Heavy Metals in bark as an indicator of atmospheric deposition near ex-tin mines in Perak

by

Norizaidah binti Kusmaniirat

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

January 2010

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

DEDICATION

To my father,
the greatest gift I ever had
came from God

Kusmaniirat Hamzah

1951 - 2007

CERTIFICATION OF APPROVAL

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Approved by,

(Dr Nurlidia binti Mansor)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

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.

NORIZAIDAH BINTI KUSMANIIRAT

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ABSTRACT

Malaysia has long been recognized as one of the world's leading tin producers in 1960's. However, over the last 15 years, the tin industry collapsed due to exhaustion of tin deposits, low tin prices and high operating costs. Generally, the former tin mines are used for housing development, agriculture and recreational purpose. However, most former mines are used for crop production. These crops can cause the heavy metal to enter the food chain. Studies have shown that crops grown on these former mining sites have high levels of arsenic, mercury, cadmium and lead. Heavy metals release will cause harmful impact to the environment especially to the human health. There are three types of heavy metals pathway from mine site released to the surrounding. The pathways are from soil, river and atmospheric deposition. The scope of study is atmospheric deposition near tin mines. Tree barks from different trees will be used as a bio-monitoring indicator. Tree barks have been used successfully to monitor the levels of atmospheric metal deposition in many areas, but rarely in Malaysia. The objective of study aims to determine the heavy metals contain in tree barks as an indicator of atmospheric deposition near several ex-tin mine at Perak in relation to mine activity and also in relation to height of barks. Barks are taken from three ex-tin mines site at Tronoh, UTP and Malim Nawar. Samples are extracted using a stainless steel knife at an average size of 15 cm x 15 cm at different tree height from ex-tin mines. The samples then were analyzed for Lead (Pb) and Zinc (Zn) using atomic absorption spectrometry (AAS). Results showed that the concentrations of heavy metals in barks are range between 13.49 mg/kg to 49.35 mg/kg for Pb and 9.46 mg/kg to 46.12 mg/kg for Zn. It is found that there are an inverse relation between height and concentration, where with increased height of barks, the concentration of heavy metals decreased. It was concluded that there still have a dispersal of heavy metal from ex-tin mine even it was a non-active site.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Heavy metals have been found in varying amounts in soils, rivers, plants and sediments. Originating from the natural component of the earth crust, heavy metals are released naturally to the environment through weathering of rocks and soils. Mining is one of the major contributors of heavy metal contamination. Due to collapse of mining industry in Malaysia, several tin mine has been reused and refilled for human activity. Therefore, an assessment of heavy metal contamination from atmospheric deposition is essential to establish the accurate level of contamination. In Perak, we can see there are several ex-tin mine that is very near to the human life. The released of heavy metals from tin mines is very dangerous.

Figure 1.1: Tree Bark as bioindicator

In order to evaluate, minimize and avoid detrimental effect of toxic metal, there has been emphasis in the use of natural bioindicators to monitor atmospheric quality in both urban and rural environment. Since biomonitoring of mosses was first introduced by Ruhling and Tyler in 1968, the use of mosses, lichen and barks for monitoring of heavy metal deposition from the atmosphere has found wide application. Since 1981, mosses are used by the Environmental Protection Agency of Bavaria (Germany) as a bioindicator for atmospheric background pollution. This research attempts to investigate the environmental atmospheric pathways, which result in dispersion of heavy metal contaminants.

1.2 Problem Statement

Malaysia used to be one of the larger producers of tin in the world. However after 1980's, the industries of tin collapsed and most of tin-mine were closed. Due to rapid population growth, the ex-tin mines has been refilled and reused back. Some of the ex-tin mines are still active until now especially in the state of Perak. To date, almost all studies on the use of lichen and barks as bio-indicators of atmospheric pollution have been undertaken in Europe and America, while equivalent studies in Asia especially in Malaysia are lacking. This study was therefore undertaken to evaluate heavy metal levels in barks as an indicator of atmospheric deposition near ex-tin mines in Perak. Measurement of the level of atmospheric deposition from ex-tin mine is very important so that the impact can be known. These may give a reflection to the harmful condition and can safe human life by avoided from living and doing such an activity near ex-tin mines.

1.3 Objectives

1) To determine aerial deposition of Pb and Zn using tree bark as a bio-indicator near several ex-tin mine in Perak.
2) To study the atmospheric dispersal of heavy metals in relation to height using tree barks.
3) To compare the concentration of heavy metals dispersal between active and non-active ex-tin mines in Perak.

1.4 Scope of Study

There are three type of heavy metals depositions from tin mining sites which are soils, rivers and atmospheric. For this research, the study is focused on dispersal of heavy metal from ex-tin mines by using tree bark as bio-monitoring of atmospheric deposition. Heavy metal deposited on surface of tree bark should be investigate because the impact of it very dangerous to environment and human health.

The uses of tree bark as an indicator because it continually exposed to the environment over a period of several years. Therefore, it can give precise information about changes that occur in the air conditions of ecosystem. This and other characteristics make tree bark a suitable material for the evaluation of heavy metals deposition from tin-mines. There are a few technologies in world to measure the level of concentration. But to minimize and avoid detrimental of toxic metal, there has been an emphasis of use tree bark.

Another focused of work is to determined concentration of heavy metals in relation to height of bark. Previous study has been shown that concentration of heavy metal have a relation with height.

1.5 Relevancy of the Project

This project is said to be relevance because it was cheap and can finish within the time duration. There is other advance technology in order to determine the concentration of heavy metals in atmosphere. But due to the cost consideration, the usage of tree bark is suitable. Barks as a natural bioindicator and has been exposed to the environment over 30 years. Besides that, the availability of the bark is very high compare to the new technology.

CHAPTER 2

LITERATURE REWIEW

2.1 Heavy Metals

Heavy metals are individual metals and metal compounds that can impact human health. There are several types of heavy metals such as arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. These are all naturally occurring substances which are often present in the environment at low levels [8]. In large amounts, they can be dangerous. Generally, humans are exposed to these metals by drinking or eating (digestion) or breathing (inhalation). Working in or living near an industrial site which utilizes these metals and their compounds increases ones risk of exposure, as does living near a site where these metals have been improperly disposed. Lifestyles can also impose higher risks of exposure and health impacts because of hunting and gathering activities [8]. Although adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues and is even increasing in some areas. Since the middle of the 19th century, production of heavy metals increased steeply for more than 100 years, with concomitant emissions to the environment [7].

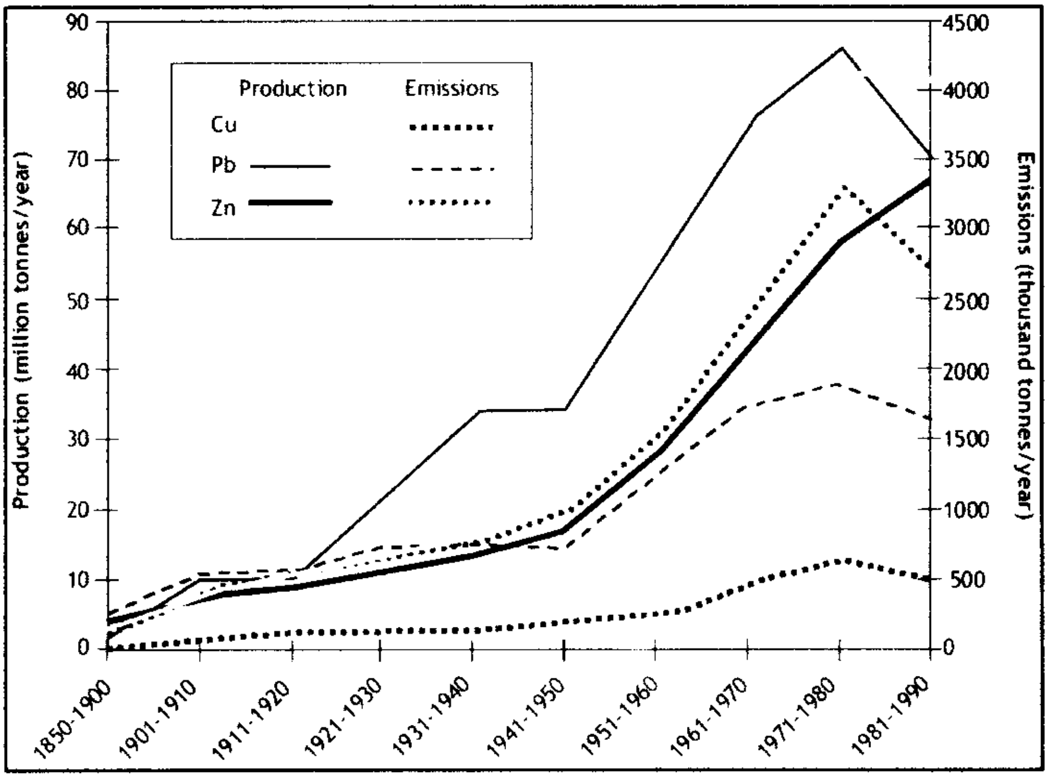

Figure 2.1 **Global production and consumption of selected toxic metals, 1850–1990.[7]**

2.1.1 Lead (Pb)

As a result of human activities, such as fossil fuel burning, mining, and manufacturing, lead and lead compounds can be found in all parts of our environment. This includes air, soil, and water. Occupational exposure to inorganic lead occurs in mines and smelters as well as welding of lead painted metal, and in battery plants. Low or moderate exposure may take place in the glass industry. High levels of air emissions may pollute areas near lead mines and smelters. Airborne lead can be deposited on soil and water, thus reaching humans *via* the food chain. Lead is used in many different ways. It is used to produce batteries, ammunition, metal products like solder and pipes, and X-ray shielding devices. Lead is a highly toxic metal and, as a result of related health concerns, its use in several products like gasoline, paints, and pipe solder, has been drastically reduced in recent years. Today, the most common sources of lead exposure in the world are lead-based paint and possibly water pipes in older homes, contaminated soil, household dust, drinking water, lead crystal, lead in certain cosmetics and toys, and lead-glazed pottery.

2.1.1.1 Health effects of Pb

Environmental Protection Agency (EPA) has determined that lead is a probable human carcinogen. Lead can affect every organ and system in the body. Long-term exposure of adults can result in decreased performance in some tests that measure functions of the nervous system; weakness in fingers, wrists, or ankles; small increases in blood pressure; and anemia.

- Exposure to high lead levels can severely damage the brain and kidneys and ultimately cause death.
- In pregnant women, high levels of exposure to lead may cause miscarriage.
- High level exposure in men can damage the organs responsible for sperm production.

2.1.2 Zn

Zinc is a very common substance that occurs naturally. Industrial sources or toxic waste sites may cause the zinc amounts in drinking water to reach levels that can cause health problems. Zinc occurs naturally in air, water and soil, but zinc concentrations are rising unnaturally, due to addition of zinc through human activities. Most zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing. Zinc is used as a white pigment in watercolours or paints, and as an activator in the rubber industry. As pigment zinc is used in plastics, cosmetics, photocopier paper, wallpaper, printing inks etc, while in rubber production its role is to act as a catalyst during manufacture and as a heat disperser in the final product. Zinc metal is included in most single tablet, it is believed to possess anti-oxidant properties, which protect against premature aging of the skin and muscles of the body.

2.1.2.1 Health effects of Zn

Zinc is a trace element that is essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc-shortages can even cause birth defects. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis.

2.2 Heavy Metals in Environments

The rapid population growth and industrial activities expansion have increasingly affected the chemical substances in our environment. Many heavy metals emitted mostly from anthropogenic sources have no exceeded or equaled their emissions and has been posing a serious threat to the ecosystems [21]. Originating from the natural component of the earth's crust, heavy metals are released naturally to the environment through weathering of rocks and soils [14]. Atmospheric emissions tend to be of greatest concern in terms of human health, both because of the quantities involved and the widespread dispersion and potential for exposure that often ensues [7].

In order to evaluate the level of metals, there has been an emphasis in the use of natural bioindicators to monitor atmospheric quality [15]. Recent investigation have shown that barks can be used effectively monitor levels of metal contamination in the atmosphere. Increased metal concentrations and decreased pH values have been reported in the tree barks from the high industrial activity, increased urbanization, increased acidity precipitation and high traffic loads [21].

2.3 Environmental Impact of Mining

Mining is one of the main contributors of heavy metal contamination worldwide. Mining and smelting of ore-bearing rocks can release large quantities of trace element bearing volatile species and dust particles into the environment. Thus, the assessment of the current level of heavy metals contamination from atmospheric deposition is essential to establish the accurate levels of heavy metals. It is carried out to consider the current level of environmental contamination by heavy metal pollutants, major emission sources and source regions, and the contribution of the atmospheric pathway to the contamination of terrestrial and aquatic environments. Heavy metals contained in residues coming from mining and metallurgical operations are often dispersed by wind and/or water after their disposal.

2.4 Mining in Malaysia

2.4.1 History of Tin Mining

Tin mining is one of the older industries in Malaya. The tin mining has started since 1820s in Malaysia after the arrival of Chinese immigrants. The Chinese immigrants settled in Perak and started tin mines. Tin was the major pillars of the Malaysian economy. Tin occurs chiefly as alluvial deposits in the foothills of the Peninsular on the western side. There were 10 mines in Perak, 13 in Selangor, 2 in Pahang, and 1 in Johor. The most important area is the Kinta Valley, which includes the towns of Ipoh, Gopeng, Kampar and Batu Gajah in the State of Perak. By 1883, Malaysia had become the largest tin producer in the world. By the end of the 19th century, it was supplying about 55% of the world's tin compared with the 1992 about 30% [18].

2.4.2 Collapsed of Tin Mining Industry

The tin industry in Malaysia collapsed in early 1988. The downfall of the tin industry is not just a result of the price drop, but also due to the escalating costs of energy, skilled manpower, environmental constraints and land availability in comparison with other industries, which may get a higher priority for development over mining. Collapse of tin mining industry is due to:

1) Falling in tin prices
2) In the food packaging industry, substitutes like aluminum, paper and plastic were used instead of tin.
3) People's awareness of environmental problems led them to recycle tin scraps and this further reduced the demand of tin.
4) The rising cost of production.
5) Rising energy cost raised the cost of mining to make it less profitable.
6) High taxes were imposed on the amount of tin produced.
7) Little land set aside for mining.
8) Fewer areas were set aside for mining because of competition from profitable use of land.

2.5 Barks as a bioindicator

Bioindicator is defined as an organism that provides quantitative information on the quality of the environment around it. Therefore, a good biomonitor will indicate the level of the pollutant and also attempt to provide additional information about the amount and intensity of the exposure. The importance and relevance of biomonitors, rather than man-made equipment, is justified by the statement: "There is no better indicator of the status of a species or a system than a species or system itself" [19]. There are several types of plant biomonitors, including mosses, lichens, tree bark, bark pockets, tree rings, leaves, and fungi.

Since biomonitoring of mosses as first introduces by Ruhling and Tyle in 1968, the use of mosses, lichen and barks for monitoring of heavy metal deposition from the atmosphere has fond wide application. The possibility of using tree barks for air pollution monitoring has been investigate since 1970 due to its advantages [2]. Tree barks are appropriate natural bio-indicators for the assessment of long-term air pollution. The bark is exposed to air pollutants either directly from the atmosphere or from steam flow [8]. Tree bark is continuously exposed to the environment over a period of several years. Therefore, if can give precise information about changes that occur in the air conditions of ecosystem [7].

2.6 Sampling

To access the changed of heavy metals in mining environment, sampling is required a long time basis, and at large sites. Distance from mines, wind directions, topography and atmospheric condition can all have an important influence on the distribution of contamination. Therefore, in order to get a good result, study will do due to different scope of sampling stations. Sampling may take from a near tree position to as far away from tin mining site and the height of tree to be monitoring also can vary. Metals introduced into the atmosphere may be deposited on the land surface by precipitation and dry fallout [14]. According to Jacob Carty, heavy metal content in lichen and barks was found to be significantly decreased at a distances from sources released [10].

Long range atmospheric transport is one of the main factors for dispersion and deposition of a wide range of pollutants [9]. The atmospheric dispersion of this research is on the tree barks in the vicinity of tin mining sites. Heavy metals are taken up to a varying degree by different plants as well as different parts of a plant species [17]. Within the barks there are two parts outside the woody body

[21]. One is the living part, the inner bark, and the other one is the dead part, the outer bark. Although the tree bark is known to absorb and accumulate airborne contaminants due to their hard, rough and thick structure [9], the relative importance of an accumulation of pollutant directly from the atmosphere compared with uptake from the soil in the different parts may be negligible.

Due to a small part of the inner bark, most previous studies except from Satake et al. (1996) have sampled the whole bark for analysis and ignored the difference between inner and outer barks [21]. Tree bark has been shown to be able to indicate levels of airborne pollutants such as Pb, Zn, Cu, Cr, Ni, Cd, Mn, Fe, U, Pt [2].

To date, almost all studies on the use of barks as bioindicators of atmospheric deposition has been undertaken in Europe and America, while equivalent studies in Malaysia are lacking. This study was therefore undertaken to evaluate heavy metals in bark near tin-mines at Tronoh to provide primary data for Malaysia.

2.7 Atomic Absorption Spectrometry (AAS)

Atomic absorption spectroscopy is a technique for determining the concentration of a particular metal element in a sample. The technique can be used to analyze the concentration of over 70 different metals in a solution. Atomic absorption is a very common technique for detecting metals and metalloids in environmental samples. It is very reliable and simple to use.

CHAPTER 3

METHODOLOGY

3.1 Sampling

To characterize heavy metals deposition, several barks near ex-tin mine around Perak has been taken as a sample. Bark sample are taken from tree species *Acacia auriculiformis* with different height from point sources which is ex-tin mine. Bark sample of approximately 15cm x 15cm was removed using stainless steel knife to a depth of approximately 1mm. Barks sample were taken from tree at heights of 2 ft, 4 ft and 6 ft. Each tree bark should be collected at a standard sampling height of 1.5 m above the ground. This height was chosen to avoid areas where soil particles may be splashed onto the trunk during periods of rainfall. However, due to so many branches and height at the tree (Figure 3.4), samples can only take up to height 6 ft above the ground. Bark samples obtained from the sampling site were placed in plastics and labeled before being taken back to the laboratory for analysis.

Table 3.1: Sampling Location and coordinate of the tree

Sample	Location	Coordinate
1	Tronoh A	4.403, 100.977
2	Tronoh B	4.403, 100.978
3	UTP Lake	4.382, 100.975
4	Malim Nawar	4.350, 101.117

Figure 3.1 and 3.2 shows the location of sampling at several ex-tin mine around Perak. At location 1, 2 and 4, there is an activity of digging the sand at the mine. So that, the location is said to be an active site. Location 4 is defined as non-active site because it does not have any activity near to the site.

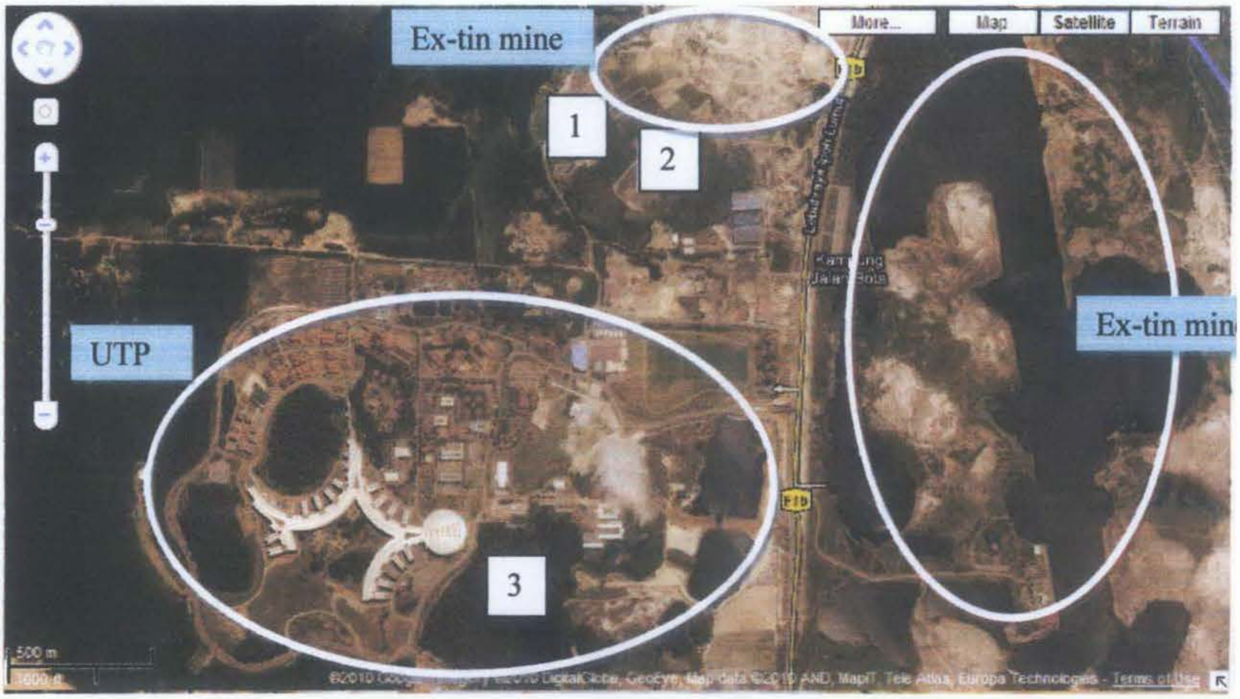

Figure 3.1: Sampling Location at Tronoh and UTP Lake from Satellite view

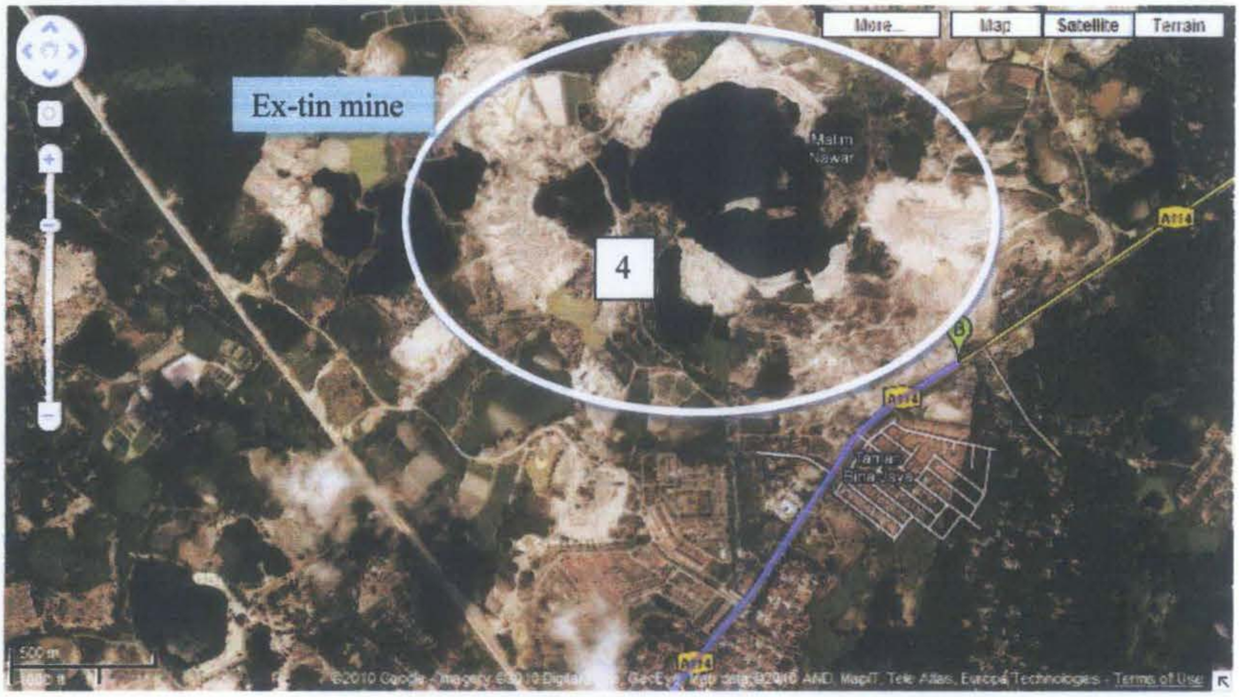

Figure 3.2: Sampling Location at Malim Nawar from Satellite view

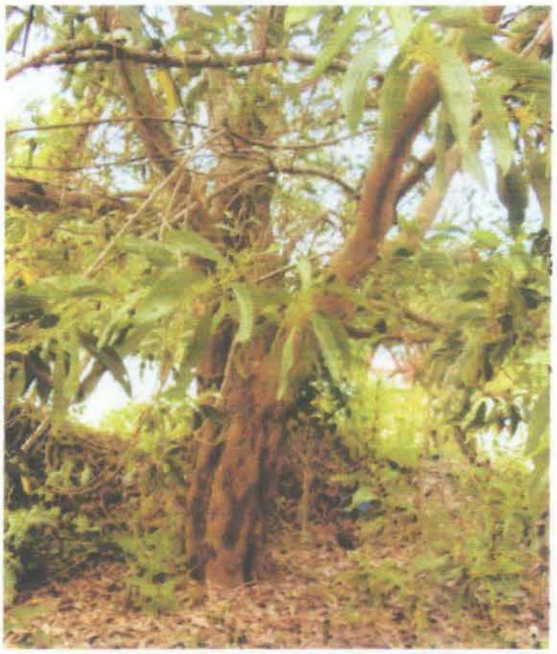

Figure 3.3: Sampling Tree: ***Acacia auriculiformis***

Figure 3.4: Structure of tree after barks taken

3.2 Sample Preparation

3.2.1 Apparatus

1. Electronic weighting (3000 gram).
2. Oven
3. Furnace
4. Grinder
5. Crucible bowl
6. Nitric acid (HNO_3)
7. Filter paper
8. Conical flask

3.2.2 Procedure

1. Weight the samples with electronic weighing.
2. Barks sample are dried in laboratory to remove dead or senescent tissues and extraneous materials: adhering bark, mosses etc [11].

3. Weight the samples with electronic weighing.
4. A sample then was put into oven at temperature 120°C for about 5 hours to get a constant weight [3].

5. Weight again the samples.
6. Dried samples then are grinded with a laboratory mill using a 2μm aperture.

7. About 2 g powders of the barks are accurately weight and transfer into a properly cleaned crucible bowl.
8. Transfer the sample into furnace at 500°C for 8 hours to remove the remaining organic matter.

9. Weight again the samples.
10. Samples digested with 10% Nitric Acid (HNO_3) and filter through acid-washed filter paper.

11. Add distilled water to bring the extract up to the total volume of the conical flask.
12. Analyze solution for total metal contain with Atomic Absorption Spectrometer (AAS).

3.3 Method for Analysis of Heavy Metals Using Atomic Absorption Spectrometer

3.3.1 Equipment / Apparatus

1. Flame Atomic Absorption Spectrometer
2. Volumetric flask
3. Pipette sucker
4. Funnel
5. Micropipettes

3.3.2 Preparation of Zero Calibration Solutions

Prepare zero calibration solution by dissolving 8 ml pure concentration HNO_3 in about 250 ml double distilled water in 1000 ml volumetric flask and then diluting it up to the mark by adding double distilled water.

3.3.3 Preparation of Working Solution

1. For preparation of 40 ppm working standard solution, pipette 1ml of standard 1000 ppm stock solution with the help of volumetric pipette into 25 ml volumetric flask. For 200 ppm working standard solution 5 ml of standard1000 ppm stock solution with the help of volumetric pipette into 25 ml volumetric flask.
2. Make the volume up to the mark by adding zero calibration solution to prepare working standard/ stock solution.
3. Switch on the AAS and operate all other steps following working instruction as per APPENDIX B.

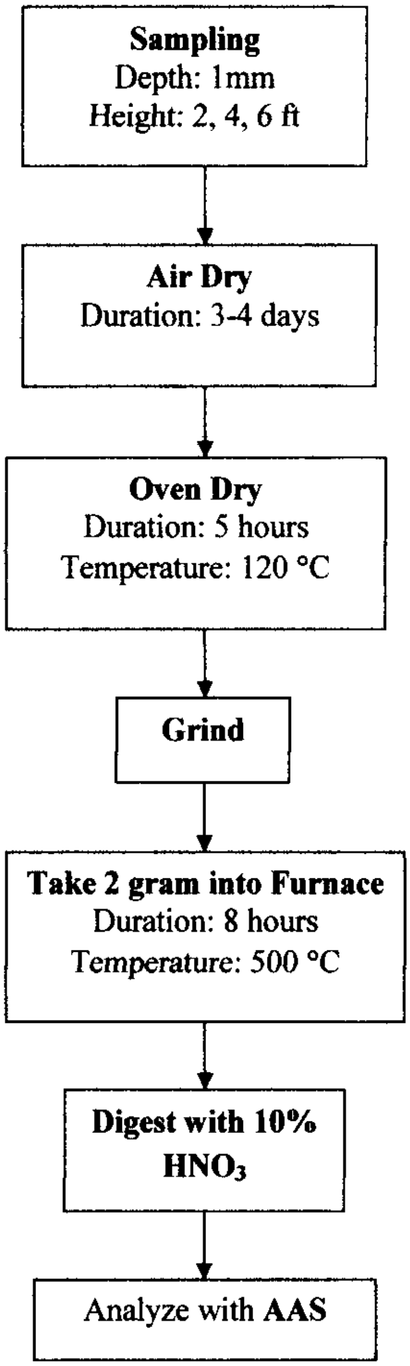

Figure 3.5: Flow diagram for the sample preparation and analysis

CHAPTER 4

RESULT AND DISCUSSION

4.1 Results

Samples of tree barks have to undergo some procedures before being analysis with AAS. This section present the result of experiment starting from drying of the tree barks until analysis with AAS.

4.1.1 Percentage of Moisture Removed

Table 4.1 below shows the percentage of moisture removed from the barks before and after the barks is dried. Weight 1 represents weight of the barks before air dried. While weight 2 represents weight of the barks after air dried. Lastly, weight 3 represents weight of the barks after being dried with oven at 120°C.

Table 4.1: Total of moisture remove after dried

Location	Height (ft)	Weight 1(g) (Before Air Dry)	Weight 2 (g) (After Air Dry)	Weight 3 (g) (Oven Dry)	% moisture removed
Tronoh A	2	26.64	25.95	21.78	18.24
	4	14.59	14.20	11.10	23.92
	6	17.74	17.40	14.12	20.41
Tronoh B	2	18.08	17.86	13.68	24.34
	4	33.18	31.28	25.19	24.08
	6	38.27	36.98	29.98	21.66
UTP lake	2	85.46	61.30	48.01	43.42
	4	43.86	31.56	23.47	46.49
	6	41.72	28.26	20.52	50.82
Malim Nawar	2	38.79	36.12	34.54	10.96
	4	44.73	43.38	41.76	6.64
	6	36.97	34.65	30.65	17.09

4.1.2 Organic Matter Removed

Table 4.2 below shows total organic matter that has been removed after it being takes out from furnace. Weight 4 represent weight of the bark before it being taken into 500°C furnace and weight 5 represent weight of the bark after taken out from furnace. Total of organic matter removed from tree barks can be seen in below table.

Table 4.2: Total of organic matter removed

Location	Height (ft)	Weight 4 (g)	Weight 5 (g)	Loss on Ignition –LOI (%)
Tronoh A	2	2.00	0.05	97.5
	4	2.00	0.01	99.5
	6	2.00	0.02	99.0
Tronoh B	2	2.00	0.07	96.5
	4	2.00	0.05	97.5
	6	2.00	0.05	97.5
UTP Lake	2	2.00	0.23	88.5
	4	2.00	0.22	89.0
	6	2.00	0.19	90.5
Malim Nawar	2	2.00	0.07	96,5
	4	2.00	0.05	97.5
	6	2.00	0.06	97.0

4.2 Discussions

This part is discussed more on the results obtained from the analysis of AAS. Here it discussed on the concentration of heavy metals in relation to height of the tree barks and also the comparison of heavy metals deposition at different activity of ex-tin mines.

4.2.1 Heavy Metals Concentration in Relation to the Height of Tree Barks.

The concentration of heavy metals may show a relation to the height of the barks. Concentration of heavy metals is decrease when height of barks is increased. Table 4.3 and 4.4 tabulates the concentration of heavy metals Pb and Zn for different barks and height.

Table 4.3: Concentration of Pb

Location	Height (ft)	Concentration (mg/l)	Concentration (mg/kg)
Tronoh A	2	0.44	21.76
	4	0.38	19.00
	6	0.32	16.24
Tronoh B	2	0.93	46.59
	4	0.66	32.80
	6	0.38	19.00
UTP	2	0.60	30.04
	4	0.41	20.38
	6	0.27	13.49
Malim Nawar	2	0.99	49.35
	4	0.96	47.97
	6	0.71	35.55

Table 4.4: Concentration of Zn

Location	Height (ft)	Concentration (mg/l)	Concentration (mg/kg)
Tronoh A	2	0.34	17.09
	4	0.33	16.30
	6	0.19	9.46
Tronoh B	2	0.33	16.60
	4	0.28	14.22
	6	0.23	11.74
UTP	2	0.92	46.12
	4	0.60	29.78
	6	0.56	27.89
Malim Nawar	2	0.47	23.63
	4	0.46	22.94
	6	0.35	17.39

From the table, we can see that the concentration of heavy metals increased when height of the bark decreases. This is because, during the dispersal of air, heavy metals from ex-tin mine is brought up together with the wind. At height of 2 ft above ground, it is shows that the concentration of heavy metals is much higher compared to 4 ft and 6 ft. This may be due to the stem flow effect where rainfall causes particles to move downwards. Therefore, heavy metals tend to accumulate at lower part of the tree. Gravitational force also causes the heavy metals to be deposit at the lower part of the tree. The results support this assumption where the trend of heavy metals deposition is quite similar for each tree for both Pb and Zn test. Figure 4.1 and 4.2 shows the concentration of heavy metals deposition for different location at different height.

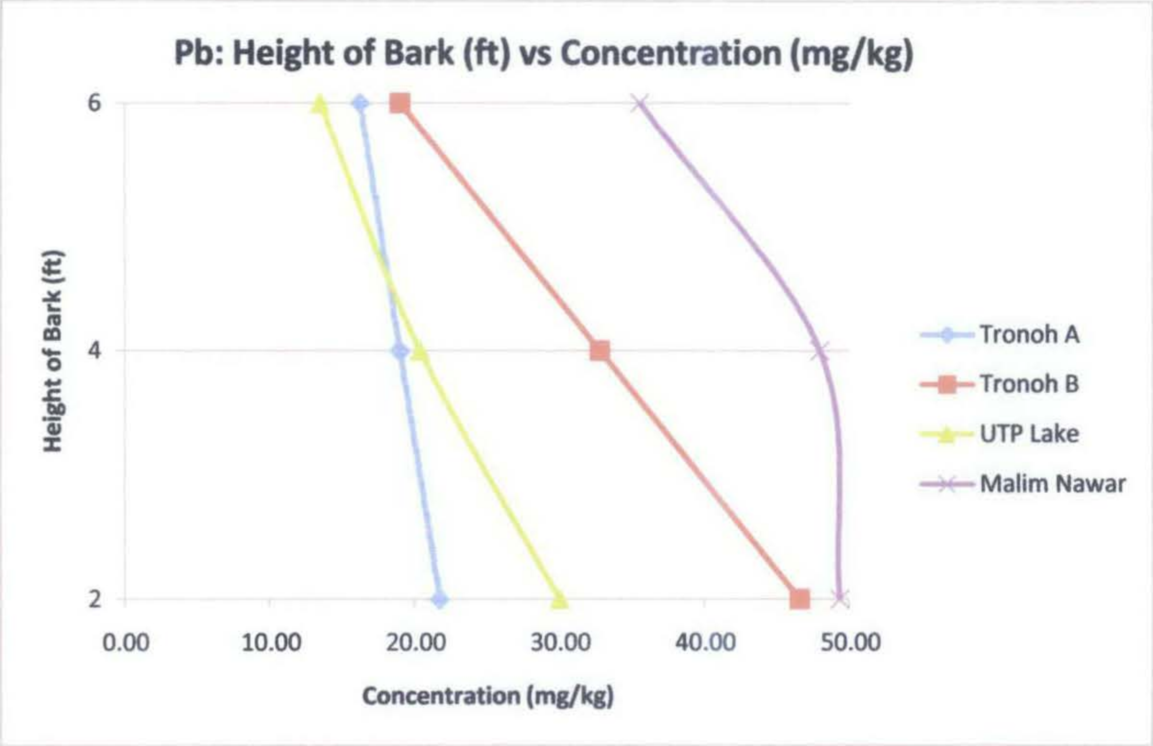

Figure 4.2: Concentration of Pb in relation to height

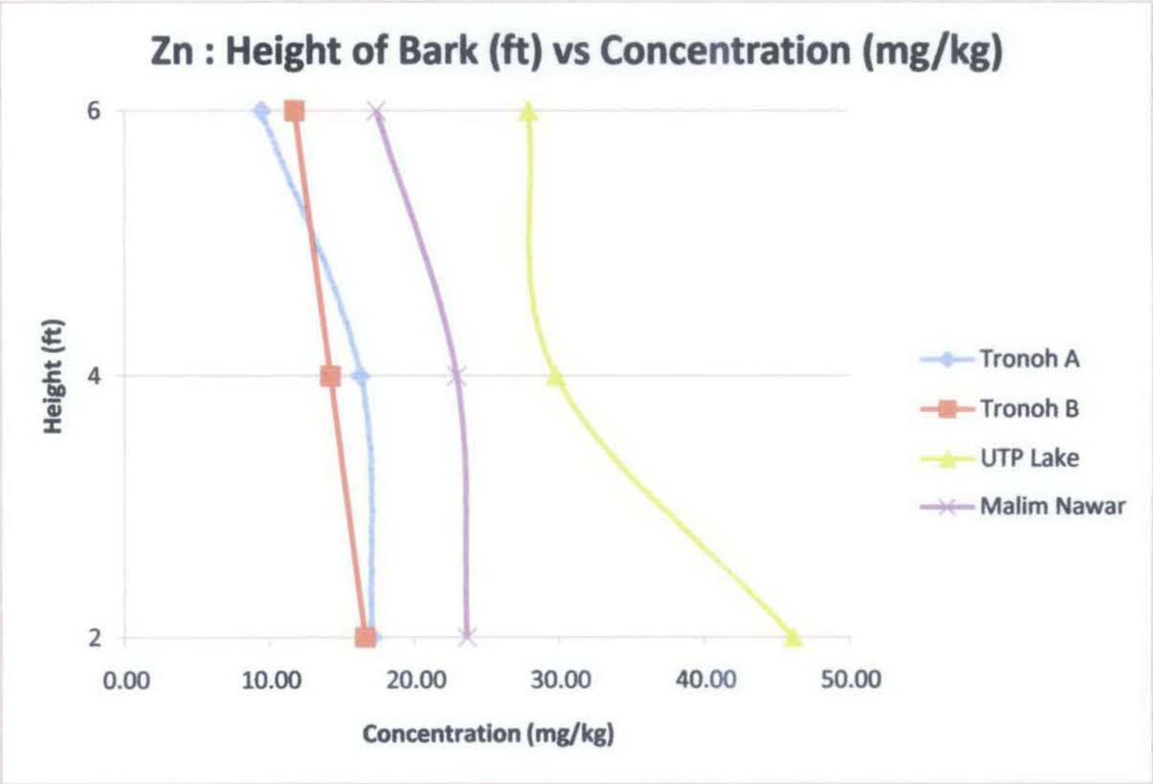

Figure 4.1: Concentration of Zn in relation to height

4.2.2 Heavy Metals Concentration in Relation to the active and non-active mine.

This section discussed the results for the heavy metals concentration in relation to the activity occurred near several ex-tin mines in Perak. Even though the tine mining activity has collapsed in Malaysia, but there are still activities near the ex-tin mines such as excavation of sand and crops and vegetation plantation. Because of all these activities, the heavy metals from ex-tin mines are still dispersed to the atmosphere. Figure 4.3 and 4.4 below shows the comparison of heavy metals concentration from active and non-active site for both Pb and Zn.

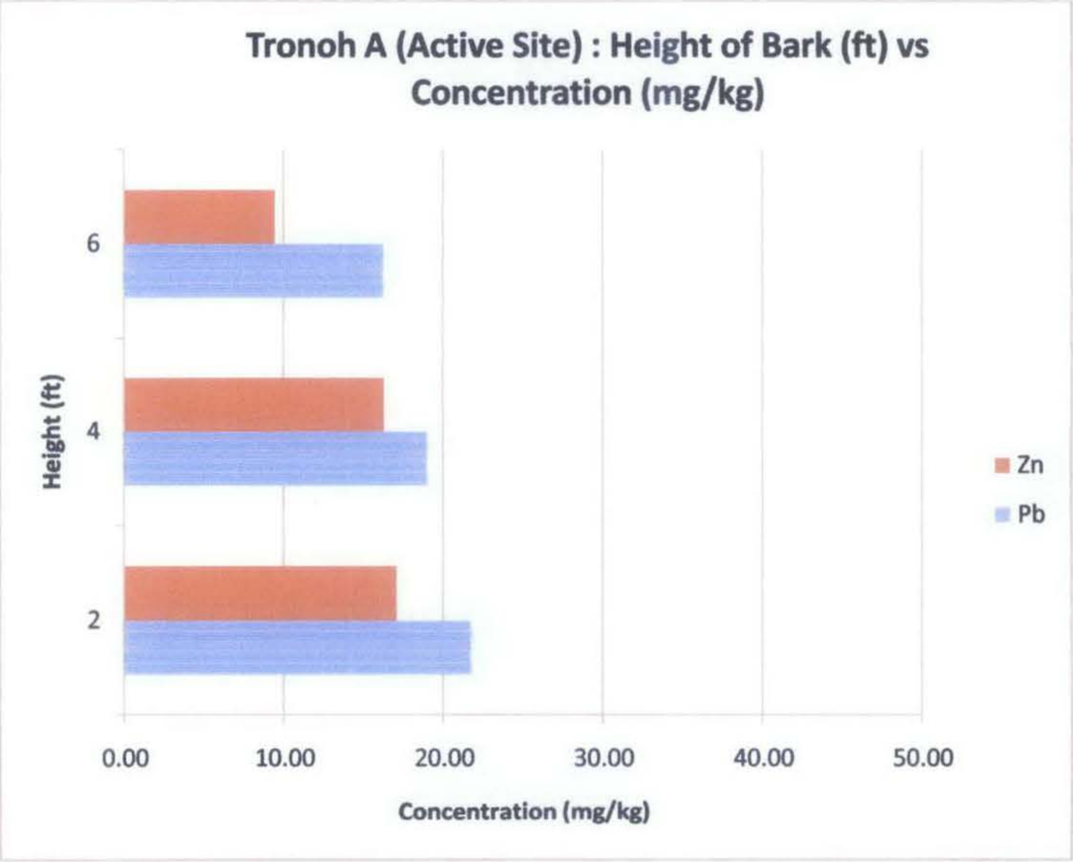

Figure 4.3: Concentration of Pb and Zn at Tronoh A

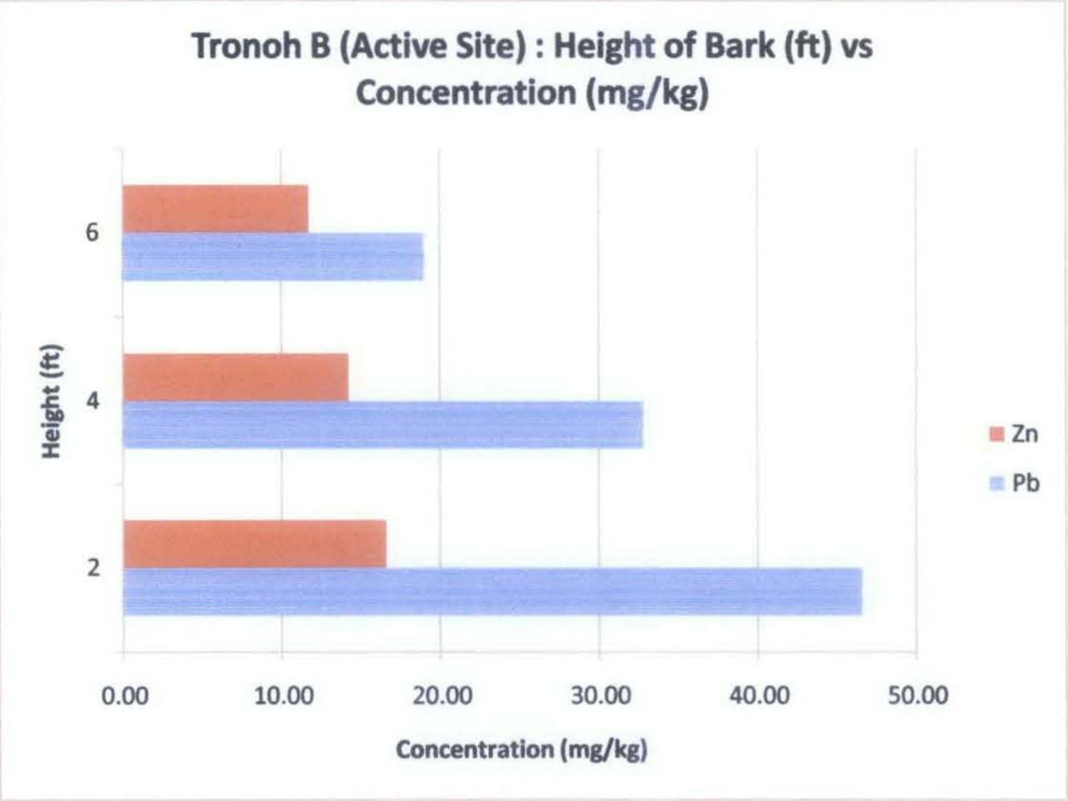

Figure 4.4: Concentration of Pb and Zn at Tronoh B

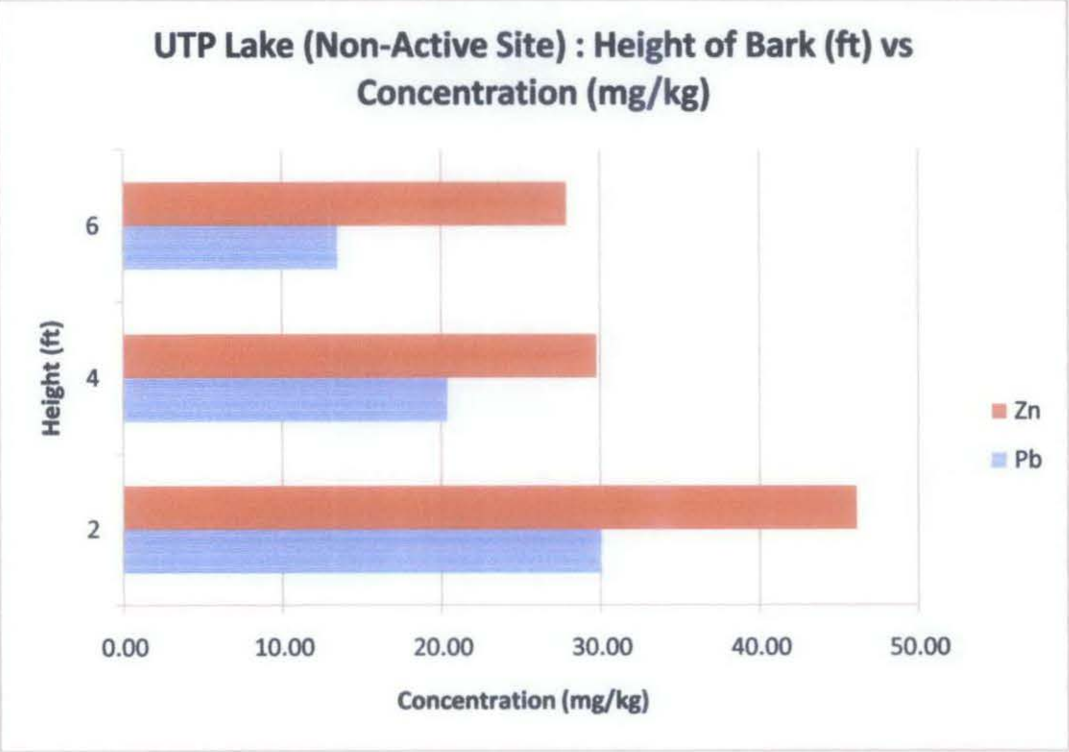

Figure 4.5: Concentration of Pb and Zn at UTP Lake

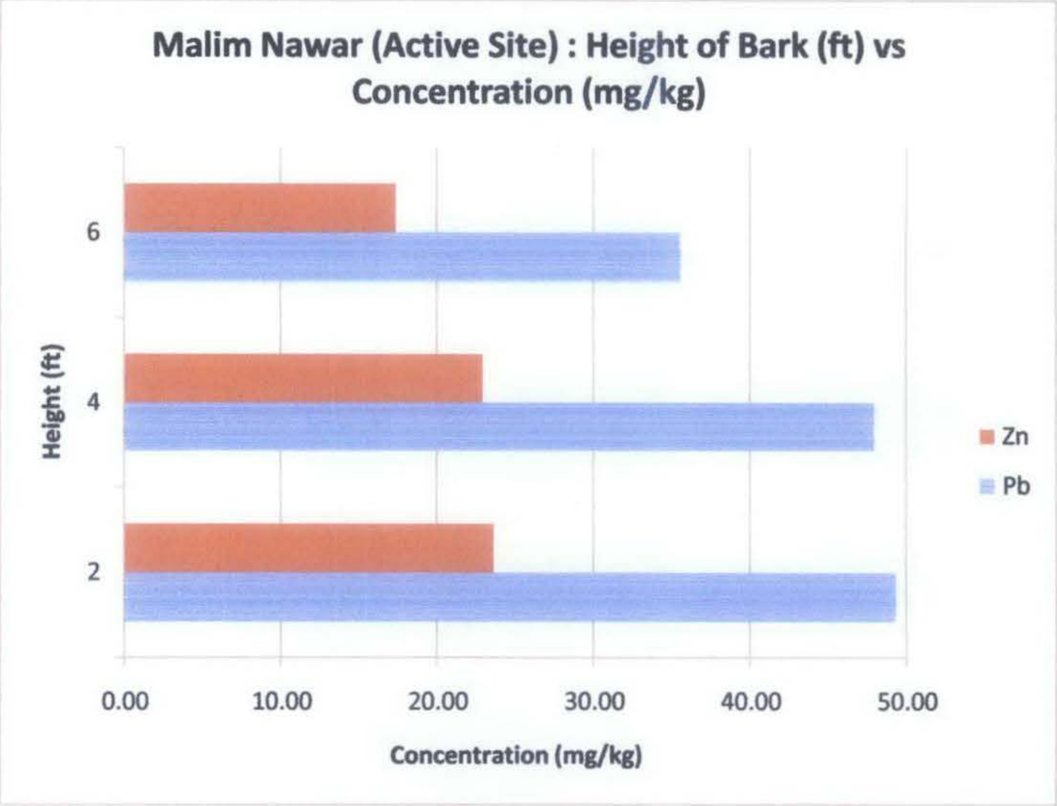

Figure 4.6: Concentration of Pb and Zn at Malim Nawar

From figure 4.3 to 4.6, highest concentration of Pb was found at active site in Malim Nawar with concentration of 49.35 mg/kg at height 2 ft. Lowest concentration of Pb was found at non-active site in UTP Lake with concentration of 13.49 mg/kg at height 6 ft. While for Zn, Highest concentration was found at active site which is UTP Lake with concentration of 46.12 mg/kg at height 2 ft. and lowest concentration of Zn was found at active site Tronoh A with concentration 9.46 mg/kg at height 6 ft.

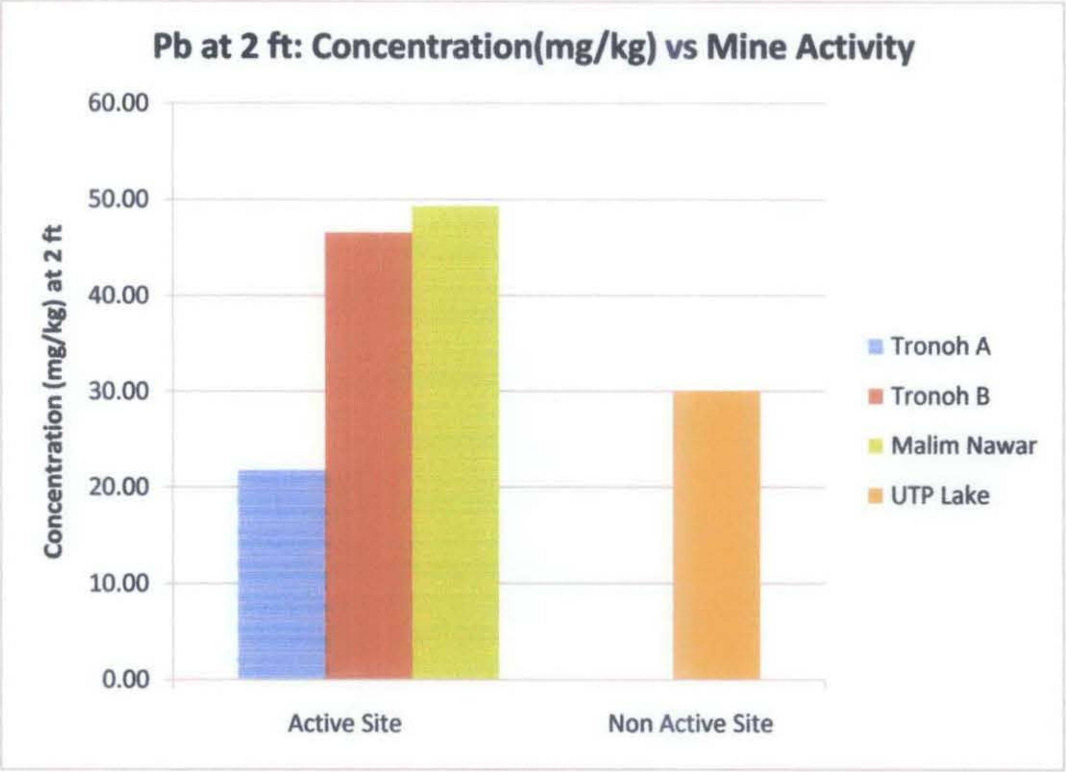

Figure 4.7: Concentration of Pb in Relation to Mine Activity

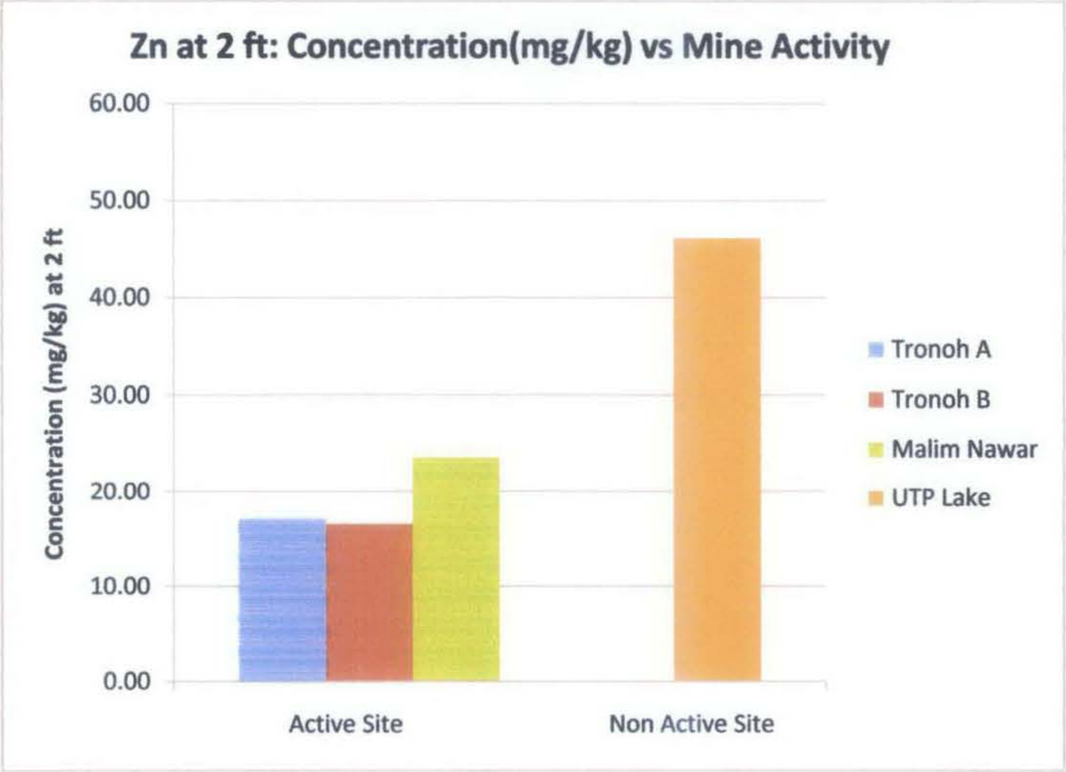

Figure 4.8: Concentration of Zn in Relation to Mine Activity

From figure 4.7, we can see that the concentration of Pb was in the range of 20 mg/kg to 50 mg/kg at active site. While at non-active site, the concentration is 30 mg/kg which is still in the range of 20 to 50 mg/kg. In figure 4.8, the concentration of Zn was in the range of 10 mg/kg to 50 mg/kg. However, the highest concentration of Zn was found at non-active site.

We can see that the concentration of Pb and Zn is within the range 10 to 50 mg/kg. This is because at all three location of active site, the activity of excavation of sand is occurred near to ex-tin mine. The activity is continuing more than 20 years. It may assume that the deposition of Pb is not only contributed from mine but also sourcing from Pb produce from vehicles such as lorry and bulldozer. Compare to concentration of heavy metals at UTP Lake, it is shows that Zn gives highest value. This may due to the re-located of the lake for the last few years ago. The lake was dug. Higher concentration of Zn is due to the exposure to the environment during relocation of lake and it dispersed in large quantity.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

There are two major focus of this study which is to determine degree of heavy metal deposition in the atmosphere near several ex-tin mine at Perak and to demonstrate the suitability of tree bark as an indicator of heavy metal deposition from the atmosphere. Based on the results, it is demonstrated that the heavy metals analysis on tree barks will provide new information and valuable data concerning the level of atmospheric deposition near several ex-tin mines at Perak.

Heavy metals concentration has an inverse relation with height. The concentration of Pb and Zn were found to be higher when height of the bark lowers.

The concentration of Pb was generally found higher at the active sites compared to the non-active site. However the concentration of Zn was found higher at the non-active site compared to active site. This shown that heavy metal is still dispersing from ex-tin mine even if there are no obvious activity at the site.

5.2 Recommendation

Further study research should be considered in relation to heavy metal dispersal from ex-tin mines for different types of tree species. This is to prove the suitability of barks as a bioindicator especially in Malaysia. Besides the use of different tree, age of tree should also be considered in future studies. By knowing the age of the tree, it is easy for the researcher to investigate the level of contamination of heavy metal from ex-tin mine. It may reflect accumulation data which shown the concentration level of heavy metal increases or decreases over the years on not.

Method of sampling also should be taken under consideration. In future studies, sampling should be taken from the tree in all direction not only focused on bark facing the point sources. This is because at the site there were more than 2 mines near the sampling tree. So the effect of heavy metal dispersal may come from all direction.

Lastly, it is recommended that more research should be done. Other ex-tin mines areas such as in the Klang Valley and Sungai Lembing should be taken under studies consideration.

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LIST OF APPENDICES

APPENDIX A

Conversion of concentration from mg/l to mg/kg

$$\frac{mg}{kg} = \frac{x\frac{mg}{l} \times Volume\ of\ Solution\ (l)\ \times Dilution\ Factor}{Mass\ (kg)}$$

APPENDIX B

Standard Method for Analysis of Heavy Metals & Minerals using Flame Atomic Absorption Spectrophotometer

1. **Purpose:**

   This standard testing method is to explain step by step procedure to analyze the metals (Cr, Mg, Ni, Cd, Ca, Pb, Sb, Zn, Fe, Cu, Na, K, Mn, As, Hg) in the samples of raw materials and finished products of different nature and matrix using Flame Atomic Absorption Spectrophotometer

2. **Scope:**

   This procedure describes all steps involved in the analysis of heavy metals & minerals in the samples of raw materials and finished products of different matrix using Atomic Absorption Spectrophotometer. This standard testing method is applicable to water, waste water, foods, herbal and pharmaceutical products for determination of followings.

Sr No	Element	Detection Limit
1	Cr	0.1ppm
2	Mg	0.1ppm
3	Ni	0.5ppm
4	Cd	0.1ppm
5	Ca	0.5ppm
6	Pb	0.5ppm
7	Sb	5ppb
8	Zn	0.1ppm
9	Fe	0.5ppm
10	Cu	0.1ppm
11	Na	0.5ppm
12	K	0.1ppm
13	Mn	0.1ppm

14	As	5ppb
15	Hg	5ppb

3. Equipment/Apparatus:

3.1 Flame Atomic Absorption Spectrophotometer (with all related standard solutions and accessories)

3.2 Volumetric flasks (10mL, 50mL, 100mL & 1000 mL)

3.3 Volumetric pipettes (5 & 10 mL)

3.4 Pipette Sucker

3.5 Funnel

3.6 Micropipette (up to 1 mL Capacity)

4. Reagents/Chemicals required:

4.1 Conc HNO_3 (Analytical/ Reagent grade)

4.2 Standard Stock Solution (NIST traceable)

4.3 Double distilled water

4.4 5% Lanthanum Solution

To prepare 5% (w/v) solution of Lanthanum weigh accurately 58.65 g of La_2O_3 in a 1 Litre beaker, wet the powder with DD water, add slowly and in small amounts 250ml conc HCl, quantitatively transfer and make to 1 Lt in volumetric flask with DD water.

4.5 2% Cesium Solution

To prepare 2 % (w/v) Cesium solution weigh accurately 25.335g CsCl in a 1 Lt volumetric flask, add 86ml conc. HCl and make up the volume using double distilled water.

Standard Method for Analysis of Heavy Metals & Minerals using Flame Atomic Absorption Spectrophotometer

5. Procedure:

5.1. **Environmental Conditions:**

Temperature (25 ± 5 °C)

5.2. **Preparation of Sample Solution:**

5.2.1 Drinking water samples are not required to prepare by ashing while other samples (Herbal and food Products) should be prepared as described in standard method for sample preparation for elemental analysis (Doc. # *TEC-/PL-SMS-01*)

5.3. **Preparation of Zero Calibration Solutions:**

5.3.1 Prepare zero calibration solution by dissolving 8 mL pure conc. HNO_3 in about 250 mL double distilled water in a 1000 mL volumetric flask and then diluting it up to the mark by adding double distilled water.

5.4. **Preparation of Working Solutions:**

5.4.1 For 40ppm working standard solution pipette 1mL of standard 1000ppm stock solution with the help of volumetric pipette into clean 25mL volumetric flask and for 200ppm working standard solution pipette 5mL of standard 1000ppm stock solution with the help of volumetric pipette into clean 25mL volumetric flask.

5.4.2 For 1000ppb working standard solution pipette 25µL of standard 1000ppm stock solution with the help of Micropipette pipette into clean 25mL volumetric flask.

5.4.3 Make the volume up to the mark by adding zero calibration solution to prepare working standard/ stock solution.

5.4.4 For determination of Na & K also add 1 ml 2% Cesium solution/ 10ml while for determination of Ca & Mg add 1ml 5 % Lanthanum solution/10ml of standard samples while making up to the final volume.

***Note:** All the glassware should be properly washed with detergent and tap water followed by rinsing thrice with distilled water, twice with double distilled water and once with zero calibration soln.*

5.5 Standard Curve:

5.5.1 Switch on the Atomic Absorption Spectrophotometer and operate all other steps following work instructions (*TEC-IPL-WI-16*).

5.5.2 Aspirate the zero calibration solution and auto zero the instrument.

5.5.3 Aspirate different standard solutions in ascending order for preparation of standard calibration curve applying standard conditions for the mineral to be analyzed.

Diluted Standard Solutions (For Standard Curve):

Working Standard Solution	**Diluted Standard Solutions**
40ppm	0.1ppm, 0.2ppm, 0.4ppm, 0.8ppm
200ppm	0.5ppm, 1ppm, 2ppm, 4ppm
1000ppb	5ppb, 10ppb, 20ppb, 40ppb

5.6. Sample analysis:

5.6.1 Aspirate the zero Calibration solution (Ref 5.3) or sample blank as blank.

5.6.2 Aspirate the sample solution to be analyzed into the flame and in case of default of software note data in lab note book.

6 Quality Checks/ Verification:

6.1 Calibration Curve:

Normally three types of Working Solutions (200ppm, 40ppm, and 1000ppb) are made from stock. Diluted Standard solutions of 0.5ppm, 1ppm, 2ppm and 4ppm are made from 200ppm solution while diluted Standard solutions of 0.1ppm, 0.2ppm, 0.4ppm and 0.8ppm are made from 40ppm solution. A new calibration curve with freshly prepared standard solutions to be drawn for new estimation

6.2. Internal quality control (IQC):

For uniformity and stability of the value among samples and triplicales IQC must be run in-between samples and triplicales as well as before and after sample analysis.

6.3. Checking Reproducibility / Verification:

Take reading of the standard solutions periodically in between the samples to ensure proper functioning and reproducibility of instrument response.

NOTE: Especially in case of elements having very low absorption e.g. Ni , Pb etc take extra reading of IQC or Standards after each sample to verify the instrument performance.

6.4. Repeatability of Analysis:

Repeatability of analysis may be determined through replicate sample; at least three replicate must be prepared for each analysis. *

6.5. Analysis Of Old Samples:

Analyze the old samples (previously analyzed at the same conditions using the same procedure in order to verify performance qualification of the instrument and to check the test method

6.6. CRM Analysis (optional):

Periodic analysis of CRM after every three months to assure the system

6.7. Proficiency Testing:

Participation in PT/ ILC for elemental analysis to verify lab results

7. Precautions/Safety requirements:

8.1 All the acids should be of analytical grade

8.2 Use acids and strong / toxic reagents and chemicals with care, under fume hood and with exhaust "TURN ON"

8.3 In case of emergency follow directions given in Instruction manual."

8. **References/Related documents:**

9.1 AOAC (1990) Official Methods of Analysis of the Association of Official Analytical Chemists. 15th Ed. pp. 42, 84, 237,312,498,708

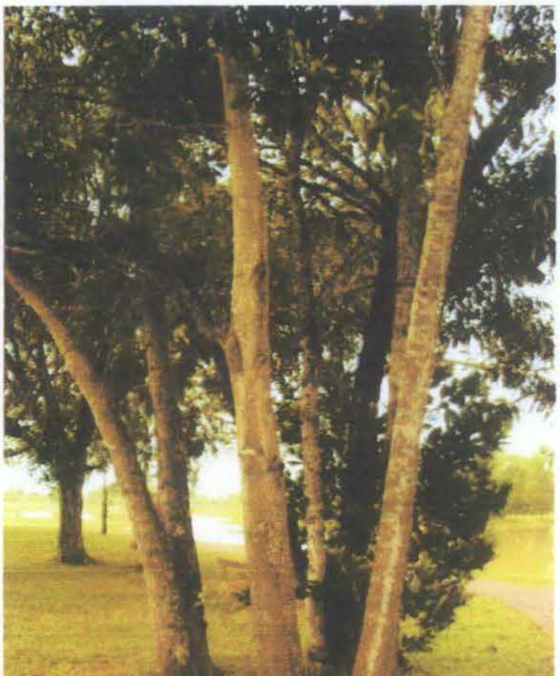
9.2 Atomic Absorption Spectrophotometery Cookbook Section 1, 2000 Basic Conditions for Analysis of Principle of Atomic Absorption Spectroscopy, Shimadzu Corporation, Japan. (Document of external origin HTL-04)

9.3 Work Instructions for Atomic Absorption (AA 6650) Shimadzu. Standard Method for sample preparation for elemental analysis

APPENDIX C

1. **Sampling Tree at Tronoh**

2. **Sampling Tree at UTP Lake**



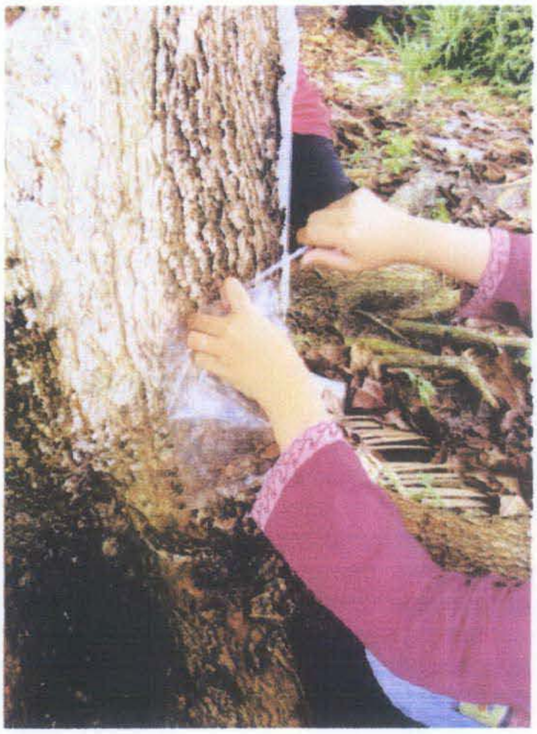
3. Sampling Tree at Malim Nawar

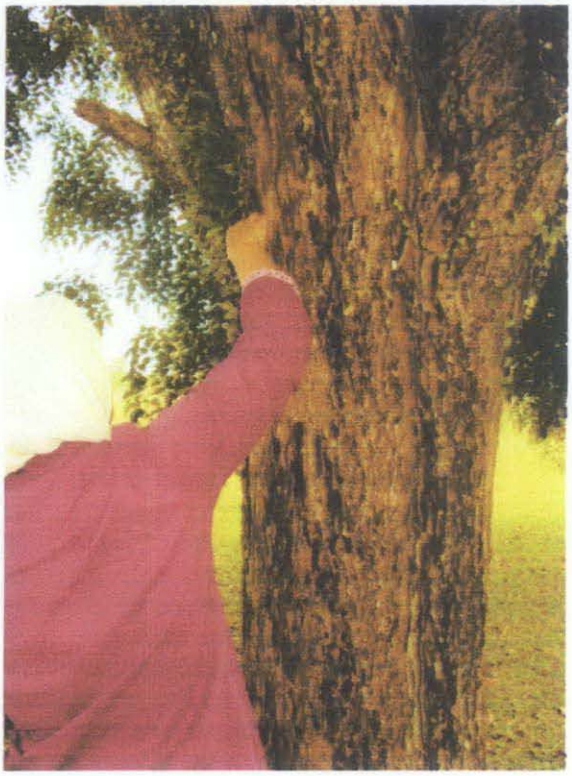
4. Height of Bark (6ft)

5. **Height of Tree (4 ft)**

6. **Height of Tree (2 ft)**

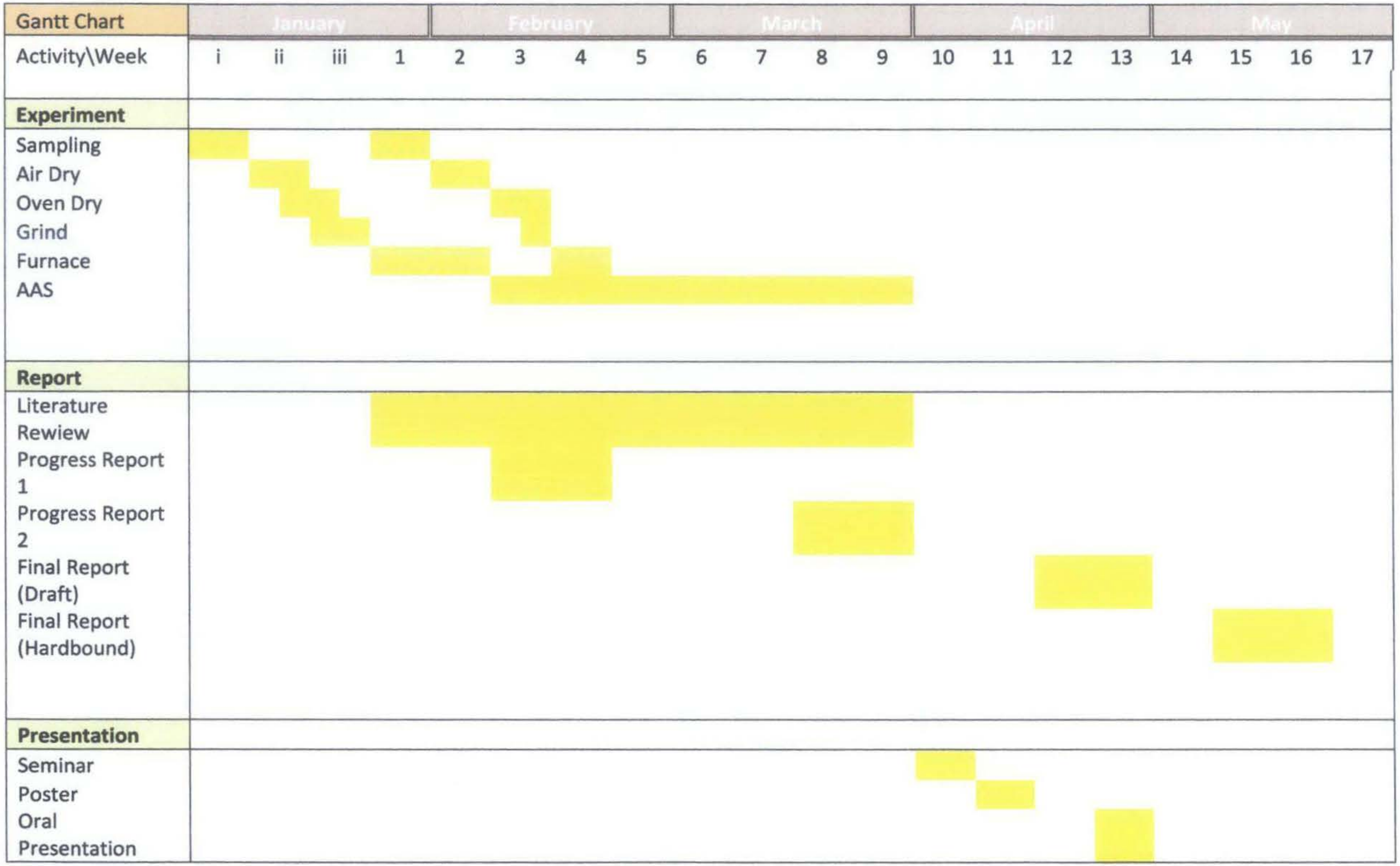
7. Process remove barks





8. Structure of tree after barks removed

APPENDIX D



Gantt Chart	January				February				March				April				May			
Activity\Week	i	ii	iii	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Experiment																				
Sampling	🟨			🟨																
Air Dry		🟨			🟨															
Oven Dry		🟨	🟨			🟨														
Grind			🟨			🟨														
Furnace				🟨	🟨		🟨													
AAS						🟨	🟨	🟨	🟨	🟨	🟨	🟨								
Report																				
Literature Rewiew				🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨								
Progress Report 1						🟨	🟨													
Progress Report 2											🟨	🟨								
Final Report (Draft)															🟨	🟨				
Final Report (Hardbound)																		🟨	🟨	
Presentation																				
Seminar													🟨							
Poster														🟨						
Oral Presentation																🟨				