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CHARACTERIZATION AND DETERMINATION OF LIPOPHILIC HYDROCARBONS IN THE CHAO PHRAYA, BANG PAKONG AND THA-CHIN RIVERS AND THE UPPER GULF OF THAILAND

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SUMMARY

Carbon tetrachloride extracts of water samples collected from the Chao Phraya, Bang Pakong and Tha-Chin rivers and the Upper Gulf of Thailand in the rainy season (1983) and dry season (1984) were studied in order to characterize and determine the lipophilic hydrocarbons. The major lipophilic organic compounds present were *n*-alkanes (C_{17}–C_{33}), dibutyl phthalate and di(2-ehtylhexyl) phthalate. However, polyaromatic hydrocarbons were hardly detectable level (0.1 μg/l by high-performance liquid chromatography). The concentrations of these lipophilic hydrocarbons were correlated with the effective rainfall content of the river. These data suggest a multiplicity of sources ranging from indigenous biological materials to petroleum activities.

INTRODUCTION

There are four important rivers draining into the Upper Gulf of Thailand, namely the Chao Phraya, Bang Pakong, Tha-Chin and Mae Klong, which have been used for agricultural and recreational purposes or as a source of potable water. Pollution from industrial and domestic waste-waters including heavy metals and various organic contaminants has increased over the last 10 years due to the development of industries and the concentration of population in these areas. Although the major

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inorganic components, *i.e.*, heavy metals, total N, total P and chemical-biochemical behaviour have been well characterized by earlier workers[1–3], the specific organic components are usually not known[4,5].

Crude oil and other petroleum products represent a significant form of water pollution, both as acute spillages and as chronic inputs. In general, crude oil is an exceedingly complex mixture and no single oil has ever been completely defined chemically. Several hundred individual compounds accounting for about half of the oil sample have been identified[6]. Most of these components are hydrocarbons (straight-chain and branched alkanes, cycloalkanes and aromatics) and other components are oxygen-, sulphur- and nitrogen-containing compounds. The composition of crude oil is known to change due to weathering[7] and biodegradation[8] in the aquatic environment. It is also recognized that the aquatic environments in estuarial and coastal regions are widely polluted with such compounds[9–33], and that these contaminants are taken up by fish and shellfish. When the fish are harvested an human health hazard may result.

The present work is, therefore, designed to characterize and determine lipophilic components present in the river- and sea-waters collected from the Chao Phraya, Bang Pakong and Tha-Chin rivers and the Upper Gulf of Thailand. These findings provided necessary background information that will undoubtedly be required in assessing the impacts and trends of organic compounds in the aquatic environment.

EXPERIMENTAL

Chemicals

Analytical grade carbon tetrachloride and *n*-hexane were purified by fractional distillation. They were checked for purity by evaporating 100 ml to 100 μl and gas chromatographic (GC) analysis. The methanol used for high-performance liquid chromatography (HPLC) was a Cica-Merck HPLC grade solvent (Kanto Chemicals Co., Tokyo, Japan). Water for HPLC was obtained from Nakarai Chemicals Ltd. (Kyoto, Japan). *n*-Alkanes, phthalate ester plasticizer and polyaromatic hydrocarbon (PAH) standards were commercially available. Standard solutions of these compounds both alone and as mixtures were prepared by dissolving the compounds in methanol or *n*-hexane, with subsequent serial dilutions.

Sample collection and extraction of lipophilic components

Water samples were collected from the Chao Phraya, Bang Pakong and Tha-Chin rivers and the Upper Gulf of Thailand (Fig. 1 and Table I). In the rainy (September and October 1983) and dry (March 1984) seasons. Great care was taken to avoid contamination: all utensils and containers were scrupulously cleaned and rinsed with purified carbon tetrachloride before use. Heyroth sample bottles were employed and all these 3-l samples were taken from the bow of a boat at a depth of 1 m to avoid contamination from the boat exhaust. A 50-ml volume of carbon tetrachloride was immediately added to each water sample to avoid biodegradation, and the bottle was shaken vigorously to disperse the carbon tetrachloride throughout the water.

In the laboratory, to a 3-l water sample was added a further 50-ml volume of

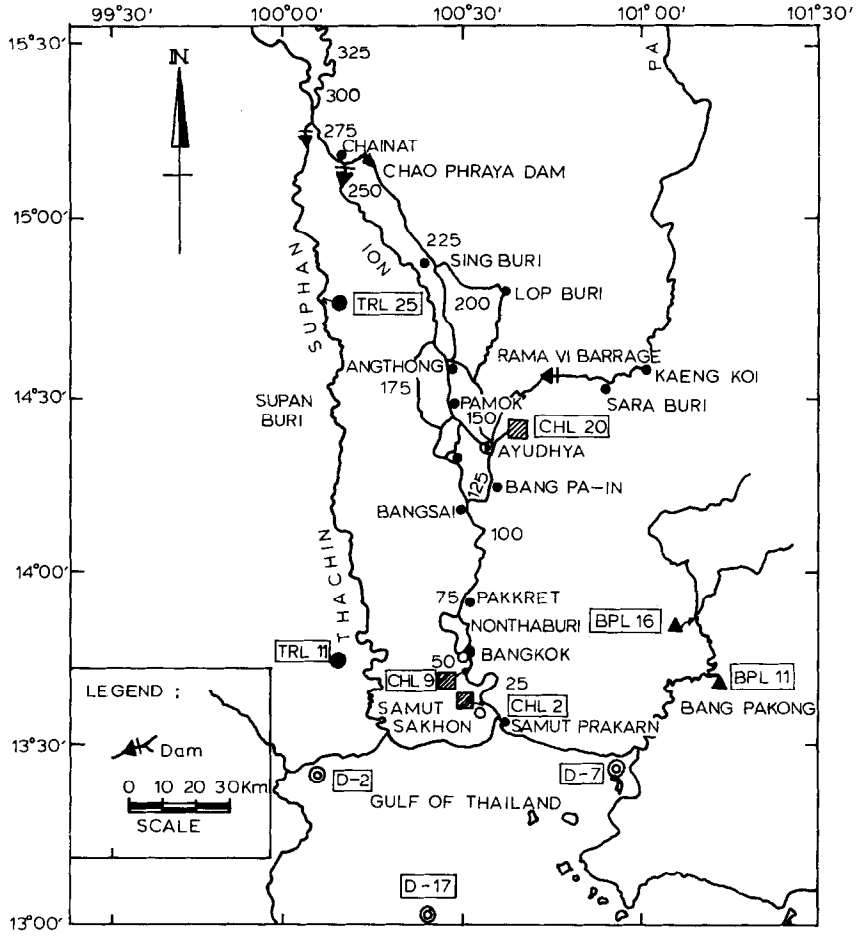

Fig. 1. Locations of sampling sites in the Chao Phraya, Bang Pakong and Tha-Chin rivers and the Upper Gulf of Thailand.

carbon tetrachloride and the mixture was mechanically stirred for 1 h. The carbon tetrachloride fraction was separated and the process was repeated with other 100 ml of carbon tetrachloride. The pooled carbon tetrachloride extracts were dried over anhydrous sodium sulphate and evaporated to dryness using a rotary evaporator, at low temperature (below 40°C). The residue was dissolved in 5 ml of *n*-hexane for GC and HPLC analyses.

Analysis of lipophilic hydrocarbons

The carbon tetrachloride extracts were analyzed using a Shimazu GC-6A gas chromatograph equipped with a flame ionization detector. A glass column (2 m × 0.3 cm I.D.) packed with 2% silicon OV-1 on Uniport HP (60–80 mesh) was employed. The temperature of the column oven was increased from 120 to 250°C at 5°C/min. The injector and detector temperatures were 260°C. The carrier gas (nitro-

TABLE I

RIVER- AND SEA-WATER SAMPLES FOR LIPOPHILIC HYDROCARBON DETERMINATIONS

Source	*Sample*	*Sampling site*	*Collection date*
Chao Phraya	CHL 2 (I)	South Electric Generation Plant	17/10/83
	CHL 2 (II)	(14 km)	06/03/84
	CHL 9 (I)	Tabacco Factory (44 km)	17/10/83
	CHL 9 (II)		06/03/84
	CHL 20 (I)	Pom Phetek (142.6 km)	17/10/83
	CHL 20 (II)		06/03/84
Bang Pakong	BPL 11 (I)	Bang Khla (85 km)	25/10/83
	BPL 11 (II)		24/03/84
	BPL 16 (I)	Bang Nam Prieo (115 km)	25/10/83
	BPL 16 (II)		24/03/84
Tha-Chin	TRL 11 (I)	Sampran (60 Km)	18/09/83
	TRL 11 (II)		12/03/84
	TRL 25 (I)	Samchook District (marker area)	18/09/83
	TRL 25 (II)		12/03/84
Upper Gulf of Thailand	D-2	Mae Klong river estuary	13/09/83
	D-7	Near Bang Sean beach (resort) Cholbuli	13/09/83
	D-17	Between Chantaburi Province and Prachab Keeree Khun Province	13/09/83

* L = At low tide; I, rainy season; II, summer season.

gen) flow-rate was 50 ml/min. A Shimazu Model Chromatopac-1A data system was used to determine the retention times and the peak areas on the chromatograms. *n*-Alkanes, phthalate esters and PAHs were identified by comparison of their retention times with those of authentic standards injected under the same GC conditions (Table II).

Polyaromatic hydrocarbons in the carbon tetrachloride extracts were analyzed by means of HPLC with UV detection (Nippon Seimitsu Scientific Co. Tokyo, Japan). The column (10 cm × 6 mm) was packed with SSC-ODS-262 (Senshu Scientific Co., Tokyo, Japan), grain size 5 μm. The following conditions were employed: column temperature, ambient; mobile phase; methanol–water (80:20, v/v); flow-rate, 1 ml/min. Individual PAHs were identified by comparison of their retention times with those of authentic samples (Table II).

An Hitachi M-80 mass spectrometer-gas chromatograph equipped with an Hitachi M-003 data processing system was used for characterization of samples under the following conditions: ion source (250°C) current, 70 μA; electron energy, 70 eV. A glass column (2 m × 0.3 cm I.D.) packed with 2% silicon OV-1 on Uniport HP (60–80 mesh) was used for the GC separations of the lipophilic components from water samples. The oven temperature of the gas chromatograph was increased from 120 to 240°C at 5°C/min. Compounds were identified by comparison of their retention times and mass spectra with those of authentic compounds.

Recovery tests were performed by spiking water with *n*-alkanes, phthalate esters and PAHs and carrying out the entire analytical procedure (Table II), in order

to evaluate the total analytical precision for individual hydrocarbons. Although drastic precautions were taken during evaporation steps, loss of the more volatile compounds occurred. Consequently data given for *n*-alkanes having less than eighteen carbon atoms and aromatic compounds having only one ring are only semiquantitative.

The corresponding detection limits were 1 μg/l for *n*-alkanes and phthalate esters by GC and 0.1 μg/l for PAHs by HPLC.

RESULTS AND DISCUSSION

Characterization of lipophilic hydrocarbons

Typical GC (with flame-ionization detection) and GC–mass spectrometric (MS) (total ion current) traces of carbon tetrachloride extracts of water samples collected from the Chao Phraya and Bang Pakong rivers in the rainy and dry seasons are shown in Figs. 2 and 3. Since no preliminary chemical and physical separations were performed for water samples and the extracts, these extracts may contain not only both dissolved and particulate hydrocarbons but also a variety of lipophilic components. However, some of the peaks in the chromatograms of Figs. 2 and 3 could be identified by comparison of their retention times and mass spectra with those of authentic standards. Typical mass spectra of these peaks are shown in Fig. 4.

Fig. 4A shows the mass spectrum of the compound corresponding to the peak

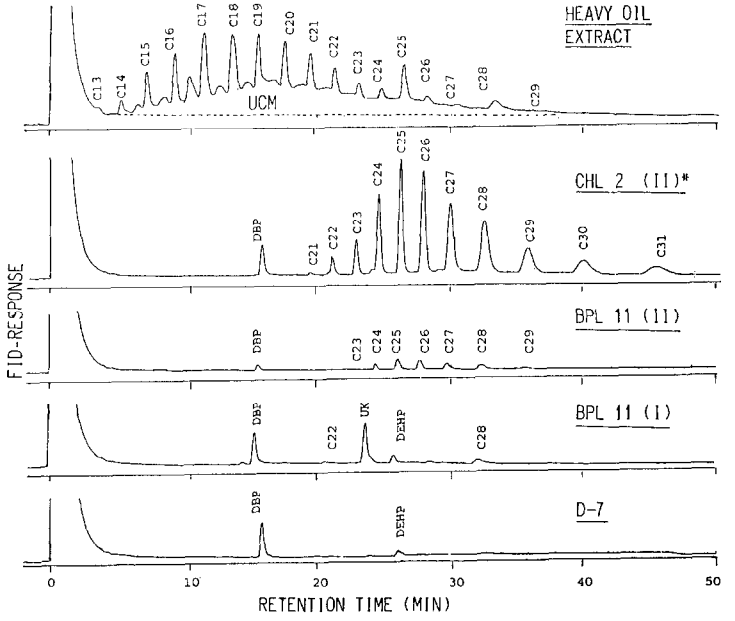

Fig. 2. Typical gas chromatograms (with flame ionization detection) of carbon tetrachloride extracts of heavy oil and water samples collected from the Chao Phraya (CHL 2), Bang Pakong (BPL 11) rivers and the Upper Gulf of Thailand (D-7). Sample names as in Table I, compounds as in Table II. For GC conditions, see Experimental. UCM = Unresolved complex mixture; UK = unknown.

TABLE II

CHROMATOGRAPHIC BEHAVIOUR AND RECOVERY DATA FOR HYDROCARBONS WHICH MAY BE FOUND IN AQUATIC ENVIRONMENTS

Compound tested	*Retention time (min)*	*Recovery (%)**	*Compound tested*	*Retention time (min)*		*Recovery (%)**
Paraffins			*Phthalates*			
n-Decane (*n*-C_{10})	0.89**	11.0	Di-*n*-butyl phthalate (DBP)	16.59**	(9.0)***	88.0
n-Undecane (*n*-C_{11})	1.39	18.5	Di-*n*-amyl phthalate (DAP)	19.43	(17.8)	89.7
n-Dodecane (*n*-C_{12})	2.37	35.5	Benzyl butyl phthalate (BBP)	22.76	(8.3)	90.5
n-Tridecane (*n*-C_{13})	3.65	28.0	Di-*n*-heptyl phthalate (DHP)	24.55		90.5
n-Tetradecane (*n*-C_{14})	5.36	37.1	Di(2-ethylhexyl) phthalate (DEHP)	26.06		98.5
n-Pentadecane (*n*-C_{15})	7.29	40.1	Dicyclohexyl phthalate (DCHP)	25.43	(18.6)	95.5
n-Hexadecane (*n*-C_{16})	9.37	46.8	Di-*n*-octyl phthalate (DOP)	29.56		93.5
n-Heptadecane (*n*-C_{17})	11.56	53.7	Di-*n*-nonyl phthalate (DNP)	27.80		96.3
n-Octadecane (*n*-C_{18})	13.67	58.6	*Polyaromatic hydrocarbons (PAHs)*			
n-Nonadecane (*n*-C_{19})	15.71	77.8	Naphthalene	1.99	(6.7)	47.0
n-Eicosane (*n*-C_{20})	17.69	75.8	Biphenyl	4.55	(9.6)	65.0
n-Heneicosane (*n*-C_{21})	19.61	87.6	1-Methylnaphthalene	3.52	(9.8)	55.8
n-Docosane (*n*-C_{22})	21.46	85.6	2-Methylnaphthalene	3.71	(10.2)	61.2
n-Tricosane (*n*-C_{23})	23.19	88.9	1-Ethylnaphthalene	4.83	(12.5)	74.0
n-Tetracosane (*n*-C_{24})	24.90	95.2	2-Ethylnaphthalene	4.85	(13.1)	76.5
n-Pentacosane (*n*-C_{25})	26.59	89.9	2,3-Dimethylnaphthalene	5.60	(14.2)	74.3
n-Hexacosane (*n*-C_{26})	28.29	88.5	1,4-Dimethylnaphthalene	5.61	(14.5)	88.1
n-Heptacosane (*n*-C_{27})	30.46	82.5	Fluorene	8.26	(12.6)	82.6
n-Octacosane (*n*-C_{28})	33.26	94.2	Anthracene	10.87	(15.3)	82.7
n-Nonacosane (*n*-C_{29})	36.72	90.0	Phenanthrene	12.30	(13.5)	98.0
n-Triacontane (*n*-C_{30})	41.19	95.5	Fluoranthene	17.85	(19.2)	96.6
n-Hentriacontane (*n*-C_{31})	47.33	90.7	Pyrene	18.73	(21.8)	76.3
n-Dotriacontane (*n*-C_{32})	54.85	86.4	Chrysene	25.22	(26.7)	88.0
n-Tritriacontane (*n*-C_{33})	64.90	79.8	Benzo[*a*]pyrene	31.62	(54.0)	85.5

* Average of three recovery tests.

** GC Retention time; for operating conditions, see Experimental.

*** HPLC retention time; for operating conditions, see Experimental.

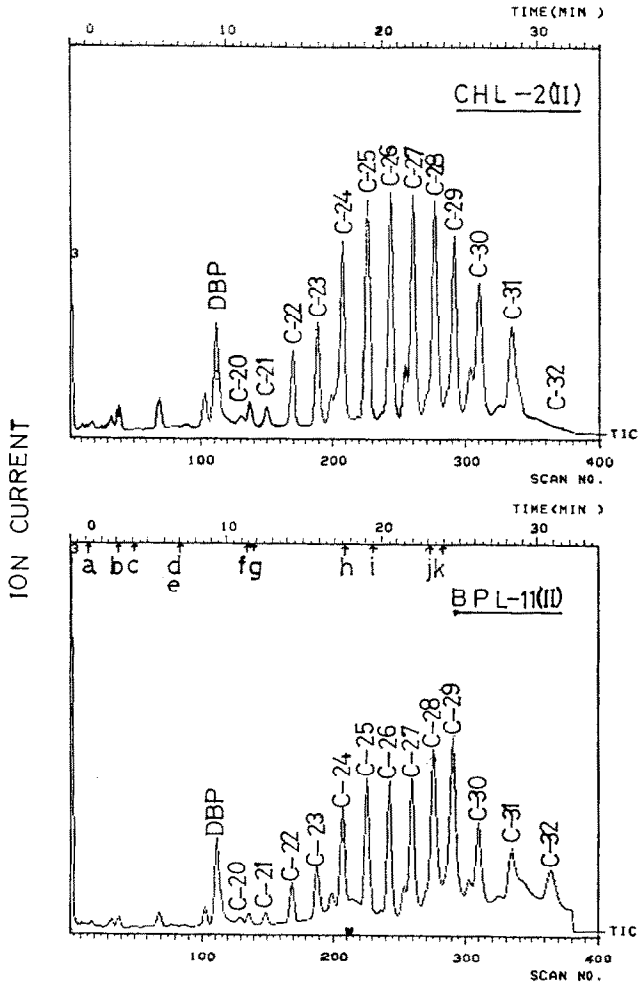

Fig. 3. Reconstructed mass chromatograms (total ion current) of carbon tetrachloride extracts of water samples collected from the Chao Phraya (CHL 2) and Bang Pakong (BPL 11) rivers in the dry season. Compounds as in Table II. a = Methylnaphthalene; b = dimethylnaphthalene; c = Fluorene; d = anthracene; e = phenanthrene, f = fluoranthene; g = pyrene; h = chrysene; i = DEHP; j = benzo-[*a*]pyrene; k = Benz[*a*]anthracene standard.

of scan 111 in Fig. 3. The molecular ion (M^+) is at *m/e* 278 and the most abundant fragment ion at *m/e* 149, which arises by the loss of butyl and butoxyl groups from the molecular ion. Other fragment ions at *m/e* 205 ($M^+ - OC_4H_9$) and 223 ($M^+ - C_4H_7$) are observed. On the basis of its retention time and mass spectral interpretation, this compound was identified as di-*n*-butyl phthalate (DBP). A similar mass fragmentation pattern, with a molecular ion at *m/e* 390, to that in Fig. 4A was also observed for the chromatographic peak of scan 232, indicating the presence of di(2-ethylhexyl) phthalate (DEHP) in the extracts. Since these phthalate esters are frequently encountered in the laboratory as artifacts, it should be pointed out that

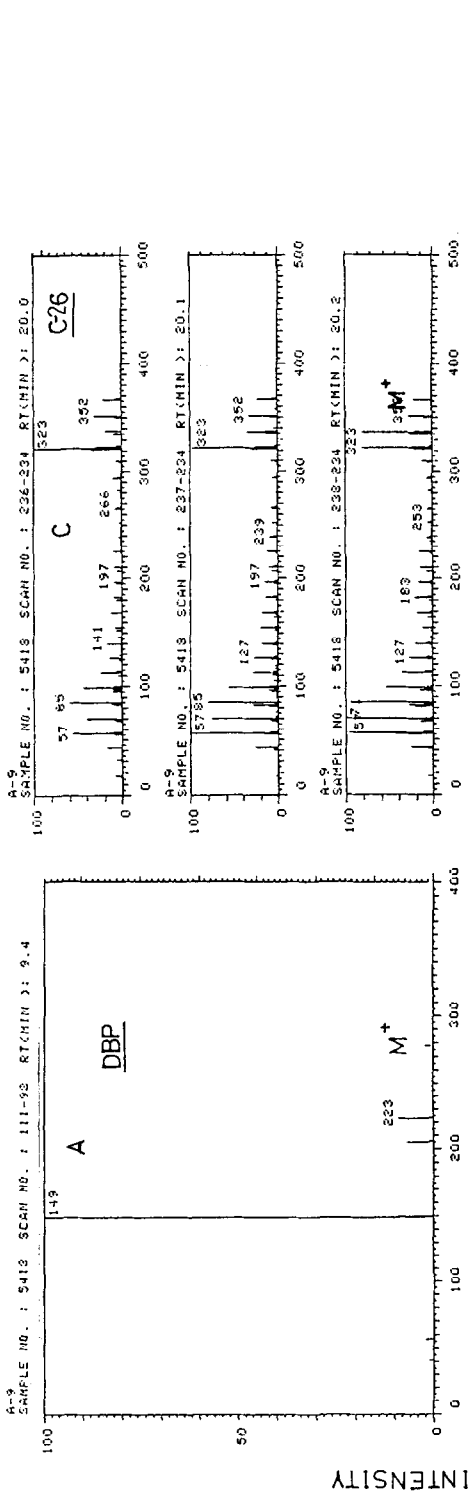

Fig. 4. Mass spectra of di-*n*-butyl phthalate (A), *n*-pentacosane (B), branched/or cyclic hydrocarbons (C) and *n*-hexacosane (D) in the chromatograms of Fig. 3.

they were not found in the procedural blank, therefore, these widely used plasticizers do seem to be present in the water samples.

The mass spectra of the compounds corresponding to the peaks of scans 226, 236 and 243 show the C_nH_{2n+1} ions characteristic of normal and branched/or cyclic alkanes (Fig. 4B–D). On the basis of their retention times and mass spectra as compared with those of authentic standards, the compounds corresponding to the peaks of scan 226 and 243 were identified as *n*-pentacosane (*n*-C_{25}) and *n*-hexacosane (*n*-C_{26}), respectively. Similar mass fragmentation patterns, but having different molecular ions, to those in Fig. 4B and D were also observed for the major peaks (C_{20}–C_{33}) on the chromatograms in Figs. 2 and 3. On the other hand, the mass spectrum of the compound corresponding to the peak of scan 237 was interpreted as being that of a branched C_{26} alkane (Fig. 4C). Similar mass fragmentation patterns, but having different molecular ions, to that in Fig. 4C were also observed for these smaller and shoulder peaks of scans 254, 268, 285, 302 and 324 in the chromatograms of Fig. 3. These aliphatic hydrocarbons are known to enter into the aquatic environment through both anthropic transport and the use of petroleum products, and natural sources, soil, continental vegetation and algal production.

Polycyclic aromatic hydrocarbons are introduced into the aquatic environment by petroleum activities and combustion processes[34–38]. Since no GC and GC–MS peaks due to the presence of these PAHs in the carbon tetrachloride extracts were detected on the chromatograms in Figs. 2 and 3, the extracts were subsequently checked by means of HPLC with UV detection at 254 nm. However, no peaks corresponding to the PAHs were detected for the extracts of water samples collected in the present work. In the HPLC analyses, only DBP was identified. These results, therefore, indicate that the pollution of the river- and sea-waters by pyrolytic-like products is low.

Hydrocarbon levels in water

On the basis of the qualititative information given above (Figs. 2 and 3), quantitative analyses of carbon tetrachloride extracts from water samples were performed by means of GC with flame ionizaton detection. The data for the samples collected from the three rivers and the Upper Gulf of Thailand in the rainy (September and October 1983) and dry (March 1984) seasons are listed in Table III as the concentrations of *n*-alkanes, phthalate ester plasticizers and other components. Since the lipophilic hydrocarbons were not first separated into the dissolved and particulate ones in the present work, the data presented are expressed as the sum of both hydrocarbon sources in water. Seasonal and regional variations in the concentrations of the hydrocarbons in water are also presented graphically in Fig. 5. The GC analyses of the carbon tetrachloride extracts showed that compositions of the non-aromatic hydrocarbons occurring in water taken in the rainy season were quite complex, whereas the most abundant hydrocarbons in water collected in the dry season were *n*-alkanes, with the exception of water samples taken from the Tha-Chin river.

Water samples collected in the rainy and dry seasons from the Chao Phraya, Bang Pakong and Tha-Chin Rivers and the Upper Gulf of Thailand showed non-aromatic hydrocarbon concentrations of 0.001–0.213 and 0.106–1.200 mg/l, respectively (Table III and Fig. 5). The concentrations of the hydrocarbons in water samples taken in the dry season were found to be 4–20 times higher than those in the rainy

TABLE III

GAS CHROMATOGRAPHIC DETERMINATIONS OF CARBON TETRACHLORIDE EXTRACTS OF WATER SAMPLES FROM THE CHAO PHRAYA, BANG PAKONG AND THA-CHIN RIVERS AND THE UPPER GULF OF THAILAND

Values are concentrations in mg/l; ND = not detected.

Compounds detected	*CHL 2*		*CHL 9*		*CHL 20*		*BPL 11*		*BPL 16*		*TRL 11*		*TRL 25*		*D-2*	*D-7*	*D-17*
	Oct.	*March*	*Oct.*	*March*	*Oct.*	*March*	*Oct.*	*March*	*Oct.*	*March*	*Sept.*	*March*	*Sept.*	*March*	*Sept.*	*Sept.*	*Sept.*
n-Alkanes																	
C_{17}	ND	0.002	ND	0.001	ND	0.001	0.003	ND	ND	ND	ND	0.003	ND	0.007	ND	ND	ND
C_{20}	ND	0.001	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C_{21}	ND	0.007	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C_{22}	0.004	0.029	0.001	0.009	ND	0.016	0.006	0.003	ND	0.005	ND	0.005	0.002	0.005	0.003	0.004	ND
C_{23}	0.001	0.053	0.002	0.013	ND	0.034	0.002	0.006	ND	0.011	ND	0.003	ND	0.002	0.005	ND	ND
C_{24}	0.002	0.107	0.002	0.032	ND	0.072	ND	0.011	ND	0.020	ND	ND	ND	0.001	0.007	ND	ND
C_{25}	0.003	0.167	0.002	0.043	0.001	0.101	0.006	0.020	0.003	0.034	0.003	0.005	0.004	0.004	0.004	0.003	0.002
C_{26}	0.002	0.176	0.005	0.038	ND	0.103	0.004	0.020	0.002	0.037	0.003	ND	ND	0.004	0.004	ND	ND
C_{27}	0.002	0.156	0.002	0.035	ND	0.085	0.002	0.018	0.003	0.037	0.003	0.001	ND	0.002	0.001	0.001	ND
C_{28}	0.012	0.158	0.007	0.039	ND	0.075	0.023	0.022	0.011	0.037	0.002	0.024	0.006	0.011	ND	0.017	ND
C_{29}	ND	0.103	ND	0.021	ND	0.052	0.007	0.015	ND	0.023	ND	ND	ND	0.019	ND	ND	ND
C_{30}	ND	0.074	ND	0.015	ND	0.037	ND	0.013	ND	0.018	ND	ND	ND	ND	ND	ND	ND
C_{31}	ND	0.067	ND	0.018	ND	0.030	0.007	0.010	ND	0.017	ND	0.008	ND	ND	ND	ND	ND
C_{32}	ND	0.031	ND	0.007	ND	0.014	ND	ND	ND	0.006	ND	ND	ND	ND	ND	ND	ND
C_{33}	ND	0.010	ND	0.001	ND	0.002	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Subtotal	0.026	1.141	0.027	0.271	0.001	0.639	0.063	0.137	0.019	0.232	0.012	0.049	0.012	0.047	0.024	0.025	0.002
Unknown	0.013	0.020	0.001	0.026	ND	0.023	0.094	0.001	0.003	0.013	ND	0.011	0.009	0.038	0.002	0.022	ND
Phthalates																	
DBP	0.021	0.049	0.004	0.019	ND	0.007	0.046	0.011	0.005	0.005	ND	0.041	0.008	0.019	0.004	0.053	ND
DEHP	0.005	ND	0.004	ND	ND	ND	0.001	ND	ND	0.004	ND	0.005	ND	0.004	0.005	0.010	ND
Subtotal	0.026	0.049	0.008	0.019	ND	0.007	0.056	0.011	0.005	0.009	ND	0.046	0.008	0.023	0.009	0.063	ND
PAHs	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total	0.065	1.200	0.036	0.315	0.001	0.667	0.213	0.149	0.028	0.251	0.012	0.106	0.029	0.109	0.034	0.110	0.002

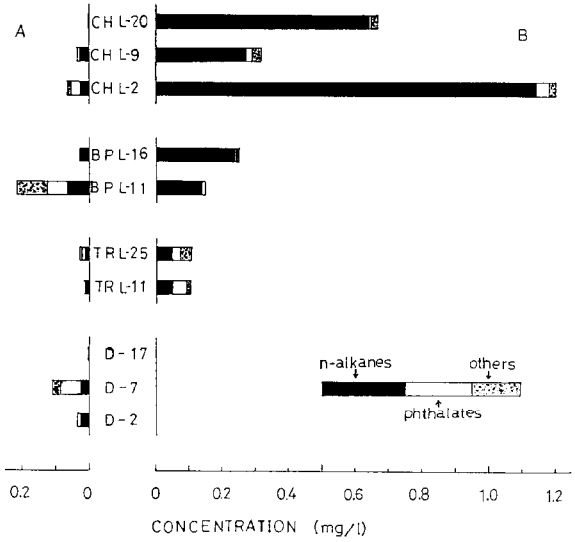

Fig. 5. Composition of lipophilic hydrocarbons found in water samples collected from the Chao Phraya, Bang Pakong and Tha-Chin rivers and the Upper Gulf of Thailand in the rainy (A) and dry (B) seasons.

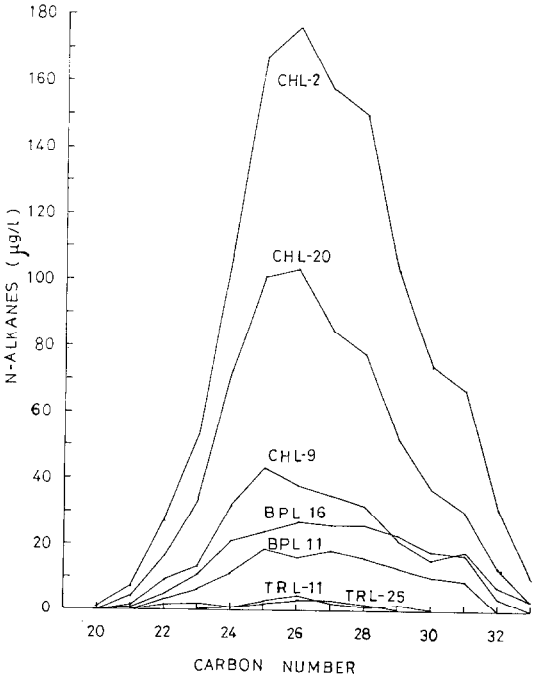

Fig. 6. Distribution patterns of *n*-alkanes found in water samples collected from the Chao Phraya, Bang Pakong and Tha-Chin rivers in the dry season as a function of carbon number.

season, with the exception of one sample collected from the station BPL 11. The highest concentration (1.200 mg/l) was found for a water sample collected in the dry season from station CHL 2, whereas the lowest values were observed in the rainy season at stations CHL 20 (0.001 mg/l) and D 17 (0.002 mg/l). Mean values of monthly rainfall in the dry and rainy seasons in these river basins have been reported to be <20 and >200 mm, respectively[2,3]. Therefore, these results can be explained in terms of the dilution of these components by heavy rain during the rainy season in Thailand.

Water from the Chao Phraya, Bang Pakong and Tha-Chin rivers and the Upper Gulf of Thailand showed phthalate ester plasticizer concentrations ranging from non-detectable to 63 μg/l. These results correspond to those reported from North America[39], Japan[40] and Western Europe[41,42]. The higher values originated from samples taken from stations CHL 2 and TRL 11 in the dry season and BPL 11 and D 7 in the rainy season (Table III and Fig. 5). Stations D 2 and D 7 are located near the Mae Klong and Bang Pakong river estuaries. Therefore, it seems that phthalate esters occurring in sea-water originate from these rivers as well as the Chao Phraya river which passes through the BKK metropolitan area. Detectable levels of phthalate esters were observed for water samples collected in the rainy season from stations CHL 20, TRL 11 and D 17. The source of the phthalate esters is not yet known. Their concentrations are quite variable and do not seem to be correlated with the effective run-off. Locating their sources is of particular interest because of their unusual ubiquity, their possible teratogenicity[43,44] and mutagenicity[45].

The concentrations of *n*-alkanes in water samples collected from the Chao Phraya, Bang Pakong and Tha-Chin Rivers and the Upper Gulf of Thailand in the rainy and dry seasons were in the ranges of 0.002–0.063 and 0.001–1.141 mg/l, respectively (Table III and Fig. 5). The values for the rainy season correspond to those reported from North America[21], Japan[46] and Western Europe[19,20,22], but were somewhat higher in the dry season.

The carbon preference index (CPI), *i.e.*, the total concentration of *n*-alkanes with odd-numbered carbon chains divided by that with even-numbered chains and the carbon number showing the maximum (C_{max}), L/H ratio, *i.e.*, the total concentration of *n*-alkanes having less than 20 carbon atoms divided by that of those having greater than 21 carbon atoms have been recognized as significant diagnostic tools to distinguish between different sources, natural and anthropic[47–49]. Figs. 6 and 7 show histograms of the *n*-alkanes expressed in terms of their amounts (μg/l) as a function of the carbon number. *n*-Alkanes in water collected in the dry season show uniform distribution patterns without predominance of odd or even numbered chains, maximizing at *n*-C_{25} or *n*-C_{26} (Fig. 6), whereas in the rainy season these compounds exhibit variable patterns maximizing at *n*-C_{28} (Fig. 7). Of note is the absence of large amounts of typical compounds such as the biologic *n*-C_{15}, *n*-C_{17}, *n*-C_{19} or prystane. The CPI values calculated in the range C_{21}–C_{33} is approximately 1. This may indicate the major input by microbial or petroliferous sources. Nevertheless, we cannot exclude a natural contribution from algal or microbial sources which could lead to regular distributions of *n*-alkanes as previously described by Clark and Blumer[50].

Although the study reported here is quite limited in scope (two or three sites sampled two times only for each river and sea, and major components only identified) and, therefore, must be considered as preliminary it has demonstrated that lipophilic

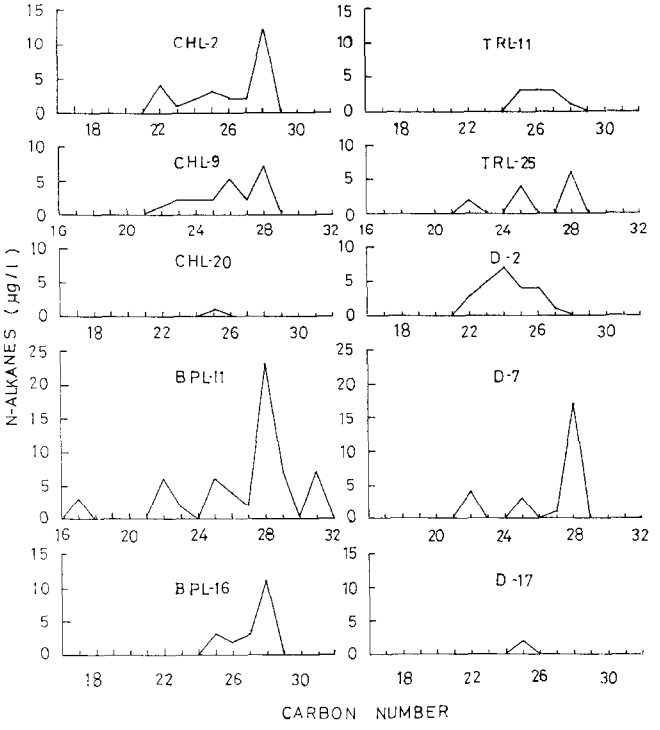

Fig. 7. Distribution patterns of *n*-alkanes found in water samples collected from the Chao Phraya, Bang Pakong and Tha-Chin rivers and the Upper Gulf of Thailand in the rainy season as a function of carbon number.

hydrocarbons occurring in water can be separated into three components, *n*-alkanes, phthalate ester plasticizers and others, by using GC, GC–MS and HPLC techniques. Furthermore, it has shown that the level of pollution of the Chao Phraya river estuary with these contaminants is very high in the dry season, as compared with those values observed for other regions surveyed in the dry and rainy seasons.

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