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Validation of a method for the analysis of 77 priority persistent organic pollutants in river water by stir bar sorptive extraction in compliance with the European Water Framework Directive

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ABSTRACT

A multi-residue method for the analysis of semi-volatile organic pollutants in inland groundwater (river water) at ultra-trace levels in compliance with the European Water Framework Directive (WFD) has been developed and validated by stir bar sorptive extraction (SBSE) and thermal desorption coupled with gas chromatography–triple quadrupole mass spectrometry (SBSE-TD–GC–MS/MS(QqQ)). The method includes various families of compounds included in the WFD and other compounds listed as persistent organic pollutants that are banned in the Stockholm Convention of Persistent Organic Pollutants, such as polychlorinated biphenyls, polycyclic aromatics hydrocarbons, and other pesticides not included in the WFD. The method also can be applied for compliance with regional environmental laws. Extraction conditions were optimised in order to analyse simultaneously analytes with very different polarities and octanol–water partition coefficients, which is an important parameter in the optimisation of a SBSE method. The quantification limits (LOQs) obtained ranged from 0.14 to 10 ng L^{-1}, lower that others presented in previous publications, and complies with the requirement for analytical methods to be used in the analysis of the compounds included in the WFD. Several quality parameters as linearity, trueness and precision were studied with good results, and also uncertainty was estimated. The WFD requires that the level of uncertainty must be lower than 50%, and this requirement was met for all compounds. Precision (in terms of RSD) was lower than 30%, recoveries ranged between 74 and 111%, and determination coefficients were higher than 0.990 for all analytes. Different factors that affect the SBSE procedure were optimised. GC–MS/MS parameters have also been revised. The accuracy of the method was tested participating in a proficiency testing scheme for each group of analytes.

1. Introduction

Water is the mainstay of the environment and its degradation has serious consequences: protecting the water means protecting the ecosystems of which it forms an inseparable part. Waters are subject to great risk, primarily due to pollution and the growing need for quality water. These risks compromise their sustainable long-term availability so measures are needed to reverse negative trends, enable the protection of water, prevent deterioration and restore those waters that are in poor condition. The European Union is going to great lengths to improve water quality, one sign of which is the European Water Framework Directive (WFD) adopted in the year 2000 [1].

The purpose of this directive is to establish a protective framework for all inland surface waters, transitional waters, coastal waters, and groundwater in order to prevent deterioration and promote their sustainable use through protection in the medium and long term. This target must be achieved in each hydrographic basin by the year 2015. Therefore, by 2015 all EU waters should be in good condition. Decision No. 2455/2001/EC approved the list of priority substances that should be tested [2], which was followed by Directive 2008/105/EC, which established environmental quality standards (EQS) in the field of the WFD [3]. The latter establishes the maximum allowable concentrations of priority substances in different types of waters.

The WFD is a highly complex legal and technical document and the quantification limits required are extremely low. The WFD states that the methods used for the control of substances must comply with a LOQ equal to or less than 30% of the annual average environmental quality standard (AA-EQS), which are in the pg L^{-1} range of in some cases. The listed substances are classified into

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three main groups: metals (Cd, Pb, Hg and Ni), volatile organic compounds (benzene, carbon tetrachloride, 1,2-dichloroethane, dichloromethane, tetrachloroethene, trichloroethene naphthalene, and trichlorobenzenes), and semi-volatile organic compounds.

For metals the most appropriate technique is ICP-MS and for volatile organic compounds the most suitable technique is purge and trap and subsequent analysis by gas chromatography–mass spectrometry (GC–MS). Semi-volatile compounds belong to very different families, and sometimes each must be analysed by an exclusive technique or method, such as tributyltin [4–7] or C_{10-13} chloroalkanes (short-chained chlorinated paraffins (SCCP)) [8,9]. For the rest of the compounds, some multi-residue methods employing different techniques [10–19] have been proposed and many of them are international standard methods. But, to our knowledge, no method analyses all the compounds together. Some compounds are amenable to analysis by GC (PBDEs, organophosphorous pesticides), by liquid chromatography (PAH) or by both (tributyltin). Multi-residue methods that can analyse a larger number of substances with low detection limits are needed [20–22].

The technique of stir bar sorptive extraction extractive (SBSE) [23] has proven effective for all the compounds that we need to analyse, and there is practically one method for each family of compounds documented, from which good results were obtained in all cases [24–33], but no publication presents a multi-residue method where all semi-volatile compounds included in the WFD were analysed, and publications that do analyse a great number of them, do not meet the limits of quantification required.

The main objective of the present work is to establish and validate a multi-residue method for analysing semi-volatile compounds amenable to analysis by SBSE. In order to analyse polar and non-polar analytes with only one extraction step the main influencing factors were evaluated and optimised. One important improvement over previously published methods is that the determination of the analytes was performed by triple quadrupole mass spectrometry (QqQ), two transitions for each analyte were measured simultaneously, and better identification and confirmation of the compounds even at ultra-trace levels can be achieved. Using the multi-residue possibilities of these techniques other pollutants not listed in the WFD, for example, persistent contaminants and endocrine disruptors such as PCBs, pesticides and PAHs, were also included in the method. These pollutants were considered organic pollutants in the Stockholm Convention [34–36] or included in local regulations [37].

2. Experimental

2.1. Chemicals and reagents

Water was purified with a Milli-Q plus system (Millipore, Bedford, USA). Pesticide quality solvents (methanol and acetone) and sodium chloride analytical grade were purchased from Panreac (Barcelona, Spain). A mixture of 20 organochlorine pesticides with a concentration of 1000 mg L^{-1} in toluene:hexane (EPA 8081 organochlorine pesticides mix containing aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, α-chlordane, γ-chlordane, 4,4′-dichlorodiphenyl trichloroethane (4,4′-DDT), 4,4′-dichlorodiphenyldichloroethylene (4,4′-DDE), 4,4′-dichlorodiphenyldichloro ethane (4,4′-DDD), α-endosulfan, β-endosulfan, endosulfan sulphate, heptachlor, heptachlor epoxide, α-hexachlorocyclohexane (α-HCH), β-hexachlorocyclohexane (β-HCH), δ-hexachloro cyclohexane (δ-HCH), lindane and methoxychlor); a mixture of 12 polycyclic aromatic hydrocarbons at a concentration of 100 mg L^{-1} in acetonitrile (EPA 610 PAH mix containing phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluorantene, benzo[g,h,i]perylene, dibenz[a,h]anthracene benzo[a]pyrene, and indeno[1,2,3-cd]pyrene); and ten individual polychlorinated biphenyls (PCB 8, 20, 28, 35, 52, 101, 118, 138, 153, and 180) at a concentration of 100 mg L^{-1} in isooctane were purchased from LGC Standard (Teddington, Middlesex, UK). A mixture of six polybrominated diphenyl ether congeners (PBDE 28, 47, 99, 100, 153 and 154) at a concentration of 20 mg L^{-1} in isooctane was purchased from Accustandards (New Haven, CT, USA). Individual pure standards of the rest of the analytes were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

Three of the four surrogates selected (triphenylphosphate (TPP), dibenz[a,h]anthracene D14 and simazine D10) were purchased individually at a concentration of 10 mg L^{-1} in methanol from Dr. Ehrenstorfer GmbH, and 2,2′,3,4,4′,5,6-heptabromodiphenyl ether was purchased from Accustandard at a concentration of 50 μg L^{-1} in isooctane.

For the individual solid pesticides, standard solutions were prepared by weighing 20 mg of pure standard and diluting in 50 mL of acetone. From these individual solutions, a 100 mL multi-compound methanolic standard stock solution (No. 1) was prepared, at a concentration of 2 mg L^{-1}. Stock solution No. 2 includes the six PBDEs at 0.2 mg L^{-1} in acetone, the No. 3 the 12 PAHs at 1 mg L^{-1} in methanol and the No. 4 the ten PCBs at 1 mg L^{-1} in acetone. Finally, stock solution No. 5 was a mixture of organochlorine pesticides and o,p′-DDT at 0.5 mg L^{-1}, and isodrin at 1.0 mg L^{-1} in methanol. A mixture of the four surrogates was also prepared in methanol at a concentration of 10 μg L^{-1} for heptabromodiphenyl ether, 300 μg L^{-1} for Simazine D10, 50 μg L^{-1} for TPP and 20 μg L^{-1} for dibenz[a,h]anthracene D14.

Proficiency testing samples for PBDE, organochlorinated and organophosphorous pesticides and triazines were provided by Resource Technology Corp (Laramie, Wyoming, USA). For PAH and PCBs, samples were provided by LGC (Teddington, Middlesex, UK).

2.2. Instrumentation and software

The gas chromatograph was an Agilent 7890 GC (Agilent Technologies, Palo Alto, CA, USA) equipped with a CIS-4 programmable temperature vaporisation (PTV) inlet, a thermal desorption unit (TDU), and a multipurpose (MPS) autosampler to automatically introduce the twisters into the TDU system (Gerstel, Mülheim an der Ruhr, Germany). The detector was an Agilent 7000B triple quadrupole mass spectrometer with inert electron-impact ion source. The mass spectrometer worked in selected reaction monitoring (SRM) mode and electron impact (EI) mode at 70 eV. For control and data analysis, Agilent MassHunter B.03.02 was used. Helium with a purity of 99.9999% was used as carrier gas and quenching gas (a special gas employed in the Agilent 7000 mass spectrometer), and nitrogen with a purity of 99.999% as collision gas, both of which were supplied by PRAXAIR España S.L. (Madrid, Spain). The capillary column was a HP-5MS 30 m × 0.25 mm i.d. × 0.25 μm d_f.

For aqueous sample extraction, PDMS stir bars (twisters) were provided by Gerstel and two different sizes were tested: 0.5 mm (PDMS thickness) × 10 mm (length) and 0.5 mm × 20 mm. After method optimisation, 0.5 mm × 20 mm twisters were selected for further analysis because they had the highest sensitivity. Water samples were stirred with a nine-position digital multiple stirrer purchased from Ovan (Badalona, Spain).

2.3. Sample extraction procedure

Prior to extraction, all samples were filtered through a filter paper in order to remove particulate material. Then, 200 mL of the sample or blank was placed in an Erlenmeyer flask, 10 g of NaCl

Table 1
Mass spectrometry parameters for the GC–MS/MS method.

Compound	Precursor (Da)	Product (Da)	Dwell time (ms)	CE (V)	t_R (min)	TS
Isoproturon (degradation)	146.0	128.0	60	10	5.06	1
Isoproturon (degradation)	161.1	146.0	60	5		
Diuron (degradation)	186.9	124.0	60	20	6.50	
Diuron (degradation)	186.9	159.0	60	10		
Mevinphos	127.0	109.0	50	10	7.13	2
Mevinphos	192.0	127.0	50	10		
Pentachlorobenzene	249.8	215.0	50	25	8.50	
Pentachlorobenzene	249.8	179.0	50	25		
Trifluralin	305.9	264.1	40	5	11.16	3
Trifluralin	263.9	160.1	40	15		
PCB 8	221.9	152.1	40	20	11.53	
PCB 8	223.9	152.1	40	20		
HCH alfa isomer	218.8	183.0	40	5	11.60	
HCH alfa isomer	180.9	145.0	40	12		
Hexachlorobenzene	286.0	251.0	40	20	11.89	
Hexachlorobenzene	284.0	249.0	40	20		
Simazine	201.0	172.1	20	10	12.65	4
Simazine	186.0	68.1	20	25		
Simazine D10 (*IS*)	211.0	193.0	20	10	11.56	
Simazine D10 (*IS*)	211.0	179.0	20	10		
Atrazine	200.1	103.9	20	20	12.88	
Atrazine	200.1	94.1	20	20		
HCH beta isomer	218.8	183.0	20	5	12.98	
HCH beta isomer	180.9	145.0	20	12		
Lindane	218.8	183.0	20	5	13.12	
Lindane	180.9	145.0	20	12		
Phenanthrene	178.0	152.1	20	25	13.37	
Phenanthrene	178.0	176.1	20	25		
Terbuthylazine	229.0	173.0	20	20	13.51	
Terbuthylazine	229.0	138.0	20	10		
Trietazin	229.0	200.0	20	10	13.48	
Trietazin	229.0	186.0	20	20		
Fonofos	246.0	137.0	20	5	13.54	
Fonofos	246.0	109.1	20	15		
Antharecene	178.0	152.1	20	25	13.59	
Antharecene	178.0	176.1	20	25		
Diazinon	304.0	179.1	20	12	14.04	
Diazinon	179.0	137.2	20	20		
HCH delta isomer	218.8	183.0	20	5	14.39	
HCH delta isomer	180.9	145.0	20	12		
PCB 28	255.9	186.1	10	20	15.75	5
PCB 28	257.9	186.1	10	20		
PCB 20	255.9	186.1	10	20	16.35	
PCB 20	257.9	186.1	10	20		
Chlorpyrifos methyl	286.0	270.9	10	20	16.17	
Chlorpyrifos methyl	286.0	93.0	10	20		
Heptachlor	274.0	239.0	10	20	16.33	
Heptachlor	272.0	237.0	10	20		
Simetryn	213.0	170.0	10	10	16.59	
Simetryn	213.0	155.0	10	20		
Alachlor	160.1	131.1	10	10	16.85	
Alachlor	160.1	130.0	10	30		
Fenchlorphos	285.0	270.0	10	15	16.93	
Fenchlorphos	285.0	93.0	10	20		
Prometryn	241.2	183.9	10	10	17.06	
Prometryn	241.2	111.2	10	25		
PCB 52	289.9	255.0	10	10	17.60	
PCB 52	289.9	220.0	10	25		
Terbutrin	241.0	185.0	10	15	17.70	
Terbutrin	241.0	170.0	10	20		
Fenitrothion	277.1	124.9	10	15	17.65	
Fenitrothion	277.1	109.0	10	20		
Pirimiphos methyl	305.0	290.0	10	10	17.91	
Pirimiphos methyl	305.0	180.0	10	5		
Aldrin	263.0	193.0	30	30	18.05	
Aldrin	263.0	191.0	30	30		
PCB 35	255.9	186.1	10	20	18.25	
PCB 35	257.9	186.1	10	20		
Malathion	173.1	117.1	10	15	18.24	
Malathion	173.1	99.0	10	15		
Metolachlor	162.2	133.1	10	15	18.36	
Metolachlor	162.2	132.1	10	25		
Chlorpyrifos	314.0	286.0	10	15	18.68	

Table 1 (*Continued*)

Compound	Precursor (Da)	Product (Da)	Dwell time (ms)	CE (V)	t_R (min)	TS
Chlorpyrifos	314.0	258.0	10	15		
Parathion	291.1	81.0	10	40	18.72	
Parathion	291.0	109.0	10	10		
Isodrin	192.9	157.1	20	25	19.45	6
Isodrin	192.9	123.0	20	35		
Heptachlor epoxide	352.9	281.9	20	15	20.16	
Heptachlor epoxide	352.9	262.9	20	10		
Fluoranthene	202.0	176.1	20	25	20.40	
Fluoranthene	202.0	152.1	20	30		
Pendimethalin	252.1	162.1	20	10	20.64	
Pendimethalin	252.1	161.2	20	20		
Chlorfenvinphos	267.0	159.0	20	20	21.11	
Chlorfenvinphos	267.0	81.0	20	40		
Chlordane, trans- (alpha)	372.7	266.1	20	25	21.31	
Chlordane, trans- (alpha)	272.0	237.0	20	20		
Pyrene	202.0	176.1	20	30	21.54	
Pyrene	202.0	152.1	20	30		
Bromophos-ethyl	358.7	331.0	20	5	21.76	
Bromophos-ethyl	358.7	303.0	20	15		
PCB 101	324.0	254.0	20	20	21.80	
PCB 101	325.8	291.0	20	15		
Endosulfan (alpha)	240.8	206.0	20	15	21.85	
Endosulfan (alpha)	238.8	204.0	20	15		
Chlordane, cis- (beta)	372.7	266.1	20	25	22.00	
Chlordane, cis- (beta)	372.7	264.1	20	25		
Dieldrin	263.0	193.0	20	30	23.24	7
Dieldrin	263.0	191.0	20	30		
p,p′-DDE	248.0	176.0	20	30	23.39	
p,p′-DDE	246.0	176.1	20	30		
Endrin	263.0	193.0	20	30	24.13	
Endrin	263.0	191.0	20	30		
Endosulfan (beta)	241.0	206.0	20	15	24.53	
Endosulfan (beta)	195.0	159.0	20	5		
PCB 118	325.8	256.0	20	20	24.70	
PCB 118	325.8	256.0	20	20		
PBDE 28 (triBr)	248.0	139.0	20	25	24.72	
PBDE 28 (triBr)	406.0	246.0	20	15		
p,p′-DDD	237.0	165.0	20	20	25.02	
p,p′-DDD	235.0	165.1	20	20		
o,p′-DDT	237.0	165.0	20	20	25.02	
o,p′-DDT	235.0	165.1	20	20		
PCB 153	358.0	288.0	20	20	25.65	
PCB 153	359.8	324.5	20	15		
Triazophos	257.0	162.0	20	5	25.92	
Triazophos	161.0	134.0	20	5		
Endosulfan sulfate	272.0	236.9	20	15	26.21	
Endosulfan sulfate	272.0	234.9	20	15		
p,p′-DDT	237.0	165.0	20	20	26.42	
p,p′-DDT	235.0	165.1	20	20		
PCB 138	359.8	289.9	20	20	26.80	
PCB 138	358.0	288.0	20	20		
TPP (*IS*)	326.0	233.0	50	10	27.30	8
Endrinketone	316.9	280.9	50	5	27.71	
Endrinketone	316.9	245.0	50	15		
Benzo(a)anthracene	228.0	226.2	50	30	27.79	
Benzo(a)anthracene	228.0	202.1	50	30		
Chrysene	228.0	226.2	50	30	27.95	
Chrysene	228.0	202.2	50	30		
Methoxychlor	227.0	169.0	50	25	28.06	
Methoxychlor	227.0	141.1	50	32		
PCB 180	393.8	358.9	50	15	28.70	9
PCB 180	392.0	322.0	50	20		
PBDE 47 (tetraBr)	486.0	326.0	60	15	28.69	
PBDE 47 (tetraBr)	326.0	219.0	60	25		
Phosalone	182.0	138.0	50	5	29.28	
Phosalone	182.0	111.0	50	15		
PBDE 99 (pentaBr)	566.0	406.0	50	15	31.05	10
PBDE 99 (pentaBr)	406.0	297.0	50	30		
Benzo(b)fluoranthene	252.0	250.1	50	30	31.51	
Benzo(b)fluoranthene	252.0	226.1	50	30		
Benzo(k)fluoranthene	252.0	250.1	50	30	31.59	
Benzo(k)fluoranthene	252.0	226.1	50	30		
PBDE 100 (pentaBr)	566.0	406.0	50	15	31.66	
PBDE 100 (pentaBr)	406.0	297.0	50	30		

Table 1 (*Continued*)

Compound	Precursor (Da)	Product (Da)	Dwell time (ms)	CE (V)	t_R (min)	TS
Benzo(a)pyrene	252.0	250.1	50	30	32.43	
Benzo(a)pyrene	252.0	226.1	50	30		
PBDE 153 (HexaBr)	644.0	484.0	80	5	33.60	11
PBDE 153 (HexaBr)	484.0	324.0	80	35		
PBDE 154 (HexaBr)	644.0	484.0	80	5	34.85	
PBDE 154 (HexaBr)	484.0	217.0	80	35		
Heptabromodiphenylether (IS)	722.0	561.0	80	5	35.36	
Heptabromodiphenylether (IS)	561.0	406.0	80	35	35.36	
Indeno[1,2,3-cd]pyrene	276.0	274.0	70	30	35.46	12
Indeno[1,2,3-cd]pyrene	276.0	275.0	70	30		
Dibenz[a,h]anthracene	278.0	276.0	70	30	35.70	
Dibenz[a,h]anthracene	278.0	277.0	70	30		
Dibenz[a,h]anthracene D14 (IS)	288.3	286.3	30	30	36.43	
Dibenz[a,h]anthracene D14 (IS)	288.3	284.3	30	30		
Benzo[g,h,i]perylene	276.0	274.0	30	30	35.98	
Benzo[g,h,i]perylene	276.0	275.0	30	30		

CE, collision energy; t_R, retention time; TS, time segment number.

was dissolved and 400 μL of the internal standard solution (surrogate) was added to the flask. The twister was then placed into the Erlenmeyer, and stirred at 800 rpm for 24 h. Then, the twister was removed and washed with deionised water to remove any remaining salt, dried on a lint-free tissue, and introduced into a clean glass desorption tube. The twister can be stored frozen without loss or degradation of the adsorbed compound, but in our case all samples and standard were analysed directly after extraction.

2.4. Calibration

The calibration graphs were established for each compound using 200 mL of spiked water at seven concentration levels. First, seven calibration standard mixtures of the compounds and surrogates were prepared in pure methanol by dilution of the stock standard solutions. Then, 400 μL of the corresponding standard in methanol were added to 200 mL of deionised water containing 10 g of NaCl. The spiked calibration samples were treated following the sample-treatment procedure described above. Calibration curves were built plotting the analyte/surrogate peak area ratio versus analyte concentration.

2.5. Thermal desorption and GC–MS/MS analysis

Desorption tubes were placed in the MPS autosampler, which automatically place them into the thermal desorption unit. Desorption was carried out in the solvent vent mode at 300 °C for 8 min. The sample was transferred under a 50 mL min^{-1} helium flow and cryofocused into the CIS-4 inlet at −15 °C. Finally, the inlet ramped to 325 °C at 12 °C s^{-1} to transfer the analytes into the GC column. The carrier gas was helium in constant pressure mode, at 20 psi. The initial oven temperature was 70 °C (held for 2 min). Then, three linear ramps were established: to 150 °C at 25 °C min^{-1}, then 3 °C min^{-1} to 200 °C, and finally 8 °C min^{-1} to a final temperature of 300 °C held for 10 min. Total time for the analysis was 41.9 min.

A SRM acquisition method was created in the QqQ mass spectrometer. Two transitions were monitored for each analyte, the first for quantification and the second for confirmation. Table 1

shows the individual experimental conditions for the mass spectrometer and for the analysis.

The method was divided into 12 segments to obtain enough sampling points for each chromatographic peak and adequate dwell times to obtain an adequate sensitivity and signal–noise relationship. Resolution was adjusted to 1.0 Da for quadrupole 1 and 3. Temperatures of the transfer line, ion source and quadrupole 1 and 2 were 290 °C, 290 °C and 180 °C respectively. Mass spectrometer autotune was performed on a weekly basis.

2.6. Validation requirements

The method performance requirements were established as follows: (1) Linearity, the determination coefficient (R^2) must be equal or greater than 0.990 and maximum residual deviation must be less than 25%. (2) Precision, expressed as RSD (inter-day precision) must be ≤30%. (3) Trueness, expressed as mean recovery, must be in the range of 70–120%. (4) The LOQ must comply with requirements 2, 3 and 5, and must be equal to or less than 30% of the Annual Average Environmental Quality Standard (AA-EQS) value specified in Annex I of the European Directive 105/2008/EC. (6) Uncertainty must be less than 50%. Those requirements are in accordance with Commission Decision 2002/657/EC [38].

3. Results and discussion

3.1. SBSE extraction optimisation

A study of the variables affecting the extraction procedure was carried out to obtain the optimum conditions for all analytes in order to improve precision and sensitivity. Methanol and sodium chloride amounts, volume of the stationary phase (twister dimensions), sample volume and extraction time were optimised. Initial conditions of 0% (v/v) MeOH, 0% (w/v) NaCl, 100 mL of sample volume, 24 h extraction time and 20 mm × 0.5 mm twister dimensions were established. All samples were spiked at 10 ng L^{-1} of each analyte.

3.1.1. Effect of methanol addition

Six samples with methanol contents of 0, 5, 10, 15, 20 and 30% (v/v) were analysed in triplicate. Only a slight increase in response was obtained for most non-polar ($\text{Log}\,K_{o/w} > 7.0$) and higher molecular weight compounds: benzo[g,h,i]perylene, dibenz[a,h]anthracene, PBDE 153, PBDE 154, PCB 138, PCB 153 and PCB 180, although the increase in response was less than 20% in all cases. For compounds with a $\text{Log}\,K_{o/w}$ between 5.5 and 7.0, the effect of the methanol concentration was not significant. For compounds with a $\text{Log}\,K_{o/w}$ lower than 5.5, a progressive decrease in the extraction rate was observed when the concentration of MeOH was increased. For more polar analytes, decreases of up to 90% were obtained. A 0% (v/v) MeOH content was selected because its negative effect on recovery, and the number of analytes affected was more greater than the small enhancement effect induced in only

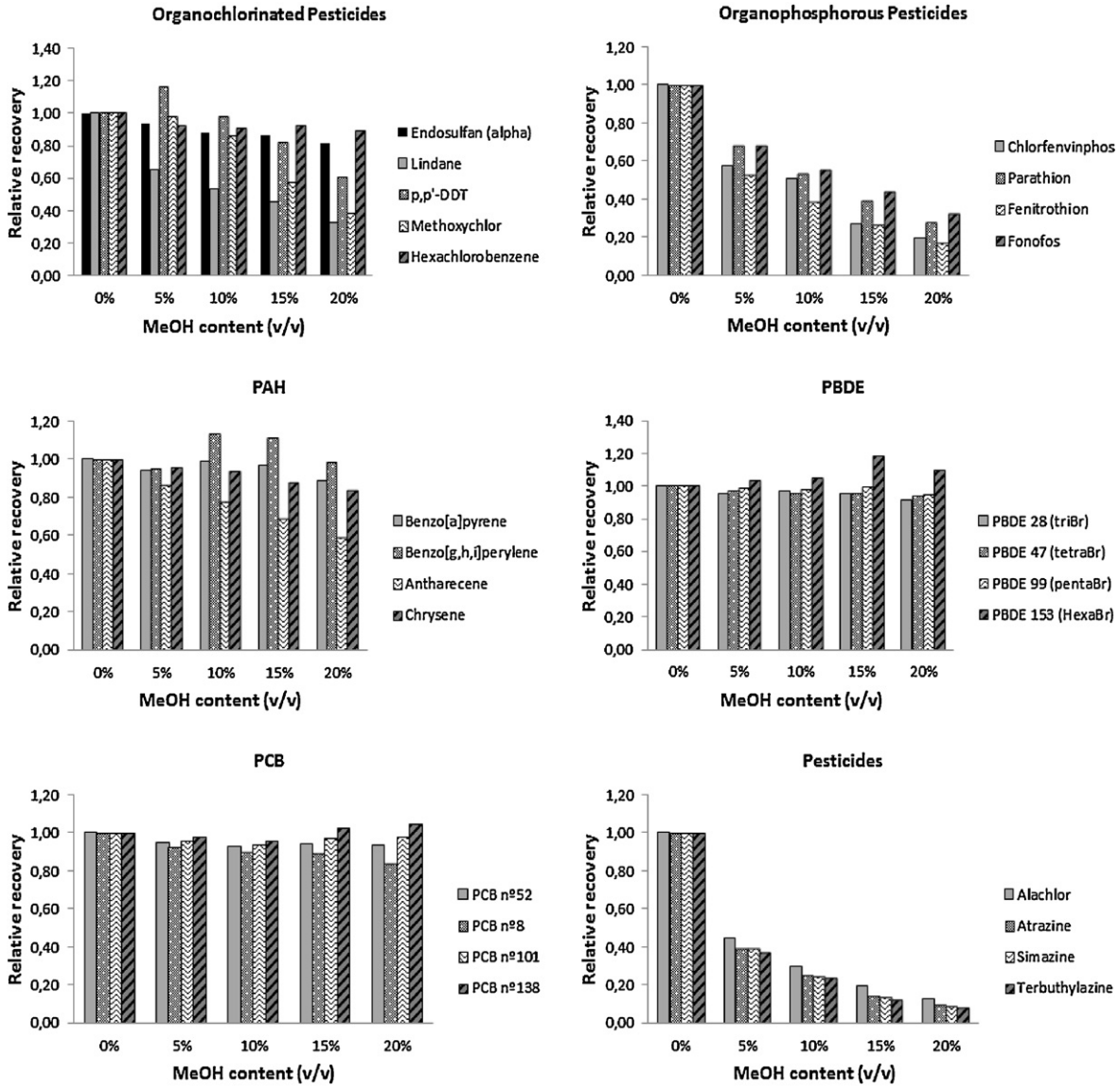

Fig. 1. Effect of MeOH concentration over the extraction of the selected compounds. Responses normalised to signals obtained with 0% (v/v) MeOH.

a few of them. Fig. 1 shows the effect of the MeOH concentration on the extraction of analytes. The responses are normalised to signals obtained with 0% MeOH. In addition, a table with the relative responses of all analytes as a function of methanol content is included as supplementary material.

3.1.2. Effect of NaCl addition

After studying the influence of the methanol concentration, the role of the ionic strength of the matrix was investigated using sodium chloride. Six samples in triplicate with 0, 5, 10, 15, 20 and 30% (w/v) NaCl concentrations were analysed. Three effects were observed, which could be correlated with the polarity of the analyte. For salt concentrations over 20% (w/v), the analytical response decreased between 80 and 90% for compounds with a high $\text{Log } K_{o/w}$ ($\text{Log } K_{o/w} > 6.5$). For some compounds with a $\text{Log } K_{o/w}$ between 4.0 and 6.0 (endosulfan sulphate, fenchlorphos, pirimiphos-methyl, chlorpyriphos, metoxichlor, etc.) a maximum in the response level was obtained for NaCl concentrations ranging between 5 and 15% (w/v). For slightly polar and polar analytes (generally $\text{Log } K_{o/w} < 4.0$) an up to five to eight-fold increase in response was observed when NaCl concentrations were increased to 30% (w/v). Therefore, it can be concluded that the addition of the salt is essential for the determination of polar compounds such as triazines and some organophosphorous pesticides. A table with the relative responses as a function of NaCl concentration for all analytes is included in supplementary material. In addition, Fig. 2 shows the effect of NaCl content for selected analytes. The responses are normalised to signals obtained with 0% NaCl. A concentration of 5% (w/v) NaCl was selected. At this concentration, non-polar analytes are not too negatively affected and an improvement in the extraction of more polar compounds, which are less efficiently extracted by the PDMS, was achieved. In turn, the fact that the lowest limits of quantification established in the WFD are for non-polar compounds as PBDE, PAH and some organochlorinated pesticides, which were negatively affected by NaCl addition, was taken into account.

3.1.3. Sample volume and stir bar dimensions

To optimise the sample volume and stir bar size, three volumes of sample (50, 100 and 200 mL) and two sizes of Twister (0.5 mm film thickness × 10 mm length and 0.5 mm × 20 mm) were studied. Spiked samples were analysed in triplicate and extracted over 48 h to ensure equilibrium was reached, combining different

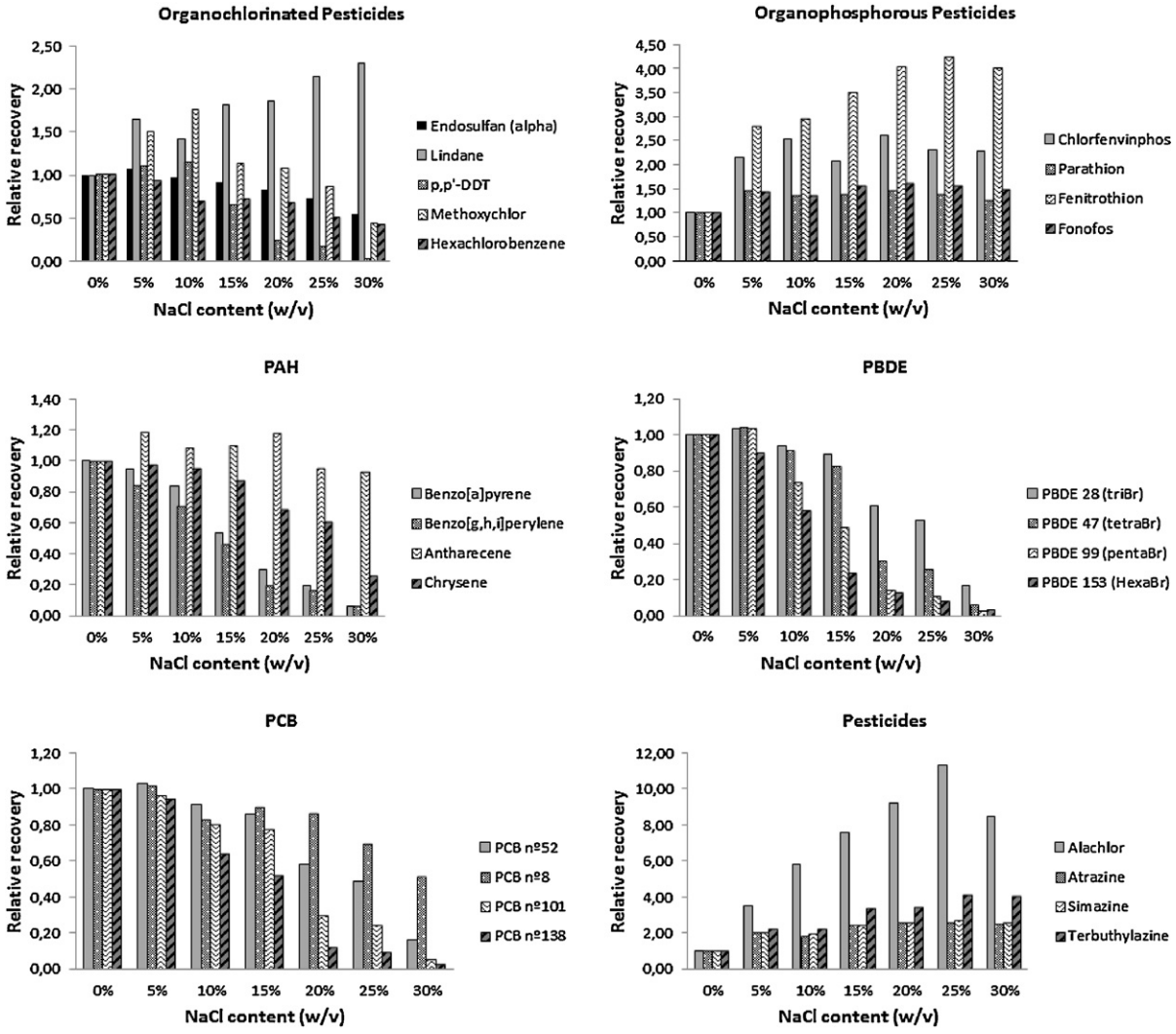

Fig. 2. Effect of NaCl concentration over the extraction of the selected compounds. Responses normalised to signals obtained with 0% (w/v) NaCl.

sizes of twister and sample volume. It was noted that for almost all analytes the signal increased with the sample volume, this is because, although the concentration was the same in all samples, the amount of analyte is greater the larger the sample volume. We also noticed that when the sample volume was doubled, and therefore the amount of analyte, the signal did not double. This indicates that the recovery efficiency is reduced as the sample volume increases, which is consistent with SBSE theory [23], but in terms of sensitivity, a greater response was achieved by increasing sample volume even though extraction is less efficient. For some analytes, such as HCH isomers, the opposite effect was observed. Although some analytes are negatively affected when sample volume is increased, 200 mL was chosen because for the majority of the compounds, maximum responses were achieved. In all cases, the signals obtained with 0.5 mm × 20 mm twisters were higher than those obtained with 0.5 mm × 10 mm twisters. The largest twister was selected.

3.1.4. Effect of extraction time

To study the effect of extraction time, the conditions selected in the previous optimisation steps were established and seven samples were fortified and extracted. Agitation was stopped and the twister was removed from the sample at different times. The experiments were performed in triplicate stopping the extraction at 1, 2, 4, 8, 16, 24 and 48 h. The equilibrium times for the highest molecular weight compounds (dibenz[a,h]anthracene, benzo[g,h,i]perylene, indeno[1,2,3-cd]perylene, PBDE 153, PBDE 154, PCB 180) and the most polar compounds (triazines) were the highest; after 48 h of extraction the steady state was not reached. The equilibrium was reached in 24 h by all compounds, except those specified, so this was the extraction time selected. Fig. 3 shows the effect of extraction time on some representative analytes. The results are also included in supplementary material section.

A very poor precision was obtained for those analytes in which the equilibrium had not been reached, and their variations were not corrected with the employed surrogate (TPP). Previous optimisation steps showed that all of these substances were very dependent on changes in extraction conditions and uncontrollable parameters such as the condition of the twister, which deteriorate with successive desorptions and the volume of available PDMS is reduced affecting the extraction rate. These analytes were corrected with a specific surrogate (heptabromodiphenyl ether for PBDE, Simazine D10 for triazines and polar pesticides, and dibenz[a,h]anthracene for PAH and PCB 180) which corrected the effects in the recovery induced by variations in the conditions or by the sample matrix. TPP was used for the rest of compounds.

3.1.5. Optimisation of desorption conditions

The effect of desorption time was evaluated analysing three samples in duplicate at three desorption times: 5, 8 and 10 min.

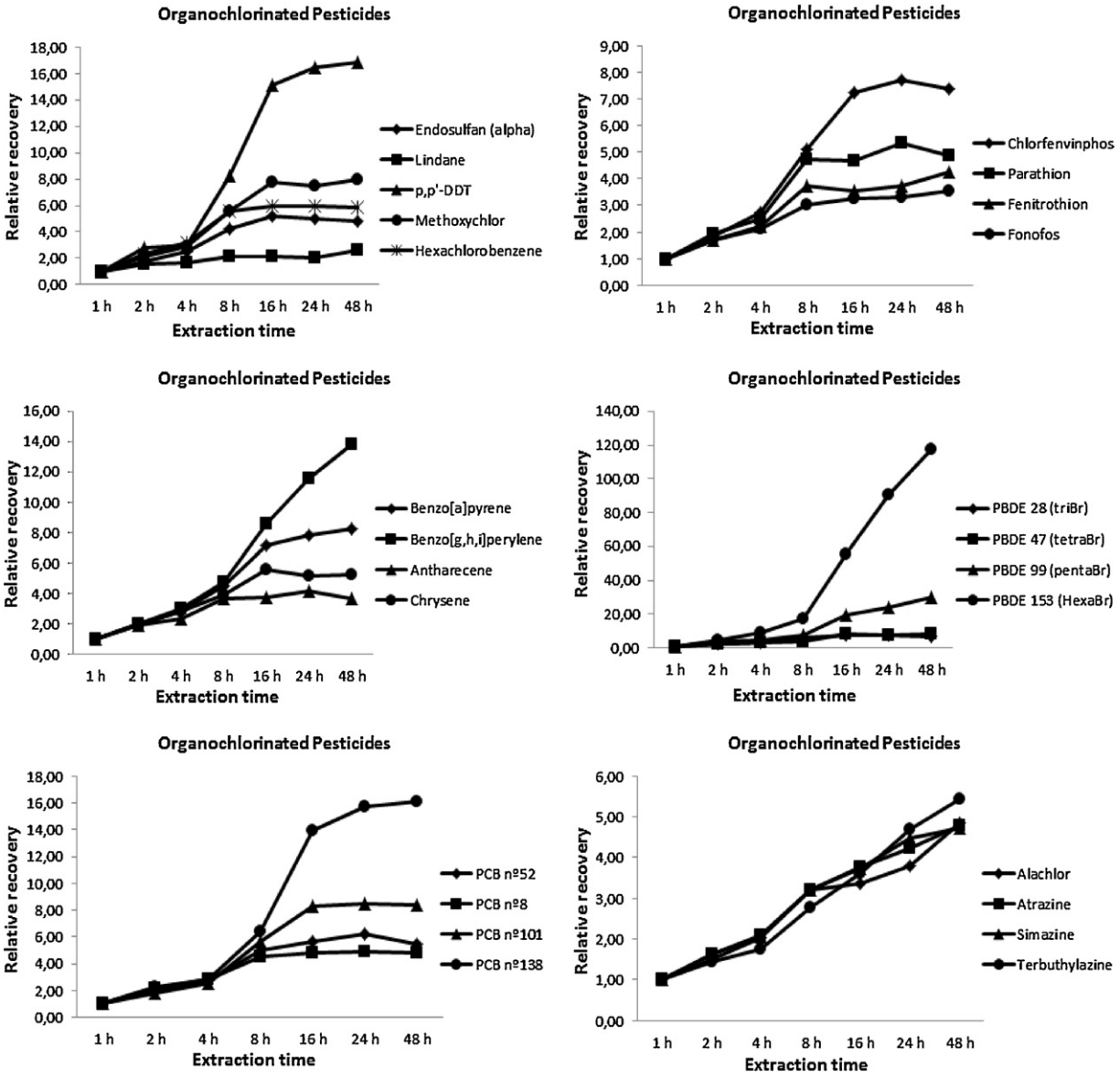

Fig. 3. Extraction profiles of studied contaminants. 0% (v/v) MeOH, 5% (w/v) NaCl, 200 mL sample volume and 20 mm × 0.5 mm stir bar.

In order to evaluate memory effect on the twister, two consecutive desorption steps were carried out. Lower signals were obtained at 5 min while no differences were observed between 8 and 10 min. After the re-analysis of each twister, at 8 and 10 min, only benzo[g,h,i]perylene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene were found at a 1.5% level of the signals obtained in the first desorption; higher levels were obtained at 5 min. The rest of analytes were undetectable in all cases.

3.2. GC–MS/MS method development

The MS/MS detection method was optimised first with individual injections in full scan mode of each analyte in order to obtain their retention times and to select the optimal precursor ions. The most intense ion with the higher *m*/*z* relationship was selected in most cases. Then, six product ion scan methods were automatically created by the MassHunter Software, each with different collision energy in order to find the best product ions. In each method, groups of about 20 pesticides were simultaneous analysed, and the collision energy (CE) ranged from 5 to 30 V, in 5 V increments. After running all groups, the software for data evaluation automatically extracted the MS/MS spectra for each analyte and selected the two most intense transitions and their optimal collision energy. The most intense product selected was a quantifier ion, and the second as well. The collision gas flow was 2.25 mL min^{-1} and the quenching gas 1.5 mL min^{-1}, the optimal values recommended by the manufacturer. A 12-segment SRM method was created, and the cycle time for each segment was set at 500 ms. For the less intense transitions, dwell time was increased in order to improve their signal and, for the most intense transitions, dwell time was decreased to keep the cycle time constant. Table 1 also shows the analytes, number of transitions per segment and dwell time.

A 1.0 mL min^{-1} flow was selected because it is the optimal flow recommended for the mass spectrometer turbopump. Compound identification was made according to relative retention times (RRT, ratio between the analyte retention time and that of the surrogate standard), with a ±0.5% maximum error in respect of the average RTT of the calibration standards.

In this method, one precursor ion and two product ions were monitored (MS/MS transitions) and four identification points

Table 2
Validated and estimated limits of quantification, linear dynamic ranges and surrogates.

Analyte	Estimated LOQ (ng L^{-1})	LOQ (ng L^{-1})	L.D.R. (ng L^{-1})	Surrogates
Aldrin	0.21	0.25	0.25–12.0	TPP
HCH alfa isomer	0.18	0.25	0.25–12.0	TPP
HCH beta isomer	0.23	1.50	1.50–12.0	TPP
HCH delta isomer	0.25	1.50	1.50–12.0	TPP
Chlordane, trans- (gamma)	0.04	0.25	0.25–12.0	TPP
Chlordane, cis- (alpha)	0.10	0.25	0.25–12.0	TPP
Dieldrin	0.18	0.25	0.25–12.0	TPP
Endosulfan (alpha isomer)	0.23	0.25	0.25–12.0	TPP
Endosulfan (beta isomer)	0.13	1.50	1.50–12.0	TPP
Endosulfan sulfate	0.07	0.25	0.25–12.0	TPP
Endrin	0.16	1.50	1.50–12.0	TPP
Endrin ketone	0.09	0.25	0.25–12.0	TPP
Heptachlor	0.11	0.25	0.25–12.0	TPP
Heptachlor epoxide	0.01	0.25	0.25–12.0	TPP
Hexachlorobenzene	0.49	2.50	0.25–12.0	TPP
Isodrin	0.18	0.50	0.50–24.0	TPP
Lindane	0.02	0.25	0.25–12.0	TPP
Methoxychlor	0.09	0.25	0.25–12.0	TPP
o,p′-DDT + p,p′-DDD	0.08	0.50	0.50–24.0	TPP
p,p′-DDE	0.14	0.25	0.25–12.0	TPP
p,p′-DDT	0.08	0.25	0.25–12.0	TPP
Pentachlorobenzene	0.06	0.25	0.25–12.0	TPP
Chlorfenvinphos	1.50	5.00	5.00–200	TPP
Chlorpyrifos	0.26	5.00	5.00–200	TPP
Chlorpyrifos methyl	0.27	5.00	5.00–200	TPP
Fenchlorphos	0.34	5.00	5.00–200	TPP
Fenitrothion	0.69	5.00	5.00–200	TPP
Fonofos	0.28	5.00	5.00–200	TPP
Malathion	0.75	10.0	10.0–200	Simazine-D10
Mevinphos	3.70	10.0	10.0–200	Simazine-D10
Parathion	0.46	5.00	5.00–200	TPP
Phosalone	2.00	5.00	5.00–200	TPP
Triazophos	0.42	10.0	10.0–200	TPP
Antharecene	0.14	3.00	3.00–20.0	TPP
Benz[a]anthracene	0.03	3.00	3.00–20.0	TPP
Benzo[a]pyrene	0.06	3.00	3.00–20.0	TPP
Benzo[b]fluoranthene	0.13	3.00	3.00–20.0	TPP
Benzo[g,h,i]perylene	0.19	0.30	0.30–20.0	Dibenz[a,h]anthracene-D14
Benzo[k]fluoranthene	0.14	3.00	3.00–20.0	TPP
Chrysene	0.03	3.00	3.00–20.0	TPP
Dibenz[a,h]anthracene	0.24	3.00	3.00–20.0	Dibenz[a,h]anthracene-D14
Fluoranthene	0.23	3.00	3.00–20.0	TPP
Indeno[1,2,3-cd]pyrene	0.18	0.30	0.30–20.0	Dibenz[a,h]anthracene-D14
Phenanthrene	0.04	3.00	3.00–20.0	TPP
Pyrene	0.09	3.00	3.00–20.0	TPP
PBDE 28	0.02	0.14	0.14–4.00	TPP
PBDE 47	0.02	0.14	0.14–4.00	TPP
PBDE 99	0.02	0.14	0.14–4.00	Heptabromodiphenylether
PBDE 100	0.03	0.14	0.14–4.00	Heptabromodiphenylether
PBDE 153	0.03	0.14	0.14–4.00	Heptabromodiphenylether
PBDE 154	0.03	0.14	0.14–4.00	Heptabromodiphenylether
PCB 8	0.36	10.0	10.0–200	TPP
PCB 20	0.39	10.0	10.0–200	TPP
PCB 28	0.50	10.0	10.0–200	TPP
PCB 35	0.06	10.0	10.0–200	TPP
PCB 52	0.27	10.0	10.0–200	TPP
PCB 101	0.33	10.0	10.0–200	TPP
PCB 118	0.46	10.0	10.0–200	TPP
PCB 138	0.22	10.0	10.0–200	TPP
PCB 153	0.04	10.0	10.0–200	TPP
PCB 180	0.32	10.0	10.0–200	Dibenz[a,h]anthracene-D14
Alachlor	4.90	10.0	10.0–200	Simazine-D10
Atrazine	6.40	10.0	10.0–200	Simazine-D10
Bromophos methyl	0.22	10.0	10.0–200	TPP
Diazinon	0.21	10.0	10.0–200	TPP
Diuron	9.10	10.0	10.0–200	Simazine-D10
Isoproturon	2.40	10.0	10.0–200	Simazine-D10
Metolachlor	0.94	10.0	10.0–200	Simazine-D10
Pendimethalin	0.32	10.0	10.0–200	TPP
Pirimiphos methyl	0.40	10.0	10.0–200	TPP
Prometryn	7.20	10.0	10.0–200	Simazine-D10
Simazine	2.70	10.0	10.0–200	Simazine-D10
Simetryn	5.70	10.0	10.0–200	Simazine-D10
Terbuthylazine	5.00	10.0	10.0–200	Simazine-D10
Terbutrina	1.60	10.0	10.0–200	Simazine-D10
Trietazin	3.20	10.0	10.0–200	Simazine-D10
Trifluralin	0.11	10.0	10.0–200	TPP

LOQ, limit of quantification; L.D.R., linear dynamic range.

Table 3
Accuracy of the method (precision and trueness).

Analyte	LOQ		High limit	
	%R[a]	%RSD[b]	%R	%RSD
Aldrin	111	8	97	16
HCH alfa isomer	98	14	105	14
HCH beta isomer	99	12	101	18
HCH delta isomer	100	16	106	18
Chlordane, trans- (gamma)	100	15	101	6
Chlordane, cis- (alpha)	100	12	102	7
Dieldrin	100	16	103	4
Endosulfan (alpha isomer)	100	13	100	4
Endosulfan (beta isomer)	96	16	96	10
Endosulfan sulfate	100	13	99	13
Endrin	92	14	98	9
Endrin ketone	99	14	104	13
Heptachlor	100	10	102	11
Heptachlor epoxide	98	12	102	4
Hexachlorobenzene	105	11	99	11
Isodrin	91	18	81	3
Lindane	99	19	106	18
Methoxychlor	85	29	96	16
o,p′-DDT + p,p′-DDD	97	14	100	9
p,p′-DDE	103	15	102	17
p,p′-DDT	101	10	99	23
Pentachlorobenzene	101	24	92	17
Chlorfenvinphos	101	12	101	9
Chlorpyrifos	103	8	100	7
Chlorpyrifos methyl	101	6	102	3
Fenchlorphos	99	6	101	4
Fenitrothion	101	11	89	24
Fonofos	108	8	100	5
Malathion	103	17	110	13
Mevinphos	116	10	104	19
Parathion	111	13	106	11
Phosalone	111	15	74	13
Triazophos	105	11	109	16
Antharecene	94	10	99	7
Benz[a]anthracene	92	13	95	10
Benzo[a]pyrene	98	19	90	20
Benzo[b]fluoranthene	89	17	91	16
Benzo[g,h,i]perylene	100	23	92	15
Benzo[k]fluoranthene	96	17	90	14
Chrysene	93	13	96	11
Dibenz[a,h]anthracene	102	20	89	16
Fluoranthene	93	9	101	7
Indeno[1,2,3-cd]pyrene	99	22	90	13
Phenanthrene	105	9	99	8
Pyrene	92	8	101	8
PBDE 28	102	9	99	7
PBDE 47	102	13	91	12
PBDE 99	111	29	107	27
PBDE 100	107	30	100	19
PBDE 153	99	30	90	29
PBDE 154	100	28	100	13
PCB 8	105	7	104	12
PCB 20	104	6	104	7
PCB 28	104	8	104	7
PCB 35	100	8	103	7
PCB 52	104	7	105	6
PCB 101	99	12	100	6
PCB 118	100	13	97	10
PCB 138	97	20	92	20
PCB 153	100	21	92	20
PCB 180	76	24	94	20
Alachlor	102	9	100	12
Atrazine	103	11	97	9
Bromophos methyl	99	8	102	4
Diazinon	102	6	103	5
Diuron	105	16	94	14
Isoproturon	99	14	92	18
Metolachlor	106	11	97	10
Pendimethalin	104	9	100	5
Pirimiphos methyl	104	9	100	6
Prometryn	112	19	91	9
Simazine	94	19	98	7
Simetryn	100	19	103	8
Terbuthylazine	104	12	99	7
Terbutrina	98	17	96	20
Trietazin	101	13	101	12
Trifluralin	98	16	104	19

LOQ, limit of quantification (ng L^{-1}).
[a] *R*, mean recovery.
[b] RSD for ten determinations.

Table 4
Evaluation of proficiency testing results.

Analito	Reported value (ng L^{-1})	Assigned value (ng L^{-1})	SDPA[a] (ng L^{-1})	Acceptance limits (ng L^{-1})	*Z*-score	Error %
Alpha-HCH	55.8	55.0	8.3	30.3–79.8	0.10	1
Lindane	107.7	97.2	14.6	53.5–140.9	0.72	11
Heptachlor	22.5	29.6	4.4	16.3–42.9	−1.60	−24
Delta-HCH	104	80.9	12.1	44.5–117.3	1.90	29
Aldrin	34.4	42.9	6.4	23.6–62.2	−1.32	−20
Heptachlor epox	35.4	38.4	5.8	21.1–55.7	−0.52	−8
Chlordane (gamma)	40.4	47.4	7.1	26.1–68.7	−0.98	−15
Chlordano (alpha)	66.4	75.3	11.3	41.4–109.2	−0.79	−12
Endosulfan (alpha)	128	152	22.8	83.6–220.4	−1.05	−16
p,p′-DDE	66.4	67.3	10.1	37.0–97.6	−0.09	−1
Dieldrin	16.6	20.5	3.1	11.3–29.7	−1.27	−19
Endrin	61.3	79.4	11.9	43.7–115.1	−1.52	−23
p,p′-DDD	88.5	71.6	10.7	39.4–103.8	1.57	24
Endosulfan (beta)	99.2	121	18.2	66.6–175.5	−1.20	−18
p,p′-DDT	70.6	82.9	12.4	45.6–120.2	−0.99	−15
Metoxychlor	37	42.5	6.4	23.4–61.6	−0.86	−13
Endrin ketone	47.4	46.2	6.9	25.4–67.0	0.17	3
Atrazine	40.8	36.7	5.5	20.2–53.2	0.74	11
Clorfenvinphos	52.3	61.5	9.2	33.8–89.2	−1.00	−15
Clorpyrifos	79	79.2	11.9	43.6–114.8	−0.02	0
Diazinon	68.7	73.1	11.0	40.2–106.0	−0.40	−6
Malathion	76.2	79.2	11.9	43.6–114.8	−0.25	−4
Parathion	68.7	68.7	10.3	37.8–99.6	0.00	0
Pendimethalin	43	47.3	7.1	26.0–68.6	−0.61	−9
Simazine	185.2	180	27.0	99.0–261.0	0.19	3
Trietazin	81	65.6	9.8	36.1–95.1	1.57	23
PBDE 47	416	433	72	217–649	−0.24	−4
PBDE 100	358	308	51	155–461	0.98	16
PBDE 99	423	356	59	179–533	1.14	19
PBDE 154	398	387	64	195–579	0.17	3
PBDE 153	332	251	42	125–377	1.93	32
Phenanthrene	237	228	34	125–331	0.26	4
Anthracene	233	190	29	105–276	1.51	23
Fluoranthene	170	160	24	88–232	0.42	6
Pyrene	257	243	36	134–352	0.38	6
Chrysene	126	120	18	66–174	0.33	5
Benzo[b]fluoranthene	165	153	23	84–222	0.52	8
Benzo[k]fluoranthene	196	195	29	107–283	0.03	1
Benzo[k]fluoranthene	196	195	29	107–283	0.03	1
Benzo[a]pyrene	79	71	11	39–103	0.75	11
Indeno[1,2,3-cd]pyrene	253	246	37	135–357	0.19	3
Dibenz[a,h]anthracene	218	210	32	116–305	0.25	4
Benzo[g,h,i]perylene	212	206	31	113–299	0.19	3
PCB 28	303	340	51	187–493	−0.73	−11
PCB 52	331	370	56	204–537	−0.70	−11
PCB 101	958	914	137	503–1.325	0.32	5
PCB 118	693	638	96	351–925	0.57	9
PCB 153	625	537	81	295–779	1.09	16
PCB 138	987	817	123	449–1.185	1.39	21

[a] Standard deviation of proficiency assessment.

were achieved in compliance with European Commission Decision 2002/657/EC. Confirmation of the detected analytes was performed by calculating the relative ion intensities between the area of the quantification transition and the area of the confirmation transition (ion ratio). The maximum allowed tolerances for relative ion intensities were ±25% in relation to the average ion ratio of the calibration standards. p,p′-DDD and o,p′-DDT were registered as the sum of both because these compounds have the same SRM transitions and cannot be separated in non-polar capillary columns. Diuron and isoproturon are thermo-labile compounds and degrade into the desorption tube during the desorption process. Since best RSD and linearity results for degradation products were obtained, these products were selected for the validation process.

3.3. Method validation and results

Two ion transitions (quantification and confirmation) were selected for each analyte. LOQs were estimated as the analyte concentration with a signal-to-noise-ratio of 10 for the transition with the least intensity. The signal-to-noise ratio for each analyte was calculated using the root-mean-square (RMS) method, and then the LOQs were estimated. The validated LOQs were set at 30% of the Annual Average Environmental Quality Standard (AA-EQS) value specified in Annex I of European Directive 105/2008/EC. This LOQ must be validated and an uncertainty of less than 50% must be obtained in accordance with WFD requirements. The estimated LOQs were only for performance and sensitivity evaluation and have no analytical use and the uncertainties at these levels were not evaluated and could be much higher than the 50% required.

The first standard for calibration was 40% less concentrated than the LOQ. This point is only for the validation step in order to obtain best accuracy in the quantification of samples spiked at LOQ, and it may be left out in routine analysis. In routine analyses, all samples with calculated concentrations below the second calibration point (LOQ) will be reported as <LOQ. Linearity of the calibration graphs was tested according to the Analytical Methods Committee [39]. Intercept (a), slope (b), determination coefficient (R^2), maximum residual deviation and relative standard deviation of response factors (RSD_{RF}) were established. Determination coefficients (R^2) were higher than 0.990 for all analytes, maximum residue deviation of

±25% and standard deviation of response factors lower than 20% were obtained in all cases. Table 2 shows the estimated and validated LOQ for each substance, the evaluated calibration range and the internal standard used.

For linearity evaluation, calibration curves with two replicates for each calibration level were made and the lack-of-fit test was also applied. The P_{lof} value was calculated. If the lack-of-fit test is not significant, $P_{lof} > 5\%$, a straight line function describes the calibration data appropriately. A P_{lof} (%) higher than 5% was obtained for all analytes, indicating that the data are well modelled by a line in all cases.

Accuracy was evaluated in terms of precision and trueness. Precision was evaluated by analysing river water samples spiked at two concentration levels: at LOQ (30% of AA-EQS) and at the highest concentration level of the calibration range. The samples were analysed in different days (inter-day reproducibility). A reagent blank and a matrix blank were extracted and analysed daily. Inter-day precision was estimated as RSD (%) of ten determinations and was between 3 and 30% for all analytes. Trueness was calculated in terms of recovery. For both levels, the recovery for all analytes was in the range of 74–116%. Table 3 shows the results.

Uncertainty was calculated following the guidance of EURACHEM contained in the document "Guide for the expression of uncertainty in measurement" [40] and was calculated individually for each. The values ranged between 40% and 46% and comply with the requirements of the WFD of a maximum uncertainty of 50%.

3.4. Participation in proficiency testing assays

Proficiency testing (PT) is a very important tool that must be used by all testing laboratories to evaluate their methods of routine analysis and to assess the validity of the methods being validated. This is true of both standard methods that are implemented in a routine laboratory and new methods being developed so that results may be compared to a reference value that has been established by a trusted entity (the organizer must be accredited for the distribution of PT). It also allows the results to be compared to those obtained by other laboratories or obtained with different methods.

To assess the validity, the method was applied in one proficiency test for each family studied: PAH, OCP, PCB, PBDE, and pesticides. The evaluation of the obtained results is included in Table 4. The Z-scores for all evaluated analytes were less than 2, no questionable ($-2 \leq Z \leq 2$) or unsatisfactory Z-scores ($Z < -3$ or $Z > 3$) were obtained in any case. This indicates that the method was not affected by any significant systematic error and was comparable to the results obtained by other laboratories that have participated in the round. Thus, the validity of the method is demonstrated.

4. Conclusions

The developed method based on SBSE-TD–GC–MS/MS allows for the simultaneous detection and quantification of almost all semivolatile compounds amenable to analysis by gas chromatography that are considered priority pollutants under the European Water Framework Directive. The extremely low quantification limits for inland surface water required by this directive were achieved and validated, and the requirement of uncertainty was also fulfilled for all analytes. A larger number of analytes, and at lower LOQ, than with other previous methods proposed in the literature based on the use of SBSE–GC–MS [25,26,30,31,41] has been validated. Quality parameters such as accuracy (precision and trueness) and linearity were evaluated for this method, and good RSD values (less than 30%) and acceptable recoveries (between 74 and 116%) were shown in all cases. The uncertainty of the measurement was lower than 50% in all cases, which is in accordance with the requirements of the WFD. Also, the method was evaluated through participation in several proficiency testing analyses and no questionable or unsatisfactory results were obtained. The method is simple, quick (a large number of analytes can be analysed in one run), and fully automated. No solvents or toxic reagents were necessary, making the method safe and not harmful to the environment. Furthermore, the proposed method is versatile because it can be applied to ensure compliance with other regional environmental laws besides WFD. Also the use of MS/MS detection leads to enhanced specificity with respect to other methods that employ SIM detection.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.12.037.

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