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Floating plastics in oceans : a matter of size

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Current opinion in green and sustainable chemistry

Summary

The amount and characteristics of plastic waste in the environment are closely monitored, with regular expansion of their collection to smaller debris sizes and new compartments such as atmosphere, soil and even food. These data, subject to constant re-evaluation, are necessary to assess the threat that plastic particles pose. In this article, we take stock of the most recent measurements of their size distribution on the ocean surface. We confront the observed size distribution to the commonly invoked degradation modes of plastics and propose a scenario that accounts for the quite unusual features of the size distribution of floating debris. We conclude that delamination alone could be a major mechanism explaining the large amount of small microplastics (< 150 μm) in the ocean.

I-Introduction

Pollution by plastic litter has become a major environmental challenge resulting from their accumulation in atmospheric, terrestrial and marine environments. The amount of plastic debris in the environment is regularly re-evaluated, due to the improvement of the detection methods as well as a wider exploration of new compartments such as the atmosphere or the soil [1-3]. If the plastic pollution awareness initially stemmed from the ubiquitous presence of macro-waste, it has now become clear that the most problematic pollution is 'invisible' i.e. due to smaller size debris (< 5 mm), and the literature exploring microplastics (MPs) and nanoplastics (NPs) quantities and effects is rapidly increasing. There are many different definitions for MPs and NPs in the literature and on-going debates to where the size limit between NPs and MPs should stand [4] ; in this paper, we opted for a frontier between NPs and MPs set at 1 micron, based on their physical properties, which determine to a large extent their behavior in the environment such as high aggregation ability due to high surface/volume ratio, brownian type motion, ability to cross biological membranes [5,6]. Regarding MPs, we use the commonly admitted upper limit of 5 mm. There is a general acknowledgement that size influences the uptake, retention and toxicity of particles on organisms [7-11]. First, particle size controls the probability of consumption or entry by respiration. Once MPs enter the body, they can go through or accumulate in different locations and induce trouble such as satiety, clogging, inflammation, ulcers... [11]. If particles are small enough (NPs), there is the additional possibility of crossing the intestinal barrier and migrating towards other organs [12,13]. Transit through the digestive tract and translocation, combined with the potential leaking of additives, induce undesirable effects on physiological functions such as growth, defense and reproduction [7,9,10,14]. In both cases of accumulation and translocation, studies show a systematic size dependent effect: the smaller the particles, the larger their toxicity [8,10]. However, Kogel et al. [8] underlines the difficulty to attribute the observed effects to size only since most studies adjust the exposure amounts for different sizes by keeping the mass constant, which results in a very large number of small particles compared to bigger ones. MPs have also been shown to constitute persistent long-distance carriers for potentially pathogenic or

invasive microorganisms [15]. Finally, hetero-aggregation of contaminants (heavy metals, organic contaminants, ...) on MPs or NPs and their further potential bio-availability constitutes another negative impact of plastic particles which depends on their size [5,15-17]. When particles fragment into smaller pieces, the adsorption capacity dramatically increases, hence the related impacts. The toxicity of plastic particles being dependent on their size and their concentration, it is crucial to know these two parameters in the natural environment in order to better predict their impacts. Laboratory results to date are difficult to translate into environmental risks because the actual amounts of the smallest plastic particles are not yet accurately measured, so researchers do not know the relevant exposure doses [10,18-20].

In this article, along with a recap of the latest data on the size distribution of plastic waste, from MPs to NPs, we come back to the reasons why these measurements are delicate. We then take stock of the mechanisms that drive the macro-waste transformation into smaller and smaller particles and finally propose a global explanation for the size distribution features that have been recently observed.

II-What do we know about the size distribution of plastic waste in the ocean?

From calculations of mismanaged waste at the global level, it is estimated that around 10 million tons of plastics are discharged into the ocean each year and that between 100 and 250 million tons of plastic will be present in the oceans in 2025 [21]. Numerous studies [2] have compared these estimated quantities to the plastic debris concentrations extrapolated from the measures made in the various ocean locations and compartments. Until recently, these quantities were not consistent, the mass found in the ocean being at least one order of magnitude smaller [21] of what was supposed to have leaked there. This difference is due, on the one hand, to the fact that the estimates of mismanaged litter are marred by great uncertainties; on the other hand, to the fact that plastic quantities actually present in the ocean are constantly reassessed, as the detection methods improve. From a methodological point of view, the extrapolation of the total amount of plastic litter in the oceans, from local measurements at a given moment, is delicate, because this waste circulates on a large and small scale with a dynamic still incompletely known [22-24] and which depends in particular on their sizes [25]. In addition to horizontal transport, one needs to take into account the size dependent vertical dynamics of particles and its effect on particle distribution in the water column, which leads to an under-representation of MP at the surface [24,26]. Moreover, not all compartments have been explored as much: there are many more measurements available at the ocean surface than at depth or on the seabed, which is less accessible. Last but not least, for technical reasons, collection and detection can only be carried out for waste above a given minimum size: most of the data available until recently consisted of debris larger than the classical nets mesh size (330 or 500 microns). Some authors [27] have shown recently that the MPs concentration increases quickly when the mesh size decreases, so that the systematic exploration at smaller sizes is of great importance.

Many authors have analyzed the waste collected at sea and, in particular, tried to establish the size distribution of floating plastic particles [23,26,28-32]. The comparison between different distributions is often made difficult because of lack of harmonization regarding the sorting criteria: whether or not the collected samples are sorted according to their chemistry, inclusion / exclusion

of certain types of waste such as fibers, choice of the characteristic dimension used for categorizing the samples (largest dimension, equivalent diameter...). Moreover, some papers produce a size distribution, others a mass distribution.

In spite of these limitations, some facts that can be reliably drawn from the latest data from the field [23,26,28-30] are summarized on Fig. 1. When browsing the sizes from the largest to the smallest, a first abundance peak is observed around 1 mm [23,29], that cannot be accounted for by the net mesh-size cut-off, which is at a much smaller value. Between 1 mm and approximately 150 μm , very few particles are found [28,30]. The abundance increases again from 150 μm down to 10 μm , with an amount of particles which is several orders of magnitude larger than what is found around 1 mm. The precise distribution for sizes between 150 μm and 10 μm is still under investigation; for instance, a recent paper mentions a second abundance peak around 70 μm [30]. It is interesting to point out that, even though small particles have a much smaller mass than big ones, due to their big amount, they could contribute to a larger extent than expected to the total mass of plastic debris in the ocean [26,30].

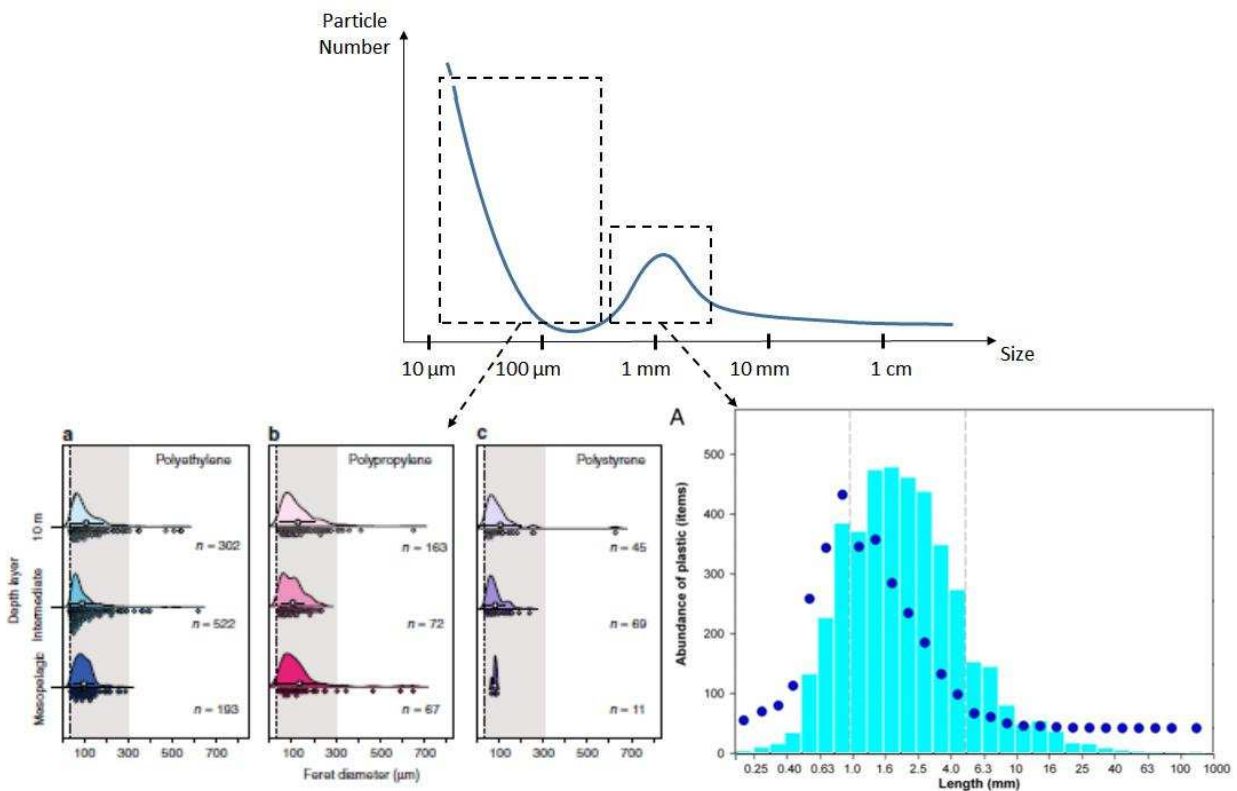


Fig. 1: Overall shape of the size distribution of particles collected in marine environments. The inserts come from [30] (left) et [23] (right), which illustrates the two main features of the curve. Note that due to the methodological reasons mentioned above, one cannot quantitatively compare the experimental data from the inserts. However, the overall shape does reflect the relative values of the particle abundance.

Regarding nanoplastics, it is widely admitted that colloidal particles ($<1 \mu\text{m}$) and soluble molecules (additives, monomers and oligomers) are inevitably released during the degradation of plastic waste: several laboratory experiments have recently demonstrated the generation of such by-products, following UV exposure in water for various polymers (polyethylene, polypropylene, polystyrene) [33-38]. Dissolved organic carbon measurements show that the amount of organic carbon based compounds passing through a filter with a given mesh size, typically $0.45 \mu\text{m}$, increases with exposure time [33-35]. It has also been shown by dynamic light scattering experiments that particles of typically a few hundred nanometers are generated by photo-oxidation [36]. Finally, McLeod et al [37] have identified which oligomers are produced during UV ageing. As far as the environment is concerned, no data was available on nanoplastic concentrations until recently [38]. Some papers reported new results on the occurrence of nanoplastics in soil and in the oceans [39-41]. Their chemical nature and size make these products yet still extremely difficult to detect, to separate from organic matter and therefore to quantify in a complex natural environment [5,42]. Quantifying nanoplastics and modeling their behavior remains a major challenge for the future if one wants to establish a complete balance of plastic pollution and assess its impacts.

III - Degradation and fragmentation mechanisms of plastics in the ocean

The set of abiotic processes that lead to the degradation of a plastic in the environment has been described in a phenomenological way by Andrady [43] and explains why by-products are generated over a very wide range of sizes throughout degradation (cf. Fig. 2). Under the combined actions of solar exposure and water, a series of oxidation and hydrolysis reactions leads to the scission of the macromolecules hence to the gradual release of monomers, oligomers or very small polymer colloidal fragments (NPs). On a larger scale, scission events also cause alterations (recrystallization, cross-linking) in the polymer, generally leading to an increase of its brittleness. Most plastics are semi-crystalline (e.g. polypropylene and polyethylene) and microcracks are preferably initiated in inter-crystalline regions due to a faster degradation rate in the amorphous phase. Internal mechanical stresses (linked to the product processing or to its deterioration) or external ones (exerted in particular by the combined action of wind, waves and sand) then easily provoke the fragmentation of the embrittled polymer [44,45]. For a plastic piece subject to stresses, two modes of fragmentation can occur [43]. The first mode corresponds to the propagation of one main crack through the bulk of the material, splitting the piece into two, which can be called bulk fragmentation. The second mode of fragmentation comes from the existence of a surface layer, whose mechanical properties have been modified by weathering. The typical thickness of this layer has been evaluated to be of the order of $100 \mu\text{m}$ [45,46]. Delamination then occurs through crack propagation at the interface between this brittle layer and the bulk of the material, leading to the release of smaller fragments from the surface. The two modes occur simultaneously except for thin films (such as plastic bags or packaging), whose thickness is of the order of the altered surface layer depth and where only the first mode will take place.

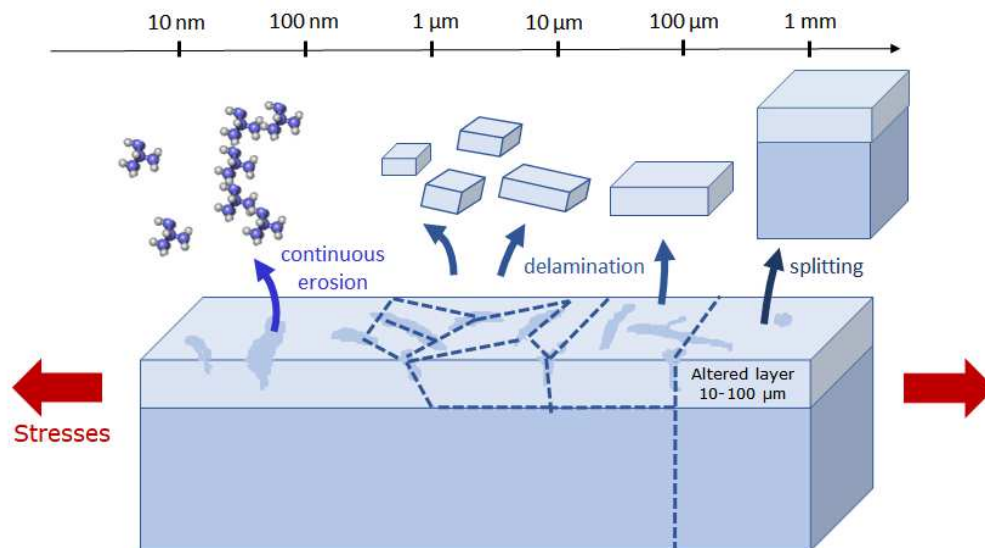


Fig. 2 : Summary diagram of the three degradation modes (erosion, bulk fragmentation and delamination) and their by-products: different sizes are obtained concomitantly depending on the different modes of fracturing and erosion involved. In dotted lines are represented the fractures likely to develop in the plastic debris from the eroded zones shown in blue.

Biodegradation mechanisms are not discussed here since, on the one hand, they are marginal for conventional polymers, and on the other hand, the amount of biodegradable polymers on the market today is extremely small, therefore their potential amount in the ocean. These mechanisms may nevertheless play a significant role in the ultimate degradation of highly oxidized fragments of conventional plastics, produced by the processes mentioned above.

IV - Do we understand the size distribution of plastic waste in the ocean?

Let us now discuss whether the bulk fragmentation and delamination mechanisms are able to explain on their own the observed MPs size distribution in the ocean and its characteristic features (cf. Fig. 1).

Bulk fragmentation proceeds through iterative splitting of one piece into two ‘daughters’ of roughly half the volume of the initial piece, meaning that the number of pieces of half size doubles at each iteration. With reasonable assumptions, bulk fragmentation thus leads to a power-law for the abundance–size distribution, with a scaling exponent equal to the spatial dimension of the plastic objects (fibers, films or lumps) [23,29,47]. However, a power-law type behavior obviously does not properly describe the experimental data, since the debris numbers decrease again below 1 mm. Several explanations have been invoked based on the idea that particles below 1 mm were removed by one mechanism or another, such as consumption by animals, biofouling and sinking or accelerated fragmentation [23,29,47,48]. Pursuing further the fragmentation argument allows us to propose an alternative explanation. Indeed, one should not forget that the mechanics of bulk fragmentation is in itself size dependent: the smaller a piece, the larger the force to break it, as we all experience when breaking sugar lumps. This hand-waving argument can be formalized by introducing a threshold, related to the average stresses occurring in the ocean and the mechanical properties of the polymer, below which the breaking probability decreases. This simple model allows us to predict the occurrence of a peak whose position is typically of the order 1 mm (George

et al, to be published). The fact that bulk fragmentation naturally slows down below a certain size then accounts for the abundance peak at 1 mm.

Looking now at the recent data about the large number of particles below 150 μm , it can be explained, to our opinion, with the second mode of fragmentation suggested by Andradý [43]. Under the action of stresses, delamination and disintegration of the altered surface layer can generate in one go many smaller 'daughters', whose characteristic size is determined by the depth of the altered layer and the polymer microstructure size. A simple calculation allows us to estimate that a 1 mm size particle can generate in one go 500 to 50 000 daughters of typical size 10-100 μm , constituting a very large source of small MPs. Due to their small size, these particles will undergo very little further fragmentation; on the other hand, the smaller the particles, the larger their specific surface area and therefore their degradation or even bio-degradation rate through erosion should be increased by a factor inversely proportional to the ratio of their diameter (a factor of 10 for a 1 mm particle generating 100 μm fragments). One can suspect that erosion is much slower than delamination for millimetric objects, otherwise altered layers would never be built. However, for small particles, whether the high rate of production of fragments by delamination will outweigh the increased rate of degradation by erosion remains an open question. The recent data on small particle abundance seems to indicate that the high production rate of daughter particles by delamination could largely compensate for this accelerated degradation.

The size distribution data of floating plastic debris in the ocean can thus be interpreted mainly with simple mechanical arguments. Even though numerous other phenomena obviously contribute to the particle size distribution, such as particles interactions with micro-organisms, transport dynamics between environmental compartments, homo- and hetero- aggregation, it is argued that they are not necessary at that stage to consistently interpret the current data. Further studies or simulations will be required to assess the relative importance of all phenomena at play.

V- Conclusion

One cannot deny the reality of the massive plastic pollution and of its prescribed increase in the coming years. A major cause of concern is that the plastic currently being dumped into the environment is gradually degraded into smaller and smaller sizes: one single plastic bag can produce up to 10 million MPs or 10^{16} NPs. Recent data on floating micro-debris seem to indicate that a lot of those are indeed small NPs and MPs. It is explained here how the delamination mechanism alone, particularly relevant for photo-oxidized floating debris, could account for the observed features of the abundance curve, mainly because small MPs are produced much faster than they are degraded. It is, in particular, by understanding the way in which particles are generated from macro-waste, added to the knowledge of plastic flux between different compartments, that one will eventually be able to properly assess the current and future state of ocean contamination.

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This paper is a complete and recent review on microplastics in the environment. The authors address the different issues of sources, distributions, fate and impact. They underline that scientific challenges include improving microplastic sampling and characterization approaches, understanding long-term behavior, additive bioavailability, and organisms and ecosystem health risks.

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This paper shows how the nanometric size range has important consequences for both the analytical challenges of studying nanoscale plastics and the environmental implications of these incidental nanomaterials. In particular, the authors emphasize that nanoplastics are distinguished from microplastics with respect to their transport properties, interactions with light and natural colloids, a high fraction of particle molecules on the surface, bioavailability and diffusion times for the release of plastic additives. Moreover, they are distinguished from engineered nanomaterials because of their high particle heterogeneity and their potential for rapid further fragmentation in the environment.

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The authors have performed a comprehensive review of the main determining factors for plastic particle toxicity in the relevant exposure systems, from publications until including the year 2018. They show also that for the currently unquantified plastic particles below 10 µm, more toxic effects were reported in all aquatic life, as compared to plastic particles of larger size.

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The authors assess the literature to determine the current weight of evidence about the effects of plastic pollution across all levels of biological organization. Their data spans marine, freshwater, and terrestrial environments. Based on their analyses, there is no doubt that macroplastics are causing ecological effects, however, the effects of microplastics are much more complex. They also assess the environmental relevancy of experimental studies by comparing the doses used in each exposure to the concentrations and sizes of microplastics found in the environment and determined that only 17% of the concentrations used in experimental studies have been found in nature, and that 80% of particle sizes used in experiments fall below the size range of the majority of environmental sampling.

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