi úza, 2011).

According to the research of Voutsa and Samara (2002), concentration of heavy metals such as Cd, Mn, Ni and Zn, were found significantly higher at industrial sites as a result of pyrometallurgical processes taking place in the area, as well as a manganese ore treating plant; while concentration of Pb was found to be relatively higher at urban sites due to high traffic load in the area.

Heavy metals in tailings can be transported to, dispersed to, and accumulated in plants and animals, then can be passed up the food chain to human beings as a final consumer (Kim *et al.*, 2001). Heavy metals are essential for human, animals and plants as nutrients at low concentrations, but some if present at higher quantities and in certain forms may become toxic and cause harm to life (Crounse *et al.*, 1983). For instance, Cu and Zn are both being essential for normal metabolism, but can be toxic in high concentrations (Thornton, 1996). High level of Cu and Zn in the body can result in damaging and malfunctioning human organs. Besides, As, Cd and Pb are believed to cause cancer, neural and metabolic disorders and other diseases (Getaneh & Alemayehu, 2006).

According to Alshaebi (2009), heavy metals contained in residues coming from mining and metallurgical processes are often dispersed by wind and/or water after their disposal. Heavy metals contained in the tailings are mobilized and migrate to the surroundings which will cause severe and widespread contamination of soils, surface waters, ground waters, rivers and the atmosphere. This research will be conducted to determine whether a tin mining tail would bring effect on the concentration of heavy metals in the atmosphere. Heavy metals include Pb, As, Hg, Cd, Zn, Al and Sn will be focused in this study.

#### 2.2.3 Pathways

Generally, air and water are the main pathways of heavy metals entry and diffusion into the environment. Heavy metals associated with particulate matters or in the water would disperse and transport up to several kilometers away from their sources. Besides air and water, soil and biota can be the media for transportation of heavy metals through wet or dry deposition (Pachana *et al.*, 2010).

One of the studies by Pachana *et al.* (2010) indicated that heavy metals both in the terrestrial or the marine environment, which are transported to the lakes and to the oceans via water (fluvial) are many times greater than that by air (atmospheric). This certainly reflects the prevalence of wastewater discharges from sewagemunicipal-industrial inputs that are so common in our industrialized society. But it does not mean that heavy metals in the atmosphere can be neglected.

Heavy metals which are introduced into the environment are transported and may be transformed into other forms of chemical. Transport can occur within a compartment or between compartments. Transformation processes in the environment involve photo-degradation, chemical degradation and biodegradation. Heavy metals may also be transformed within organisms and this is called biotransformation (Pachana *et al.*, 2010).

#### 2.2.4 Sources and Effects

#### 2.2.4.1 Lead

Lead is well known as one of the toxic heavy metals. Lead can stay in the environment for longer time (Joshi and Balasubramanian, 2010). As lead additive size diameter in gasoline is less than 1  $\mu$ m; it can transport to far distance more than 30 km. Although these lead additives were presently cancelled, they are still found and detected in dust particles (Boonsaner, 2006). According to Zhao *et al.* (2015), lead in the atmosphere originates mainly from mining, smelting, industrial uses, waste incineration, coal combustion, and leaded gasoline. Thus, vehicle emission, especially the leaded gasoline combustion, is generally considered as one of the dominant sources of lead in the atmosphere. Thus, lead is primarily an atmospheric pollutant enters soils and waters as fallout.

Lead is known as a probable human carcinogen. Exposure to high level of lead can severely damage the brain and kidneys and ultimately cause death. Longterm exposure can lead to anemia; decrease in performance that affects the functions of the nervous system; weakness in ankles, wrists or fingers; and small increases in blood pressure. Inorganic lead is normally absorbed in digestion and respiratory systems of organism, while organic lead e.g. alkyl lead is mostly absorbed by skin. But, the toxicity testing has declared that the lead intake by oral is more six-times toxic than absorbed by skin (Boonsaner, 2006).

#### 2.2.4.2 Arsenic

Arsenic is released into the atmosphere both from natural sources which include volcanoes and forest fires, and also from various anthropogenic sources which include coal combustion, smelter, mining activities and pesticide application. Arsenic in air mainly exists in the form of particulate matter that is mostly less than 2 µm in diameter and is often a mixture of arsenite and arsenate (European Commision, 2000). These particles can be transported by air currents and wind until they are brought back to earth surface by dry or wet deposition.

Soluble inorganic arsenic is extremely toxic. Intake of inorganic arsenic over a long period can result in chronic arsenic poisoning. Effects such as cardiovascular disease, cancer, diabetes, gastrointestinal symptoms, peripheral neuropathy, renal system effects and skin lesions, can take years to develop depending on the level of exposure; while organic arsenic which is abundant in seafood, is less harmful to health and is eliminated by the body rapidly (WHO, 2010).

#### 2.2.4.3 Mercury

Natural sources of mercury result from the degassing of the earth's crust, evaporation from natural bodies of water and present in many rocks including coal. Therefore, coal-burning power plants are responsible for high level of mercury emissions to the atmosphere, also to all domestic human-caused mercury emissions. Mining processes also cause mercury discharges indirectly to the atmosphere. Besides, incineration of hazardous wastes, chlorine production, spilling mercury and breaking mercury products, as well as the improper treatment and disposal of mercury contained products or waste, can contribute to its discharge into the environment (USEPA, 2009).

Mercury mostly exists as a gaseous element in the atmosphere (Dinis & Fi úza, 2011). Due to its long lifetime more or less than one year in the atmosphere, transportation, deposition and dispersion of mercury in the environment will cause harmful effects on human health and ecosystems (Dinis & Fi úza, 2011).

Mercury exists in the inorganic form as free mercury or as organic mercury compounds, such as phenyl mercuric salts. The EPA (2009) has determined that both organic and inorganic form of mercury are possible human carcinogens. Exposure to high level of mercury can permanently damage the brain, kidneys, and developing fetuses. Effects on brain functioning may result in changes in vision or hearing, irritability, tremors, shyness and memory problems; while short-term exposure may cause skin rashes and eye irritation, increases in blood pressure or heart rate, lung damage, diarrhea, nausea, vomiting.

#### 2.2.4.4 Cadmium

Cadmium has long been recognized as a toxic element. A major environmental source of cadmium is vapor emissions accompanying with dust that contaminate surrounding water and soil through fallout during smelting (Boonsaner, 2006). According to the World Bank Group (1998), the largest contributors to the contamination of cadmium are from metal productions and mines, followed by waste incineration and other sources, including the nickel-cadmium batteries productions and combustion of fossil fuel. Mine tailings generated as the result of the potential of zinc mining to transfer cadmium to the ambient environment.

Inhaling high level of cadmium can cause severe damage to the lungs; while ingesting high level of cadmium can severely irritates the stomach, leading to diarrhea and vomiting (World Bank Group, 1998). Long-term exposure to low level of cadmium leads to a buildup in the kidneys and possible kidney disease, fragile bones and lung damage (World Bank Group, 1998).

#### 2.2.4.5 Zinc

Zinc is commonly found in the Earth's crust. Zinc is released naturally to the environment, as well as from anthropogenic activities. But, anthropogenic releases of zinc are greater than those from natural sources. Zinc mostly enters the environment as the result of mining, steel production, purifying ores, coal burning, and waste incinerations. These activities can increase concentration of zinc in the atmosphere (ATSDR, 2005). Besides, emission of zinc in the atmosphere are usually associated

with the vehicular petrol fuel combustion and also the use of car brakes (Norela *et al.*, 2005; Alahmr *et al.* 2012).

Exposure to high level of zinc (as zinc dust or fumes from smelting or welding) can lead to a specific short-term disease namely metal fume fever, which is able to be reversed once exposure to zinc ceases (ATSDR, 2005). But, there is only very little knowledge about the long-term effects of inhaling zinc dust or fumes. Furthermore, ingesting high level of zinc for months may cause anemia, damage to pancreas and decrease high-density lipoprotein (HDL) cholesterol level. (ATSDR, 2005).

#### 2.2.4.6 Aluminium

Aluminium can be discharged naturally to the environment, as well as by anthropogenic activities. Due to its prominence as a main component of the earth's crust, natural processes have exceeded many folds greater than the contribution of anthropogenic releases of aluminium in the environment (Lantzy and MacKenzie, 1979). Aluminium enters the atmosphere as a major constituent of atmospheric particulates and settle to the ground or wash out of the air by rain. Yet, very small aluminium particles can remain in the atmosphere for several days. The largest source of aluminium particles is the weathering of rocks and the flux of dust from soil (Sorenson *et al.*, 1974). Mining and agriculture activities are presumably contributed to wind-blown dust (Filipek *et al.*, 1987). The main anthropogenic sources of aluminum particles include aluminum production, coal burning and other industrial activities for instance smelting, which process crustal minerals (Lee and Von Lehmden, 1973).

Exposure to aluminium can lead to "metal fume fever". This is a flu-like illness with symptoms of metallic taste in the mouth, headache, fever, chills, cough, aches and chest tightness (ATSDR, 2008). In addition, inhalation of aluminium as fine dust can cause scarring of the lungs with symptoms of cough and shortness of breath; while in contact with aluminium also can cause irritation of skin and eyes (ATSDR, 2008).

#### 2.2.4.7 Tin

Tin can be naturally found in the Earth's crust, with an average concentration of approximately 2–3 mg/kg (Budavari, 2001). Tin occurs in both inorganic and organic forms. Tin can be released to the environment from natural and anthropogenic sources. Tin is a component of many soils and inorganic tin may be released in dusts from roads, wind storms and agricultural activities. Tin is seldom detected in air and at low concentration (WHO, 2005). Other less significant natural sources include forest fires and volcanic emissions. Tin can be discharged into the environment through the production, recovery, use and disposal of tin and tin compounds. Dusts, fumes and gases containing tin may be discharged from refining and smelting processes, waste incineration, fossil fuel combustions and industrial uses of tin (WHO, 2005).

According to ATSDR (2005), inorganic tin compounds normally enter and leave human body rapidly after inhalation or ingestion and do not cause harmful effects. But, human who ingested large quantities of inorganic tin in will cause anemia, suffered stomachaches, liver and kidney problems (ATSDR, 2005). Besides, inhalation, ingestion or skin contact to some organotin compounds has been revealed to cause harmful effects in human such as neurological problems, skin and eye irritation and respiratory irritation, but the main effect will depend on the particular organotin compound (ATSDR, 2005).

#### 2.3 The Previous Studies of Heavy Metals in the Atmosphere

Research by Alahmr *et al.* (2012) indicated that high concentration of zinc in the Kajang and Bangi, which is most likely both areas are considered as a semi-urban area which associated with vehicle combustion. Another research by Cheng and You

(2010) showed that high concentration of heavy metal in typhoon rain such as Pb had large variability compared to normal period, which changed more than several hundred times during the typhoon events. Ozsoy and Ornektekin (2009) found that relative high concentration of Fe and Al in Mersin were influenced by the natural and marine sources, rather than the anthropogenic factors.

Joshi and Balasubramanian (2010) showed that Al, Fe and Zn were found to be abundant in both residential and industrial runoff. However, the concentration of most heavy metals in industrial runoff was found to be many times greater than that of residential runoff. This is due to the emissions of vehicles in the industrial area are much greater than those of residential area, as well as metal intensive activities and the extensive use of metals such as Pb and Zn in industries are reflected in elevated concentrations of these metals in the runoff. Another research by Al-Momani (2003) indicated concentration of Al in Northern Jordan was relative high compared to other rural sites. This is due to sporadic, intense incursions of Saharan dust and the long dry summer season in the region which increases the atmospheric loading of soil particles which gets washed out by precipitation.

The results from Table 2.3 will be used as guidance and comparison to investigate the significant of heavy metals in dust fall between the regions of Kampar, Malaysia.

Site	Pb	Cd	Fe	Zn	Al	Cr	References
Semi-urban	$4.10 \pm 1.20$	$0.76 \pm 0.60$	18.11 ±	47.93 ±	17.17 ±	$0.52 \pm 0.31$	Alahmr et. al., 2012
			8.10	26.10	13.86		
Urban	1710	nd	nd	64.2	13.8	0.4	Cheng and You,
							2010
Urban	11.36 ±	$0.81 \pm 0.09$	743.2 $\pm$	$50.2 \pm 6.06$	$484.5~\pm$	5.72 ±0.43	Ozsoy and
	0.81		115		49.5		Ornektekin, 2009
Industrial	90.25	4.57	3146	1127	769.30	213.80	Joshi and
							Balasubramanian,
							2010
Industrial	6.17 ±4.47	4.49 ±4.57	nd	nd	nd	$3.02 \pm 3.83$	Latif <i>et al.</i> , 2001
Rural	9.60	0.02	15.30	65.20	34.70	0.04	Cheng <i>et al.</i> , 2011
Rural	$2.57 \pm 2.33$	$0.42 \pm 0.63$	92 ±104	$6.52 \pm 7.84$	382 ±323	$0.77 \pm 0.84$	Al-Momani, 2003
Desert	$51 \pm 36.40$	$42 \pm 22.86$	$21.50~\pm$	$32 \pm 32.61$	nd	nd	Alkhashman, 2005
			32.84				

## Table 2.2: Summary of selected heavy metal research results (µg/L)

nd: no data

#### 2.4 Guidelines

The concentration of heavy metals in dust fall collected in this study were compared with the Drinking Water Quality Standard recommended by Malaysia, WHO and USEPA as shown in Table 2.3 below. It was used as a reference for heavy metal standard in dust fall due to the dust fall samples collected were in the form of rainwater and there is no suitable standard can be used to determine the concentration of heavy metals in the dust fall. In this study, dust fall samples in the form of rainwater were analyzed to obtain the concentration of heavy metals in the dust fall.

# Table 2.3: Malaysia, WHO and USEPA Drinking Water Quality Standard (Ministry of Health Malaysia, 2010; WHO, 2011;USEPA, 2014)

ELEMENT	Mala	ysia	WHO	USEPA	
	Recommended Raw	Drinking Water	Drinking Water	National Primary	National Secondary
	Water Quality	Quality Standard	Guideline Value	Drinking Water	Drinking Water
				Regulations	Regulations
	Acceptable Value	Maximum	Maximum	Maximum Acceptable	Maximum Acceptable
	(µg/l)	Acceptable Value	Acceptable Value	Value (µg/l)	Value (µg/l)
		(µg/l)	(µg/l)		
Arsenic (As)	10	10	10	10	-
Aluminium (Al)	-	200	-	-	200
Boron (B)	-	-	2400	-	-
Cadmium (Cd)	3	3	3	5	-
Chromium (Cr)	50	50	50	100	-
Copper (Cu)	1000	1000	2000	-	1000
Iron (Fe)	1000	300	-	-	300
Lead (Pb)	50	10	10	15	-
Magnesium (Mg)	150000	150000	-	-	-
Manganese (Mn)	200	100	-	-	50
Mercury (Hg)	1	1	6*	2	-
Nickel (Ni)	-	20	70	-	-
Zinc (Zn)	3000	3000	-	-	5000

\* For inorganic mercury

## CHAPTER 3

## **RESEARCH METHODOLOGY**

## 3.1 Study Area

In this study, eight sampling stations around Kampar area were chosen for dust fall collection which included resident area, workshop area and UTAR Perak campus. The eight sampling locations and the coordinates are stated clearly as shown in Table 1.

Tuble etter sumpling location	Table	3.1:	Sam	pling	location
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Station	Study Area	Description	Geographic
			Coordinates
А	UTAR Perak	University Area	4 °20'19.5"N
		(Block E)	101 08'35.8"E
В	UTAR Perak	University Area	4 °20'08.3"N
		(Block A)	101 °08'30.0"E
С	UTAR Perak	University Area	4 °20'26.8"N
		(Block M)	101 08'15.5"E
D	Kampar Putra	Residential Area	4 °19'12.2"N
		(Exposed to Construction)	101 °07'46.2"E
Е	Taman Bandar Baru	Residential Area	4 °19'27.5"N
			101 08'15.8"E

F	Taman Naga Emas	Residential Area	4 °18'55.1"N
			101 09'14.5"E
G	Taman Melayu Jaya	Workshop Area (Close to	4 °18'04.4"N
		Train Station)	101 09'20.8"E
Н	Taman Mahsuri Jaya	Residential Area	4 °19'41.2"N
		(Construction since March	101 <sup>0</sup> 9'09.7"E
		2015)	



Figure 3.1: Map of Kampar, Perak, Malaysia (Google Maps, 2015)

#### 3.2 Sampling for Dust Fall and Preparation of Reagent

#### **3.2.1** Sampling for Dust Fall

Dust fall consisting of wet and dry deposition was collected monthly, from February 2015 to June 2015, using polyethylene bottles (2 L) equipped with a plastic filter funnel (diameter size 20 cm). The polyethylene bottles were mounted at least a height of 2 m from ground surface to avoid accumulation of soil or surface dust. 10 mL of 0.02 M copper sulfate (CuSO<sub>4</sub>.5H<sub>2</sub>O) was added to each sampling bottles in order to prevent lichen growth during the sampling period. The amount of dissolved Cu<sup>2+</sup> from CuSO<sub>4</sub>.5H<sub>2</sub>O has been considered for Cu<sup>2+</sup> determination in the dust fall. After the collection of all samples, they were filtered using Whatman glass microfiber filters GF/C (47 mm diameter with a 1.2 µm pore size) to determine the amount of undissolved solids. Then, all samples were stored in 4°C prior to other analysis.

#### 3.2.2 Preparation of 0.02 M Copper Sulfate (CuSO<sub>4</sub>.5H<sub>2</sub>O)

Copper (II) Sulfate Pentahydrate (Grade AR), 4.9936 g was mixed with 1 L of distilled water in a volumetric flask. The solution was stirred using a magnetic stirrer on a hot plate at 55°C for 10 minutes in order to have a homogeneous mixture.

#### 3.3 Determination for Undissolved Solids and Dissolved Solids in Dust Fall

#### **3.3.1** Determination for Undissolved Solids

After the filtration of the sample in 3.2.1, the filter paper was dried in an over at 105°C for 2 hours and it was allowed to cool in a desiccator until a constant weight is
achieved. The concentration of undissolved solids was calculated based on the method stated by Norela *et al.* (2009) as Eq. (1):

Concentration of undissolved solids  $(mg/m^2/day) = (M_2 - M_1) / (AT)$  Eq. (1)

Where:

M<sub>1</sub> = Weight of the filter without sample (mg)
M<sub>2</sub> = Weight of the filter with dry undissolved solids after filtration (mg)
A = Funnel surface area (m<sup>2</sup>)
T = Period of sampling days (days)

## 3.3.2 Determination for Dissolved Solids

The filtrated sample (100 mL) was transferred to a beaker. The sample was concentrated to less than 50 mL on a hot plate. The beaker was subsequently dried in an oven for 4 hours at 105°C and allowed to cool in a desiccator until constant weight is achieved. The concentration of dissolved solids was calculated based on the method stated by Latif and Rozali (1999) as Eq. (2):

Concentration of dissolved solids  $(mg/m^2/day) = [(M_4 - M_3) (V_1 / V_2) - 18.5] / (AT)$ 

Eq. (2)

Where:

 $M_3$  = Weight of beaker without the dissolved solids (mg)

 $M_4$  = Weight of dissolved solids with the weight of the beaker (mg)

 $V_1$  = Volume of all the rainwater collected (mL)

 $V_2$  = Volume of rainwater which evaporated (100 mL)

A = Funnel surface area (m<sup>2</sup>)

T = Period of sampling (days)

18.5 = Factor for dissolved solids from 10 mL 0.02 N CuSO4.5H2O

### **3.4** Determination of Heavy Metals in Dust Fall

#### 3.4.1 Pretreatment of Dust Fall Samples

In order to analyze heavy metals by using inductively coupled plasma-mass spectrometer (ICP-MS, Perkin Elmer NexION<sup>TM</sup> 300Q), pre-treatment of sample was needed. Two milliliter of concentrated HNO<sub>3</sub> and 5 mL of concentrated HCl were added into the sample. The sample was then heated at  $95^{\circ}$ C by using hot plate until the sample was concentrated to 25 mL. Final volume of the digested sample was filled to 100 mL with distilled water. Samples were filtered with a 0.45 µm filter.

#### 3.4.2 Assessment of Heavy Metals by ICP-MS

#### **3.4.2.1 Preparation of Stock Solutions**

Prior to analysis by ICP-MS, standard solutions such as Multi-Element Calibration Standard 2 (PerkinElmer Pure Plus, 10 mg/L, 5% HNO<sub>3</sub>), Mercury (SPEX CertiPrep, 1000 mg/L, 10% HNO<sub>3</sub>) and Boron (SPEX CertiPrep, 1000  $\mu$ g/mL) were used to prepare stock solutions according to desirable range of concentrations encompassing expected sample concentrations which include 50 ppb, 100 ppb, 500 ppb and 1000 ppb.

#### 3.4.2.2 Setting of ICP-MS

Prior to analysis, daily performance check was performed and a new quantitative analysis method was created. Desirable elements which wish to be quantified were selected and other related fields were populated automatically. The method was saved in the machine. Each element was calibrated and recorded in the machine by using blank solution (ultra-pure water) and stock solutions. After the calibration, all samples were analyzed and data was obtained.

### **3.5 Quality Control and Assurance**

To ensure the reliability of the results of dust fall measurements, quality control measures were taken to avoid any interference in both field and laboratory. All polyethylene bottles, filter funnels and glassware were pre-washed several times with tap water, then rinsed two times with nitric acid to get rid inorganic substances, lastly rinsed with distilled water for two times, and then dried in a clean laboratory. Prior to filtration to determine undissolved solids in the collected samples, Whatman glass microfiber filters GF/C were dried in an oven at 105°C for 2 hours subsequently cooled in a desiccator for 30 minutes. Samples were recommended to store at 4°C to avoid degradation of substances.

## 3.6 Statistical Analysis

The one-way ANOVA test was used to analyze correlation coefficient and correlation significance so as to estimate differences between the mean concentration of total dust fall, undissolved solids, dissolved solids and heavy metals in rainwater.

## **3.7 Enrichment Factors**

Enrichment factors (EF) are good pollution indicators used to determine whether the heavy metals detected in the rainwater samples originated from natural or anthropogenic sources (Duce *et al.*, 1975). Enrichment factors were calculated using Eq. (3), used by Al-Momani (2007) and Latif *et al.* (2015) for similar purposes. This calculation was based on averaged heavy metal concentrations for the Earth's crust and dust fall.

where  $C_x$  is the concentration of the element of interest and  $C_{ref}$  is the concentration of the reference element (Taylor and McLennan, 1985). The unit for  $C_x$  and  $C_{ref}$  in rainwater is in ppb and the unit for  $C_x$  and  $C_{ref}$  in Earth's crust is in ppm. Based on the hypothesis that crustal material is the only source of Al (Al-Momani, 2003), therefore Al was used as the reference element in this study. EF values can be classified into five categories: (i) EF approaching 1 shows the element is of crustal origin; (ii) EF < 2 shows a low enrichment; (iii) EF = 2–5 shows a moderate enrichment; (iv) EF = 5–20 shows a significant enrichment; and (v) EF = 20–40 shows an extremely high enrichment (Han *et al.*, 2009).

## **CHAPTER 4**

## **RESULTS AND DISCUSSIONS**

## 4.1 Dust Fall Concentration

Figure 4.1 shows the mean concentration of undissolved solids, dissolved solids, as well as total solids in dust fall at the eight sampling locations.



Figure 4.1: Mean concentration of undissolved solids, dissolved solids and total solids in dust fall in Kampar

## 4.1.1 Total Solids

The overall range for total solids was between  $5.87 \pm 1.73 \text{ mg/m}^2/\text{day}$  and  $32.17 \pm 4.86 \text{ mg/m}^2/\text{day}$ . Station G had the highest concentration of total solids with  $32.17 \pm 4.86 \text{ mg/m}^2/\text{day}$  while station A had the lowest concentration at  $5.87 \pm 1.73 \text{ mg/m}^2/\text{day}$ . Overall, the mean concentration of total solids in this study was to be found  $20.39 \pm 2.60 \text{ mg/m}^2/\text{day}$ , which was 6.5 times lower than the value recommended by the DOE Malaysia which is at  $133 \text{ mg/m}^2/\text{day}$ . The high concentration of total solids in dust fall at station G is most probably due to it being located near to car workshops and train station which a high level of deposited particulates are emitted from car repairing activities and moving vehicles. On the contrary, the low concentration of total solids in dust fall at station A may be the result of a low amount of passerby due to the access door to this area is always locked and outsiders are prohibited.

The concentration of total solids in this study was far lower when compared to other studies that were conducted by Latif and Rozali (1999) for both Teluk Kalung and Air Keroh, Momani *et al.* (1999), Latif and Rozali (2000), Norela *et al.* (2004), Norela *et al.* (2009) and Alahmr *et al.* (2012). In this study, lower concentration of dust fall can be mainly due to the fact that the other studies were conducted near the urban area, industrial area and power station, which most likely to have emitted more particulate matter from the combustion of fossil fuels. While Kampar is still a developing town that has low population, less amount of vehicles and industrial activities if compared with other urban areas and developed towns.

### 4.1.2 Dissolved Solids

For dissolved solids, station G had the highest concentration compared to station A which had the lowest concentration with a range between  $2.83 \pm 0.92 \text{ mg/m}^2/\text{day}$  and  $27.35 \pm 2.19 \text{ mg/m}^2/\text{day}$ . The high concentration at station G is mostly due to the result

of car repairing activities and emissions from moving vehicles as mentioned earlier. Moreover, station G is located near to car workshops and train station where a high level of dust is present and where vehicular emissions around the study area influence air quality.

## 4.1.3 Undissolved Solids

Meanwhile, station F was recorded the highest concentration of undissolved solids with  $6.33 \pm 3.49 \text{ mg/m}^2/\text{day}$  and station A was recorded the lowest concentration with  $3.04 \pm 0.81 \text{ mg/m}^2/\text{day}$ . Station F is a residential area which is located nearby jungle area. The reason for the high concentration of undissolved solids in station F was believed to be the emissions from vehicles due to it is a pathway that linked to the school direction, as well as plant residues from nearby jungle (Alahmr *et al.* 2012) compared to station A which is mostly considered as isolated area (which has less passerby and traffics).

## 4.2 Heavy Metals in Rainwater

Concentration of heavy metals in rainwater at Kampar from eight different sampling locations was recorded in Table 4.1 below. Based on the data collected, Zn was recorded the highest concentration compared to the other heavy metals with a mean concentration of  $81.81 \pm 15.55$  ppb during the sampling period, followed by As, Al, B, Fe, Cr, Pb, Ni, Mn, Hg, Sn and Cd. Cd had the lowest concentration at  $0.30 \pm 0.16$  ppb. According to Dinis & Fiuza (2011), there are three common heavy metals that are Pb, Hg and Cd, which are of great concern to human health and the environment, due to their ability to travel long distances in the atmosphere before deposition. Therefore, Pb, Hg, Cd, As, Zn, Al and Sn will be discussed in the section below.

Heavy	А	В	С	D	E	F	G	Н	Mean
Metals		D	C	D	L	Ĩ	0	11	Weah
В	$60.91 \pm 15.78$	$44.29 \pm 7.08$	48.61 ±13.20	59.10 ±25.71	$73.13 \pm 3.38$	$40.64 \pm 12.18$	$57.65 \pm 6.74$	$50.51 \pm 13.84$	$54.36 \pm 12.24$
Al	$81.59 \pm 32.40$	$78.54\ \pm 12.89$	$65.05 \ \pm 6.81$	$62.54 \pm 12.04$	$78.52\ {\pm}18.18$	$67.31 \pm 8.64$	$60.42 \pm 5.20$	$76.02 \pm 8.50$	$71.25 \pm 13.08$
Cr	$19.27 \pm 1.07$	$18.62 \pm 4.68$	$19.75 \pm 2.97$	$16.57 \pm 2.93$	$21.41 \pm 7.05$	$17.09 \pm 1.91$	$17.56 \pm 5.64$	$15.42 \pm 1.66$	$18.21 \pm 3.49$
Mn	$2.41\ \pm 0.88$	$2.96 \pm 1.26$	$2.43 \pm 0.87$	$2.63 \pm 0.95$	$3.01\ \pm 0.88$	$2.57\ \pm 1.05$	$2.88 \pm 0.61$	$2.63 \pm 0.65$	$2.69 \pm 0.89$
Fe	$56.14 \pm 23.18$	$54.61 \pm 13.70$	$49.76 \pm 3.06$	$48.05 \pm 5.50$	$56.13 \pm 12.85$	$46.24 \pm 1.43$	$43.32 \pm 3.06$	$49.44 \pm 8.42$	$50.46 \pm 8.90$
Ni	$7.65~\pm7.80$	$3.58 \pm 0.72$	$3.94 \pm 0.38$	$3.22 \pm 0.43$	$9.18~{\pm}8.61$	$4.34 \pm 0.64$	$5.22 \pm 3.63$	$3.76 \pm 0.53$	$5.11 \pm 2.84$
Zn	$69.14 \pm 21.08$	$79.20\pm7.98$	$77.45 \pm 27.35$	$80.13 \pm 26.72$	$124.28 \pm 19.62$	$68.42 \pm 2.81$	$71.57 \pm 9.15$	$84.30 \pm 9.70$	$81.81 \pm 15.55$
As	$78.74 \pm 4.98$	$80.62 \pm 4.25$	$65.72 \pm 30.70$	$73.86 \pm 2.70$	$77.77\ \pm 10.69$	$66.42 \pm 21.47$	$72.91 \pm 3.65$	$68.28 \pm 3.01$	$73.04 \pm 10.18$
Cd	$0.23 \pm 0.12$	$0.29 \pm 0.19$	$0.38 \pm 0.15$	$0.22 \pm 0.13$	$0.41\ \pm 0.24$	$0.34 \pm 0.13$	$0.24 \pm 0.09$	$0.34 \pm 0.23$	$0.30\pm 0.16$
Sn	$1.61 \pm 1.28$	$1.18 \pm 0.68$	$0.63 \pm 0.25$	$0.70\ \pm 0.36$	$0.64\ \pm 0.14$	$0.44\ \pm 0.18$	$0.80\ \pm 0.13$	$0.73 \pm 0.66$	$0.84\ \pm 0.46$
Hg	$3.41 \pm 0.85$	$2.62 \pm 2.15$	$1.09\ \pm 0.31$	$0.90\ \pm 0.47$	$0.98 \pm 0.42$	$1.30\ \pm 1.04$	$0.66 \pm 0.11$	$0.73 \pm 0.37$	$1.46 \pm 0.71$
Pb	$8.33 \pm 1.02$	$8.92 \pm 0.57$	$10.48 \pm 1.56$	$8.28 \pm 1.07$	$9.36 \pm 2.88$	$9.54 \pm 2.67$	$8.36 \pm 1.17$	$10.54 \pm 2.94$	$9.23 \pm 1.74$

 Table 4.1: Mean concentration of heavy metals in rainwater in Kampar (ppb)

## 4.2.1 Lead

Based on Figure 4.3, highest concentration of Pb in station H, which found to be  $10.54 \pm 2.94$  ppb had slightly exceeded the value recommended by Malaysia and WHO drinking water quality standard which is 10 ppb, but is still in the range for raw water quality standard by Malaysia and drinking water quality standard by USEPA. High levels of Pb in the atmosphere are frequently observed in industrial, residential and commercial areas which includes all the eight sampling locations. One of the possibility that causes the high concentration of Pb in Kampar was the high traffic load due to Kampar is considered as developing town. The concentration of Pb increases with respect to the amount of vehicular emissions. Former tin mining activities might also be one of the source of Pb in the atmosphere.

Yet, when comparing the results obtained in the current study, the concentration of Pb is noticeably lower compared to Joshi and Balasubramanian (2010). This may be due to the fact that the location of this study was not affected by factories that can contribute certain metal concentrations in rainwater. Furthermore, a study undertaken by Cheng and You (2010) found that the concentration of Pb is about 185 times greater than that found in this study, which was affected by the Mindulle and Aere typhoon events in 2010 and 2011 respectively.



Figure 4.3: Concentration of lead in rainwater in Kampar

### 4.2.2 Arsenic

Based on Figure 4.4, highest concentration of As can be found in station B, which recorded to be  $80.62 \pm 4.25$  ppb that had exceeded 8 times the maximum acceptable value in Malaysia and USEPA drinking water quality standard which is 10 ppb. Although station B had the highest concentration of As, the concentration of As in other seven sampling locations had also exceeded the standard with the range of  $65.72 \pm 30.70$  ppb –  $78.74 \pm 4.98$  ppb. In this study, it was observed that concentration of As in Kampar was extremely high. Hence, as the surrounding of Kampar was covered by former tin mine lake, it was proved that past tin mining activities has the possibility to bring the effect on the concentration of As in the atmosphere as As can be found in the form of particulate matter as reviewed in Chapter 2.



Figure 4.4: Concentration of arsenic in rainwater in Kampar

### 4.2.3 Mercury

Based on Figure 4.5, the highest concentration of Hg was found to be  $3.41 \pm 0.85$  ppb in station A. Station A and station B ( $2.62 \pm 2.15$  ppb) was found to be exceeded the recommended value of drinking water quality standard by Malaysia and USEPA which is 1 ppb even without undergoing full extraction due to limitation of resources. Mining metals can cause mercury indirectly discharge to the atmosphere through the evaporation from natural bodies of water (USEPA, 2009). Therefore, it was believed that high concentration of Hg in station A and station B was due to both stations were located nearest to the abandoned tin mining lake, thus Hg in the atmosphere was brought down by rainfall.



Figure 4.5: Concentration of mercury in rainwater in Kampar

## 4.2.4 Cadmium

Based on Figure 4.6, Cd recorded as the lowest concentration among all other heavy metals. The highest concentration of Cd can be found in station D which is  $0.22 \pm 0.13$  ppb, lower than the value recommended by Malaysia, WHO and USEPA drinking water quality standard which is 3 ppb for Malaysia and WHO and 5 ppb for USEPA. In this study, Kampar as a mining tail does not seem affected much on the concentration of Cd by the former tin mining activities.



Figure 4.6: Concentration of cadmium in rainwater in Kampar

## 4.2.5 Zinc

Based on Figure 4.7, zinc recorded as the highest concentration in station E, with the range  $68.42 \pm 2.81$  ppb –  $124.28 \pm 19.62$  ppb. The highest concentration of Zn was found to be  $124.28 \pm 19.62$  ppb at station E, which did not exceed the maximum acceptable value in Malaysia and USEPA drinking water quality standard which is 3000 ppb. Station E is a residential area that exposed to vehicular emissions during sampling period. It is a point that connects New Town and Old Town, whereby there is a small industrial area in between. This is an alternative pathway to Old Town, but is a main pathway that leads the lorries and trucks into the small industrial area. The amount of vehicles such as motorcycles, cars, lorries and trucks increases with respect to the population growth and also industrial activities. According to Norela *et al.* (2005) and Alahmr *et al.* (2012), emission of Zn in the atmosphere was associated with use of car brakes and petrol fuel as used in these vehicles. Besides, soil dust is expected to be one of the factors which contributes to the high concentration of Zn in the rainwater.

Abandoned mining area around the study area also has capacity to contribute to the amount of soil blown dust containing high amount of Zn.



Figure 4.7: Concentration of zinc in rainwater in Kampar

#### 4.2.6 Aluminium

Based on Figure 4.8, concentration of Al from eight sampling locations was found to be in the range of  $60.42 \pm 5.20 \text{ ppb} - 81.59 \pm 32.40 \text{ ppb}$ , which both values are below the drinking water quality standard set by Malaysia and USEPA which is 200 ppb. Station A showed the highest concentration of Al with a concentration of  $81.59 \pm 32.40$  ppb, while station G showed the lowest concentration of Al with a concentration of  $60.42 \pm 5.20$  ppb. This is most likely a direct consequence of the area itself, where station A is located nearby the abandoned tin mining lake (which is rich in minerals, along with the weathering process of rocks) compared to station G which is far away from the lake.

The concentration of Al in this study was lower compared to the study results from Ozsoy and Ornektekin (2009) and Joshi and Balasubramanian (2010) as shown in Table 2.3. It can be concluded that industrial areas tend to discharge more Al to the atmosphere as compared to a semi-urban town like Kampar, which the area is free of any local industries.



Figure 4.8: Concentration of aluminium in rainwater in Kampar

### 4.2.7 Tin

Based on Figure 4.9, overall concentration of Sn was ranged between  $0.44 \pm 0.18$  ppb and  $1.61 \pm 1.28$  ppb. This showed a relatively low value for an abandoned tin mining area that assumed to contain a high level of Sn in the rainwater, but there is no drinking water guidelines can be found to compare for Sn in this study. This might due to Sn properties itself is insoluble and strongly corrosion and weathering. This explains the relatively low amount of Sn present in soils, water bodies and atmosphere even though the study was conducted around an abandoned tin mining area.



Figure 4.9: Concentration of tin in rainwater in Kampar

## 4.3 Correlation

The correlation coefficient between heavy metals in dust fall at Kampar was studied in order to predict the possibility of a common source. The  $r^2$  value was generally high recording extreme correlation and significance for Al-Fe ( $r^2 = 0.76$ , p < 0.05) as shown in Figure 4.10. Table 4.2 indicated that there was strong significant correlation for Sn-Hg ( $r^2 = 0.47$ , p < 0.05) and B-Zn ( $r^2 = 0.44$ , p < 0.05) as shown in Figure 4.10. This may indicate that these heavy metals are originated from the same source, possibly the former mining activities.



Figure 4.10: Correlation of heavy metal between Al-Fe, Sn-Hg and B-Zn

	B 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
B 11	1											
Al 27	0.08	1										
Cr 52	0.01	0.00	1									
Mn 55	0.22	0.07	0.00	1								
Fe 57	0.09	0.76	0.00	0.08	1							
Ni 60	0.11	0.07	0.02	0.05	0.07	1						
Zn 66	0.44	0.17	0.01	0.25	0.17	0.17	1					
As 75	0.01	0.00	0.09	0.00	0.00	0.01	0.03	1				
Cd 111	0.04	0.06	0.00	0.09	0.03	0.01	0.21	0.04	1			
Sn 188	0.01	0.10	0.00	0.01	0.22	0.01	0.06	0.03	0.02	1		
Hg 202	0.02	0.05	0.00	0.01	0.17	0.03	0.07	0.07	0.12	0.47	1	
Pb 208	0.00	0.01	0.01	0.00	0.00	0.09	0.01	0.01	0.27	0.01	0.06	1

 Table 4.2 Correlation between heavy metals in dust fall in Kampar

## 4.4 Enrichment Factors

The enrichment factor (EF) results are shown in Figure 4.11. This study revealed that the heavy metals in the rainwater samples were derived from anthropogenic sources, except for Mn and Fe. The EF value for Mn was within the moderate enrichment factor (EF = 2-5) which shows that the Mn originated from natural Earth's crust and minimally from anthropogenic activities; while the EF value for Fe was in the range EF < 1 which was believed that the Fe was most probably originated only from Earth's crust.

As was recorded to have highest EF values of 40028.60, while the lowest EF value recorded was for Fe with an EF value of 0.92. A study by Cheng and You (2010) revealed that the EF values for Pb, Zn, and Ni are extremely high: Pb = 10,202,566, Zn = 27,921 and Ni = 3047. Therefore, the results obtained in this study demonstrate that there is an extremely high probability of the B, Zn, As, Cd, Hg and Pb originating from anthropogenic activities rather than distribution from soil dust. The probable anthropogenic sources that influence the EF results are mining activities, including soil excavation from construction sites, which released a large amount of dust into the surrounding area.

	EF <sub>rain</sub>	EFearth	EF
В	0.76295	0.0001061	7191.00
Al	1	1	1.00
Cr	0.25558	0.0017073	149.70
Mn	0.03775	0.0134146	2.81
Fe	0.70821	0.7682927	0.92
Ni	0.07172	0.0010976	65.34
Zn	1.14821	0.0009634	1191.81
As	1.02512	2.561E-05	40028.60
Cd	0.00421	1.829E-06	2301.75
Sn	0.01179	2.683E-05	439.43
Hg	0.02049	8.171E-07	25078.82
Pb	0.12954	0.000122	1062.26

Table 4.3: Enrichment Factor (EF) of heavy metals in dust fall in Kampar

## **CHAPTER 5**

## CONCLUSION AND RECOMMENDATIONS

## 5.1 Conclusion

This finding indicated that the mean concentration of total solids collected from eight sampling locations was  $20.39 \pm 2.60 \text{ mg/m}^2/\text{day}$ , which found to be under the permissible limit of 133 mg/m<sup>2</sup>/day as recommended by the Department of Environment Malaysia. The mean concentration for undissolved solids was  $4.08 \pm 1.50 \text{ mg/m}^2/\text{day}$ , while for dissolved solids was  $16.31 \pm 1.10 \text{ mg/m}^2/\text{day}$ . However, toxic heavy metals such as Pb, As and Hg (without full extraction) in the relative low concentration of dissolved samples were found to be exceeded the permissible limit as recommended in Drinking Water Quality Standard by Malaysia, WHO and USEPA; while Cd was found to have a relative low concentration in the dissolved samples.

From the results it could be concluded that the concentration of dust fall and heavy metals in the study area most possibly originated from the former mining activities and also vehicular emissions. Several precautionary procedures therefore need to be implemented by local authorities so as to maintain the concentration of dust fall around the study area. The quantity of vehicles and construction activities were shown to significantly increase the concentration of dust fall and its composition.

## 5.2 **Recommendations**

There are several improvements and recommendations could be done in future studies. In this research, mercury was determined by using the same procedures as to determine heavy metals which stated in USEPA Method 3005A: Acid Digestion of Waters for Total Recoverable or Dissolved Metals. However, USPEA standard operating procedures stated that one ppm of gold should be added into the sample in order to recover mercury for ICP-MS analysis to obtain a more precise result which gold is a limited resource in this research. Therefore, mercury could be analyzed by undergoing a proper full extraction procedures if there are resources available in the future studies.

Besides, heavy metals in other types of particulate matter such as  $PM_{2.5}$  and  $PM_{10}$  could be studied in future. For the past twenty years, the effects of these particulate matters on human health has been widely studied to assess and regulate air quality (Cincinelli *et al.*, 2003). Fine particles ( $PM_{1-2.5}$ ) or less in diameter have been proven to have the greatest health significance (Li and Lin, 2003). Therefore, assessment of heavy metals in particulate matters and dust fall should be carried out frequently in order to understand the air quality in Kampar, which might be affected by some factors such as increase in population growth, amount of vehicles, construction activities and etc.

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# APPENDICES

Period:	16/2/15 -			
	Weig	Weight (g)		
Sample	Before	After	Weight (g)	
А	0.1787	0.2024	0.0237	
В	0.2728	0.3079	0.0351	
С	0.1806	0.2014	0.0208	
D	0.2672	0.291	0.0238	
Е	0.2694	0.2934	0.024	
F	0.269	0.3132	0.0442	
G	0.1802	0.1981	0.0179	
Н	0.1801	0.2006	0.0205	

Appendix A: Weight of filter paper before and after filtration of collected samples.

Period:	17/3/15 -	15/4/15

	Weig	Actual	
Sample	Before	After	Weight (g)
А	0.1781	0.1988	0.0207
В	0.1803	0.192	0.0117
С	0.2676	0.2914	0.0238
D	0.3583	0.3798	0.0215
E	0.2694	0.2926	0.0232
F	0.1814	0.2218	0.0404
G	0.1786	0.1937	0.0151
Н	0.3589	0.3889	0.03

Period: $18/4/15 - 16/5/1$	15
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	Weig	Actual	
Sample	Before	After	Weight (g)
А	0.2674	0.2803	0.0129
В	0.179	0.202	0.023
С			
D	0.3608	0.3734	0.0126
Е	0.2678	0.2818	0.014
F	0.1784	0.2055	0.0271
G	0.2706	0.3032	0.0326
Н	0.181	0.1984	0.0174

Period: 18/5/15 - 16/6/15

	Weig	Actual		
Sample	Before	After	Weight (g)	
А	0.1783	0.194	0.0157	
В	0.1805	0.202	0.0215	
С	0.1791	0.2089	0.0298	
D	0.1793	0.2005	0.0212	
E				
F	0.179	0.2554	0.0764	
G	0.7162	0.7662	0.05	
Н	0.3555	0.3773	0.0218	

Period:		16/2/15 - 17/3/15		
	Sample	Weight (g)	Average (g)	
	A1	0.0018	0.0015	
	A2	0.0012	0.0015	
	B1	0.0029	0.002	
	B2	0.0031	0.005	
	C1	0.0075	0.0069	
	C2	0.0061	0.0008	
	D1	0.006	0.0062	
	D2	0.0064	0.0062	
	E1	0.0038	0.004	
	E2	0.0042	0.004	
	F1	0.0071	0.0075	
	F2	0.0079	0.0075	
	G1	0.0106	0.0102	
	G2	0.0098	0.0102	
	H1	0.0079	0.0002	
	H2	0.0085	0.0082	

Appendix B:	Weight of	beaker with	dissolved	solids.
Appendix D.	weight of	beaker with	uissoiveu	sonus

Period:	17/3/15 - 15/4/15		
Sample	Weight (g)	Average (g)	
A1	0.0024	0.0021	
A2	0.0018	0.0021	
B1	0.0038	0.0026	
B2	0.0034	0.0056	
C1	0.0073	0.0068	
C2	0.0063	0.0008	
D1	0.0068	0.0066	
D2	0.0064	0.0000	
E1	0.0035	0.0030	
E2	0.0043	0.0039	
F1	0.0071	0.0073	
F2	0.0075	0.0075	
G1	0.0092	0.0005	
G2	0.0098	0.0095	
H1	0.0072	0.008	
H2	0.0088	0.008	

Period:	18/4/15 -	- 16/5/15
Sample	Weight	Average
Sample	(g)	(g)
A1	0.0014	0.0016
A2	0.0018	0.0016
B1	0.004	0.0027
B2	0.0034	0.0037
D1	0.0059	0.00565
D2	0.0054	0.00565
E1	0.0033	0.0025
E2	0.0037	0.0035
F1	0.0068	0.0071
F2	0.0074	0.0071
G1	0.0104	0.0107
G2	0.011	0.0107
H1	0.0077	0.00775
H2	0.0078	0.00775

Period:	18/5/15 -	- 16/6/15
Sample	Weight	Average
1	(g)	(g)
A1	0.002	0.0010
A2	0.0018	0.0019
B1	0.0044	0.0041
B2	0.0038	0.0041
C1	0.007	0.0066
C2	0.0062	0.0000
D1	0.0068	0.0065
D2	0.0062	0.0003
F1	0.0076	0.00755
F2	0.0075	0.00733
G1	0.0108	0.011
G2	0.0112	0.011
H1	0.0079	0.0077
H2	0.0075	0.0077

Sampla	Co	ncentratior	$n (mg/m^2/d)$	lay)
Sample	M1	M2	M3	M4
А	3.95	3.45	2.15	2.61667
В	5.85	1.95	3.8333	3.58333
С	3.46667	3.96667		4.96667
D	3.96667	3.58333	2.1	3.53333
E	4.0000	3.86667	2.3333	
F	7.36667	6.73333	4.51667	12.7333
G	2.98333	2.51667	5.43333	8.3333
Н	3.41667	5.0000	2.9	3.63333

Appendix C: Concentration of undissolved solids in dust fall collected for 4 months.

Appendix D: Concentration of dissolved solids in dust fall collected for 4 months.

Sampla	Co	Concentration (mg/m <sup>2</sup> /day)									
Sample	M1	M2	M3	M4							
А	1.91667	3.91667	2.25	3.25							
В	6.91667	8.91667	9.25	10.5833							
С	19.5833	19.5833		18.9167							
D	17.5833	18.9167	15.75	18.5833							
E	10.25	9.91667	8.58333								
F	21.9167	21.25	20.5833	22.0833							
G	30.9167	28.5833	32.5833	33.5833							
Н	24.25	23.5833	22.75	22.5833							

		54	

Sampla	Con	centration (mg/m <sup>2</sup> /da	ay)
Sample	Undissolved Solids	<b>Dissolved Solids</b>	Total Solids
А	$3.04 \pm 0.81$	$2.83 \pm 0.92$	$5.87 \pm 1.73$
В	$3.80 \pm 1.60$	$8.92 \pm 1.52$	$12.72 \pm 3.12$
С	$4.13 \pm 0.76$	$19.36 \pm 0.38$	$23.49 \pm 1.14$
D	$3.34 \pm 0.82$	$17.71 \pm 1.42$	$21.05 \pm 2.24$
E	$3.40 \pm 0.93$	$9.58 \pm 0.88$	$12.98 \pm 1.81$
F	$6.33 \pm 3.49$	$21.46 \pm 0.69$	$27.79 \pm 4.18$
G	$4.82 \pm 2.67$	$27.35 \pm 2.19$	$32.17 \pm 4.86$
Н	$3.74 \pm 0.90$	23.29 ±0.77	27.03 ±1.67
Mean	$4.08 \pm 1.50$	$16.31 \pm 1.10$	$20.39 \pm 2.60$

Appendix E: Mean concentration of undissolved solids, dissolved solids and total solids in dust fall collected for 4 months.

Sample	B 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
A1	49.692	73.784	21.161	2.538	41.194	3.837	36.65	85.984	0.087	0.436	2.485	8.764
A2	73.988	61.419	19.854	2.869	41.197	3.161	93.487	80.744	0.229	0.628	2.311	8.889
B1	41.238	76.987	14.571	2.396	48.761	3.278	87.93	84.932	0.913	0.653	0.746	9.555
B2	39.524	73.372	14.02	2.821	42.805	3.361	85.351	81.862	0.197	0.99	0.795	9.435
C1	58.854	63.151	20.084	3.234	47.225	4.515	93.879	71.262	0.13	0.392	0.556	10.435
C2	53.562	51.226	18.131	3.138	48.218	4.219	99.844	65.054	0.992	0.289	0.924	10.804
D1	90.142	68.848	14.758	3.934	52.758	3.552	108.248	71.935	0.3	0.348	0.459	7.831
D2	78.745	73.084	16.208	3.875	50.61	3.463	110.783	68.958	0.215	0.242	0.428	7.754
E1	86.403	71.634	20.869	2.817	49.126	3.733	122.579	68.724	0.759	0.288	0.72	7.146
E2	67.1	72.826	18.362	1.97	40.123	3.343	121.043	69.507	0.443	0.691	0.304	7.955
F1	53.049	65.96	18.123	1.123	43.922	4.153	73.772	32.127	0.524	0.071	0.831	9.58
F2	51.963	65.893	16.176	1.362	46.48	4.211	71.067	37.182	0.184	0.278	0.269	12.816
G1	65.351	69.376	18.745	3.758	48.556	3.432	64.171	75.635	0.502	0.94	0.758	8.453
G2	68.036	66.115	19.146	3.358	42.869	3.587	72.241	78.769	0.127	0.935	0.491	7.904
H1	61.235	71.524	15.9	2.89	50.864	3.257	95.552	62.984	0.496	0.227	0.413	8.243
H2	69.033	76.005	17.762	2.962	48.89	3.176	90.468	65.837	0.515	0.186	0.457	10.677

Appendix F: Concentration of heavy metals in dust fall collected from eight sampling locations (ppb).

Period: 16/2/15 - 17/3/15

# Appendix G: Concentration of heavy metals in dust fall collected from eight sampling locations (ppb).

## Period: 17/3/15 - 15/4/15

Sample	B 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
A1	74.811	77.732	17.407	2.701	52.269	18.747	79.727	82.939	0.188	0.559	4.169	9.31
A2	77.915	70.04	18.782	2.777	47.268	19.757	74.693	81.164	0.21	0.588	3.34	9.577
B1	50.6	68.97	14.943	3.529	58.489	4.021	83.442	75.425	0.162	1.498	3.802	7.69
B2	56.314	91.794	14.823	3.894	83.484	5.274	86.015	74.812	0.285	2.825	7.381	9.466
C1	62.059	76.055	20.778	2.79	60.882	4.328	92.648	33.628	0.212	0.806	1.563	9.412
C2	50.446	62.05	13.537	2.481	45.68	3.264	85.99	34.115	0.36	0.648	0.932	8.286
D1	72.734	68.127	15.754	2.795	55.719	3.654	85.213	79.448	0.126	1.319	0.808	6.958
D2	78.512	81.413	13.779	2.591	51.867	3.615	93.862	73.625	0.087	0.821	0.667	7.71
E1	69.183	117.511	13.695	4.561	59.051	21.396	144.381	70.523	0.326	1.001	1.074	11.266
E2	70.907	80.506	17.183	3.466	80.94	16.792	145.649	78.4242	0.636	0.496	1.08	14.102
F1	40.901	78.128	20.382	3.771	49.287	3.63	73.54	71.606	0.358	0.487	0.957	9.755
F2	44.227	78.697	14.742	3.69	45.307	3.899	62.436	72.49	0.118	0.428	1.035	7.08
G1	51.272	66.25	13.011	2.388	47.185	11.139	85.409	72.132	0.302	0.285	0.615	8.855
G2	52.009	54.685	13.224	2.282	44.322	10.18	76.272	68.328	0.301	1.231	0.671	10.776
H1	54.318	86.398	14.89	3.353	53.491	3.762	87.719	63.655	0.476	1.974	0.751	11.884
H2	64.445	90.815	18.734	3.305	68.816	3.871	81.25	73.857	0.662	1.359	0.978	17.704

# Appendix H: Concentration of heavy metals in dust fall collected from eight sampling locations (ppb).

## Period: 18/4/15 - 16/5/15

Sample	B 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
A1	75.466	113.069	19.766	3.366	110.934	5.803	99.567	74.126	0.678	3.249	3.144	8.958
A2	57.302	144.733	19.746	2.799	70.03	4.306	84.58	70.853	0.141	1.088	3.121	5.257
B1	46.292	62.143	23.292	4.236	42.245	3.251	75.557	82.245	0.289	0.705	1.669	8.318
B2	45.691	65.372	22.88	4.09	40.021	3.309	76.343	76.718	0.214	0.578	1.059	10.301
C1												
C2												
D1	49.874	52.474	21.912	2.144	45.023	2.738	70.571	73.909	0.292	0.55	0.929	7.316
D2	46.017	50.601	19.976	2.444	40.605	3.368	80.488	72.194	0.475	0.481	0.767	12.273
E1	58.716	62.196	33.204	2.575	48.453	4.81	105.866	83.215	0.151	0.688	1.028	7.866
E2	86.489	66.431	25.16	2.664	59.089	5.031	106.141	96.217	0.122	0.688	1.655	7.813
F1	47.433	70.676	18.532	3.125	47.276	5.576	71.471	75.309	0.32	0.625	0.79	9.567
F2	40.302	64.354	19.719	2.73	42.388	4.938	60.245	84.878	0.715	0.506	0.861	14.848
G1	61.54	62.567	29.4	3.394	42.006	3.802	65.028	72.602	0.224	0.806	0.617	7.683
G2	45.5	50.235	20.541	3.05	42.912	3.416	55.695	66.489	0.158	0.922	0.485	6.241
H1	43.238	86.12	16.059	2.648	41.984	4.93	98.813	75.668	0.276	0.413	0.527	9.04
H2	30.935	56.132	12.945	2.262	43.113	3.985	79.146	60.794	0.161	0.291	0.325	7.057

# Appendix I: Concentration of heavy metals in dust fall collected from eight sampling locations (ppb).

# Period: 18/5/15 - 16/6/15

Sample	<b>B</b> 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
A1	47.864	61.226	19.921	1.296	44.93	3.195	51.025	83.274	0.033	4.249	4.177	8.371
A2	30.277	50.701	17.495	0.924	41.333	2.363	33.408	70.822	0.251	2.05	4.57	7.516
B1	33.344	92.334	21.237	1.326	70.602	2.919	67.249	80.457	0.136	1.051	2.743	7.966
B2	41.344	97.321	23.206	1.352	50.492	3.191	71.702	88.488	0.093	1.145	2.785	8.659
C1	28.135	62.735	21.942	1.374	40.921	2.714	42.448	87.181	0.318	0.704	1.272	11.946
C2	38.584	75.061	24.025	1.58	55.618	4.593	49.877	103.055	0.29	0.917	1.309	11.992
D1	38.575	64.324	17.55	1.737	59.405	3.112	57.89	83.562	0.174	1.411	2.261	9.586
D2	18.192	41.459	12.658	1.535	28.411	2.278	33.993	67.245	0.077	0.437	0.854	6.817
E1												
E2												
F1	21.95	58.327	14.78	2.454	53.847	3.167	70.123	77.49	0.243	0.639	3.505	9.335
F2	25.259	56.424	14.28	2.282	41.408	5.154	64.727	80.274	0.226	0.474	2.16	3.358
G1	69.831	59.08	13.21	2.434	44.669	3.287	84.396	78.581	0.092	0.41	0.679	7.982
G2	47.672	55.016	13.21	2.342	34.049	2.92	69.329	70.731	0.179	0.892	0.944	8.978
H1	38.998	67.592	13.293	1.661	45.017	3.535	68.545	72.226	0.152	0.49	0.924	10.975
H2	41.869	73.61	13.807	1.966	43.338	3.573	72.894	71.249	0.014	0.873	1.469	8.725

Location	Months	B 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
А	1	61.84	67.6015	20.5075	2.7035	41.1955	3.499	65.0685	83.364	0.158	0.532	2.398	8.8265
	2	76.363	73.886	18.0945	2.739	49.7685	19.252	77.21	82.0515	0.199	0.5735	3.7545	9.4435
	3	66.384	128.901	19.756	3.0825	90.482	5.0545	92.0735	72.4895	0.4095	2.1685	3.1325	7.1075
	4	39.0705	55.9635	18.708	1.11	43.1315	2.779	42.2165	77.048	0.142	3.1495	4.3735	7.9435
	Mean	60.91	81.59	19.27	2.41	56.14	7.65	69.14	78.74	0.23	1.61	3.41	8.33
	SD	15.78	32.40	1.07	0.88	23.18	7.80	21.08	4.98	0.12	1.28	0.85	1.02

Appendix J: Mean concentration of heavy metals of dust fall collected in station A (ppb).

Appendix I: Mean concentration of heavy metals of dust fall collected in station B (ppb).

Location	Months	B 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
В	1	40.381	75.1795	14.2955	2.6085	45.783	3.3195	86.6405	83.397	0.555	0.8215	0.7705	9.495
	2	53.457	80.382	14.883	3.7115	70.9865	4.6475	84.7285	75.1185	0.2235	2.1615	5.5915	8.578
	3	45.9915	63.7575	23.086	4.163	41.133	3.28	75.95	79.4815	0.2515	0.6415	1.364	9.3095
	4	37.344	94.8275	22.2215	1.339	60.547	3.055	69.4755	84.4725	0.1145	1.098	2.764	8.3125
	Mean	44.29	78.54	18.62	2.96	54.61	3.58	79.20	80.62	0.29	1.18	2.62	8.92
	SD	7.08	12.89	4.68	1.26	13.70	0.72	7.98	4.25	0.19	0.68	2.15	0.57
Location	Months	B 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
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С	1	56.208	57.1885	19.1075	3.186	47.7215	4.367	96.8615	68.158	0.561	0.3405	0.74	10.6195
	2	56.2525	69.0525	17.1575	2.6355	53.281	3.796	89.319	33.8715	0.286	0.727	1.2475	8.849
	3												
	4	33.3595	68.898	22.9835	1.477	48.2695	3.6535	46.1625	95.118	0.304	0.8105	1.2905	11.969
	Mean	48.61	65.05	19.75	2.43	49.76	3.94	77.45	65.72	0.38	0.63	1.09	10.48
	SD	13.20	6.81	2.97	0.87	3.06	0.38	27.35	30.70	0.15	0.25	0.31	1.56

Appendix K: Mean concentration of heavy metals of dust fall collected in station C (ppb).

Appendix L: Mean concentration of heavy metals of dust fall collected in station D (ppb).

Location	Months	B 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
D	1	84.4435	70.966	15.483	3.9045	51.684	3.5075	109.516	70.4465	0.2575	0.295	0.4435	7.7925
	2	75.623	74.77	14.7665	2.693	53.793	3.6345	89.5375	76.5365	0.1065	1.07	0.7375	7.334
	3	47.9455	51.5375	20.944	2.294	42.814	3.053	75.5295	73.0515	0.3835	0.5155	0.848	9.7945
	4	28.3835	52.8915	15.104	1.636	43.908	2.695	45.9415	75.4035	0.1255	0.924	1.5575	8.2015
	Mean	59.10	62.54	16.57	2.63	48.05	3.22	80.13	73.86	0.22	0.70	0.90	8.28
	SD	25.71	12.04	2.93	0.95	5.50	0.43	26.72	2.70	0.13	0.36	0.47	1.07

Location	Months	B 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
Е	1	76.7515	72.23	19.6155	2.3935	44.6245	3.538	121.811	69.1155	0.601	0.4895	0.512	7.5505
	2	70.045	99.0085	15.439	4.0135	69.9955	19.094	145.015	74.4736	0.481	0.7485	1.077	12.684
	3	72.6025	64.3135	29.182	2.6195	53.771	4.9205	106.004	89.716	0.1365	0.688	1.3415	7.8395
	4												
	Mean	73.13	78.52	21.41	3.01	56.13	9.18	124.28	77.77	0.41	0.64	0.98	9.36
	SD	3.38	18.18	7.05	0.88	12.85	8.61	19.62	10.69	0.24	0.14	0.42	2.88

Appendix M: Mean concentration of heavy metals of dust fall collected in station E (ppb).

Appendix N: Mean concentration of heavy metals of dust fall collected in station F (ppb).

Location	Months	B 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
F	1	52.506	65.9265	17.1495	1.2425	45.201	4.182	72.4195	34.6545	0.354	0.1745	0.55	11.198
	2	42.564	78.4125	17.562	3.7305	47.297	3.7645	67.988	72.048	0.238	0.4575	0.996	8.4175
	3	43.8675	67.515	19.1255	2.9275	44.832	5.257	65.858	80.0935	0.5175	0.5655	0.8255	12.2075
	4	23.6045	57.3755	14.53	2.368	47.6275	4.1605	67.425	78.882	0.2345	0.5565	2.8325	6.3465
	Mean	40.64	67.31	17.09	2.57	46.24	4.34	68.42	66.42	0.34	0.44	1.30	9.54
	SD	12.18	8.64	1.91	1.05	1.43	0.64	2.81	21.47	0.13	0.18	1.04	2.67

Location	Months	B 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
G	1	66.6935	67.7455	18.9455	3.558	45.7125	3.5095	68.206	77.202	0.3145	0.9375	0.6245	8.1785
	2	51.6405	60.4675	13.1175	2.335	45.7535	10.6595	80.8405	70.23	0.3015	0.758	0.643	9.8155
	3	53.52	56.401	24.9705	3.222	42.459	3.609	60.3615	69.5455	0.191	0.864	0.551	6.962
	4	58.7515	57.048	13.21	2.388	39.359	3.1035	76.8625	74.656	0.1355	0.651	0.8115	8.48
	Mean	57.65	60.42	17.56	2.88	43.32	5.22	71.57	72.91	0.24	0.80	0.66	8.36
	SD	6.74	5.20	5.64	0.61	3.06	3.63	9.15	3.65	0.09	0.13	0.11	1.17

Appendix O: Mean concentration of heavy metals of dust fall collected in station G (ppb).

Appendix P: Mean concentration of heavy metals of dust fall collected in station H (ppb).

Location	Months	B 11	Al 27	Cr 52	Mn 55	Fe 57	Ni 60	Zn 66	As 75	Cd 111	Sn 188	Hg 202	Pb 208
Н	1	65.134	73.7645	16.831	2.926	49.877	3.2165	93.01	64.4105	0.5055	0.2065	0.435	9.46
	2	59.3815	88.6065	16.812	3.329	61.1535	3.8165	84.4845	68.756	0.569	1.6665	0.8645	14.794
	3	37.0865	71.126	14.502	2.455	42.5485	4.4575	88.9795	68.231	0.2185	0.352	0.426	8.0485
	4	40.4335	70.601	13.55	1.8135	44.1775	3.554	70.7195	71.7375	0.083	0.6815	1.1965	9.85
	Mean	50.51	76.02	15.42	2.63	49.44	3.76	84.30	68.28	0.34	0.73	0.73	10.54
	SD	13.84	8.50	1.66	0.65	8.42	0.53	9.70	3.01	0.23	0.66	0.37	2.94

SUMMARY						
Groups	Count	Sum	Average	Variance		
Al 27	30	2136.34	71.2115	248.242		
Fe 57	30	1508.89	50.2962	119.306		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	6561.7	1	6561.7	35.7053	1.49641E-07	4.00687
Within Groups	10658.9	58	183.774			
Total	17220.6	59				

## Appendix Q: One-way ANOVA for Al and Fe

## Appendix R: One-way ANOVA for Sn and Hg

SUMMARY						
Groups	Count	Sum	Average	Variance		
Sn 188	30	25.6255	0.85418	0.41849		
Hg 202	30	44.6995	1.48998	1.68051		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	6.06362	1	6.06362	5.77765	0.019448053	4.00687
Between Groups Within Groups	6.06362 60.8708	1 58	6.06362 1.0495	5.77765	0.019448053	4.00687
Between Groups Within Groups	6.06362 60.8708	1 58	6.06362 1.0495	5.77765	0.019448053	4.00687

SUMMARY						
Groups	Count	Sum	Average	Variance		
B 11	30	1617.63	53.921	244.186		
Zn 66	30	2416.21	80.5405	474.131		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	10629	1	10629	29.5941	1.11794E-06	4.00687
Within Groups	20831.2	58	359.159			
Total	31460.2	59				

## Appendix S: One-way ANOVA for B and Zn