HEAVY METALS CONTENT IN PAHANG RIVER STREAM SEDIMENT; UPPER AND LOWER BASELINE STUDIES

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ABSTRACT

Stream sediment has an important role in the essential nutrients cycle of aquatic environments as well as in the transport of the nutrients and pollutants. Human activities, such as mining, farming, logging, and industrialization, may adversely affect stream sediment quality. These activities can cause heavy metals toxic pollutant that can be dangerous to the environment. The present study was carried out to determine concentrations of heavy metals content in the upper and lower river stream sediments of Pahang River. Three sampling sites were chosen from upper which are in Sungai Tembeling, Sungai Jelai and Temerloh and three sampling sites for lower regions which are Kampung Belimbing, Kampung Temai and Pekan at Pahang River. These samples were analyzed using Atomic Absorption Spectrometry (AAS) to determine the concentration of heavy metals in sediment. The observed stream sediment heavy metals contamination is further evaluated which is higher concentration of heavy metals contamination is in lower Pahang River than upper region.

ABSTRAK

Mendakan sungai mempunyai peranan penting dalam kitaran nutrisi dari persekitaran akuatik terutama dalam pengangkutan nutrisi dan pencemaran. Aktiviti manusia seperti perlombongan, pertanian, penebangan dan industrialisasi boleh menjejaskan kualiti mendakan sungai. Aktiviti ini boleh menyebabkan pencemaran toksik logam berat di mana ia boleh membahayakan persekitaran. Penyelidikan ini akan dilakukan untuk menentukan kadar kepekatan kandungan logam berat di dalam mendakan di bahagian atas dan bawah Sungai Pahang. Tiga tempat lokasi sampel dipilih dari bahagian atas di sekitar Sungai Tembeling, Sungai Jelai dan Temerloh dan di bahagian bawah iaitu Kampung Belimbing, Kampung Temai dan Pekan di Sungai Pahang. Sampel ini dianalisis menggunakan Spektrometri Serapan Atom (AAS) untuk menentukan kepekatan logam berat di dalam mendakan.Pencemaran mendakan sungai dinilai lebih lanjut di mana ia mempunyai kadar kepekatan tinggi pencemaran logam berat di bahagian bawah Sungai Pahang.

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LIST OF SYMBOLS

α	Alpha

LIST OF ABBREVIATIONS

μm	Micrometer
AAS	Atomic Absorption Spectrometry
ANOVA	Analysis of Variance
Cu	Copper
g	Gram
HCl	Hydrochloric acid
HNO_3	Nitric acid
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
km	Kilometer
ml	Mililiter
Ni	Nickel
nm	Nanometer
Pb	Lead
ppm	Part per million
SRM	Standard Reference Material
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Sediment is naturally-occurring material that is broken down by processes of weathering and erosion, and is subsequently transported by the action of fluids such as wind, water, or ice, and/or by the force of gravity acting on the particle itself. In general, sediment comprises many shapes and sizes. The sediment size can be small, such as sand, small pebbles and silt, or large such as boulders, which are normally found upriver. Sediments found in estuaries are mostly fine-grained, such as sand and silt. The speed at which water flows in rivers plays an important part in determining its capacity to carry away sediments. Slower moving rivers will have a lower rate of sediment movement.

The river is one of the most important sources of water for all living things in addition to lakes, seas, water catchments and underground water. Rivers are very important to humans and other organisms as they are essential resources for living. For Pahang's resident, Pahang's Rivers are very important for them. With 459 km in length, it is the longest river on the Malay Peninsula. The river begins at the confluence of Jelai and Tembeling rivers on the Titiwangsa Mountains and drains into the South China Sea. Thus, the resident can do some activities besides the river bank such as farming, mining and many more.

Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. Higher concentration of heavy metals can gives impact to the environment. It is very dangerous if the river contain higher concentrations of heavy metals in it.

1.2 PROBLEM STATEMENT

Sediment usually contains heavy metals toxic pollutant. Human activities, such as mining, farming, logging, and industrialization, may adversely affect stream sediment quality. These activities may lead to an increase of heavy metals in stream sediments. Such an increase affects water plants and animals which later also affect human health and life because heavy metals that contain in stream sediments are dangerous. Currently, there are limited numbers of information available regarding heavy metals' content in the Pahang River stream sediments. This research addresses the needs on such valuable information.

1.3 HYPOTHESIS

Pahang River is considered as one of the non-polluted rivers in the Malaysian Peninsula. Consequently, the heavy metals content in the stream sediments of Pahang River result from mostly natural origin, however, some anthropogenic sources may contribute to the increase of the heavy metals. Generally, lower river sediments have higher concentrations of heavy metals than upper river ones.

1.4 SCOPE OF STUDY

This research limits the measurand parameter of heavy metals to lead, copper, nickel and zinc in sediments, because it may occur naturally or by human activities along the Pahang River. The sampling locations are chosen to represent the two regions of upper and lower Pahang River. The upper river includes Sungai Jelai, Sungai Tembeling and Sungai Pahang at Temerloh. The lower river includes three sampling locations in Sungai Pahang, namely Kampung Belimbing, Kampung Temai, and Pekan.

1.5 OBJECTIVE/AIM

1. To determine the concentrations of heavy metals in upper and lower stream sediment.
2. To establish information baseline on heavy metals in Pahang River stream sediment.

CHAPTER 2

LITERATURE REVIEWS

2.1 PAHANG RIVER

Pahang River or (Sungai Pahang in Malay) is a river in the state of Pahang, Malaysia on the Malay Peninsula. With 459 km in length, it is the longest river on the Malay Peninsula. The river begins the confluence of Jelai and Tembeling rivers on the Titiwangsa Mountains and drains into the South China Sea. [1] There are many activities along the Pahang River that can be harmful to the human and living. In recent year, Pahang River estuary has been heavily impacted by discharges from municipal and industrial overflows, in addition to sand mining and aquaculture. The sediment contain heavy metals due to the human activities. The studies regarding geochemical profile of such sediments in east coast of Malaysia is still scanty. [2]

2.2 SEDIMENT

Sediment is naturally-occurring material that is broken down by processes of weathering and erosion. It is subsequently transported by the action of fluids such as wind, water, or ice, and/or by the force of gravity acting on the particle itself. Sediment is most often transported by water (fluvial processes), by wind (aeolian processes) and glaciers. Beach sands and river channel deposits are examples of fluvial transport and deposition. Though, sediment also often settles out of slow-moving or standing water in lakes and oceans. Desert sand dunes and loess are examples of Aeolian transport and deposition. Glacial moraine deposits and till are ice transported sediments.

Sediment usually contains heavy metals contaminant. Most common heavy metals that are usually found in sediment are copper (Cu), lead (Pb), zinc (Zn) and nickel (Ni). [3] These contamination is due to the human activities and nature.

2.3 HEAVY METALS

2.3.1 Copper (Cu)

Copper is widely used in electrical wiring, roofing, various alloys, pigments, cooking utensils, and piping and in the chemical industry. Copper is present in munitions, alloys (brass, bronze) and coatings. Copper compounds are used as or in fungicides, algicides, insecticides and wood preservatives and in electroplating, azo dye manufacture, engraving, lithography, petroleum refining and pyrotechnics. Copper compounds can be added to fertilizers and animal feeds as a nutrient to support plant and animal growth Copper compounds are also used as food additives. [3] The contemporarily presence of small or medium sized urban centres, together with agricultural activities, although not intensive, represent the characteristics of the Pahang River area that can be mainly defined tourist and recreational. [4] In Pahang, there are many human activities along its river such as agricultures, mining and many more. This can cause Copper contamination. [2]

2.3.2 Lead (Pb)

Lead is non essential for plants and animals and is toxic by ingestion-being a cumulative poison. Lead may cause irreversible neurologic damage to renal disease, cardiovascular effects, and reproductive toxicity. [5] Human has been mining and using this heavy metal for thousands of years, poisoning them in the process. Although lead poisoning is one of the oldest known work and environmental hazards, the modern understanding of the small amount of lead necessary to cause harm did not come about until the latter half of the 20th century. [6]

Lead from the atmosphere or soil can end up in groundwater and surface water. [7] Lead in water comes from industrial, mines and smelter discharges before being deposited in the sediment sinks. Lead is also used in the production of lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors, ammunition, glazes and plastic stabilizers. Lead (II) sulfide or galena is the sources of contamination of lead in sediment. Galena is the primary ore mineral of lead. Galena is a common and popular mineral for rock hounds. [8] In Kechau Tui near Gua Musang but still in Pahang, there are tin mining occur. This can cause galena naturally. Galena can overflows thru Pahang River by human activities which is tin mining. Thus, it can cause lead contamination. [9]

2.3.3 Zinc (Zn)

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. [10][11] Many human activities have a negative impact on several biological processes and there is no doubt that these will continue to affect the functioning of highly productive river and coastal ecosystems. Contamination caused by zinc affects both ocean waters, those of the continental shelf and the coastal zone where, besides having a longer residence time, metal concentrations are higher due to input and transport by river runoff and the proximity to industrial and urban zones.[12][13]In recent years, especially for the first kilometre along the Kuala Pahang estuary has been heavily impacted by discharges from municipal and industrial outflows. This was due to the rapid development of the area via expansion of the industrialization area as well as the increase in population. On the other hand, Pahang River can be contaminant by zinc due to the industrial overflows and human activities. [14]

2.3.4 Nickel (Ni)

Nickel is the 24th element in order of natural abundance in the earth's crust and it is widely distributed in the environment. Natural sources of aqueous nickel derive from biological cycles and solubilization of nickel compounds from soils. [15][16] Nickel is used principally in its metallic form combined with other metals and nonmetals as alloys. Nickel alloys are characterized by their hardness, strength and resistance to corrosion and heat. Nickel is also used mainly in the production of stainless steels, non-ferrous alloys and super alloys. Other uses of nickel and nickel salts are in electroplating, as catalysts, in nickel-cadmium batteries, in coins, in welding products and in certain pigments and electronic products. The common aqueous species found in water is predominantly Ni^{2+}. It is suspected to be essential trace elements for plants and animals. Nickel may be present in some ground waters as a consequence of dissolution from nickel ore-bearing rocks.[3] Nickel can affect the stomach, lungs, kidneys and blood of the body. Nickel caused increased red blood cells. The most serious effect of nickel has been cancer of the lungs and nasal sinus. [17] Nickel contamination can occur in Pahang River because of industrial waste that overflows through the river. [2]

CHAPTER 3

METHODOLOGY

3.1 EXPERIMENTAL DESIGN

3.1.1 Experimental Parameters

The parameters that were observed are heavy metals including lead (Pb), copper (Cu), nickel (Ni) and zinc (Zn). The research aimed to characterize the contamination of heavy metals in Pahang River sediments.

3.1.2 Sampling Method and Design

Sampling of stream sediments follows EPA 3000 series method of stream sediment sampling. The following protocol is adapted:

1) Three sampling sediment sites for each upper and lower Pahang's River were collected.
2) The sediments samples were collected using sediment scoop.
3) The sediments sample was put in a plastic bag.
4) The average of sediment for upper and lower were homogenized and acid digested according to EPA 3000 series method for acid digestion.
5) The digested samples were analyzed by using atomic adsorption spectrometry (AAS) in laboratory.

3.1.3 Data Collection Methods

The data were obtained by using Atomic Absorption Spectrometry (AAS) Perkin Elmer Analyst 800.

3.1.4 Data Analysis and Evaluation Methods

Concentrations of the heavy metal that contain in sediment were analyzed. The AAS data were evaluated using two-way analysis of variance (ANOVA) to test the differences among the parameters.

3.2 EQUIPMENT AND INSTRUMENTS

Atomic Absorption Spectrometry (AAS), sediment scoop, plastic bags, beaker, oven, hot plate, magnetic stirrer, pestle and mortar.

3.3 MATERIALS

Nitric acid (HNO_3), hydrochloric acid (HCl) and distilled water.

3.4 PROCEDURES

The sediment samples were collected at three stations for each upper and lower. For upper region the samples were collected at Temerloh, Sungai Jelai and Sungai Tembeling while for lower region the samples were collected at Pekan, Kampung Temai and Kampung Belimbing (near Tasik Chini). The samples were dried in the oven at 100 °C for 24 hours. After that, the samples were digested by mortar and pestle and sieved using 425 µm sieve shaker. 50 g of each sample were weighed into a 250 ml beaker. 15 ml of distilled water, 8 ml concentrated HNO_3 and 24 ml concentrated HCl were added to the each sample and blank. The samples were digested with two times digestion by added the same amount of acid and 10 ml of distilled water for 2 hours with 1 hour for each digestion.

The digestion was carried out on a hot plate in a fume chamber avoiding splattering. Digestions were continued until the sample become paste. The beakers were cooled at room temperature. The digests then were filter into a 100 ml volumetric flask and made up to volume with distilled water. After that the analysis were carried out using Atomic Absorption Spectrometry (AAS) Analyst 800 Perkin Elmer.

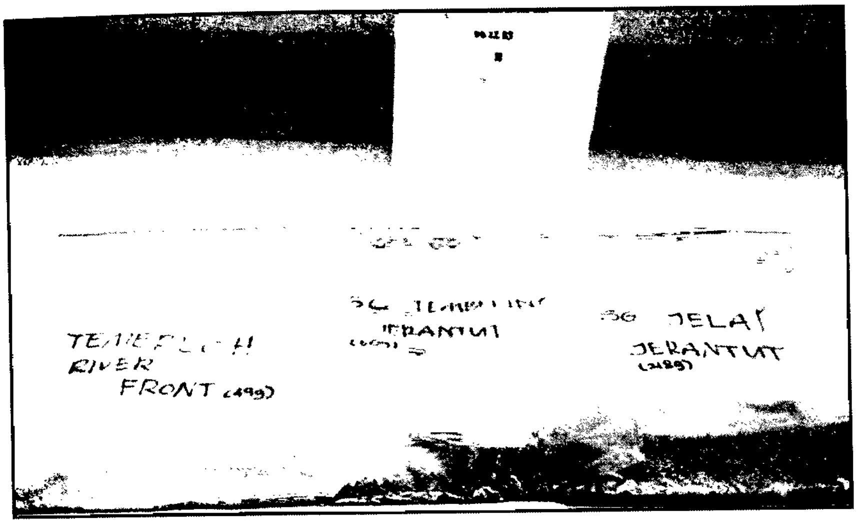

Figure 3.1: Samples after sieving

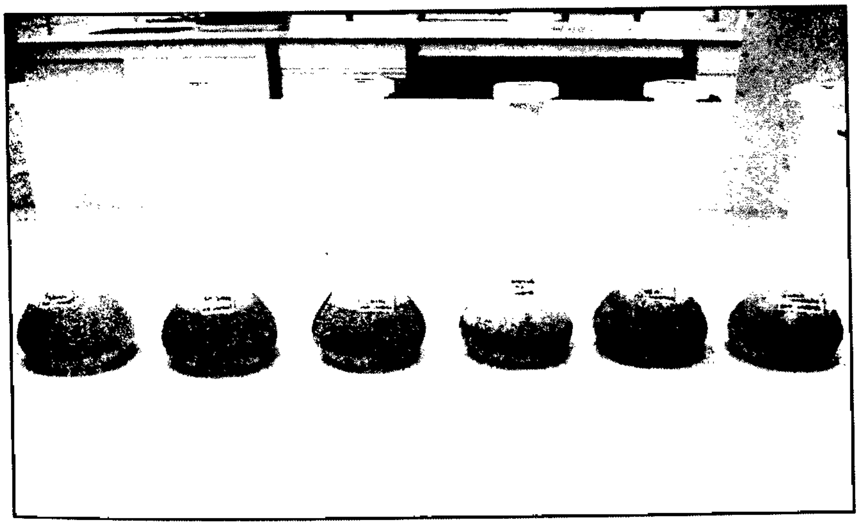

Figure 3.2: Samples after digestion method

CHAPTER 4

RESULTS AND DISCUSSION

4.1 SAMPLING SITES

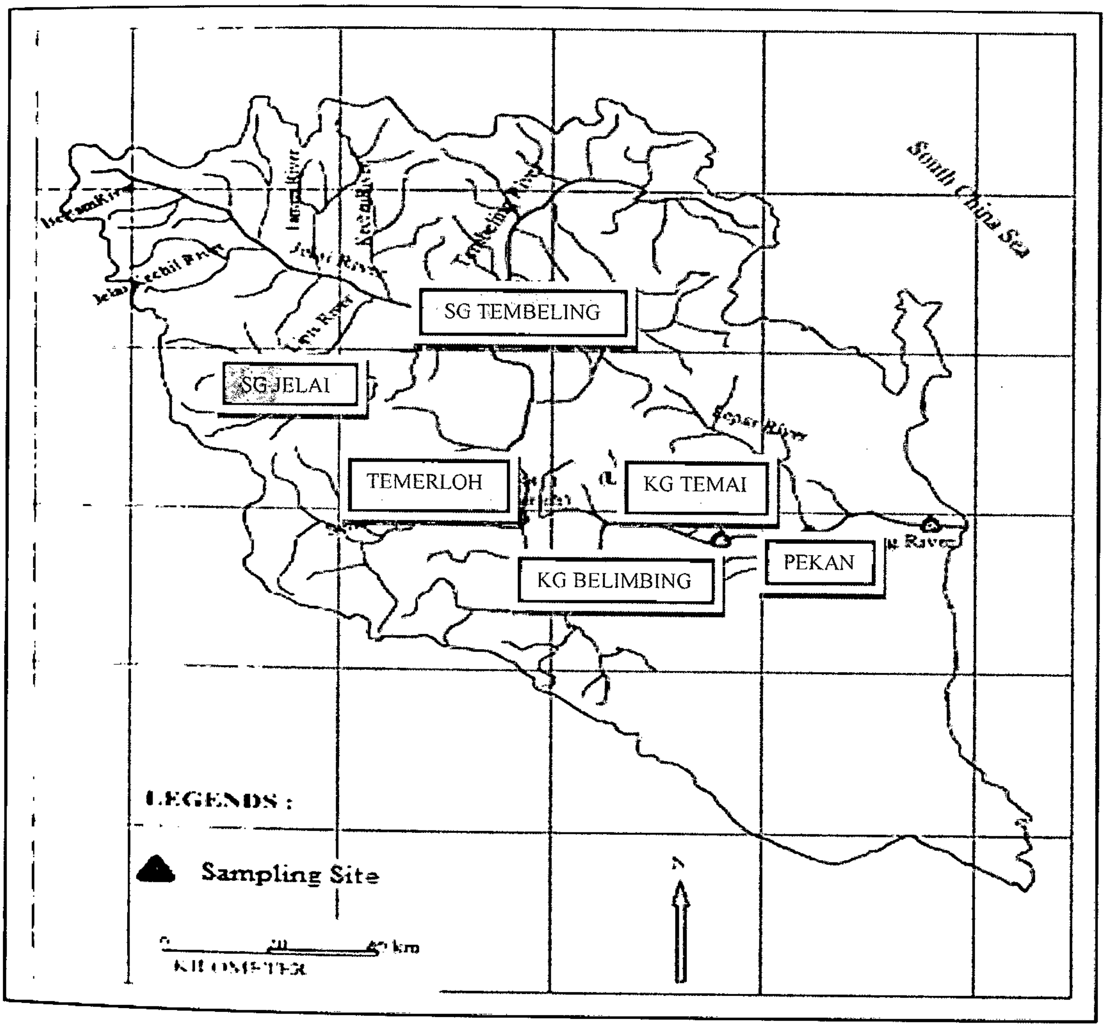

Figure 4.1: Map of sampling sites

Figure 4.1 shows the map of sampling sites. The sampling sites can be divided into two regions which is upper and lower Pahang's River. The six stations were chosen as sampling sites. In upper region, the samples were collected at three sites, including Sungai Jelai, Sungai Tembeling and Temerloh. Meanwhile, in lower region the samples were collected at Kampung Belimbing, Kampung Temai and Pekan. The stations were determined by the flows of Pahang River. The Pahang river system begins to flow in the south east and south directions from the north passing along such major towns as Kuala Lipis, Jerantut and Temerloh, finally turning eastward at Mengkarak in the central south flowing through Pekan town near the coast before discharging into the South China Sea.

4.2 LEAD (Pb)

Table 4.1 shows the relationship between lead concentration and its AAS absorbance. The lead absorbance was measured at 283.3 nm on acetylene-air mixture (4 litres acetylene per minute).

Table 4.1: Lead (Pb) concentration vs absorbance. Pb stock solution 1000 $\pm$ 2 ppm

Concentration of the standard (ppm)	Absorbance
0	0
4	0.031
8	0.056
16	0.113

Figure 4.2 shows the calibration curve for the stock solution 1000 ppm of lead versus its AAS absorbance.

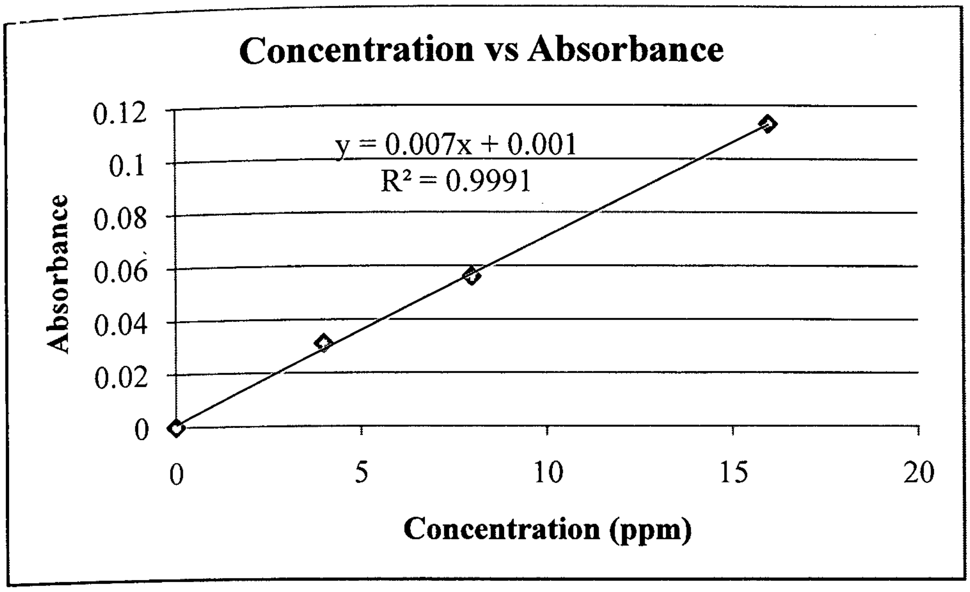

Figure 4.2: Calibration curve for lead (Pb)

Table 4.2: Concentration of sample (Pb)

Sample	Concentration (ppm)
Sungai Tembeling	1.71
Sungai Jelai	2.71
Temerloh	2.57
Kampung Belimbing	4.14
Kampung Temai	5.14
Pekan	1.71

Table 4.2 shows the results of lead concentration contained in the samples. The concentration of each sample was calculated using linear equation based on the calibration curve of concentration standard versus absorbance in Figure 4.2. From the Table 4.2, we can see that the highest concentration of lead is at Kampung Temai. The lowest concentrations were observed at two stations, in examples Sungai Tembeling (Upper River) and Pekan with 1.71 ppm. The contribution of these metals in the study area would likely be due to the anthropogenic activities such as boating, sand mining and sea dumping activities. The lead of concentration between Sungai Tembeling and Pekan were the same because in Pekan there much dilution factor

from surrounding or rain while in Sungai Tembeling the river flow lead to the lower region.

4.3 COPPER (Cu)

Table 4.3 shows the relationship between copper concentration and its AAS absorbance. The lead absorbance was measured at 324.8 nm on acetylene-air mixture (4 litres acetylene per minute).

Table 4.3: Copper (Cu) concentration vs absorbance. Cu stock solution 1000 $\pm$ 2 ppm

Concentration of the standard (ppm)	Absorbance
0	0
2	0.115
4	0.231
8	0.475

Figure 4.3 shows the calibration curve for the stock solution 1000 ppm of copper versus its AAS absorbance.

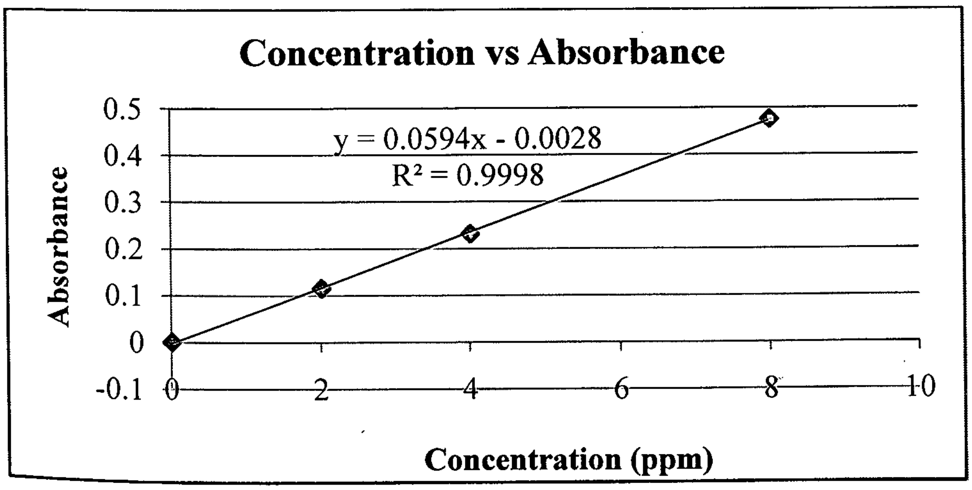

Figure 4.3: Calibration curve for copper (Cu)

Table 4.4: Concentration of sample (Cu)

Sample	Concentration (ppm)
Sungai Tembeling	1.04
Sungai Jelai	1.19
Temerloh	2.25
Kampung Belimbing	2.60
Kampung Temai	1.88
Pekan	0.62

Table 4.4 shows the concentrations of copper for each sample. The calculation for concentrations used linear equation like lead. Based on the table above, the highest concentrations was in Kampung Belimbing with 2.60 ppm. Meanwhile, the lowest concentration was in Pekan which is 0.62 ppm. Although Kampung Belimbing contains higher concentration of copper, is of the up flow of Pekan. This is due to the human activities in Kampung Belimbing as this place is near jetty to Lake Chini. Lake Chini has been developed as a tourism destination in Pahang. Activities such as the continuous development of eco-tourism facilities, farming and logging have negatively affected the lake and river near Lake Chini. When the river flows to the downstream in Pekan, the metal is absorbed by surrounding and gives low concentration of copper.

4.4 ZINC (Zn)

Table 4.5 shows the relationship between zinc concentration and its AAS absorbance. The lead absorbance was measured at 213.9 nm on acetylene-air mixture (4 litres acetylene per minute).