INdIGO

INnovative fIshing Gear for Ocean

T3.1.2 Natural and accelerated ageing of the materials in the marine environment

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Summary

I. Introduction

Abandoned, Lost or otherwise Discarded Fishing Gear at sea (ALDFG) is a growing problem due to its negative impact on the marine environment. The INdIGO (INnovative fIshing Gear for Ocean) project aims to develop the first fishing gear with a controlled lifespan that is biodegradable in the marine environment. It also aims to define a strategy for improving the recycling of fishing gear at the end of its life and to promote the circular economy. The alternative solutions proposed by INdIGO are both preventive and curative to achieve good ecological status in the France-Channel-England (FCE) zone by reducing the plastic pollution generated by the fishing and aquaculture industries.

The INdIGO project is a 45-month project funded by the Interreg VA France (Channel) England programme, a European Union programme that encourages economic development between the south of the UK and the north of France. As part of activity 1 of WP3, several ageing studies of the materials developed (monofilaments and multifilaments) have been carried out to study their behaviour when exposed to extreme conditions (UV, seawater, etc.) over relatively long periods.

Initially, the samples were immersed in the marine environment at two different locations: Lorient (Southern Brittany - France) at a depth of 1 m and West Gabbard (UK) in the North Sea at a depth of 15 m. The main objective was to compare the degradation kinetics of the prototypes as a function of the marine environment, with contrasting water quality parameters such as temperature, salinity, conductivity, turbidity, and UV radiation.

Samples will be taken at regular intervals over a 12-month period to identify the mechanisms and kinetics of material degradation. The protocols for the soak tests will be described in detail in this report, as will the sampling intervals and the monitoring of water temperature. The samples will be characterized in such a way as to determine the initial properties at t=0, to establish the reference before ageing in seawater. After each sample is taken, the same tests will be carried out to monitor changes in the properties of the samples. All the results obtained will be presented in this report.

At the same time, the prototypes were also exposed to UVs, both naturally and artificially. The natural ageing was carried out by IRMA on the Lorient site, while the accelerated ageing tests were carried out by CEFAS in a specialised enclosure. The evolution of the properties of the samples will be characterised and the results compared.

A study on alternating air and water immersion will be presented and the results will also be compiled in this report. The tests involve alternating exposure of the samples at different frequencies (4 and 8 days), to simulate the real conditions associated with use on a fishing boat.

Finally, during use or degradation of the filaments, they are likely to release microplastics into the environment. The INdIGO partnership therefore wanted to study this phenomenon through Cefas, which analysed the potential formation of microplastics in biodegradable samples exposed to a marine environment.

The partners involved in the deliverable are: UBS, IRMA and Cefas.

II. Materials and Methods

1. Presentation of materials

In agreement with the project partnership, three samples have been selected (Figure 1) two formulations are being studied for the monofilament, referenced mono 1 AC and mono 2 AH, and one formulation for the multifilament, referenced multi Y.

Figure 1: Presentation of the samples selected for the ageing studies.

As indicated in deliverable T2.1.1 "selection of formulations", the monofilaments are mainly composed of PBS. Multifilament Y is also made of PBS, with a specific viscosity better suited to the spinning process.

2. Ageing protocols

a) Ageing platform in natural seawater

It is important to remember that the prototypes will be in direct contact with sea spray, sand and seawater, all aggressive factors that influence the rate at which polymers degrade. This is why ageing in a marine environment has been studied.

➔ **Ageing in the Lorient Bay**

IRMA has an offshore platform for carrying out ageing tests in natural seawater (in static or dynamic mode) to study the degradation of plastics over time. The samples were immersed in Japanese lanterns in the port of Kernevel in the harbour of Lorient (Figure 2) and the assembly has been placed vertically under the pontoons of the marina since 17 March 2022 (static mode).

Samples were taken every 3 months for a total ageing period of 12 months. Various characterisations were carried out on the samples to compare the properties before and after ageing in a marine environment, including tensile tests to monitor changes in mechanical properties, and microscopic observations using the SEM to monitor changes in surface condition, etc.)

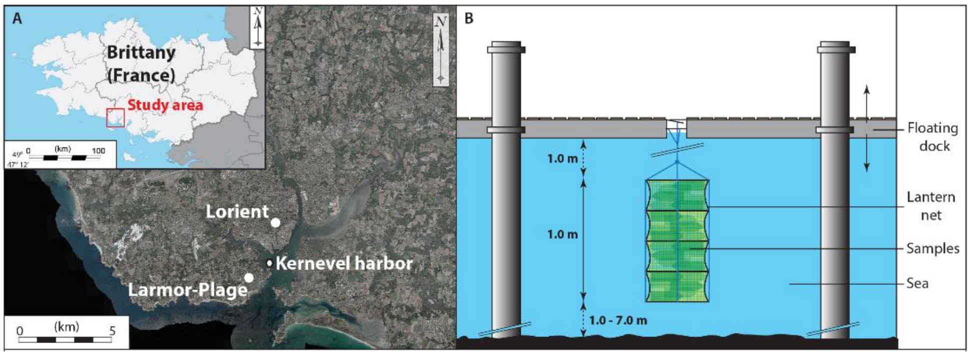

Figure 2: location of nets for the study of natural ageing in the marine environment.

➔ Ageing in the North Sea

Cefas has a network of fully equipped buoys that it uses to deploy equipment at sea via its SmartBuoys system. SmartBuoys are autonomous, moored systems that record water quality parameters and are deployed at coastal sites as part of the UK's marine eutrophication monitoring programme. The Warp and West Gabbard buoys are in the areas covered by the North Sea and English Channel sites.

Water samples are collected and stored on board for subsequent analysis of nutrients and phytoplankton species. The SmartBuoys are serviced 4 times a year and the data recorded at a depth of 1 m includes: high-frequency real-time measurements of parameters such as surface salinity, temperature, turbidity, O2 saturation, chlorophyll fluorescence and nutrient concentrations. A description of the instruments and sensors used to collect high-frequency data on water quality parameters is presented in Appendix II.

The buoy connected to West Gabbard 2 (51°57'.25N 002°06'.65E) was selected because of the low turbidity in the area (Figure 3).

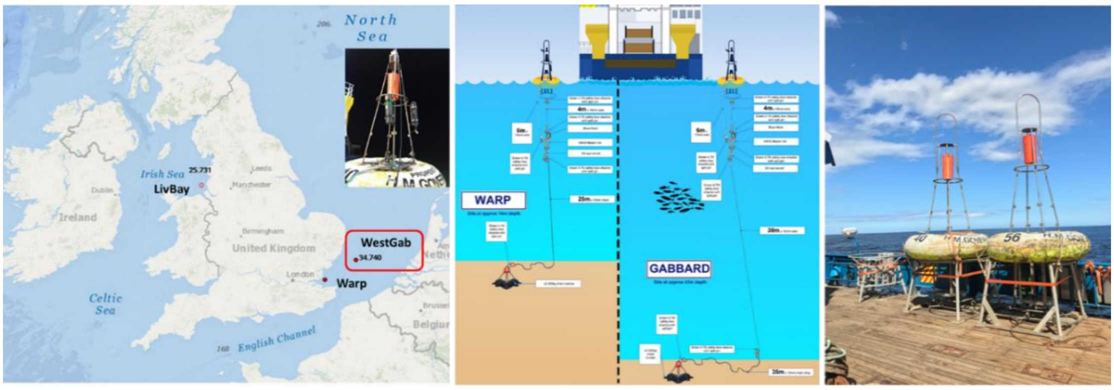

Figure 3: Location of the West Gabbard SmartBuoy and setting up the equipment deployment system at sea.

The configuration of the deployment of materials at sea is illustrated in Figure 4. It consists of a metal frame deployed at a depth of 15 m to simulate the ageing behaviour of lost fishing gear when present in the water column. This configuration was also complementary to the configuration applied by the French partners (UBS) with the deployment at sea of samples at the sea surface.

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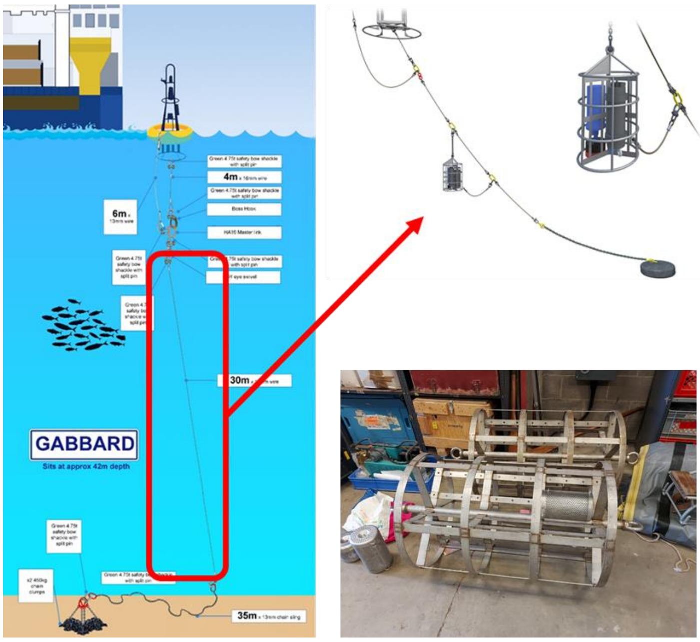

Figure 4: Deployment configuration at sea for ageing INdIGO samples.

Intelligent sensors were also installed on the frame of the median attachment to collect seawater parameters at a depth of 15 m for comparison with data collected at the surface at a depth of 1 m (Table 1). The initial deployment strategy was to deploy the equipment at sea for a period of 12 months. Samples were taken every 3 months for a period of 9 months. Deployment of the materials at sea is still underway and samples will be collected for t=12 months.

Sensor	Parameter	Resolution	Sampling Frequency (Seconds)	Frequency data acquisition (min)
Seapoint Turbidity	**Turbidity**	**0.03 FTU**	**1**	**30**
Aandreaa CT	**Conductivity**	0.0002 S/m (0.002 mS/cm)	10	30
Aandreaa CT	**Temperature**	0.01°C	10	30
Druck Pressure	**dBar**	0.006105m	1	30
Licor Underwater Quantum sensor	**Par**	20 µmol m-2 s-1	1	30

Table 1: Water quality parameters recorded at 15m depth.

Samples were immersed using modified passive sampling cages with sample holders shown in Figure 5. The cage openings are large enough to allow free access to the seawater and microorganisms present.

➔ Special case of monitoring the formation of microplastics

To study the fragmentation of microplastic materials, smaller cages were also designed and built by Cefas. These consisted of a 300 µm mesh held in place by a metal frame with a lid (Figure 6). The sample holders and the cage containing the samples were fixed by means of an internal metal rod in the cage of the modified passive sampler.

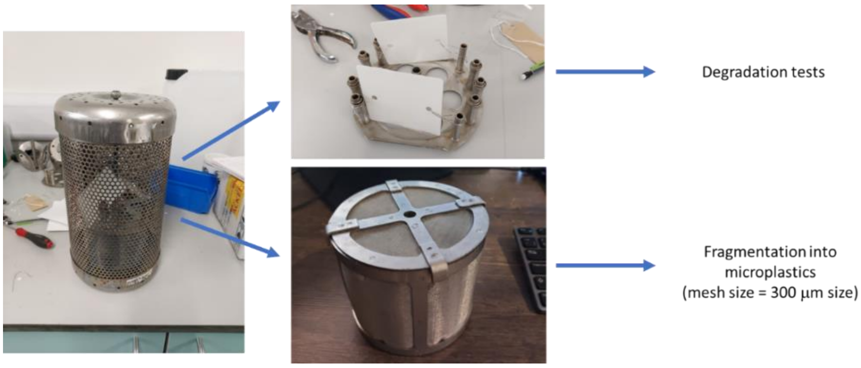

Figure 5: Modified passive sampling cage for the deployment of biodegradable materials at sea.

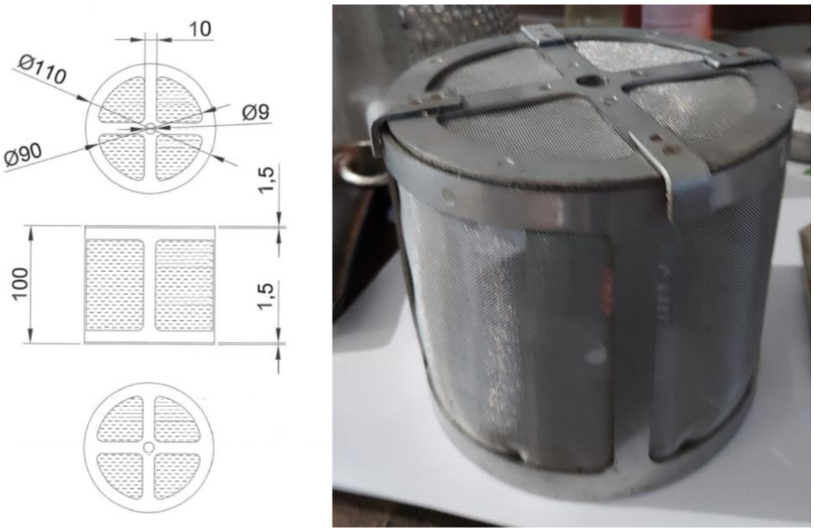

Figure 6: Sample cage for studying the fragmentation of microplastic materials.

At each sampling, i.e. every 3 months, the chemical and physical degradation profile of the various aged samples is analysed. Chemical characterisation was carried out using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), while physical degradation was carried out using scanning electron microscopy (SEM). The methods applied are detailed below. Control (unaged) samples were also stored in a cabinet, protected from light and moisture to prevent degradation during the experiment. Due to the time constraints of this project, only infra-red analysis (ATR-FTIR) was carried out on the materials aged at sea.

b) UV natural ageing platform

The products developed as part of the INdIGO project will also be exposed to UV rays, both monofilaments for fine nets and multifilaments for aquaculture nets.

It makes sense to study their behaviour when they are exposed to natural light, with a view to anticipating any early degradation of the samples. IRMA has therefore installed a device at the back of the building to monitor the natural ageing of the samples in contact with UV light (Figure 7). This device will also be used for alternating water/air ageing.

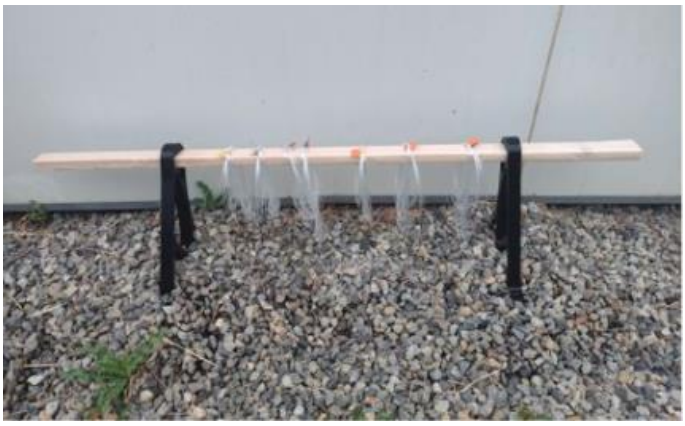

Figure 7: Mounting for exposure of wires to the sun's UV rays with natural ageing.

c) Accelerated ageing in climatic chambers

➔ **Sample preparation**

Monofilament and multifilament samples were placed in pre-cleaned 200 mm borosilicate glass tubes (Figure 8). To facilitate subsequent study of biodegradation and ecotoxicity tests, some samples were transformed into powder form by grinding under liquid nitrogen. The powdered samples were also placed in individual borosilicate glass tubes to be exposed to xenon, air and seawater in the accelerated ageing chamber for 3 months.

In order to study the leaching of potentially hazardous chemicals into the environment, mono and multifilaments and powdered materials were removed by filtration through a Whatman® 47mm regenerated cellulose filter (0.2mm pore size). The filtered seawater and controls (seawater alone and reverse osmosis water alone) were sent to IRMA for biodegradation and ecotoxicity tests. The recovered samples were then characterised by microscopic observation of the surface (SEM), infra-red analysis (ATR-FTIR).

Figure 8: Exposure of materials in glass tubes installed in the ageing chamber.

➔ **Accelerated ageing protocol in climatic chambers**

Artificial ageing of the materials was carried out using a Q-SUN Xenon ageing chamber (Model Xe-1, Q-lab), shown in Figure 9 below. The xenon arc, fitted with filters, was used to simulate the relative spectral irradiance of daylight in the ultraviolet (UV) and visible regions of the spectrum. The Xe-1 model is not equipped with a spraying system and the materials were exposed either in air or in seawater. The tubes were rotated daily to ensure even exposure of the samples to the light source. The xenon test chamber was programmed to follow the standard ISO 4892-2 method, which specifies test conditions that reproduce the effects of weathering on plastic materials using humidity and xenon arc light. Irradiance was set at 0.51 W/m2 with a temperature set at 63°C.

Figure 9: Q-SUN ageing chamber for accelerated ageing of biodegradable materials.

d) Ageing in alternating air/water conditions

One of the aims of this study is to carry out ageing by alternating contact with water and UV rays to simulate real-life fishing gear conditions as closely as possible. In fact, when a net is in use, it is immersed in water, then stored on the deck of the boat, and so on... This alternating ageing study was carried out via a 3-month internship during 2022, with intern Jeremy Baribeault-St-Germain being supervised by the UBS (all the results are described in detail in his internship report, which has already been imported into eMS during period 5). It is appropriate here to present the most interesting results obtained in connection with this deliverable.

Four series of studies were therefore launched in parallel on the samples selected above, i.e., two types of monofilaments and one multifilament, described below:

- Hydrothermal ageing in distilled water at 30°C
- UV ageing via exposure to natural light
- Alternating 8-day ageing in water and air
- Alternating 4-day ageing in water and air

Hydrothermal ageing took place in a water bath filled with distilled water, where the temperature was maintained at 30°C throughout the 2-month study.

3. *Characterisation techniques*

A wide range of experimental methods will be used in the project, including thermal, mechanical and physico-chemical characterisation techniques.

a) Thermal properties

- *Differential Scanning Calorimetry (DSC)*

Differential scanning calorimetry is a thermal analysis technique that measures the differences in heat exchange between a sample to be analysed and a reference. It is used to determine phase transitions such as the glass transition temperature (Tg) of amorphous materials, melting temperatures (Tm), crystallisation temperatures (Tc) and enthalpies of reaction. The samples have an average mass of around 10 mg and are placed in aluminium crucibles. The sampling zone is a fragment representing the entire sample. The curves obtained were processed using STARe software.

- **Machine**: METTLER type DSC 822e
- **Method used:**

  First heating: from 0 to 200°C at 20°C/min, step at 200°C for 3 minutes,

  Cooling: from 200 to 0°C at 20°C/min, step at 0°C for 3 minutes,

  Second heating: from 0 to 200°C at 20°C/min.

This technique can also be used to determine the crystallinity of samples:

$$\chi = \Delta H_m / \Delta H_{100\%}$$

with ΔHm the enthalpy of fusion (J/g) calculated from the melting peak and ΔH100% the enthalpy of fusion for a totally crystalline polymer.

- *Thermogravimetric analysis (TGA)*

Thermogravimetric analysis (TGA) is a complementary thermal analysis technique used to monitor polymer degradation temperature. The principle involves measuring the variation in mass of a sample as a function of time.

- **Machine**: METTLER ATG-DSC 1
- **Method used**: air flow and simple heating from 20 to 800°C at 10°C/min.

b) Morphological and physico-chemical properties

- *Molecular mass analysis*

Monitoring the molar mass is essential for defining the degradation mechanism of the material. The presence of water and/or UV light can weaken the material through chain cutting mechanisms (see Figure 10), leading to material degradation. As a function of immersion time, the molar mass can therefore change.

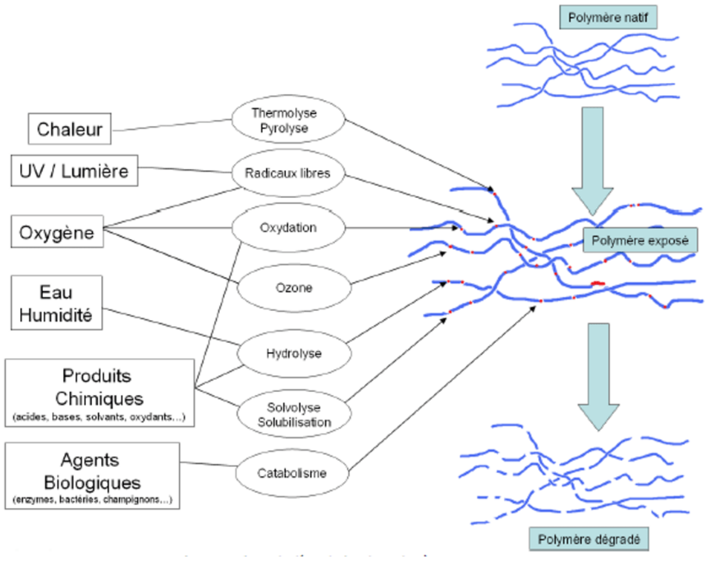

Figure 10: Major polymer degradation agents leading to changes in molecular mass.

The samples are prepared by dissolving the polymer in chloroform for 24 hours at room temperature, then filtered and analysed by steric exclusion chromatography (SEC). These analyses are subcontracted to a partner laboratory.

- *Scanning Electron Microscope (SEM)*

Microscopic observations can also be made on the surface of the sample using a scanning electron microscope (SEM). These observations are necessary because they enable us to look as closely as possible at the sample, to check whether attack by micro-organisms has taken place during marine ageing via a surface erosion mechanism, for example. The samples are first metallised with a thin layer of gold.

Machine: Jeol JSM IT500-HR/LA

For samples aged at Cefas, SEM analysis was carried out at the University of East Anglia, UK. The samples were also gold-coated using a Polaron SC7640 high-resolution sputter coater manufactured by Quorum Technologies. The samples were then imaged under vacuum with a ZEISS Gemini 300 scanning electron microscope using the secondary electron detector.

- *Infrared spectrometry*

La caractérisation chimique des échantillons fournis par UBS a été réalisée à l'aide de la spectroscopie infrarouge à transformée de Fourier à réflexion totale atténuée (ATR-FT-IR)

- **Machine**: Thermo Fisher Scientific Nicolet iS5 ATR-FTIR
- **Software:** OMNIC (version 9.9.473).
- **Method used**: absorbance mode in the 4000-400 cm^{-1} ranges, a resolution of 4 cm^{-1}

The ATR-FTIR spectra were superimposed for the same virgin and aged material to study all the chemical changes associated with accelerated ageing in the xenon lamp ageing chamber. The spectra were processed with Bruker OPUS version 8.5.

c) Mechanical properties

- *Tensile tests*

The tensile tests were carried out on an Instron 5566A machine equipped with a 1kN load cell. The monofilaments were tested using the same protocol as that specified in standard NF EN ISO 2062, in a controlled atmosphere (23°C, RH50%). The main test parameters are as follows:

- Specific jaws for 1kN monofilament
- Initial length between jaws: 250 mm
- Tensile speed: 250 mm/min, Diameter: average of 5 measurements for each test
- Results based on a minimum of 5 tests

The main mechanical characteristics calculated using these tensile tests are Young's modulus, stress at break, strain at break and force at break. The tensile tests carried out before and after each sample are used to highlight changes in mechanical properties over time: whether the material becomes more rigid and brittle over time (e.g., hydrolysis), or on the contrary, whether it deforms more (e.g., plasticisation, etc.).

- *Abrasion resistance measurement*

The machine used to carry out these tests is an adaptation of the machine described in the ASTM D6611 standard for measuring the abrasion resistance of multifilaments. According to this standard, abrasion is caused by the filament rubbing against itself when subjected to a defined weight and driven by a motor at 1 rpm (Figure 11a).

In our case, the monofilament does not slide against itself, preventing the abrasion resistance measurement. After discussions with Le Drezen (France's leading net manufacturer, based in Le Guilvinec - Finistère), we were able to adapt the standard by replacing the lower pulley with an abrasive surface such as a grinding wheel (Figure 11b), allowing the abrasion resistance of the monofilament to be measured at this level. This machine was custom designed at UBS by Mr Hervé Bellegou.

In this project, we carried out a qualitative study to compare the abrasion resistance of the 2 monofilaments selected. The main parameters used are as follows:

- 4 different weights: 26 g, 42 g, 71 g, 91 g
- 10 repetitions per weight, same series performed in water immersion.

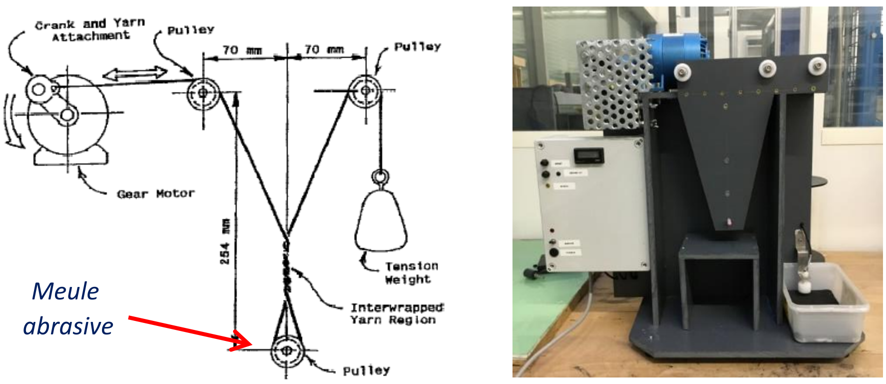

Figure 11: Diagram corresponding to the ASTM standard where abrasion takes place filament against filament (left) and machine used with an abrasive surface instead of a pulley (right)

III. Study of filament degradation

1. *Natural ageing*

This section looks at the ageing of the monofilaments studied. Initially, the various monofilaments were placed in natural ageing conditions in a marine environment to understand the various phenomena involved during their degradation. The results will concern two monofilaments of different diameters designed for slow degradation and one multifilament designed for faster degradation in the marine environment. The different samples taken depend on the formulation studied:

- Monofilament degradation: 3 months, 6 months, 9 months, and 12 months
- Multifilament degradation: 1 month, 3 months

a) Study of ageing in a marine environment

- **Microscopic observations**

The microscopic observations obtained using a Scanning Electron Microscope (SEM) were carried out to study and understand the behavior of the monofilaments after long-term immersion in a marine environment for 12 months. Figure 12 and Figure 13 below show the images taken of the surface of the AC and AH monofilaments, unaged and then after each sample, 3, 6, 9 and 12 months, respectively.

Before ageing, for both samples, the unaged monofilaments have a homogeneous and uniform surface. After only 3 months of ageing in natural seawater, the AC and AH monofilaments already show some surface irregularities for the same immersion time. As they age, the surface condition of the monofilaments changes, with a significant increase in surface roughness. After 9 months of immersion, the surface becomes increasingly heterogeneous, with an increase in the number and size of pores, and after 12 months of immersion, the AC and AH monofilaments appear weakened...

Figure 14 represents the SEM images obtained from the surface of the multifilaments before and after ageing for 3 months in a marine environment. An intermediate sample after 1 month was added in view of the rapid degradation rate of the multifilaments. Before immersion, the surface of the multifilaments was smooth and uniform. After only 1 month of ageing, surface irregularities appeared and after 3 months, the surface condition of the multifilaments was severely degraded. Mechanical tests are even impossible because the samples have become very brittle. The diameter of a multifilament strand is between 25 and 35 µm, which could explain this very rapid degradation. However, it is important to remember that the ageing process applied is one of complete immersion. These filaments, intended for the manufacture of catinage nets, will not undergo complete immersion but will alternate between immersion and air, which should slow the rate of degradation.

These images enable us to highlight one of the degradation mechanisms of biodegradable plastics, namely enzymatic degradation occurring heterogeneously on the surface. This phenomenon has already been described in the literature in the degradation of PHAs, for example. The degradation kinetics of these monofilaments appear to be rather rapid in a marine environment, which may also be an added value for the targeted application.

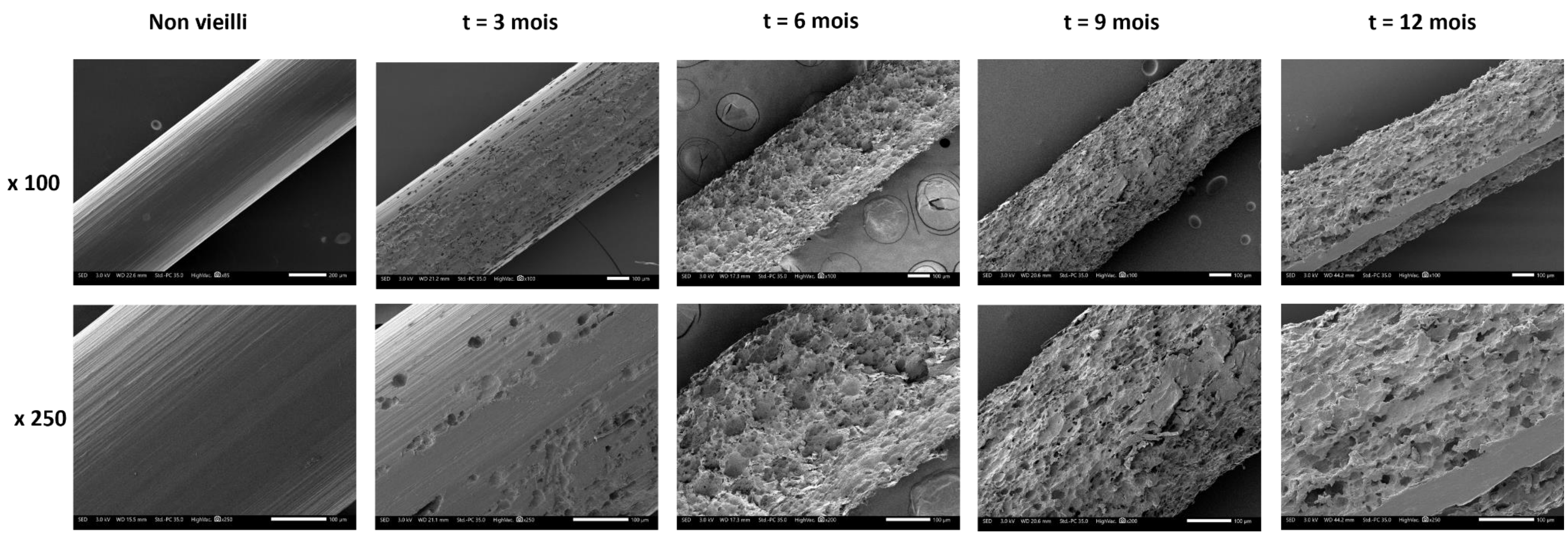

Figure 12: Microscopic observations of the surface condition of AC monofilaments before and after natural ageing in a marine environment at two magnifications (x100 et x250)

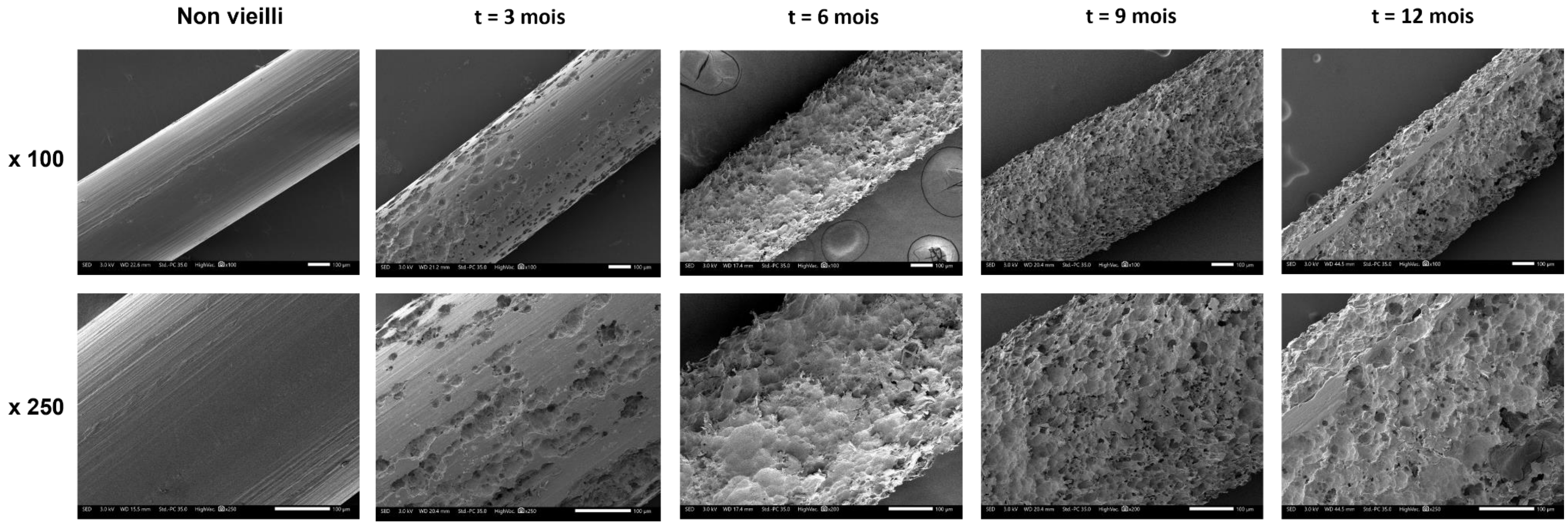

Figure 13: Microscopic observations of the surface condition of AH monofilaments before and after natural ageing in a marine environment at two magnifications ((x100 et x250)

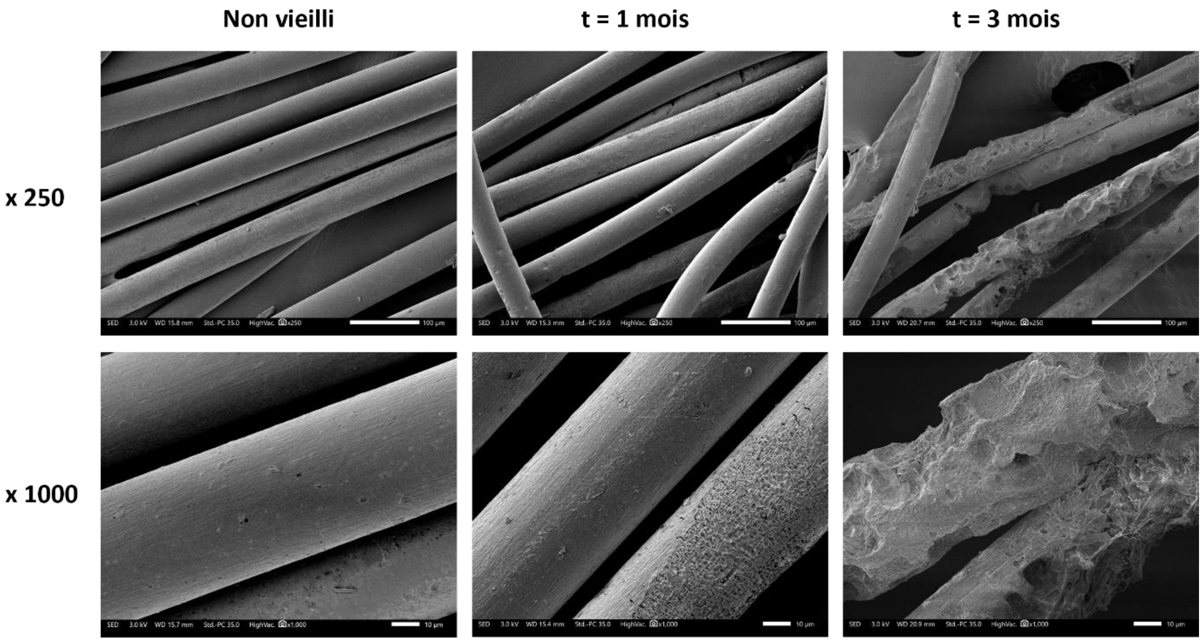

Figure 14: Microscopic observations of multifilaments before and after ageing in a marine environment.

- **<u>Changes in monofilament diameter</u>**

The SEM images show that the surface condition changes significantly during degradation, as does the diameter. The evolution of the size of the AC and AH monofilaments, and more precisely the diameter, was therefore calculated using image processing software (ImageJ) on the different images obtained. The results obtained are presented in Table 2 below for the two monofilaments studied:

Durée (mois)	**Mono AC** ø (µm)	**Mono AH** ø (µm)
0	606,0 ± 0,76	528,9 ± 1,61
3	566,6 ± 1,464	522,6 ± 0,87
6	452,4 ± 10,11	487,5 ± 13,24
9	517,2 ± 1,24	535,9 ± 11,98
12	496,6 ± 12,91	525,4 ± 10,65

Table 2: Evolution of monofilament diameters calculated using IMAGE J software.

Over the immersion period, the diameter of the AC monofilament appears to decrease progressively, with a diameter of around 500µm after 12 months, compared with 600µm for the unaged monofilament. The diameter of the AH monofilament appears to be more stable over time. It is important to note that during the transformation process, i.e. during the extrusion-spinning of the monofilaments, the output diameter is checked and variations in diameter are sometimes observed. Diameter measurements are therefore given for information only.

Additional analysis, such as gravimetric monitoring of the samples, would make it possible to track the loss of mass of the samples more accurately.

- **<u>Evolution of mechanical properties</u>**

The evolution of the mechanical properties of AC and AH monofilaments as a function of ageing time in a marine environment is shown in the Table 3 below.

	Durée (mois)	**diamètre (µm)**	**Module E (Mpa)**	**σ_b (Mpa)**	**ε_b (%)**	**F (N)**
AC	0	475,0 7,1	1393,1 28,7	242,4 5,3	43,7 6,1	43,3 0,9
	3	488,0 29,0	1230,9 136,8	195,0 29,1	18,0 0,2	36,2 0,9
	6	466,0 26,8	1137,5 105,5	149,5 17,6	16,8 0,6	25,3 0,4
	9	447,0 5,0	1353,5 65,8	158,5 11,6	17,0 0,5	24,9 1,5
	12	443,8 7,5	1190,0 76,0	116,7 10,0	14,4 0,8	18,0 1,6
AH	0	498,0 31,1	1254,6 130,9	214,9 20,7	50,2 8,4	41,6 1,7
	3	490,6 21,0	1072,5 57,7	176,6 17,2	21,4 0,5	33,3 0,8
	6	511,3 15,5	949,5 53,8	129,6 10,6	20,5 0,8	26,5 0,5
	9	498,8 15,5	1032,9 84,0	107,9 7,3	18,0 0,4	21,0 0,3
	12	452,0 24,0	1049,3 113,8	111,6 15,7	17,5 1,2	17,7 1,1

Table 3 : Evolution of the mechanical properties of AC and AH monofilaments as a function of immersion time

Firstly, the diameter values measured in micrometers are slightly different from those obtained using the image processing software (Table 2). However, the trends appear to be similar, with a gradual decrease in the diameter of the AC monofilament, and a stabilisation of the diameter of the AH monofilament up to 9 months of ageing, with a decrease observed after 12 months.

The most interesting mechanical property for our discussions with end-users concerns the breaking strength, expressed in Newtons, which can be converted into kilograms (a more meaningful value), using the ratio 10N = 1kg. The evolution of the breaking force is represented more specifically on the Figure 15:

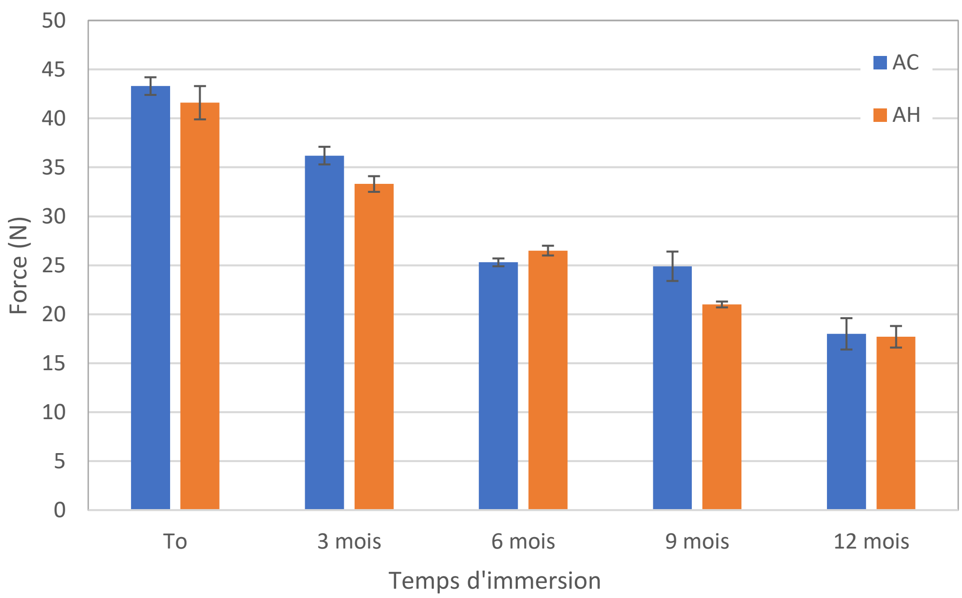

Figure 15 : Progressive changes in the breaking strength of the 2 monofilaments studied

Over the period of immersion in natural seawater, the tensile strength decreased progressively, with a loss of 50% of the properties after 12 months of ageing, compared with the properties of the unaged monofilaments. It is important to note that there were no significant differences in degradation kinetics between the 2 monofilaments. Figure 16 shows the evolution of stress at break and strain at break over time for the AC and AH monofilaments. In the same way as for the force at break, the decrease in stress at break appears to be progressive over time. Strain at break drops rapidly after only 3 months of immersion, with a loss of more than 50% compared with the properties of unaged monofilaments, while the values change little or not at all between 3 and 12 months of ageing.

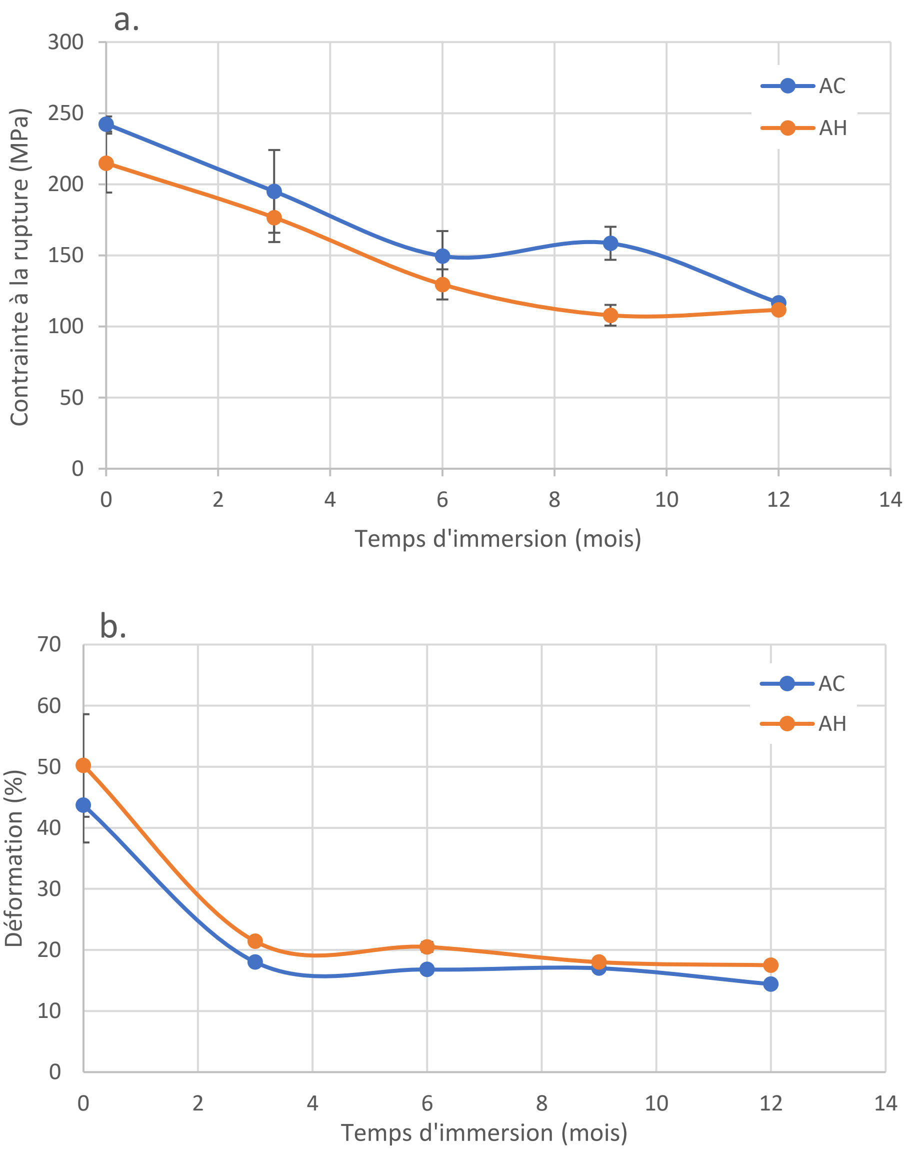

Figure 16 : Evolution of stress at break (a) and strain at break (b) as a function of immersion time in natural seawater for AC and AH monofilaments.

Tensile tests on multifilaments are more difficult to carry out because of the need to measure diameters, detect breakage, etc. For this type of sample, the traditional methods used in the technical textiles sector on fibres were therefore applied.

For each multifilament studied, the linear mass, which corresponds to the length of yarn in kilometres contained in one kilogram, was calculated, as well as the tex, which indicates the weight in grams of 1000 m of yarn. These parameters are used to calculate the strength and tenacity of the multifilaments.

Strength is the force measured when the wire breaks under tension and is expressed in newtons (N). Tenacity corresponds to the strength measured in 1 tex and is therefore expressed in newtons (or centinewtons) per tex. This makes it possible to compare the strength of wires independently of their size.

The other properties studied are like the conventional tensile test: elongation at break expressed as a percentage (%) and stiffness or modulus of elasticity, characterised by Young's modulus (E).

Tensile tests after ageing were not possible, as the samples were far too brittle after 3 months' ageing in natural seawater, in line with the microscopic observations obtained on the surface of the multifilaments.

- **Evolution of thermal properties**

The evolution of the thermal properties of AC and AH monofilaments as a function of ageing time in a marine environment is monitored by DSC.

For the two monofilaments studied, the melting temperatures on initial heating and the crystallization temperatures on cooling appear to be stable over the immersion time. Two peaks associated with melting temperatures appear on 1st and 2nd heating, already observed in the literature for polyester formulations such as PBS [1].

However, the precision of the calorimetric analysis of the thermal properties does not reveal any chemical degradation after 12 months of ageing in a marine environment.

Confidential results

- **Molecular mass evolution**

Molar mass analyses were subcontracted, and a choice was made by the partnership to select the most relevant samples. Whatever the formulation studied, the molar masses appear to be stable after 12 months' immersion in natural seawater. These results are in line with those obtained after thermal analysis, which did not reveal any chemical degradation linked to breaks in macromolecular chains caused by hydrolysis. [2].

Confidential results

- **Assessment: degradation mechanism identified**

During natural ageing, microscopic observations reveal a significant increase in the surface roughness of monofilaments. Mechanical properties also change gradually over time. Thermal analysis and monitoring of the molar mass of samples aged in a marine environment did not reveal any chemical degradation by chain cutting linked to hydrolysis. These results enable us to identify the degradation mechanism of monofilaments when exposed to a marine environment: biotic degradation (linked to the action of marine micro-organisms), via an enzymatic hydrolysis mechanism [3].

The fungi, bacteria and algae in our environment have a large exo-enzymatic arsenal capable of degrading organic macromolecules that they are unable to bio-assimilate directly because of their high molar mass. It is necessary to reduce this polymer into much smaller elements (low molar masses) before considering consuming it (Figure 17).

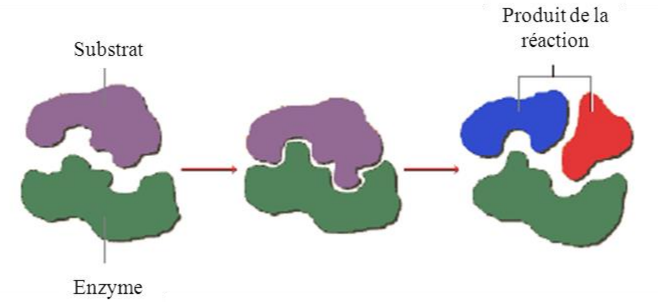

Figure 17 : how an enzyme works.

What's more, a number of these exo-enzymatic actions catalyse hydrolysis: this is the case, for example, with the action of amylases, proteases, nucleases, cellulases, esterases and other hydrolases.

Enzymatic hydrolysis can take place in several ways. In the first case, endo-enzymes cause random breaks in the ester bonds of the polyester's carbon chain, releasing polymers with a lower molar mass. In the second case, exo-enzymes specifically hydrolyse the ester bonds at the end of the chain, releasing monomers. In this case, the average molar mass of the polymer is only slightly affected, although an overall loss of mass can be observed. In the scientific literature, Tsuji and Suzuyoshi observed this case on a PHB aged at sea for 10 weeks with a mass loss of more than 10% without any change in molar mass [4].

Additional analyses, such as gravimetric monitoring of the monofilaments, would make it possible to follow the evolution of mass loss and confirm the degradation mechanism.

b) Influence of the immersion environment

The incubation environment is one of the parameters that can influence the rate of degradation of a biodegradable material. Depending on the microorganisms present, the temperature of the water and physico-chemical parameters such as salinity, composition, pH, etc., the rate of degradation of samples can differ from one place to another. The following results therefore present the evolution of the mechanical properties of monofilaments immersed at Lowestoft in the North Sea. A comparison is then made with the monofilaments immersed at Lorient in Brittany.

All the samples deployed at sea at a depth of 15 m were intact and showed signs of biological fouling (Figure 18).

- **Physico-chemical factors**

Some water quality parameters were superimposed to understand the potential impact of variation in marine physico-chemical parameters. Individual graphs for conductivity, salinity, irradiance and photosynthetically active radiation are presented in Appendix III. No differences in conductivity, temperature and salinity were observed for the recording date at 1 m and 15 m depth. No photo-synthetically active radiation (PAR) values were measured at 15 m depth as opposed to 1 m depth, indicating a limited impact of solar radiation on the materials deployed at 15 m depth.

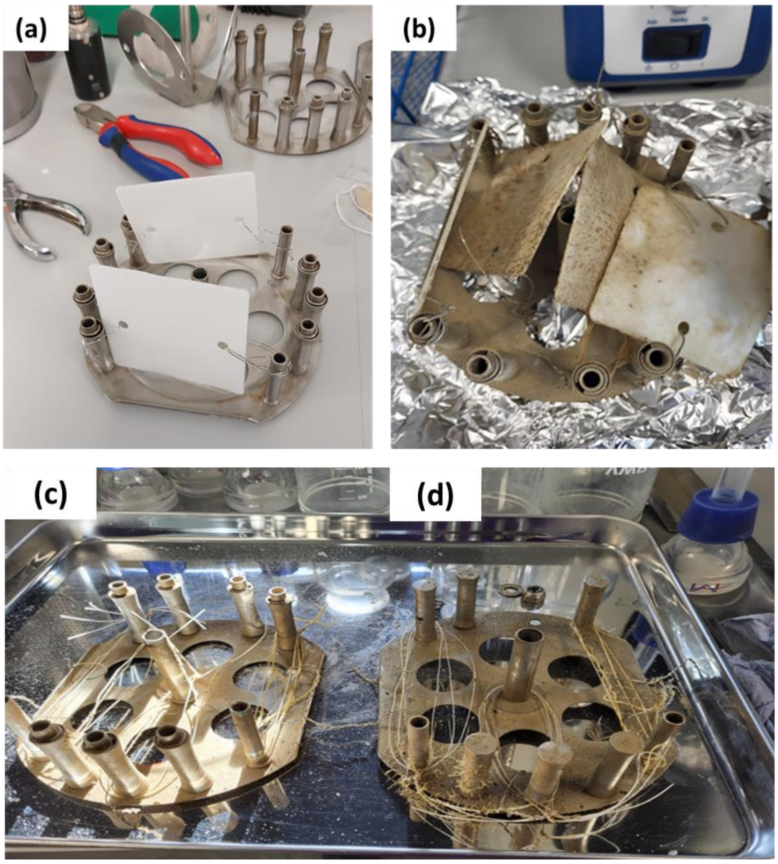

Figure 18. Fixation of samples before deployment (a/ b) and after deployment at sea (b/ d) for samples in the form of plates (a/ b) and mono and multifilaments (c/d).

- **<u>Evolution of mechanical properties</u>**

The evolution of the mechanical properties of AC and AH monofilaments aged in the North Sea, as a function of immersion time, is shown in the Table 4 below.

	Durée (mois)	diamètre (µm)	Module E (Mpa)	σ_b (Mpa)	ε_b (%)	F (N)
AC	0	475,0 7,1	1393,1 28,7	242,4 5,3	43,7 6,1	43,3 0,9
	3	487,5 17,1	1014,9 159,2	214,9 16,7	23,7 1,0	40,0 0,9
	6	485,0 7,1	997,2 25,7	214,2 10,5	23,8 1,6	39,6 0,8
AH	0	498,0 31,1	1254,6 130,9	214,9 20,7	50,2 8,4	41,6 1,7
	3	488,8 18,4	1155,0 91,7	209,6 16,5	22,1 1,3	39,2 2,0
	6	496,0 5,7	1058,6 25,8	195,0 11,6	22,1 0,9	37,6 1,4

Table 4: Evolution of the mechanical properties of AC and AH monofilaments immersed in the North Sea

After 6 months of immersion in the North Sea, the diameter of the AC and AH monofilaments appears stable. A gradual decrease in stress at break is observed during ageing, as well as a drop in deformation from the first few months of immersion, in the same way as for monofilaments aged in Southern Brittany.

Figure 19 below shows the evolution of the breaking strength of AC and AH monofilaments between the two environments studied: natural ageing in Lorient (VN Lorient) and natural ageing at Cefas (VN Cefas).

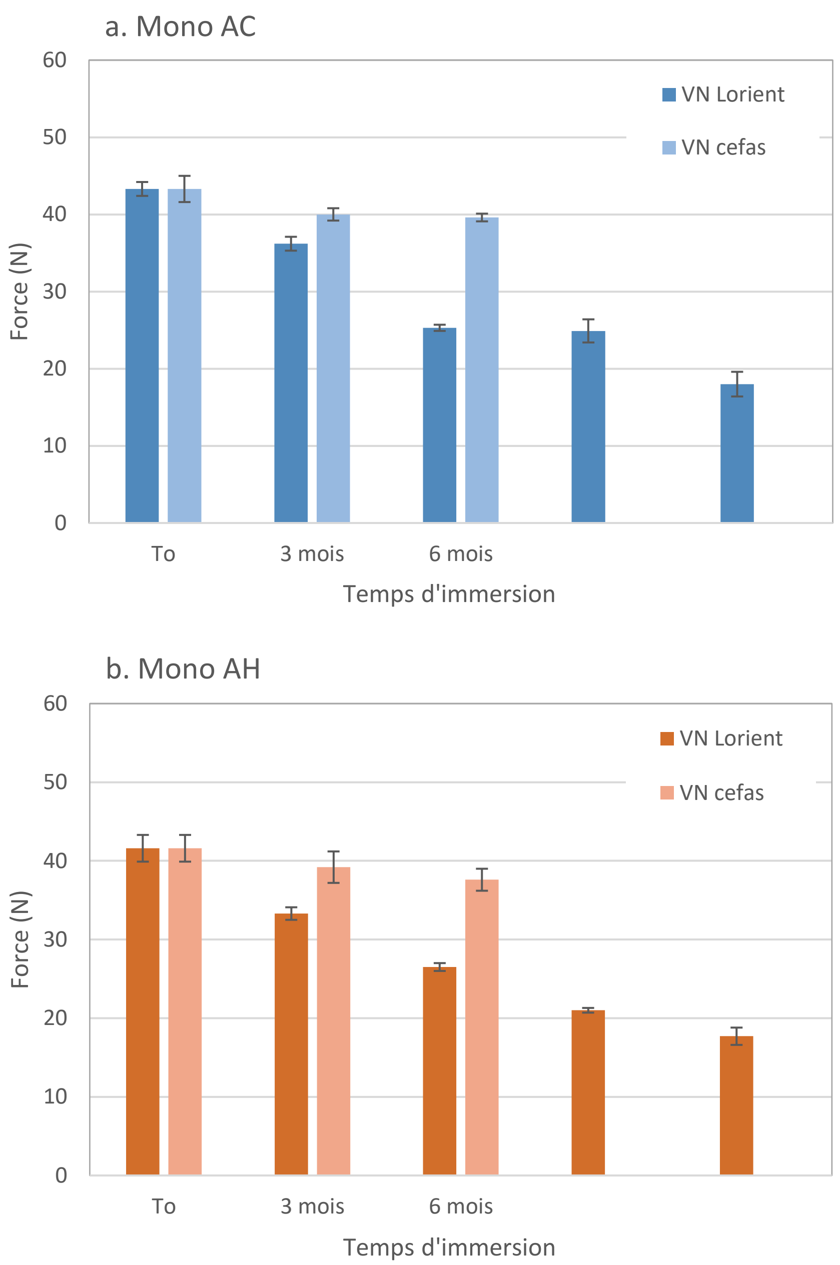

Figure 19: Comparison of the evolution of the breaking strength of AC (a) and AH (b) monofilaments as a function of the immersion environment: natural ageing at Lorient and natural ageing at Cefas.

The influence of the immersion medium in this study is highlighted by a difference in degradation kinetics. The breaking strength decreased for the 2 monofilaments and for the two environments studied, but the loss was greater for the natural ageing in Lorient.

- **<u>Infrared analysis (ATR-FTIR)</u>**

FTIR spectra of mono and multifilaments aged in the North Sea for 9 months are shown in Figure 20.. In all cases, no obvious changes were observed between the unaged reference samples and the aged samples. It is therefore not possible to identify any chemical degradation in these analyses after immersion for 9 months at a depth of 15 m. In addition, handling the aged monofilaments and multifilaments did not cause any breakage due to loss of material integrity. All the samples retained their flexibility.

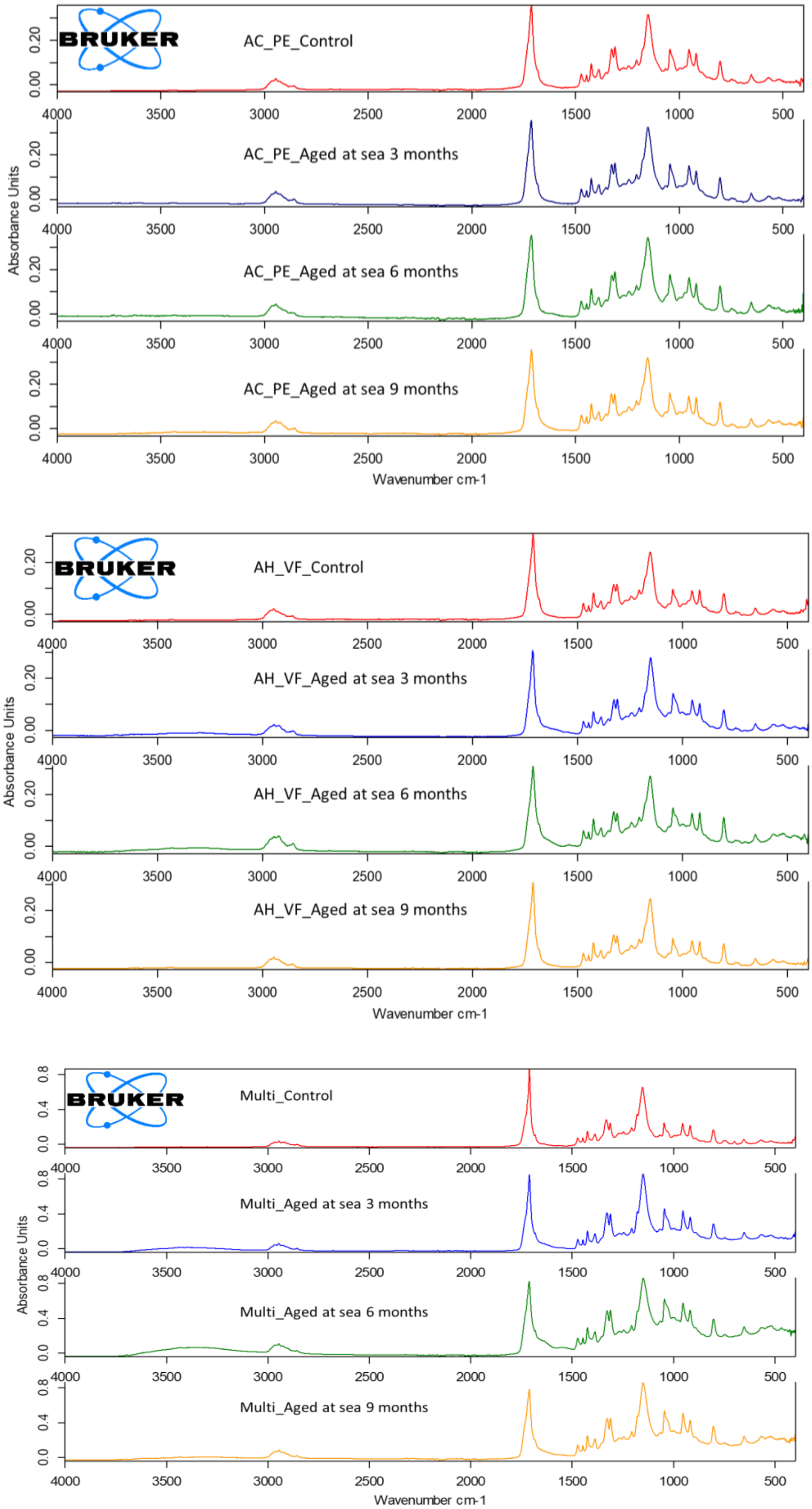

Figure 20: Infrared spectra of AC, AH monofilaments and biodegradable multifilaments obtained before and after ageing as a function of immersion time.

The degradation behaviour will therefore be compared with materials deployed on the sea surface by the UBS partner (experiment in progress). However, these results seem to indicate that solar activity, which is not present at a depth of 15 m, does not accelerate the degradation of biodegradable materials.

- **Fragmentation into microplastics**

Regarding the study of the possible formation of microplastics in submerged cages, no evidence of fragmentation of microplastics above 300 µm (i.e., the mesh size) was recorded for materials submerged at sea for 9 months. However, it is possible that particles smaller than 300 µm were produced and therefore would not have been retained by the mesh sieve.

- **Summary**

These tests show that the degradation of monofilaments depends on the environment in which they are placed. Differences were observed, such as the absence of surface roughness and a rather stable evolution of mechanical properties after 6 months of immersion, for samples aged in the North Sea.

Several factors could explain this difference, such as seasonality, which could be a factor that speeds up or slows down the rate of degradation of monofilaments. For the study carried out in Lorient, the samples were immersed at the end of March, just before the summer period, which favours the proliferation of micro-organisms and could explain the surface condition of the degraded AC and AH monofilaments (Figure 12). For the tests conducted in the North Sea, the samples were immersed in July 2022. Other explanations include the activity of the micro-organisms, which may be slowed down at a depth of 15 metres, or the temperature...

Another factor to consider is the difference in the depth of ageing. No photo-synthetically active radiation (PAR) values were measured at a depth of 15 m, as opposed to 1 m, indicating a limited impact of solar radiation on the materials deployed at 15 m depth.

A longer study would initially provide more information on the behaviour of monofilaments in the North Sea and would also provide a better understanding of the different degradation mechanisms from one environment to another.

2. *Artificial ageing*

- **Infrared analysis**

The spectrometers obtained before and after ageing of the samples exposed to air and seawater in the xenon ageing chamber for 3 months are shown in Figure 21. Initially, no difference in the FTIR spectra was observed for the intact filaments and for the same materials in powder form, suggesting no impact of the grinding process on chemical degradation.

For monofilaments and multifilaments, no obvious changes were observed compared with unaged samples, suggesting no chemical degradation of the samples. The 3-month exposure period would correspond to more than a year's ageing under natural conditions.

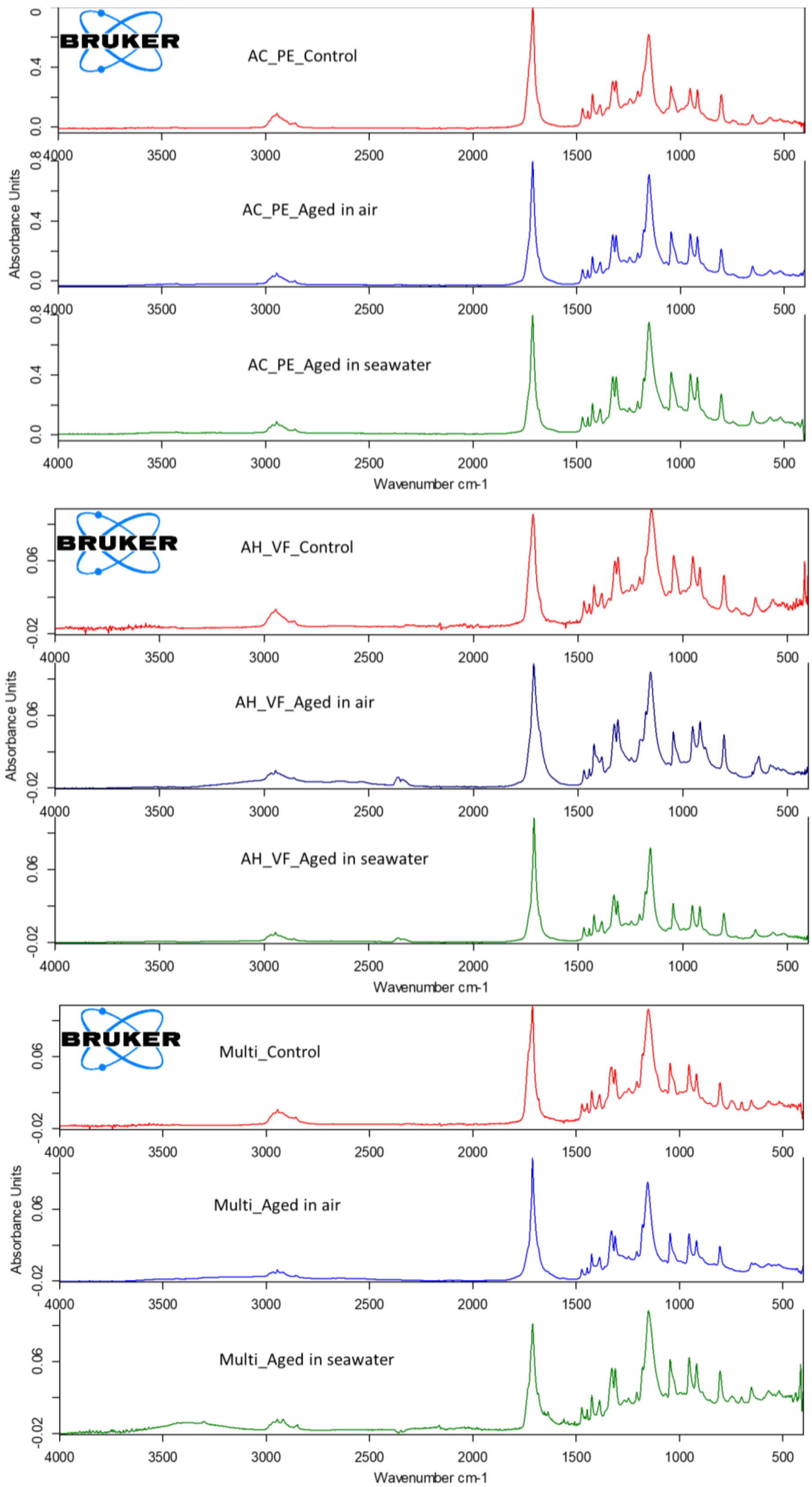

Figure 21. ATR-FTIR profiles of the mono and multi-filaments after ageing in air for 3 months using the Xenon-test chamber.

Handling of the samples for ATR-FTIR analysis, however, indicated a significant loss of material integrity, with fragmentation of the monofilaments observed, and the production of microplastics. The multifilament materials, on the other hand, retained a degree of flexibility and did not fragment during handling.

- **<u>Microscopic observations</u>**

Microscopic observations of the surface condition of Y monofilaments and multifilaments before and after accelerated ageing in air and water are shown in the Figure 22 below.

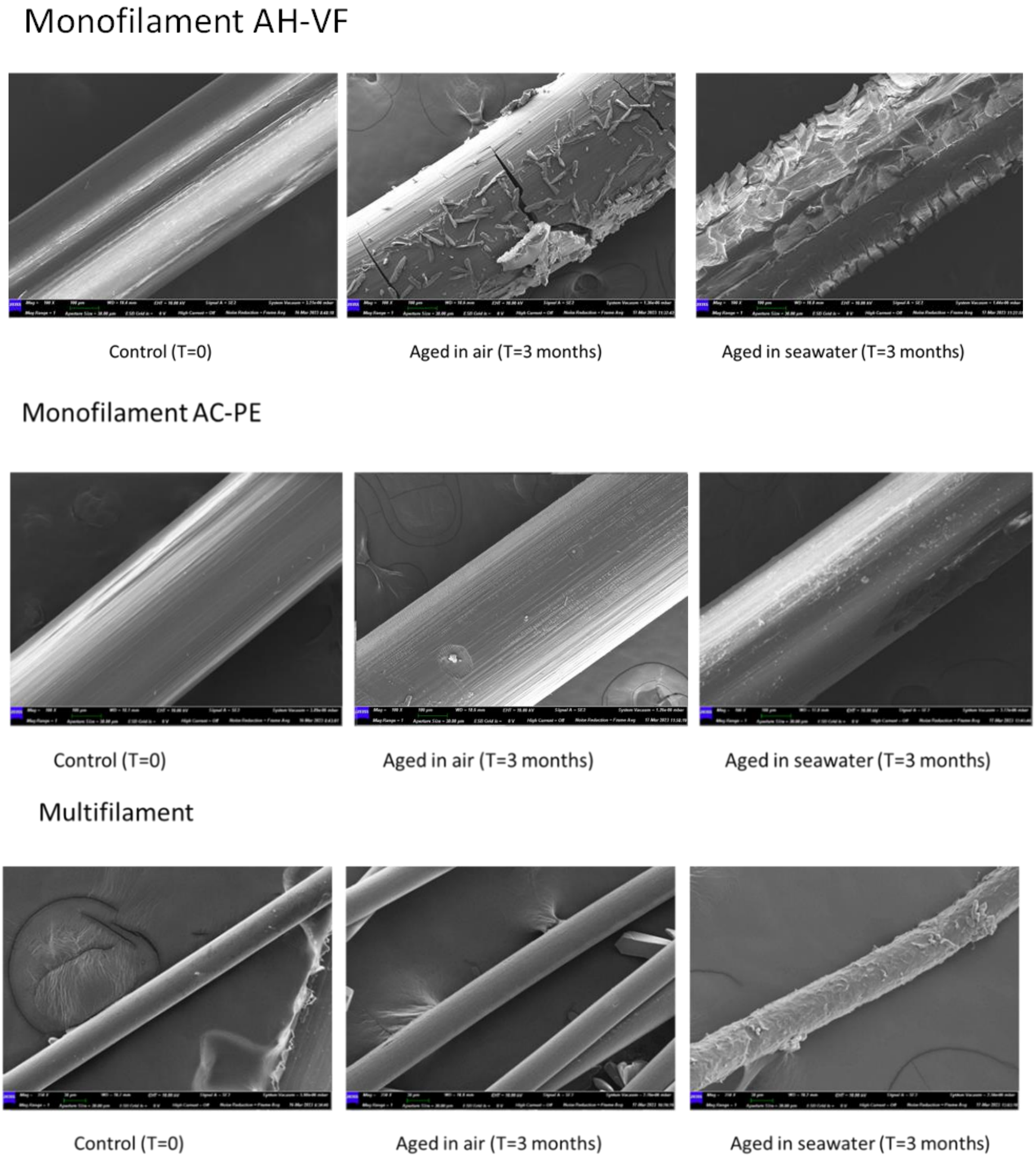

Figure 22 : Microscopic observations of the surface condition of monofilaments and multifilaments before and after accelerated ageing exposed to air and seawater in the ageing chamber (magnification x100).

SEM analysis revealed significant morphological changes on the surface of AH monofilaments for both treatments (air and seawater) after 3 months of ageing compared with unaged samples. The air-aged AH samples showed major cracks perpendicular to the fibre axis. The cracks are deep, going well beyond simple surface cracking, which would potentially lead to rapid fragmentation of the monofilaments. Samples aged in seawater showed signs of surface erosion, associated with the appearance of numerous microcracks (see Appendix 3). The degradation mechanism therefore seems to differ from one medium to another, from a liquid medium to air. In view of the surface condition of samples aged in seawater, this environment is aggressive for AH monofilaments.

In contrast, visual inspection of the AC monofilaments showed limited signs of degradation, compared to the AF monofilament (Figure 22 and SEM observations in Appendix 3). At high magnification (x100), there are nevertheless signs of small-scale surface cracks, perpendicular to the fibre axis, beginning to form in the air-aged sample, not observed in the seawater-aged sample.

Finally, analysis of the surface state of the multifilaments showed a modification of the surface with an increase in roughness for samples aged in seawater, suggesting degradation due to microbial activity.

3. Ageing in alternating air/water conditions

As part of this specific study, which was the subject of an internship, one of the objectives was to study the behavior of monofilaments when exposed to real conditions on a fishing boat. Ageing in alternating water/air conditions therefore makes it possible to simulate the conditions in which a net is used. All the results obtained are described in detail in the internship report, and only the results relating to this deliverable will be mentioned in this section.

Several ageing conditions were studied. Firstly, two continuous ageing processes were conducted: immersion in a thermostatic bath (demineralised water at 30 °C) and continuous exposure of the filaments to UV rays to obtain the reference behaviour in either environment. Two alternating ageing were then studied: exposure to UV rays and immersion in distilled water alternately at different frequencies of 4 and 8 days.

The duration of the study was 2 months, except for the continuous ageing, which lasted 11 months.

- **Microscopic observations**

Microscopic observations of the surface condition of AC and AH monofilaments (x250 magnification) and Y multifilaments (x1000 magnification) before and after continuous ageing (ED = distilled water and UV) and alternating ageing (Alt 4 and 8 days) are shown in Figure 23 below.

Regarding the evolution of the surface condition of the monofilaments, there was no change after 2 months of ageing, whatever the series studied.

The multifilaments that had been aged alternately showed some changes, in particular some surface irregularities.

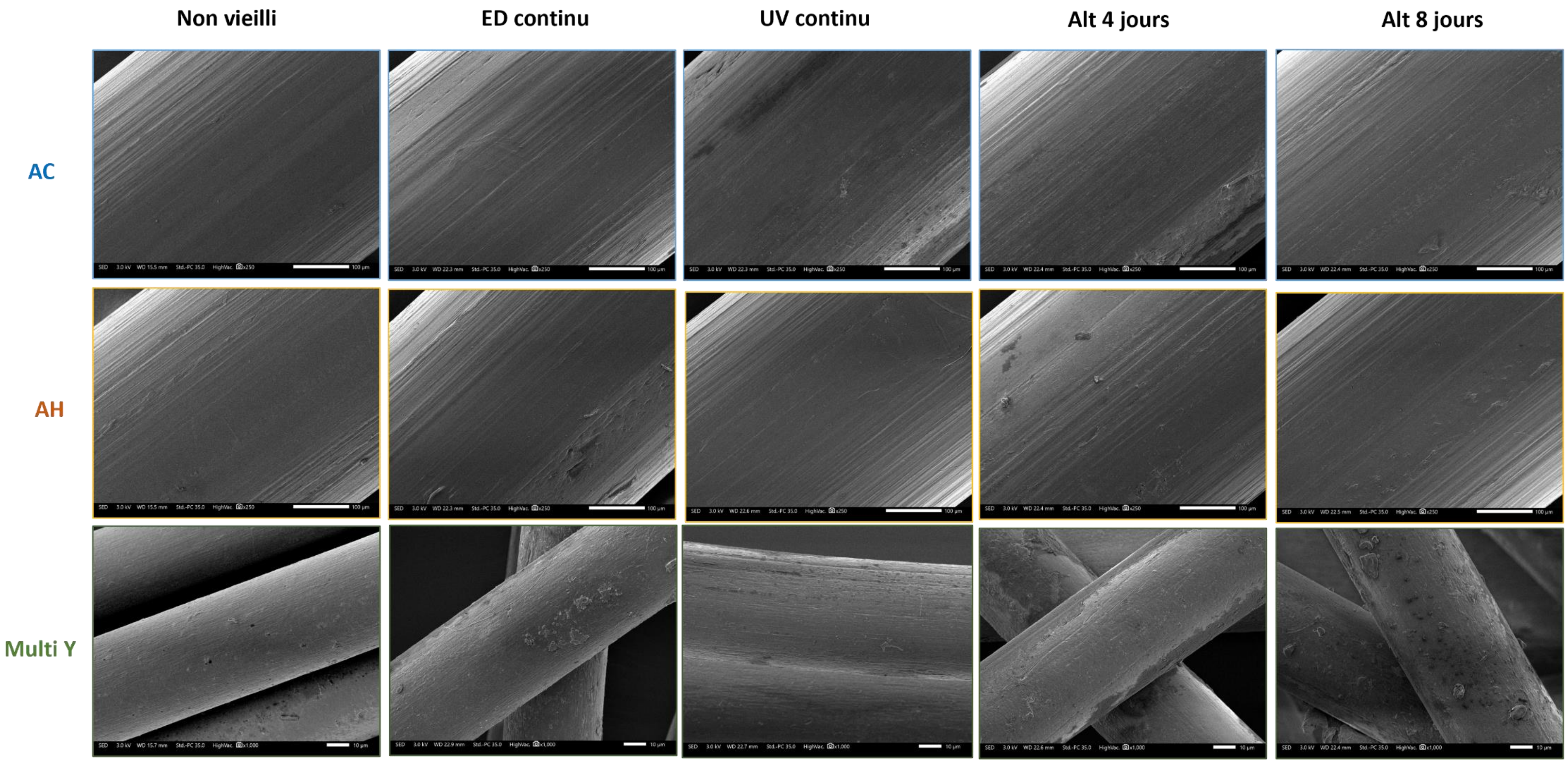

Figure 23 : Microscopic observations of the surface condition of AC and AH monofilaments (magnification x250) and Y multifilaments (magnification x1000) before and after continuous ageing (ED = distilled water and UV) and alternating ageing (Alt 4 and 8 days).

- **Evolution of mechanical properties**

The evolution of the mechanical properties of the monofilaments studied according to the 4 series are shown in the Table 5 below:

ED continu

	Durée (mois)	diamètre (µm)	Module E (Mpa)	σ_b (Mpa)	ε_b (%)	F (N)
AC	0	475,0 7,1	1393,1 28,7	242,4 5,3	43,7 6,1	43,3 0,9
	1	467,3 15,5	1360,6 56,2	248,1 11,4	38,9 6,9	42,5 1,5
	2	493,0 23,2	1259,4 95,0	228,1 19,8	40,5 12,4	43,4 1,6
	11	478,8 13,1	1364,0 44,4	236,7 16,2	32,9 5,3	42,5 0,8
AH	0	498,0 31,1	1254,6 130,9	214,9 20,7	50,2 8,4	41,6 1,7
	1	498,3 17,6	1117,7 62,5	198,1 15,2	42,4 4,9	38,5 0,4
	2	482,5 11,9	1155,6 84,2	216,7 17,2	30,9 7,6	39,5 1,4
	11	496,8 8,3	1176,7 43,1	204,6 4,5	27,5 1,9	39,6 0,5

UV Continu

	Durée (mois)	diamètre (µm)	Module E (Mpa)	σ_b (Mpa)	ε_b (%)	F (N)
AC	0	475,0 7,1	1393,1 28,7	242,4 5,3	43,7 6,1	43,3 0,9
	1	485,0 18,7	1297,1 117,1	239,8 29,0	42,4 15,1	44,0 3,0
	2	506,6 20,2	1232,7 87,9	228,8 8,2	49,8 7,1	46,1 2,0
	11	470,0 13,7	1451,8 93,7	237,5 12,9	27,4 1,9	41,1 0,4
AH	0	498,0 31,1	1254,6 130,9	214,9 20,7	50,2 8,4	41,6 1,7
	1	496,3 13,4	1152,6 57,3	211,8 17,1	37,5 11,0	40,9 1,9
	2	506,6 11,5	1166,4 63,0	204,5 7,8	31,1 4,6	41,2 0,3
	11	469,3 22,1	1262,3 51,8	200,9 19,5	25,8 0,4	38,7 0,3

Alternance 4 jours

	Durée (mois)	diamètre (µm)	Module E (Mpa)	σ_b (Mpa)	ε_b (%)	F (N)
AC	0	475,0 7,1	1393,1 28,7	242,4 5,3	43,7 6,1	43,3 0,9
	1	469,0 7,8	1399,5 53,9	271,4 7,1	50,5 4,5	46,9 0,6
	2	490,8 32,0	1465,2 480,7	233,6 25,5	39,0 13,7	43,9 1,9
AH	0	498,0 31,1	1254,6 130,9	214,9 20,7	50,2 8,4	41,6 1,7
	1	485,3 28,0	1229,9 93,6	212,3 22,0	27,1 3,6	39,0 0,6
	2	462,7 4,6	1281,4 32,0	244,3 7,8	24,3 1,4	41,1 0,6

Alternance 8 jours

	Durée (mois)	diamètre (µm)	Module E (Mpa)	σ_b (Mpa)	ε_b (%)	F (N)
AC	0	475,0 7,1	1393,1 28,7	242,4 5,3	43,7 6,1	43,3 0,9
	1	489,2 7,6	1361,4 58,9	241,1 15,6	51,4 16,3	45,3 2,8,
	2	506,7 20,0	1240,3 82,7	222,2 17,0	49,8 3,2	44,3 0,8
AH	0	498,0 31,1	1254,6 130,9	214,9 20,7	50,2 8,4	41,6 1,7
	1	489,0 20,0	1231,2 96,5	221,7 16,7	39,7 13,3	41,5 0,5
	2	511,8 37,0	1185,8 132,7	203,5 28,5	33,3 5,7	41,4 1,2

Table 5 : Evolution of the mechanical properties of AC and AH monofilaments according to the 4 series of ageing applied.

About the continuous ageing of AC and AH monofilaments in distilled water and natural light, the mechanical properties, i.e., Young's modulus, stress, and strength at break, appear to be stable after 11 months of immersion. However, a slight decrease in strain at break was observed after 11 months in immersion for the AC monofilament, and a more gradual decrease was noted for the AH monofilament.

Regarding the continuous ageing of the monofilaments in UV light, the observations are generally similar to those obtained for ageing in distilled water.

Regarding ageing in alternating water/air, the 2-month duration of the study did not reveal any significant differences between a medium change frequency of 4 and 8 days. However, the deformation of the AH monofilament over time decreased more rapidly for the 4-day alternating ageing.

These observations reveal the beginnings of the chemical degradation mechanism by cutting macromolecular chains, impacting for the moment only the ductility of the monofilament, the force and stress at break still being stable. A study lasting a few months longer would certainly have shown early degradation linked to alternating environments.

Figure 24 compares the evolution of the breaking force between the 4-ageing series studied in this section and that of the natural ageing studied in Lorient. Although the ageing period is 3 months (and not 2 months as for the 4 series), natural ageing in a marine environment seems to have a greater influence on the breaking strength of monofilaments, with a more significant decrease.

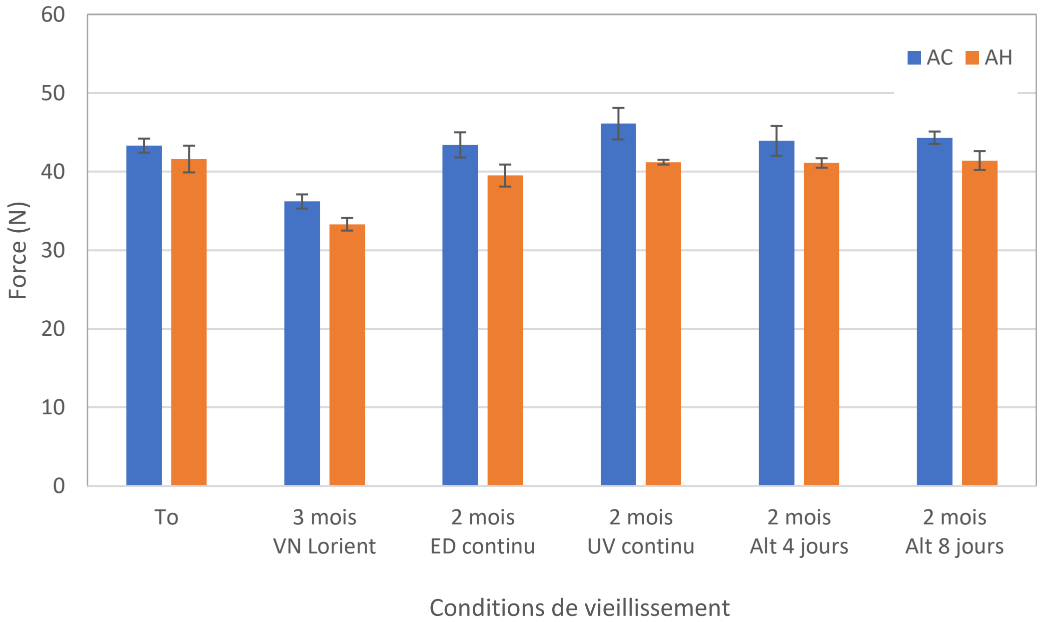

Figure 24 : Comparison of the evolution of the breaking strength of AC and AH monofilaments as a function of the ageing conditions studied over short periods of time.

- **<u>Comparison with natural ageing over the long term</u>**

Figure 25 compares the evolution of the breaking strength of AC and AH monofilaments between the two series of continuous ageing and natural ageing in the environment over a longer period.

A slight decrease is observed after 11 months of exposure to natural light, while a loss of more than 50% in breaking strength is obtained for AC and AH monofilaments immersed in natural seawater.

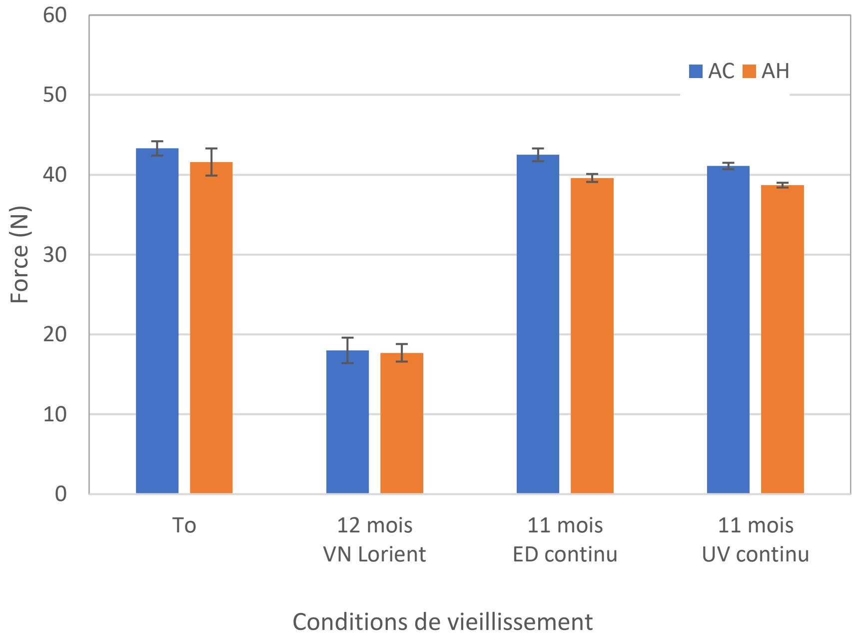

Figure 25 : Comparison of the evolution of the breaking strength of AC and AH monofilaments as a function of the ageing conditions studied over extended periods of time.

- **<u>Assessment</u>**

The alternating ageing study revealed premature wear of the monofilaments with a slight drop in mechanical properties, such as a reduction in strain at break. These observations reveal the beginnings of a chemical degradation mechanism involving cuts in macromolecular chains, which for the time being has only an impact on the ductility of the monofilament, while the force and stress at break are still stable. A study lasting a few months longer would certainly have shown early degradation linked to alternating environments.

Over the long term, natural ageing under immersion in natural seawater leads to greater degradation of the monofilaments. Concomitant factors of different origins, such as microbial activity, the action of water with hydrolysis and UV exposure, seem to accelerate the degradation kinetics of monofilaments in the natural environment.

IV. Study of the formation of microplastics

1. *Literature review*

a) Relative importance of fishing related items as sources of microplastics

Pollution by microplastics has been reported for all environmental compartments worldwide and has raised public awareness in recent years due to its wide distribution and harmful ecological and economic effects.

Plastics can be present at different size scales, from large (e.g. mega > 1 m) and macroplastics (25 - 50 mm) to smaller particles of meso (5 mm to 2.5 cm), micro (less than 5 mm in size) and nanoplastics (1 - 1000 nm) [5,6]. Their ubiquity has led to heightened concerns about their potential negative environmental impacts. Microplastics can be ingested by terrestrial, freshwater and marine organisms with evidence of bioaccumulation in tissues [7]. Microplastics have also been shown to enter the food chain [8] via atmospheric vectors [9] as well as combined routes through food, water and air [10]. The results of correlative studies in subjects exposed to high concentrations of microplastics, such as animal models and cell cultures, suggest that the effects of microplastics could in particular provoke immune and stress responses and induce reproductive and developmental toxicity [11].

Microplastic sources are difficult to identify and control due to their small size, diffuse sources, and high mobility in the marine environment (Figure 26). Fishing activities have been identified as a major source of marine microplastics from degradation of ALFDG or abrasion of fishing gear, including ropes and buoys [12].

Wright et al. [13] investigated the potential release of microplastics from stranded fishing gear on the south-west peninsula of England, considered to be an accumulation site for ALDFG. The authors suggested a potential release of 1277 ± 431 items/m-1 with fishing line and net as the largest emitters with 44% and 49% respectively [13]. Napper et al. [14] also studied the potential release of microplastics due to the abrasion effect of ropes during fishing activities. The authors compared a variety of ropes (differing in age, wear surface and material) to quantify and characterise the production of microplastics during their use. This was achieved by simulating, in laboratory and field experiments, the rope hauling activity that is typically conducted on board maritime vessels, such as fishing boats. The results indicated that new and one-year-old PP ropes released significantly fewer microplastic fragments (14 ± 3 and 22 ± 5 particles) and less microplastic mass (11 ± 2 and 12 ± 3 µg) per metre pulled compared with two-year-old (720 ± 51, 247 ± 18 µg) or ten-year-old (767 ± 55, 1052 ± 75 µg) ropes [14].

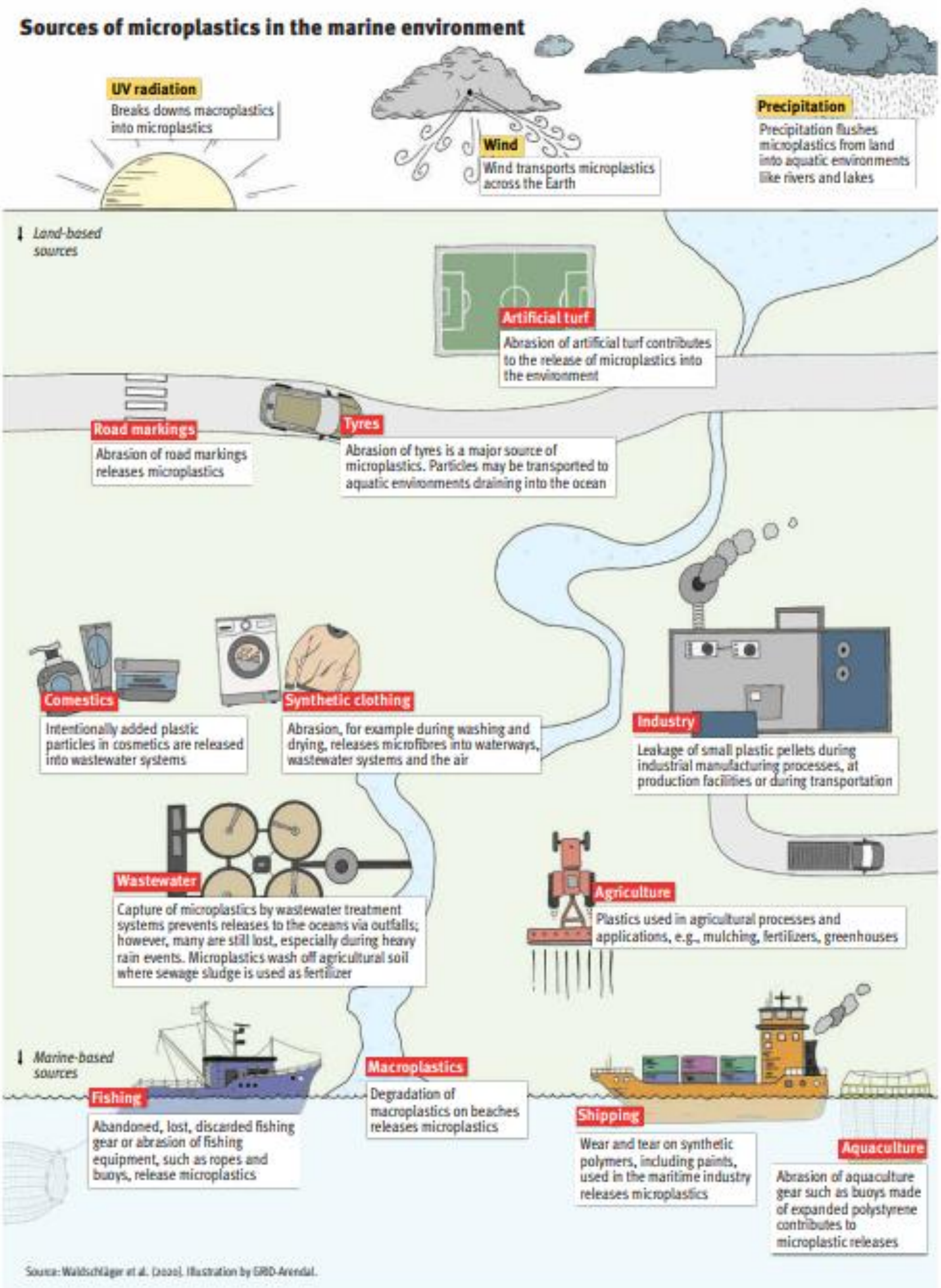

Figure 26 : Sources of microplastics in the marine environment. Source: (UNEP, 2021) [15].

The development of fishing gear with a controlled lifespan has been suggested as a promising step towards reducing fishing-related marine waste. The use of biodegradable materials would, in theory, prevent the production of persistent microplastics in the marine environment, as is the case with conventional materials [16,17]. Further scientific evidence is therefore needed to investigate the environmental impacts of biodegradable fishing gear, including the formation of microplastics [18]. The production of microplastics from biodegradable materials developed as part of the INdIGO project has therefore been studied and the results are also presented in this report.

b) Detection of microplastics in environmental samples

Detection of microplastics in the environment can be challenging depending on the complexity of the matrix under investigation [19]. Nile Red (NR) was developed as a low cost and fast approach for the detection and quantification of microplastics in environmental samples by the University of East Anglia and Cefas [20]. Since its development, the application of NR in relation to microplastic research has increased substantially. Shruti et al. [21] recently published a review on the application of NR for the analysis of microplastics in environmental samples including food products. While the need for standardised protocols for NR use was highlighted in the review, the authors concluded that NR tagging of microplastics was a promising approach for a low-cost and fast screening of microplastics from environmental samples, especially for laboratories lacking more advanced and often costly infrastructure (e.g., pyrolysis GC-MS or m-FTIR, m-Raman facilities). NR has also previously been used for the large-scale mapping of microplastics from sediment, indicating its suitability in a monitoring context [22–25]. NR has also been applied to the detection and quantification of microplastics in biota [22,26–29] and water [22,24].

2. Materials and methods

a) Sample processing and fluorescence tagging of polymers using Nile Red (NR)

Fragmentation of the mono and multi-filaments into microplastics was carried out following the exposure of the materials using the xenon test chamber. The tubes containing the filaments in sweater were filtered using 47 mm Whatman regenerated cellulose filters (0.2 µm pore size). The filters were stained using NR (0.01g L^{-1} in ethanol) and the filters imaged as detailed in Bakir et al. [30]. List of chemicals, manufacturers and suppliers is shown in Table 6.

Chemicals	Molecular formula	Manufacturer/Supplier	Purity (%)
Ethanol	C2H6O	Acros organics ThermoFisher scientific	95% purity
Nile Red	C20H18N2O2	Acros organics ThermoFisher scientific	99% purity

Table 6 : List of chemicals, manufacturers, and suppliers.

b) Particle characterization using micro-FTIR

Microplastics were identified for composition confirmation. Particles of interest were transferred to 25 mm Anodiscs filters (0.2 µm porosity, Whatman, VWR, UK). A LUMOS II (Bruker, UK) using micro-ATR and transmission FTIR with a liquid nitrogen cooled MCT detector. For micro-ATR FTIR, spectra (32 scans) were collected in reflectance mode in the range 4000 – 500 cm-1 at a resolution of 4 cm-1. Spectra (32 scans) were collected in transmission mode in the range 4000 – 1250 cm-1 at a resolution of 4 cm-1. Polymer identification was carried out against an in-house database using pristine samples of the mono and multi-filaments as reference materials.

3. *Results and discussion*

- <u>**Fragmentation and characterisation of microparticles**</u>

The study of fragmentation and the formation of microplastics was conducted on samples of AC and AH monofilaments that had undergone accelerated ageing in a Xenon chamber. All the materials produced fluorescence when stained with NR (Figure 27).

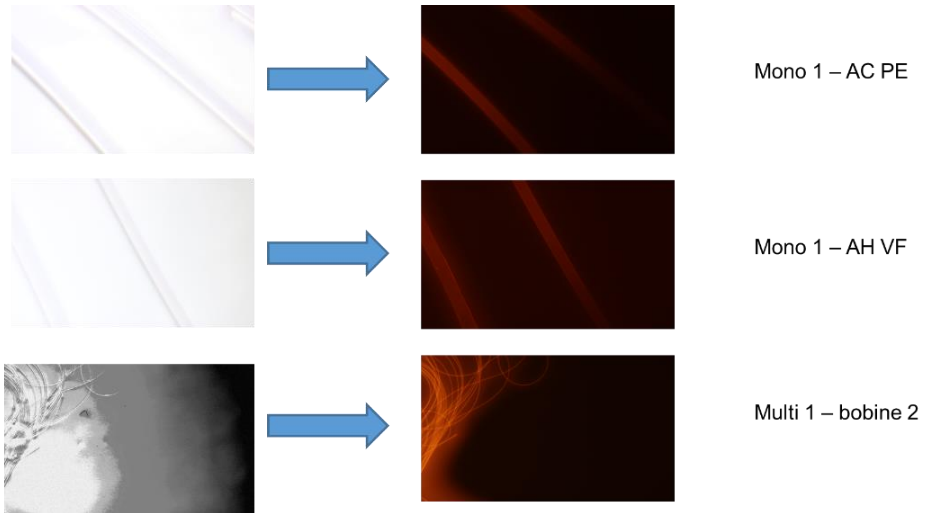

Figure 27. Example of the fluorescence tagging of the newly formulated materials using NR

Fragmentation was assessed on monofilaments only (Figure 28). Visual inspection of the tubes confirmed the presence of secondary microplastics resulting from degradation of the original elements.

Further work will therefore be required to understand the formation of microplastics from multifilaments and to identify the mechanisms and kinetics of fragmentation over time.

The microplastics produced correspond well to the original compounds. A complete quantification was not conducted in this study and was qualitative.

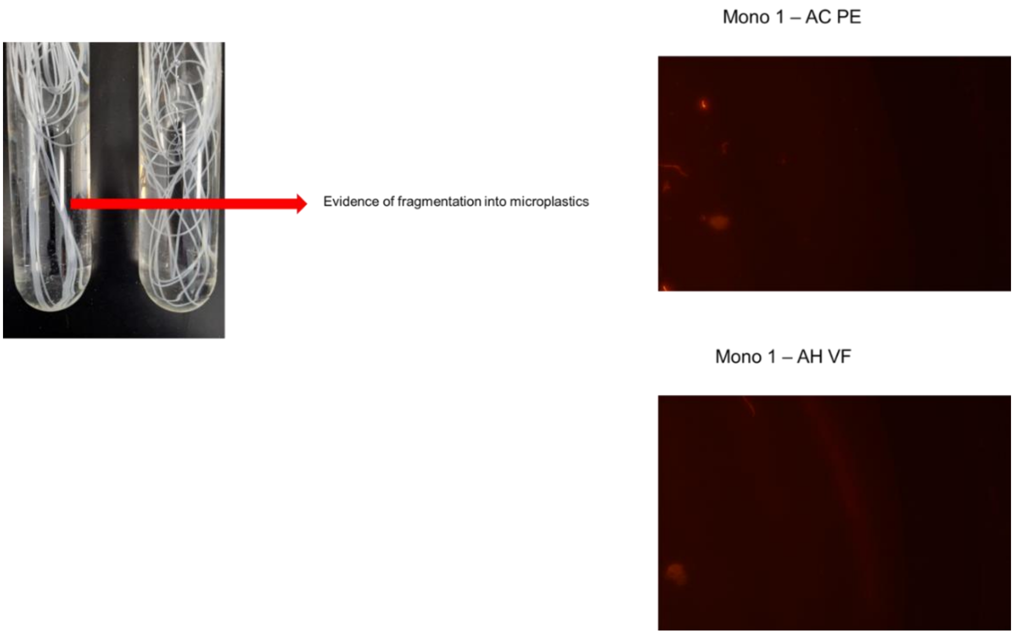

Figure 28. Evidence of fragmentation of the monofilaments as confirmed by micro-FTIR.

- **<u>Summary</u>**

The potential formation of microplastics during the degradation of biodegradable monofilaments was studied in this project. The analyses carried out at sea did not reveal any evidence of microplastic formation, but it is possible that pieces smaller than 300 µm have escaped surveillance. A longer study would undoubtedly enable changes to be observed. Accelerated ageing in a xenon ageing chamber revealed the presence of microplastic after 3 months.

Replacing conventional fishing gear with fishing gear made from biodegradable plastics will not prevent the formation of microplastics, a degradation mechanism common to plastics and caused by exposure to UV light. However, the durability of microplastics from biodegradable fishing gear in the marine environment will be less. Deliverable T3.2.1, which presents the biodegradation and toxicity results in the marine environment, confirms that the samples returned in powder form are biodegraded after 1 year's incubation in the marine environment.

V. Conclusion

In this report, the ageing of the prototypes was studied under several conditions. The aim is to study and understand their behaviour when exposed to extreme conditions over relatively long periods. The samples selected for this study were 2 AC and AH monofilaments and 1 Y multifilament. While all the analyses could be carried out on the monofilaments, the tests on the multifilaments were much more complex to carry out because of the fineness of the strands, the entanglement of the strands and the rapidity of degradation.

Initially, the samples were immersed in natural seawater in the port of Lorient (France). During natural ageing, microscopic observations revealed a significant increase in the surface roughness of the monofilaments. Mechanical properties also change progressively over time, with a 50% drop in breaking strength after 12 months. However, thermal analysis and monitoring of the molar mass of samples aged in a marine environment did not reveal any chemical degradation by chain cutting, linked to hydrolysis. These results enable us to identify the degradation mechanism of monofilaments when exposed to a marine environment: biotic degradation (linked to the action of marine micro-organisms), via an enzymatic hydrolysis mechanism.

The influence of the immersion environment was also monitored between the study carried out in Lorient (Southern Brittany - France) at a depth of 1 m and that carried out in West Gabbard (UK) in the North Sea at a depth of 15 m. The choice of ageing study zone is important because the degradation kinetics of monofilaments depend on the environment in which they are placed. The results show that several parameters, such as temperature, depth and the presence of UV radiation from micro-organisms, are key factors in the degradation process of monofilaments made from biodegradable plastic. The degradation kinetics of samples aged in the North Sea at a depth of 15 m are much better than those obtained in Lorient.

Secondly, the INdIGO samples were placed in a climatic ageing chamber, some conditioned in tubes in contact with air, others in tubes in contact with seawater. The exposure period was set at 3 months, corresponding to more than a year's ageing under natural conditions. Microscopic observations revealed some changes to the surface of the monofilaments, with the appearance of major cracks perpendicular to the axis of the AH monofilament and only a few microcracks for the AC monofilament.

A study of alternating immersion in water and air was then carried out. The tests consisted of alternately exposing INdIGO samples to air and water, at different frequencies (4 and 8 days), to simulate conditions closer to those associated with use on a fishing boat. The results highlighted premature wear of the monofilaments, which underwent alternating ageing, with a slight drop in mechanical properties, such as a reduction in strain at break. These observations reveal the beginnings of a chemical degradation mechanism involving cuts in macromolecular chains, which for the time being has only an impact on the ductility of the monofilament, while the force and stress at break remain stable. A study lasting a few months longer would certainly have shown early degradation linked to alternating environments.

Finally, the partnership wanted to study the possible formation of microplastics during the degradation of monofilaments in the marine environment, to prevent the transfer of pollution into the marine environment. This pollution is a real scourge for marine flora and fauna. Analyses carried out in the natural environment did not reveal the formation of microplastics after 9 months, but it is possible that pieces smaller than 300 µm escaped surveillance. A longer study would undoubtedly enable changes to be observed. In addition, the study conditions at a depth of 15 m appear to be less aggressive for the samples than those encountered in Lorient at a depth of 1 m. As for the samples aged in a climatic chamber, particles were observed after 3 months of artificial ageing and IR analyses confirmed that these were indeed the polymer used in the monofilaments. Replacing conventional fishing gear with gear made from biodegradable plastics will not prevent the formation of microplastics. However, the durability of microplastics from biodegradable fishing gear in the marine environment will be significantly reduced. Deliverable T3.2.1, which presents the biodegradation and toxicity results in the marine environment, confirms that the samples brought back in powder form are biodegraded after 1 year's incubation in the marine environment.

The monofilaments and multifilaments developed as part of the INdIGO project to produce prototypes of fine nets for the fishing industry and catcher nets for aquaculture therefore have little or no long-term impact.

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VII. Appendices

Appendice I. Deployment of the biodegradable materials at sea

Figure A2. Deployment of the mid-tether frame alongside the SmartBuoy**.**

Table A1. Description of instruments and sensors on SmartBuoys for the collection of high frequency time series of water quality parameters.

Instrument	Measured Parameter(s)	Elevation / Depth	Sampling	Frequency of data recovery

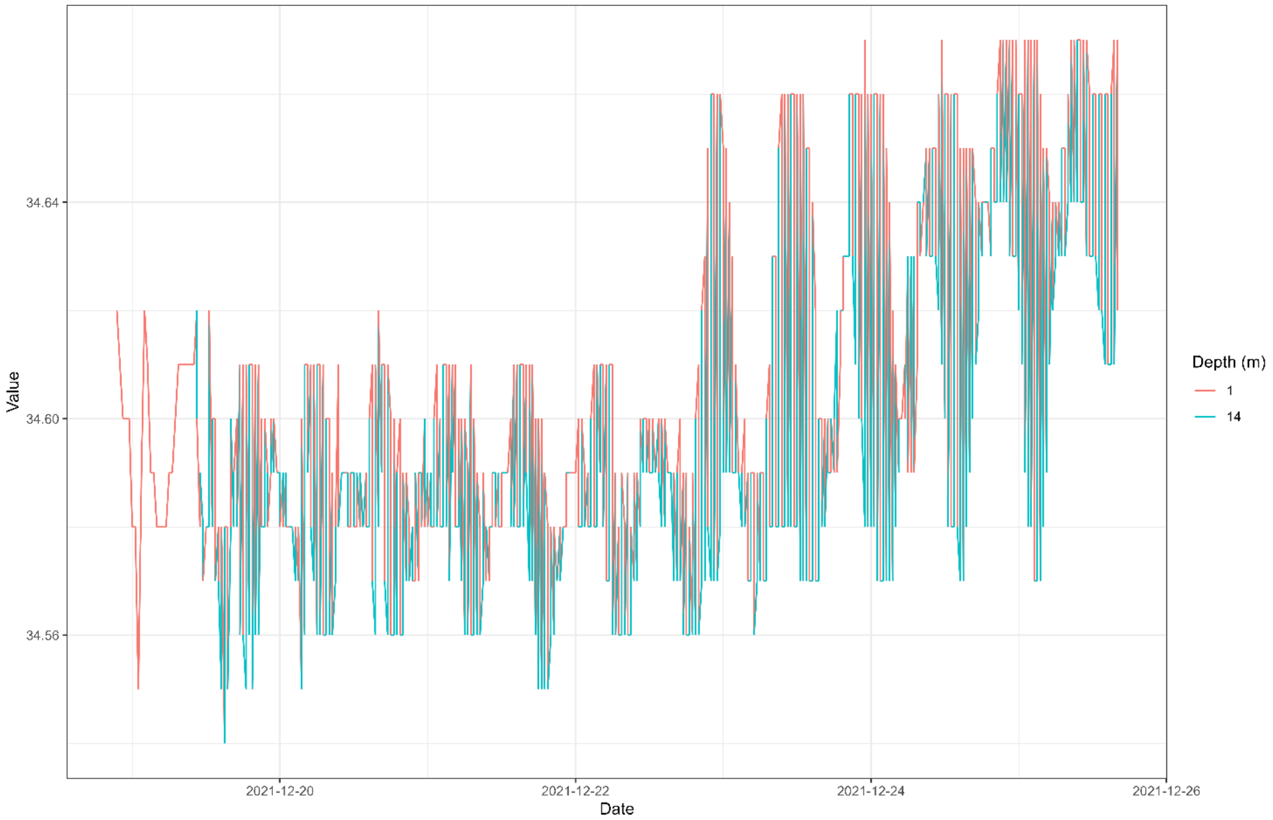
Cefas SmartBuoy

Instrument	Parameters	Depth (m)	Sampling frequency	Data availability
Aanderaa CT	Conductivity, temperature, salinity	-1	Burst average of 1Hz for 10 minutes, every 30 minutes	Data telemetry every 2 hours (basic QC) Full QC data available after recovery every 3 months
Druck PDCR4000	pressure	-1	Burst average of 1Hz for 10 minutes, every 30 minutes	Data telemetry every 2 hours (basic QC) Full QC data available after recovery every 3 months

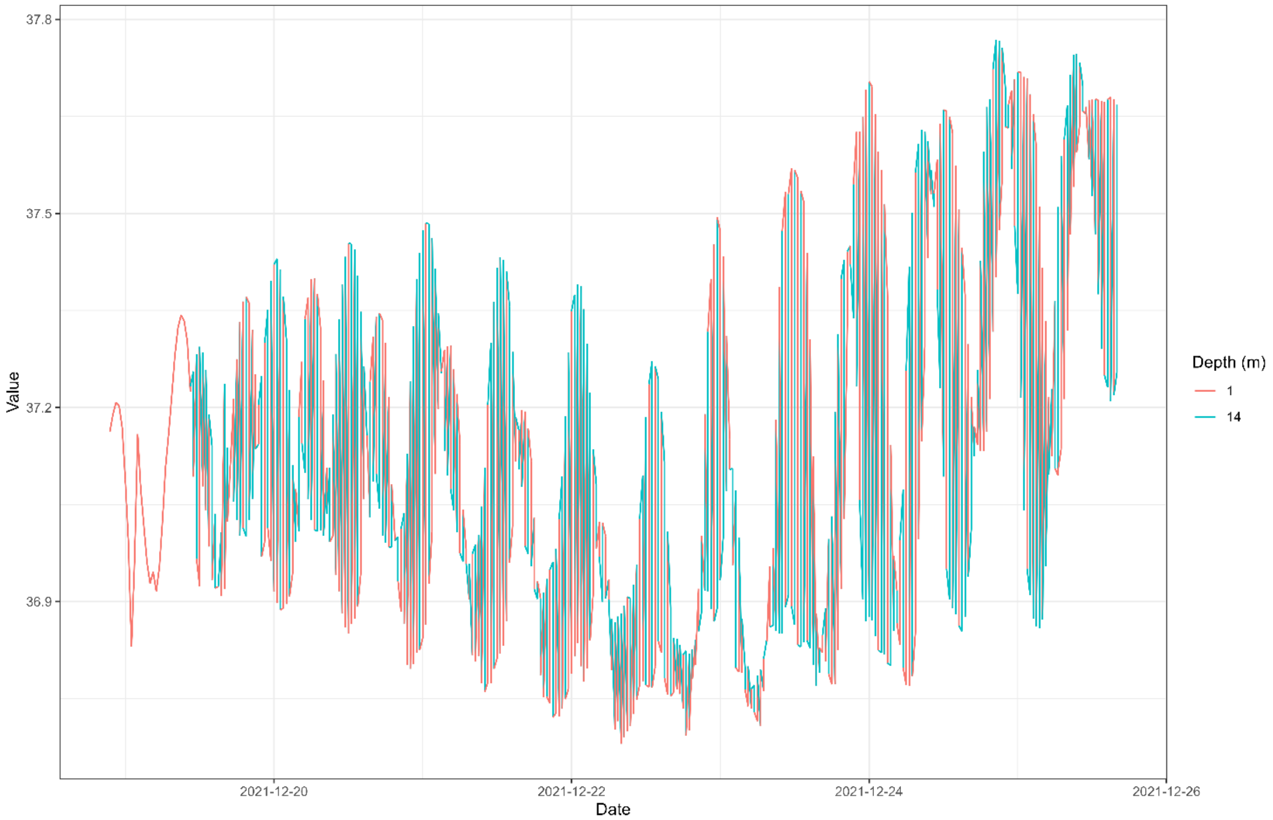
Analogue Devices ADXL202	Roll, pitch	-1	Burst average of 1Hz for 10 minutes, every 30 minutes	Data telemetry every 2 hours (basic QC) Full QC data available after recovery every 3 months
Seapoint SCF	Chlorophyll fluorescence, calibrated to chlorophyll in mg l^{-1} after recovery	-1	Burst average of 1Hz for 10 minutes, every 30 minutes	Data telemetry every 2 hours (basic QC) Full QC data available after recovery every 3 months
Seapoint OBS	Turbidity (FTU), calibrated to suspended particulate matter in mg l^{-1} after recovery	-1	Burst average of 1Hz for 10 minutes, every 30 minutes	Data telemetry every 2 hours (basic QC) Full QC data available after recovery every 3 months
Aanderaa optode	Oxygen concentration Oxygen percent saturation temperature	-1	Burst average of 0.2Hz for 10 minutes, every 30 minutes	Data telemetry every 2 hours (basic QC) Full QC data available after recovery every 3 months
Licor PAR	Photosynthetically active radiation	0, -1, -2	Burst average of 1Hz for 10 minutes, every 30 minutes	Data telemetry every 2 hours (basic QC) Full QC data available after recovery every 3 months
Discrete water sampler	Nitrate, silicate, phytoplankton species composition and abundance	-1	Every 4-8 days	Data available after recovery every 3 months

Previous ad hoc sensor trials include pCO$_2$, uv nitrate, settling plates for invasive species, passive samplers

WESTGAB2/024 SAL mid tether comparison



WESTGAB2/024 COND mid tether comparison



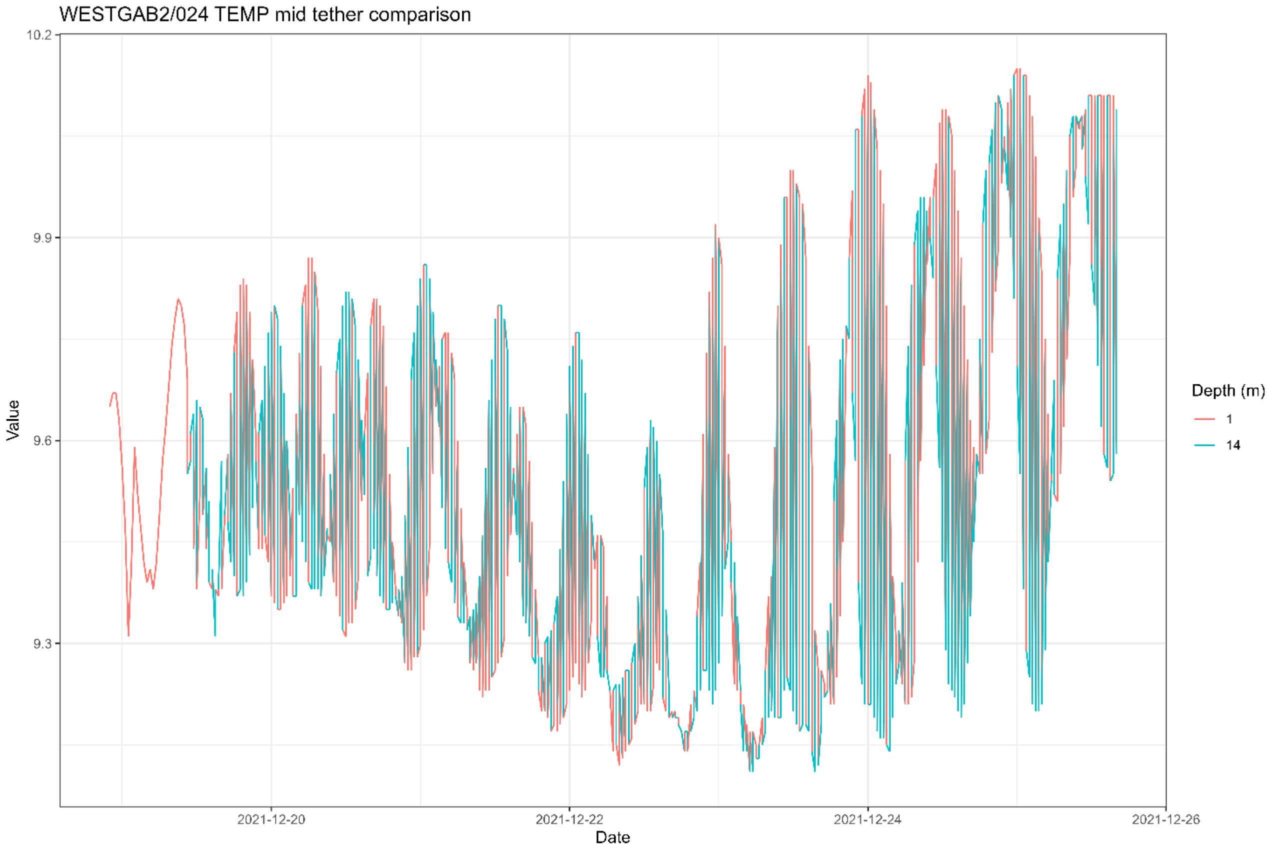


Figure A3. Selected water quality parameters at 1 and 14 m depth