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Plastics in the Ocean: Perspectives for their Biodegradation

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Introduction[1]

I devoted 25 years of my career as a research scientist to study the biodegradation of lignin, by far the most recalcitrant natural polymer on earth. Today, I will refer to the biodegradation of plastics, which are highly recalcitrant synthetic polymers. More specifically, since this plenary session is about science and sustainability, I would like to address a topic of increasing concern, which is the heavy contamination of the oceans with plastic material. This appears as a paradigmatic case in which scientific knowledge is deemed to play an essential role in the design of public policies for the protection of the environment.

I would like to start my presentation by quoting Pope Francis in his encyclical *Laudato si'*, precisely devoted to the environment and human ecology. In #21 of the encyclical, the Pope asserts that each year hundreds of millions of tons of waste are generated, much of it non-biodegradable. Then, in #174 he adds that the growing problem of marine waste and the protection of the open seas represent particular challenges. As you well know, *Laudato si'* also includes an urgent appeal to protect our common home by bringing the whole human family together to seek a sustainable and integral development.

Assessing the problem

Now, I will say a few words concerning the plastic industry and the final destination of plastic waste. Plastics are a suitable material for multipurpose use due to their low cost, high durability and resistance to physical breakdown. At present, global plastic production reaches about 300 million metric tons per year.[2] Unfortunately, disposal of waste plastic is problematic due to its inherent resistance to decomposition. Some plastic is recycled, although the majority is placed in landfills where it may take centuries to breakdown.

Of particular concern are plastic debris that end up in the marine environment. This outcome may result from accidental loss, deliberate release or poor waste management practices. As revealed in a recent study published in *Science*, an estimated 4.8-12.7 million tons of plastics entered the oceans from land-based sources in 2010.[3] This is equivalent to one municipal garbage truck dumping its content in the ocean every minute. If ocean-based sources such as fishing and shipping are included, the input of plastic increases by 20%.[4]

Marine plastic debris include mainly beverage bottles, bags, toys, tires, cigarette filters, nets, ropes, traps, fishing lines, etc. However, although less evident to visual inspection, a severe impact is exerted by microplastics, with a particle size of up to 5 mm. These may consist of fragments deriving from larger plastics, microbeads used in cosmetics, resin pellets employed in the production of plastics (so-called “nurdles”), remnants of ship coatings, etc.

There have been some surveys to estimate the amount of plastic debris in the ocean. For example, a study published by Eriksen *et al.* in PLOS One a couple of years ago,[5] shows that there are more than 5 trillion plastic pieces weighing over 250,000 tons floating in the ocean. Of these, 92% correspond to microplastic particles within a size range between 0.33 and 4.75 mm, which comprises 13% of the total by weight. This figure does not include plastics in the seabed or particles below 0.33 mm.

The same group, as well as others, have found that plastics of all sizes concentrate mainly near five ocean gyres, where converging surface currents trap and mobilize floating debris towards the vortex centers. The highest concentrations are found at the North Pacific gyre, also known as the Great Pacific garbage patch. Plastic debris also cluster along the coasts near human communities. For these studies, plastics were classified in four size classes: 0.33 to 1 mm, 1 to 5 mm, 5 to 200 mm and bigger than 200 mm.

There is another global inventory of floating plastic debris published by van Sebille *et al.*,[6] which yielded a higher limit of 51 trillion pieces weighing 236,000 tons. Both studies agree on a similar figure for the total weigh of plastic debris floating in the ocean: about 250 kilotons. But this is only between 1 and 2% of the global plastic waste estimated to have entered the ocean in the year 2010. The question is then: Where is the missing plastic litter? Four main possible sinks have been proposed for the substantial losses of floating plastic from the

surface: shore deposition, nano fragmentation, biofouling and ingestion. However, as suggested by Woodall *et al*.,[7] deep-sea is the most likely fate of microplastic debris.

We may ask how do plastics affect the marine environment. They do so in various ways: entanglement of birds, fish, seals and whales in fishing gear (lines and nets); floating plastics transport microbial communities to new environments, threatening native ecosystems; micro plastics decrease growth of fish larvae;[8] plastics are ingested by fish and seabirds. It has been found that zooplactivorous fishes may contain up to 30% plastics in their gut.[9] On the other hand, plastics in the ocean adsorb persistent hydrophobic organic pollutants such as DDT, PCBs, PBDEs, which when ingested by the trophic fauna bioaccumulate in the food chain. Moreover, plastic manufacture involves the use of potentially toxic additives, such as antioxidants, UV stabilizers, flame retardants and antimicrobial agents. Since most of these chemicals are lipophilic, they penetrate cell membranes when ingested.[10]

All these facts confirm that we are in the presence of a threat not only to the environment, but also to animal and human health. According to a study published in the journal *Australian Quarterly*, more than 100,000 sea animals die each year from eating or being caught in plastic debris.[11] There are also recent publications demonstrating the consumption of plastic by deep sea fauna[12] and also the presence of plastics in seafood intended for human consumption,[13] confirming that the environmental problem is also turning into a human health hazard.

What are the possible solutions for the problem of plastic contamination of the oceans? First, public policies and agreements to prevent marine pollution, of which there are several. The question is to what extend the citizens of all signing nations comply with these agreements.[14] In addition, a better waste management is required, including cutting down the amount of plastic microbeads in personal care products. Third, plastic recycling, although it has a cost because it requires sorting different plastics comprising the waste. Also, clean up of existing marine debris: various countries and NGOs perform periodical clean-up programs at a high cost. Efforts should concentrate near the coasts before it sinks or is ingested by wildlife. And finally, use of biodegradable plastics and polymer blends: for example, starch- and cellulose-based plastics, bio-based polyesthers such as polylactic acid, polyhydroxybutirate, etc.

Plastic biodegradation[15]

First, a few words about the structure of plastics. There are those with a carbon-carbon backbone, such as polyethylene and polystyrene. These are highly resistant to microbial attack, most likely because during their short residence time in natural environments evolution could not design new degradative enzymes. Besides, their solid nature results in an extremely low exposure to potential enzymes. However, when long polymers are fragmented by abiotic means, small oligomers can enter the cell where they are metabolized. On the other hand, there are plastics with ester (polyethylene terephthalate, PET) and amide (nylon, polyurethane) bonds, which are attacked by extracellular hydrolases. For example, PET can be hydrolyzed by cutinase, an enzyme that cleaves the esther linkages in cutin, the main constituent of the plant cuticle. In this case, one of the products is further metabolized and enters the Krebs cycle. On the other hand, Yoshida *et al.* recently published the degradation of the same polymer by a single bacterium which produces two enzymes, yielding aliphatic and aromatic monomers, both of which are used as carbon source for growth.[16]

Another example of a degradable plastic is polyurethane, which possesses amide and ester bonds. Both are hydrolysable and therefore the type of product will depend on the specificity of the enzyme catalyzing bond cleavage, which can be a urease, esterase or protease.

Decay of plastics in the ocean

In marine environments, plastic deterioration takes place by a combination of four mechanisms: photo degradation, thermal degradation, mechanical action and biodegradation. Weathering of plastics by sunlight and mechanical action leads to the production of smaller fragments and particles, thus increasing the surface area susceptible to microbial attack.

In particular, light and temperature lead to the formation of highly reactive free radicals, which can be either carbon or oxygen centered. Among the latter, peroxyl and hydroxyl radicals are the most reactive. Some reactions end up with the fragmentation of the polymer, sometimes possessing alcohol or ketone groups.[17] Others are crosslinking reactions that lead to products of higher molecular weight. Typically, an oxygen-centered radical may react with a non-radical plastic polymer producing ketone and olefin fragments, plus a carbon centered radical that will in turn react with oxygen to produce a peroxi radical, and so on. It is expected that the small fragments produced in reactions involving free radicals enter the cells of microorganisms to be further biodegraded to CO2 plus water.

What do we know about marine microorganisms metabolizing plastic-derived oligomers? At present, not much. However, there is promising work conducted by the group led by Erik Zettler, from Woods Hole, Massachusetts, which refers to the characterization of the microbial community that colonizes microplastics in the ocean. He has called these communities the platisphere.[18] Platisphere communities vary with location, season and polymer type.[19] Microorganisms differ from those of the surrounding seawater, being bacillus and diatoms the most abundant. It has been calculated that the platisphere represents about 6% of the total mass of microplastic debris. It is still debatable whether the biofilm might protect plastic from photo degradation. However, pits conforming to bacterial shape visualized on the surface strongly suggest plastic biological decay. In addition, ribosomal RNA surveys confirm the presence of hydrocarbon-degrading bacteria.

This work is only starting and there is much to be learned with respect to biochemical mechanisms leading to plastic degradation by these communities. Whatever these mechanisms may be, plastic biodegradation is an intrinsically slow process, even under ideal laboratory conditions. One may ask then what can be done to make plastics more prone to biodegradation not only in the ocean but in any environment and thus decrease their harmful impact.

There are several options to reach this objective. One is to use only plastics of petrochemical origin that are biodegradable, as the ones mentioned previously. There is also the possibility of using biodegradable plastics based on starch and cellulose, or plastics based plastics. Another option is to blend conventional plastics with bio-based biodegradable plastics, or use oxo-biodegradable plastics, so-called because they contain pro-oxidant additives (organic salts of Fe, Co, Ni or Mn) that facilitate weathering by light and heat.[20] Bio-based plastics seem to be a promising solution. However, their actual presence in the market is only marginal.

On the other hand, we must keep in mind that bio-based plastics are not a panacea, as asserted in a recent report entitled “Biodegradable plastics and marine litter” issued by UNEP – the United Nations Environmental Program.[21] According to this account, among other drawbacks, bio-based plastics tend to be more expensive; they must be separated from fossil fuel-based plastics for recycling; their efficient biodegradation occurs under conditions that are rarely, if ever, met in the marine environments; and labelling a product as biodegradable may result in a greater inclination to litter on the part of the public. Only time will tell whether bio-based plastics succeed in replacing non-hydrolysable synthetic plastics.

Final remarks

To conclude, it is worthwhile to outline some future tasks that may be relevant in this very critical issue of plastics in the ocean. First, reiterate the need for better waste management, for recycling, for cleaning-up the existing marine debris and for proper public policies to prevent marine pollution. Confidently, the latter must be based on scientific evidence.[22] Then, to continue studies of plastic biodegradation in the oceans. To date, most work reported in the literature corresponds to experiments conducted under conditions that are not relevant to the marine environment. Finally, to study the fate and environmental impact of plastic biodegradation by-products (some may be toxic or more recalcitrant) and also of additives and persistent organic pollutants that sorb to the plastics in the ocean.

END NOTES

[1] This text corresponds to the transcript of the oral presentation at the Plenary Session.

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[14] Among them, the International Convention for the Prevention of Pollution from Ships, so called MARPOL convention adopted in 1973 by the International Maritime Organization, the Regional Seas Programme launched in 1974 by the UNEP, Global Programme of Action for the Protection of the Marine Environments from Land-based Activities created by UNEP in 1995, Marine Strategy Framework Directive (EU 2008), Sustainable Development Goals of the UN (2015, #14 addressed to protect life under water).

[15] For recent review, see Muthuk, S., Veerappapillai, S. Biodragradation of plastics: A brief review. *Int. J. Pharm. Sci. Rev. Res*., 31(2), 204-209, 2015; Ghosh, S.K., Pal, S., Ray, S. Study of microbes having potentiality for biodegradation of plastics. *Environ Sci Pollut Res*. 20, 4339-4355, 2013; Tokiwa, Y., Calabia , B.P., Ugwu, C.U., Aiba, S. Biodegradability of plastics. *Int. J. Mol. Sci. 10*, 3722-3742, 2009.

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