

## Conference paper

Agnieszka Dąbrowska\*, Iwona Łopata and Magdalena Osiał\*

# The ghost nets phenomena from the chemical perspective

<https://doi.org/10.1515/pac-2020-1102>

**Abstract:** The XXIst century might be called the Plastic Era. With the continually growing consumption and production, low recycling level, one observes the continuous transformation of the Blue Planet into the Ocean of Plastics. Among various problems related to the presence of synthetic materials in the environment, the ghost nets draw particular attention. They are present in the global ocean due to lost or abandoned fishing gear. Their impact on the environment is represented by the tones of animals caught. Moreover, they are an abundant source of secondary marine microplastic and release a considerable amount of toxic chemical compounds. To resolve this issue, an interdisciplinary approach is needed. Chemical research enables a better understanding of polymer behaviour and their weathering, whereas spectroscopy helps in qualitative analyses and proposes solutions. This paper aims to present the interdisciplinary study of this phenomenon and its broad context, including social awareness but underlines the crucial role of chemical research. One focuses on the basic studies of chemical and physical properties as this knowledge provides the first and essential step to tackle the problem.

**Keywords:** ChemRAWN; ghost nets; marine microplastic; polymer materials; Raman spectroscopy; sustainability; weathering.

## Introduction

### From the natural fishing gears to the ghost netting phenomena

The chemistry of fishnets evolved in time. Starting from the natural sources, dominated synthetic materials during the last decades, it will probably partially switch to the more sustainable materials.

At the beginning of fishery, fishing nets were made of natural, biodegradable materials such as hemp, sisal, cotton, flax or coconut fibres and other plant-based materials [1]. Once lost or abandoned they were decomposed within weeks. Biodegradable nets were not as efficient as modern, synthetic nets [2] and were soon replaced by polymers such as nylon, which dominated the market. Whereas previously, the lost natural nets decomposed easily in the environment being biodegraded, the durable and resistant polymer materials persist in the oceans. Synthetic nets are more durable and enable more effective fishing. Together with the growing demand for fish and seafood, modern nets have contributed to the fishing industry growing at a great rate [3].

Ghost nets are quite a new phenomenon and started occurring around the time of the popularisation of synthetic materials. They can be easily described as all lost or left synthetic fishing nets in the aquatic systems.

---

\***Corresponding authors:** **Agnieszka Dąbrowska**, Faculty of Chemistry, University of Warsaw, Laboratory of Spectroscopy and Intermolecular Interactions, Pasteura 1, 02-093 Warsaw, Poland; and Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland, E-mail: [adabrowska@chem.uw.edu.pl](mailto:adabrowska@chem.uw.edu.pl); and **Magdalena Osiał**, Faculty of Chemistry, University of Warsaw, Chemistry Teaching Laboratory, Żwirki i Wigury 101, 02-089 Warsaw, Poland, E-mail: [mosial@chem.uw.edu.pl](mailto:mosial@chem.uw.edu.pl)

**Iwona Łopata**, Faculty of Chemistry, University of Warsaw, Laboratory of Spectroscopy and Intermolecular Interactions, Pasteura 1, 02-093 Warsaw, Poland

They cause an uncontrolled bycatch being abandoned and wandering in oceans and release of multiple chemicals and microplastic fibres while weathering under environmental conditions. Mass production of synthetic materials started in the 1950s reaching a total production of 280 mln tonnes by the year 2017 [4] and still growing nearly to 400 mln tonnes. It is estimated that during the last 15 years, over 50 % of plastic was produced. As an effect of bad waste management, large quantities of plastic end up in the oceans. After being mixed with abandoned fishing gear and shifted by currents, they form large garbage patches. Waste can also be found accumulating on the shores and beaches. Both locations are places where plastic is exposed to weathering conditions such as UV radiation, temperature, waves and currents [5]. Another factor contributing to ghost netting is a constantly growing demand for fish and seafood, which puts pressure on fisheries to produce more supply at the lowest possible cost. This stands in opposition to the idea of sustainable fishing, the aim of which is to ensure biodiversity preservation.

Currently ubiquitous (Fig. 1), ghost nets are described as lost, abandoned or otherwise discarded fishing gear (FAO) remaining in the oceans causing a great threat for wildlife and the environment. Most fishing nets are lost by accident due to storms and other weather conditions or collisions. The aquacultures and oil platforms are also significant contributors to plastics pollution. In the Polish economic zone, fishing gear is usually caught in shipwrecks originating from World War II. What is more, the Baltic is a shelf sea and therefore is very shallow in comparison to other fishing grounds such as the North Sea. Mapping of shipwrecks is currently being developed in order to avoid collisions. It is estimated that 20–40 % of plastic waste in the oceans is of fishing origin [6]. This includes nets along with expanded polystyrene waste (EPS). EPS is a material used for buoys and other floating elements, as well as fish containers [7].

As the World Wildlife Fund estimates, abandoned fishing nets remaining in the water, create a catch of 6–20 % of the primary fishing capacity. An investigation conducted by Swedish scientists in 1998 and 1999 shows that the fishing capacity of gillnets drops by 80 % during the first three months after being abandoned and then remains at the level of 5–6 % [8]. This figure remained static until 27 months later when the investigation was completed. The numbers above are not taken into consideration when calculating the Total Allowable Catch (TAC) for species. Doing so leads to destabilisation of fish populations and unnecessary mortality of target and non-target species. Moreover, ghost nets are a great threat to marine mammals such as seals, porpoises and dolphins that can easily become entangled and unable to reach the surface for air [9]. Porpoises find a way thanks to echolocation but are unable to detect thin and almost invisible fibres of modern fishing nets. Fishing gear and nets were found e.g. in Greenland shark (*Somniosus microcephalus*).

Large quantities of plastic waste have been the cause of plastisphere formation. Plastisphere is a term that first occurred in a scientific paper in 2011 in *The Microbial Community on Marine Plastic Debris: Life in the “Plastisphere”* [10]. It is the first ecosystem at the origin of which stands human activity. Plastisphere is said to be the eighth continent due to its great available surface and particular physical and chemical properties. Because of the constant break-down of polymers and rapid surface growth (without gaining volume or weight), plastic is becoming increasingly attractive to sedentary animals and can become a new place for primary



**Fig. 1:** The polymer netting in the marine environment; (a–d) the ghost netting at different levels of decomposition and biofilm growth on a beach of Gdynia, (e) the fishing gear in Plymouth, (f) the polymer materials as a floating island and a substrate for the growth of the mussels, (g) aquacultures as a source of polymers and synthetic materials in the environment.

succession. This leads to the Plastisphere being a new ecological niche yet to be examined. It provides great conditions for living organisms as due to the hydrophobic nature of polymers, biofilm can easily be formed on its surface [11]. Biofilm consists of microorganisms stuck together and with the polymer surface, creating a base for the development of further, more complex organisms such as algae, fungi and diatoms. The unique properties of the Plastisphere cause the specific conditions for the species and, for instance, the rapid horizontal gene exchange [12], antibiotic resistance [13] or biodegradation [14] are observed. In addition to small plastic particles being attractive for microorganisms, stands a threat that microplastic poses to larger animals. Microplastic is a term describing plastic particles not larger than 5 mm [15], that originate from primary or secondary sources. Primary sources include beauty products with scrubbing properties or medical products, fibres detached during laundry and other household waste [16]. Secondary sources are mostly broken-down plastic waste, including fishing nets. Polymers are subject to weathering as well as physical, biological and chemical processes, which are later described in this paper. Due to its small size, microplastic can easily be ingested by animals such as filtering ones.

One also has to consider the problem of invasive marine species that are mostly transported in ballast water tanks. These are used to control the ships' buoyancy and are filled or emptied depending on salinity. It is an increasingly worrying issue, due to the steady increase in travel and trade. In 1970, 200 tons of cargo was shipped per year and the number has grown to 10 000 tons in 2010. Even though invasive species, once brought into a different body of water, are expected to fail to survive, there have been many cases of not only survival but also rapid population growth. The round goby (*Neogobius melanostomus*) managed to persist until today. The round goby (*N. melanostomus*) is native to European seas and was introduced to the Laurentian Great Lakes with discharged ballast waters. It is a good example of an invasive species with a great impact on local ecosystems. Their populations were found equally numbered at both low and high contamination sites proving that highly contaminated areas are not an obstacle in the establishment of round goby [17]. In the pristine Arctic regions [18], where the equilibria are easy to be destroyed, exotic species such as barnacle (*Semibalanus balanoides*) and bryozoan (*Membranipora membranacea*) were found. Moreover, the 87.5% of fulmars (*Fulmarus glacialis*) in Svalbard have plastics in the stomach showing the scale of pollution.

Raman spectroscopy is a tool that allows one to easily analyse the chemical components of fishing nets [19]. Knowing the exact ingredients is a key for one to effectively plan a recycling programme. Measurements show that fishing nets are mostly made of polymers such as polyethylene (PE) and polypropylene (PP). All additional components such as pigments, plasticizers or combustion retarders are an obstacle and disable a complete homogenization of the material. Remains of catalysers of polymer synthesis such as sulphur compounds can also be found. Chemical quantitative and qualitative analysis is crucial and should be stressed in researching the ghost nets phenomenon. It is so due to ghost net retrieval and recycling being the number one solution to this problem.

The ghost nets phenomenon is not stressed enough socially. Social awareness is yet to be raised. A survey was held in March 2020, the results of which are presented further in the paper. Overall, social awareness is extremely low, which may be a result of not bringing up the issue in public. One can stress also the crucial role of science engagement and citizen science in monitoring the derelict fishing gear.

Ghost netting or lost fishing gears, ropes, deteriorated lines are ubiquitous in the environment. They are also a source of microplastics while deteriorating. In Svalbard, they entangled dead seabirds, seals and even reindeers (*Rangifer tarandus platyrhynchus*) [20].

Interestingly, one may observe the renaissance of traditional methods and increasing usage of natural fibres also in the composite materials for the maritime industry.

## Chemistry of fishing nets

Fishing nets became a huge environmental problem causing mainly water pollution. The microplastic that is released from them can adhere to aquatic plants, animals and various microbes that can colonize it forming microfilms increasing the number and local concentration of pathogenic microorganisms in water systems [21]. Moreover, many animals living in water tanks tend to consume microplastic which affects their digestive tract [22].

Finally, microplastic particles and fibres that are released from the fishing nets can be accumulated in the soft tissues like the brain or muscles, not only in the digestive system [23, 24].

- Fishing nets are full of twisted and/or braided fibres that are commonly made of synthetic polymers like:
- Polyamide (PA) also known as nylon, amilan, anزالon, perlon; aromatic polyamide or polyaramides - Kevlar, Tehnora, Twaron are the restricted brand names popular on the sailors market,
  - High-density polyethylene (HDPE),
  - Polyethylene terephthalate (PET),
  - Polypropylene (PP), popular in the lines and parts of gears,
  - Polyester (PES).

Some new brands experiment with PA, PET and PE modifications in order to provide excellent products for the most exigent clients (e.g. sailors of the world-class regatta). Kevlar, Dyneema and Spectra are the most common names of ropes and lines materials in the sailing world of today. Currently, there are a dozen types of Kevlar (PA) available, and just a few of Dyneema and Spectra, both being the PE variations. All exhibit high mechanical resistance and small elongation. As kevlar is prone to UV radiation and degrades easily, it is used for cores and provided with polyester braids. This type of lines is also significantly weaker with knots on it. One of the biggest advantages is the high thermal resistance and scant creep. That is not the case of Dyneema, which in contrast is resistant, light and has buoyancy. The optimal choice is polyamide or dyneema core and braid from polyester to protect from UV radiation or mechanical damage.

All those materials are non-biodegradable and degrading release large quantities of their fragments, marine microplastics, or added compounds. Also, green or biopolymers are usually persistent in the ocean environment. Synthetic polymers used for the formation of marine ropes and nets contain different chemical compounds like pigments or toxic additives that are incorporated in the polymer during production and formation of the final object [25–27]. Within the fabrication process many chemical additives are added like bisphenol-A (BPA), flame retardants (FRs), for instance, polybrominated diphenyl ethers (PBDEs), non-ylphenol (NP), phthalates [28] – dibutylphthalate (DBP), diethyl phthalate (DEP), di-(2-ethylhexyl)phthalate (DEHP); polychlorinated biphenyls (PCBs) [29]. Their role is the improvement of plasticity, resistance against UV radiation or oxidative processes. Some are flame retardants, lubricate materials or maintain and stabilize the colour. Depending on the requirements of the polymer that is used for the production of the fishing nets.

Despite the enhancement of performance properties, these additives harm the living organisms having a neurotoxic effect, causing lipid oxidative effect and many disorders. Bisphenol-A is one of the most common additives used for the polymerization of different monomers. Such compounds leach from the fishing nets, while it is an endocrine-disrupting molecule that also has a mutagenic effect [30]. Due to its toxicity, its analogues like bisphenol-B and bisphenol-F are both used for the production of marine plastics. Nevertheless, despite lower toxicity, they are also harmful to living organisms [31]. Phthalates are also one of the most bioavailable compounds for marine organisms because they are not bound chemically into the polymer [32]. For that reason, they tend to leach from polymer affecting living organisms [33]. They are endocrine disruptors and can influence the release of reproductive hormones. Following a group of compounds are industrial chemicals commonly used to reduce inflammability of plastics that are neurotoxic endocrine disruptors that also have negative reproductive and immunological effect [34]. Compounds like PBDEs are genotoxic affecting wildlife and humans [35].

Other groups of chemicals that can be found in the fishing nets are heavy metals and trace metals that can be accumulated in plastic during its production and released in the aquatic media. The most common are aluminium (Al), copper (Cu), lead (Pb), zinc (Zn), manganese (Mn), iron (Fe) and silver (Ag) [36–38]. They might be accumulated with living organisms what can lead to different diseases. Pb has a devastating influence on the body causing neurotoxicity, cardiac and pulmonary disorders [39]. Al agglomerate in the organism leading to neurotoxicity, immunological disorders, and pulmonary problems [40], while an excess of macroelements like Cu, Mn, Fe, Zn is also dangerous leading to neurotoxicity, hepatic, kidneys, and cardiovascular system disorders [41, 42].

Furthermore, one has to be aware that the fishing equipment does not consist only of the nets. They contain several other components of the fishing gear that are gradually released and accumulate in the environment together with lost nets. Finally, the bycatch accumulates on the surface and forms the biological and organic layer at different stages of decomposition.

## Weathering of synthetic materials in natural and laboratory conditions

The synthetic materials, currently dominant on the market of fishing gear, are persistent and durable. Although they do not decompose easily in the environment, nothing is eternal. The gradual effect of weathering is observed. The main factors contributing to the decomposition of polymers in the maritime environment are the following: UV radiation, oxidation, chemical and physical interactions with the saltwater, mechanical abrasion, biodegradation. One may observe also the interactions with biota and leakage of added compounds. The most common changes include fragmentation, structural and morphological changes. As the current state of material will significantly influence its properties, biocompatibility, toxicology, transport and fate, it is crucial to characterize polymers at different stages of weathering. That is a challenge due to the complex chemistry and physics of materials itself combined with non-linear behaviour in the environment. To resolve that problem, weathering in controlled laboratory conditions is helpful. Chosen parameters can both resemble the natural ones or model selected expected environmental conditions or any needed for basic science. The aim is to understand processes in order to better design materials considering their life-time, model the Plasticsphere, transport and fate of microplastics, provide a valuable source for recycling and re-use.

Overall, the weathering of polymer materials in environmental conditions, especially in oceans, differs from the well-known theoretical mechanisms. The majority of naturally decomposed samples included the small debris, porous surfaces, roughness at the interphase, adsorbed compounds, oxidised functional groups, etc. The Raman and FTIR spectroscopy [43] can be used as a precise tool for the monitoring of the current stage of material by looking at the changes between the bands in spectra (for instance, ratio, intensity, surface, position) of the old and pristine sample. Furthermore, the electrochemical approach enables the detection of leaking compounds with a very low detection limit.

The aim of weathering material can be at least one of those:

- the design of structures degrading in a controlled manner,
- the better understanding of the samples behaviour in the environment, interaction of biota and possible toxicity,
- the efficient recycling,
- the control of materials parameters at different stages of its lifetime,
- the calibration of analytical methods and characterization techniques before measurement of the naturally decomposed materials.

In particular, the weathering of the fishing net is not yet fully understood and a variety of phenomena and mechanism correlated with this process were observed in this study on the naturally changed and artificially pre-treated samples.

## Materials and methods

### The sources of ghost nets

The variety of new naturally and artificially deteriorated netting and sailing lines were collected and studied. Among many others, there were three complementary sources of the representative materials for this research and the following aims:



- Raman spectroscopy of the “real” material collected by WWF in the environment within the Marelitt Baltic project held in the years 2016–2019, in particular from the bottom sediments of Baltic and the North Sea; samples gathered in this project are mainly parts of fishing nets hooked to the shipwrecks and the bottom of the Baltic Sea; they were pulled onto shipping vessels and examined along with the organic matter included; one fishing net sample manually extracted by the author during diving in the Laccadive Sea, along the Maldivian coast was included in the research,
- Identification of the specimens of deteriorated ropes found at the Słowiński National Park at “Wydma Czolpino” (the protected area, one of the biggest wandering dune, in the central part of the Polish coastline, a region of the Southern Baltic),
- Naturally weathered lines from fisherman and tall ships, which potentially might end up in the sea – identification and detection of the weathering signs,
- Pristine materials (PP, PA, PET) weathered in the laboratory conditions to observe the results and the effect of leakage of added compounds.

All measurements were repeated a few times for each specimen and in the case of the macro-objects, the sampling occurred at different points.

## Laboratory weathering

The pristine net samples were washed with ethanol ( $\geq 98\%$ , POCH) and water (Milli-Q water filtering system) to remove potential organic stain from the surface, then dried on-air and cut into pieces about 5 mm in length. Next, 3 g of the net was immersed into 10 mL of Milli-Q water, warmed up to 50 °C for 1 h. Then, the sample was stirred at 300 rpm for 72 h. There were three different PP ropes, two PA and one PET what enables the comparison between various polymers, and on the other hand, within the same macromolecular chain, the differences between added compounds might be observed. The PP 1 and PET were also weathered for 3 days in hydrogen peroxide to simulate the intensive oxygen impact (see Fig. 2).

## Characterization by spectral analysis

The Raman [44] and IR spectroscopies [45] are the complementary methods [46] efficiently used for the qualitative and quantitative characterization of polymer materials and marine microplastic. Both provide the standard for polymers identification. Within this research, Raman spectroscopy was used as a prime technique of characterization. Measurements were carried out on the Thermo Scientific Nicolet iN10MX Raman microscopy with four laser lines accessible: 455, 532, 633 and 780 nm. The most popular green 532 nm laser line (working at 10 mW) was used for the identification of samples from Słowiński National Park (SNP) and ghost nets variety. In order to avoid the self-luminescence, the laboratory weathered samples and their pristine materials were characterized under a 780 nm laser beam (working at 24 mW). The 10 mm lenses were used with the 50  $\mu\text{m}$  diaphragm opening for all measurements.



**Fig. 2:** The macroscopic view of six different pristine ropes and their samples weathered in the laboratory, on the right the same material new and after weathering with changes in colour and shape.

In the case of the PP popular and naturally weathered line, the additional FTIR measurement was performed to present the possibility of spotting the deterioration of materials on a spectrum. Measurements were performed for numerous samples of the same material to confirm the reproducibility of a signal. The Thermo Scientific Nicolet iN10MX microscope was used in a reflectance mode, with a cooled detector dedicated for mapping. It provided a spatial resolution 2–5  $\mu\text{m}$ .

UV–vis absorption spectra were recorded using a Perkin Elmer Lambda 35 in quartz glass cuvettes to avoid contamination of the sample with classical single-use plastic cuvette. They provided additional information about the laboratory weathered materials.

## Cyclic voltammetry of added compounds

Electrochemical measurements were performed in the three-electrode system using an Autolab electrochemical setup (Eco-ChemieNetherlands) with GPES software. Platinum disc electrode was applied as a working electrode, 3 M Ag|AgCl|KCl electrode was used as reference electrode and a Platinum wire served as the auxiliary electrode. 0.1 M LiClO<sub>4</sub> ( $\geq 98\%$ , Sigma-Aldrich) was used as a basic electrolyte and electrochemical experiments were performed with Milli-Q water. Samples were investigated with the use of cyclic voltammetry. All solutions were bubbled with argon for 5 min before electrochemical experiments to remove the oxygen from the studied solution.

## Local perspectives, environmental issues and science engagement

As the ghost netting phenomena concerns not only material scientists but has a significant impact on the biota and human wellbeing, the monitoring of social awareness of the problem seems crucial. No global social investigations were yet conducted. Locally, fishing industry workers were questioned. Studies show, that fishermen are not currently familiar with the threats, that ghost nets pose on the environment [47].

A public survey is one of the tools to promote knowledge of chosen topics. According to Stratton, almost 40 % of survey participants do at least little and sometimes extensive research on the topic they were questioned on [48].

A study conducted aiming for this paper does not meet the needs of worldwide research, but has great local potential. It has awareness on local basic and provided information for organisations such as the World Wildlife Fund regarding topics that should be addressed.

## Results and discussion

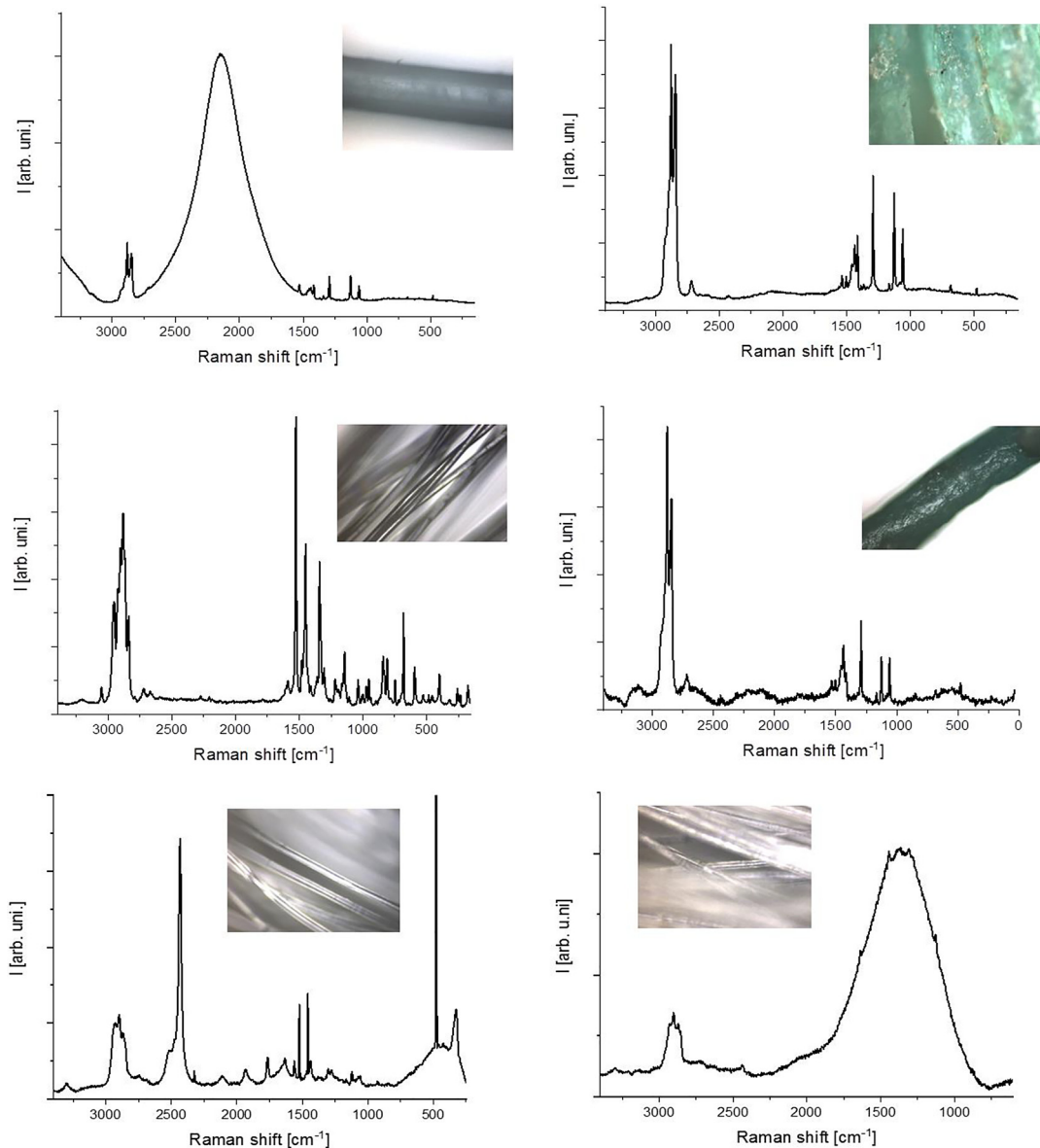
### Raman spectroscopy of ghost nets

The Raman spectroscopy studies enable both the qualitative distinction between the various types of polymers and the quantitative estimation of the weathering stage. Usually, the region of Raman shift between 2600 and 3200  $\text{cm}^{-1}$  is the most informative. For the ghost nets from the Baltic and the North Sea the spectra were collected with the laser line (532 nm) and the results are presented in Fig. 3.

The most characteristic bands are summarized in Table 1.

### Natural weathering of synthetic lines

The weathering processes that occur in a marine environment are not yet fully understood. Currently, there are just partial models or not verified hypothesis. However, as already shown, the Raman and FTIR spectra are



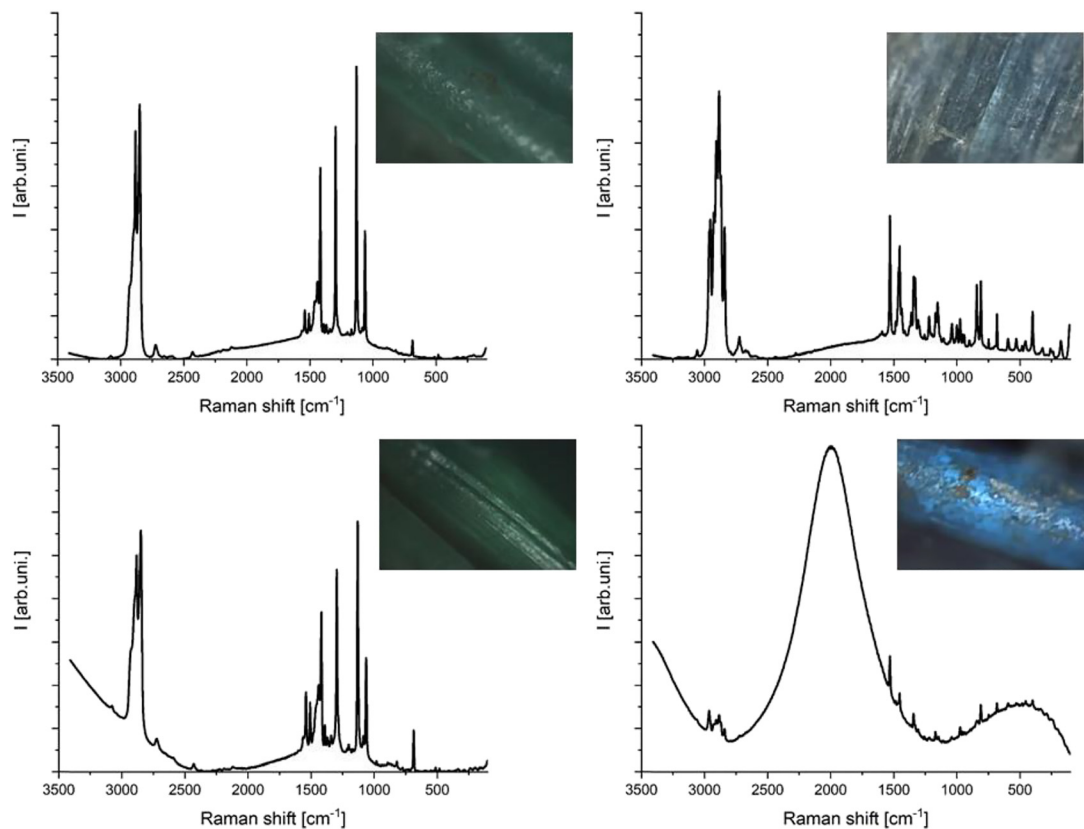
**Fig. 3:** The ghost net spectra identified as low-density polyethylene (upper left), polypropylene (middle left), new polyethylene (upper right), naturally weathered polyethylene (middle right) along microscopic images; in the lower row the PA examples.

susceptible methods and an advisable approach to model those changes [49]. The decomposition of lines, ropes and nets was studied on the three examples: a collection of samples from Słowiński National Park (Czołpino Dune), the polypropylene sailing rope from the tall ship STS Pogoria and samples collected from the sailors and fishermen. The fibres found in SNP were identified as PP and PE (Fig. 4). The fluorescence and enhanced background noise are typical for naturally weathered materials. Presented data corresponds to the particular type of synthetic fibres that were gathered in a chosen geographical location. The ageing of PE is frequently described by the changes in its density and the ratio of amorphous to crystal domains in material. The most common method to distinguish high-density (HDPE) and low-density (LDPE) polypropylene samples consists of the monitoring of  $-\text{CH}_2$  peaks  $\sim 1416 \text{ cm}^{-1}$  and  $1440 \text{ cm}^{-1}$  for crystalline and amorphous bending, respectively. The  $-\text{CH}_2$  asymmetric stretching ( $\sim 2882 \text{ cm}^{-1}$ ) grows in HDPE in respect to the symmetric band  $\sim 2848 \text{ cm}^{-1}$ .



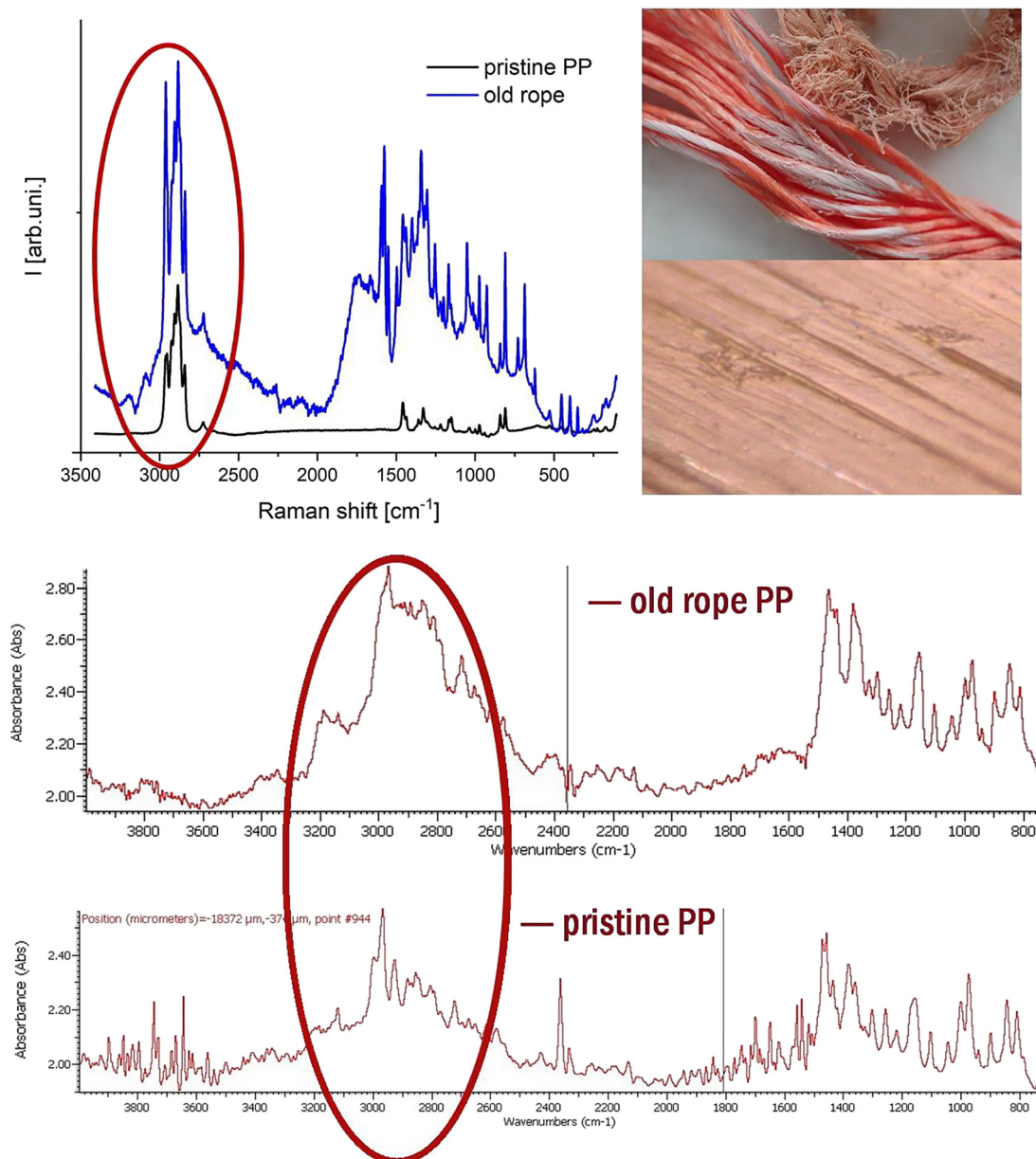
**Table 1:** Ranges of spectral bands specific for polymers shown on samples of different origin.

Sample name and specifications	Range ( $\text{cm}^{-1}$ )	Compound or group
<b>S2</b> Marelitt Baltic	3000–2854 3400–3330 1689–1644	alkanes
<b>S3</b> Marelitt Baltic	3000–2854 1473–1446 1196–1188	alkanes alkanes sulphur compounds
<b>S6</b> Marelitt Baltic	1515–1490 1350–1330 1150–1000 1070–1040	chlorine compounds isopropyl alkanes sulfoxides
<b>S7</b> New synthetic rope	3000–2854 835–747	alkanes isopropyl
<b>S8</b> New synthetic rope	3000–2854	alkanes
<b>India</b> Unknown origin, picked at the Lakkadivian Sea	2850–2700 1196–1188 1030–1010	aldehyde alkyl sulfites pyridine derivative

**Fig. 4:** The naturally weathered lines found at the Słowiński National Park (Poland) and identified as polyethylene (left column) and polypropylene (right column) at different stages of deterioration.

One can conclude about the deterioration of PP by comparison of the relative peak ratio intensities  $-CH_2-CH_3$  which decreases as the fragmentation occurs. Moreover, the FTIR spectra changes in the polymer region (Fig. 5). The spectral changed due to the weathering is frequently observed during the MMs mapping and might be used as a part of the library for the future identifications of environmental samples.

The majority of fibres are difficult to characterize by Raman spectroscopy due to the strong self-luminescence or deterioration under the laser beam, however, the main components of ropes and sailing lines can still be characterized in details. The PA and PET signals were registered from nets and ropes weathered at sea. Old material in respect to the pristine one exhibits stronger luminescence and background noise. The peaks separation decreased. In the case of the PA line, the green core was identified as being PP (see Fig. 6).



**Fig. 5:** The Raman (upper row) and FTIR (bottom row) spectra of the polypropylene line naturally weathered at sea (from the tall ship STS Pogoria).

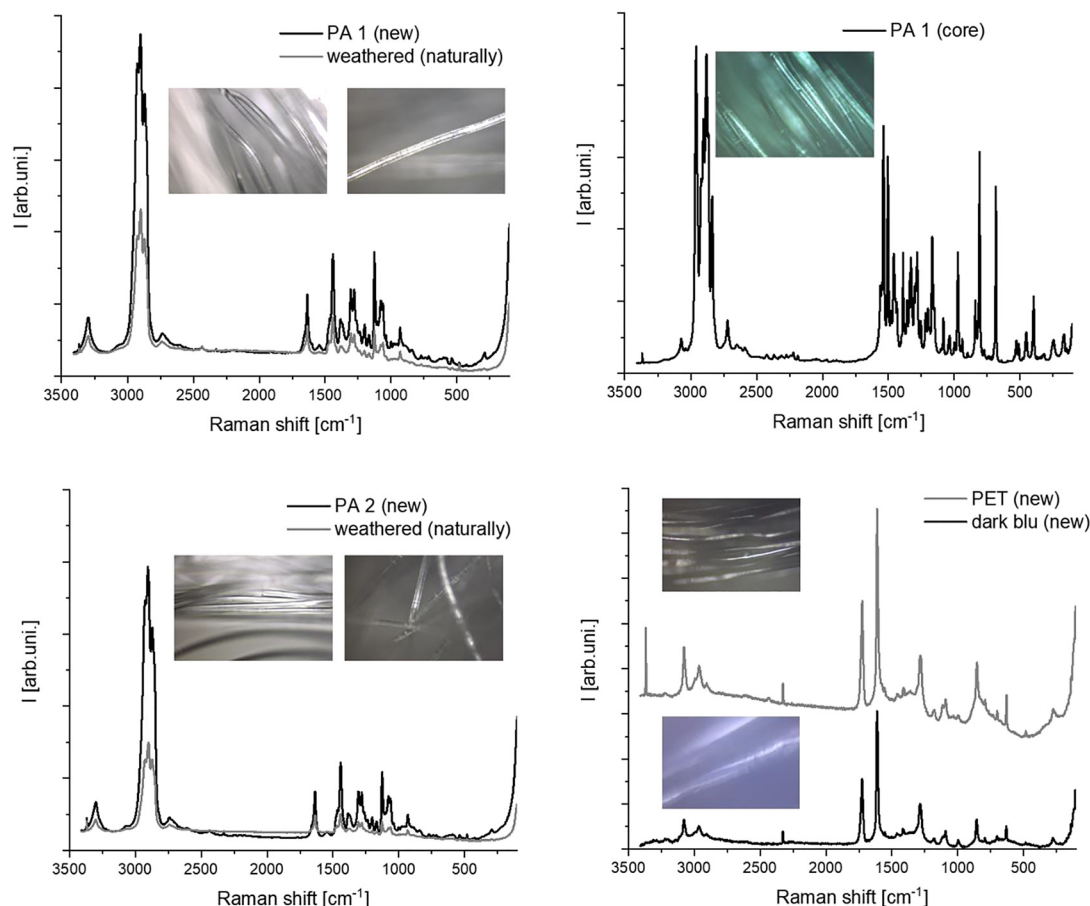


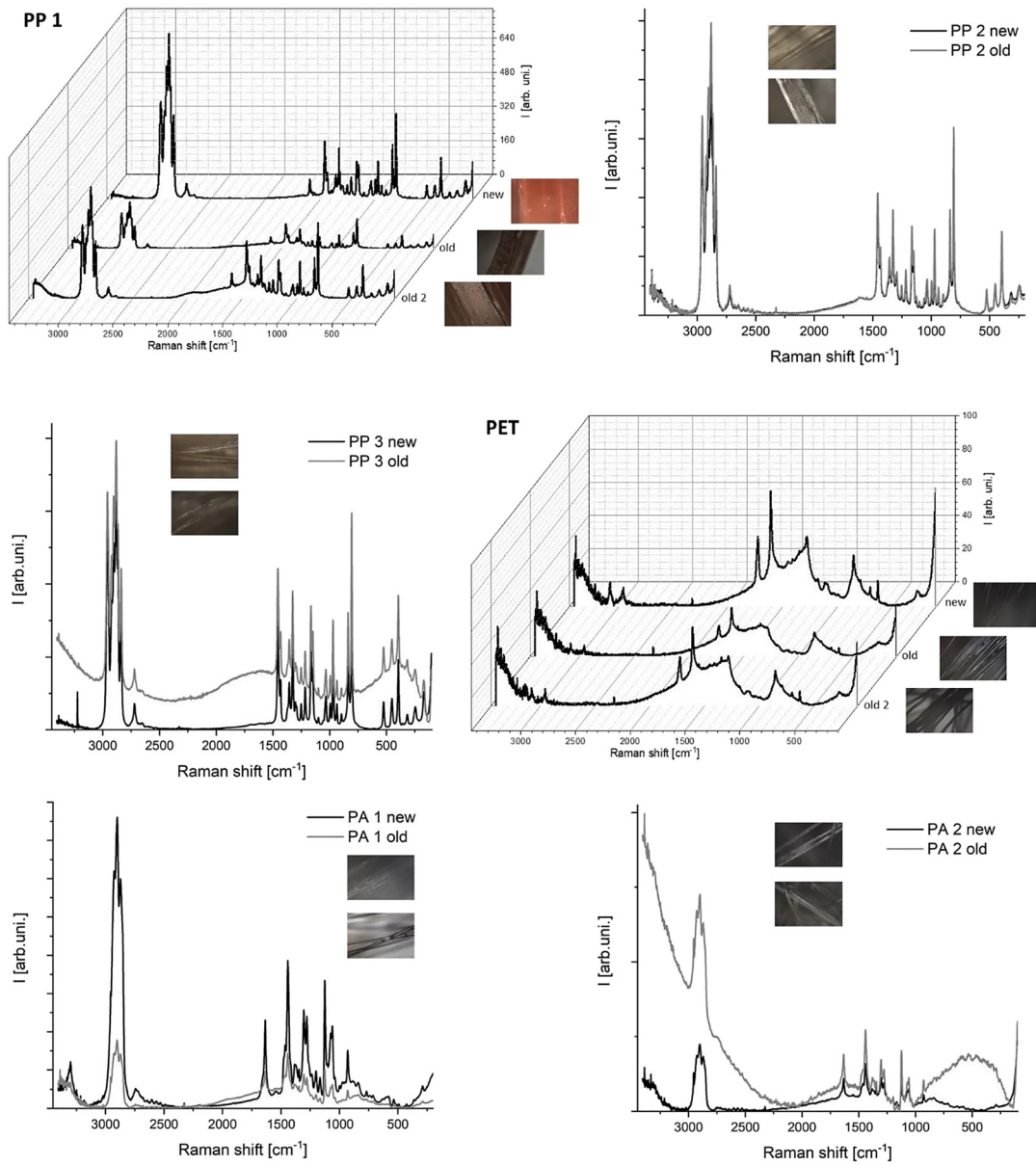
Fig. 6: Raman spectroscopy (532 nm) of the selected (two types of PA and PET) pristine new and naturally weathered lines.

### Raman spectroscopy of laboratory weathered lines

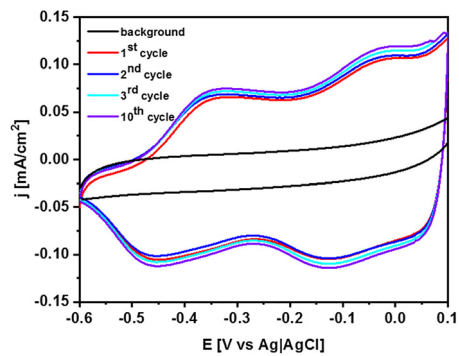
The Raman spectroscopy is an efficient tool for monitoring the results of weathering. In particular, the ratio between  $-CH_2$  and  $-CH_3$  band decreased due to the fragmentation of the chain. That is why the observations of the relative intensities are the first parameter to be taken into account (PP 1, PP 3). In the case of six types of lines and net materials decomposed in laboratory conditions, one may observe the different changes in spectra (Fig. 7). In particular: the increase of background noise (PP 1, PP 3, PA 2), strong luminescence around  $500\text{ cm}^{-1}$  (PP 3, PA 2),  $-CH_3$  increase (PP 1, PP 3). Interestingly, from all three PP lines, one (PP 2) does not exhibit any difference.

### Electrochemical studies of laboratory weathered lines

The electrochemical measurements were performed to check if any chemical compounds were released from the samples during weathering. Although the Raman spectroscopy may provide the information of deterioration of a polymer chain, for the monitoring of leakage of added compounds the other techniques might be more suitable, for instance, the cyclic voltammetry that is widely used for electrosensing. Fig. 8 presents an investigation of the aqueous solution of the weathered PP line gained within the weathering of sample PP 1. No significant change in the colour of the solution after weathering was observed. The cyclic voltammetry response from the pigment leaching from the sample was recorded in the range from  $-0.6$  to  $0.1\text{ V}$  vs. Ag|AgCl



**Fig. 7:** The Raman spectroscopy (780 nm) of the lines (PP 1, PP 2, PP 3, PET, PA 1, PA 2) weathered in the laboratory conditions.



**Fig. 8:** CV recorded for sample PP 1 at the potential range from -0.6 to 0.1 V at 0.1 M LiClO<sub>4</sub> aqueous solution at 20 mV·s<sup>-1</sup>.

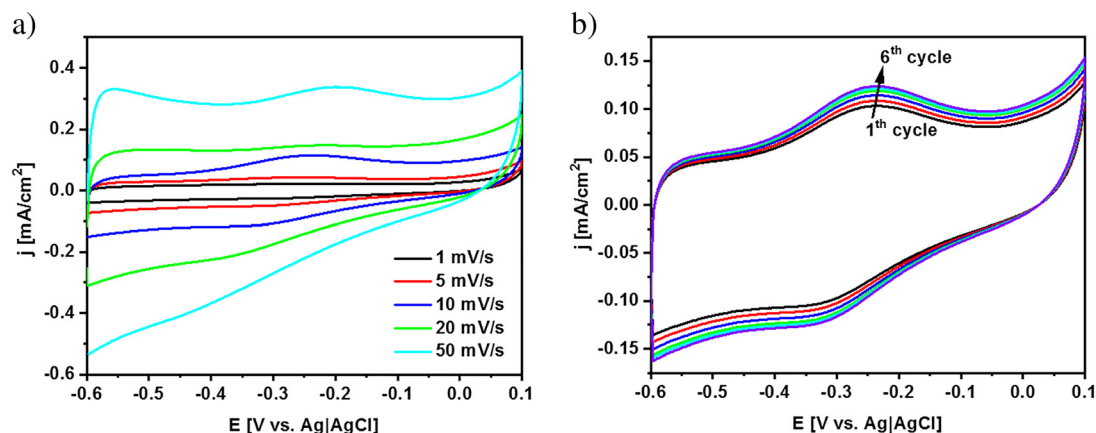
electrode. CV curves show two redox pairs, where the anodic peaks appear at  $-0.32$  and  $0.0$  V, while the cathodic peaks appear at  $-0.45$  V and  $-0.13$  V. Widening of the potential range into the anodic region about  $0.5$  V did not give any additional signals. Based on these studies the peaks can be ascribed to the chemical compound that is electroactive and has a characteristic redox couple.

It is possible that Neutral Red released from the sample, while it also might be a combination of some other pigments like Nile Red. Both are derivatives of phenazine that is a highly reversible electrochemical system [50, 51]. Neutral Red is an electron mediator and its reduction undergoes in aqueous media in two stages [52, 53]. That compound has two redox pair, so the stain observed on the electrode may come from such pigment. It is not excluded that both above-mentioned pigments release from the PP sample. The Nile Red and Neutral Red give electrochemical response in the similar potential range [54, 55]. Following cycles with  $20 \text{ mV}\cdot\text{s}^{-1}$  show a very small rise in the current density.

Following the sample, that was also PP, revealed different electrochemical response. The line has a beige colour and looks similar to natural fibres. As can be seen in Fig. 9 with the increase of the scan rate, cathodic peak shifts cathodically and anodic bulk signal shifts anodically. The peak that appears in the range from  $-0.6$  V to  $-0.4$  V may correspond to the hydrogen adsorption and desorption that takes place onto the electrode, due to the high overvoltage of Pt electrode [56, 57], however, the polarization in the above mentioned potential range of potentials leads to the appearance of the greyish stain onto the surface of the electrode. It may come from the poisoning of the surface or deposition of some electrochemical species, while their chemical composition is not clear.

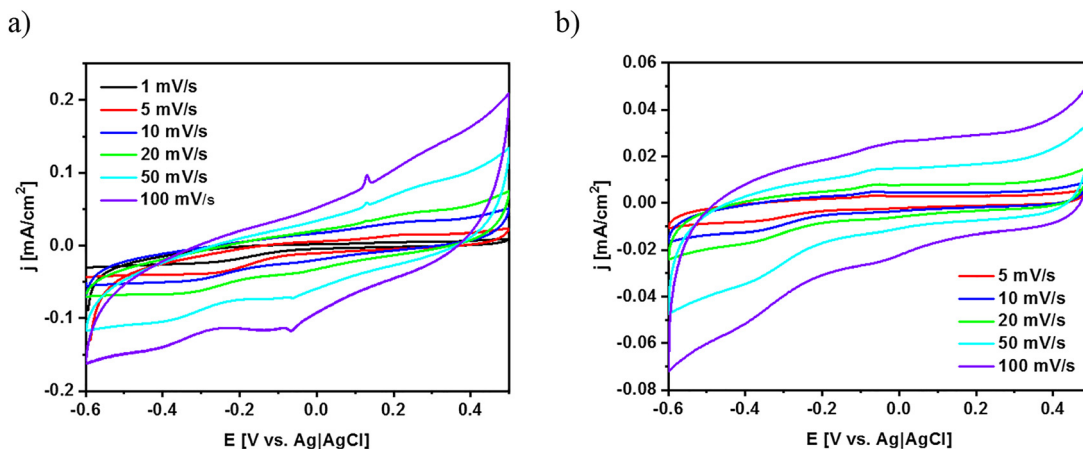
Next sample – PA 1 was studied as previously in the range from  $-0.6$  to  $0.1$  V. No electrochemical response was observed, while an extension of the potential range into the anodic region up to  $0.5$  V revealed some electrochemical response (Fig. 10a). According to the broad signal that appears below  $-0.2$  V it may come from the hydrogen adsorption onto the Pt electrode surface, while the small peaks that appear at both: anodic and cathodic region are not clear. They tend to appear only for high scan rates like  $50$  and  $100 \text{ mV}\cdot\text{s}^{-1}$ , while it is difficult to ascribe them to particular species.

The following sample that was investigated electrochemically was sample PET. Initially, It was expected that the black pigment or mixture of pigments will be released from the sample, while no change of the colour of the solution was observed within weathering. Only the tiny fibres were visible in the solution. Usually, PET gets black colour after carbon addition or various pigments, while electrochemical studies did not confirm any release of them. However, as can be seen in Fig. 11 the weathered line releases some chemical compound that gives electrochemical response at the anodic range of CV curve in the potential range from  $0.2$  to  $0.8$  V, where the measurement was performed with  $20 \text{ mV}\cdot\text{s}^{-1}$ . The anodic peak appears at  $0.66$  V and it tends to decrease with the following scans. No redox pair is observed. Based on the literature the peak that appears on the anodic curve may be ascribed to the bisphenol A [58].

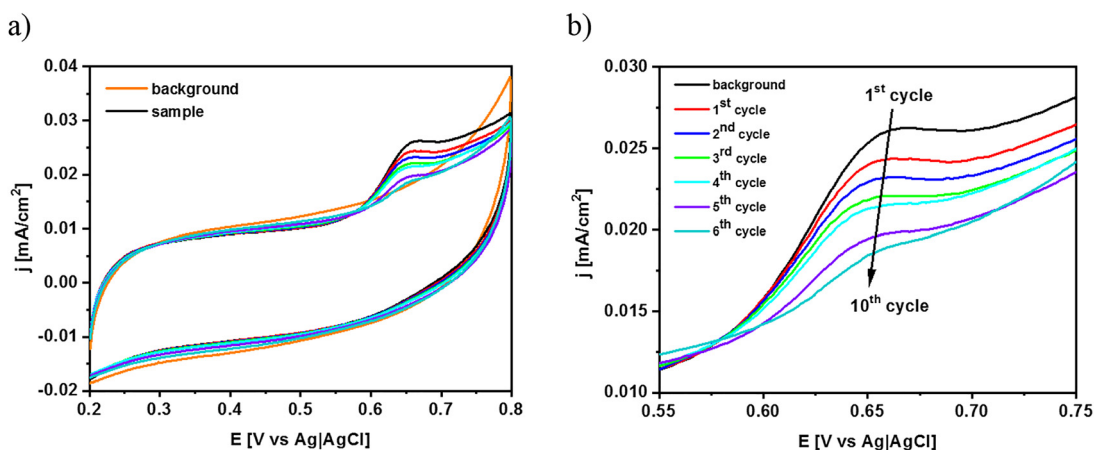


**Fig. 9:** CV recorded for sample PP 2 at the potential range from  $-0.6$  to  $0.1$  V at  $0.1 \text{ M LiClO}_4$  aqueous solution at (a)  $1, 5, 10, 20,$  and  $50 \text{ mV}\cdot\text{s}^{-1}$ , and (b)  $20 \text{ mV}\cdot\text{s}^{-1}$ .





**Fig. 10:** CV recorded at potential range from  $-0.6$  to  $0.5$  V at  $0.1$  M  $\text{LiClO}_4$  aqueous solution for sample (a) PA 1 at scan rate  $1, 5, 10, 20, 50$  and  $100$   $\text{mV}\cdot\text{s}^{-1}$ , (b) 2 PA scan rate  $5, 10, 20, 50$  and  $100$   $\text{mV}\cdot\text{s}^{-1}$ .



**Fig. 11:** CV recorded for sample PET at  $0.1$  M  $\text{LiClO}_4$  aqueous solution at  $20$   $\text{mV}\cdot\text{s}^{-1}$  (a) at the potential range from  $0.2$  to  $0.8$  V, and (b) enlarged potential range.

Literature refers that the anodic peak in the proposed potential range tends to decrease with the following scans, which can be caused by direct oxidation of the BPA and following the blocking of the electrode surface by the oxidation products of BPA [59].

## UV-vis analysis of leaking compounds

Phenazine derivatives are widely used as a fluorescent probe for their absorption of the visible range. To confirm the presence of the species that were released from the PP 1 sample into the solution within the weathering the UV-Vis absorption spectrum was recorded. As can be seen in Fig. 12 the broad appears in the range from about  $550$  to  $700$  nm with a maximum of about  $630$  nm. The band can be ascribed to the Nile Red or Neutral Red, or their mixture that is widely studied within spectroscopic techniques in literature [60, 61]. So, the presence of such a band confirms that some phenazine derivative releases from the sample. Due to the colour of the PA 1 sample, only the red phenazines can be ascribed to recorded bands. Following PET sample releases the bisphenol A, which is in good agreement with electrochemical studies. Based on the literature recorded bands at  $275$  and  $286$  nm confirm the presence of bisphenol A in the solution after laboratory

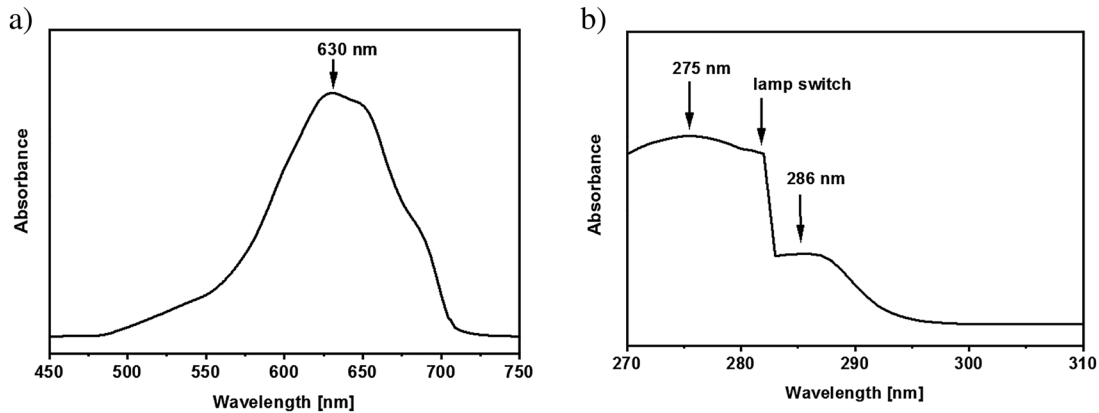


Fig. 12: UV-vis spectrum of aqueous solution gained from weathering of (a) PA 1, and (b) PET.

weathering of the PET sample [62, 63]. UV-vis results for PET sample also are in good correlation with the electrochemical results.

## Sustainability and social awareness

Due to the growing number of scholar and popular publications, social awareness of plastic marine debris (PMD) has increased in recent years [64]. This includes the influence of policy recommendations given by The Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP). GESAMP aims to prevent and reduce the degradation of marine environments and therefore published a list of recommendations on how to contribute less to it.

In contrast, a pilot study on social awareness in Poland showed that there is still a lot to be done. A survey performed on 537 Polish citizens showed that the social awareness of the ghost nets phenomenon is close to none. The average percentage of correct answers was 32.75 %, which clearly shows that the issue should be brought up more in public. Among the questions asked were: the size of microplastics particles, amount of gillnets discarded in the Baltic, main threats of ghost nets, catchability of abandoned fishing nets, etc. The summary of the obtained results is presented in Table 2.

Respondents were asked whether they consume fish and seafood and interestingly, the number of correct answers varied depending on the respondents' diet. Those who refuse animal products in day-to-day life tend to have a better knowledge of sustainable food production, fish and seafood included. This may suggest; that promoting more plant-based diets is a way of reducing demand for fish, which should lead to smaller growth of the fishing industry, and therefore less fishing gear being dumped into oceans [65].

Table 2: The aggregate results of a survey.

Question	No. of correct answers (%)
What is the main material that builds fishing nets?	54.1
How much abandoned fishing gear can be found in the Baltic Sea	49.7
What is the catchability of abandoned fishing nets?	29.6
What is the size of microplastic?	17.9
How many gillnets per year are abandoned in the Baltic Sea?	33.3
What is the main cause of fishing nets being abandoned?	11.9
The average percentage of correct answers given	32.75

Further, respondents were asked to give potential solutions to abandoned fishing gear and gave some ideas worth trying. Among them were: biodegradable fishing nets, an “in/out” record for fishing nets to track down lost nets, the “polluter cleans” policy, fishermen education, etc.

Fish production is a sector growing more rapidly than any other animal food-producing sector. The wild catch is becoming less popular due to aquacultures constantly having to fill the gap between supply and demand for seafood and fish oil. Aquaculture is predicted to replace wild catches by 90 % in the next decade [66]. This is why we focus on developing sustainable aquaculture infrastructure and policy, including waste management is crucial. The world today faces many different problems that are not always environment-related. Undoubtedly though, the human race is highly dependent on the food of aquatic origin. Marine based products currently provide a major part of animal protein requirements in many human communities [67]. Especially, the poor, third world countries depend entirely on the sea as a food provider. According to researchers modelling the supply-demand relation, global demand for the most consumed species worldwide such as tuna, salmon and shrimp is to be reduced [66]. Diversification of food sources would also have a positive effect on ecosystems by reducing monocultures, which are and artificial sites [66].

A global future perspective includes an educated society, international law determining the chemical ingredients of fishing gear and much bigger stress on sustainability. According to the Food and Agriculture Organisation of the United Nations, countries should cooperate and take action towards Responsible Consumption and Production of food, which is one of the 20 Sustainable Development Goals, that is supposed to transform food and agriculture [67].

One of the partial solutions is biodegradable nets. Biodegradable polymers such as filaments based on polylactide (PLA) have already been used for marine purposes [68]. Two innovative products have been produced using PLA: rope Organic by FSE Robline and Elite BioTwine by LankHorst Yarns. Unfortunately, PLA can only biodegrade under specific conditions. An alternative may be found in polyhydroxyalkanoates (PHA) as studies showed that they biodegrade within a month in marine environments [69].

Protecting the marine environment against ghost nets and other ecological problems, such as climate change and ocean acidification is such a complex issue, that it is difficult to include all perspectives at once. Scientific research and chemical analysis are crucial because knowing the cause and consequences, one can suggest solutions. What is more, results should not only be kept in scientific surroundings but also presented to the public for social awareness to raise constantly. Stress should be put on the education of society and its role in global change underlined.

## Conclusions and future perspectives

The increasing problem of ghost nets requires a holistic approach. Although the economic and social perspective is already well described and defined, the issue of physical and chemical properties changing in time needs to be properly addressed. Obtained results indicate that Raman spectroscopy is an efficient tool to identify the type of polymer in a ghost netting and provide information on the stage of decomposition. One can obtain knowledge about main net components and their chemistry what is crucial for a proper understanding of weathering, designing the recycling strategies, further changes in the chemistry of materials available on the market. For instance, the polypropylene lines are a substantial source of marine microplastics. The supplementary research on social awareness revealed the strong need for science engagement in this field. Finally, the preliminary results on using the electrochemical methods for the marine microplastics characterization seem promising, especially for added compounds, and this approach will be developed within future studies.

**Acknowledgments:** Authors would like to thank the members of WWF Poland for the cooperation and all materials given, Barbara Palys for the expert’s consultations on Raman spectra and access to the laboratory equipment.

**Author contributions:** **Agnieszka Dąbrowska** (Raman Spectroscopy & Ghost Nets): Conceptualization, Data Curation, Formal Analysis, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing – Original Draft Preparation, Writing – Review & Editing; **Iwona Łopata**: Investigation, Writing – Original Draft Preparation; **Magdalena Osial** (Electrochemistry): Data Curation, Investigation, Methodology, Resources, Visualization, Writing – Original Draft Preparation, Writing – Review & Editing.

## References

1. P. Rajewski, C. Behrendt, P. Krause. *Eksplatacja i Niezawodność-Maiten. Reliab.* **2**, 76 (2009).
2. E. Grimaldo, B. Herrmann, B. Su, H. M. Føre, J. Vollstad, L. Olsen, R. B. Larsen, I. Tatone. *Fish. Res.* **213**, 67 (2019).
3. A. Wenaty, F. Mabiki, B. Chove, R. Mdegela. *Int. J. Fish. Aquat. Stud.* **6**, 247 (2018).
4. Z. Akdogan, B. Guven. *Environ. Pollut.* **254**, 113011 (2019).
5. Wright R. J., Langille M. G. I., Walker T. R., *ISME J.* **15** (2020) 789–806.
6. L. Lebreton, B. Slat, F. Ferrari, B. Sainte-Rose, J. Aitken, R. Marthouse, S. Hajbane, S. Cunsolo, A. Schwarz, A. Levivier, K. Noble, P. Debeljak, H. Maral, R. Schroeneich-Argent, R. Brambini, J. Reissner. *Sci. Rep.* **8**, 1 (2018).
7. P. Ryan. *Mar. Pollut. Bull.* **135**, 159 (2018).
8. V. Tschernij, P. O. Larsson. *Fish. Res.* **64**, 151 (2003).
9. K. J. Wyles, S. Pahl, L. Carroll, R. C. Thompson. *Mar. Pollut. Bull.* **144**, 48 (2019).
10. E. R. Zettler, T. J. Mincer, L. A. Amaral-Zettler. *Environ. Sci. Technol.* **47**, 7137 (2013).
11. J. Reisser, J. Shaw, G. Hallegraef, M. Proietti, D. K. A. Barnes, M. Thums, C. Wilcox, B. D. Hardesty, C. Pattiaratchi. *PLoS One* **9**, 1 (2014).
12. P. Laganà, G. Caruso, I. Corsi, E. Bergami, V. Venuti, D. Majolino, R. La Ferla, M. Azzaro, S. Capello. *Int. J. Hyg. Environ. Health* **222**, 89 (2019).
13. Y. Yang, G. Liu, W. Song, C. Ye, H. Lin, Z. Li, W. Liu. *Environ. Int.* **123**, 79 (2019).
14. J. Zhang, D. Gao, Q. Li, Y. Zhao, L. Li, H. Lin, Q. Bi, Y. Zhao. *Sci. Total Environ.* **704**, 1 (2020).
15. J. Q. Jiang. *Sustain. Prod. Consum.* **13**, 16 (2018).
16. K. Lei, F. Qiao, Q. Liu, Z. Wei, H. Qi, S. Cui, X. Yue, Y. Deng, L. An. *Mar. Pollut. Bull.* **123**, 122 (2017).
17. E. S. McCallum, R. E. Charney, J. R. Marenette, J. A. M. Young, M. A. Koops, D. J. D. Earn, B. N. Bolker, S. Balshine. *Biol. Invasions* **16**, 2449 (2014).
18. C. Halsband, D. Herzke. *Emerg. Contam.* **5**, 308 (2019).
19. L. Lv, L. He, S. Jiang, J. Chen, C. Zhou, J. Qu, Y. Lu, P. Hong, S. Sun, C. Li. *Sci. Total Environ.* **728**, 138449 (2020).
20. E. M. Jepsen, P. J. N. de Bruyn. *Mar. Pollut. Bull.* **145**, 295 (2019).
21. S. Oberbeckmann, M. Loder, M. Labrenz. *Environ. Chem.* **12**, 551 (2015).
22. J. S. Weis. *Water* **12**, 1475 (2020).
23. M. A. Browne, S. J. Niven, T. S. Galloway, S. J. Rowland, R. C. Thompson. *Curr. Biol.* **2**, 2388 (2013).
24. N. Von Moos, P. Burkhardt-Holm, A. Köhler. *Environ. Sci. Technol.* **46**, 11327 (2012).
25. R. E. Engler. *Environ. Sci. Technol.* **20**, 12302 (2012).
26. C. M. Rochman, E. Hoh, B. T. Hentschel, S. Kaye. *Environ. Sci. Technol.* **47**, 1546 (2013).
27. T. S. Galloway, M. Cole, C. Lewis. *Nat. Ecol. Evol.* **20**, 116 (2017).
28. S. Net, R. Sempéré, A. Delmont, A. Paluselli, B. Ouddane. *Environ. Sci. Technol.* **49**, 4019 (2015).
29. A. Lusher, P. Hollman, J. Mendoza-Hill. *FAO Fish. Aquacult. Technol.* **615**, 1 (2017).
30. M. Y. Chen, M. Ike, M. Fujita. *Environ. Toxicol.* **17**, 80 (2002).
31. A. Usman, S. Ikhlas, S. Ahmad. *Toxicol. Lett.* **312**, 222 (2019).
32. C. E. Talsness, A. J. M. Andrade, S. N. Kuriyama, J. A. Taylor. *Philos. Trans. R. Soc. B* **364**, 2079 (2009).
33. L. Hermabessiere, A. Dehaut, I. Paul-Pont, C. Lacroix, R. Jezequel, P. Soudant, G. Duflos. *Chemosphere* **182**, 781 (2017).
34. P. O. Darnerud. *Environ. Int.* **29**, 841 (2003).
35. K. Ji, K. Cho, J. P. Giesy, J. Musarrat, S. Takeda. *Environ. Sci. Technol.* **45**, 5003 (2011).
36. L. A. Holmes, A. Turner, R. C. Thompson. *Mar. Chem.* **167**, 25 (2014).
37. D. Brennecke, B. Duarte, F. Paiva, I. Caçador, J. Canning-Clode. *Estuar. Coast Shelf Sci.* **178**, 189 (2016).
38. J. Murphy. *Additives for Plastics Handbook*, Elsevier Science Ltd, Oxford, UK, 2nd ed. (2001).
39. A. L. Wani, A. Anmura, J. A. Usmani. *Interdiscipl. Toxicol.* **8**, 55 (2015).
40. I. O. Igbokwe, E. Igwenagu, N. A. Igbokwe. *Interdiscipl. Toxicol.* **12**, 45 (2019).
41. S. L. O'Neal, W. Zheng. *Curr. Environ. Health Rep.* **2**, 315 (2015).
42. L. M. Gaetke, H. S. Chow-Johnson, C. K. Chow. *Arch. Toxicol.* **88**, 1929 (2014).
43. J. L. Xu, K. V. Thomas, Z. Luo, A. A. Gowen. *TrAC - Trends Anal. Chem.* **119**, 115629 (2019).
44. C. F. Araujo, M. M. Nolasco, A. M. P. Ribeiro, P. J. A. Ribeiro-Claro. *Water Res.* **142**, 426 (2018).

45. J. Yu, P. Wang, F. Ni, J. Cizdziel, D. Wu, Q. Zhao, Y. Zhou. *Mar. Pollut. Bull.* **145**, 153 (2019).
46. F. Corami, B. Rosso, B. Bravo, A. Gambaro, C. Barbante. *Chemosphere* **238**, 124564 (2020).
47. C. P. Liao, H. W. Huang, H. J. Lu. *Ocean Coast. Manag.* **172**, 1 (2019).
48. S. J. Stratton. *Prehospital Disaster Med.* **27**, 1200115 (2012).
49. A. B. Silva, A. S. Bastos, C. I. L. Justino, J. P. da Costa, A. C. Duarte, T. A. P. Rocha-Santos. *Anal. Chim. Acta* **1017**, 1 (2018).
50. D. Benito, J. J. García-Jareño, J. Navarro-Laboulais, F. Vicente. *J. Electroanal. Chem.* **446**, 47 (1998).
51. K. C. Lin, Y. C. Lin, S. M. Chen. *Analyst* **137**, 186 (2012).
52. A. N. Azariah, S. Berchmans, V. Yegnaraman. *Bull. Electrochem.* **14**, 309 (1998).
53. M. M. Barsan, M. E. Ghica, C. M. A. Brett. *Anal. Chim. Acta* **881**, 1 (2015).
54. O. Sadak, A. K. Sundramoorthy, S. Gunasekaran. *Biosens. Bioelectron.* **89**, 430 (2017).
55. C. Batchelor-McAuley, A. A. Little, S. V. Sokolov, E. Kästelhön, G. Zampardi, R. G. Compton. *Anal. Chem.* **88**, 11213 (2016).
56. P. Daubinger, J. Kieninger, T. Unmüssig, G. A. Urban. *Phys. Chem. Chem. Phys.* **16**, 8392 (2014).
57. O. Diaz-Morales, T. J. P. Hersbach, C. Badan, A. C. Garcia, M. T. M. Koper. *Faraday Discuss* **201**, 301 (2018).
58. A. Ghanam, A. A. Lahcen, A. Amine. *J. Electroanal. Chem.* **789**, 58 (2017).
59. Z. Yan, B. Fu, J. Chen, T. Liu, L. Kang. *Int. J. Electrochem. Sci.* **13**, 1556 (2017).
60. M. K. Goftar, K. Moradi, N. Moradi-Kor. *Eur. J. Exp. Biol.* **4**, 71 (2014).
61. A. Bag, S. Bhattacharya, A. N. Aa, R. Shunmugam. *MOJ Res. Rev.* **2**, 69 (2019).
62. H. Ali, S. Mukhopadhyay, N. R. Jana. *New J. Chem.* **43**, 1536 (2018).
63. S. Babu, S. Uppu, B. Martin, O. A. Agu, R. M. Uppu. *Toxicol. Mech. Methods* **1537-6516**, 1 (2015).
64. L. A. Amaral-Zettler, E. R. Zettler, B. Slikas, G. D. Boyd, D. W. Melvin, C. E. Morrall, M. Proskurowski, T. J. Mincer. *Front. Ecol. Environ.* **13**, 541 (2015).
65. Wijkstrom U. N., *Vet. Res.* **27** (2003) 461–468.
66. J. K. Ipinjolu, I. Magawata, B. A. Shinkafi. *J. Fish. Aquat. Sci.* **9**, 338 (2014).
67. M. Boliko. *J. Nutr. Sci. Vitaminol.* **65**, S4 (2019).
68. M. Deroiné, I. Pillin, G. Le Maguer, M. Chauvel, Y. Grohens. *Polym. Test* **74**, 163 (2019).
69. M. Breen, N. Graham, M. Pol, P. He, D. Reid, P. Suuronen. *Fish. Res.* **184**, 2 (2016).