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Characterization of organic micropollutants in the River Cinca (Spain) by using granular activated carbon and liquid–liquid extraction

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Abstract

The results obtained in the characterization of the micropollutants in the River Cinca by adsorption on granular activated carbon (GAC) and liquid–liquid (LL) extraction are presented. Gas chromatography–mass spectrometry was used for the identification of the various components in the water. Nineteen organochloride compounds [the complete series of chlorobenzenes, DDTs and their metabolites, dichlorobenzophenone (DCBF) and tetradifon] were quantified by gas chromatography–electron-capture detection. In the River Cinca, 229 and 74 compounds were identified by GAC and LL extraction, respectively, fifteen of which appear in the group of substances in List I of the 76/464/EEC European Council Directive as Priority Pollutants.

Keywords: Water analysis; Environmental analysis; Extraction methods; Chlorobenzenes; Organochlorides; Pesticides; Dichlorobenzophenone; Tetradifon

1. Introduction

Owing to the industrial and agricultural activities in Spain, more and more toxic substances are entering the rivers. In the European Directive 76/464/EEC [1], relative to the pollution caused by noxious substances, maximum contaminant levels (MCLs) for individual compounds have been stipulated in surface water (at $\mu\text{g/l}$ levels) and in wastewater (at mg/l levels)

[2,3]. As a consequence, to control the contamination coming from the industrial activities [4] which generate substances included in these directives, it is necessary to develop and improve analytical methods in order to identify and quantify these pollutants in the river water [5–8] at trace levels.

In this study, the characterization of the organic material in water from the River Cinca was carried out [9]. The principal pollutants of the water in this river emanate from agriculture and many industrial waste spillages such as pesticide [10] and resin manufacture and electrolytic and tanning industries.

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2. Experimental

2.1. Reagents

The complete series of chlorobenzenes, dichlorobenzophenone, tetradifon, DDTs and their metabolites were supplied by Cromlab (Barcelona, Spain). The organic solvents used were of special grade for pesticide analysis: acetone, hexane, methylene chloride and diethyl ether (Mallinckrodt, Paris, KY, USA). Florisil, anhydrous sodium sulphate, granular activated carbon (2514) and BF_3 -methanol, were supplied by Merck (Darmstadt, Germany). N-55 nitrogen and N-50 helium were supplied by SEO (Zaragoza, Spain).

2.2. Sampling and extraction

A comparative study between two organic micropollutant extraction techniques was carried out: liquid–liquid (LL) extraction of precise samples and granular activated carbon (GAC) extraction of average river samples from the riverbed.

Liquid–liquid extraction

Method 625, of the US Environmental Protection Agency (EPA), based on liquid–liquid extraction with methylene chloride, was used. A 1-l volume of surface water at pH 10 (6 M sodium hydroxide) was extracted with 3×60 ml of methylene chloride. The organic extract was dried over anhydrous sodium sulphate and passed through a column of Florisil in order to remove the interfering substances. Elemental sulphur was removed by adding activated copper. The extract was dried by passing it through a column of sodium sulphate and eluting with 10 ml of hexane. The extract was concentrated to 2 ml with a stream of nitrogen and analysed by GC–MS and GC–electron-capture detection (ECD).

The aqueous fraction at pH 2 (32% HCl) was extracted with 3×2 ml of methylene chloride, dried over anhydrous sodium sulphate and evaporated using a gentle stream of nitrogen. This acid fraction was derivatized using 3 ml of BF_3 -methanol for 12 h. The reaction was

stopped by addition of 20 ml of ultra-pure water and extracted with 2×2 ml of hexane. The organic extract was dried over anhydrous sodium sulphate and concentrated to 2 ml with a stream of nitrogen. This extract was analysed by GC–MS and GC–ECD.

GAC extraction

A GAC module was installed in the River Cinca in order to adsorb the majority compounds from the riverbed [11]. A 2000-l volume of surface water was passed through a carbon column (60 cm) containing 100 g of GAC at a rate of 35 ml/min. The activated carbon was Soxhlet extracted with 500 ml of dichloromethane over a period of 48 h. The eluate was dried using a rotary evaporator and a stream of nitrogen and the residue was dissolved in 8 ml of diethyl ether. The ether extract was extracted with 4×1 ml of 5% NaOH in order to fractionate the compounds into a basic plus neutral fraction (organic fraction) and an acidic (aqueous) fraction.

Aqueous fraction. The aqueous fraction at pH 2 (32% HCl) was extracted with 3×2 ml of methylene chloride, dried over anhydrous sodium sulphate and evaporated using a gentle stream of nitrogen. This acid fraction was derivatized using 3 ml of BF_3 -methanol for 12 h. The reaction was stopped by addition of 20 ml of ultrapure water and extracted with 2×2 ml of hexane. The organic extract was dried over anhydrous sodium sulphate and concentrated to 2 ml with a stream of nitrogen. This extract was analysed by GC–MS [12] and GC–ECD.

Organic fraction. The ether fraction was dried over anhydrous sodium sulphate and the interfering substances were removed by passing the extract through a column of Florisil by elution with 10 ml of methylene chloride. The elemental sulphur was removed by adding activated copper. The extract was dried by passing it through a column of sodium sulphate and eluting with 10 ml of hexane. The extract was concentrated to 2 ml with a stream of nitrogen and analysed by GC–MS [12] and GC–ECD.

The concentration ratio (initial volume/final

volume) was 10^3 and 10^6 in precise samples and average river samples, respectively.

2.3. GC–ECD analysis

The gas chromatograph was a Hewlett-Packard (HP) Model 5890-II equipped with an electron-capture detector and splitless injection. An HP-5 column was used. A 2- μ l volume of sample was injected and the splitless time was 0.8 s. Helium was used as the carrier gas. The injector and detector temperature were 250 and 350°C, respectively. The temperature programme was 60°C (1 min)–4°C/min–280°C (0 min).

2.4. GC–MS analysis

The gas chromatograph was a Varian Model 3300, coupled with a FinniganMat Model 800 ITD mass spectrometer. The column and conditions were the same as those for GC–ECD.

3. Results

3.1. GC–ECD analysis

In the surface water, nineteen organochlorine compounds were quantified by the external standard method: *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DCBF, *p,p'*-DCBF, *o*-tetradifon, *p*-tetradifon, 1,2-dichlorobenzene (1,2-DCB), 1,3-DCB, 1,4-DCB, 1,2,3-trichlorobenzene (1,2,3-TCB), 1,2,4-TCB, 1,3,5-TCB, total tetrachlorobenzene (TetraCB), pentachlorobenzene (PentaCB) and hexachlorobenzene (HCB)—substances included in the Priority Pollutant List of the 464/76/EEC European Directive and used in the pesticide industry in the Cinca basin (Spain). The concentration of the quantification standards was 5 μ g/l–0.5 mg/l in hexane.

Table 1 gives the results obtained in the quantification by means of the two different methods, LL extraction and GAC extraction of four duplicate different samples. The results are given as average values. GC–MS was used as a confirmation technique. In all cases the concen-

Table 1

GC–ECD determination of nineteen organochlorine compounds in River Cinca water

Compound	Concentration (μ g/l)	
	LL	GAC
1,3-DCB	0.031	0.020
1,4-DCB	0.142	0.025
1,2-DCB	0.051	0.008
1,3,5-TCB	0.022	0.011
1,2,4-TCB	0.149	0.000
1,2,3-TCB	0.014	0.001
TetraCB (Σ isom.) ^a	n.d. ^b	0.000
1,2,3,4-TetraCB	n.d.	0.000
PentaCB	0.014	0.002
HCB	n.d.	0.000
<i>o,p'</i> -DCBF	n.d.	n.d.
<i>p,p'</i> -DCBF	n.d.	n.d.
<i>o,p'</i> -DDE	0.027	0.017
<i>p,p'</i> -DDE	0.088	0.077
<i>o,p'</i> -DDD	n.d.	n.d.
<i>p,p'</i> -DDD	n.d.	n.d.
<i>o,p'</i> -DDT	n.d.	0.001
<i>p,p'</i> -DDT	n.d.	n.d.
Tetradifon	14.938	0.007

^a Σ isom = 1,2,4,5-TetraCB + 1,2,3,5-TetraCB.

^b n.d. = not detected.

tration obtained by GAC was lower than that found by LL extraction.

The same results were achieved by using standards solutions, recovery studies being carried out. The nineteen organochlorine compounds were added to ultrapure water at concentrations of 3–300 μ g/l (five different samples), in order to study the percentage recoveries achieved with the extraction techniques previously described and their duplicate analysis by GC–ECD. Samples of 1 l were extracted by LL extraction and 10 l by GAC extraction.

Table 2 gives the recovery results, the standard deviations (S.D.) and the method detection limits (MDL) for the nineteen organochlorine compounds (MDL calculated as $3.14 \times$ S.D.).

GAC extraction was a very effective technique for the identification of the compounds in surface water owing to the high concentration ratio, but it was not a good quantification method because the recovery was only about 5–10%, compared

Table 2

Liquid–liquid and GAC extraction recoveries, standard deviations (S.D.) and method detection limits (MDL)

Compound	GAC			LL		
	Recovery (%)	S.D. (%)	MDL ($\mu\text{g/l}$)	Recovery (%)	S.D. (%)	MDL ($\mu\text{g/l}$)
1,3-DCB	5 \pm 1.0	1.41	4.43	94 \pm 0.4	0.57	1.79
1,4-DCB	5 \pm 1.0	1.41	4.43	104 \pm 0.5	0.71	2.23
1,2-DCB	8 \pm 1.0	1.41	4.43	95 \pm 0.4	0.57	1.79
1,3,5-TCB	4 \pm 1.0	1.41	4.43	98 \pm 0.5	0.71	2.23
1,2,4-TCB	17 \pm 0.6	0.85	2.67	100 \pm 0.4	0.57	1.79
1,2,3-TCB	8 \pm 0.7	0.99	3.11	102 \pm 0.5	0.71	2.23
TetraCB	6 \pm 0.5	0.71	2.23	110 \pm 0.4	0.57	1.79
1,2,3,4-TetraCB	6 \pm 0.9	1.27	3.99	122 \pm 0.7	0.99	3.11
PentCB	3 \pm 0.6	0.85	2.67	135 \pm 0.7	0.99	3.11
HCB	1 \pm 0.3	0.42	1.32	135 \pm 0.7	0.99	3.11
<i>o,p'</i> -DCBF	26 \pm 0.3	0.42	1.32	126 \pm 0.5	0.71	2.23
<i>p,p'</i> -DCBF	26 \pm 0.5	0.71	2.23	94 \pm 0.4	0.57	1.79
<i>o,p'</i> -DDE	7 \pm 0.6	0.85	2.67	87 \pm 0.3	0.49	1.54
<i>p,p'</i> -DDE	6 \pm 0.6	0.85	2.67	75 \pm 0.3	0.42	1.32
<i>o,p'</i> -DDD	8 \pm 0.4	0.57	1.79	77 \pm 0.7	0.99	3.11
<i>p,p'</i> -DDD	8 \pm 0.2	0.28	0.88	71 \pm 0.5	0.71	2.23
<i>o,p'</i> -DDT	6 \pm 0.4	0.57	1.79	75 \pm 0.3	0.42	1.32
<i>p,p'</i> -DDT	6 \pm 0.7	0.99	3.11	79 \pm 0.5	0.71	2.23
Tetradifon	5 \pm 0.4	0.57	1.79	44 \pm 0.3	0.42	1.32

with LL extraction, which gave recoveries of about 80–100% with standard samples.

In order to establish whether the compounds not extracted by GAC remained in the water or were not removed from the activated carbon, the water passed through the carbon column was analysed by LL extraction and GC–ECD and GC–MS analysis. These compounds were not in the out-water. They had been adsorbed on the carbon column and the Soxhlet extraction was not capable of removing them effectively; there had been irreversible adsorption, as also reported by other authors [13–16].

In our forthcoming investigations, work will be dedicated to optimizing the GAC methodology, checking solvent mixtures or even using the backflush mode in the elution step.

3.2. GC–MS analysis

In four different samples and by means of GAC, a total of 229 organic compounds were identified, fifteen of which are regulated by the

EEC [1] and/or US EPA [17]. In precise samples and by LL extraction, 74 organic substances were determined, fifteen of which were EEC and/or US EPA Priority Pollutants. Table 3 gives a classification of the compounds detected in the surface water samples: organohalide compounds, phenols, ketones, acids, esters, alcohols, aldehydes, plasticizers, pesticides, hydrocarbons, nitrogen-derived organic compounds, polynuclear aromatic hydrocarbons, phthalates, etc.

By means of GAC, the majority of compounds found were acids and esters (28%), organohalide compounds (14%), aromatic hydrocarbons (13%) and ketones and aldehydes (9%). Phenols (3%), plasticizers (2%), surfactants (3%) and pesticides (1%) were minor components (see Fig. 1).

Liquid–liquid extraction determined as majority compounds acids and esters (22%), organohalide compounds (14%), plasticizers (14%) and aromatic hydrocarbons (16%). Phenols and alcohols were not detected and pesticides were minority compounds in the samples (3%) (see Fig. 1).

Table 3
Pollutants in River Cinca water detected following GAC and LL extraction

Compound	GAC	LL
<i>Organohalides</i>		
Benzene, chloro- ^{a,h}	×	×
Benzene, 1,3-dichloro- ^{a,h}	×	
Benzene, 1,4-dichloro- ^{a,h}	×	×
Benzene, 1,2-dichloro- ^{a,h}		×
Benzene, 1,2,4-trichloro- ^{a,h}		×
Benzene, dichloromethyl-		×
Methanone, (3-chlorophenyl)phenyl-	×	
4,4'-Dichlorobenzophenone	×	
Methanone, bis(3-chlorophenyl)-	×	
Ethanone, 2-chloro-1-phenyl-	×	
Ethanone, 1-(2,5-dichlorophenyl)-	×	
Methyl bis(<i>p</i> -chlorophenyl)acetate	×	
1-Propanone, 3-chloro-1-phenyl-	×	
1-Propanone, 2-chloro-1-(4-ethylphenyl)-2-methyl-	×	
2,4-Pentadiyl-1-one, 1,5-bis(4-chlorophenyl)-	×	
Benzaldehyde, <i>n</i> -chloro-	×	×
Benzoyl chloride, <i>n</i> ,4-dichloro-	×	
Butanoic acid, 2,3-dichloro-, methyl ester	×	
Benzoic acid, 2-chloro-, methyl ester	×	×
Benzoic acid, 2, <i>n</i> -dichloro-, methyl ester	×	
Benzoic acid, 2, <i>n</i> -dichloro-, ethyl ester	×	
Benzamide, 2,6-dichloro, N,N-dimethyl-	×	
Benzamide, 2-chloro-N-phenyl-	×	
Benzene, 1-chloromethyl-4-(2-propenyl)-	×	
Benzene, 1,1'-sulphonyl bis(4-chloro-	×	
Benzene, (2-chloro-1-methylethyl)-	×	
Phenol, <i>n</i> -chloro-	×	
Phenol, 2,3-dichloro- ^a	×	
Phenol, 4,4'-(1-methylethylidene)bis(2,6-dichloro)-	×	
Dodecane, 1-chloro-		×
6-Bromo-1,1a,6,6a-tetrahydrocyclopropane[<i>a</i>]indeno-	×	
Undecanoic acid, 11-bromo-, methyl ester		×
Naphthalene, 2-bromo-		×
Quinolinium, 1-ethyl-, iodide	×	
<i>Phenols and quinones</i>		
Phenol, 2-amino-4-methyl-	×	
Phenol ^b	×	
Phenol, 4-methyl-	×	
Phenol, 2-(2-methyl-2-propenyl)-	×	
Phenol, 2-nitro- ^b	×	
Phenol, <i>n</i> -methyl- <i>n</i> -nitro	×	
2,6-di- <i>tert</i> -butyl- <i>p</i> -quinone	×	
Phenol, 3-(1,1-dimethylethyl)-		×
Phenol, 2-methyl-5-(1-methylethyl)-	×	
Phenol, 3,5-bis(1,1-dimethylethyl)-	×	
Phenol, 2, <i>n</i> -bis(1,1-dimethylethyl)-4-methyl-	×	
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methoxy-		×
Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl-		×
<i>Acids and esters</i>		
Acetic acid, (2-methylphenoxy)-	×	

(Continued on p. 164)

Table 3 (continued)

Compound	GAC	LL
2-Propenoic acid, 3-(4-methoxyphenyl)-, 2-ethylhexyl ester	×	×
Cyclopropanecarboxylic acid, 2,2-dimethyl-3-(2-propenyl)-, ethyl ester	×	
2-Butenoic acid, methyl ester	×	
2-Butenedioic acid, diethyl ester		×
2-Butenoic acid, 3-methyl-, methyl ester	×	
Butanoic acid, 2,3-dimethyl-, methyl ester	×	
Butanoic acid, 3,3-dimethyl-, methyl ester	×	
2-Butenedioic acid, 2-ethyl-3-methyl-, dimethyl ester	×	
Pentanoic acid, methyl ester	×	
2-Pentenoic acid, methyl ester	×	
3-Pentenoic acid, methyl ester	×	
4-Pentenoic acid, 2-methoxy-, methyl ester	×	
2-Pentenoic acid, 4,4-dimethyl-, methyl ester	×	
Pentanedioic acid, 2,2-dimethyl-, dimethyl ester	×	
Hexanoic acid, methyl ester	×	×
Hexanoic acid, 5-methyl, methyl ester	×	
Hexanoic acid, 3-oxo-, methyl ester		×
Hexanedioic acid, mono(2-ethylhexyl) ester	×	
Cyclohexanecarboxylic acid, methyl ester	×	
3-Cyclohexene-1-carboxylic acid, methyl ester	×	
1,2-Cyclohexanedicarboxaldehyde	×	
Heptanoic acid, methyl ester	×	
Heptanoic acid, docosyl ester	×	
Octanoic acid, methyl ester	×	
Nonanedioic acid, dimethyl ester	×	
Decanoic acid, methyl ester	×	×
Undecanoic acid, methyl ester	×	
Undecanoic acid, <i>n</i> -methyl-, methyl ester	×	
Dodecanoic acid, methyl ester	×	×
Dodecanoic acid, <i>n</i> -methyl-, methyl ester	×	
Dodecanoic acid, <i>n</i> -methyl-, methyl ester	×	
Tridecanoic acid, 12-methyl-, methyl ester	×	
Tetradecanoic acid, methyl ester	×	×
Tetradecanoic acid, 12-methyl-, methyl ester	×	×
Tetradecanoic acid, 3-hydroxy-, methyl ester	×	
Tetradecanoic acid, tetradecyl ester	×	
Pentadecanoic acid, methyl ester	×	
Pentadecanoic acid, 14-methyl-, methyl ester	×	×
Pentadecanoic acid, 13-methyl-, methyl ester	×	
14-Pentadecynoic acid, methyl ester	×	
Hexadecanoic acid, ethyl ester	×	×
Hexadecanoic acid, 14-methyl-, methyl ester	×	
Hexadecanoic acid, 15-methyl-, methyl ester	×	
<i>n</i> -Hexadecenoic acid, methyl ester	×	
Heptadecanoic acid, methyl ester	×	×
Heptadecanoic acid, 16-methyl-, methyl ester	×	
Heptadecanoic acid, 15-methyl-, methyl ester	×	×
Heptadecanoic acid, 2-ethyl, methyl ester		×
Octadecanoic acid, octyl ester	×	
Octadecanoic acid, 9-methyl-, methyl ester	×	
<i>n</i> -Octadecnoic acid, methyl ester	×	×
Eicosanoic acid, methyl ester	×	×
Docosanoic acid, methyl ester	×	

Table 3 (continued)

Compound	GAC	LL
Tricosanoic acid, methyl ester	×	
Tricosanoic acid, 2-methoxy-, methyl ester	×	
Tetrasanoic acid, methyl ester	×	
Hexacosanoic acid, methyl ester	×	
Benzoic acid, methyl ester	×	×
Benzoic acid, 3-methyl-, methyl ester	×	
Benzoic acid, 2-hydroxy-, methyl ester	×	
Benzeneacetic acid, α -methoxy-, methyl ester	×	
Benzeneacetic acid, $\alpha,\alpha,2$ -trimethyl-, methyl ester	×	
Benzenepropanoic acid, methyl ester	×	
Carbanilic acid, <i>p</i> -phenyl-	×	
1 <i>H</i> -Indole-1-carboxaldehyde, 2,3-dihydro-	×	
1 <i>H</i> -Indole-3-carboxyaldehyde	×	
<i>Alcohols</i>		
1,2-Cyclopentanediol, 3-methyl-	×	
1,2,6-Hexanetriol	×	
Cyclohexanol, 4-methyl-	×	
Cyclohexanol, 3,5-dimethyl-	×	
Cyclohexanol, 2-(1,1-dimethylethyl)-	×	
3-Cyclohexene-1-methanol, 4-trimethyl	×	
Ethanol, 2-(9-octadecenyl)-	×	
Benzenemethanol	×	
1-Phthalanol, 1,3,3-trimethyl-	×	
1,1'-Biphenyl-2-ol	×	
<i>Ketones and aldehydes</i>		
Ethanone, 1-(methylphenyl)-	×	
Methanone, 1,4-phenylenebis(phenyl)-		×
Ethanone, 1-(<i>n</i> -aminophenyl)-	×	
Ethanone, 1-(<i>n</i> -hydroxyphenyl)-	×	
2-Propenal, 2-methyl-3-phenyl-	×	
1-Butanone, 1-(2,4,5-trihydroxyphenyl)-	×	
3-Buten-2-one, 4-phenyl-		×
1,3-Cyclopentadione, 2-methyl-	×	
2-Cyclohexen-1-one, 3-methyl-	×	×
Cyclohexanone, 2-(1-methylheptyl)-	×	
2-Cyclohexen-1-one, 3-methyl-	×	
Benzaldehyde	×	
Benzaldehyde, 4-ethyl-	×	
Belzaldehyde, 3,4,5-trimethoxy-	×	
Benzophenone	×	×
Bicyclo[5.1.0]heptan-2-one	×	
Triciclo[3.3.1.0.2.8]nona-3,6-dien-9-one	×	
<i>Elasticizers</i>		
Dimethyl phthalate ^b	×	×
1,3-Benzenedicarboxylic acid, dimethyl ester		×
Diethyl phthalate ^b	×	×
1,2-Benzenedicarboxylic acid, butyl-2-methylpropyl ester	×	×
1,2-Benzenedicarboxylic acid, butyl methyl ester		×
Dibutyl phthalate ^b	×	×
Benzyl buthyl phthalate ^b		×
1,2-Benzenedicarboxylic acid, decyl hexyl ester		×

(Continued on p. 166)

Table 3 (continued)

Compound	GAC	LL
1,2-Benzenedicarboxylic acid, bis(1-methylheptyl) ester		×
Bis(2-ethylhexyl) phthalate	×	×
Phosphoric acid, ethylhexyl ester	×	
Phosphoric acid, tributyl ester ^a	×	×
<i>Pesticides</i>		
<i>o,p'</i> -DDE ^a	×	×
<i>p,p'</i> -DDE ^b	×	×
Tetradifon	×	×
<i>Nitrogen derived</i>		
Benzamide, <i>n</i> -methyl-	×	
Benzenamine, N,N-dimethyl		×
Benzenamine, N,N-diethyl		×
Benzenamine, 2-methyl-5-nitro-	×	
Benzenamine, 4-methyl-2,6-dinitro-	×	
Benzenamine, 4-(4-morpholinyl)-	×	
Benzene, 1-methyl-3-nitro		×
Methylamine, <i>n</i> -cyclopentylidene	×	
1-Butanamine, N,N-dimethyl-	×	
Cyclohexanamine, <i>n</i> -cyclohexyl- <i>n</i> -nitroso-	×	
<i>Aliphatic hydrocarbons</i>		
Byciclo[4.2.0]octa-1,3,5-triene	×	×
Bicyclo[5.1.0]octane, 8-methylene-	×	
7-Oxabicyclo[2.2.1]heptane, 1-methyl-4-(1-methylethyl)-	×	
Cyclopentane, (2-methylpropyl)-	×	
Squalene		×
<i>Aromatic hydrocarbons</i>		
Benzene, methyl- ^{a,b}	×	×
Benzene, ethyl- ^{a,b}	×	×
(<i>m</i> + <i>p</i>)-Xylene ^{a,b}	×	×
<i>o</i> -Xylene ^{a,b}	×	×
Benzene, 1, <i>n,n</i> -trimethyl-	×	
Alkylbenzene C ₉ H ₁₂	×	×
Benzene, 1-ethyl- <i>n</i> -methyl-C ₉ H ₁₂	×	
Alkylbenzene C ₁₀ H ₁₄	×	×
Alkylbenzene C ₁₀ H ₁₅		×
Alkylbenzene C ₁₀ H ₁₇		×
Alkylbenzene C ₁₁ H ₁₆	×	
Benzene, 2-methyl-1-methylenepropyl-	×	
Alkylbenzene C ₁₆ H ₁₆		×
Alkylbenzene C ₁₄ H ₂₂	×	
Benzene, methoxy-	×	
Benzene, 1-methoxy-4-methyl-	×	
Benzene, 1-methoxyethyl-	×	
Benzene, 1,2-dimethoxyethyl-	×	
Benzene, 1-ethenyl-4-methoxy-	×	
Benzene, 2,4-bis(1,1-dimethylethyl)-1-methoxy	×	×
Benzene, 2-ethoxyethyl-	×	
Benzene, 1,1'-(1,2-cyclobutanediyl)bis-	×	
Cyclobutane, 1,3-diphenyl-, <i>cis</i>	×	×
Cyclobutane, 1,3-diphenyl-, <i>trans</i>	×	×
Benzene, 1,1'-(1-cyclobutene-1,2-diyl)bis-	×	
1,4-Diphenyl-1,3-butadiene	×	
1,1-Biphenyl, 3,3'-dimethoxy-	×	

Table 3 (continued)

Compound	GAC	LL
<i>Terpenes and other natural compounds</i>		
Cyclohexanol, 5-methyl-2-(methylethyl)-	×	
Cyclohexanol, 1-methyl-4-(1-methylethyl)-	×	
Bicyclo[2.2.1]heptan-2-one, 1,3,3-trimethyl-	×	
Bicyclo[2.2.1]heptan-2-ol, 1,3,3-trimethyl-	×	
Cineole (VAN)	×	
Camphor C ₁₀ H ₁₆ O		
<i>PAHs and derivatives</i>		
1 <i>H</i> -Inden-1-ol, 2,3-dihydro-	×	
2 <i>H</i> -Inden-2-one, 1,3-dihydro-	×	
1 <i>H</i> -Inden-1-one, 2,3-dihydro-3-methyl-	×	
1 <i>H</i> -Indene, octahydro-2,2,4,4,7,7-hexamethyl-	×	
5,6-Dimethoxy-1-indenone	×	
1,4-Methanonaphthalen-9-ol, 1,4-dihydro-	×	
Naphthalene, 1,2-dihydro-1,1,6-trimethyl-	×	
Naphthalene, 1,2,3,4-tetrahydro-5,6-dimethyl-	×	
Naphthalene, 1-(phenylmethoxy)-		×
2-Naphthalenenitrilo	×	
Naphthalene, 3-benzyl-1,2-dihydro-	×	
Anthracene, 9-dodecyltetradecahydro-	×	
<i>Heterocyclics</i>		
2(5 <i>H</i>)-Furanone, 5,5-dimethyl-	×	
Furan, 2,5-dihydro-2,5-dimethoxy-	×	
2,5-Furandiene, 3-ethyle-4-methyl-	×	
2(4 <i>H</i>)-Benzofuranone,5,6,7,7a-tetrahydro-4,4,7a-trimethyl-	×	
3-Pyridinecarboximide, 1,6-dihydro-1-methyl-6-oxo-	×	
Benzothiazole	×	×
Quinazoline, <i>n</i> -methyl-	×	
2(1 <i>H</i>)-Quinoline	×	
4(1 <i>H</i>)-Quinoline, 1-methyl-	×	
2-Quinolinenitrilo	×	
Quinoline, 2-(2-methylpropyl)-	×	×
<i>n</i> -Isoquinolinenitrilo	×	
Thiophene, 3-methyl-2-pentadecyl-(111)	×	
Thiophene, 3-methyl-2-pentadecyl-		×
<i>Miscellaneous</i>		
Sulphur (S ₈)	×	×
Diazepam (USAN)	×	
Benzenesulphonamide, <i>n</i> -butyl-	×	
Piperazine, 2,6-dimethyl-	×	
Hydrazinecarboxamide, N,N-diphenyl-		×
Trisulphide, dimethyl-	×	
Benzene, methylthio-		×
Benzenethiol, 4-(1,1-dimethylethyl)-2-methyl-	×	
Benzene, isocyano-	×	
Benzene, isothiocyanatomethyl-	×	×
Caffeine		×
Propanenitrile, 3,3'-oxybis-	×	
Benzene, 1,1'-sulphonyl bis-	×	×

^a EEC Priority Pollutant.

^b US EPA Priority Pollutant.

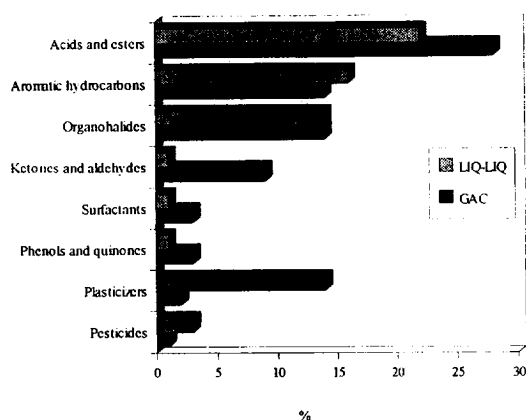


Fig. 1. Chemical species in River Cinca water: monitoring of 229 compounds using GAC and 74 using liquid–liquid extraction.

The main components of the organic extracts were as follows:

(i) volatile fatty acids derived from catabolic degradation of lipids (C_4 – C_8 acids), proteins (benzeneacetic and benzenepropionic acid) and lignins (cyclohexanecarboxylic and benzoic acids);

(ii) organohalide compounds from the pesticides industry: chlorobenzene, dichlorobenzene and trichlorobenzene used as raw materials in dicofol and tetradifon manufacture; DCBF, a degradation product of dicofol; and chlorobenzaldehyde and chlorobenzene acid, oxidation products of the organic material;

(iii) surfactants and related compounds such as alkylphenols and aromatic hydrocarbons such as toluene, xylenes, ethylbenzene and other alkylbenzenes used in the resins industry;

(iv) plasticizers, also used in resin manufacture, such as dimethyl, dimethyl and dibutyl phthalate;

(v) pesticides, such as DDE, used as a raw material in dicofol production; tetradifon was also detected;

(vi) urban waste compounds such as squalene (from steroid degradation), diazepam (with pharmaceutical activity), nitrogen-derived compounds, caffeine and aliphatic hydrocarbons (from petrol and oils); and

(vii) natural organic compounds such as terpenes present in vegetables and trees, bicyclics and some hydrocarbons.

The GAC technique could adsorb a large number of compounds, their polarity being greater than those identified in the case of precise samples. There was coincidence for 40 compounds in the two techniques, these being substances present at higher concentrations in the extracts and whose source could have a natural origin such as the complete series of acids and esters: hexanoic, decanoic, dodecanoic, tetradecanoic, methyldecanoic, methylheptanoic, octadecanoic and eicosanoic acids. However, other compounds could be attributed to industrial spillages such as chlorobenzene, dichlorobenzene, benzoic acid, *o,p'*-DDE, *p,p'*-DDE and tetradifon from pesticide manufacture and 3-methyl-2-cyclohexen-1-one, 2,4-bis(1,1'-dimethylethyl)-1-methoxybenzene, methylbenzene, xylene, ethylbenzene, diphenylcyclobutane and 2-(2-methylpropyl)quinoline from resin production.

4. Conclusions

By means of the two extraction techniques and subsequent GC analysis of surface water from the River Cinca, a large number of organic compounds were detected (229 with GAC and 74 with LL extraction), acids and esters (with a natural origin), organohalides and aromatic hydrocarbons (with an industrial origin) being the majority components.

Other detected compounds could have industrial or urban origin such as phenols, alcohols, some ketones, aldehydes, plasticizers, pesticides, organonitrogen and surfactants. Other substances such as bicyclics and hydrocarbons could have a natural origin.

In order to carry out a study of the micropollutants in real waters, extraction with activated carbon provided a greater number of different chemical species than the extraction of precise samples with methylene chloride. However, to quantify individual compounds, liquid–liquid extraction was the most suitable method.

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