# **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 acknowledgement, and that the original work contained herein have not been undertaken or done by unspecified source or person.

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### ABSTRACT

Repeating urbanization shows that the amount of vehicles is increasing day by day and contributes to the heavy metal contaminant to the atmosphere. The existence of heavy metal contaminant by vehicular emission in atmosphere has become one of the serious environmental issues. Heavy metals such as Pb, Zn, Ni and Cd cause ill effect on human health and the environment. Thus, many countries already manage and arrange control programmes due to the concern of this atmospheric pollutant. Unfortunately, nowadays the controlling air pollutants are a very complex. Hence in Malaysia, data monitoring for heavy metal contaminant are very scarce. In order to get an alternative for this controlling program, bioindicator become one of the green technology solution. Much attention is given for the tree barks specifically Acacia Mangium sp as the bioindicator alternative due its availability. In order to investigate the heavy metals trace by tree bark, bark sample are taken from specified high density traffic, medium and rural are collected and analyzed by Atomic Absorption Spectroscopy (AAS). As the result, when the numbers of vehicles are increasing, the concentrations of heavy metal also increase. Vehicular emission might be the direct contributor for the heavy metal contaminant. Thus, the suitability for the tree bark is discussed in this further study.

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# <u>CHAPTER 1</u> PROJECT BACKGROUND

#### 1.1 Background of Study

Repeating urbanization shows that the important of vehicle on the road especially in stimulating social and economic activities. The result of statistic by Malaysia Automotive shows that the number of vehicles in Malaysia is increasing day by day. The increasing number of vehicle contributes the increment of heavy metal contaminant in the environment.

### (Sumber: Malaysia Automotive Association, 2010)

Summary of New Passenger and Commercial Vehicles <u>REGISTERED</u> In Malaysia f the Year 1980 to 2009

Year	Passenger Vehicles	Commercial Vehicles	4x4 Vehicles	Total Vehicle
1980	80,420	16,842		97,262
1985	63,857	26,742	4,400	94,999
1990	106,454	51,420	7,987	165,861
1995	224,991	47,235	13,566	285,792
2000	282,103	33,732	27,338	343,173
2005	416,692	97,820	37,804	552,316
2006	366,738	90,471	33,559	490,768
2007	442,885	44,291	-	487,176
2008	497,459	50,656		548,115
2009	486,342	50,563	· .	536,905

Figure 1 : Statically of Vehicle Registered in Malaysia

Thus, it will probably lead to the increasing of major environmental and human health hazard in future .Lead (pb), Zinc (Zn), Copper (Cu), Nickel (Ni) and Chromium (Cr) are the five major heavy metal that are closely related to motor vehicles. In addition, anthropogenic heavy metals can be find from lubricating oil combustion in the engine .All the heavy metals depends a great deal on their chemical form, concentration and residence time (Tayel El-Hasan, 2002).

Most of the countries try to develop and established control program due to concern of atmospheric pollutants. As practiced by most of the countries, the necessary information can be obtained by dispersion modeling (source-orientation, known as emission source) and by the field measurement of the emission (receptor/effect orientation). In practice, controlling (anthropogenic) air pollutions is a very complex problem: sources and emission have to be identified, analytical method have to evaluated, risk to be assessed, critical emission have to be controlled, and economical aspect have to integrated .(Sloof,1993; Wolterbeek and Freitas,1999).

This project will covered the study of tree barks as the bio indicator for heavy metal dispersal from vehicular emission. There are a lot of studies about bio monitor technology around the world such as mango tree bark as bio indicator in China (Wanaruk Saipunkaew ,2001) and Biomonitoring in Spain.Tree bark can be used as a biomonitoring for other various pollutants, such as electrical conductivity, pH, sulphur, nitrogen, and heavy metals. Thus, tree bark is very porous, and the absence of metabolic process makes it almost inert in the presence of inorganic and organic substance. (H.Schulz, 1999)

Through this project three areas will be covered as the area background which are Medan Gopeng, Ipoh, Jalan Lagenda, Ipoh and Kampung Layang-Layang, Bota. *Acacia mignium s.p.* will be used as the tree for the sampling due some available factors. As the result, we could see later on the area which contain high concentration of heavy metal can be considered as the polluted area and the result might be used for the some of future taken to solve the pollution problem. By the development of tree barks as the bio monitor perhaps it will lead to the better and efficiency the monitoring of air quality.

#### **1.2 Problem Statement**

#### **1.2.1 Identify the Problem**

Anthropogenic heavy metals can be find from lubricating oil combustion in the engine and released in high level of concentration. It consists of Lead, Cadmium, Chromium, Copper and Zinc. Therefore, the exposure to high concentrations of heavy metals in environment will cause health hazard to human being such as adversely affecting the nervous, blood forming, cardiovascular, renal and reproducing. Thus, we need tools to monitor the heavy metal concentration that emitted to the environment.

In practice, controlling (anthropogenic) air pollutions is a very complex problem: sources and emission have to be identified, analytical method have to evaluated, risk to be assessed, critical emission have to be controlled, and economical aspect have to integrated (Sloof,1993; Wolterbeek and Freitas,1999).

#### **1.2.2 Significant of the Project**

From beginning to end of this project the *acacia mignium* tree are taken as the tree bark sample due to the some availability factors. These trees bark also measurable to physiological change, which can be seen at behavioral level that reveal its present or past exposure to pollution.

By this study also, an experiment will be conducted in order to analyze the influence of the heavy metal concentration to the environment. The sample will be covered with the three areas will be covered as the area background which are Medan Gopeng, Ipoh, Jalan Lagenda,Ipoh and Kampung Layang-Layang, Bota.. This can be benefitted to the industries as well as to the environment by the result of the heavy metal concentration. Thus, this study of the biomonitoring is significant to the environment and will be one of the alternative for the current monitor which is might release toxic to the environment.

#### **1.3 Objectives**

- To investigate the heavy metal dispersal from vehicular emission using tree barks.
- To compare the heavy metal dispersal between high density traffic, medium density traffic area and rural area.
- To study on the potential of *Acacia Mangium sp* as a suitable bioindicator for heavy metal dispersal.

#### 1.4 Scope of Study

From beginning to end of this project the *acacia mignium* tree are taken as the tree bark sample due to the some availability factors. These trees bark also measurable to physiological change, which can be seen at behavioral level that reveals its present or past exposure to pollution.

The study will focus on obtaining the concentration of heavy metal which are Pb, Cu, Ni, Zn, and Cr in the tree bark in the specified points of three different areas which are Medan Gopeng, Ipoh, Jalan Lagenda, Ipoh and Kampung Layang-Layang, Bota.. Some of the heavy metal emitted by vehicular emissions and will be deposited and accumulated into the tree barks which located surrounding. Hence, tree barks are collected to investigate the heavy metal concentrations.

The results obtained from the experimental work are used to assess the influence of vehicular emission towards the level of heavy metal in tree barks. As the result, we could see later on which area contain high concentration of heavy metal can be considered as the polluted area and the result might be used for the some of future taken to solve the pollution problem.

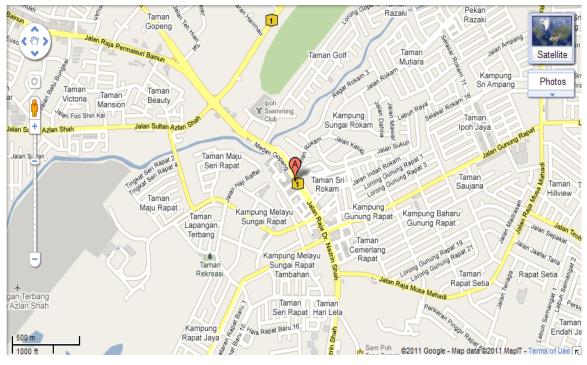


Figure 2: Location of Medan Gopeng, Ipoh



Figure 3: Location of Kampung laying-layang Kiri, Bota

#### CHAPTER 2

#### **LITERATURE REVIEW**

#### 2.1 Tree Bark as the Bio Indicator

Most of the countries such as New Zealand, Ireland, United States and many more really struggling in put their effort to establish the technology for air pollution monitoring. In many countries, dispersion modeling has gained more interest based on the economic reason compare to the technical field measurement. It also have some problem such as lack of sufficiently sensitive and inexpensive techniques. This measurement requires long-term sampling at large number of sampling site.

In practice, controlling (anthropogenic) air pollutions is a very complex problem: sources and emission have to be identified, analytical method have to evaluated, risk to be assessed, critical emission have to be controlled, and economical aspect have to integrated (Sloof, 1993; Wolterbeek and Freitas, 1999). Thus, many of the countries start to study and doing the research on th bio trace element.

Bio monitoring can be difined as the use of bio-organism to obtain information on ceratin characteristic. In this study, tree bark has been choose as considered for different factors such as the effect on the collecting of heavy metals in bark surface, such as heavy metal quantities in air, physiological and chemical properties of the bark, Barnes et al. (1976) showed that rough barks accumulate metals more than smooth barks.

Tree bark are excellent adsorbents of airbone pollution, including anthropogenic heavy metal. The bark surface is porous and the absence of metabolic process makes it almost inert in the presence of inorganic and organic substance. Monitoring with tree barks supplies low-cost information on the composition and quantity of the deposition of pollutants.

Through this project, *Acacia Mignium sp* has been chosen as the tree bark sample. These species are native range to Queensland, Australia. Thus, it go to the global distribution and introduce to Bang;ladesh, China, Indonesia and Malaysia. This tree has been selected because it is measurable to the physiological change. In other hand, it can be seen at a behavioral level that reveals its present or past exposure to pollution. It also probably capable for the range from tropical very dry to moist through subtropical dry west forest life zone.



Figure 4: Acacia Mignium sp. Tree



Figure 5 : The flower of Acacia Mignium Tree

#### 2.2 Heavy Metal Dispersal from The Vehicular Emission

Anthropogenic heavy metals such as Lead(Pb), Cooper(Cu), Cromium (Cr), Nickel (Ni) and Zinc(Zn) can be in the automobile industries, either as the main element for the fabrication in a vehicle or as additive such as lubricants for engine operation. Even though, there are less motor vehicle that used Lead as the additive, but there still in a small quantity of motor vehicle. These heavy metals, might be deposited constantly in small rates over long periods of time ago, and will be accumulate.

Lead particulate pollution from automotive emissions and other industrial sources has been extensively investigated inrecent years (1-7). Apart from lead, very little attention has been paid to the possibility of pollution from other heavy metals derived from automobiles. However, Lagerwerff and Specht (8) reported the presence of cadmium, nickel, and zinc (as well as lead) in soils and grasses at roadsides. These elements were presumably derived from motor vehicle exhausts and, for a site with 48 000 vehicles per day (Neil 1. Ward, Robert R. Brooks\*, and Edward Roberts',1977).

Metal	Calculated urban background concentration due to local road traffic (ng m <sup>-3</sup> )	Rural background <sup>a</sup> (ng m <sup>-3</sup> )	Measured total concentration in urban background (ng $m^{-3})$	Fraction due to local road traffic	Fraction due to other local sources <sup>t</sup>
Chromium (Cr)	0.53	0.28	2.3	23%	65% (59%)
Copper (Cu)	7.0	0.83	7.7	91%	-2% (-7%)
Nickel (Ni)	0.084	0.57	2.3	4%	72% (59%)
Lead (Pb)	0.53	1.6	3.4	16%	37% (13%)
Zinc (Zn)	3.4	3.9	17.0	20%	57% (46%)
Wolfram (W)	0.19	No data	1.9	10%	-
Mercury (Hg, part phase)* IVL	1.1 <sup>c</sup>	5.2°	11.1 <sup>c</sup>	10%	43% (20%)

Calculated contribution from local road traffic in Stockholm to the total urban background concentrations in Stockholm.

<sup>a</sup> Measurements at Birkenes in southern Norway (Aas and Breivik, 2005).

<sup>b</sup> Values in paranthesis refer to the contribution from other local sources if rural concentrations were 50% higher in the Stockholm area.

° pg m⁻³.

### Table 2: Concentration of Heavy Metal at Stockholm

In the centre of road highways is likely to make the most important contribution to people's exposure. Emissions from road traffic occur at ground level along streets in the most densely populated parts of the cities. They are due to wear of brakes, tires, other vehicle components, road pavement and also due to exhaust emissions. Corrosion of metallic material alongside streets may also contribute (Christer Johansson,2008)

From the study of the Cypress tree (Cupressus semervirens L.) bark as an indicator for heavy metal pollution in the atmosphere of Amman City, Jordan found that all heavy metals are higher in industrial and road highways comparative to residential and clean air area. The traffic emission was found to be the main source of metal pollution in the atmosphere where the area are dominated by elevated concentrations of Pb, Cd, Fe, and Cr.

Lead can be found as the additive in lubrication oil for motor vehicle. The use of such compound however, ends up leaving an enormous amount of lead oxide, a very toxic metal, into the environment. The chief source of lead also is mainly the use of leaded gasoline in the 20th century (Satake et al., 1996). The lead deposition has diminished considerably in Europe in the last decades because of the common use of unleaded gasoline and lower dry deposition rate, as humid climate is prevailing.

Full use of unleaded fules however, does not put to stop the use of lead compounds in monitoring activities. This compound still detected in the environment, fortunately in a small amount owing to its use anti-wear agent in lubricant oils for engines. (Hidayah,2008).Although Pb has been banned in petrol for a numbers of years, it might be deposited constantly in small rates over long periods of time ago, and accumulate in the tree barks.

Pb remains a significant indicator to study the effect of vehicular emission towards the tree barks content. The exposure of the high lead levels can severely damage the brain and kidneys ultimately cause death. It also effect on the pregnant mother which the high exposure of the metal will lead for the miscarriage. For the long-term exposure it can effect on the decreasing of the nervous function ,wrist and ankle, small increase in blood pressure and anemia. Zn and Ni occurred in a wide range and relatively low concentrations in all sites. The low concentrations could be due to the very limited use of unleaded gasoline in Jordan (Jiries etal., 2002a). The possible sources of these metals are the addition of tetraethyl lead to petrol to boost the octane number of gasoline used. Zn and Ni are higher in industrial and residential areas, which might be attributed to the fact hat Ni are fuel additives just as Pb, especially in burning fuels (diesel) used in factories and residential eating systems (Loranger and Zayed, 1994).Ni also used for plating the outer part of a vehicle such as tyre rim. The plated surface does not only become long lasting but also resistant to high heat, thus providing a very good platform for heat conductivity . When people absorb too little zinc they can experience a loss appetite, decreased sense of taste and smell, slow wound healing and skin sores. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis.

Cromium related with the chrome platting of some vehicle part. The brake wear and exhaust emission are the important sources of Cr. Cr might originated from lubricant oils and car metal plating and could contribute roadside pollution.

### CHAPTER 3

#### **METHODOLOGY**

#### 3.1 Research Methodology

The research for this project is based on the tree barks as the bio indicator for the heavy metal dispersal from vehicle emission. All academic journal and textbooks used for the reference is published from year 1995 until 2010 to make sure that the information is relevant for further study and in line with the changes of technology trend besides taking account the extensive problem figures.

Along the way of this project, experiments will be conducted to full fill the research. The sample will be taken from two different are which are highway road (near Lumut) and Clean air area (Kampung Layang-Layang, Bota). Starting with small scale laboratory work moving to the real equipment (AAS Spectometer), data collected will be compared that obtained from the literature review made. efficiency and the mixture of the solvent will be examined and analyzed.

At the end of each experiment, the data will be analyzed. The parameter used is the concentration of the heavy metal. Based on the result we can determine the air quality for both area.

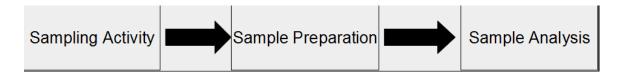


Figure 6 : Process for the sample experiment

# **3.2 Project Activities**

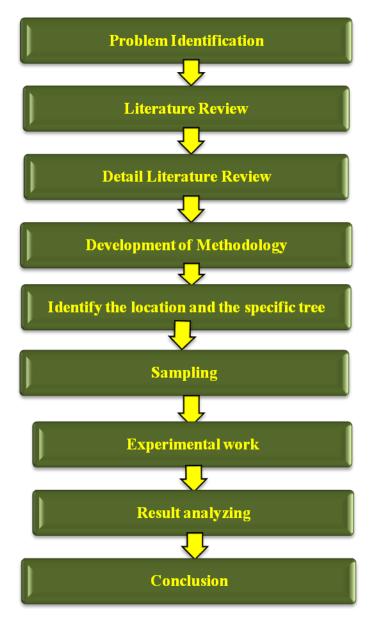


Figure 7 : Project Activity

### **3.3 Experimental Work**



Figure 8 : Experimental Work

### a) Sampling Activities

The sampling activity had been done on 21<sup>st</sup> April. On that time the area covered are Bandar Industri Gopeng,Perak and Near by Medan Gopeng. The activity was conducted by Unfortunately, while waiting for the exam and the supervisor, Dr Lidia. The area is about 40 minutes from UTP. About 100 gram tree bark of Acasia had been collected with different height. Which are 0.5m,1.0m and 1.5m. The sample had been pack in the plastic and labeled. Since the time duration gap between the AAS training are quite long, new sample are taken. For this time, the sample taken in front of Medan Gopeng. Medan Gopeng has been chosen since the road are the most busy traffic in Perak. The another sample are taken in Kampung-kampung Layang Kiri, Perak.



Figure 9 : Sample Taken with Different Height



Figure 10 : Sample Taken with using Knife

### b) Sampling Preparation



Figure 11 : Sample of dried bark

1) The sample of tree bark are dried in the open air about one days. The weight for the initial are noted. Then, the tree bark are dried in open air, the tree bark are collected and ready to dried in oven. The Temperature used is about 110  $^{\rm O}$ C. The sample dried about 8-10 hours. After the sample reach the constant weight, the sample are removed. The final weight are recorded as below

	Intial (g)	Final (g)
Medan Gopeng		
0.5m	76.2	83
1.0m	73.8	54.3
1.5m	116	98
In front of Hill City		
0.5m	126	0.5

1.0m	73.8	63.7
1.5m	116	98
Kampung Layang-Layang, Bota		
0.5m	128.5	110.13
1.0m	137	118
1.5m	73.9	63.72

Table 3 : The weight of sample before and after dried



Figure 12 : sample of bark powder.

3) Then, the sample are grind used Morter Grinder located in the mechanical Block. Now, the sample turns into powder.

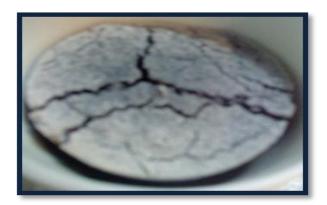
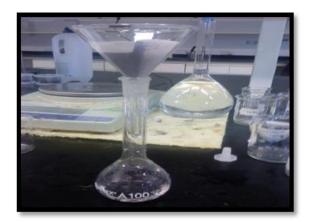


Figure 13 : Bark Ash

4) The 2 g sample are weight and placed into a crucible bowl. The, the sample are dried in the furnace. Organic matter will be remove.



5) The sample ready for the digestion. 10% of HNO3 are used. 20 ml of HNO3 are added in the 2g of Heavy Metal Organic. The samples are filter using filter paper and funnel. The sample placed in the 100ml flask. The water then pour into the 100ml flask until reach the volume of 100ml.



Figure 14 : Atomic Absorption Spectrometer

# **CHAPTER 4**

# **RESULT AND DISCUSSION**

## **4.1 Experimental Result**

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

Concentration of metals (mg/kg) =

Concentration(ppm) x volume extract of 0.1 L x Dilution Factor

Weight of samples of 0.002kg

The Safe Limit based on : Analysis of National Bureau Standard (NBS), US

Heavy Metal	Safe Limit (mg/kg)
Zinc	25
Lead	45
Cadmium	0.11
Nikel	1.3
Ferum	30

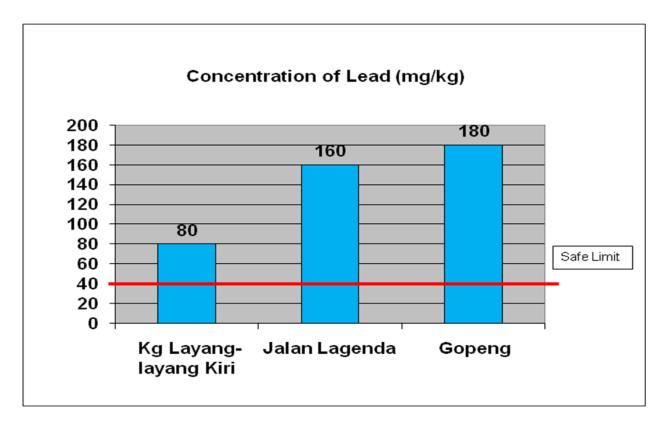
Table 3 : Safe Limit By NBS

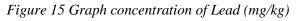
# 4.1.1 Heavy Metals : Pb

Point	Dilution Factor	Conc (ppm)	Conc (mg/kg)
Kg Layang-layang Kiri (Rural Density Traffic)	10	0.19	80
Jalan Lagenda, Gopeng (Medium Traffic Density)	10	0.5	160
Gopeng (High Density Traffic)	10	0.58	180

Discussion on the Result

Based on the result, a graph of Pb Concentration has been constructed as below.





All the concentrations for Pb are above safe limit. The safe limit stated by National Bureau Standard (NBS),US is 45 ppm. Medan Gopeng has the higher concentration which is 180 mg/kg and it is 4 times of the safe limit. Medan Gopeng is one of the busy area in Perak and heavy traffic in that which is the main bus sation located at the centre point. There is also a lots of shops, offices and also a more than3 of traffic lights which reduces traffics speeds and contributes to the traffic congestion. Higher numbers of vehicle is considered to contribute more heavy metal.Thus, more Kampung Layang-Layang Kiri which has lowest traffic density shows the lowest concentration of heavy metal.

Currently, most of vehicles used the unleaded feul. Li et al (2004) said although has been banned in petrol for number of years, the result for concentration of Pb maybe reflects the significance degree of historical Pb contaminant and the long half-life in bio indicator.

Jalan Lagenda which is located about 2 km from the centre of Gopeng recorded that the result of Pb is 160 mg/kg and Kg Layang-Layang Kiri is 80 mg/kg. It can said the it might be a possiblity the Pb also come from other sources such as industries, plantation and factory.

# 4.1.1 Heavy Metals : Pb

The Detection Limit of AAS analysis of Pb is between 4ppm

Point	Dilution Factor	Conc (ppm)	Conc (mg/kg)
Kg Layang-layang Kiri (Rural Density Traffic)	10	0.088	44
Jalan Lagenda, Gopeng (Medium Traffic Density)	10	0.17	85
Gopeng (High Density Traffic)	10	0.19	95

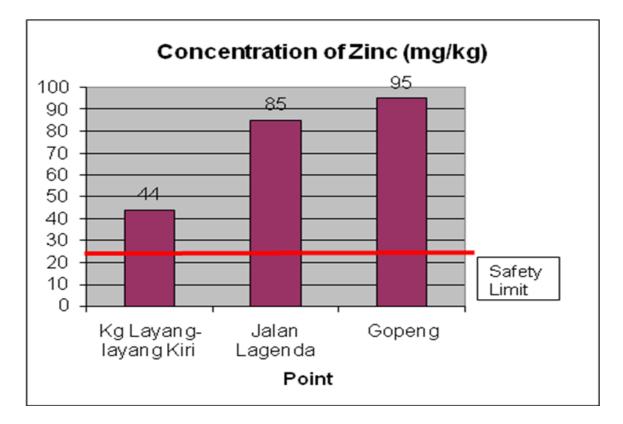


Figure 16 Graph concentration of Zinc (mg/kg)

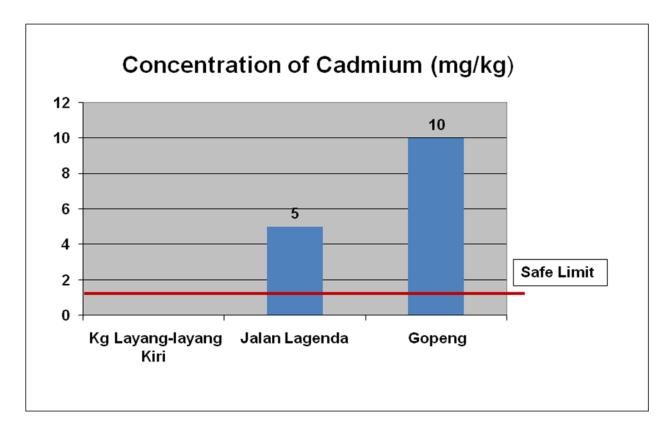
Based on the graph, it shows that the pattern graph for Pb is same with Zinc which Gopeng shows the highest concentration of Zinc. The concentration of Zn is 95 mg/kg which are 3 times of the safe limit. Jalan lagenda The concentration of Jalan Medan is lower than Gopeng due to less traffic density. The pattern of result for Zn is same with Pb. Kampung Layang-Layang Kiri which represents the lowest density area recorded the lowest value which is 44 mg/kg. The result also shows that the value is above safe limit.

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 mean that more vehicles will contributes the concentration of Zinc in atmosphere. All of the area shows that there are some influential and direct effect of vehicular activities of Zn Concentration. Medan Gopeng lead the highest result. As mention before, the area has very slow and heavy traffic which will be contributes more Zn contaminant to the atmosphere.

# 4.1.1 Heavy Metals : Pb

Point	Dilution Factor	Conc (ppm)	Conc (mg/kg)
Kg Layang-layang Kiri (Rural Density Traffic)	10	BDL	0
Jalan Lagenda, Gopeng (Medium Traffic Density)	10	0.01	5
Gopeng (High Density Traffic)	10	0.02	10

The Detection Limit of AAS analysis of Pb is between 4ppm



# Figure 17 Graph concentration of Cadmium(mg/kg)

Based on the result, there is slightly different result for Jalan Lagenda and Medan Gopeng which is 5 mg/kg. Both of the areas show the concentration for Cd is above the safe limit. The safe limit stated is 0.11 mg/kg. Medan Gopeng still lead the highest result which is 10 mg/kg while Jalan Lagenda is 5mg/kg. Kampung Layang-layang Kiri shows

that the result is below detection Limit. The sample cannot be detected by AAS equipment. The sample might be already contaminant or the concentration is very low.

By referring the result of study, the result for Cd is lower compared to Pb and Zinc. Thus, the reading of result for Cd, Pb And Zinc are quite obviously difference. It is about 40 mg/kg. There some possibility that the tree bark of Acasia is not too good to trace Cadmium or the sample Cd are not properly AAS detectable with AAS.

#### **Recommendation and Limitation.**

Recommendation is important base on the study. That is because it can be used for further study or research. Based on the some recommendation has been made. Firstly, the study for Acasia Should be done deeply research. There are some uncertainties over the length of exposure. Hence, the difficulties in standardizing sampling with respect depth should be covered. Due the time constraint, the process to deal with FRIM is immovable. The most important info is how long the element has been trap in bark. Thus, the result can be pattern year by year.

Besides, the sample that going to be analyzes need to be limited due to the limited services of AAS. The waiting duration for used the AAS is about 4 month. The sample for first sampling cannot be used since the duration between sampling and analyzed is too long. Thus, the samples cannot be duplicated for better result. Hence, only 3 area can be covered for the sampling due the time constraint. Most of the area near by UTP are ex-tin mining. It might infflunce the result of trace element. Thus, the possible area for sampling is about more than half hour.

Thirdly, there should be a based control which it can be represented any the forest that free from any vehicles. Unfortunately, the clear forest are quite far from UTP and its take a times. Based control is important where by we can get the better comparison.

### CHAPTER 4

### **CONCLUSION**

Based on the results, tree bark is able to detect the heavy metal dispersal from vehicular emission. The result also shows that when the amount of vehicles are increasing, the value of concentration also increasing. The higher traffic density shows the higher heavy metal dispersal compare to the rural area. This may indicate that the high number of vehicle contribute the high heavy metal contaminant. Hence, the rural area which less vehicle on the road produce the less concentration value of heavy metal. Tree bark has the potential as the alternative for bioindicator to monitor the heavy metal. Finally, people are easily highly exposed to the vehicular emission especially the heavy metal dispersal by vehicular emission because the vehicles in Malaysia are increasing day by day.