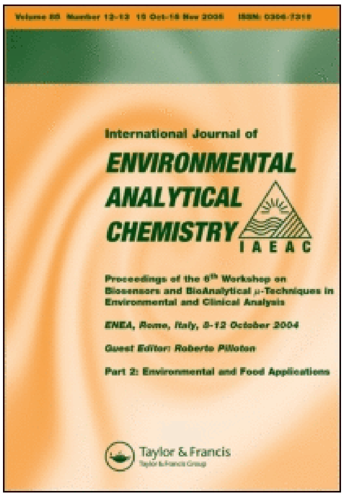

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BROAD SPECTRUM ANALYSIS OF IONIC AND NON-IONIC ORGANIC CONTAMINANTS IN URBAN WASTEWATERS AND COASTAL RECEIVING AQUATIC SYSTEMS

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A comprehensive analytical protocol for the qualitative and quantitative assessment of ionic and non-ionic organic contaminants in urban wastewaters, coastal seawater, and sediments is outlined. Liquid–liquid extraction (LLE) and adsorption onto polymers (polyurethane foam) or macroreticular resins (Amberlite, XAD-2) for the extraction of a wide variety of dissolved contaminants are evaluated. Organic extracts are resolved into fractions of increasing polarity by a combination of silica-alumina adsorption and gel permeation chromatography. HRGC-MS analysis of these fractions, using different ionization techniques, namely electron impact (EI), positive (PICI) and negative ion chemical (NICI) ionization, and the direct use of FAB-MS on the original extracts enabled the identification of a broad spectrum of anthropogenic compounds (290) in the different aquatic compartments. The decoupling of these contaminants between the water-dissolved and particulate phases is discussed.

KEY WORDS: Organic pollutants, surfactants, urban and coastal waters, water extraction, HRGC-MS chemical ionization techniques.

INTRODUCTION

A major part of the more than 2000 organic compounds already identified in the aquatic environment[1] is contributed by urban and industrial wastewaters which find their final deposition in rivers and coastal areas.[2,3] The main concern, however, is currently focused on a limited number of components which have been selected according to several criteria (i.e. occurrence, toxicity, bioaccumulation, human exposure) and are included in priority pollutants lists for monitoring. In this respect, the U.S. EPA and the EEC have issued blacklists containing, respectively 114 and 118 organic compounds of environmental concern. Nevertheless, it has been recognized that further research is needed in order to identify other refractory, toxic, and widely distributed contaminants, resulting from the continuous development of industrial activities. Consequently, the U.S. EPA has established a "target list" of compounds which should be tested for occurrence, with the aim of the implementation of a further priority pollutants list.[5]

This raises the need for the development of analytical methodologies enabling

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the detection and control of pollutants present in waters not routinely considered in environmental sample screening. These comprehensive protocols should be well suited for both urban and industrial effluents, as well as for the receiving aquatic systems, where concentrations are in the range of mg–pg l^{-1}. This is particularly critical for the preconcentration techniques which should provide intercomparable results for all types of samples, a question that has already been addressed in previous papers.[6,7].

The aim of the present paper is to report further results on the extraction, fractionation and chemical characterization of organic extracts of urban wastewaters, coastal receiving waters and sediments, based on samples collected in the northwestern Mediterranean. Special emphasis is given to ionic and non-ionic contaminants that can be used as markers of urban wastewaters in the aquatic environment, such as petroleum hydrocarbons and domestic surfactants and related products. The composition of these fractions has been examined by capillary GC-MS using different ionization mass spectrometric techniques and GC detection systems (NPD, ECD and FPD), in order to obtain an adequate selectivity for a large variety of organic contaminants. Moreover, selective procedures are developed for the determination of ionic contaminants based on the use of soft ionization mass-spectrometric techniques, namely positive and negative ion fast atom bombardment (FAB-MS).

EXPERIMENTAL

Chemicals and Reagents

Dichloromethane, *n*-hexane, methanol and acetonitrile were pesticide grade (SDS, Peypin, France). Acetone and diethylether were glass distilled (Carlo Erba Farmitalia, Milan, Italy). Silica and neutral alumina (70–230 mesh) purchased from Merck (Darmstadt, FRG), were soxhlet-extracted (dichloromethane–methanol) and activated at 120 and 350 °C, respectively. Amberlite XAD-2 was obtained from Rohm and Haas (Philadelphia, PA, USA).

The derivatization reagents *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and (*N*,*N*′,*N*)-1-methyl-3-nitro-1-nitrosoguanidine were obtained from Fluka (Buchs, Switzerland) and Aldrich Chemie (Stenheim, FRG), respectively. Nonylphenolpolyethoxylates (NPEOs), linear alkylbenzenesulphonates (LASs), linear alkylbenzenes (LABs) and alkyl and arylphosphates (APs) were purchased from Merck. Polycyclic aromatic hydrocarbons (PAHs) were supplied by Scharlau (Barcelona, Spain). *p*,*p*′-DDE, *p*,*p*′-DDD, *p*,*p*′-DDT, endrin and dieldrin were obtained from Polyscience Corp. (Niles, IL, USA). Benzo[*c*]quinoline and 1,8-naphthalic anhydride were purchased from Aldrich (Steinheim an Albuch, FRG). The polychlorinated biphenyls (PCBs) (I.U.P.A.C. numbers 28, 52, 101, 118, 153, 138, and 180) were obtained from Prochem (Wesel, FRG). The benz[*de*]anthracen-7-one, fluoren-9-one and *p*-nitrophenol were a gift of Prof. Milton L. Lee (Brigham Young, Univ., Provo, UT, USA). The heptadecylnitrile and *N*,*N*-dioctadecylmethylamine were obtained by synthesis.[8,9]

Samples Origin

Wastewaters were collected monthly in the influent of the Barcelona primary treatment plant (March–July, 1987). Sediment samples were collected off-Barcelona, in the Besos river estuary and at 4 km offshore of the river mouth with a van Veen dredge and frozen immediately at −20 °C until analysis. Seawater was collected at 1.5 km offshore from a sailing boat in order to prevent sample contamination.

Sample Handling

About 1 l of wastewater was filtered through a Whatman GF/C glass fiber filter kiln-fired at 350 °C overnight. Filtered water was saturated with NaCl and sequentially extracted with (a) dichloromethane (3 × 75 ml) and (b) by percolation through an Amberlite XAD-2 glass column (10 × 0.6 cm i.d.; 1.5–2 g). Adsorbed organic matter onto the Amberlite column was eluted with 25 ml acetone containing 10% water. This solution was concentrated to 3 ml and back extracted with dichloromethane (2 × 25 ml).

Extraction of larger samples (e.g. coastal waters, up to 500 l) was performed *in situ* from a vessel as previously described.[6] In summary, the particulate material was collected onto glass fiber filters (Watman GF/C) and the dissolved organic matter was recovered by using polyurethane foam (PUF) plugs packed into a PTFE column (30.5 × 5.08 cm i.d.). The adsorption column was eluted successively with 500 ml of acetone and hexane. The combined solutions were evaporated to near dryness.

The glass fiber filters containing the particulate material were Soxhlet extracted using dichloromethane–methanol (2:1). On the other hand, the sediments were freeze-dried extracted with dichloromethane–methanol (2:1) and methanol.

Fractionation

The organic extracts previously recovered were concentrated to 50 ml and partitioned into acids and bases + neutrals by treatment with 2 M KOH (3 × 25 ml) and extraction with dichloromethane (3 × 30 ml), before and after acidification with aq. HCl. The neutral + bases fraction was further fractionated by column chromatography using 8 g of each 5% water deactivated silica and alumina (25 × 1 cm i.d.). The following fractions were collected (Figure 1): (I) 20 ml hexane; (II) 20 ml 10% dichloromethane in hexane; (III) 40 ml 20% dichloromethane in hexane; (IV) 30 ml 50% dichloromethane in hexane; (V) 30 ml dichloromethane; (VI) 20 ml 10% methanol in dichloromethane and (VII) 40 ml diethylether. Acid and polar (V–VII) fractions were derivatized prior to high resolution GC (HRGC) analysis using diazomethane and BSTFA, respectively. Sililation was performed with 200 μl of BSTFA and isooctane at 70 °C for 1 h in a nitrogen atmosphere. After derivatization, solvents and the excess of reagents were evaporated under a gentle nitrogen stream. Diazomethane was prepared by alkaline hydrolysis of (*N*,*N*′,*N*)-1-methyl-3-nitro-1-nitrosoguanidine and was transferred as ethereal solu-

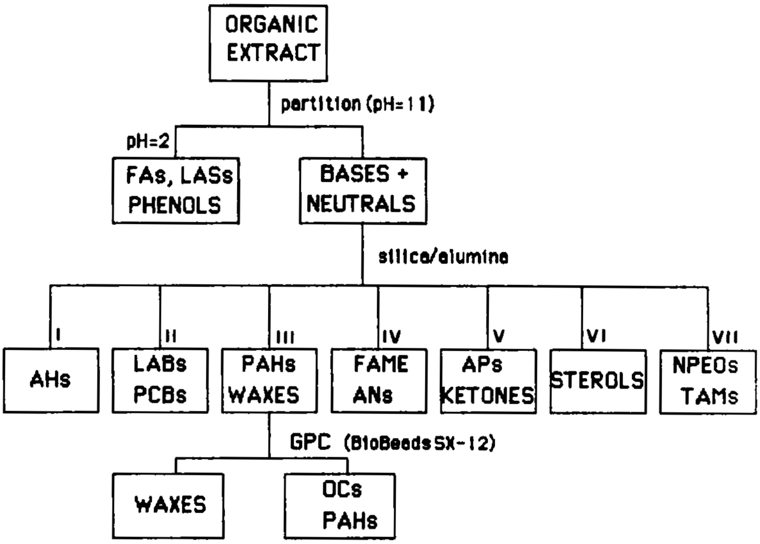

Figure 1 Fractionation scheme for organic extracts. The eluents used for fractions I–VII are indicated in the experimental part.

tion onto the dried acid fraction and kept at room temperature for 2 h. Blanks were processed in parallel with real samples and analyzed using the same analytical techniques.

HRGC and HRGC-MS Analyses

Organic fractions were analyzed in a Carlo Erba Mega 5300 series gas chromatograph equipped with a split–splitless and on column injectors and FID, ECD, FPD and NPD detectors. Injector and detector temperatures were held at 300 and 320 °C, respectively. Column temperature was programmed from 60 to 300 °C at 6 °C min^{-1}, holding the final temperature for 10 min. A 25 m × 0.32 mm i.d. fused silica column coated with 0.3 μm of SE-54 was used (Alltech Assoc.). Quantitative analyses were performed in duplicate using as external standards: *n*-dodecylbenzene for LABs; *n*-heneicosanoic acid methyl ester for LASs; *n*-tributylphosphate (*n*-TBP) for APs; and NP3EO for NPEOs assuming the same response factor for all the ethoxamers, *n*-alkanes of the same carbon number for trialkylamines (TAMs), the U.S. National Institute of Science and Technology (NIST) reference material 1647 for PAHs, and IUPAC congener numbers 28, 52, 101, 118, 153, 138, and 180 for PCBs. Recovery data were obtained from the ratio of concentrations of target compounds recovered by both extraction systems from real samples.

HRGC-MS analyses were performed in a Hewlett-Packard 5985A instrument interfaced to a 9825A data system. Electron impact (EI) mass spectra were obtained at 70 eV of ionization energy. Helium was used as carrier gas (30 cm s^{-1}) and a fused silica capillary column coated with SE-54 was fitted directly into the ion source. Other chromatographic conditions were identical to those described in the GC analysis.

Methane was used as reagent gas at 0.5 and 1.0 torr in the ion source for PICI and NICI, respectively. The injector GC port, ion source, and mass analyzer were held at 300, 180 and 110 °C, respectively. Electron energy for PICI and NICI was typically 110 or 230 eV, respectively, and the electron emission current was kept at 300 μA. The mass axis was calibrated with perfluorobutylamine using fragments at m/z: 41, 414 and 652 for PICI, and 264, 414 and 633 for NICI. Scans were obtained from 30–600 amu at 0.9 scans per second. Multiple ion detection (MID) was used in the EI and PICI ionization except for the NPEOs, which were analyzed using selected ion monitoring (SIM) detection mode (dwell time 150 msec per ion). The EI mass spectra assignments were accomplished by library search using the PBM algorithm (match quality above 0.85) in the John Wiley spectral data base ($\sim$120000). NICI mass spectra were also compared with reported data[10] (less than 10% fragment abundance variability). Positive identifications were accomplished by coinjection of authentic standards.

FAB-MS analyses were performed in a VG updated MS9 instrument equipped with a saddle field source (Ion Tech Ltd.). Methanolic extracts (1–2 μl) were dissolved within a small amount of thioglycerol saturated with NaCl and inserted onto the tip probe. Ions were produced by a primary beam of atomic xenon (8 keV), extracted and accelerated with 8 kV.

RESULTS AND DISCUSSION

Extraction and Fractionation of Organic Extracts

A particular requirement for the analysis of organic microcontaminants in coastal waters when a broad-spectrum screening is intended, is preconcentration, to increase the detectability of the target compounds. In any case, the technique used should provide representative extracts from large volumes of seawater. Previous studies[6,7] have shown that liquid–liquid and solid-phase extraction systems (e.g., Amberlite XAD-2 and polyurethane foam) exhibit major differences in the recovery of homologous series of compounds with a wide range of molecular weight distributions and/or polarities. In this respect, liquid–liquid extracts are enriched in the higher homologs of aliphatic and aromatic hydrocarbons compared with those obtained by sorption onto Amberlite XAD-2. This has been attributed to selective association of the hydrophobic species with seawater fulvic materials and the effects of the dissolved organic molecules on sorbent properties. On the other hand, on a polarity basis, liquid–liquid extraction (LLE) exhibits preference for the hydrophobic solutes, while the most hydrophilic ones can only be satisfactorily recovered by sorption onto organic polymers. Irrespective of whether LLE is performed after or before XAD-2 adsorption, the results obtained exhibited similar trends for a series of surfactants and related products of interest as urban waste markers. This is illustrated in Figure 2 where the efficiency of the extraction of a previously filtered wastewater sample using XAD-2 resin or dichloromethane (LLE) is compared. LASs (log K_{ow}=2.0) and nonylphenolethoxylates (NPEOs)

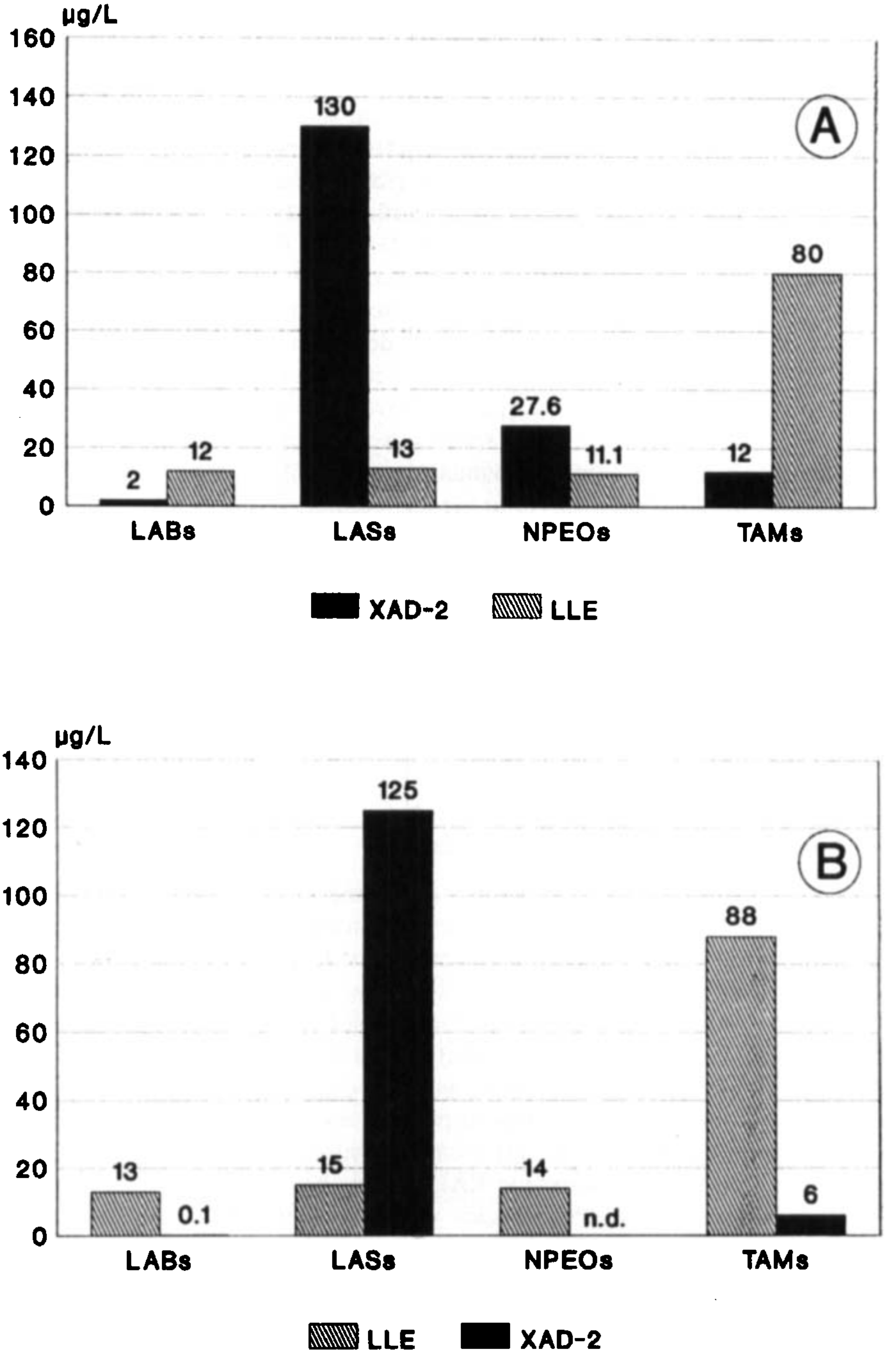

Figure 2 Absolute concentrations of surfactants and related products recovered from the dissolved phase of wastewater by (A) sequential solid-phase (XAD-2) and liquid–liquid extraction (LLE) and (B) sequential LLE and XAD-2 adsorption.

were recovered with higher efficiencies in the XAD-2 column (91–94% of the total amount recovered), whereas LABs and TAMs ($\log K_{ow} \geqq 8$) were mostly recovered by LLE, with NPEO exhibiting ($\log K_{ow} = 4$–6) intermediate results. Accordingly, a combination of LLE and adsorption onto Amberlite XAD-2 or polyurethane foam was used for the extraction of the dissolved components as described in the experimental section.

Extraction of sediments by soxhlet extraction with dichloromethane–methanol (2:1) provides good recoveries for low- to moderate-polarity compounds.[11] However, when highly polar ($\log K_{ow} \leqq 4$) or ionic species (e.g. tetraalkylammonium surfactants) need to be determined, an additional extraction step with methanol was performed.

Partitioning of the organic extracts at $\mathrm{pH} = 11$ is not sufficient to hydrolyse esters, such as alkylphosphates, alkylesters and triglycerides, the latter being biogenic or natural components. Therefore, a further separation of these compounds from analytes of similar polarity (e.g. PAHs) should be performed to avoid interferences in their determination. This is accomplished by low-resolution gel permeation chromatography (GPC)[12] (Figure 1), which has also the advantage, in the case of sediment extracts, of removing the interference due to elemental sulphur, which interferes in the HRGC-ECD NICI MS analyses. Recoveries of PCBs and 3–6-ring PAHs from 60–80% in the pg–ng range have been obtained using BioBeads SX-12 or SX-3[12], respectively. The GPC stationary phases were selected according to the molecular weight of the analytes.

The chromatographic system used for obtaining fractions of increasing polarity has been extensively used in our laboratory.[13] Typical recoveries were in the range of 80–90% for PAH and TBPs, and higher than 90% for aliphatic hydrocarbons and ANs, both at the μg level. However, consistently lower recoveries were obtained for TAMs (50–60%), so that data were corrected accordingly.

Mass Spectrometric Analyses

Electron impact (EI) mass spectrometry coupled to HRGC is the conventional procedure for analysing volatile organic pollutants.[4] However, the identification of compounds which do not constitute a routine target in environmental sample screening requires the combined application of other ionization techniques. HRGC-MS using negative ion chemical ionization (NICI) enhances both selectivity and sensitivity in the determination of electrophilic compounds in complex matrices, most of which are of environmental concern.[14] Typical profiles obtained from coastal seawater collected in the western Mediterranean are shown in Figure 3. Organochlorinated compounds (compounds 72–90 in Table 1) have been identified at the $\mathrm{pg\,l^{-1}}$ level. Most of the 4–6-ring PAHs (compounds 42–47 in Table 1) and polar substituted aromatic compounds (PAC) (compounds 54–69 in Table 1) were also selectively identified at the $\mathrm{pg\,l^{-1}}$ level by application of this technique (Table 2).

HRGC-MS in the positive ion chemical ionization mode (PICI) has also been useful for the characterization of certain organic microcontaminants. Usually the

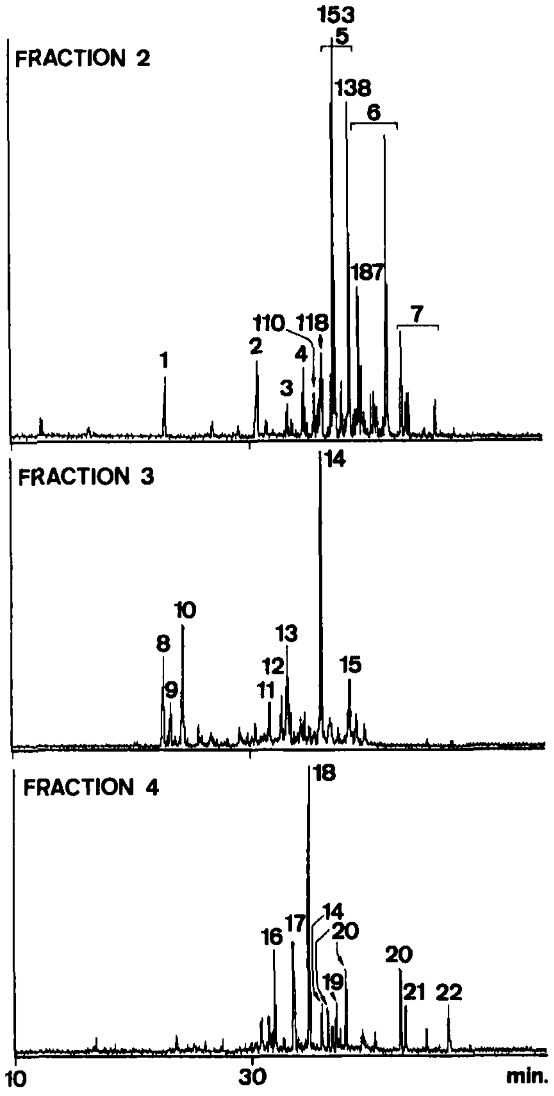

Figure 3 TIC obtained by HRGC-MS using NICI from an extract of the seawater dissolved phase. Identification: 1, HCB; 2, elemental sulphur; 3, *t*-nonachlor; 4, *p,p'*-DDE; 5, hexachlorobiphenyl substituted isomers; 6, heptachlorosubstituted biphenyl isomers; 7, octachlorosubstituted biphenyl isomers; 8, α-HCH; 9, β-HCH; 10, γ-HCH; 11, fluoranthene; 12, γ-chlordane; 13, endosulfan I; 14, endosulfan II; 15, *p,p'*-DDT; 16, heptachlor epoxide; 17, unknown (338, 340); 18, dieldrin; 19, unknown (309); 20, unknown (376); 21, unknown (410); 22, benzo[*a*]pyrene.

Table 1 Summary of contaminants identified in wastewaters (W), seawater (SW), and sediments (S)

Compound no.	*Compartment*[a]	*Identification*	*Number of isomers*	*Mass spectra*[b]		
				EI	*PICI*	*NICI*
Surfactants						
1	W, SW, S	phenyldecane	4	91, 218		
2	W, SW, S	phenylundecane	5	91, 232		
3	W, SW, S	phenyldodecane	5	91, 246		
4	W, SW, S	phenyltridecane	5	91, 260		
5	W, SW, S	phenyltetradecane	5	91, 274		
6	W, SW, S	tetradecanenitrile	1	110	223	
7	W, SW, S	hexadecanenitrile	1	110, 194	251	
8	W, SW, S	octadecenenitrile	2	110	263	
9	W, SW, S	octadecanenitrile	1	110, 222	265	
10	W, SW, S	*N*,*N*-dimethylhexadecylamine	1	269, 58	268	
11	W, SW, S	*N*,*N*-dimethyloctadecylamine	1	297, 58	296	
12	W, SW, S	*N*,*N*-dihexadecylmethylamine	1	479, 268	478	
13	W, SW, S	*N*,*N*-tetradecylmethylamine	1	479, 240	478	
14	W, SW, S	*N*-hexadecyl-*N*-octadecylmethylamine	1	507, 268	506	
15	W, SW, S	*N*,*N*-dioctadecylmethylamine	1	535, 296	534	
16	W, S	decylsulphonic acid methyl ester	4	270, 185		
17	W, S	undecylsulphonic acid methyl ester	4	284, 185		
18	W, S	dodecylsulphonic acid methyl ester	4	298, 185		
19	W, S	tridecylsulphonic acid methyl ester	5	312, 185		
20	W, SW, S	nonylphenol TMS	7	292	293	
21	W, SW, S	nonylphenolmonoetoxyl TMS	7	336	337	
22	W, SW, S	nonylphenoldietoxyl TMS	7	384	381	
23	W, SW	nonylphenoltrietoxyl TMS	7		425	
24	W, SW	nonylphenoltetraethoxyl TMS	7		469	
25	W, SW	nonylphenolpentaethoxyl TMS	7		513	
26	W, SW	nonylphenolhexaethoxyl TMS	7		557	
Aromatic compounds						
27	W, S	biphenyl	1	154		
28	W, S	C_1-biphenyl	2	168		
29	W, S	C_2-biphenyl	3	182, 155		
30	W, S	C_3-biphenyl	5	196, 181		
31	W, S	C_1-dibenzothiophene	3	198		
32	W, S	C_1-naphthalene	2	142, 127		
33	W, S	C_2-naphthalene	6	156, 141		
34	W, S	C_3-naphthalene	11	170, 155		
35	W, S	fluorene	1	166		
36	W, S	C_1-fluorene	4	180, 165		
37	W, SW, S	phenanthrene	1	178		
38	W, SW, S	C_1-phenanthrene	4	192, 177		
39	W, SW, S	C_2-phenanthrene	8	206, 191		
40	W, SW, S	fluoranthene	1	202		202
41	W, SW, S	pyrene	1	202		
42	W, SW, S	chrysene	1	228		
43	W, SW, S	benzo[*b*]fluoranthene	1			252
44	W, SW, S	benzo[*a*]pyrene	1			252
45	W, SW, S	benzo[*c*]chrysene	1			276
46	W, SW, S	indenol[1,2,3-*cd*]pyrene	1			276
47	W, SW, S	benzo[*ghi*]perylene	1			276

Table 1 (continued)

Compound no.	*Compartment*[a]	*Identification*	*Number of isomers*	*Mass spectra*[b]		
				EI	*PICI*	*NICI*
48	W, S	diphenylether	1	$\underline{170}$, 141		
49	W, S	azobenzene	1	182, $\underline{77}$		182
50	S	azabiphenyl	2	155		
51	W, S	dibenzofuran	1	168		
52	W, S	C_1-dibenzofuran	4	182, $\underline{167}$		
53	W, S	C_2-dibenzofuran	2	196, 165		
54	S	fluoren-9-one	1			180
55	S	C_1-fluorenone	4			194
56	S	C_2-fluorenone	6			208
57	S	benz[*de*]anthracen-7-one	1			230
58	S	4*H*-cyclopenta[*def*]phenanthren-4-one	1			204
59	S	benzacridine isomer	3			229
60	S	benzo[*c*]quinoline	4	179		
61	S	C_1-benzoquinoline	3	193		
62	S	1,8-naphthalic anhydride	1			198
63	S	C_1-naphthalic anhydride	3			212
64	S	benzonaphthalic anhydride	1			248
65	S	phenanthrene carboxaldehyde	2			206
66	W	fluoranthene carboxaldehyde	3			230
67	W	pyrene carboxaldehyde	2			230
68	S	nitroindane	3		163	
69	S	C_1-nitronaphthalene	2			187
70	S	*N*,*N*-dimethyl aminoazobenzene	1		225	
71	S	*N*-phenyl-naphthylamine	1	219		
Organochlorinate compounds						
72	W, SW, S	tetrachlorobiphenyl	4			292
73	W, SW, S	pentachlorobiphenyl	7			326
74	W, SW, S	hexachlorobiphenyl	7			360
75	W, SW, S	heptachlorobiphenyl	9			394
76	W, SW, S	octachlorobiphenyl	6			430
77	W, SW, S	hexachlorobenzene	1			284
78	SW	hexachlorocyclohexane	4			255
79	W, SW, S	*p,p′*-DDE	2			318
80	S	*p,p′*-DDD	2			320, $\underline{248}$
81	W, SW	*p,p′*-DDT	2			$\underline{318}$, 283
82	SW, S	chlordane	4			410
83	SW	nonachlor	2			444
84	SW	endrin	1			380
85	W, SW, S	dieldrin	1			380, $\underline{346}$
86	SW	heptachlor	1			374
87	SW, S	heptachlor epoxide	1			388
88	SW	endosulfan	2			406
89	W, S	tetradifon	1			356, $\underline{320}$
90	W, S	dichlorobenzofenone	2			250
Esters						
91	W, SW, S	*i*-tributylphosphate	1	211, $\underline{99}$	267	
92	W, SW, S	*n*-tributylphosphate	1	211, $\underline{99}$	267	
93	W, SW, S	tris(2-ethylhexylphosphate)	1	435		
94	W	triphenylphosphate	1	327		
95	W	tricresylphosphate	1	369		

Table 1 (continued)

Compound no.	*Compartment*[a]	*Identification*	*Number of isomers*	*Mass spectra*[b] *EI*	*PICI*	*NICI*
96	W, SW, S	dimethylphthalate	1			194
97	W, SW, S	diethylphthalate	1	177, $\underline{149}$		236, $\underline{148}$
98	W, SW, S	ethylhexylphthalate	1			206, $\underline{148}$
99	W, SW, S	dibutylphthalate	1	223, $\underline{149}$		221, $\underline{148}$
100	W, SW, S	butylbenzylphthalate	1	206, $\underline{149}$		221, $\underline{148}$
101	W, SW, S	dioctylphthalate	1	167, $\underline{149}$		390, $\underline{148}$
Miscellaneous						
102	W, S	trichloroaniline	2			197
103	W, S	2,4-dichloro-4-nitroaniline	1			206
104	S	diphenylsulphone	1			218
105	S	caffeine	1	$\underline{194}$, 109		
106	W	3,3′-dichlorobenzidine	1			
107	S	p-nitrophenol TMS	1			211
108	S	C_1-nitrophenol TMS	1		225	
109	S	di-*t*-butylmethylphenol	1	220, $\underline{205}$		
110	S	tri-*t*-butylphenol	1	262, $\underline{247}$		
111	S	methylparaben	1			152

[a] P: particulate (≥0.45 μm), D: dissolved and S: sediment.

[b] Diagnostic ions used in the electron impact (EI), positive ion (PICI) and negative ion chemical ionization (NICI). The base peak of the mass spectra is underlined.

Table 2 Concentration of microcontaminants in different aquatic compartments

Compounds	*log K_{ow}*	*Wastewater ($\mu g\,l^{-1}$)* *D*[a]	*P*	*Coastal waters ($ng\,l^{-1}$)* *D*[a]	*P*	*Sediments ($\mu g\,g^{-1}$)*
LABs	8.8	3–33	15–52	2	10	50.3
LASs	2.0	127–400	n.d.	—	n.d.	—
NPEOs	6.6	37–123	—	845	n.d.	6.6
TAMs	—	17–189	129–210	5	30	0.3–35
ANs	—	0.4–2.2	4.1–7.1	0.3	7.2	0.07–2.2
PCBs	5.7–7.4	—	0.07	11.6	1.1	11–653
PAHs	4.6–6.1	1.0	62.9	10.1	13.3	9–190
TBPs	4.0	28–84	2–3	2.8	0.1	0.35

[a] Total concentration of dissolved microcontaminants recovered by XAD-2 and LLE.

n.d. = not detected.

molecular ion, ($[M+1]^+$ or $[M-1]^+$), is the base peak of the mass spectra of compounds containing nucleophilic functional groups, in contrast with a low abundance or even their absence in the EI ionization mode. For instance, alkylphosphates (compounds 91–93), long-chain alkylnitriles (LANs) (compounds 6–9) and NPEO, (compounds 22–26), widely represented in the analyzed samples (Table 2), exhibited $[M+1]^+$ as base peak. In contrast, the long-chain trialkylamines (TAMs) exhibited a more prominent $[M-1]^+$ in agreement with the aliphatic moiety of these molecules (compounds 10–15 in Table 1).

Finally, fast atom bombardment-mass spectrometry (FAB-MS) was also used for

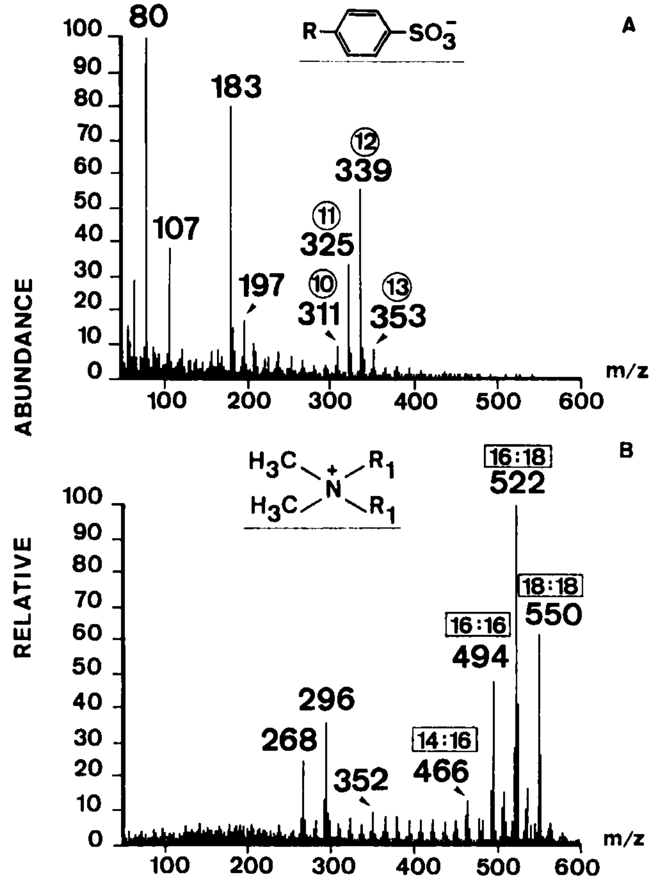

Figure 4 FAB mass spectra of a methanolic sediment extract obtained in negative and positive ion detection modes, respectively. (A) LASs (C_{10}–C_{13}; m/z=311–353) and (B) DMDTA $[(CH_3)_2NR_1R_2]^+$ where $R_1, R_2 = C_{14}$–C_{18} (m/z=466–550).

the direct characterization of ionic surfactants in sediment methanolic extracts. As shown in Figure 4, positive ion detection provides an excellent selectivity for cationic compounds, which exhibit their molecular ions and those corresponding to the α-cleavage (m/z 268, 296).[15] In their turn, the anionic compounds are detected in the negative ion mode. In this case, in addition to the molecular ion distribution (m/z: $311 + n \times 14$), significant fragments at m/z 80 and 183 corresponding to $[SO_3]^-$ and the β-cleavage of the alkyl-chain, respectively, are obtained.

Chemical Composition

Surfactants and related products

These compounds are among the more ubiquitous and abundant in urban wastewaters. Consistently, several components (Table 1), including nonionic, (NPEOs; fraction VI), anionic, (LASs) and cationic species (dimethylditallowammonium chloride, DMDTAC) have been identified in the different aquatic compartments studied. Other related products such as linear alkylbenzenes (LABs, fraction II) and trialkylamines (TAMs, fraction VII) have also been identified. These components are traces of the raw chemicals used in the synthesis of the corresponding ionic derivatives, so that they have been proposed as markers of anionic[16] and cationic[17] surfactants, respectively, because due to their hydrophobicity they are more persistent in the aquatic environment. In this respect, the decoupling of TAMs and NPEOs between the particulate and the dissolved phases of seawater, which is illustrated in Figure 5, is very significant. Both surfactant markers are eluted, in our fractionation scheme (Figure 1), in fraction VII. Their occurrence in different aquatic compartments determines their ultimate fate, because TAMs will preferentially find their way towards the sediment, whereas NPEO will be more available for degradation.

The determination of NPEOs in wastewaters is usually accomplished using HPLC coupled to UV, fluorescence or light-scattering detection[18–20] or, alternatively, by HRGC-MS.[21] Although the former method allows the detection of the whole series up to 20 ethoxamers, the latter, restricted to lower-molecular oligomers (NP7EO), provides resolution of alkyl-chain and ring positional isomers. HRGC-MS also exhibits higher selectivity than HPLC, but the molecular ion abundance of the corresponding EI mass spectra is only significant for the lowest homologs, so that PICI is the preferred technique for tracing the whole NPEOs series in complex mixtures.[21] In this sense, using selected ion monitoring detection, we have been able to identify for the first time NPEOs in coastal waters, as shown in Figure 5. The oligomeric distribution in sediments is rather simple, with nonylphenol as the major component and the low-ethoxylated homologs present.[7]

LASs were identified by HRGC-MS, mainly in the dissolved phase (Table 2), in agreement with QWASI fugacity models.[23] Their distribution in the area of study exhibited an homologous series encompassing all possible C_{10} to C_{14} alkyl-chain isomers. The concentrations (Table 2) were of the same order of magnitude as those reported by Takada and Ishiwatari (230–1500 $\mu g\,l^{-1}$),[24] but one order of magnitude lower than those reported by Marcomini *et al.* ($4.8 \pm 0.2\,mg\,l^{-1}$)[25] for influent wastewaters. Consistently with their predicted short life in the aquatic environment (2 days)[23] we found very low levels in coastal sediments. Their occurrence was evidenced by FAB-MS in the negative ion detection mode (Figure 4A).

LABs, ranging from C_{10} to C_{14}, exhibited a similar distribution pattern as LASs, as they are their synthetic precursors. However, they were identified mostly in the particulate phase of wastewater and seawater and also at significant concentrations in sediments, in agreement with their high K_{ow} values (Table 2) and resistance to biodegradation.[26] Concentrations of these compounds are given in Table 2, and are comparable to others reported previously.[16–24]

The DMDTAC ($[(CH_3)_2NR_1R_2]^+Cl^-$, where R_1 and $R_2 = C_{16}H_{33} - C_{18}H_{37}$) was found widely distributed in wastewaters and coastal sediments of the area of

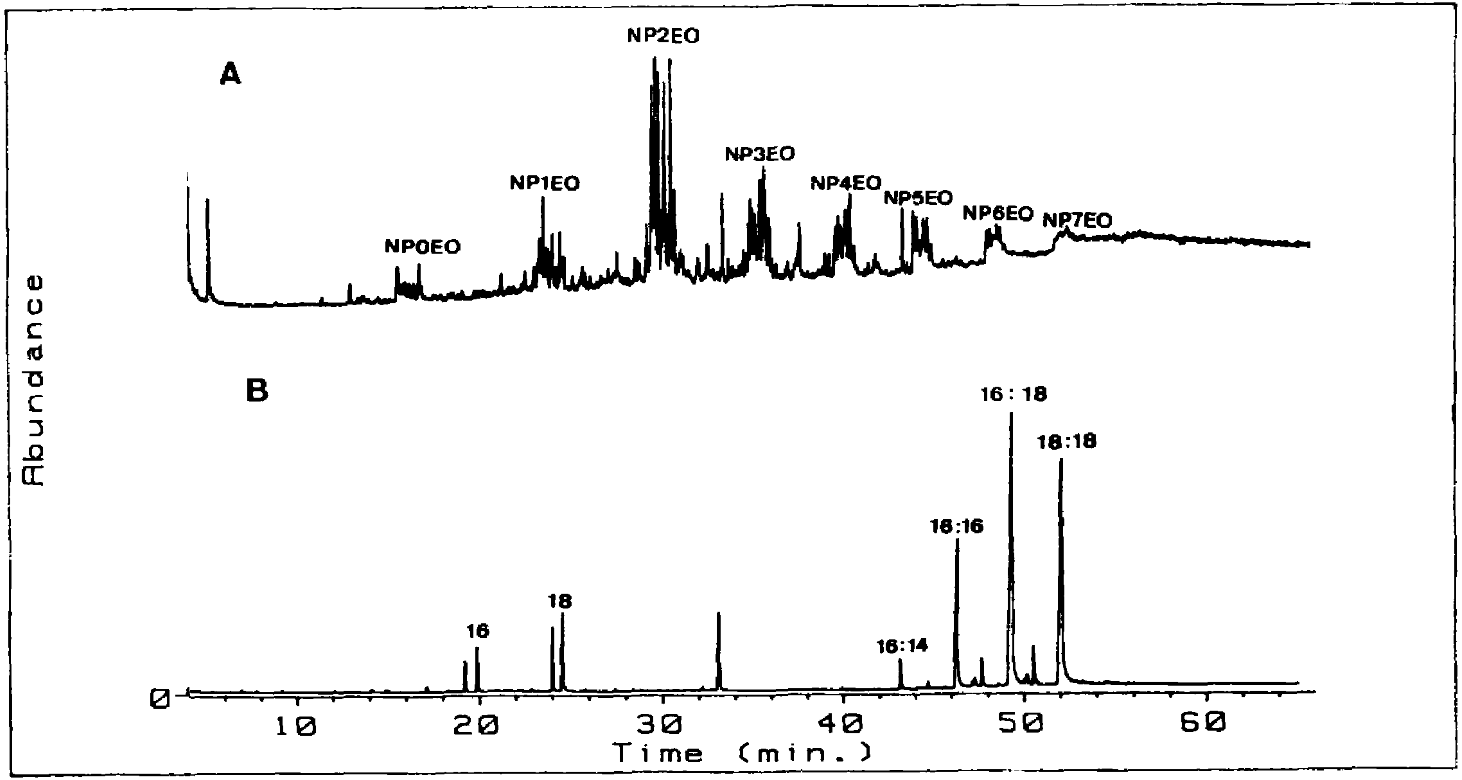

Figure 5 TIC GC-MS profiles corresponding to fraction VII. (A) Oligomeric distribution of NPEOs as TMS derivatives, recovered from the dissolved phase of seawater. (B) Long-chain trialkylamines identified in the particulate phase of seawater. Numbers indicate the carbon numbers of the alkyl-chain substituents.

study, exhibiting a higher abundance of the $[(CH_3)_2NC_{16}H_{33}C_{18}H_{37}]^+$ homolog (Figure 4B).

TAMs ($CH_3NR_1R_2$, where $R_1=CH_3$, $C_{14}H_{29}-C_{18}H_{37}$ and $R_2=C_{14}H_{29}-C_{18}H_{37}$) have also been proposed as markers of cationic surfactants,[17] because they are always present as impurities in these products. They exhibited an homologous distribution of odd–even carbon number alkylderivatives (Figures 5B and 7), where the two long-chain substituents (C_{16}—C_{18}) are the major components. The high concentration found in the seawater particulate phase correlate with the high levels found in sediments (Table 2) indicating that adsorption onto particles and precipitation is the favoured elimination mechanism from the water column. It is worth mentioning the environmental stability of this class of compounds taking into account that, although cationic and anionic surfactants account for 7% and 65%, respectively, of the total industrial output of surfactants, the environmental concentrations of TAMs exceeded those of LABs (Table 2).

Long-chain alkylnitriles (LANs) constitute another class of widely distributed contaminants related to cationic surfactants. In fact, they are intermediates in their production and have also been identified as impurities in cationic surfactant formulations. Figure 7 shows a characteristic distribution of these compounds, which is similar to the precursor fatty acids. Although the physical–chemical properties of LANs are unknown, apparently they are more strongly associated to the particulate phase of seawater than TAMs (Table 2). Therefore, the lower concentrations found in sediments may indicate a shorter half-life of those compounds in this compartment.

Polycyclic aromatic compounds (*PACs*)

A variety of polycyclic aromatic hydrocarbons (PAHs) and polar substituted aromatic compounds (PACs) were identified by EI and NICI-MS in medium-to-polar fractions (fractions III–VI). Coastal seawater exhibited similar concentrations of the total PAHs in the dissolved and particulate phases (Table 2), but their composition was decoupled according to the different water solubility of the components. In this sense, the more condensed PAHs (over 4 aromatic rings) were preferentially associated to the particulate phase and, consequently, to the sediments. For example, benzo[*a*]pyrene was detected in both compartments ($16\,pg\,l^{-1}$ in the particulate seawater) but not in the dissolved phase, where phenanthrene was 20 times more abundant ($690\,pg\,l^{-1}$). In addition, a source-related decoupling in the water phases was observed. As is shown in Figure 6, the dissolved phase is enriched in alkylated species compared with the particulate material, thus reflecting a predominant petrogenic origin, whereas the pyrolytic sources are preferentially associated with the particulate phase.

Several chemical classes of PACs were also identified as indicated in Table 1. Among them, aromatic ketones (compounds 54–58), carboxaldehydes (compounds 65–67), nitroarenes (compounds 68–69), aromatic amines (compounds 70–71), azaarenes (compounds 59–61), and aromatic anhydrides (compounds 62–64). These aromatic compounds are characteristic of combustion processes, energy-related or intermediate industrial products.

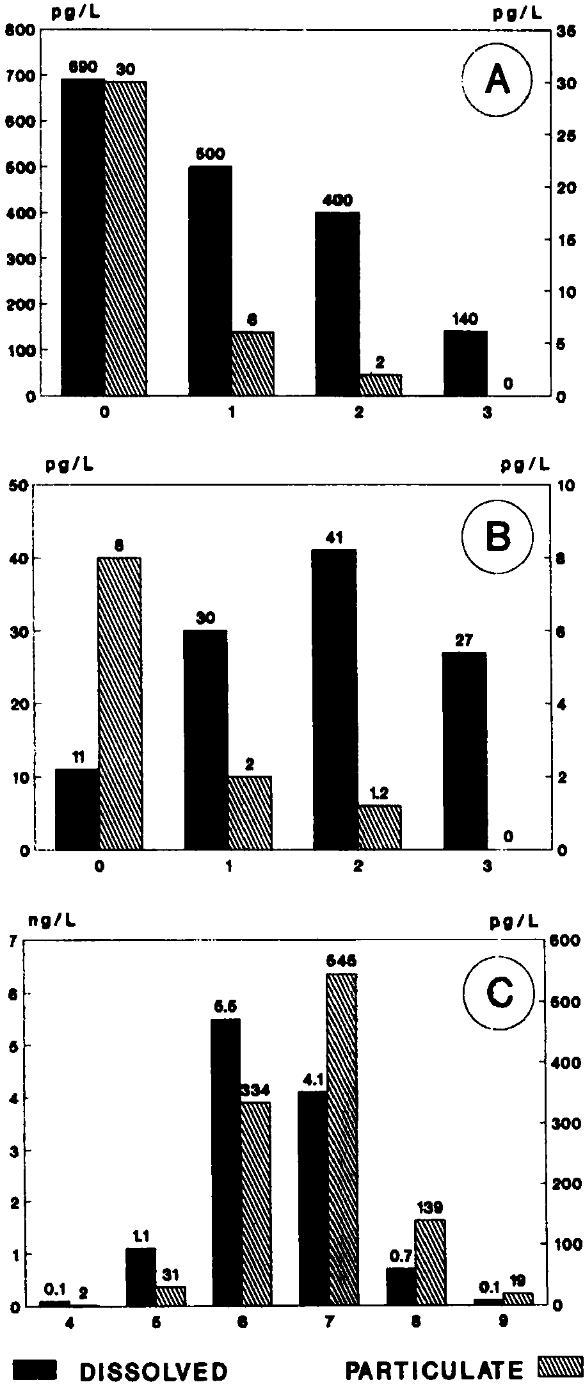

Figure 6 Distribution of alkylated phenanthrenes (A), dibenzothiophenes (B) and polychlorinated biphenyls (C) between the dissolved and particulate phases of coastal seawater. The number of alkyl carbons and chlorine substituents in the aromatic rings are indicated.

Organochlorinated compounds

PCBs, HCHs and DDTs were identified in the low polarity fractions II–III. Chlorinated cyclopentadiene derivatives and sulphonated compounds (e.g. 84–88 in Table 1) were found in the next fractions (III–IV). Most of the organochlorinated pesticides were concentrated in the dissolved phase of seawater, although the more hydrophobic species, like PCBs and DDTs, exhibited a higher preference for the particulate phase. In this respect, the relative enrichment of the highly substituted PCBs in the particulate phase (Figure 6) explains the qualitative distributions found in sediments. In fact, the role played by organic-rich material in scavenging hydrophobic organic contaminants from the water column towards the sediment has been extensively reported.[28,29]

Dieldrin was the most abundant of the organochlorinated cyclopentadiene derivatives. Some degradation products of *p,p'*-dicofol and *p,p'*-DDT were also identified (compounds 79 and 90 in Table 1). In addition, a novel acaricide, tetradifon was found widely distributed in the area of study (compound 89 in Table 1). A characteristic distribution of dissolved compounds identified in seawater is shown in Figure 2.

Esters

Alkyl and aryl phosphates were recovered in the slightly polar fractions V–VI. They have many industrial applications[30] and, consequently, they have been found in significant quantities in all samples, although they are not found in the priority pollutant lists. The alkylphosphates (compounds 91–93 in Table 1) were found at higher concentrations in the water-dissolved phase (Table 2). In Figure 7 a characteristic distribution of these compounds is shown, based on HRGC-NPD. The limit of detection was as low as $0.6\,\mathrm{ng\,l^{-1}}$ and $50\,\mathrm{pg\,l^{-1}}$ for wastewater and seawater, respectively.

The phthalic acid esters are recovered in the medium-polarity fractions IV–V. Small quantities of phthalic acid were also recognized in the acid fraction. They are widely distributed in all aquatic compartments considered. The NICI mass spectra presented a base peak at m/z 148 in contrast with that 149 in EI (Table 1). Most of this class of compounds are included in the priority pollutant lists.

Miscellaneous

Two butylated phenols, both of them widely used as antioxidants, were identified in fraction III of wastewaters and sediments (compounds 109–110 in Table 1). Caffeine was also identified in wastewaters, but below detection limit in seawater (compound 105 in Table 1). Chlorinated anilines were also identified in both wastewater and marine sediments (compound 102). Finally, *p*-nitrophenol and dichlorobenzidine (compounds 106–108 in Table 1) were identified in sediments. The former may be a degradation product of parathion, and both are included in the U.S. EPA priority pollutants list.

CONCLUSIONS

Different analytical procedures including combinations of continuous liquid–liquid

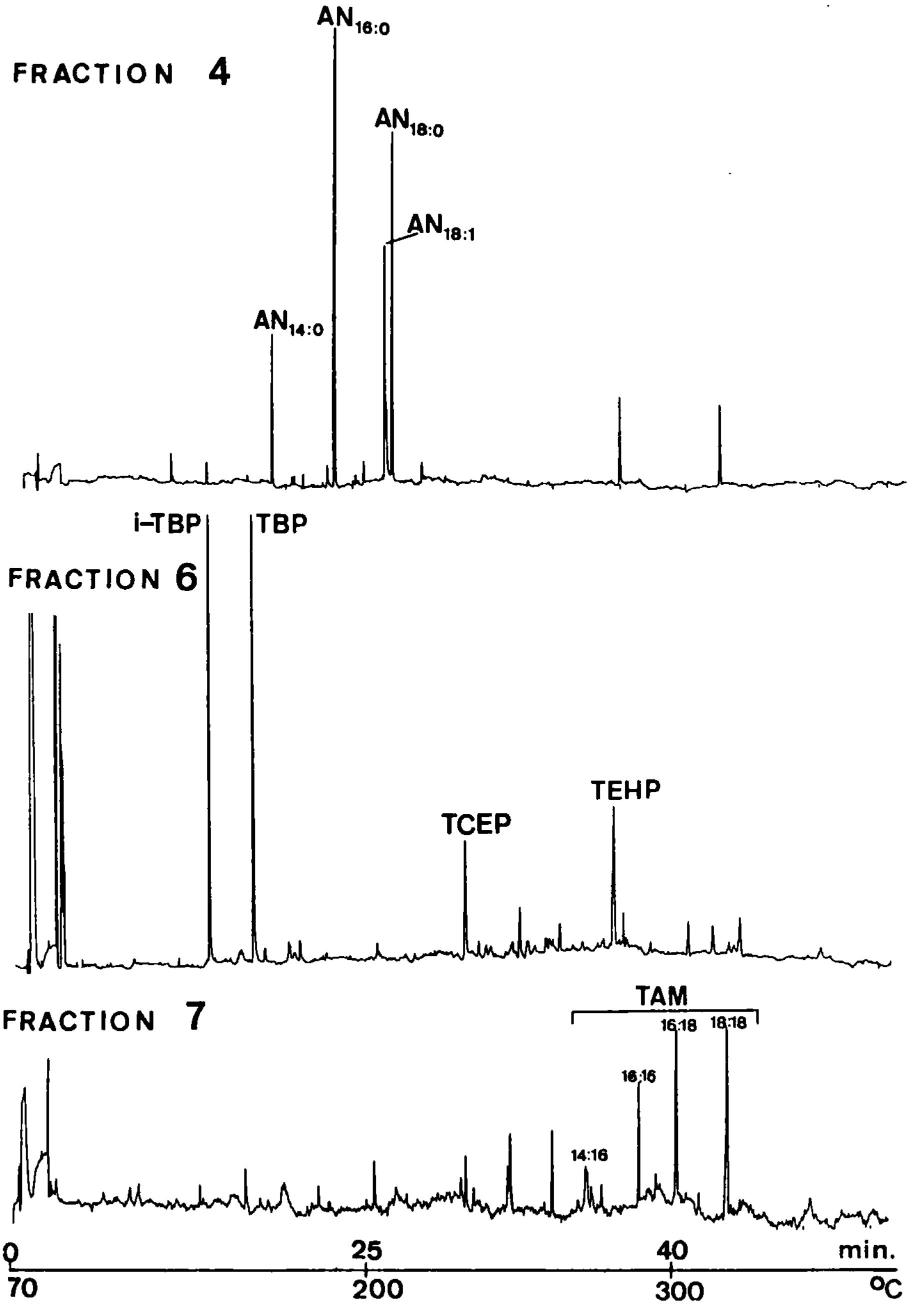

Figure 7 HRGC-NPD of coastal sediment fractions (IV–VI). Peak identification: *i*-TBP, branched tributylphosphate; *n*-TBP, linear tributylphosphate; TCEP, tris(2-chloroethylphosphate); and TEHP, tris(2-ethylhexylphosphate). The total carbon number of alkylnitriles (AN) (fraction IV) and alkyl-substituents of TAMs (fraction VII) is indicated.

extraction and adsorption onto Amberlite XAD-2 have been investigated for the systematic characterization of organic contaminants in municipal sewage waters, and the receiving coastal waters. A wide variety of ubiquitous contaminants, namely aromatic hydrocarbons, chlorinated pesticides, industrial additives, and, particularly, ionic surfactants and related products (e.g. LAS-LAB, DMDTAC-TAM) were investigated.

Significant qualitative and quantitative differences were obtained with the different sampling methods, which are attributable to the particular hydrophobicity of these contaminants, thus suggesting the need for the development of common analytical protocols enabling the determination of a broad range of organic contaminants present in these aquatic systems. The adequate application of ionization techniques in MS, others than conventional EI, namely NI and PICI and FAB in the positive and negative ion modes, enables the identification of a broad range of organic wastewater components that could be considered for inclusion in monitoring programmes.

The decoupling of organic contaminants among the aquatic compartments has been realised and interpreted in terms of the physicochemical properties of the components (e.g. log K_{ow}), or their particular sources. In any case, the consideration of both the dissolved and particulate phases is of considerable interest for a better understanding of the processes involved. Depending on the phase association of the organic species, they may be remineralized, recycled into the food web, incorporated onto the underlying sediments or transported towards the open sea.

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