DETERMINATION OF SELECTED HEAVY METAL IN ROAD DUST ALONG GAMBANG - KUANTAN ROAD

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ABSTRACT

Some heavy metals help important role in our body but it also can be a dangerous treat if it been taken for too much. The uncontrolled emission of heavy metal that been discharge by human activities can be transported by water, air and deposited to land surface as road dust. Due to we use road almost every day in purpose go to work or any event, the increases of heavy metal concentration in road dust are might affect human health through inhalation. Since 2009 there is much development and construction activities actively grow in kuantan, especially in Kuantan – Gambang road including industrial and residential area. Review from literature showed that heavy metal concentrations are greater at area closer to industrial and construction activities. It also shows that communities who live near highway might be having higher asthma and allergy rate. The objective of this study is to determine the concentration of heavy metal in road dust of Kuantan - Gambang road. Road dust samples were collected from several sites covering residential area, industrial area, airport, campus UMP, bus terminal and agriculture area. Heavy metals, including Cr (chromium), Mn (manganese), Fe (ferum), Ni (nickel), Zn (zinc), Pb (plumbum), Cu (cuprum) and Cd (cadmium) have been selected in this study. After sampling, the samples were heated in muffle furnace up to 550°C for 4 hours to remove any possible organic matter. After that, the samples were digested using aqua regia and were determined by using atomic absorption spectrometer (AAS). Results showed that heavy metals concentration in road dust samples were ranged from 0.01 μg/g to 60.00 μg/g. Sampling site with the highest concentration of heavy metals was the road that far from Kuantan. Meanwhile, for site that contain lowest concentration of heavy metals was the mining area at Gambang which located far away from Kuantan. In addition, cadmium and chromium were below the detection limit.

ABSTRAK

Sebahagian logam berat memainkan peranan penting dalam badan kita tetapi boleh juga menjadi berbahaya jika diambil terlalu banyak. Pembebasan logam berat yang tidak terkawal oleh aktiviti manusia dapat dipindahkan melalui air, udara dan terutama sekali tanah atau lebih khusus iaitu debu jalan. Disebabkan penggunaan jalan raya hampir setiap hari dengan tujuan untuk pergi bekerja atau peristiwa apapun. Ini menyebabkan peningkatan kepekatan logam berat dalam debu jalan berkadar langsung dengan kawasan yang hampir dengan Bandar. Dalam ekonomi baru di mana terdapat banyak pembangunan dan pembinaan yang giat dijalankan bermula tahun 2009 sehingga sekarang, terutamanya di kawasan kuantan-gambang. Kawasan industri, perumahan dan kawasan awam merupakan penyumbang besar pada masalah kesihatan dan pencemaran alam sekitar. Dapat disimpulkan bahawa kepekatan logam berat menjadi semakin tinggi jika semakin hampir dengan kawasan kegiatan industri dan pembinaan. Hal ini juga menunjukkan bahawa masyarakat yang tinggal berdekatan jalan raya kemungkinan besar mengalami asma dan alahan yang tinggi. Objektif utama kajian ini adalah untuk menentukan kepekatan logam berat dalam debu jalan di jalan kuantan-gambang. Sampel debu akan dikumpulkan dari beberapa kawasan yang telah dipersetujui meliputi kawasan perumahan, kawasan industri, lapangan terbang, kampus UMP, terminal bas dan kawasan pertanian sebagai kawasan kawalan. Di dalamnya berkemungkinan mengandungi logam berat seperti Cr (kromium), Mn (mangan), Fe (besi), Ni (nikel), Zn (zink), Pb (plumbum), Cu (tembaga) dan Cd (kadmium). Setelah selesai mengutip sampel, sampel debu jalan dipanaskan dalam tungku sehingga 550°C selama 4 jam untuk membuang kebarangkalian benda organik. Setelah itu, sampel dicerna menggunakan aqua regia dan ditentukan dengan menggunakan spektrometer serapan atom (AAS). Hasil penelitian menunjukkan bahwa konsentrasi logam berat dalam sampel debu jalan di dalam lingkungan 0.01 µg/g sehingga 60.00 µg/g. Kawasan ujian dengan konsentrasi tertinggi logam berat adalah jalan yang jauh dari Kuantan. Sementara itu, untuk kawasan yang mengandung konsentrasi terendah logam berat adalah dari area perlombongan di gambang yang terletak jauh dari Kuantan. Tambahan, untuk kadmium dan kromium, kedua dua elemen ini berada di bawah batas deteksi.

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LIST OF SYMBOLS

mg / L	Milligram per Litre
ppm	Parts per million
μg / g	Microgram per Gram

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
LOD	Limit of Detection
LOQ	Limit of Quantitation

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Metals generally can be divided into light metals and heavy metals. Light metals are metals that contain low atomic weight. Lithium, beryllium, sodium, magnesium and aluminium are harmless light metal in tiny quantity. Metals heavier than nickel are usually called heavy metals. Light metals are generally less toxic than heavy metals. Beryllium is toxic, but it is rarely found in large concentrations. Vanadium, not always counted as a light metal, is also toxic. Other light metals are toxic in large amounts. Metals are defined chemically as "elements which conduct electricity, have a metallic luster, are malleable and ductile, form cations, and have basic oxides" (Atkins and Jones, 1997). Heavy metal can be described as element that exhibit metallic properties and has an unstable electronic configuration. Due to its unstable orbital, its tend to donate or sharing electron between another element to reach equilibrium. Those heavy metal that release freely will react to atmosphere and some of them are dangerous to health or to the environment (e.g. cadmium, lead, chromium), some may cause corrosion (e.g. zinc, lead), and some metals are harmful in other ways. In addition, some of these elements are actually necessary for humans in tiny amounts (cobalt, copper, chromium, manganese, nickel) while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth (nickel, cadmium, copper, chromium).

Heavy metal pollution can arise from many sources but most commonly arises from the purification of metals, e.g., the smelting of copper, the preparation of nuclear fuels and electroplating. The sad thing about the pollution of the environment with heavy metals is that they can't be biologically degraded, they can only be transformed from one oxidation state or organic complex to another (Lone et al., 2008; Jing et al., 2007). Heavy metals are found naturally in the soil mostly in its complexes or bound form such as in $ZnS0_4$, ZnCl and Zinc Oxides. They enter the environment by human activities such as mining, purification of zinc, lead and cadmium, steel production, coal burning, burning of wastes, discharges from industrial effluents, excessive use of fertilizer, pesticide application and use of raw sewage waste in farming, (Lone et al., 2008; Okoronkwo et al., 2005; Jing et al., 2007). Through precipitation of their compounds or by ion exchange into soils and mud, heavy metal pollutants can localize and leave hidden in road dust. Incomplete reaction of inorganic materials from different urban sources is responsible for surface road dusts contamination with heavy metal.

Automobile exhaust, lubricating oils, atmospheric depositions, power plants, domestic heating systems, petrol and diesel engines, refuse burning and various industrial activities, concentrations of heavy metal in street dust are assumed to be influenced by traffic density and rate of deposition. Diesel vehicle exhaust, tire and pavement are expected to be the major contributors of heavy metal in road dust in Pahang state. Unfortunately, it has unconformities that there was a major difference in the Heavy metal profiles between locations rather than between size-fractions and sampling times. Heavy metal concentration in road dust was may be different according to the distance from the source of pollution.

1.2 Problem Statement

Air pollution is composed of many environmental factors. They include carbon monoxide, nitrates, sulfur dioxide, ozone, lead, secondhand tobacco smoke and particulate matter. Particulate matter, also known as particle pollution, is composed of solid and liquid particles within the air. There are different sized dust particles. Coarser particles affect the mouth, throat and nostrils but cannot be inhaled.

Fine and very fine particles can be inhaled and enter the lungs and respiratory tract, which is a health risk. A research professor in the division of atmospheric sciences at Nevada's Desert Research Institute said that Particles smaller than 2.5 microns go deeper into the lungs, where they can damage epithelial cells and even pass into the bloodstream. Particles larger than 2.5 microns can lodge in the upper respiratory area, where they may cause severe irritation. Effects may be especially pronounced in infants, the elderly, and those with pre-existing conditions such as asthma. Particles this size may also be linked to some respiratory cancers. Dust particles this small can elude all but the most specialized of filters. So those who live near unpaved roads aren't the only people at risk from these particles but vehicle passengers also are exposed, even if they ride with their windows rolled up. And the dust impacts not only the air, but the water as well, as it settles into nearby streams and rivers. A series of road dust particles will be investigate to evaluate the ratio between metal content in each fraction of particle size and total metal content.

1.3 Research Questions

This study embraces some research questions, which are;

1. What is a major source of heavy metals deposited on the main road of kuantan – gambang?
2. What is the relation between human activities and level of contamination of heavy metals in road dust?

1.4 Objective of the Study

Many heavy metals become bound to the surface of soil and roadside dust. Elevated emissions and their depositions over time can lead to anomalous enrichment, causing metal contamination of the surface environment (Pagotto et al., 2001; Sabiha et al., 2009). The objectives of this study are:

1. To measure the concentration of selected heavy metals in road dust of kuantan – gambang road

2. To compare distribution of heavy metals at different area (with different daily activities)

1.5 Rationale and Significance

Gambang - Kuantan road, which is also known as Jalan Gambang and Jalan Tanah Putih, is the major highway that connects Gambang to Kuantan. At Gambang exit, the roads interchange with Segamat - Kuantan highway and also the east coast expressway, connecting KL and Terengganu. Heavy traffic flow at this road has drawn public concern on the pollution and possible health effect. Therefore this study will focus on determination of selected heavy metals in road dust along Kuantan - Gambang road.

CHAPTER 2

LITERATURE REVIEW

2.1 Dust

Dust is an earth or other matter in fine, dry particles. Powdery earth or other matters in fine, dry particles are easily suspended in air, raised and wafted by the wind. Airborne particulate matter, ranging in diameter from 10 to 50 microns, is generated by activities such as cutting, crushing, detonation, grinding, and handling of organic and inorganic matter such as coal, grain, metal, ore, rock, wood. Industrial dust generated by cutting, drilling, grinding, or sawing (which are usually less than 10 microns in diameter) can pose health risks if inhaled and would be more hazardous due to its ability to embed deep into lungs and other tissue (Segerstedt and Forsberg, 2006). It is true that dust has been around since the dawn of time caused by wind sweeping across the desolate landscape.

This type of dust is scientifically described as particular matter. This is airborne debris that can adversely affect the health of people and the environment. The most common particulate matter is smaller than 10 micron in diameter and is called PM10. The second most common is PM2.5. This is debris that is smaller than 2.5 microns in diameter.

2.1.1 Road dust

Road dust has been acknowledged as a dominant source of PM10 (Segerstedt and Forsberg, 2006). Particles are also formed in the mechanical processes in the tire-road interface, brakes, and engine, but vehicles affect the concentrations of ambient airborne particles through exhaust emissions. Cadmium contaminations in the process of vulcanization were reported that the cadmium level in car tires is in the range of 20 to 90 μg/g (Yu et al., 2003). The emissions from vehicular traffic, heating systems, building deterioration, construction and renovation, corrosion of galvanized metal structures, sinking particles in air and etc. contribute directly to the road dust load (Howari et al., 2004; Al-Khashman, 2004). Particles deposited on or in the surrounding area of the road may be entering into air through vehicle-induced turbulence and shearing stress of the tires. A commonly used term for these particles is 'road dust'.

The quantity of dust that is produced by unpaved roads is five times greater than two other contributors, which are construction activities and wind erosion. Not only is dust from these roads a trouble, but they have been cited in many cases of respiratory illness for humans that live near areas in need of road dust control.

A study was conducted in the state of Iowa (Morgan, 2005) to see exactly how much an unpaved road without road dust control and associated traffic would cause particulate air pollution. The results showed that for every vehicle that travels over an unpaved road for one mile, one ton of dust is created annually. This is interpreted as for every 500 trucks or cars that travel over 100 miles of these roads that 50,000 tons of dust is thrown up into the surrounding air every year. This also means that for every mile of unpaved road lacking road dust control, that a ton of material from that road is removed every year for every automobile that travels on it. Without the help of wind, this nuisance dust can travel up to 500 feet from the road into the air. Not only is this affecting the inhabitants near a busy unpaved road, but this dust also negatively impacts the growth of plant life. Besides that, study by Chong (1986) showed that stainless steel and alloy steel contain Fe, Cr, Co, Al and Cu. Exhaust emission from both gasoline and diesel fueled vehicles contain variable quantities of these elements

2.2 Heavy metals

Metals are defined chemically as "elements which conduct electricity, have a metallic luster, are malleable and ductile, form cations, and have basic oxides" (Atkins and Jones, 1997). The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb).

Heavy metal is a general collective term which applies to the group of metals and metalloids with an atomic density greater than 4 g/cm^3 (Duffus, 2002). Although it is a loosely defined term, it is widely recognized and usually applies to the common contaminants of terrestrial and freshwater ecosystems. Heavy metals are elements which occur naturally in the Earth's crust. They are therefore found naturally in soils and rocks with a following range of natural background concentrations in soils, sediments, waters and organisms. Anthropogenic releases can give rise to higher concentrations of the metals relative to the normal background values. The heavy metals which are included in air pollution information system (APIS) are cadmium, chromium, copper, mercury, lead, zinc, arsenic, boron and the platinum group metals, which comprises Platinum, Palladium, Rhodium, Ruthenium, Osmium, and Iridium.

2.2.1 Sources of heavy metal in environment

Although heavy metals differ in their chemical properties, they are used widely in electronic components, machinery and materials. Two main sources of road dust, and consequently of the heavy metals found therein, are deposition of previously suspended particles (atmospheric aerosols) and displaced soil (Ferreira and DeMiguel, 2005). Consequently, they are emitted to the environment from a variety of anthropogenic sources to supplement natural background geochemical sources. Some of the oldest cases of environmental pollution in the world were caused by heavy metal extraction and use, for example, copper, mercury and lead mining, and smelting.

The amounts of most heavy metals deposited to the surface of the Earth are many times greater than depositions from natural background sources. Combustion processes are the most important sources of heavy metals, particularly, power generation, smelting, incineration and the internal combustion engine (Battarbee et al 1988; Duce et al. 1991; Galloway et al. 1982; Hutton & Symon 1986; Nriagu 1989; Nriagu & Pacyna 1988).

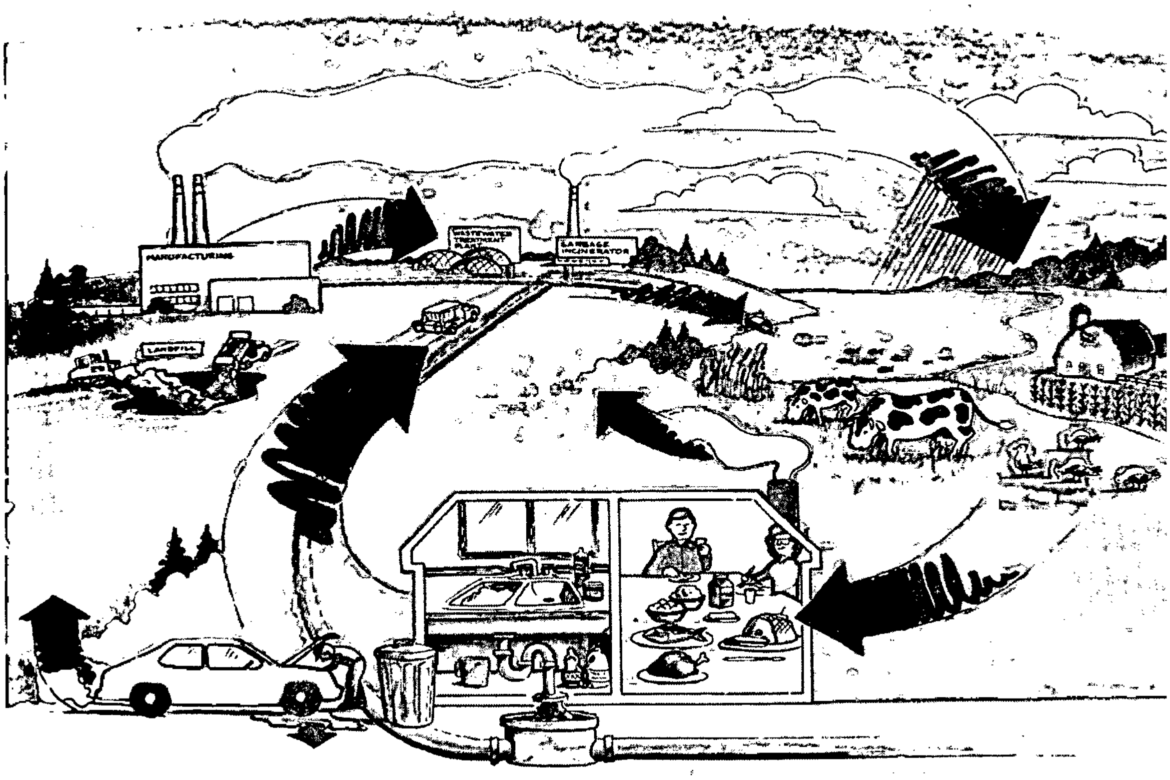

Figure 2.1: The sources of heavy metal

Many heavy metals become bound to the surface of soil and roadside dust. Elevated emissions and their depositions over time can lead to anomalous enrichment, causing metal contamination of the surface environment (Pagotto et al., 2001; Sabiha et al., 2009). The sources of heavy metal are shown in figure 2.1.

2.2.2 Health Effect of heavy metal

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination, high ambient air concentrations near emission sources, or intake via the food chain. Heavy metals accumulate in organisms as a result of direct uptake from the surroundings across the body wall. Uptake via food is most important in terrestrial organisms and it may also be important in the aquatic environment. Dietary uptake can include heavy metals adsorbed on particulates present on the surface of leaves etc, which have not been absorbed by the plant.

Heavy metals are dangerous because they tend to bioaccumulate. It means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized). The free ion is generally the most bioavailable form of a metal, and the free ion concentration if often the best indicator of toxicity. However, there are exceptions, such as the well known case of mercury, where the organic form, (methylmercury) is more toxic than the inorganic ion. Metals apply toxic effects if they enter into biochemical reactions in the organism and typical responses are inhibition of growth, suppression of oxygen consumption and destruction of reproduction and tissue repair.

Metal contamination in street dust has a high vulnerability of causing cough in both children and adults during inhalation. Inhalation of siliceous dust causes siliceous disease of the lungs (Leke, 1999). Besides, chromium and its compounds are known to cause cancer of the lungs, nasal cavity and para nasal sinus and suspected to cause cancer of the stomach and larynx (ATSDR, 2000).

2.3 Spectroscopy

Spectroscopy is the use of the absorption, emission, or scattering of electromagnetic radiation by matter to qualitatively or quantitatively study the matter or to study physical processes. The matter can be atoms, molecules, atomic or molecular ions, or solids. The interaction of radiation with matter can cause redirection of the radiation and/or transitions between the energy levels of the atoms or molecules. The technique is as below:

- Absorption: A transition from a lower level to a higher level with transfer of energy from the radiation field to an absorber, atom, molecule, or solid.
- Emission: A transition from a higher level to a lower level with transfer of energy from the emitter to the radiation field. If no radiation is emitted, the transition from higher to lower energy levels is called nonradioactive decay.
- Scattering: Redirection of light due to its interaction with matter. Scattering might or might not occur with a transfer of energy, i.e., the scattered radiation might or might not have a slightly different wavelength compared to the light incident on the sample.

2.3.1 Atomic Absorption Spectroscopy (AAS)

Atomic-absorption spectroscopy (AAS) uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporized in a flame or graphite furnace. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption. Applying the Beer-Lambert law directly in AAS is difficult due to variations in the atomization efficiency from the sample matrix, and nonuniformity of concentration and path length of analyte atoms (in graphite furnace AAS). Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration. Figure 2.2 shows the schematic diagram of atomic absorption spectroscopy (AAS).

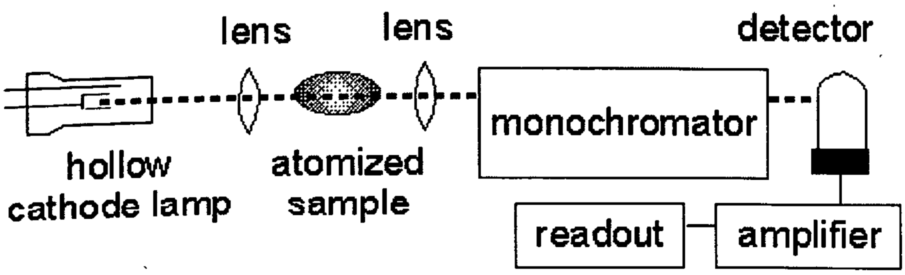

Figure 2.2: Schematic diagram of atomic absorption spectroscopy (AAS)

2.3.1a Light source

The light source is usually a hollow-cathode lamp of the element that is being measured. Lasers are also used in research instruments. Since lasers are intense enough to excite atoms to higher energy levels, they allow AAS and atomic fluorescence measurements in a single instrument. The disadvantage of these narrow-band light sources is that only one element is measurable at a time.

2.3.1b Atomizer

AAS requires that the analyte atoms be in the gas phase. Ions or atoms in a sample must undergo desolvation and vaporization in a high-temperature source such as a flame or graphite furnace. Flame AAS can only analyze solutions, while graphite furnace can accept solutions, slurries, or solid samples.

Flame AAS uses a slot type burner to increase the path length, and therefore to increase the total absorbance (Beer-Lambert law). Sample solutions are usually aspirated with the gas flow into a nebulizing/mixing chamber to form small droplets before entering the flame.

The graphite furnace has several advantages over a flame. It is a much more efficient atomizer than a flame and it can directly accept very small absolute quantities of sample. It also provides a reducing environment for easily oxidized elements. Samples are placed directly in the graphite furnace and the furnace is electrically heated in several steps to dry the sample, ash organic matter, and vaporize the analyte atoms.

2.3.1c Excitation

A flame provides a high-temperature source for desolvating and vaporizing a sample to obtain free atoms for spectroscopic analysis. In atomic absorption spectroscopy ground state atoms are desired. For atomic emission spectroscopy the flame must also excite the atoms to higher energy levels. The following table lists temperatures that can be achieved in some commonly used flames.

Table 2.1: List for temperature of some common flame

Temperatures of Some Common Flames		
Fuel	**Oxidant**	**Temperature K**
Hydrogen	Air	2000-2100
Acetylene	Air	2100-2400
Hydrogen	Oxygen	2600-2700
Acetylene	Nitrous Oxide	2600-2800

2.3.1d Light separation and detection

AAS use monochromators and detectors for uv and visible light. The main purpose of the monochromator is to isolate the absorption line from background light due to interferences. Simple dedicated AAS instruments often replace the monochromator with a bandpass interference filter. Photomultiplier tubes are the most common detectors for AAS.

2.4 Previous studies

These are the several studies that have been used to determine the heavy metal in road dust, including their location and result.

Table 2.2: Table of previous study in different locations

References	Location	Result
Apeagyei E., Michael S. Bank, John D. Spengler (2011)	Massachusetts cities: Boston, Somerville and Greenfield.	Zn was the only significant element found in tire dust, accounting for 0.02% - 0.06% of the PM10 mass
Trang T.T. Duong & Byeong-Kyu Lee (2011)	12 urban locations in the metropolitan city of Ulsan, Republic of Korea	14.1 - 34.6% for Cd, 19.3 - 45.5% for Cu, 11.1 - 20.7% for Pb, 8.8 - 18.7% for Zn 13.5 - 23.5% for Ni most road dust particles were between 180 and 850 mm
Wei B., Jiang F., Li X., Mu S. (2009).	the city of Urumqi, the capital of Xinjiang Uygur Autonomous north-west Region of China	60% of all samples had high pollution levels with IPI in the range from2 to 5, while low pollution levels with IPI lower than 2 accounted for about 35.9% of all samples.
Mohammed A. Khairy, Assem O. Barakat, Alaa R. Mostafa, Terry L. Wade (2011).	7 different sites in the delta region, Egypt	Concentrations of Al ranged an average concentration of 30,260 mg/kg, whereas concentrations of Fe ranged an average concentration of 32,041 mg/kg

Cumulative frequency distribution graphs showed distribution of Fe, Ba, Cu, and Mo were similar regardless of road traffic rating. However, Zn, Ti, and Zr varied significantly ($p < 0.05$) with traffic ratings of roadways (heavy > moderate > low traffic). Fe, Ba, Cu, and Mo also had similar distributions regardless of road class while composition of Zn, Ti, and Zr varied significantly across road class ($p < 0.05$) (Major roads > Minor roads > highway). In comparing urban road dust to rural road dust (Apeagyei, 2011). The concentrations of heavy metals in the road dust from the circulation roads were dependent upon their traffic volume, vehicle speeds and the surrounding environment which may have included industrial emissions. The lowest heavy metal concentrations among the different rotary areas were identified in the samples from the riverside rotary which had high atmospheric dispersion of dust to the riverside and air dilution by winds from the riverside (Trang, 2011).

Most of the road dust samples were in low levels of pollution in the new urban area and city side. Moreover, the areas closed to manufactories were also in high levels of pollution. These trends can be attributed to urbanization, distribution of industrial areas and commercial areas. The integrated pollution index (IPI) is defined as the mean value of the pollution index (PI) of an element. It is classified as: IPI≤1 low level of pollution; 1bIPI≤2 middle level of pollution; IPIN2 high level of pollution. Extremely high pollution levels with IPI higher than 5. These road dust sample sites with extremely high pollution levels were all located in the areas closed to manufactories such as petrochemical factory, power plant, tire manufacturing plant, cement plant, textile mill or others (Wei, 2009).

High concentrations of trace metals were observed in the road dust samples from Delta region, Egypt, which were higher than concentrations recorded worldwide in major developed cities for most of the investigated metals. The output of the PCA revealed that Al, Fe, Be and Mn are produced from natural sources and that all the other metals were produced from anthropogenic activities such as industrial, construction and traffic emissions. Road dust samples were found to be heavily to extremely contaminate with Cd, Pb, Sn and Zn when compared to the background values reflecting the influence of the traffic and industrial activities on alteration of the atmospheric quality of the Delta region (Mohammed, 2011).

CHAPTER 3

METHODOLOGY

3.1 Sampling locations

Several sites were selected for the study along the major roads from gambang to kuantan. Several replicate samples were collected from the sampling sites as shown in Figure 1. It shows the major roads. Street dust samples were taken from bus terminal, airport, industrial area, residential areas and agricultural area.

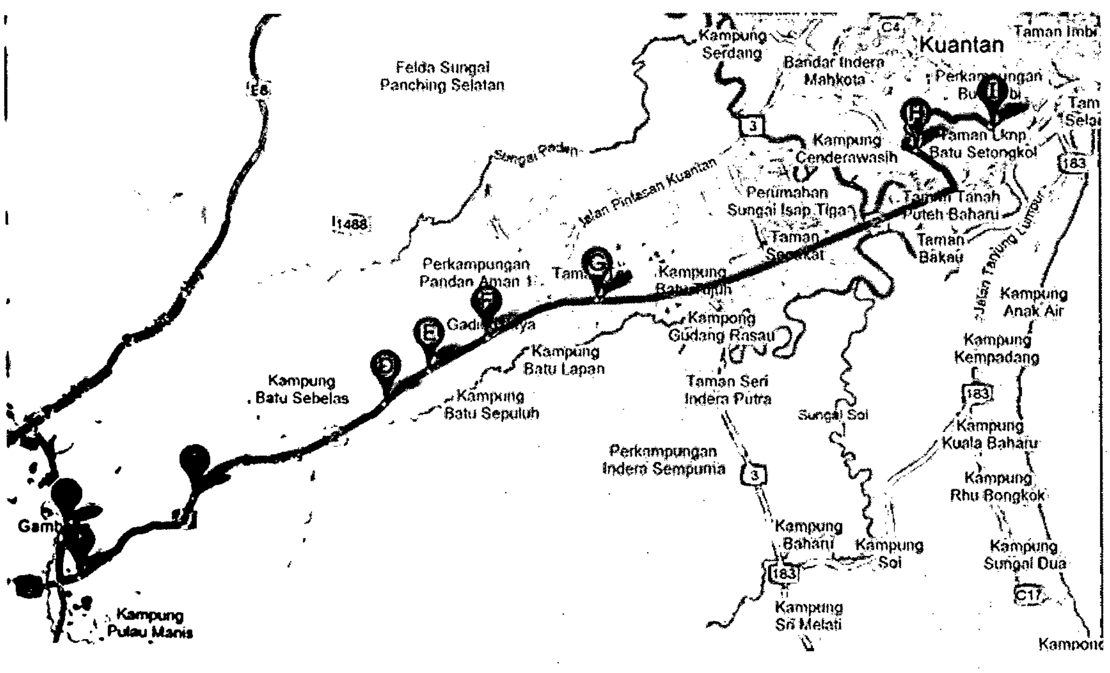

Figure 3.1: The road from gambang to kuantan