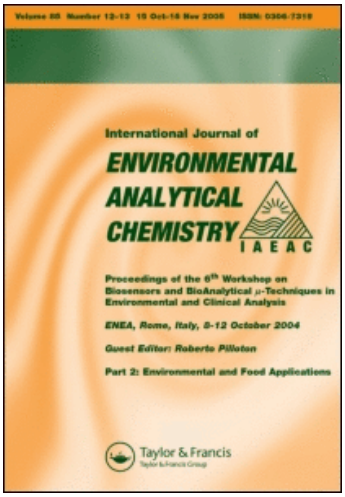

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Josep Rivera[a]; Francesc Ventura[a]; Josep Caixach[a]; Mariona De Torres[a]; Albert Figueras[a]; Joaquím Guardiola[b]
[a] Laboratori d'Espectrometria de Masses, Departament de Química Ambiental, C.S.I.C., Barcelona, Spain [b] Sociedad General de Aguas de Barcelona, Barcelona, Spain

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GC/MS, HPLC and FAB Mass Spectrometric Analysis of Organic Micropollutants in Barcelona's Water Supply†

JOSEP RIVERA, FRANCESC VENTURA, JOSEP CAIXACH, MARIONA DE TORRES and ALBERT FIGUERAS

Laboratori d'Espectrometria de Masses, Departament de Química Ambiental, C.S.I.C., Jorge Girona Salgado, 18–26, 08034-Barcelona, Spain

and

JOAQUÍM GUARDIOLA

Sociedad General de Aguas de Barcelona, Passeig de Sant Joan, 39, 08009-Barcelona, Spain

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Water samples from Llobregat river entering two water work plants, Barcelona tap water and waste dumping samples taken along the river course were analyzed for trace organic contaminants by different procedures, liquid–liquid extraction, adsorption on granular activated carbon followed by GC/MS/DS. Ether insoluble organic fractions were analyzed and fractionated by HPLC with diode-array detection, followed by FAB and FAB-CID-MIKE characterisation. Results, after two years monitoring, proved that surfactants, plasticizers, ethyleneglycol derivatives, phos-

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phates, hydrocarbons and other miscellaneous compounds can be considered as chronic pollutants of Llobregat river. Some of the identified compounds by GC/MS and FAB mass spectrometry have not been previously reported to occur in water.

KEY WORDS: Water, organic pollutants, GC/MS, HPLC Diode-Array, FAB mass spectrometry.

INTRODUCTION

Analysis of organic micropollutants in water has received much attention due to the presence of many organic compounds, coming from both anthropogenic and biogenic sources, which might be harmful (toxic, carcinogenic and/or mutagenic) even at very low trace levels.

Gas chromatography with specific detectors and coupling GC/MS has been routinely employed as a tool for the identification of organic micropollutants.[1-11] Although this technique has proved to be very suitable for many compounds, it is not for ionic, polar or thermally unstable compounds. Moreover, the so called non volatile organic fraction still remains unknown, but represents 70–80% of the total organic material.[12] The use of LC/MS[13] or new soft ionisation techniques such as field desorption[5,14] or FAB mass spectrometry[15] is an interesting alternative approach that could overcome some of these lacks.

Llobregat river and its tributaries (Cardener and Anoia) supply water for domestic and industrial uses for Barcelona and surroundings (3.2 million inhabitants). The river passes by heavy industrialized areas therewith receiving industrial and municipal wastewaters with little epuration. Sant Joan Despí and Abrera, 7 and 40 km far from the mouth respectively, are the main water work plants (see Figure 1). Salt works, textile, galvanic, leather, surfactants and pharmaceutical industries are probably the major sources of pollution in the river. The present study has been understaken to set up the quality of the water, identifying the chronic industrial pollutants and their sources in order to force the involved industries to improve their wastewater purification processes. Figure 1 shows the geographical situation and the selected points along the river course. Table I is a summary of the different analyzed points.

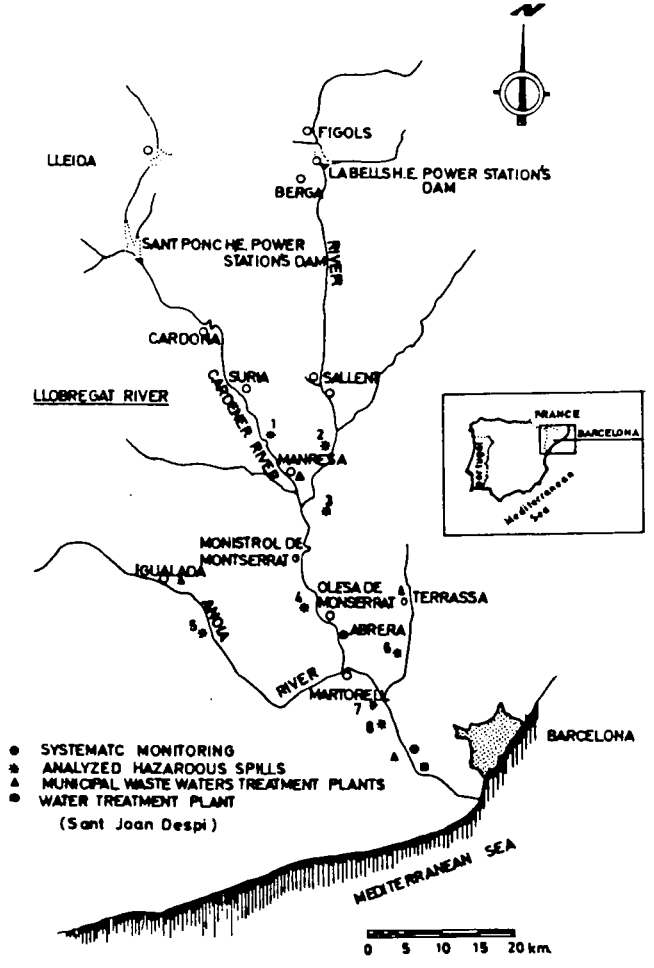

FIGURE 1 Geographical situation.

Analytical techniques used in this study includes liquid–liquid extraction for "grab" samples, and adsorption on granular activated carbon, as that used in the water works plants, for monthly average water samples, in order to know the nature of organic compounds removed in the water treatment process. For the identification of

pollutants, gas chromatography (FID and ECD), computerized GC/MS, HPLC analysis and fractionation by diode array detection, FAB and FAB-CID-MIKE spectrometry have been used. Future work will include quantitative analyses of identified organic compounds, improvement of adsorption procedures and detailed study of HPLC fractions by FAB mass spectrometry.

TABLE I

Sampling points	Type of discharge
1 and 2	Salt mines
3	Sanitary landfill (industrial and urban wastes)
4	Surfactants and pesticide industrial area
Abrera	Water works plant for cities around Barcelona
5	Flavour and perfume industry
6	Miscellaneous ind. activity (textile, galvanic)
7	Miscellaneous ind. activity (galvanic, pharmac.)
8	Surfactants and textile industries
S. Joan Despí	Barcelona's water works plant

EXPERIMENTAL

Sampling and extraction procedures

Wastewater or spill water samples from industries suspected as major sources of pollution in Llobregat river and water samples taken at the major confluences of Llobregat river with its tributaries, were usually collected as grab samples in ambar glass bottles fitted with Teflon-lined screw caps. Methylene chloride and hydrochloric acid were added to the samples in order to minimize biological degradation at the collection site.

On the other hand, monthly average water samples were collected at Abrera's water works plant and at different stages of S. Joan Despí water works plant, by passing 2000 liters of water through a column of granular activated carbon Pittsbourgh F–200 as that used in the water works plants.

Grab samples, were fractionated in acid and base+neutral fractions according to EPA method 625.[16]

Organic extracts from water entering the water works and tap water were disadsorbed from granular activated carbon with dichloromethane by Soxhlet extraction. The total extract was concentrated to *ca* 2 ml with a rotary evaporator, followed by evaporation using a gentle stream of nitrogen. The residue, once elemental sulphur was removed by passing the extract through a minicolumn of activated copper, is redissolved in ether. The ether soluble compounds are fractionated in acids and base + neutrals and analyzed by GC/MS/DS, whereas the ether insoluble residue is redissolved in methanol and fractionated by HPLC monitored with UV-Diode Array detection. These HPLC fractions were analyzed by FAB mass spectrometry or FAB-CID-MIKE.

Analytical instrumentation

GC analysis GC analysis were performed on a Konik-2000 gas chromatograph equipped with a ^{63}Ni ECD (Tracor 560) and FID detectors respectively. For trihalomethane analysis (ECD detector), a 25 m × 0.25 mm DB-1 (S.G.E. Australia) was employed. Hydrogen was the carrier gas (0.8 bar) and nitrogen was used as make-up gas (30 ml/min). Split injection 1/20. Column temperature was 40°C isotherm, being injector and detector temperatures 200°C and 250°C respectively. For FID analysis, the same conditions as described below for GC/MS analysis were used, being injector and detector temperatures 250°C and 280°C respectively. Splitless injections were carried out for 45 sec.

GC/MS analysis A Konik-200 gas chromatograph coupled with a MS-9 VG updated mass spectrometer and VG 11/250 data system was used. GC/MS analyses were carried out with a DB-1 fused silica column (25 m × 0.22 mm) (S.G.E. Australia) coupled directly to the ion source. Helium was the carrier gas with a back pressure of 0.8 bar. Temperature program was 60°C (3 min) to 275°C at 4°C/min. For the EI mode, the conditions were as follows: ionisation energy 70 eV, mass range 40–500, scan time 2 sec/dec and 1000 of resolving power.

Liquid chromatographic separations (analytical and preparative) were performed with a dual pump gradient system (LKB-2150). Ultraviolet absorbance detection was accomplished with a LKB-

2140 diode array detector. Chemical separations were performed on a 7.8 mm × 30 cm u-Bondapack C-18 (Water Assoc.) for semipreparative scale and two columns in series, 4 mm × 25 cm Lichrosorb RP18 (Merck) for analytical purposes. The gradient elution scheme used for LC separation was as follows: 10% to 95% B in A in 45 min being A = Water/MeOH (90:10) and B = acetonitrile.

FAB spectra were obtained using a ZAB-HF spectrometer (VG England) using a monothyoglycerol saturated with NaCl matrix. Conditions and more detailed explanations are given elsewhere.[17]

RESULTS AND DISCUSSION

The organic compounds identified in Llobregat River and their tributaries are listed in Table II.

Concentration ranges

Sampling point No. 3: Acids (1–10 ppm), base + neutrals (1–25 ppb)
No. 4: 10 ppb–10 ppm

Abrera water works: Monthly average concentration (0.5–50 ppb)
No. 5: 1 ppb–50 ppm
No. 6–8: 1–100 ppb

S. Joan Despí and tap water: Monthly average concentration 0.5–10 ppb
For trihalomethanes: 20–700 ppb
For pesticides: 0.5–20 ppt.

Sampling point No. 3 (see Figure 1) was the leachate from a sanitary landfill near a little tributary. This landfill is mainly used for disposal of domestic and industrial wastes. The leachate percolates through the landfill to the tributary and finally to the river.

The analyses allowed to distinguish between the products originally present in the refuse after being washed out by the percolating waters (or arising from industrial activity) and those derived of metabolic products formed by aerobic or anaerobic degradation or organic matter. The major components of the organics extracts were volatile fatty acids derived from catabolic degradation of lipids (C_4–C_8 acids), proteins (benzeneacetic and benzenepropionic acids) and lignins (cyclohexanecarboxylic and benzoic acids). Phenol and

TABLE II

Organic compounds in Llobregat river and Barcelona's tap water

	Tap water	S. Joan Despí water works	8	7	6	5	Abrera	4	3
Halogenated compounds									
[ba]Chloroform	×	×					×		
Bromodichloromethane	×						×		
[a]Dibromochloromethane	×						×		
[a]Bromoform	×						×		
[ba]Tetrachloroethylene	×	×					×		
[ba]Trichloroethylene	×	×					×		
[ba]Carbon Tetrachloride	×	×							
[ba]1,1,1-Trichloroethane	×	×							
[ba]1,2,4-Trichlorobenzene	×	×					×		
3-chloropyridine		×							
2,6-dichlorobenzamide							×		
[b]1-chloro-3-nitrobenzene		×							
2-chlorobenzyl alcohol	×			×		×			
(2-chlorophosphate)ethanol	×						×		
6-chloro-2-nicotinic acid	×	×					×		
alfa-chloromethylbenzyl alcohol						×			
[b]2-chlorotoluene						×			
1-chloro-2-(chloromethyl)benzene						×			
4-chlorobenzaldehyde						×			
2,4-dichlorotoluene						×			
2,3,5,6-tetrachlorophenol			×						
[ba]Pentachlorophenol			×						
[ba]2,4,5-Trichlorophenol				×					
4-chlorophenol					×				
2,4-dichlorobenzyl alcohol						×			
2-chloro-5-methylphenol						×			
4-chloro-2-methylphenol						×			
3,4-dichlorobenzoate							×		
[ba]Hexachloroethane	×								
Aromatic Hydrocarbons									
[ba]Toluene					×				
[b]Xylenes	×	×					×		
Styrene			×						
2-nitrovinylbenzene			×						
Alkylbenzenes	×	×					×		
[ba]Naphtalene		×					×		
Tetrahydronaphtalene	×	×							

TABLE II (continued)

	Tap water	S. Joan Despí water works	8	7	6	5	Abrera	4	3
[b]Biphenyl			×				×		
4-vinylbenzene			×						
1-methylnaphtalene			×						
2-methylnaphtalene			×						
1,7-dimethylnaphtalene			×						
1,1′-oxybisbenzene							×		
1,1′,2′,2″-terpenyl	×	×							
[ba](9H)-fluorene			×						
(9H)-carbazole			×						
1,1′-(methylenebis(oxymethylene)				×		×			
bisbenzene						×			
Phenantrene			×						
Phenols and quinones									
[a]Phenol									×
4-methylphenol									×
p-tertbutylphenol							×		
2,5-dimethylphenol			×			×			
2,2-methylenebisphenol									×
4,4′methylenebisphenol									×
1-ethoxy-2-methylphenol									×
2,6-di-tbutyl-p-dibenzo quinone		×							
Acids and esters									
Propionic acid									×
Butyric acid									×
Iso-butyric acid									×
Valeric acid									×
Iso-valeric acid									×
Caproic acid									×
Heptanoic acid									×
2-ethylhexanoic acid									×
Benzoic acid									×
Phenylacetic acid									×
Phenylpropionic acid									×
Cyclohexane carboxylic acid									×
iso-hepatanoic acid									×
6-aminohexanoic acid									×
3-oxobutanoic acid, methyl ester									×

TABLE II (continued)

	Tap water	S. Joan Despí water works	8	7	6	5	Abrera	4	3
Acetic acid, phenylmethyl ester									×
Benzoic acid, phenyl methyl ester									×
Mirystic acid	×	×			×		×		
Palmitic acid	×	×			×		×		
Oleic acid	×	×			×		×		
Stearic acid	×	×			×		×		
Alcohols									
Benzyl alcohol	×	×						×	
Triacetin			×						
Decanol								×	
Lauryc alcohol			×					×	
Tetradecanol								×	
Alfa-terpineol			×			×			
2-phenoxyethanol								×	
Ketones and Aldehydes									
Benzophenone	×	×					×		
[a]Isophorone	×						×		
Benzaldehyde	×	×		×		×	×		
Cuminaldehyde		×							
2,5-dimethylbenzaldehyde	×								
4-methyl benzaldehyde						×			
4-methyl-E-oximebenzaldehyde					×				
Plasticizers									
[a]Dimethylphtalate	×	×						×	
[a]Diethylphtalate	×	×	×				×		
[a]Di-n-butylphtalate	×	×	×				×		
Butyl, i-propylphtalate	×	×					×		
[a]Bis(2-ethylhexyl)phtalate	×	×					×	×	
[a]Di-n-ocytlphtalate	×	×					×		
Di-i-octylphtalate	×	×	×				×		
[b]tri(tert-butyl)phosphate	×	×					×		
2-butoxyphosphate, ethanol	×	×					×		
Pesticides and herbicides									
Atrazine	×	×					×	×	
[b]Trifluralin	×	×					×	×	
[b]Simazine								×	
[ba]α-BHC	×	×					×		
[ba]Lindane	×	×					×		

TABLE II (continued)

	Tap water	S. Joan Despi water works	8	7	6	5	Abrera	4	3
[ba]β-BHC	×	×					×		
[ba]Aldrin	×	×					×		
[ba]Heptachlor	×	×							
[ba]pp′-DDE	×	×					×		
[ba]pp′-DDD	×	×					×		
[ba]pp′-DDT	×	×					×		
Amines and amides									
3-nitroaniline		×		×					
NN′-dimethylaniline			×						
N-ethyl acetamide									×
Benzamide									×
2-methyl-3,5-dinitrobenzamide (Dinitolmide)									×
N,N′-diethyl-3-pyridincarboxamide (Coramine)									×
3-methylpyridine					×				
2,4-dimethylpyridine					×				
Ethyleneglycol derivatives and surfactants									
1-(2-(2-methoxy-1-methylethoxy)-1-methylethoxy)2-propanol									
1-(2-butoxyethoxy)ethanol									
2-(2-(2-methoxyethoxy) ethoxy, ethanol									
Polyethylenglycols PEG200, 400, 600	×	×					×		
Poly(ethylenpropylen)glycol block copolymers	×	×					×		
Polyethoxylated alkylphenols (C_8-C_{10}) with $n=0$–13	×	×					×		
Polyethoxylated alcohols (C_{12}–C_{15}) with $n=0.18$	×	×					×		
Polyethoxylated fatty acids (ricinoleic acid) $n=12$							×		
Poly(ethoxypropxy)lated alkylphenols (C_8 and diC1-C_9) with $n=1$–8 and $m=1$-4	×								
Alkylether sulfates (C_8 and C_9) with $n=10$	×	×					×		
Dimethyldistearylammonium chloride								×	

TABLE II (continued)

	Tap water	S. Joan Despí water works	8	7	6	5	Abrera	4	3
Miscellaneous compounds									
Benzofurazan	×	×							
Benzofuroxan	×	×							
Benzothiazole									
Benzodithiazole		×					×		
1,2-benzoisothiazole		×					×		
1-methyl-4-amino-(1H)-benzothiazole		×							
2-methyltiobenzothiazole	×	×							
2-(4-hidroxybutyl)phtalimide							×		
N-ethylphtalimide	×	×					×		
N-methylphtalimide									
Clofibrate					×				
Caffeine	×								
Fenchone		×							
Borneol	×								
Nicotin									×
Nicotin oxide									×
Caprolactam									×
1-acetyl pyrrolidine									×
Aminopyrine									×
5-ethyldihydro-2-(3H)-furanone									×
1,7,7-trimethyl-3-phenylene-bicyclo (2.2.1)-heptan-2-one					×				×

[a]EPA Priority pollutants list.
[b]Black list. Journal officiel des Communautés Européennes C176/7, 14/7/82.

cresol were also present. These results are in agreement with those obtained from other sanitary landfills.[18,19] More interesting and complex, although less abundant was the the bases + neutral fraction. The main identified compounds includes caprolactam, used in the manufacture of synthetic polyamide type fibers[8] and its degradation product 6-aminohexanoic. Other identified compounds, such as Aminopyrine used as analgesic and antypiretic[20] and Coramine, a

respiratory stimulant prepared by heating nicotinc acid were indicatives of pharmaceutical wastes. Thus, the presence of nicotine-oxide could be explained from industrial activity.

Sampling point No. 4 (see Figure 1) was selected as a representative wastewater of an industrial area near a water plant (6 km downstream) supplying drinking water to cities around Barcelona. Wastewaters from a common pipeline of two factories, developed to pesticide manufacturing and surfactants' industry allowed us to identify a wide range of commercial herbicides, such as atrazine, trifluralin, simazine, 0,0,S-trimethyl phosphorothioic, whereas long chain alcohols (C-10, C-12, C-14), nonylphenols, monoethoxylated lauryl alcohol and phenols and dodecylbenzenes were closely related with the other one. All these compounds were identified by GC/MS/DS and comparison with authentic standards. Total organic extract without any treatment was directly analyzed by FAB and FAB-CID-MIKES mass spectrometry Figure 2 shows the main presence of dimethyldistearylammonium chloride, a cationic surfactant present in textile softeners.[15,21] Recently, both factories were suspected of causing environmental impacts as pollution in groundwaters wells, as well as extensive fish poisoning and small spots of burned off forestal areas.[22,23]

Abrera sampling point (see Figure 1) is located at the entering to plant water works. Main identified compounds include a wide range of plasticizers (dimethyl, diethyl, di-n-butyl, bis-2-ethylhexyl and di-n-octyl phtalates), dye carriers, such as trichlorobenzenes, biphenyl and alkylphtalimides.[1] Other miscellaneous compounds such as 1,1'-oxybisbenzene, used in perfume soaps and organic syntheses,[20] 2,4-dichlorobenzamide and 3,4-dichlorobenzoic acid methyl ester were also identified. GC chromatograms of Abrera water works samples were dominated by surfactants being polyethoxylated nonylphenols the major ones. This was not surprising as surfactants' and textile industries are placed in the banks of the river. Figure 3 shows the mass fragmentogram of representative ions of these compounds up to $n=7$ (degree of polyethoxylation), maximum identified in our conditions. Nevertheless, the total organic extract was also analyzed by FAB mass spectrometry showing polyethoxylated nonylphenols up to $n=12$ as major components.

From sampling point No. 5 were collected water samples corresponding to an industrial area where all kind of residues are dumped

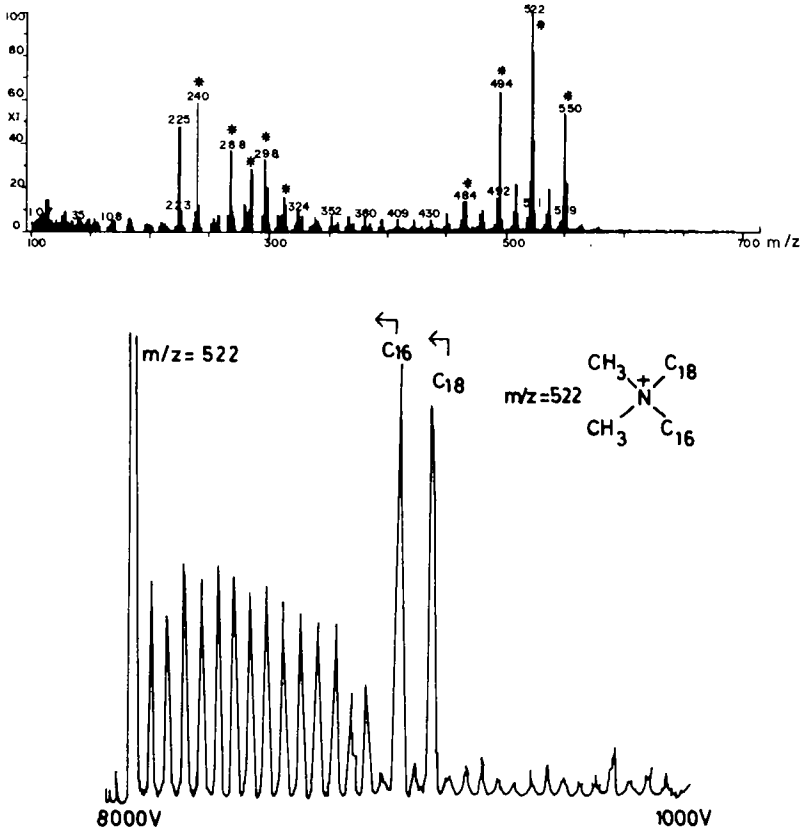

FIGURE 2 Top: FAB(+) spectrum of a wastewater dumping at Llobregat river. Bottom: CID-MIKE spectrum of m/z=552 corresponding to $(CH_3)_2N^+(C_{18}H_{37})(C_{16}H_{33})$ and showing alkyl chain cleavage.

into the river (among them the wastes from a flavouring industry). Some compounds found in drinking water were closely related with this factory. The major identified compounds in the organics extracts were benzaldehyde and benzylic alcohol. Chlorinated derivatives of these compounds (p-chlorobenzaldehyde, 2-chloro benzylic alcohol, 2,4-dichlorobenzylic alcohol), alkyl derivatives (p-methylbenzaldehyde, p-ethylbenzyl alcohol), other chlorinated compounds (2-chlorotoluene, 2,4-dichlorotoluene, 2-chloroethylbenzene, 1-chloro-

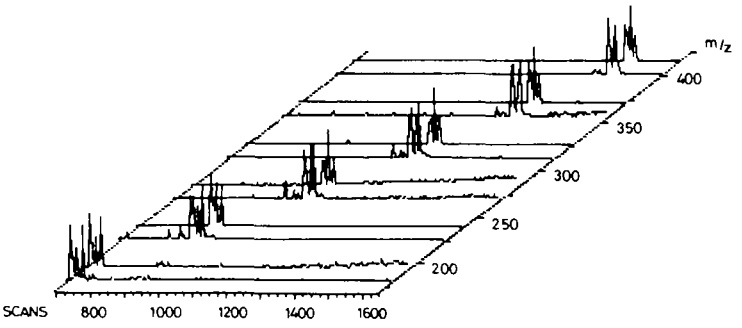

FIGURE 3 Mass fragmentograms of polyethoxylated nonylphenols at Abrera's water works plant. (for $n=1$ m/z = 179, 193; $n=2$ m/z = 223, 237; $n=3$ m/z = 267, 281, $n=4$ m/z = 311, 325; $n=5$ m/z = 355, 269; $n=6$ m/z = 399, 413.

2-(chloromethyl)benzene), phenols (acetylphenol, 2,5-dimethylphenol, 2-chloro-5-methylphenol, 2-methyl-4-chlorophenol) and miscellaneous as well as condensation products, such as alfa-terpineol, benzamide and 1,1'-methylene-bis-(oxymethylene)-bis-benzene were also identified.

Water samples collected in the conjunction of the ditch of the industrial area mentioned above and the river (sampling point No. 7) allowed us to identify other different compounds. Although the major compound peak was benzyl alcohol, benzofurazan and benzofuroxan were also found. These two last compounds, to our knowledge, have not been reported to occur so far in water samples. Other miscellaneous compounds, such as 2-chlorobenzyl alcohol, 3-nitroaniline (dyestuff intermediate) and Dinitolmide (2-methyl-3,5-dinitrobenzamide) were also identified.

Sampling point No. 8 receives wastewaters coming from some industries, a petrol station and tank washing of petrol-trucks. Organic micropollutants identified in the extracts include some compounds coming from the industrial area (such as benzyl alcohol, 2,5-dimethylphenol, alfa-chloromethyl benzylalcohol), surfactants and related compounds. Other organic compounds from this point are: polycyclic aromatic hydrocarbons (methylnaphtalenes, (9H)-

fluorenone, (9H)-carbazone, phenantrene), chlorinated phenols (2,3,5,6-chlorophenol, pentachlorophenol), plasticizers (diethyl, n-butyl. i-propyl, dibutyl, di-i-octylphtalates), dye's industry related compounds (biphenyl, NN'-dimethylaniline, triacetin) and miscellaneous compounds such as styrene and 2-nitrostyrene.

Sant Joan Despí sampling point relates to monthly average water samples entering to the main water works plant. Plasticizers (dimethyl, diethyl, di-n-butyl, bis-(2-ethylhexyl) and di-n-octylphtalates and tributyl phosphate), surfactants and related compounds (alkylbenzenes, polyethoxylated nonylphenols, 2-butoxyphosphate ethanol) are the major ones. Other compounds are related with pharmaceutical activity: Clofibrate, used by older people to control *atherosclerosis*[24] is coming from a laboratory located in 6. Benzofurazan and benzofuroxan, intermediates of N-(2-hydroxyethyl)-3-methyl-2-quinoxalinecarboxamide and 3-(2-quinoxalinylmethylene)carbazaic acid methyl ester N,N'-dioxide are used as growth stimulant. Organic compounds related with dye's industry (trichlorobenzenes, biphenyl, benzoic acid), rubber industry (benzothiazole, 1-methyl-4-amino-(1H)-benzothiazole, benzoditiazole, 1,2-benzoisotiazole, 2-methyl-tiobenzotiazole, 2,6-di-t-butyl-p-di-benzoquinone), and flavour industry (benzyl alcohol, benzaldehyde, 2-chlorobenzyl alcohol) were also identified. The last group of compounds come from point No. 4 whereas those compounds derived from rubber industry are mainly discharged by a tire manufacturing plant located in Manresa (see Figure 1). More difficult is to determine the origin of dye products due to the wide number of industries located in the banks of the river. Pyridin derivatives (2,4-dimethylpyridine, 3-chloropyridine), nitroderivatives (3-nitroanaline, 1-chloro-3-nitrobenzene) probably coming from an an industry located near sampling point No. 5 (manufacturing nitroderivatives) were also identified. Last group of miscellaneous compounds includes naphthalene, tetrahydronaphtalene, 1,1', 2',2''-terpenyl, xylenes, 4,4'-dichloro-1,1'-biphenyl-2-carboxylic acid and t-butylphenol, an intermediate in the manufacture of varnish and lacquer resins and also used in motor oil additives.[20] Figure 4 shows a reconstructed ion chromatogram of raw water as an example.

Drinking water samples showed brominated trihalomethanes (max 714 μg/l) as major species. Figure 5 shows an ECD chromatogram of Barcelona's tap water. The origin and abnormal high amounts of

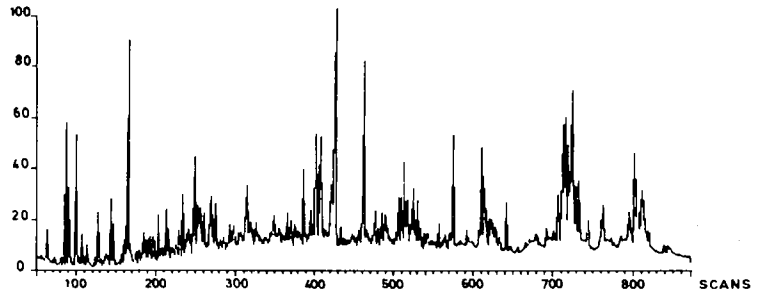

FIGURE 4 Reconstructed ion chromatogram of a typical GC/MS analyses of raw water entering Barcelona's water works plant.

these compounds was proved to be salt water discharges 140 km upstream the water works plant (points 1 and 2).[25]

Other chlorinated solvents such as carbon tetrachloride 1,1,1-trichloroethane and mainly tetrachloroethylene were regularly present in drinking water. The same group of plasticizers identified in water samples entering the water works plant were observed. Flavour and perfume industry related compounds (benzaldehyde, benzyl alcohol, 2-chlorobenzyl alcohol, 2,5-dimethyl benzaldehyde, borneol and fenchone) and miscellaneous compounds (caffein, trichlorobenzenes, xylenes, 4-vinylcyclohexene, N-ethylphtalimide, 6-chloro-2-nicotinic acid and hexachloroethane used as rubber vulcanization accelerator were also identified. Alkylbenzenes and polyethoxylated alkylphenols were identified by GC/MS but an interesting approach was obtained when HPLC fractionated extracts by diode-array detection (see Figure 6). Ether insoluble fractions of raw and drinking water were analyzed by FAB and FAB-CID-MIKE mass spectrometry. Polyethylenglycols (PEG 200–600), polyethoxylated alkylphenols (C_8–C_{10} and $n=0$–13), alcohols (C_{12}–C_{15} $n=0$–12), polyethoxypropoxylated alkylphenols and fatty acids, polyethylenpropylenglycol block copolymers and alkylether sulfates were identified in raw water entering the water works plant whereas the same compounds with lower polyethoxylation degree were present in drinking water. More detailed information is given elsewhere.[17] Figure 7 shows a positive FAB spectrum of one HPLC fraction of tap water with the main identified products.

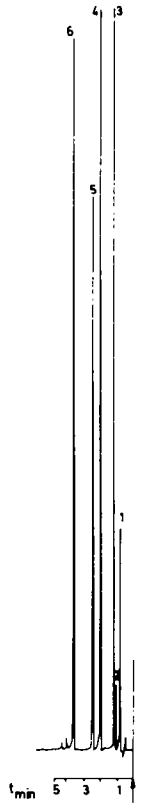

FIGURE 5 ECD chromatogram of Trihalomethanes of Barcelona's tap water. Identified peaks are 1-$CHCl_3$; 2-CCl_4; 3-$CHCl_2Br$; 4-$CHClBr_2$; 5-$Cl_2C{=}CCl_2$; 6-$CHBr_3$.

The FAB spectrum was obtained using monothioglycerol + NaCl as a matrix. Peaks m/z 237 and 295 are background of the matrix, but other peaks such as m/z 217, 311 and so on are unidentified compounds. The observed background arises from the sample, because thioglycerol peaks over m/z 300 are negligible.

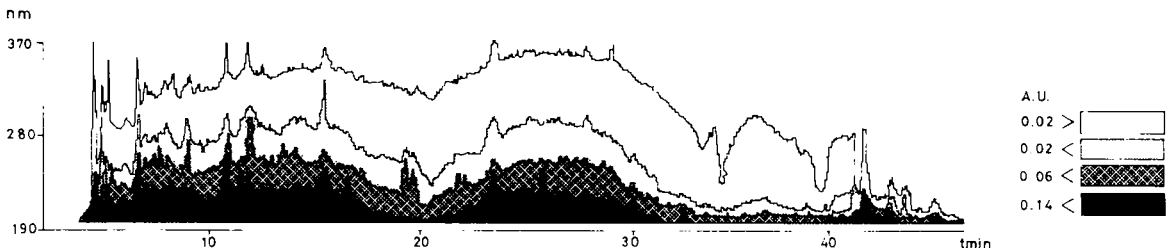

FIGURE 6 Isoabsorbance map of ether insoluble fraction of final drinking water by HPLC-diode array detection. Conditions are described in text.

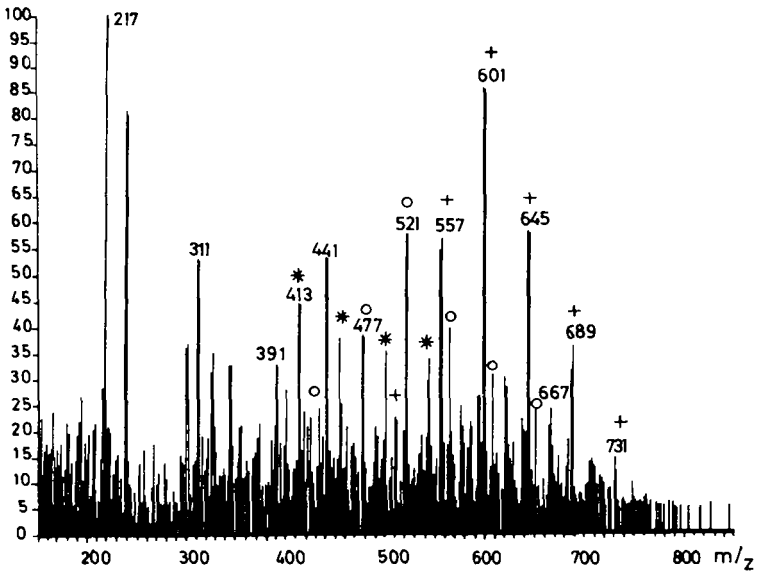

FIGURE 7 FAB(+)spectrum of an HPLC fraction of tap water showing the main identified compounds, confirmed by FAB-CID-MIKE. Peak identification: *Polyethoxylated myristic alcohol ($M+Na^+=413$ for $n=4$) 0 Nonylphenol ethersulfates ($M+Na^-=521$ for $n=5$); + unidentified polyethoxylated compounds.

CONCLUSIONS

Survey of organic micropollutants in Llobregat river and Barcelona's tap water has demonstrated the presence of some compounds that could be considered as chronic pollutants, the major ones, being halogenated compounds (mainly brominated trihalomethanes), hydrocarbons, phosphates, plasticizers, benzothiazoles, polyethoxylated compounds, ethyleneglycol derivatives. These products are mainly related to surfactants, textile, rubber and dye industry located in the banks of the river.

The use of GC/MS has been widely used for monitoring organic micropollutants but FAB and FAB-CID-MIKE offers an advantadge for those compounds not amenable to gas chromatography.

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References

1. R. A. Hites, *J. Chromatogr. Sci.* **11,** 570 (1973).
2. G. A. Junclaus, L. M. Games, R. A. Hites, *Anal. Chem.* **48**(13), 1894 (1976).
3. L. S. Sheldon and R. A. Hites, *Environ. Sci & Techn.* **12**(10), 1188 (1978).
4. L. S. Sheldon and R. A. Hites, *Environ. Sci & Techn.* **13**(5), 574 (1979).
5. A. Yasuhara, H. Shirashi, M. Tsuji and T. Okuno, *Environ. Sci. & Techn.* **15**(5), 570 (1981).
6. V. A. Elder, B. L. Proctor and R. A. Hites, *Biomed. Mass Spectrom.* **8**(9), 409 (1981).
7. A. Guiraud and J. Larnicol, *Water Sci. & Techn.* **14,** 127 (1982).
8. J. C. Peterson, F. Guiochon, C. Democrate and M. Dutang. *Intern. J. Environ. Anal. Chem.* **14,** 23 (1983).
9. R. A. Moore and F. W. Karasek, *Intern. J. Environ. Anal. Chem.* **17,** 203 (1984).
10. H. Shirashi, A. Otsuki and K. Fuwa, *Biomed. Mass Spectrom.* **12**(2), 86 (1985).
11. J. C. Peterson, D. F. Clarck and P. S. Sleevi. *Anal. Chem.* **58**(1), 70A (1986).
12. National Academy of Sciences (1977). "Drinking water and Health," p. 489–856. *Acad. Sci.*, Washington, D.C.
13. A. D. Thruston Jr. and J. M. McQuire, *Biomed. Mass Spectrom.* **8**(2), 47 (1981).
14. B. Crathorne, C. D. Watts and M. Fielding, *J. Chromatog.* **185,** 671 (1979).
15. K. Levsen and S. A. McLuckey. In: *Analysis of Organic Micropollutants in Water* (G. Angeletti and A. Bjorseth, eds.) (D. Reidel Publishing Co., Dordrecht, Holland,), pp. 132–140.
16. U.S.E.P.A. Federal Register 44, 69464-575 (Dec., 3, 1979).
17. J. Rivera, D. Fraisse, F. Ventura, J. Caixach, A. Bruchet, in press.
18. W. D. Burrows, R. S. Rowe, *J. Water Pollut. Control Fed.* **47,** 921 (1975).
19. W. J. Dunlap, D. C. Shew, M. R. Scalf, R. L. Cosby, J. M. Robertson. In: *Identification and Analysis of Organic Pollutants in Water* (L. H. Keith, ed.) (Ann Arbor Science Publishers, Michigan, 1976), pp. 453–476.
20. The Merck Index (Merck & Co. Inc., Rahway, N.J., 1983), 10th ed.
21. C. D. Watts, B. Crathorne, M. Fielding and C. P. Steel. In: *Analysis of Organic Micropollutants in Water* (G. Angeletti and M. Bjorseth, eds.) (D. Reidel Publishing Co., Dordrecht, Holland), pp. 120–131.

22. J. Rivera, J. Caixach, F. Ventura, I. Espadaler, *Chemosphere* **14**(5), 395 (1985).
23. J. Rivera, J. Caixach, M. de Torres and F. Ventura, *Int. J. Environ. Anal. Chem.* **24,** 183 (1983).
24. A. W. Garrison, J. D. Pope and F. R. Allen. In: *Identification and Analysis of Organic Pollutants in Water* (L. H. Keith, ed.) (Ann Arbor Science Publishers, Michigan, 1976), pp. 517–556.
25. F. Ventura and J. Rivera, *Bull. Environ. Contam. & Toxicol.* **35,** 73 (1985).