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## Organophosphate ester additives and microplastics in benthic compartments from the Loire estuary (French Atlantic coast)

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### ABSTRACT

We report the first empirical confirmation of the co-occurrence of organophosphate esters (OPEs) additives and microplastics (MPs) in benthic compartments from the Loire estuary. Higher median concentrations of MPs (3387 items/kg dw),  $\sum_{13}$ tri-OPEs (12.0 ng/g dw) and  $\sum_{4}$ di-OPEs (0.7 ng/g dw) were measured in intertidal sediments with predominance of fine particles, and under higher anthropogenic pressures, with a general lack of seasonality. Contrarily, *Scrobicularia plana* showed up to 4-fold higher  $\sum$ tri-OPE concentrations in summer (reaching 37.0 ng/g dw), and similar spatial distribution. Polyethylene predominated in both compartments. Tris (2-ethylhexyl) phosphate (TEHP), its degradation metabolite (BEHP) and tris-(2-chloro, 1-methylethyl) phosphate (TCIPP) were the most abundant OPEs in sediments, while TCIPP predominated in *S. plana*. The biota-sediment accumulation factors suggest bioaccumulation potential for chlorinated-OPEs, with higher exposure in summer. No significant correlations were generally found between OPEs and MPs in sediments suggesting a limited role of MPs as in-situ source of OPEs.

### 1. Introduction

Organophosphate ester (OPEs) flame retardants and plasticizers are nowadays detected in virtually all environmental compartments from oceans and seas, including atmosphere, water, sediment and marine organisms (including seafood) (Wei et al., 2015; Xie et al., 2022). The increasing global environmental ubiquity and hazardous effects shown by these plastic additives (Van Der Veen and De Boer, 2012; Wei et al., 2015) have risen concerns regarding the exposure of marine organisms and humans (Gbadamosi et al., 2021; Castro-Jiménez and Tornero, 2023). These chemicals present multiple sources in the environment, including direct leakage from plastic manufacture industries and electronic recycling sites (e-waste) (Wei et al., 2015; Xie et al., 2022), atmospheric deposition (Castro-Jiménez et al., 2014, 2016), riverine inputs, which are mostly derived from waste water treatment plant (WWTP) effluents (Li et al., 2019; Schmidt et al., 2020; Fu et al., 2020; Chen et al., 2022). Other urban sources, such as runoff (Rodgers et al., 2023), and leaching from marine plastics could also inject OPEs to

coastal areas. (Nurlatifah et al., 2021; Fauvelle et al., 2021). Another emerging threat to the marine environment is microplastics (MPs). Substantial loading from rivers, coastal cities, maritime traffic and fishing activities (Lebreton et al., 2017; Schmidt et al., 2017) and atmosphere (Liu et al., 2019) have been reported. Moreover, several hazardous effects associated to MPs have been documented (Wang et al., 2021; Li et al., 2023).

OPEs and MPs co-occur in our oceans and seas. Marine sediments are thought to be a sink for both OPEs (Ma et al., 2017; Li et al., 2019; Liao et al., 2020; Alkan et al., 2021) and MPs (Van Cauwenberghe et al., 2015; Peng et al., 2018; Phuong et al., 2021), representing a reservoir and main route of exposure to benthic organisms. Very few investigations have focused on the co-occurrence of OPEs and MPs, and their interactions, particularly in areas subject to high sedimentary mediated transport of contaminants, such as estuaries. This knowledge become crucial to understand the environmental cycling and ultimate inputs of these two families of contaminants of emerging concern to the marine environment (Wu et al., 2023).

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Estuaries are considered as ecosystems of high ecological value as well as an ocean/land interface for sea trade and associated industrial activities. In this work we focus on one of the largest European macrotidal estuaries: the Loire estuary. This ecosystem is under important anthropogenic pressures (Section 2.1), and contaminants of different nature have been reported in the Loire estuary, raising high concern. For example, the presence of trace metals in the water dissolved and particulate phases (Briant et al., 2021) and sediments (Coynel et al., 2016) have been confirmed. Different families of organic contaminants, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), alkylphenols and bisphenol A have been measured in subtidal sediments as well (Couderc et al., 2016). Moreover, a recent investigation suggested that the Loire estuary may constitute a long-lasting reservoir of plastic litter, pointing to intertidal areas as accumulation hotspots (Ledieu et al., 2022). The presence of MPs in sediments and bivalves from adjacent areas to the Loire estuary have been also confirmed (Phuong et al., 2018b, a). However, the co-occurrence and spatial-temporal trends of widespread distributed plastic additives such as OPEs and MPs have never been studied in benthic compartments from the estuary, neither the OPE-MP interactions nor the contaminant transfer potential from sediment to benthic species.

The major objectives of this investigation were: (1) to determine the current levels of OPEs and MPs in benthic compartments (i.e. intertidal sediments and the clam *Scrobicularia plana*) from the Loire estuary; (2) to explore potential links between MP abundance and OPE concentrations in sediments; (3) to investigate the OPE bioaccumulation (transfer sediment-benthos). To achieve these objectives around 100 samples (all

zones and matrixes) were gathered in two sampling campaigns. Intertidal sediments and the bivalve *Scrobicularia plana*, also known as Peppery furrow shell, were collected in contrasted sites of the estuary and analysed for OPEs and MPs. *S. Plana* exhibits high densities in intertidal mudflats and is a primary consumer, feeding on benthic (at low tide) and planktonic (at high tide) micro-organisms. As such, it is a relevant sentinel species of contamination at low trophic levels, and has been used for biomonitoring purposes (Buffet et al., 2015). Being an important part of the diet of wading birds, crabs and benthic fish, it is also at the bottom of estuarine food webs and a better understanding of *S. plana* contamination levels and processes can support the later assessment of trophic transfer in those sensitive ecosystems.

## 2. Material and methods

### 2.1. Study area and sampling

The Loire River drains a catchment covering around 20 % of the French territory (117,800 km<sup>2</sup>) (Dhivert et al., 2016), with a mean annual water discharge of about 850 m<sup>3</sup>/s, varying from 80 to 5,500 m<sup>3</sup>/s (National water monitoring “Banque Hydro” database; station Montjean-sur-Loire) (Coynel et al., 2016) (Fig. 1). Its estuary, located in the North-East edge of the Bay of Biscay (Atlantic Ocean), is a macrotidal and highly turbid estuary, one of the largest in France, and one of the major European estuaries (Jalón-Rojas et al., 2017). Like most rivers in North-Western Europe, the sub-catchments of the Loire River contributing to the estuary are industrialised (industrial port, oil refineries, coal-fired thermal electricity production and various industries, such as

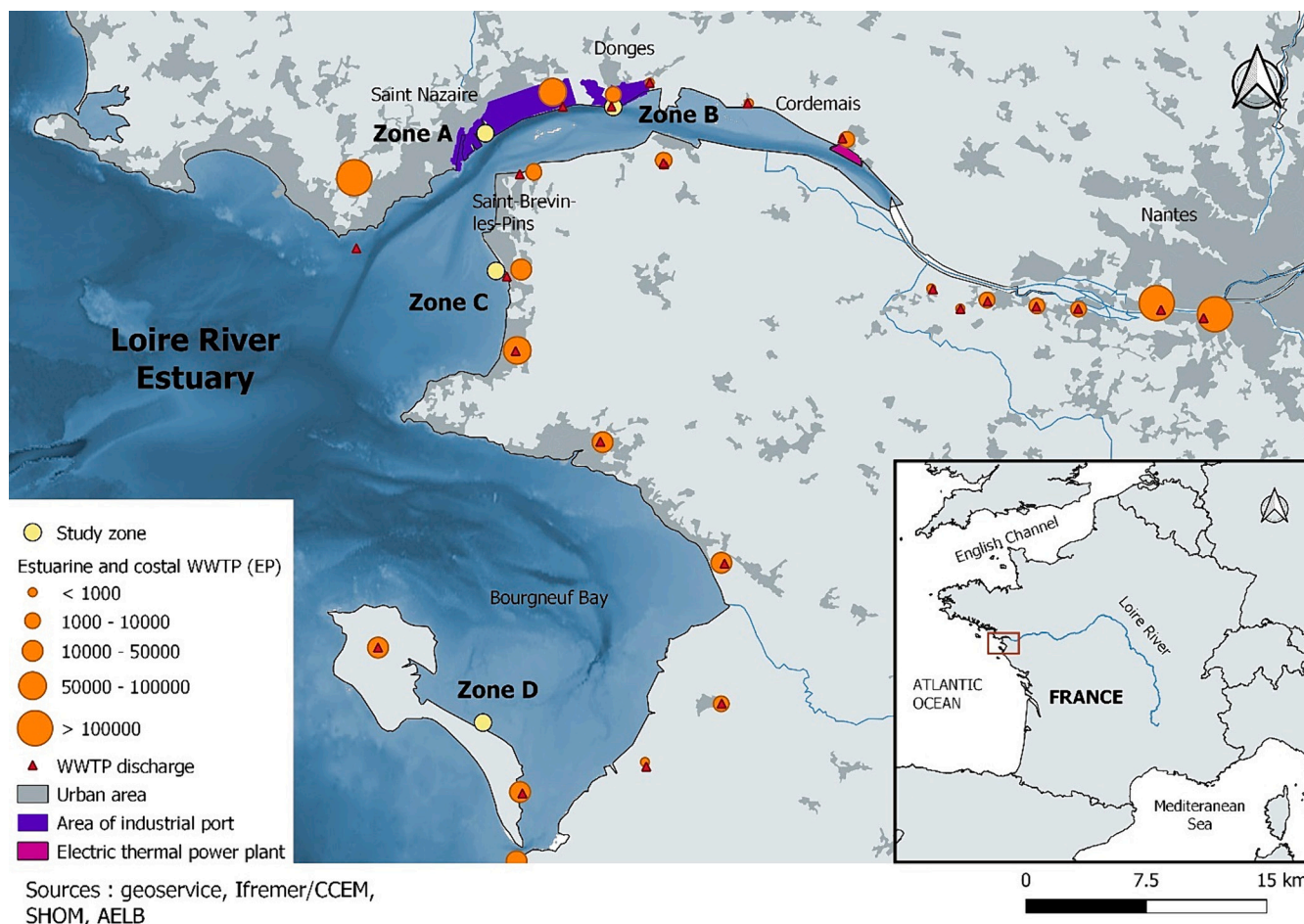


Fig. 1. Study area (the Loire estuary) and sampling zones, including details on anthropogenic activities in the area. For waste water treatment plants (WWTP), the capacity as equivalent person (EP), and the exact location of the effluent reject (discharge) are shown.

gas storage, aircraft, shipyard and fertilizers production). In addition, agricultural and urban pressures affect the estuary, including the metropolitan areas of Nantes (around 670,000 inhabitants) and Saint-Nazaire (about 71,800 inhabitants). Four sampling zones were selected, three of them directly located inside the estuary (downstream part of the Loire estuary: zones A, B and C), and one located along the coast in the Bourgneuf Bay (zone D). A brief description of the zones is presented hereafter: *Zone A*: located on a mudflat (Vasière de Méan) in a polyhaline area, under the influence of seawater, Loire River water and a local small stream named “Le Brivet” (33 km long). Sediment from this site is highly rich in organic matter (Table S1) and dominated by polychaete and *S. plana*. It is located next to the main navigation channel which is dredged all year round, next to the urban area of St Nazaire and the industrial port of Nantes – Saint-Nazaire (including shipyards); *Zone B*: located on a mudflat in a polyhaline area, this site is under the influence of seawater, Loire River water and a local small channel named “Canal de Martigné”. It is also located next to the navigation channel, next to a petrochemistry complex site (Donges), directly under the discharge of the urban waste water treatment plant (WWTP) of Donges (about 8,700 equivalent person -EP) and downstream the coal-fired thermal power station of Cordemais (12 km); *Zone C*: this sampling site is the most marine site of the three estuarine sites. It is located in a euhaline and polyhaline zone depending on the tide and the river flow. This site is sandy (Table S1) and with a higher influence of marine water than the two other sites. It is located close to the urban area of Saint-Brevin-les-Pins and next to its WWTP discharge point (around 22,000 EP). This area is rather touristic in summer; *Zone D*: this rather muddy sampling site is located in coastal waters in a shallow area named Bourgneuf Bay. Depending on the current conditions, suspended solids from the Loire River plume can settle in this bay, that is a semi-enclosed system. The main human activities of this area are shellfish farming, agriculture and salt marshes. There are two urban WWTP discharges close to the sampling zone (SE and NW of the site, Fig. 1), representing a cumulative capacity of around 65,000 EP. This area is rather touristic in summer too.

Two sampling campaigns were conducted, in September 2021 and February 2022. Intertidal surface sediment (0–5 first cm) was collected by directly filling a pre-cleaned 600 ml glass container in the aforementioned zones of the Loire Estuary (Fig. 1). Sediments were collected in five sites distant of 20–50 m for each zone (in duplicates) following a grid pattern (Fig. S1). *S. Plana* was only present in two zones (A, D). Individual specimens were collected by hand in the same area where sediments were sampled (within the grid). Exact coordinates for each sample are reported in Table S1. Once in the lab, sediments were homogenized and frozen until further processing. *S. Plana* individuals were externally rinsed with MQ water, then shelled, and the flesh was further rinsed with mili-Q (MQ) water in a Buchner funnel until complete removal of the sediment particles trapped inside the shells. The samples were freeze-dried (dry weight  $11.3 \pm 1.7\%$ ) and further stored at room temperature in the dark until further analysis. An entire set of sediment samples and most of *S. Plana* individuals were devoted to OPE analyses. The other duplicate of sediment samples and selected *S. Plana* individuals were devoted to MP analyses. For each zone where *S. Plana* was present, individuals of similar shell length were split in 3 pools of 35 or 36. Individuals from zone D in September 2021 and from zones A and D in February 2022 had similar sizes ( $29.8 \pm 2.6$  mm altogether), while individuals from zone A in September 2021 were marginally but significantly smaller ( $26.6 \pm 1.5$  mm).

## 2.2. OPE extraction and analysis

### 2.2.1. Sediments

Sediments were freeze-dried and sieved (500  $\mu$ m stainless steel mesh). Separated extractions were performed for tri-OPE and di-OPE analyses. For tri-OPEs, 1 g (dry weight - dw) was loaded into a 30 ml glass centrifuge tube and spiked with tri-OPE labelled standards

(surrogates) at 1 ng/sample (Table S2). After few minutes of stabilisation, 5 ml of a mixture of ethyl acetate/cyclohexane (80/20, v/v) was added, the sample was vortexed for 30 s and then ultrasound extracted (30 min) by using a XtraTT 120HT sonicator –Elma (200 W of effective ultrasonic power) (Singen, Germany). The extract was transferred to another tube and a second extraction was performed in the same conditions. The combined extracts were concentrated to 100  $\mu$ l under gentle  $N_2$ . Clean-up was performed using SPE-NH<sub>2</sub> columns (500 mg, 6 ml Discovery® DSC-NH<sub>2</sub>). The SPE-NH<sub>2</sub> cartridges were washed and conditioned with 5 ml of ethyl acetate/cyclohexane (1:1, v/v) followed by 5 ml of cyclohexane before adding the extract. Elution was performed with 4 ml of ethyl acetate/cyclohexane (1:4, v/v) followed by 5 ml of ethyl acetate/cyclohexane (1:1, v/v). The fractions were concentrated to 100  $\mu$ l under  $N_2$  and transferred to injection vials. Isotopically labelled injection standards were added at 1 ng/sample (Table S2), the final extract was evaporated to dryness and reconstituted with 100  $\mu$ l of methanol and 100  $\mu$ l of water. For di-OPEs, 1 g dw was spiked with di-OPE labelled standards at 1 ng/sample (Table S2) and extracted twice with 5 ml of methanol and the volume reduced to 100  $\mu$ l as above indicated. The extracts were cleaned-up by using SPE-HLB columns (500 mg, 6 ml Oasis HLB). The SPE-HLB cartridges were washed and conditioned with 5 ml of methanol followed by 5 ml of MQ water. After the addition of the sample the columns were washed with 5 mL of MQ water, dried for 20 min and eluted with 10 ml of methanol. This fraction was concentrated to 100  $\mu$ l under  $N_2$  and transferred to a glass vial. Isotopically labelled injection standards were added (1 ng/sample) (Table S2) the final extract was evaporated to near-dryness, and 100  $\mu$ l of methanol and 100  $\mu$ l of MQ water were added.

### 2.2.2. Biota

Samples were analysed as described previously (Aminot et al., 2023). Briefly, *S. Plana* samples (1 g dw) were processed by accelerated solvent extraction (ASE) with in-cell Florisil clean-up followed by sequential SPE-NH<sub>2</sub> and SPE-ENVI-Carb (500 mg, 6 ml, Supelclean™ ENVI-Carb™). Quantification was done against isotopically labelled OPE homologues (Table S2).

### 2.2.3. Instrumental analysis

Twenty-one tri-OPEs (eleven in *S. Plana*) and seven di-OPE (only in sediments) were quantified by isotopic dilution LC-ESI-MS/MS (LC coupled with a triple quadrupole Xevo TQS- $\mu$  from Waters, Milford, MA, USA) (Table S2). Tri-OPEs were analysed using a 50 mm  $\times$  2.1 mm BEH C18 1.7  $\mu$ m column (Waters, Milford, MA, USA) maintained at 50 °C. The gradient from solvent A (ammonium acetate 20 mM) to solvent B (100 % methanol), at a 0.5 ml / min flow rate, was as follows: 0 min (25 % B), 0.5 min (25 % B), 5 min (85 % B), 5.1 min (100 % B), 6 min (100 % B), 6.1 min (25 % B), 9 min (25 % B). The LC-MS/MS was operated in positive electrospray ionization mode (ESI+). Di-OPEs were analysed using a 100 mm  $\times$  2.1 mm HSS T3 2.5  $\mu$ m column (Waters, Milford, MA, USA) maintained at 40 °C. The gradient from solvent A (ammonium acetate 20 mM) to solvent B (100 % methanol), at a 0.3 ml / min flow rate, was as follows: 0 min (2 % B), 1 min (2 % B), 3 min (100 % B), 10 min (100 % B), 10.5 min (2 % B), 15 min (2 % B). The LC-MS/MS was operated in negative electrospray ionization mode (ESI-).

## 2.3. MP extraction and analysis

### 2.3.1. Sediments

The procedure used for MP extraction and identification in sediments was described in a recent study (Dhivert et al., 2022). Briefly, homogenized wet sediment was subsampled at a mass equivalent to approximately 10 g dw. Water content in sediments was determined in parallel and independently with MP evaluation. Firstly, organic matter in the sample was eliminated using pre-filtered hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 %). Samples were heated at 45 °C during 24 h. The liquid phase was then removed through the filtration on a metallic filter (10  $\mu$ m mesh size and



47 mm diameter). MPs were extracted from the digested sediment using iodide sodium (NaI) solution (density > 1.6 g/cm<sup>3</sup>) and microplastic sediment separator (Nakajima et al., 2019). In order to optimize the quality of MP spectra, a second digestion using H<sub>2</sub>O<sub>2</sub> at 45 °C for 24 h was performed on supernatant particles. Finally, digested solution was filtered on Anodisc membrane filter (0.2 µm and 25 mm diameter).

Chemical composition of particles on the Anodisc filter was determined by µ-FTIR imaging (Thermo Nicolet iZ10) in transmission mode using a 25 × 25 µm pixel resolution. The whole filtration area was mapped with 16 MCT detector. Based on this methodology, we considered a size limit of around 25 µm for MPs. Spectrum acquisition with 1 scan from 4,000/cm to 1,200/cm. The acquired maps were then treated with siMPle software (version 1.1.β). Reference spectrum included >30 polymer types and also some natural materials. The number of MPs and characteristics (type, size) were provided by the software.

### 2.3.2. Biota

The method used for the analysis of MPs in *S. Plana* has been previously detailed (Phuong et al., 2018b). Briefly, soft tissue of *S. Plana* (pool of 5 individuals) was digested using KOH solution (10 %, 45 °C, 24 h). After this digestion, samples underwent the same analytical train as described above for sediments.

### 2.4. TOC, particle-size and lipid determinations

Total organic carbon (TOC) determinations in sediments were conducted at the Laboratory of Environmental Marine Science (France). Briefly, particulate inorganic carbon was first eliminated from freeze-dried sediments under steaming HCl for a few hours according to (Nieuwenhuize et al., 1994). Samples were combusted (950 °C), under a flow of oxygen/helium, and TOC was determined using a Flash 2000 elemental analyser (Thermo). Sediment granulometry was determined by using a laser particle size analyser/LS 13320 (Beckman Coulter). Briefly, aliquots of fresh sediment were sonicated in MQ water for 20 s to promote particle dispersion. Obscuration was between 6 and 10 %. Analyses were carried out in triplicate for each sample. Total lipid content (TLC) was determined gravimetrically as the dry weight of a dichloromethane extract after pressurised liquid extraction.

### 2.5. Chemicals and reagents

Ethyl acetate, cyclohexane and methanol were purchased from Promochem (Germany). Ultrapure water (MQ) was taken from a Millipore (resistivity >18.2 MΩ) Milli-Q system. H<sub>2</sub>O<sub>2</sub>, 30 %, was from Honeywell, Fluka, iodide sodium was from VWR, Anodisc membrane filters were purchased from Whatman. Labelled OPEs were purchased from Wellington Laboratories (Guelph, Canada), TRC Canada (Toronto, Canada). Native OPEs were obtained from Wellington Laboratories (Guelph, Canada), Accustandards (New Haven, USA), Chiron AS (Trondheim, Norway) and Dr. Ehrenstorfer GmbH, (Augsburg, Germany). All labelled and native compounds used are presented in Table S2.

### 2.6. Quality assurance/quality control (QA/QC)

All laboratory recommendations were strictly respected during MP analysis. Briefly, lab cotton coats and nitrile gloves were used in the whole analytical procedure. Experiments were carried out in a closed fume hood and maximizing the protection of samples with aluminium foil. Before utilisation, all materials were rinsed three times with ultrapure water. Solutions (H<sub>2</sub>O<sub>2</sub>, NaI) were filtered on glass fibre filters (0.7 µm, Fisher Scientific). Blank analyses were performed on two tests. Firstly, a blank identification ( $n = 1$ ; clean filter instead for sample filter) was measured, in which no MP was found. Procedural blanks ( $n = 3$ ; water instead of samples, i.e. sediment or biota) were performed in the same conditions. A maximum of three MP particles were found in these

blanks. This value was considered negligible in comparison to MP concentration in sediment and *S. Plana* samples, so results were not blank-corrected.

Strict measures were taken to minimize potential cross-contamination during OPE analysis. First, the entire analytical procedure was conducted in clean laboratories, under a low-dust atmosphere and positive pressure (ISO 8 class according to NF EN ISO 14644). The use of plastic material was minimized as much as possible. The few elements of plastic employed (e.g. micropipet tips) were previously blank-tested to assure no contamination problems. All glassware was cleaned with detergent, rinsed with tap water + MQ water and then baked at 450 °C for a minimum of 6 h before using. Procedural blanks ( $n = 2$ ) following all steps were prepared for each extraction batch. A method validation was performed for sediment by assessing the accuracy of the calibration function, and the intermediate precision and associated bias (details in Text S1, and Table S3). Validation criteria were met for seventeen out of twenty-one targeted OPEs. The analysis was considered semi-quantitative for BEHP and BDCIPP due to a higher absolute bias (47 and 29 %, respectively), and for 3TBPDPP and 3IPDPP, which showed a relative standard deviation (RSD) over the 20 % threshold (21 and 24 %, respectively). The method was previously validated for biota (Aminot et al., 2023). The retention times and the response factors by LC-MS/MS were evaluated for each analytical sequence by regularly injecting different calibration levels and injections of the LC mobile phase were regularly performed to check and monitor potential cross contamination along the injection sequence. A delay column was installed between the pump and the injector to separate instrument- and mobile phase-related peaks from the actual sample peaks (Aminot et al., 2023).

The median method recoveries of labelled surrogates in sediments ( $n = 40$ ) varied from 19 to 86 % and from 70 to 128 % for tri-OPEs and di-OPEs, respectively (Fig. S2A), while these for tri-OPE in *S. Plana* ( $n = 12$ ) ranged from 18 to 123 % depending on the compound (Fig. S2B). Average blank values varied from non-detected (nd) to 653 ± 97 pg in sediments ( $n = 4$ ) and from nd to 981 ± 229 pg in *S. Plana* ( $n = 10$ ), depending on the compound (Tables S4, S5). The limits of quantification (LOQ) were determined as blank average values +3xSD. When a compound was not detected in the blank, the LOQ corresponded to a S/N ≥ 10 in the lowest calibration level. All concentrations were blank corrected (in pg) by subtracting the corresponding blank average values. LOQs ranged from 1 to 597 pg/g dw in sediments and from 21 to 686 pg/g dw in *S. Plana*, depending on the compound and sample (Table S6).

### 2.7. Statistical analyses

Statistical data treatment was performed with the software STATA/SE 16.1. Non-parametric tests (Kruskal-Wallis) were used in order to investigate possible significant differences ( $p < 0.05$ ) of the different contaminants among zones and seasons. Results were further compared by pairs of zones (Wilcoxon rank-sum test). Each contaminant level was compared among 4 zones resulting in a total of 6 pairs of comparisons. The False Discovery Rate (FDR) correction (Benjamini and Hochberg, 1995; Benjamini and Yekutieli, 2001), with Simes's method (1986) was used to account for the effect of the multiple comparisons. Only OPEs showing overall detection frequencies (DF) ≥ 50 % were considered to study their individual spatial-temporal patterns. Non-detected values were imputed to the LOD/2 to run these tests. However, the concentration sums presented in Sections 3.2 and 3.4 consider only the detected values.

## 3. Results and discussion

### 3.1. MPs occurrence in sediments and biota

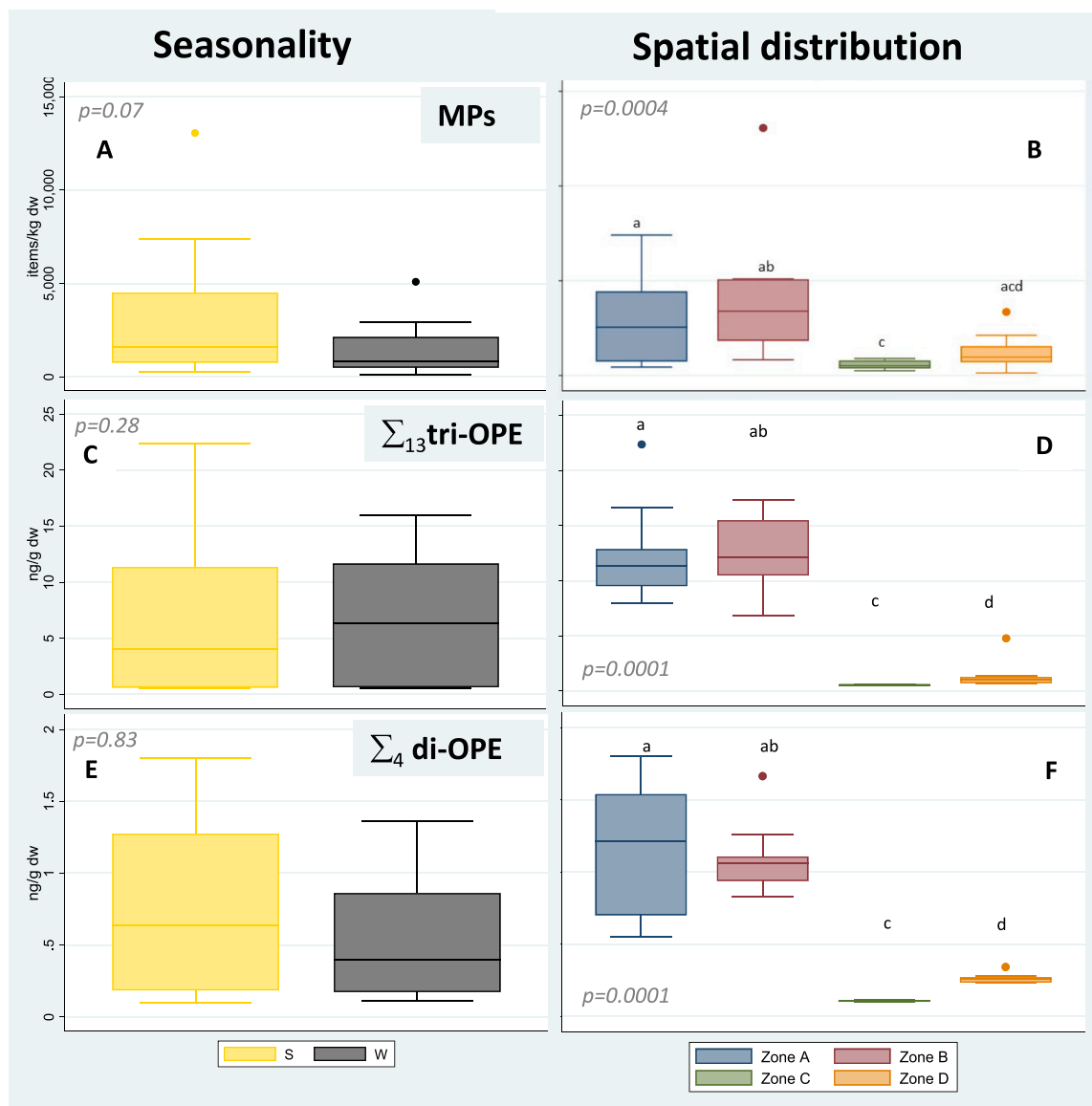
MPs were detected in all sediment samples, with a large variability of concentrations in the study area (131 to 13,062 items/kg dw)

(Table S7). Overall (all sites considered,  $n = 20$ ), no significant differences were found between summer and winter (Fig. 2A), although higher levels were generally found in summer. This is probably due to the fact that in Zone A, a significantly higher median MP concentration ( $p = 0.02$ ) in summer (4,440 items/kg dw) compared to winter (1,443 items/kg dw) ( $n = 5$ ) was observed (Fig. S3).

Significant differences ( $p = 0.0004$ ) were found among the sampling zones, with higher median levels in zone B (3,387 items/kg dw) compared to zones C (514 items/kg dw) and D (968 items/kg dw), and zone A (2,544 items/kg dw) in comparison to zone C (Fig. 2B). The lowest MP concentration was found at zone C, which is a sandy site. Indeed, the observed spatial trends are consistent with the sediment particle-size distribution in the study area (Fig. S4). The finest sediment fractions, more efficiently ‘trapping’ microplastics (Enders et al., 2019; Li et al., 2024), predominated in Zones A and B, which exhibited a median particle-size (D50) of 11.7  $\mu\text{m}$  and 11.6  $\mu\text{m}$ , respectively. Larger median particle-sizes were measured in Zones C (D50 = 178.1  $\mu\text{m}$ ) and Zone D (D50 = 167.9  $\mu\text{m}$ ), which reflected lower MP concentrations. In addition, the higher anthropogenic pressures in Zones A and B, leading to potentially larger MP emissions could contribute to the observed

spatial trends. TOC content in sediments from the study area varied from 0.03 to 3.2 % (Table S1). Interestingly, only polyethylene (PE) concentrations were correlated with the TOC content in the sediments ( $r^2 = 0.33$ ,  $p = 0.0002$ ), while no correlations were observed for the other polymers, suggesting the preferential capacity of this organic matter fraction to accumulate PE. Likely, the interplay of various factors namely, polymer type, TOC content, sediment granulometry and zone-specific sources could offer a reasonable explanation of the observed trends in the study area.

Our results are in agreement with those reported on Hong Kong sediment samples (Lo et al., 2018). MP levels were 268 items/kg in mudflat compared to 17 items/kg in sandy shore sediment. The authors argued that the different concentrations found may be influenced by sediment’s grain size and organic matter content (Vermeiren et al., 2023). Overall, the concentrations measured were 6 to 200-fold higher than previous measurements in other sites from the estuary (Phuong et al., 2018a). These differences are probably due the larger size range (MP > 25  $\mu\text{m}$ ) of MP investigated in this study compared to the previous study in the Loire estuary (MP > 300  $\mu\text{m}$ ). To compare to other studies worldwide, the MP concentration from the sediment collected at the



**Fig. 2.** Seasonal and spatial variability of MPs (A, B),  $\Sigma_{13}$  tri-OPE (C, D) and  $\Sigma_{4}$  di-OPE (E, F) concentrations in sediment of the study area. Kruskal–Wallis test ( $n = 20$  for seasonal analysis,  $n = 10$  for spatial analysis). S = summer; W = winter.

Lima River estuary (Portugal) ranged 200 to 2500 items/kg of dry sediment (Almeida et al., 2023). Other study demonstrated that MP level in mudflat sediment from Canada was 15 items/kg (Alava et al., 2021). While MP abundance in estuarine sediment from South Carolina (USA) ranged from 2 to 65 MP/kg of wet sediment (Leads et al., 2023). However, different protocols were used for the MP determination potentially leading to a methodological associated variability (Phuong et al., 2021). The higher MP concentrations measured in the Loire estuary compared to other studies may be also related to the method used, especially to the identification step. In our study, particles ( $> 25 \mu\text{m}$ ) were measured automatically. In contrast, the procedure of other studies (cited above) is based on visual observation under the microscope, separation of suspected MPs and measuring the various subsamples.

Regarding the polymer size, most abundant MPs were smaller than  $500 \mu\text{m}$ . While a very similar size-distribution pattern in summer and winter was observed in the more polluted Zones A and B, some seasonal variations were observed in the less impacted zones, with a more polydisperse distribution in summer (higher % of MPs  $< 100 \mu\text{m}$  and higher % of larger fragments) (Fig. S5).

PE was the most abundant polymer, followed by polypropylene (PP), accounting between 37 and 89 % and 5 to 50 % of the sum of total polymer types, respectively (Fig. S5). Other polymers found at lower percentages were polyamide (PA), polystyrene (PS), polyurethane, polyvinyl chloride, polyester and acrylic.

The MP determination in *S. Plana* was performed in a reduced number of samples, collected during the winter campaign, due to limited material availability ( $n = 2$  per zone). Concentrations in zone A (1.8 items/g wet weight (ww)) were slightly higher than in zone D (0.8 items/g ww), consistent with sediment trends, and PE was the predominant polymer. However, the low number of replicates does not allow a robust comparison between sites.

### 3.2. OPE occurrence in sediments

Overall, seventeen out of twenty-eight target OPEs were detected in the study area ( $n = 40$ ). The chlorinated OPE (Cl-OPE) TDCIPP was the most frequently detected compound (DF = 79 %), and was found in the four zones at both seasons. The other two Cl-OPEs were also detected at high frequencies, 70 % (TCEP) and 57 % (TCIPP). TEHP, TMPP and EHDPP exhibited also high DFs in the area, ranging 68 % to 77 %. The most frequently detected di-OPE was BEHP (DF = 61 %). These overall DFs were mostly driven by the highest DFs found in Zones A and B, where many OPEs were ubiquitous (Fig. S6). On the contrary, only two OPEs were detected in Zone C (TDCIPP at both seasons and EHDPP only in winter), both at DF = 60 %. Zone D represented an intermediate situation, with a few OPEs reaching DF  $> 80$  % (i.e. TEHP, TDCIPP, TMPP) while many were non-detected. BEHP was the only di-OPE detected in Zone D (DF = 33–50 %) (Fig. S6).

The concentrations measured for the sum of detected tri-esters ( $\sum_{13}\text{tri-OPEs}$ ) and di-esters ( $\sum_{4}\text{di-OPEs}$ ) exhibited a large variability, ranging from 0.01 to 22.1 ng/g dw and from 0.03 to 1.4 ng/g dw, respectively (Tables S8 and S9). Overall, non significant differences were found between summer and winter seasons for the sum of tri-OPEs ( $p = 0.28$ ) and sum of di-OPEs ( $p = 0.83$ ) (Fig. 2C, E). Individual OPEs followed the same pattern, with the exception of EHDPP, which showed concentrations  $\sim 2$ -fold higher in winter than in summer ( $p = 0.028$ ) (Fig. S7). We don't have a clear explanation for this trend, but it could either be due to a higher use of this particular OPE in winter season, particularly in zone A and B which are under the influence of important industrial activities, or to a more pronounced degradation rate in summer in the study area, or a combination of both.

Concentrations of  $\sum_{13}\text{tri-OPEs}$  and  $\sum_{4}\text{di-OPEs}$  were significantly higher ( $p = 0.0001$ ) in the most impacted zones (i.e. Zones A and B) (Fig. 2D, F), as observed for MPs.  $\sum_{13}\text{tri-OPEs}$  reached similar median concentrations of 11.0–12.0 ng/g dw in zones A and B, while levels of  $\sum_{4}\text{di-OPEs}$  were of  $\sim 1.0$  ng/g dw in the same zones. The lowest

concentrations were measured in Zone C, with 0.02 ng/g dw for  $\sum_{13}\text{tri-OPEs}$ . Di-OPEs were not detected at all in this zone. This is not surprising due to the absence of major contamination sources in this zone, as well as the sandy nature of the sediment (Table S2). These trends are consistent with the sediment particle-size distribution (Fig. S4), as for MPs, pointing again to the finest particles as driver of the contaminant burden in sediments from the Loire estuary. Individual OPE concentrations generally follow the same trend (Fig. S8). In addition, TBOEP and TDCIPP showed 1.1 to 1.5-fold significantly higher concentrations ( $p = 0.01$ – $0.04$ ) in zone B compared to zone A, while IDDPP exhibit 1.5-fold higher levels ( $p = 0.01$ ) in zone A than B (Fig. S8, Table S10). These results highlight the strong site-specific dependency of sources for some OPEs in the study area. Significant correlations with TOC were found only for TEHP ( $r^2 = 0.929$ ,  $p < 0.0001$ ) and BEHP ( $r^2 = 0.493$ ,  $p < 0.002$ ). Very weak or no correlations were observed for the rest of OPEs (results not shown). These point to the limited role of TOC affecting the spatial distribution of most OPEs in the study area. The relatively high log  $K_{ow}$  for TEHP (9.49) and BEHP (6.07) could explain their correlation with TOC in sediments. Other authors have reported the absent of TOC and OPE correlations in marine sediments (Liang et al., 2024).

Very few studies have investigated the OPE occurrence in estuarine sediments, and are limited to tri-esters to the best of our knowledge, so the following comparisons are made for tri-OPEs. Concentrations ranging from 2.5 to 181 ng/g dw were reported in sediments from European river basin estuaries and deltas (Wolschke et al., 2018). Interestingly, the Gironde River (France), with its estuary located  $\sim 200$  km south from the Loire estuary, was part of the survey. Our measurements, particularly the most polluted zones, were within the range of concentrations reported for the Gironde River (2.5 to 73.0 ng/g dw for  $\sum_{8}\text{OPEs}$ ). However, many sampling sites were upstream estuary for all rivers. OPE concentrations reported in sediments from the Yangtze River estuary and adjacent East China Sea varied from 1.0 to 19.0 ng/g dw ( $\sum_{8}\text{OPEs}$ ), also in line with our measurements (Ji et al., 2022). Higher OPE levels (41.4–1,930 ng/g dw) were reported in sediments from the Yellow River estuary (Yang et al., 2024), and other marine coastal areas such as the Gulf of Lion in the Mediterranean Sea, (4.0–227 ng/g dw for  $\sum_{9}\text{OPEs}$ ) (Alkan et al., 2021) and the Korean coast (2.0–347 ng/g dw) ( $\sum_{13}\text{tri-OPE}$ ) (Choi et al., 2020). Comparable values (0.1 to 32.2 ng/g dw,  $\sum_{12}\text{OPEs}$ ) were reported in sediments from the East China Sea (Liang et al., 2024). The authors of that investigation also measured di-esters, with concentrations ranging from 0.5 to 15.0 ng/g dw for ( $\sum_{8}\text{di-OPE}$ ), which are slightly higher than those measured for di-OPEs in the Loire estuary. Some extra variability is expected considering the fact that different amount (and types, sometimes) of OPEs were measured in the various studies.

The role of tri-OPEs as potential relevant environmental source of di-OPE, due to degradation processes, have been discussed by some authors (Liang et al., 2024). The investigation of di/tri-ratios (R) could provide some clues about this hypothesis. Considering the most impacted zones from our study area (zones A and B), for which the higher DFs of tri/di-OPE allowed their paired measurements, the following median ratios were estimated:  $R_{\text{BEHP/TEHP}} = 0.13$  ( $n = 10$ ),  $R_{\text{DPhP/TPHP}} = 0.74$  ( $n = 7$ ) and  $R_{\text{Dn-IBP/TnBP}} = 1.10$  ( $n = 10$ ). This relative di/tri-OPE occurrence may suggest a minor role of the studied tri-esters as significant sources of their corresponding transformation products. A consequent tri-ester degradation would have resulted into higher ratios, which is not the case. In spite of some agreement with the limited number of di/tri-OPE available ratios in marine sediments, our values were generally lower. For example, a median  $R_{\text{DPhP/TPHP}}$  of 0.9 was reported in sediments from the East China Sea (Liang et al., 2024), while values ranging from 0.2 to 1.2 for oceanic sediments in the Arctic (Fu et al., 2023). Contrary, median  $R_{\text{BEHP/TEHP}}$  and  $R_{\text{DBP/TnBP}}$  values of 1.3 and 3.5, respectively, were reported in the East China Sea and slightly higher  $R_{\text{DBP/TnBP}}$  values ranging from 1.4 to 2.6 in Arctic oceanic sediments. The authors of those studied argued that tri-OPE transformation in the environment could be a source of di-OPEs in their studied areas. However, the interplay of

various factors and environmental processes may affect the representativeness of these ratios, as already discussed by the authors. For example, the different physical-chemical properties and therefore partitioning behaviour between tri- and di-OPEs in the sediment, as the log  $K_{ow}$  values of di-esters are generally lower, and the potential direct input of di-OPEs, particularly in impacted areas are among these factors (Liang et al., 2024). Additionally, in the most impacted zone of our study area, continuous inputs of tri-OPEs are very likely, also affecting the di/tri ratios. The differential degradation rates of OPEs in marine sediment could also increase variability. Very few studies have investigated OPE degradation in marine sediments at relevant environmental conditions. Results from an incubation experiment investigating the chemical and microbial degradation of widely occurring tri-OPEs in coastal marine sediments reported experimental half-lives ( $t_{1/2}$ ) of 47–77, 19–46 and 17–27 days for TEHP, TnBP and TPhP, respectively (Castro-Jiménez et al., 2022). This could offer a partial explanation to some of our estimated ratios, with lower values for more persistent OPEs, like TEHP. Certainly, the interplay of the above-mentioned factors may affect the di/tri-OPE ratios.

A quite consistent pattern was observed in the more contaminated zones (A, B) in summer and winter (Fig. 3), with TEHP accounting for  $41.0 \pm 14.0$  % to  $43.0 \pm 10.0$  % (summer) and  $38 \pm 8.0$  % to  $42 \pm 10.0$  % (winter) of  $\sum$ tri-OPEs. TCIPP, which accounted for  $17.0 \pm 13.0$  % to  $21.0 \pm 6.0$  % (summer) and  $25.0 \pm 8.0$  % to  $26 \pm 11.0$  % (winter) of  $\sum$ tri-OPEs, predominated also in the pattern. The higher relative abundance of BEHP in these areas, both in winter ( $67.0 \pm 18.0$  % to  $77.0 \pm 12.0$  % of  $\sum$ di-OPEs) and summer ( $89.0 \pm 16.0$  % to  $96.0 \pm 6.0$  %), seems consistent with the predominance of its parent compound, TEHP, in the same zones and seasons, but direct BEHP inputs cannot be excluded, as previously discussed. The OPE relative distribution in zone D in summer resembled very much this of zones A and B, but with a higher predominance (around 60 %) of TCIPP, while the pattern in zone C in summer was entirely dominated by TDCIPP. Indeed, this chlorinated compound was the only tri-OPE measured in this zone and season. In winter, the predominance of EHDPPP ( $92.0 \pm 13.0$  %) in zone C and

higher contribution of TBOEP (61 %, but detected only in one site) emerged (Fig. 3). These differences in patterns may suggest different OPE sources in the region and certain degree of seasonality for a few OPEs, most probably also driven by a differential environmental processing depending on the zone-specific characteristics (e.g sediment composition, tidal regimes, etc). However, we cannot elucidate these differences with the present data.

### 3.3. MP-OPE field interactions in sediments

One potential OPE source in the sediment could be the direct leaching from plastic fragments. However, no significant correlations were generally found between the concentration of individual OPEs and the MP abundance (all polymer type confounded), except for TEHP and BEHP, which exhibited weak but significant positive correlations ( $p = 0.01$ ,  $p = 0.003$ , respectively) (Table S11). Similar trends were generally observed when plotting the additive concentrations versus the MP size-classes (results not shown), suggesting that the particle size did not have a marked influence in our study area. However, the polymer type seemed to have an influence in the correlations between additive concentration and MP abundance for the above mentioned OPEs. For example, in the case of TEHP, a significant positive correlation ( $p = 0.01$ ) with PE abundance in the sediment was found, while no correlations were found with PP, PA or PS abundances (Table S11). Since this OPE is used as additive in different kinds of polymers, the general predominance of PE in sediment was most probably driving its overall correlation. On the other hand, BEHP showed a positive significant correlation with PP ( $p = 0.02$ ) and PS ( $p = 0.002$ ) particles, and not with PE and PA. Interestingly, MPDPP exhibited a significant positive correlation ( $p = 0.005$ ) with PS abundance only. These results suggest that the role of MPs as effective in-situ source of OPEs in sediments from our study area seem to be quite limited as well as compound and polymer type dependent. Only one previous study discussed the correlations between OPEs and MP concentrations in marine sediments, and the authors claimed a positive correlation (Liang et al., 2024). However, the

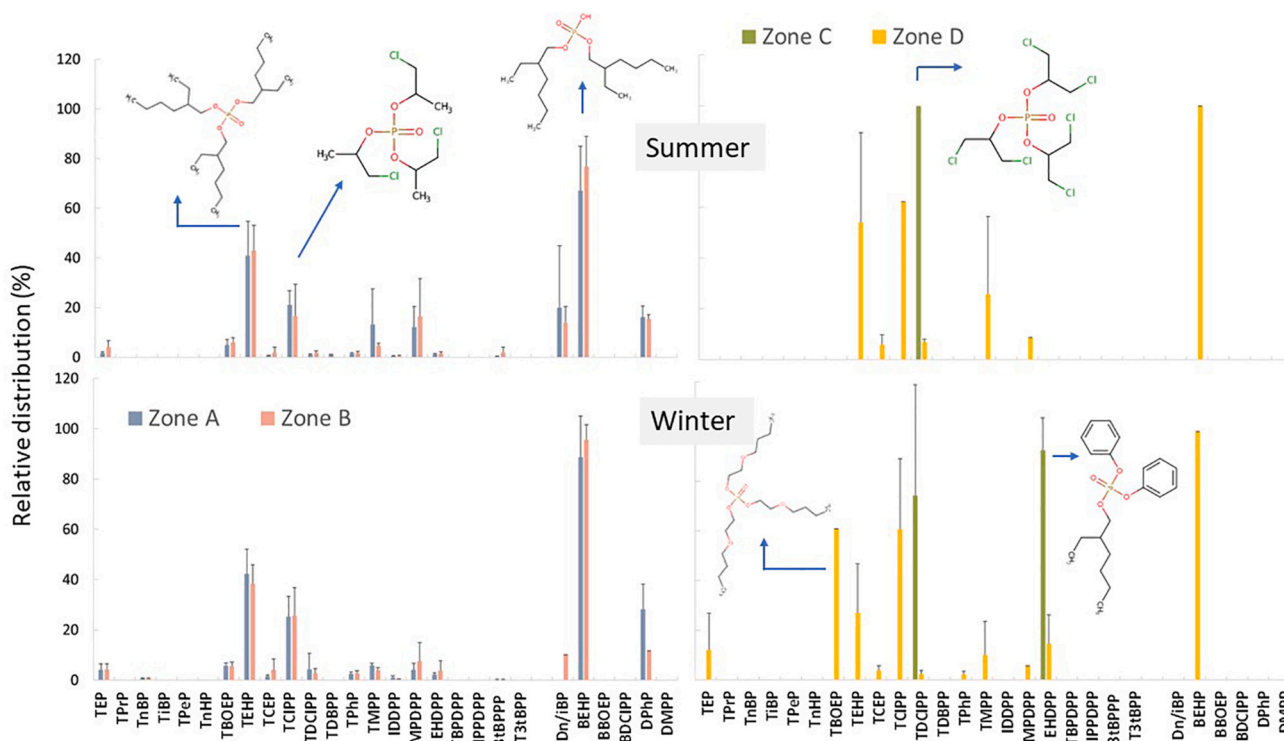


Fig. 3. OPE patterns in sediments from the four studied zones. The plots show the relative contribution of tri-OPEs to  $\sum$ tri-OPEs (left side) and the relative contribution of di-OPEs to  $\sum$ di-OPEs (right side).



data provided is very limited (e.g. no MP results shown or absent of number of samples considered). Moreover, the authors only studied the correlation for the  $\sum$ OPEs. We have demonstrated that these correlations may be different depending on the specific OPE and polymer type. A recent review compiling studies on fresh water sediments, highlighted that while there seems to be an apparent correlation between concentrations of MPs and additives, it is not clear if MPs act as a source or a sink of lipophilic chemicals, such as most of OPEs, to the aquatic environment (Onoja et al., 2022). Indeed, the elucidation of the role of MPs as in-situ sources of OPEs in marine sediments is a complex issue due to the interplay of different factors. For example, the additive could be released from a given plastic fragment but it could be potentially re-adsorbed by other plastic fragments or by other active components from the matrix, such as organic carbon and/or mineral particles coated by organic matter. The sorption of some OPEs by MPs in seawater has been reported (Chen et al., 2019). No reports exist for marine sediments to the best of our knowledge, but it seems a plausible process. The understanding of the partitioning of OPEs in sediments, between sediment particles and the MPs themselves, has been already identified as a research priority (Onoja et al., 2022). In addition, the relative role of additive leaching in sediments compared to direct inputs (waterborne and airborne) is poorly understood. Last, detailed information on additive quantities and diversity in polymers is still missing, as this information is usually declared as confidential by producers (Maes et al., 2023).

### 3.4. OPE occurrence in the benthic bivalve *S. Plana*

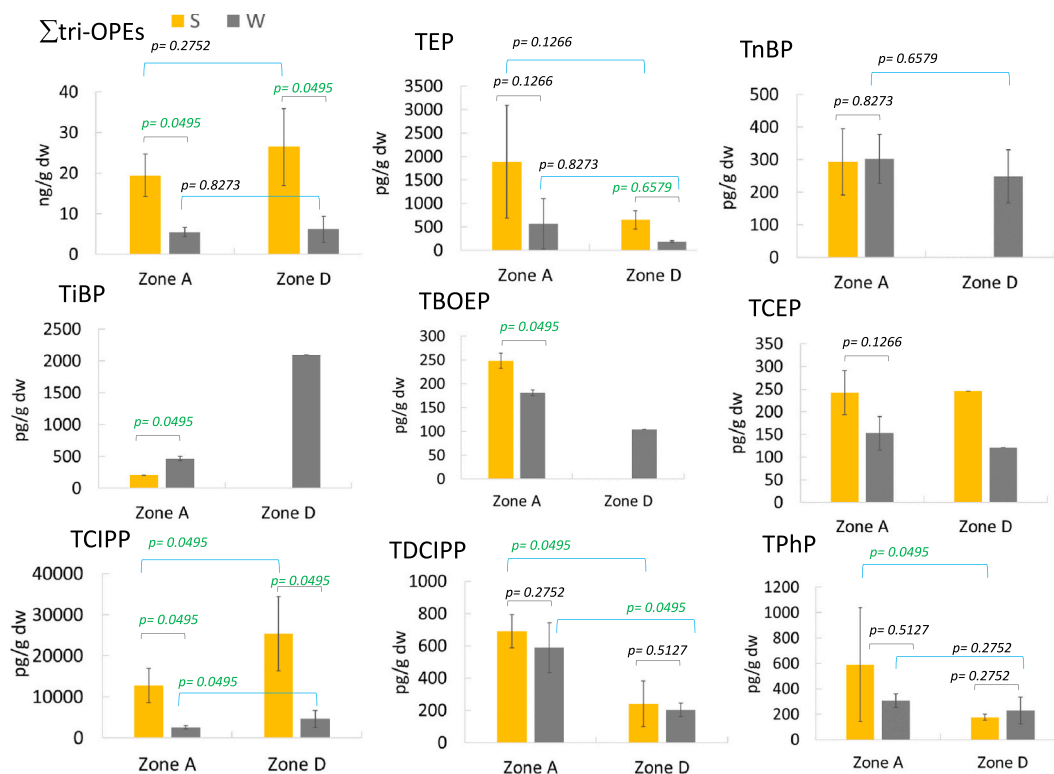
Overall, ten out of twelve target OPEs were quantified in *S. Plana* ( $n = 12$ ). DF > 50 % were observed for most OPEs, with the highest found for the chlorinated TDCIPP and TCIPP (100 %), TPHP (92 %) and TEP (83 %). TMPP and EHDPP exhibited lower DF (33 and 25 %, respectively). TEHP and MPDPP were also detected in *S. Plana*, although the analytical method used didn't allow accurate quantification. TPrP and

TDBPP were not detected at all (Fig. S9). Concentrations for  $\sum$ tri-OPEs varied from 4.1 to 37.3 ng/g dw (59.7 to 680.3 ng/g lipid weight, lw). TCIPP clearly dominated the OPE pattern (47–96 % of  $\sum$ tri-OPEs) (Fig. S10), reaching values from 2.2 to 35.7 ng/g dw (29.7 to 651.0 ng/g lw). Individual concentrations are presented in Table S12. Contrary to sediments, a general seasonality was observed for OPEs, with 3 to 4-fold higher concentrations measured in summer for  $\sum$ tri-OPEs in both sites (Fig. 4).

This trend was also observed for most individual OPEs, although it was not statistically significant in all cases. TnBP and TDCIPP showed comparable levels in both seasons, and TiBP was the only compound exhibiting around 2-fold higher levels in winter compared to summer in zone A ( $p = 0.0495$ ).

The generally higher levels in summer may be related to the enhancement of the feeding activity (pumping and filtering rates) of *S. Plana* at higher temperatures (Hughes, 1969), which would lead to a higher dietary exposure from microphytobenthos. It was also considered if the reproductive cycle of *S. plana* could affect the contamination levels by inducing physiological changes. In the studied area, the spawning period has been established as being between May and July, with sexual repose from November to January (Mouneyrac et al., 2008). Our sampling was performed in late September and early February, which is outside of the spawning period. No significant differences were found in lipid content between either zones or seasons, with an average of  $6.4 \pm 0.9$  % of dry weight (Table S1), suggesting the tissue composition would not affect lipophilic contaminant levels.

Also, in contrast to the concentration trends found in sediments, no significant difference was found between Zones A and D ( $p = 0.275-0.823$ ) for  $\sum$ tri-OPEs. However, when examining individual OPEs, TDCIPP and TPhP exhibited significantly higher concentrations ( $p = 0.0495$ ) in Zone A than in zone D (3-fold both in summer and winter and 1.3-fold only in summer, respectively). Interestingly, the opposite trend was observed for the most abundant OPE, the chlorinated TCIPP, which showed ~2-fold higher concentrations ( $p = 0.0495$ ) in Zone D,



**Fig. 4.** Spatial and seasonal variation of OPE concentrations in *S. Plana* (Zones A, D). Statistical comparisons (Wilcoxon,  $n = 3$ ) were performed only for OPEs with DF  $\geq 67$  % in each zone and/or season S = summer; W = winter.

both in summer and winter (Fig. 4), when sediment concentrations were significantly higher in zone A than in zone D in both summer and winter. We do not have a complete explanation of this trend, but a degree of uncertainty should be constrained. Intertidal sediments are daily covered by seawater at regular periods of different extent depending on the tidal regimes. During these episodes, *S. Plana* stays preferentially in contact with the water phase, behaving as suspension feeder and obtaining some of its food by filtering suspended matter from the seawater (Buffet et al., 2015). Indeed, some authors consider that *S. Plana* can inform about the waterborne chemicals (Solé et al., 2009). In our investigation, OPE occurrence in the water phase and/or sediment pore water was not evaluated. A potential bioconcentration of dissolved water phase OPE could occur, particularly for OPE with relatively low log  $K_{ow}$  and high water solubility (WS), such as TCIPP (log  $K_{ow}$  = 2.6, WS = 1, 200 mg/l). However, the extent of this process as well as its relative importance compared to the transfer from sediment particle-bound OPE cannot be evaluated with present data. Likely, a combination of processes may provide a more complete explanation of the observed patterns in *S. Plana*. Our observations show again that considering only the  $\Sigma$ tri-OPEs masks contrasting trends of individual OPEs. We acknowledge the limitations of these comparisons due to the reduced number of replicates. A larger study in the area should be conducted to confirm these trends.

A systematic review on OPE concentrations in marine bivalves was recently published (Aminot et al., 2023), and although it also includes filter-feeding bivalves such as mussels, our results were compared to those gathered from their work. Concentrations found in the clam *S. plana* from our studied sites were globally comparable to those reported worldwide, which span 2–3 orders of magnitude (Fig. 5). In particular, the benthic bivalve *Cerastoderma edule* was studied in the Western Scheldt estuary, Netherlands (Brandtsma et al., 2015), and the authors reported median concentrations very close to ours, with the exception of TBOEP, reaching 8.1 ng/g dw when we found no values >0.3 ng/g dw. Also predominant in their sediment, it may reflect a site specificity. The concentrations determined in our study were lower than those reported for mussels and oysters used in biomonitoring in France, except for TCIPP, TEP and TMPP, which could suggest local sources in the Loire estuary or a peculiarity of burrowing vs. water-column filtering bivalves. It is also noteworthy that TEP, rarely studied or found elsewhere and of limited hydrophobicity (log  $K_{ow}$  = 0.8), was ubiquitous in our study. On the contrary, TnBP and TBOEP were more frequently studied, and concentrations elsewhere were found to be higher than in our study.

In order to gain insight in the bioaccumulation potential of OPEs by *S. Plana*, the biota-sediment accumulation factors (BSAFs) were

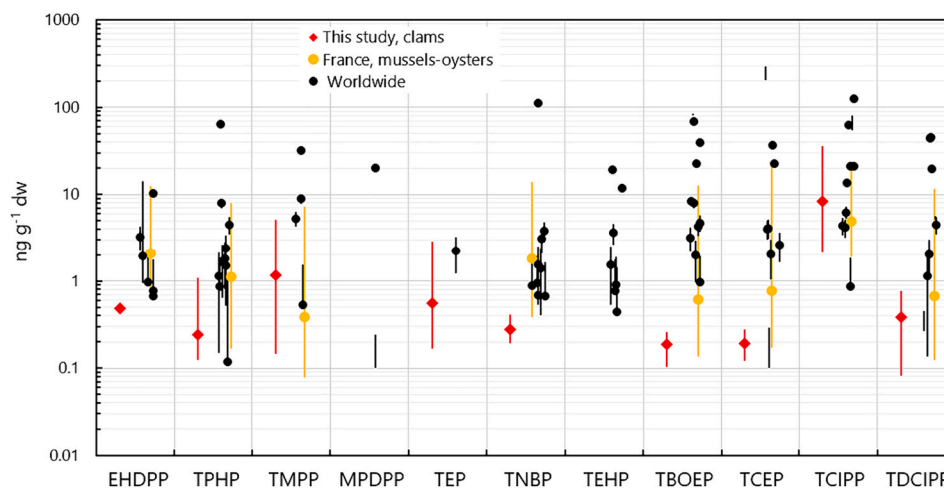
tentatively determined as the OPE concentration in *S. Plana* divided by the OPE concentration in sediment (Morrison et al., 1996). Here, two calculations were performed: (1) using the OPE dry weight concentrations (ng/g dw) for both matrixes (BSAF<sub>dw</sub>); and (2) using lipid-normalized OPE (ng /g lw) and TOC-normalized (ng /g TOC) values for *S. Plana* and sediments, respectively (BSAF<sub>norm</sub>). Due to the absence of paired observations for most OPEs in Zone D, we present results for Zone A only (Table 1).

BSAF values for most OPEs were generally higher in summer than winter, consistent with the observed seasonal patterns in *S. Plana*. BSAF<sub>dw</sub> values in summer and winter ranged from 0.36 ± 0.09 and 0.28 ± 0.04 (TBOEP) to 5.43 ± 0.79 and 4.07 ± 1.33 (TDCIPP), respectively. TDCIPP showed the highest potential for bioaccumulation from sediment, in both seasons. High BSAF were also observed for TCIPP, TPHP and TEP in summer, and TnBP in winter. EHDPP exhibit a BSAF<sub>dw</sub> of 2.51 ± 0.94 (only winter value available) indicating too its potential bioaccumulation. BSAF<sub>norm</sub> showed the same trends but values were systematically 2.5-fold and 3.3-fold lower in summer and winter compared to BSAF<sub>dw</sub>, respectively. These differences mostly resulted from the quasi-constant lipid/TOC ratios in both seasons in Zone A. The lipid (*S. Plana*) and TOC (sediment) contents in this zone were very similar in summer (6.4 ± 0.4 and 2.5 ± 0.1 %, respectively) and winter (7.1 ± 0.4 and 2.2 ± 0.1 %, respectively) and no significant differences were observed. The lowest BSAF<sub>norm</sub> corresponded to TBOEP (0.15 ± 0.04 summer and 0.08 ± 0.01 winter) and the highest to TDCIPP (2.20 ± 0.27 summer and 1.23 ± 0.45 winter). Indeed, TDCIPP was the compound exhibiting the highest bioaccumulation potential as derived from the BSAF estimations and considering the uncertainty of our calculations, and only in summer. No correlations were found between the

**Table 1**  
Mean (n = 3) biota-sediment accumulation factors (BSAFs) for OPEs in Zone A.

	BSAF <sub>dw</sub>		BSAF <sub>norm</sub>	
	Summer	Winter	Summer	Winter
TEP	4.28 ± 3.84	1.25 ± 1.19	1.70 ± 1.48	0.38 ± 0.35
TnBP	2.47 ± 2.36	3.56 ± 1.11	1.00 ± 0.93	1.07 ± 0.37
TBOEP	0.36 ± 0.09	0.28 ± 0.04	0.15 ± 0.04	0.08 ± 0.01
TCEP	2.81 ± 1.61	1.16 ± 0.40	1.12 ± 0.61	0.35 ± 0.14
TCIPP	4.02 ± 1.82	0.69 ± 0.09	1.61 ± 0.68	0.21 ± 0.03
TDCIPP	5.43 ± 0.79	4.07 ± 1.33	2.20 ± 0.27	1.23 ± 0.45
TPhP	4.05 ± 3.81	1.02 ± 0.41	1.62 ± 1.49	0.30 ± 0.11
TMPP	2.91 ± 2.74	/	1.18 ± 1.08	/
EHDPP	/	2.51 ± 0.94	/	0.74 ± 0.26

‘/’ = not possible to calculate due to the absence of paired measurements



**Fig. 5.** Comparison of OPE concentrations (ng/g dw) in this study (median and minimum – maximum) and in other studies on marine bivalves worldwide (median or mean, and minimum – maximum when available). MPDPP and TEHP, not quantified in this study. Amended from (Aminot et al., 2023).

log  $K_{ow}$  and  $BSAF_{dw}$  or  $BSAF_{norm}$  suggesting that the bioaccumulation of OPEs in *S. Plana* could be the result of combined process, as explained above. Very few studies report  $BSAF$  for bivalve in marine environments. For comparison, an investigation conducted in mussels and oysters from the Korean coast reported lower  $BSAF$ s of  $0.06 \pm 0.08$ ,  $0.6 \pm 0.3$  and  $0.8 \pm 1.3$  for TCIPP, TCEP and EHDPP, respectively (Choi et al., 2020), although these organisms are non-burrowing species as *S. Plana*.

#### 4. Conclusion

Estuarine zones under higher anthropogenic pressures showed higher levels of MPs and OPEs suggesting an apparent relationship between these two families of contaminants of emerging concern. The finest sediment particles seem to be a major driver of the contaminant burden, both MPs and OPEs, in sediments from the Loire estuary. However, the fact that no significant correlations were generally found between the concentration of individual OPEs and the MP abundance points to a limited role of MPs as effective in-situ source of OPEs in the study area. We hypothesize that the interplay of various factors, such as the OPE partitioning in sedimentary material containing as well MPs, direct inputs and/or similar accumulation patterns of both families of contaminants may drive these apparent relationships. No clear evidence of a significant role of tri-OPEs as environmental source of di-OPEs in estuarine sediments was found. The seasonal and spatial trends of OPEs in sediments and *S.Plana* were different in the study area suggesting a certain degree of decoupling of the OPE concentrations in both compartments, in spite of relatively high  $BSAF$  for some OPEs, particularly the chlorinated TDCIPP. In any case, higher exposure of this benthic organisms is expected in summer. The occurrence of OPE in the water dissolved and particle phases should be studied in order to apportion the OPE sources in *S. Plana*.

#### CRedit authorship contribution statement

**J. Castro-Jiménez:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Y. Aminot:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Data curation, Conceptualization. **N. Bely:** Methodology, Formal analysis. **C. Pollono:** Writing – review & editing, Supervision, Methodology, Formal analysis. **B.I.T. Idjaton:** Writing – review & editing, Methodology, Investigation, Formal analysis. **L. Bizozero:** Writing – review & editing, Writing – original draft, Conceptualization. **O. Pierre-Duplessix:** Resources, Methodology, Conceptualization. **N.N. Phuong:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis. **J. Gasperi:** Writing – review & editing, Writing – original draft, Methodology, Investigation.

#### 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.marpolbul.2024.116256>.

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