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Gas chromatographic–mass spectrometric analysis of urban-related aquatic and airborne volatile organic compounds

Study of the extracts obtained by water closed-loop stripping and air adsorption with charcoal and polyurethane foam

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ABSTRACT

The distribution of volatile organic compounds (VOC) in urban-influenced air and river waters was investigated. The aquatic VOC were extracted with the closed-loop stripping technique (CLST) and the airborne compounds were studied using two methods, charcoal and polyurethane foam adsorption. In both types of samples, C_1–C_5 alkylbenzenes and *n*-alkanes constitute the two major VOC groups, and the presence of these groups indicates a predominance of petroleum products in these two environmental compartments. Chlorinated compounds such as polychlorobenzenes, polychloronaphthalenes and hexachlorobutadiene are abundant in water samples, whereas tetrachloroethene is the predominant chlorinated airborne VOC. The compounds collected with each sampling system can be described in terms of ranges of volatility. These ranges (expressed as mmHg vapour pressure at 25°C) can be defined approximately as 140 (methylcyclopentane)–0.65 (*n*-undecane) for charcoal, 5.1 (*n*-nonane)–0.000061 (*n*-docosane) for polyurethane foam and 29 (toluene)–0.00029 (*n*-eicosane) for the CLST. Parallel air sampling with charcoal and polyurethane foam is therefore needed to cover a VOC range similar to that afforded by the CLST in water.

INTRODUCTION

Volatile organic compounds (VOC) constitute the major organic species in air and water. Many of these compounds are proven bacterial mutagens and suspected carcinogens [1,2]. Therefore, major efforts are being made to assess their environmental occurrence and health hazards [3,4].

Because VOC are ubiquitous, integrated studies encompassing water and air systems may contribute significantly to the understanding of the sources and physico-chemical processes determining their distribution in the environment. This approach has rarely been addressed [5] and thus requires a preliminary comparison of the performance of the methods used for VOC determination in aquatic and air samples. Such evaluations are not simple. Although the closed-loop stripping technique (CLST) is widely accepted as the standard method for

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the analysis of aquatic VOC [6–8], various techniques involving a wide diversity of solid adsorbents are currently used for the study of airborne volatile compounds [9].

In this situation, charcoal adsorption is the air sampling method to be primarily compared with the CLST because a charcoal microcolumn is used for the extraction of aquatic VOC in the stripping technique. However, this adsorption method is dedicated essentially to the analysis of low air volumes, which requires a general-purpose large-volume adsorbent to be included in the comparison. Polyurethane foam is perhaps the most representative adsorbent having these characteristics [10–12].

We report here a comparative study of the VOC occurring in the atmosphere and river waters of an urban area, Barcelona. Air samples were collected in the centre of the city by means of parallel charcoal and polyurethane foam adsorption. Water samples were collected by the CLST in the Besos and Llobregat rivers, near the discharge sites. These rivers are located north and south of Barcelona, respectively, their waters share multiple uses (domestic, industrial, agricultural, etc.) and they receive a wide range of wastes.

EXPERIMENTAL

Materials

Glass microfibre filters (GF/A) (1.6-μm pore size) (20.3 × 25.4 cm) and cellulose filters Grade 1 (11 μm) (7-cm diameter) were purchased from Whatman (Maidstone, U.K.). Coconut charcoal tubes (Lot 120) were purchased from SKC (Eighty Four, PA, U.S.A.). Polyurethane foam of density 0.022 g/cm^3 was obtained from a regular upholstery provider. Pestipur-grade *n*-hexane, methanol and isooctane were purchased from SDS (Peypin, France). Resi-analyzed grade dichloromethane was from Baker (Phillipsburg, NJ, U.S.A.). Analytical reagent grade acetone and carbon disulphide were from Carlo Erba (Milan, Italy) and Merck (Darmstadt, F.R.G.), respectively. Analytical-reagent grade hydrochloric acid (25%, w/w), neutral silica gel (Kieselgel 40, 70–230 mesh) and alumina (aluminum oxide 90 active, 70–230 mesh) were from Merck, pentylcyclohexane, octacosane and C_4, C_6, C_8, C_{10}, C_{12}, C_{16} and C_{18} 1-chloroalkanes from Fluka (Buchs, Switzerland) and perdeuterated naphthalene and anthracene from ICN Stable Isotopes (Innerberg, Switzerland).

The filters were kiln-fired at 400°C for 12 h, then wrapped in solvent-rinsed aluminium foil until use. The individual polyurethane plugs (height 7.5 cm, diameter 5 cm) were compressed/decompressed in water and acetone (ten times). Following this step, they were Soxhlet extracted with acetone (24 h) and *n*-hexane (24 h) and dried in a vacuum desiccator with phosphorus pentoxide. Each plug was wrapped with aluminium foil and stored in a clean Teflon-sealed glass jar.

Silica gel and alumina were extracted with dichloromethane–methanol (2:1, v/v) in a Soxhlet apparatus for 24 h. After solvent evaporation, they were heated for 12 h at 120 and 350°C, respectively. A total of 3% (w/w) of Milli-Q-grade water was then added to the chromatographic adsorbents for deactivation.

The purity of the solvents was checked by concentrating under vacuum 100 ml of solvent to 10 μl for gas chromatographic (GC) analysis. Blank requirements were as follows: splitless injection of 2.5 μl should result in chromatograms with no unresolved GC envelope and only very few peaks, representing up to 0.1 ng in terms of their flame ionization detector response. This threshold, under the above dilution factor, is equivalent to a level of artifacts below 0.05 ng/l when referred to a volume of 2 l of water (CLST), or to levels below 0.4 and 0.01 ng/m^3 for the air volumes collected with the charcoal and polyurethane foam samplers, respectively.

Glassware was washed by sonication in a detergent solution and rinsed with Milli-Q-grade water and acetone.

Sampling

Water sampling was carried out from a rowed dinghy. Subsurface river and marine waters were collected by immersion of 2-l amber-glass bottles. These were rinsed thoroughly with the field water being sampled, filled completely (without headspace), closed with glass stoppers and stored at 4°C until analysis, which was performed within 24 h.

Air sampling was performed by parallel adsorption on charcoal and polyurethane foam. The former technique involved a sampling circuit composed of a Model CPV-1 low-volume MCV pump, a filtering system equipped with cellulose filters and the charcoal tubes. After sampling, the tubes were stored at -20°C and analysed within 48 h. Volumes of 0.1–1 m^3 were collected at a flow-rate of 4 l/min. The polyurethane foam circuit was composed of a Model CAV-P high-volume MCV pump, a filtering system equipped with Whatman GF/A filters and a Teflon column filled with two foam plugs. Air volumes of 40 m^3 were collected at a flow-rate of 20 m^3/h.

Extraction and fractionation

The volatile organics were obtained by the CLST in a commercially available apparatus (Brechbuhler, Schlieren, Switzerland) designed according to Grob [13] and Grob and Zürcher [14]. The water samples were spiked with 5 μl of a methanol standard solution containing 15–40 ng/μl (marine samples) or 160–400 ng/μl (river samples) of C_4, C_6, C_{12} and C_{18} 1-chloroalkanes. The VOC were then stripped for 30 min at 45°C according to the optimized parameters reported by Gomez-Belinchon and Albaigés [15]. The gas stream leaving the water was always heated about 10°C above the bath temperature to prevent water condensation and to optimize the adsorption of organics on the charcoal filter. This filter was loaded with various amounts of adsorbent according to the samples to be analysed (1.5 or 5 mg for marine or river waters, respectively). The filters were extracted using 5 μl of another carbon disulphide standard solution containing 30–40 ng/μl (marine samples) or 320–370 ng/μl (river samples) of C_8, C_{10} and C_{16} 1-chloroalkanes, followed by an additional extraction with 10 μl (marine samples) or 30 μl (river samples) of redistilled carbon disulphide.

After air sampling, the open charcoal tubes were capped and stored at −20°C until analysis. Before extraction, the tubes were scored with a file at both ends and the ends broken off. Each charcoal section was removed, placed in separate vials and sealed. After addition of 2 ml of carbon disulphide, these vials were shaken for 30 min and the solutions were submitted to instrumental analysis.

After air sampling, the polyurethane plugs were removed from the Teflon columns, wrapped in aluminium foil and stored in Teflon-sealed glass jars at −20°C. These plugs were always analysed within 48 h. An internal standard containing pentylcyclohexane, octacosane and perdeuterated naphthalene and anthracene was added before Soxhlet extraction with 700 ml of *n*-hexane for 24 h. The extract was vacuum-evaporated to 0.3 ml and then fractionated by column chromatography. A 30 cm × 0.5 cm I.D. column packed with 0.8 g each of 3% water-deactivated alumina (top) and silica (bottom) was used. The aliphatic and aromatic hydrocarbons were eluted with 3 ml of *n*-hexane and 6 ml of *n*-hexane–dichloromethane (4:1, v/v), respectively. These fractions were concentrated under a current of nitrogen to a small volume (0.3 ml) and reconstituted to 1 ml with *n*-hexane. Special attention was paid to avoid evaporation to dryness.

Instrumental analysis

All samples were analysed by GC with a Carlo Erba Mega Series HRGC 5300 instrument equipped with a flame ionization detector and a split–splitless injector. The separation was carried out on a 45 m × 0.32 mm I.D. SE-52 fused-silica capillary column (0.45-μm film thickness) prepared in the laboratory according to described deactivation and stationary phase immobilization methods [16,17]. Injections were made in the splitless mode (split valve closed for 35 s) with the column held at 30°C for 1 min, then heated quickly (40°C/min) to 50°C and at 3°C/min to 220°C. The carrier gas was hydrogen (0.5 m/s linear velocity). The injector and detector were maintained at 225 and 250°C, respectively.

Selected samples were analysed by GC coupled with mass spectrometry (GC–MS) using a Vacuum Generators Model MS9 mass spectrometer coupled to a Konik-200 gas chromatograph. This system was provided with a VG 11/250 data station. Operating conditions were as follows: ionization energy, 70 eV; mass range, m/z 40–500; scan time, 2 s per decade; electron multiplier, 2000–2500 V; ion source temperature, 220°C; and interface temperature, 250°C. Alternatively, the GC–MS analyses were performed with a Hewlett-Packard 5995 instrument coupled with an HP-300 data system. Mass spectrometer temperatures were as follows: transfer line, 300°C; ion source, 200°C; and analyser, 230°C. Data were also acquired in the electron impact mode (70 eV), scanning from 50 to 650 mass units at 1 s per decade. In both instances the chromatographic conditions were the same as described above, except that helium was used as the carrier gas.

Compound identification and quantitation

Compound identification was based on the GC–MS data and, in most instances, coinjection with authentic standards. Quantification was performed using the GC profiles after correction for recoveries using the internal standards mentioned above. A reproducibility of *ca.* 95–97% was obtained. Detection limits were *ca.* 1 ng/l (CLST), 1 ng/m^3 (charcoal adsorption) or 0.1 ng/m^3 (polyurethane adsorption).

RESULTS AND DISCUSSION

Major VOC in air and water samples

The average concentrations of the VOC found regularly in the waters of the Besos and Llobregat Rivers and in the atmosphere of Barcelona are given in Table I. C_1–C_5 alkylbenzenes and *n*-alkanes constitute the two major groups of VOC present in both types of samples. Alkylbenzenes are found in vehicle exhausts [18,19], fuels [20] and the fumes of other combustion processes [21]. *n*-Alkane distributions without odd-to-even carbon number preference usually correspond to petrogenic contributions [18,22]. Therefore, petroleum sources determine the composition of the major VOC found both in air and water samples.

In addition to these compounds the mono-, di- and trichlorobenzenes constitute an important group of aquatic VOC; these compounds, together with chloronaphthalenes and hexachlorobutadiene, encompass the organochlorinated species found regularly in the river waters. Conversely, in the atmospheric samples, tetrachloroethene is the predominant chlorinated species, and chlorobenzenes are only found at trace levels. Other VOC groups found regularly in both types of samples are the alkylnaphthalenes and the alkylbiphenyls, which occur together with some terpenes, namely α-pinene and limonene. C_{10}–C_{14} alkylbenzenes, *tert.*-butylphenols, anisole and tributyl phosphates are common in the waters, but they are not found in the air samples. Further information on the occurrence of some of these species, *e.g.*, tributyl phosphates, in the Besós and Llobregat Rivers has been reported elsewhere [23].

VOC chromatographic patterns

Two chromatograms of the VOC present in the waters of the Besos and Llobregat Rivers are displayed in Fig. 1. They constitute representative examples of the series of monthly samples collected in both rivers during a period of 13 months. Gas chromatograms are also used to illustrate the composition of volatile organics in the air of Barcelona. Fig. 2 shows an example of the extracts obtained by charcoal adsorption and Fig. 3 displays the chromatograms corresponding to the aliphatic and aromatic hydrocarbons obtained after column chromatographic fractionation of the polyurethane extracts. These profiles represent atmospheric situations of intermediate traffic pollution among those observed during the study. Peak identifications are given in Table II, where all the compounds identified are listed.

TABLE I

MEAN CONCENTRATIONS OF THE VOLATILE ORGANIC COMPOUNDS IDENTIFIED IN THE WATERS OF THE BESÓS AND LLOBREGAT RIVERS AND IN THE AIR OF BARCELONA

Numbers in parentheses refer to the chromatograms in Figs. 1–3.

Compound	Water (CLSA)				Barcelona City air			
	Besós		Llobregat		Charcoal adsorption		Polyurethane adsorption	
	Mean (ng/l)	S.D.[a]	Mean (ng/l)	S.D.	Mean (ng/m^3)	S.D.	Mean (ng/m^3)	S.D.
n-Octane (12)	1100	96	530	170	Id[b]		Id	
n-Nonane (22)	4500	110	490	110	3000	160	Id	
n-Decane (31)	26000	95	1700	70	1000	200	11	120
n-Undecane (52)	13000	100	1100	78			9	140
n-Dodecane (63)	13000	100	915	87			16	140
n-Tridecane (79)	11000	92	1300	96			29	86
n-Tetradecane (89)	19000	120	3400	90			265	67
n-Pentadecane (98)	8500	110	1900	140			255	83
n-Hexadecane (106)	2300	82	1100	120			240	86
n-Heptadecane (117)	2200	90	720	89			235	70
Pristane (118)	460	64	300	90			110	85
n-Octadecane (121)	790	77	350	80			150	53
Phytane (122)	230	64	150	77			75	63
n-Nonadecane (133)	300	90	170	79			105	53
n-Eicosane (141)	8.5	340	52	120			52	38
Toluene (7)	22000	120	4100	110	23000	96		
Ethylbenzene (16)	15000	130	1900	210	9000	130		
o-Xylene (20)	8100	120	830	100	7000	130		
m- + *p*-Xylene (17,18)	24000	110	4700	130	17000	76		
Propylbenzene (25)	2000	110	160	90	5000	160	14	100
1,3,5-Trimethylbenzene (28)	Id		Id		4000	120	38	76
1,2,4-Trimethylbenzene (30)	Id		Id		9000	120	110	115
1,2,3-Trimethylbenzene (34)	5500	130	750	180	2000	200	25	140

Ethyltoluenes (26,27,29)	9900	120	710	90	7000	130	79	105
C_4benzenes (40–45,48–50,53–56,58)	15000	130	2000	81			270	130
C_5-benzenes (59,60,67–72)	10000	120	400	84			70	170
Naphthalene (62)	1300	150	180	130			400	97
Methylnaphthalenes (77,78)	930	93	170	88			440	110
C_2-Naphthalenes (82,84,85,87,88,93)	3800	110	430	120			475	130
C_3-Naphthalenes (94,107–112)	830	74	240	80			400	110
Acenaphthylene (92)							170	110
Acenaphthene (95)							28	140
Phenanthrene (143)							110	76
Anthracene (144)							22	110
C_{10}-Benzenes (103)	570	96	140	140				
C_{11}-Benzenes (115)	1300	88	870	97				
C_{12}-Benzenes (119)	210	120	240	130				
C_{13}-Benzenes (126)	150	270	98	110				
Chloronaphthalenes (80)	650	140	760	110				
Dichloronaphthalenes (102)	260	140	150	140				
Chlorobenzene (14)	260	210	210	170				
p-Dichlorobenzene (33)	600	200	310	120			Id	
o-+*m*-Dichlorobenzene (32)	5000	260	1.7	350				
1,2,3-Trichlorobenzene (65)	1100	140	200	100				
1,2,4-Trichlorobenzene (61)	8100	120	1200	140				
Hexachlorobutadiene (64)	3200	120	370	120				
Tetrachloroethene (11)	Id		Id		3000	100		
α-Pinene (24)	3400	150	520	110	4000	200		
Limonene (35)	1600	120	590	150	Id			
Biphenyl (81)	1500	150	4.2	350			66	130
Methylbiphenyls (96,97)	740	180	230	160			140	120
C_2-Biphenyls (104,105)	240	270	28	270			195	110
1,2-Dimethyl-4-(phenylmethyl)benzene (114)	150	200	50	96				
2,5-Di-*tert*.-butyl-4-methylphenol (100)	84	140	21	270				
2,5-Di-*tert*.-butyl-4-ethylphenol (120)	120	190	65	120				
Anisole (23)	91	180	34	91				
Diethyl phthalate (127)	95	97	460	91				
Tributyl phosphate (116)	2200	200	240	140				

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[a] Standard deviation expressed as 100 × coefficient of variation (standard deviation/average).

[b] Identified but not quantified.

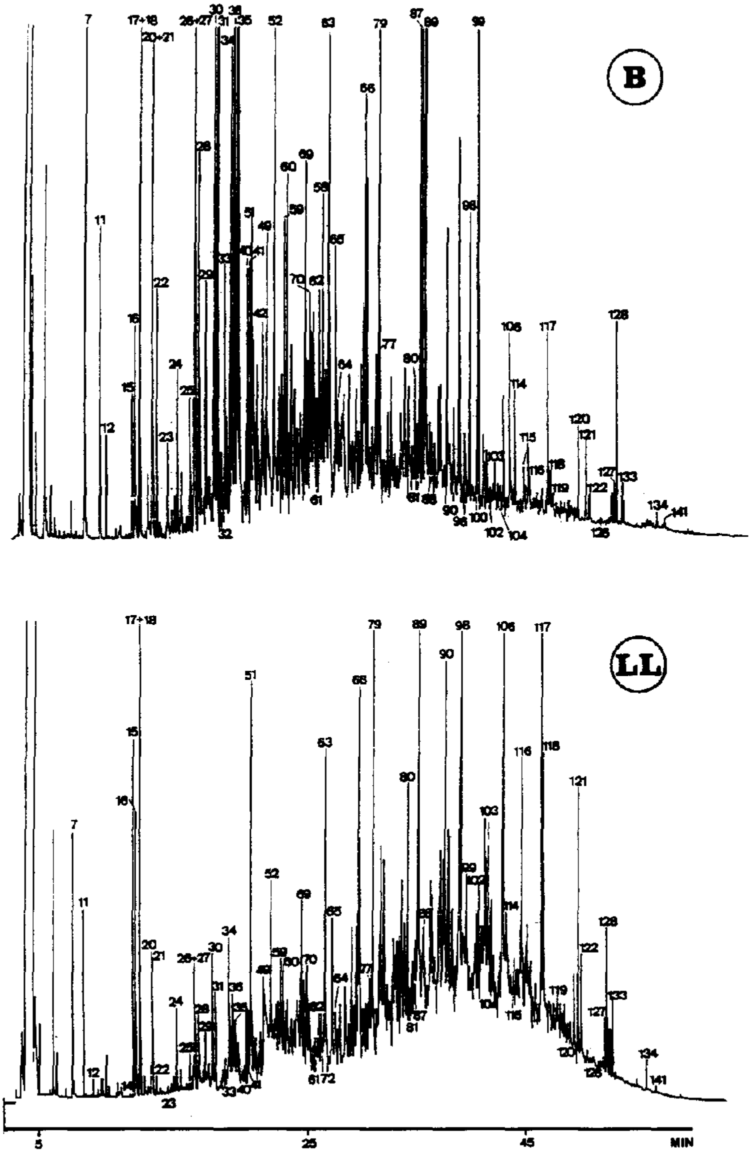

Fig. 1. Representative gas chromatograms of the closed-loop stripping extracts corresponding to the volatile organic compounds present in the waters of the Besós (B) and Llobregat (LL) Rivers. Numbers refer to Table II.

VOC retention in low-polarity columns

The compounds in Table II are ordered according to the elution order which, as corresponds to the low polarity of the SE-52 coated columns, is essentially in agreement with their relative volatilities. However, some solute–stationary phase

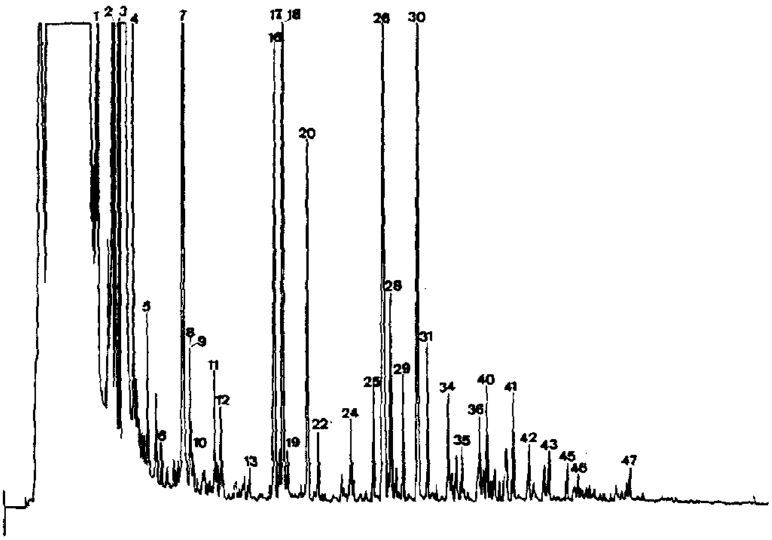

Fig. 2. Representative gas chromatogram of the charcoal extracts corresponding to the volatile organic compounds present in the air of Barcelona City. Numbers refer to Table II.

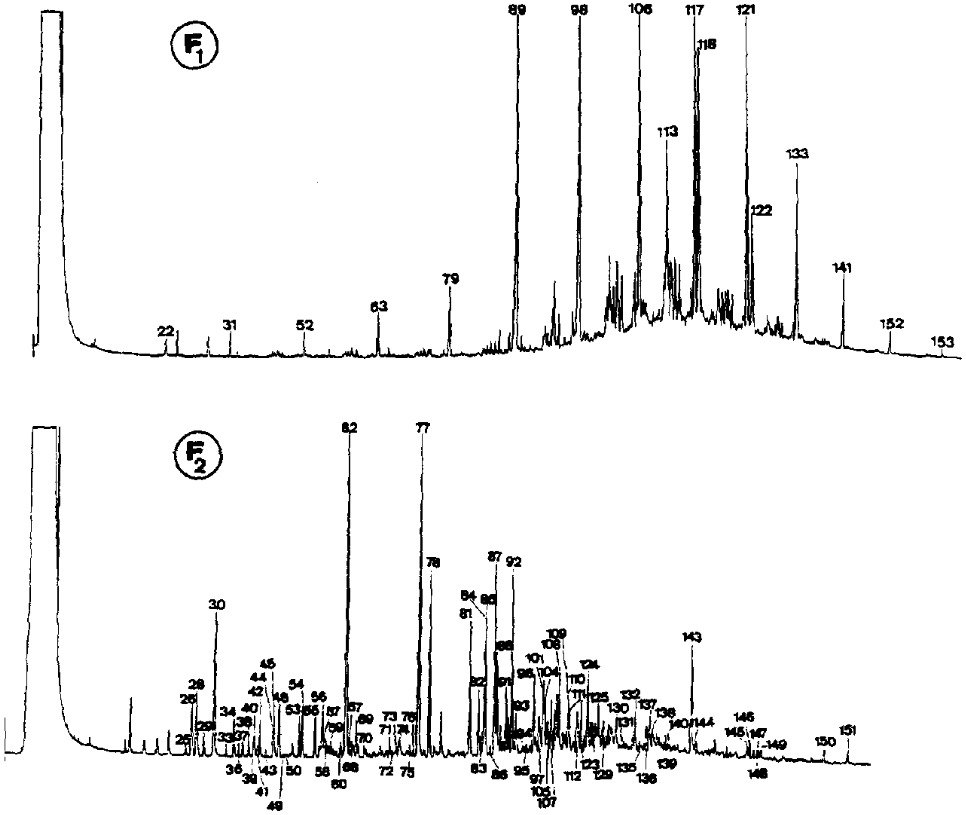

Fig. 3. Representative gas chromatograms of the volatile aliphatic (F_1) and aromatic (F_2) hydrocarbons obtained from the polyurethane extracts of air samples collected in Barcelona City. Numbers refer to Table II.

TABLE II

VOLATILE ORGANIC COMPOUNDS IDENTIFIED IN THE WATERS OF THE BESÓS AND LLOBREGAT RIVERS AND IN THE AIR OF BARCELONA

Numbers refer to the chromatograms in Figs. 1–3.

No.	Compound	No.	Compound
1	Methylcyclopentane	77	2-Methylnaphthalene
2	2-Methylhexane	78	1-Methylnaphthalene
3	3-Methylhexane	79	*n*-Tridecane
4	*n*-Heptane	80	Chloronaphthalene
5	Methylcyclohexane	81	Biphenyl
6	Ethylcyclopentane	82	2-Ethylnaphthalene
7	Toluene	83	$m/z = 152$
8	2-Methylheptane	84	2,6-Dimethylnaphthalene
9	4-Methylheptane	85	2,7-Dimethylnaphthalene
10	3-Methylheptane	86	Dimethylnaphthalene
11	Tetrachloroethene	87	Dimethylnaphthalene
12	*n*-Octane	88	Dimethylnaphthalene
13	2,5-Dimethylheptane	89	*n*-Tetradecane
14	Chlorobenzene	90	1-Chlorododecane[a]
15	1-Chlorohexane[a]	91	$m/z = 154$
16	Ethylbenzene	92	Acenaphthylene
17	*p*-Xylene	93	Dimethylnaphthalene
18	*m*-Xylene	94	Trimethylnaphthalene
19	Methyloctane	95	Acenaphthene
20	*o*-Xylene	96	3-Methylbiphenyl
21	Styrene	97	4-Methylbiphenyl
22	*n*-Nonane	98	*n*-Pentadecane
23	Anisole	99	Triisobutyl phosphate
24	α-Pinene	100	2,5-di-*tert.*-butyl-4-methylphenol
25	Propylbenzene	101	β,β'-Ethylmethylnaphthalene
26	4-Ethyltoluene	102	Dichloronaphthalene
27	3-Ethyltoluene	103	*n*-Decylbenzene
28	1,3,5-Trimethylbenzene	104	C_2-biphenyl
29	2-Ethyltoluene	105	C_2-biphenyl
30	1,2,4-Trimethylbenzene	106	*n*-Hexadecane
31	*n*-Decane	107	1,3,7-Trimethylnaphthalene
32	*m*-Dichlorobenzene	108	1,3,6-Trimethylnaphthalene
33	*p*-Dichlorobenzene	109	1,3,5-Trimethylnaphthalene
34	1,2,3-Trimethylbenzene	110	1,4,6-Trimethylnaphthalene
35	Limonene	111	2,3,6-Trimethylnaphthalene
36	C_4-benzene	112	1,6,7-Trimethylnaphthalene
37	Vinyltoluene	113	Norpristane
38	Indene	114	1,2-Dimethyl-4-(phenylmethyl)benzene
39	1,3-Diethylbenzene	115	*n*-Undecylbenzene
40	C_4-benzene	116	Tri-*n*-butyl phosphate
41	C_4-benzene	117	*n*-Heptadecane
42	C_4-benzene	118	Pristane

TABLE II (*continued*)

No.	Compound	No.	Compound
43	C_4-benzene	119	*n*-Dodecylbenzene
44	Unsat. C_4-benzene	120	2,5-Di-*tert*.-butyl-4-ethylphenol
45	C_4-benzene	121	*n*-Octadecane
46	Alkane	122	Phytane
47	Alkane	123	Fluorene
48	C_4-benzene	124	3,3′-Dimethylbiphenyl
49	C_4-benzene	125	3,4′-Dimethylbiphenyl
50	Unsat. C_4-benzene	126	*n*-Tridecylbenzene
51	1-Chlorooctane[a]	127	Diethyl phthalate
52	*n*-Undecane	128	1-Chlorohexadecane[a]
53	1,2,4,5-Tetramethylbenzene	129	C_3-biphenyl
54	1,2,3,5-Tetramethylbenzene	130	C_3-biphenyl
55	Unsat. C_4-benzene	131	C_3-biphenyl
56	Unsat. C_4-benzene	132	C_4-naphthalene
57	Methylindene	133	*n*-Nonadecane
58	C_4-benzene	134	Phthalate ester
59	C_5-benzene	125	C_4-naphthalene
60	C_5-benzene	136	Methylfluorene
61	1,2,4-Trichlorobenzene	137	C_4-biphenyl
62	Naphthalene	138	C_4-biphenyl
63	*n*-Dodecane	139	C_4-biphenyl
64	Hexachlorobutadiene	140	C_3-biphenyl
65	1,2,3-Trichlorobenzene	141	*n*-Eicosane
66	1-Chlorodecane[a]	142	1-Chlorooctadecane[a]
67	Unsat. C_5-benzene	143	Phenanthrene
68	Unsat. C_5-benzene	144	Anthracene
69	C_5-benzene	145	3-Methylphenanthrene
70	C_5-benzene	146	2-Methylphenanthrene
71	Unsat. C_5-benzene	147	9-Methylphenanthrene
72	C_5-benzene	148	4*H*-Cyclopenta[*def*]phenanthrene
73	C_6-benzene	149	4-Methylphenanthrene
74	Unsat. C_5-benzene	150	Fluoranthene
75	C_6-benzene	151	Pyrene
76	C_6-benzene	152	*n*-Heneicosane
		153	*n*-Docosane

[a] Internal standard.

interactions are reflected in retention time–volatility deviations [*e.g.*, the higher retention of α-pinene (No. 24) or limonene (No. 35)]

Despite the considerable number of studies related to the analysis of VOC in air and water samples, the chromatograms corresponding to the total extracts of volatile compounds have been reported only in a few instances [5,7,24,25]. This small number limits the possibilities of comparison between results obtained in different environmental systems.

As observed in the Besos and Llobregat Rivers, petrogenic mixtures of *n*-alkanes, alkylbenzenes and to a lesser extent alkylnaphthalenes and alkylbiphenyls are commonly found in CLST extracts [5,7,22,25,26]. Accordingly, the chromatograms in Fig. 1 show important similarities with those reported for other aquatic systems [5,7,25]. However, despite the low polarity of the columns used currently for these studies (*i.e.*, SE-54 [5,7] and CP-Sil 8 [25]), careful attention must be paid to the different elution behaviours of some compounds. Thus, tetrachloroethene (No. 11 in Table I) elutes before *n*-octane (No. 12) with CP Sil 8 [25] and SE-52 columns, but the elution order of these compounds is reversed on SE-54 columns [5,7]. A similar result is observed with 1,2,4.trimethylbenzene (No. 30) and *n*-decane (No. 31), which show the same elution order on CP-Sil 8 [25] and SE-52 columns, but the reverse on SE-54 [5].

VOC charcoal and polyurethane extracts

Important qualitative and quantitative differences are observed between the compositions of the charcoal- and polyurethane-extracted airborne VOC (see Table I). The compounds collected with these adsorbents can be grouped according to their volatilities, which were calculated using a form of the Kistiakowsky equation that, in the case of solid compounds at 25°C, gives the vapour pressures of the corresponding subcooled liquids [27]. Comparison of Table I and II shows that the charcoal-trapped products encompass a group of compounds with vapour pressures (in mmHg at 25°C) between 140 (methylcyclopentane) and 0.65 (*n*-undecane), whereas the compounds contained in the polyurethane extracts range from *ca.* 5.1 (*n*-nonane) to 0.000061 (*n*-docosane). The lower volatility range of charcoal corresponds to the smaller number of species collected with this adsorbent (see Table I).

On the other hand, the CLST gives a range of compounds that cover a wide intermediate portion of those compounds collected with both air adsorbents: from toluene (29 mmHg at 25°C) to *n*-eicosane (0.00029). The contrast between the greater number of water-stripped VOC and the airborne charcoal-extracted species is particularly interesting, because charcoal is also used as the adsorbent in the CLST. The same elution solvent, carbon disulphide, is used in both techniques, but the solvent volume-to-adsorbent ratios are different. A range of 0.007–0.01 ml/mg is commonly used for the CLST microcolumns, whereas in the regular charcoal packings the ratios are about 0.002 ml/mg. The higher CLST ratios result in the elution of a larger number of low-volatility compounds and therefore in a higher range of analysable VOC. However, this ratio cannot be increased in air sampling with regular charcoal columns. An increase in the solvent elution volume involves higher VOC dilution and therefore a decrease in sensitivity. On the other hand, a decrease in the amount of adsorbent represents a decrease in retention efficiency because air sampling with charcoal columns is not operated under the closed-loop principle and recycling effects are not produced [28].

The results in Tables I and II illustrate that parallel air sampling with charcoal and polyurethane adsorption is needed to cover a range of VOC similar to that afforded by the CLST in water. However, the relatively small group of airborne charcoal-extracted VOC is very significant from an environmental standpoint because most of these compounds represent the dominant petrogenic inputs observed in both air and water samples, and their concentrations (average total concentration 94 $\mu g/m^3$; see Table I) are generally one or two orders of magnitude higher than those collected with polyurethane foam (average total concentration 4.6 $\mu g/m^3$ in Table I). Further, many VOC in this group are usually selected as target compounds in monitoring studies dealing with atmospheric health hazards [4,29–31].

CONCLUSIONS

C_1–C_5 alkylbenzenes and *n*-alkanes constitute the two major groups of VOC in both air and water samples, and they occur together with mixtures of alkylnaphthalenes and alkylbiphenyls. These hydrocarbons indicate that petroleum sources are predominant among the VOC collected in urban-influenced air and waters. Chlorinated species are present in both types of samples, but they show a contrasting composition: mono-, di- and trichlorobenzenes, mono- and dichloronaphthalenes and hexachlorobutadiene are abundant in the river waters, but tetrachloroethene is the predominant chlorinated VOC in the air samples. C_{10}–C_{14} alkylbenzenes and tributyl phosphates are two major VOC groups that have been identified only in the waters.

The compounds collected with the air adsorbents and using the CLST can be described in terms of ranges of volatility. Thus, the charcoal extracts are composed of mixtures encompassing from *ca.* 140 mmHg (at 25°C) (methylcyclopentane) to 0.65 (*n*-undecane), whereas the polyurethane extracts correspond approximately to a range between 5.1 (*n*-nonane) and 0.000061 (*n*-docosane). The CLST compounds constitute an intermediate range between 29 mmHg (at 25°C) (toluene) and 0.000029 (*n*-eicosane).

Parallel air sampling with charcoal and polyurethane foam is therefore needed to cover a VOC range similar to that afforded by the CLST in water. However, the charcoal extracts are very significant from an environmental standpoint. Their VOC represent the dominant petrogenic sources in the urban atmosphere, being between one and two orders of magnitude more concentrated than the compounds collected by polyurethane adsorption. Further, the charcoal VOC are currently selected as target compounds in monitoring studies on atmospheric health hazards.

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