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Analytical Method Development and Validation for Some Persistent Organic Pollutants in water and Sediments by Gas Chromatography Mass Spectrometry

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ABSTRACT: Many of the persistent organic pollutants (POPs) with endocrine disrupting properties are monitored regularly by risk assessors with limited resources, where analytical procedures are usually laborious, expensive, and not ecofriendly. Moreover, these analyses were frequently advanced aiming one class of pollutants, consequently inefficient to correspond the demand of monitoring a quickly rising number of pollutants in the environment. The objective of this study was to develop a single sample extraction procedure and multiple gas chromatography-mass spectrometry runs for the detection of various groups of semi volatile organics; Polychlorinated Biphenyls (28, 52, 101, 118, 138, 153, 180), Polybrominated Diphenyl Ethers (17, 47, 66, 100, 153, 183) and Organochlorine Pesticides (α-HCH, HCB, γ-HCH, Heptachlor, p,p-DDD, p,p-DDE, p,p-DDT) in sediment and water samples simultaneously. Extraction for water involved solid phase extraction using C18 and for sediment using homemade column with florisil, primary secondary amine and magnesium sulfate with ultrasonication step by acetone. This procedure was validated and applied to water samples from tap, river and lake; and sediment samples from river and lake. For both matrices and all analytes, high linearity, recovery (88-106%) with all relative standart deviation values <20% and limit of quantification levels below the tested limits were achieved. This reliable and cost effective procedure for monitoring selected multiple POP levels in water and sediment; do not require complicated device nor intensive manual efforts, which would also minimize the depletion of the organic solvents, could be used for routine detection of selected POPs.

Key words: PCB, PBDE, OCPs, GC-MS, Method development

INTRODUCTION

Among the most hazardous chemicals with endocrine-disrupting properties, persistent organic pollutants (POPs) are characterized by low water solubility, high lipophilicity, resistance to biodegradation, ability for long distance travel from the source, toxicity on human and animal health, and bioaccumulation (Environmental Protection Agency, 2015). Polychlorinated Biphenyls (PCBs), Polybrominated Diphenyl Ethers (PBDEs) and Organochlorine Pesticides (OCPs) among the POPs list, received importance for the development of new research areas regarding detection and screening (Kuzukiran and Filazi, 2016). Hazardous chemicals are generally present at very low levels in environmental samples. Thus, their precise analysis require selective and sensitive methods (Guo and Kannan. 2015). Conventionally, several techniques have been performed for the extraction of PCBs, PBDEs and OCPs in environmental matrices. For PCBs, PBDEs and OCPs, the most commonly used extraction methods are Soxhlet pressurized liquid extraction (Dai et al., 2012) and Soxhlet extraction (Covaci et al., 2005), despite of some disadvantages such as over solvent depletion and extraction time or cost. Different techniques such asmicrowave-assisted extraction (Smalling andKuivila, 2008), matrix solid phase dispersion (Stanley et al., 2009), dispersive liquid-liquid microextraction(Rezaee et al., 2006)and ultrasound assisted extraction (Kuzukiran et al., 2016;Yurdakok-Dikmen et al., 2016) have been used because of their speed, simplicity and low solvent depletion. For satisfactory purification of sample extracts, the choice of an appropriate adsor-

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bent and eluent solution is important and depends mainly on the chemical properties of the target analytes as well as the sample matrix (Guo and Kannan, 2015).

The objective of this present study was to examine a reliable, simple, time saving and cost-effective extraction procedure based on SPE-assisted by ultrasound for the analyses of multiple groups of semi volatile organics (PCBs, PBDEs and OCPs) in sediment and water samples. The SPE method for extraction of selected POPs was developed by optimizing instrumentation conditions, clean-up phase, elution solvents and their volume. The analysis of the selected POPs in water and sediments are difficultto obtain due to the count of co-extracted compounds, which would expectedly affect the procedure and apparatus performance adversely. In order to overcome this issue,in the current study a sensitive, selective and efficient method have been developed and implemented, based on GC-MS principles for the simultaneous determination of several POPs including PCBs, PBDEs and OCPs, in water and sediment samples.

MATERIALS & METHODS

All chemicals and solvents used were of analytical grade. Indicator PCBs (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180), PCB 118 (dioxin like PCB), PBDEs (PBDE 17, PBDE 47, PBDE 66, PBDE 100, PBDE 153, PBDE 183, PBDE209) and OCPs [alfa- hexachlorocyclohexane (α-HCH), gamma-hexachlorocyclohexane or lindane (αΤαβλε 1. Ρετεντιον τιμεσ ανδ ΣΙΜ ιονσ οφ ταρ–γετ αναλψτεσ.-HCH), hexachlorobenzene (HCB), heptachlor,p,p'-dichlorodiphenyl dichloroethane (p,p'-DDD), p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE), andp,p'- dichlorodiphenyl trichloroethane(p,p-DDT)] were targeted. All individual standards of OCPs and PCBs were taken from Dr Ehrenstorfer Laboratories (Augsburg, Germany), while PBDE standards were purchased as mixed (BDE-MXD) at the concentrations 74% nonane/26% toluene from Wellington Laboratories (Guelph, Canada). The internal standard (IS) 2,2',4,4',5,5' hexachlorobiphenyl (PCB153-labeled 13C12)was purchased from Cambridge Isotope Laboratories (Andover, MA, USA).PCB 30, PCB 209and PCB153-labeled 13C12were used as the internal standards for samples. C18, florisil (60-100 mesh), magnesium sulfate and Bondesil-Primary Secondary Amine (PSA) (40 µm) for solid-phase extraction(SPE) were taken from Agilent Technologies (Santa Clara, California-USA).Acetone, acetonitrile, methanol, n-hexane, dichloromethane, ethyl acetate, pentane and isooctane were purchased from Merck (Darmstadt, Germany).Standard stock solutions of target compounds (100µg L^{-1} of each target analyte as mixture) or internal standards [PCB 30 (1 mg L^{-1}) and PCB209 (1 mg L^{-1}) and PCB153-labeled 13C12 (400 µg L^{-1})]were prepared in acetonitrile and stored in the dark at ≤4°C. Standard working solutions were prepared daily.

A Polaris Q External Ionization Ion Trap GC-MS was used in combination with a split/splitless (SSL) injector (Thermo Finnigan, San Joe, CA, USA). The injector, transfer line and external ion source temperatures were kept at 280°C, 270°C and 250°C, respectively. The injector was equipped with a 12-cm × 5-mm i.d. Silcoseeve liner (Thermo Finnigan, San Joe, CA, USA) and was employed in the splitless mode, and 2 ?L of sample was injected. Chromatographic separation was carried out using an HP-5MS capillary column fused the (5%-phenyl)-methylpolysiloxane (30 m × 0.25 mm id, 0.25 µm film thickness) (Agilent Technologies, Palo Alto, CA, USA). The carrier gas was He (purity 99.995%) at a constant flow rate of 1.0 mL min-1.The solvent delay time was adjusted to 8 min. GC oven program started at 70°C (hold time 2 min), which was raised at 25°C min-1 to 150°C, at 5°C min-1 to 200°C (hold time 5 min), at 5°C min-1 to 270°C (hold time 2 min), finally at 25°C min-1 to 290°C (hold time 6 min). Oven program time was totally 43 min. Mass spectra (m/z100-800) were recorded at a rate of five scans per second with an ionization energy of 70 eV. Mass spectrometric analysis for quantitative measurement of the analytes was performed in selected ion monitoring (SIM) mode by use of 3 characteristic fragment ions for each chemical (1 target ion and 2 qualifier ions)(Table 1).

All samples (6 lake sediments, 6 river sediments, 6 tap water, 6 lake water and 6 river water) were collected in sterile glass. Sediment samples were collected from Kosrelik Lake and Ankara River; meanwhile water samples were collected both from these areas and city tap water. The distance between sample collection locations in lake and river was about 500 m. Each surface sediment (depth: 0-5 cm) samples were picked up using a stainless steel grab sampler.Sediment samples, dried at room temperature for 24 h, and water samples processed within 24 h after collection. Water samples used unfiltered.

The extraction method used for the detection of target analytes in water samples was adopted from prior described methods for extraction of PCBs and PBDEs from water (Barco-Bonilla et al,. 2015; Sanchez-Avila et al., 2009). Homemade SPE cartridge (10-mL glass syringe)included 500 mg C18 prepared for purification, and conditioned by passing 10 mL of n-hexane, 10 mL of dichloromethane, 10 mL of methanol and 10 mL deionized water avoiding dryness (flow rate 5 mLmin-1). 10 mL of unfiltered water sample was allowed to pass through the cartridge under vacuum at a flow rate of 5 mL min-1, and cartridgewasrinsed with 5 mL deionized water, and air-dried,using vacuum for at least 30 min, and then eluted with 2x5mLof dichloromethane:hexane

Table 1. Retention times and SIM ions of target analytes

Compound	Retention times (min)	Selected Ion Monitoring ions
Alfa- hexachlorocyclohexane	10.76	**183***, 181, 219
Hexachlorobenzen	10.81	**286***, 284, 282
PCB30**	11.59	**256***, 258, 186
Gamma-hexachlorocyclohexane	11.74	**181***, 183, 219
PCB28	13.59	**256***, 258, 186
Heptachlor	13.98	**272***, 274, 270
PCB52	14.80	**292***, 220, 257
PCB101	18.37	**326***, 328, 254
p,p'-dichlorodiphenyldichloro ethylene	19.96	**246***, 248, 318
PBDE17	21.06	**248***, 246, 406
PCB118	21.93	**326***, 328, 254
p,p'-dichlorodiphenyl dichloroethane	22.55	**235***, 165, 237
PCB153-labeled $^{13}C_{12}$***	23.04	**372***, 302, 374
PCB153	23.09	**360***, 290, 288
PCB138	24.42	**360***, 290, 288
p,p'- dichlorodiphenyl trichloroethane	24.60	**235***, 165, 237
PCB180	27.62	**394***, 396, 324
PBDE47	27.90	**488***, 486, 484
PBDE66	28.68	**488***, 486, 484
PBDE100	31.39	**404***, 406, 566
PCB209**	33.80	**500***, 498
PBDE153	36.72	**484***, 482, 486
PBDE183	40.01	**562***, 564, 721

*Quantifier ion, ** Internal injection standards, *** Internal Standard

mixture (1:1, v/v). The extractcollected was evaporatedunder a gentle nitrogen stream at 35°C and collected in 100 µL of isooctane and lastly spiked with 1 µg mL-1 of injector internal standard PCB 30. The final extract obtained was then injected into the GC-MS. For method optimization and validation, deionized water was used as the blank sample and validated for tap, lake and river water.

The sediment samples,dried at room temperature for 24 h, were homogenized using a porcelain mortar and passed through a 0.4-mm stainless steel sieve. The sediment indicating the lack of the target PCBs, PBDEs and OCPs was utilized as the blank sample for extraction optimization, calibration and validation purposes. At the beginning of extraction used ultrasound procedure such as Kuzukiran et al. (2016). 5 g of sedimentwas weighed in a 15-mL glass centrifuge tube, and then 10 mL of acetone was added and mixed. The mixture was immersed in an ultrasonic bath (frequency 35 kHz, 0.32 kW, Super RK 510, Sonorex, Bandelin, Germany) for 10 min at 25±2 °C. Next, the mixture was centrifuged at 4000 rpm for 10 min. The supernatant was taken and dried under nitrogen pressure at 35 °C. The dried extract was dissolved using 1 mL of acetone, and loaded onto homemade SPE cartridge packed from bottom to top with 1 g of florisil, 500 mg of PSA and 0.8 g of magnesium sulfate. SPE cartridge was conditioned by passing 5 mL of ethyl acetate/ acetone/hexane (5:2:1, v/v/v) mixture. To prepare SPE cartridge was also tested from bottom to top with 1 g of florisil and 1 g of magnesium sulfate, however this combination was not used because of the eluat was not clean. After loading onto cartridge, extracts were eluted with 5 mL of ethylacetate:acetone:hexane (5:2:1, v/v/v) mixture. For conditioning and elution, ethyl acetate:acetone (5:2, v/v), pentane:dichloromethane (4:1, v/v) and hexane:dichloromethane (2:2, v/v) mixtures were also tested, but the best results were obtained by ethyl acetate:acetone:hexane mixture. The eluate collected was evaporated under a gentle nitrogen stream at 35°C and collected in 100 µL of isooctane, and spiked with 1 µg mL-1 of injector internal standard PCB 30, and applied into the GC/MS.

To validate the developed method such parameters as selectivity,linearity, trueness, precision, limits of detection (LODs) and limits of quantification (LOQs) were determined using fortified sediment and water samples according to Eurachem Guide (Magnusson and Ornemark, 2014).The linearity of the method for water was assessed using spiked deionized water at six concentrations (0.25, 0.5, 1.0, 2.0, 5.0 and 10.0 ng mL^{-1}) (Table 2).

Table 2. The validation parameters in the water of method

Analyte	Linearity (ng/mL)	r^2	Mean Recovery (%)	LOD (ng/mL)	LOQ (ng/mL)	Intermediate precision (RSD* %)	Repeatability (RSD* %)
PCB 28	0.25-10	0.997	103	0.03	0.09	5.1	4.9
PCB 52	0.25-10	0.998	99	0.04	0.13	6.2	8.2
PCB 101	0.25-10	0.998	102	0.04	0.12	5.7	5.2
PCB 118	0.25-10	0.999	101	0.04	0.14	4.2	4.5
PCB 138	0.25-10	0.999	102	0.07	0.24	5.1	5.0
PCB 153	0.25-10	0.995	102	0.06	0.21	5.8	5.6
PCB 180	0.25-10	0.999	100	0.06	0.20	7.6	6.8
PBDE 17	0.25-10	0.997	99	0.03	0.09	4.3	5.3
PBDE 47	0.25-10	0.998	94	0.04	0.14	6.1	6.1
PBDE 66	0.25-10	0.998	97	0.04	0.14	6.1	5.7
PBDE 100	0.25-10	0.999	93	0.07	0.22	7.2	7.4
PBDE 153	0.25-10	0.995	74	0.08	0.28	7.6	7.7
PBDE 183	0.25-10	0.999	73	0.12	0.41	5.5	6.1
α-HCH[1]	1-10	0.999	94	0.03	0.09	5.1	4.9
HCB[2]	1-10	0.998	103	0.11	0.38	7.1	7.3
γ-HCH[3]	1-10	0.995	97	0.20	0.66	6.1	5.1
Heptachlor	1-10	0.999	97	0.24	0.81	7.7	7.9
p,p'-DDE[4]	1-10	0.998	99	0.05	0.15	9.4	9.0
p,p'-DDD[5]	1-10	0.998	103	0.07	0.25	7.6	7.8
p,p'-DDT[6]	1-10	0.998	101	0.19	0.64	5.4	5.2

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For the linearity of the method for sediment was assessed using matrix matched standard calibration by analyzing spiked blank samples at six concentration levels (0.5, 1.0, 2.0, 5.0, 10.0 and 20 ng g^{-1}). The slope ratios of the matrix/solvent for each compound were calculated to estimate the matrix effect (Table 3).

LODs and LOQs for all target analytes were calculated in the same blank extracts used to examine the selectivity of the method. LODs and LOQs were expressed as the analyte concentration that corresponded to the mean of 10 blank measurements plus 3-fold and 10-fold their standard deviation, respectively.Precision were evaluated at two levels as repeatability and intermediate precision. They were confirmed by assessing 6 replicates at 6 varied concentrations representative of the designed validation range across 4 days of analysis; the results were stated as the relative standard deviation (RSD%) of the measurements. Trueness was evaluated at three or four concentration levels for water (0.25, 1, 2 and 10 ng mL^{-1}) and sediments (0.5, 2, 5 and 20 ng g-1) using blank samples spiked with appropriate volume of working standard solution (Tables 4 and 5). Ten replicates per level were performed. To eliminate possible matrix effects, the standard addition method was used for thequantitative determination of the PCBs, PBDEs and OCPs in different water samples (tap water, and river and lake waters). Watersamples were fortified with a level of 0.25, 1, 2 and 10 ng mL-1 for each analyte and recoveries and RSD% were determined.

RESULTS & DISCUSSION

The instrument conditions of the method described in this paper were adapted from previously described methods for the extraction of PCBs from water (Yurdakok-Dikmen et al., 2016) and sediment (Kuzukiran et al., 2016). In order to improve the performance of the target analytes, some modifications were implemented. Different oven temperature programs, flow rate, injec-

Table 3. The validation parameters in sediment of method

Analyte	Linearity (ng/mL)	r^2	Mean Recovery (%)	LOD (ng/g)	LOQ (ng/g)	Intermediate precision (RSD* %)	Repeatability (RSD* %)
PCB 28	0.5-20	0.997.	100	0.09	0.31	3.2	3.2
PCB 52	0.5-20	0.998	102	0.05	0.17	4.3	4.1
PCB 101	0.5-20	0.998	100	0.13	0.44	4.8	4.4
PCB 118	0.5-20	0.999	101	0.14	0.47	7.7	7.4
PCB 138	0.5-20	0.999	96	0.08	0.28	5.3	5.3
PCB 153	0.5-20	0.995	98	0.15	0.49	6.1	5.8
PCB 180	0.5-20	0.999	94	0.07	0.22	5.4	5.4
PBDE 17	0.5-20	0.997	101	0.14	0.45	7.1	6.8
PBDE 47	0.5-20	0.998	99	0.11	0.36	4.0	4.0
PBDE 66	0.5-20	0.998	99	0.11	0.37	5.6	4.9
PBDE 100	0.5-20	0.999	95	0.12	0.41	5.1	5.4
PBDE 153	0.5-20	0.995	98	0.13	0.43	3.5	3.5
PBDE 183	1-20	0.999	100	0.17	0.57	2.2	2.6
α-HCH[1]	1-20	0.996	99	0.22	0.72	4.5	5.2
HCB[2]	1-20	0.998	104	0.19	0.62	6.4	6.5
γ-HCH[3]	1-20	0.998	98	0.39	1.31	6.1	5.1
Heptachlor	1-20	0.999	97	0.28	0.95	6.1	6.7
p,p'-DDE[4]	1-20	0.999	96	0.08	0.26	7.2	7.1
p,p'-DDD[5]	1-20	0.998	100	0.19	0.64	5.1	4.9
p,p'-DDT[6]	1-20	0.994	98	0.37	1.25	6.1	5.3

1alfa-hexachlorocyclohexane, 2hexachlorobenzen, 3 gamma-hexachlorocyclohexane,4 p,p'-dichlorodiphenyldichloro ethylene, 5p,p'-dichlorodiphenyl dichloroethane, 6p,p'- dichlorodiphenyl trichloroethane, *Relative Standard Deviation

Table 4. Average recovery and Relative Standard Deviation for analyte -spiked water samples

Analyte	Mean Recovery (%) (n=6)				Relative Standard Deviation % (n=6)			
	0.25 ng/mL	1.0 ng/mL	2.0 ng/mL	10.0 ng/mL	0.25 ng/mL	1.0 ng/mL	2.0 ng/mL	10.0 ng/mL
PCB 28	100	101	106	104	5.3	6.5	3.6	7.5
PCB 52	96	101	103	97	7.4	10.7	3.4	10.5
PCB 101	101	101	106	100	5.3	6.1	6.9	8.0
PCB 118	99	102	104	102	5.3	4.4	7.6	4.1
PCB 138	101	101	105	101	6.9	6.2	5.5	4.2
PCB 153	96	104	104	104	7.5	6.6	2.9	8.2
PCB 180	104	96	98	100	5.4	6.6	11.0	7.5
PBDE17	92	101	103	99	6.5	7.3	2.9	5.5
PBDE47	88	88	101	98	11.5	6.8	6.5	6.2
PBDE66	92	94	104	96	7.4	9.7	4.4	6.8
PBDE100	88	89	102	93	4.6	7.7	8.2	6.3
PBDE153	-	96	101	100	-	7.1	6.6	6.0
PBDE183	-	102	97	92	-	3.9	6.7	8.0
α-HCH[1]	-	90	95	91	-	11.0	3.3	9.5
HCB[2]	-	88	104	91	-	13.3	3.8	6.2
γ-HCH[3]	-	106	95	98	-	8.8	8.4	7.3
Heptachlor	-	98	98	94	-	9.8	3.8	14.3
p,p'-DDE[4]	-	98	103	103	-	11.4	6.8	9.5
p,p'-DDD[5]		98	100	97	-	19.0	6.4	6.6
p,p'-DDT[6]	-	94	99	100	-	12.8	6.3	9.0

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Table 5. Average recovery and Relative Standard Deviation for analyte-spiked sediment samples

Analyte	Mean Recovery (%) (n=6)				Relative Standard Deviation % (n=6)			
	0,5 ng/g	2,0 ng/g	5,0 ng/g	20,0 ng/g	0,5 ng/g	2,0 ng/g	5,0 ng/g	20,0 ng/g
PCB 28	99	100	100	102	6.0	3.6	2.6	4.4
PCB 52	98	105	100	103	2.7	10.1	3.8	3.1
PCB 101	95	103	103	100	9.7	3.4	2.1	4.0
PCB 118	98	102	101	102	8.8	2.9	9.9	10.2
PCB 138	98	96	100	99	6.2	7.4	3.4	5.2
PCB 153	95	94	98	99	9.9	8.6	2.7	5.3
PCB 180	93	97	91	95	2.8	4.1	3.5	7.8
PBDE17	97	102	103	100	9.5	4.7	2.2	8.7
PBDE47	97	96	100	102	8.9	3.6	3.1	6.6
PBDE66	96	101	98	99	9.9	5.6	4.6	6.6
PBDE100	95	91	96	100	9.0	2.0	6.6	5.6
PBDE153	-	98	98	99	-	2.1	3.7	3.1
PBDE183	-	100	100	100	-	1.0	2.4	3.5
α-HCH[1]	-	96	97	104	-	9.7	4.2	6.6
HCB[2]	-	106	104	100	-	6.1	2.7	6.9
γ-HCH[3]	-	97	95	101	-	8.7	3.6	10.0
Heptachlor	-	97	95	99	-	2.7	3.3	8.1
p,p'-DDE[4]	-	102	99	98	-	7.5	3.6	6.3
p,p'-DDD[5]	-	99	92	97	-	10.1	4.3	6.1
p,p'-DDT[6]	-	100	93	101	-	3.5	6.3	3.5

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tor temperature, injection volume, were tested in order to achieve optimum chromatographic performance. For this, the standards at high concentration levels had to be injected into instrument to carry out a single method. As a beginning, the oven program was altered because the original program for PCBs did not permit the accurate resolution of PBDEs and OCPs, and a longer total running time were needed, but initial temperature were suited for all the analytes. The initial temperature was similar to PCBs because PCBs and OCPs need lower temperatures than PBDEs to elute from the column, but final temperature was increased from 260 °C to 290 °C. The temperature program was prolonged for obtain complete resolution of all analytes. In the optimized oven program, which is remarked in the apparatus section, the total running time was determined to be 43 min.

To equilibrate the solvent elimination from the injector, the temperature and flow rate must also be optimized. At high injector temperatures, low molecular weight compounds can be lost through solvent discharge and at high flow rates, the risk of analyte loss increases (Stapleton, 2006). Thus, flow rate was also optimized for the simultaneous determination of three types of contaminants, in order to minimize the carryover effect. Better results were obtained with a flow rate of 1.0 mL min-1which was similar to our previous studies (Kuzukiran et al., 2016; Yurdakok-Dikmen et al., 2016). Following the flow rate,the injector temperature was optimized.For PBDEs, the high inlet temperature can lead to thermal degradation and discrimination of higher molecular weight PBDEs, particularly the fully brominated PBDE 209 (Björklund et al., 2004). Because it was seen that the sensitivity of the compounds was not affected, 280 °C was preferred as the injector temperature for prevent faster septa and head column distortion. However, despite all efforts, PBDE 209 could not be detected. The determination of highly brominated compounds (especially Deca-BDE) is hard due to thermal degradation (Covaci et al,. 2002), and this is the main factor that a number of studies do not contain PBDE-209 in their results. Typically, PBDE-209 is detected in short columns, which however are damaging for the separation of the other brominated compounds (Besis and Samara, 2012).

Relating to the SIM conditions, three ions per compound were selected from the full scan spectra according to some valuation criteria such as intensity, selectivity and interferences (Barco-Bonilla et al.,2015). So, the three selected ions (a quantifier and two qualified

ions) were monitored.

For optimization of the extraction procedure, ultrasound procedure and a homemade SPE cartridge were used. Another important issue for extraction procedure is purification. In literature searches, the most common used technique for purification of PCBs, PBDEs or OCPs was found to be SPE. Indeed SPE reduced the matrix interference of surface water and sediment samples before pre-concentration. The efficiency of SPE depends on the type and quantity of sorbent. Several materials including C18, PSA, Florisil, alumina and like that commonly used. C18 is known for its strong ability to remove protein interference (Wang et al., 2014). For this, it was preferred for analysis of water samples. SPE cartridge involved 500 mg C18 using by Portales et al (2011) and Barco-Bonilla et al (2015) was prepared for extraction of water samples, and conditioned such as Sanchez-Avilla et al (2009). Water samples were not filtered to prevent losses in the total amount and therefore considered both dissolved and particulate bound chemicals. All the targeted analytes showed the same behavior, and when described procedure was tested, suitable results were obtained. Thus, this extraction procedure was exposed to validation to check if it was reproducible and suitable for the simultaneous extraction of PCBs, PBDEs and OCPs from water samples.

For the extraction of the target analytes in sediment,various techniques were tested in the current study including;homemade SPE cartridgespacked with florisil:PSA:magnesium sulfate or florisil: magnesium sulfate. The magnesium sulfat:florisil ensured good recovery, but a clean eluate was not obtained. With florisil:PSA:magnesium sulfate cartridge a good recovery and a clean eluate was obtained. With the current available literature, no study was found using this combination which revealed good results. PSA is a weak anion-exchanger which removes fatty acids, sugars and other co-extractives interferences based on hydrogen bond formation (Wang et al., 2014).

Several solvent mixtures were tested for the extraction efficiency from sediment and it has been found that the mixtures ethyl acetate:acetone:hexane (5:2:1, v/v/v) and hexane:dichloromethane (1:1, v/v) gave similar recoveries for reference standards, while the use of a mixture ethyl acetate:acetone (5:2, v/v) or pentane:dichloromethane (4:1, v/v) resulted in significantly lower values. Although mixture of hexane:dichloromethane was obtained a good recovery, it was showed matrix effect in chromatogram, especially for α-HCH, α-HCH, HCB and PCB28. For this reason,the mixture of ethyl acetate:acetone:hexane for both a good recovery and a clean eluate was preferred. Also different volumes(5 and 10 mL) of this solvent mixture were tested; where 10 mL was not found to increase the recovery of analytes, but increased the cleaning of the pollution in eluate.Polar solvents such as acetone, ethyl acetate, acetonitrile were found to increase the extraction efficiency of selected POPs from sediment, and penetrate the sediment better than non-polar solvents. Hexane is a non-polar solvent, with a good separation ability of oily compounds from matrices. Moreover, hexane, ethyl acetate and acetone were being favored because of their low cost, low toxicity, and agreeable odor (Covaci et al., 2002). Therefore, the mixture of ethyl acetate: hexane:acetone for the extraction of PCBs, PBDEs and OCPs from sediments was selected in the current study.

Surface water and sediments are matrices including a broad array of interferences which might affect the determination of the selected analytes. Also, these analytes may occur in a wide range of amounts in water and sediments, so it is very substantial to provide a high sensitivity and reproducible of the procedure (Covaci et al., 2002, 2005, Sanchez-Avilla et al., 2009). For this, the developed method was validated according to Eurachem Guide. All target compounds indicated significant matrix effect for sediments. Therefore, matrix-matched standard calibration was used for PCBs, PBDEs and OCPs quantification for compensate this case in sediment samples. Since deionized water for validation of method was used for the optimization of target analytes from water samples, no matrix-matched analysis were performed. Calibration curves provided good linearity with a coefficient of determination (r2) >0.99 for selected PCBs, PBDEs and OCPs compounds in water and sediment over a concentration range from 0.25 to 10 ng mL-1 and from 0.5 to 20 ng g^{-1}, respectively (Tables 2 and 3).Repeatability and intermediate precision were investigated through RSD studies, and the same concentration levels as in linearity assays (n=6) were measured. As shown in Tables 2 and 3, RSD values were ≤10% and ≤8% for intermediate precision and repeatability in water and sediments, respectively. LODs and LOQs were 0.03-0.24 and 0.09-0.81 ng mL^{-1} in water, 0.05-0.39 and 0.17-1.31 ng g-1 in sediment, respectively (Table 2 and 3). Covaci et al. (2005) has obtained similar limits for PBDEs using GC-MS and for PCBs and OCPs using GC-Electron Capture Detector in sediments; whereas the detection limits of PCBs and PBDEs were higher than the study by Barco-Bonilla et al (2015), who used Gas Chromatography High Resolution Mass Spectrometry; which could be explained by the sensitivity of the device.

Trueness was considered as suitable those values between 70 and 120%. In water, all compounds indicated recoveries over the range of 88-106% (Table 4). The recoveries for target analytes from spiked tap and surface water samples to eliminate matrix effects

were obtained between 97-107% for PCBs, 74-102 for PBDEs, 92-102 for OCPs with RSD below 11%. Data was not presented. For sediment, all compounds showed recovery values between 91 and 106%(Table 5). It was seen that the developed method gave satisfactory results. The selectivity of the method is shown in Figs 1 and 2. Retention times of α-HCH with HCB, PCB153-labeled 13C12 with PCB 153, PCB138 with p,p'-DDT are very close together. But this phenomenon was discarded due to perform SIM mode for quantification of this analytes.

The developed method was used to measure selected PCBs, PBDEs and OCPs in 6 lake sediments, 6 river sediments, 6 tap water, 6 lake water and 6 river water samples. No target compound were found in tap water samples, but all another water samples were positive. Regarding sediment, 4 out of the 6 sediment ob-

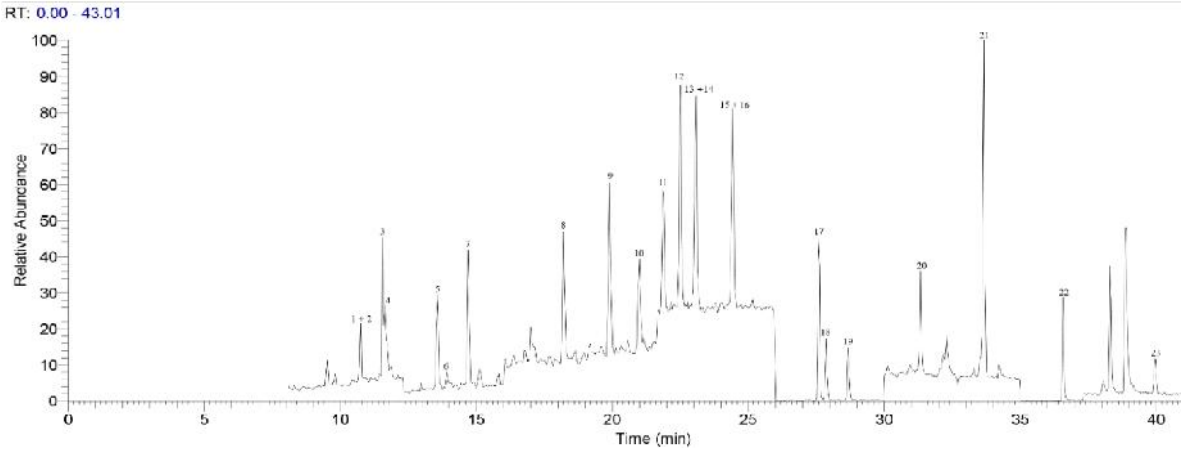

Fig. 1. The chromatogram of fortified water samples (0,5 ng mL-1) and selectivity of proposed method. 1 and 2) Alfa- hexachlorocyclohexane and hexachlorobenzene, 3) PCB 30, 4) Gamma-hexachlorocyclohexane, 5) PCB 28, 6)Heptachlor, 7) PCB 52, 8)PCB 101, 9) p,p'-dichlorodiphenyldichloro ethylene, 10) PBDE 17, 11) PCB 118, 12) p,p'-dichlorodiphenyl dichloroethane, 13 and 14) PCB153-labeled 13C12 and PCB 153, 15 and 16) PCB138 and p,p'- dichlorodiphenyl trichloroethane, 17) PCB 180, 18) PBDE 47, 19) PBDE 66, 20) PBDE 100, 21) PCB209, 22) PBDE 153, 23) PBDE 183.

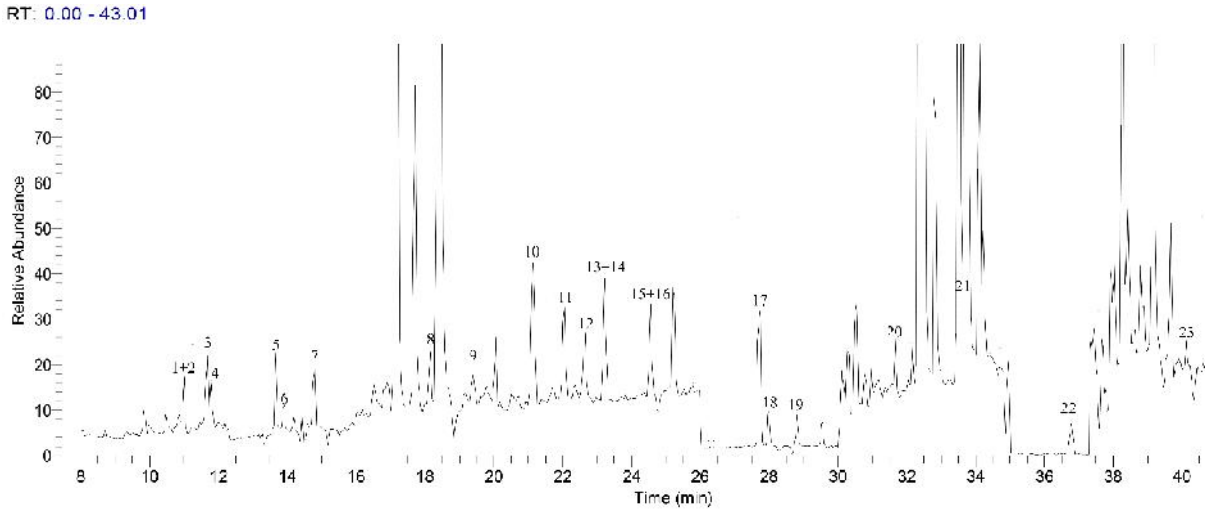

Fig .2. The chromatogram of fortified sediment sample (0,5 ng g-1) and selectivity of proposed method. 1 and 2) Alfa- hexachlorocyclohexane and hexachlorobenzene, 3) PCB 30, 4) Gamma-hexachlorocyclohexane, 5) PCB 28, 6)Heptachlor, 7) PCB 52, 8)PCB 101, 9) p,p'-dichlorodiphenyldichloro ethylene, 10) PBDE 17, 11) PCB 118, 12) p,p'-dichlorodiphenyl dichloroethane, 13 and 14) PCB153-labeled 13C12 and PCB 153, 15 and 16) PCB138 and p,p'- dichlorodiphenyl trichloroethane, 17) PCB 180, 18) PBDE 47, 19) PBDE 66, 20) PBDE 100, 21) PCB209, 22) PBDE 153, 23) PBDE 183.

tained by Ankara River, and all sediments obtained by Kösrelik Lake analyzed were positive. The detected compounds in water and sediment samples were p,p'-DDE, PBDE 17, PBDE 47, PBDE 66, PBDE 100 and PBDE 153, and PCB 101, PBDE 17, PBDE 66 PBDE 100 and PBDE 153, respectively, which were found at low concentration levels ranging from 0.24 to 2.90 ng mL-1 in water, and from 0.77 to 6.94 ng g-1 in sediment samples. p,p'-DDE was detected in most of the water, however PBDE 17 was detected in most of the sediment. A study reported that the most detected compounds in water samples from Almeria province (southeast of Spain) were PCBs and PBDEs with a low halogenationlevel, which werefound at low concentration levels ranging from 0.05 and0.20 ng L-1(Barco-Bonilla et al., 2015).

The high concentrations of total DDTs and related compounds in surface water showed that DDT usage wasunfortunately intense; yet lake or river have suffered significant inputs of DDTs. p,p'-DDE, the decomposition product of DDT in natural environment (Barakat et al., 2002), was predominant in surface water and detected in all the river and lake water. Erdogrul et al (2005) also reported the same compoundas the most abundant in fish samples from Sir Dam Lake, Kahramanmara?,-Turkey. The results indicate that, DDTs were not newly released into those locations, and the metabolite residues are due to their possible use previously. PBDE 17 was clearly the predominant PBDE congener in lake water and sediment. It was concluded that Ankara River and Kosrelik Lake have been affected by municipal and industrial discharges.

CONCLUSIONS

The combination of SPE and ultrasonic extraction with GC-MS ensures highly sensitive analytical procedures for the simultaneous determination of PCBs, PBDEs and OCPs in surface water samples and sediments. Ultrasound extraction procedure ensures simplicity and speed for extract organic compounds from very complex matrices such as sediments. Purification using SPE cartridge loaded with C18 for water and florisil/PSA/magnesium sulfate for sediment had notably a highersensitivity for the clean-upprocedure and prevention of thedeterioration of the GC-MS system. The developed method was validated and appropriate results were attained, with favorable recoveries (70-120%) and precision values (RSD<20%). The developed and validated method was successfully applied on surface water and sediments from lake and river; where the effects of the pollution were observed in both matrices.

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