Environmental occurrence of organophosphate esters and micro-plastics in sediments and benthic organisms from the Loire Estuary (France)

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INTRODUCTION AND OBJECTIVES

Organophosphate ester (OPE) flame retardants and plasticizers and microplastics (MPs) are emerging threats to the marine environment, presenting multiple sources in the environment and being widely distributed in sea and ocean of the planet [1-3]. Marine sediments are thought to be a sink for both OPEs and MPs. In addition, leaching from MPs could constitute in-situ sources of OPEs [2]. Therefore, determining their environmental occurrence in sediments becomes crucial to better understand their current stocks, the exposure of benthic organisms, and possible impacts on the global functioning of marine ecosystems. The Loire is the longest river in France representing an important freshwater discharge to the North-East Atlantic Ocean. Its estuary is considered as an ecosystem of high ecological value as well as an ocean/land interface for sea trade and associated industrial activities.

The overall objectives of this work were: (1) to determine the current environmental levels of OPEs and MPs in sediments and selected benthic organisms from the Loire estuary; (2) to investigate the OPE bioaccumulation (transfer sediment-benthos); and (3) to explore the links between MPs abundance and OPE concentrations in the study area. Two sampling campaigns conducted in September 2021 and November 2022 allowed the collection of surface sediments and the deposit feeder clam *Scrobicularia plana* (SP) in four study areas subjected to different anthropogenic pressures (Fig.1). Preliminary results from the first campaign in September are presented in this poster.

RESULTS

Organophosphate esters

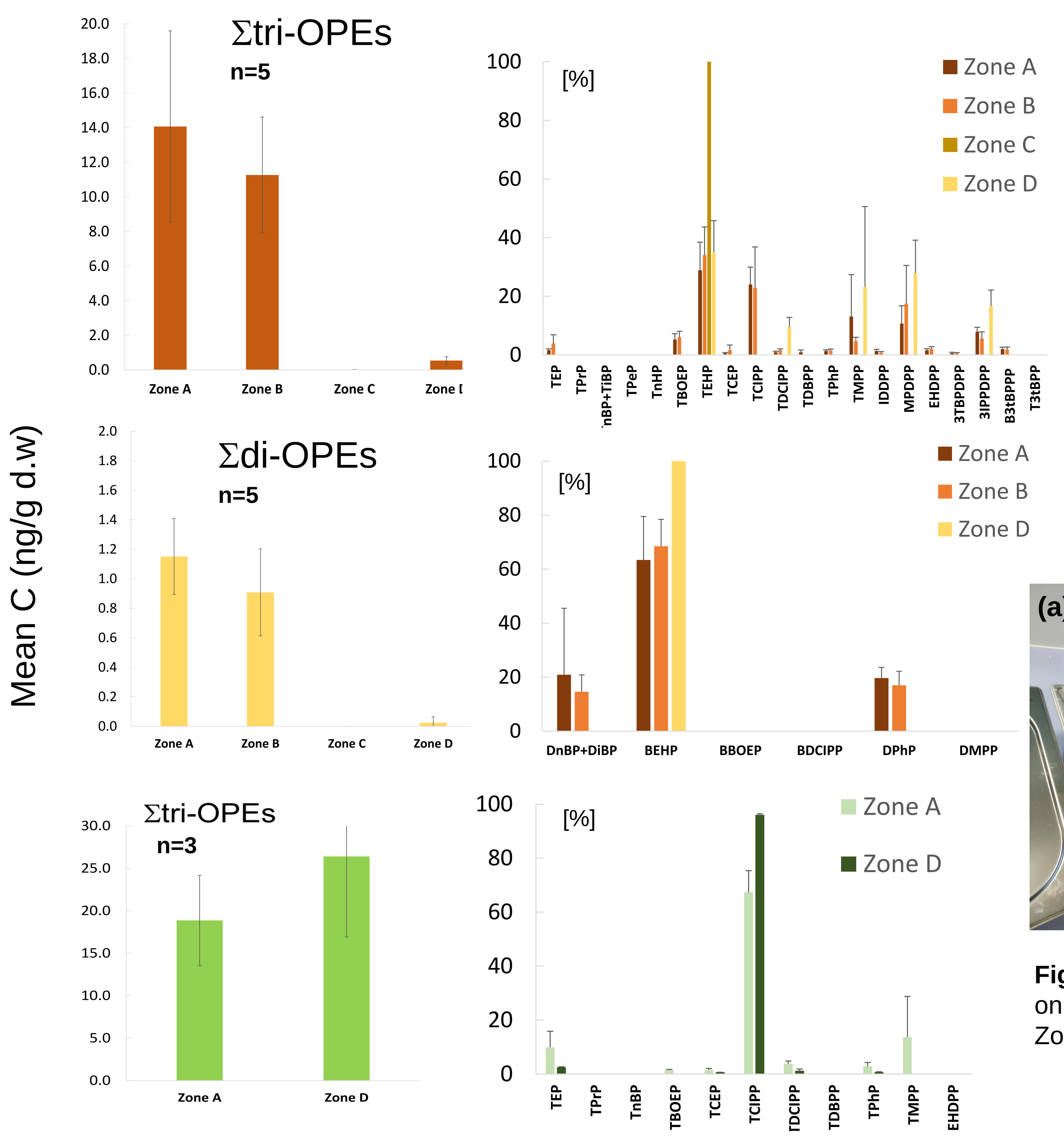
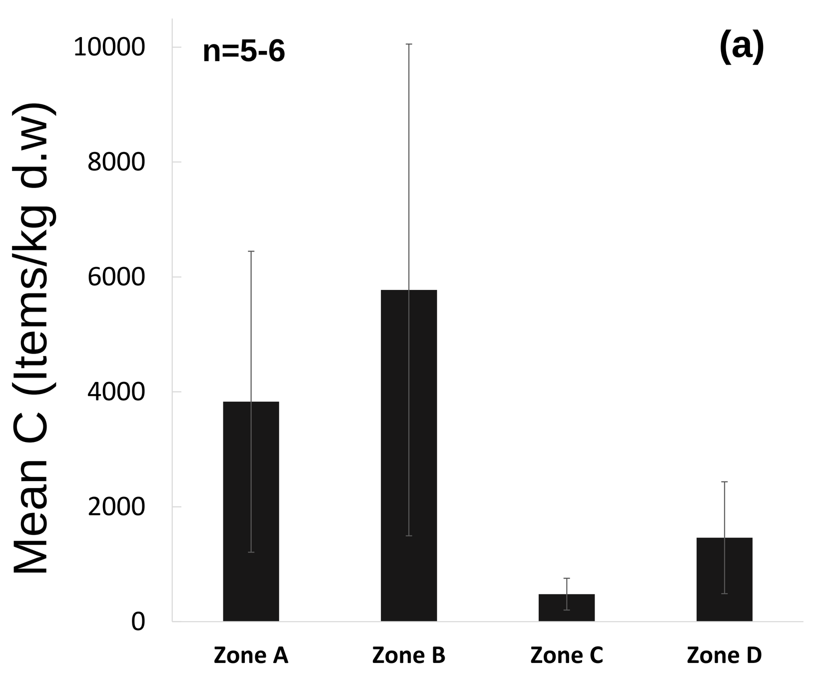


Fig. 2. Mean concentrations (ng/g d.w and distribution patterns (%) of tri-OPEs and di-OPEs in sediments (upper and mid panels, respectively) and tri-OPEs in *Scrobicularia plana* (lower panel). Vertical bars are standard deviation.

Fig. 1. Study area, sampling zones and detail on *Scrobicularia plana* individuals collected in Zone A (a) and sediments from Zone B (b)

Microplastics (sediments)



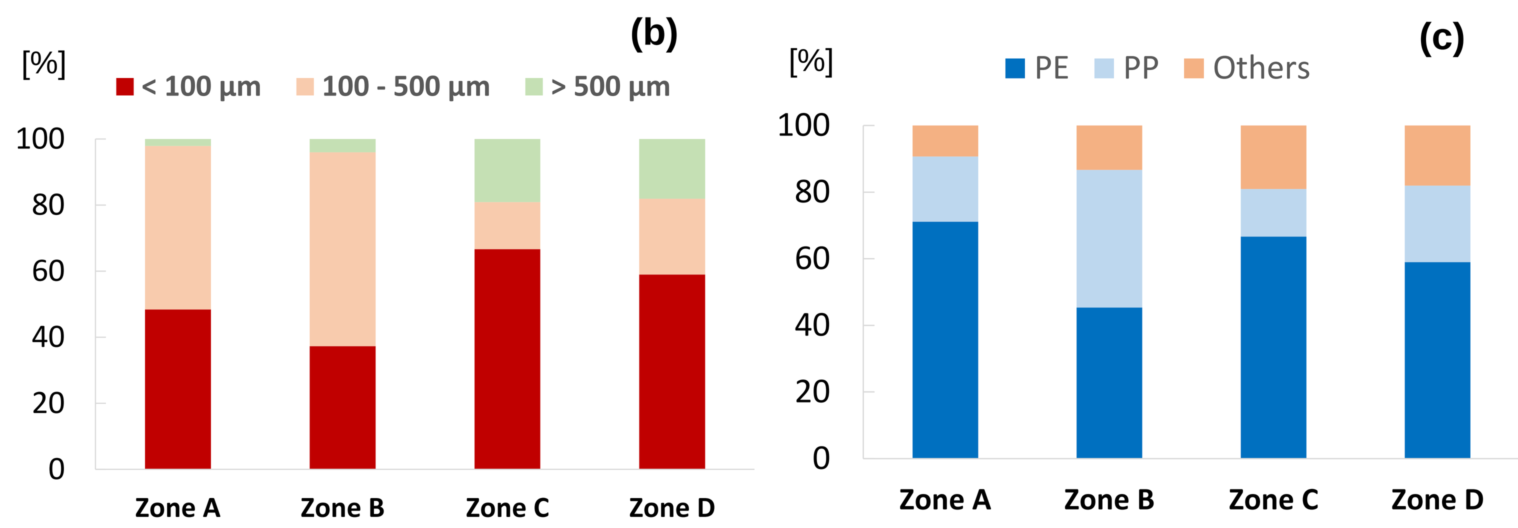


Fig. 3. Microplastic concentrations (items/kg sediment d.w -a-), relative particle size distribution (%, -b-) and polymer type relative distribution (%, -c-) in the study area. PE= polyethylene , PP=polypropylene, Others includes (polyamide, polystyrene, polyvinyl chloride, acrylic, polyester)

MAIN FINDINGS

- ✓ OPE presence confirmed in sediments and *Scrobicularia plana* in the Loire Estuary for the first time
- ✓ Higher OPE median levels in sediments under industrial harbor & petrochemical pressures (∑tri-OPEs = 10-12 / ∑di-OPEs = 0.8-1.2 ng/g d.w)
- ✓ Comparable levels (∑tri-OPEs) for *Scrobicularia plana* in industrial harbor (17 ng/g d.w) and bivalve fishing (22 ng/g d.w.) zones
- ✓ Tris(2-ethylhexyl) phosphate (TEHP) and tris-(2-chloro, 1-methylethyl) phosphate (TCIPP) most abundant tri-OPEs in sediments
- ✓ Predominance of TCIPP in *Scrobicularia plana*, although TEHP was also confirmed (but not quantitatively)
- ✓ Predominance of degradation metabolite bis(2-ethylhexyl) phosphate (BEHP) in sediments, consistent with high abundance of TEHP
- ✓ MPs in sediments were also ubiquitous following a similar concentration trend as OPEs in sediments, with higher levels in impacted zones
- ✓ Despite difference of MP concentrations, a similar size distribution and polymer pattern was found in the four zones (PE, PP predominated)
- ✓ The coupling of OPE and MPs concentrations in the study area point to MPs as potential OPE sources, but further research needed to confirm

- On-going work: Determinations of TOC (sediments) and lipid (SP) contents, analysis of samples from second campaign, derivation of BSAFs…

METHODS

Surface sediment (1-5 first cm) was collected at four different zones from the Loire Estuary subjected to different anthropogenic pressures (Fig.1). Five sites were collected in each zone following a grid pattern. The benthic organism *Scrobicularia plana* (SP) was only present in two zones (A, D). Both sediment and SP were freeze-dried. Sediments were sieved (500µm), spiked with OPE labelled standards, and ultrasound extracted (1 g d.w.). Separated extractions were performed for tri-OPE analysis (EtOAc/Cyclohexane 80/20) and di-OPE (MeOH). Clean-up was performed using SPE-NH2 (500mg, 6 ml Discovery® DSC-NH2) and SPE-HLB (500mg, 6 ml Oasis HLB) cartridges for tri-OPE and di-OPE, respectively. SP samples (1 g d.w.) were processed by accelerated solvent extractaction (ASE) with in-cell florisil clean-up and followed by sequential SPE-NH2 and SPE-ENVI-Carb cartridges (500mg, 6 ml, Supelclean™ ENVI-Carb™). Twenty-one tri-OPEs (eleven in SP) and seven degradation metabolites (di-OPE, only in sediments) were quantified by isotopic dilution LC-MS/MS (UPLC coupled with a triple quadrupole Xevo TQS-µ from Waters, Milford, MA, USA) . MP abundance was determined after sediment digestion (10g w.w.) with H_2O_2 (30%) and polymer isolation (NaI) and the fragments were characterized by µ-FTIR (Thermo_nicolet iZ10). Method median recoveries varied from 29 to 130% and limits of quantification ranged from 0.01 to 1.2 ng/g d.w depending on the specific OPE.

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Acknowledgements
We would like to acknowledge Nadège Bely and Lauriane Ledieu for their help in the sampling campaign

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