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Residue Levels of Phthalate Esters in Water and Sediment Samples from the Klang River Basin

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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 water supply to an estimated population of two million people in this region, together with its growing industrial activities.

According to the Environmental Quality Report (Department of Environment 1989), the Klang River is regarded as one of the rivers which has been seriously affected by 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. Earlier studies of this river system have indicated the presence of organochlorine pesticide residues (Tan et al. 1991), PAHs (Tan et al. 1992) and phenolics (Tan et al. 1993) in the water samples collected from this waterway.

Phthalate esters (PEs), which are known to be substances of low toxicity (Giam et al. 1984) are ubiquitous pollutants in the environment owing to their widespread use as plasticizers in the plastics fabricating industry (Larsson et al. 1986; Preston and Al-Omran 1989). The present survey on residue levels of phthalate esters covers the period from January 1992 to February 1993.

MATERIALS AND METHODS

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 were adopted for this particular study. Sampling stations were selected to represent water outlets for domestic, agricultural and industrial use at the present time. All water and sediment samples were analyzed to determine the residue levels of seven phthalate esters, namely, dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), diisobutyl phthalate (DIBP), di-2-ethylhexyl phthalate (DEHP), di-n-octyl phthalate (DOP) and dioctyl isophthalate (DOIP).

The grab sample technique was used whereby the surface water (0.5 to 1.0 m deep) was collected from the middle of the river with a pail and filled into 2.5-L amber bottles. All sampling bottles used in this study were thoroughly rinsed with dilute nitric acid and then washed with glass distilled water to avoid contamination. Prior to actual filling, the bottles were pre-rinsed with some sample water. Sediment samples were collected from the

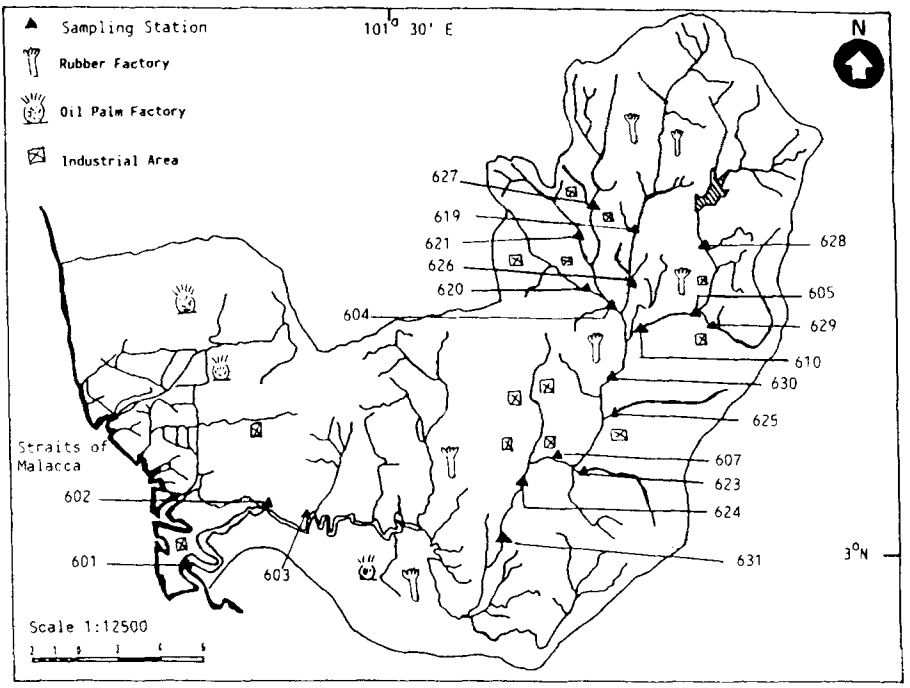

Figure 1. KLANG RIVER BASIN - SAMPLING STATIONS

various sampling stations along the Klang River. The sediments were dug out of the river bed using an excavator and then stored in wide-mouthed amber bottles. Sediment samples were taken near the river bank, which is covered by shallow water and only surface sediment samples (approximately 0 to 10 cm deep) were collected. The excavator was a home-made hoe-shaped device consisting of a 1.5-m pole fixed to a diagonally truncated metal can. Duplicate water and sediment samples were obtained every 3 months during the survey period from January 1992 to February 1993.

Phthalate esters standards (Theta Kit, Theta Corp, Penn, USA), anhydrous sodium sulfate (Merck, Darmstadt, Germany), dichloromethane (Lab Scan, Dublin, Ireland, redistilled), petroleum ether 60 to 80°C (Lab Scan, Dublin, Ireland redistilled), hexane (BDH, Poole, UK, GC-grade), acetonitrile (Romil, Leicester, UK, redistilled) and Florisil (Sigma, St. Louis, MO, USA, pesticide-grade) were used in the analysis. Diethyl ether (b.p. 34 to 40°C) from Riedel de-Haen (Seelze, Germany, GP grade, 99% purity) was passed through a chromatographic column packed with alumina to eliminate peroxides and was glass distilled twice prior to use. Doubly distilled water from an all-glass distiller and stored for not longer than 7 d in a glass storage tank was used as reagent water.

All glassware were thoroughly cleaned by the following procedure to avoid contamination of phthalates from laboratory apparatus. First, all glassware were washed and then immersed in a chromic acid bath overnight. After this, the glassware was rinsed with redistilled acetone before being wrapped up in an acetone rinsed aluminium foil and then dried in the oven at 110°C for 48 hr. After this, all glassware were properly kept in a clean metal box and further rinsed with the respective organic solvent each time before use.

Table 1. Recovery of phthalates from fortified water samples. Amount of phthalate added is 10 µg each.

Substance	% Recovery			
	Sample			
	I	II	III	Average
DMP	32	45	35	37
DEP	54	64	77	65
DBP	61	72	53	62
DEHP	82	95	90	89
DIBP	46	62	78	62
DOP	48	54	63	55
DOIP	72	84	93	83

A 500-mL volume of river water sample was extracted with 2 x 25 mL of dichloromethane. The extracts were combined and filtered through a funnel with a solvent-moistened double phase filter paper containing approximately 2g of anhydrous sodium sulfate into a 250-mL round-bottomed flask. An additional 10 to 15-mL of dichloromethane was used to wash the filter paper with the sodium sulfate to ensure a quantitative transfer of the extract compounds. The solvent was then evaporated from the flask using a rotary vacuum evaporator. 5-mL of petroleum ether was added to transfer the sample extract for Florisil column chromatographic clean-up.

Sediment samples were extracted by using the procedure developed by Thuren (1986). Florisil column chromatographic clean-up was used for fractionation of the phthalate esters from the water and sediment extracts by elution with solvents of increasing polarity. A glass column (35 cm x 8 mm i.d.) was charged with deactivated Florisil (3 g, 3% water w/w). The extract was introduced onto the column and eluted with 10-mL of petroleum ether followed by 25-mL of 20% diethyl ether in petroleum ether. The first fraction (0 to 15-mL) contains organochlorine compounds such as PCBs and DDT, and the second fraction (16 to 35-mL) contains the phthalates. The second fraction was collected and evaporated to dryness and then transferred quantitatively to a sample vial with 5-mL of hexane. The extract was concentrated to 2-mL under nitrogen.

Table 2. Recovery of phthalates from fortified sediment samples. Amount of phthalate added is 10 µg each.

Substance	% Recovery			
	Sample			
	I	II	III	Average
DMP	23	20	34	26
DEP	35	28	40	34
DBP	45	47	60	51
DEHP	85	75	90	83
DIBP	45	52	58	52
DOP	35	41	48	41
DOIP	68	62	75	68

Table 3. Blank recovery of phthalates from glass distilled water. Amount of phthalate added is 10 µg each.

Substance	% Recovery			
	Sample			
	I	II	III	Average
DMP	45	38	37	40
DEP	54	64	77	65
DBP	71	74	69	71
DEHP	80	75	82	79
DIBP	55	67	63	62
DOP	68	60	75	68
DOIP	64	85	62	70

Duplicate water and sediment samples were analyzed on each sampling occasion during the survey period. For each sample, triplicate analyses were carried out for the phthalate ester residue levels.

The separation and determination of the phthalate esters in the cleaned up extracts were performed with the Shimadzu GC 14A chromatograph fitted with a flame ionization detector using a Supelco SPB-608 fused silica capillary column (15 m, 0.53 mm ID). The injector and detector temperatures were 250°C. The oven temperature for the column was maintained at 115°C for 3 min, then programmed at 5°C min^{-1} to 165°C and then further programmed at 10°C min^{-1} to 245°C and held at this final temperature of 245°C for 7 min. The flow rate of the carrier gas was maintained at 5 mL min^{-1}. The sample size was 0.6 µL.

Table 4. Residue levels of phthalates in Klang River water (from January 1992 to February 1993; average of four data sets).

Station no.	Distance from estuary (km)	Phthalates (µg/L) DMP	DEP	DBP	DIBP	DEHP	DOP	DOIP	Total PEs
601	1.2	nd[a]	nd[a]	1.2	0.3	13.8	nd[a]	nd[a]	15.3
602	10.8	0.1	0.1	3.2	0.2	5.8	0.3	nd[a]	9.7
603	15.0	nd[a]	nd[a]	0.8	0.6	3.1	0.5	nd[a]	5.0
624	41.6	0.1	0.1	4.8	2.1	19.9	0.8	nd[a]	27.8
607	44.1	nd[a]	0.2	2.0	nd[a]	27.5	1.5	nd[a]	31.2
625	48.3	nd[a]	nd[a]	1.2	0.1	9.8	0.1	nd[a]	11.2
610	56.1	0.1	nd[a]	1.1	0.3	34.9	0.4	nd[a]	36.7
630	51.2	nd[a]	nd[a]	0.8	nd[a]	19.3	0.3	nd[a]	20.4
626	58.3	0.1	nd[a]	3.2	3.3	62.2	0.2	nd[a]	69.2
604	60.4	nd[a]	nd[a]	2.1	2.8	64.3	nd[a]	nd[a]	69.2
620	61.5	nd[a]	nd[a]	1.9	nd[a]	7.5	nd[a]	nd[a]	9.4
628	63.0	nd[a]	nd[a]	1.3	nd[a]	13.3	nd[a]	nd[a]	14.6

[a]nd = not detected

Table 5. Residue levels of phthalates in sediment samples of Klang River water (from January 1992 to February 1993, average of four data sets)

Station no.	Distance from estuary (km)	Phthalates (ng/g dry wt.) DMP	DEP	DBP	DIBP	DEHP	DOP	DOIP	Total PEs
601	1.2	3.3	1.1	398	181	3881	23	nd[a]	4487
624	41.6	1.5	3.4	248	41	896	62	nd[a]	1252
607	44.1	nd[a]	nd[a]	637	400	15015	193	nd[a]	16244
625	48.3	nd[a]	nd[a]	67	7	493	nd[a]	nd[a]	568
630	51.2	nd[a]	nd[a]	114	56	1632	nd[a]	nd[a]	1801
604	60.4	3.4	nd[a]	101	nd[a]	609	7	nd[a]	720
620	61.5	10.1	3.3	406	58	7521	nd[a]	nd[a]	7798

[a]nd = not detected

The water and sediment samples were analyzed for the residues of the seven phthalate esters, namely, DMP, DEP, DBP, DIBP, DEHP, DOP and DOIP. The direct comparison technique using external standards was used to identify and quantity the phthalate ester levels in the samples.

Recovery studies of these phthalates were also carried out using fortified water and sediment samples. Blank recovery studies using glass distilled water were also carried out.

RESULTS AND DISCUSSION

Using the stipulated conditions the phthalates eluted from the gas chromatographic column in the order of DMP (7.8 min), DEP (10.5 min), DIBP (15.1 min), DBP (16.4 min), DEHP (21.3 min), DOP (23.4 min) and DOIP (24.4 min) with baseline resolution of all the peaks. The detection limit (signal/noise ratio of 3:1) was 0.01 ng for DMP, DEP and DBP; 0.05 ng for DOP; 0.1 ng for DEHP and DIBP; and 0.4 ng for DOIP.

Recovery of phthalates from fortified water samples ranged from 32 to 45% for DMP, 54 to 77% for DEP, 53 to 72% for DBP, 82 to 95% for DEHP, 46 to 78% for DIBP, 48 to 63% for DOP and 72 to 93% for DOIP. Tables 1 and 2 show the recovery of phthalates from fortified water and sediment samples. Table 3 shows the blank recovery data using glass distilled water.

Tables 4 and 5 show the average results of the residue levels of phthalates present in the water and sediment samples of the Klang River during the period from January 1992 to February 1993. The results are averaged over four sampling occasions during this period.

DBP and DEHP were present in all the water and sediment samples collected at the various sampling stations. These two compounds are important materials in the plastics manufacturing industry, since they are used as plasticizers for making all kinds of plastic devices. It is possible that the location of various plastics manufacturing factories near some of the monitoring stations could be the contributing factor for some of the high levels of DBP and DEHP in the water and sediment samples. The phthalate levels in the water and sediment samples collected near industrial areas are relatively high as can be

seen in samples from stations 607 and 624. The phthalates found in these stations could have come from untreated industrial waste discharge from the factories around these stations. The results of this survey also indicate that the industrial section dealing with plastics manufacturing have ignored the treatment of their waste water effluents. This is especially true in view of the fact that there are some 3000 to 4000 illegal factories operating without proper license from the local authorities in the Klang Valley region (Department of Environment 1989).

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. Figure 1 shows the locations of the various sampling stations in the Klang River basin.

The present survey results for phthalates in the water and sediment samples in the Klang River correspond to those reported from North America and Western Europe (Giam et al. 1984; Schwartz et al. 1979; Thuren 1986). The DEHP levels in freshwater sediment samples range from 180 ng/g to 30,000 ng/g (Giam et al. 1984). In the Klang River the sediment samples were found to contain DEHP ranging from 493 ng/g to 15,014 ng/g. (Table 5). The levels of DEHP were only high at or around a station where direct discharge points were found. This could have been the case for the high levels at stations 624 and 607.

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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