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Chapter 11

The Effect of Fishing Nets Aging on Metal Uptake



Ana Teresa Macas Lima , Ida Maria Gieysztor Bertelsen ,
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Abstract Fishing nets are mainly constituted of Polyethylene (PE), Polyamide, Polyethylene terephthalate (PET), Polypropylene (PP), and Nylon. While new, these plastics exhibit pristine mechanical performance but lose it as they age. But what about their metal adsorptive performance? Literature finds that plastics like PET and PVC accumulate Al, Cr, Mg, Fe, Co, Ni, Zn, Cd, and Pb, even when exposed to very low concentrations. This is mainly true for aged PVC (Kedzierski et al. Adsorption/desorption of Micropollutants. *Mar Pollut Bull.* 127:684–694, 2018). In this study, we look at the effect of age on the properties of fishing nets, including their capacity to adsorb metals. Because fishnets are in great part constituted by PE, we used standardized PE pellets as our reference. In calorimeter signaling, we observed that end-of-life fishing nets display a very different differential scanning calorimetry (DSC) pattern; both new and old fishing nets are very different from standardized PE polymer. Preliminary results show that Cr, Cu, Pb, and Se adsorption onto fishing nets occurs in the first 10 min to 6 h of exposure (24 h for Se). The maximum uptake was registered at 11 mg Cr kg⁻¹, 38 mg Cu kg⁻¹, 27 mg Pb kg⁻¹, and 15 mg Se kg⁻¹. All these concentrations refer to *old* end-of-life PE fishing nets, where *new*, unused PE fishing nets adsorb 2–20 times less (*Old* in this chapter refers to used fishing nets. The term is not attempting to attribute a particular life span/age to the nets). A comparison to different EU directives that regulate metal content in plastics for different end-uses shows that the old end-of-life PE fishing nets, after exposure to heavy metals, do not meet the regulations for hazardous waste. We believe that Greenlandic old waste

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fishing nets can be used to clean the wastewater, or metal-contaminated water, in Greenland and eventually, the rest of the world.

Keywords Fishnets · Polyethylene · Metal adsorption · End-of-life · Wastewater

11.1 Introduction

Fishing nets are mainly comprised of Polyamide, Polyethylene (PE), Polyethylene terephthalate (PET), Polypropylene (PP), or Nylon (reference). Production of plastics is currently around 381 million tons annually (Amirkhanian 2020), with production estimated to increase annually if no ban is officially set by governments (Geyer et al. 2017). Approximately 8 million tons of these plastics end up in the oceans (Jambeck et al. 2015), with an estimated 10–20% of global ocean plastic waste coming from marine sources, such as fishing nets (Hannah and Roser 2018; Moore 2008). Ghost nets are fishing nets found in the seawater, floating or deposited together with sediment after usage (Moore 2008). In Greenland, where 50% of plastic waste on the shores is from marine sources (McGwin 2021), fishing nets pose a great threat to local fisheries. The ministry suggests starting clean-up efforts in three of the most heavily fished areas, covering 420 km² (McGwin 2021).

It is known that metals adsorb directly to plastic surfaces or co-precipitate with or adsorption to hydrous iron and manganese oxides (Mitchell et al. 2019). In 1978, Cutter observed a loss of 59% of selenate in Polyethylene bottles within five days. Longer-term adsorption of metals onto plastics has been studied in situ to understand the impact of plastics on the ocean and its role in the cycling, retention, and desorption of elements in the ocean environment (Kedzierski et al. 2018; Rochman et al. 2014). Plastics like PET and PVC have been widely studied for metal adsorption, in particular, and accumulated Al, Cr, Mg, Fe, Co, Ni, Zn, Cd, and Pb (Rochman et al. 2014; Zhang et al. 2020). Ashton et al. (2010) considered that the possible mechanisms for metal adsorption were due to the direct adsorption of cations (or complexes) onto charged sites or neutral regions of the plastic surface. They also concluded that heavy metals have a high affinity for plastics since plastics are composed of organic polymers. The reactivity of plastic pellets toward trace metals is attributed to the short-term adsorption of organic matter and the long-term aging and modification of the plastic pellet surface. Quantitatively, adsorption constants on a mass basis are lower than respective constants defining adsorption to suspended sediments; however, it must be appreciated that the specific surface area of weathered or modified plastics is orders of magnitude lower than that of fine sediment (Holmes et al. 2014). From these studies, Kedzierski et al. (2018) found that aged PVC adsorbs large amounts of heavy metals. This is a curious result since most plastics at sea are used and aged to a certain degree (Holmes et al. 2012).

Plastics, or polymers, can be characterized by different techniques. One of them uses thermal treatments. Thermal gravimetric analysis (TGA), coupled with differential scanning calorimetry (DSC), is a method which has been previously used as a polymer characterization tool, where a unique endothermic/exothermic signal characterizes individual polymers (Kayacan and Doğan 2008; Kannan et al. 2014). These signals create a fingerprint to the material that depends on (i) the molecular weight distribution and branching, (ii) crystallinity, and/or (iii) crystallite morphology of the polymer. The wear and tear of fishnets, i.e., the usage of the polymers, may be detected by thermal treatment.

In the BCE project, we looked at ways to reuse/recycle these fishing nets because of the increasing amount of fishing nets found at shores and drifting in the ocean. In this chapter, we look if EOL fishing nets are hazardous after increased exposure to metals. We test the hypothesis that they can be (re)used one last time as adsorbents for metals in, e.g., wastewater. Conventional methods for heavy metal removal from wastewater include reduction, precipitation, ion exchange, filtration, electrochemical treatment, membrane technology, and evaporation removal, all of which may be either ineffective or prohibitively costly, especially in the case of the metals dissolved in large volumes of solution at relatively low concentrations (Özcan et al. 2005; Feng et al. 2009). With this in mind, we test the hypothesis that *old* end-of-life PE fishing nets can be used to adsorb metals and treat industrial wastewater. This hypothesis stems from previous findings, where studies have observed that metals and hydrophobic organic chemicals adsorb onto plastic (Holmes et al. 2012; Koelmans et al. 2016).

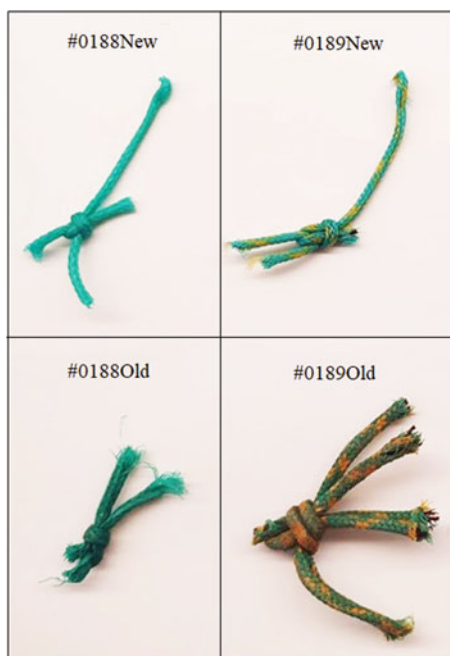
11.2 Methodology

11.2.1 Materials

Four different types of Polyethylene (PE) fishnets were chosen to carry out this study. Figure 11.1 shows the 2 types of PE polymer. New, unused fishnets were collected at the producer—EURONETE, Denmark. The main factory characteristics are listed in Table 11.1. These fishnets were chosen because of their widespread use by Greenlandic fishermen. Discarded fishnets were collected at a dumpsite in Sisimiut in April 2016, at the end of their usage by local fishermen (Fig. 11.2).

We characterized 4 fishing net samples as illustrated in Fig. 11.1: 2 unused (new) fishing nets and 2 used (old) fishing nets of the same type. The next sections describe the methods used.

Fig. 11.1 Visual representation of unused and discarded, end-of-life fishnets. Photograph by the authors



11.2.2 TGA and Fishing Nets Visualization

Thermal gravimetric analysis (TGA), coupled with differential scanning calorimetry (DSC), uses between 3 and 1000 mg of sample to determine accurate mass loss from exposure to the rising temperature. These tests are standard for determining PE kinetics, namely dynamic methods (Kayacan and Doğan 2008; Aboulkas et al. 2010; Cai et al. 2008) and isothermal methods (Encinar and González 2008). In these studies, sample weight loss data is obtained by heating the sample under controlled conditions of desired temperature and gaseous environment, adopting non-isothermal (dynamic) or isothermal techniques. In this study, we used dynamic settings in which the sample is submitted to a thermal program that includes a temperature range from 30–600 °C at the heating rate of 10 K min⁻¹. All experiments used a constant flow rate of nitrogen as a purge gas, as described in (Kannan et al. 2014), followed by an N₂ flow rate of 250 cm² min⁻¹. The initial mass of each sample was approximately 20 mg.

High-resolution pictures were made with a macro lens, Nikon D 610 (24 Megapixel), Kaiser RB 5000 Daylight Copy Light Set at 5.5 cm between lens and sample.

Table 11.1 Description of the unused fishnets, their composition as described by the seller, physical performance, and applications (described in http://www.euronete.com/products/view_product/1/5/)

Internal ref.	Name	Composition	Diameter (mm)	Breaking strength (kg)	Applications
#0188	Twisted Polyethylene	Polyethylene	2.5	100	Bottom Trawling (Cod-ends, upper and lower panels) Aquaculture' (Bird Netting)
#0189	Euroline	Polyethylene	2.2	100	Bottom Trawling (Cod-ends, upper and lower panels) Aquaculture (Predator Netting, Bird Netting)



Fig. 11.2 Dumpsite containing discarded fishing nets in Sisimiut, Greenland. Photographs by the authors taken in April 2016

11.2.3 Adsorption Experiments (1)

Of the selected fishnets, we exposed #0188 and #0189 fishnets, both new and old, to a known concentration of metals. The metal solution was prepared from a standard concentrated solution of 0.5 mg L^{-1} of Cr, Cu, Pb, and Se aqueous solution, at a neutral pH (≈ 7). These concentrations are approximately two orders higher than those in contaminated inshore waters (Jonas and Millward, 2010). Still, we chose those values for determining the maximum adsorption of Cr, Cu, Pb, and Se onto PE.

The experimental procedure was adapted from Holmes et al. (2012). 0.25 g of fishnet PE was put in contact with 20 ml of 0.5 mg L^{-1} Cr, Cu, Pb, and Se aqueous solution in glass vials with Teflon caps for 5, 10 and 30 min, 1, 3, 6, 24, 48, 113, and 163 h. The vials were kept at a shaking table, as exemplified in Fig. 11.3. The (kinetic) experiments were undertaken in duplicate and included a metal-free control, with the same 0.25 g of fishing net PE, and added to 20 ml of ultra-pure deionized water. Blank vials were also added with only 20 ml of 0.5 mg L^{-1} Cr, Cu, Pb, and Se aqueous solution (no PE fishing nets added). After the contact time, liquid and solid PE were separated and analyzed. Liquid samples were transferred to polypropylene flasks and acidified to $\text{pH} < 2$ with $50 \mu\text{l}$ of HNO_3 . Then, liquid solutions were analyzed directly in an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). A solid PE fishing net was first microwave digested, and then, the solution was analyzed in ICP-OES. Pellets were transferred to 8 ml glass vials with 2.5 ml of ultra-pure deionized water and ultrasonicated for 3 min to extract adsorbed trace metals and minimize digestion of pre-existent metals. After this, fishnet PE was transferred to Teflon vials (Fig. 11.3b) and then digested in a Multiwave GO microwave digestion system (Fig. 11.3c). Plastics were digested in a mixture of concentrated HNO_3 and HCl (Hildebrandt et al. 2020). Finally, digested fishnet PE was diluted and measured in the ICP-OES.



Fig. 11.3 Illustration of the instruments used in obtaining metal adsorption curves. **a**—fishnet PE in contact with metal solution in a shaking table; **b**—PE in a Teflon vial in preparation for microwave digestions; **c**—multiwave GO microwave digestion system. Photograph by the authors

11.3 Results and Discussion

11.3.1 Evidence of PE Fishing Nets Aging

The aging of fishnets is visible in Fig. 11.4. We show the effect of aging at the microscale by comparing unused fishnets provided directly by the supplier (Table 11.1) from the supplier clearly shows the aging of fishing nets at the microscale.

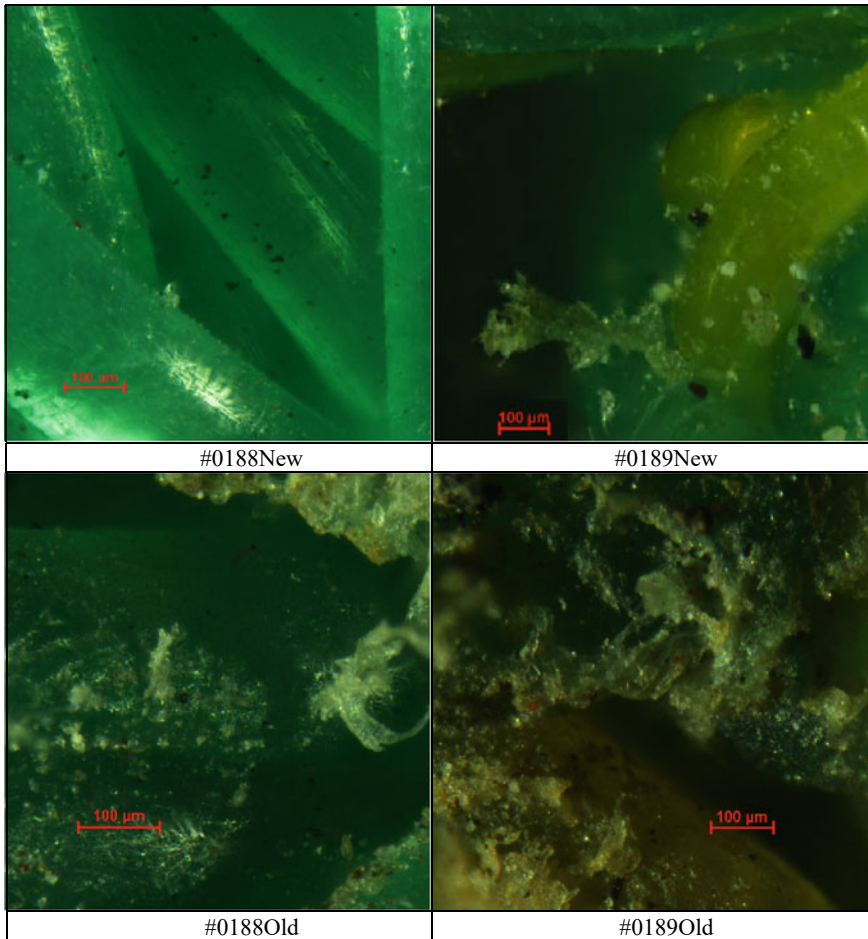


Fig. 11.4 Images of PE fishing nets #0188 and #0189 both in unused and end-of-life conditions. Pictures were made with a macro lens, Nikon D 610 (24 Megapixel), Kaiser RB 5000 daylight copy light set at 5.5 cm between lens and sample. Microscope pictures by the authors

By comparing the old and new #0188 and #0189 fibers, we see that the old PE fishing net shows a higher surface rugosity and increased fiber tear (Fig. 11.4). This effect is a consequence of the wear and tear of plastics, widely reported as one of the pathways to increased microplastics in the marine environment (Kedzierski et al. 2018; Hildebrandt et al. 2020; Brennecke et al. 2016). In addition, we also performed TGA analysis, where DSC signals when endothermic or exothermic changes occur in the sample—while exposure temperature increases. This method has been previously used as a polymer characterization tool, where a unique endothermic/exothermic signal characterizes individual polymers (Kayacan and Doğan 2008; Kannan et al. 2014). Figure 11.5 shows the spectra for a reference PE plastic and #0188 and #0189 old and new PE fishing net samples. There are several striking results from these graphs:

- Standardized PE presents a very different DSC signal from the studied PE fishing nets, but the weight loss curve is identical;
- In terms of gravimeter differences between new and old PE fishing net fibers, the weight loss differences are minimal – only #0189 old PE fiber shows a slightly more attenuated curve, perhaps due to increased adsorption of foreign elements;
- Drastic differences between DSC signals of old and new PE fishing nets fibers. The peaks do not precisely match the same sample's old and new samples (#0188 or #0189). One endothermic peak appears around 250 °C in both #0188 and #0189 old PE fishing nets absent in the new sample. And one exothermic peak in both old samples was around 410 °C.

We can then conclude that the aged PE fishing nets are physically and chemically altered (Figs. 11.4 and 11.5). The melting temperature of a polymer is usually associated with the peak temperature, about 258 °C in this case. In the temperature range between 350 and 500 °C, several overlapping endothermic and exothermic effects are observed in the DSC signal, which are due to the pyrolytic decomposition of the polymer content of the sample (Schindler et al. 2017). Polymers melt in the range of 200–300 °C (Schindler et al. 2017), but our samples do not show an obvious peak in this range (Fig. 11.5). Because the peak at 150 °C matches perfectly between #188 and #189 and standard PE, we conclude that the melting point occurs around 150 °C (Fig. 11.5). Exothermic (positive) peaks are associated with crystallization reactions while endothermic (negative) peaks are associated with glass transition or melting reactions. Crystallization is molten amorphous material changing to crystalline material upon cooling, with two distinct phases: nucleation and crystal growth (Ipiná et al. 2018). In summary, the main point of this part of the study is to prove that fishnets change properties at the EOL when compared to the “new” unused material. And here we show that both crystallization and melting moments differ in the old, used fishnets compared to the new, unused ones. This might imply new crystalline phases in the old, used fishnets that could act as nuclei for metal ions. In the next sub-chapters we will explore the use of old, used fishnets as sinks for metals, in comparison to new, unused ones.

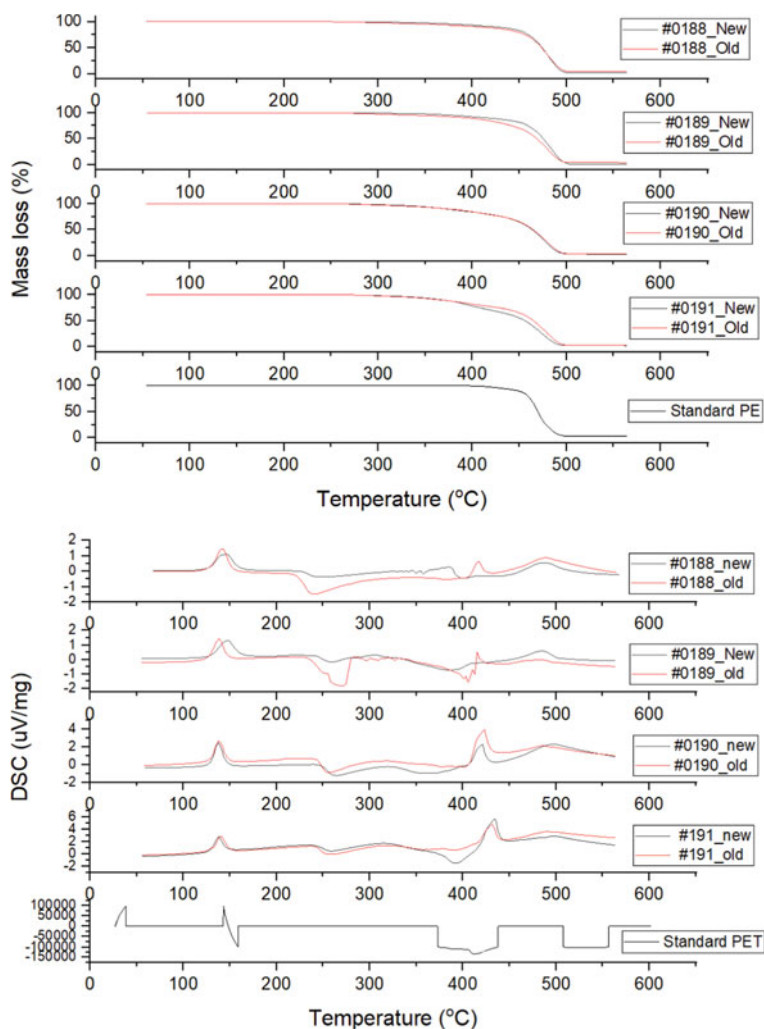


Fig. 11.5 Mass loss and DSC changes in the #0188, #0189, and PE reference samples with temperature performed in TGA, up to 550 °C. Data treatment by the authors

11.3.2 Adsorption Experiments (2)

11.3.2.1 Chromium

Cr can be found in the environment in varied speciation because of its Cr use in various industries such as metallurgical (steel, ferro-, and nonferrous alloys), refractories (chrome and chrome-magnesite), and chemical (pigments, electroplating, tanning, and other) (Kotaś and Stasicka 2000). In the environment, Cr can form and be

adsorbed onto different minerals depending on its oxidation state: Cr(III) and Cr(VI) (Nagajyoti et al. 2010; Alloway 1995; Burke et al. 1991). But while Cr(III) is a trace element essential for the proper functioning of living organisms, Cr(VI) exerts toxic effects on biological systems (Kotaś and Stasicka 2000). The soluble Cr(VI) species depend on pH and vary as H_2CrO_4 at pH less than 1, HCrO_4^- at pH between 1 and 6, and CrO_4^{2-} at pH above 6 (Arar and Pfaff 1991). $0.79 \mu\text{g Cr L}^{-1}$ can be found in seawater (Tao et al. 2021), while up to $1 \mu\text{g Cr L}^{-1}$ can be found in wastewater (Lesage et al. 2007).

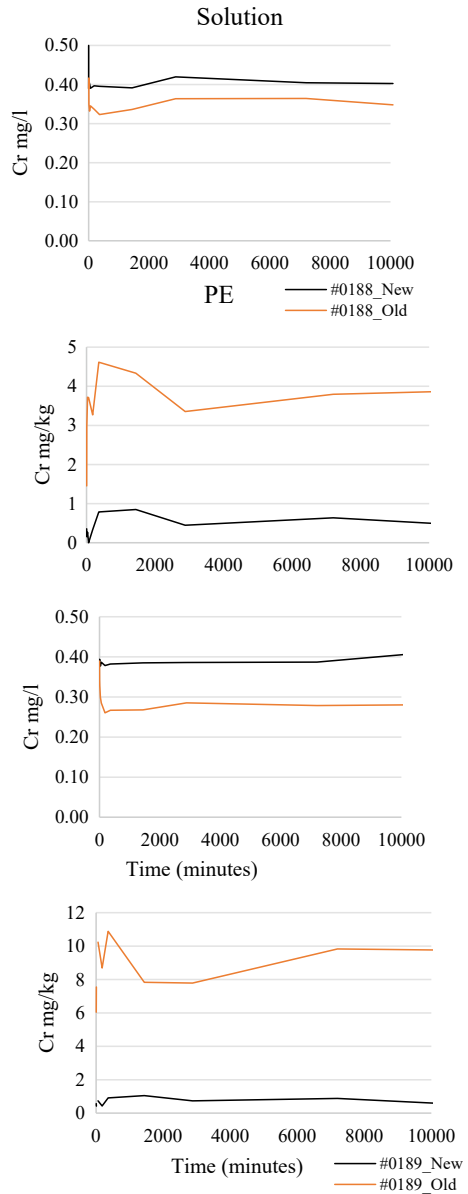
Cr(III) was investigated in this study. When we subject a relatively high concentration of 0.5 mg Cr L^{-1} of soluble Cr(III) to the fishing nets, we are clearly above the threshold of dissolved Cr found in seawater ($0.000,104\text{--}0,00,026 \text{ mg Cr L}^{-1}$) and wastewater ($0.014\text{--}0.113 \text{ mg Cr L}^{-1}$) (Lesage et al. 2007). Nevertheless, this gives us an idea of the limiting adsorption capacity PE fishing nets possess in the present study. Figure 11.6 shows both Cr concentrations in the solution and the fishing nets after each contact point. We assume that metals are adsorbed and uptake by the fishing nets (and not the other way around, as some authors suggested). Indeed, Fig. 11.6 shows a decline of Cr in the solution with increasing contact times, while a rise in Cr concentrations can be observed in the PE fishing nets fibers. While the new, unused fishing nets adsorb negligible amounts of dissolved Cr (for both #0188 and #0189 types), the *old* end-of-life PE fishing nets seem to uptake around 0.1 mg Cr L^{-1} from the solution (Fig. 11.6). Analogously, the *new*, unused PE fishing net fibers seem to increase $2 \text{ mg of Cr kg}^{-1}$ after being in contact with dissolved Cr, while *old* end-of-life PE fishing nets fibers seem to uptake $4 \text{ mg of Cr kg}^{-1}$ extra than their initial Cr content. The uptake happens in the first 5–10 min of contact with the solution.

11.3.2.2 Copper

Copper (Cu) has been extensively researched, especially regarding water quality (Crane et al. 2007; USEPA 2000). Cu is a trace element (micronutrient) for plants and animals, including humans, and has relatively low toxicity (except for invertebrates and microorganisms) when compared to other metals (Artiola 2005). But acute copper poisoning can show effects such as hemolysis, liver and kidney damage, and fewer with influenza syndrome (Feng et al. 2009). Local effects reported include irritation of the upper respiratory tract, gastrointestinal disturbance with vomiting, diarrhea, and a form of contact dermatitis (Rengaraj et al. 2004). Copper at the concentration of $10 \mu\text{g L}^{-1}$ greatly impacts the growth and reproduction of the sea anemone (Trenfield 2017). At a concentration higher than 1 mg L^{-1} , CuO nanoparticles negatively impact zebrafish hatching and increase malformation prevalence (Vicario-Parés et al. 2014).

Copper is found in natural surface waters at an average concentration of 0.002 mg L^{-1} , ranging from 0.001 to $\sim 0.1 \text{ mg L}^{-1}$. Cu in seawater is at the upper end of the range (Alcacio et al. 2001). In wastewater, however, Cu concentrations can reach $2\text{--}32 \mu\text{g Cu L}^{-1}$ (Lesage et al. 2007). Once released into the water environment, Cu^{2+} ions will hydrolyze and form soluble Cu hydroxides that dominate at

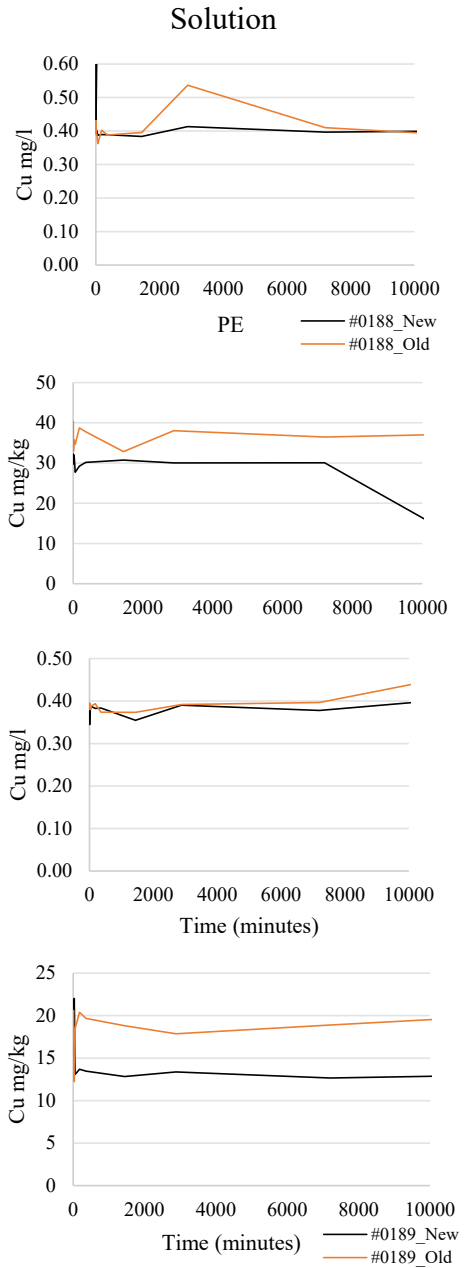
Fig. 11.6 Cr time series uptake by the #0188 and #0189 fishing nets, both unused (New) and end-of-life (old) samples. Visual representation of unused and discarded, end-of-life fishnets. Photograph by the authors



pH > 7 (Artiola 2005) and can be easily assimilated by invertebrates. Therefore, it is necessary to treat wastewater containing copper before being discharged into water streams.

Cu adsorption onto plastics follows the same tendency as Cr (Fig. 11.7). Cu dissolved in solution decreases about 0.1 mg Cu L⁻¹ (in both #0188 and #0189 fibers),

Fig. 11.7 Cu time series uptake by the #0188 and #0189 fishing nets, both unused (New) and end-of-life (old) samples. Visual representation of unused and discarded, end-of-life fishnets. Photograph by the authors



while concentrations in both *new* unused and *old* end-of-life PE fishing nets fibers increases, again in the first 5–10 min of the experiment. The curves are not as clear as in the case of Cr, but again with Cu we observe that the old end-of-life PE fishing nets fibers adsorb higher amounts of Cu than the unused PE fibers counterpart. #0189 *new*, unused fishing nets seem to desorb Cu from the fibers (Fig. 11.7). Nevertheless, the *old* end-of-life PE fishing nets fibers adsorb up to 5 mg kg^{-1} of Cu from the solution.

11.3.2.3 Lead

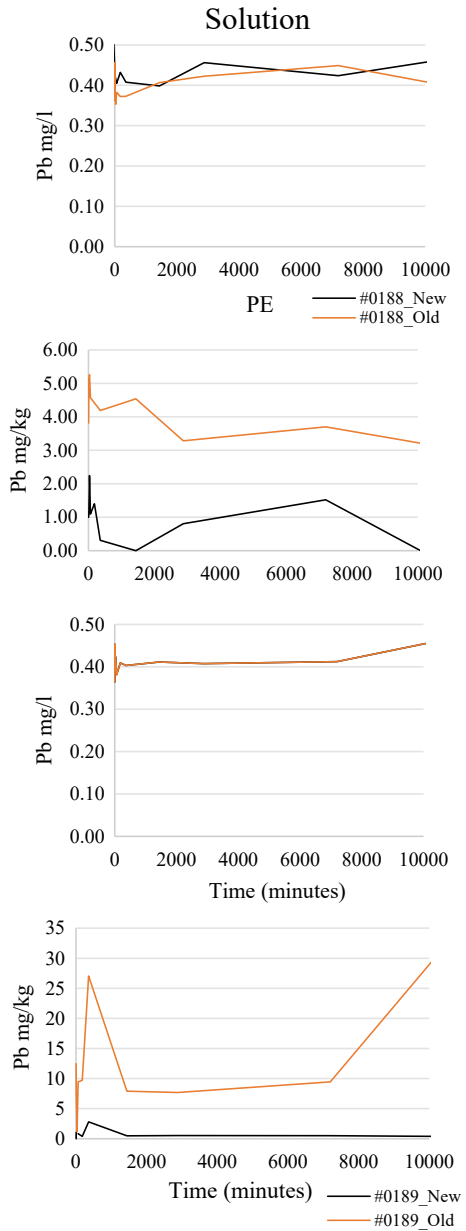
Lead (Pb) in the environment may derive from either natural or anthropogenic sources (Hoet 2005). Although the use of Pb has been declining since the Roman period, it is still widely used in batteries, cable sheathing, medical equipment, paints and pigments, ceramic glazes, metal rolled and extruded products like pipes, military equipment, ammunition and lead fishing weights, crystal glass, and alloys (Hoet 2005). The usual valence state in inorganic lead compounds is +2, but inorganic Pb rarely exists in its elemental state but is found in the environment in various complexes (Hill 1997). In water, these include simple inorganic species such as $\text{Pb}(\text{OH})_2$, $\text{Pb}(\text{OH})_3^-$, and polymeric lead ions such as $\text{Pb}_2(\text{OH})_3^+$ and $\text{Pb}_4(\text{OH})_4^{4+}$ (Artiola 2005). Concentrations in seawater are $0.002\text{--}0.2 \text{ mg L}^{-1}$ (Lavilla et al. 2015), and in wastewater, it can range from 2 to $5 \text{ } \mu\text{g Pb L}^{-1}$ (Lesage et al. 2007).

Lead is also widely used in the plastic industry to extend the temperature range at which it can be processed without degradation (thermal stabilizer) (Hoet 2005). All these lead compounds are pigmentsing white powders and thus cannot be used when clear or translucent articles are required (Hoet 2005). In terms of dissolved Pb adsorption onto PE polymers, we observe slight differences from the previously studied Cr and Cu. Pb adsorption seems to decline with time (Fig. 11.8). While Pb in solution shows an approximately constant concentration – with a slight rise at the end (around the 10,000 min), Pb in PE fishing net fibers seem to in fact desorb with time (Fig. 11.8). Nevertheless, if we continue to consider the initial 5–10 min of contact between PE fishing nets and the 0.5 mg Pb L^{-1} solution, we conclude that $1\text{--}10 \text{ mg Pb kg}^{-1}$ are adsorbed onto the *old* end-of-life PE fishing net fibers.

11.3.2.4 Selenium

Selenium is essential to living organisms (Tan et al. 2016). The interest in selenium has risen in the last decades due to its application in health areas (Tan et al. 2016), mainly due to its narrow beneficial range for living organisms, where toxic vs safe concentrations only have a 3–fivefold (Brozmanová et al. 2010) up to tenfold (40–400 μg in one day) (El-Ramady et al. 2015) difference. Studies highlight excess Se

Fig. 11.8 Pb time series uptake by the #0188 and #0189 fishing nets, both unused (New) and end-of-life (old) samples. Visual representation of unused and discarded, end-of-life fishnets. Photograph by the authors



in wastewater as a potential environmental concern (Tan et al. 2016), namely as toxicity for human beings and provoking physical deformities, mutations, reproduction failures, and even death in aquatic fauna (Ellis et al. 2003). USEPA has established $20 \mu\text{g Se L}^{-1}$ for acute aquatic life toxicity (USEPA 2016). It is then important to clean wastewater of excess Se.

Se adsorbs to untreated plastic and ferrous and manganese oxides (Balistrieri et al 1992; Missana et al. 2009), and by biofilm growing on ocean plastic debris (Mitchell et al. 2019). In this study, we find that both #0188 and #0189 *old* end-of-life PE fishing net fibers show Se adsorption with time, but not the *new* #0188 and #0189 unused PE fishing net fibers (Fig. 11.9). We observed a drop of $0.5\text{--}0.2 \text{ mg Se L}^{-1}$ in the solution and a peak of Se adsorption in the first 6–24 h of contact, followed by a constant concentration comparable to the initial one (before contact was started). The peaks represent a $3\text{--}10 \text{ mg Se kg}^{-1}$ increase of the initial Se concentration in the PE plastics. Again, this effect was only observed in the *old* end-of-life PE fishing net fibers.

11.3.3 Are Metal-Enriched Fishing Nets Hazardous Waste?

After exposing the old end-of-life PE fishing net fibers, we can now compare the total metal amounts that are adsorbed into the PE fibers to the different plastic regulations. The *Toy Safety Directive* and its amendments list criteria that toys must meet before being marketed in the EU (Council of the European Union 2017). The *Restriction of Hazardous Substances (RoHS)* Directive includes electronic and electrical plastic housings and insulation (European Parliament and Council 2011), and the *End-of-Life Vehicles (ELV)* Directive, encompasses plastic components of vehicles (Commission Directive 2017), sets total concentration limits for metals (see Table 11.2). The *Packaging and Packaging Waste (PPW)* Directive is also restricted to these metals. Still, it sets a combined total concentration limit of 100 mg kg^{-1} (European Parliament and Council of the EU 1994), while the Directive relating to plastics intended to come into *Contact with Foodstuffs (CFS)* stipulates different but substantially lower total concentration limits for five metals (Commission Directive 2002). To learn more about the regulations, please see Turner and Filella (2021).

The metal solution in contact with the *old* end-of-life and *new*, unused PE fishing nets was 0.5 mg L^{-1} , which was (depending on the metal) 1000 times higher than the amounts found in seawater and wastewater (see Sect. 11.3.2). Old end-of-life fishing nets adsorbed the highest quantities of metals onto the PE fibers (Figs. 11.6, 11.7, 11.8 and 11.9), but that amount is still below the *RoHS* and *PPW* directives (Table 11.2). The concentrations for Cr and Pb are well below these directives—which indicates that the old end-of-life PE fishing nets are not hazardous waste—even after being in direct contact with a high concentration of these metals in a liquid and available form for up to 7 days. These concentrations would be more in the order of the CFS requirements for plastics (contact with foodstuffs). But compared to plastics found in the environment, these numbers are still on the lower end of the spectrum.

Fig. 11.9 Se time series uptake by the #0188 and #0189 fishing nets, both unused (New) and end-of-life (old) samples. Visual representation of unused and discarded, end-of-life fishnets. Photograph by the authors

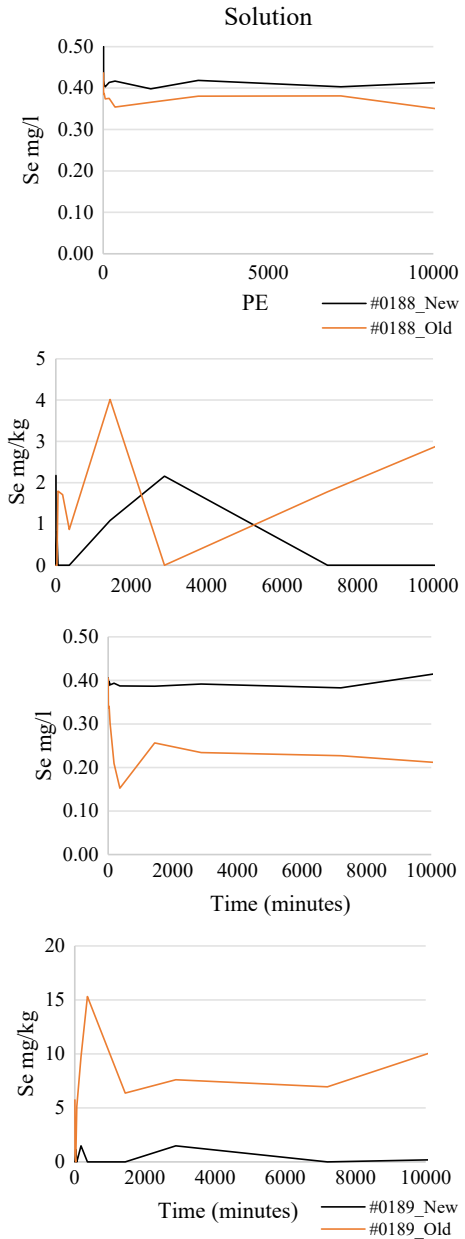


Table 11.2 Metals in plastics are regulated in Europe, and current limit values (in mg kg⁻¹) are according to various directives. Adopted from (Turner and Filella 2021) and comparison to the maximum achieved metal concentrations

	Toy safety directive	Restriction of hazardous substances	End-of-life vehicles	Packaging and packaging waste	Contact with foodstuffs	Hazardous	Maximum achieved in #old fishing nets
Cr (mg kg ⁻¹)	0.2	1000	1000	100	1	yes	5–12
Cu (mg kg ⁻¹)	7700				5	No current regulation	20–40
Pb (mg kg ⁻¹)	23	1000	1000	100	2	yes	5–30
Se (mg kg ⁻¹)	460					No current regulation	4–15

In PE beads used for water treatment, Pb concentrations were found in the order of 5380 mg Pb kg⁻¹ (Turner et al. 2019) or 23 500 mg Pb kg⁻¹ in beached plastic litter in Lake Geneva (Filella and Turner 2018). More research is needed for more conclusive remarks.

11.4 Final Considerations

This study is a stepping stone to understanding metal adsorption onto PE fibers. To the author's knowledge, such high concentrations of 0.5 mg L⁻¹ of Cr, Cu, Pb, and Se have never been tested before. Overall, the results of this study corroborate previous findings. Holmes et al. (2012) found that virgin PE pellets could adsorb trace metals rapidly but that aged beach pellets had much higher equilibrium partition coefficients. The same authors also considered adsorption to virgin and beached (aged) pellets (PE) in an estuarine environment and found that the adsorption rate for Cd, Co, Ni, and Pb decreased with increasing salinity and decreasing pH (Zhang et al. 2020; Holmes et al. 2012). Cu was not significantly affected by these factors. They also found an increase in Cd, Co, Ni, and Pb adsorption, with increasing pH (Zhang et al. 2020). This study does not corroborate this effect since the solution used possessed a neutral pH (≈7). However, we observe a stagnation (Se) or desorption behavior (Pb) with increasing contact between dissolved metals and PE fishing net fibers.

We therefore recommend using old end-of-life fishing nets to remove excess Cr, Cu, Pb, and Se from polluted waters, such as industrial wastewater and contaminated surface waters, on any solution with high metals levels. Hamadi et al. (2001) suggested using waste tyres and a sawdust pyrolysis product to adsorb aqueous Cr(VI) present in complete wastewater removal at low pHs. We did not observe complete metal removal, but our study had concentrations 100-fold higher than those in Hamadi et al. (2001). We believe that Greenlandic old waste fishing nets can be used to clean the wastewater, or metal-contaminated water, in Greenland. This would be a circular cheap solution for one last use of EoL fishing nets, without the fishnets becoming hazardous waste. As shown in the study, a comparison to different EU directives that regulate metal content in plastics for different end-uses shows that the old end-of-life PE fishing nets, after exposure to heavy metals, do not meet the regulations for hazardous waste. Eventually, this could be used worldwide as a circular option for EoL fishing nets.

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