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Determination of selected organic contaminants in soil by pressurized liquid extraction and gas chromatography tandem mass spectrometry with in situ derivatization

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ABSTRACT

The determination of organic contaminants in soil is a real challenge due to the large number of these compounds with quite different physico-chemical properties. In the present work, an analytical method was developed for the simultaneous determination in soil of 40 organic contaminants belonging to different chemical classes: polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polybrominated diphenyl ethers, UV filters, parabens, bisphenols and triclosan. Soil was extracted by pressurized liquid extraction and the extracts, without the need of a clean-up step, were analyzed by gas chromatography–tandem mass spectrometry after in situ derivatization in the gas chromatographic system. In the pressurized liquid extraction step, two extraction cycles were performed with a mixture of ethyl acetate–methanol (90:10, v/v) at 80 °C. Recovery of these contaminants from soil samples spiked at levels ranging from 30 to 120 ng g^{-1} was satisfactory for most of the compounds. The developed procedure provided detection method limits from 0.1 to 2.5 ng g^{-1}. The analysis of soil samples collected in different agricultural fields confirmed the presence of some of the studied contaminants. Polycyclic aromatic hydrocarbons were the main contaminants detected, parabens and polychlorinated biphenyls were also found but at relatively low concentration levels, 2-ethylhexyl salicylate was the UV filter that appeared most frequently at levels ranging from 17.2 to 43.4 ng g^{-1} and triclosan was found in eight out of fourteen samples, at relatively low concentration levels (0.8–28.6 ng g^{-1}).

1. Introduction

The fate of organic contaminants and their adverse environmental and human health effects has attracted the attention of scientists and regulatory bodies; however, the simultaneous determination of these contaminants is a real challenge due to the large number of these compounds with quite different physico-chemical properties. Among the various types of contaminants, persistent organic pollutants (POPs) are a very important group of compounds with a high potential of bioaccumulation in living organisms and resistance to degradation. POPs are prone to long-range atmospheric transport and deposition and as a result they have been detected in remote areas. In the Stockholm Convention of 2001, polychlorinated biphenyls (PCBs), organochlorine pesticides, and polychlorinated dibenzofurans and dibenzodioxins, among others, were included as POPs. In 2009, polybrominated diphenyl ethers (PBDEs), perfluorinated compounds, hexachlorocyclohexane and pentachlorobenzene were added to this list. Polycyclic aromatic hydrocarbons (PAHs) are not considered POPs because they usually are not bioaccumulated and are naturally-occurring substances. Nevertheless, it is important to monitor these compounds in the environment because they are toxic substances which are resistant to degradation and have been included in the European Union (EU) list of priority pollutants [1]. Another group of contaminants, which have been increasingly studied in the last decade in view of the number of papers published, are the so-called emerging organic contaminants (EOCs). EOCs comprise a rather large range of compounds that have not been regulated yet and are widely used. EOCs have caused widespread concerns due to their extensive use and their entry into the environment through effluents of wastewater treatment plants (WWTPs), surface water runoffs and soil leaching after agricultural application of sludge and manure as amendments. Soil is an important reservoir of these contaminants, due to their low solubility and great ability to be adsorbed or associated to soil particles.

Several analytical methodologies are already available in the literature for the determination of individual or a combination of several of these compounds in soil [2–4]. Among the different extraction procedures available, ultrasound assisted extraction (UAE) has been used in the determination of parabens [5] and

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endocrine disrupting compounds [6–8] whereas Soxhlet has been applied in the extraction of PAHs, PCBs and PBDEs from soil [1,9,10]. Pressurized liquid extraction (PLE) is a well-established technique that provides excellent extraction yields and the possibility of integrating extraction and clean-up in one step. It was applied to the determination in soil of PAHs and PCBs [10,11] or the antimicrobials triclosan and triclocarban [12].

Quantification of contaminants in soil extracts can be achieved by employing gas chromatography–mass spectrometry (GC–MS) [7,10,13,14], gas chromatography–tandem mass spectrometry (GC–MS/MS) [11], comprehensive two-dimensional gas chromatography coupled to micro-electron capture detection (GC × GC–μECD) [15], liquid chromatography–mass spectrometry (LC–MS) [16] or liquid chromatography–tandem mass spectrometry (LC–MS/MS) [5,12]. Except for some neutral compounds, many EOCs are polar, non-volatile and thermally labile compounds and are unsuitable for GC separation. Thus, a derivatization step before GC analysis is necessary to improve their volatility and chromatographic behavior. Derivatization procedures are sometimes laborious and time-consuming; thus, in situ derivatization in the GC injector is an attractive alternative because it avoids preparative steps, accelerates reaction rates and reduces evaporative losses [17,18].

Due to the concern regarding the presence and fate of both persistent and emerging contaminants in the environment as well as the high cost and duration of analysis, there is a need to introduce fast and sensitive multiresidue methods capable of analyzing different classes of contaminants within one analytical procedure. Simultaneous analysis of several groups of compounds with different physico-chemical properties generally requires a compromise in the selection of experimental conditions, but the resultant multiresidue method increases the number of contaminants that can be determined in routine analyses. Nowadays, LC–MS/MS has become a widely used tool for the determination of a broad number of compounds. Nevertheless, GC–MS or GC–MS/MS are an interesting alternative to LC due to the high resolution, lower operation costs and reduced solvent waste. Moreover, matrix effects occurring in LC–MS/MS produce not only ion enhancement but ion suppression that hinders the quantification of target compounds.

The aim of this work was to develop an efficient method for the simultaneous analysis in soil of forty organic compounds, considered either persistent or emerging contaminants, belonging to various chemical classes and having different physico-chemical properties. To the best of our knowledge, a multiresidue method for the determination of all the compounds listed in this study in soil is not yet available. The selection of the analytes object of study was partly based on our previous works where many of the compounds were frequently detected in soil. Method development was based on the extraction of samples with PLE followed by in situ derivatization in the injection port to improve the response of the polar analytes. GC–MS/MS was selected to determine a high number of compounds of different classes in a single run with a high selectivity making unnecessary a clean-up step before the analysis. The validated method was used to monitor these contaminants in soil samples collected from agricultural fields located in different Spanish regions.

2. Experimental

2.1. Reagents and standards

Ethyl acetate, acetone and methanol, residue analysis grade, were purchased from Scharlab (Barcelona, Spain). Diatomaceous earth, 30/40 mesh, was purchased from Resprep Corporation (Bellefonte, PA). Fat free quartz sand was supplied by Buchi Labortechnik AG (Switzerland). Spe-ed™ PSE matrix (hydroscopic samples dispersing agent) was purchased from Applied Separations (Allentown, PA). A mixture of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) (99:1, v/v), supplied by Aldrich (Steinheim, Germany), was used as silylation reagent.

A standard solution of the 16 EPA-priority PAHs (2000 μg mL^{-1} each) was supplied by Sigma–Aldrich. EPA 525 fortification solution B from Supelco (Bellafonte, PA), containing acenaphthene-d_{10} (Ace-d_{10}), phenanthrene-d_{10} (Phen-d_{10}), perylene-d_{12} (P-d_{12}) and chrysene-d_{12} (Chr-d_{12}) at 500 μg mL^{-1} in acetone, was used as internal standard. A mixture of 7 PCBs (Code BP-D7) at a concentration of 10 μg mL^{-1} in nonane:toluene (96.5:3.5, v/v) (PCB 28, 52, 101, 118, 138, 153 and 180), and a 5 μg mL^{-1} nonane:toluene (93:7, v/v) solution of seven $^{13}C_{12}$-labeled PCBs (Code MBP-D7) were purchased from Wellington Laboratories (Guelph, Ontario, Canada). A standard solution of PBDEs (Code BDE-MXD) containing BDE 17, 47, 66, 100, 153 and 183 (5 μg mL^{-1} each in nonane:toluene (74:26, v/v)), and a 5 μg mL^{-1} nonane solution of three $^{13}C_{12}$-labeled PBDEs (BDE 47, 99 and 153) (Code MBDE-MXA), were supplied by Wellington Laboratories (Guelph, Ontario, Canada).

Methylparaben (MeP), ethylparaben (EtP) and propylparaben (PrP) were obtained from Sigma–Aldrich (St Louis, MO, USA). Propylparaben-d_4 (PrP-d_4) was purchased from CDN Isotopes (Quebec, Canada). Individual UV filter standards, 2-hydroxy-4-methoxybenzophenone (HMB), 2-ethylhexyl salicylate (EHS) and 3,3,5-trimethylcyclohexyl salicylate (HMS), purity > 97%, were obtained from Sigma–Aldrich (St Louis, MO, USA). Triclosan (TCS) and methyl triclosan (MTCS), purity > 97%, were obtained from Riedel-de Haën (Seelze, Germany), whereas $^{13}C_{12}$-labeled TCS and MTCS used as internal standards (100 μg mL^{-1} in nonane, purity > 98%) were supplied by Cambridge Isotope Laboratories (Andover, MA, USA). Bisphenol A (BPA), tetrachlorobisphenol A (TCBPA), tetrabromobisphenol A (TBBPA) and $^{13}C_{12}$-labeled standards of these compounds were purchased from Cambridge Isotope Laboratories (Andover, MA, USA).

The list of investigated compounds along with some of their physico-chemical characteristics is shown in Table 1.

A working mixture solution at 200 ng mL^{-1} was prepared in ethyl acetate. TBBPA and TCBPA, due to their low chromatographic response, were made up to 400 ng mL^{-1}. A standard solution containing all the labeled compounds used as internal standards was prepared in ethyl acetate at the same concentration as the working mixture solution. All standard solutions were stored at 4 °C prior to use.

2.2. Apparatus

2.2.1. GC–MS/MS

The analysis was performed with an Agilent 7890A (Waldbronn, Germany) gas chromatograph equipped with two 7693 automated liquid samplers (ALS) and coupled to a tandem triple quadrupole mass spectrometer, Model 7000. A fused silica capillary column ZB-5MS, 5% phenyl polysiloxane as nonpolar stationary phase (30 m × 0.25 mm i.d. and 0.25 μm film thickness), from Phenomenex (Torrance, CA, USA), was used. Helium (purity 99.995%) was used as carrier gas at a constant flow-rate of 1 mL min^{-1}. Injections were carried out with the following injection port temperature program: 80 °C of initial temperature, held 0.1 min, increased at 900 °C min^{-1} until 270 °C and decreased again until the initial temperature (80 °C) applying cooling with compressed air. Two-layer sandwich injections drawing 1 μL of sample and 1 μL of the derivatization reagent (BSTFA:TMCS (99:1, v/v)) were done in pulsed splitless mode in a single-taper glass liner with a nominal volume of 800 μL. The injections were carried out at a pulse pressure of 25 psi until 0.5 min with the splitless injector purge

Table 1
Physico-chemical properties of the target compounds.

IUPAC name	Abbreviation	MW[a]	Log K_{ow}[b]	pK_a	Water solubility (mg L^{-1})
PAHs					
Naphthalene	Naph	128.2	3.30		3.20E+1
Acenaphthylene	Acyl	152.2	3.94		1.61E+1
Acenaphthene	Ace	154.2	3.92		5.30E+0
Fluorene	Fl	166.2	4.18		1.85E+0
Phenanthrene	Phen	178.2	4.46		1.24E+0
Anthracene	Anth	178.1	4.45		6.40E−2
Fluoranthene	F	202.3	5.16		2.42E−1
Pyrene	Py	202.3	4.88		1.32E−1
Chrysene	Chr	228.3	5.81		1.80E−3
Benzo[a]anthracene	BaA	228.3	5.76		1.40E−2
Benzo[b]fluoranthene	BbF	252.3	5.78		1.00E−3
Benzo[k]fluoranthene	BkF	252.3	6.11		0.80E−3
Benzo[a]pyrene	BaP	252.3	6.04		1.60E−3
Indeno[1,2,3-c,d]pyrene	IcdPy	276.3	6.70		1.90E−3
Dibenzo[a,h]anthracene	DBahA	278.4	6.75		6.00E−5
Benzo[g,h,i]perylene	BghiP	276.3	6.63		2.65E−4
PCBs					
2,4,4′-Trichlorobiphenyl	PCB-28	257.5	5.51		1.17E−1
2,2′,5,5′-Tetrachlorobiphenyl	PCB-52	292.0	6.26		1.10E−1
2,2′,4,5,5′-Pentachlorobiphenyl	PCB-101	326.4	5.92		7.00E−3
2,3′,4,4′,5-Pentachlorobiphenyl	PCB-118	326.4	6.49		1.03E−4
2,2′,4,4′,5,5′-Hexachlorobiphenyl	PCB-153	360.9	6.66		2.54E−5
2,2,3,4,4′,5′-Hexachlorobiphenyl	PCB-138	360.9	7.44		6.60E−6
2,2′,3,4,4′,5,5′-Heptachlorobiphenyl	PCB-180	395.3	7.21		4.70E−4
PBDEs					
2,2′,4-Tribromodiphenyl ether	BDE-17	474.1	7.20		1.20E−2
2,2′,4,4′-Tetrabromodiphenyl ether	BDE-47	485.1	8.81		1.50E−2
2,3′,4,4′-Tetrabromodiphenyl ether	BDE-66	485.8	8.81		1.80E−2
2,2′,4,4′,6-Pentabromodiphenyl ether	BDE-100	564.7	8.90		4.00E−3
2,2′,4,4′,5,5′-Hexabromodiphenyl ether	BDE-153	643.0	7.90		1.00E−3
2,2′,3,4,4′,5′,6-Heptabromodiphenyl ether	BDE-183	728.0	8.27		2.00E−3
Parabens					
Methylparaben	MeP	152.2	1.66	8.17	2.45E+0
Ethylparaben	EtP	166.2	2.19	8.22	0.96E+0
Propylparaben	PrP	180.2	2.71	8.35	3.90E−1
UV filters					
2-Hydroxy-4-methoxybenzophenone	HMB[c]	228.2	3.52	7.56	
2-Ethylhexyl salicylate	EHS[c]	250.4	5.97	8.13	
3,3,5-Trimethylcyclohexyl salicylate	HMS[c]	262.3	6.16	8.09	
Bisphenols					
Bisphenol-A	BPA	228.3	3.40	9–11	1.20E+2
Tetrachlorobisphenol-A	TCBPA	366.1	6.22	6.42	7.20E−1
Tetrabromobisphenol-A	TBBPA	543.9	5.60	6.33	2.80E−1
Triclosan					
Triclosan	TCS	290.1	4.76	8	1.97–4.6
Methyl triclosan	MTCS	304.0	5.20		

[a] MW, molecular weight.
[b] K_{ow}, octanol–water partition coefficient at 25 °C and pH 7.
[c] INCI, International Nomenclature for Cosmetic Ingredient elaborated by COLIPA (Committee de Liaison des Associations Europeans de L'industrie de la Perfumerie, de Products Cosmetics et de Toilette).

valve activated 1 min after sample injection (purge flow to split vent 50 mL min^{-1}). The column temperature was initially set at 80 °C (held for 0.5 min), increased at 8 °C min^{-1} to 230 °C and finally programmed at 5 °C min^{-1} to 280 °C (held for 10 min). The total analysis time was 39.25 min and the run was carried out with a solvent delay of 4 min.

First of all, mass spectra and retention times of each of the analytes were acquired operating in full scan mode with a mass range from 50 up to 700 *m*/*z*, scan time of 100 ms and an ion source temperature of 230 °C. The mass spectrometer was operated in electron impact (EI) ionization mode at 70 eV. The electron multiplier was set 200 eV above the autotune. Analyses were performed in the Multiple Reaction Monitoring (MRM) mode with 12 time segments (TS). The optimized program consisted on three MS/MS transitions, one quantifier and two qualifier transitions, for most of the target compounds. Table 2 lists the compounds studied along with their retention times, the quantifier and qualifier transitions and the optimized collision energy for each transition. Analytes were confirmed by their retention time and the identification of target and qualifier transitions. Retention times must be within ±0.2 min of the expected time and qualifier-to-target ratios within a 20% range for positive confirmation.

2.2.2. Extraction equipment

PLE was performed with a SpeedExtractor E-916 system (Buchi Labortechnik AG, Switzerland) furnished with 20 mL stainless-steel cells and 60 mL collection vials. Extracts were concentrated with a Multivapor P-12 equipped with a vacuum pump V-700 and a Controller V-855 (Buchi Labortechnik AG, Switzerland).

2.3. Samples

2.3.1. Sample collection

Various soil samples were collected from agricultural fields located in different Spanish provinces (Madrid, Guadalajara, Badajoz and Castellón). Soil was sampled from the upper layer (0–30 cm)

Table 2
Mass spectrometry parameters for the GC–MS/MS method.

TS[a]	Dwell time	Compound	t_R (min)	Q[b]	q1[c]	q2[d]	IS[e]
1	100	Naph	6.846	128.0 > 102.0 (25)	128.0 > 127.0 (20)	128.0 > 78 (30)	Ace-d_{10}
2	35	Acyl	10.983	152.0 > 151.0 (25)	152.0 > 150.0 (25)	152.0 > 126.0 (30)	Ace-d_{10}
		Ace-d_{10}	11.401	164.0 > 162.0 (25)	164.0 > 160.0 (40)	164.0 > 158.0 (50)	
		MeP-d_4	11.434	212.5 > 139.0 (10)	227.0 > 139.0 (25)		
		MeP	11.462	208.4 > 149.0 (10)	208.4 > 177.0 (20)	208.4 > 91.0 (15)	MeP-d_4
		Ace	11.489	154.0 > 153.0 (20)	154.0 > 152.0 (40)	154.0 > 151.0 (50)	Ace-d_{10}
3	50	EtP	12.539	194.4 > 151.1 (10)	222.4 > 151.1 (5)	222.4 > 134.9 (20)	MeP-d_4
		Fl	12.989	166.0 > 165.0 (25)	166.0 > 164.0 (40)	166.0 > 139.0 (50)	Ace-d_{10}
		PrP	13.966	194.4 > 151.1 (10)	237.0 > 195.0 (10)	237.0 > 151.0 (20)	MeP-d_4
4	55	Phen-d_{10}	15.703	188.0 > 160.0 (30)	188.0 > 186.0 (25)	188.0 > 184.0 (40)	
		Phen	15.771	178.0 > 152.0 (30)	178.0 > 177.0 (25)	178.0 > 176.0 (30)	Phen-d_{10}
		Anth	15.921	178.0 > 152.0 (30)	178.0 > 177.0 (25)	178.0 > 176.0 (30)	Phen-d_{10}
5	30	$^{13}C_{12}$-PCB-28	16.890	267.3 > 197.2 (35)	267.3 > 198.2 (35)	269.3 > 198.1 (35)	
		PCB-28	16.898	185.7 > 150.1 (40)	185.7 > 151.1 (30)	255.6 > 186.1 (30)	$^{13}C_{12}$-PCB-28
		EHS	17.609	194.4 > 75.0 (30)	194.4 > 177.0 (15)	194.4 > 159.0 (25)	$^{13}C_{12}$-BPA
		$^{13}C_{12}$-PCB-52	17.736	231.4 > 162.2 (40)	231.4 > 197.1 (30)	303.3 > 269.0 (15)	
		PCB-52	17.743	291.5 > 220.1 (30)	291.5 > 222.1 (30)	219.7 > 185.1 (25)	$^{13}C_{12}$-PCB-52
		HMS	18.109	194.5 > 75.1 (30)	194.5 > 177.1 (15)	194.5 > 159.1 (25)	$^{13}C_{12}$-BPA
6	20	F	19.282	202.0 > 200.0 (50)	202.0 > 201.0 (30)	202.0 > 176.0 (40)	Phen-d_{10}
		HMB	19.353	284.3 > 285.1 (5)	284.3 > 242.1 (25)	284.3 > 241.2 (35)	$^{13}C_{12}$-BPA
		$^{13}C_{12}$-PCB-101	19.822	265.3 > 266.1 (5)	337.2 > 303.0 (15)	337.2 > 268.1 (35)	
		PCB-101	19.826	327.5 > 256.0 (30)	325.5 > 256.0 (30)	325.5 > 290.9 (15)	$^{13}C_{12}$-PCB-101
		$^{13}C_{12}$-MTCS	19.846	313.7 > 264.0 (20)	315.6 > 266.0 (20)	263.7 > 200.0 (25)	
		MTCS	19.852	251.3 > 189.0 (25)	251.3 > 161.0 (35)	301.2 > 252.1 (20)	$^{13}C_{12}$-MTCS
		$^{13}C_{12}$-TCS	19.881	356.4 > 206.1 (15)	356.4 > 322.1 (5)	356.4 > 225.1 (5)	
		TCS	19.888	199.5 > 170.1 (35)	199.5 > 185.1 (20)	346.4 > 200.1 (15)	$^{13}C_{12}$-TCS
		Py	19.932	202.0 > 200.0 (50)	202.0 > 201.0 (30)	202.0 > 175.0 (45)	Phen-d_{10}
7	20	$^{13}C_{12}$-BPA	20.925	368.2 > 73.1 (40)	368.2 > 197.2 (5)	368.2 > 196.2 (5)	
		BPA	20.930	372.0 > 357.0 (10)	372.0 > 191.0 (10)		$^{13}C_{12}$-BPA
		BDE-17	21.042	247.3 > 139.2 (30)	405.3 > 248.1 (20)	405.3 > 246.0 (20)	$^{13}C_{12}$-BDE-47
		$^{13}C_{12}$-PCB-118	21.395	337.2 > 338.0 (5)	337.2 > 268.0 (35)	335.2 > 266.1 (35)	
		PCB-118	21.403	327.5 > 256.0 (30)	325.5 > 256.0 (30)	325.5 > 254.0 (30)	$^{13}C_{12}$-PCB-118
		$^{13}C_{12}$-PCB-153	21.964	371.1 > 301.9 (30)	371.1 > 301.0 (35)	301.2 > 302.0 (5)	
		PCB-153	21.973	361.4 > 289.9 (30)	359.4 > 289.9 (30)	359.4 > 287.9 (30)	$^{13}C_{12}$-PCB-153
		$^{13}C_{12}$-PCB-138	22.686	371.2 > 372.0 (5)	371.2 > 337.0 (15)	371.2 > 302.0 (35)	
		PCB-138	22.697	359.4 > 324.9 (15)	359.4 > 289.9 (30)	361.4 > 290.0 (30)	$^{13}C_{12}$-PCB-138
8	20	Chr	24.093	228.0 > 226.0 (40)	228.0 > 227.0 (25)	228.0 > 202.0 (30)	Chr-d_{12}
		Chr-d_{12}	24.121	240.0 > 236.0 (40)	240.0 > 238.0 (25)	240.0 > 212.0 (30)	
		BaA	24.214	228.0 > 226.0 (40)	228.0 > 227.0 (25)	228.0 > 202.0 (30)	Chr-d_{12}
		$^{13}C_{12}$-PCB-180	24.585	335.2 > 335.9 (5)	405.1 > 335.9 (35)	405.1 > 335.0 (35)	
		PCB180	24.596	395.4 > 325.9 (30)	395.4 > 323.9 (30)	393.4 > 323.9 (30)	$^{13}C_{12}$-PCB-180
		$^{13}C_{12}$-BDE-47	24.786	337.2 > 338.0 (5)	337.2 > 230.1 (35)	497.3 > 337.2 (25)	
		BDE-47	24.794	485.2 > 325.9 (20)	325.2 > 245.0 (20)	325.2 > 217.0 (30)	$^{13}C_{12}$-BDE-47
		BDE-66	25.344	485.2 > 325.9 (20)	325.2 > 245.0 (20)	325.2 > 217.0 (30)	$^{13}C_{12}$-BDE-99
9	35	BDE-100	27.588	403.1 > 297.0 (30)	565.3 > 405.7 (30)	565.3 > 403.7 (30)	$^{13}C_{12}$-BDE-99
		$^{13}C_{12}$-TCBPA	27.890	507.7 > 282.8 (15)	507.7 > 280.7 (15)	280.3 > 248.6 (40)	
		TCBPA	27.890	494.2 > 73.1 (30)	494.2 > 275.8 (10)	494.2 > 274.9 (10)	$^{13}C_{12}$-TCBPA
		BbF + BkF	28.095	252.0 > 250.0 (30)	252.0 > 251.0 (30)	252.0 > 226.0 (30)	Chr-d_{12}
		$^{13}C_{12}$-BDE-99	28.184	577.3 > 417.2 (25)	417.2 > 336.8 (25)	417.2 > 307.9 (35)	
10	60	BaP	29.233	252.0 > 250.0 (30)	252.0 > 251.0 (30)	252.0 > 226.0 (30)	P-d_{12}
		P-d_{12}	29.451	264.0 > 260.0 (50)	264.0 > 262.0 (30)	264.0 > 236.0 (30)	
11	50	$^{13}C_{12}$-BDE-153	31.838	247.6 > 153.5 (25)	247.6 > 167.9 (15)	655.3 > 495.7 (25)	
		BDE-153	31.853	241.6 > 148.0 (20)	241.6 > 187.7 (15)	481.3 > 402.7 (30)	$^{13}C_{12}$-BDE-153
12	30	$^{13}C_{12}$-TBBPA	33.282	684.0 > 73.0 (40)	684.0 > 74.0 (40)		
		TBBPA	33.298	672.0 > 73.9 (40)	672.0 > 73.0 (40)		$^{13}C_{12}$-TBBPA
		IcdPy	34.149	276.0 > 274.0 (50)	276.0 > 275.0 (30)	276.0 > 273.0 (50)	Chr-d_{12}
		DBahA	34.424	278.0 > 276.0 (40)	278.0 > 277.0 (25)	278.0 > 275.0 (50)	Chr-d_{12}
		BghiP	35.513	276.0 > 274.0 (50)	276.0 > 275.0 (30)	276.0 > 273.0 (50)	Chr-d_{12}
		BDE-183	37.284	280.5 > 227.6 (15)	280.5 > 226.6 (15)	280.5 > 187.0 (15)	$^{13}C_{12}$-BDE-153

[a] TS, time segment.
[b] *Q*, quantifier transition (collision energy, eV).
[c] *q*1: qualifier transition 1 (collision energy, eV).
[d] *q*2: qualifier transition 2 (collision energy, eV).
[e] IS, internal standard.

with a stainless steel corer and transported to the laboratory where it was air dried, sieved through a 2 mm mesh, thoroughly mixed and kept frozen (−18 °C) in glass containers until analysis. Soil used in the recovery assays was collected from the plough layer of an experimental plot located in the region of Madrid (Spain) that had the following characteristics: pH, 7.69; organic matter content, 0.97%; sand, 44.34%; silt, 37.44%; and clay, 18.22%.

2.3.2. Extraction and derivatization procedures

A metal frit and a cellulose disk were placed on the bottom of each extraction cell that was filled with 1 g of sieved soil and 7 g of Spe-ed™ PSE matrix that were previously homogenized in a glass mortar. For the recovery studies, samples were spiked with the working solution to reach concentrations of 120 ng g^{-1}, 60 ng g^{-1} or 30 ng g^{-1} (for TBBPA and TCBPA the concentration was doubled)

and the solvent was allowed to evaporate at room temperature. In all experiments, an isotope labeled internal standard solution was added to each soil sample prior to extraction. The cell was tightly closed and placed into the PLE system. Analytes were extracted with ethyl acetate–methanol (90:10, v/v) at 80 °C performing two 10 min cycles with the cell pressurized at 120 bar (1740 psi) and a purge time of 2 min. PLE extracts were concentrated in a Multivapor P-12 and adjusted to a final volume of 1 mL with ethyl acetate. Analyses of extracts were carried out by GC–MS/MS performing the derivatization of those analytes that required an improvement of their chromatographic response in the inlet of the GC system as described above.

3. Results and discussion

3.1. Optimization of the PLE procedure

Analytes binding to the matrix depends on their physico-chemical properties, as well as, on the characteristics of the matrix. Hence, it is important to know some basic physico-chemical properties such as acidity (pK_a), water solubility and octanol–water distribution (K_{ow}) of analytes. As shown in Table 1, K_{ow} values of the analytes studied in this work vary over a relatively wide range and, for this reason, finding an optimum strategy enabling their simultaneous isolation is not an easy task.

To achieve a fast and efficient extraction procedure, PLE variables such as temperature, pressure, solvent, dispersant and number of extraction cycles were evaluated. PLE was performed by dispersion of the sample with an inert material in order to avoid sample aggregation and thereby improve contact between solvent and matrix. Three of the most commonly used dispersion agents in PLE were studied. Sand, diatomaceous earth and Spe-ed™ PSE matrix (a type of cleaned and sieved diatomaceous earth) were evaluated in this study. In general, sand is a good choice for dry samples, whereas diatomaceous earth provides best results for samples with residual moisture. For air dried soil samples, both types of dispersing agents could be suitable. To evaluate solvent consumption, PLE cells, with 1 g of soil, were packed with the corresponding dispersant and extracted with ethyl acetate in the same run. The extraction carried out with Spe-ed™ PSE matrix generated the lowest solvent volume and was more cost effective than the others; therefore, Spe-ed™ PSE was chosen as dispersion agent.

Extraction solvent is one of the most important parameters to optimize in the development of an efficient extraction procedure. Initially, acetone and ethyl acetate were selected based on published literature. Ethyl acetate has been employed in our works to extract different organic pollutants from soil with very good results [2,8], whereas acetone has been used in a PLE procedure for the determination of TCS in soil [12]. In the case of acetone, the best results were obtained for parabens and BPA; however, for PAHs the recoveries were low (<50%) especially for those with higher molecular weight. Ethyl acetate provided good recoveries (>80%) for most of the compounds except for bisphenols (BPA, TCBPA, and TBBPA) and the UV filters that were < 60%. To improve the recovery of these compounds, the polarity of the extraction solvent was increased and mixtures of ethyl acetate:methanol were evaluated. Although ethyl acetate–methanol (80:20, v/v) provided the best results for those compounds with a low recovery in ethyl acetate a decrease in the extraction yield was observed for the other compounds. Hence, a mixture of ethyl acetate:methanol (90:10, v/v) was selected because it yielded acceptable extraction efficiency for bisphenols and UV filters from soil whereas good recoveries of the rest of the compounds were achieved.

Extraction temperature also plays an important role in PLE with regard to the solubility and mass transfer effect. Three extraction temperatures (60, 80 and 100 °C) were evaluated and low recoveries (<60%) were obtained for 60 °C whereas recoveries > 80% were obtained with the other two temperatures tested. Therefore, 80 °C was selected as extraction temperature because, although the recovery results obtained were similar to those achieved at 100 °C, a possible thermal degradation of the analytes was minimized.

The next step was to establish the optimal number of cycles. Three extraction cycles (10 min each) were carried out with a soil sample spiked at 60 ng g^{-1} and the extracts, after each cycle, were collected and analyzed separately. Negligible amounts of the studied compounds were detected in the third cycle and two cycles were selected as the optimum number.

In PLE, pressure is used to keep solvents as liquids at temperatures above their atmospheric boiling point. Some researchers do not optimize the applied pressure because it does not appear to be a critical parameter [19]. In the present work, the effect of pressure on the recoveries was checked by performing extractions at two different pressures 120 bar (1740 psi) and 100 bar (1450 psi) of soil samples spiked at 60 ng g^{-1}. The effect of the pressure was negligible and 120 bar was selected because it was the value recommended by manufacturer.

After extraction, each PLE extract was concentrated to 1 mL before the chromatographic analysis using an evaporator that allowed the concentration of twelve samples simultaneously. The effect of evaporation on the recovery of the target analytes was carried out concentrating 20 mL of ethyl acetate standards to 1 mL and comparing the chromatographic response with that of a standard freshly prepared. The evaporation was done at 95 mbar with the water bath at 60 °C without adding labeled standards. Losses were higher than 28% for all the compounds studied and higher than 67% for bisphenols. In order to reduce these losses, the temperature of the water bath was set at 40 °C and losses were lower than 8% for most of the compounds, except for Acyl, PrP and Anth, which were <15%. In order to correct recoveries, labeled standards were used.

3.2. Derivatization

Silylation is one of the derivatization procedures widely used to improve GC behavior of polar compounds containing phenolic groups, such as parabens and bisphenols. Silylation replaces active hydrogens by trimethylsilyl groups, producing derivatives which are more volatile and thermally stable. Derivatization is a time-consuming procedure which often requires the use of toxic reagents; therefore, the automatization of this step has many advantages, including less manipulation and increased productivity. Silylation using BSTFA containing 1% TMCS has been optimized in our previous works [2,4]. In summary, 50 μL of derivatizing agent were added to a 2 mL vial containing the sample (100 μL) and kept at 60 °C (10 min). This procedure, when carried out manually, has to be done in a fume hood and skin exposure has to be avoided. An interesting alternative to benchtop derivatization is the possibility of carrying out the reaction in the inlet of the gas chromatograph. The ALS is capable of making multilayer (sandwich) injections of the silylation reagent and the sample, so the derivatization takes place in the GC inlet [20]. Multilayer injections applying three different standard:reagent volume ratios (1:1, 1:0.5 and 1.5:0.5) were assayed for the in situ derivatization. The 1:1 ratio provided the highest response for all the compounds, not only those susceptible to react with the silylation reagent but those that do not contain active hydrogens. In some cases, such as parabens and BPA, a two-fold response improvement was found when working with the 1:1 ratio in comparison to the other two ratios tested. In general, the 1.5:0.5 ratio provided the lowest chromatographic response of the target analytes. Once the conditions for the in situ derivatization were selected it was compared with manual derivatization. Five standards were prepared manually by mixing 50 μL of a 60 ng mL^{-1} standard with 50 μL of BSTFA, left to react at 60 °C for 10 min and

Table 3
Validation data of the analytical method.

Compound	Recovery (%)[a]						MDL (ng g^{-1})	LOQ (ng g^{-1})
	120 ng g^{-1}		60 ng g^{-1}		30 ng g^{-1}			
	Mean	RSD	Mean	RSD	Mean	RSD		
Naph	99	5	98	12	44	6	1.9	6.4
Acyl	97	16	113	2	85	1	1.3	4.3
Ace	93	14	70	8	87	1	0.6	2.0
MeP	92	6	83	4	77	5	1.1	3.8
EtP	91	6	80	1	89	4	0.2	0.7
Fl	101	8	113	2	98	2	0.6	2.1
PrP	94	2	85	3	92	5	0.6	2.1
Phen	96	4	85	3	93	11	0.9	2.9
Anth	81	10	72	5	76	2	0.4	1.3
PCB-28	90	4	92	10	94	3	0.5	1.7
PCB-52	91	4	87	6	99	6	0.1	0.4
EHS	108	11	85	11	65	8	1.2	3.9
HMS	109	9	84	5	95	10	0.5	1.7
F	101	11	85	5	109	4	0.2	0.7
HMB	93	14	86	7	77	10	1.7	5.7
Py	99	8	73	1	106	4	0.9	3.0
PCB-101	88	3	90	9	97	9	0.4	1.3
MTCS	93	8	81	3	74	3	0.7	2.3
TCS	87	3	88	7	100	8	0.1	0.4
BDE-17	93	5	98	7	102	4	0.6	1.9
BPA	89	4	82	8	71	2	1.3	4.2
PCB-118	88	3	94	2	96	5	0.9	2.9
PCB-153	89	2	92	8	96	9	0.4	1.3
PCB-138	91	3	98	8	97	8	0.3	1.1
Chr	97	5	82	2	112	4	0.8	2.6
BaA	100	5	82	2	114	8	2.0	6.6
PCB-180	95	9	100	9	95	1	0.2	0.8
BDE-47	91	3	88	8	94	6	0.2	0.6
BDE-66	86	4	81	2	98	8	0.5	1.8
BDE-100	86	4	81	6	96	6	0.9	2.8
BbF + BkF	103	4	86	4	114	5	0.9	2.9
TCBPA[b]	104	5	90	5	95	4	0.4	1.3
BaP	80	9	84	9	107	15	1.2	3.9
BDE-153	88	4	75	3	95	6	2.0	6.8
IcdPy	102	6	89	4	108	3	2.3	7.6
TBBPA[b]	98	6	89	5	93	5	1.1	3.8
DBahA	96	2	93	4	112	3	1.2	4.2
BghiP	95	4	83	4	99	9	1.5	5.2
BDE-183	96	7	80	5	91	7	2.5	8.3

[a] Number of replicates ($n = 5$).
[b] Recovery assays were carried out at 240, 120 and 60 ng g^{-1}.

finally 2 μL were injected into the GC–MS/MS system. On the other hand, five in situ derivatizations were performed using a 2 μL multilayer injection. By examining the peak areas after analysis, the relative response was higher when the derivatization was carried out in situ with relative standard deviation (RSD) < 9%, whereas for manual derivatization RSD were < 15%. Thus, in situ derivatization was selected since it presents several advantages over manual derivatization, such as higher chromatographic response, reduction of reagent usage and less time and manipulation required for sample preparation, which reduces laboratory costs. Nevertheless, a potential drawback of the in situ derivatization is the somewhat higher proportion of reagent injected that might influence the performance of the chromatographic column over time. Although BSTFA is an aggressive agent to the stationary phase, a very small amount is injected into the column and the lifetime of the column is acceptable.

3.3. Gas chromatographic determination

Precursor ions for each analyte were selected taking into consideration a high ion m/z and abundance. Once selected the precursor ions, product ion spectra were obtained by collision induced dissociation at collision energies ranging from 5 to 50 eV and the experiment design software automatically selected the optimal collision energy for each transition tested. Three transitions were selected, one as quantifier and two as qualifiers, for most of the compounds. The chromatographic method was divided in 12 time segments where the dwell time was adjusted to maintain the cycle time constant.

Prior to the analysis of samples, contamination arising from the presence of contaminants in certain parts of the gas chromatograph, such as the inlet septum and the stationary phase of the capillary column, was studied. To reduce the possible memory effects of the column, everyday, prior to the analysis of samples, the inlet was flushed by heating at 300 °C for 30 min and procedural blanks were analyzed after every four samples.

Quantification was carried out with internal standard calibration. The isotopically labeled compounds used as internal standards for each analyte are shown in Table 2. BbF and BkF were quantified as the sum of both because they co-eluted and had the same transitions.

The chromatographic response of target analytes may be affected by the presence of matrix components that may produce an improvement in analyte transfer into the column. Matrix effect was evaluated preparing two sets of standard solutions ranging from 10 to 200 ng mL^{-1}, one set of standards was solvent-based and the other was prepared spiking blank soil extracts. The slopes obtained by plotting concentration at five levels against peak area,

following linear regression analysis, were compared. A significant increase of the chromatographic response was observed for PCBs 28, 118, 138, BDE 100, IcdPy, DBahA, BghiP, and the three UV filters (EHS, HMS and HMB). Rodil et al. [21] reported high matrix effects in the determination of EHS and HMS when PLE was used. There are several approaches to counteract matrix-induced effects, such as exhaustive clean-steps to reduce the amount of matrix components extracted, the use of inert surfaces in the GC system, and different calibration methods [22]. Among the calibration methods employed to overcome matrix effects, matrix-matched standards are often used in spite of its main drawback, which is the lack of appropriate blank matrix. An alternative to matrix-matched calibration is the use of isotopically labeled standards, which avoids the dependence of the results obtained from the sample matrix, although they are usually expensive and sometimes not available for environmental analysis.

Isotopically labeled standards of most of the target analytes of this study were available. To evaluate if isotope labeled internal standards could minimize matrix effects, calibration curves for standards prepared in neat solvent and in spiked soil blanks at the range from 10 to 200 ng mL^{-1}, which included internal standards at 60 ng mL^{-1}, were obtained. Fig. 1 shows the slope ratios between matrix-matched and solvent calibration for compounds with a significant matrix effect using external and internal standard quantification. Isotope labeled standards, used as internal standards, can overcome the increase in the chromatographic response due to matrix components achieving slope ratios of ca. 1.0 for most of compounds. Therefore, quantification was carried out using labeled standards as internal standards.

3.4. Method validation

After optimization, the developed method was evaluated in terms of linearity, precision, accuracy and detection limits before it was used to determine contaminant residues in soil from agricultural fields.

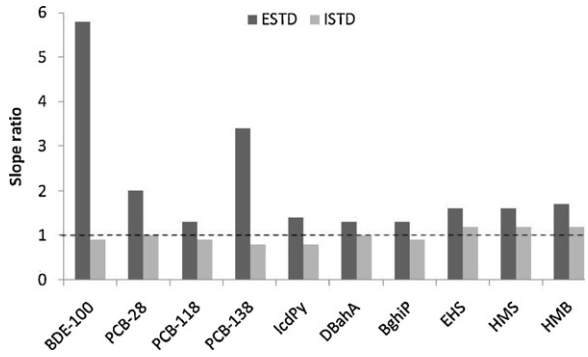

Fig. 1. Slope ratios between matrix-matched and solvent-based standards of a selection of target analytes applying external standard (ESTD) or internal standard (ISTD) quantification.

3.4.1. Linearity

The linearity of the method was evaluated injecting five standard solutions prepared at 10, 25, 50, 100 and 200 ng mL^{-1} levels for all the studied compounds except for TCBPA and TBBPA that were prepared at double-concentration due to their low response. All the set of standards contained isotopically labeled internal standards at 60 ng mL^{-1} (120 ng mL^{-1} for $^{13}C_{12}$-TBBPA and $^{13}C_{12}$-TCBPA). Standards were silylated with BSTFA using 2-layer sandwich injection and inlet derivatization. A good linearity was obtained in the range 10–200 ng mL^{-1} with correlation coefficients equal or higher than 0.990 for all the compounds studied.

3.4.2. Accuracy and precision

The accuracy of the method was evaluated performing the recovery of target analytes from soil samples spiked at three concentration levels 30, 60 and 120 ng g^{-1}. As can be seen in Table 3, the recovery results obtained were satisfactory (>70%) for most of the compounds at the levels assayed except for naphthalene with a 44% recovery at the lowest concentration assayed. Loss of this

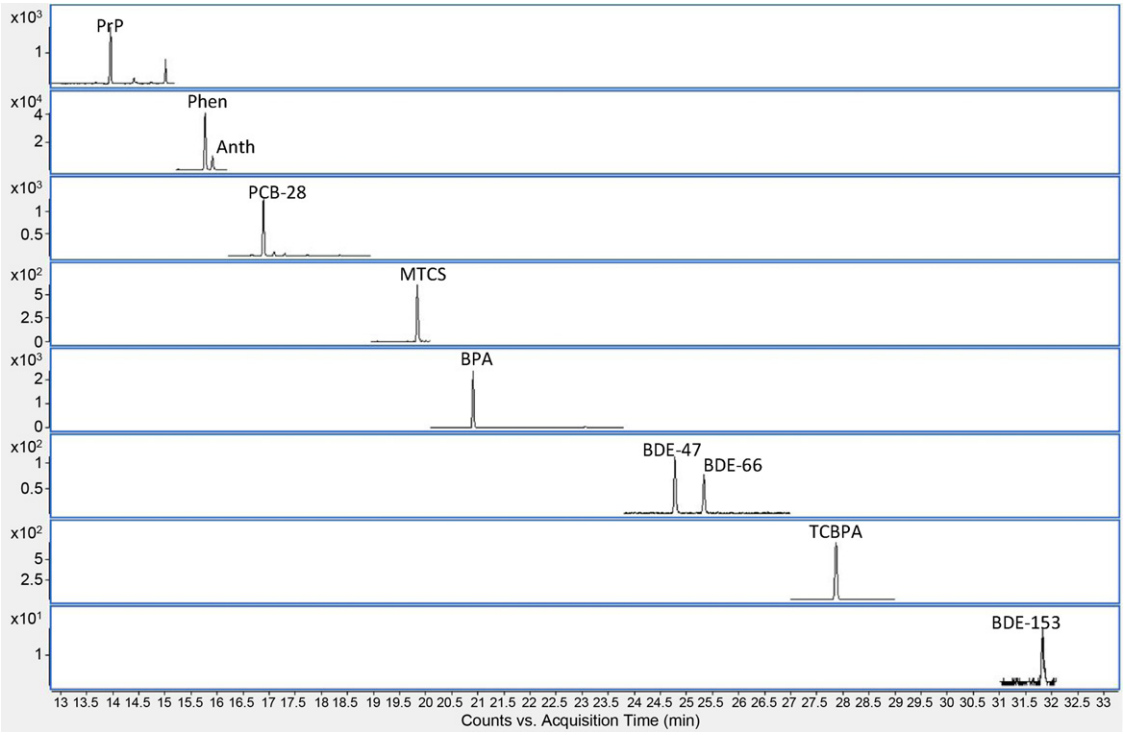

Fig. 2. Representative GC–MS/MS chromatograms, quantifier transition, of a soil sample spiked at 10 ng g^{-1} of each compound except for TCPBA (20 ng g^{-1}). See Table 1 for abbreviations and Table 2 for quantifier transitions.

Table 4
Concentration of the studied compounds (ng g^{-1}) detected in soils collected in agricultural fields from different areas of Spain.[a]

Compound	Soil													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Naph	21.1 ± 0.2	15.5 ± 0.1	16.8 ± 2.5	19.8 ± 1.9	NQ[b]	NQ	7.4 ± 0.2	13.5 ± 0.5	17.5 ± 0.3	15.2 ± 0.3	15.4 ± 0.7	15.1 ± 0.2	NQ	16.2 ± 0.3
Acyl					6.7 ± 0.1				16.6 ± 0.1					
Ace	NQ	NQ	NQ	NQ	2.4 ± 0.1			NQ	NQ	NQ	NQ	NQ		NQ
Fl	3.0 ± 0.1	NQ	2.2 ± 0.3	2.9 ± 0.1	5.1 ± 0.1	NQ	NQ		4.0 ± 0.1		NQ			4.1 ± 0.1
Phen	14.8 ± 1.3	9.5 ± 0.6	9.8 ± 2.0	23.7 ± 4.3	13.2 ± 0.4				50.2 ± 0.2		10.2 ± 1.2			17.2 ± 0.4
Anth					19.2 ± 0.6									
F	4.2 ± 0.4	1.7 ± 0.1	1.4 ± 0.1	31.5 ± 1.2	239.2 ± 1.6	1.1 ± 0.2	NQ		141.9 ± 1.1		2.7 ± 0.3		NQ	4.1 ± 0.2
Py	5.1 ± 0.4	NQ	NQ	27.6 ± 1.3	258.2 ± 0.5	NQ			173.3 ± 2.1		NQ			6.0 ± 0.2
Chr				18.8 ± 0.3	241.7 ± 2.6				57.9 ± 1.0				NQ	
BaA				18.2 ± 0.6	454.0 ± 1.7				74.4 ± 0.5				NQ	
BbF + BkF				5.7 ± 1.0	236.5 ± 1.8				51.6 ± 8.2				NQ	
BaP					227.9 ± 3.3				110.3 ± 0.6					
IcdPy					55.8 ± 1.1				47.6 ± 1.2					
DBahA					17.8 ± 0.9				10.6 ± 0.3					
BghiP				12.7 ± 0.3	32.7 ± 6.0				44.4 ± 0.7					
MeP	NQ			NQ					NQ	NQ	NQ	NQ		4.9 ± 1.2
PrP			NQ	NQ							2.5 ± 0.2			NQ
EHS	43.4 ± 0.6	17.8 ± 0.9	17.2 ± 3.9	29.2 ± 3.2							30.9 ± 4.0			37.8 ± 2.0
HMS									NQ					
HMB														NQ
TCS	0.9 ± 0.1	0.8 ± 0.1	0.8 ± 0.1	1.0 ± 0.1		3.4 ± 0.2			28.6 ± 1.4		0.9 ± 0.1		NQ	1.0 ± 0.1
BPA	7.3 ± 1.2		70.2 ± 10.8					5.5 ± 0.5						
PCB-28					2.2 ± 0.1	1.9 ± 0.6	2.7 ± 0.4	2.2 ± 0.1	2.0 ± 1.0	2.3 ± 0.1		1.9 ± 0.1	1.7 ± 0.1	
PCB-101						0.4 ± 0.1			NQ					
PCB-118						0.4 ± 0.1			0.5 ± 0.1					
PCB-153					NQ	2.1 ± 0.3	NQ		1.9 ± 0.1					
PCB-138					NQ	1.7 ± 0.5			2.2 ± 0.1					
PCB-180						2.3 ± 0.3	NQ		1.1 ± 0.1					

[a] Soil samples 1–9 were collected in agricultural fields in Madrid, soil sample 10 in Castellón, soil samples 11–13 in Badajoz and soil sample 14 in Guadalajara.
[b] NQ, not quantified (<LOQ).

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compound, due to its high volatility, during the extraction process or the concentration step has been previously reported [11]. The addition of labeled internal standards before the extraction procedure counteracted the evaporative losses at the two higher concentration levels assayed; however, at the lowest concentration the evaporation rate for naphthalene was higher than for the internal standard, and hence the low recovery obtained for this compound. Fig. 2 shows representative GC–MS/MS chromatograms of a soil sample spiked at 10 ng g^{-1} of each compound except for TCPBA (20 ng g^{-1}).

The intra-day precision was determined by analyzing five spiked samples on the same day ($n = 5$). The inter-day precision was evaluated by determining five replicates on four consecutive days ($n = 20$). The intra- and inter-day precisions RSD were lower than 12% and 17%, respectively.

3.4.3. Method detection limit (MDL) and limit of quantification (LOQ)

Eight replicates of soil extracts spiked at the lowest calibration level (10 ng g^{-1}) were analyzed in order to determine MDLs and LOQs of the developed method. The equation to calculate the MDL was the following: MDL = $t_{99} * S$, where t_{99} is the Student's t value for a 99% confidence level and $n - 1$ degrees of freedom and S is the standard deviation of the replicate analyses [23]. The LOQ was calculated as 10 times the standard deviation of the results of the replicate analysis used to determine MDL. As shown in Table 3 the MDL values ranged from 0.1 to 2.5 ng g^{-1}, which are lower than those previously reported by other authors [11,15].

3.5. Real samples

Once the method was optimized and validated it was used to monitor the contaminants object of this study in soil samples collected in 14 agricultural fields. Soil samples 1–3 were collected from fields that were amended with sludge at a 12 Tn/ha dose. Fields near the course of four rivers in the Madrid region were also sampled (soils 6–9). Reagent blanks were prepared together with the soil samples analyzed to check for contamination. As shown in Table 4, PAHs were the compounds found in soil at higher concentrations and parabens were also found but at relatively low levels. Soil 5 samples were collected from a field bordering a highway with heavy traffic, which could explain the high molecular weight PAHs found. PCBs were detected at concentrations up to 2.3 ng g^{-1} and these levels are similar to those reported in soils from southeast Spain [11] but the levels of PCB-28 were higher than those reported in an agricultural soil in China [9]. Although PBDEs have been detected in sewage sludge from Spanish WWTPs [24], they were not found in any of the soil samples analyzed. EHS was the UV filter most frequently detected at levels ranging from 17.2 to 43.4 ng g^{-1}. Triclosan was found in eight out of fourteen samples, at relatively low concentration levels (0.8–29 ng g^{-1}).

4. Conclusions

A multiresidue method for the determination in soil of forty selected organic contaminants belonging to different chemical classes was developed and validated. Isotope labeled internal standards were used to compensate the matrix induced chromatographic response enhancement observed avoiding the use of matrix-matched calibrations. In situ derivatization carried out in the injection port of the GC system was used as an attractive alternative to manual procedures because it simplifies the sample preparation and avoids the manipulation of hazardous reagents. The high selectivity of MS/MS detection allowed the identification and quantification of the diverse analytes selected without performing a clean-up step. The method was applied to soil samples collected in Spanish agricultural fields and the analysis confirmed the presence of some of the studied contaminants, PAHs being the compounds mainly detected at the highest levels.

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