Influence of Vehicular Emission on Road Dust in Urban and Rural Roads

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CERTIFICATION OF APPROVAL

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January 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

The increasing amount of motored vehicles in Malaysia is believed to be a contributor to the drastic increment of heavy metals contamination in the environment especially at high traffic density area. This critical domestic environmental issue need for more detailed information to have an understanding on the problem and consequently triggers the proper pollution prevention to be undertaken to avoid any adverse effect to human's health. Lead (Pb), Copper (Cu), Nickel (Ni), Chromium (Cr) and Zinc (Zn) are elements that many researchers claims as the major heavy metals contributed by vehicular emissions. In order to investigate the influence of vehicular emissions towards the level of heavy metals concentration in the environment, road dust samples from specified urban and rural locations are collected which represent high and low traffic density areas respectively. The concentration of Pb, Zn, Cu, Cr and Ni from the road dust samples will be analyzed using Atomic Absorption Spectroscopy (AAS). The experimental results shows that as the number of motored vehicles increases on the road, the concentrations of Zn and Cr in the road dust also increase. Thus, it shows that the vehicular emission could be a direct contributor and responsible to the emission of heavy metals to environment particularly Zn and Cr. Ni contents in road dust are too low to be interpreted and analyzed by AAS system owing to its high mobility property. Meanwhile, Pb concentration in road dust shows that the vehicular emission is not a sole contributor to the Pb level in road dust as it might be originated from various sources such as industrial and agricultural activities

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1.0 INTRODUCTION

1.1 Background

Vehicular emission is a long debated environmental issue since the Industrialization Era. Malaysia as one of the developing nations in the world and listed as one of the Asian Tigers in term of economic growth could not run away from the issue of vehicular emission. Statistic shows that Malaysia experiences drastic increases in the number of motored vehicles on the road. Malaysian Institute of Road Safety Research (MIROS) issued a statistic that the number of registered vehicles in Malaysia is approximately 9 million in 1997 and increased to 17 million in 2007. This significant increase in the amount of motored vehicles in Malaysia is believed to be the major contributors to the increment of heavy metal contamination in the road dust. Hence, this study is undertaken to study the influence of vehicular emission towards the level of heavy metal contents in road dust. The concentration of heavy metals in road dust for high and low traffic roads are compared to investigate the effect of the increment of the number of vehicles on the road from which high and low traffic densities are represented by the urban and rural roads respectively.

Road dust is the indicators of heavy metal contamination from atmospheric deposition Christoforidis (2009). It is a complex mixture of multiple source contributions; anthropogenic materials such as automobile/truck exhaust particles, lubricating oil residues, tire wear particles, weathered road surface particles, brake lining wear particles, and natural biogenic materials such as leaves and other plant matter that can pulverized by the passing traffic (Rogge et al. 1993a). All of these sources are direct contributors to road dust (Rogge et al, 1993b). Hence, road dust deposition from vehicular emissions provides a record of the combustion, mechanical abrasion, and automobile and road wear and tear. These heavy metals are emitted into the atmosphere where some can be absorbed onto the particulate phase and other incorporated in road dust. The particulate will then settle to the ground by dry or wet deposition. Once emitted, the heavy metals can reside in the environment for hundreds of years unless they are partially transported through surface runoff and ends in the aquatic environment (Jiries, 2003). Furthermore, Christoforidis (2009) insisted that the road dust investigation is of particular importance for two main reasons. First, road dust is freely being inhaled by those traversing the roads and those residing within the vicinity of the roads. The more the dusts on such roads become contaminated with heavy metals, the more such people are exposed to health hazards associated with such heavy metals. Secondly, when rains are received, the dust usually gets discharged in the adjoining marine environment, could seriously pollute the water and concentrate in the surface sediments of the coastal area. This might prove toxic to marine life, and at worst it may contaminate fish or shellfish, which could have adverse direct impacts on the health of individuals that consume seafood

Lead (Pb), Zinc (Zn), Copper (Cu), Nickel (Ni) and Chromium (Cr) are five major heavy metals that are closely related with motored vehicles (Al Kashman, 2007). Sources of these metals are fossil fuel and lubricating oil combustion, as well as wear and tear of the road surface and tires through traffic activity. Harrison *et al*, (1981) reported that Pb, Cu, and Zn are essential for motored vehicle engine and released onto the roadside environment due to motor abrasion and fuel combustion. Hence, it is obvious that the vehicular emission contributes to the heavy metals contamination in the environment.

In some cities, the heavy metals mentioned might originated from steel plants, industrial activities, foundries, waste incinerating plants and energy production plants (Espinosa et al, 2004; Shah et al, 2006; Querol et al, 2007). But, in the centre of urban areas, road traffic is likely to make the most important contribution to people's exposure (Johansson et al, 2009). Al-Kashman, (2007), also emphasized that Pb, Zn, Cu, Ni and Cr in road dust are most likely attributed from traffic activities. Hjortenkrans (2006) claimed that metals dispersed in the anthrosposphere are caused by the traffic sector. For example, the traffic sector in Sweden is estimated to contribute about 90% of cadmium (Cd), 40% of Cu, more than 99% of both chromium (Cr) and Ni, 85% of Pb, and 80% of Zn. The European Environmental Agency (EEA, 2004) has also highlighted that the road traffic is a significant source of metal emissions to environment.

As mentioned earlier, Pb, Zn, Ni, Cu and Cr are the major metals that are highly associated with the traffic density and hence could be the parameter to investigate the influence of vehicular emission towards the level of heavy metals concentrations in road dust. However, some people may argue the relevance of Pb to be used as such parameter because it has been banned to be used as an anti-knocking additive in fuels worldwide. For instance, the European Union (EU) has banned the use of Pb since 2000. In Malaysia, the leaded fuel is totally banned in

1998 which caused environmental lead exposure dramatically decreased (Zailina *et al*, 1998). However, Hidayah, (2008) stated that the use of unleaded fuel does not put to stop the use of lead compounds in motoring activities. This compound could still be detected in the environment, fortunately in a smaller amount owing to its use as anti-wear agent in lubricant oils for engines. Hidayah, (2008) also emphasized that Pb emissions are still one the most important parameters for the study of influence of traffic activities as Pb could still be traced in the road dust samples.

This study is necessary to assess the environmental pollution especially in Malaysia. The results obtained from the study can be used as a basis for controlling, managing and reducing the pollution level as emphasized by Tuzen (2003) which stated that the determination of metal in environmental samples including dusts, plants, soil and surface water is very necessary for monitoring environmental pollution.

1.2 Problem Statement

The main issue that Malaysia experiences currently is regarding the significant increment in the number of motored vehicles on the road. From various studies conducted as mentioned in the background section, the heavy metals such as Pb, Zn, Cu, Ni and Cr are closely associated with the vehicular emissions, (Al Kashman, 2007). The current problem in Malaysia is that there is a lack of study, information and standards regarding the effect of vehicular emission on the contents of heavy metals in road dust. Currently, the domestic studies of vehicular emission are focus more on the emission of organic compounds such as n-alkanes and polycyclic aromatics hydrocarbons (PAH) in particulate matters (PM), which are the fine particles with an aerodynamic diameter of 10 μm or less that settle very slowly and remain suspended in the atmosphere for considerable time (Omar et al, 2007). The study of heavy metals contents in road dust seems underestimated and neglected by the local researchers and environmentalist. Therefore, this study is conducted to contribute and provide data and information for the present issue of environmental pollution in Malaysia. Furthermore, the exposure to high concentrations of heavy metals in environment cause health hazard to human being such as adversely affecting the nervous, blood forming, cardiovascular, renal and reproductive systems. Other includes reduced intelligence, attention deficit and behavioral abnormality, as well as its contribution to cardiovascular disease in adults Christoforidis (2009). It becomes more critical issue in Malaysia because large population is likely to reside in the location alongside roadways and highways which are highly exposed to heavy metals contamination. Consequently, an immediate study should be conducted to assess population exposure and health effects.

1.3 Objectives

1. To investigate the influence of vehicular emission towards the level of heavy metals in the environment.
2. To investigate the influence of high and low traffic density towards the level of heavy metals contamination in road dust represented by urban and rural roads respectively.
3. To investigate the concentrations of heavy metals in road dust that is related to vehicular emission.

1.4 Scope of Study

The study will focus on obtaining the concentration of heavy metals which are Pb, Cu, Ni, Zn and Cr in the road dust in the specified points of urban and rural roads. Urban and rural roads reflect the high and low traffic densities respectively. Some of the heavy metal emitted by vehicular emissions will be deposited and incorporated in road dust and will settle to the ground by dry or wet depositions and could reside for hundreds of years. Hence, road dust is collected to investigate the heavy metal concentrations. The results obtained from experimental work are used to assess the influence of vehicular emission towards the level of heavy metals contents in road dust.

2.0 LITERITURE REVIEW

Well-known road traffic related metal emissions sources of concern are brake linings, tyres, road pavement and exhaust fumes. Pb, Cu, Ni, Zn and Cr are among the commonly used elements in automobile industries, either as the main elements for parts or components fabrication in a vehicle or as additives such as lubricants for engine operation.(Hidayah, 2008). Traffic activities also appear to be responsible for the high levels of Pb, Zn, Cu, Barium (Ba), Cr (Manno, 2006). Al-Khashman (2007) has investigated the concentrations of metals Fe, Zn, Cu, Cr, Pb, Cadmium (Cd), Ni, Manganese (Mn) and Cobalt (Co) from 140 street dust samples which were collected from Aqaba city, Jordan which were analyzed using flame atomic absorption spectrophotometry (AAS). The results of the study show that the highest level of metal concentration was found in the samples from heavy traffic roads while the lowest level of metal ions were noted in the street dust samples from hospital, health centers and school gardens. According to Hidayah (2008), Al-Khashman (2007), Manno (2006), Pb, Zn, Ni, Cu and Cr are the group of metals that are closely related with vehicular emission. Therefore, the concentrations of those metals should be the parameters to investigate the influence of vehicular emission on the level of heavy metals in the road dust.

Pb compounds, particularly lead tetraethyl $(C_2H_5)_4Pb$, are known to be effective additive in fuels as an antiknocking agent. The use of such compound however, ends up leaving an enormous amount of lead oxide, a very toxic metal, into the environment (Hidayah, 2008). This set out the effort, by petroleum companies to find alternative additive of the same effectiveness, which results in the use of unleaded fuels. In this type of fuels, agents such as benzene and toluene, having better ability to boost octane number in fuel replaces the use of lead compounds as antiknocking agents. Later, enforcement benzene and toluene as antiknock agents took place immediately following the affective of Clean Air Act 1990. Full use of unleaded fuels however, does not put to stop the use of lead compounds in motoring activities. This compound could still be detected in the environment, fortunately in a smaller amount owing to its use as anti-wear agent in lubricant oils for engines (Hidayah, 2008). In Sweden, Pb content is mainly a historical residue from the combustion of petrol (Hjortenkrans, 2006). Li et al (2004) claims that the concentration of Pb in Hong Kong is related to Hong Kong’s high traffic volumes. Although Pb has been banned in petrol for a number of years, the concentration of Pb in urban soils still reflects the significance degree of historical Pb contamination and the long half-life of Pb in soils. Therefore, despite its phasing-out and observed decreasing trend in concentration, Pb remains a significant indicator to study the effect of vehicular emission towards the road dust contents.

Zn compound is used in the lubricant oil as Zinc dialkyldithiophosphate (ZDDP) agent which provides additional protection under extreme-pressure or in a heavy-duty performance situation. (Hidayah, 2008). Its other functions are to protect the lubricant itself from oxidative breakdown and to prevent the formation of deposits in engines in the lubricating oil. The lubricants' function is to smooth each component movements as well as to prevent damages by creating a layer of oil on engine surfaces and have the ability to provide protection even under great pressure (Hu, 2002). Zn may be also derived from mechanical abrasion of vehicles and from tyres of motored vehicles (Manno, 2006). According to Jiries (2003), a very high concentration of Zn was found in closed car parking areas although higher traffic densities existed in the city center and tunnels. This can be attributed to the wear of tires.

Ni is also used for plating the outer part of a vehicle such as tyre rims. It is also one of the elements used to fabricate a special alloy for plating surfaces of cylinders and pistons of an engine. The plated surfaces does not only became long lasting but also resistant to high heat, thus providing a very good platform for heat conductivity as well as offers resistance from damages and scratches (Ward 1997). Moreover, Ni pollution on a local scale is caused by emissions from vehicle engines that use Ni gasoline and by the abrasion and corrosion of Ni from vehicle parts.

Cu, it is one of the elements used in spark plugs. The demanded criteria for spark plug are for it to be long lasting and capable of igniting in any condition. Thus, Cu is the element commonly used as an electrode in spark plugs as it is able to fulfill all of the demanded criteria. Cu compounds is also used in lubricants as anti-wear agent by providing a protective layer on engine surface to reduce friction and prevent damages due to continuous rubbing between engine parts (Hidayah, 2008). Cu, is also used in the brakes to control heat transport (Manno, 2006). Furthermore, Cu in the street dust was indicated by research as being due to corrosion of metallic parts of cars derived from engine wear, thrust bearing, brushing, and bearing metals (Al-Khashman, 2007). Johansson et al (2009) claims that Cu emission is due to brake wear as the locations that record high concentration of Cu are road traffic crossing, sloping road and traffic light areas that requires the use of brake to control the maneuvers of vehicles.

Cr in dust is associated with the chrome plating of some motor vehicle parts. (Al-Shayep and Seaward, 2001). Johansson et al (2009) claimed that brake wear and exhaust emission are the important sources of Cr. Affum et al (2008) stated that Cr might originated from lubricating oils and car metal plating and could therefore contribute to roadside pollution. From various study mentioned, Cr might originated from various aspect of vehicle which has potential to pollute the enviro8ent.

One of the important properties that greatly affect the concentration of heavy metals in road dust is the mobility property of such heavy metals. Schafer et al (1998) have classified several heavy metals according to its mobility properties. He observed that mobility properties of Pb are the lowest, followed by Zn, Cu and lastly Ni. Ni has the highest mobility and is the easiest to be transferred or transported from one medium to another. With the mobility properties, it is important to be aware of the poisoning factors possess by each element. Baker (1993) stated that there are various transport pathways of heavy metals such as airborne dust, coating of edible food, dissolution in surface and ground water and the particles containing heavy metals.

It is undeniable that certain heavy metals, such as Cu, Zn and Ni are required by our body to maintain a good health. Biological demand for these elements however, is in trace level and unnecessary entry of these elements at a high concentration from the environment into any biological system will cause adverse health effects. Existence of such elements in any biological system: human, animals or plants, however does happen either through a deliberate introduction, such as for medical reasons in human or through contamination of the environment, in animals and plant. (Hidayah, 2008). Medical data suggests that it is the fine dusts which becomes deeply imbedded in human lung tissue, causes respiratory problems, and exacerbates other cardiovascular diseases (Miller et al 1979; Utell and Samet 1996). Some trace metals such as Cu and Zn at small amounts are harmless, but some mainly Pb, As, Hg and Cd even at extremely low concentrations are toxic and are potential cofactors, initiators or promoters in many diseases and cancer (Dockery and Pope, 1996; Willers et al, 2005). Baragli, 1998 elaborate further that young children are more likely to ingest significant quantities of dust than adults because of the behavior of mouthing non-food objects and repetitive hand/finger sucking. Children also have much higher absorption rate of heavy metals from digestion system and higher hemoglobin sensitivity to heavy metals than adults. Acu-Cell Nutrition website lists the adverse health effect of overecposure of Zn, Ni, Pb, Cu and Cr to human being.

Table 2.1; The health effect of overexposure of Zn, Ni, Pb, Cu and Cr.

Heavy Metals	**Health effect of overexposure**
Zn	Skin irritation
	Anaemia
Ni	Allergy reactions such as skin rashes
	Irritant contact dermatitis
Pb	Anaemia
	Damage of kidneys and brain cells
	Miscarriage and subtle abortions
	Disruption of nervous system
	Behavioral disruptions of children such as aggression Impulsive behavior and hyperactive
Cu	Physical and mental fatigue
	Sleep disorders
	Depression and other mental problems
	Schizophrenia
Cr	Spinal / joint degeneration
	Depressed immune system
	Lymphatic swelling

3.0 METHODOLOGY

3.1 Sampling Location

3.1.1 Urban Roads

1. Medan Kidd Bus Station, Ipoh.

Medan Kidd Ipoh at Jalan Leong Boon Swee, Ipoh is selected to be a sampling of urban location. Ipoh is capital city of Perak State, Malaysia. It is the second largest city in Malaysia. Medan Kidd bus station Ipoh is one the major and oldest bus station in Ipoh that handles buses and taxis. It is a very busy area with Perak Roadways bus station and Ipoh Railways Station nearby. There is a roundabout besides bus station which reduces traffic speeds and contributes to traffic congestion. There are also a lot of shops, workshops, offices and school surrounding the bus station which contributes to the heavy traffic in that area. Thus, two points are selected to collect the road dust samples which are the pave way near the bus station and area inside the Medan Kidd Bus Station which are congested with buses and taxis.

Figure 3.1: The front view image of Medan Kidd Bus Station, Ipoh

2. Medan Gopeng Bus Station, Ipoh

The Medan Gopeng Bus Station is the second busiest bus station after Medan Kidd bus station in Ipoh that handle express buses which travel around peninsular Malaysia. Along the roads of Medan Gopeng bus station, there are three junctions with the traffic lights which slow down the traffic speed and cause heavy traffic in that area. There are also a lot of shops, banks, offices and fast food restaurants besides and adjacent to the bust station. Therefore, there are two points selected at this location, the first point is the bus station car-park while the second point is inside the bus station.

Figure 3.2: The location of road dust sampling at Medan Gopeng Bus Station car-park, Ipoh

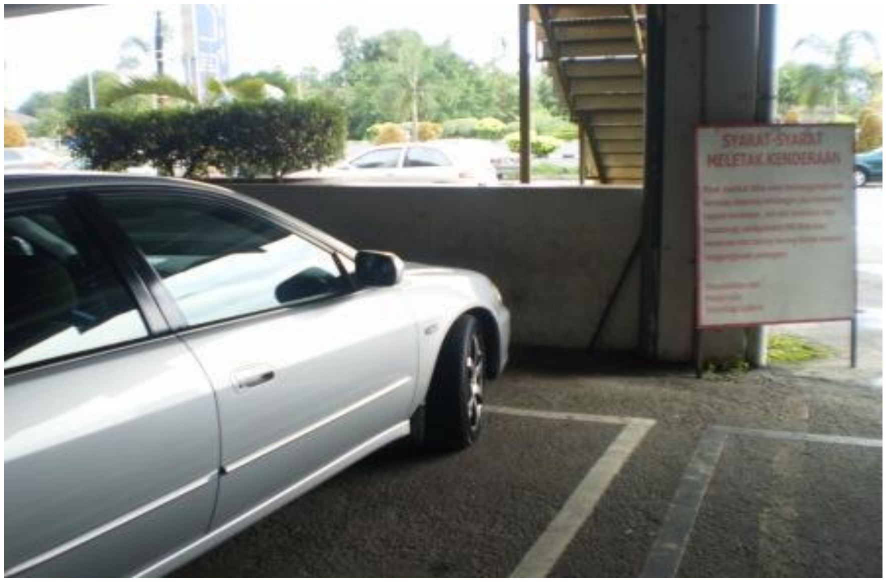

Figure 3.3: Other view of the location of road dust sampling at Medan Gopeng Bus Station car-park, Ipoh

Figure 3.4: More clear view of the point of road dust sampling at Medan Gopeng Bus Station car-park, Ipoh

3. Simpang Pulai Road

Figure 3.5: The location of road dust sampling at Simpang Pulai roadside

Figure 3.6: Another view of the location of road dust sampling at Simpang Pulai roadside

This road of Simpang Pulai is the north entrance to the capital city of Ipoh near North-South Highway. The traffic of this road is heavy with tankers, trucks and light vehicles heading to the industrial and residential areas at the outskirt of Ipoh. The conditions during the sampling are non-wind and cloudy. There was the sampling took place about 1.5 m along the roadside and 50 cm from the paved road. There was, no rain recorded on the day of sampling and the day before.

3.1.2 Rural Area

The sampling location for rural area was at Kampung Kubang Condong, Bota Kanan, Perak. This village is the midway from Universiti Teknologi PETRONAS to the historical place of Pasir Salak, Perak. The location is remote from heavy traffic influence and industrial activities which is suitable for rural-type roads. There are three points selected for sampling the road dust. The sampling took place in cloudy and non-wind condition and no rain recorded on the day of sampling and the day before.

Figure 3.7: First point (Rural 1) for rural area sampling at Kg Kubang Condong, Bota Kanan, Perak.

Figure 3.8: Second Point (Rural 2) for rural area sampling (paddy field) at Kg Kubang Condong, Bota Kanan, Perak.

Figure 3.9: Third point (Rural 3) for rural area sampling at Kg Kubang Condong, Bota Kanan, Perak.

Therefore, to summarize all the points of road dust sampling locations, the results are tabulated below:

Table 3.1: List of sampling locations for road dust samples

Sample No.	**Sampling Points**	**Type of roads**
1	Kg. Kubang Condong, Bota Kanan (Rural 1)	Rural
2	Kg. Kubang Condong, Bota Kanan (Rural 2)	Rural
3	Kg Kubang Condong, Bota Kanan (Rural 3)	Rural
4	Medan Kidd Pave way	Urban
5	Medan Kidd Bus Station	Urban
6	Simpang Pulai Road	Urban
7	Medan Gopeng Car-park	Urban
8	Medan Gopeng Bus Station	Urban

3.2 Sampling Methods

Based on Hidayah Shahar *et al* (2008) and Al-Khashman (2007), the sampling procedure as below:

1. For each location, the road dust is collected at road side or road edges using the plastic brush, tray and container. The sampling point is determined for each road location and recorded. The road dust is collected along 5 m of the road. The samples will be kept in airtight bottles or bags. The sampling points are dictated on the container. Safety precaution is required during sampling task especially at high traffic area.
2. Samples are kept into the plastic bag and sent to the laboratory for heavy metals analysis.
3. Samples are left to dry at room temperature for 3 days. The weights of the samples are recorded before and after the air drying process.

Figure 3.10: The samples are air dried for 3 days to remove moisture from soil pellets

3.3 Experimental Procedure

Based on Hidayah Shahar *et al* (2008) and Chen et al (2001), the sampling procedure is per below:

1. Samples are dried further using the oven for 24 hours long. The weight of the road dust is recorded.
2. Samples are sieved with 2-mm plastic sieve to remove extraneous matter such as small pieces of brick, paving stone, and other debris. Care is to be taken to reduce the disturbance of the fine particles, which are readily lost by resuspension.
3. For each sample, 1.0 g of the sieved road dust is weighed and divided into two more portions called duplicate.

Figure 3.11: Road Dust Samples being measured as required using weight balance

4. 12 ml of aqua regia solution (1 HNO_3 and 3 HCL) is added to the sample. The mixture swirled slowly and left for a few minutes until bubbles from the reaction appeared. Figure below is the aqua regia solution prepared.

Figure 3.12: The solution of Aqua regia which being prepared in 1 Litre volumetric flask

5. The mixture is heated until it is quite dry which take about 3 hours for aqua regia digestion to complete using hot plate methods, Chen et al (2001)

Figure 3.13: The road dust samples being added with aqua regia solution before digested using hot-plate method

Figure 3.14: The solution of road dust sample is digesting using hot plate to extract the heavy metals

6. The mixture is added with 20 ml of 20% nitric acid (HNO_3) when it is quite dry.
7. The mixture is filtered using filtration funnel and Whatman filter and the residue is diluted with de-ionized water in the 100 ml volumetric flask.

Figure 3.15: The digested solution is being filtered using filtration funnel and Whatman filter paper

8. All of the digestion procedures are done in the fume hood.
9. The final solution is analyzed using the Atomic Absorption Spectroscopy (AAS). The detail procedure to use the AAS could be viewed at Appendix I.

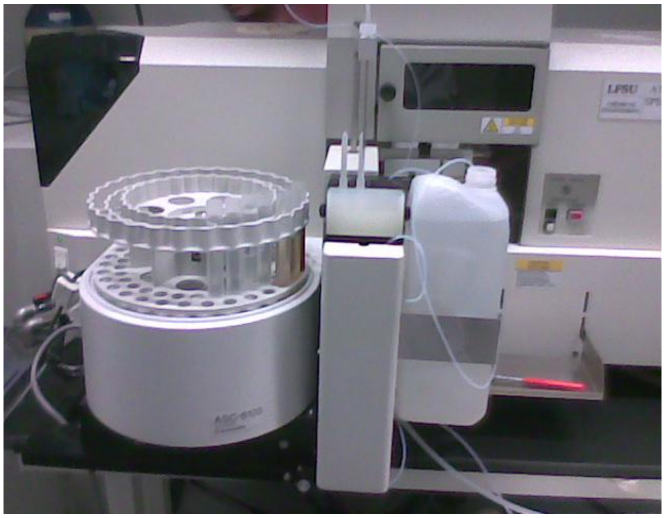

Figure 3.16: The diagram of AAS system to analyzed heavy metals in samples

10. Standard solutions of desired metals: Zn, Cu, Pb, Cr and Ni were prepared fresh from stock solutions before analysis for calibration and qualitative purposes.

Figure 3.17: The apparatus and chemicals required to prepare the standard solution of particular heavy metals

11. To minimize the sources of error, blanks are run simultaneously for analysis of all the elements.
12. The equipments such as volumetric flask and tubes are washed several times with soap, de-ionized water and diluted nitric acid to remove any impurities.
13. All procedures of sampling and handling are carried out without contact with metals, to avoid potential contamination of the samples.

*The procedure above is synchronized with the time line according to the UTP academic weeks; therefore the Gantt chart is produced to monitor the progress of the experimental work. Gantt chart could be viewed at the Appendix II.

3.4 Atomic Absorption Spectrophotometry (AAS)

The AAS is used to analyze the heavy metals content in the solid matters such as road dust, due to its availability and easiness of usage in the laboratory. Based on Tom Huff (1998), AAS determines the presence of metals in liquid sample and also measures the concentrations of metals in the samples. Its typical concentrations range is in the low range of unit mg/L.

In their elemental form, metals will absorb ultraviolet light when they are excited by heat. Each metal has a characteristic wavelength that will be absorbed. The AAS instrument looks for a particular metal by focusing a beam of UV light at a specific wavelength through a flame and into a detector. The sample of interest is aspirated into the flame. If the metal presents in the sample, it will absorb some of the light, thus reducing the light intensity. Hence the instrument measures the change in intensity. A computer data system converts the change in intensity into an absorbance. As concentration goes up, absorbance goes up. A calibration curve is constructed by running standards of various concentrations on the AAS and observing the absorbance and the computer data system will produce the standard curve. Samples can then be tested and measured against this curve.

In atomic absorption, there are two methods of adding thermal energy to a sample. A graphite furnace AAS uses a graphite tube with a strong electric current to heat the sample. In flame AAS; the sample is aspirated into a flame using a nebulizer. The flame is lined up in a beam of light of the appropriate wavelength. The flame (thermal energy) causes the atom to undergo a transition from the ground state to the first excited state. When the atoms make their transition, they absorb some of the light from the beam. The more concentrated the solution, the more light energy is absorbed.

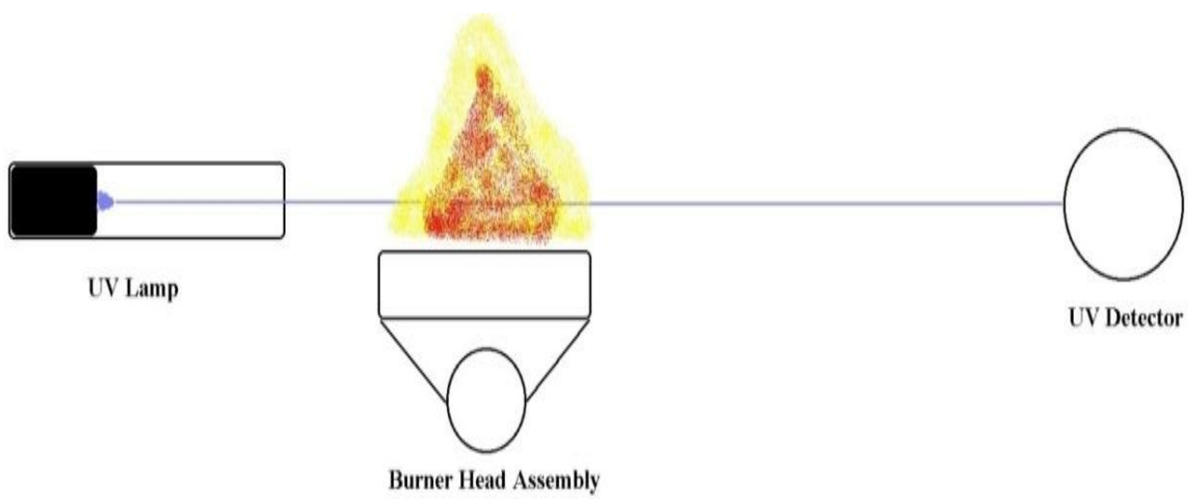

Figure 3.18 : A simplified schematic diagram for the basic operation of Atomic Adsorption Spectroscopy (AAS)

The light beam is generated by a lamp that is specific for a target metal. The lamp must be perfectly aligned so the beam crosses the hottest part of the flame and travels into the detector. The detector measures the intensity of the beam of light. When some of the light is absorbed by a metal, the beam's intensity is reduced. The detector records that reduction as absorption. That absorption is shown on readout by the data system. The figure above shows the schematic diagram of a flame AAS. The diagram indicates that there are four primary parts to the system which are the light source, flame apparatus, detector, and data system. Fortunately, it is not need to separate solutions containing different metals. No chromatography is required for this instrument. It is merely change the lamps and adjust the detector wavelength.

The concentrations of metals can be found in a sample running a series of calibration standards through the instrument. The instrument will record the absorption generated by a given concentration. By plotting the absorption versus the concentrations of the standards, a calibration curve can be plotted. The absorption will be viewed for a sample solution and use the calibration curves to determine the concentration in that samples.

4.0 RESULTS AND DISCUSSION

4.1 Experimental results

4.1.1 Heavy Metals: Pb

Table 4.1: Concentration of Pb for various sampling points in mg/kg unit

Sample Point	Duplicate No	AAS reading conc. (mg/l)	Average Conc. (mg/l)	Dilution Factor	Conc. (mg/kg)
Rural 1	1 2	1.526 1.6753	1.60065	1	320.13
Rural 2	1 2	1.856 1.9542	1.9051	1	381.02
Rural 3	1 2	1.413 BDL	1.431	1	286.2
Medan Kidd Bus Station	1 2	0.7151 2.0737	1.3944	1	278.88
Medan Kidd Pavement	1 2	1.9542 1.5956	1.7749	1	354.98
Simpang Pulai	1 2	1.8347 1.6753	2.0339	1	406.78
Medan Gopeng Bus Station	1 2	2.2331 2.7112	2.47215	1	494.43
Medan Gopeng Car Park	1 2	2.4721 1.0378	1.75495	1	350.99

* The range of detection limit of AAS analysis of Pb is between 0.5 to 4 ppm

* Below Detection Limits (BDL)

The calculation of concentration in unit mg/kg from the unit concentration of ppm is as follows;

Concentration of metals (mg/kg) =

$$\frac{Concentration\ (mg/l) x\ Volume\ extract\ of\ 0.1\ L\ x\ Dilution\ factor}{Weight\ of\ samples\ of\ 0.0005\ kg}$$

From above table, the graph of Pb concentrations for various sampling points is constructed to analyze the pattern between the rural and urban samples.

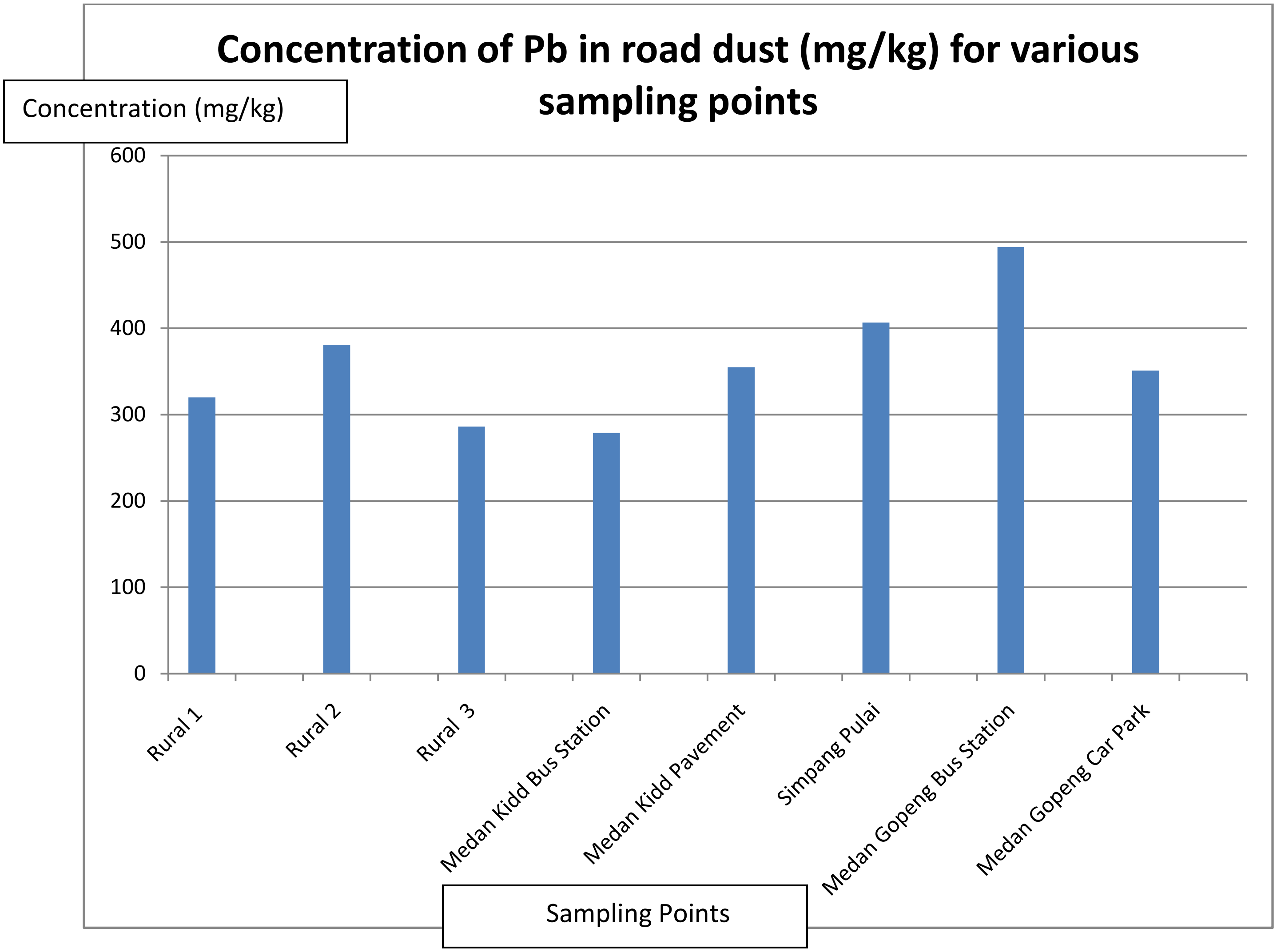

Figure 4.1: The bar chart of Pb concentration for various sampling points

Explanation and Discussion on the results

From Table 4.1 and Figure 4.1 presented above, it is found that there is no obvious difference between the rural samples (Rural 1, Rural 2, and Rural 3) and urban samples because the range of Pb concentration of both samples is similar which is between 270 mg/kg to 500 mg/kg. Even, two of the rural samples (Rural 1 and Rural 2) record the values higher than urban samples except Simpang Pulai and Medan Gopeng Bus Station samples. The urban sample of Medan Kidd Bus Station records the lowest concentration of Pb (278 mg/kg). Meanwhile, Medan Gopeng Bus Station shows the highest value of Pb level among others which is 494 mg/kg. The trends of rural roads that records high Pb concentration might due the fact that the rural roads are very close in proximity with wide paddy field area that contribute to the emission of Pb via paddy fertelizers, harvest machines, pesticides and insecticides (Anasco 2010). Besides, Pb possesses the lowest mobility properties compare to other significant heavy metals such as Cu, Ni and Zn as been reported by Schafer *et al* (1998). Thus, Pb is hard to be transferred to another site through the dissolution in surface water or in airborne dust particles (Baker, 1993) which also could contribute to the high concentration of Pb in rural road dust samples.

Other highly associated and relevant researches have been referred to compare the results obtained for this study in term of Pb concentrations in road dust in variety of sampling points. The first is Al-Kashman (2007) who did the study of ‘The Investigation of Metal Concentration in Street Dust Samples in Aqaba City, Jordan’. This study was to investigate the influence of traffic activities to the metal concentration in street dust. The concentrations of metals under concern are (Iron (Fe), Zn, Cu, Cr, Pb, Cadmiun (Cd), Ni, Manganese (Mn) and Cobalt (Co)) in 140 street dust samples which are collected from Aqaba city, Jordan. Hence the plot of Pb concentrations as follows:

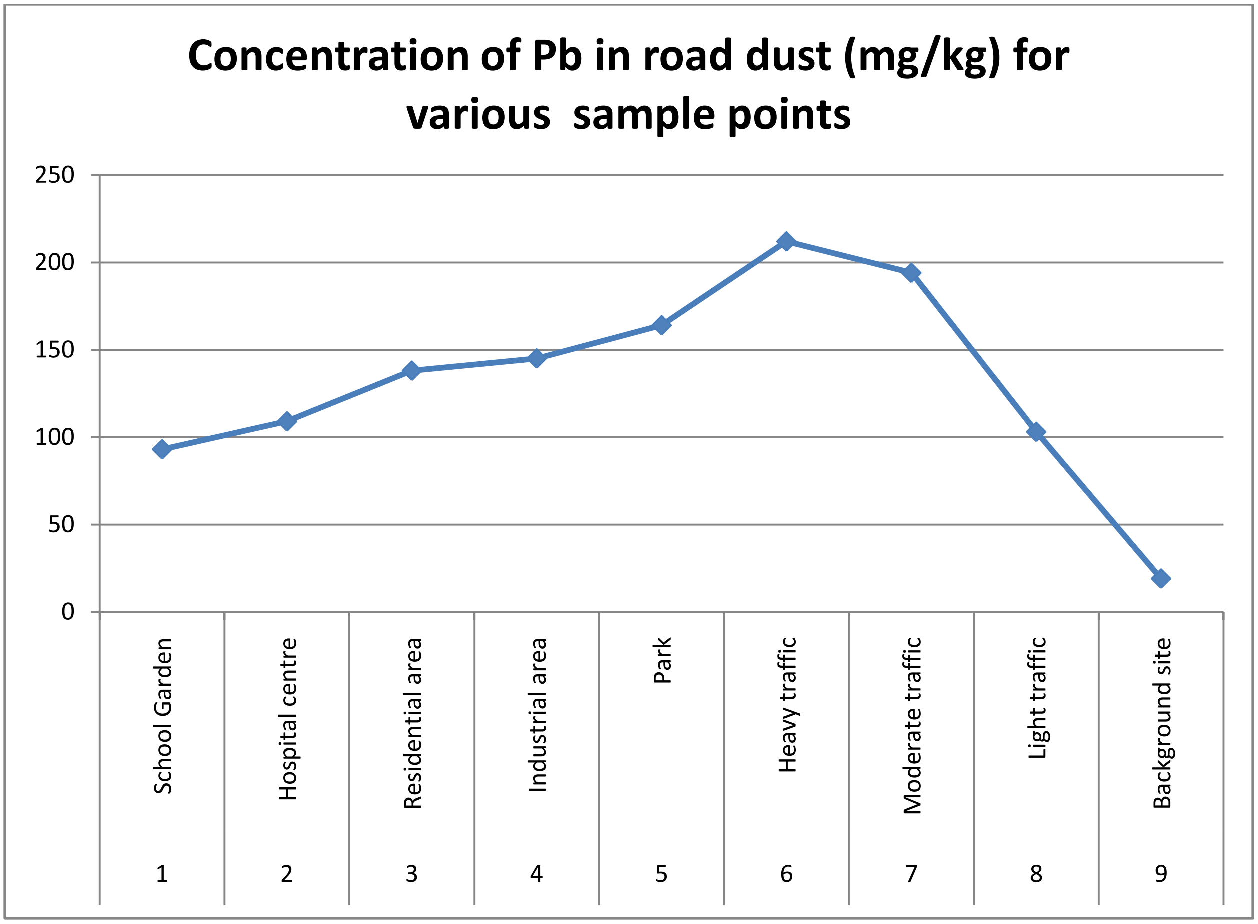

Figure 4.2: The bar chart of Pb concentration for various sampling points by Al-Kashman (2007)

Secondly, Jiries (2003) who did the study on 'Vehicular Contamination of Dust in Amman, Jordan' has collected samples of road dust from various traffic areas such as city center, tunnels, closed car parks and a residential area. His study also being referred to compare the level of Pb concentration in those related sites; the results as follows;

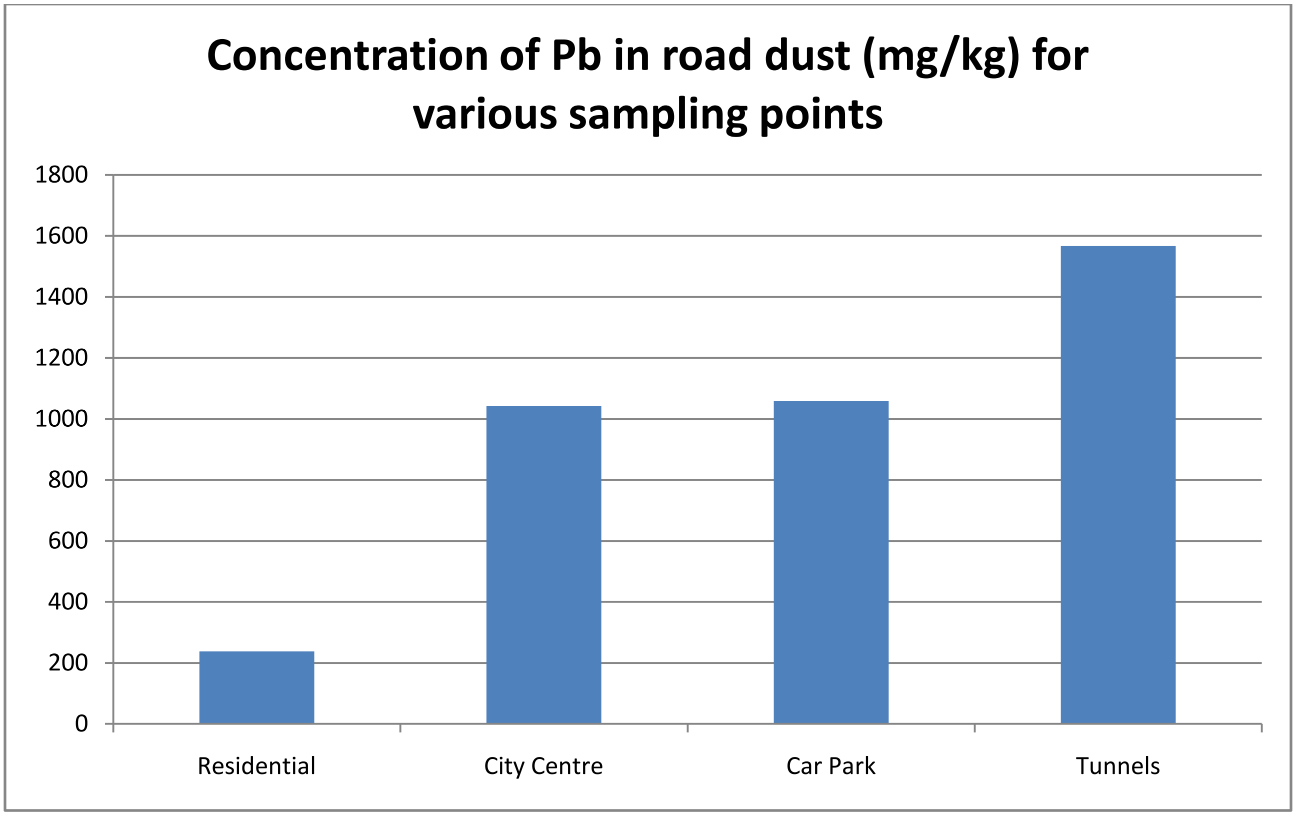

Figure 4.3: The bar chart of Pb concentration for various sampling points by Jiries (2003)

From both studies, the difference in Pb concentration between high and low traffic density areas is obvious. The concentration of Pb highly affected by the traffic density from which Al-Kashman recorded the highest value of Pb is at heavy traffic area (220 mg/kg) while Jiries's results shows that Pb recorded the highest in concentration for tunnel area (1590 mg/kg). Both of them recorded the low concentration at school garden, light traffic and residential area. From the result of this study, it shows that Medan Gopeng Bus Station records higher value of Pb concentration (494 mg/kg) than heavy traffic roads but lower than the concentration of Pb at tunnel area.

From the results of this study, vehicular emission is not a sole contributor to the Pb level in road dust as Pb might be originated from various sources such as industrial and agricultural activities as indicated by rural roads' values. Besides, the influence of high and low traffic density towards the level of Pb is not apparent and obvious. The results also differ in Pb concentration trend with both reference studies.

4.1.2 Heavy Metal: Ni

Table 4.2: Concentration of Ni for various sampling points in mg/kg unit

Sampling Point	Duplicate No	AAS reading conc. (mg/l)	Average Conc. (mg/l)	Dilution Factor	Conc. (mg/kg)
Rural 1	1 2	BDL BDL	-	1	-
Rural 2	1 2	BDL BDL	-	1	-
Rural 3	1 2	BDL BDL	-	1	-
Medan Kidd Bus Station	1 2	BDL BDL	-	1	-
Medan Kidd Paveway	1 2	BDL BDL	-	1	-
Simpang Pulai	1 2	BDL BDL	-	1	-
Medan Gopeng Bus Station	1 2	BDL BDL	-	1	-
Medan Gopeng Car Park	1 2	BDL BDL	-	1	-

* The range of detection limit of AAS analysis of Ni is between 0.5 to 4 ppm

* Below Detection Limits (BDL)

Explanation and Discussion on the results

From the table above, it is found that all sampling points record very low Ni concentration as it could not be detected by AAS with the detection range of 0.5 to 4 ppm. It is due to the fact that Ni possesses the highest mobility properties as reported by Schafer *et al.* (1998). Thus, it is the easiest to be transferred from one place to another either as sediment by surface water or in airborne dust particles (Baker, 1993) which contributes to its low concentration in road dust.

The studies of Al-Kashman (2007) and Jiries (2003) are also used to be compared with the results obtained above. Al-Kashman reported the concentration of Ni as follows:

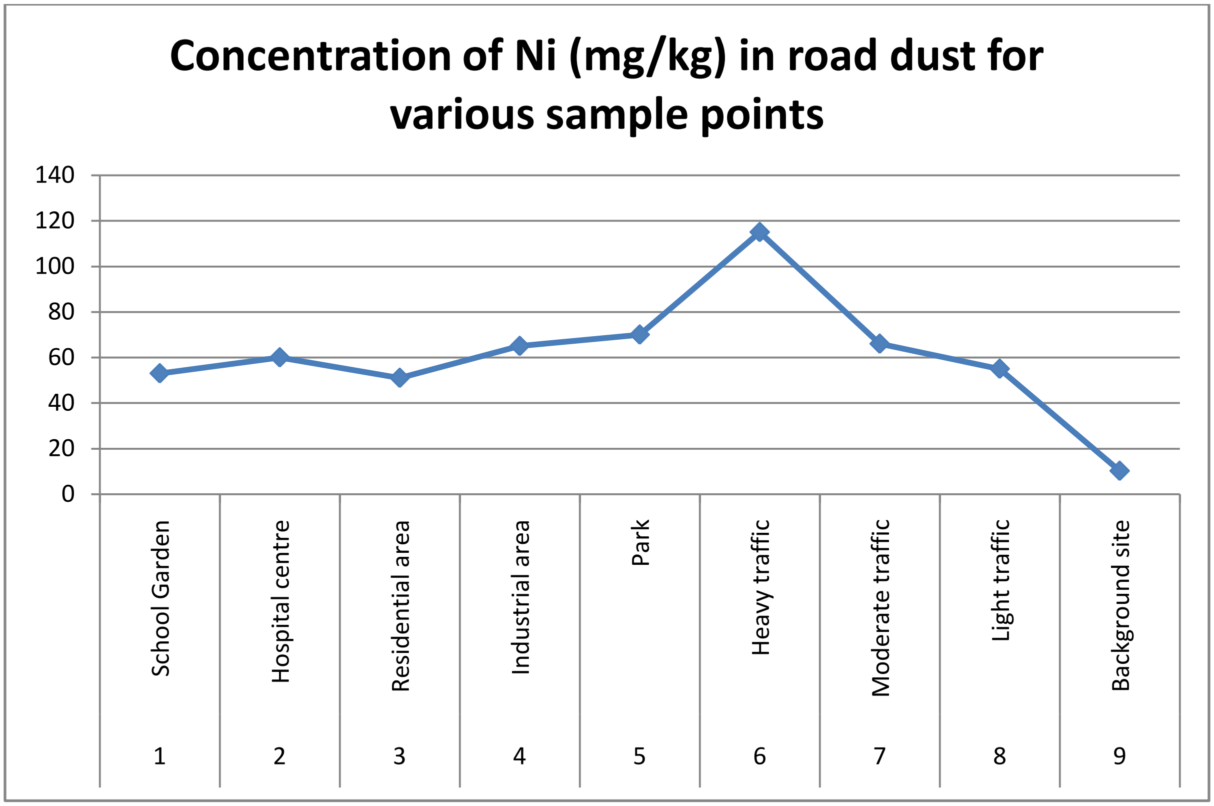

Figure 4.4: The bar chart of Ni concentration for various sampling points Al-Kashman (2007)

Meanwhile, Jiries (2003) reported the Ni concentrations plot as per figure below:

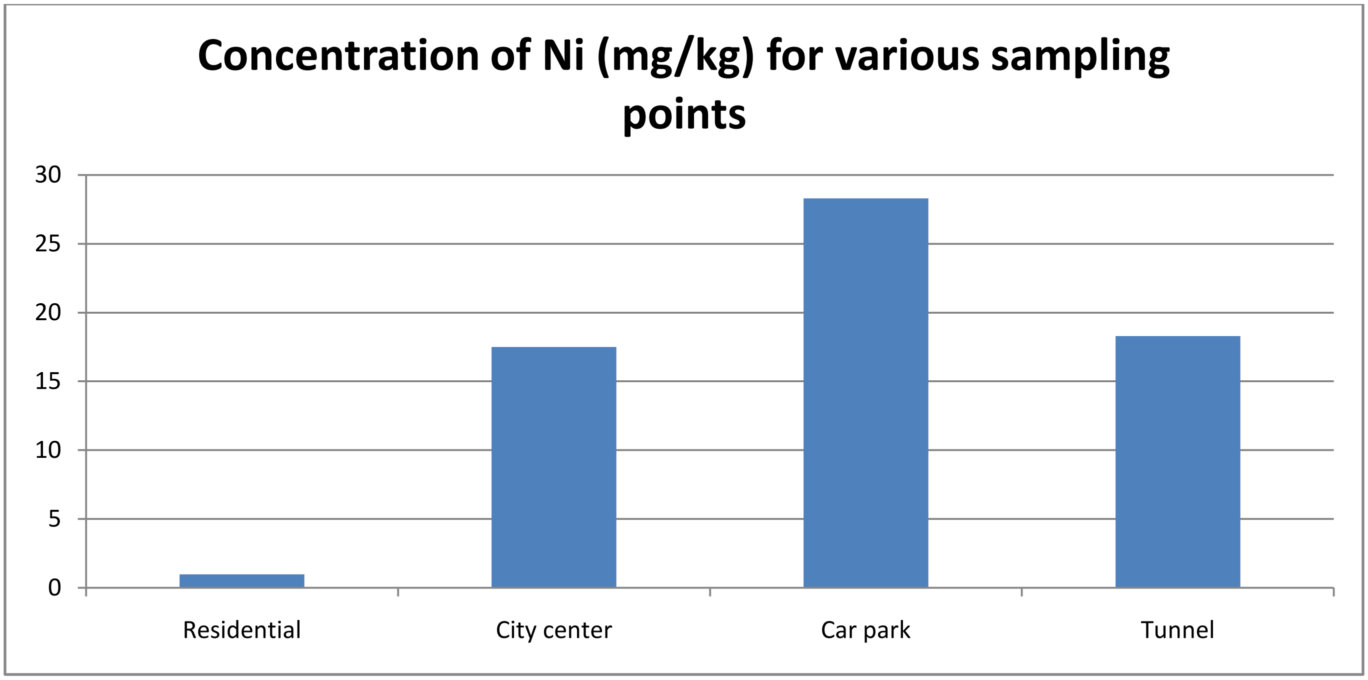

Figure 4.5: The bar chart of Ni concentration for various sampling points Jiries (2007)

According to both studies, Ni concentration in road dust is effected by the traffic density because the highest value of Ni concentration recorded at heavy traffic density, tunnel and car park areas. The results are in contrast with this study which records very low concentration of Ni at all sampling points. However, the Jiries's study shows quite low Ni concentration which in the range of 1 mg/kg to 28 mg/kg. By referring to the results of this study, there is a possibility that is no influence of vehicular emission on the Ni contents in road dust which differ with the results of both reference studies. The road dust samples from both of the studies might be naturally enriched with Ni contents.

4.1.3 Heavy Metal: Zn

Table 4.3: Concentration of Zn for various sampling points in mg/kg unit

Sampling Point	Duplicate No	AAS reading conc. (mg/l)	Average Conc. (mg/l)	Dilution Factor	Conc. (mg/kg)
Rural 1	1	0.2238	0.21015	1	42.03
	2	0.1965			
Rural 2	1	0.2131	0.2026	1	40.52
	2	0.1921			
Rural 3	1	0.2323	0.2331	1	46.62
	2	0.2339			
Medan Kidd Bus Station	1	0.5177	0.3745	1	74.9
	2	0.2313			
Medan Kidd Paveway	1	0.5465	0.5443	1	108.85
	2	0.5420			
Simpang Pulai	1	0.6192	0.61835	1	123.67
	2	0.6175			
Medan Gopeng Bus Station	1	0.5168	0.54715	1	109.43
	2	0.5775			
Medan Gopeng Car Park	1	0.5456	0.54575	1	109.15
	2	0.5459			

* The range of detection limit of AAS analysis of Zn is between 0.1 to 0.8 ppm

* Below Detection Limits (BDL)

From above table, the graph of Zn concentrations for various sampling points is constructed to analyze the pattern between the rural and urban samples.

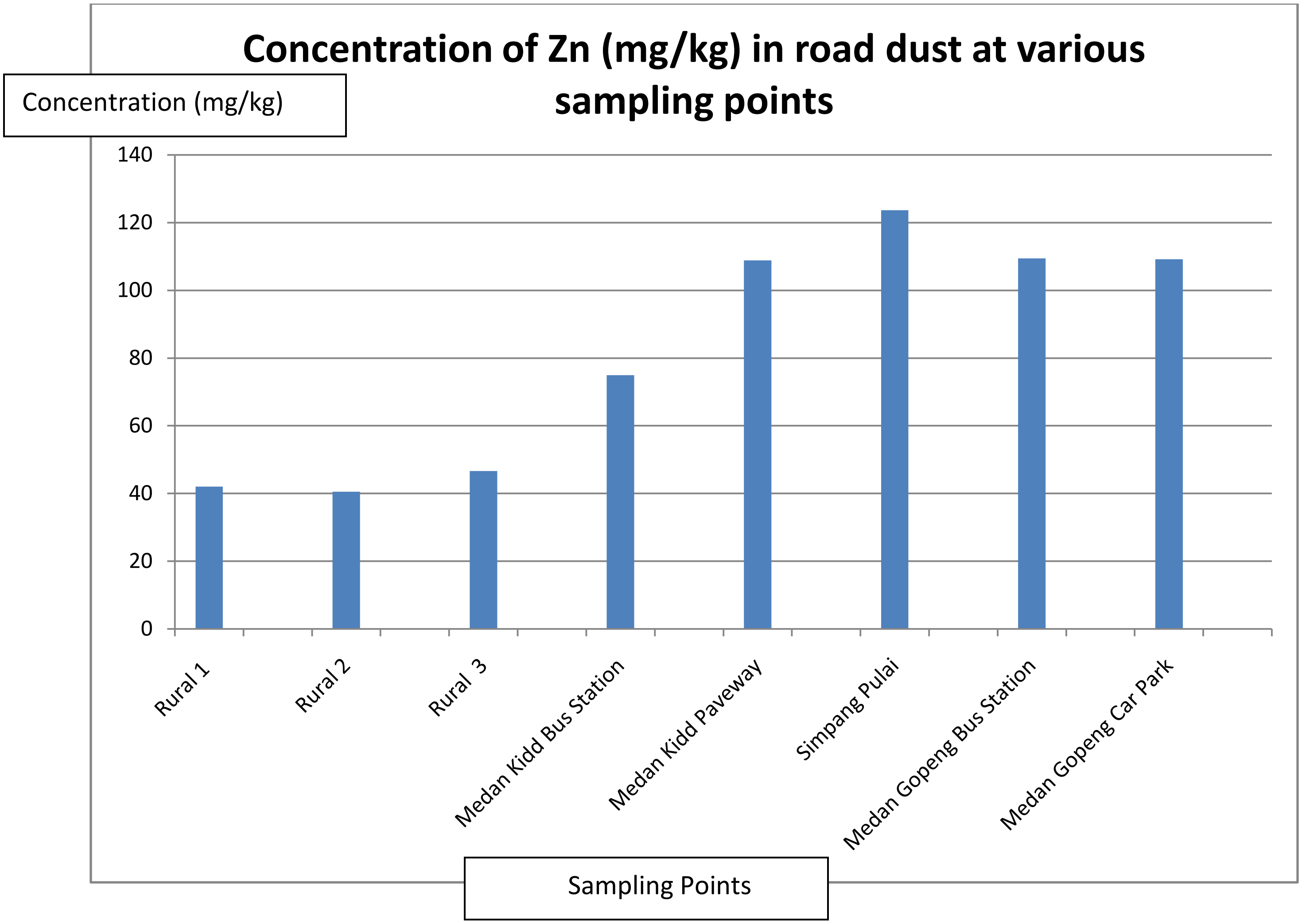

Figure 4.6: The bar chart of Zn concentrations in road dust for various sampling points

Explanations and Discussion on the results:

From the table and graph above, there is an obvious and clear difference of Zn concentrations between rural and urban roads samples. Rural road samples (Rural 1, Rural 2 and Rural 3) record the concentration below 50 mg/kg while the urban samples records the concentration higher that 70 mg/kg up to 125 mg/kg of Zn concentration. The highest concentration of Zn is found at Simpang Pulai roads which is 123 mg/kg while the lowest value is recorded by Rural 2 sample (40.52 mg/kg). Medan Kidd Bus Station sample shows the lowest value of Zn concentration (74.9 mg/kg) among urban samples. This sampling point also records the lowest value of Pb concentration earlier which can be attributed to the road dust of that investigated area being low in Zn and Pb. The high values of Zn concentration for the urban samples clearly shows the direct effect of vehicular emission towards Zn contents such as from lubricant oil, vehicle engines and tyres abrasion Hidayah, (2008). Johansson (2009) emphasized that that wear of tires is an important source of Zn emission. The second highest Zn concentration is at Medan Kidd pave way where it is just besides the roundabout. Thus, the use of brake is high at roundabout due to slow speed of traffic and might cause the higher emission of Zn from brake linings. Hence, the increment of vehicles on the road causes the increment of Zn emission to urban road areas.

The results obtained in this study are to be compared with the prominent studies of Al-Kashman's and Jiries's studies. Al-Kashman (2007) recorded the Zn concentration for various sampling points as follows;

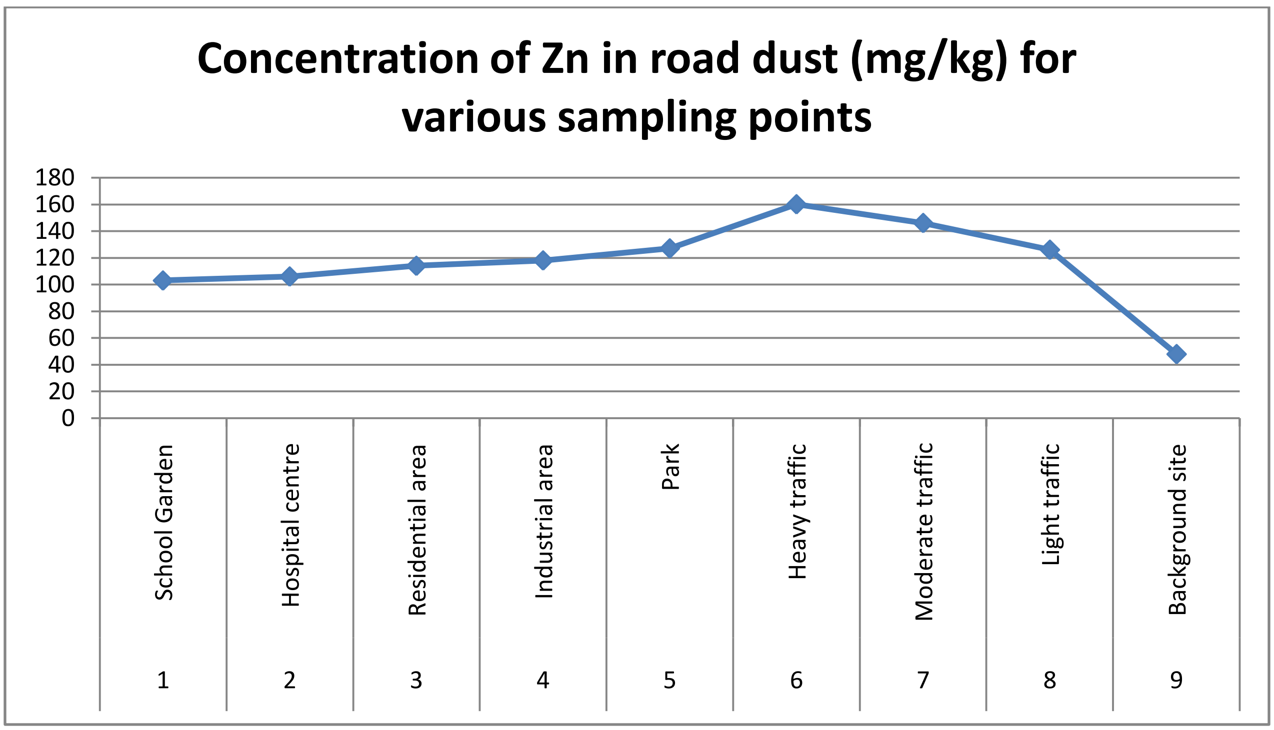

Figure 4.7: The graph of Zn concentrations in road dust for various sampling point Al-Kashman (2007)

Meanwhile, Jiries (2003) also reported on the Zn concentration in various sampling points as per figure below:

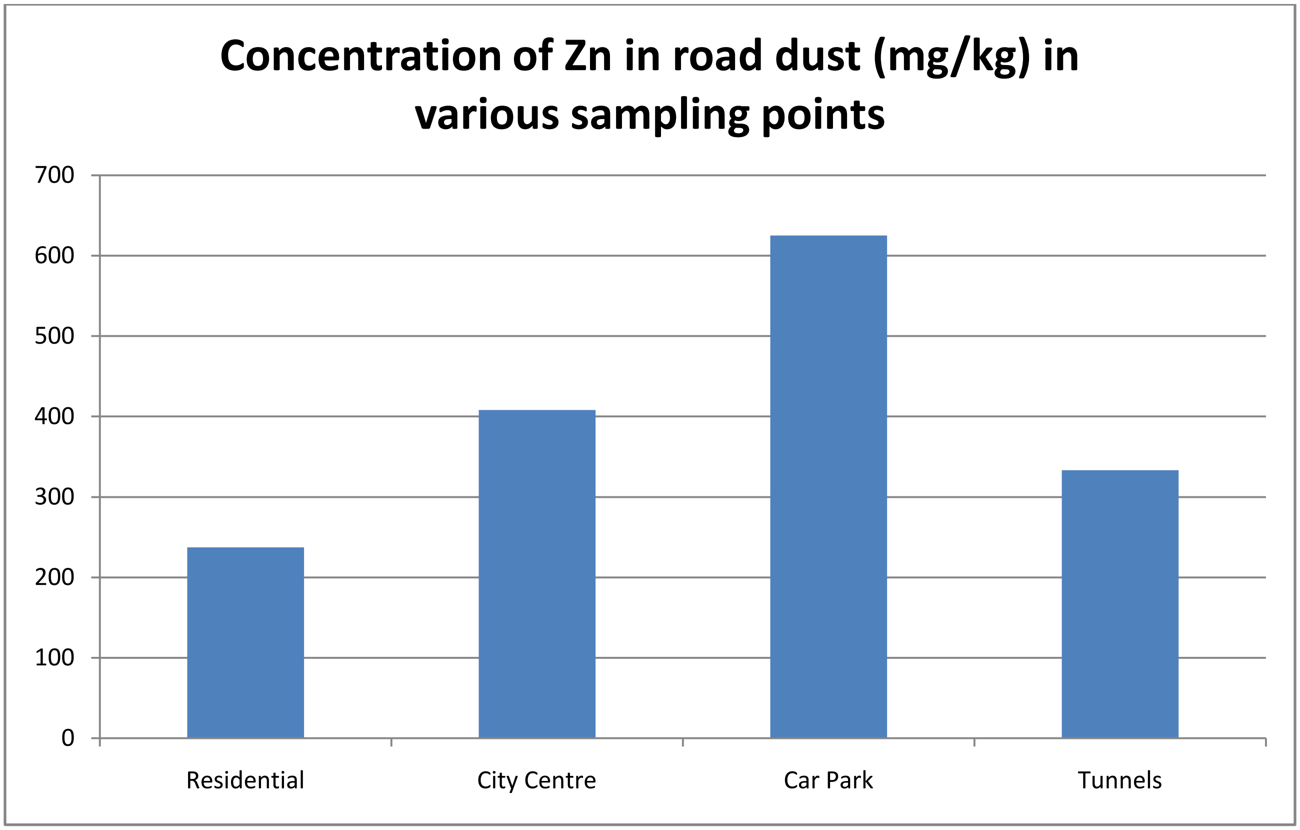

Figure 4.8: The graph of Zn concentrations in road dust for various sampling points Jiries (2003)

Al-Kashman (2007) reported that the heavy traffic area records the highest concentration of Zn of 160 mg/kg that are close with the highest Zn contents for this study which is Simpang Pulai samples (123 mg/kg) while Jiries (2003) claimed that the car park area recorded the highest value of Zn concentration which is 620 mg/kg although higher traffic densities existed in the city centre and tunnels. This can be attributed to wear of tires (Carlosena,1998). Both studies show that the areas with low traffic density such as school garden and residential area recorded low Zn concentration. Besides, the Zn concentration in rural samples of this study is well below the concentration in background sites of Al-Kashman's.

Hence, from the results obtained from this study, the influence of vehicular emission on Zn level in road dust is highly significant and there is an obvious difference of Zn contents in road dust between rural and urban roads. High traffic density represented by urban roads show higher values of Zn concentration than the rural roads. Hence, it clearly shows that the increase in the amount of vehicles causes an increment of Zn concentration in road dust. These claims are supported by the findings of both reference studies mentioned previously.

4.1.4 Heavy Metal: Cr

Table 4.4: Concentration of Cr for various sampling points in mg/kg unit

Sampling Point	Duplicate No	AAS reading Conc. (mg/l)	Average Conc. (mg/l)	Dilution Factor	Conc. (mg/kg)
Rural 1	1 2	0.15588 0.1093	0.13259	1	26.518
Rural 2	1 2	BDL BDL	-	1	-
Rural 3	1 2	0.1093 0.1712	0.14025	1	28.05
Medan Kidd Bus Station	1 2	0.3021 0.2879	0.295	1	59
Medan Kidd Paveway	1 2	0.2131 0.2425	0.2278	1	45.56
Simpang Pulai	1 2	0.2132 0.1892	0.2012	1	40.24
Medan Gopeng Bus Station	1 2	0.2262 0.2252	0.2257	1	45.14
Medan Gopeng Car Park	1 2	0.2425 0.2291	0.2358	1	47.16

* The range of detection limit of AAS analysis of Cr is between 0.1 to 0.8 ppm

* Below Detection Limits (BDL)

From above table, the graph of Cr concentrations for various sampling points is constructed to analyze the pattern between the rural and urban samples.

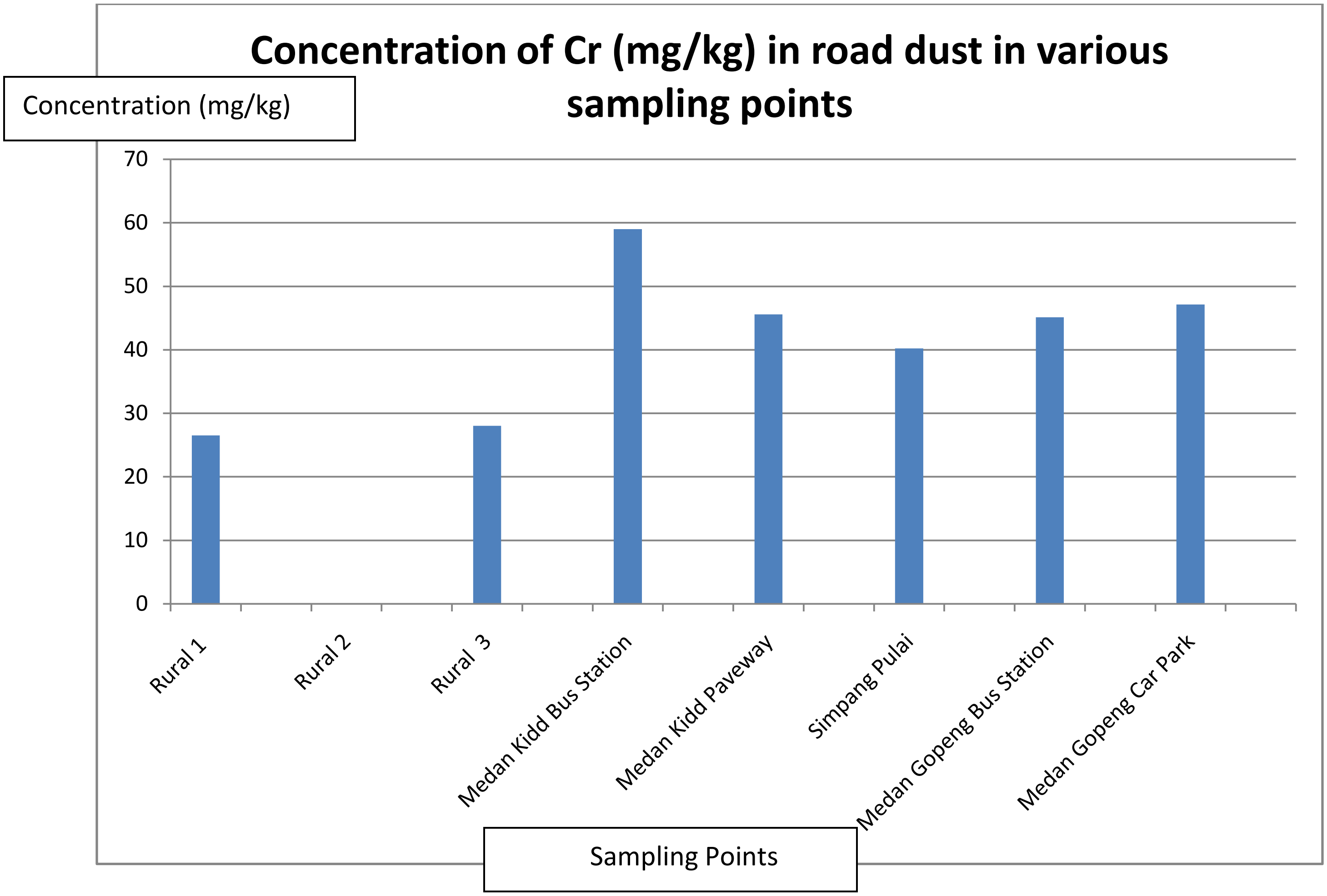

Figure 4.9: The concentration of Cr in mg/kg in road dust in various sampling points

Explanations and Discussion on the results

There is an obvious difference of Cr level between urban and rural road dust samples. The rural road dust samples records the Cr concentration in the range between 25 to 30 mg/kg while the range for urban samples is higher than rural samples range which is between 40 to 60 mg/kg Cr concentration. This shows an influential and direct effect of vehicular activities towards the Cr contents in road dust. Such level of Cr in the dust samples is associated with the chrome plating of some motor vehicle parts. (Al-Shayep and Seaward, 2001) while Johansson et al (2009) claimed that brake wear and exhaust emission are the important sources of Cr. Besides, Affum et al (2008) stated that Cr might be originated from lubricating oils and car metal plating. Therefore, there are various parts of vehicles that contribute to Cr emission to environment as claimed by various researchers wordwide. Medan Kidd Bus Station records the highest concentration of Cr in road dusts (59 mg/kg) although it shows the lowest level of Pb and Zn among urban samples. It is observed that Simpang Pulai samples shows lowest Cr concentration (40.24 mg/kg) among urban samples due to its smooth and fast flow of traffic. The traffic flow and speed at Medan Kidd and Medan Gopeng Bus Station are relatively very slow and consequently the potential of wear from metal plating and brake is high at those areas. For Rural 2 road dust samples, the Cr concentration is very low which could not be detected by AAS system with the detection limit of Cr is between 0.l ppm to 0.8 ppm.

The results of this study are going to be compared with the studies of Al-Kashman and Jiries similar as done in previous metals. Al-Kashman (2007) recorded the Cr concentration for various sampling points as follows;

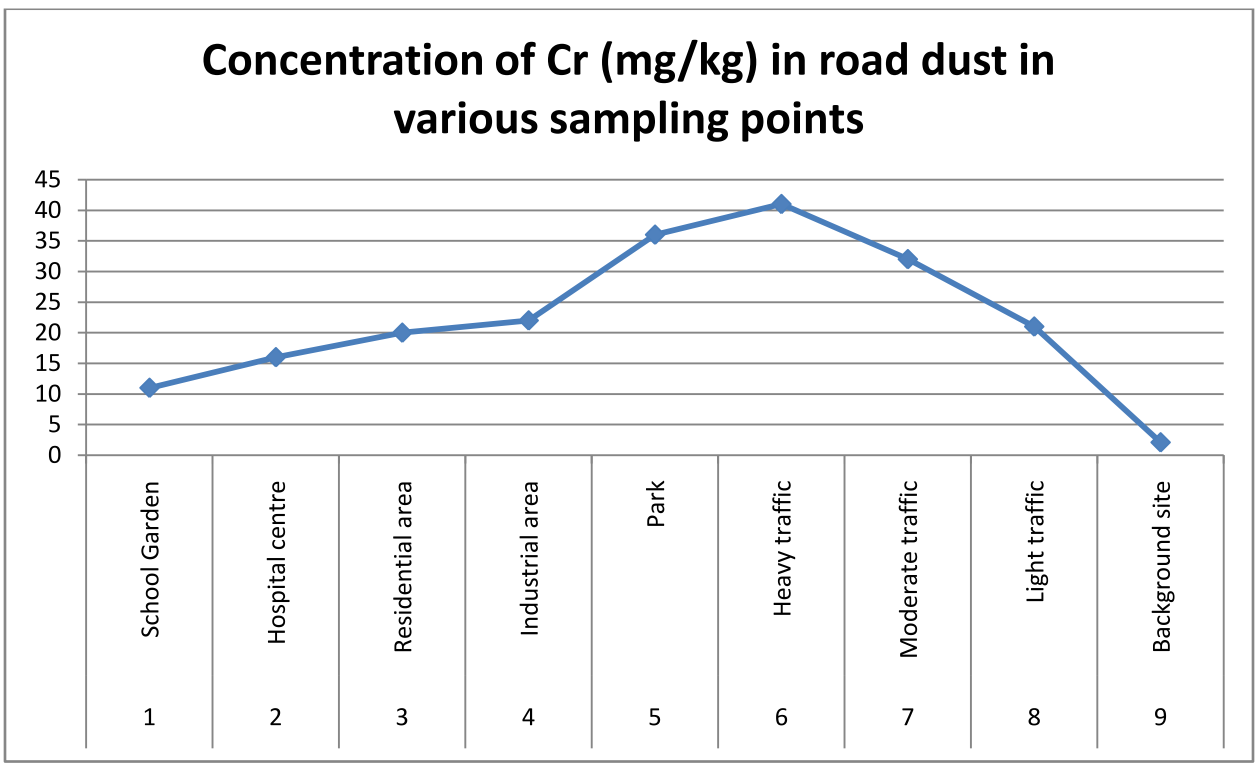

Figure 4.10: The graph of Cr concentrations in road dust for various sampling point Al-Kashman (2007)

Jiries (2003) reported on the Cr concentration in various sampling points as per figure below:

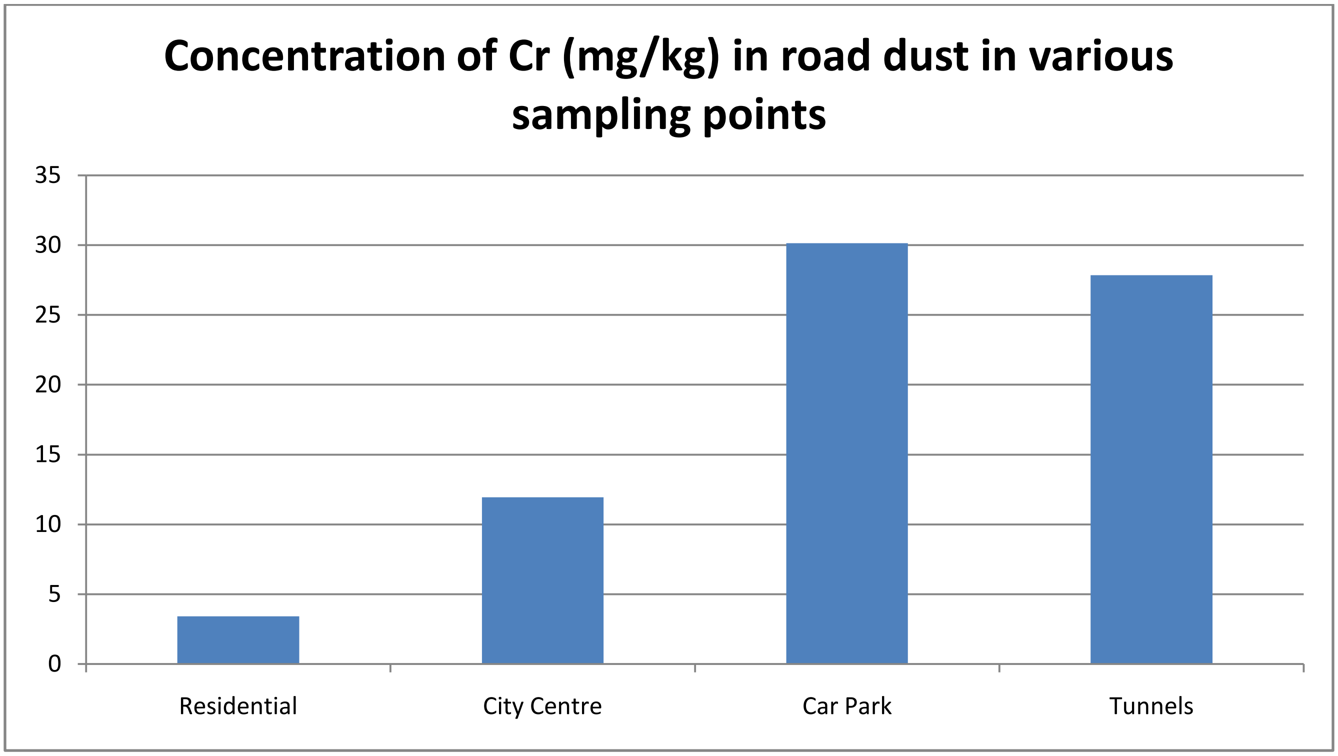

Figure 4.11: The graph of Cr concentrations in road dust for various sampling point Jiries (2003)

The highest Cr concentration in road dust is found at heavy traffic and car park areas as reported by Al-Kashman and Jiries respectively. Both studies shows that Cr concentrations in road dust for all sampling point are below 100 mg/kg which is consistent with the results presented by this study. Thus, it shows that concentration of Cr in road dust is lower compare to Pb and Zn.

By referring to the results of this study, vehicular emission highly affects the Cr concentration in road dust. This claim is supported by both relevant and related studies of Al-Kashman and Jiries. It is also found that Cr level is high in urban road dust samples compare to rural samples. Thus, it shows that the increment of traffic density causes the increment of Cr concentration in road dust.

5.0 CONCLUSION

From the results obtained from this study, it is concluded that vehicular emission could be a direct contributor and responsible towards the emission of heavy metals to the environment particularly Zn and Cr. Besides, high and low traffic densities which are represented by urban and rural roads respectively affect the level of heavy metal especially Zn and Cr concentrations in road dust. The results show that the increment of the number of motored vehicles on the road causes the concentrations of Zn and Cr in the road dust also increase. In the other hand, the results of Pb concentration in road dust shows that the vehicular emission is not a sole contributor to the Pb level in road dust as it might be originated from various sources such as industrial and agricultural activities. Hence, the difference between high and low traffic density towards the level of Pb in road dust is not apparent and obvious. Furthermore, by referring to the results of Ni concentration in this study, there is a possibility that is no influence of vehicular emission on the Ni contents in road dust as the concentrations are too low to be interpreted and analyzed by AAS system owing to its high mobility property. Finally, it is found that people are highly exposed to the vehicular emission especially heavy metals because the number of vehicles keeps increasing every year in Malaysia. Thus, practical solution and pollution prevention strategy need to be undertaken seriously as the heavy metals emitted by vehicular emission could cause adverse effect to people's health.

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