

***Microplastics in the Aquatic Environment :
Green Analytical Protocols, Risks and Sustainable Solutions***

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Plastic pollution is nowadays a global and ubiquitous problem being detected everywhere: marine environment, sand beaches, wastewaters, surface waters, soils, sludges, sediments, biota, food and air. The word plastic comes from the Greek term *plastikos*, which means that it can remain shaped in various systems. Global plastic production did hit approximately 348 million tonnes in 2017, being China the largest producer responsible of 27% of worldwide pollution. It is estimated that more than 8300 million tonnes of virgin plastic have been produced to date. Many consumers are not aware that plastic goods are usually made in petrochemical plants. According to the 2019 Centre for International Environmental Law Report, its production will contribute approximately to 850 million tons greenhouse emissions. Plastic is part of our daily life and worldwide we use 4 trillion plastic bags annually and 1 million plastic bottles every minute.

Plastics in the environment are divided into Macro-Plastics (with particles >2.5 cm), Meso-Plastic (with particles 2.5cm-5mm), Micro-Plastics (MPs) (with particles between micron- 5mm) and Nano-Plastics (with particles between 1-100nm). Macro-Plastics include everything identified as litter, such as plastic bags, bottles discarded fishing nets, plastic toys among other items and they can be usually observed. MPs are commonly invisible to the naked eye, particularly when mixed with sediment. Macro-Plastics enter the marine environment via rivers, poor waste management or being dumped into the marine waters.

MPs are directly released into the water or formed by degradation of Macro-plastics. In short, annually between 4 and 12 millions of tonnes of plastics are going into the oceans and most probably in 2050 will exceed the amount of fish. The amount of anthropogenic debris in the marine and coastal environments is steadily increasing with an estimation of 270,000 of plastic floating. In consequence international organizations, as well as NGOs recognize marine litter as a global issue of major concern. Plastic litter enters the marine environment from diverse points and diffuse sources and it can be transported through rivers long distances before being deposited in the bottom of seas. Few studies suggest that river litter can contribute up to 40% of all marine litter input, being estimated over 1.2-2.5 million tonnes of plastic every year (1,2).

MPs, are made from diverse molecules and correspond to diverse product types. MPs are composed of diverse suite of polymer type, being the most produced and consumed ones polypropylene (PP), low density polyethylene (LDPE), high density polyethylene (HDPE), polyvinyl chloride (PVC), polyurethane, polyethylene terephthalate (PET) , polystyrene (PS) and polyamide (PA) are diverse and come from a multitude of sources, also they are in different sizes, colours, shapes and types of materials. MPs contain additives, i.e. phthalates and they can be as well a vector of organic contaminants and pathogens that can be ingested by organisms and introduced into the food web. Airborne fibrous MPs may enter our respiratory system with risk to the environment and humans.

Having said that , this presentation will cover in the first part different aspects of MPs and Macro-Plastic litter pollution in coastal waters , rivers ,sediments and lakes . Case studies of MP pollution in several coastal environments, sediments and catchments of China,. Saudi Arabia, India, Europe and Australia will be reported (2,3,4). It is well-known that MPs affect communities, biological diversity, and ecosystem processes will be reported. MPs increase the abundance of some taxa but decrease the abundance of some other taxa, indicating trade-offs among taxa and altered microbial community composition in both the natural environment and animals' gut. The alteration of community composition by microplastics is highly conserved across taxonomic ranks, while the alpha diversity of microbiota is often reduced or increased, depending on the microplastics dose and environmental conditions, suggesting potential threats to biodiversity. Biogeochemical cycles, greenhouse gas fluxes, and atmospheric chemistry, can also be altered by microplastics pollution. These findings suggest that microplastics may impact the U.N. Sustainability Development Goals (SDGs) to improve atmospheric, soil, and water quality and sustaining biodiversity (5).

The second part of this lecture will discuss green analytical chemistry (GAC) protocols for the analysis of MPs in water (6,7). Within the last years aspects such as green, eco-friendly and sustainable are making their way into analytical chemistry. The field has changed with the introduction of these concepts. Information on the consumption of toxic solvents and energy is now a part of everyday life. This green analytical chemistry could be playing a pioneering role in the analysis of micro(nano)plastics, MP(NPs) in the environment. We discuss the roles of green analytical and sustainability within MP(NPs) determination and its possible applications. We explain its many advantages, like their function to preserve the environment and operator health or their role in the so called eco-friendly methodologies, but we also highlight points such as an efficiency in the determination that should be viewed critically. Finally, we describe how micro(nano)plastics analysis is implementing the GAC and the challenges faced. We would like to emphasize here the importance of implementing GAC for determination micro(nano)plastics to ensure that the intensive study of these contaminants carried out nowadays does not became a source of others pollutants that can be even worse. These aspects have hardly been considered in the methods developed so far and they should. It is important to know that in all steps of the method (i) sampling, (ii) sample preparation and (iii) identification and quantification measures can be taken to make the method more environmentally friendly and sustainable, safer for the operator. In this sense the Green Analytical Chemistry (GAC) aspects have been little considered in the MPs analysis. In the end, GAC has to be considered as a more global aspect, in which

laboratory safety, good practices, and the implementation of systems for the proper disposal of waste and equipment can play a more important role than the reagents used in a particular analysis. The impact that the methodologies used to isolate and determine MPs and NPs have on the environment due to the consumption of reagents and energy and the generation of waste will be addressed as well in this presentation. Examples reported will include analytical methodologies applied to MPs and NPs determination assessing their greenness through National Environmental Methods Index, Analytical Eco-scale and AGREE metrics and discussing green issues related to the consumption of solvents/reagents, etc. In the greenness of analytical methods for micro(nano)plastics several issues that can contribute to that remain to be addressed such as in situ sampling, use of direct methods, miniaturization and automation of methods, replacement of hazardous reagents by less hazardous ones, and application of chemometrics to reduce the number of samples analyzed. It is to be hoped that future studies dedicated to the analysis of these compounds will address this problem and implement these solutions for a more sustainable future.

The last part of this lecture will discuss as well plastic litter and its increase use under Covid-19 outbreak. In this sense the excessive use and consumption of single-use plastics (including personal protective equipment such as masks and gloves) due to COVID-19 pandemic. This review aimed to provide an integrative and synthesized overview on the effects of COVID-19 on macroplastic pollution and its potential implications on the environment and human health in a long-term scenario; addressing the main challenges and discussing potential strategies to potentially overcome them. It emphasizes that future measures, involved in emergent health crisis or not, should reflect the balance between public health and environmental safety as they are both undoubtedly connected. Although the use and consumption of plastics significantly improved our quality of life, it is crucial to shift towards sustainable alternatives, such as bio-based plastics. Plastics should remain in the top of the political agenda in Europe and across the world, not only to minimize plastic leakage and pollution, but to promote sustainable growth and to stimulate both green and blue- economies (8).

Landfilling and illegal waste disposal have risen to deal with the Covid-19 potentially infectious waste, particularly in developing countries. The intense use of such a disposal method drives us apart from the envisioned 2030 circular economy and environmental sustainability. It is estimated that 3.5 million metric tons of masks have been landfilled worldwide in the first year, which can generate up to 2.3×10^{21} microplastics of 7 μm in the coming year. This presentation addresses the challenges raised in the pandemic and post-pandemic scenarios on landfills; while discussing the potential environmental and health implications that might drive us apart from the 2030 U.N. sustainable goals. Also, it highlights some innovative mitigation technologies and improved management strategies that can pave the way to environmental recovery (9).

MPs and macro litter pollution is nowadays in the radar not only of the scientific community but also of the public, the so-called citizen science. Media coverage helps to push such initiatives being complementary to scientific approaches. Such synergistic combination of academia, the public as well as policy actions should help to mitigate MP and macroplastics litter pollution in the next coming years. It

is important to note that there are still many gaps in knowledge and we do not know well how plastics and MPs are transported and distributed and in what quantity. However, all these programs together with the modelling will allow us to know it soon. Monitoring and sampling systems also need to be improved especially in coastal areas and all existing programs will help. This is urgently needed in the next coming years due to the impact of plastic waste due to Covid-19 outbreak. Previous monitoring program will need to be repeated again to measure and evaluate in the field the real impact of plastic under almost two years of pandemic.

The detailed study of the strictly technological alternatives to the solution of this problem, show that they are not sufficient, and that in many cases they just transfer the problem of water to the generated sludge. More studies in these aspects are absolutely necessary, because although the number of publications is enormous, the gaps in knowledge are also enormous. Another solution that is expected to be developed and that could bring more definitive results is the degradation of MPs by microorganisms (fungi and bacteria). Many studies are being carried out, although the complexity of these studies means that progress in this field is slow. In this context, we would like to add few recommendations : (i) law and waste management strategies, such as exploring new removal technologies and avoid landfilling if this is economically feasible (ii) education, outreach and awareness, (iii) source identification, (iv) increasing monitoring and risk assessment to better understand the threat to biodiversity by reporting additional case studies where showing the impact of MP around the globe and (v) further innovative research lines like the development of bioplastics to replace SUPs in our daily life. In short a greater awareness and responsibility of the general public, stakeholders, industries is needed. Discussions on this topic, particularly considering the excessive use of plastic, should start soon with the involvement of the scientific community, plastic producers and politicians in order to be prepared for the near future.

References

1. Damià Barcelo and Yolanda Picó, Case studies of macro- and microplastics pollution in coastal waters and rivers: Is there a solution with new removal technologies and policy actions? *Case Studies in Chemical and Environmental Engineering*, 2 (2020) 100019.
2. Bianying Zhou, Jiaqing Wang, Haibo Zhang, Huahong Shi, Yufan Fei, Shunying Huang, Yazhi Tong, Dishu Wen, Yongming Luo, Damià Barceló, Microplastics in agricultural soils on the coastal plain of Hangzhou Bay, east China: Multiple sources other than plastic mulching film, *Journal of Hazardous Materials*, 368(2020)121814.
3. Gabriella F. Schirinzi , Marianne Köck-Schulmeyer , María Cabrera , Daniel González-Fernández , Georg Hanke , Marinella Farré , Damià Barceló Riverine anthropogenic litter load to the Mediterranean Sea near the

metropolitan area of Barcelona, Spain, *Science of the Total Environment*, 714 (2020) 136807

4. Yolanda Picó, Vasiliki Soursou, Ahmed H. Alfarhan, Mohamed A. El-Sheikh, Damià Barceló, First evidence of microplastics occurrence in mixed surface and treated wastewater from two major Saudi Arabian cities and assessment of their ecological risk, *Journal of Hazardous Materials*, 416(2021)125747.

5. Evgenios Agathokleous, Ivo Iavicoli, Damià Barceló, Edward J. Calabrese, Ecological risks in a 'plastic' world: A threat to biological diversity? *Journal of Hazardous Materials*, 417 (2021)126035.

6. Damià Barceló and Yolanda Picó, Analysis of microplastics and nanoplastics: how green are the methodologies used? *Current Opinion in Green and Sustainable Chemistry*, 31 (2021) 100503.

7. Damià Barceló and Yolanda Picó, Micro(Nano)plastic analysis: a green and sustainable perspective, *Journal of Hazardous Materials Advances*, 6 (2022) 100058

8. Ana L. Patricio Silva, Joana C. Prata, Tony R. Walker, Armando C. Duarte, Wei Ouyang, Damià Barceló, Teresa Rocha-Santos, Increased plastic pollution due to COVID-19 pandemic: Challenges and recommendations, *Chemical Engineering Journal*, 405 (2021)126683.

9. Ana L.P. Silva, Joana C. Prata, Armando C. Duarte, Amadeu M.V.M. Soares, Damià Barceló, Teresa Rocha-Santos, Microplastics in landfill leachates: The need for reconnaissance studies and remediation technologies, *Case Studies in Chemical and Environmental Engineering*, 3 (2021) 100072