

Metallic Constituents in Water Samples from the Michu and Langat Rivers

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ABSTRACT The concentrations of the metals Cr, Mn, Fe, Ni, Cu, Zn, Pb, Mg, Ba, K and Cd in water samples from the Michu and Langat Rivers were measured using the Inductively-Coupled Plasma (ICP) technique. Samples were taken at six locations on the rivers, on five different days between May and July of 1999 in relation to the closure of the Ampang Municipal Landfill. Mn, Fe, Zn, Mg, Ba and K were detected in all the samples. Cr, Cu and Cd were present in most samples while Ni and Pb were only found in six and four samples, respectively, out of a total of 35 samples analyzed for each metal. With a few exceptions, samples from locations furthest away from the leachate source were often lower in the metallic content compared to other locations. There was no consistent indication of the effect of time from landfill closure on metal concentration.

ABSTRAK Kepekatan logam Mn, Fe, Ni, Cu, Zn, Pb, Mg, Ba, K dan Cd dalam sampel air daripada Sungai Michu dan Sungai Langat telah disukat dengan menggunakan teknik "Inductively-Coupled Plasma" (ICP). Sampel telah diambil daripada enam lokasi di sungai tersebut, pada lima hari berbeza di antara Mei dan Julai tahun 1999, berkait dengan penutupan Tapak Pelupusan Perbandaran Ampang. Mn, Fe, Zn, Mg, Ba dan K telah dikesan dalam kesemua sampel. Cr, Cu dan Cd ada dalam kebanyakan sampel manakala Ni dan Pb hanya ditemui, masing-masing dalam enam dan empat sampel daripada sejumlah 35 sampel yang telah dianalisis bagi setiap logam. Kecuali bagi beberapa kes, sampel dari lokasi yang lebih jauh daripada punca leachate tapak pelupusan kerap menunjukkan kandungan logam yang lebih rendah daripada lokasi lain. Tiada petunjuk konsisten dapat dilihat tentang kesan jangka masa penutupan tapak pelupusan terhadap kepekatan logam.

(River pollution, metallic constituents, Ampang Landfill, Michu River, Langat River, ICP analysis)

INTRODUCTION

Trace quantities of many metals such as cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), and zinc (Zn) are found in most waters. Some metals such as calcium (Ca), cobalt (Co), molybdenum (Mo), potassium (K), sodium (Na), tungsten (W), vanadium (V), Cr, Pb, Mg, Mn, Ni, Fe, Cu and Zn are essential macro and micronutrients, necessary for proper growth of living organisms. However, excessive doses of metals in inorganic or chelated forms can be toxic to living cells, and the threshold concentration of inhibitory effect on heterotrophic organisms has been identified [1].

Metal toxicity will certainly interfere with any beneficial use of potable water. The control of the concentrations of these substances is therefore of prime importance.

The metals barium (Ba), Cd, Cr, Pb, Hg and silver (Ag) are among 129 elements and compounds which have been classified by the United States Environmental Protection Agency as priority pollutants. Priority pollutants, which include inorganics and organics (eg. chemical compounds such as pesticides), were selected on the basis of their known carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity [2]. Metals are often introduced into aquatic systems as a result of the weathering of soils and rocks, from volcanic eruptions, and groundwater infiltration. Domestic, commercial

and industrial discharges are significant sources of metal contamination in water. As the use of treated wastewater effluent for irrigation and landscape water increases, it becomes increasingly important to monitor the levels of these metals in the water, as their presence may have adverse effects. For instance, Ca, Mg and Na are of importance in determining the sodium adsorption ratio (SAR), which is used to assess the suitability of treated effluent for agricultural use. The use of composted sludge in agriculture would require the assessment of arsenic (As), Cu, Pb Hg, Mb, Ni, Se and Zn [1].

The Michu River is of interest due to its location adjacent to the former Ampang Municipal Landfill, which was closed in 1998. The river can be considered a direct recipient of the leachate generated from the dumpsite. This is of particular concern since the Michu River flows into the Langat River about 2 km upstream from the 10th mile Langat River Puncak Niaga Water Intake Point. The intent of this study is to analyse water from the Michu and Langat Rivers for their metallic contents. The Langat River system is known to be among the most polluted in the country with a multitude of human activities generating large cumulative amount of effluents, from sewage and farm refuse to chemical laden wastewater and leachate. The work of Lim *et. al* [3] showed the extent of anthropogenic activities on the Langat River system and how this had significantly impacted on the quality of the river water, compared to areas with less such development.

The work reported here is part of an investigation on the pollution parameters of the Michu and Langat Rivers in relation to the closure of the Ampang Landfill [4]. There were various constraints in the collection of data and extent of analyses. Pollution causes are also multifactorial, thus it would not be possible to directly link the observations to specific anthropogenic or geogenic activities taking place around the location of this study. Nonetheless, the results have shown to some extent the possible impact of leachate and other discharges on the quality of the Michu and Langat Rivers.

MATERIALS AND METHOD

Figure 1 shows the seven sampling stations along the Michu River and the section of Langat River.

On visiting the vicinity of the dumpsite, leachate was seen to seep (from the landfill) on the ground, and made its way to the lower ground as it followed the land topography. Being an unplanned dumpsite the landfill was not equipped with a proper channel for leachate. The flow of leachate in various directions thus classifies it as a non-point source of pollution. Eventually making its way to the nearest river, the contamination of the Michu River was evident from the rust brown colour of the river water upstream, not attributable to other factors. Sampling station S1 was the furthest upstream point accessible beyond the inhabited area. For this study it was the closest point to the landfill, i.e. the leachate source. Houses were found between points S1 and S2, and their number progressively increased towards stations S3 and S4. Station S4 was at the confluence between the Michu and Langat Rivers and C2 was a point on the Langat River prior (upstream) to S4. The last two sampling stations were the Puncak Niaga (PN) water intake point and treated pipe water taken from residences after the water treatment plant. All the samples were collected after the landfill closure.

Sampling was done at each station once every two weeks in the months of May, June and July of 1999. The samples were collected in duplicates in 1-liter high-density polyethylene (HDPE) bottles, which were washed with concentrated nitric acid to prevent the sorption of metal ions onto the sides of the container prior to metal analyses. All the samples were stored temporarily at 4°C in the laboratory while awaiting analyses.

The metals tested were those for which standards were available for the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) at the Environmental Laboratory of the Department of Civil Engineering, University of Malaya. 100 mL of each sample was filtered using a preconditioned plastic filtering device with vacuum containing a filter support made of plastic. The ungridded acetate membrane filter paper with 0.45 µm pore diameter was pre-washed with 2N HNO₃ before use. After filtration the filtrate was acidified to pH 2 with concentrated nitric acid and measurements were made with the ICP-AES, Model Optima 3000.

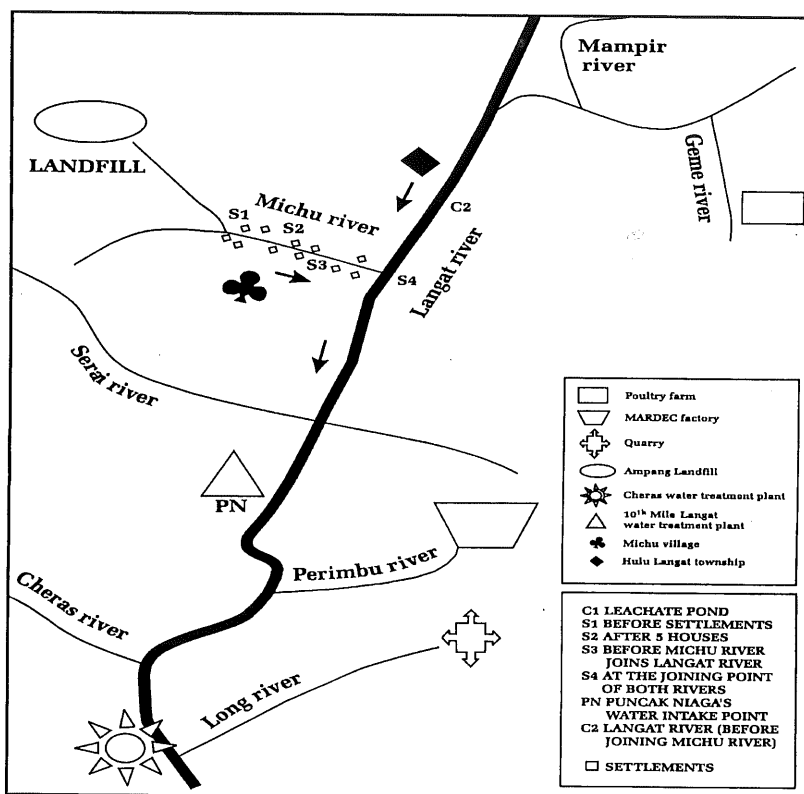


Figure 1. Sungai Langat's River Basin

RESULTS AND DISCUSSION

Figures 2 to 12 show the mean concentrations of the metals at all stations on different sampling dates. The absence of data means that the metal was not detected in the samples of the respective date.

Chromium

Chromium (Figure 2) was detected most frequently in the samples from station S1; and never in the treated pipe water. The leachate chromium concentration after the landfill closure was 115 ppb [4]. For the water samples the average level was about 9 ppb, with the highest (16 ppb) occurring at S1 on 24.5.99 and the lowest (4 ppb) at C2. There is no limit set in the National Water Quality Standard (NWQS) for this metal. Hexavalent chromium compounds are carcinogenic and corrosive on tissue.

The presence of chromium in Langat River, detected at stations S4, C2 and PN, can also be

attributed to industrial effluents. Timber factories along the river may use chromium in the impregnation process of wood and timber. Chromium is also a constituent of inorganic pigments and steel, and is an alloying and plating element for corrosion resistance. Such metal related industries, which may be found on the river upstream, could be a contributive factor.

Manganese

The concentration of manganese (Figure 3) in the water samples collected at the Michu and Langat Rivers fell in the range between 10.5 ppb and 74.0 ppb, which meant that at times the values were higher than the leachate Mn concentration of 41 ppb after landfill closure [4], but lower than the NWQS of 100 ppb. Every station, including pipe water, showed the presence of manganese at each sampling. The concentration at C2 and the pipe water samples were distinctly lower (10 to 20 ppb).

The other stations showed an increase in Mn concentration on 19.6.99, the day after a heavy rainfall. Soil erosion could have contributed to the increased level of this mineral.

As a comparison, in a similar study done on the water bodies within the vicinity of Taman Beringin and Jinjang Utara Landfill, it was found that the mean concentration of manganese was in the range of 0-175 ppb in the former and 50 ppb in the latter [6]. These values were reasonably close to the manganese concentration in the water samples collected from Michu and Langat rivers.

Iron

Iron (Figure 4) was one of the metals present in high concentration in the leachate (22 ppm after closure) [4], and exceeded the EQA 1974 Standard A limit of 1.00 ppm. Possibly due to continuous influx of leachate into the Michu River, the concentration of Fe at station S1 was the highest during each sampling with values exceeding 1000 ppb.

Stations S2, S3 and S4 had relatively lower Fe levels, but exceeded the Standards limits on the last two and three sampling dates. The samples of 19.6.99 showed markedly high readings at S1, S2 and S4. As explained for manganese, this could be from soil erosion during heavy rainfall the previous day. Domestic refuse from the villagers may also account for iron in the Michu River. The levels at C2 and PN were consistently low, which could probably be due to dilution with higher water volume at these stations. The pipe water level remained the lowest at all time, with the concentration averaging about 250 ppb.

Nickel

Nickel (Figure 5) was not detected in most of the samples collected. Interestingly, its presence was detected in the first and the last samplings. On 8.5.99, the concentration of nickel recorded at stations S1 and S2 were 9.48 ppb and 4.9 ppb. On 17.7.99, nickel was detected at S1, C2 and PN, with C2 recording the highest concentration of 7.75 ppb followed by S1 (3.61 ppb) and pipe water (2.88 ppb). The presence of nickel at C2 could be attributed to the untreated waste discharged by the industries operating along the Langat River. Nickel is widely used in the production of alloys, as pigments in ceramics, catalysts in chemical industries and batteries. Overall the nickel concentration in the water samples complied with the National Water

Quality Standard of 50 ppb. The leachate nickel concentration after closure was about 26 ppb [4].

Copper

The copper (Figure 6) concentrations in the water samples were found to be within the National Water Quality Standard of 1000 ppb. S1 showed the presence of copper at every sampling with the sample on 24.5.99 having the highest level of 34.1 ppb, more than twice the next highest concentration of about 17 ppb. The other stations had copper in the samples on two or three occasions with the levels ranging from 1.96 ppb at C2 to 16.8 ppb at S4. The concentration of copper detected in the pipe water samples ranged between 4.56 and 11.9 ppb. The leachate had a concentration of 71 ppb after closure [4].

Zinc

The Zn (Figure 7) concentration in water fluctuated slightly about a mean of around 50 ppb. High readings of 120 ppb, 180 ppb and 250 ppb were detected at S4, PN, and S1, respectively on 24.5.99. The highest level (275 ppb) occurred on 8.6.99 at S1. The pipe water had the lowest zinc level of about 10 ppb for all samples.

Considering the leachate Zn concentration was only 95 ppb after landfill closure [4], the high Zn concentration observed in the water samples could be from sources other than leachate or natural causes.

Lead

Lead (Figure 8) is used widely in the production of batteries. Other uses of significance from the standpoint of environmental pollution and human health are the use of lead in cable covering, ammunition, piping, tank linings, solder and fusible alloys, paint pigments, and gasoline additives. Pb is toxic by ingestion or inhalation, and can cause brain and kidney damage in the long term.

On 8.5.99, lead was detected at S1 with a concentration of 2.67 ppb. The presence of lead was not detected in the next three samplings, but it was present in the last sampling done on the 17.7.99. At 12.8 ppb, this was the highest concentration of lead found in the samples, but it was within the National Water Quality Standard set for lead, which allows a maximum concentration of 50 ppb in the river water for Class IIA. Only 2 other samples showed the presence of lead (S3 and S4 on 17.7.99).

However, the average concentrations were lower than at S1.

The lead concentrations of water bodies in the vicinity of Jinjang Utara and the active Taman Beringin Landfill were found to be higher with mean concentration of 79 ppb at Jinjang Utara and 0-260 ppb in the Taman Beringin Landfill [6].

Magnesium

Overall, the levels of magnesium (Figure 9) detected in the river water samples were quite high above the National Water Quality Standard of 50 ppb. The pipe water also charted an average of greater than 200 ppb. The leachate had a concentration of 9100 ppb.

Referring to Figure 9, in the first sampling the concentration of magnesium were found to be highest at station C2 with an average of 747 ppb and this was followed by S4 with 665 ppb, S3 with 652 ppb, PN with 650 ppb, S1 with 539 ppb and S2 with 498 ppb. But in the next sampling done on 24.5.99, there was increase in the concentration of magnesium at S1 and S2 stations. A higher concentration was also detected at PN. On 8.6.99, S3 recorded the highest level of magnesium with an average concentration of 1030 ppb followed by S4 (987 ppb), S1 (895 ppb), C2 (747 ppb), S2 (615 ppb) and PN (537 ppb). On 19.6.99 the magnesium level in almost all the samples showed a decrease with the concentration ranging between 551 ppb and 605 ppb. Similarly the samples collected in the last sampling also recorded lower concentration of magnesium ranged between 550 ppb and 661 ppb.

The presence of high magnesium content in the river water samples collected from S3 station can be attributed to the domestic waste disposal into the river. Its presence at C2 station is most likely due to the industrial discharges, which contains high levels of magnesium. Leachate could be the main pollutant at S1 station because the level of magnesium found in the leachate was recorded high at 9100 ppb.

Barium

Figure 10 shows that barium concentrations were similar and lower than 10 ppb in most cases, although on 24.5.99, there was a distinct rise at

all stations except S2, with PN recording the highest value of nearly 70 ppb followed by C2 (40 ppb), S1 (37 ppb), S4 (34 ppb), pipe water (22 ppb) and S3 (19 ppb). In general, the concentration of barium in the river water samples was within the limit set in the National Water Quality Standard of 1000 ppb.

Barium is used in vacuum tubes, spark-plug alloys, and deoxidizer for copper amongst other uses. Flammable at room temperature in powder form, it is a priority pollutant and can increase blood pressure and nerve block upon long-term exposure.

Potassium

Potassium (Figure 11) is naturally found in abundance in water, and is normally harmless if present in small quantities. The leachate had a post-closure concentration of 350 ppm [4] while the water samples from stations S1 to S4 recorded concentrations of 5.0 ppm to 16 ppm. Lower readings of about 2.0 ppm were recorded for PN and pipe water samples as well as C2. But for C2 the level rose by factors of 8 and 5 on 8.5.99 and 19.6.99, respectively. The presence of high potassium concentration in the leachate samples could explain the high concentration of potassium at station S1. Food is the main source of potassium.

Cadmium

In the first sampling done on 8.5.99, cadmium (Figure 12) was found present at S1, S2, C2 and pipe water with concentrations of 2.98 ppb, 1.72 ppb, 4.36 ppb and 3.99 ppb, respectively. Overall the mean concentration of cadmium was found to be the highest at PN with 6.64 ppb and this was followed by station S1 with mean concentration of 5.4 ppb, S4 with 4.21 ppb and S3 with 4.0 ppb. In a later study [5] on the quality of raw and treated river water from treatment plants in Selangor, the average Cd concentrations measured over a 3 months period for the PN sampling station were about an order of magnitude lower. High Cd concentrations could be due to industrial or sewage pollution. Fecal excretion appears to represent unabsorbed cadmium from food. Cadmium is also widely used in batteries, radios, calculators, portable appliances, tires, and discharge of these materials into the river by the residents may also be the cause of cadmium pollution.

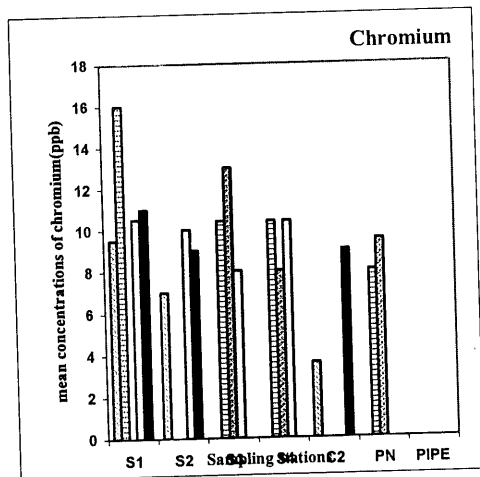


Figure 2. Chromium

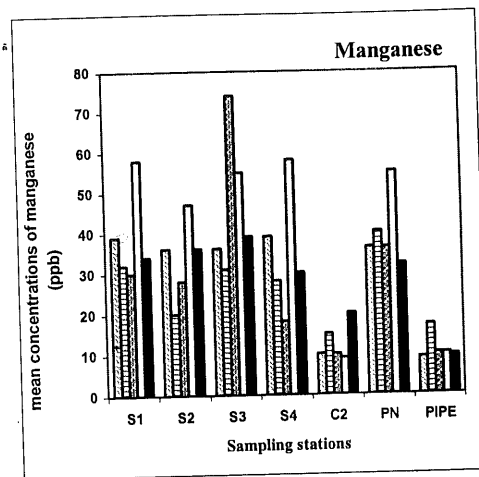


Figure 3. Manganese

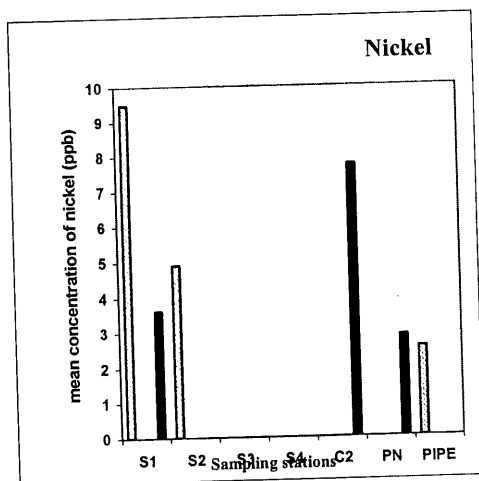


Figure 4. Iron

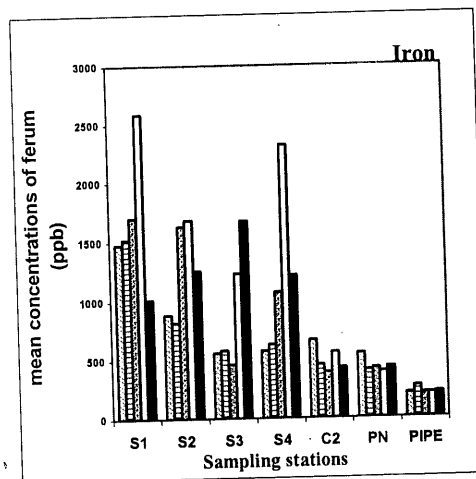


Figure 5. Nickel

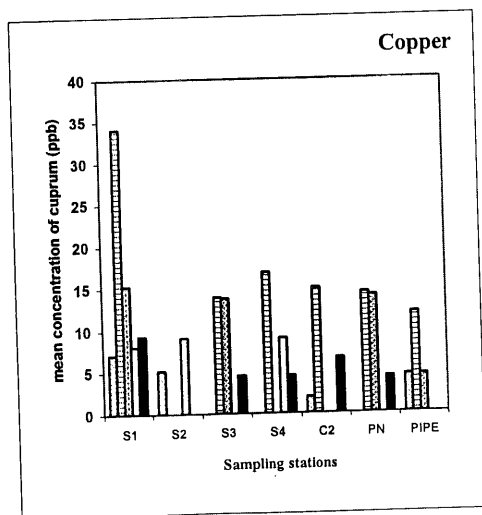


Figure 6. Copper

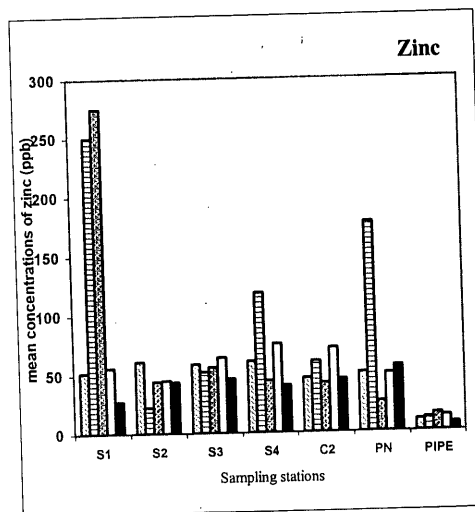


Figure 7. Zinc

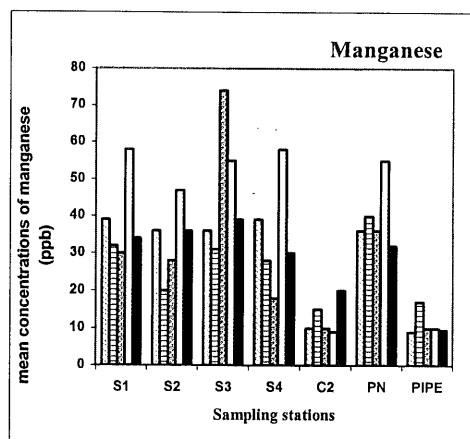


Figure 8. Lead

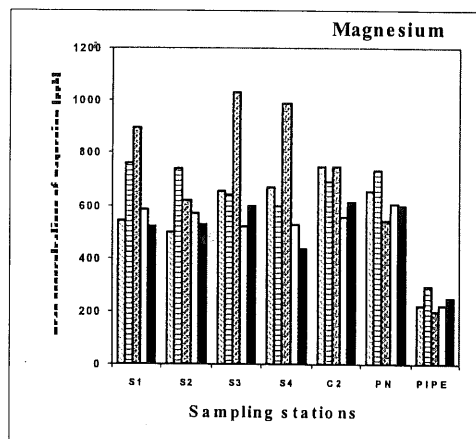


Figure 9. Magnesium

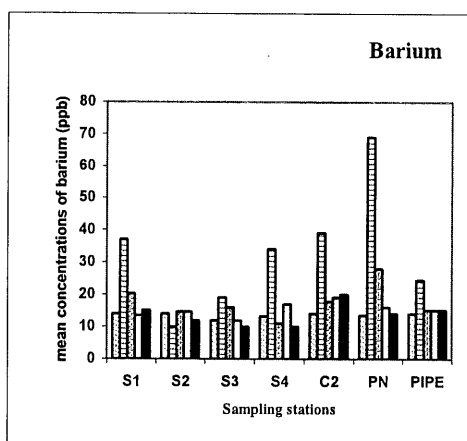


Figure 10. Barium

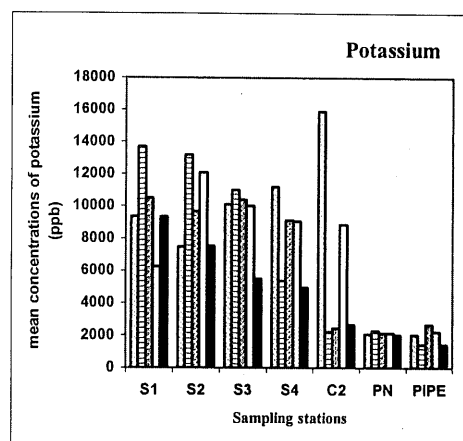


Figure 11. Potassium

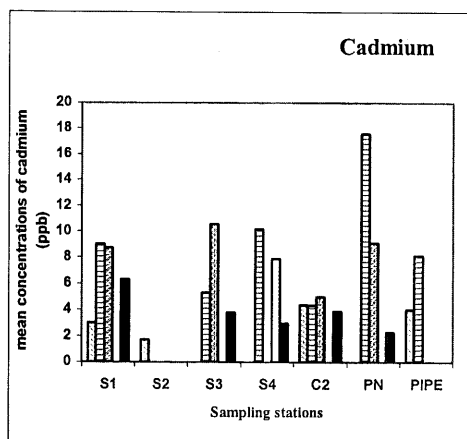
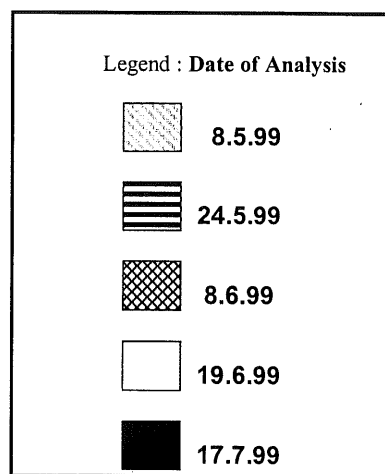


Figure 12. Cadmium



Figures 8 - 12. Mean concentrations of metals in water samples along the Michu and Langat Rivers over a 3-month period after landfill closure.

CONCLUSION

The data reported here may reflect the overall condition of the Michu River and a section of the Langat River in terms of metal distribution for a period of about three months after the closure of the Ampang Municipal Landfill, which was adjacent to the Michu River. The concentrations of metals were not alarmingly high and most parameters complied with the EQA 1974 Standard A. For the sampling station PN, which is the Sg. Langat Puncak Niaga water treatment plant, the concentrations of Cr, Mn, Fe and Ni the concentrations are in the same order of magnitude to data obtained in a more recent study [3, 5].

The presence of metals in the Michu River can be attributed to leachate influx, domestic discharge and possibly dissolution from soil. Station S1, located closest to the landfill before any residential dwelling began, often had the highest concentrations and persistent presence of metals. At stations S2 and S3 additional metals could come from domestic discharge from villagers along the Michu River. On the Langat River, added sources of pollution at points S4, C2 and PN could be the multitude of commercial, agricultural and industrial activities taking place upstream from the stations.

Many factors influence the parameter levels in the dynamic river system. In the set of data obtained during this study, a number of days had showed marked increase in the concentration compared to the values on the other sampling dates. Such "unusual" surges were recorded for K, Ba and Zn at C2 and PN. The concentrations of these parameters are not only affected by the rate of pollutant discharge into the river but also river hydraulics, including water volume, flow rate, and flow patterns that determine dead zones and high flow regions, which are in turn dependent on other factors such as weather conditions. Due to the limited scope of this work

it was not possible to detect or explain the causes for the abrupt changes observed.

The pipe water samples have shown the occurrence of all metals except Cr and Pb. Ni and Cd occurred on two occasions each. Zn, Mg and Fe had the lowest concentrations in pipe water compared to the other samples, while Cu, Mn, K and Ba levels were comparable to samples from other points. In general the levels comply with the Department of Health standard [3].

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