



Pesticides in sediments of the Ebro River Delta cultivated area (NE Spain): Occurrence and risk assessment for aquatic organisms[☆]

A. Peris^a, M.V. Barbieri^a, C. Postigo^a, M. Rambla-Alegre^b, M. López de Alda^a, E. Eljarrat^{a,*}

^a Dep. of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-26, 08034, Barcelona, Spain

^b Institute of Agriculture and Food Research and Technology (IRTA), Ctra. Poble Nou, Km 5.5, Sant Carles de La Ràpita, Tarragona, 43540, Spain

ARTICLE INFO

Keywords:

Environmental risk assessment
Risk quotient method
Plant protection products
Sediments
Ebro river delta

ABSTRACT

Intense agricultural activities are performed in the Ebro River Delta (NE Spain) with extensive use of pesticides. Medium to highly polar pesticides have not been studied intensively in sediments despite its larger use in the recent years. This work aimed at assessing the occurrence of 69 pesticides, including medium to highly polar compounds, in sediments collected from drainage and irrigation channels of the Ebro River Delta during the main rice growing season. In addition, an environmental risk assessment was performed to evaluate the potential adverse effects to sediment-dwelling organisms with the risk quotient approach. A total of 24 pesticides were detected in sediments with bentazone and cypermethrin exhibiting high detection frequencies (79%) as well as high mean concentration levels (61.9 and 81.8 ng g⁻¹ dw, respectively). Overall, the Alfacs bay, in the South of the delta, presented higher pesticide contamination than the Fangar bay, in the North. A similar pesticide distribution profile was observed in both bays, with oxadiazoles, organochlorines, pyrethroids, benzothiazinones and organophosphates as major, predominant classes. The presence of oxadiazon, pendimethalin and thifensulfuron methyl in the sediments may pose a moderate risk to sediment-dwelling organisms while bentazone, chlorpyrifos, and cypermethrin exhibited a potential high risk. Thus, the importance of the inclusion of medium to highly polar pesticides in the analysis of sediments is emphasized since some polar pesticides such as bentazone, imidacloprid, and thifensulfuron-methyl have been detected at concentrations that may pose a risk to aquatic organisms. Moreover, the co-occurrence of pesticides may potentially pose a high risk to sediment-dwelling organisms in 13 out of the 14 investigated locations. Finally, it could be concluded that the risk derived from the presence of pesticides in sediments must be assessed since some pesticides not detected at concerning levels in water, may pose a moderate/high risk in the sediments.

1. Introduction

The global burden of pesticides on the environment is widely known. Due to their potential toxicity, they may pose a risk to non-target organisms through their presence in water, accumulation in sediments, soils and potential biomagnification through the food chain (Ccanccapa et al., 2016; Terrado et al., 2007). Water contaminated with pesticides from cultivated land can reach groundwater and surface water by percolation and runoff/drift, respectively (Katagi, 2006; Pérez et al., 2021), and pollute related water systems (Gavrilescu, 2005). Upon release into the aquatic environment, pesticides distribute among the various compartments of the aquatic ecosystems (water, suspended matter, biota) depending on their physicochemical properties such as

solubility and octanol-water partition coefficient (K_{OW}) (Katagi, 2006). Suspended matter, together with those pesticides that are likely to sorb onto it, eventually deposits on the bottom of the water bodies forming the sediment layers (Barbieri et al., 2019). Thus, sediments act as a pollution sink. However, sediments can also act as a pollution source, because retained contaminants can be bioaccumulated by sediment-dwelling organisms and subsequently pose a risk to higher trophic organisms through biomagnification among the food chain (Parolini et al., 2010). Moreover, retained pollutants can be released at any time via re-suspension by natural processes or human actions (Gavrilescu, 2005; Pinto et al., 2016), and it is thus important to consider the sediment phase of the aquatic environments (Warren et al., 2003; Gavrilescu, 2005; Katagi, 2006; Masiá et al., 2013).

[☆] This paper has been recommended for acceptance by Charles Wong.

* Corresponding author.

E-mail address: ethel.eljarrat@idaea.csic.es (E. Eljarrat).

The European Union (EU) has included various pesticides within the List of Priority Substances in the field of Water Policy (Directive 2013/39/EU (EC, 2013)) and within the Watch Lists (Commission Implementing Decisions (EU) 2015/495, 2018/840 and 2020/1161 (EC, 2020)). Priority substances are those that pose a significant risk to the aquatic environment or through it, while the substances listed within the Watch List are those that may pose a significant risk to the aquatic environment or through it, but current available data are insufficient to determine the risk (EC, 2020, 2013). Directive 2013/39/EU provides environmental quality standards (EQS) for priority substances in water and biota, which are concentration values that must not be exceeded to reach a good chemical status of freshwater bodies. There are currently no EQS for pesticides in sediments but the Directive 2013/39/EU states that the monitoring of these substances must be performed in order to provide enough data to adopt measures aimed to reduce the concentration of priority substances in sediments.

The Ebro River is located in the northeastern part of Spain and occupies an area of approximately 85,000 km². It is 928 km long and forms a delta in the Mediterranean Sea with an area of more than 300 km² (Cancapá et al., 2016). The main economic activity in the delta is agriculture, with rice cultivation as the predominant activity (Terrado et al., 2007). Pesticides have been used extensively as previous studies have reported with high levels of propanil, molinate, bentazone, organophosphate pesticides (Barbieri et al., 2021; Campo et al., 2013; Kuster et al., 2008), and pyrethroid insecticides (Feo et al., 2010), among others, in water exceeding, in some cases, EQS. The presence of these compounds may pose a risk to aquatic organisms, since some of them are persistent, toxic, and have endocrine disrupting properties. There are a few studies on the occurrence of pesticides in sediments from the Ebro River Basin (Cancapá et al., 2016; Feo et al., 2010; Lacorte et al., 2006; Navarro-Ortega et al., 2010; Veses et al., 2012), but only one of them focused on the Ebro River Delta region (Feo et al., 2010).

Most of the few works that have studied the fate of pesticides in sediments focus on non-polar pesticides, while little attention has been paid to medium and highly polar pesticides (Barbieri et al., 2019). In the last years, the large use of the latter pesticides in agriculture has led to their persistence in the water ecosystems (Barbieri et al., 2019; Kuster et al., 2009; Narendran et al., 2019; Taylor et al., 2020). Thus, the screening of these substances in sediments is critical to better understand and assess their fate and potential risks to aquatic organisms (Pinto et al., 2016).

In this context, the aim of this study was to assess the occurrence of a variety of pesticides, including medium to highly polar pesticides, in sediments from the Ebro River Delta and their associated risks. To study the implications of the sediment pesticide contamination for freshwater organisms, an environmental risk assessment was performed using the risk quotient (RQ) approach. This type of risk assessment based on experimental concentrations in the sediment is scarce for polar pesticides where the values in surface waters are generally used. Finally, the environmental risk assessment was complemented, thanks to a previous study by Barbieri et al. (2021), with results in water collected in the same sampling areas and at the same time to give a complete view of the risk status.

2. Materials and methods

2.1. Standards and solvents

Sixty-nine pesticides and 51 isotopically labelled pesticides used as internal standards (IS) were purchased from Fluka (Honeywell Specialty Chemicals Seelze GmbH, Germany), Sigma Aldrich (Merck KGaA, Darmstadt, Germany), Toronto Research Chemicals (North York, ON, Canada), Cambridge Isotope Laboratories (Tewksbury, MA, USA) and Dr. Ehrenstorfer (LGC Standards, Teddington, UK). Selected pesticides and IS used for quantification can be found in Tables S1 and S2 (Supporting Information (SI)), respectively. Pesticides were carefully chosen

to cover a wide range of applications (herbicides, acaricides, insecticides, fungicides, etc.), classes (organophosphates, neonicotinoids, pyrethroids, triazines, organochlorines, etc.), physico-chemical properties (persistence, solubility, volatility, polarity, etc.), and legal status (approved and banned). The list includes: 18 organophosphates (azinphos-ethyl, azinphos-methyl, azinphos-methyl-oxon, chlorfenvinphos, chlorpyrifos, diazinon, dichlorvos, dimethoate, fenitrothion, fenitrothion oxon, fenthion, fenthion oxon, fenthion oxon sulfone, fenthion oxon sulfoxide, fenthion sulfone, fenthion sulfoxide, malathion, malafoxon), 12 organochlorines (2,4'-DDD, 4,4'-DDD, 2,4'-DDE, 4,4'-DDE, 2,4'-DDT, 4,4'-DDT, dicofol, endosulfan, heptachlor epoxide, hexachlorobenzene, lindane, mirex), 8 triazines (atrazine, deisopropylatrazine, desethylatrazine, cyanazine, irgarol, simazine, terbutylazine, terbutryn), 5 neonicotinoids (acetamiprid, clothianidin, imidacloprid, thiacloprid, thiamethoxam), 4 phenylureas (chlorotoluron, diuron, isoproturon, linuron), 2 chloroacetamides (alachlor, metolachlor), 2 diphenyl ethers (bifenoxy, oxyfluorfen), 2 pyrethroids (cyhalothrin, cypermethrin), 2 aryloxyalkanoic acids (MCPA, mecoprop), 2 thiocarbamates (molinate, triallate), 2 dinitroanilines (pendimethalin, trifluralin), and 10 pesticides of other classes (2,4-D, bentazone, bromoxynil, diflufenican, fluroxypyr, methiocarb, oxadiazon, propanil, quinoxifen, thifensulfuron methyl). All purchased standards were of high purity (96–99.9%).

For polar compounds, individual stock solutions were prepared at a concentration of 1000 µg mL⁻¹ in methanol (MeOH), while non-polar compounds solutions were prepared at 100 µg mL⁻¹ in ethyl acetate (EtAc). As an exception, simazine and its isotopically labelled analogue were prepared in dimethyl sulfoxide. Mixtures containing all the analytes and/or the IS were used to prepare the calibration solutions and the spiking of the samples and the procedural blanks. All solutions were stored in amber glass bottles at -20 °C, protected from light.

Pesticide-grade solvents of MeOH, EtAc, hexane, acetone (ACE), acetonitrile (ACN), dichloromethane (DCM), formic acid (FA) and LC-grade water were supplied by Merck (Darmstadt, Germany). Hydro-matrix, florisis (FL) and alumina (Al₂O₃) were purchased from Merck (Darmstadt, Germany).

2.2. Sample collection

Sampling was conducted in the Ebro Delta in June 2017 during the main rice-growing season when the highest use of pesticides occurs in the area (Köck et al., 2010). Sampling sites included seven locations in the northern part (Fangar bay) and seven in the southern part (Alfacs bay). Details on the sampling locations are shown in Fig. 1 and Table S3. A series of 13 drainage channels discharging the output water from the rice fields were sampled. Only one irrigation channel was analyzed. The irrigation channels bring water to the agricultural fields and it is later collected by the drainage channels discharging the water ultimately straight to the sea (Terrado et al., 2007).

The sediment samples were taken at the bottom in the center, whenever possible, of the irrigation or drainage channel with a Van Veen grab sampler, placed in aluminum trays, and wrapped with aluminum foil. The samples were kept refrigerated at 4 °C until they arrived at the laboratory, where they were frozen at -20 °C and lyophilized with a LyoAlfa 6–50 freeze-dryer (Telstar) to eliminate the water content. Once lyophilized, they were sieved (125 µm) and kept frozen at -20 °C in the dark until analysis.

2.3. Extraction procedures and instrumental analysis

Two different analytical methodologies were employed for the determination of the selected analytes. Medium to highly polar compounds were analyzed according to Barbieri et al. (2019). Briefly, sediment samples (5 g) were PLE-extracted using a Dionex accelerated solvent extraction (ASE) 350 apparatus (Vertex Technics S.L, Barcelona) with an acidified mixture of ACE/DCM (1:1 and 1% FA, v/v). The

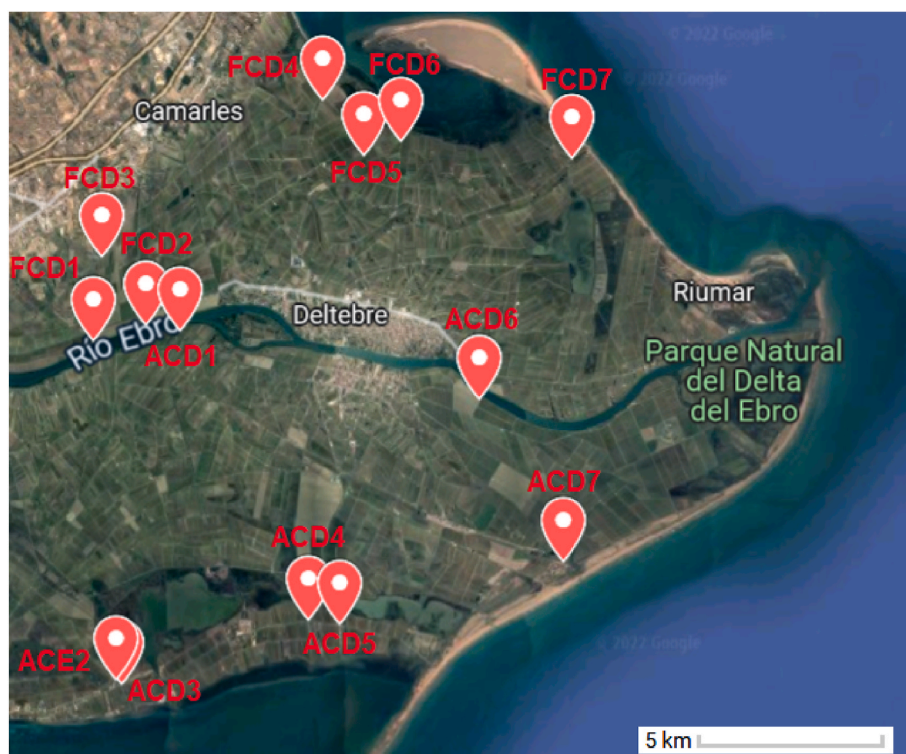


Fig. 1. Map of the Ebro Delta showing the sampling locations. A: Alfacs bay. F: Fangar bay. CD: drainage channel. CE: irrigation channel.

extracts were purified using Oasis HLB cartridges (500 mg, 6-cc cartridges, Waters, Milford, MA, USA), and the resulting extracts were reconstituted in 5 mL of MeOH. LC-MS/MS analysis was performed using a reversed phase Purospher® STAR RP-18 end-capped column (150 × 2.1 mm, 2 μm particle size) from Merck with an Aria™ LC system equipped with two Transcend quaternary pumps (Thermo Fisher Scientific Inc.) and coupled to a TSQ Quantiva triple-quadrupole mass spectrometer (Thermo Fisher Scientific Inc.). The ionization of the analytes was achieved with a heated electrospray ionization source (HESI) operated in both positive and negative modes, while mass acquisition was performed in the selected reaction monitoring (SRM) mode.

As for non-polar pesticides, their analysis was done following a method previously described by Peris and Eljarrat (2021) based on PLE and gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) determination. Sediment samples (1 g) were extracted by PLE with a mixture of hexane/DCM (1:1) and FL to perform a clean-up step within the extraction cell. Extracts were evaporated until dryness, reconstituted with EtAc, and analyzed by GC-MS/MS using a 7890 B GC system coupled to a 7000C triple quadrupole detector (Agilent Technologies, Santa Clara, CA, USA). Acquisition was performed in the SRM mode, while chromatographic separation was achieved with a DB-5MS column (30 m × 250 μm × 0.25 μm) from Agilent Technologies.

Analyte quantification was performed using an isotope dilution method. Table S2 summarizes the IS used for quantification. Details on the analytical limits of detection (LODs) and quantification (LOQs) achieved with the aforesaid methodologies can be found in Table S4.

2.4. Risk assessment

The potential ecotoxicological risk derived from the presence of pesticides in the sediments was assessed with the RQ approach. This approach compares the measured environmental concentration (MEC) with the predicted no-effect concentration (PNEC) at which no adverse/harmful effects are expected. $PNEC_{sed}$ values were derived following the

equilibrium partitioning approach (Eq. (1)) as stated in the NORMAN Ecotoxicology Database (Dulio and von der Ohe, 2013).

$$PNEC_{sed} = \text{Lowest } PNEC_{fresh} * 2.6 * (0.615 + 0.019 * K_{oc}) \quad (1)$$

Where $PNEC_{fresh}$ is the predicted no-effect concentration in freshwater and K_{oc} is the organic carbon-water partition coefficient. $PNEC_{fresh}$ and K_{oc} values were extracted from the NORMAN Ecotoxicology database (Dulio and von der Ohe, 2013) (lowest PNEC predicted by QSAR models or obtained experimentally) and the Pesticide Properties DataBase (Lewis et al., 2016), respectively.

In this study, two scenarios were evaluated, the normal-case scenario and the worst-case scenario that were assessed using the mean concentration (MEC-Mean) and the maximum concentration (MEC-Max) of pesticides found in the investigated locations, respectively. The risk evaluation of the pesticides found in sediments was performed considering RQ values below 1 to pose a low risk to aquatic organisms, between 1 and 10 as moderate risk, and above 10 as high risk for aquatic organisms (Aydin et al., 2019). Furthermore, an additive model was applied to assess the total pollution by pesticides in the samples. Therefore, each individual RQ associated with each site was summed accordingly obtaining the RQ of each sampling site (Pérez et al., 2021). Then, risk evaluation was performed using the same criteria described above.

3. Results and discussion

3.1. Occurrence of pesticides

Table 1 summarizes the results of the analysis of the 69 target pesticides in the 14 sediment samples collected from the Ebro River Delta (for detailed sample results see Table S5). Pesticides were detected in all samples analyzed, at total concentration levels ranging between 50.8 and 1912 ng g⁻¹ dry weight (dw).

Twenty-four of the 69 target pesticides were detected in the investigated samples. Eight out of the 24 detected compounds (acetamiprid,

Table 1

Pesticides found in the sediments from the Ebro River Delta: detection frequency and mean, maximum and minimum concentrations measured (expressed in ng g⁻¹ dw).

Pesticides	Detection Frequency (%)	Concentration (ng g ⁻¹ dw)		
		Mean ^a	Maximum	Minimum ^b
<i>Benzothiazinones</i>				
Bentazone	79	61.9	232	2.57
<i>Carboxamides</i>				
Diflufenican	7.1	0.04	0.59	0.59
<i>Chloroacetamides</i>				
Metolachlor	86	0.33	0.50	0.25
<i>Dinitroanilines</i>				
Pendimethalin	7.1	44.8	627	627
Trifluralin	7.1	0.16	2.29	2.29
<i>Diphenyl ethers</i>				
Oxyfluorfen	14	6.03	59.0	25.4
<i>Neonicotinoids</i>				
Acetamiprid	21	0.25	2.35	0.39
Imidacloprid	14	0.36	3.76	1.26
Thiamethoxam	7.1	0.03	0.46	0.46
<i>Organochlorines</i>				
2,4'-DDD	93	4.08	10.8	1.92
4,4'-DDD	93	11.3	42.2	4.26
4,4'-DDE	36	16.7	89.7	8.84
2,4'-DDT	14	2.49	24.0	10.9
4,4'-DDT	86	8.33	17.9	3.56
Hexachlorobenzene	57	0.12	0.70	0.01
<i>Organophosphates</i>				
Chlorpyrifos	86	26.8	274	0.80
Fenthion Oxon	7.1	0.004	0.06	0.06
Fenthion Oxon Sulfoxide	7.1	0.02	0.31	0.31
<i>Oxadiazoles</i>				
Oxadiazon	57	303	1252	57.0
<i>Pyrethroids</i>				
Cypermethrin	79	81.8	327	4.00
<i>Sulfonylureas</i>				
Thifensulfuron Methyl	14	2.82	21.5	18.0
<i>Thiocarbamates</i>				
Molinate	50	1.21	8.15	0.49
<i>Triazines</i>				
Irgarol	7.1	0.01	0.16	0.16
Terbutryn	43	0.10	0.49	0.06

^a For mean values calculation, n. d. were assigned as zero, and n. q. as LOQ/2.

^b Minimum values obtained, excluding n. d.

bentazone, cypermethrin, diflufenican, imidacloprid, oxyfluorfen, pendimethalin and thifensulfuron methyl) are currently allowed for use as pesticides and hence, their presence in the environment could be expected. Among these, bentazone and cypermethrin stand out, since they presented a high detection frequency in the samples, 79%, as well as high levels of contamination, with mean values of 62 and 82 ng g⁻¹ dw, respectively. A high level of pendimethalin was also found in the Alfacs area, 627 ng g⁻¹ dw, but in only one sample (ACD3).

The presence of banned pesticides among the detected substances is indicative of their persistence in the environment. Among these, chlorpyrifos, metolachlor, hexachlorobenzene, oxadiazon, and molinate stand out due to their high frequency of detection in the samples (≥50%), and the latter two also due to their high mean concentration levels (303 and 27 ng g⁻¹ dw, respectively).

Five TPs were found among the detected compounds: 2,4'-DDD, 4,4'-DDD, 4,4'-DDE, fenthion oxon and fenthion oxon sulfoxide. DDDs (2,4'-DDD and 4,4'-DDD) and DDEs (2,4'-DDE and 4,4'-DDE) are TPs of DDTs (2,4'-DDT and 4,4'-DDT), pesticides that, despite being banned for a long time, were also detected in the investigated samples due to their high persistence in the environment (DT50 of 17 years in soils) (Lewis et al., 2016). In general, the total amount of DDDs and DDEs in the samples was higher than that of DDTs, which suggests their origin from a legacy contamination of DDTs in the area. DDTs and their metabolites (DDXs) presented a high detection frequency in the samples, especially,

DDDs metabolites (93%) and 4,4'-DDT (86%) with mean levels of 4.08, 11.3, 16.7, 2.49, and 8.33 ng g⁻¹ dw for 2,4'-DDD, 4,4'-DDD, 4,4'-DDE, 2,4'-DDT, and 4,4'-DDT, respectively. As for the fenthion TPs, namely fenthion oxon and fenthion oxon sulfoxide, their presence could be also attributed to legacy contamination of fenthion in the area, although fenthion was not found in any sediment sample. Note that these TPs were only found in one sample (FCD5 and FCD6, respectively) and at very low levels (0.06 and 0.31 ng g⁻¹ dw in the case of fenthion oxon and fenthion oxon sulfoxide, respectively).

Most of the detected pesticides have a non-polar character, with log K_{ow} values higher than 3, K_{oc} values higher than 1000 mL g⁻¹, water solubility values lower than <50 mg L⁻¹, and present a high persistence in soils (DT50 values higher than 100 days). Therefore, they are more likely to accumulate in sediments than in water. Notable exceptions are the highly polar pesticides bentazone (log K_{ow} of -0.46), thiamethoxam (log K_{ow} of -0.13), and thifensulfuron methyl (log K_{ow} of -1.65). Nevertheless, despite that these pesticides tend to remain more in the aqueous phase than in the particulate phase, this fact does not exempt the possibility that they get also absorbed in the sediments. In fact, their behavior is reflected in the low concentrations of these pesticides found in the sediment samples (mean concentrations of 0.03 and 2.82 ng g⁻¹ dw for thiamethoxam, and thifensulfuron methyl, respectively) with bentazone as an exception (mean concentration of 61.9 ng g⁻¹ dw). This could be attributed to an extensive use of bentazone in the area since a mean concentration in waters collected in the same site at the same time of 53,000 ng L⁻¹ has previously been reported (Barbieri et al., 2021).

3.2. Main pesticide classes and spatial distribution

The pesticides detected have mostly herbicidal (11) and insecticidal (7) activity being hexachlorobenzene the only pesticide with fungicidal activity. The class with the highest number of detected congeners in the investigated area was organochlorines (6 compounds), followed by neonicotinoids (3), organophosphates (3), triazines (2), and dinitroanilines (2). Fig. 2 shows the mean contribution of each class of pesticides to total pesticide concentrations in the samples. The highest contribution corresponds to oxadiazoles (30%) followed by organochlorines (25%), benzothiazinones (18%), pyrethroids (17%), dinitroanilines (5%), and organophosphates (4%). The other classes (10 pesticides belonging to 7 different classes) constitute the remaining 2%. Oxadiazon represents the 100% of the oxadiazoles contribution, being the pesticide detected at the highest concentrations in the samples, with a maximum value of 1252 ng g⁻¹ dw. Likewise, cypermethrin and bentazone represent the 100% of the pyrethroids and benzothiazinones contributions. Regarding organochlorines, DDTs metabolites (DDD and DDEs) are responsible for 75% of the organochlorine contribution, while hexachlorobenzene only makes 0.3% of the organochlorine total amount. Chlorpyrifos represents the 99.9% of the organophosphate contribution with a mean concentration of 26.8 ng g⁻¹ dw and a maximum value of 274 ng g⁻¹ dw. These results are expected since both oxadiazon and bentazone have been extensively used in the area as herbicides to protect rice crops. The advantage of analyzing sediment over water is that this matrix reflects long-term contamination and hence the presence of legacy pesticides such as DDXs, hexachlorobenzene, metolachlor, and molinate, among others.

Regarding geographical distribution of pesticides, in general, Alfacs bay presented higher pesticide contamination than Fangar bay (see Fig. 3 and Table S6). Higher levels of benzothiazinones, dinitroanilines, diphenyl ethers, neonicotinoids, organophosphates, oxadiazoles, pyrethroids and sulfonylureas were found at sampling locations in the Alfacs bay compared to those in the Fangar bay. However, the pesticide distribution profile is similar in both bays, with oxadiazoles, organochlorines, pyrethroids, benzothiazinones, and organophosphates among the pesticides that contribute the most to total pesticide concentrations in each location. Nonetheless, some differences were observed: oxadiazoles represent the major pesticide class in the Alfacs bay, while

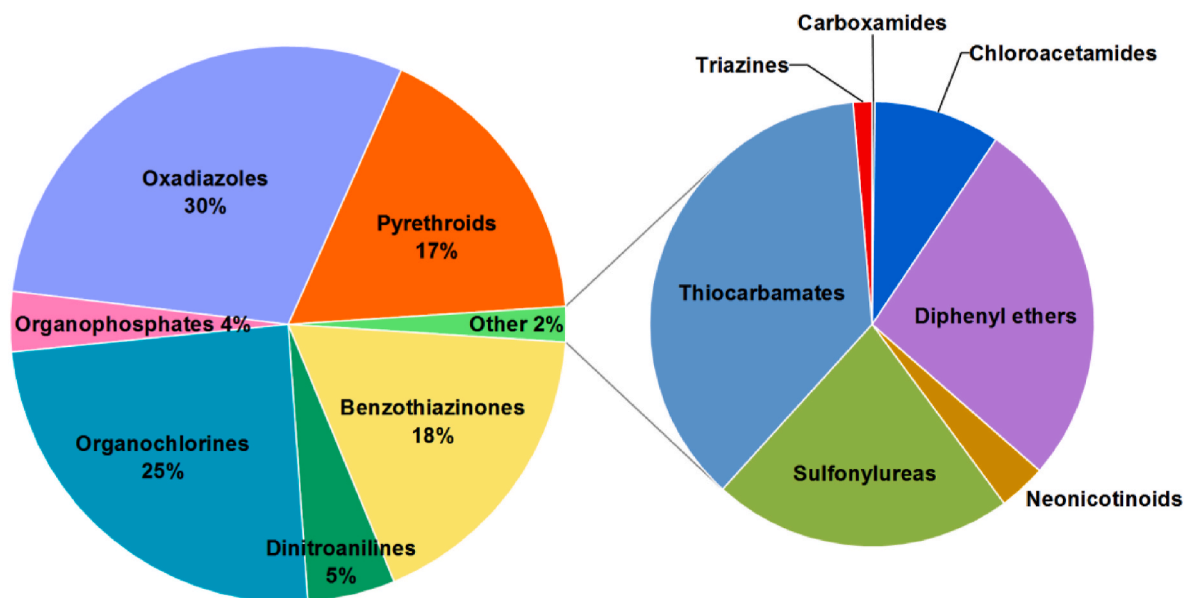


Fig. 2. Contribution of the different pesticide classes investigated to total pesticide levels in the sediments.

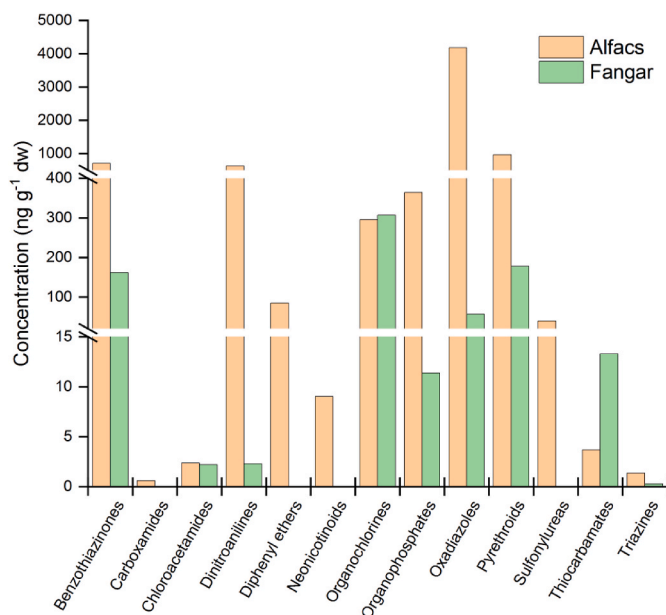


Fig. 3. Total pesticide concentrations in each sampling location of the Alfacs and Fangar Bays.

organochlorines is the main chemical class in the Fangar bay, with a mean contribution in the samples of 56% and 44%, respectively. This difference is mainly attributed to a higher contamination of oxadiazon in the Alfacs bay since organochlorine contamination is similar in both bays. Oxadiazon is an oxadiazole herbicide, largely used in rice crops against both mono and dicotyledonous weeds (Pietrzak et al., 2019). Therefore, oxadiazon presence in the samples is likely related with the predominant rice cultivation in the Ebro River Delta. These differences between Alfacs and Fangar bay could be related with a higher use of dry seeding in the Fangar bay, a technique that could reduce the use of herbicides. In addition, a lower mean contribution of dinitroanilines in the Fangar area (0.6%) was observed compared to the Alfacs bay (10%). However, this is due to a high level of contamination with pendimethalin in one sediment sample from the Alfacs bay.

Also, an apparent increase of pesticide levels in the river direction

(ACD1-ACD7) to the bay can be observed (Table S5). The most contaminated samples were ACD5 and ACD7 with total pesticide concentrations of 1682 and 1912 ng g⁻¹ dw, respectively. These levels result from the high amount of oxadiazon detected in these samples (1252 and 1230 ng g⁻¹ dw in ACD5 and ACD7, respectively). ACE2, the only irrigation channel analyzed, presented contamination levels similar to the samples from the drainage channels. This is because, when the water level decreases, it is filled with water from the drainage channels to cover the water demand of the adjacent fields.

This work is complementary to the study conducted by Barbieri et al. (2021) in which the occurrence of the target pesticides was evaluated in water samples collected in the same sampling locations at the same time. In Barbieri et al.'s study, 35 pesticides were detected in the Ebro Delta surface waters with bentazone showing the highest concentrations in all analyzed samples (up to 177 µg L⁻¹), followed by propanil, MCPA, acetamiprid, triallate, imidacloprid and 2,4-D. In general, pesticides detected in aqueous phase are more polar (log K_{ow} values lower than 3) than those detected in the particulate phase, and hence their presence is less relevant in sediments.

Furthermore, experimental sediment-water distribution coefficients (K_d) were calculated in order to evaluate the pesticide partition between the sediment and the aqueous phase. K_d was only calculated for the analytes that were present in both phases in at least 30% of the samples. Results of experimental K_d are summarized in Table S7. Based on these results, oxadiazon presented the highest tendency to be absorbed into the sediments (K_d: 17,733 L kg⁻¹; Log K_d: 4.25), followed by chlorpyrifos (K_d: 3270 L kg⁻¹; Log K_d: 3.51), terbutryn (K_d: 96.7 L kg⁻¹; Log K_d: 1.99), molinate (K_d: 67.1 L kg⁻¹; Log K_d: 1.83), metolachlor (K_d: 14.9 L kg⁻¹; Log K_d: 1.17), and bentazone (K_d: 1.41 L kg⁻¹; Log K_d: 0.15).

Several experimental sediment-water K_d values have been published for diverse pesticides around the world. In the case of chlorpyrifos, Zhen et al. (2019), who studied the fate and ecological effects of current-use pesticides in the Xiaqing River, reported a Log K_d of 2.21, lower than the one obtained in this study (Log K_d 3.51). Gebremariam et al. (2012) reviewed the sorption of chlorpyrifos to aquatic sediments and reported values ranging from 40 L kg⁻¹ to 767 L kg⁻¹, lower than the one from this study (3270 L kg⁻¹). Carazo-Rojas et al. (2018) reported K_d values for chlorpyrifos and terbutryn of 326.04 L kg⁻¹ and 97.28 L kg⁻¹, respectively. The K_d value of terbutryn is similar to that obtained in the present study (96.7 L kg⁻¹) despite that the K_d reported by Carazo-Rojas et al. (2018) was derived from the K_{oc} value and the fraction of total

organic carbon measured in the sediment samples. [Cruzeiro et al. \(2016\)](#) reported a log K_d value of terbutryn from samples collected from the Tagus River Estuary of 2.91, higher than the one obtained in this study of 1.99. In [Cruzeiro et al.](#)'s study, K_d values were calculated with suspended sediments concentration instead of bottom sediments. [Xue et al. \(2005\)](#) reported a sediment-water K_d of 3.3 L kg^{-1} for metolachlor derived from the analyses of both water and sediments from the Beijing Guanting reservoir. This value is lower than the one obtained in the present study (14.9 L kg^{-1}). [Chaumet et al. \(2021\)](#) reported higher mean K_d values for metolachlor than this study, calculated from sediments collected from the Bassioué Pond (Gers, France) in autumn (480 L kg^{-1}) and summer (210 L kg^{-1}).

The variability among peer-reviewed data and those generated in our study could be explained by different environmental conditions in each location such as the organic carbon content of the sediments, or the ionic strength, temperature, and pH of the water, which affect compound sorption ([Warren et al., 2003](#); [Zhen et al., 2019](#)). Additional differences can also be attributed to the fact that the experimental K_d derived from flowing systems cannot be assumed to be at equilibrium. Moreover, exceptional events (e.g. storms, floods, delivered disposal) altering surface water concentrations and normal diffusion rates of compounds can affect sediment-water K_d ([López-García et al., 2021](#)).

3.3. Historical data of pesticide occurrence in sediments from the ebro river basin

A comparison between our results with previously published pesticide levels in sediments from the Ebro River basin can be found in [Fig. 4](#) (for detailed information see [Table S8](#)). For this comparison, the studied area was expanded to the whole Ebro River basin since there are very few studies focused on the occurrence of pesticides in sediments from the delta area. Most of these studies targeted non-polar pesticides, while only two studies ([Ccancapa et al., 2016](#); [Navarro-Ortega et al., 2010](#))

included pesticides with a broader range of polarity.

[Ccancapa et al. \(2016\)](#) analyzed 50 pesticides (23 of which were also analyzed in our study) in sediments collected in two consecutive years (2010 and 2011) along the Ebro River basin. However, only four pesticides were detected: terbutryn, chlorpyrifos, diazinon, and malathion. Diazinon and malathion presented lower concentrations in 2011 than 2010. This decreasing trend is confirmed in our study, since none of them were detected in 2017. Similar results were found for terbutryn since the mean found in this study ($0.10 \text{ ng g}^{-1} \text{ dw}$) was similar to the one single measured concentration in 2011 ($0.10 \text{ ng g}^{-1} \text{ dw}$) when the overall mean was near zero and lower than that calculated in 2010 ($1.16 \text{ ng g}^{-1} \text{ dw}$). On the other hand, an increasing trend of chlorpyrifos is observed since the mean concentration in this study ($26.8 \text{ ng g}^{-1} \text{ dw}$) was higher than that obtained in 2011 and 2010 (7.66 and $1.06 \text{ ng g}^{-1} \text{ dw}$, respectively). In addition, an apparent increase of cypermethrin can be observed since higher ranges were obtained in this study compared to the one obtained in June 2009 (4.00 – 327 vs. 8.27 – $71.9 \text{ ng g}^{-1} \text{ dw}$) by [Feo et al. \(2010\)](#) that analyzed pyrethroid insecticides in sediments collected in the Ebro Delta.

On the other hand, compared to [Navarro-Ortega et al. \(2010\)](#) that analyzed polycyclic aromatic hydrocarbons (PAHs), pesticides and alkylphenols in sediments collected in the Ebro River basin between 2004 and 2006, a decrease in lindane, diazinon, propanil, and alachlor has been observed since they were not detected in the present study. This could be attributed to the low presence in the environment of these pesticides, since their use, except that of propanil ([Spanish Ministry of Agriculture, 2017](#)), has been already banned for years. However, substances such as hexachlorobenzene, DDXs, and molinate were also detected in the present study despite being banned. Nonetheless, a considerable decrease in hexachlorobenzene concentrations has been observed (0.12 vs. $88.48 \text{ ng g}^{-1} \text{ dw}$) as well as some DDXs (4.08 vs. $11.92 \text{ ng g}^{-1} \text{ dw}$ for 2,4'-DDD, 2.49 vs. $15.10 \text{ ng g}^{-1} \text{ dw}$ for 2,4'-DDT, 8.33 vs. $48.38 \text{ ng g}^{-1} \text{ dw}$ for 4,4'-DDT, and below LOD vs. 2.78 ng g^{-1}

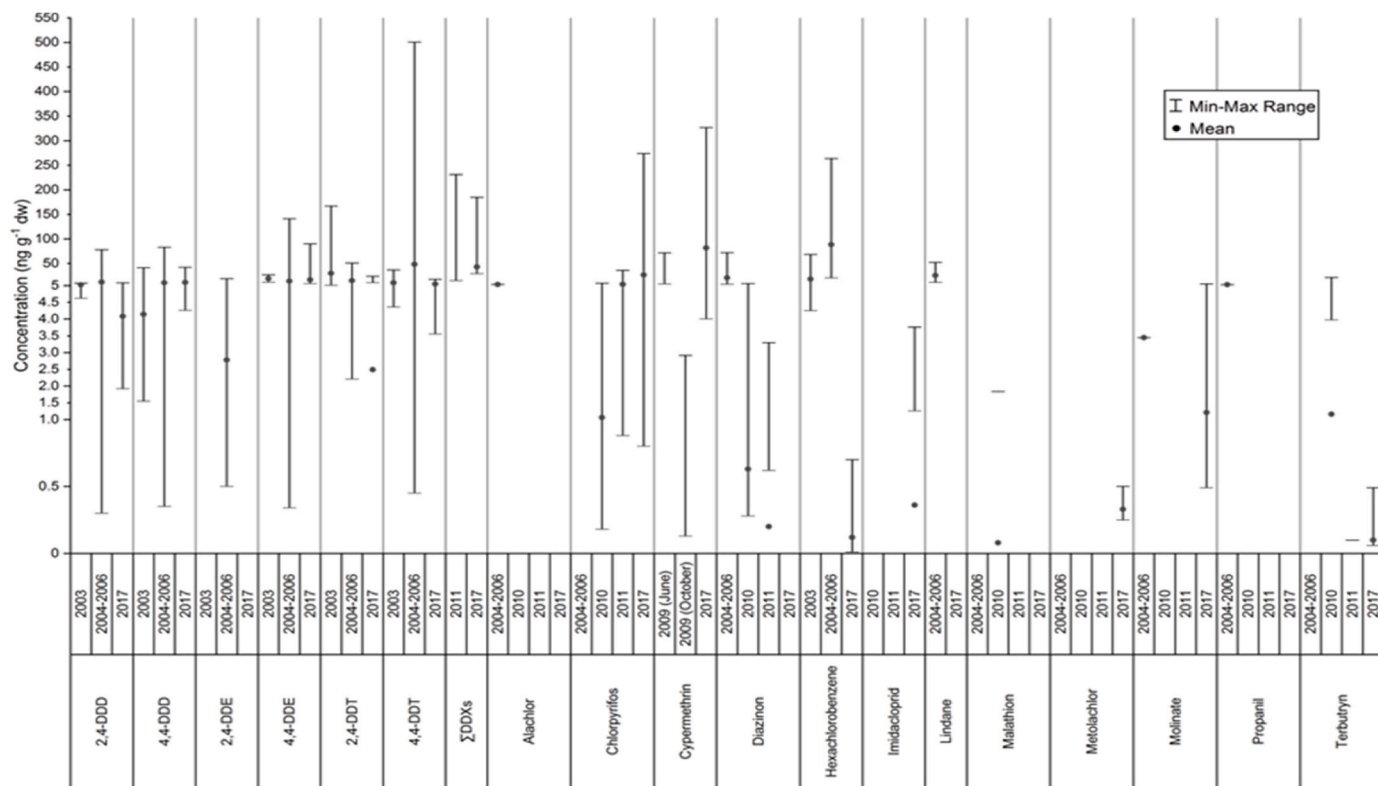


Fig. 4. Summary of data, mean, minimum (min) and maximum (max) pesticide concentrations, expressed in $\text{ng g}^{-1} \text{ dw}$, in sediments from the Ebro river basin. References: year 2003 ([Lacorte et al., 2006](#)), 2004–2006 ([Navarro-Ortega et al., 2010](#)), 2009 ([Feo et al., 2010](#)), 2010–2011 ([Ccancapa et al., 2016](#)), 2011 ([Veses et al., 2012](#)), and 2017 (present study).

dw for 2,4' DDE), and molinate (1.21 vs. 3.45 ng g⁻¹ dw). However, similar levels of some TPs of DDT such as 4,4'-DDD and 4,4'-DDE were obtained in our study (11.3 vs. 10.52 and 16.7 vs. 14.09 ng g⁻¹ dw, respectively) as well as metolachlor and trifluralin (0.33 and 0.16 ng g⁻¹ dw vs. below LODs). This decreasing trend of hexachlorobenzene and DDXs is also supported by Lacorte et al. (2006) and Veses et al. (2012) studies. Moreover, an apparent increase in chlorpyrifos has also been observed since it was detected in our study with a mean concentration of 26.8 ng g⁻¹ dw that was absent in the sediments analyzed between 2004 and 2006.

In general, it can be concluded a decreasing tendency of DDXs, hexachlorobenzene, diazinon, lindane and malathion levels in the sediments of the Ebro River basin, and an increasing trend of pesticides such as chlorpyrifos, cypermethrin, and imidacloprid. However, it must be noted that most of the samplings of aforementioned studies were conducted along the Ebro River basin while the present study only focuses on the Ebro Delta area, hence results should be taken with caution.

3.4. Environmental risk assessment

The results from the evaluation of the potential ecotoxicological risk derived from the presence of pesticides in the sediments with the RQ method are summarized in Table 2.

Regarding the “normal-case” scenario, where MEC-Mean was used for evaluation, six out of the 24 detected pesticides presented RQs higher than 1 indicating at least a moderate risk to sediment-dwelling

organisms. These pesticides are bentazone, pendimethalin, chlorpyrifos, oxadiazon, cypermethrin, and thifensulfuron methyl. Among these, bentazone, oxadiazon and cypermethrin presented RQs higher than 10 indicating that they can pose a potential high risk. A high RQ can be a result of a high environmental concentration of the pollutant and/or a low PNEC. The high RQ values of aforementioned pesticides are mainly a result of their high concentrations in the sediment samples. These results are not only of concern for sediment-dwelling organisms but also for higher trophic organisms through bioaccumulation and biomagnification of pesticides along the food chain potentially affecting humans. Moreover, four out of the six aforementioned pesticides (bentazone, pendimethalin, cypermethrin, and thifensulfuron methyl) are still in use, in accordance with Regulation (EC) No 1107/2009 (EC, 2009), hence an increase of their environmental concentrations in the near future could be speculated, as seen in the case of pesticides such as cypermethrin and chlorpyrifos (Fig. 4). The observed toxicological effects in fish include developmental malformations, cellular damage, behavioral alterations, and alterations of biochemical and hematological parameters among others (Burgos-Aceves et al., 2019; Fathy et al., 2019; Gupta and Verma, 2020; Jee et al., 2005; Oliveira et al., 2017; Saglio et al., 2001; Shankar Murthy et al., 2013; Tabassum et al., 2015).

Similar results were obtained when assessing the “worst-case” scenario, where MEC-Max was used for evaluation, since all six aforementioned pesticides presented RQs higher than 10 indicating that they can pose a potential high risk to sediment-dwelling organisms. Only one of the remaining 18 pesticides, imidacloprid, had a RQ higher than 1

Table 2
Risk quotients (RQs) for the worst-case (RQ-Max) and the normal (RQ-mean) contamination scenarios.

Pesticides	PNEC _{fresh} ^a (µg L ⁻¹)	PNEC _{sed} ^b (ng g ⁻¹)	MEC-Mean ^c (ng g ⁻¹)	MEC-Max ^c (ng g ⁻¹)	RQ-Mean ^d	RQ-Max ^d
<i>Benzothiazinones</i>						
Bentazone	0.1	0.43	61.9	232	144	538
<i>Carboxamides</i>						
Diflufenican	0.009	2.46	0.04	0.59	0.02	0.24
<i>Chloroacetamides</i>						
Metolachlor	0.2	1.51	0.33	0.50	0.22	0.33
<i>Dinitroanilines</i>						
Pendimethalin	0.018	15.6	44.8	627	2.89	40.2
Trifluralin	0.03	23.5	0.16	2.29	0.007	0.10
<i>Diphenyl ethers</i>						
Oxyfluorfen	0.094	218	6.03	59.0	0.03	0.27
<i>Neonicotinoids</i>						
Acetamiprid	3.74	42.9	0.25	2.35	0.006	0.06
Imidacloprid	0.0083	2.77	0.36	3.76	0.13	1.37
Thiamethoxam	2.96	12.9	0.03	0.46	0.002	0.04
<i>Organochlorines</i>						
2,4'-DDD	0.0039	30.0	4.08	10.8	0.14	0.37
4,4'-DDD	0.025	192	11.3	42.2	0.06	0.22
4,4'-DDE	0.025	188	16.7	89.7	0.09	0.48
2,4'-DDT	0.025	187	2.49	24.0	0.01	0.13
4,4'-DDT	0.01	74.6	8.33	17.9	0.11	0.24
Hexachlorobenzene	0.05	124	0.12	0.70	0.001	0.006
<i>Organophosphates</i>						
Chlorpyrifos	0.03	8.21	26.8	274	3.29	33.4
Fenthion Oxon	0.2	0.34	0.004	0.06	0.01	0.18
Fenthion Oxon Sulfoxide	0.48	0.77	0.02	0.31	0.03	0.40
<i>Oxadiazoles</i>						
Oxadiazon	0.088	14.1	303	1252	21.6	89.1
<i>Pyrethroids</i>						
Cypermethrin	0.00008	1.22	81.8	327	67.5	269
<i>Sulfonylureas</i>						
Thifensulfuron Methyl	0.2	0.60	2.82	21.5	4.70	36.9
<i>Thiocarbamates</i>						
Molinate	3.8	41.7	1.21	8.15	0.03	0.20
<i>Triazines</i>						
Irgarol	0.0025	0.20	0.01	0.16	0.05	0.81
Terbutryn	0.065	7.91	0.10	0.49	0.01	0.06

^a PNEC_{fresh}: water predicted no-effect concentration. Data extracted from the NORMAN Ecotoxicology database (Dulio and von der Ohe, 2013).

^b PNEC_{sed}: sediment predicted no-effect concentration.

^c MEC-Mean: Mean concentration of detected pesticides in the samples; MEC-Max: Maximum concentration of detected pesticides in the samples.

^d RQ values > 10 are highlighted in bold.

indicating that it may pose a moderate risk to sediment-dwelling organisms at high concentrations (MEC-Max of $3.76 \text{ ng g}^{-1} \text{ dw}$), while the remaining pesticides would not represent ecological risk (RQ below 1). As mentioned above, these results are not only of concern for stream ecology but also for higher trophic organisms potentially affecting humans through bioaccumulation and biomagnification along the food chain. Among toxicological effects in humans are endocrine and estrogenic effects (cypermethrin), blood, liver and kidney toxicity (bentazone), thyroid and liver toxicity (pendimethalin), and possible human carcinogenic effects (cypermethrin, pendimethalin) (Lewis et al., 2016).

Similar results were obtained by Eissa et al. (2022) that detected chlorpyrifos ($13\text{--}360 \text{ ng g}^{-1} \text{ dw}$), cypermethrin ($10\text{--}38 \text{ ng g}^{-1} \text{ dw}$), and pendimethalin ($10 \text{ ng g}^{-1} \text{ dw}$), among others, in sediments from the Rosetta branch of the Nile River (Egypt). Results of the ecotoxicological risk assessment revealed that chlorpyrifos and cypermethrin could pose a potential high risk for aquatic organisms at all sites while pendimethalin presented a medium risk for aquatic organisms. High RQs posing a potential high risk to aquatic organisms have also been reported in water and sediments for chlorpyrifos and cypermethrin (León et al., 2020; Tsaboula et al., 2016; Vryzas et al., 2011).

In addition, similar results were obtained by Pérez et al. (2021) that reported imidacloprid in sediments at concentrations ranging between 7.00 and $8.00 \text{ ng g}^{-1} \text{ dw}$ (mean of $4.85 \text{ ng g}^{-1} \text{ dw}$) that could pose potential acute toxicity to sediment-dwelling organisms. Other studies have reported imidacloprid at concentrations ranging from 0.02 to $25.2 \text{ ng g}^{-1} \text{ dw}$ (Calvo et al., 2021; Matic Bujagic et al., 2019; Zhang et al., 2019) in line with reported concentrations in the present study. Moreover, other studies like Wang et al. (2021) have reported imidacloprid at concentrations in water posing a potential high risk to aquatic organisms.

Furthermore, bentazone was reported in sediments from The Natural Park of the Albufera (Spain) at high concentrations up to $898 \text{ ng g}^{-1} \text{ dw}$ (mean of $82 \text{ ng g}^{-1} \text{ dw}$) by Calvo et al. (2021) in line with reported concentrations in this study. Bentazone has already been reported to cause a high risk to aquatic organisms in Palma et al. (2021) study derived from its presence in surface waters collected in the Guadina Basin (Southern of Portugal) with mean concentrations ranging from 44.8 to 795.9 ng L^{-1} . On the other hand, other studies have reported oxadiazon in sediments with concentrations ranging from 1.3 to $382 \text{ ng g}^{-1} \text{ dw}$ (Crane and Youngmans-Haug, 1992; Le Gaudu et al., 2022; Peris and Eljarrat, 2021) in line with our study. Oxadiazon was already reported to cause a potential high risk to aquatic organisms by Peris and Eljarrat (2021) in sediments collected from several Catalan river basins with a mean concentration of $44 \text{ ng g}^{-1} \text{ dw}$. Moreover, thifensulfuron methyl was detected in sediment samples collected from wetlands of Saskatchewan and Manitoba (Canada) with concentrations below LOQ ($1 \text{ ng g}^{-1} \text{ dw}$) (Degenhardt et al., 2010). Reported concentrations in our study are slightly higher with a mean of $2.82 \text{ ng g}^{-1} \text{ dw}$. Nevertheless, thifensulfuron methyl has already been reported to cause a potential moderate risk to aquatic organisms derived from its presence in surface waters at mean concentrations ranging from 44.0 to 78.0 ng L^{-1} (Palma et al., 2021).

Moreover, a tentative risk assessment derived from the simultaneous presence of pesticides in the sediments was performed through a simple additive model of the RQ values (Fig. 5, Table S9). As mentioned by other authors (Backhaus et al., 2000; Barbieri et al., 2021; Belden et al., 2007), this model may underestimate the risk since synergistic effects that may occur between contaminants are not considered. Nevertheless, this model can be useful as a first picture of the risk status that can lead to further studies. Results are of concern since all monitored sites, except one (FCD2), presented RQs higher than 10 indicating that the simultaneous presence of pesticides in the sediments may pose a potential high risk to sediment-dwelling organisms. Nevertheless, calculated risk was obtained using a conservative approach since predicted PNECs in sediment were derived from the lowest freshwater PNECs obtained experimentally or predicted by QSAR models extracted from the NORMAN

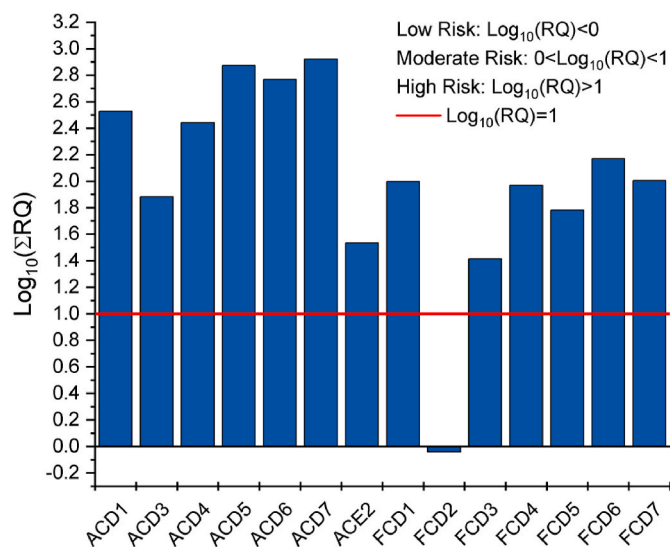


Fig. 5. Total risk quotient (RQ) associated to pesticide presence in each sampling location.

Ecotoxicology database (Dulio and von der Ohe, 2013). In addition, an apparent increase in the RQ was also observed in the river direction (ACD1-ACD7) as previously observed with total pollution by location. Moreover, the highest contribution to the total RQ in the samples corresponded to the class of benzothiazinones (49.7%) followed by pyrethroids (23.3%), oxadiazoles (12.6%), dinitroanilines (4.53), organochlorines (3.91%), and organophosphates (3.14%). The other classes (10 pesticides belonging to 7 different classes) constitute the remaining 3%. Interestingly, this result differs slightly from the contribution to total pesticide contamination where oxadiazoles was the main class followed by organochlorines, benzothiazinones, pyrethroids, dinitroanilines, and organophosphates. These results remark that despite oxadiazoles and organochlorines presented higher concentrations in the samples than benzothiazinones and pyrethroids their concentrations represented less risk to sediment-dwelling organisms, respectively.

Results of the comparison between the environmental risk assessment in the sediments from this study and the water samples from Barbieri et al. (2021)'s study are summarized in Fig. 6. Results from the environmental risk assessment in the water samples by Barbieri et al. (2021) indicated that acetamiprid, azinphos-ethyl, bentazone, cybutryne, dicofol, imidacloprid, MCPA, and propanil could pose, at least, a moderate risk to aquatic organisms. Out of these, bentazone, dicofol, imidacloprid, and propanil exhibited RQs higher than 10 indicating a potential high risk to aquatic organisms. In sediments, bentazone and imidacloprid also exhibited levels that could pose a potential high and moderate risk to aquatic organisms, respectively. However, no risk is expected from the presence of acetamiprid in sediments. On the other hand, the presence of chlorpyrifos, oxadiazon, and pendimethalin in the sediments could pose, at least, a moderate risk to aquatic organisms while no risk was concluded from their presence in surface waters. These differences between water and sediment could be attributed to differences in the application of pesticides since a recent use of a pesticide would reflect high concentrations in water compared to sediment and vice versa for a past-used pesticide.

Similar results were obtained for both water and sediment when comparing the cumulative risk at each sampling location. All sampling locations exhibited RQs higher than 10 in water. Furthermore, in general, Alfacs bay presented higher RQs than the Fangar bay in the sediments while in water no apparent differences could be appreciated.

Nevertheless, additional research needs to be conducted to assess the risk derived from the presence of mixtures of pesticides in both the water

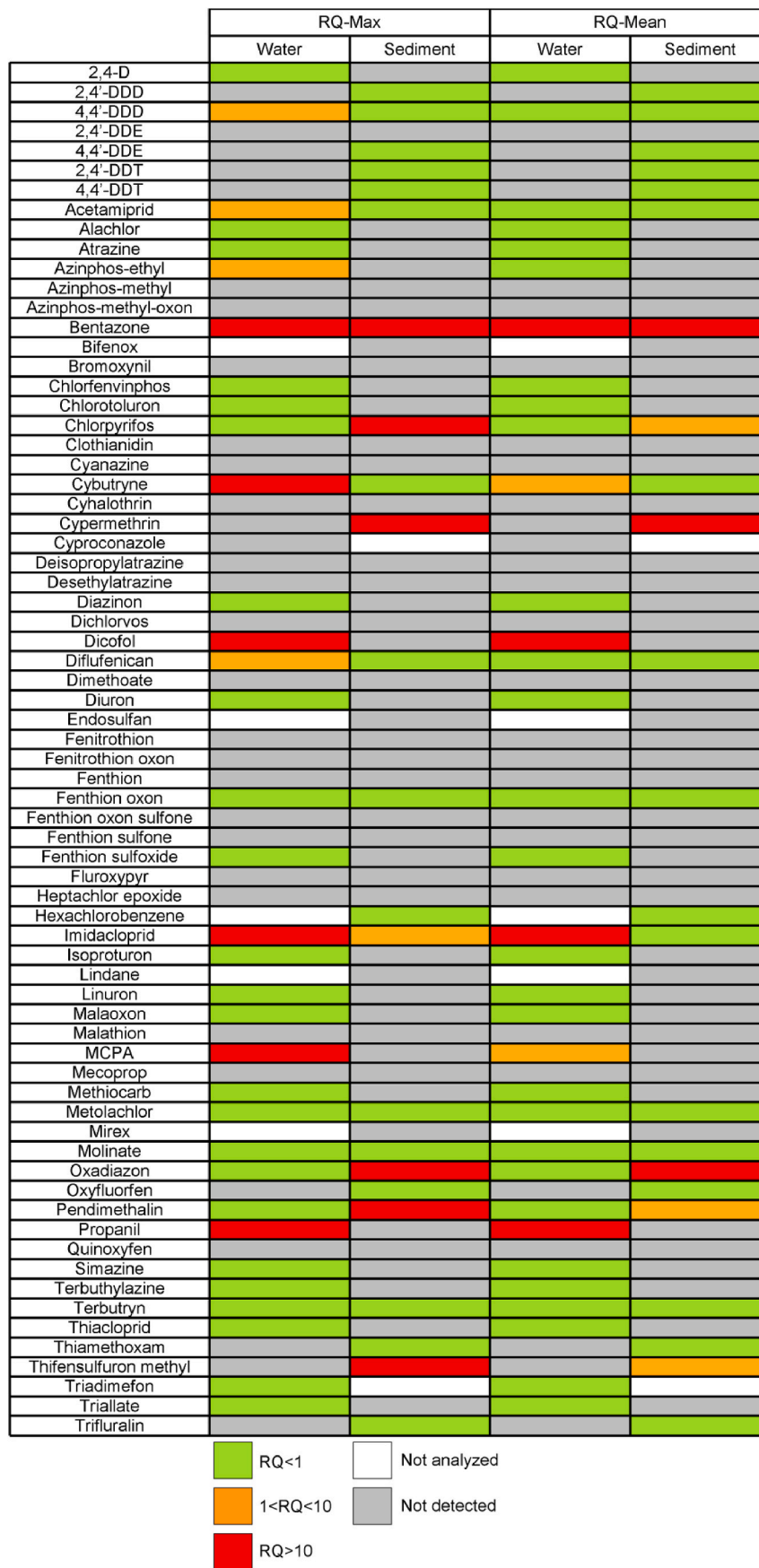


Fig. 6. Environmental risk assessment of water and sediment samples.

and the sediment compartments. In addition, results from this study should be taken with caution since sediment PNECs were derived from freshwater PNECs as toxicity data on sediments was limited for our selection of pesticides. Therefore, the risk could be overestimated or underestimated in some cases. In fact, a comparison of the results was performed with available toxicity data of sediment-dwelling organisms (Table S10) and revealed that chlorpyrifos and pendimethalin risks were underestimated and overestimated, respectively. Nevertheless, the use of predicted PNECs was preferred in order to assess the risk status of the area derived from the presence of all detected pesticides in the sediment that can lead to further studies. Moreover, results from this study highlight the importance of their simultaneous evaluation in both matrices since some pesticides, which are not detected at concerning levels in water, may pose a moderate/high risk in the sediments and vice versa.

4. Conclusions

Twenty-four of the 69 target pesticides were detected in the sediment samples analyzed with bentazone and cypermethrin exhibiting high detection frequencies, 79%, as well as high mean levels of 61.9 and 81.8 ng g⁻¹ dw, respectively. In general, the Alfacs bay presented higher pesticide contamination than the Fangar bay, but exhibiting similar distribution profiles, with oxadiazoles, organochlorines, pyrethroids, benzothiazinones and organophosphates among the major classes of detected pesticides. A historical comparison of pesticide levels in sediments collected from the Ebro River basin showed a decreasing tendency of DDXs, hexachlorobenzene, diazinon, lindane and malathion levels as well as an increasing trend in the levels of chlorpyrifos, cypermethrin, molinate and imidacloprid. The presence of chlorpyrifos, pendimethalin and thifensulfuron methyl in the sediments represents a potential moderate risk to aquatic organisms based on the RQ method, while bentazone, cypermethrin and oxadiazon exhibit a potential high risk. As a complement to the study of Barbieri et al. (2021) it could be concluded that additional work is needed to assess the risk derived from the simultaneous presence of pesticides in both the water and the sediment compartments since the results obtained suggest that some pesticides, not detected at concerning levels in water, may pose a moderate/high risk in the sediments, and vice versa for the water matrix. In addition, the importance of the inclusion of medium to highly polar pesticides in the analysis of sediments is emphasized since some polar pesticides such as bentazone, imidacloprid, and thifensulfuron-methyl have been detected at concentrations that may pose a risk to aquatic organisms. Moreover, aforementioned pesticides should be prioritized for further consideration of pesticide control and management interventions in the studied area and other areas of the world as they have been reported at similar levels by other studies. To the best of the author's knowledge, this is the most complete risk assessment of pesticide contamination in sediments from the Ebro Delta, and the first report of the occurrence of bentazone, oxadiazon, pendimethalin and thifensulfuron methyl, with mean concentrations of 61.9, 303, 44.8 and 2.82 ng g⁻¹ dw, respectively, that may pose a moderate risk (pendimethalin and thifensulfuron methyl) and high risk (bentazone and oxadiazon) to sediment-dwelling organisms.

Credit author statement

A. Peris: Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing **M.V. Barbieri:** Methodology, Formal analysis, Investigation, Review & Editing **C. Postigo:** Investigation, Review & Editing **M. Rambla-Alegre:** Sampling, Review & Editing **M. López de Alda:** Conceptualization, Methodology, Validation, Investigation, Resources, Review & Editing, Project administration, Funding acquisition **E. Eljarrat:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding

acquisition

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work has been funded by the Spanish State Research Agency (AEI) and the European Regional Development Fund (ERDF) through the project BECAS (grant number CTM 2016-75587-C2-2-R), and by the Generalitat de Catalunya (Consolidated Research Group Water and Soil Quality Unit 2017 SGR 1404). IDAEA-CSIC is a Center of Excellence Severo Ochoa (Spanish Ministry of Science and Innovation, Project CEX 2018-000794-S). IRTA members acknowledge the support from CERCA Programme/Generalitat de Catalunya.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2022.119239>.

References

- Aydin, S., Aydin, M.E., Ulvi, A., Kilic, H., 2019. Antibiotics in hospital effluents: occurrence, contribution to urban wastewater, removal in a wastewater treatment plant, and environmental risk assessment. *Environ. Sci. Pollut. Res.* 26, 544–558. <https://doi.org/10.1007/s11356-018-3563-0>.
- Backhaus, T., Altenburger, R., Boedeker, W., Faust, M., Scholze, M., Grimme, L.H., 2000. Predictability of the toxicity of a multiple mixture of dissimilarly acting chemicals to *Vibrio fischeri*. *Environ. Toxicol. Chem.* 19, 2348–2356. <https://doi.org/10.1002/etc.5620190927>.
- Barbieri, M.V., Peris, A., Postigo, C., Moya-Garcés, A., Monllor-Alcaraz, L.S., Rambla-Alegre, M., Eljarrat, E., López de Alda, M., 2021. Evaluation of the occurrence and fate of pesticides in a typical Mediterranean delta ecosystem (Ebro River Delta) and risk assessment for aquatic organisms. *Environ. Pollut.* 274, 115813. <https://doi.org/10.1016/j.envpol.2020.115813>.
- Barbieri, M.V., Postigo, C., Monllor-Alcaraz, S., Barceló, D., de Alda, M.L., 2019. Reliable LC-MS/MS-based method for trace level determination of 50 medium to highly polar pesticide residues in sediments and ecological risk assessment. *Anal. Bioanal. Chem.* 411, 7981–7996. <https://doi.org/10.1007/s00216-019-02188-0>.
- Belden, J.B., Gilliom, R.J., Lydy, M.J., 2007. How well can we predict the toxicity of pesticide mixtures to aquatic life? *Integrated Environ. Assess. Manag.* 3, 364–372. [https://doi.org/10.1897/1551-3793\(2007\)3\[364:HWCWPT\]2.0.CO;2](https://doi.org/10.1897/1551-3793(2007)3[364:HWCWPT]2.0.CO;2).
- Burgos-Aceves, M.A., Lionetti, L., Faggio, C., 2019. Multidisciplinary haematology as prognostic device in environmental and xenobiotic stress-induced response in fish. *Sci. Total Environ.* 670, 1170–1183. <https://doi.org/10.1016/j.scitotenv.2019.03.275>.
- Calvo, S., Romo, S., Soria, J., Picó, Y., 2021. Pesticide contamination in water and sediment of the aquatic systems of the Natural Park of the Albufera de Valencia (Spain) during the rice cultivation period. *Sci. Total Environ.* 774, 145009. <https://doi.org/10.1016/j.scitotenv.2021.145009>.
- Campo, J., Masiá, A., Blasco, C., Picó, Y., 2013. Occurrence and removal efficiency of pesticides in sewage treatment plants of four Mediterranean River Basins. *J. Hazard Mater.* 263, 146–157. <https://doi.org/10.1016/j.jhazmat.2013.09.061>.
- Carazo-Rojas, E., Pérez-Rojas, G., Pérez-Villanueva, M., Chinchilla-Soto, C., Chinchilla, J.S., Aguilar-Mora, P., Alpizar-Marín, M., Masiá-Mora, M., Rodríguez-Rodríguez, C.E., Vryzas, Z., 2018. Pesticide monitoring and ecotoxicological risk assessment in surface water bodies and sediments of a tropical agro-ecosystem. *Environ. Pollut.* 241, 800–809. <https://doi.org/10.1016/j.envpol.2018.06.020>.
- Cancaccapa, A., Masiá, A., Navarro-Ortega, A., Picó, Y., Barceló, D., 2016. Pesticides in the Ebro river basin: occurrence and risk assessment. *Environ. Pollut.* 211, 414–424. <https://doi.org/10.1016/j.envpol.2015.12.059>.
- Chaumet, B., Probst, J.-L., Eon, P., Camboulive, T., Riboul, D., Payré-Suc, V., Granouillac, F., Probst, A., 2021. Role of Pond sediments for trapping pesticides in an agricultural catchment (auradé, SW France): distribution and controlling factors. *Water* 13, 1734. <https://doi.org/10.3390/w13131734>.
- Crane, D.B., Youngmans-Haug, C., 1992. Oxadiazon residue concentrations in sediment, fish, and shellfish from a combined residential/agricultural area in Southern California. *Bull. Environ. Contam. Toxicol.* 48, 608–615. <https://doi.org/10.1007/BF00199081>.
- Cruzeiro, C., Pardal, M.A., Rodrigues-Oliveira, N., Castro, L.F.C., Rocha, E., Rocha, M.J., 2016. Multi-matrix quantification and risk assessment of pesticides in the longest river of the Iberian peninsula. *Sci. Total Environ.* 572, 263–272. <https://doi.org/10.1016/j.scitotenv.2016.07.203>.

- Degenhardt, D., Cessna, A.J., Raina, R., Pennock, D.J., Farenhorst, A., 2010. Trace level determination of selected sulfonylurea herbicides in wetland sediment by liquid chromatography electrospray tandem mass spectrometry. *J. Environ. Sci. Health Part B Pestic. Food Contam. Agric. Wastes* 45, 11–24. <https://doi.org/10.1080/03601230903404291>.
- Dulio, V., von der Ohe, P.C., 2013. NORMAN Prioritisation framework for emerging substances. <https://bit.ly/2ZICWRW>.
- EC, 2020. COMMISSION IMPLEMENTING DECISION (EU) 2020/1161 of 4 August 2020 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council. *Off. J. Eur. Union L* 257, 32–35.
- EC, 2013. DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. *Off. J. Eur. Union L* 226, 1–17.
- EC, 2009. REGULATION (EC) No 1107/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC. *Off. J. Eur. Union L* 309, 1–50.
- Eissa, F., Al-Sisi, M., Ghanem, K., 2022. Occurrence and ecotoxicological risk assessment of pesticides in sediments of the Rosetta branch, Nile River, Egypt. *J. Environ. Sci. (China)* 118, 21–31. <https://doi.org/10.1016/j.jes.2021.08.047>.
- Fathy, M., Mohamed, I.A., Farghal, A.I.A., Temerak, S.A.H., Sayed, A.E.D.H., 2019. Hemotoxic effects of some herbicides on juvenile of Nile tilapia *Oreochromis niloticus*. *Environ. Sci. Pollut. Res.* 26, 30857–30865. <https://doi.org/10.1007/s11356-019-06280-x>.
- Feo, M.L., Ginebreda, A., Eljarrat, E., Barceló, D., 2010. Presence of pyrethroid pesticides in water and sediments of Ebro River Delta. *J. Hydrol.* 393, 156–162. <https://doi.org/10.1016/j.jhydrol.2010.08.012>.
- Gavrilescu, M., 2005. Fate of pesticides in the environment and its bioremediation. *Eng. Life Sci.* 5, 497–526. <https://doi.org/10.1002/elsc.200520098>.
- Gebremariam, S.Y., Beutel, M.W., Yonge, D.R., Flury, M., Harsh, J.B., 2012. Adsorption and desorption of chlorpyrifos to soils and sediments. In: *Reviews of Environmental Contamination and Toxicology*, pp. 123–175.
- Gupta, P., Verma, S.K., 2020. Impacts of herbicide pendimethalin on sex steroid level, plasma vitellogenin concentration and aromatase activity in teleost *Clarias batrachus* (Linnaeus). *Environ. Toxicol. Pharmacol.* 75, 103324. <https://doi.org/10.1016/j.etap.2020.103324>.
- Jee, J.H., Masroor, F., Kang, J.C., 2005. Responses of cypermethrin-induced stress in haematological parameters of Korean rockfish, *Sebastes schlegelii* (Hilgendorf). *Aquac. Res.* 36, 898–905. <https://doi.org/10.1111/j.1365-2109.2005.01299.x>.
- Katagi, T., 2006. Behavior of pesticides in water—sediment systems. In: *Reviews of Environmental Contamination and Toxicology*. Springer, New York, pp. 133–251.
- Köck, M., Farré, M., Martínez, E., Gajda-Schranz, K., Ginebreda, A., Navarro, A., Alda, M.L. de, Barceló, D., 2010. Integrated ecotoxicological and chemical approach for the assessment of pesticide pollution in the Ebro River delta (Spain). *J. Hydrol.* 383, 73–82. <https://doi.org/10.1016/j.jhydrol.2009.12.029>.
- Kuster, M., López de Alda, M., Barceló, D., 2009. Liquid chromatography-tandem mass spectrometric analysis and regulatory issues of polar pesticides in natural and treated waters. *J. Chromatogr. A* 1216, 520–529. <https://doi.org/10.1016/j.chroma.2008.08.031>.
- Kuster, M., López de Alda, M.J., Barata, C., Raldúa, D., Barceló, D., 2008. Analysis of 17 polar to semi-polar pesticides in the Ebro river delta during the main growing season of rice by automated on-line solid-phase extraction-liquid chromatography-tandem mass spectrometry. *Talanta* 75, 390–401. <https://doi.org/10.1016/j.talanta.2007.11.027>.
- Lacorte, S., Raldúa, D., Martínez, E., Navarro, A., Diez, S., Bayona, J.M., Barceló, D., 2006. Pilot survey of a broad range of priority pollutants in sediment and fish from the Ebro river basin (NE Spain). *Environ. Pollut.* 140, 471–482. <https://doi.org/10.1016/j.envpol.2005.08.008>.
- Le Gaudu, M., Thiebault, T., Quénéa, K., Alliot, F., Guigon, E., Le Callonnec, L., 2022. Trace organic contaminants within solid matrices along an anthropized watercourse: organo-mineral controls on their spatial distribution. *Sci. Total Environ.* 822, 153601. <https://doi.org/10.1016/j.scitotenv.2022.153601>.
- León, V.M., Viñas, L., Concha-Graña, E., Fernández-González, V., Salgueiro-González, N., Moscoso-Pérez, C., Muniategui-Lorenzo, S., Campillo, J.A., 2020. Identification of contaminants of emerging concern with potential environmental risk in Spanish continental shelf sediments. *Sci. Total Environ.* 742, 140505. <https://doi.org/10.1016/j.scitotenv.2020.140505>.
- Lewis, K.A., Tzilivakis, J., Warner, D.J., Green, A., 2016. An international database for pesticide risk assessments and management. *Hum. Ecol. Risk Assess.* 22, 1050–1064. <https://doi.org/10.1080/10807039.2015.1133242>.
- López-García, E., Mastroianni, N., Ponsà-Borau, N., Barceló, D., Postigo, C., López de Alda, M., 2021. Drugs of abuse and their metabolites in river sediments: analysis, occurrence in four Spanish river basins and environmental risk assessment. *J. Hazard Mater.* 401, 123312. <https://doi.org/10.1016/j.jhazmat.2020.123312>.
- Masiá, A., Campo, J., Vázquez-Roig, P., Blasco, C., Picó, Y., 2013. Screening of currently used pesticides in water, sediments and biota of the Guadalquivir River Basin (Spain). *J. Hazard Mater.* 263, 95–104. <https://doi.org/10.1016/j.jhazmat.2013.09.035>.
- Matić Bujagić, I., Grujić, S., Laušević, M., Hofmann, T., Micić, V., 2019. Emerging contaminants in sediment core from the iron gate I reservoir on the danube river. *Sci. Total Environ.* 662, 77–87. <https://doi.org/10.1016/j.scitotenv.2019.01.205>.
- Narendran, S.T., Meyyanathan, S.N., Karri, V.V.S.R., Babu, B., Chintamaneni, P., 2019. Multivariate response surface methodology assisted modified QuEChERS extraction method for the evaluation of organophosphate pesticides in fruits and vegetables cultivated in Nilgiris, South India. *Food Chem.* 300, 125188. <https://doi.org/10.1016/j.foodchem.2019.125188>.
- Navarro-Ortega, A., Tauler, R., Lacorte, S., Barceló, D., 2010. Occurrence and transport of PAHs, pesticides and alkylphenols in sediment samples along the Ebro River Basin. *J. Hydrol.* 383, 5–17. <https://doi.org/10.1016/j.jhydrol.2009.12.031>.
- Oliveira, J.M.M., Galhano, V., Henriques, I., Soares, A.M.V.M., Loureiro, S., 2017. Basagran® induces developmental malformations and changes the bacterial community of zebrafish embryos. *Environ. Pollut.* 221, 52–63. <https://doi.org/10.1016/j.envpol.2016.10.028>.
- Palma, P., Fialho, S., Lima, A., Catarino, A., Costa, M.J., Barbieri, M.V., Monllor-Alcaraz, L.S., Postigo, C., de Alda, M.L., 2021. Occurrence and risk assessment of pesticides in a Mediterranean Basin with strong agricultural pressure (Guadiana Basin: southern of Portugal). *Sci. Total Environ.* 794, 148703. <https://doi.org/10.1016/j.scitotenv.2021.148703>.
- Parolini, M., Binelli, A., Matozzo, V., Marin, M.G., 2010. Persistent organic pollutants in sediments from the Lagoon of Venice—a possible hazard for sediment-dwelling organisms. *J. Soils Sediments* 10, 1362–1379. <https://doi.org/10.1007/s11368-010-0277-4>.
- Pérez, D.J., Iturburu, F.G., Calderon, G., Oyesqui, L.A.E., De Gerónimo, E., Aparicio, V.C., 2021. Ecological risk assessment of current-use pesticides and biocides in soils, sediments and surface water of a mixed land-use basin of the Pampas region, Argentina. *Chemosphere* 263. <https://doi.org/10.1016/j.chemosphere.2020.128061>.
- Peris, A., Eljarrat, E., 2021. Multi-residue methodologies for the analysis of non-polar pesticides in water and sediment matrices by GC-MS/MS. *Chromatographia* 84, 425–439. <https://doi.org/10.1007/s10337-021-04026-x>.
- Pietrzak, D., Kania, J., Malina, G., Kmiecik, E., Ważor, K., 2019. Pesticides from the EU first and second watch lists in the water environment. *Clean* 47, 1800376. <https://doi.org/10.1002/clen.201800376>.
- Pinto, M.L., Burrows, H.D., Sontag, G., Vale, C., Noronha, J.P., 2016. Priority pesticides in sediments of European coastal lagoons: a review. *Mar. Pollut. Bull.* 112, 6–16. <https://doi.org/10.1016/j.marpolbul.2016.06.101>.
- Saglio, P., Olsén, K.H., Bretaude, S., 2001. Behavioral and olfactory responses to prochloraz, bentazone, and nicosulfuron-contaminated flows in goldfish. *Arch. Environ. Contam. Toxicol.* 41, 192–200. <https://doi.org/10.1007/s002440010237>.
- Shankar Murthy, K., Kiran, B.R., Venkateswarlu, M., 2013. A review on toxicity of pesticides in Fish. *Int. J. Open Sci. Res.* 1, 15–36.
- Spanish Ministry of Agriculture, 2017. Resolución de autorización excepcional para la comercialización y el uso de los productos fitosanitarios formulados a base de propanil 48% [SC] P/V, para el control de malas hierbas de hoja estrecha en arroz. <https://bit.ly/3eHexab>.
- Tabassum, H., Afjal, M.A., Khan, J., Raisuddin, S., Parvez, S., 2015. Neurotoxicological assessment of pendimethalin in freshwater fish *Channa punctata* Bloch. *Ecol. Indic.* 58, 411–417. <https://doi.org/10.1016/j.ecolind.2015.06.008>.
- Taylor, A.C., Fones, G.R., Mills, G.A., 2020. Trends in the use of passive sampling for monitoring polar pesticides in water. *Trends Environ. Anal. Chem.* 27, e00096. <https://doi.org/10.1016/j.teac.2020.e00096>.
- Terrado, M., Kuster, M., Raldúa, D., Lopez De Alda, M., Barceló, D., Tauler, R., 2007. Use of chemometric and geostatistical methods to evaluate pesticide pollution in the irrigation and drainage channels of the Ebro river delta during the rice-growing season. *Anal. Bioanal. Chem.* 387, 1479–1488. <https://doi.org/10.1007/s00216-006-1038-5>.
- Tsaboula, A., Papadakis, E.N., Vryzas, Z., Kotopoulou, A., Kintzikoglou, K., Papadopoulou-Mourkidou, E., 2016. Environmental and human risk hierarchy of pesticides: a prioritization method, based on monitoring, hazard assessment and environmental fate. *Environ. Int.* 91, 78–93. <https://doi.org/10.1016/j.envint.2016.02.008>.
- Veses, O., Mosteo, R., Ormad, M.P., Ovelheiro, J.L., 2012. Potential toxicity of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments from the ebro river basin in Spain. *Bull. Environ. Contam. Toxicol.* 88, 644–650. <https://doi.org/10.1007/s00128-011-0519-1>.
- Vryzas, Z., Alexoudis, C., Vassiliou, G., Galanis, K., Papadopoulou-Mourkidou, E., 2011. Determination and aquatic risk assessment of pesticide residues in riparian drainage canals in northeastern Greece. *Ecotoxicol. Environ. Saf.* 74, 174–181. <https://doi.org/10.1016/j.ecoenv.2010.04.011>.
- Wang, T., Zhong, M., Lu, M., Xu, D., Xue, Y., Huang, J., Blaney, L., Yu, G., 2021. Occurrence, spatiotemporal distribution, and risk assessment of current-use pesticides in surface water: a case study near Taihu Lake, China. *Sci. Total Environ.* 782, 146826. <https://doi.org/10.1016/j.scitotenv.2021.146826>.
- Warren, N., Allan, I.J., Carter, J.E., House, W.A., Parker, A., 2003. Pesticides and other micro-organic contaminants in freshwater sedimentary environments—a review. *Appl. Geochem.* 18, 159–194. [https://doi.org/10.1016/S0883-2927\(02\)00159-2](https://doi.org/10.1016/S0883-2927(02)00159-2).
- Xue, N., Xu, X., Jin, Z., 2005. Screening 31 endocrine-disrupting pesticides in water and surface sediment samples from Beijing Guanting reservoir. *Chemosphere* 61, 1594–1606. <https://doi.org/10.1016/j.chemosphere.2005.04.091>.
- Zhang, C., Tian, D., Yi, X.H., Zhang, T., Ruan, J., Wu, R., Chen, C., Huang, M., Ying, G.G., 2019. Occurrence, distribution and seasonal variation of five neonicotinoid insecticides in surface water and sediment of the Pearl Rivers, South China. *Chemosphere* 217, 437–446. <https://doi.org/10.1016/j.chemosphere.2018.11.024>.
- Zhen, X., Liu, L., Wang, X., Zhong, G., Tang, J., 2019. Fates and ecological effects of current-use pesticides (CUPs) in a typical river-estuarine system of Laizhou Bay, North China. *Environ. Pollut.* 252, 573–579. <https://doi.org/10.1016/j.envpol.2019.05.141>.