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Determination of organic priority pollutants in sewage treatment plant effluents by gas chromatography high-resolution mass spectrometry

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ABSTRACT

In this work, we report the development and validation of an analytical method for the trace level determination of 14 selected (EU-directive) priority organic pollutants (namely, 1,2,3-trichlorobenzene (1,2,3-TCB), 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, hexachloro-1,3-butadiene, pentachlorobenzene, hexachlorobenzene, alachlor, α-hexachloro-cyclohexane (α-HCH), β-HCH, γ-HCH (lindane), δ-HCH, tetra-brominated diphenyl ether (tetra-BDE), penta-brominated diphenyl ether and hepta-brominated diphenyl ether) in wastewater samples from 5 different sewage treatment plants (STPs) located in Spain. The proposed methodology is based on liquid–liquid extraction with n-hexane followed by identification and confirmation of the selected pollutants by gas chromatography high-resolution mass spectrometry in selected ion recording acquisition mode. Recovery studies performed with spiked wastewater samples at two different concentration levels (0.1 and 1 $\mu g\,L^{-1}$) gave mean recoveries in the range 80–120% (except for trichlorobenzenes, *ca.* with 50%) with RSD values below 10% in most cases, thus confirming the usefulness of the proposed methodology for the analyses of this kind of complex samples. The obtained detection limits in effluent wastewater matrices were in the low nanogram per liter range, with values as low as 0.09 $ng\,L^{-1}$ for tetra-BDE and 0.3 $ng\,L^{-1}$ for hexachlorobenzene. Finally, the proposed methodology was successfully applied to a monitoring study intended to characterize wastewater effluents of 5 different sewage treatment plants with different major activities (Industrial, Coastal, Urban). Most of the compounds targeted were detected in the $ng\,L^{-1}$ range at concentrations ranging from 0.19 $ng\,L^{-1}$ to 135 $ng\,L^{-1}$ (hexachlorobenzene).

1. Introduction

The contamination of the aquatic environment by organic pollutants is of paramount concern for citizens and environmental authorities. The main tool of the European water policy to reduce chemical pollution of surface water is the water framework directive (WFD) 2000/60/EC [1,2], which establishes guidelines against pollution of water by sorting out a list of priority substances that involves a significant risk to or via the aquatic systems. In this context, urban wastewaters may have a strong contaminating effect on the natural aquatic systems. With the aim of improving the quality of the effluents by removal of potentially hazardous substances, sewage treatment plants include various stages of wastewater treatments. However, several studies have demonstrated that many organic compounds such as persistent organic pollutants, pharmaceuticals, personal care products, hormones and other disrupting compounds escape treatments becoming ubiquitous in the environment [3–9]. This impact can be reduced with enhanced wastewater treatment technologies using advanced oxidation processes [10,11]. The development of these thorough wastewater treatment technologies combined with comprehensive quality control strategies comprising chemical and microbiological markers is required in order to fully characterize these systems, with the late goal of possible wastewater reuse of the effluents for selected applications such as agriculture, to apply in regions or countries with water shortage.

For a detailed chemical characterization related to the presence and amount of priority pollutants, analytical methodologies should be able to both confirm the presence and accurately determine low levels of any pollutant detected. Gas chromatography (GC) has been the technique of choice for the analysis of non-polar and relatively volatile substances in environmental samples, because of its high selectivity, precision and sensitivity, particularly when combined with mass spectrometry (GC–MS) as detection technique [12,13]. GC–MS is a powerful tool for the identification and quantitation of organic compounds in complex samples. Several methods have been developed for the analyses of organic contaminants in water samples based on GC–MS [14–23], typically using single quadrupole analyzer in selected ion monitoring acquisition mode.

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Due to the high complexity of wastewater samples in comparison to surface waters a particularly sensitive and selective detection methods are required [24,25]. This extra selectivity can be provided during the detection step using GC–MS instruments operating in MS/MS acquisition mode using an ion trap [26] or a triple quadrupole instrument [27], or with high resolution capabilities [28,29]. In both cases, excellent selectivity and sensitivity is achieved enabling the simultaneous unambiguous confirmation (according to EU guidelines [30]) and quantitation of the targeted analytes.

Double focusing magnetic sector mass spectrometers are most often used for applications where high resolution and sensitivity are the primary requirements. As far as we know, it has not been explored in wastewater analysis, where the reliable quantification and confirmation of many organic pollutants is required at very low concentration levels, according to the present and future environmental regulations. The high resolution enables many chemical background masses to be eliminated and consequently allows a lower level of detection for a number of specific target compounds to be achieved. The highest sensitivity can be achieved by performing selected ion recording as this provides a better duty cycle than scanning. In the present work, an analytical methodology for the determination of 14 selected priority organic pollutants in effluent wastewater samples using gas chromatography high-resolution mass spectrometry (GC–HRMS) is reported for the first time. The 14 EU priority substances included were: trichlorobenzenes isomers, pentachlorobenzene, hexachloro-1,3-butadiene, hexachlorobenzene, HCH isomers, alachlor and polybrominated diphenyl ethers (PBDEs). The proposed methodology comprised a sample treatment step based on liquid–liquid extraction followed by identification and quantitation of the target species by GC–HRMS in high resolution selected ion monitoring mode. The proposed method was applied to monitor the selected priority pollutants in different effluent wastewater samples from 5 Spanish sewage treatment plants with different profiles in terms of main activity (urban, industrial, coastal, etc.).

2. Experimental

2.1. Chemicals and reagents

1,2,3-Trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, hexachloro-1,3-butadiene, pentachlorobenzene, hexachlorobenzene, alachlor and mixture (1:1:1:1) of hexachlorocyclohexane isomers (α-hexachloro-cyclohexane α-(HCH), β-HCH, γ-HCH (lindane), δ-HCH), were purchased from Riedel-de-Haën (Seelze, Germany), PESTANAL™ quality. Polybrominated diphenyl ether (PBDEs) mixture (tetra-brominated diphenyl ether (tetra-BDE), penta-brominated diphenyl ether (penta-BDE) and hepta-brominated diphenyl ether (hepta-BDE)) was obtained from Dr. Ehrenstorfer (Ausburg, Germany). Individual stock standard solutions of the target compounds were prepared in methanol (HPLC-grade, Merck, Darmstadt, Germany) at a concentration of 1 mg mL^{-1} and stored at −20 °C. Working solutions, at different concentrations, were prepared by appropriate dilution of the stock solutions in n-hexane. n-Hexane was obtained from Riedel-de-Haën (Seelze, Germany), PESTANAL™ quality. Sodium chloride and anhydrous sodium sulfate (pesticide residue analysis quality) were ordered to J.T. Baker (Phillipsburg, NJ, USA). Sulphuric acid was purchased from Panreac (Barcelona, Spain).

2.2. Wastewater sampling

Wastewater samples used in this study were collected from 5 municipal sewage treatment plants (STPs) (Fig. 1). Two were located in North Spain (Castro Urdiales and Santander (Cantabria), both mainly with urban activity), two located in the centre (both in Alcalá de Henares, Madrid; one STP mainly with urban activity, and the other mainly with industrial activity), and one located in the southeast of Spain (El Ejido, Almería). This later plant treats urban wastewater with important contributions from greenhouses, plastic industry also related to greenhouses, and from a local hospital. Input wastewater undergoes a physical pre-treatment to remove coarse solids and greases, primary settling of particulates, and secondary treatment with activated sludge, after which the water is discharged to the sea. They are representative of different activities (urban, agricultural, industrial). All plants apply a pre-treatment for solid removal, a primary treatment to eliminate suspended material, an activated sludge biological treatment, and a final clarification. Integrated samples representative of 1-day work in the STP were taken. They were taken at 3-h intervals. Sampling was carried out by an automatic device (0.5 L/3 h). Effluent samples were collected by using pre-rinsed amber glass bottles and sent to the laboratory for sample treatment and for analysis. All samples were filtered through a 0.7-μm glass fiber filter (Millipore, Milford, MA, USA) and extracted within 48 h in all the cases. Before the extraction, samples were kept at +4 °C in the fridge.

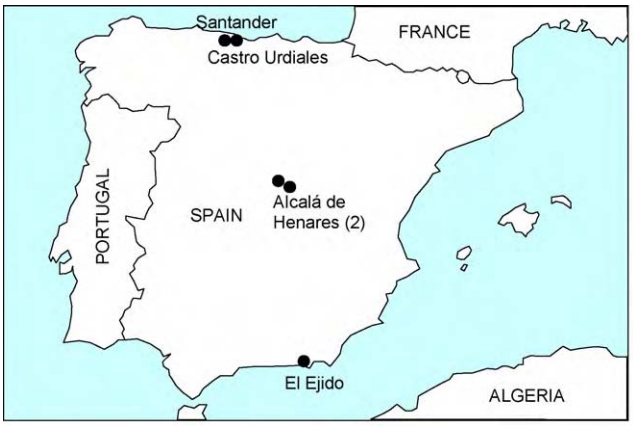

Fig. 1. Geographical location of the studied sewage treatment plants.

2.3. GC–HRMS system and operating conditions

GC–HRMS analyses were run on a HP 6890 Series gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA) interfaced to a double focusing magnetic sector mass analyzer (Micromass AutoSpec NT (Micromass, Manchester, UK)), operating in high resolution selected ion recording mode (HR SIR) with the following operating parameters: ionization mode: electron ionization with 70 eV energy; ion repeller (V) = −134 V; detector: 300 V. Perfluorokerosene (mass-lock) were used for accurate mass calibration purposes. Data acquisition and processing, and instrumental control were performed by MassLynx 4.1 software (Micromass, Manchester, UK).

Analytes were separated in a ZB-5MS capillary column (5% diphenyl/95% dimethylsiloxane), 30 m × 0.25 mm i.d., 0.25 μm film thickness (Phenomenex, Torrance, CA, USA). A split/splitless injector was used in pulse splitless mode. The injector operating conditions were as follows: injection volume 1 μL; injector temperature 250 °C; initial pulse pressure: 30 psi (1.5 min). The helium (99.9999% purity) carrier gas flow was maintained at 1 mL min^{-1}. The oven temperature programme was 2.0 min at 70 °C, 10 °C min^{-1} to 180 °C (keeping 180 °C for 5 min), 6 °C min^{-1} to 260 °C and 4 °C min^{-1} to 300 °C.

Table 1
Identification of priority organic pollutants in wastewater by gas chromatography high-resolution mass spectrometry using two ions for identification and confirmation purposes.

Compound	Ret. time (t_R)	m/z ion 1 (Q)	Elemental composition ion 1	m/z ion 2 (q) (relative abundance (%))	Elemental composition ion 2
1,3,5-Trichlorobenzene	5.45	179.929	$C_6{}^{35}Cl_3H_3$	181.926 (96)	$C_6{}^{35}Cl_2{}^{37}ClH_3$
1,2,4-Trichlorobenzene	6.12	179.929	$C_6{}^{35}Cl_3H_3$	181.926 (96)	$C_6{}^{35}Cl_2{}^{37}ClH_3$
1,2,3-Trichlorobenzene	6.66	179.929	$C_6{}^{35}Cl_3H_3$	181.926 (96)	$C_6{}^{35}Cl_2{}^{37}ClH_3$
Hexachloro-1,3-butadiene	6.73	224.844	$C_4{}^{35}Cl_5$	222.841 (63)	$C_4{}^{35}Cl_4{}^{37}Cl$
Pentachlorobenzene	11.27	249.849	$C_6{}^{35}Cl_5{}^{37}ClH$	251.846 (65)	$C_6{}^{35}Cl_4{}^{37}Cl_2H$
α-HCH	13.14	180.934	$C_6{}^{35}Cl_3H_4$	182.934 (96)	$C_6{}^{35}Cl_2{}^{37}ClH_4$
β-HCH	13.83	180.934	$C_6{}^{35}Cl_3H_4$	182.934 (96)	$C_6{}^{35}Cl_2{}^{37}ClH_4$
γ-HCH	13.97	180.934	$C_6{}^{35}Cl_3H_4$	182.934 (96)	$C_6{}^{35}Cl_2{}^{37}ClH_4$
δ-HCH	14.71	180.934	$C_6{}^{35}Cl_3H_4$	182.934 (96)	$C_6{}^{35}Cl_2{}^{37}ClH_4$
Hexachlorobenzene	12.80	283.809	$C_6{}^{35}Cl_5{}^{37}Cl$	285.807 (80)	$C_6{}^{35}Cl_4{}^{37}Cl_2$
Alachlor	16.53	160.1126	$C_{11}H_{14}N$	188.107 (71)	$C_{12}H_{14}NO$
Tetra-BDE	28.18	485.711	$C_{12}O^{79}Br_2{}^{81}Br_2H_6$	487.709 (65)	$C_{12}O^{79}Br^{81}Br_3H_6$
Penta-BDE	31.02	563.621	$C_{12}O^{79}Br_3{}^{81}Br_2H_5$	565.619 (98)	$C_{12}O^{79}Br_2{}^{81}Br_3H_5$
Hepta-BDE	31.81	563.621	$C_{12}O^{79}Br_3{}^{81}Br_2H_5$	565.619 (98)	$C_{12}O^{79}Br_2{}^{81}Br_3H_5$

2.4. Sample treatment

2.4.1. Liquid–liquid extraction (LLE) procedure for the isolation and preconcentration of priority organic pollutants

Samples without filtration were acidified up to pH 3 (with H_2SO_4 1 M). An aliquot of 200 mL of influent or effluent wastewater sample were loaded in a 250-mL separatory funnel with 250 mg of NaCl in which a three-step liquid–liquid extraction was undertaken. 25 mL of n-hexane were added and the mixture was vigorously shaken for 3 min being then the organic phase (upper) separated from the aqueous one. Then, this extraction step was repeated three times. The organic phases were combined and water traces were removed by adding sodium sulfate anhydrous. The extract was then carefully evaporated up to near dryness using a vacuum rotary evaporator (Büchi Rotavapor R200) equipped with a heating bath (Büchi B-490) operating at 30 °C and a vacuum controller (Büchi V800) operating at 150–175 mm Hg. Finally, the residue was re-dissolved with 2 mL of n-hexane.

2.5. Validation of the proposed method

All the validation studies were performed by using sewage extracts taken from a mixture of the STP effluents from the 5 different STPs. Because of the impossibility to obtain blanks, the samples were previously analyzed and the presence of the target compounds considered. To minimize matrix effects, matrix-matched calibration curves were used for quantitative determinations. The linearity in the response was studied by using matrix-matched calibration solutions prepared by spiking effluent wastewater effluent extracts at five concentration levels, ranging from the determination limit of each analyte to 200 $\mu g\,L^{-1}$ in the final extract (note 100:1 preconcentration factor from the sample treatment). Each point was obtained as the average of three injections. Integrated peak area data of the selected accurate masses of ions (see Table 1) were used to construct the curves. To optimize the analytical procedure, the recovery studies were carried out by spiking effluent wastewater samples at the concentration level of 0.1 and 1 $\mu g\,L^{-1}$ ($n = 6$), in accordance with the approximate maximum concentration levels established by EU regulations for water intended for human consumption [31]. The method detection limit (MDL) and method quantification limit (MQL) were determined experimentally from the injection of spiked wastewater samples and calculated using the minimum concentration of analyte providing signal-to-noise ratios of 3 and 10, respectively. They were estimated from the spiked extracted ion chromatograms at the lowest analyte concentration assayed. Confirmation criteria applied to the target compounds in the wastewater effluent samples were as follows: presence of two characteristic ions at the correct retention time, with the characteristic relative ion abundances and the correct targeted accurate mass. Quantification was performed by external standard calibration.

3. Results and discussion

3.1. Identification and confirmation of selected target priority pollutants by gas chromatography high-resolution mass spectrometry

The aim of this article is to develop a multi-residue method for ultratrace detection of multiclass priority pollutants in sewage wastewater treatment plants effluents. Fourteen compounds of the EU-Water Framework Directive were selected. The identification of the targeted species was performed using GC/high-resolution mass spectrometry with a double focusing magnetic instrument. The analyzer used has a three-sector, double focusing geometry of type electrostatic analyzer/magnet/electrostatic analyzer. This instrument was used in high-resolution selective ion recording HRSIR at a resolution value of 10.000 permitting the accurate identification of the targeted compounds. For identification and confirmation purposes, the accurate mass of two characteristic ions and their relative abundances were combined with retention time matching. Therefore, the proposed criteria is in compliance with the EU criteria (Commission Decision 2002/657/EC) [30] related to the confirmation of veterinary chemicals in food/feed based on identification points (IPs) (2 points gained per detection ion with high resolution MS; 3–4 IPs required for unambiguous confirmation depending on the substance). In most cases, molecular ions were chosen for the HRMS analysis in order to enhance selectivity and sensitivity. Table 1 includes the selected ions used for identification and quantitation purposes and their corresponding elemental compositions.

Instrument dwell time was optimized with the aim of obtaining a good chromatographic peak shape (with at least 10 points recorded per peak) while maintaining satisfactory sensitivity for each compound. To obtain the maximum possible analyte signal, a 50-ms dwell time was selected for each of the monitored ions. To some extend, this might become a limitation of the method/instrument when dealing with large-scale multi-residue methods (i.e. >80 targeted species) using GC–HRMS. The average width of the chromatographic peaks is *ca.* 4 s, which involves a maximum acquisition time per point of 0.4 s – assuming 10 point peak for an appropriate peak shape. This involves that only 8 ions (4 compounds) can be screened at the same time (time segment window). In contrast, the typical dwell time of state-of-the-art GC–MS/MS (triple quadrupole) instruments is 10–25 ms (*ca.* 1/5 or 1/2 compared to GC–HRMS dwell time). Therefore, the capacity of monitoring compounds is between 2 and 3 times

higher. The main drawback associated with this issue is that a dedicated effort would be required if it is required to develop a large-scale multi-residue method, including several scheduled time segments throughout the chromatographic run. On the other hand, the sensitivity and selectivity provided by high resolution are remarkable as demonstrated by the analytical features of the method.

3.2. Performance of the sample treatment procedure

Optimization of the extraction procedure was made with the aim of reaching good recoveries for the widest group of compounds in a single extraction step. To extract the targeted species from sewage wastewater treatment plant effluents, liquid–liquid extraction (LLE) method was developed. Before selecting the LLE procedure, different procedures based on solid-phase extraction were tested. Using C_{18} (500 mg, 6 mL, BondElut™, Varian Inc., Palo Alto, CA, USA) cartridges and elution with 1:1 ethyl acetate/dichloromethane (v/v) or with hexane:acetone, poor recoveries (<15%) were obtained in the case of trichlorobenzenes, hexachlorobenzene and pentachlorobenzene. Note that the compounds included in the method have very different physico-chemical properties. Therefore, it was not straightforward to obtain optimized conditions, in which all the compounds were quantitatively recovered. Finally, LLE using n-hexane was assayed with 200 mL of sample volume and three extractions with 25 mL of solvent. The effluent sample was not filtered before LLE. The pre-treatment was limited to adjust the pH to 3–4. With that approach the overall recoveries for the different classes of compounds tested were satisfactory. Only for trichlorobenzenes and hexachloro-1,3-butadiene the recovery rates (shown in Table 2) are relatively lower. The recovery studies were performed at two concentration levels: 0.1 μg L^{-1} and 1 μg L^{-1} level, obtaining satisfactory recovery rates in the range 39.5–117.5% with RSD (%) values (n = 6) between 2.1 and 15.3%. Only trichlorobenzenes and hexachlorobutadiene displayed relatively low recovery rates probably due to their high volatility and vapor pressure [32].

Table 2
Recovery studies of the targeted priority compounds in effluent wastewater samples spiked at two concentration levels: 0.1 and 1 μg L^{-1}.

Compound	Recovery (%) (n = 6)			
	Conc. level. 0.1 μg L^{-1}	RSD (%)	Conc. level. 1 μg L^{-1}	RSD (%)
1,3,5-TCB	47.7	8.2	43.1	9.6
1,2,4-TCB	53.2	10.5	58.8	9.3
1,2,3-TCB	58.7	9.7	63.6	7.1
Hexacloro-1,3-butadiene	39.5	11.9	42.0	12.5
Pentachlorobenzene	88.2	5.7	84.2	7.1
α-HCH	93.0	6.3	109.3	2.1
β-HCH	96.3	4.9	92.4	9.1
γ-HCH	91.5	6.7	108.1	6.1
δ-HCH	89.7	7.5	99.0	11.8
Hexachlorobenzene	85.2	5.5	79.7	6.6
Alachlor	109.3	6.3	117.5	4.4
Tetra-BDE	97.1	12.1	84.7	14.6
Penta-BDE	81.3	11.8	94.5	15.3
Hepta-BDE	96.5	10.6	106.8	9.5

3.3. Analytical performance of the proposed method

To evaluate the analytical performance of the proposed method based on GC–HRMS, a detailed study was carried out including the linearity, accuracy and limits of detection of the selected contaminants. The results obtained are shown in Table 3. The linearity of the proposed method was studied in the range 0.01–2 μg L^{-1} (note that the sample volume used was 200 mL and the preconcentration factor 100:1). Correlation coefficients (r) > 0.99 were obtained in most cases.

Inter-day and intra-day accuracy was studied with matrix-matched standards spiked at 50 μg L^{-1}. The results obtained for intra-day study were below 15% in most cases. Limits of detection (LODs) were estimated from the injection of matrix-matched standard solutions at 0.01 μg L^{-1} concentration level. LODs and LOQs were assigned taking into account signal-to-noise (S/N) ratio criterion (S/N of about 3 for LOD and S/N of about 10 for LOQ) in the qualifier ion. The results obtained for each compound are included in Table 3. In preliminary studies, we also tested GC-ECD (Varian CP3800 GC) detection with the same chromatographic method, as long as it is a cheaper instrument that can be implemented in routine laboratories. Nevertheless, considering the concentration levels that are usually found in the samples, the use of a GC-ECD may not provide enough analytical performance in terms of sensitivity to detect the species. In addition, a confirmatory MS analysis is necessary due to the complexity of the matrix (note the low preconcentration factor implemented in the method (100:1) due to the relatively complexity of the extracts). The results in terms of LOQs for GC-ECD analysis are also shown in Table 3. From the data shown in Table 3, it can be observed the low detection levels achieved by using GC–HRMS, as low as 90 pg L^{-1} for tetra-BDE, and overall in the low ng L^{-1} level. An example of the identification of the target species in wastewater samples by GC–HRMS is shown in Fig. 2.

Table 3
Analytical parameters of the proposed method for the quantitation in effluent wastewater samples by gas chromatography high-resolution mass spectrometry.

Compound	Conc. range tested (ng L^{-1})[a]	Regression (correlation coefficient) (r)	MLOD (ng L^{-1})	MLOQ (ng L^{-1})	LOQ (ng L^{-1}) (GC-ECD)[b]
1,3,5-TCB	10–2000	0.997	0.9	3	100
1,2,4-TCB	10–2000	0.989	0.9	3	100
1,2,3-TCB	10–2000	0.996	0.9	3	60
Hexachloro-1,3-butadiene	10–2000	0.999	0.225	0.75	30
Pentachlorobenzene	10–2000	0.995	0.3	1	30
α-HCH	10–2000	0.997	1.2	4	200
β-HCH	10–2000	0.999	1.8	6	250
γ-HCH	10–2000	0.999	1.2	4	200
δ-HCH	10–2000	0.994	1.8	6	200
Hexachlorobenzene	10–2000	0.999	0.3	1	30
Alachlor	10–2000	0.997	3	10	250
Tetra-BDE	10–2000	0.990	0.09	0.3	100
Penta-BDE	10–2000	0.999	0.15	0.5	50
Hepta-BDE	10–2000	0.996	0.3	1	50

[a] Preconcentration factor (100:1) considered.
[b] GC-ECD analyses were performed using the same chromatographic method, injection volume, column and instrument.

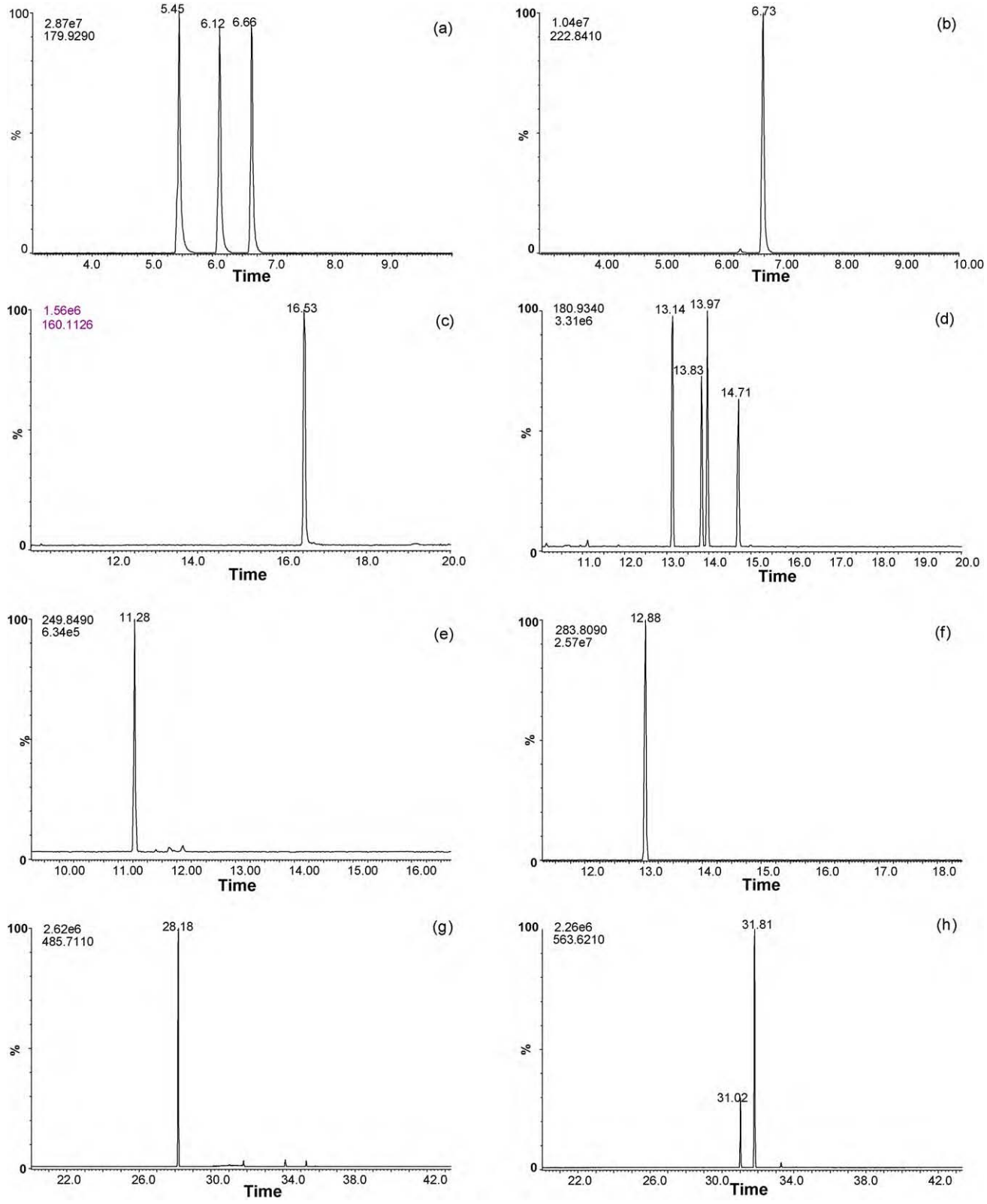

Fig. 2. GC–HRMS extracted ion chromatograms of a sewage effluent matrix-matched standard mixture at 0.5 μg L^{-1} containing all target compounds: (a) trichlorobenzene; (b) hexachlorobutadiene; (c) alachlor; (d) HCHs; (e) pentachlorobenzene; (f) hexachlorobenzene; (g) tetra-BDE; (h) penta- and hepta-BDE.

3.4. Application of the proposed method for the monitoring of 5 selected Spanish STPs

The proposed method was successfully tested on a monitoring program in order to control the presence of these species in sewage treatment plants effluents. Table 4 shows preliminary results obtained from the monitoring program initiated. Concentration range and mean values of the target compounds detected in 36 samples collected in the studied STPs are shown. All the compounds initially selected were detected with the exception of

Table 4
Results of the monitoring of priority pollutants from five Spanish sewage treatment plants.

Location/compound(s)	Samples tested	% positives	Concentration range (ng L^{-1}) of positive samples	Average concentration (ng L^{-1})
STP Alcalá de Henares, Madrid (mainly urban)				
Σ TCBs	15	100	2.71–25.6	6.96
Hexachlorobutadiene	15	20	8.3–109.32	14.00
Hexachlorobenzene	15	100	5.3–135.89	38.69
Pentachlorobenzene	15	73	0.22–1.80	0.63
Σ Hexachloro-cyclohexane	15	66.7	0.46–9.28	2.30
Alachlor	15	0	–	0.00
Σ PBDEs	15	20	0.37–0.63	0.10
STP Alcalá de Henares, Madrid (urban-industrial)				
Σ TCBs	13	92.3	2.41–48.9	8.57
Hexachlorobutadiene	13	15.4	9.3–77.32	19.28
Hexachlorobenzene	13	100	8.15–81.72	41.00
Pentachlorobenzene	13	76.9	0.19–1.91	0.53
Σ Hexachloro-cyclohexane	13	61.5	0.67–9.35	2.52
Alachlor	13	0	–	0.00
Σ PBDEs	13	23.1	1.73–11.29	1.21
STP El Ejido, Almeria (coastal-agricultural)				
Σ TCBs	4	100	5.36–15.31	12.16
Hexachlorobutadiene	4	0	–	0.00
Hexachlorobenzene	4	100	16.34–113.78	49.59
Pentachlorobenzene	4	75	1.18–1.82	1.10
Σ Hexachloro-cyclohexane	4	100	2.03–33.14	18.84
Alachlor	4	0	–	0.00
Σ PBDEs	4	50	1.82–2.48	1.08
STP Castro Urdiales, Cantabria (mainly urban)				
Σ TCBs	2	100	5.97–14.05	10.01
Hexachlorobutadiene	2	0	–	0.00
Hexachlorobenzene	2	100	17.23–20.22	18.73
Pentachlorobenzene	2	100	0.69–0.70	0.70
Σ Hexachloro-cyclohexane	2	100	11.31–17.74	14.53
Alachlor	2	0	–	0.00
Σ PBDEs	2	0	–	0.00
STP Santander, Cantabria (mainly urban)				
Σ TCBs	2	100	15.25–18.12	16.69
Hexachlorobutadiene	2	0	–	0.00
Hexachlorobenzene	2	100	12.58–17.86	15.22
Pentachlorobenzene	2	100	0.53–0.68	0.61
Σ Hexachloro-cyclohexane	2	100	10.61–30.43	20.52
Alachlor	2	0	–	0.00
Σ PBDEs	2	50	0.77	0.39

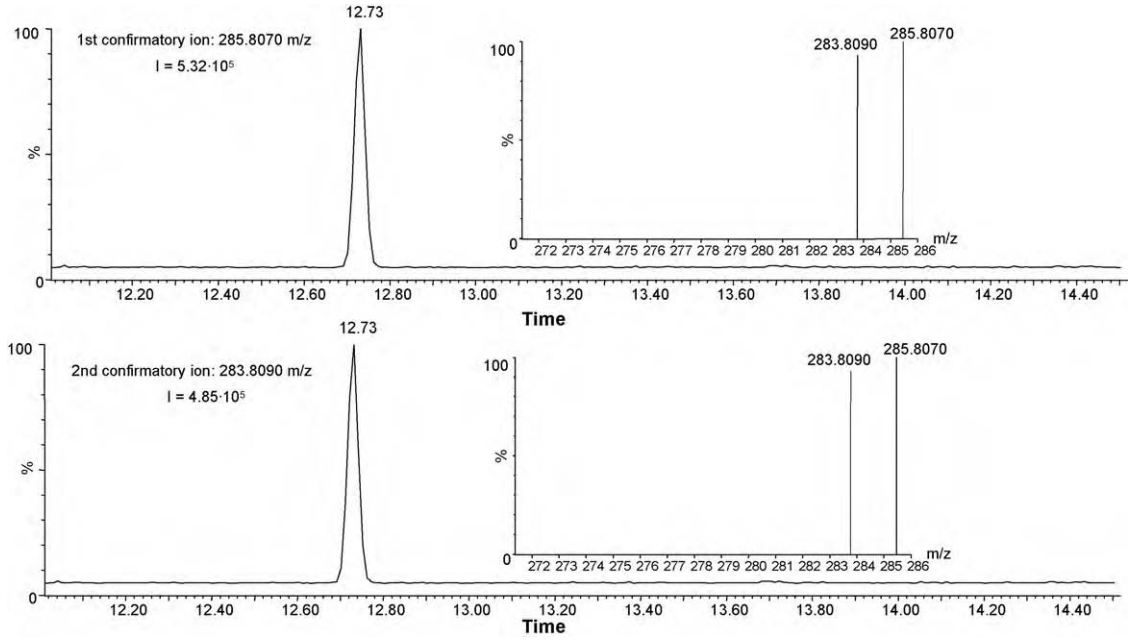

Fig. 3. Determination of priority organic pollutants in wastewater treatment plants effluents by GC–HRMS. Example of a positive in an effluent WW sample (San Roman (Santander)), containing 45 ng L^{-1} of hexachlorobenzene.

alachlor. The more frequently detected one was hexachlorobenzene, which was found in all the studied samples at concentrations in the range 5–135 ng L^{-1}. As an example, Fig. 3 shows the chromatograms obtained in an effluent wastewater sample containing 45 ng L^{-1} of hexachlorobenzene. From the preliminary data collected, it can be remarked that, in general, the concentration levels are relatively low, and represents a small amount when compared to the load of the so-called emerging contaminants, which can be found in the microgram per liter level according to different studies [6,33,34]. Anyhow for a comprehensive evaluation and risk analysis, the data on priority contaminants is very important, because of their high relative toxicity in comparison with emerging contaminants [6].

4. Concluding remarks

In this work, an analytical methodology for the ultratrace detection and quantitation of priority organic pollutants in wastewater samples has been described. The data shown in the article with the ability to determine as low as a few picograms per liter of the selected contaminants in wastewater samples reveals the usefulness of GC–HRMS as a powerful tool to monitor priority pollutants (2455/2001/CE Directive) in wastewater samples. The proposed methodology was applied to the characterization of effluents from various STPs. The concentration levels found are in most cases below the maximum concentration permitted for these species in water samples intended for human consumption [31]. Further work should be accomplished to monitor emerging contaminants since they are usually present at higher concentration levels, as they represent the major contribution to the charge of contaminants in wastewater samples (>25000 ng L^{-1}) [6,33,34]. An exhaustive knowledge and characterization of the behavior of main organic pollutants in sewage treatment plants will prompt the development of technologies for the promotion of the sustainable wastewater treatment and reuse.

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