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Multi-residue Methodologies for the Analysis of Non-polar Pesticides in Water and Sediment Matrices by GC–MS/MS

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Abstract

A multi-residue method for the analysis of non-polar pesticides by GC–MS/MS in water and sediment matrices has been successfully developed, including 33 and 27 compounds, respectively. Water analysis method is based on a classic liquid–liquid extraction with recoveries ranging between 39 and 102%, with RSDs lower than 13%, LODs of 0.42–15.2 ng L^{-1} and LOQs of 0.72–50.8 ng L^{-1}. Sediment analysis method is based on a pressurized liquid extraction with recoveries ranging between 37 and 133%, RSDs lower than 18%, LODs of 0.01–0.16 ng g^{-1} dry weigth (dw) and LOQs of 0.02–0.54 ng g^{-1} dw. Reported LODs were lower than the maximum acceptable detection limits set by the EU Watch Lists for selected pesticides. Applicability of both methodologies has been evaluated in real water and sediment samples collected in Catalonian river basins reporting oxadiazon for the first time in sediments from Catalonian river basins with a range of n.d. to 382 ng g^{-1} dw and a mean concentration of 44.0 ng g^{-1} dw. The importance of the simultaneous evaluation of both water and sediment has been emphasised since ten out of the 15 detected pesticides in the sediments can pose a high risk to aquatic organisms according to the Risk Quotient (RQ) method. Further detailed work needs to be done to better understand and assess the environmental impact of pesticide-contaminated sediments on aquatic organisms.

Keywords GC–MS/MS · Multi-residue · Oxadiazon · Pesticides · Sediment · Water

Introduction

Pesticides have been widely used since the mid-twentieth century to pest control. They present a wide range of physico-chemical diversity and can be persistent in water, accumulate in sediments, and bio-accumulate in biota, which poses an environmental and health issue due to its potential toxicity on non-target organisms [1]. Polar compounds tend to remain in water, potentially contaminating aquifers while the more non-polar ones tend to adsorb in sediments, soils and bio-accumulate in organisms entering the food chain, endangering environmental and human health. Pesticides can cause acute and chronic effects to aquatic life among which are injuries, inhibition or reproductive failure, suppression of the immune system, disruption of endocrine system, cellular damage, and physical deformities [2].

Regulation of pesticides is important due to environmental reasons. European Union classifies some pesticides within the List of Priority Substances under the water policy according to Directive 2013/39/EU [3] and the Watch List under the Commission Implementing Decision (EU) 2018/840 [4]. Priority substances are those that pose a significant risk to aquatic environment or through it. Current directive classifies 45 substances, 22 of which are pesticides. Directive 2013/39/EU updated the environmental quality standards (EQS) of the priority substances in line with the latest scientific and technical knowledge concerning the properties of those substances. EQS are limits on the concentration of the priority substances which must not be exceeded if a good chemical status is to be met concerning their presence in surface water. There are currently no established EQS for sediments, but the Directive 2013/39/EU states that EU Members shall monitor these substances in sediments with the optimal frequency to provide sufficient data for a reliable long-term trend analysis and to take measures aimed at ensuring that concentrations of priority substances do not increase significantly in sediments. The substances listed on the Watch List are those

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that EU has information that may pose a significant risk to aquatic environment or through it but monitoring data is insufficient to determine the risk. Moreover, a maximum acceptable detection limit is provided for monitoring of each substance. In this case, three of the eight class of listed substances are pesticides. Despite its regulation, pesticides represent an environmental issue difficult to solve due to its diffuse nature of origin (mainly runoff waters); to the widespread use at domestic, urban and agricultural level; to its extensive use in developing countries; to the illegal sale of banned products; and to its potential toxicity on non-target organisms [2].

Non-polar pesticides analysis' methods are based on GC–MS although, in recent years, GC–MS/MS methods have been developed to improve sensitivity and selectivity. There are several methods applied to water and sediment samples for specific families of pesticides. For example, Feo et al. [5] developed a method to analyze 12 different pyrethroid insecticides in water and sediments. However, due to the high number of pesticides of interest, including a wide range of families, and their regulation, it is necessary the development of multi-residue analysis methods with higher sensitivity than legislated levels. There are several multi-residue methods for pesticide analysis in water [6–25] and sediments/soils [6, 26–32] through GC–MS/MS.

For water matrices, there are studies that use classic liquid–liquid extraction methods [6, 7], SPE [8–19] and SPME [20–25]. Liquid–liquid extraction methods developed by Mondal et al. [6] and Robles-Molina et al. [7] obtained good recovery percentages (70–120%), RSDs lower than 20% and LOQs between 0.03 and 80 ng L^{-1} using as extracting solvents a mixture of ethyl acetate (EtAc)/dichloromethane (DCM) (8:2) and n-hexane, respectively. Regarding SPE, those methods using cartridges of HLB [8–14] and C18 [15–19] stand out. SPE methods with HLB cartridges [8–11] obtain recoveries between 60 and 120%, RSDs lower than 20% and LOQs that range between 10 and 500 ng L^{-1}. On the other hand, methods that use C18 cartridges [15–19] obtain recoveries between 65 and 120%, RSDs lower than 35.4% and LOQs between 3 and 80,000 ng L^{-1}. SPME methods generally use PDMS fibers. These methods [20–25] obtain recoveries ranging between 70 and 120%, RSDs lower than 34% and LOQs between 2 and 500 ng L^{-1}. Therefore, currently available methods offer LOQs between 0.03 and 80,000 ng L^{-1}. In general, LODs reported in the literature are lower than established EQS of priority substances except for pesticides, such as dicofol, cypermethrin, dichlorvos, and heptachlor epoxide. However, selected pesticides of the Watch Lists (methiocarb, oxadiazon, and triallate) are not included in most published methods including, to the best of the authors knowledge, only methiocarb in two methods [11, 17], but with LODs higher than the maximum acceptable detection limit of the EU Watch list of 2018.

For sediment and soil matrices, there are several published studies that use, in general, pressurized liquid extraction (PLE) [26, 27], QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) [6, 28–31], and ultrasound extraction [32]. Zhang et al. [32] developed a method using ultrasound extraction with a mixture of hexane/DCM (1:1) followed by a clean-up step using Florisil (FL) cartridges. Obtained recoveries ranged between 70 and 130% with RSDs lower than 20% and LODs between 0.1 and 57.1 pg g^{-1} dry weight (dw). PLE methods used different extracting solvents, such as DCM [26] or methanol [27]. Recoveries ranged between 63 and 119% with RSDs lower than 35% and LODs lower than 1 ng g^{-1} dw. Regarding QuEChERS, recoveries ranged between 65 and 120% with RSDs lower than 28%. LODs and LOQs are quite variable and range between 4.9 and 21.7 ng g^{-1} dw [28], and between 5 and 10 ng g^{-1} dw [29]. Fernandes et al. [30] obtained LODs lower than 7.6 ng g^{-1} dw while Yu et al. [31] obtained LOQs between 0.1 and 5 ng g^{-1} dw. However, some pesticides of recent interest, such as those included in the Watch List, are not included.

The objective of the present work was to develop analytical methodologies for the analysis of 38 non-polar pesticides, chosen based on the priority substances and Watch Lists, in water and sediment samples. Selected analytes belong to different classes and applications, with molecular weights ranging between 201.7 and 545.5 g mol^{-1}, and Log K_{OW} values between 1.90 and 6.80 (Table 1). Moreover, another objective of our study was to obtain lower LODs and LOQs than those previously reported and lower than the maximum acceptable detection limits of the Watch List pesticides and priority substances' EQS (Table S1).

Materials and Methods

Standards and Solvents

Native standards of 2,4′-DDD, 4,4′-DDD, 2,4′-DDE, 4,4′-DDE, 2,4′-DDT, 4,4′-DDT, cyhalothrin, bifenthrin, and permethrin were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Trifluralin, methiocarb, fenitrothion, chlorpyrifos, fenthion, dicofol, pendimethalin, oxadiazon, oxyfluorfen, quinoxyfen, diflufenican, cypermethrin, isoproturon, dichlorvos, simazine, diazinon, triallate, propanil, terbutryn, malathion, triadimefon, chlorfenvinphos, cyproconazole, hexachlorobenzene, lindane, endosulfan, and mirex were purchase from Sigma-Aldrich (Steinheim, Germany). Heptachlor epoxide and bifenox were purchased from LGC standards (Teddington, Middlesex, UK).

Internal standards of d_{14}-trifluralin, d_{10}-chlorpyrifos, phenoxy-d_5-cyhalothrin, d_{10}-simazine, d_{10}-diazinon, s-methyl-d_3-terbutryn, diethyl-d_{10}-malathion, $^{13}C_6$-hexachlorobenzene, and phenoxy-d_5-fenvalerate were purchased

Table 1 Chemical name, CAS, molecular weight, Log K_{ow}, molecular formula, application, and class of selected analytes

Application[a]	Class[a]	Name	CAS	Molecular weight[a]	Log K_{ow}[a]	Molecular formula[a]
Acaricides[b]	Organochlorine	Endosulfan[c]	115-29-7	406.9	4.75	$C_9H_6Cl_6O_3S$
		Dicofol[c]	115-32-2	370.5	4.30	$C_{14}H_9Cl_5O$
		Lindane[c]	58-89-9	290.8	3.50	$C_6H_6Cl_6$
	Organophosphate	Chlorfenvinphos[c]	470-90-6	359.6	3.80	$C_{12}H_{14}C_{13}O_4P$
		Diazinon	333-41-5	304.4	3.69	$C_{12}H_{21}N_2O_3PS$
		Malathion	121-75-5	330.4	2.75	$C_{10}H_{19}O_6PS_2$
		Dichlorvos[c]	62-73-7	221.0	1.90	$C_4H_7Cl_2O_4P$
	Pyrethroid	Bifenthrin	82,657-04-3	422.9	6.60	$C_{23}H_{22}ClF_3O_2$
Fungicides	Azole	Triadimefon	43,121-43-3	293.8	3.18	$C_{14}H_{16}ClN_3O_2$
		Cyproconazole	94,361-06-5	291.8	3.09	$C_{15}H_{18}ClN_3O$
	Organochlorine	Hexachlorobenzene[c]	118-74-1	284.8	3.93	C_6Cl_6
	Quinoline	Quinoxyfen[c]	124,495-18-7	308.1	5.10	$C_{15}H_8Cl_2FNO$
Herbicides	Amide	Diflufenican	83,164-33-4	394.3	4.20	$C_{19}H_{11}F_5N_2O_2$
		Propanil	709-98-8	218.1	2.29	$C_9H_9Cl_2NO$
	Carbamate	Triallate[d]	2303-17-5	304.7	4.06	$C_{10}H_{16}Cl_3NOS$
	Diphenyl ether	Bifenox[c]	42,576-02-3	342.1	3.64	$C_{14}H_9Cl_2NO_5$
		Oxyfluorfen	42,874-03-3	361.7	4.86	$C_{15}H_{11}ClF_3NO_4$
	Urea	Isoproturon[c]	34,123-59-6	206.3	2.50	$C_{12}H_{18}N_2O$
	Nitroaniline	Pendimethalin	40,487-42-1	281.3	5.40	$C_{13}H_{19}N_3O_4$
		Trifluraline[c]	1582-09-08	335.3	5.27	$C_{13}H_{16}F_3N_3O_4$
	Oxidiazole	Oxadiazon[d]	19,666-30-9	345.2	5.33	$C_{15}H_{18}Cl_2N_2O_3$
	Triazine	Terbutryn[c]	886-50-0	241.4	3.66	$C_{10}H_{19}N_5S$
		Simazine[c]	122-34-9	201.7	2.30	$C_7H_{12}ClN_5$
Insecticides	Carbamate	Methiocarb[e]	2032-65-7	225.3	3.18	$C_{11}H_{15}NO_2S$
	Organochlorine	Mirex	2385-85-5	545.5	5.28	$C_{10}C_{11}2$
		2,4′-DDE[f]	3424-82-6	318.0	6.00 [g]	$C_{14}H_8C_{l4}$
		4,4′-DDE[f]	72-55-9	318.0	6.00 [g]	$C_{14}H_8Cl_4$
		2,4′-DDT[f]	789-02-6	354.5	6.79 [g]	$C_{14}H_9Cl_5$
		4,4′-DDT[f]	50-29-3	354.5	6.79 [g]	$C_{14}H_9Cl_5$
		2,4′-DDD[f]	53-19-0	320.0	5.87 [g]	$C_{14}H_{10}C_{l4}$
		4,4′-DDD[f]	72-54-8	320.0	5.87 [g]	$C_{14}H_{10}C_{l4}$
		Heptachlor epoxide[c]	1024-57-3	389.3	4.98	$C_{10}H_5Cl_7O$
	Organophosphate	Chlorpyrifos[c]	2921-88-2	350.6	4.70	$C_9H_{11}Cl_3NO_3PS$
		Fenitrothion[c]	122-14-5	277.2	3.32	$C_9H_{12}NO_5PS$
		Fenthion	55-38-9	278.3	4.84	$C_{10}H_{15}O_3PS_2$
	Pyrethroid	Cyhalothrin	68,085-85-8	449.9	6.80	$C_{23}H_{19}ClF_3NO_3$
		Cypermethrin[c]	52,315-07-8	416.3	5.55	$C_{22}H_{19}Cl_2NO_3$
		Permethrin	52,645-53-1	391.3	6.10	$C_{21}H_{20}Cl_2O_3$

[a]Data extracted from The PPDB, pesticide properties database. https://sitem.herts.ac.uk/aeru/ppdb/en/search.htm

[b]Selected acaricides are also insecticides except Dicofol

[c]Included into the Priority substances list in the field of Water policy under Directive 2013/39/EU

[d]Included into the Watch List of substances under Commission Implementing Decision (EU) 2015/495 and removed later by Commission Implementing Decision (EU) 2018/840

[e]Included into the Watch List of substances under Commission Implementing Decision (EU) 2018/840

[f]Data extracted from ChemSpider. http://www.chemspider.com/

[g]Data estimated using the US Environmental Protection Agency EPISuite™. http://www.chemspider.com/

from Sigma-Aldrich (Steinheim, Germany). d_3-bifenox, d_{10}-chlorfenvinphos, d_7-oxadiazon, d_6-dichlorvos, d_6-permethrin, d_6-fenitrothion, and d_6-fenthion were purchased from LGC standards (Teddington, Middlesex, UK). d_4-endosulfan was purchased from Cambridge Isotope Laboratories Inc. (Andover, Massachusetts, EEUU).

EtAc, acetone, water, DCM, hexane, and methanol solvents were purchased form J. T. Baker (Waltham, Massachusetts, EEUU). Chloroform was purchased from Carlo Erba (Val De Reuil, Eure, France). All solvents were purchased for organic trace analysis.

All standard solutions were prepared at a concentration of 100 ng μL^{-1} with EtAc by weight or dilution. A solution mixture of all standard solutions was prepared at a concentration of 10 ng μL^{-1} and working solutions were prepared by dilution of the later.

Sample Collection

To evaluate the applicability of the developed methods to real samples, pesticide levels were determined in sediment and water samples from Catalonian river basins collected during pesticide application seasons, between February and June 2017.

Water and sediment samples were taken at the center bottom of the channel with a water sampler and a dredger, respectively. Water samples were collected in amber bottles of polyethylene terephthalate (PET) and were kept at 4 °C until they reached the laboratory where they were stored at − 20 °C until analysis was performed. Sediment samples were collected in aluminum trays and were kept at 4 °C until they reached the laboratory where they were frozen and lyophilized to eliminate the water content. Once lyophilized, they were sieved (125 μm) and stored at − 20 °C until analysis.

Sample Preparation

Different recovery experiments were planned testing different extraction methods. Extraction solvents were targeted for optimization since they heavily influence analyte recoveries. Therefore, different solvent mixtures were chosen to cover a wider range of polarities within extraction.

Following this criterion, SPE, ultrasound-assisted emulsification extraction (UAEE), and classic liquid–liquid extraction were chosen for water matrix. UAEE was carried out as described by Feo et al. [5] testing chloroform and a mixture of EtAc/chloroform (1:1) as extracting solvents. SPE methods were carried out with 100 mL of sample and C18 cartridges testing hexane, EtAc, and a mixture of EtAc/chloroform (1:1) as extracting solvents. Liquid–liquid extraction was carried out with 50 mL of sample testing chloroform and a mixture of EtAc/chloroform (1:1) as extracting solvents. On the other hand, PLE and ultrasound extraction were chosen for sediment matrix. Ultrasound extraction was carried out as described by Feo et al. [5] testing different solvents, such as chloroform and a mixture of EtAc/chloroform (1:1). PLE extraction was carried out as described by Barón et al. [33] testing two common adsorbents of alumina and FL. All recovery assays were performed on spiked water and sediments with 10 ng of native standards and 15 ng of IS. Native standards were added before extraction while IS were added before GC–MS/MS injection. Methods were evaluated by recovery and RSD and, considering obtained results, the following methods were established as optimal.

Water Samples

A 50 mL of sample was spiked with 15 ng of IS and left 2 h at laboratory temperature. Extraction was carried out by classic liquid–liquid extraction with 25 mL of a mixture of EtAc/chloroform (1:1). Extraction step is repeated twice. Obtained extracts were pooled and evaporated under nitrogen steam until dryness. Extracts were then reconstituted with 50 μL of EtAc.

Sediment Samples

A 1 g of sample was mixed with 2 g of copper and left spiked with 15 ng of IS refrigerated overnight. Extraction was carried out by PLE extraction. Extraction cell was filled with 6 g of FL, mixed sample with 2 g of FL, and hydromatrix. Extraction was performed on two cycles of 10 min at 100 °C of temperature and 1650 psi of pressure with a mixture of hexane/DCM (1:1). Extracts were then evaporated until dryness and reconstituted with 50 μL of EtAc.

Instrumental Conditions

GC–MS/MS analysis was performed on a 7890B GC coupled to a 7000C triple quadrupole (Agilent Technologies, Santa Clara, CA, USA). For chromatographic separation, a DB-5MS (30 m × 250 μm × 0.25 μm) column was used. Helium at a flow of 1 mL min^{-1} was used as a gas carrier. Volume of injection was 2 μL on splitless mode. Injector temperature was 280 °C with a chromatographic ramp as follows: 80 °C initial (held 2 min) until 180 °C at 25 °C min^{-1} (held 6 min), 240 °C at a 5 °C min^{-1} (held 5 min), 280 °C at 10 °C min^{-1} (held 5 min) until 325 °C at a 30 °C min^{-1} (held 2 min). Total instrumental analysis time was 41.5 min.

Mass detection was carried out with MS/MS working on electron ionization (EI) mode with a collision energy of 70 eV. Ion source and transfer line temperature were 280 and 300 °C, respectively. Confirmation and quantification transitions have been monitored for every analyte and IS.

Analytical Parameters

Linearity was determined by a six-point calibration curve including all the analytes, with concentrations ranging from 0.01 to 2 ng μL^{-1} with IS at a concentration of 0.3 ng μL^{-1}. Reproducibility was measured by RSD of five consecutive injections (intra-day) and five different days (inter-day). Instrumental detection limits (IDLs) and instrumental quantification limits (IQLs) were determined for each compound as the minimum amount of analyte that gave S/N of 3 and 10, respectively. Recovery and reproducibility were measured on spiked samples at 200 ng L^{-1} and 10 ng g^{-1} for water and sediments, respectively. Recovery was evaluated as the percentage ratio of the experimentally obtained concentration of analyte and the spiked concentration of analyte. Reproducibility was evaluated as the %RSD of four replicates for each matrix. LODs and LOQs were calculated for water and sediment samples with the same method used to calculate IDLs and IQLs.

Results and Discussion

Optimization of Extraction

For water matrices, classic liquid–liquid extraction using a mixture of EtAc/chloroform (1:1) as extracting solvent was chosen as the optimal method of extraction since obtained recoveries and RSD percentages were the best (see Supporting Information, Table S2). Ultrasound extraction results showed that, when using chloroform as extracting solvent, one analyte was lost and 13 had recoveries below 50%. Results got worse when the EtAc/chloroform (1:1) mixture was used since three analytes were completely lost and 31 had recoveries lower than 50%. SPE extraction results showed that, when using the mixture of EtAc/chloroform (1:1) as eluent, four analytes were lost and 20 had recoveries below 50%. Results got worse when using EtAc and hexane as eluents since 22 compounds were completely lost for hexane and seven were lost with 19 compounds having recoveries below 50% when using EtAc. Classic liquid–liquid extraction results showed that, when using chloroform as extracting solvent, 16 analytes had recoveries below 50% while using an EtAc/chloroform (1:1) mixture only seven compounds had recoveries below 50%. Taking as a quality criterion when working with isotopic dilution methods, a minimum recovery of 40%, our methodology for water would then be applicable to 33 selected analytes. However, there would be five compounds for which our methodology could not be applied. These are: mirex (18.8% of recovery), hexachlorobenzene (24.5% of recovery), endosulfan (24.9% of recovery), bifenox (25.6% of recovery), and lindane (26.2% of recovery).

For sediment matrices, PLE using FL as adsorbent was chosen as the optimal method of extraction since obtained recoveries and RSD percentages were the best (see Supporting Information, Table S3). Ultrasound extraction results showed that one of the analytes was lost with 19 compounds having recoveries below 50% when using chloroform as extracting solvent. Results got worse when a mixture of EtAc/chloroform (1:1) was used since all had recoveries lower than 50% except oxyfluorfen with 52%. On the other hand, PLE extraction results showed that, when using alumina as an adsorbent, seven compounds were completely lost while ten had less than 50% of recovery. Results got better when using FL as adsorbent since only four compounds were lost (dichlorvos, triallate, terbutryn, and cyproconazole) and 11 had recoveries below 50%. Following the same quality criteria as above, discarding analytes with recoveries below 40%, our methodology will be applicable to 27 analytes. The four lost compounds will be discarded as well as triadimefon (3.8% of recovery), chlorfenvinphos (3.9% of recovery), isoproturon (19.1% of recovery), simazine (19.2% of recovery), diazinon (24.4% of recovery), propanil (25.4% of recovery), and malathion (27.9% of recovery).

As expected, for water sample methodology, we had problems with high Log K_{OW} compounds (discarded analytes presented values between 3.50 and 5.28). However, in the case of sediments, recovery problems have been found with lower Log K_{OW} analytes (discarded compounds presented values between 1.90 and 4.06) (see Table 1).

GC–MS/MS Conditions

Several MS parameters were optimized to maximize the signal. Product ion scans were performed for all analytes to achieve the transitions with maximum signal. As EI mass spectra presented a lot of fragmentation since EI is a hard ionization technique, most of selected precursor ions are fragments due to the loss or low signal of the molecular ion. Selected transitions for each analyte with identification of each fragment are presented in Table 2. Every analyte has its own distinctive fragments originated by the rupture of the molecule. The most recurrent observed ruptures are the loss of Cl [M-35] (heptachlor epoxide, hexachlorobenzene, dicofol, endosulfan, DDTs, DDEs, DDDs, mirex, oxadiazon, triallate, chlorpyrifos, and propanil), C_2H_4 [M-28] (simazine and chlorpyrifos), and C_2H_5 [M-29] (pendimethalin and trifluralin). Regarding DDTs and DDDs, obtained fragments are the same but originated differently. For DDTs, precursor ion is generated due to the loss of CCl_3 [M-119] and their product ions correspond to a successive loss of chlorine. On the other hand, DDDs precursor ion is generated due to the loss of $CHCl_2$ [M-85] and their product ions correspond to a successive loss of chlorine.

Table 2 Mass and chemical formula for each pesticide and their *m/z* and chemical formula of their precursor and product ions

Compound	Mass	Formula	Precursor ion		Product ion 1		Product ion 2	
			m/z	Formula	*m/z*	Formula	*m/z*	Formula
Isoproturon	206.3	$C_{12}H_{18}N_2O$	146	$C_9H_8NO^+$	128	$C_9H_6N^+$	91	$C_7H_7^+$
Dichlorvos	221.0	$C_4H_7Cl_2O_4P$	109	$C_2H_6O_3P^+$	79	$CH_4O_2P^+$	47	PO^+
Methiocarb	225.3	$C_{11}H_{15}NO_2S$	168	$C_9H_{12}OS^+$	153	$C_8H_9OS^+$	109	$C_7H_7O^+$
Trifluralin	335.3	$C_{13}H_{16}F_3N_3O_4$	306	$C_{11}H_{11}F_3N_3O_4^+$	264	$C_8H_5F_3N_3O_4^+$	43	$C_3H_7^+$
Hexachlorobenzene	284.8	C_6Cl_6	284	$C_6Cl_6^+$	249	$C_6Cl_5^+$	214	$C_6Cl_4^+$
Simazine	201.7	$C_7H_{12}ClN_5$	201	$C_7H_{12}ClN_5^+$	173	$C_5H_8ClN_5^+$	44	$C_2H_6N^+$
Lindane	290.8	$C_6H_6Cl_6$	181	$C_6H_4Cl_3^+$	145	$C_6H_3Cl_2^+$	109	$C_6H_3Cl^+$
Diazinon	304.4	$C_{12}H_{21}N_2O_3PS$	179	$C_{10}H_{15}N_2O^+$	121	$C_6H_8N_2O^+$	137	$C_7H_9N_2O^+$
Triallate	304.7	$C_{10}H_{16}Cl_3NOS$	268	$C_{10}H_{16}Cl_2NOS^+$	226	$C_7H_9Cl_2NOS^+$	184	$C_4H_4Cl_2NOS^+$
Propanil	218.1	$C_9H_9Cl_2NO$	161	$C_6H_5Cl_2N^+$	99	$C_5H_4Cl^+$	63	$C_5H_3^+$
Terbutryn	241.4	$C_{10}H_{19}N_5S$	185	$C_6H_{11}N_5S^+$	170	$C_5H_8N_5S^+$	68	$C_2H_2N_3^+$
Fenitrothion	277.2	$C_9H_{12}NO_5PS$	277	$C_9H_{12}NO_5PS^+$	260	$C_9H_{11}NO_4PS^+$	109	$C_2H_6O_3P^+$
Malathion	330.4	$C_{10}H_{19}O_6PS_2$	173	$C_8H_{13}O_4^+$	99	$C_4H_3O_3^+$	117	$C_4H_5O_4^+$
Chlorpyrifos	350.6	$C_9H_{11}Cl_3NO_3PS$	314	$C_9H_{11}Cl_2NO_3PS^+$	286	$C_7H_7Cl_2NO_3PS^+$	258	$C_5H_3Cl_2NO_3PS^+$
Fenthion	278.3	$C_{10}H_{15}O_3PS_2$	278	$C_{10}H_{15}O_3PS_2^+$	169	$C_8H_9S_2^+$	109	$C_2H_6O_3P^+$
Triadimefon	293.8	$C_{14}H_{16}ClN_3O_2$	208	$C_9H_7ClN_3O^+$	181	$C_8H_6ClN_2O^+$	75	$C_6H_3^+$
Dicofol	370.5	$C_{14}H_9Cl_5O$	139	$C_7H_4ClO^+$	111	$C_6H_4Cl^+$	75	$C_6H_3^+$
Pendimethalin	281.3	$C_{13}H_{19}N_3O_4$	252	$C_{11}H_{14}N_3O_4^+$	191	$C_8H_7N_2O_4^+$	162	$C_6HN_2O_4^+$
Heptachlor epoxide	389.3	$C_{10}H_5Cl_7O$	353	$C_{10}H_5Cl_6O^+$	263	$C_7H_2Cl_5^+$	217	$C_9H_4Cl_2^+$
Chlorfenvinphos	359.6	$C_{12}H_{14}Cl_3O_4P$	267	$C_8H_6O_4Cl_2P^+$	159	$C_7H_5Cl_2^+$	81	$H_2O_3P^+$
2,4-DDE	318.0	$C_{14}H_8Cl_4$	246	$C_{14}H_8Cl_2^+$	211	$C_{14}H_8Cl^+$	176	$C_{14}H_8^+$
4,4-DDE	318.0	$C_{14}H_8Cl_4$	246	$C_{14}H_8Cl_2^+$	211	$C_{14}H_8Cl^+$	176	$C_{14}H_8^+$
Endosulfan	406.9	$C_9H_6Cl_6O_3S$	339	$C_9H_5Cl_5SO^+$	195	$C_7H_4Cl_3^+$	159	$C_7H_4Cl_2^+$
Oxadiazon	345.2	$C_{15}H_{18}Cl_2N_2O_3$	175	$C_6H_3Cl_2NO^+$	112	$C_6H_5Cl^+$	76	$C_6H_4^+$
Oxyfluorfen	361.7	$C_{15}H_{11}ClF_3NO_4$	252	$C_{13}H_7O_2F_3^+$	224	$C_{11}H_3O_2F_3^+$	117	$C_7H_3ClF_3^+$
2,4-DDD	320.0	$C_{14}H_{10}Cl_4$	235	$C_{13}H_9Cl_2^+$	199	$C_{13}H_9Cl^+$	165	$C_{13}H_9^+$
4,4-DDD	320.0	$C_{14}H_{10}Cl_4$	235	$C_{13}H_9Cl_2^+$	199	$C_{13}H_9Cl^+$	165	$C_{13}H_9^+$
2,4-DDT	354.5	$C_{14}H_9Cl_5$	235	$C_{13}H_9Cl_2^+$	199	$C_{13}H_9Cl^+$	165	$C_{13}H_9^+$
4,4-DDT	354.5	$C_{14}H_9Cl_5$	235	$C_{13}H_9Cl_2^+$	199	$C_{13}H_9Cl^+$	165	$C_{13}H_9^+$
Cyproconazole	291.8	$C_{15}H_{18}ClN_3O$	222	$C_{10}H_9N_3OCl^+$	125	$C_7H_6Cl^+$	82	$C_3H_4N_3^+$
Quinoxyfen	308.1	$C_{15}H_8Cl_2FNO$	237	$C_{15}H_8FNO^+$	208	$C_{13}H_3FNO^+$	181	$C_{11}H_3FNO^+$
Bifenthrin	422.9	$C_{23}H_{22}ClF_3O_2$	181	$C_{14}H_{13}^+$	166	$C_{13}H_{10}^+$	165	$C_{13}H_9^+$
Diflufenican	394.3	$C_{19}H_{11}F_5N_2O_2$	266	$C_{13}H_7F_3NO_2^+$	218	$C_{12}H_7NF_2O^+$	183	$C_{12}H_9NO^+$
Bifenox	342.1	$C_{14}H_9Cl_2NO_5$	341	$C_{14}H_9Cl_2NO_5^+$	311	$C_{13}H_6Cl_2NO_4^+$	189	$C_8H_6Cl_2O^+$
Mirex	545.5	$C_{10}Cl_{12}$	272	$C_5Cl_6^+$	237	$C_5Cl_5^+$	235	$C_5Cl_5^+$
Cyhalothrin	449.9	$C_{23}H_{19}ClF_3NO_3$	181	$C_{13}H_9O^+$	152	$C_{11}H_4O^+$	77	$C_6H_5^+$
Permethrin	391.3	$C_{21}H_{20}Cl_2O_3$	163	$C_7H_9Cl_2^+$	127	$C_7H_{10}O_2^+$	91	$C_7H_7^+$
Cypermethrin	416.3	$C_{22}H_{19}Cl_2NO_3$	163	$C_7H_9Cl_2^+$	127	$C_7H_{10}O_2^+$	91	$C_7H_7^+$

Collision energy was optimized to obtain the product ions with the highest intensity at the highest possible mass to minimize interference while avoiding disappearance of the precursor ion. The optimal transitions and collision energies for all selected pesticides are reported in Table 3. Instrumental method was successfully developed with the elution of all analytes before minute 35 and good linearity, sensitivity, intra- and inter-day variations (Table 3). Correlation coefficients ranged between 0.9859 and 0.9999 within the studied concentration range of 0.01–2 ng μL^{-1}. IDLs and IQLs ranged between 0.01 and 2.68 injected pg and between 0.03 and 8.93 injected pg, respectively. As expected, inter-day variation was higher than intra-day variation with RSD percentages between 0.7 and 8.4% and between 2.0 and 10%, respectively.

Table 3 Retention time, precursor ion, product ions, collision energies, correlation coefficients, instrumental detection and quantification limits and reproducibility (RSD, %) for intra- and inter-day

Compound[a]	t_R (min)	Precursor	MS_1	CE_1 (eV)	MS_2	CE_2 (eV)	R^2	IDL (pg)	IQL (pg)	Intra-day (% RSD)	Inter-day (% RSD)
Analytes											
Isoproturon	5.7	146	128	5	91	20	0.9965	0.02	0.05	1.9	3.1
Dichlorvos	5.8	109	79	5	47	40	0.9999	0.24	0.79	1.8	2.9
Methiocarb	8.2	168	153	10	109	20	0.9977	0.29	0.80	2.1	5.8
Trifluralin	9.5	306	264	5	43	20	0.9962	0.15	0.50	1.5	2.6
Hexachlorobenzene	10.5	284	249	20	214	40	0.9996	0.04	0.12	3.0	5.4
Simazine	11.0	201	173	5	44	10	0.9998	0.25	0.82	0.9	2.8
Lindane	11.6	181	145	10	109	20	0.9998	0.09	0.29	2.3	3.4
Diazinon	12.0	179	121	40	137	20	0.9993	0.20	0.65	1.8	2.5
Triallate	12.9	268	226	5	184	20	0.9990	0.16	0.53	5.0	6.3
Propanil	13.9	161	99	20	63	40	0.9983	0.44	1.46	5.2	7.6
Terbutryn	15.5	185	170	5	68	40	0.9998	0.15	0.50	1.8	3.9
Fenitrothion	15.5	277	260	10	109	20	0.9995	0.21	0.66	2.4	6.1
Malathion	16.0	173	117	5	99	10	0.9974	0.33	1.11	1.3	3.2
Chlorpyrifos	16.3	314	286	10	258	40	0.9999	0.12	0.41	5.2	7.8
Fenthion	16.5	278	169	10	109	20	0.9995	0.11	0.37	1.9	4.3
Triadimefon	16.8	208	181	5	75	40	0.9979	0.11	0.36	6.8	7.9
Dicofol	16.9	139	111	20	75	20	0.9998	0.24	0.80	1.2	2.9
Pendimethalin	17.7	252	191	5	162	5	0.9940	0.02	0.07	2.7	4.5
Heptachlor epoxide	18.0	353	263	10	217	40	0.9989	0.30	1.01	0.8	2.0
Chlorfenvinphos	18.2	267	159	10	81	40	0.9996	0.03	0.11	3.5	5.9
2,4′-DDE	19.2	246	211	20	176	40	0.9982	0.17	0.55	8.4	10
4,4′-DDE	20.6	246	211	20	176	40	0.9996	0.09	0.30	0.7	2.2
Endosulfan	19.5	339	195	20	159	40	0.9992	0.11	0.40	1.6	3.3
Oxadiazon	20.7	175	112	10	76	40	0.9990	0.01	0.03	2.1	4.6
Oxyfluorfen	20.9	252	224	10	177	40	0.9859	2.68	8.93	4.5	6.9
2,4′-DDD	20.8	235	199	20	165	20	0.9999	0.03	0.09	1.7	3.5
Cyproconazole	21.4	222	125	20	82	10	0.9960	0.03	0.08	4.0	7.6
4,4′-DDD	22.3	235	199	20	165	20	0.9996	0.03	0.09	1.8	3.4
2,4′-DDT	22.3	235	199	20	165	20	0.9940	0.03	0.09	1.8	3.9
4,4′-DDT	23.7	235	199	20	165	20	0.9959	0.45	1.48	3.5	6.7
Quinoxyfen	23.5	237	208	40	181	40	0.9993	0.03	0.09	0.9	3.1
Bifenthrin	24.4	181	166	10	165	10	0.9930	0.62	2.08	–	–
Diflufenican	24.6	266	218	20	183	20	0.9958	0.06	0.18	3.2	5.6
Bifenox	26.7	341	311	5	189	5	0.9886	2.39	7.96	3.7	5.7
Mirex	28.5	272	237	20	235	20	0.9998	0.02	0.08	2.2	4.3
Cyhalothrin	29.1	181	152	20	77	40	0.9989	0.56	1.86	1.9	4.6
Permethrin	29.6	163	127	10	91	10	0.9994	0.76	2.52	–	–
Cypermethrin	33.0	163	127	5	91	5	0.9942	0.01	0.04	0.7	2.7
Internal standards											
d_6-dichlorvos	5.8	226	115	20	191	5					
d14-trifluralin	9.4	315	163	20	267	5					
$^{13}C_6$-hexachlorobenzene	10.5	290	220	40	255	10					
d_{10}-simazine	10.8	211	179	5	144	20					
d_{10}-diazinon	11.9	314	183	10	199	5					
d_6-fenitrothion	15.4	283	266	5	115	10					
s-methyl-d_3-terbuthryn	15.5	188	170	5	112	20					
diethyl-d_{10}-malathion	15.8	183	132	5	100	10					

Table 3 (continued)

Compound[a]	t_R (min)	Precursor	MS$_1$	CE$_1$ (eV)	MS$_2$	CE$_2$ (eV)	R^2	IDL (pg)	IQL (pg)	Intra-day (% RSD)	Inter-day (% RSD)
d$_{10}$-chlorpyrifos	16.1	324	260	10	292	10					
d$_6$-fenthion	16.4	284	115	20	131	20					
d$_{10}$-chlorfenvinphos	18.0	333	269	20	160	40					
d$_4$-endosulfan	19.5	343	271	10	198	10					
d$_7$-oxadiazon	20.6	351	176	20	259	10					
d$_3$-bifenox	26.6	344	314	10	192	20					
phenoxy-d$_5$-cyhalothrin	29.1	185	156	20	131	20					
d$_6$-permethrin	29.5	169	133	10	97	10					
phenoxy-d$_5$-fenvalerate	35.2	424	230	5	167	10					

[a]Dwell time for all compounds was 20 ms

QA of Developed Methods

Optimized methods include 33 and 27 compounds for water and sediment samples, respectively. Obtained recoveries ranged between 39 and 102% for water and between 37 and 133% for sediments (Table 4).

Reproducibility of the method has been shown to be satisfactory with RSDs lower than 13% for water and lower than 18% for sediments (except for methiocarb, with a value of 28%). On the other hand, good LODs and LOQs have been obtained. For water, LODs and LOQs range between 0.42 and 15.2 and between 0.72 and 50.8 ng L^{-1}, respectively. LODs and LOQs for sediments range between 0.01 and 0.16 and between 0.02 and 0.54 ng g^{-1} dw, respectively.

If we compare obtained LOQs in our method for water matrices with other published data in the literature, we can observe similarities with those obtained by Mondal et al. [6] and Robles-Molina et al. [7] with ranges between 0.03 and 80 ng L^{-1} whom also used classic liquid–liquid extraction. Moreover, our values were 10 times more sensitive in comparison with other published LOQs from SPE extraction methods [8–11] ranging between 10 and 500 ng L^{-1}.

He and Aga [12] analyzed endocrine disrupting chemicals, including pesticides, in water samples through GC–MS/MS and LC–MS/MS with SPE (HLB) reporting LODs between 0.4 and 4.5 ng L^{-1} for a selection of pesticides through GC–MS/MS. Reported LODs are lower than our method. However, only four compounds are also included in our method. Reported values were 2.1, 2.9, 1.8, and 0.4 for simazine, dichlorvos, diaiznon, and chlorpyrifos, respectively. Comparing with our reported values of 2.98, 7.30, 0.54, and 1.01 ng L^{-1}, only for diazinon our LOD was better.

Cruzeiro et al. [13] analyzed 54 pesticides in surface waters through GC–MS/MS with SPE (HLB) considering their content in both dissolved aqueous phase (DAP) and suspended particulate matter (SPM) fractions. Reported recoveries were above 71% and LODs ranging between 0.4 and 1.3 ng L^{-1} for DAP. Reported LODs are lower than our method. However, no individual datum was provided for each pesticide and EU Watch List' pesticides, such as methiocarb, triallate, and oxadiazon, are not included in the method.

Zhang et al. [14] analyzed 450 pesticides in precipitation through GC–MS/MS with SPE (HLB). However, no comparison could be achieved with our method since neither recoveries nor detection limits were reported since their main focus was occurrence and distribution of pesticides in precipitation and did not focused on analytical concentrations.

Regarding SPME extraction methods [20–25], obtained LOQs were higher than those obtained with our method since published LOQs ranged between 2 and 500 ng L^{-1}.

Despite LLE poses a limitation when analyzing a large number of samples, LLE was the method that produced the best results in terms of recovery and reproducibility. Moreover, LODs lower than the maximum acceptable detection limits set by the EU Watch List in 2018 (Table S1) have been obtained for methiocarb with a value of 0.81 ng L^{-1}. Despite the recent removal of oxadiazon and triallate from the EU Watch List in 2018, obtained LODs of 0.23 and 2.12 ng L^{-1} were lower than the maximum acceptable detection limits set by the EU Watch List in 2015 with values of 88 and 670 ng L^{-1}, respectively. In general, obtained LODs were lower than established EQS of surface waters set by the Directive 2013/39/EU (Table S1) with the exception of some compounds, such as dicofol, cypermethrin, dichlorvos, and heptachlor epoxide, as previously reported methods in the literature.

Regarding sediments, published methods using PLE [26, 27] obtained LODs lower than 1 ng g^{-1} while our values were ten times lower. Regarding QuEChERS methods, sensitivity is much lower than ours with LODs values of up to 10 ng g^{-1} dw [28, 29]. However, there are other parameters that might affect the LODs and LOQs values, such as

Table 4 Recoveries, RSDs, LODs, and LOQs for water and sediment matrices of each pesticide

Compound	Water				Sediment			
	Recovery (%)	RSD (%)	LOD (ng L^{-1})	LOQ (ng L^{-1})	Recovery (%)	RSD (%)	LOD (ng g^{-1} dw)	LOQ (ng g^{-1} dw)
Isoproturon	70.0	8.1	4.84	16.1	19.1	18	–	–
Dichlorvos	52.0	4.4	7.30	24.2	0	0	–	–
Methiocarb	76.8	4.0	0.81	2.61	56.9	28	0.04	0.13
Trifluralin	74.6	4.6	15.2	50.8	46.5	12	0.11	0.35
Hexachlorobenzene	24.5	4.1	–	–	39.4	14	0.01	0.02
Simazine	96.8	3.6	2.98	9.60	19.2	3.8	–	–
Lindane	26.2	4.6	–	–	74.1	5.8	0.02	0.07
Diazinon	60.0	9.9	0.54	1.73	24.4	8.8	–	–
Triallate	59.5	8.1	2.12	7.02	0	0	–	–
Propanil	92.1	1.6	1.53	5.12	25.4	15	–	–
Terbutryn	94.7	2.1	2.32	7.74	0	0	–	–
Fenitrothion	102	3.3	3.03	10.1	36.9	13	0.03	0.11
Malathion	80.2	5.6	0.42	1.23	27.9	4.2	–	–
Chlorpyrifos	66.9	6.6	1.01	3.21	37.2	1.4	0.02	0.05
Fenthion	98.2	6.0	1.50	4.94	63.5	9.9	0.04	0.13
Triadimefon	85.4	7.7	1.22	4.01	3.8	89	–	–
Dicofol	81.2	6.3	2.21	7.34	85.9	18	0.05	0.17
Pendimethalin	81.7	4.7	0.62	2.03	77.9	13	0.03	0.10
Heptachlor epoxide	48.7	8.1	0.53	1.61	63.0	13	0.01	0.04
Chlorfenvinphos	70.1	4.6	2.61	8.73	3.9	173	–	–
2,4′-DDE	38.9	13	1.24	4.02	53.3	13	0.05	0.17
4,4′-DDE	60.7	7.3	1.60	5.32	76.7	14	0.06	0.20
Endosulfan	24.9	5.2	–	–	96.5	13	0.08	0.26
Oxadiazon	90.0	5.4	0.23	0.72	103	12	0.03	0.09
Oxyfluorfen	97.5	4.3	7.01	23.5	133	15	0.12	0.38
2,4′-DDD	53.9	2.6	1.12	3.81	83.1	14	0.10	0.33
Cyproconazole	64.5	7.1	1.63	5.30	0	0	–	–
4,4′-DDD	67.3	3.4	0.73	2.43	80.1	16	0.06	0.21
2,4′-DDT	62.1	4.9	1.72	5.81	80.1	16	0.06	0.21
4,4′-DDT	79.5	4.0	1.03	3.32	110	11	0.04	0.13
Quinoxyfen	91.8	6.4	0.72	2.21	51.8	17	0.12	0.39
Bifenthrin	74.5	11.7	1.24	4.13	76.2	5.0	0.16	0.54
Diflufenican	95.3	6.3	1.42	4.72	70.8	6.9	0.04	0.12
Bifenox	25.6	2.1	–	–	83.8	13	0.08	0.25
Mirex	18.8	2.0	–	–	44.7	8.5	0.07	0.25
Cyhalothrin	79.5	6.5	7.86	25.9	82.7	10	0.16	0.52
Permethrin	81.1	8.9	2.66	8.87	64.2	5.1	0.16	0.54
Cypermetrin	80.0	7.0	1.51	4.94	121	13	0.04	0.15

volume of sample, extracting solvents, clean-up, etc., since all variability cannot be attributed to one factor.

Applicability to Real Samples

To demonstrate the applicability of our developed methodologies, both methods were applied to the analysis of ten water and ten sediment samples collected in different Catalonian river basins. Results are shown in Figs. 1 and 2 (detailed results are summarized in Table S4).

Twenty-six of the 38 analyzed pesticides have been detected. Among the no-detected ones were dichlorvos, lindane, propanil, heptachlor epoxide, endosulfan, cyproconazole, quinoxyfen, bifenthrin, bifenox, mirex, cyhalothrin,

Fig. 1 Total concentration in ng L^{-1} of detected pesticides in the water samples
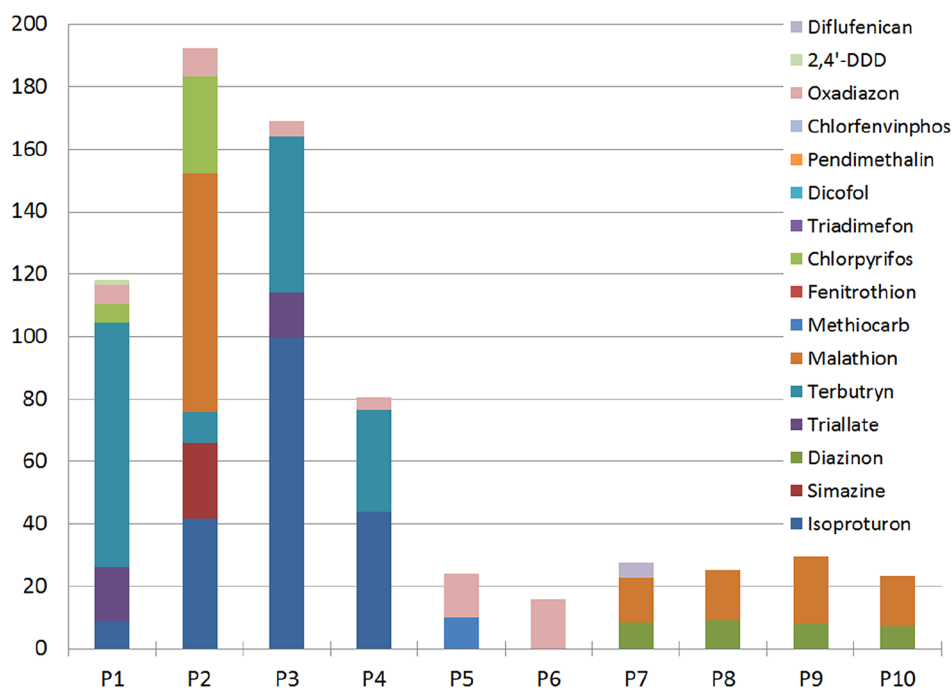
and permethrin. This result is consistent since the vast majority of these pesticides are not approved in accordance with Regulation (EC) No 1107/2009 [34].

Sixteen and 15 pesticides have been detected in water and sediments, respectively. In general, pesticides with higher non-polarity have been detected more in sediments than water. Only five analytes, chlorpyrifos, dicofol, pendimethalin, oxadiazon, and 2,4′-DDD have been detected in both matrices. These are highly non-polar pesticides since their log K$_{ow}$ range between 4.30 and 5.87, hence their higher presence in sediments than water. Dicofol and pendimethalin were detected in water below LOQs while in sediments they were detected with mean concentrations of 0.11 and 1.7 ng g^{-1} dw, respectively. 2,4-DDD was only detected in one water sample at 1.9 ng L^{-1} while in sediments, it was detected in three samples with a mean value of 2.5 ng g^{-1} dw. On the other hand, oxadiazon and chlorpyrifos were among the most frequently detected pesticides in the samples probably due to their extensive use as pesticides, therefore their presence in both matrices.

Diflufenican was the most frequently detected pesticide in water with a 70% of detection frequency followed by chlorpyrifos (60%), oxadiazon (60%), diazinon (60%), and malathion (50%). However, diflufenican was detected below LOQs in 90% of the samples, while oxadiazon and malathion had the highest frequency of quantification in the samples with 60 and 50%, respectively. The highest concentration level of a pesticide in the samples corresponded to terbutryn with 78.2 ng L^{-1} followed by malathion with 76.6 ng L^{-1}. Obtained results were lower for oxadiazon with a range between n.d. and 15.8 ng L^{-1} (mean value of

5.4 ng L^{-1}) in comparison with other previously published results in water from Catalonian river basins like Gusmaroli et al. [35] who detected oxadiazon between 21.1 and 592 ng L^{-1} (mean value of 270 ng L^{-1}) in 2016. Regarding malathion, our results were lower, with a range between n.d. and 76.6 ng L^{-1} (mean value of 14.5 ng L^{-1}), in comparison to Masiá et al. [36] who detected malathion between 3.01 and 320 ng L^{-1} (mean value of 57.6 ng L^{-1}) in 2010. Moreover, Köck-Schulmeyer et al. [37] detected malathion in water from various sampling campaigns of 2009 and 2010 with mean concentrations ranging between 2.6 and 16.7 ng L^{-1}, similar to our results. Concerning terbutryn, our results were lower, with a range between n.d. and 78.2 ng L^{-1} (mean value of 17.1 ng L^{-1}), in comparison with other published results like Navarro et al. [38] who detected terbutryn with a range between 5 and 184 ng L^{-1} (mean value of 53 ng L^{-1}) in the Ebro river basin in 2010.

On the other hand, the pesticides with the highest detection frequency in the sediments were hexachlorobenzene with a 100% of detection frequency followed by 4,4′-DDE (50%), pendimethalin (40%), and dicofol (40%). The highest concentration level of a pesticide in the samples corresponded to oxadiazon with 382 ng g^{-1} dw. Mean concentrations of DDXs were n.d., 9.09, 0.75, 1.94, 0.42, and 2.36 ng g^{-1} dw for 2,4′-DDE, 4,4′-DDE, 2,4′-DDD, 4,4′-DDD, 2,4′-DDT, and 4,4′-DDT, respectively. Obtained results were lower for hexachlorobenzene, with a range between 0.1 and 1.3 ng g^{-1} dw (mean value of 0.53 ng g^{-1} dw), in comparison with other previously published results in sediments from Catalonian river basins like Navarro-Ortega et al. [39] who detected hexachlorobenzene at

Fig. 2 Total concentration in ng g^{-1} dw of detected pesticides in the sediment samples
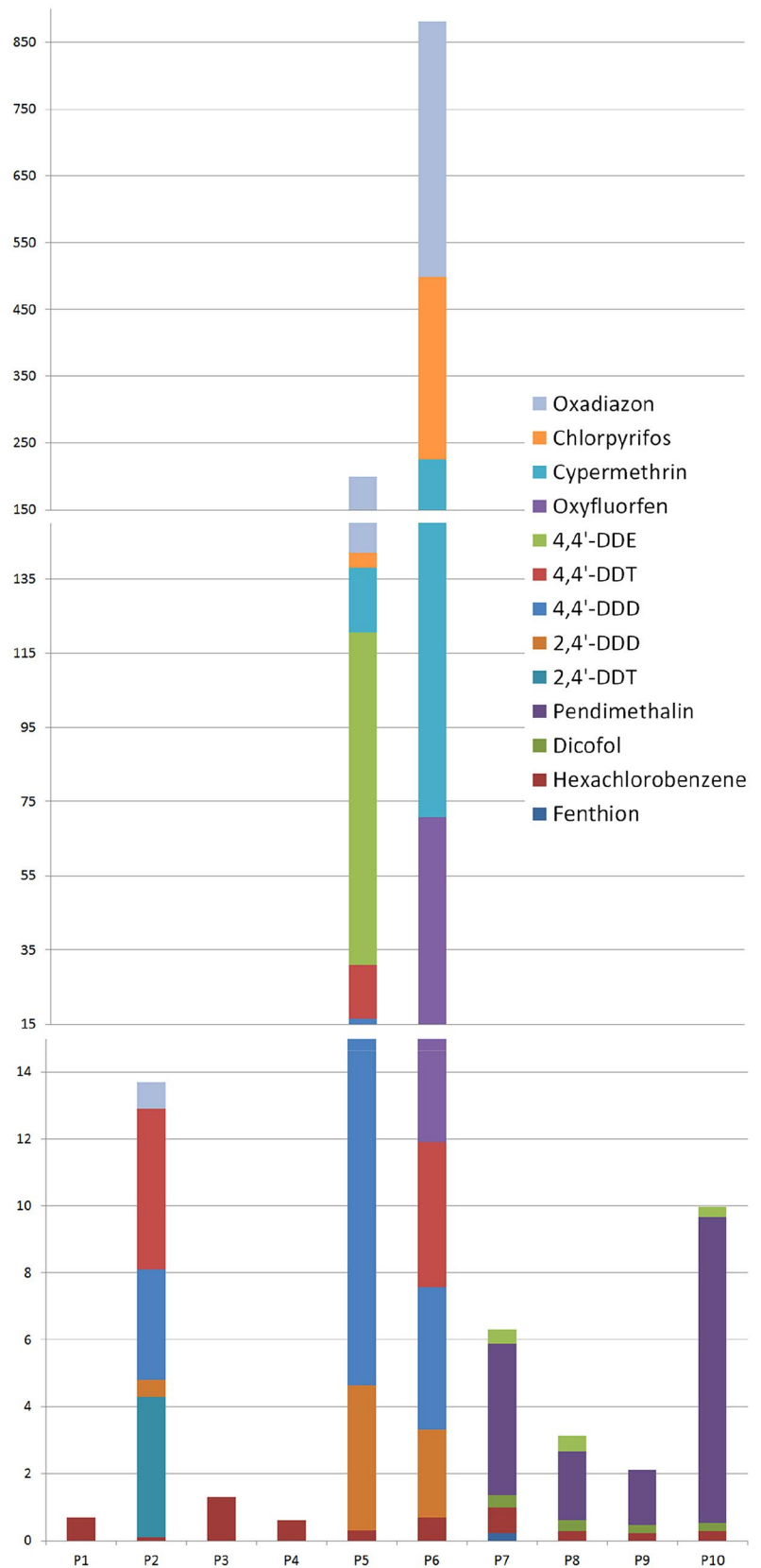
concentrations between 20.7 and 264 ng g^{-1} dw (mean value of 88.1 ng g^{-1} dw) from various sampling campaigns between 2004 and 2006. Regarding DDXs, our results were lower in comparison to Navarro-Ortega et al. [39] who obtained levels of 4,4′-DDT between 0.45 and 501 ng g^{-1} dw (mean value of 48.4 ng g^{-1} dw); 4,4′-DDE between 0.34 and 141 ng g^{-1} dw (mean value of 14.1 ng g^{-1} dw); 2,4′-DDD between 0.30 and 77.9 ng g^{-1} dw (mean value of 11.9 ng g^{-1} dw); 4,4′-DDD between 0.35 and 83.0 ng g^{-1} dw (mean value of 10.5 ng g^{-1} dw); 2,4′-DDE between 0.50 and 18.9 ng g^{-1} dw (mean value of 2.78 ng g^{-1} dw); and between 2.21 and 50.9 ng g^{-1} dw (mean value of 15.1 ng g^{-1} dw) for 2,4′-DDT. Oxadiazon is an organochlorine herbicide largely used in rice crops against mono- and dicotyledonous weeds [40]. Despite being removed from the second EU Watch List of substances (2018/840/EU) [4], oxadiazon is considered to be very toxic to aquatic organisms, with algae and fish reproduction as the most sensitive endpoints [40]. To our knowledge, this is the first time the presence of oxadiazon has been reported in sediments from Catalonian river basins with a range of n.d. to 382 ng g^{-1} dw and mean concentration of 44 ng g^{-1} dw. These results show the importance of the analytical multi-residue methodologies development's applicability for an easier screening of these compounds in water and sediments that can be used later for a better evaluation and understanding of the presence and behavior of these compounds in the environment. Moreover, these results emphasize the importance of the inclusion of selected pesticides, such as those included in the EU Watch Lists (methiocarb, oxadiazon, and triallate), since the presence in several samples of pesticides, such as oxadiazon, has been determined at concentration levels that can pose a high risk to aquatic organisms.

Environmental Risk Assessment

The potential ecotoxicological risk derived from the presence of pesticides to aquatic organisms was assessed with the risk quotient (RQ) method. This method evaluates the ratio of the measured environmental concentration (MEC) with the predicted no-effect concentration (PNEC) at which no toxicological effects are expected. In this work, we used both the mean and the maximum concentration of detected pesticides in the samples as MEC-Mean and MEC-Max, respectively. Evaluation of RQ values was assessed considering RQs below 1 as not hazardous to aquatic organisms, between 1 and 10 to pose a moderate risk, and higher than 10 are considered to pose a high risk to aquatic organisms. The worst-case scenario evaluation was assessed using MEC-Max. Obtained RQs of detected pesticides in water and sediments from Catalonian river basins are summarized in Table 5.

Regarding water samples, obtained RQs were below 1 indicating the presence of detected pesticides poses a low risk to aquatic organisms with the exception of malathion with an RQ of 2.4, higher than 1, indicating that its presence can pose a moderate risk to aquatic organisms. As expected, worse results are obtained when evaluating the worst-case scenario since malathion now poses a high risk to aquatic organisms while the presence of terbutryn, methiocarb, and chlorpyrifos can pose a moderate risk to aquatic organisms.

Regarding sediment samples, obtained RQs were higher than 1 in all cases and higher than 10 for ten out of the 15 detected pesticides indicating a high risk due its presence in the sediments. Similar results are obtained when evaluating the worst-case scenario since now all samples can pose a high risk to aquatic organisms. These obtained high RQ values are explained due to the low PNEC values of each pesticide even for fenthion with a maximum detected concentration of 0.21 ng g^{-1} dw. These results are concerning and remarks the importance of the simultaneous evaluation of both water and sediment since sediments can act as a pollution sink of contaminants that can be released to the aqueous phase at any time through re-suspension by natural or human actions [41, 42].

Conclusion

A multi-residue method for the analysis of non-polar pesticides by GC–MS/MS in water and sediment matrices has been successfully developed for the analysis of 33 and 27 compounds for water and sediments, respectively. This method showed good recovery percentages, reproducibility, and low detection limits, lower than the maximum acceptable method detection limits of the Watch Lists' pesticides and most of the selected priority substances' EQS. The proposed method has been applied successfully for the analysis of real water and sediment samples from Catalonian river basins confirming the applicability of the method for the analysis of pesticides at trace level in environmental samples of water and sediment. The need to include recent interest pesticides, such as those included in the Watch Lists, has been emphasized since the presence in several samples of pesticides, such as oxadiazon, has been demonstrated at concentration levels that can pose a high risk to aquatic organisms according to the RQ method as well as the importance of the simultaneous evaluation of both water and sediments since almost all detected pesticides in the sediments can pose a high risk to aquatic organisms. However, further studies need to be done to better understand and assess the environmental impact of contaminated sediments to aquatic organisms.

Table 5 RQs of detected pesticides for the worst-case scenario (RQ-Max) and the normal (RQ-Mean) with their respective MEC-Max and MEC-Mean as well as PNEC values for water and sediment

Compound	Water				
	PNEC (ng L^{-1})[a]	MEC-Mean (ng L^{-1})	RQ-Mean	MEC-Max (ng L^{-1})	RQ-Max
Isoproturon	300	19.4	0.065	99.5	0.332
Simazine	1000	2.44	0.002	24.4	0.024
Diazinon	10	3.28	0.328	9.12	0.910
Triallate	470	3.19	0.007	17.3	0.037
Terbutryn	65	17.1	0.262	78.2	1.20
Malathion	6	14.5	2.41	76.6	12.8
Methiocarb	10	1.02	0.102	10.2	1.02
Chlorpyrifos	30	3.71	0.124	30.9	1.03
Oxadiazon	88	5.39	0.061	15.8	0.180
2,4′-DDD	3.9	0.19	0.049	1.87	0.487
Diflufenican	9	0.48	0.053	4.79	0.533
Compound	Sediment				
	PNEC (ng g^{-1})[a]	MEC-Mean (ng g^{-1})	RQ-Mean	MEC-Max (ng g^{-1})	RQ-Max
Hexachlorobenzene	0.08	0.53	6.61	1.27	16.3
Fenthion	0.0064	0.02	3.28	0.21	32.8
Chlorpyrifos	0.048	27.8	579	274	5708
Dicofol	0.000051	0.11	2216	0.35	6863
Pendimethalin	0.029	1.74	60.0	9.14	315
4,4′-DDE	0.00064	9.09	14,203	89.7	140,156
Oxadiazon	0.14	44.0	314	382	2729
Oxyfluorfen	0.15	5.90	39.3	59.0	393
2,4′-DDD	0.0063	0.75	118	4.34	689
4,4′-DDD	0.0008	1.94	2420	11.8	14,750
2,4′-DDT	0.0000096	0.42	43,750	4.16	437,500
4,4′-DDT	0.016	2.36	148	14.5	906
Cypermethrin	n/a[b]	17.1	–	154	–

[a]Data extracted from the NORMAN Ecotoxicology Database. https://www.norman-network.com/nds/ecotox/

[b]Data not available

Declarations

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