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Determination of organic contaminants in L'Albufera Natural Park using microporous polyethylene tube passive samplers: An environmental risk assessment

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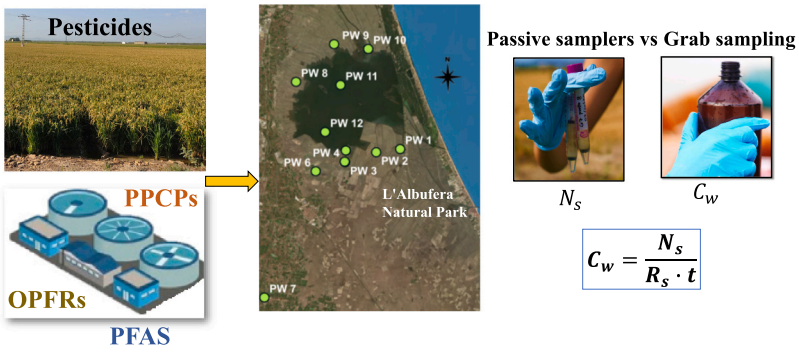
HIGHLIGHTS

- 45 pesticides, 30 PPCPs, 22 PFAS and 7 OPFRs detected in L'Albufera Natural Park
- Pesticides were the dominant contaminants in the area.
- Spatial distribution showed more contaminants at higher concentrations in the North of the Lake.
- Risk Quotient factors showed that contamination is of concern within the Natural Park.

GRAPHICAL ABSTRACT



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ABSTRACT

L'Albufera Natural Park (Valencia, Spain) is a protected wetland of international significance that provides critical habitats to endemic and threatened bird and plant species. This study aims to use multiple cross-validation techniques to generate an accurate estimation of the environmental risk of organic contaminants (OCs) in an internationally important coastal wetland, to identify compounds of concern and their potential sources and risk factors. Microporous polyethylene tube (MPT) passive samplers were deployed at 12 locations across L'Albufera Natural Park with concurrent grab samples collected. A subset of MPT samplers were also analysed by an additional laboratory in Australia to widen the range of contaminants and assess interlaboratory reproducibility of results. Forty-three pesticides, 20 pharmaceuticals and personal care products (PPCPs), 20 *per*- and polyfluoroalkyl substances (PFAS) and 4 organophosphorus flame retardants (OPFRs) were detected in the MPT samplers. The fungicides tebuconazole and difenoconazole were detected at the highest concentrations in passive samplers (maximum concentrations, 153 ng sampler^{-1} and 106 ng sampler^{-1}, respectively). Several other pesticides were detected in all locations (mean concentrations >1 ng sampler^{-1}). The compounds fenamiphos, propyzamide, difenoconazole, propiconazole, metsulfuron methyl, sodium bis (perfluorohexyl) phosphinate (6:6 PFPiA), 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB), 6:2 fluorotelomersulfonate (6:2

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FTS), citalopram desmethyl and citalopram were reported in the wetland for the first time. Spatial distribution analysis revealed higher pesticide concentrations in the North of L'Albufera. A risk quotient (RQ) analysis showed that ibuprofen is of concern in the area. Overall, the MPT sampling approach is promising as a risk assessment tool for better understanding the transport and fate of OCs in protected areas.

1. Introduction

L'Albufera, a Mediterranean coastal wetland, was declared a Natural Park in 1986 for its ecological value, providing a critical habitat to endemic and migratory endangered species. Only three years later, in 1989, it was recognized as Wetland of International Importance especially as a Waterfowl Habitat (Ramsar, 1971). It is also an integral part of the Natura 2000 Network - having been designated as a Special Protection Area for Birds (Directive 2009/147/EC), and as a Site of Community Importance by the Habitat Directive (Council Directive 92/43/EEC).

Mediterranean coastal wetlands play an additional, important ecological role, acting as natural filters that retain and/or eliminate pollution, such as, metals (Li et al., 2022), runoff sediments and nitrogen (Gargallo et al., 2017). However, these systems can also experience deleterious effects from organic contaminants (OCs) pollution. The increasing scarcity of water in these areas has led to the utilization of non-conventional water resources that are typically discharged into the water system in large quantities and intermittently, mostly through irrigation channels to maintain the ecological flow (Martín et al., 2020). The presence of OCs in recycled or reclaimed water from industry or agriculture and wastewater could negatively impact the environment, biota or human health (Pascual-Aguilar et al., 2015).

The occurrence of several OCs within the sub-ecosystems of L'Albufera have previously been reported, including pesticides such as terbumeton, terbuthylazine and their metabolites (Calvo et al., 2021; Lorenzo et al., 2019; Sadutto et al., 2021; Andreu Sánchez, 2008). Land-use surrounding the ecosystem consists of various urban, agricultural and industrial activities, contributing to non-conventional waste release to the wetland. A wide range of OCs belonging mainly to four relevant use classes were identified as important for investigation in this study (pesticides, pharmaceuticals and personal care products (PPCPs), perfluoroalkyl substances (PFAS) and organophosphorus flame retardants (OPFRs)). The high scientific and ecological value of this ecosystem coupled with the potential threat of OCs from surrounding land uses justify an in-depth assessment of the types and concentrations of OCs for a comprehensive risk assessment.

Sensitive monitoring tools that can detect a broad range of OCs are crucial to ensure risk assessment and adequately preserve threatened ecosystems such as L'Albufera. So far, water quality monitoring has been performed mainly by analyzing grab (spot) samples that provide information on a singular moment within the system. Consequently, this method may fail to capture the presence of certain substances or variations in their concentrations over time (Brack et al., 2017). The occurrence of events such as contamination plumes, accidental spills or deliberate industrial releases can also be missed (Vrana et al., 2005). Representative sampling is an essential requirement for accurately estimating the concentration of OCs and to evaluate risks they may pose to ecosystems.

Passive sampling can overcome many of the limitations of grab sampling by accumulating chemicals in situ over an extended time-period. These samplers can also provide additional information through time-weighted average or equilibrium concentrations of the freely dissolved contaminant fraction (Booij et al., 2007; Liu et al., 2011; Vrana et al., 2005). Different passive sampler configurations (e.g. Polar Organic Chemical Integrative Sampler (POCIS), Chemcatcher®, Microporous Polyethylene Tubes (MPT), organic-diffusive gradients in thin films (o-DGT), etc.) have been used in wastewater influent, wastewater effluent, surface waters, seawaters, and urban waterways to establish the occurrence of contaminants such as PFAS, pesticides, PPCPs, and so on (Benedetti et al., 2022; MacKeown et al., 2022; Alvarez et al., 2021; Hageman et al., 2019; MacKeown et al., 2022; Martínez Bueno et al., 2016; Menger et al., 2021; Niemi et al., 2022; Novic et al., 2017; Overdahl et al., 2021; Quintana et al., 2021; Rico et al., 2019).

MPT passive samplers have demonstrated high versatility for a range of contaminants owing to interchangeable sorbents and reduced flow-dependence. This is achieved due to the thicker diffusive layer used (Fauvelle et al., 2017; Brack et al., 2017), i.e. the thicker diffusive membrane dictates the majority of the diffusion rate thus limiting the water boundary layer's influence. MPT samplers have been applied for sampling of pesticides, illicit drugs, PPCPs, PFAS and glyphosate, by adapting a variety of sorbent phases to target compounds (Hageman et al., 2019; McKay et al., 2020; Verhagen et al., 2021; Kaserzon et al., 2019; Clokey et al., 2023; Fauvelle et al., 2017). Due to the MPT's versatility and its cost-effectiveness in monitoring projects, these passive samplers were selected for deployment in this study to investigate contaminants in L'Albufera Natural Park.

The aim of this study was to use multiple complementary sampling methods to increase understanding of the presence and concentrations of OCs in L'Albufera Natural Park. In order to achieve this aim, four specific objectives were formulated (i) to determine the presence and concentration of a wide range of OCs at multiple sites within L'Albufera Natural Park using grab sampling and two configurations of MPT passive samplers (ii) to compare the analytes detected and their concentrations in grab samples and MPT passive samplers to establish the degree of complementarity between these two sampling approach in monitoring OCs in the Natural Park (iii) to map the spatial variability of OCs in the Natural Park to assess the effects of different OC inputs (iv) to assess combined risk posed to the Natural Park by detected OCs considering their presence, concentrations, and spatial distribution.

2. Materials and methods

2.1. Reagents and chemicals

A total of 229 contaminants were analysed, including 57 PFAS, 11 OPFRs (7 non-halogenated and 4 halogenated), 50 PPCPs and 111 pesticides (refer to Supplementary Information (SI) Text S1 and Tables S1-S4 for a detailed list of compounds and the laboratory where they were analysed). Other reagents and chemicals are also detailed in the SI (Text S2).

2.2. Passive sampler assembly

Two configurations of the MPT passive sampler were used in this study; one for sampling glyphosate and its metabolite aminomethylphosphonic acid (AMPA) (filled with agarose gel and titanium (IV) oxide (TiO_2) powder, Sigma-Aldrich, China) and another for the sampling of pesticides, PPCPs, OPFRs and PFAS (filled with hydrophilic lipophilic sorbent phase – Strata-X, a reversed phase surface modified polymer of styrene and divinylbenzene functionalized with N-vinyl-2-pyrrolidone) (Phenomenex, Melbourne, Australia). The assembly of the MPT sampler for glyphosate and AMPA has been described in Fauvelle et al. (2017) and the MPT configuration for PPCPs, OPFRs and PFAS is described in McKay et al. (2020). Microporous polyethylene tubes were purchased from Pall Corp. Crailsheim, Germany (Filterplast®, 8 mm ID, 35 % porosity, 2.5 μm in size, 12 mm OD, and 0.6 gcm^{-3} density) (Hageman et al., 2019; Kaserzon et al., 2019). Exposed tube length was

4 cm with a sorbent mass 400 ± 10 mg.

2.3. Description of the sampling area

L'Albufera Natural Park (Valencia, Spain) is one of the most representative and valuable coastal wetlands in the Valencian Community and the Mediterranean basin covering over 21 thousand hectares. It is located 10 km from Valencia City and extends between the mouth of the rivers Turia and Júcar (Fig. 1).

L'Albufera Natural Park comprises: a lake separated from the sea by a sand bar, rice paddies that now occupy the primitive marshy lands (a potential source of contaminants), and a smaller area dedicated to citrus orchards. The main crop bounding the Natural Park is citrus. The area has an important network of irrigation channels and canals that supply water to the fields (especially rice fields that are flooded most of the time) and collect excess water after irrigation or when rice paddies are emptying. Near the lake, some rice paddies have been repurposed into artificial wetlands to recover the primitive habitats of the marshland. The lake has a maximum diameter of ~8 km, an estimated surface area of 2.3 ha and its average depth is approximately 1.2 m.

2.4. Sampling

Twelve sampling points were selected as representative sites within L'Albufera Natural Park (Fig. 1). These cover three different habitats: lake (sites 11, 12), artificial wetland (sites 3, 4, 5) and channels (sites 2, 6, 8, 9, 10). Sites with different contaminant sources were also investigated: PPCPs through wastewater treatment plants (WWTPs) effluent (sites 3, 10) and pesticides from agricultural runoff reaching the wetlands and channels. Two points were selected as a control (i) the fish farm for autochthonous species preservation belonging to the local government (site 1) and (ii) the Royal Jucar channel that transports freshwater from the Jucar River to the orchards and rice paddies (site 7); its average flow during irrigation periods is 15 m^3/s. Further details can be found in Table S5.

Sampling was conducted between September 21, 2020, and October 15, 2020. At each site two configurations of MPTs were deployed in triplicate: for polar and moderately polar compounds (PPCPs, pesticides and PFAS) and for glyphosate and AMPA. One sampler of each configuration was collected after 14 days and the other two were collected after 28 days of deployment. The MPT samplers were submerged in the middle of the water column (between 0.3 and 0.7 m deep depending on the depth of the sampling point) so that the passive samplers were completely submerged but did not touch the sediment. Upon retrieval the MPTs were removed from the water, rinsed with deionised water and transferred to separately labelled, single-use 15 mL centrifuge tubes. Samples were transported to the laboratory in a cooler with ice bricks. Once in the laboratory, the MPTs were frozen at −20 °C until extraction. One 28-day sample from each site was sent to the University of Queensland (UQ) in Australia for analysis. The two remaining samplers

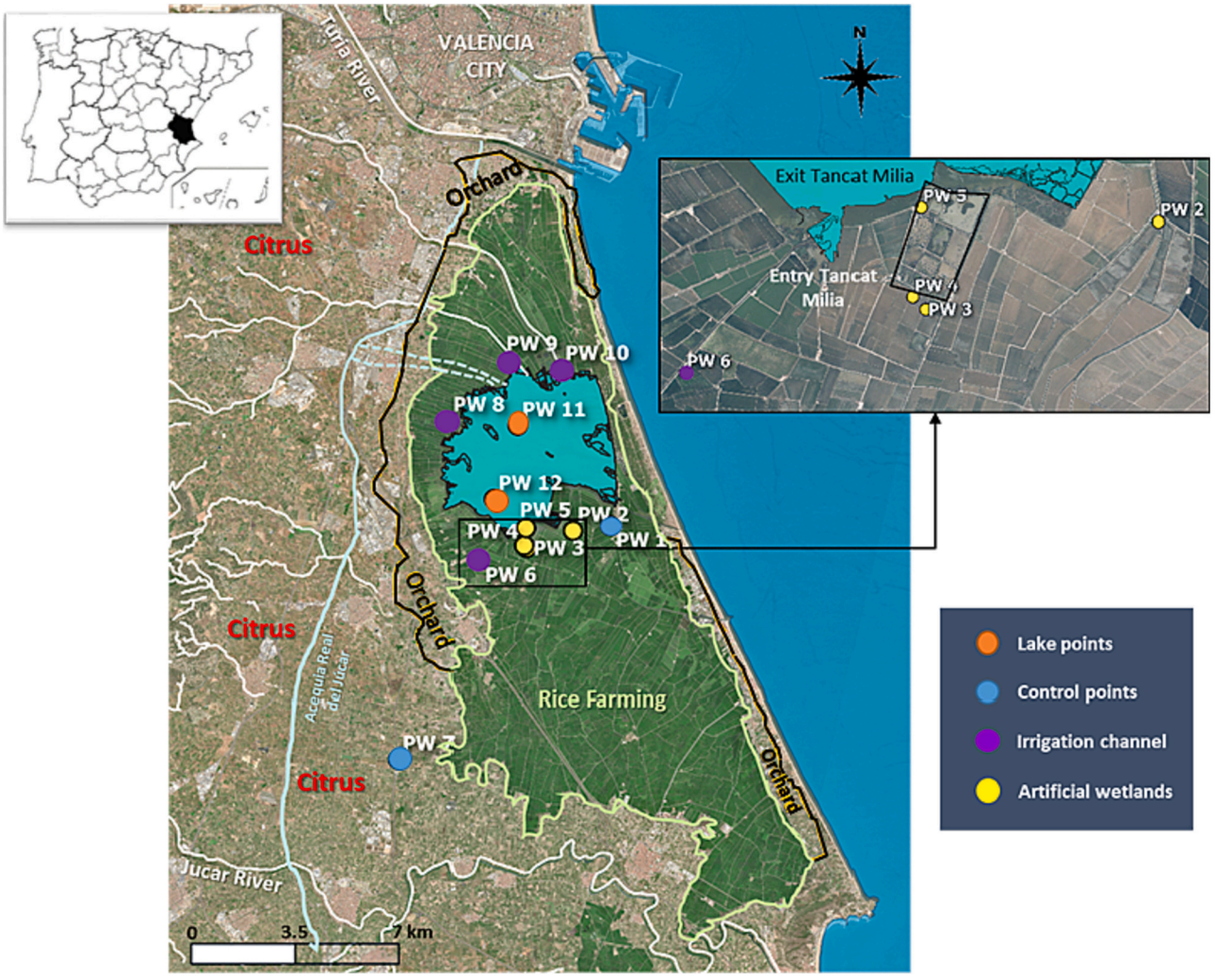

Fig. 1. Map of L'Albufera Natural Park. Location of the sampling sites are highlighted in orange, blue, yellow and violet. Three closely clustered sites are shown zoomed in in the top left. Satellite image by Orthopnea 2018 CC-BY 4.0 scne.es (National Cartographic System).

(collected at 14 and 28 days, respectively) were analysed at the University of Valencia (UV). Images showing the sampling process are available in Fig. S1 of the supplementary material. At each sampling point, 1 L of surface water was collected in clean polyethylene terephthalate amber bottles from the middle of the water column. Grab samples were collected during deployment of the passive samplers (day zero) and at days 14 and 28.

The following water quality parameters were measured in situ: dissolved oxygen (DO) (15.0–153 % or 1.30–12.5 mg L^{-1}), pH (7.30–8.50), temperature (15.6–26.6 °C), salinity (0.53–1.63 PSU), conductivity (1.06×10^3 - 3.13×10^3 μS cm^{-1}), chlorophyll A (0.07–37.5 μg L^{-1}), phycoerythrin (0.38–77.2 μg L^{-1}) (Table S6 lists these parameters for each sampling points at days 0, 14 and 28 days). These values were obtained using a portable multiparametric meter (model HI9829, HANNA Instruments).

2.5. Sample treatment and extraction

2.5.1. Grab water

Grab samples were analysed at UV. Grab water samples were defrosted for 24 h at room temperature in darkness, followed by filtration of 250 mL using a 0.45-μm glass fiber filter under vacuum (Advantec MFS, Dublin, CA, USA). Then, 50 μL of mixed isotopically labelled internal standards at a concentration of 1 μg mL^{-1} was spiked into each sample (Text S1 and Text S3). The samples were extracted by solid phase extraction (SPE) using Phenomenex Strata-X-33 μm Polymeric Reversed Phase (200 mg/6 mL) SPE cartridges according to the method previously reported by Carmona et al. (2017).

2.5.2. Passive sampler extraction

Passive samplers were extracted at UV and UQ following the methods described by Fauvelle et al. (2017) and McKay et al. (2020) (Text S4). Briefly, sorbent in the tube was spiked with a mix of isotopically labelled internal standards (50 μL of internal standards mix at a concentration of 1 μg mL^{-1}) prior to extraction (See Text S1). Samples were then extracted using methanol (MeOH).

Extracts were concentrated to 1 mL in different solvents (MeOH/water:MeOH) as reported in the supplementary information (Text S4) prior to analysis via liquid chromatography-mass spectrometry (LC-MS/MS).

2.6. LC-MS/MS analysis

Analysis was performed by liquid chromatography-mass spectrometry in both laboratories. The instruments used were an Agilent 6410 (Santa Clara, CA, USA) at UV and the API5500 and API6500 QTRAP (Sciex, Melbourne, Australia) at UQ. The compounds analysed as well as the specific conditions of each determination are detailed in the SI (Text S1, S5 and Table S7).

2.7. Calculation of analyte concentrations in water from passive samplers

If chemical uptake into the sampler is linear with time over the deployment period, accumulation can be reduced to a linear approximation model. Time-weighted average concentrations in water (C_w) over the deployment periods were calculated using Eq. (1) (Alvarez, 2010).

$$C_w = \frac{N_s}{R_s \bullet t} \quad (1)$$

where N_s is the mass of the compound in the sampler receiving phase or sorbent (ng $sampler^{-1}$), C_w is the concentration of the compound in the water (ng mL^{-1}), R_s is the sampling rate (mL d^{-1} $sampler^{-1}$) at the time of deployment (t, days). R_s values were compiled from literature and are shown in Table S8 for the detected analytes.

2.8. Calculation of risk quotient (RQ) and predicted no effect concentrations (PNEC)

Risk Quotients (RQ) were calculated for OCs of concern in this study according to Eq. (2) (Anagnostopoulpou et al., 2022; Picó et al., 2021).

$$RQ = \frac{C_w}{PNEC} \quad (2)$$

where C_w is water concentration (ng L^{-1}) and PNEC is the Lowest Predicted No Effect Concentrations (ng L^{-1}). PNEC values were extracted from the NORMAN Ecotoxicology Database (https://www.norman-network.com/nds/ecotox/lowestPnecsIndex.php) (Table S9). RQ > 1 suggests high ecological risk. For $0.1 \leq RQ \leq 1$ suggests medium ecological risk and RQ < 0.1 suggests low ecological risk.

2.9. Quality assurance/quality control

Procedural blanks were prepared to check for possible contamination from reagents, MPT tubes or equipment. Results showed that no relevant OCs were detected.

The quality control followed with grab samples involved the processing of laboratory blanks and field blanks collected alongside the samples. The field blank samples consisted of MilliQ water that was taken to the field. Only negligible amounts of PFOS (up to 0.05 ng L^{-1}) were detected in the blanks and these were subtracted from the signals observed in the samples to eliminate any background noise or contamination effects. The analytical validation of the methods for analysis of grab water samples for pesticides, PPCPs, PFAS and OPFRs was previously reported (Picó et al., 2021; Sadutto et al., 2020; Lorenzo et al., 2016a; Picó et al., 2020; Lorenzo et al., 2016b). Average recovery percentage of the internal standards obtained in grab water samples of these studies for pesticides, PFAS, PPCPs and OPFRS ranged from 57 % -107 %, 85–102 %, 57 %–104 % and 70–112 %, respectively. The limits of detections (LODs) and quantification (LOQs) were calculated using spiked matrix samples and ranged from 1 to 5 ng L^{-1} for water. These limits were calculated as the concentration that provides a response 3 and 10 times higher, respectively, than the standard deviation of the average field blank concentration. To validate the quality of the chemical analysis of these samplers, the recoveries of the isotopically labelled internal standard spiked into passive samplers prior to extraction were established. These recoveries ranged from 57 to 107 %. Laboratory blank MTP passive samplers were prepared alongside samplers and kept in the refrigerator until the processing and extraction of the MPT samplers. In the blanks no contamination was observed. The LODs and LOQs were estimated with the grab sample results. The MPT interlaboratory analysis (Text S6) provides an idea of the reproducibility within the deployment and reliability of the MPT across laboratories. Collected data shows compound percentage variations on a site-by-site basis from −200 % to 198 % (Fig. S2A). The average ratio was between 0.5 (terbuthylazine) and 15 (desethyl atrazine) (Fig. S2B).

2.10. Statistical analysis

Concentrations are expressed as ng L^{-1} or in ng $sampler^{-1}$. Concentrations below the LOQ were considered as the average between LOQ and LOD while n.d. were consider as half of the LOD for statistical treatment. In the case of UQ laboratory, LORs, represent three times the LODs. In the case of blank detection LOR were calculated as the average blank plus three times the standard deviation of the blanks. LODs are calculated using three times the standard deviation from a repeated injections ($n = 7$) of a low analytical standard.

Statistical analysis was conducted using IBM SPSS version 26.0. The differences between the results obtained from both laboratories (UQ and UV), as well as between grab and passive sampling, were assessed using a paired t-test. Furthermore, to compare the spatial differences in

concentrations of OCs, analysis of variance (ANOVA) and Tukey's multiple range test at $\alpha = 0.05$ were performed. To assess the positive relationships between water quality and OC levels, bivariate correlation analysis was conducted at both 95 % and 99 % significance levels. Pearson's correlation analysis was used for variables with normal distribution, while Spearman Rho correlation analysis was used for variables without normal distribution. The R2 and standard deviation of residuals (Sy.x) were calculated as well.

To establish the weight and dependence among variables and recognize possible behavioral patterns, multiple stepwise linear correlation analysis, discriminant analysis, and categorical principal component analysis (PCA) were used.

3. Results and discussion

3.1. Presence of OCs in L'Albufera Natural Park

One hundred and four OCs (45 pesticides, 30 PPCPs, 22 PFAS and 7 OPFRs) were detected between grab and passive samplers in L'Albufera Natural Park (detailed in Table S10–18). Also, results for the inter-laboratory comparison study are provided in the Text S6, Tables S19-S20 and Fig. S2. Frequency and concentration showed similar patterns with pesticides >PPCPs > PFAS> OPFRs. Results showed that 87 compounds (43 pesticides, 20 PFAS, 20 PPCPs, 4 OPFRs) were detected in MPT passive samplers. Mass accumulated in the MPTs ranged from 0.10 ng sampler^{-1} for atrazine desisopropyl, 1-(3,4-Dichlorophenyl)-3-methylurea (DCPMU), PFBS, PFHpS, PFUnDA, sulfadiazine, atenolol and temazepam to 153 ng sampler^{-1} for tebuconazole (Table S10–12). In grab samples, 61 compounds were detected (24 pesticides, 14 PFAS, 16 PPCPs, 7 OPFRs). Concentration in grab samples ranged from 0.11 ng L^{-1} for TnBP to 1470 ng L^{-1} for ibuprofen (Table S13). Of these compounds, 44 were detected in both grab and MPT samplers.

In passive samplers 43 pesticides were detected after 28 days deployment with compound mass accumulated ranging from LOQ to 153 ng sampler^{-1} (tebuconazole) (see Tables S10 and S12). Globally, samples contained highest concentrations of conazoles fungicides (tebuconazole, difenoconazole and propiconazole). 3,4-Dichloroaniline, DEET, propiconazole, difenoconazole, MCPA, chlorpyrifos, acetamiprid, tebumeton desethyl, terbuthylazine-2OH, tebuconazole, dichlofenthion and prochloraz were detected at a frequency ≥ 50 % of samples and the highest value measured for all of these compounds was ≥3.0 ng sampler^{-1}. Herbicides and their metabolites (3,4-dichloraniline, MCPA, terbumeton desethyl and AMPA), insecticides (DEET, chlorpyriphos and dichlofenthion) and one fungicide (propiconazole) were also frequently detected in passive samplers (frequency of detection of >70 % in the samples and median ≥ 1 ng sampler^{-1}). Herbicides were previously reported in L'Albufera Natural Park as being widely used in rice cultivation, especially at the beginning of cultivation cycle (end of May/beginning of June) (Calvo et al., 2021). In addition to the herbicides used for the rice, glyphosate was used on field margins, which are planted with lilies and other ornamentals, to eliminate weeds.

In grab samples, 24 pesticides were detected ranging from <LOQ to 71.0 ng L^{-1}. Imidacloprid, acetamiprid, atrazine-desethyl, carbendazim, thiabendazole, terbumeton desethyl, terbuthylazine-2OH, terbuthylazine desethyl, tebuconazole and prochloraz presented the highest value measured ≥10 ng L^{-1} and detected at a frequency ≥ 50 % (see Tables S13 and S15-S17). Bromacil, metalaxyl, fenamiphos, propyzamide, metsulfuron methyl were reported here for the first time in the Natural Park.

Twenty PFAS were detected in passive samplers ranging from 0.10 (PFHpS) to 10.2 (PFOPA) ng sampler^{-1}. PFOS, PFOPA, 6:2 FTAB were at a frequency of ≥50 % and the highest value measured for all of these compounds was ≥3.0 ng sampler^{-1}. PFOS (median 2.07 ng sampler^{-1}, Table S10) was present in 100 % of the sites investigated.

Long-chain PFAS (i.e., PFNA, PFDA, PFUndA) were only detected at levels of <0.85 ng sampler^{-1} in some MPTs. It has been reported that long-chain PFAS were less common in water than short-chain (C ≤ 8) (Onghena et al., 2012). 6:2 FTAB, 6:6 PFPiA and 6:2 FTS were detected here for the first time in the Natural Park. PFTeDA, FBSA, PFTeDA, PFHxDA, and PFHxA were only detected in the passive samplers. Again, the pattern in passive samplers is different to that of grab samples where 14 PFAS were detected ranging from 0.13 (PFHxS) to 10.2 (PFOS) ng L^{-1}. PFTrDA and PFDS were only detected in grab samples. Results obtained in grab water samples showed the high occurrence of PFHxS and PFOA (100 % of the samples). However, PFOA (maximum concentration 4.51 ng L^{-1}) was at concentrations lower than PFOS (maximum concentration 10.2 ng L^{-1}). PFPeA was detected in ≥50 % of the samples and the highest concentration was ≥3 ng L^{-1}. This pattern was similar to that already reported in other Spanish rivers and in L'Albufera Natural Park using grab sampling with PFOA generally showing higher frequency than PFOS (Pico et al., 2012).

Twenty PPCPs were detected in the MPTs, ranging from 0.10 (Sulfadiazine, atenolol, temazepam) to 13.5 ng sampler^{-1} (salicylic acid). Caffeine, temazepam, acesulfame, gabapentin and tramadol were detected at frequency ≥ 50 % and the highest value measured for all of these compounds was ≥3.0 ng sampler^{-1}. Iopromide, oxazepam, and triclosan were detected in MPTs with a frequency of detection of 25, 42 and 33 %, respectively at the sampling points (Table S10). The results indicate that acidic OCs are less efficiently extracted than neutral or basic OCs with this passive sampler configuration. In grab water samples, 16 PPCPs were detected ranging from 1.34 ng L^{-1} (caffeine) to 1470 ng L^{-1} (ibuprofen). Salicylic acid, naproxen, diclofenac and ibuprofen were detected at frequency ≥ 50 % in the samples and the highest value measured for all these compounds was ≥100 ng L^{-1}.

Four OPFRs were detected in passive samplers deployed for 28 days with mass accumulated in samplers ranging from 0.28 to 1.48 ng sampler^{-1}. TDCIPP and TPhP were detected at a frequency of ≥50 % in samples and an amount ≥ 1.0 ng sampler^{-1}. In the grab water samples, 7 OPFRs were detected ranging from 0.11 to 816 ng L^{-1} for TnBP and TClPP, respectively. The OPFR detected at the highest concentration was TCIPP with a frequency of detection of 42 % in passive samplers. TCIPP, TDCIPP, TnBP and TPhP were detected in grab water samples and in passive samplers. In grab water samples TnBP (median 1.45 ng L^{-1}) was present in at least 75 % of the samples. TCEP, TPP and TBEP were only detected in grab water samples. TnBP and TBEP were detected at a frequency of detection of ≥50 % in the samples and the highest value measured for all these compounds was ≥10 ng L^{-1}.

3.2. Comparison of the performance of MPT passive samplers and grab samples

Fig. 2 compares the individual OCs detected in grab samples and passive samplers. It highlights the OCs that were exclusively identified in the passive samplers, namely buprofezin, chlorpyrifos, clothianidin, dichlofenthion, hexythiazox, fluvalinate, and flumethrin. Additionally, it also indicates the OCs that were only detected in the grab samples, including propanil, spinosad A, PFDS, PFTrDA, methylparaben, ethylparaben, naproxen, bezafibrate, propylparaben, ibuprofen, flufenamic acid, paracetamol, ofloxacin, lorazepam, TCEP, TPP, and TBEP. Two possible explanations could be considered as to why some OCs were detected in grab sampling and not in passive sampling even through the same sorbent was used to concentrate analytes. The first is that certain OCs may have higher interactions with the microporous polyethylene material and are therefore hindered in accumulating onto the sorbent material. The second, more straightforward explanation may be that the concentration factors between MPT and grab samples are different. With grab samples 250 mL of water is extracted providing a x250 concentration factor. MPT samplers can accumulate contaminants with sampling rates of 10's of milliliters per day. Considering the reported R_s range of 3 to 30 mL d^{-1}, this yields 84 to 840 mL for 28-day deployments. Although the value of 84 mL is only three times lower than that of 250 mL, it cannot be ruled out that it has some influence on the

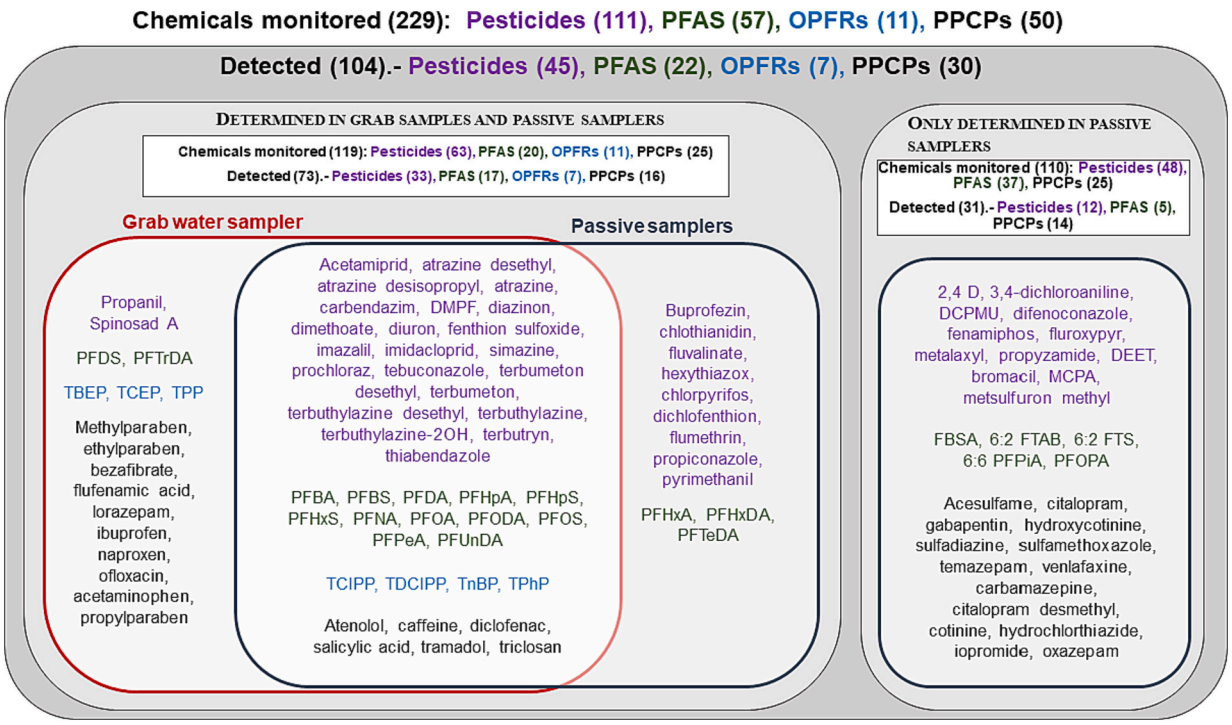

Fig. 2. Diagram of organic contaminants (OCs) [Pesticides, pharmaceutical care products (PPCPs), perfluoroalkyl substances (PFAS) and organophosphorus flame retardants (OPFRs)] detected in grab water samples and microporous polyethylene tubes (MPT) passive samplers. The compounds only analysed and detected in passive samplers are not used for comparison purposes between the sampling methods.

missing of some compounds from the passive samplers. Therefore, MPT samplers may be less sensitive in comparison depending on the R_s of the compounds and the deployment duration.

The pesticides pattern in L'Albufera differs between passive samplers and grab samples. While neonicotinoid insecticides and herbicides are primarily detected in grab samples, passive samplers also identify these compounds, along with additional ones such as chlorpyrifos, dichlofenthion, and flumethrin. These latter pesticides, characterized by being nonpolar, water insoluble, and having a log $P > 4$, were consistently found in passive samplers throughout our study. This displays the benefit of simultaneous passive deployment, allowing the detection of chemicals which may otherwise not be detected. The chlorpyrifos results contradict those reported for Hageman et al. (2019) who detected chlorpyrifos mostly in grab samples and not in POCIS. Other studies have demonstrated adequate quantification of chlorpyrifos using several types of passive samplers (Quintana et al., 2021; Rico et al., 2019). The pattern of OPFRs is similar in grab samples and passive samplers with TClPP and TDClPP as predominant compounds as also pointed out a previous study. This study also indicated that most relevant compounds in water were TCIPP and TDCIPP (Lorenzo et al., 2018). Overall, the disparity between different sampling types reinforces the benefits of simultaneous deployment of MPTs with grab samples.

Therefore, water concentration estimates (C_w) were calculated for 16 compounds detected in MPTs for which previously calibrated sampling rates were available (Cárdenas-Soracá et al., 2020; Clokey et al., 2023; Hageman et al., 2019; McKay et al., 2020). Table S14 reports the values of C_w (ng L^{-1}) at 14 and 28 days of pesticides, PPCPs and PFAS in water obtained from passive samplers using Eq. (1), and sampling rates are reported in Table S8. The C_w calculated during both periods varies depending on the compound and the sampling point. At some sites certain compounds C_w decrease with time by more than a factor of 2 (e.g., atrazine desethyl in sampling points 4 and 5). Contrasting significant increases were observed at other sites from 14 to 28 days (e.g., tebuconazole at sites 11 and 12). Differences in C_w estimates between days 14 and 28 would indicate that compounds could have dissipated from passive samplers. This may be due to a decrease in chemical concentrations in the water of the Natural Park over time. It is possible there could have been a dilution event, or that concentrations of some compounds dissipated from water. C_w is an average of the previous 14 days and day 28 is the same (i.e. average of the previous 28 days), therefore reductions could be due to a lack of further input of a compound. Without costly and time-demanding high resolution grab sampling we can only hypothesize this was the case. The MPTs only sample tens of mL of water per day, so the samplers would be nowhere near their capacity to sorb compounds (i.e., using 400 mg of sorbent phase provides significant further sorption capacity). Changes in C_w observed are likely reflecting changes in the system over time.

Grab samples were collected at 0, 14 and 28 days (detailed concentration of the three sampling days are outlined in Tables S15-S17). The concentrations obtained also showed fluctuations dependent on the compound and site. Grab samples displayed a general decrease in concentrations from 14 to 28 days. Furthermore, the grab samples represent a point in time concentration estimate and therefore it is not possible to evaluate intermittent dilution or concentration of the compounds that instead may influence the concentrations in passive samplers.

The MPT C_w at 28 days were compared to those from grab samples (mean concentration of samples taken at 0, 14 and 28 days). The comparison of each detected compound site by site revealed variations in percentage ranging from −198 % to 195 % (refer to Table S21 for the paired *t*-test results and Table S22 for the specific percentage differences). The results showed variations for individual OCs when comparing the ratio of water concentrations (Cw) in grab samples and passive samplers to the concentrations in grab samples (see Figs. S3-S5). Similarly, differences were observed for each OC when comparing water concentrations (Cw) in grab samples to those in passive samplers (see Figs. S6-S8). Additionally, differences can be also observed in the site-by-site comparison of the concentrations in grab samples and passive samplers (see Figs. S9-S11). It is worth mentioning that the largest mismatch between grab and passive sampling occurs for PFOA, PFDA, and PFOS (see Fig. S10). However, when considering the average

concentrations of the different compounds over all sites, better results were observed for most compounds with normalized differences >33 % except for diuron, atenolol, tramadol and PFHxS (Fig. S12 for the average value of 12 points).

3.3. Spatial assessment of organic contaminants in the wetland

To better understand occurrences and concentrations, spatial distribution of the concentrations of pesticides, PFAS, PPCPs and OPFRs in twelve sites of the wetland was examined. Fig. 3 and Fig. S13 show the spatial distribution of contaminants in the Natural Park (Fig. S13 is

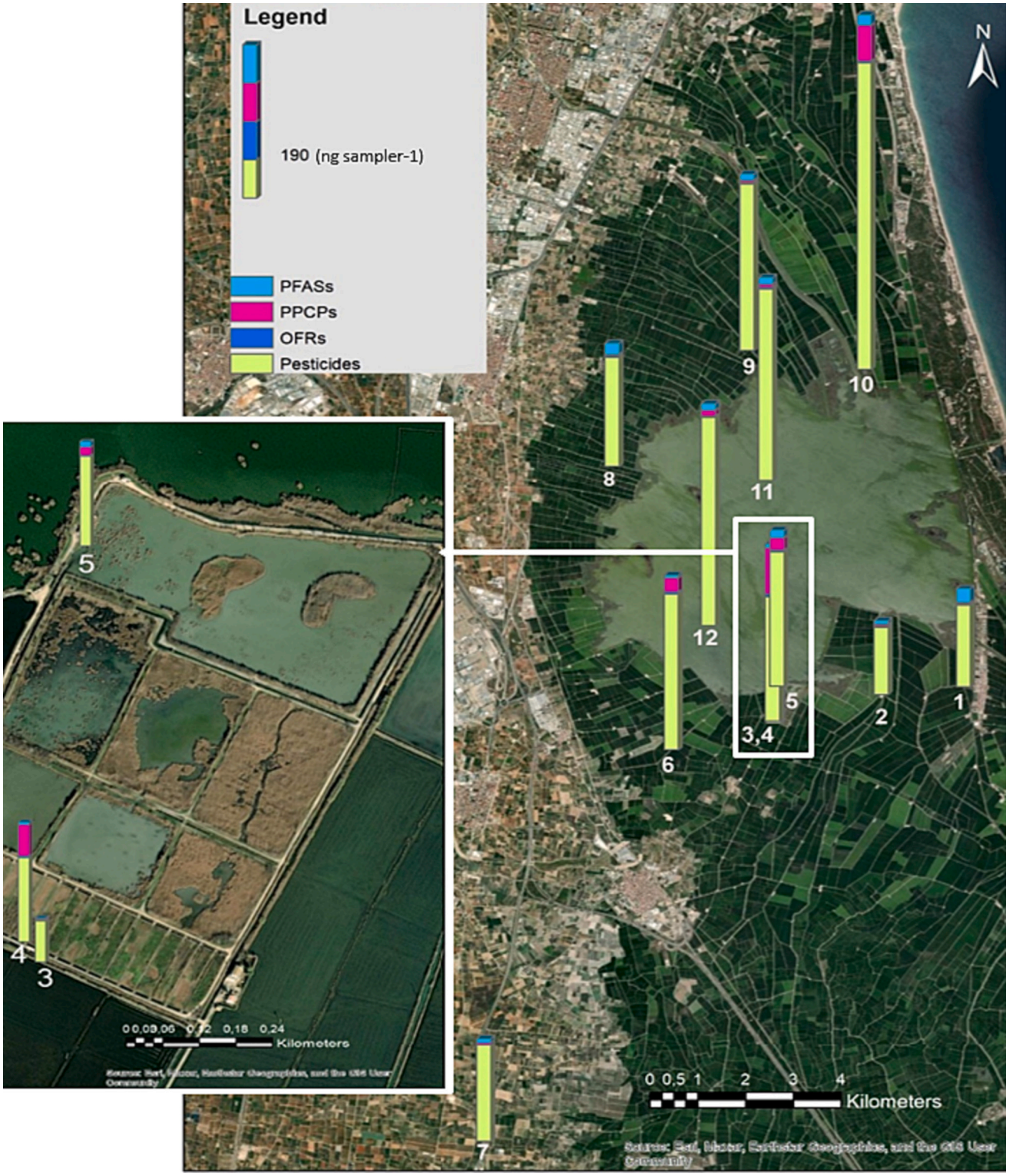

Fig. 3. Sum of the mass per sampler (ng sampler^{-1}) accumulated in microporous polyethylene tube (MPT) passive samplers of target pesticides, pharmaceuticals (PPCPs), *per*-and polyfluoroalkyl substances (PFAS) and organophosphorus flame retardants (OPFRs) across twelve sampling sites of L'Albufera Natural Park, Valencia, Spain.

equal to Fig. 3 but without the pesticides). The statistical analysis applied to these spatial assessment is also shown in the Supplementary Material (see Annex 1).

Pesticides were the most notable contaminants in L'Albufera. This is in line with nearby agricultural land-use devoted to rice and citrus cultivation. Pesticide treatment is matched to the plant, differing with each cultivar grown. Pesticides were detected at every site tested. It should be taken into account that aerial treatments on rice cause diffuse contamination throughout the area. Prochloraz, propiconazole and tebuconazole are post emergence fungicides usually sprayed from the mid-term of July until the harvest of the rice depending on the strength of the Pyricularia infection in the year of the cultivation (they had low or moderate solubility and are bioaccumulative). Carbendazim, imazalil, and thiabendazole were detected in the samples, despite not being used in rice cultivation. These compounds are typically employed in pest management for other crops such as citrus, specifically oranges and tangerines, which also aligns with the crop profile of L'Albufera.

Fewer pesticides were detected in control sites (sites 1, 7) but typically, these pesticides had higher concentrations compared to Obera (Site 2) and Els campets (Site 3). One potential explanation for these results is that grab water samples were taken in September when harvesting had not been completed in the north; the fields in the Obera and Els campets channels had already been harvested (in the south of the Natural Park).

Sites 4 and 5 correspond to the entrance and exit of the Milia artificial wetland. This is an old rice field bordering L'Albufera, which has been transformed into an artificial wetland or green filter for purification of the water that reaches the lagoon. This artificial wetland (Site 4) is fed by treated water from the L'Albufera Sur treatment plant (located 10 km from the artificial wetland). Pesticide levels were lower at the inlet and highest at the outlet. The treated water from the WWTP may have been contaminated by pesticides due to drift from overhead spraying, or upstream application. This shows a limited capacity for the artificial wetland to remove certain pesticides. The other irrigation channels corresponding to Sites 6, 7, 8 and 9, present comparable levels of pesticides in the east of the Natural Park. The levels increase slightly within the lake (Sites 11 in the north and 12 in the south) and in the points located in the irrigation channel of Tancaeta (Site 10, the most northerly point,), which carries treated water from the city of Valencia via the Pinedo II treatment plant in addition to that from rice cultivation. The differences were only significant for tebuconazole that showed higher levels in the channels and lake than in the controls. In the case of grab samples there were also statistically significant differences for atrazine and diazinon.

Figs. 3 and S13 provide at-a-glance fingerprints of contaminant groups at each site derived from the MPTs. The difference in the concentration of PPCPs between Site 3 (an irrigation channel that collects the outflows of the rice field) and Site 4 (the irrigation channel that transport the treated wastewater) is notable considering their proximity. Site 4 corresponds to the channel that carries the tertiary treatment water from the L'Albufera Sur treatment plant (urban treatment plant) to the Tancat de Milia (artificial wetland) for its final treatment before being discharged into the lake, likely leading to Site 4's elevated levels. The reduction in concentration at Site 5 (90 % lower), which corresponds to the outlet of the artificial wetland, gives credence to the efficacy of the wetland's purification capabilities. Sites 6 and 10 showed relatively high levels of PPCPs, likely attributable to wastewater discharges. The level of PPCPs was higher in the South part of the lake than in the North. This may indicate that the hydrology of the lake attenuates contaminants in the south. However, differences are not statistically significant for passive samplers or grab samples. This division has already been noted in other studies for PPCPs (Sadutto et al., 2021) and PFAS (Pico et al., 2012; Lorenzo et al., 2019). Levels of PFAS and OPFRs are much lower and less variable in L'Albufera. However, it is noteworthy that the highest levels of PFAS were observed in Sites 1 and 8. The observed higher levels present in Site 1 may indicate that the materials used in the construction, maintenance and operation of the fish farm (aquaria, tanks, etc.) may contain PFAS. Site 8's contamination might be linked to its location within Valencia city's industrial belt. Differences were only significant for 6:2 FTS that was at lower concentrations in the lake. The completed results of the special analysis including grab samples and passive samplers are presented in the Annex 1 of the supplementary material. Please see Figs. S14-S21). The PCA differentiate two groups for passive samplers in the case of PPCPs and pesticides (see Figs. S18 and S19) noting the influence of phycoerythrin and chlorophyll A in some OCs and the influence of conductivity and salinity in others. In the case of PPCPs these explain variance at 99.8 % and in the pesticides 80.8 %. PFAS variance is explained at 76.26 % by two groups of parameters (one group include salinity, conductivity, phycoerythrin and chlorophyll A and the other pH and DO) (see Fig. S20). Instead, salinity, conductivity and temperature are driven variables that influence the behavior of OPFRs (see Fig. S21). This study demonstrates the significant variability within the Park, elucidating the variety of OCs sources. In addition, it demonstrates the north/south division and the importance of broad understanding of contamination across the entire Natural Park.

3.4. Risk assessment for the wetland

For individual contaminants, RQs were calculated by dividing the C_w (mean or maximum concentration of OC detected in the grab water samples) by the corresponding predicted no-effect concentration (PNEC), as shown in Eq. (2). The results of the ecotoxicological risk assessment derived from the presence of the different OCs in grab water samples with the RQ method are outlined in Table 1.

For average C_w (grab samples) in the park, PFOS, diclofenac and ibuprofen showed RQ >1 indicating that these are OCs of concern for aquatic biota. Demonstrated toxicological effects of these OCs in fish comprise developmental malformations, oxidative stress, cellular damage, behavioral alterations and alterations of biochemical, immunological and hematological parameters among others (Abdel Rahman et al., 2023; Jo et al., 2014; Mathias et al., 2018; Muñoz-Peñuela et al., 2022).

Ibuprofen (RQ >15 at the average concentration and RQ > 100 at maximum concentration) as well as diclofenac (RQ >10 at maximum concentrations) could be of particular concern to aquatic biota. These PPCPs have recently also been described as of high concern in two other Spanish hydrological systems — the Guadiana River Basin (Palma et al., 2020) and the Ebro delta (Barbieri et al., 2021). Worldwide studies on risk assessment performed on these contaminants showed risk to a variety of aquatic biota (Lin et al., 2022; Naumann et al., 2022; Stehle et al., 2023).

Acetamiprid, and terbumeton desethyl exhibited mean concentrations within the range of $0.1 \leq RQ < 1$ while flufenamic acid, triclosan, dimethoate and terbutryn displayed their maximum concentrations within the same range in L'Albufera Natural Park. This indicates a moderate risk to the Natural Park's ecosystem. The other compounds detected have RQ <0.1 and are thus considered to be of negligible risk.

This risk assessment is limited and low RQ may be the result of low concentrations and/or too high a PNEC in the absence of experimental values. Some experimental PNEC data were not available, so it was not possible to calculate the RQ of some OCs. The RQ does not consider certain phenomena that affect higher trophic levels such as bioaccumulation and biomagnification of OCs along the food chain. In addition, the OCs were considered individually, however in the environment, a mixture of compounds is present that can add up or even potentiate their effects. Several studies that conducted a cumulative risk assessment of OCs that by themselves did not represent any hazard to biota concluded that instead the mixtures are of concern (Barbieri et al., 2021; Nantaba et al., 2020; Sadutto et al., 2021; Wang et al., 2021; Yu et al., 2023). Therefore, additive, antagonistic and synergistic effects may need to be considered to better assess if there is additional risk posed to aquatic biota by OCs.

Table 1
Risk quotient (RQ) values for individual organic contaminants (OCs) detected in grab samples at mean and maximum concentrations found in L'Albufera Natural Park. Results are categorized by high, medium and low risk.

Contaminant	RQ (mean environmental concentrations)	RQ (max environmental concentrations)
At mean concentration. $1 \leq RQ$		
PFAS		
PFOS	1.1	5.1
PPCPS		
Diclofenac	2.5	14
Ibuprofen	16	103
At maximum concentration. $1 \leq RQ$		
Pesticides		
Imidacloprid	0.63	3.5
At mean concentration. $0.1 \leq RQ < 1$		
Pesticides		
Acetamiprid	0.68	3.0
Terbumeton desethyl	0.31	0.94
At maximum concentration. $0.1 \leq RQ < 1$		
Pesticides		
Diazinon	$4.4 \cdot 10^{-2}$	0.35
Diuron	$6.0 \cdot 10^{-2}$	0.41
Dimethoate	$1.0 \cdot 10^{-2}$	0.13
Terbutryn	$2.0 \cdot 10^{-2}$	0.13
PPCPs		
Flufenamic acid	$5.0 \cdot 10^{-2}$	0.23
Triclosan	$7.5 \cdot 10^{-2}$	0.21
At any concentration. $RQ < 0.1$		
OPFRs		
TCEP	$3.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$
TPhP	$5.0 \cdot 10^{-3}$	$1.7 \cdot 10^{-2}$
TnBP	$3.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$
Pesticides		
Atrazine	$1.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$
Atrazine-Desethyl	$1.6 \cdot 10^{-2}$	$5.9 \cdot 10^{-2}$
Atrazine-Desisopropyl	$7.0 \cdot 10^{-3}$	$2.3 \cdot 10^{-2}$
Carbendazim	$7.0 \cdot 10^{-3}$	$2.7 \cdot 10^{-2}$
Imazalil	$6.0 \cdot 10^{-4}$	$4.0 \cdot 10^{-3}$
Prochloraz	$3.9 \cdot 10^{-3}$	$1.4 \cdot 10^{-2}$
Propanil	$1.0 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$
Simazine	$1.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$
Tebuconazole	$2.2 \cdot 10^{-2}$	$4.5 \cdot 10^{-2}$
Terbumeton	$4.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-3}$
Thiabendazole	$7.0 \cdot 10^{-3}$	$2.7 \cdot 10^{-2}$
PFAS		
PFBA	$3.0 \cdot 10^{-5}$	$1.0 \cdot 10^{-4}$
PFBS	$1.0 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$
PFDA	$4.7 \cdot 10^{-3}$	$3.0 \cdot 10^{-2}$
PFDS	$4.1 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$
PFHpA	$1.2 \cdot 10^{-3}$	$3.1 \cdot 10^{-3}$
PFHpS	$1.4 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$
PFHxS	$8.0 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$
PFNA	$4.0 \cdot 10^{-3}$	$3.4 \cdot 10^{-2}$
PFOA	$9.1 \cdot 10^{-3}$	$1.6 \cdot 10^{-2}$
PFODA	$4.4 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$
PFTrDA	$7.4 \cdot 10^{-3}$	$1.4 \cdot 10^{-2}$
PFUnDA	$1.1 \cdot 10^{-2}$	$3.3 \cdot 10^{-2}$
PPCPs		
Atenolol	$3.0 \cdot 10^{-6}$	$2.0 \cdot 10^{-5}$
Bezafibrate	$3.4 \cdot 10^{-3}$	$3.6 \cdot 10^{-2}$
Caffeine	$7.0 \cdot 10^{-4}$	$4.8 \cdot 10^{-3}$
Ethylparaben	$1.0 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$
Lorazepam	$1.4 \cdot 10^{-2}$	$5.8 \cdot 10^{-2}$
Methylparaben	$2.3 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$
Naproxen	$2.11 \cdot 10^{-2}$	$9.26 \cdot 10^{-2}$
Ofloxacin	$2.47 \cdot 10^{-3}$	$1.90 \cdot 10^{-2}$
Acetaminophen	$6.00 \cdot 10^{-5}$	$4.00 \cdot 10^{-4}$
Propylparaben	$4.70 \cdot 10^{-4}$	$1.50 \cdot 10^{-3}$
Salicylic acid	$1.60 \cdot 10^{-3}$	$2.70 \cdot 10^{-3}$
Tramadol	$2.66 \cdot 10^{-3}$	$9.50 \cdot 10^{-3}$

The sum of exposure to the detected OCs present at each sampling point may suggest environmental concern for some biota in the wetlands. Therefore, to overcome some of the previous drawbacks and to improve this risk assessment, the cumulative risk of the simultaneous presence of several OCs in the 12 grab water samples was spatially represented (Fig. 4).

The risk assessment for the individual compounds showed that some compounds (ibuprofen, imidacloprid, acetamiprid, PFOS and diclofenc) might be of environmental concern. Concentration and number of contaminants that were present in each sample are of environmental concern. These results highlight the importance of examining the whole mixture of organic contaminants to assess the environmental risk. If all the compounds are considered, the RQ for all sampling points would be >1 for all sites. In this calculation, RQ were highest for sites 3 and 10 (Fig. 4). The lack of information on the effects of this mixed contamination makes this an appropriate area for future studies.

4. Conclusions

The determination of a wide range of contaminants in L'Albufera Natural Park revealed that pesticides are the most abundant OCs with the highest observed masses followed by PPCPs>PFAS>OPFRs. MPT passive samplers showed themselves to be comparable and complementary tool for the assessment of medium-term pollution status within coastal wetlands. The passive samplers provide good agreement with information from the grab samples and in some cases additional information on compounds that were not successfully sampled via grab sampling. The passive samplers integrate water concentrations only during the sampling period and can help reflect the pollution situation in a water body. The need to apply compound specific sampling rates means that some OCs detected at elevated concentrations in passive samplers could not be quantified because sampling rates have not yet been calibrated for certain compounds. Future work will include measurement of sampling rates for additional analytes with MPT samplers.

The spatial variability of many of the OCs in the studied region was relatively small, indicating greater contributions from diffusive sources than point sources in most locations. Agricultural contaminants were the exception to this, with greater prevalence in the open lake and the north of the Natural Park.

The risk assessment of individual compounds to aquatic biota showed that imidacloprid, acetamiprid, PFOS, PFDA, diclofenac and ibuprofen pose the highest individual risk quotients. However, when calculating RQ based on the sum of exposure to all the OCs detected in the sampling sites, all samples were of environmental concern.

CRediT authorship contribution statement

Yolanda Soriano: Data curation, Writing- Original draft preparation.

Rodrigo Alvarez-Ruiz: Writing- Reviewing and Editing, Visualization.

Joseph Clokey: Writing- Reviewing and Editing, Investigation.

Sara Ghorbani Gorji: Writing- Reviewing and Editing.

Sarit Kaserzon: Conceptualization, Methodology, Visualization.

Yolanda Picó: Conceptualization, Methodology, Reviewing and Editing, Supervision, Project Administration; Funding acquisition,

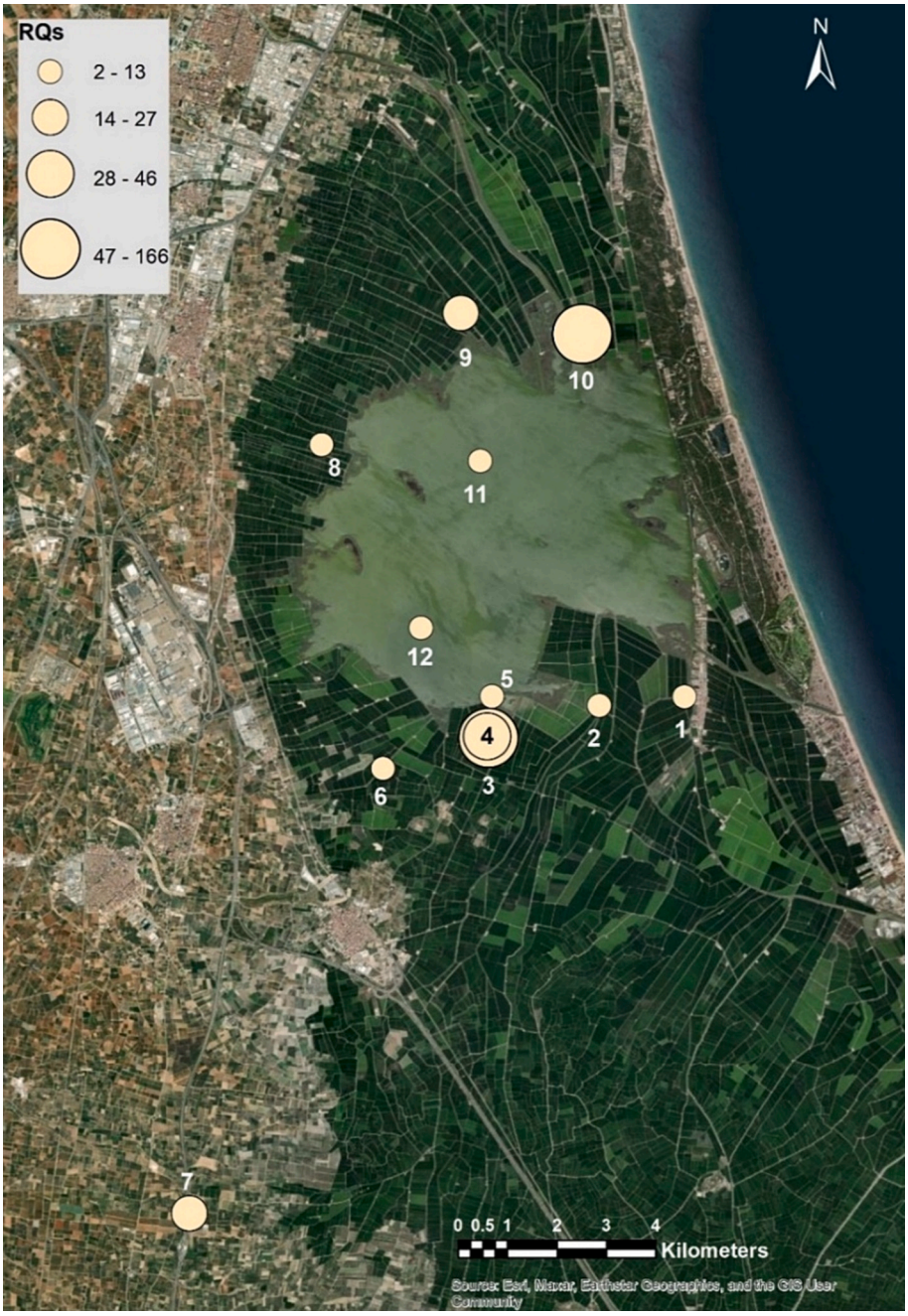

Fig. 4. ΣRisk Quotients (RQs) at each sampling point showing the differences between the sampling points.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.166594.

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