TRACE MONITORING OF WATER-BORNE PHENOLICS IN THE KLANG RIVER BASIN

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Abstract. The Klang River Basin is located in the most densely populated region in Malaysia, with its heavy concentration of industries and population. A systematic study of the pollution to this river system caused by phenolic compounds have been carried out under this project. Analyses of water samples from the Klang River by high performance liquid chromatography (HPLC) with an ultraviolet (UV) detector at 280 nm have shown the presence of some priority phenolic pollutants.

1. Introduction

The Klang River, which is located on the West coast of central Peninsular Malaysia, is regarded as an important waterway. It flows through the capital city, Kuala Lumpur, and the suburban area of the densely populated and highly industrialized Klang Valley. The upper reaches of the Klang River serve as an important source of the water supply to an estimated population of two million people in this region, together with its growing industrial activities. Figure 1 shows the location of the Klang River basin on the west coast of Peninsular Malaysia.

According to the Environmental Quality Report (Department of Environment, 1988), the Klang River is regarded as one of the rivers which have been seriously affected by organic pollution. Discharges of wastewater from industrial activities in the Klang River Basin have also contributed to increasing levels of organic chemical pollutants in the waterways. An earlier study of this river system has indicated the presence of organochlorine pesticide residues, phthalates and PAHs in the water samples collected from this waterway (Tan *et al.*, 1990). The present survey covers the period from October 1990 to January 1991.

High performance liquid chromatography (HPLC) has been developed by Alarcon *et al.* (1987) and Li *et al.* (1988) for the analysis of priority pollutant phenolic compounds in water samples.

2. Experimental

2.1. Selection of Water Samples

The Malaysian Department of Environment (DOE) has established a network of sampling stations for the determination of some water quality criteria and these stations and their coding system was adopted for this particular study. Sampling

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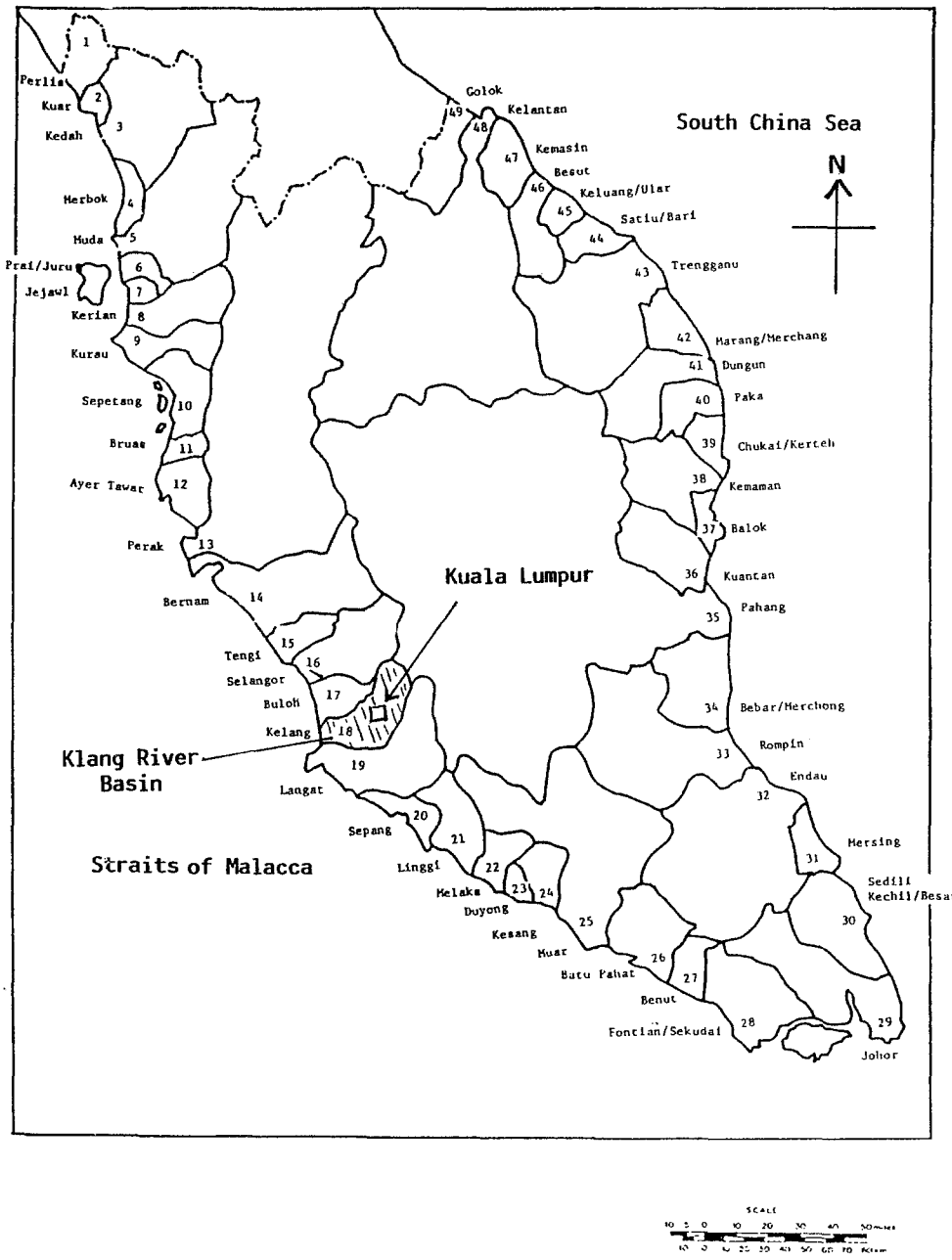

Fig. 1. Classified water quality control regions in Peninsular Malaysia.

stations were selected to represent water outlets for domestic, agricultural and industrial use at the present time. All water samples were analysed to determine the residue levels of priority pollutant phenols.

The grab sample technique was used whereby the surface water (0.5–1.0 m deep) was fished out from the middle of the river and filled into 2.5 L amber bottles. Water samples were collected in duplicates and were acidified to pH 2 with sulfuric acid to eliminate biological activity in the water. Table I shows the sampling record for the various stations along the Klang River basin.

2.2. Apparatus

An Altex Model 334 HPLC pump fitted with a Rheodyne 7125 injector was connected to a Macherey-Nagel Nucleosil 5 C_{18} column (12.5 cm × 4.0 mm i.d.) The eluent from the column was connected to a Linear model 200 UV–vis detector set at 280 nm. Data acquisition was performed with a Hewlett-Packard HP 3396A Integrator.

2.3. Reagents

HPLC-grade solvents were used. The impurity levels of all solvents and reagents did not exceed an acceptable blank when subjected to the complete procedure without the sample.

(a) Methanol, CH_3OH, from Lab-Scan Analytical Sciences;

(b) Acetonitrile, CH_3CN, from Romil Chemicals;

(c) Hexane, C_6H_{14}, from Fisher Scientific;

(d) Concentrated hydrochloric acid, HCl, from Fisher Scientific;

(e) Ammonium acetate, NH_4OAc, from Sigma Chemicals;

(f) Zerolit FFIP SRA69 anion exchange resin from BDH Chemicals Ltd.

2.4. Sample Clean-up and Preconcentration Procedure

2.4.1. Solvent Extraction

All glassware in this procedure was washed with the extraction solvent.

A 1000 mL volume of each water sample was adjusted to pH 11 with 0.5 M sodium hydroxide using a pH meter. If a precipitate forms in solution, it was coagulated by allowing the sample solution to sit for about 20 minutes. A 500 mL portion of the supernatant liquid was then transferred to a separating funnel through a filter funnel with cotton wool to act as a filter. Hexane (80 mL) was then added to the separating funnel. The funnel was shaken vigorously for about 2 minutes and the layers were allowed to separate. The aqueous layer was drained into a clean conical flask. The hexane layer was discarded. This procedure was repeated with another 80 mL of hexane for the aqueous layer. The same procedure was then applied to the other 500 mL portion of the water sample.

TABLE I
Sampling record

Date of sampling	Station no.	pH	Water condition	Weather
31 Oct '90	624	7	fast flow and muddy	rainy previous night
	610	6	fast flow and muddy	rainy previous night
	604	6	fast flow and muddy	rainy previous night
	629	7	fast flow and muddy	rainy previous night
	605	8	fast flow and muddy	rainy previous night
	628	6	fast flow and muddy	rainy previous night
	626	7	fast flow and muddy	rainy previous night
	621	6	fast flow and muddy	rainy previous night
	627	8	fast flow and brownish	rainy previous night
15 Jan '91	623	6	slow flow and brownish	fine and hot
	607	7	slow flow and brownish	fine and hot
	631	6	slow flow and brownish	fine and hot
	601	6	stagnant flow, foul-smelling and greenish yellow	fine and hot
	602	6	slow flow and brownish	fine and hot
	603	6	slow flow and brownish	fine and hot

2.4.2. Preconcentration

Preconcentration was performed using a 150 mm × 15 mm glass column fitted with a 100 mL solvent reservoir and packed with 10 g of anionic exchanger. The extracted water samples were poured into the reservoir of the column and allowed to flow through the resin column at a rate of 10–15 mL min^{-1}. The column was

previously conditioned by:

(a) washing successively with 2M sodium hydroxide, then water and then 4M hydrochloric acid;
(b) washing with acetone; and
(c) repeating step (a) and finally by washing with distilled water at pH 11. After successively washing with 20 mL of methanol, water at pH 11 and 0.1 M hydrochloric acid, the phenols were eluted with 20 mL of CH_3OH/4M HCl (9 : 1). The eluate was filtered through 0.45 μm filters (Millipore). Five microlitres of the eluate were then injected into the HPLC.

The above procedure was then repeated for the duplicate water sample collected at each station.

Blanks using all-glass double-distilled water were spiked with the standard priority pollutant phenols at a known concentration before carrying out the same extraction, clean-up, preconcentration and HPLC analytical procedure as described above. The percentage recovery of each phenol was then calculated using the formula:

$$\% \text{ recovery} = A/(B \times C) \times 100$$

where A = peak area of recovered phenol following the extraction and clean-up procedure; B = concentration of phenol for 100% recovery (15 mg/L); and C = calibration factor obtained from calibration curve.

2.4.3. Identification and Quantification of Phenols

The direct comparison technique (Van Hall, 1985) using external standards was chosen for this study because the phenols identified in the samples clearly matched known phenol standards on the basis of their retention times (Figure 2). The calibration curve method was employed for the quantitative determination of phenols in the water samples. Since the conditions of the HPLC can vary from time to time, the working calibration curve or calibration factor for each individual phenol has to be verified for each working session.

The phenol concentration is calculated as follows:

$$\text{concentration, } \mu\text{g/mL} = \frac{P}{C \times D}$$

where P = peak area count; C = calibration factor; D = dilution factor (50).

2.4.4. HPLC Conditions

Column: Macherey-Nagel Nucleosil 5 C_{18} (125 × 4 mm)

Mobile phase: 30 mM NH_4 OAc : CH_3CN : CH_3 OH

56 : 34 : 10

Wavelength: 280 nm

Range (AUFS): 2.0 – 0.005

Flow rate: 0.8 mL min^{-1}

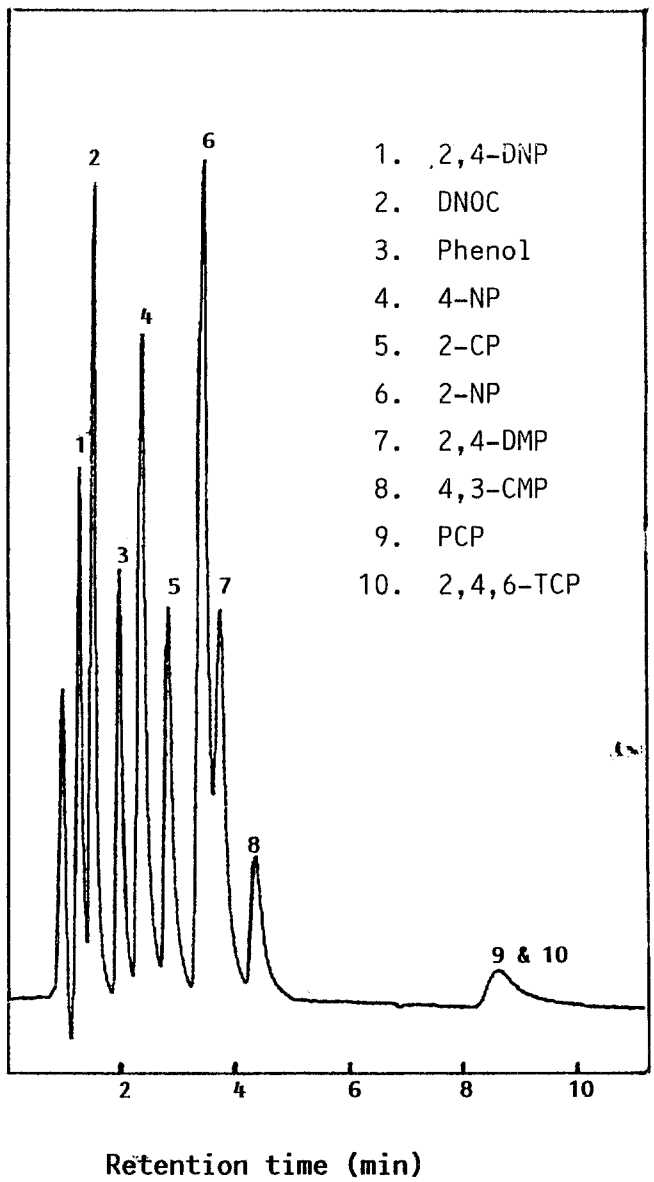

Fig. 2. HPLC chromatogram of phenol standards.

3. Results and Discussion

Table I gives the sampling record of the water samples collected from the various stations along the Klang River. On the first sampling date (31 Oct. 1990) it was raining on the previous night. This time of the year coincided with the onset of

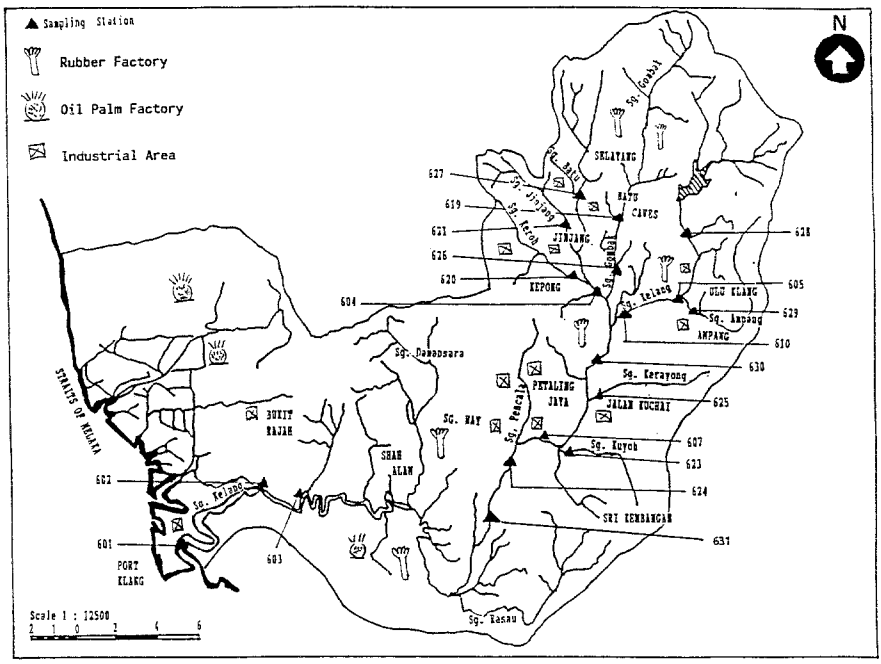

Fig. 3. Klang River basin: sampling stations.

the Northeast monsoon season during which the Klang River basin is subjected to heavy rainfall. Hence the water conditions at the various stations were all very fast flowing and muddy due to the run-off rain water from the surrounding areas.

On the subsequent sampling date (15 Jan 1991) the weather conditions coincided with the dry season for the Klang River basin. The water conditions at the sampling stations were all slow flowing with some brownish colour. Figure 3 shows a detailed map of the Klang River basin with the respective water sampling stations.

Table II gives the percentage recovery data of the phenols from the blank water samples, the determinations being carried out in triplicate. The average recovery of all the phenols exceeded 50%.

Table III shows the average results of the level of priority pollutant phenols and the total phenol concentration present in the water samples obtained from the various sampling stations in the Klang River basin during the survey period from October 1990 to January 1991.

There is a wide range of phenols present in the water samples in addition to the 10 priority pollutant phenols (PPPs) (one of them has been omitted because of unavailability of the standard). It is quite possible that the other unknown peaks, apart from the 10 PPPs, were also phenols. The clean-up procedure employed was developed in such a way as to eliminate almost all of the interference, even though a number of neutral organic compounds can be retained by the anion exchange resin.

TABLE II
Percentage recovery of phenols

Compound	% recovery			
	I	II	III	Average
2,4–DNP	86.3	94.6	90.2	90.4
DNOC	44.3	86.9	52.8	61.3
Phenol	60.5	54.5	52.5	55.8
4–NP	62.5	60.4	65.0	62.3
2–CP	55.6	59.7	56.0	57.1
2–NP	65.0	69.6	68.0	67.5
2,4–DMP	51.4	50.9	52.4	51.6
4,3–CMP	70.5	69.8	67.5	69.3
PCP & 2,4,6–TCP	70.2	72.4	78.2	73.6

TABLE III
Level of priority pollutant phenols and total phenols in Klang River Basin (μg/L)

Station no	Distance from estuary (km)	2,4–DNP	DNOC	Phenol	4–NP	2–CP	2–NP	2,4–DMP	4,3–CMP	PCP	2,4,6–TCP	Unk. Phenols	Total Phenols
627	65.38	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	18.0	18.0
621	63.98	nd	nd	15.6	nd	nd	nd	nd	nd	nd	nd	nd	15.6
628	62.97	131.2	24	25.2	2.4	nd	2	nd	nd	nd	nd	76.4	261.2
604	60.48	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	24.4	24.4
629	59.62	131.2	78.8	13.6	nd	nd	nd	nd	2.8	nd	nd	66.4	292.8
605	58.62	43.6	15.6	20.4	2.8	2.4	nd	2.4	nd	nd	nd	57.2	144.4
626	58.30	39.2	nd	138.4	nd	nd	4.4	nd	nd	nd	nd	106.8	288.8
610	56.13	33.6	9.2	nd	nd	nd	nd	nd	16.4	nd	nd	28.4	87.6
623	45.42	nd	6	nd	nd	nd	nd	nd	nd	nd	nd	53.2	59.2
607	44.12	16.8	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	16.8
624	41.62	nd	3.6	4.8	1.6	nd	nd	nd	nd	nd	nd	nd	10.0
631	39.15	29.6	nd	1.2	nd	nd	nd	nd	nd	nd	nd	9.2	40.0
603	14.91	6.4	5.6	nd	0.4	1.2	nd	0.4	nd	nd	nd	nd	14.0
602	10.77	8.4	3.2	4	1.2	2.4	2.8	nd	nd	nd	nd	44.8	66.8
601	1.24	100.8	26.8	16.4	18.8	17.6	7.2	1.6	3.6	nd	nd	98.4	291.2

However, none of these compounds were extracted. They were eluted from the resin by methanol prior to elution of the phenols and, similarly, any basic organic compounds were removed by hydrochloric acid and thus did not interfere with the HPLC determination of phenols. The quantification of the unknown phenols was carried out by assuming that the unknown phenols have very similar properties in terms of the molar absorptivities to those of the known phenols which are adjacent to them. The calibration factor of the particular known phenol was then used to calculate the concentration of the unknown phenols.

From the results given in Table III, it is found that all stations were polluted with phenols to some extent. Two major areas where polution by phenols have

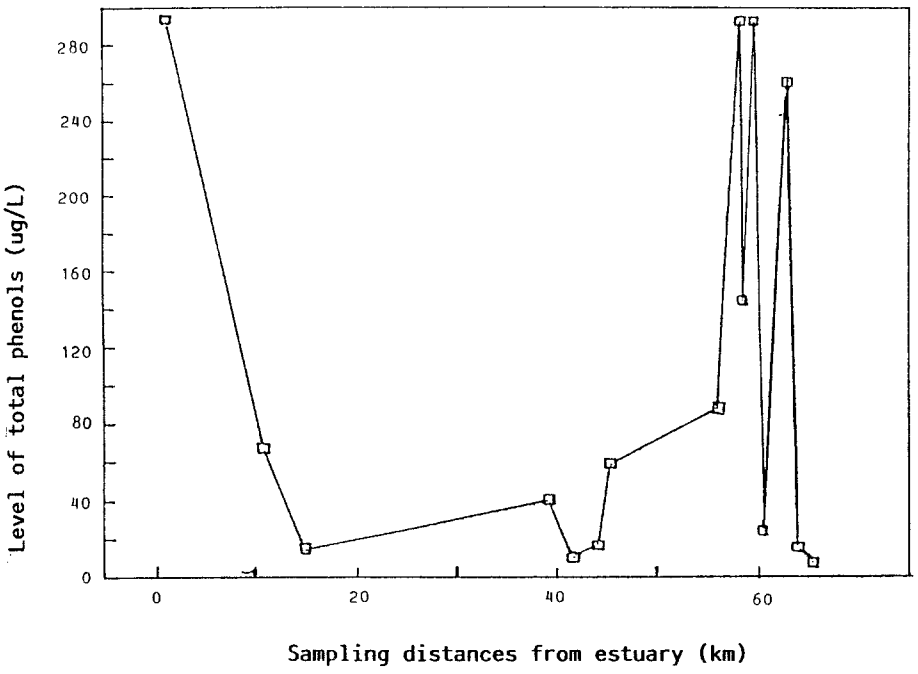

Fig. 4. Level of total phenols in Klang River on 31 Oct 1990 and 15 Jan 1991.

reached an alarming level are Ulu Klang, Ampang (Stations 628, 605, 629, 626 and 610) and a stretch from the river mouth (601) of Port Klang to Station 602 (see Figure 4). In these two highly populated and industrial areas it is possible to infer that most of the industries in the highly polluted area are involved with some phenolic compound, either directly or indirectly. The results of this survey also indicate that the industrial section from these two areas have ignored the treatment of their waste water effluents. This is especially true in view of the fact that there are some 3000–4000 illegal factories operating without proper license from the local authorities in the Klang Valley region (Department of Environment, 1988). These small and medium-sized factories often lack the expertise or resources to install the appropriate waste water treatment facilities for their effluents. Inevitably the raw effluents from such industrial activities are discharged directly to nearby drains and streams which flow directly into the Klang River.

The present survey results for phenols on the Klang River Basin correspond quite well with the results for other parameters such as phthalates, organochlorine pesticide residues, oil and grease and PAHs obtained earlier for the stations in terms of their levels of pollution (Tan *et al.*, 1990).

As the water flows downstream to Station 624 (see Figure 3) it gets diluted by run off rain water as well as from the tributaries of the Klang River. The sampling record in Table I tends to support this as it was raining on the previous night. The

TABLE IV
Chromatographic results and method detection limit

Peak No.	Compound	Abbrev.	Retention Time (min)	Method Detection Limit (mg/L)	Linearity 5–40 mg/L (Regression)
1	2,4–Dinitro phenol	2,4–DNP	1.32	0.1	0.9973
2	4,6–Dinitro-2–methylphenol	DNOC	1.56	0.1	0.9994
3	Phenol	Phenol	2.06	0.2	0.9954
4	4–Nitrophenol	4–NP	2.47	0.1	0.9938
5	2–Chlorophenol	2–CP	2.99	0.2	0.9927
6	2–Nitrophenol	2–NP	3.61	0.15	0.9955
7	2,4–Dimethyl-Phenol	2,4–DMP	3.95	0.3	0.9997
8	4–Chloro–3-methyl phenol	4,3–CMP	4.63	0.7	0.9999
9	Pentachloro-phenol	PCP	9.21	5.0	–
10	2,4,6–Trichloro-phenol	2,4,6–TCP	9.21	3.0	–

water flow was also very fast on the sampling date. A closer look at Figure 3 also tends to support the contributing factor from tributary dilution at station 624. Hence a low estimated total phenols of 10 μg/L was recorded for this station.

The physical appearance of the water at station 601 is consistent with the data obtained for the phenolic content. It is among the most polluted stations covered in this study at the Klang Valley. The high total phenolic content (291 μg/L) is to be expected as the water is still and is at a place where all the effluents accumulate from a nearby dense industrial area. Some of the factories in this industrial area deal with wood-based products such as plywood, sawn timber and furniture where phenolic resins and phenolic compounds are known to be used.

The most commonly encountered priority pollutant phenols in this study were 2,4–dinitrophenol, 4,6–dinitro–2–methylphenol and phenol (Table III). These three phenols are most probably commonly used phenolic compounds in the industries of the surrounding areas. They could also be major by-products and perhaps the main component of other phenolic compounds from domestic sewage which includes house hold disinfectants.

However PCP and 2,4,6–TCP were not detected for the water samples collected in this study. This may be due to the low concentrations present which is well below the detection limit for the two phenols combined (Table IV). A closer examination of the persistence or fate of PCP and 2,4,6–TCP may well explain the results. PCP is known to undergo photochemical degradation in solution in the presence of sunlight (USEPA, 1980). 2,4,6–TCP has a similar behaviour to PCP.

According to the US Environmental Protection Agency, the total phenolic content in domestic water supplies should not exceed 1 μg/L. The Malaysian National Drinking Water Guidelines have set a limit of 2 μg/L for total phenolic content (Ministry of Health, 1983). Therefore from the results of this study, all the Klang river water are unfit for drinking without extensive treatment (see Table III).

4. Conclusion

As can be seen from data obtained in this study, there is a definite need to set up a properly planned and systematic approach to water pollution control in the Klang Valley. Such control should include more stringent controls of effluent discharges into the river. One possible way whereby this could be achieved is to re-locate some of these small- and medium-scale factories in a properly planned industrial zone with a centrally located effluent treatment facility to handle the discharges from their activities.

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