Marine Pollution Bulletin 209 (2024) 117291

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

# Potential of fishing nets for adsorption of inorganic (Cu and Pb) and organic (PAHs) pollutants

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## ABSTRACT

This study aimed to evaluate metals and polycyclic aromatic hydrocarbons (PAHs) adsorption on new plastic fishing nets in both laboratory and quasi-real scenario (nets submersed in marina seawater) experiments as well as in situ monitoring of these contaminants in water and sediments in lost fishing gears hotspots. The latter was inconclusive as environmental contaminants levels were very low. Laboratory experiments showed metals (copper and lead) and PAHs adsorption depended on the thickness and polymeric composition of the net, being lower in thinner nylon nets. Experiments in the marina, also showed significant contaminants adsorption, which increased over time, probably due to biofilm formation on net surface. This work showed the potential role of fishing gears as skins of pollutants, increasing organisms' exposition to contaminants present in the environment. So, initiatives to prevent the loss of fishing gear and to retrieve them are needed to reduce and/or eliminate their environmental impact.

## 1. Introduction

Marine litter derived from fisheries such as abandoned, lost or discarded fishing gear (ALDFG) (e.g., nets, long lines, fish traps) are an important kind of marine litter that can comprise up to 10 % of global marine litter (Giskes et al., 2022). Nowadays, a significant amount of fishing gear is made of plastics or has plastic components. Plastic is an inert material, however, environmental dynamics can induce modifications on its surface, making it suitable for adsorbing pollutants (Rafa et al., 2024). Persistent pollutants, such as polycyclic aromatic hydrocarbons (PAHs) (Tan et al., 2019), polychlorinated biphenyls (PCBs) (Llorca et al., 2020), polybrominated diphenyl ethers (PBDEs) (Xu et al., 2019) and nonylphenol (NP) (Chen et al., 2018) have been detected on floating plastics, raising concern for marine environmental health. These pollutants can be associated with ocean plastics by direct addition during production processes (e.g., flame retardants) or by sorption to plastics from the marine environment through partitioning mechanisms (Chen et al., 2024). Considering that fishing gear is mostly made of plastic, they can have the potential to adsorb contaminants such as metals or organic pollutants (e.g. PAHs).

Some studies have reported the adsorption of both inorganic (e.g., metals) and organic pollutants by microplastics of different composition, including by microplastics of polymers used in fishing net manufacturing, e.g., polyamine and polyethylene (e.g., Llorca et al., 2018; Ahechti et al., 2020; Yu et al., 2019). Adsorption of metals and PAHs by microplastics in brackish and saline waters has already been observed (Almeida et al., 2020 and unpublished results). In addition, metals such as Cd, Cu, Cr, Ni, Pb and Zn were detected in fragments of fishing nets collected from beaches on SW English coast (Turner, 2017), and ALDFG in Palk Bay, India (Pasumpon and Vasudevan, 2022). So, one can assume that ALDFG made of plastic can adsorb pollutants from the surrounding water, and become itself a hotspot for those pollutants. By floating around from one place to the other, ALDFG can carry contaminants from one place to the other also. Besides, adsorbed organic contaminants can degrade with time and their metabolites can even be more toxic. In addition, by adsorbing and desorbing contaminants ALDFG can increase contaminants concentrations in sites where they are located, comparatively to sites with no ALDFG. Therefore, hotspots of ALDFG can

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https://doi.org/10.1016/j.marpolbul.2024.117291
Received 7 July 2024; Received in revised form 10 November 2024; Accepted 10 November 2024

constitute a new pollution point.

ALDFG is a problematic issue as after being lost this fishing gear can continue to trap fish and other marine organisms, catching target and non-target species, in a phenomenon called ghost fishing (Lively and Good, 2019), being also responsible for serious entanglements of marine animals (turtles or mammals, like whales and dolphins) (Ramos et al., 2023). Apart from this, the harmfulness of ALDFG as a pollutant of the marine environment is still largely unknown. To our knowledge, chemical and biological pollution accumulation in ALDFG (composed of plastics) has not yet been sufficiently explored, however, it is essential to obtain a better understanding of the ecological implications of fishing-related debris. Although some laboratory studies showed the potential of microplastics to adsorbed pollutants, conditions are controlled and not always reflect environmental dynamics. Besides, studies in field conditions are still lacking and more research is needed. For instance, the formation of biofilms on submerged materials can significantly affect contaminants adsorption and biofilm formation will depend on water environmental conditions (Qin et al., 2024). Biofilms are dynamic systems, that comprise microorganisms and associated extracellular products, and their formation is also dependent on material surface. So biofilm formation can differ among gears materials and plastic polymers all of which can influence contaminants adsorption (Qin et al., 2024).

In this study, we aimed to assess the potential of plastic fishing nets for adsorption of pollutants, like metals and PAHs, evaluating the potential of these nets to act as a sink of metals and/or PAHs, by adsorbing pollutants and/or concentrating them in surrounding water (with possible higher levels in waters of ALDFG hotspots), and to act as a carrier of the pollutants, with potential to release them afterwards. Research was carried under different setups, through a combination of laboratory, quasi-real scenario and in situ studies that complement each other, a novel approach. Linking these three scenarios and integrating obtained results allows to evaluate the impact of ALDFG as a potential new pollutant due to the adsorption and possible concentration of contaminants.

Initially, a set of controlled laboratory experiments were carried out to evaluate the possible adsorption of metals and PAHs on new plastic fishing nets, submersing for a short period of time fragments of nets of different structures and polymers in seawater doped with selected pollutants and evaluate afterwards a possible release of those adsorbed pollutants.

Afterwards, an in situ experiment was carried out in a quasi-real scenario. For that, three different fishing nets were submerged in the water of Marina of Leixões, Matosinhos, Portugal, and pollutants adsorption over time was assessed, including on formed biofilm, along with pollutant levels in surrounding water.

Finally, an in situ monitoring of chemical pollutants in water and sediments in ALDFG hotspots was done, comparing pollutant levels with those observed at sites without ALDFG. For that, two hotspots in NW Portuguese coast were selected as case studies.

## 2. Materials and methods

All material used was previously decontaminated to avoid cross contaminations: washed with deionised water, submersed in a 20 % $HNO_3$ solution for 24 h, rinsed again with deionised water and placed in an oven at 30 °C to dry.

### 2.1. Laboratory experiments

To investigate if fishing nets have the potential for adsorption of metals and/or PAHs, laboratory experiments were carried out in controlled conditions by doping seawater with the selected contaminants and submerging fragments of new (not used) fishing nets in the doped seawater. The fishing nets (supplied by a manufacturer of fishing nets) had different polymeric composition and thickness (Table 1), being commonly used in different fishing sectors and activities. The seawater was collected in Matosinhos beach, in NW Portugal (41°10′33.50”N; 8°41′36.15”W).

#### 2.1.1. Metals adsorption experiments

Seawater was doped with 50 μg L$^{-1}$ of either Cu or Pb. The concentration was based on those reported for environmentally polluted sites (Bakke et al., 2010). The metals selected are among those commonly detected on the NW Portuguese coast (Vasconcelos et al., 2011; Gouveia et al., 2018; Almeida et al., 2008) and represent metals with different properties and impacts. Cu is a micronutrient that can be toxic at high concentrations whereas Pb is a toxic metal with no known biological function. For each net type, three treatments were prepared: (i) metal control - seawater doped with the respective metal (Cu or Pb) without net fragments; (ii) net control - fishing net fragments in seawater without metals doping; and (iii) adsorption -fishing net fragments in seawater doped with the respective metal.

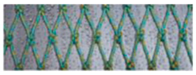
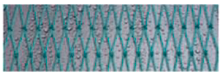
Fishing nets were cut into small fragments. Then, one net fragment was submerged in 150 mL of doped seawater (one replicate per condition). The mean weight of each fragment was ca. 0.7 g for braided PE net, 0.4 g for twisted PE net, 2.8 g for braided nylon net and 0.04 g for thin nylon net. Each net fragment included both lines and knotting portions to represent each net configuration (see photos in Table 1). Net fragments were of similar size and area to allow suitable comparison on metal adsorption, which resulted in different weights.

Flasks were placed in a mechanical shaker with low agitation (80 rpm), in the dark, for 7 days. Seawater aliquots (5 mL) were sampled at different times (see results). Samples were immediately acidified with 1 % $HNO_3$ and kept at room temperature until analysis.

Considering that the braided nylon net presented a higher potential for metal adsorption (see results section), this net was selected to repeat the adsorption experiment, preparing each treatment in triplicate (triplicate adsorption experiments). Exposure was carried out until 48 h, as no significant adsorption occurred after that (see results section).

Adsorption percentages were calculated considering the metal concentrations observed in the metal control solutions and in adsorption solutions collected at the same time, according to eq. (1).

**Table 1**
–Fishing nets, and their characteristics, used in laboratory experiments.

| | Net | | | |
|---|---|---|---|---|
| Name | 1 – Braided PE (trawling net) | 2 – Twisted PE (trawling net) | 3 – Braided Nylon (trawling net) | 4 – Thin Nylon (seine net) |
| |  |  |  |  |
| Material | High Tenacity Polyethylene fibres | Polyethylene fibres | Nylon fibres | Nylon fibres |
| Rope assembly | Braided | Twisted | Twisted | Monofilament |
| Diameter (mm) | 3 | 1.8 | 2.3 | 0.3 |
| Mesh size (mm) | 150 | 80 | 53 | 100 |

$$1-\left(\frac{\text{Adsoption solution}-\text{Net control}}{\text{Metal control solution}}\right)\times 100 \quad (1)$$

- Adsoption solution = metal concentration measured in seawater containing fishing net fragments and metal (Cu or Pb) to evaluate metal adsorption,
- Net control = metal concentration measured in seawater without metals doping containing fishing net fragments to evaluate possible metal released from fishing net,
- Metal control solution = metal concentration in seawater doped with the metal (Cu or Pb) without net fragments to evaluate possible metal losses in solution over time.

### *2.1.2. Metals desorption experiments*

To investigate possible metal desorption, at the end of the triplicate adsorption experiments (48 h), the fishing nets fragments were transferred to new flasks with clean seawater.

Samples of seawater were collected over time (same time periods as before) until 48 h.

Desorption percentages were calculated according to the eq. (2).

$$1-\left(\frac{\text{Desorption solution}-\text{Net control}}{\text{Adsorbed value}}\right)\times 100 \quad (2)$$

- Desorption solution = metal concentration in seawater containing the fishing net fragments with metal adsorbed
- Net control = metal concentration measured in seawater without metals doping containing fishing net fragments to evaluate possible metal released from virgin fishing net
- Adsorbed value = estimated metal concentration adsorbed in fishing net fragments taking in consideration metal concentration in adsorption solution

### *2.1.3. PAHs adsorption and desorption experiments*

For PAHs adsorption experiments, seawater was doped with a PAHs solution containing 10 PAHs considered a priority by United States Environmental Agency, resulting in a concentration of 1 μg $L^{-1}$ of each PAH. This concentration was selected considering levels of PAHs found in contaminated seawater (Bakke et al., 2010). The net presenting the highest adsorption rate, braided nylon (see results section), was afterwards selected for a second experiment in triplicate. Afterwards, net fragments were place in clean seawater to investigate possible PAHs desorption.

The same methodology described for metal adsorption/desorption experiments was used for the selected nets (Table 1).

In each experiment, seawater samples (10 mL) were taken over time at defined periods (assuring that no significant volume changes occurred). Collected samples were kept at −20 °C until analysis.

Adsorption and desorption percentages at a given time period were calculated using equations used for metal adsorption experiments.

### *2.1.4. Metals plus PAHs adsorption experiment*

In parallel, experiments with one metal (Cu or Pb) and PAHs (10 PAHs considered a priority by the United States Environmental Protection Agency) were carried out with braided PE net fragments to understand whether the presence of both contaminants (organic and inorganic) could alter metal or PAHs adsorption behaviour. Experimental conditions were identical to those previously described.

### *2.1.5. Metal analysis*

Metals concentrations were determined by atomic absorption spectrometry with flame (Perkin Elmer AAnalyst 200) or with electrothermal atomization (Perkin Elmer 4100ZL) depending on metal levels, by direct analysis of the samples. For metals quantification, external calibration with metal standard solutions of each metal prepared in seawater were used.

### *2.1.6. PAHs analysis*

The analysis of 10 of the PAHs considered a priority by the United States Environmental Protection Agency, naphthalene (Nap), acenaphthylene (Ace), acenaphthene (Acn), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Py), benz(*a*)anthracene (BaA) and chrysene (Ch), was carried out by headspace SPME-GC–MS (Gonçalves et al., 2016) in a Varian Saturn 2000 mass spectrometer (MS) (Walnut Creek, CA) coupled to a Varian 3900 gas chromatograph (GC) (Rocha et al., 2019). For water samples, 10 mL of each sample were first placed in glass flasks and an internal standard solution (20 μl) was added. Quantification was obtained through external calibration with PAHs standard solutions (each a mixture of the 10 PAHs) prepared similarly to the samples and with internal standard correction (with 4 deuterated internal standards composed of naphthalene d8, acenaphthene d10, phenanthrene d10, and chrysene d12), as previously optimised (Gonçalves et al., 2016).

## *2.2. Experiments in quasi-real scenario for evaluating pollutant adsorption to fishing nets*

### *2.2.1. Experimental set up and sampling*

Fishing nets were exposed to quasi-real environmental conditions in the Marina of Leixões, Matosinhos (Fig. S1). This recreational marina is in an enclosed area, being limited by the north, west, and east quays and may serve as a retention area for the pollutants released by the activities present in the commercial harbour which can differ along the year.

Three different fishing nets (section 2.1), 50 cm apart from each other, were placed in the water, namely Braided PE (Site A), Braided Nylon (Site B) and Thin Nylon (Site C) (Fig. S1). Twisted PE net tested in the laboratory experiments was not selected as its function, polymer and thickness was similar to braided PE net. To ensure the submersion of the nets at about 50 cm below the surface, each net was kept transversally open with a rope entangled on the top, which was connected to a stone at the bottom (Fig. S1). The experiment was carried out between February 2020 and July 2020, and in February (the sampling used as the baseline for initial conditions), March, May, and July 2020 water samples and net fragments were collected for metals and PAHs analysis.

Water was collected at two depths: 1) near each net at the bottom (below the net) corresponding to the control sample (no net) and 2) on the surface (near the net) corresponding to the fishing net sample, to evaluate if the net was concentrating metals in its vicinity due to its possible capacity to adsorb and desorb contaminants. Sampling took place 3 h after low tide. Water was collected with a water sample bottle and transferred into glass flasks for PAHs analysis and into plastic bottles for metal analysis. Additionally, pieces of each net were collected in all sampling campaigns. All water samples and net fragments were kept at −20 °C until analysis.

### *2.2.2. Metal and PAHs analysis*

Metals in particulate matter was determined in nitrate cellulose filters (0.45 μm porosity) used to filtrate the water sample. Filters were then dried at room temperature and afterwards digested with concentrated $HNO_3$ in a high-pressure microwave system (Ethos, Milestone) and analysed by AAS using a previously optimised sediment procedure (Almeida et al., 2004). No metal analysis was done in water as metal levels in the dissolved phase are in general below detection limits.

For metals adsorbed to the fishing nets, net pieces were thawed, cut, measured, weighed (Table S1) and placed in individual flasks with 20 mL of a 10 % solution of $HNO_3$ to gently desorb any metal on the net surface. Flasks were vortex for 1 min and sonicated (Elma, Transsonic 460/H) for 15 min. Metals were analysed directly as in section 2.1.5 but metals were quantified by external calibration with aqueous standard metal solutions.

For PAHs adsorbed to the fishing nets, nets pieces were placed in flasks with methanol (ca. 10 ml), vortex 1 min, sonicated for 15 min and analysed as described in section 2.3. PAHs concentrations in collected water samples (no PAHs analysis was done in water suspended particulate matter as levels in this matrix are in general below detection limits).

Fishing net fragments (new net, not used) were also subjected to the same procedures, to check if, eventually, some metal or PAHs were released from the net.

### 2.3. *In situ survey of metals and PAHs in ALDFG hotspots*

Two locations of ALDFG hotspots in NW Portuguese coast, were selected as case-studies, namely a coastal Marine Protected Area Parque Natural do Litoral Norte (PNLN) and a submarine wreck (Matosinhos). The first location is a natural rocky bottom area, with kelp algae and several reefs where small pieces of ALDFG (all <1 m long) are attached. The second location is an artificial reef created by the wreck of the World War II German submarine (U-1277) that sunk out of Matosinhos coast (near Porto city), being at ca. 30 m depth in a sandy bottom without rocks nearby. These two locations have intensive fishing activity, and consequently they are areas where pieces of fishing gear are lost, becoming hotspots of ALDFG.

In PNLN, bottom water samples (depth ranging between 15 and 25 m) were collected in six sites within the ALDFG hotspot area and in 3 sites outside that area (used as control sampling sites) in January (winter), March (spring) and June (summer) 2019 (Fig. 1). Sediments were collected (with a Van Veen grab) only in three sites within the ALDFG hotspot area as the area has too many rocky reefs that prevent sediment sampling. Sampling was done in January and June 2019 (as sediment have less seasonal variations). In Matosinhos, pieces of lost fishing nets and ropes (<1 m long) are trapped in the structure mainly at two sites: the torpedoes exit (site A) and the periscope (site B). Water and sediments samples were collected at these two sites and at a third site, 50 m far from the submarine, selected as control (site C). The sampling was carried out by recreational divers from the diving school *Submersus* in June and September 2019. Weather, navigability conditions and constraints of sampling at 30 m depth conditioned samples collection (several samples were lost).

For metal analysis in water suspended particulate matter and PAHs analysis in water samples, the procedures described in section 2.2.2 were followed.

All sediments were frozen at −20 °C and lyophilized before analysis. For metal analysis, dry sediment samples were subjected to high-pressure microwave digestion as described for filters. For PAHs, sediment samples were subjected to an ultrasonic extraction with methanol in an ultrasonic bath for 30 min following a previously optimised methodology (Gonçalves et al., 2016). The extract was then cleaned up with Florisil. An aliquot of the sediment extract (200 μl) was then diluted in deionised water and analysed as water samples.

### 2.4. *Data analysis*

The mean and standard deviation of the replicates of samples collected in the two hotspot locations and triplicate laboratory experiments were calculated. Significant ($P < 0.05$) differences among samples were evaluated by applying the unilateral parametric variance analysis (ANOVA) followed by the Turkey pairwise comparisons test.

## 3. Results and discussion

### 3.1. *Laboratory experiments for pollutant adsorption to fishing nets*

#### 3.1.1. *Metals adsorption/desorption laboratory experiments*

No significant ($P > 0.05$) metals were released from the net itself (Net control), with values in seawater, in general, below the detection limit for both Cu and Pb. Metal concentrations in metal control solutions (seawater doped with Cu or Pb without net fragments) showed in some cases a slight decrease over time, always lower than 10 %. Nevertheless, to compensate this decrease, metal adsorption percentages were always calculated taking in consideration metal concentrations in metal control solutions collected at the same time.

For both PE and Thin Nylon fishing nets low Cu adsorption values were generally observed (< 17 %), with an increasing trend of metal adsorption over time (Fig. 2). For the Braided Nylon net, adsorption reached 50 %. So, polymer type and Nylon net thickness showed different Cu adsorption behaviours.

For Pb, the Twisted PE net and the Braided PE presented high adsorption variability over time, but higher for the latter (Fig. 3). Braided Nylon net, with a behaviour similar to Braided PE, showed much high Pb adsorption than the Thin Nylon, for which the adsorption values were quite low (varying from 0 to 7 %). Results clearly indicate that net thickness influenced Pb adsorption.

Braided Nylon net was selected to confirm adsorption results, this time in triplicate. In this experiment, Cu and Pb showed increasing

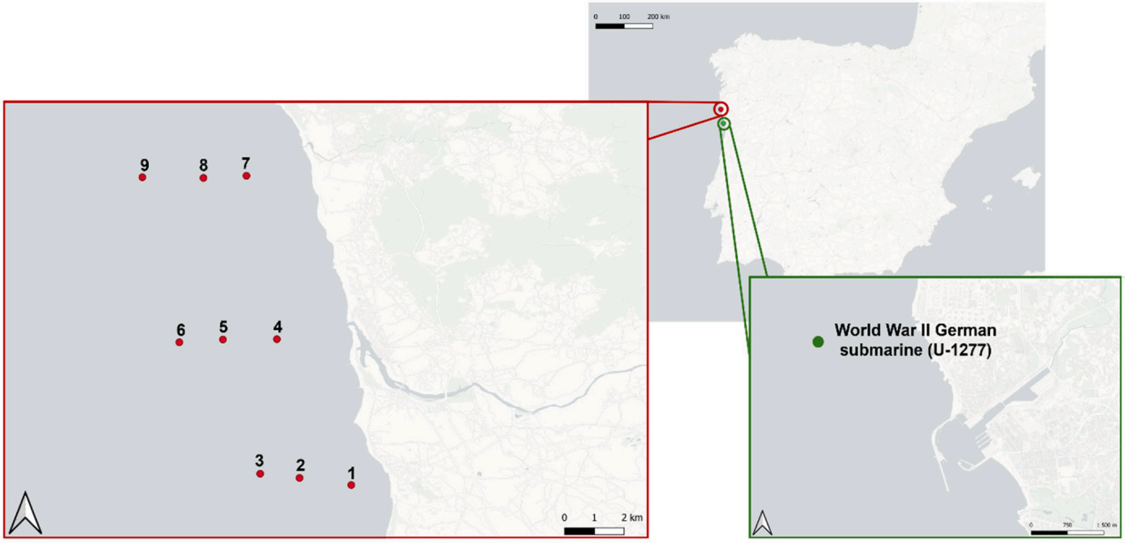


**Fig. 1.** Location of water sampling sites (1–9) at Parque Natural do Litoral Norte (site 1–6 were within ALDFG hotspot area; Site 7–9 were outside ALDFG hotspot area and were used a control) and location of the wreck of the World War II German submarine (U-1277) in Matosinhos coast.

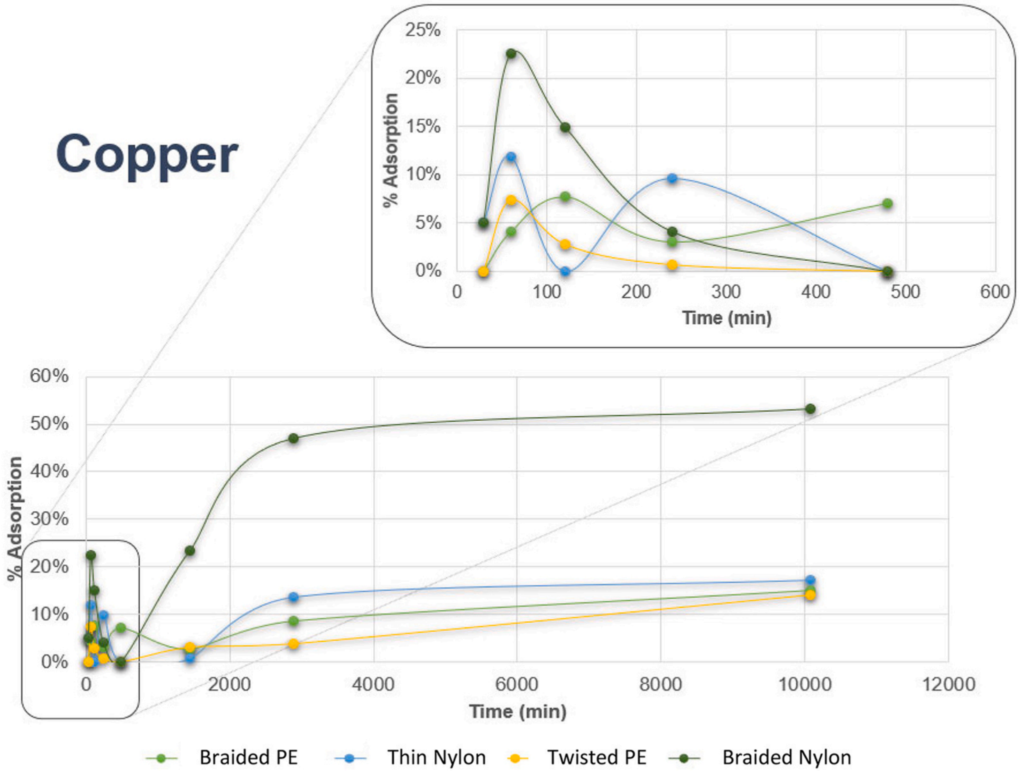


**Fig. 2.** Cu adsorption to different fishing net fragments over time. Samples collected at times 30 min, 1 h (60 min), 2 h (120 min), 4 h (240 min), 8 h (480 min), 24 h (1440 min), 48 h (2880 min) and 7 days (10,080 min).

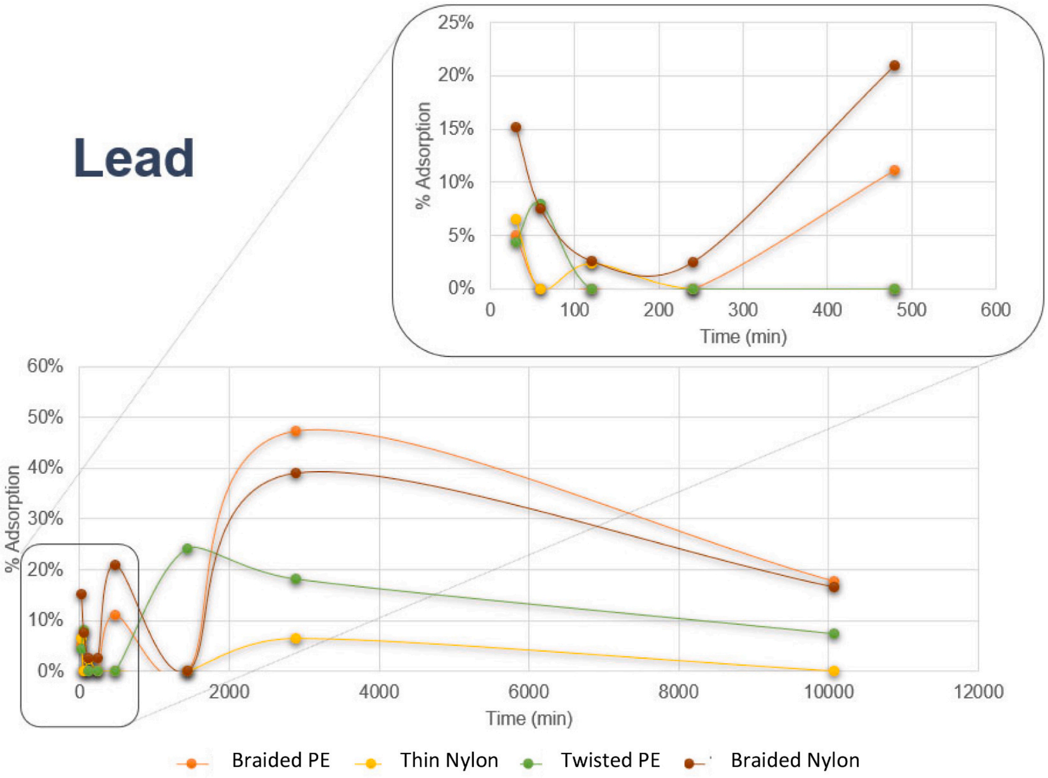


**Fig. 3.** Pb adsorption to different fishing nets over time. Samples collected at times 30 min, 1 h (60 min), 2 h (120 min), 4 h (240 min), 8 h (480 min), 24 h (1440 min), 48 h (2880 min) and 7 days (10,080 min).

adsorption over time (Fig. S2 in supplementary material), in contrast to what was observed previously, where the adsorption percentage varied over time. Variability among replicates was very low. The different results observed among experiments could be related with seawater composition, since it was used seawater collected at different times (seawater was used as collected).

In nylon fishing nets the adsorption percentages observed for Cu were generally higher when compared with those of Pb, similarly to Gao et al. (2019).

Nevertheless, results showed that PE and nylon fishing nets can adsorb Cu and Pb. These results are important, because although PE and nylon are among the most studied polymers in the laboratory context, there are still few studies on the adsorption of metals, with most studies concerning the adsorption of organic compounds (Guo and Wang, 2019), Lima et al., 2023).

Metal desorption experiments showed that for Cu, small amounts of the adsorbed metal were released from the fishing net into the surrounding seawater, but only after 24 h and 48 h (desorption percentages ca. 17±2 % and 27±2 %, respectively). For Pb, no metal was detected in seawater indicating that Pb was not released into the water.

### *3.1.2. PAHs adsorption/desorption laboratorial experiments*

Levels of PAHs in net control solutions (only seawater with net fragments) were always below detection or quantification limits.

Generally, PAHs adsorption in the Braided PE net increased until 48 h, with only a small increase after 24 h (Table S2). For the heavier hydrocarbons, adsorption percentages stabilized after 48 h. For lighter PAHs, compound degradation occurred over time, preventing the evaluation of adsorption rates after 24 h. In fact, after 48 h light PAHs concentrations in doped seawater (without net fragments) were very low. Therefore, the following adsorption experiments were only carried out until 48 h of contact.

Twisted PE net showed also PAHs adsorption but percentages did not increase regularly with PAHs molecular weight, with lower and more irregular adsorption rates after stabilization for the heaviest hydrocarbons compared to Braided PE (Table S3). Braided nylon net showed an adsorption behaviour similar to that of Braided PE net, with high adsorption percentages for each PAH at early time (Table S4). Thin nylon net showed the lower adsorption percentages of the 4 tested nets, with extremely variable adsorption over time for each PAH (Table S5). Table 2 compares the PAHs adsorption behaviour of the four nets tested.

Globally, PAHs adsorption occurred for all nets and the adsorption percentages increased with molecular weight. Heavier hydrocarbons showed higher adsorption percentages since the first sampling and until stabilization.

The Thin nylon net had the smallest diameter (0.3 mm) and the lowest weight, probably explaining the low adsorption of PAHs. Twisted PE net fibres have a diameter smaller than those of Braided PE (respectively 1.8 mm and 3 mm) and the adsorption percentages were lower. However, braided PE fibres have a bigger diameter than those of Braided Nylon but showed lower PAHs adsorptions. Results indicate that adsorption efficiency is dependent of two parameters, the net polymer, that can have more or less affinity to adsorb the pollutant, and the thickness of the net fibres, that influences the surface area available for adsorption.

Braided nylon net fibres had the highest PAHs adsorption values. So, the experiment was repeated with triplicates. Results showed again that adsorption was occurring for all PAHs, with low variability among replicates, and that adsorption rates were higher for heavier hydrocarbons throughout all sampling times (Table 3). Moreover, stabilization rates edify another phenomenon, rates evolve similarly in group: chrysene, benzo(*a*)anthracene, pyrene and fluoranthene have four benzene rings and showed the highest adsorption percentages (ca. 100 %). phenanthrene, anthracene, acenaphthylene, acenaphthene and fluorene have three benzene rings and presented slightly lower adsorption percentages (ca. 90 %). Naphthalene has two benzene rings and presented the lowest adsorption percentage (ca 74 %).

PAHs desorption rates evolve quite similarly in each group (Table S6). Heavier PAHs with four rings showed no desorption. Phenanthrene, fluorene, acenaphthene, and acenaphthylene (all with 3 benzene rings) presented low desorption rates (ca. 15 %). Naphthalene (two benzene rings) presented a slightly higher desorption rate (ca. 24 %).

So, plastic polymers have the potential to adsorb PAHs, but also to release a part of them. Lighter PAHs are more difficult to adsorb, and apparently, they are released more easily. For heavier hydrocarbons, the

**Table 3**
PAHs adsorption percentage (%, mean ± standard deviation, $n = 3$) to Braided Nylon net.

| | Collection times | | | | | | |
|---|---|---|---|---|---|---|---|
| PAHs | 0.5 h | 1 h | 2 h | 4 h | 8 h | 24 h | 48 h |
| Nap. | 33 ± 5 % | 33 ± 8 % | 32 ± 2 % | 37 ± 6 % | 45 ± 3 % | 74 ± 2 % | 66 ± 2 % |
| Ace. | 38 ± 4 % | 13 ± 8 % | 34 ± 5 % | 56 ± 7 % | 64 ± 2 % | 87 ± 1 % | 77 ± 2 % |
| Acn. | 40 ± 3 % | 13 ± 6 % | 33 ± 5 % | 54 ± 8 % | 60 ± 1 % | 87 ± 1 % | 71 ± 3 % |
| Fl. | 44 ± 5 % | 22 ± 6 % | 56 ± 3 % | 68 ± 3 % | 76 ± 2 % | 90 ± 1 % | 81 ± 1 % |
| Phe. | 61 ± 6 % | 69 ± 3 % | 77 ± 1 % | 84 ± 1 % | 87 ± 1 % | 89 ± 1 % | 88 ± 1 % |
| Ant. | 53 ± 6 % | 67 ± 3 % | 80 ± 1 % | 88 ± 1 % | 89 ± 1 % | 90 ± 1 % | 89 ± 1 % |
| Fluo. | 70 ± 12 % | 77 ± 1 % | 89 ± 1 % | 95 ± 2 % | 98 ± 1 % | 99 ± 1 % | 98 ± 1 % |
| Py. | 72 ± 12 % | 80 ± 2 % | 91 ± 1 % | 96 ± 2 % | 97 ± 1 % | 99 ± 1 % | 99 ± 1 % |
| BaA. | 70 ± 4 % | 72 ± 5 % | 89 ± 3 % | 98 ± 1 % | 97 ± 8 % | 96 ± 1 % | 98 ± 2 % |
| Ch. | 65 ± 4 % | 82 ± 6 % | 91 ± 1 % | 97 ±3 % | 97 ± 1 % | 97 ± 1 % | 97 ± 2 % |

**Table 2**
Comparison of PAHs adsorption behaviour for the 4 different nets tested. A = adsorption rate at T1 (0.5 h) (Low: adsorption <15 %; Middle: 15 % < adsorption <30 %; High: adsorption >45 %); B = Evolution over time; +/−: variable; +: always increasing until stabilization; C = adsorption percentage after stabilization.

| | Braided PE | | | Twisted PE | | | Twisted Nylon | | | Thin Nylon | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PAHs | A | B | C | A | B | C | A | B | C | A | B | C |
| Nap. | Low | +/− | 25 % | Low | +/− | 63 % | Middle | +/− | 64 % | Low | +/− | 0 % |
| Ace. | Low | +/− | 40 % | Low | + | 54 % | Middle | +/− | 80 % | Low | +/− | 0 % |
| Acn. | Low | + | 57 % | Low | + | 60 % | Middle | +/− | 77 % | Low | +/− | 0 % |
| Fl. | Low | +/− | 63 % | Low | + | 77 % | High | + | 80 % | Middle | +/− | 0 % |
| Phe. | Low | + | 89 % | Middle | +/− | 92 % | High | + | 91 % | Middle | +/− | 27 % |
| Ant. | Middle | + | 91 % | Middle | + | 89 % | High | + | 84 % | Middle | +/− | 27 % |
| Fluo. | Middle | + | 100 % | Low | + | 82 % | High | + | 99 % | High | +/− | 73 % |
| Py. | Middle | + | 100 % | Middle | + | 88 % | High | + | 99 % | High | +/− | 77 % |
| BaA. | High | + | 97 % | Low | + | 75 % | High | + | 89 % | High | +/− | 78 % |
| Ch. | High | + | 100 % | Middle | + | 74 % | High | + | 96 % | High | +/− | 86 % |

inverse phenomena occur, since they are more easily adsorbed and apparently hardly desorbed. So, adsorption/desorption is correlated to PAH molecular weight.

Some studies have shown that PAHs can be adsorbed to microplastics (e.g Bouhroum et al., 2019, Tan et al., 2019, Nguyen et al., 2022). The adsorption process and efficiency were not limited to small pieces of plastic but also occur for large plastic pieces (Bouhroum et al., 2019) and larger plastic objects such as plastic ropes, buoys, caps, packaging material and many other larger fragments (Jang et al., 2024). Plastic types found in those studies were mainly PE and PP. To our knowledge, no studies until now evaluate the potential PAHs adsorption on nylon and more specifically on nylon fishing nets.

So, obtained results show the potential of adsorption of PAHs to fishing nets.

### 3.1.3. *Metals and PAHs adsorption experiment*

PAHs adsorption percentages on Braided PE net after stabilization were different in the presence of metals and depended on the PAHs (Table 4 and Tables S7 and S8), being i) higher in the presence of metals for naphthalene, acenaphthene, acenaphthylene, fluorene; ii) identical for phenanthrene and anthracene; and iii) slightly lower in the presence of metals for fluoranthene, pyrene, benzo(*a*)anthracene and chrysene.

So, the simultaneous presence of different pollutants can change PAHs adsorption behaviours. On one hand, the compounds can interact and even form complexes that can reduce the availability of the pollutant to adsorb on the polymer and on the other hand there could be a reduction of adsorption sites as one compound can block more easily the adsorption sites. Nevertheless, the results obtained are only informative and further experiments with additional samples and different pollutant concentrations are needed.

## 3.2. *Experiments in quasi-real scenario for evaluating pollutant adsorption to fishing nets*

These experiments aimed to evaluate if plastic fishing nets could potentially adsorb PAHs or metals present in the surrounding water, acting as a sink of these pollutants in the area where nets were placed.

### 3.2.1. *Metal adsorption*

Metal concentrations in particulate matter of Marina Leixões water varied with sampling campaign and site (Table 5).

Metals detected in some cases had levels lower in surface water than in bottom water (no nets), independently of the net type, indicating that fishing nets could be removing metals from the surrounding medium (Table 5).

Nevertheless, significant variability among sampling campaigns was observed. Biological activity, physical and chemical changes resulting from hydrodynamics and seasonal changes and the individual behaviour of each metal can also influence the metal levels at the site. One should be aware that the marina of Leixões is a confined place, which can facilitate the retention of metals in suspended particulate matter. This area is also subject to several anthropogenic factors that can affect metal levels. In fact, the Leça river drains at this marina and along the course of Leça river there are several points of discharge of effluents, sometimes untreated. Downstream from Leça river the area is characterized by high industrial and urban density (Gomes et al., 2014; Rocha et al., 2011; Rodrigues et al., 2019) with two important WWTPs located in its course, discharging effluents as well as with industry of different types, such as stamping and dyeing, metallurgic, mechanical and agri-food (Gomes et al., 2014). All these anthropogenic pressures can influence the values of metals present in the marina of Leixões water. However, observed metal levels were in accordance with the values reported for the area (APA, 2019; Gomes et al., 2014).

Regarding metals extracted from fishing net pieces, in general, all were detected (Table 6). In general, metals in the extraction solution of the new (not used) nets were below the detection limit. When detected, levels were, in general, 10 times lower than values measured in the extraction solution with net pieces from the Marina experiment. In general, metals concentrations extracted from fishing nets was Braided Nylon net > Braided PE net > Thin Nylon net in March and May sampling campaigns, whereas in July sampling campaign the order was Braided Nylon net > Thin Nylon net > Braided net PE. Metal extraction amounts varied not only among nets but also among metals, with Cd and Ni showing very low retention.

Metals levels in nets from the Marina experiment were considerably different from those in the laboratory experiment. In fact, Thin Nylon showed practically no adsorption in the laboratory experiments and in the quasi-real environment metal retention seemed to occur. However, these results may be influenced by the biofilms formed on the surface of the nets (Fig. 4). Microorganisms, including bacteria, protozoa, algae, archaea, fungi, and protists, have the capacity to form biofilms on the surface of plastics (Zettler et al., 2013; Flemming, 2020). These biofilms increased overtime (the nets weight increased over time, Table S1), the same being observed in general for metal levels in PE and thin nylon nets. Thin Nylon was the fishing net where the presence of these biofilms was more significant.

These biofilms can influence metals levels either directly or indirectly. That is, directly, the sorption processes may be taking place in the biofilm itself (Gunaalan et al., 2020), or indirectly, because the formation and development of biofilms may alter the morphology and physicochemical properties of plastics, and consequently the adsorption capacity of metal can be increased (Guan et al., 2020). However, distinguish if the processes of metal sorption in quasi-real environment was occurring in the fishing net or in the biofilm was not possible. Besides, biofilm formation is dependent of the surface of the material but can also change the surface of that material, not only physically but also chemically, which ultimately can also affect contaminants adsorption (Qin et al., 2024).

**Table 4**

Comparison of PAHs adsorption behaviour for Braided PE net in the presence or absence of Pb or Cu. A = adsorption rate at T1 (0.5 h) (Low: adsorption <15 %; Middle: 15 % < adsorption <30 %; High: adsorption >45 %); B = Evolution over time; +/−: variable; +: always increasing until stabilization; C = adsorption percentage after stabilization.

| | Net Braided PE | | | Net + Cu | | | Net + Pb | | |
|---|---|---|---|---|---|---|---|---|---|
| PAHs | A | B | C | A | B | C | A | B | C |
| Nap. | Low | +/− | 25 % | Low | +/− | 47 % | Low | +/− | 55 % |
| Ace. | Low | +/− | 40 % | Low | +/− | 90 % | Low | +/− | 79 % |
| Acn. | Low | + | 57 % | Low | +/− | 92 % | Low | +/− | 83 % |
| Fl. | Low | +/− | 63 % | Low | +/− | 94 % | Low | + | 88 % |
| Phe. | Low | + | 89 % | Low | + | 90 % | Low | + | 91 % |
| Ant. | Middle | + | 91 % | Middle | + | 90 % | Middle | + | 92 % |
| Fluo. | Middle | + | 100 % | Middle | + | 91 % | Middle | + | 90 % |
| Py. | Middle | + | 100 % | Middle | + | 92 % | Middle | + | 89 % |
| BaA. | High | + | 97 % | High | + | 91 % | Middle | + | 89 % |
| Ch. | High | + | 100 % | Middle | + | 88 % | Middle | + | 87 % |

**Table 5**
Metal concentration (μg L$^{-1}$) in particulate matter of Marina Leixões water, collected in February (beginning of the experiment, T0); March (T1); May (T2) and July (T3) 2020. Control corresponds to bottom water samples without fishing nets and Fishing net corresponds to surface water samples where fishing nets are present. Net A - Braided PE, Net B - Braided Nylon and Net C - Thin Nylon. Mn and Ni were below detection limit (1.2 μg L$^{-1}$ for Mn and 0.6 μg L$^{-1}$ for Ni). Cu and Pb were in general also below detection limit (1.2 μg$^{-1}$ for Cu and 0.6 μg L$^{-1}$ for Pb). Cd was only detected in some samples in the last sampling campaign, varying between 0.37 and 0.55 μg L$^{-1}$ (Cd detection limit: 0.12 μg L$^{-1}$).

| | *Zn* | | | | *Fe* | | | | *Cr* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Sampling time* | T0 | T1 | T2 | T3 | T0 | T1 | T2 | T3 | T0 | T1 | T2 | T3 |
| Control A | 3.5 | 4.5 | 0.9 | 5.7 | 122 | 146 | 56 | 32 | 0.34 | 0.42 | 0.26 | 0.35 |
| Fishing net A | 1.0 | 0.8 | 4.3 | <LOD | 31 | 72 | 53 | 19 | 0.32 | 0.48 | <LOD | <LOD |
| Control B | 5.2 | 1.8 | 1.7 | 2.1 | 217 | 100 | 78 | 37 | 0.63 | n.d | <LOD | <LOD |
| Fishing net B | 0.7 | <LOD | <LOD | <LOD | 48 | 65 | 31 | 16 | 0.37 | <LOD | <LOD | <LOD |
| Control C | 3.0 | 2.6 | 0.8 | 1.4 | 77 | 160 | 48 | 31 | 0.34 | 0.48 | 0.29 | <LOD |
| Fishing net C | 1.3 | 0.8 | <LOD | <LOD | 36 | 87 | 51 | 18 | <LOD | 0.45 | <LOD | <LOD |

Limit of detection (LOD) for Zn: 0.60 μg L$^{-1}$; for Cr: 0.24 μg L$^{-1}$; n.d – not determined, sample lost.

**Table 6**
Metal concentration (μg L$^{-1}$, except Fe in mg L$^{-1}$) extracted from fishing nets exposed in Marina of Leixões: Site A (Braided PE), Site B (Braided Nylon) and Site C (Thin Nylon). Samples were collected in March (T1); May (T2) and July (T3) 2020. Metal levels released by new, not used, net are also included. Results are presented per litre of extraction solution.

| Net | Sampling campaign | Cu | Zn | Fe | Pb | Cd | Ni | Mn | Cr |
|---|---|---|---|---|---|---|---|---|---|
| A | New net | <50* | <25* | 0.3 | 20 | <0.50* | 7.5 | <50* | 1.9 |
| | T1 | 354 | 800 | 24.4 | 204 | 0.8 | 15.4 | 745 | 61 |
| | T2 | 424 | 915 | 22.3 | 210 | 1.6 | 15.8 | 1454 | 50 |
| | T3 | 513 | 866 | 21.2 | 386 | 1.1 | 7.8 | 1050 | 70 |
| B | New net | 57 | 0.104 | 0.4 | 32 | 0.7 | 7.7 | 229 | 2.2 |
| | T1 | 1014 | 1609 | 62.2 | 480 | 3.0 | 49.5 | 1243 | 185 |
| | T2 | 504 | 1145 | 33.9 | 256 | 2.5 | 21.9 | 1159 | 82.5 |
| | T3 | 623 | 1087 | 37.2 | 361 | 1.4 | 19.8 | 111 | 102 |
| C | New net | <50* | <25* | <0.10 | 20 | <0.50* | 4.0 | <50* | 1.4 |
| | T1 | <50* | 852 | 2.1 | 49 | <0.50* | 6.2 | 72 | 19 |
| | T2 | 124 | 372 | 10.7 | 124 | <0.50* | 6.8 | 140 | 31 |
| | T3 | 543 | 1014 | 34.7 | 411 | 1.2 | 8.9 | 773 | 91 |

[*] Detection limit.

### 3.2.2. *PAHs adsorption*

PAHs levels in surface and bottom water showed high variability among nets locations and over time with no clear trend (Table S9). Acenaphthylene, acenaphthene, fluorene and anthracene were always below detection or quantification limits. Fluoranthene, pyrene and chrysene levels were only detected at the beginning of the experiments. Phenanthrene and benzo(*a*)anthracene were detected irregularly, without difference between bottom and surface waters. Naphthalene was detected only at the end of the experiment. Therefore, the presence of the nets showed no significant influence on the PAHs levels in their surrounding waters.

In general, all PAHs were detected on the nets' extraction solution however with high variability and irregularity and with no clear differences over time or between nets (Table 7). Besides, for some PAHs, extraction solution from new nets also contained PAHs. So, only naphthalene, acenaphthene, fluorene, phenanthrene seemed to be adsorbed to braided nylon, and benzo(*a*)anthracene to braided PE.

Observed results are different from those observed in laboratory control experiments where PAHs were fully adsorbed to all fishing nets. As mentioned for metals, adsorption of pollutants to fishing nets can be dependent not only on physical-chemical processes, but also on biological processes, due to the formation of biofilm on fishing net surfaces. Biofilm formation seems to have a significant impact on PAHs adsorption, which seemed more relevant for the thick net, the braided nylon.

As mentioned for metals, PAHs levels detected can be adsorbed on the net itself or in the biofilm or even both. PAHs tend to adsorb on organic matter, including biofilms, whose amount on the nets increased over time and this can justify the slightly increase over time for some PAHs. As mention, biofilms can also change the material surface, altering the specific surface area or its hydrophobicity, which can alter contaminants adsorption, mostly increasing it (Qin et al., 2024). Nevertheless, the high variability in PAHs adsorption can also be dependent on the availability of the contaminant in the water. In fact, PAHs levels in the water were very variable, probably due to the different anthropogenic pressures affecting the marina of Leixões water as discussed for metals. PAHs levels in these waters were, however, not much higher than levels detected in nearby beaches (Rocha et al., 2017).

Globally, results did not show any correlation between PAHs levels found in the water and levels adsorbed on the nets over time.

## 3.3. *In situ survey of metals and PAHs in ALDFG hotspots*

In general, low levels of all analysed trace metals and PAHs were found throughout the seasonal campaigns, in both ALDFG hotspots (located in PNLN and in Matosinhos submarine wreck) (Tables S10 to S13). Metals and PAHs levels were, in general, considerably lower than the established guidelines (Bakke et al., 2010). Water was, in general, classified as of "good environmental conditions" and sediments in general were classified as "background" taking into consideration the two types of contaminants (Bakke et al., 2010).

The NW of Portugal is part of the Iberian Peninsula ecoregion, and receives the influence of three oceanic water masses. This area is highly urbanized, hosting the second major city of Portugal (Porto), with high population density and several industrial and urban activities, such as an oil refining industry and two maritime harbours (located at *Leixões* and *Viana do Castelo*). Moderate concentrations of metals and PAHs have been previously reported in sediments of this NW coast (Mucha et al., 2004; Guimarães et al., 2009; Gravato et al., 2010; Rocha et al., 2011; Mil-Homens et al., 2013; Reis et al., 2013). Nevertheless, some rocky shore beaches (e.g., *Carreço*, *Vila Chã*) have been used as a reference site since they show low susceptibility to human influence and low levels of environmental contamination (Cairrão et al., 2004; Rodrigues et al.,

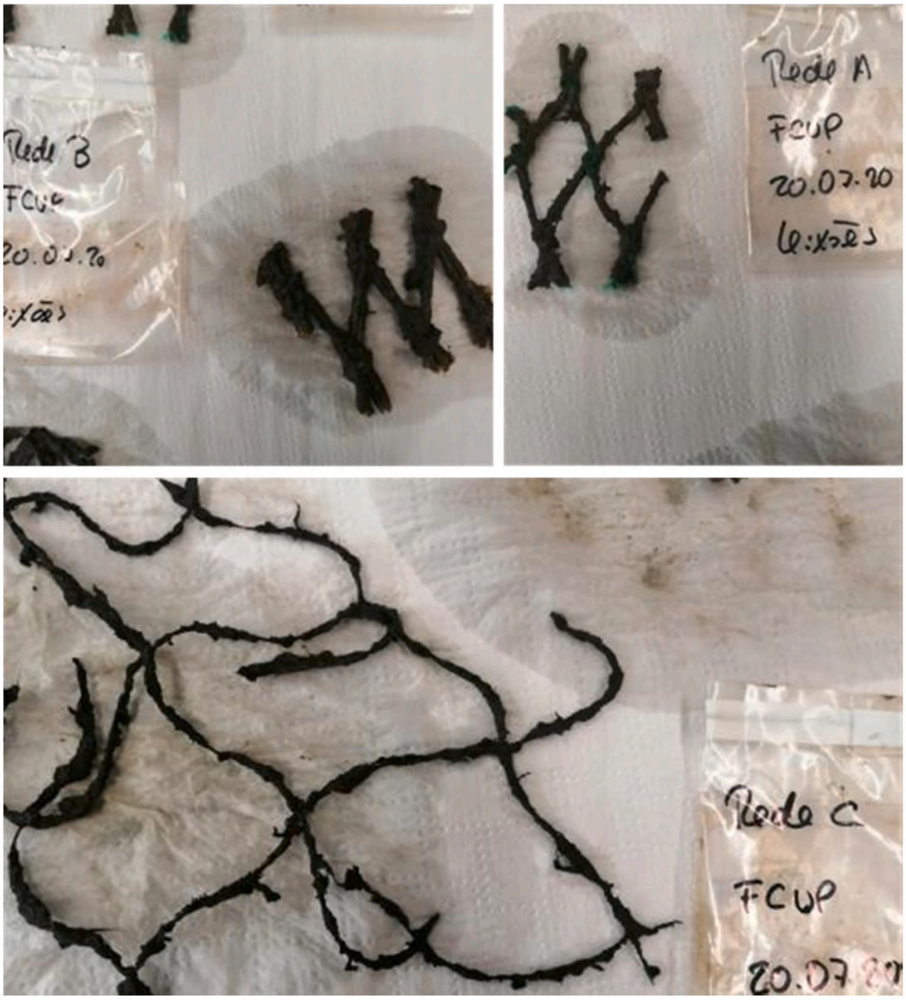


**Fig. 4.** Fishing nets collected in the Marina experiment: Braided PE (net A), Braided Nylon (B) and Thin Nylon (net C) showing biofilm formation.

**Table 7**
Levels of polycyclic aromatic hydrocarbons (PAHs (ng/g); $n = 1$) extracted from fishing nets exposed in Marina of Leixões: Site A (Braided PE), Site B (Braided Nylon) and Site C (Thin Nylon). Samples collected in March (T1); May (T2) and July (T3) 2020. PAHs levels released by new, not used, net are also included. Results are presented per litre of extraction solution.

| | Sampling campaign | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | New net | | | T1 | | | T2 | | | T3 | | |
| PAHs | A | B | C | A | B | C | A | B | C | A | B | C |
| Nap. | 3.7 | 5.1 | 11.0 | 1.8 | 13.2 | 7.1 | 4.2 | 14.6 | 3.7 | 3.2 | 16.8 | 2.0 |
| Ace. | 11.3 | 21.3 | 10.6 | <2.0* | 11.5 | <2.0* | <2.0* | 15.1 | <2.0* | <2.0* | 14.2 | <2.0* |
| Acn. | <1.0* | <1.0* | <1.0* | <3.0** | 20.5 | <3.0** | <3.0** | 26.3 | <3.0** | <3.0** | 19.2 | <1.0* |
| Fl. | 13.7 | 15.1 | 11.7 | 14.3 | 84.5 | 12.9 | 16.8 | 120.5 | 11.1 | 16.1 | 104.7 | 13.6 |
| Phe. | 10.7 | 20.3 | 7.2 | 10.3 | 130 | 14.5 | 12.6 | 201 | 5.2 | 12.1 | 161 | 8.1 |
| Ant. | 12.9 | 12.8 | 9.6 | 11.4 | 15.1 | <0.5* | 10.7 | 26.4 | <0.5* | 10.1 | 16.8 | 10.2 |
| Fluo. | 20.0 | 37.2 | 8.1 | 5.8 | 36.8 | 6.5 | 7.1 | 26.2 | 5.1 | 6.8 | 14.3 | <2.0* |
| Py. | 14.0 | 43.4 | 12.1 | 7.3 | 21.6 | <1.1* | <1.1* | 27.8 | 7.5 | 7.3 | 50.0 | 8.23 |
| BaA. | <4.3** | 55.4 | 45.3 | 41.0 | 19.5 | 7.2 | 14.8 | 65.7 | 8.8 | 31.9 | 168 | 20.8 |
| Ch. | <0.41* | 22.1 | 3.4 | <0.41* | <0.41* | <0.41* | <0.41* | 19.3 | <0.41* | <0.41* | 39.4 | <0.41* |

* Detection limit.

** Quantification limit.

2013). In fact, in general, the Portuguese northern rocky shores present minor contamination levels even with a high human activity and exploitation of the coastal resources (Rocha et al., 2018).

### 3.3.1. *ALDFG hotspot in PNLN*

Levels of Pb, Cd, Mn and Cr in water suspended particulate matter were in general below detection limits, whereas levels of Cu, Zn, Fe and Ni were detected in almost all samples (Table S10). Levels varied significantly among sites and among sampling campaigns with no clear pattern of variation. Metal levels in water suspended particulate matter depend on water hydrodynamics that can vary with the season. Besides, each metal can present a different behaviour as they are involved in different biogeochemical processes. Overall, metal levels were similar to those reported in other studies conducted in NW Portugal for seawater

(APA, 2019). At the PNLN area, the main human activities are fisheries, small-scale agriculture, small city nearby (Esposende) and maritime touristic activities. In fact, severe contamination by urban, agricultural and industrial effluents is unlikely to occur. However, the area is close to the Cávado River, which is subject to a strong industrial and anthropogenic activity along its course that can increase metal levels (Gredilla et al., 2015), this study showed relative low values for metal concentrations. Such low metal contamination observed supports the good environmental quality of PNLN area, a marine protected area. No clear influence of proximity of ALDFG was evident on metal levels as those levels were identical between sites with and without (control) lost fishing nets.

For sediments, in general, all metals were quantified above the detection limit, with the exception of Cd and Ni (for some samples) for which levels were below the detection limit (Table S11). Overall, the levels observed were in accordance with levels found around this area (APA, 2019). Summer sampling showed, in general, lower levels of metals than winter sampling. For Cu, Fe, Pb, Cd and Cr, levels were in general identical among sites, but Zn, Ni and Mn showed clear variation. The observed variability between sites could be associated with several factors, namely biological activity, physico-chemical changes derived from hydrodynamics, sediment geology or anthropogenic pressures (Rocha et al., 2019). Hence, no clear influence of ALDFG on metal levels in sediments was observed.

Regarding PAHs, among the 10 PAHs analysed, only naphthalene, phenanthrene and fluoranthene were detected in water samples, but at very low levels (Table S12). Overall, PAHs levels were similar to those reported in other studies conducted in NW Portugal for seawater (Rocha et al., 2018; APA, 2019). PAHs are semi-volatile compounds with low water solubility and therefore, they tend to adsorb to sediments, and normally are not detected in the dissolved water phase (Iglesias et al., 2020). No clear pattern of distribution among sites with and without ALDFG was observed but, in general, levels were higher in summer. As mentioned, this area is a marine protected area, but has several recreational and touristic activities, with typically have higher frequency during the summer, which may induce some anthropogenic pressures during this season. The low values detected do not allow to identify any influence of ALDFG on PAHs levels in water of this location.

As mentioned, PAHs tend to adsorb to sediments, thus justifying the occurrence of higher diversity and levels of PAHs found in sediment (Table S13) compared to water (Table S12). Four of the ten analysed PAHs were detected in several samples, the levels being in general higher in the winter sampling campaign. Considering a higher anthropogenic pressure in summer, as discussed above, it can be hypothesised that PAHs adsorption to sediment occurs and that higher adsorption reflects only in the season after. Nevertheless, levels were still low, being in the same order of magnitude as those reported for this area (APA, 2019). In general, PAHs levels were identical among sites with and without (control) lost fishing nets. Therefore, no clear influence of lost fishing nets was evident on PAHs levels.

### 3.3.2. ALDFG hotspot in Matosinhos submarine wreck

Metal levels in water suspended particulate matter were in general below detection limits (Table S14). The only element detected in all samples was Fe, which presented a high variability between sampling campaigns. Moreover, in the second sampling campaign, Fe levels varied also among sites, with a tendency for higher levels at site B. Water suspended particulate matter depends on water hydrodynamics that can vary with the season. Metal levels observed were in general lower than those reported for seawater in the NW Portuguese coast nearby (APA, 2019). The very low metal levels prevented observing any clear influence of ALDFG on metal levels. The Matosinhos submarine wreck hotspot is located near an oil refinery and a commercial harbour. Although some oil spills have occurred in the past, at the present, contaminants levels reports have shown low levels (e.g., Gouveia et al., 2018). This area can also be affected by Douro river plume. The Douro estuary is highly impacted by severe pressures (Ramos et al., 2015; Rodrigues et al., 2019), although current studies have shown a significant decrease in contaminants levels (Iglesias et al., 2020). As such, low contaminant levels were expected at this Matosinhos location, particularly being localised off shore.

Metal levels in sediments were in general low (Table S15). In fact, most levels were below the detection limits. Only Fe, an element commonly present in the Earth crust, was detected in all collected samples, similarly to what was observed in water suspended particles. Metal levels observed were in general lower than those reported for the NW Portuguese coast nearby (APA, 2019). At each site, in general, no relevant differences were observed among collected samples (two or three per site). Comparing the selected sites, in general, no differences were observed, although in some cases metal levels were slightly higher in the site selected as control, site C, which could be related to the type of sediment or the hydrodynamics of the sites. Therefore, ALDFG did not seem to contribute for an accumulation of metals around the wreck of the submarine. Comparing the two sampling campaigns, metal levels were similar, with the exception of Cr. Seasonal variability in environmental metal levels has been observed and can be due to several factors, such as biological activity and physico-chemical changes associated with water dynamics, sediments geology and anthropogenic pressures (Rocha et al., 2019).

PAHs levels in water were very low, with most PAHs levels being below detection or quantification limits (Table S16), being of the same order of magnitude as levels reported in other studies in the NW Portuguese coastal area nearby (APA, 2019). Among the ten PAHs measured only three were quantified: naphthalene, phenanthrene and benzoanthracene. Some differences were observed between sampling campaigns, mainly for naphthalene, but without a clear pattern. Although a few differences among sites were observed, for example, naphthalene was higher at site B in the June sampling campaign, no clear pattern could be established. So, no clear influence of ALDFG on PAHs levels was perceived as there was no clear differences between sites within the hotspot area and out of the area.

In general, PAHs values in sediments were below detection limits, only naphthalene was detected in several samples, with no relevant differences among sites (Table S17). Levels were of the same order of magnitude of those reported in other studies in NW Portuguese coastal area nearby (APA, 2019; Gouveia et al., 2018). As for water, no clear influence of ALDFG was observed as levels were very low and no there was no clear differences among sites within the hotspot area and out of the area.

## 4. Conclusions

The results obtained in the current work suggested that fishing nets effectively have the potential for adsorption of metals and PAHs, concentrating pollutants on their surface and potentially functioning as sinks of pollutants. Although low metal and PAHs concentrations in the environmental characterization of the ALDFG hotspots in study prevent from inferring a clear effect of ALDFG, adsorption laboratory experiments and experiments in quasi-real environment (in situ experience in Marina of Leixões), clearly showed the potential for adsorption of metals and PAHs to fishing gear.

Laboratory adsorption experiments showed that the exposure time can effectively influence pollutants adsorption, a feature observed in general for all fishing nets. Besides, adsorption is also influenced both by the fishing net polymer and by its structure and thickness, as well as by the pollutant characteristics, indicating that these sorption processes are dependent on physical-chemical processes. In addition, laboratory experiments also indicated that a percentage of adsorbed pollutants (metals or PAHs) could be released again into the medium.

On the other hand, experiments in quasi-real environment indicate that, in addition to physical-chemical processes, the biological component (biofilm) present in the fishing nets can influence and increase pollutants (metals and PAHs) retention in fishing nets. For instance, metal retention was an order of magnitude higher than that recorded in the adsorption laboratory experiment.

ALDFG pose an environmental risk, being dangerous for marine life, since several aquatic species can be easily entangled in this fishing gear and may even ingest smaller fragments of lost gear. It is known that a wide range of aquatic organisms easily confuses natural food with plastic fragments (Botterell et al., 2019; Chouchene et al., 2023; Pereira et al., 2023), accidentally ingesting them and, consequently, the upper trophic levels can accumulate these plastic fragments indirectly, by biomagnification (Gao et al., 2024). The present study showed that fishing nets can have another environmental risk, associated with their capacity to adsorb pollutants and act like a pollutant sink, which can cause harm to aquatic organisms, being an environmental hazard. As so, initiatives to prevent the loss of fishing gear as well as initiatives to retrieve ALDFG are needed to reduce and/or eliminate their environmental impact.

Although none of the results and conclusions obtained in these studies should be neglected, their interpretation needs to be taken with caution, since in laboratorial experiments it is not possible to account with all potential drivers involved in the process under analysis. Thus, we emphasize that more field studies are needed to fully understand the harmfulness that fishing nets can pose to the environment. Models that explain how these adsorptions occur and what the exact factors that make these adsorptions vary need to be clarified. Various types of plastic polymers, whether they are of higher or low density, should also be studied for sorption capacities. So, further studies are necessary to clarify these sorption processes, and for example, it would be interesting to assess the potential of fishing nets in sites known to be environmentally contaminated. For instance, a study concluded that metals concentrations in water significantly influence metals concentration in microplastics (Purwiyanto et al., 2020). Hence, the results obtained will significantly contribute to the scarce information available in the literature on the interaction of inorganic compounds (metals) and organic compounds (PAHs) with fishing nets, which are frequently detected in our rivers and oceans.

## CRediT authorship contribution statement

**C. Marisa R. Almeida:** Writing – review & editing, Validation, Supervision, Resources, Investigation, Funding acquisition, Conceptualization. **Rafaela Perdigão:** Writing – original draft, Methodology. **Bárbara Ribeiro Correia:** Writing – original draft, Investigation, Formal analysis. **Henry Van Der Gracht:** Writing – original draft, Investigation, Formal analysis, Conceptualization. **Sofia Dias:** Writing – review & editing, Validation, Formal analysis. **Catarina Magalhães:** Writing – review & editing, Resources, Funding acquisition. **Maria F. Carvalho:** Writing – review & editing, Resources, Funding acquisition. **Ana P. Mucha:** Writing – review & editing, Resources, Funding acquisition. **Francisca Espincho:** Writing – review & editing, Validation. **Sandra Ramos:** Writing – review & editing, Supervision, Resources, Investigation, Funding acquisition, Conceptualization.

## Declaration of competing interest

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

## Acknowledgments

This research was supported by NETTAG+ project funded by the European Union under the Horizon Europe Program, Grant Agreement No. 101112812, NetTag project financed by EMFF-EASME (EASME/EMFF/2017/1.2.1.12/S2/02/S12.789121) and partially by OMARE project (POSEUR-15-2016-54) and national funds through FCT - Foundation for Science and Technology within the scope of UIDB/04423/2020 and UIDP/04423/2020, a research contract to S.R. (DL57/2016/CP1344/CT0020) and by the PhD fellowship attributed to Rafaela Perdigão with the reference 2020.04689.BD (doi:10.54499/2020.04689.BD) financed by FCT. Authors acknowledge *Submersus* school divers for water samples collection and all people involved in sampling.

Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2024.117291.

## Data availability

At https://doi.org/10.5281/zenodo.14047068

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