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Characteristics, fate, and impact of marine plastic debris exposed to sunlight: A review

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Marine Pollution Bulletin

Characteristics, fate, and impact of marine plastic debris exposed to sunlight: a review.

--Manuscript Draft--

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Abstract:	<p>The increase of plastic production from the middle of the twentieth century was inevitably followed by an increase in the amount of plastic dumped in the natural environment. There, the plastic debris are exposed to sunlight, temperature, humidity, and physical stress. This can induce photo-oxidative and thermal degradation. This review discusses the mechanism of plastics UV weathering and its characteristics. Comparison of the photodegradation rate and physico-chemical properties are made according to the weathering mode (natural/accelerated) and medium (air/water). Since the photodegradation can lead to plastics fragmentation, this phenomenon is described along with the methodologies used in literature to evaluate the fragmentation. The impact of the photodegraded plastic debris on the marine environment is also presented in term of (i) photodegradation products and stabilizers leakage, (ii) organic pollutants accumulation, transfer, and leakage, and (iii) toxicity on marine organisms.</p>



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Aix-en-Provence, 30th June 2021

Dear Editor,

We would like to thank the referees for their positive answer to the publication of our paper and their last comments and suggestions to improve the quality of the paper.

Please find enclosed the final revised paper co-authored with Maria Masry, Stéphanie Rossignol, Jean-Luc Gardette, Sandrine Therias and Pierre-Olivier Bussière entitled: "***Characteristics, fate, and impact of marine plastic debris exposed to sunlight: a review***" referred MPB-D-21-00843.

With best regards, Yours sincerely.

Pr. P. Wong-Wah-Chung



Reviewer #1:

This review focused on the mechanism of plastics UV weathering and its characteristics, excluding other factors such as physical stress.

This paper is well documented, well written and well structured.

Major comments

For the different sections, from a conceptual point of view, authors review the most interesting finding and given some results/findings for a few numbers of polymer. For these different sections, I would suggest to try to generalize on all polymers and/or to conduct some more systematic comparison between polymer (--/-/+ / ++), when possible.

Thank you for this observation, a table comparing polymers behavior was added to the final manuscript line 296.

Table 1: Qualitative comparison of polymer behavior in term of weathering extent in air / water medium (IR carbonyl and hydroxyl groups bands) (Biber et al., 2019; Cai et al., 2018; Pimentel et al., 2005; Ranjan and Goel, 2019; Tang et al., 2019, 2018), fragmentation (number of generated fragments) (Kalogerakis et al., 2017; Lambert and Wagner, 2016a; Song et al., 2017; Weinstein et al., 2016) and dissolution (mass of plastics and dissolved organic carbon) (Lee et al., 2020; Ward et al., 2019; Zhu et al., 2020). Symbols: ++ resistant, -- fragile and x not mentioned.

	Air UV	Water UV	Fragmentation	Dissolution
PE	+	++	++	++
PP	+	++	++	+
PS	-	--	--	-
PET	+	++	++	x
PLA	x	x	-	x
PVC	+	++	x	x

Knowledge is required to balance contribution of the different mechanisms in plastic fragmentation, i.e. UV weathering vs. physical stress. Authors highlight that photooxidation in terrestrial environment is faster compared with other degradation processes (Lambert and Wagner, 2016a; Wang et al., 2016). How to be sur of this very strong hypothesis? New knowledge on the plastic litter dynamic in the land-to-sea continuum was recently produced, demonstrating very long residence time of litter in estuary and in bank and this assumption should be examined in light of the recent advances.

Thank you for this comment. Problems in investigation of outdoor photodegradation of various polymers are complex, due to concerted or cyclic attacks of regular as well as casual atmospheric environmental stresses and their combinations on polymers.

“It is generally considered that radiation in the ultraviolet (UV) and visible is the primary factor in outdoor polymer weathering. Effects from heat, moisture, pollutants, mechanical stresses, and biological attack can come into play, but usually the weathering process begins with a photochemical event” (J.E. Pickett, D.A. Gibson, M.M. Gardner, Effects of irradiation conditions on the weathering of engineering thermoplastics. *Polymer Degradation and Stability* 93 (2008) 1597–1606).

“Polymers exposed outdoors can degrade through the action of several agents, including solar ultraviolet (UV) radiation; water; pollutants (in gaseous form or, more potently, as acid-rain); elevated temperature; and temperature changes. In a majority of cases, the main cause of property deterioration is photooxidation, which is initiated by UV irradiation and, as a consequence, much laboratory photo-ageing testing is conducted to determine the weatherability of polymers and to test

the effectiveness of stabilisers introduced to improve their weather resistance” (Jim R. White, Polymer ageing: physics, chemistry or engineering? Time to reflect. C. R. Chimie 9 (2006) 1396–1408).

We propose the following modification from lines 87 to 91:

It is generally considered that radiation in the ultraviolet (UV) and visible is the primary factor in outdoor polymer weathering. Effects from heat, moisture, pollutants, mechanical stresses, and biological attack can come into play, but usually the weathering process begins with a photochemical event (Pickett et al., 2008; White, 2006). Giving the importance of photooxidation for determining the fate and impact of plastic debris, the aim of this work is to give an overview on plastics photodegradation in the marine environment.

In the section 2.2 Chemical modification, authors stated that oxidation leads to some modification of IR spectrum and provide very few examples. I recommended to conduct a systematic approach and to examine for the most common polymers these modifications. In a systematic way. By this way, limited or drastic modification would be better highlighted and a comparison between polymer can be done. As mentioned in the manuscript, the carbonyl band is largely employed to characterize the UV weathering extent of the most common polymers such as polyolefins PVC, PS, PLA, PET and ABS (L. 157 - 159). Labeling the modifications as limited or drastic is not possible as it depends on the exposure time, conditions and possible stabilizers added to the polymer matrix. The term dramatic in the manuscript in the description of infrared analysis was removed (L. 143).

The formation of the oxidation products leads to ~~dramatic~~-modifications of the infrared spectrum of the polymer and infrared spectroscopy has been recognized for a long time as a very useful tool in the identification of marine plastic debris and in the characterization of the chemical modifications provoked by ageing (Jung et al., 2018, 2018; Lobo and Bonilla, 2003; Pavia et al., 2008; Rugg et al., 1954).

In many parts of the manuscript, Authors mentioned "weathering degree" but no definition nor qualitative criteria are given to defined this degree. What mean weathering degree for authors?

Thank you for pointing that out, weathering extent would be better. We have changed degree by extent in the manuscript.

The weathering extent corresponds to the chemical and physical modifications that the plastic undergoes according to its UV exposure time and external weathering conditions. It is not an absolute criteria nor a given value to be determined, but rather a relative criteria allowing the comparison of the aging extent of different plastic samples as it can be defined by one or several parameters according to the study.

This definition was added to the manuscript lines 115 to 119.

As for the criteria, as mentioned in the manuscript, weathering extent can be characterized by chemical modifications and the formation of oxidation products in infrared spectroscopy (L. 140-142 *The identification and quantification of the oxidation products are essential for the understanding of the mechanism of degradation and to determine the weathering extent of plastic debris*) mainly carbonyl index (L. 157 - 159 *the carbonyl band is largely employed to characterize the UV weathering extent of polymers*) as well as spectra modifications in Raman spectroscopy (L. 174 - 175 *According to the polymer type, photodegradation mechanism and weathering extent changes in the Raman spectra can occur*). Even though in some cases, mainly after the plastic is exposed to water, it is hard to determine the weathering extent or exposure time, to our knowledge there is no other qualitative criteria for the determining of the weathering extent.

L322-323. Eventually, this process induces the splitting of the plastic, thus to the formation of plastics fragments and secondary microplastics. Was the formation of microplastics (or smaller size-particles) by the way of UV oxidation demonstrated or only suggested? This point is of prime importance.

Fragmentation of plastic debris exposed to UV in air is not likely to occur without mechanical forces. On the other hand, fragmentation of plastic debris exposed to UV in water can occur without any external mechanical forces. Thus, the fragmentation due to the formation of cracks do not correlate with the oxidation level (quantity of oxygenated functional groups at the plastics surface). This was demonstrated in two main studies: Song et al. 2017, Julienne et al., 2019 and suggested by others such as Andrady et al., 2017.

Clarification on this point was added to manuscript.

L. 339 - 345 *In the case of plastic debris exposed to UV in air, fragmentation is not likely to occur without mechanical forces (Song et al., 2017).* For water weathered plastics, cracks can propagate through the plastics, and water probably accelerates the propagation of these cracks. *Thus, for plastic debris exposed to UV in water, fragmentation can occur without any external mechanical forces (Julienne et al., 2019).* Eventually, this process induces the splitting of the plastic, thus to the formation of plastics fragments and secondary microplastics (Andrady, 2017; Julienne et al., 2019; ter Halle et al., 2016).

In the section, 4.2 dissolution of plastic, a comparison between polymer (at least about their potential to be solubilized) has to be done.

Thank you for this comment, the following was added to the manuscript L. 435 - 437: *Overall, the mass of plastics was reduced, and the dissolved organic carbon showed an increase according to UV exposure time. EPS degraded at a faster rate than PP and PE with PE being the most resistant to dissolution.*

Minor comments

Graphical abstract: mechanical stress should be also included.

Mechanical stress was added to the graphical abstract according to this comment.

L64. In 2018 more than 350 million tons of plastic were produced worldwide, China being the biggest plastic producer contributing with 30% of the world's production. Please update our figure and also included the fiber production.

Thank you for this comment. The numbers were updated according to plastics Europe latest issue and fiber production was added as well L. 64 - 66: *In 2019, 368 million tons of plastic and 73.5 million tons of synthetic fibers were produced worldwide, China being the biggest plastic producer contributing with 31% of the world's production.*

L86-88. Authors quoted "Since in the terrestrial environment, photooxidation is faster compared with other degradation processes (Lambert and Wagner, 2016a; Wang et al., 2016), the aim of this work is to give an overview on plastics photodegradation in the marine environment.

This was changed in the manuscript to the following:

L. 90 - 91 *Giving the importance of photooxidation for determining the fate and impact of plastic debris, the aim of this work is to give an overview on plastics photodegradation in the marine environment.*

136 In many cases, photodegradation mostly occurs at the surface of the polymer. Microsurface is maybe more relevant. What is the thickness of the oxidized surface?

It is a common observation that the chemical degradation in a polymer exposed to high UV irradiation is strong at the surface but falls off steeply in the interior of the sample. This is generally attributed to oxygen starvation in the interior and to a decrease of the absorbed light penetrating into the polymer. The most widespread cause of heterogeneous degradation of polymers results then from oxygen

diffusion-limited effects and limitation of the penetration of light. Oxygen diffusion-limited effects are likely to be observed in the conditions of accelerated aging, if the rate of oxygen consumption exceeds the rate of oxygen permeation; the oxidation occurs in the surface layers whereas the core remains practically unoxidized.

The importance of these effects depends then on several parameters:

- intrinsic parameters, related to the material geometry (e.g. sample thickness), coupled with the oxygen consumption rate which depends on the reactivity of the polymer, the nature of the additives, the oxygen permeability of the material;
- external parameters that result from the conditions in which the aging is carried out which include both the light intensity and the sample temperature, as well as the oxygen pressure during the weathering.

We propose the following modification: L. 138 - 140 *Depending on the polymer and on the weathering conditions (irradiance, temperature, oxygen permeability etc.) the thickness of the degraded layer can be limited to a few tens of microns or even less (Malajati, 2009; Nagai et al., 2003; Pospíšil et al., 2006; Rivaton et al., 2005; Sinturel et al., 1999).*

L113-121. Appears not so relevant in section 2.1 Visual modification. I understand that in this review, a link between plastic oxidation and microplastic scientific community needs to be woven but not relevant from my point of view

Thank you for this comment, this section was removed from the manuscript.

L199. The surface degradation increases with the UV exposure time. Yes, but very complicated to established link with time in environment.

Thank you for this remark, clarifications were added in the manuscript: L. 201 - 202 *In the case where a plastic is exposed to the same external conditions, the surface degradation should increase with the UV exposure time.*

L307-310. UV exposure can lead to the oxidation of the plastic surface and its embrittlement, after L308 "mechanical forces caused by wind action, current and tides can induce fragmentation and / or dissolution according to environmental conditions and plastic type". Mechanical forces could also favor the oxidization of the surface.

In this review, the term oxidation is used to describe the formation of oxygen containing groups in the plastic matrix. In literature, according to our knowledge, there is no direct evidence proving that mechanical forces can favor the oxidation of the surface of marine plastic debris. The oxidation is mainly affected by external conditions (temperature, UV exposure, water composition etc.).

In the case of plastic debris, a study by Song et al., 2017 showed that polyolefins were minimally fragmented by mechanical abrasion without photooxidation by UV. Thus, UV exposure combined with temperature and external conditions that causes plastics oxidation and fragilization before mechanical forces induce the fragmentation.

L369. the particle size distribution showed an increase in particle concentration with decreasing particle size. A comparison of these different size distributions could be relevant, to compared the fragmentation of different polymers.

Thank you for this comment, an example of the size distribution was added to the manuscript:

L. 398 - 401 *In this study over 73% of fragments were below 100 μm and over 97% were below 300 μm . In the case of EPS fragments, around 104 particles/pellet were below 100 μm , 1.5 particles/pellet were at 200 μm and less than a 1 particle/pellet were at 1 μm .*

Reviewer #2:

The manuscript entitled "Characteristics, fate, and impact of marine plastic debris exposed to sunlight: a review" brings an in-depth assessment of the current literature of plastic debris and its degradation and pollution effects. For sure it will be a key-reference for future studies on this subject for scientists, the general people and especially policy makers. In fact, the manuscript covers all the essential issues related to plastic properties and degradation and its effects on the environment and marine fauna. But, the issue of 'temperature' seems to be underrepresented in its importance.

As a resident and scientist living in a tropical country. i.e., where the average monthly temperature does not fall below 18°C throughout the year and near-permanent winds (called trade winds) affect beaches, the degradation of plastic would necessarily follow different paths when compared to temperate and cold weather. I searched the current literature and found very limited information of the processes involving plastic degradation speed when exposed to high temperatures of tropical beaches, that can easily reach and maintain 60 degrees Celsius for several hours (due to silica and quartz). There are open questions that should be addressed in a review paper: does intense heat break can cause plastic break (and degradation) more easily and thus make it available more quickly to the marine fauna? Does it explain why marine turtles in tropical areas consume so much plastic?

As such, there could be inserted some graphic representation of the effects of degradation on different environments, from the Arctic to the Equator and then to the Antarctic. In the same way, this section: Lines 248-255 = "Thus, the accelerated weathering presented an acceleration rate ranging overall from 2.5 to 30 times the natural weathering depending on the polymer type, the region and accelerated conditions used. It is worth noting that limits to acceleration may exist above an irradiance threshold due to the fact that recombination and/or disproportionation become predominant compared to realistic propagation (Therias et al., 2021). This was demonstrated for PE samples and we can infer that such threshold can depend on the kind of polymer. In addition, the same authors proved that temperature could be a major parameter affecting the photooxidation degradation rate of non-absorbing polymers because of its essential role in thermal activation." deserves more detailed information, as it generally touches the variability of plastic degradation by 'region' and its 'temperature'. In my opinion, the paper would greatly increase its visibility if it includes more detailed data on the temperature variability on beaches in different gradients of latitude and its effects of plastic degradation. The perception of plastic debris is different among different regions of the world, and maybe physical degradation differences is connected to this perception.

Thanks for the opportunity to revise this manuscript, for sure it will be a landmark on the theme of plastic degradation.

Dear Reviewer: We thank you for these comments which will help improve our manuscript. There are many fundamental issues in your comments concerning the role of temperature in the photo oxidation process which are of great importance and require a more detailed explanation, as you are suggesting. We thank you for giving us the opportunity to discuss this major point.

May we draw some general comments regarding thermo-oxidation vs. photo-oxidation:

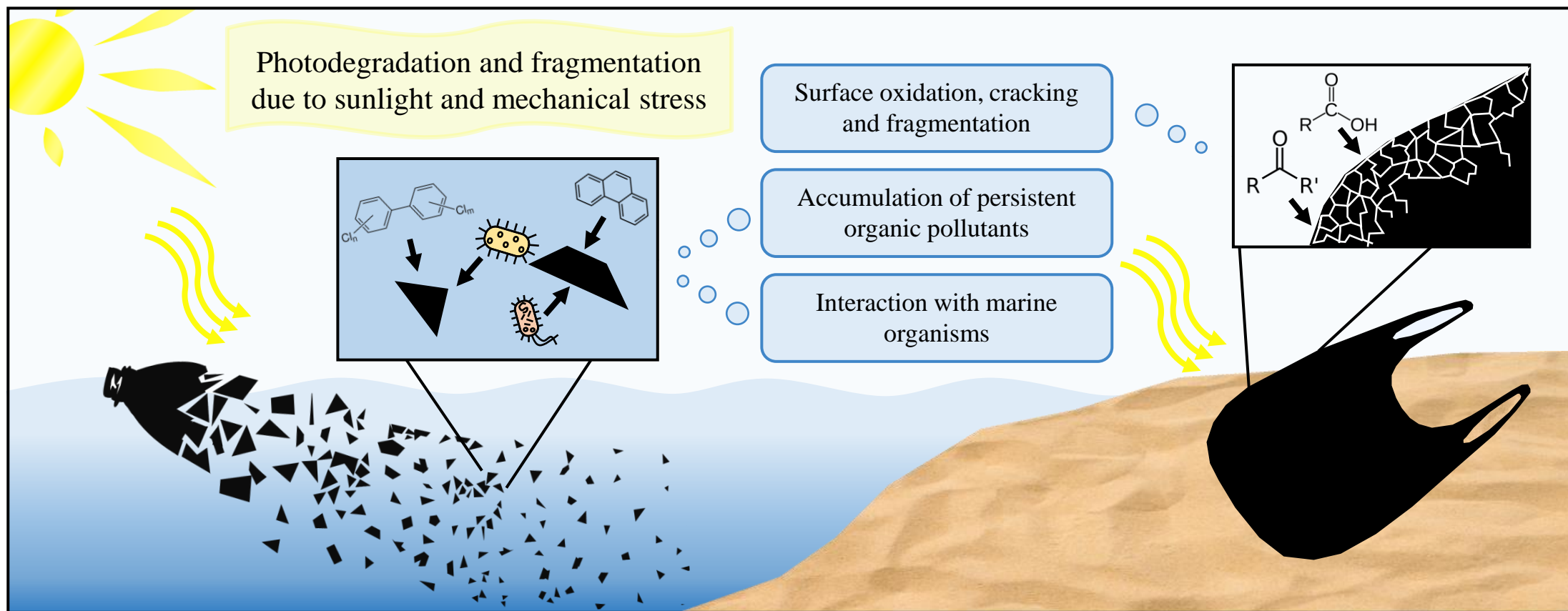
- The (apparent) activation energies measured for the photo oxidation of polyolefins are relatively high. We have measured 74 kJ/mol for LDPE in the range 51-65°C (Therias 2021). Similar values (activation energies in the range 30-50°C around 85 kJ/mol for photodegradation of HDPE) were reported by Fairbrother (A. Fairbrother et al. Polymer Degradation and Stability 165 (2019) 153-160 Temperature and light intensity effects on photodegradation of high-density polyethylene). In the case of polypropylene, Audoin had reported 55 kJ/mol (L. Audouin et al. Polymer degradation and Stability

60 (2015) 137-143 Effect of temperature on the photooxidation of polypropylene films). These values are rather important, and the consequences of high temperatures on the rate of degradation of polymers (at least polyolefins) could be underestimated. This means that, as an example, increasing the temperature from 50 to 60°C would provoke an acceleration of photo oxidation by a factor 2.3, and from 40 to 60°C by a factor around 5! On sunny days, the temperature rises quickly and is within a few degrees of maximum throughout the sunny part of the day. As you point out in your comment, when exposed at temperature around 60°C for several hours on tropical beaches, polymers would degrade faster. At the same time the irradiance is usually also very high, and depending on the polymer (non light-absorbing polymers such as polyolefins or absorbing polymers such as PC, PS, PET,...), an increase of irradiance can provoke -or not- a faster photooxidation. The consequence is that a drastic photooxidation is likely to occur within these periods of time.

- You are right when you say that intense heat can cause plastic break (and degradation) more easily and thus make it available more quickly to the marine fauna. However, this is very difficult to be quantified since there is no linear relationship between the average mean temperature and fluctuating temperatures. As temperatures are constantly changing in outdoors weathering, a direct comparison between different locations is unpractical. Many data characterizing climatic conditions in 79 locations from 19 countries can be found in the book "Weathering Handbook" published by Jerzy Wypych (ISBN 1-895198-00-3)

Considering your comments, we propose to modify our manuscript by adding the following from line 254:

It is worth noting that limits to acceleration may exist above an irradiance threshold due to the fact that recombination and/or disproportionation become predominant compared to realistic propagation (Therias et al., 2021). This was demonstrated for PE samples and we can infer that such threshold depends on the polymer type. In addition, the same authors showed that temperature affects the photooxidative degradation rate of PE with a measured apparent activation of 74 kJ/mol (Therias et al., 2021). In the case of PP, an activation energy for photooxidation around 55 kJ/mol had been determined (Audouin et al., 1998). The consequence is that, with an activation energy of 74 kJ/mol, an increase of temperature from 50 to 60°C would double the rate of photooxidation, and the rate would be multiplied by a factor 5 when passing from 40 to 60°C. Thus, the variability of temperature by region is an important parameter that should be considered, but difficult to be predicted. The rate of photooxidation of a given polymer is then expected to present strong variations depending on the location, the season, and the hour, with very important oxidation rates with higher temperatures. In other applications where temperature plays an important role on the photodegradation, i.e. solar mirrors industry, empirical models have been established to take into account how the variations of temperature and the reached maximum temperature impact the degradation (Avenel et al., 2018; Escobar and Meeker, 2006).



Highlights

Plastics exposed to sunlight undergoes visual and physico-chemical modifications.

Exposure medium (air/water) highly affects the photodegradation process.

Fragmentation depends on polymer type, formulation, exposure conditions.

The path and time spent by the plastic in the environment cannot be identified yet.

Plastics risk is associated to organic pollutants and degradation products.

1 **Characteristics, fate, and impact of marine plastic debris exposed to sunlight: a** 2 **review.**

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21 **Abstract**

22 The increase of plastic production from the middle of the twentieth century was inevitably followed by an
23 increase in the amount of plastic dumped in the natural environment. There, the plastic debris are exposed to
24 sunlight, temperature, humidity, and physical stress. This can induce photo-oxidative and thermal degradation.
25 This review discusses the mechanism of plastics UV weathering and its characteristics. Comparison of the
26 photodegradation rate and physico-chemical properties are made according to the weathering mode
27 (natural/accelerated) and medium (air/water). Since the photodegradation can lead to plastics fragmentation, this
28 phenomenon is described along with the methodologies used in literature to evaluate the fragmentation. The impact
29 of the photodegraded plastic debris on the marine environment is also presented in term of (i) photodegradation

30 products and stabilizers leakage, (ii) organic pollutants accumulation, transfer, and leakage, and (iii) toxicity on
31 marine organisms.

32 **Keywords**

33 Plastic debris, photochemistry, marine environment, oxidation, fragmentation, analytical techniques.

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53 1. Introduction

1
2 54 Mass production of plastics began as early as 1939, and increased year by year ever since. Plastic can be
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4 55 categorized according to different criteria, the first being in thermoplastics and thermosets. Thermoplastics can be
5
6 56 melted at high temperature and hardened when cooled, like polyethylene (PE), polypropylene (PP), polyvinyl
7
8 57 chloride (PVC), polyethylene terephthalate (PET), polystyrene (PS), and acrylonitrile butadiene styrene (ABS).
9
10 58 Thermoset plastics, after they were heated and formed remain in a permanent solid state like polyurethane (PU),
11
12 59 unsaturated polyester and epoxy resins. Another plastics classification is based on its source as it can be of fossil
13
14 60 origin, renewable or even mineral base. According to their structure, polymers can also be classified into carbon-
15
16 61 carbon backbone and polymers with heteroatoms in their main chain (Brydson, 1999; Geyer, 2020; Van der Vegt,
17
18 62 2002). During compounding and shaping, stabilizers can be added to improve plastics stability and mechanical
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20 63 properties (Brydson, 1999). Being lightweight, durable, strong, and cheap, plastics production increased rapidly.

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23 64 In 2019, 368 million tons of plastic and 73.5 million tons of synthetic fibers were produced worldwide, China
24
25 65 being the biggest plastic producer contributing with 31% of the world's production. It is estimated that global
26
27 66 annual primary plastic production would reach 1.1 billion tons in 2050. Plastic is mostly used in the packaging
28
29 67 industry and in building and construction. Most used plastics are PP, PE, and PVC (Geyer, 2020;
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31 68 Industrievereinigung Chemiefaser, 2020; Plastics Europe, 2020). The life cycle of a plastic product can vary
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33 69 according to the plastic's type and its properties as not all plastic products have the same service life. Depending
34
35 70 on its use the plastic's lifespan can vary from less than a year to more than 50 years. Giving this, the amount of
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37 71 plastic waste collected does not correlate with the plastics production of the same year. For example, in Europe in
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39 72 2018, 61.8 million tons were produced, and only 29.1 million tons of post-consumer plastic waste were collected.
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41 73 Collected waste was recycled, used for energy recovery, or dumped in landfills. Another part of plastic waste is
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43 74 not collected, this is due to littering and unauthorized dumping. Following the actual trends, by 2050 humankind
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45 75 would have generated 33,000 Mt of total plastic waste and that 12,000 Mt of the waste would be in landfills,
46
47 76 dumps, or the natural environment (Geyer, 2020; Kosior and Mitchell, 2020; Plastics Europe, 2019a, 2019b;
48
49 77 Welden and Lusher, 2020).

50
51
52 78 Plastic debris are transferred into the marine environment from coastal and inland sources transported by rivers,
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54 79 drainage systems or human activity (Auta et al., 2017; Peng et al., 2020). Jambeck et al. 2015 estimated that
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56 80 between 4.8 and 12.7 million tons of plastic entered the ocean from coastal environments in 2010 (Hurley et al.,
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58 81 2020; Jambeck et al., 2015; Lebreton et al., 2017; Schmidt et al., 2017). Currently, it is estimated that between 5
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82 and 50 trillion plastic pieces afloat at sea (Eriksen et al., 2014; van Sebille et al., 2015). Most of these particles are
1
2 83 more likely to be PE, PP, PS, polyester and polyamide and acrylic (Erni-Cassola et al., 2019).

3
4 84 In the marine environment, plastics are exposed to sunlight, temperature, humidity, physical stress, and
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6 85 microorganisms. This can induce photo-oxidative, thermal, mechanical, and bio-degradation (Andrady, 2011;
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8 86 Gewert et al., 2015; Jacquin et al., 2019).

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10
11 87 It is generally considered that radiation in the ultraviolet (UV) and visible is the primary factor in outdoor
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13 88 polymer weathering. Effects from heat, moisture, pollutants, mechanical stresses, and biological attack can come
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15 89 into play, but usually the weathering process begins with a photochemical event (Pickett et al., 2008; White, 2006).
16
17 90 Giving the importance of photooxidation for determining the fate and impact of plastic debris, the aim of this work
18
19 91 is to give an overview on plastics photodegradation in the marine environment. This study presents the mechanism
20
21 92 of plastics photodegradation and its characteristics according to weathering conditions and medium (air/water).
22
23 93 The study also details the fragmentation and dissolution processes of plastics exposed to UV weathering. The
24
25 94 second focus of this review is on the impact of photodegraded plastic debris on the marine environment in terms
26
27 95 of photodegradation products and stabilizers release, accumulation of organic pollutants, and their toxicity on
28
29 96 marine organisms.

30 31 32 97 **2. Photodegradation mechanism and characteristics of weathered marine plastic debris**

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34
35 98 In the marine environment, plastics are exposed to several stresses including solar ultraviolet (UV) radiation.
36
37 99 The mechanisms by which polymers photodegrade in the presence of oxygen consist of three main steps (initiation,
38
39 100 propagation, and termination) and have been the object of numerous articles, reviews, and books (Allen and
40
41 101 MacKellar, 1980; Billingham, 1993; Bolland, 1949; Feldman, 2002; Fotopoulou and Karapanagioti, 2017;
42
43 102 Gardette, 2000; Gewert et al., 2015; Norrish and Bamford, 1936; Rabek, 1995; Singh and Sharma, 2008). Thus,
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45 103 the mechanism will be discussed briefly.

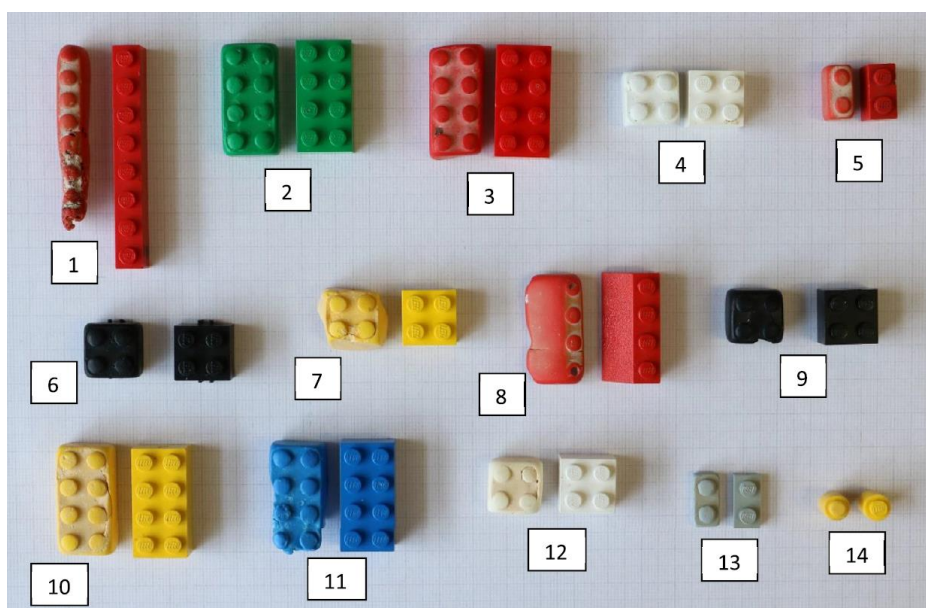
46
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48 104 Photodegradation is initiated by the absorption of UV light and the formation of free radicals. For example,
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50 105 intrinsic and extraneous chromophore groups and/or impurities in polymers can absorb light in the near UV and
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52 106 induce photodegradation (Allen and Fatinikun, 1981; Bolland, 1949; Rånby, 1989). The propagation reactions are
53
54 107 common to all carbon backbone polymers, as free polymer radical reacts with oxygen to form peroxy radicals
55
56 108 then hydroperoxides. Further radical reactions with oxygen and polymer radicals take place leading to random
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58 109 chain scission, chain branching, cross linking and formation of oxygen containing functional groups (Agboola et

110 al., 2017; Gardette et al., 2013; Gijsman et al., 1999; Torikai et al., 1986). Termination reaction is the combination
1 of two free radicals leading to non-active stable products and can be promoted by the presence of stabilizers
2 111 of two free radicals leading to non-active stable products and can be promoted by the presence of stabilizers
3
4 112 (Fechine et al., 2002; Gijsman, 2017; White and Shyichuk, 2007; Zweifel, 1998).

6 113 In short, weathering mechanisms and rates can vary depending on the polymer type, structure, and formulation
7
8 114 (presence of additives, fillers, pigments, etc.). The consequences of UV weathering on plastics visual aspect and
9
10 115 physico-chemical properties are presented here. Plastic's weathering extent corresponds to the chemical and
11
12 116 physical modifications that the plastic undergoes according to its UV exposure time and external weathering
13
14 117 conditions. It is not an absolute criteria nor a given value to be determined, but rather a relative criteria allowing
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16 118 the comparison of the aging extent of different plastic samples as it can be defined by one or several parameters
17
18 119 according to the study.

2.1. Visual modification

24 121 Plastic's colour could give an indication about its source and the time it has remained in the environment. In
25
26 122 international pellet watch campaigns in coastal waters and remote islands, volunteers noticed a yellowish colour
27
28 123 on weathered pellets, specially initially transparent and white pellets (Frias et al., 2010; Heskett et al., 2012; Le et
29
30 124 al., 2016; Mizukawa et al., 2013; Ogata et al., 2009). Other authors described a discoloration in previously coloured
31
32 125 weathered plastic debris as well as loss of gloss and texture, smoothing and denudation as shown in figure 1
33
34 126 (Bandow et al., 2017; Gauquie et al., 2015; Karkanorachaki et al., 2018; Turner et al., 2020).



128 **Figure 1:** Weathered and unweathered blocks paired from appearance (Turner et al., 2020). (double/colour)

129 In the case of previously coloured plastic, loss of colour can be attributed to the loss of organic and/or
130 inorganic colorants, pigments, or dyes due to their photodegradation or diffusion from the plastic matrix to the
131 water. The yellowing can be attributed to chemical modifications and the formation of unsaturated organic groups
132 capable of absorbing wavelengths in the visible region after being exposed to sunlight.

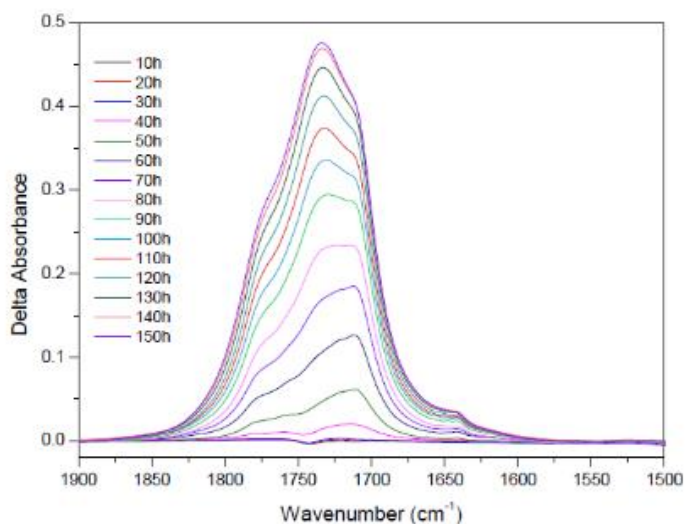
133 **2.2. Chemical modifications**

134 The ageing of polymers produces modification of the chemical structure of the polymer due to the formation
135 of a complex mixture of different oxidation products. In many cases, photodegradation mostly occurs at the surface
136 of the polymer, as a result of a control by oxygen diffusion or by the penetration of UV light, and it can be limited
137 in the bulk (Gardette, 1993; Jouan and Gardette, 1987; Malajati, 2009; Pospíšil et al., 2006; Shyichuk et al., 2003,
138 2005; Sinturel et al., 1999). Depending on the polymer and on the weathering conditions (irradiance, temperature,
139 oxygen permeability etc.) the thickness of the degraded layer can be limited to a few tens of microns or even less
140 (Malajati, 2009; Nagai et al., 2003; Pospíšil et al., 2006; Rivaton et al., 2005; Sinturel et al., 1999). The
141 identification and quantification of the oxidation products are essential for the understanding of the mechanism of
142 degradation and to determine the weathering extent of plastic debris.

143 The formation of the oxidation products leads to modifications of the infrared spectrum of the polymer and
144 infrared spectroscopy has been recognized for a long time as a very useful tool in the identification of marine
145 plastic debris and in the characterization of the chemical modifications provoked by ageing (Jung et al., 2018,
146 2018; Lobo and Bonilla, 2003; Pavia et al., 2008; Rugg et al., 1954). It can analyse plastic particles as small as 10
147 μm and was used in numerous marine plastics sampling campaigns (Bouhroum et al., 2019; Corami et al., 2020;
148 Heskett et al., 2012; Hildebrandt et al., 2020; Mecozzi et al., 2016; Rios et al., 2010, 2007; Scircle et al., 2020;
149 Silva et al., 2018; Syakti et al., 2018, 2017; Thermo Fisher Scientific, 2018).

150 According to the sample size and thickness either transmission mode or attenuated total reflectance module
151 can be applied to acquire the sample spectra (Skoog et al., 2007). For polyolefins, two main areas are correlated
152 with the formation of the photodegradation products: hydroxyl groups (O-H) with a broad peak from 3100 to 3700
153 cm^{-1} and carbonyl bands (C=O) from 1550 to 1810 cm^{-1} consisting mainly of carboxylic acids, ketones, esters and
154 lactones at 1713, 1720, 1735, and 1780 cm^{-1} , respectively (Bandow et al., 2017; Brandon et al., 2016; Gardette et
155 al., 2013; Lemaire et al., 1996; Lv et al., 2015; Pavia et al., 2008; Rouillon et al., 2016).

156 In figure 2, an infrared spectrum is presented showing an increase of absorbance in the region relative to
1 carbonyl bands representing the degradation products of polypropylene (PP). Even though other areas can be
2 157 selected to characterize the weathering extent according to polymer type, the carbonyl band is largely employed
3
4 158 to characterize the UV weathering extent of common polymers such as PVC, PS, PLA, PET and ABS (Bandow et
5
6 159 al., 2017; Brandon et al., 2016; Copinet et al., 2004; Gardette, 2000; Ioakeimidis et al., 2016; Liu et al., 2019;
7
8 160 Turner et al., 2020).
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10 161



162
163 **Figure 2:** Infrared spectra in the region 1900 - 1500 cm⁻¹ of a photooxidized PP film (Rouillon et al., 2016).
164 (single/color)

165 The chemical composition of plastic debris can also be determined by X-ray Photoelectron Spectroscopy (XPS)
166 and Energy Dispersive X-Ray Spectroscopy (EDS or EDX). These methods can give details about the elemental
167 composition of the sample's surface. For example, chlorine and carbon are the most abundant elements in the
168 PVC's surface. XPS and EDS results on UV aged plastics shows that weathered plastic's surface contains higher
169 oxygen content than unaged plastics confirming FTIR results (Gniadek and Dąbrowska, 2019; Massey et al., 2007;
170 Müller et al., 2018; Tian et al., 2019; Tiwari et al., 2019; Turner et al., 2020; Wang et al., 2017; Yang et al., 2003).

171 Among the chemical consequences of UV weathering on plastic debris, changes in some polymer structures
172 are cited in addition to the formation of oxidized function. This can be further examined by Raman spectroscopy.
173 Raman spectroscopy allows the identification of plastics based on characteristic peaks in their specific fingerprint
174 region. According to the polymer type, photodegradation mechanism and weathering extent changes in the Raman
175 spectra can occur. For some polymers such as PE, PP and PET characteristic peaks in the fingerprint region do not
176 show considerable changes with weathering, while for other polymers changes can be noticed. For example, the

177 spectrum of UV weathered PVC shows an intensity reduction for its characteristic bands at 693 and 637 cm⁻¹
178 compared to unaged PVC corresponding to C-Cl bond of the polymer. Even though Raman spectroscopy presents
179 a wider spectral range coverage, better resolution, lower water interference and can analyse smaller plastic particles
180 (down to 100 nm) when compared to FTIR, it has a limitation in the analysis of photodegraded samples. Thus, for
181 the analysis of photodegraded polymers, reference spectra of photodegraded polymers should be included in
182 Raman database (Chabert et al., 1997; Lenz et al., 2015; Ribeiro-Claro et al., 2017; Silva et al., 2018; Sobhani et
183 al., 2020).

184 Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) is also described in literature for the
185 identification of polymer type and associated organic stabilizers by analysing their thermal degradation products
186 (Fischer and Scholz-Böttcher, 2017; Fries et al., 2013; Hermabessiere et al., 2018). This method will not be further
187 discussed here since it is mostly used to identify microplastics and not their weathering extent. Nevertheless, it
188 could be interesting to develop this method by creating a database for chemically aged polymers.

189 While it is not frequently used for environmental plastic sample's analysis, Gel Permeation Chromatography
190 (GPC) is used in laboratory analysis to characterize plastics before and after UV weathering. GPC gives
191 information about the molecular weight distribution including weight and number average molecular weights.
192 Polymers studied after UV exposure showed a decrease in their molecular weight distribution to low molecular
193 weight side due to chain scission mechanism (Ceccarini et al., 2018; Copinet et al., 2004; Goedecke et al., 2017;
194 Hiejima et al., 2018; Lv et al., 2015; Müller et al., 2018; Shyichuk et al., 2005; ter Halle et al., 2017). Even though
195 environmental plastic debris can be characterized by GPC, a limitation remains in the determination of the
196 weathering extent as the molecular weight distribution of the initial plastic is more often unknown.

197 ***2.3. Modification in physical properties***

198 Surface modification of UV weathered plastics is not limited to the formation of oxidation products as the
199 fragilization of polymer structure can induce changes in the surface topography. While unaged plastics show a
200 smooth surface, as presented in figure 3, the surface of UV weathered plastic presents mostly cracks and fractures,
201 as well as flakes, grooves, adhering particles, and pits. In the case where a plastic is exposed to the same external
202 conditions, the surface degradation should increase with the UV exposure time (Cooper and Corcoran, 2010;
203 Corcoran et al., 2009; Girão et al., 2017; Liu et al., 2019; Lv et al., 2015; Rouillon et al., 2016; ter Halle et al.,
204 2017, 2016; Turner et al., 2020). For this, Scanning Electron Microscopy (SEM) is suitable to acquire high-
205 magnification images of plastic particles with a good resolution.

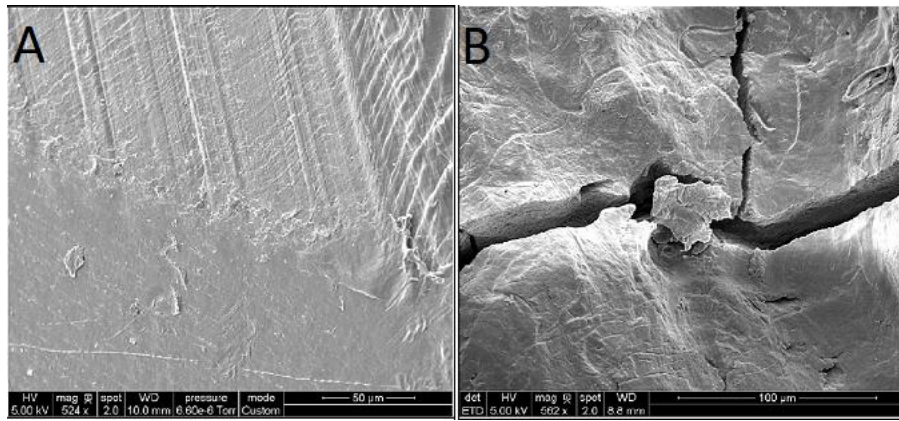


Figure 3: SEM images of (A) an unaged PE pellet and (B) a PE sample collected from the North Atlantic subtropical gyre (ter Halle et al., 2017). (double)

Atomic force microscopy (AFM) is another microscopic technique to acquire plastics surface topographies. It is mainly applied in laboratory studies to evaluate the surface condition of the photodegraded plastic before and after the application of a physical force, for example during Vickers micro-hardness test (Larché et al., 2012; Rouillon et al., 2016). Although environmental plastic samples have been rarely characterized by AFM, recent studies showed an interest for this technique to characterize environmentally weathered plastics as results showed a significant increase in the root-mean-square roughness by at least a factor 2 (Rowenczyk et al., 2020; Taghavi et al., 2021).

Plastic's density, buoyancy and location in the water column and thus exposure to UV light depends on its structure and crystallinity. Many studies concerning semi-crystalline plastic's properties during UV aging documented an increase of the crystallinity. This is explained by the fact that oxidation occurs in the amorphous phase, as oxygen cannot penetrate into the crystalline phase. Oxidation can lead to an increase of crystallinity resulting of chemi-crystallisation (crystal growth from molecules segments released by the scission of polymer chains), which is responsible for a higher density, thus a negative buoyancy for plastic debris (Rabello and White, 1997). This is confirmed in environmental conditions, as marine plastic debris show a higher crystallinity, estimated by Differential Scanning Calorimetry (DSC). compared to consumer packaging materials (Andrady, 2017; Lv et al., 2015; Müller et al., 2018; Pospíšil et al., 2006; Rouillon et al., 2016; ter Halle et al., 2017).

3. Comparison of photodegradation conditions

The influence of factors such as radiation intensity and temperature on the degradation of polymers provoked by UV-exposure has been determined for both natural and accelerated weathering (Lemaire et al., 1996, 1979).

228 Nevertheless, in the marine environment, other factors such as mechanical strain, humidity, oxygen availability,
1 229 weather conditions, and bacterial fouling can interfere and differ for beaches, surface water, deep-water and marine
2 230 sediments (Andrady, 2017; Andrady et al., 2019; Beltrán-Sanahuja et al., 2020; Kockott, 1989). While several
3 231 studies compared natural and accelerated weathering, there have been limited studies on the degradation of plastic
4 232 debris in the marine environment.
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10 233 ***3.1. Photodegradation conditions: natural vs. accelerated weathering***

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12 234 Natural weathering being time consuming and depending of several factors that are difficult to control,
13 235 alternative methods are used to accelerate weathering in controlled conditions (Andrade et al., 2019; Avenel et al.,
14 236 2017; Gardette, 2000; Malajati et al., 2011). Most publications in literature used accelerated weathering simulating
15 237 natural conditions in order to estimate the lifetime of plastic materials according to their physicochemical and
16 238 mechanical properties (Al-Salem, 2009; Al-Salem et al., 2019; Espí et al., 2007; Feldman, 1981). Natural
17 239 weathering conditions varies according to regions, climates, and seasons while accelerated weathering was
18 240 according to different conditions applied in commercial chambers such as Q-Panel, Atlas Weather-Ometer, SEPAP
19 241 12-24 and SPHERE with dry or wet/dry cycle depending on the study (Fairbrother et al., 2019; Gugumus, 1995;
20 242 Larché et al., 2011; Lv et al., 2015; Philip and Al-Azzawi, 2018; Pimentel et al., 2005; Pimentel and Gardette,
21 243 2001; Rosa et al., 2005; Scoponi et al., 2000; Tidjani, 2000, 1996; Tuasikal et al., 2014; White et al., 2011;
22 244 Wypych, 1990).
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36 245 It is important in accelerated weathering experiments to simulate as closely as possible natural weathering.
37 246 This requires that the various degradation products be produced at the same proportions and the mechanical
38 247 properties modifications comparable for both weathering modes. Several publications compared the effects of
39 248 natural and accelerated weathering at different exposure times with regular characterization. Some correlation can
40 249 be made to plastic debris weathered in the marine environment at shore and in water (Gardette, 2000; Gewert et
41 250 al., 2015). The higher radiation dose, temperature and humidity in accelerated weathering cause faster chain
42 251 scission rate and crack growth increasing the area exposed to UV radiation (Andrady, 1989; Kockott, 1989;
43 252 Maxwell et al., 2005; Philip and Al-Azzawi, 2018). Thus, the accelerated weathering presented an acceleration
44 253 rate ranging overall from 2.5 to 30 times the natural weathering depending on the polymer type, the region and
45 254 accelerated conditions used. It is worth noting that limits to acceleration may exist above an irradiance threshold
46 255 due to the fact that recombination and/or disproportionation become predominant compared to realistic
47 256 propagation (Therias et al., 2021). This was demonstrated for PE samples and we can infer that such threshold
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257 depends on the polymer type. In addition, the same authors showed that temperature affects the photooxidative
1 258 degradation rate of PE with a measured apparent activation of 74 kJ/mol (Therias et al., 2021). In the case of PP,
2 3
4 259 an activation energy for photooxidation around 55 kJ/mol had been determined (Audouin et al., 1998). The
5
6 260 consequence is that, with an activation energy of 74 kJ/mol, an increase of temperature from 50 to 60°C would
7
8 261 double the rate of photooxidation, and the rate would be multiplied by a factor 5 when passing from 40 to 60°C.
9
10 262 Thus, the variability of temperature by region is an important parameter that should be considered, but difficult to
11
12 263 be predicted. The rate of photooxidation of a given polymer is then expected to present strong variations depending
13
14 264 on the location, the season, and the hour, with very important oxidation rates with higher temperatures. In other
15
16 265 applications where temperature plays an important role on the photodegradation, i.e. solar mirrors industry,
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18 266 empirical models have been established to take into account how the variations of temperature and the reached
19
20 267 maximum temperature impact the degradation (Avenel et al., 2018; Escobar and Meeker, 2006).

268 **3.2. Photodegradation medium: air vs. water**

269 From an environmental point of view, some authors have described and compared UV weathering in air (beach)
270 and water (ocean surface) (Andrady, 2011; Biber et al., 2019; Cai et al., 2018; Malajati et al., 2011; Pimentel et
271 al., 2005; Ranjan and Goel, 2019; Tang et al., 2019, 2018). These approaches were essential to have a better
272 understanding of the weathering process at shore and in the ocean and to estimate the duration spent by plastic
273 debris in the environment.

274 Authors essentially compared plastic debris characteristics in four different exposure conditions, air-UV light,
275 air-darkness, water-UV light, and water-darkness. Plastics were weathered in natural or accelerated conditions at
276 different exposure times. Plastics used in these studies were mostly PP, PE, PET, PS and PVC as pellets or films.

277 According to FTIR results for polyolefins (based on carbonyl and hydroxyl groups absorption bands), PET and
278 PVC, the level of chemical weathering was higher in air in comparison to water, as air has higher oxygen content
279 and UV transmittance opposed to water. The slower degradation rate in water is also due to the lower temperature
280 (Andrady, 2011; Biber et al., 2019; Cai et al., 2018; Pimentel et al., 2005; Ranjan and Goel, 2019; Tang et al.,
281 2019, 2018). The lower concentration of carbonyl and hydroxyl groups in plastics weathered in water can also be
282 due to the release of the degradation products into the water (c.f. section 4.2). Thus, infrared analysis of the solid
283 polymer can be subject to errors in determining quantitatively the photodegradation state of marine plastic debris
284 as the concentrations of some photoproducts could be underestimated as a consequence of the migration of these
285 products. The other characterization methods used presented complementary results to those of FTIR. Although

286 Raman spectra did not show significant changes for the weathering of plastics in different mediums, they did show
 1 287 differences between unaged and weathered plastics. SEM and AFM analysis confirmed the presence of fractures
 3 288 and holes on the plastic's surface, similarly in both mediums. Nevertheless, mechanical properties decreased more
 5 289 for plastics exposed in air than those exposed in water (Andrady, 1989; Andrady et al., 1993; Biber et al., 2019;
 7 290 Brandon et al., 2016; Cai et al., 2018; Pimentel et al., 2005; Ranjan and Goel, 2019; Tang et al., 2019, 2018).

10 291 Opposite results occurred in the case of PS, as its photodegradation was faster in water in comparison to air.
 12 292 The authors concluded that this is possibly due to the removal of the oxidized yellow surface by water movement
 14 293 allowing the bulk beneath to be gradually exposed to UV radiation while in the air this layer prevents the UV light
 16 294 diffusion and protects the bulk (Andrady and Pegram, 1991; Tian et al., 2019). A summary of polymer behaviour
 18 295 according to the weathering medium is presented in Table 1.

21 296 **Table 1:** Qualitative comparison of polymer behaviour in term of weathering extent in air / water medium (IR carbonyl
 22 297 and hydroxyl groups bands) (Biber et al., 2019; Cai et al., 2018; Pimentel et al., 2005; Ranjan and Goel, 2019; Tang et al.,
 23 298 2019, 2018), fragmentation (number of generated fragments) (Kalogerakis et al., 2017; Lambert and Wagner, 2016a; Song et
 24 299 al., 2017; Weinstein et al., 2016) and dissolution (mass of plastics and dissolved organic carbon) (Lee et al., 2020; Ward et al.,
 25 300 2019; Zhu et al., 2020). Symbols: ++ resistant, -- fragile and x not mentioned.

	Air UV	Water UV	Fragmentation	Dissolution
PE	+	++	++	++
PP	+	++	++	+
PS	-	--	--	-
PET	+	++	++	X
PLA	X	X	-	X
PVC	+	++	X	X

301
 302 Fewer studies compared weathering behaviour in water with different salt content. FTIR and mechanical
 303 characteristics results of PE, PP and PS showed that the photodegradation rate of plastics in ultrapure or freshwater
 304 was higher than that in seawater. This is due to the salt content as the refractive index of water increase with
 305 salinity, thus the UV photonic flux for plastics in seawater is lower compared with that in pure water. Another
 306 reason can be the formation of salt crystals on plastic surface that can protect the bulk from UV radiation (Cai et
 307 al., 2018; Ranjan and Goel, 2019).

308 Some authors compared their results with environmental plastic debris to estimate how long it has been in the
 309 ocean. Brandon et al. 2016 recorded hydroxyl and carbonyl infrared bands in different plastic samples exposed to
 310 sunlight in seawater as a function of time. They did not obtain linear results, bond indices showing systematically
 311 increasing and decreasing phases under such conditions. The combination of both formation and water release and

312 / or photodegradation of the oxidized species could explain these observations. The authors concluded that this
1
2 313 approach presents a limitation for determining the weathering extent and the time spent in the environment by a
3
4 314 plastic. Nevertheless, they were able to estimate that samples from California and the North Pacific subtropical
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6 315 gyre were exposed for less than 18 months with some exposed for less than 30 months (Brandon et al., 2016). This
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8 316 approach thus allowed them to estimate a period of time in which the plastic was exposed to sunlight in the marine
9
10 317 environment but not the exact weathering time nor the path undertaken by the plastic in the environment.

11
12 318 Despite the current knowledge, it is therefore still hard to determine how long a given plastic has been in the
13
14 319 environment. Moreover, the degradation depends not only on the polymer type, its characteristics, and its initial
15
16 320 stabilizer formulation but also on the path of the plastic from its source to the ocean. In fact, before entering the
17
18 321 ocean, the plastic can be protected from ageing for years, or it can be weathered during its use or on shore. Also,
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20 322 biofilms development onto the plastic surface in the ocean can protect it from sunlight and thus from
21
22 323 photodegradation. Better understanding of the longer term, natural weathering and the variable conditions of the
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24 324 weathering process is still needed.

25 26 27 325 **4. Fate of plastic debris: Fragmentation and dissolution**

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30 326 As already mentioned, UV exposure can lead to the oxidation of the plastic surface and its embrittlement, after
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32 327 this, mechanical forces caused by wind action, current and tides can induce fragmentation and / or dissolution
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34 328 according to environmental conditions and plastic type (Cooper and Corcoran, 2010; O’Brine and Thompson,
35
36 329 2010; Pegram and Andrady, 1989).

37 38 39 330 ***4.1. Fragmentation process***

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41 331 The fragmentation process is the disintegration of the material, it is described as the degradation of plastic
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43 332 debris into smaller particles. Two fragmentation processes are described in literature and are presented in figure
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45 333 4: plastic splitting and surface ablation (Andrady, 2017; Yakimets et al., 2004).
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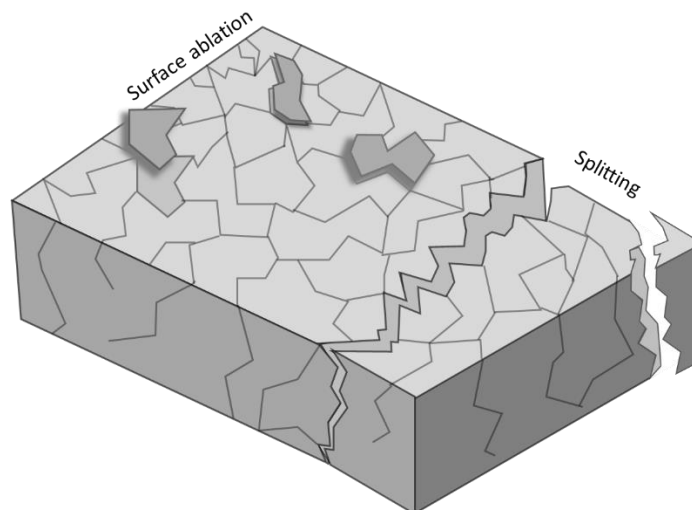


Figure 4: Fragmentation processes. (double)

After the plastic surface was weathered, cracks on the surface can propagate deeper into the plastic and cause the split of the plastic into two or more fragments. This process was described for semi-crystalline polyolefins as they have a heterogeneous surface consisting of crystalline and amorphous phases. After the degradation of the amorphous phase due to UV exposure, cracks develop in inter-crystalline region. In the case of plastic debris exposed to UV in air, fragmentation is not likely to occur without mechanical forces (Song et al., 2017). For water weathered plastics, cracks can propagate through the plastics, and water probably accelerates the propagation of these cracks. Thus, for plastic debris exposed to UV in water, fragmentation can occur without any external mechanical forces (Julienne et al., 2019). Eventually, this process induces the splitting of the plastic, thus to the formation of plastics fragments and secondary microplastics (Andrady, 2017; Julienne et al., 2019; ter Halle et al., 2016).

For surface ablation, the weathered surface of the plastic usually presents different characteristics than the bulk of the material and is more susceptible to mechanical stress as repeated wet and dry cycles fragilize the interface between the surface and the bulk which can cause fragmentation by surface ablation (Andrady, 2017; Feldman, 2002). An example for this type of weathering was described as oxidized PS surface layer is removed by water movement leading to the graduate degradation of the plastic's bulk (Andrady and Pegram, 1991). This is also confirmed by SEM analysis of marine plastic debris consisting of PP, PE, PS and PVC as the surface texture of most samples presents pits, conchoidal fractures, linear fractures, subparallel ridges and grooves (Corcoran et al., 2009; Kedzierski et al., 2018; ter Halle et al., 2017). This can generate particles as small as nano-plastics (Gigault et al., 2016).

355 4.1.1. *Fragmentation of environmental samples*

1
2 356 Ter Halle et al. 2016 characterized environmental plastic samples from the North Atlantic gyre in order to
3
4 357 better understand microplastics fragmentation. The authors suggested that the fragmentation of plastic debris
5
6 358 depends on their buoyancy in water: big parallelepipeds float flat at the surface with one face exposed to the sun
7
8 359 while smaller cubic pieces tend to roll at water surface. This is confirmed by their SEM results, as 80% of the
9
10 360 parallelepipeds plastics had one face with more cracks than the other while cubic plastics presented the same
11
12 361 characteristics on all faces (ter Halle et al., 2016). Corcoran et al. 2009 also sampled environmental plastics. Their
13
14 362 SEM and FTIR results indicate that the mechanical process was mostly responsible of the surface erosion and that
15
16 363 this process was more favourable when the surface was oxidized from UV exposure (Corcoran et al., 2009). This
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18 364 is confirmed in a lab study by Song et al. 2017 that stated that polymer fragmentation increase with UV exposure
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20 365 time in combination with mechanical abrasion (Song et al., 2017).

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22
23 366 Ter Halle et al. 2016 noted that in fragmentation studies the mass of the plastic should be considered and not
24
25 367 its size since mass is conservative and unequivocal while size can be dependent of the measuring method (Filella,
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27 368 2015; ter Halle et al., 2016). Resmeriță et al. 2018 measured weight loss of PP pellets exposed to UV radiation for
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29 369 500 hours in air and seawater at ocean like conditions (Resmeriță et al., 2018). The author noted that weight loss
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31 370 was more significant in samples weathered in seawater while no significant decrease was noted in samples
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33 371 weathered in air. Despite this, the author was not able to detect any released particles by optical microscopy.

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36 372 4.1.2. *Comparison of polymers fragmentation behaviour*

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39 373 Fragmentation rate depends mostly on the polymer type, additives used in compounding, UV exposure medium
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41 374 and mechanical conditions (Song et al., 2017). In general, laboratory fragmentation studies consist of exposing
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43 375 plastic material to natural weathering or accelerated UV degradation combined with mechanical force. Two
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45 376 approaches are described in literature.

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47
48 377 The first one consists on the exposure of plastic to natural weathering, for example in a salt marsh habitat for
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50 378 Weinstein et al. 2016, then placing the photodegraded samples in closed seawater amber jug while shaking to
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52 379 induce fragmentation (Weinstein et al., 2016). Since plastic fragments can be lost during weathering in open
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54 380 exposure system, this approach can induce an underestimation of the number of particles produced. Other authors
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56 381 studied the fragmentation in a closed simulated environment. In this second approach, plastic samples are exposed

382 to UV light directly in closed simulated beach/ocean environment in laboratories with and/or without mechanical
383 abrasion (Kalogerakis et al., 2017; Lambert and Wagner, 2016a, 2016b; Song et al., 2017).

384 Plastic types studied were mostly PE, PP, PS, PET and PLA as pellets, films, strips, and consumer materials.
385 After weathering in both approaches, the surface of the plastic is analysed by FTIR and SEM while the fragments
386 generated are collected from sand and/or water and characterized by dissecting scope, particle counter (Coulter
387 counter, nanoparticle tracking analysis) or density separation followed by Nile red stain and fluorescence
388 microscopy (Lambert and Wagner, 2016a; Song et al., 2017; Weinstein et al., 2016).

389 FTIR results showed in all cases an increase for hydroxyl and carbonyl groups peaks while SEM results showed
390 surface cracks due to photooxidation. For all plastics, identified fragments sizes varied overall from 30 nm to 1000
391 μm , and the particle size distribution showed an increase in particle concentration with decreasing particle size.
392 For polyolefins, fragmentation did not occur without the mechanical abrasion (Song et al., 2017). They also
393 produced the least number of particles in the smaller size range. This is attributed to the initial composition of the
394 plastic as polyolefins could contain stabilizers, such as anti-UV and antioxidants, that could impede UV
395 degradation compared to PS and PLA (Lambert and Wagner, 2016a; Song et al., 2017; Weinstein et al., 2016).

396 For example, in the study by Song et al. 2017 and in the size range of 50 - 1000 μm , expanded polystyrene
397 (EPS) was the most fragmented and released $10,501 \pm 1718$ particles/pellet, the PP 6084 ± 1061 particles/pellet,
398 while PE was the least fragmented with 20 ± 8.3 particles/pellet (Song et al., 2017). In this study over 73% of
399 fragments were below 100 μm and over 97% were below 300 μm . In the case of EPS fragments, around 10^4
400 particles/pellet were below 100 μm , 1.5 particles/pellet were at 200 μm and less than a 1 particle/pellet were at 1
401 μm . In another study by Lambert and Wagner 2016a in the size range from 2 to 60 μm , PS and PLA generated the
402 most plastic particles at respectively 92,465 and 61,750 particles mL^{-1} , while PE and PP pellets produced
403 respectively 39,619 and 26,380 particles mL^{-1} (Lambert and Wagner, 2016a). Data from these studies can only be
404 compared qualitatively, considering the fragmentation order of polymers as presented in Table 1, as a limitation
405 remains in data expression and unit (Hidalgo-Ruz et al., 2012; Lambert and Wagner, 2016a).

406 Efimiva et al. 2018 and Chubarenko et al. 2020 in two complementary publications studied the effect of bottom
407 marine sediments with different characteristics and grain-size on the fragmentation of unaged single-use plastic
408 (LDPE, PP and PS). They placed plastic with water and sediments in a rotating mixer and characterized generated
409 fragments in term of mass, number, shape, and surface (Chubarenko et al., 2020; Efimova et al., 2018). PS
410 produced the most fragments as it has lost 99.8% of its initial mass, while PP was the least degraded. In another

1
2 412 study, Beltrán-Sanahuja et al., 2020 showed that PLA based materials degrade 5 times more in sediment than in
3 water (Beltrán-Sanahuja et al., 2020).

4 413 Some publications suggested that plastic debris could be fragmented not only into microplastics but also into
5 nano-sized plastic particles (Andrady, 2017, 2011). In a complementary study, Lambert and Wagner 2016b
6 414 developed the nano aspect from 30 to 2000 nm by analysing the fragments produced by PS after accelerated UV
7 exposure in water. In this study, the nano plastics concentration was 1.2×10^8 particles mL⁻¹ with an average
8 415 particle size of 224 nm (Lambert and Wagner, 2016b). So far, no lower size limitation was mentioned in literature
9 and several challenges remain concerning the nano fragments detection, identification and quantification (Gigault
10 416 et al., 2018).

11 417
12 418
13 419
14 420 Giving this, fragmentation rate and generated particle sizes depends on the polymer type, shape, composition
15 and on external conditions. In the studies described herein weathering conditions and medium as well as plastics
16 421 shape differs, thus the tendencies for plastics fragmentation cannot be fully established. More fragmentation
17 422 research should be done as particle formation may differ according to weathering conditions (Kalogerakis et al.,
18 423 2017; Lambert and Wagner, 2016a).

19 424 20 425 **4.2. Dissolution of plastic debris**

21 426 Photochemical dissolution of plastic debris was also studied (Ward et al., 2019; Zhu et al., 2020). Ward et al.
22 427 2019 studied the dissolution of PS in the marine environment (Ward et al., 2019). They exposed PS samples to
23 428 accelerated UV weathering and measured CO₂ and dissolved organic carbon production. They noted in their main
24 429 results that UV degradation can oxidize PS completely into CO₂ and partially into dissolved organic carbon.
25 430 According to studies concerning PS photodegradation products, these compounds are likely to be carboxylic acids
26 431 and ketones (Watanabe et al., 2009; Yuzawa et al., 2013). After their leaking into the water, these hydrophilic
27 432 products undergo further photodegradation or mineralization (Tian et al., 2019).

28 433 In other studies by Zhu et al. 2020 and Lee et al. 2020, post-consumer plastics such as PP, PE and EPS as well
29 434 as plastic fragments collected from the North Pacific gyre were exposed in fresh and seawater to simulated sunlight
30 435 and dissolved organic carbon was analysed (Lee et al., 2020; Zhu et al., 2020). Overall, the mass of plastics was
31 436 reduced, and the dissolved organic carbon showed an increase according to UV exposure time. EPS degraded at a
32 437 faster rate than PP and PE with PE being the most resistant to dissolution, as presented in Table 1. Surface oxidation
33 438 was also noticed by FTIR analysis and fragmentation was observed by SEM analysis. The dissolution effect was

439 also documented on environmental plastic samples that were analysed by SEM. The presence of pits on the plastic
1 surface was attributed to a dissolution mechanism of the plastic floating at sea (Corcoran et al., 2009).
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4 441 **5. Impact of photodegraded plastic debris on the marine environment**

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7 442 Since there is a continuous increase in plastic production and thus in the amount of plastic debris polluting the
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9 443 marine environment, it is essential to understand the impact of these plastic debris on the marine ecosystems.
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11 444 The first described impact of plastic litter was the entanglement and ingestion of plastics by vertebrates
12
13 445 especially sea birds, marine mammals, turtles, fish and other marine biota (Clunie and Hendricks, 1996; Hofman,
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15 446 1995). Plastic debris affects many species of marine organisms worldwide. The number of organisms identified to
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17 447 be affected is more likely to increase as the effect of micro and nano plastics is being assessed on smaller organisms
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19 448 (Moore, 2008).
20
21

22 449 Another risk is the toxic chemicals associated with plastic debris (Fred-Ahmadu et al., 2020; Hong et al., 2018).
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24 450 More than 60 pollutants were indeed found in some plastic samples (León et al., 2018). Associated pollutants can
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26 451 be:
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29 452 - Intentionally added substances (IAS) like stabilizers and additives intentionally incorporated in the plastic
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31 453 during its manufacturing, compounding, or processing.
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- 33 454 - Non intentionally added substances (NIAS) for example residual monomers and oligomers, from
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35 455 incomplete polymerization and degradation products of the polymer due to UV, thermal, and mechanical
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37 456 weathering during the plastic's lifetime use or in the marine environment.
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- 39 457 - Persistent organic pollutants (POPs) present in the environment and sorbed onto plastic debris.
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42 458 Plastic's toxicity, in literature is mainly described as associated with the accumulation, transfer, and release of
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44 459 these pollutants, as presented in figure 5. Since the main studied risk of plastic debris is associated with the sorbed
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46 460 pollutants, it is essential to investigate the accumulation (sorption) and leakage (desorption) of these pollutants in
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48 461 marine like conditions (Gallo et al., 2018; Hong et al., 2018; Liu et al., 2020b; Rochman et al., 2014; F. Wang et
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50 462 al., 2018).
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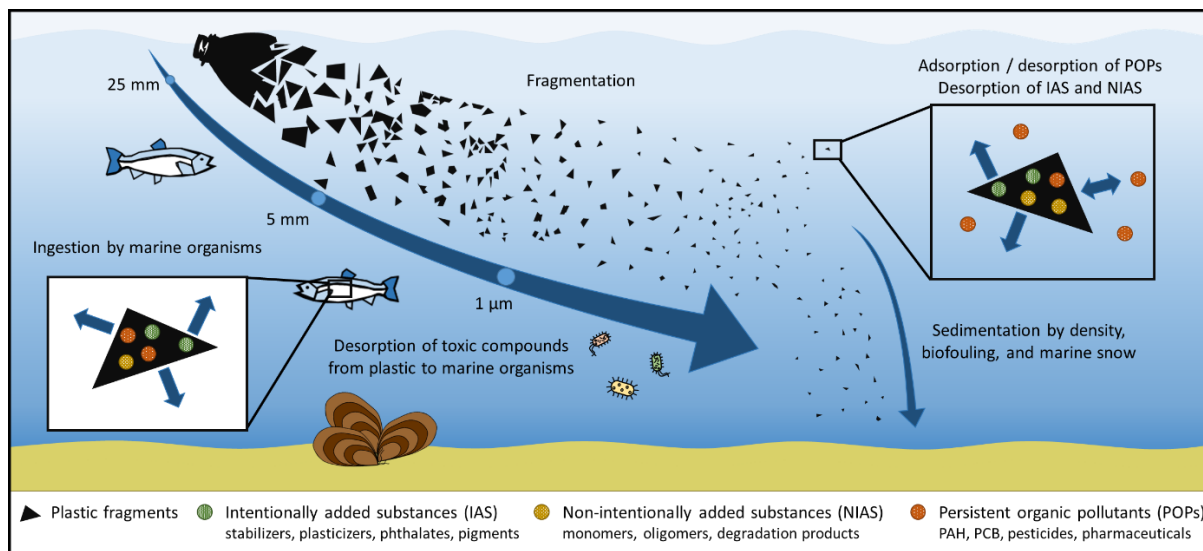


Figure 5: The effect of fragmentation and the sorption of toxic organic compounds onto plastic fragments on marine organisms. (double/colour)

5.1. Consequences of fragmentation

Fragmentation of marine plastic debris into micro and nano plastics requires not only UV weathering but also external mechanical forces caused by waves, wind etc. So far, plastic fragments were present in seawater, surface water, beaches, sediments and even in animals in all continents, oceans, and seas. Plastics abundance is up to 279 items m^{-3} in seawater samples and grows with time (Peng et al., 2020; Yu et al., 2020). Fragmentation is responsible of such trend and it can affect bioavailability and wildlife. In fact, as fragments size decreases, their ingestion by a wide diversity of organisms is favoured. For example, smaller particle size makes it available to lower trophic marine organisms such as mussels and zooplanktons (Auta et al., 2017; Barnes et al., 2009; Kalogerakis et al., 2017; Moore, 2008). Moreover, smaller particles were found to be more readily transfer through the different barriers of the organisms, thus reaching a wider range of organs (Kögel et al., 2020).

These physical impacts of plastic debris and micro and nanoplastics on marine organisms has been largely studied and recently reviewed (Haegerbaeumer et al., 2019; Jacquin et al., 2019; Kögel et al., 2020; Wright et al., 2013). As a consequence, this aspect will not be further developed here and, in the following, the impacts of the plastic photodegradation on the release and sorption of chemicals in/from the marine environment will be more specifically reviewed as well as the related toxicity aspects.

5.2. Photodegradation products, additives and stabilizers leakage

Additives and stabilizers are introduced intentionally in plastic's formulations to obtain certain desired properties depending on the final application. These include antioxidant agents, anti-UV, plasticizers, phthalates,

484 pigments, and flame retardants. These compounds can be released into the plastic's environment. On the other
1
2 485 hand, NIAS such as monomers, oligomers with low molecular weight, degradation products, even heavy metals
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4 486 can also be released into the ocean. Studies showed that these compounds can be transported and leaked into the
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6 487 marine environment depending on their solubility in water, polarity, and affinity with the plastic. This is also
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8 488 controlled by external conditions such as temperature, water salinity, pH and water turbulence (Aminot et al.,
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10 489 2020; Cao et al., 2020; Eyheraguibel et al., 2018; Koelmans et al., 2014; Kwon et al., 2015; Nakashima et al.,
11
12 490 2016; Suhrhoff and Scholz-Böttcher, 2016; Verma et al., 2016). The leakage rate and leaked compound's
13
14 491 concentrations are higher for UV weathered samples compared with unaged pristine plastics (Bandow et al., 2017;
15
16 492 Kedzierski et al., 2018; Luo et al., 2020). This can be due to the fact that UV-aged polymers contain a wider range
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18 493 of NIAS (c.f. section 2.2) and/or that changes in the polymers matrix (c.f. section 2.3) can modify the diffusion
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20 494 rate of compounds from the polymer to the water.

21 22 23 495 ***5.3. Organic pollutants accumulation, transfer, and leakage***

24 25 496 *5.3.1. Sorption of organic pollutants*

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28 497 Organic pollutants sorption consists of the adsorption of the pollutant to the plastic's surface and absorption of
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30 498 the pollutant to the material bulk. The sorption of organic pollutants in water depends mostly on the pollutant's
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32 499 nature and abundance, and the plastic's type, size, physical, and chemical properties (Allen et al., 2018; Fries and
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34 500 Zarfl, 2012; Hüffer and Hofmann, 2016; Lee et al., 2014; Li et al., 2018; Llorca et al., 2014; Razanajatovo et al.,
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36 501 2018). It depends also on external factors such as salinity, pH, temperature, and water movement (Booij et al.,
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38 502 2003; Goedecke et al., 2017; Guo and Wang, 2019; Shen et al., 2018; Wang et al., 2015; F. Wang et al., 2018). It
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40 503 can also vary due to the cocktail effect, as there can be a competition in a mixture of organic pollutants for sorption
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42 504 sites (Bakir et al., 2012).

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44
45 505 In recent years, there have been an increase of plastic debris sampling campaigns in the marine environment.
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47 506 This was usually followed by the characterization of plastics and the analysis of their chemical compositions. This
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49 507 was done mainly by solvent extraction followed by gas chromatography coupled with mass spectrometry analysis.
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51 508 Target contaminants consists mostly of polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyl (PCBs)
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53 509 and pesticides. Other sorbed contaminants can be pharmaceutical products and heavy metals.

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56 510 According to polymer type, PE generally exhibits a greater sorption capacity to environmental pollutants than
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58 511 other plastic types (O'Connor et al., 2016; F. Wang et al., 2018). According to size, although decreasing particle

512 size leads to higher specific surface area and thus higher sorption rate, the analysis of environmental samples
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2 513 showed that POPs concentrations did not vary significantly according to plastic's size (Chen et al., 2019; Endo
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4 514 and Koelmans, 2016; Goedecke et al., 2017).

5
6 515 As for POPs, PAHs showed higher concentrations in plastic debris than PCBs and pesticides (Antunes et al.,
7
8 516 2013; Gauquie et al., 2015; Rios et al., 2010, 2007; Taniguchi et al., 2016; Van et al., 2012). The sum of 16 PAHs
9
10 517 concentration can vary up to more than 119 $\mu\text{g g}^{-1}$ depending on the plastic's type, the region and near
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12 518 contamination sources, while the concentration of PCBs can vary up to 4 $\mu\text{g g}^{-1}$ (Gregory, 1978; Hong et al., 2018;
13
14 519 Mai et al., 2018). For PAHs, the most abundant ones were two to four rings such as phenanthrene and chrysene.
15
16 520 As for PCBs, the most abundant congeners varied according to regions and are mainly PCB 110, 187, 138, 101
17
18 521 and 170 (Bouhroum et al., 2019; Frias et al., 2010; Rios et al., 2010).

19
20
21 522 Concerning the spatial distribution, POPs concentrations near greater cities such as Porto and Sidney were
22
23 523 higher than those observed near smaller and remote cities and islands such as Hawaiian Islands (Gómez et al.,
24
25 524 2020; Heskett et al., 2012; Mizukawa et al., 2013; Ogata et al., 2009; Pozo et al., 2020; Taniguchi et al., 2016; Yeo
26
27 525 et al., 2015; Zhang et al., 2015). Plus, POPs concentrations were significantly higher in plastic debris from coastal
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29 526 beaches than those from open ocean areas (Bouhroum et al., 2019; Chen et al., 2019; Hirai et al., 2011; Rios et al.,
30
31 527 2007). POPs concentrations varied also according to sampling period (Karkanorachaki et al., 2018).

32 33 34 528 *5.3.2. Effect of aging on sorption*

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36
37 529 Theoretically, weathering can enhance the adsorption capacity by increasing the surface specific area. On the
38
39 530 other hand, the absorption capacity is reduced by polymer crystallinity growth. The formation of hydrophilic
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41 531 groups onto the plastic's surface can decline its affinity towards hydrophobic pollutants, but these hydrophilic
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43 532 groups (organic compounds, oligomers, polymer chain) in the natural environment are more likely to migrate to
44
45 533 the surrounding water.

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47
48 534 Giving the competing polymer changes and the complexity of factors in the marine environment, the sorption
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50 535 behaviour of POPs onto UV weathered plastics is still not fully understood. In order to investigate the sorption
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52 536 behaviour on weathered plastic, sorption laboratory tests are essential to understand the process even though they
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54 537 do not simulate exactly the complexity of the marine environment.

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56
57 538 Recent laboratory studies showed that hydrophobic pollutants such as aliphatic compounds, fuel aromatics,
58
59 539 and ethers sorbed less on UV aged PS than on pristine PS while no change in the sorption capacity was noted in

540 the case of PP. Although the authors attributed the case of PS to the increase in surface polar functionalities such
1
2 541 as carbonyl and hydroxyl groups, it can also be due to the polymer crystallinity growth (Hüffer et al., 2018; Müller
3
4 542 et al., 2018). The sorption of hydrophilic organic compounds on UV weathered PS and PVC is favoured compared
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6 543 to pristine materials. This was explained by the change in interactions, as in pristine plastics the sorption mainly
7
8 544 involved π - π interactions while in UV weathered plastics it was controlled by electrostatic interactions and
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10 545 hydrogen bonding (Liu et al., 2019, 2020a).

11
12 546 In the case of environmental plastic debris, weathered plastic pellets were found to contain higher pollutants
13
14 547 concentration than unaged pellets (Antunes et al., 2013; Frias et al., 2010; Karapanagioti and Klontza, 2008; Ogata
15
16 548 et al., 2009). This can be attributed to the increase of the specific surface area of the weathered pellet and thus the
17
18 549 favoured adsorption or to the changes in the polymer properties from weathering. But considering results from
19
20 550 laboratory studies in this case, it is more likely attributed to the time spent in the ocean. In laboratory studies, both
21
22 551 pristine and UV weathered plastics are exposed to organic pollutants for the same duration. Thus, the differences
23
24 552 in sorption properties are attributed only to the weathering extent. While in marine plastic samples, weathered
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26 553 pellets which have been present for a longer time in the ocean hence their higher UV weathering degree. The
27
28 554 longer time spent in the ocean would increase the concentration of POPs sorbed onto the pellet through absorption
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30 555 and the diffusion of POPs into the bulk of the plastic (Mato et al., 2001).

31 555 32 33 556 *5.3.3. Transfer and leakage*

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36 557 Floating marine plastic debris can act as vectors for pollutants transfer in the environment. Polyolefins being
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38 558 lighter than water and the most abundant in the marine environment, can accumulate organic pollutants enriched
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40 559 in the sea surface microlayer. Then floating plastics can be easily transported by wind or wave action on water
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42 560 surface into remote areas and open ocean. Due to biofouling plastics can also sink via marine snow and transport
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44 561 the contaminant deeper into the water column (Hartmann et al., 2017; Kaiser et al., 2017; Kowalski et al., 2016;
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46 562 Mato et al., 2001; Sadri and Thompson, 2014; Teuten et al., 2007; Zarfl and Matthies, 2010; Zhang, 2017).

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48
49 563 Highly contaminated plastic debris can transfer contaminants into seawater or biota (Bakir et al., 2014; León
50
51 564 et al., 2018; Teuten et al., 2009, 2007). For example, high abundance of fibers was found to lead to higher
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53 565 contaminant transfer to sediments and cultured seafood (Z. Wang et al., 2018). Results of PCB content of the
54
55 566 International Pellet Watch campaign was positively correlated with those from Mussel Watch campaign (Ogata et
56
57 567 al., 2009). Thus, the transfer of POPs by plastic debris into the marine environment must be further investigated
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59 568 taking into account the influence of weathering extent and chemical content.

569 **5.4. Effect of aging on plastics toxicity**

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2 570 The studies described here are limited to the effect of UV weathered plastic on the marine organisms.
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4 571 Bioavailability of plastic debris for filter feeders depends on its size, density, abundance, and colour (Wright et
5
6 572 al., 2013).
7

8
9 573 As previously discussed, UV weathering affects the surface of the plastic and its chemical properties. This can
10
11 574 change its affinity towards plastisphere communities, and increase the development of biofilm that can be linked
12
13 575 to the formation of the photodegradation products possibly utilized by microorganisms (Rummel et al., 2017;
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15 576 Zettler et al., 2013). Developing biofilm can affect the affinity of colonized plastic particle towards marine
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17 577 organisms, thus affecting the ingestion of the particle. For example, UV weathering promotes biofilm development
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19 578 that promotes its ingestion by zooplankton but decreases its ingestion by marine larva (Kaposi et al., 2014; Vroom
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21 579 et al., 2017).
22
23

24 580 UV weathering can also contribute to the toxicity of plastic debris on marine organisms due to the possible
25
26 581 leakage of NIAS and / or IAS (potential estrogenic and endocrine disruptors) in seawater (Chen et al., 2019; Coffin
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28 582 et al., 2018; Kedzierski et al., 2018). The leakage can be utilized by marine bacteria, but it can also inhibit microbial
29
30 583 activity (Zhu et al., 2020). The leakage can also inhibit cell growth and photosynthesis of marine algae (Luo et al.,
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32 584 2020). Another study on brown mussels showed that leakage from aged beach pellets is more toxic than that of
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34 585 pristine pellets (Gandara e Silva et al., 2016).
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37 **6. Conclusion**

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39 587 This work reviews the mechanism of plastics UV weathering and its characteristics, compares plastic's
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41 588 characteristics according to the natural/laboratory UV weathering medium, and provides an overview on the
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43 589 environmental impacts of UV weathered plastics. The fate of plastics depends on their initial characteristics, their
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45 590 weatherability and the weathering conditions. Even though several spectroscopic and microscopic techniques are
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47 591 used to characterize marine plastic debris, there are still limitations in the determination of the weathering extent.
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49 592 The path taken by the plastic and the time spent in the marine environment are difficult to be assessed as
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51 593 photodegradation products leakage and plastic fragmentation can occur. More research and models should be
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53 594 employed in order to determine the exact weathering extent of marine plastic debris.
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595 UV weathering can lead to fragmentation and the formation of smaller plastic particles down to the nano scale.
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2 596 Little is still known on the nano fraction and its impact on the environment. Thus, it is important to conduct more
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4 597 research concerning the formation and impact of this nano fraction.
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6 598 The impact of UV weathered plastics was briefly discussed in term of additives and photodegradation products
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8 599 leakage, interaction with POPs, and its effect on marine organisms. Plastic debris, according to their weathering
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10 600 extent and / or time spent in the marine environment, can accumulate POPs that can eventually be transferred with
11
12 601 the plastic to remote unpolluted areas. These weathered plastics can also release photodegradation products, NIAS
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14 602 and IAS into the water that can be toxic to certain marine organisms. Nonetheless, some of the photodegradation
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16 603 products can be utilized by other marine microorganisms and induce their growth. Thus, the toxicological effect
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18 604 of the cocktail plastic - POPs - photodegradation products depends mostly on the organisms studied.
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21 605 Actually, there are over than 150 Mt of plastic debris in the ocean, without significant intervention, by 2050
22
23 606 there could be more plastic than fish in the sea (Kosior and Mitchell, 2020). Thus, it is important to raise awareness
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25 607 among people and reinforce global legislation concerning the impact of plastic waste on the marine environment.
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28 608 7. References

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Declaration of interests

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

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: