

Micro(nanoplastics) in the marine environment: Current knowledge and gaps

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Abstract

The topic of Micro(nanoplastics) in the marine environment is attracting attention because of their potential impact in sea organisms and humans. There are several sources of Micro(nanoplastics) such as micro and nanoparticle production or fragmentation off bigger plastics. Nanoplastics can have a bigger capacity to concentrate toxic compounds either associated with its production or sorbed from the environment has not been extensively evaluated. Indications suggest that nanoplastics carry more toxics than microplastics (more than million times than seawater). These nanoplastics can also carry microorganisms. There is no harmonization of methodologies for sampling and analysis of micro(nanoplastics) and there are limits in the accuracy of sizes of these particles that can be detected. Calculation of their possible concentrations in the environment is biased by the analytical instrumentation. This paper summarizes the knowledge gaps in the analysis and repercussions of micro(nanoplastics) in the environment and organisms.

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Introduction

Plastic debris pollution is a worldwide environmental issue that lately became an emergent contaminant and many research topics are growing around its sources, fate and ecological consequences with the potential

implications in human health. Synthetic polymers or plastics were synthesized and commercialized since the 19th century. After the mid-20th century, their global production was increasing to reach approximately 322 tonnes in 2015 (PlasticsEurope. *Plastics – The Facts 2016. An Analysis of European plastics production, demand and waste data.* (Plastics Europe: Association of Plastic Manufacturers. Available at <http://www.plasticseurope.org/Document/plastics—the-facts-2016-15787.aspx?FolID=2>). Their high durability and their low or null biodegradation lead geologists to suggest this era to be named as Plasticene age or Age of Plastics [1,2]. Inadequate disposal resulted in plastic debris even in the tropics and polar regions [3,4], with high concentrations in the oceanic gyre, [5,6]. It is known that most of the plastic debris found in the marine environment originates from land-based sources [7]. Plastic debris was suggested to be classified as hazardous materials when found in the environment [8]. Microplastics (MP) have physical, chemical and biological effects on marine organisms with potential impact in the food web and human health [9,10]. Persistent organic pollutants adsorbed onto MP from the North Pacific were identified and quantified [11] and it is suggested that these MP can release additive that are toxic compounds such as phthalates and bisphenol A, to the environment [12,13]. One of the consequences of the excess of plastics used is the formation of MP and nanoplastics (NP). The size of plastic particles is an important key in the concentration of toxic compounds because the smaller the plastic the bigger its capacity to adsorb higher concentrations of contaminants [14]. Plastic particles in a range of 50 nm can adsorb more toxic compounds than plastic particles around 10 µm in size [15]. The objectives of the present review are to summarize the existing knowledge on micro (nano)plastics and to outline the knowledge gaps related to their consequences and impacts in the marine environment.

Definition of Micro(nanoplastics)

MP are synthetic polymers that are becoming the most persistent contaminant in the marine and freshwater environment and are produced intentionally (plastic pellets or preproduction plastics that are raw material for the production of bigger plastic items, microbeads in cosmetic products, blasting abrasive, ink for 3D laser printing) or by fragmentation of large piece of plastic products (photodegradation or mechanically fragmentation). MP are defined as particles lower than 5 mm in

any one dimension (by the National Oceanic and Atmospheric Administration (NOAA) in Ref. [16] Arthur et al., 2009; also in Ref. [17] GESAMP, 2015). However, there are studies as Wagner et al., 2014 [18] that defined NP as plastic particles < 20 μm in a similar way as nanoplankton, or as Pinto et al., 2016 [19] that decided to use NP as <1 μm in at least one of its dimensions. Koelemans et al., 2015 [20] defined NP as <100 nm particles in size. In this paper, NP definition is based on the European Commission definition of the nano-material size that is 1–100 nm [21], differentiating between MP and NP particles.

Sources of Micro(nanoplastics)

There are three main sources of plastic particles in micro and nano sizes in the marine environment: 1) Polymer nanoplastics that are produced intentionally for specific purposes such as cosmetic product, ink for 3D printers, drug delivery [22,23], 2) Fragmentation of plastics due to UV photodegradation, mechanical action, hydrolysis and microorganisms actions [24,25], and 3) Wastewater Treatment Plants (biosolids and effluent water) [26]. In Fig. 1, it is showed the micro and nanoplastic particles from St. Louis River Estuary as an example of these particles and polystyrene particles of 10 μm size.

The first source results to particles that demonstrate totally different properties than the ones resulting from the other two sources. For example, polystyrene (PS) NP refers to particles at nano scale dimension with a PS core and variable functional groups. Common functionalized PS NP include anionic carboxylated ($-\text{COOH}$) and cationic unsaturated amino ($-\text{NH}_2$). Their chemical reactivity and particle surface charge is analogous to these functional groups [22].

For the second source, exposure to sunlight and oxygen are the most important factors that initiate polymer degradation. For example, polyethylene (PE) and polypropylene (PP) preproduction pellets and PS,

polyethylene terephthalate (PET), and polylactic acid (PLA) plastic products, the particle size distribution generated during degradation display and increase in particle concentration with decreasing particle diameter, and also greater variability between the replicate measurements with increasing particle size [24]. Song and collaborators (2017) [25] also did lab experiment using UV and mechanical abrasion to show the formation of NP from MP.

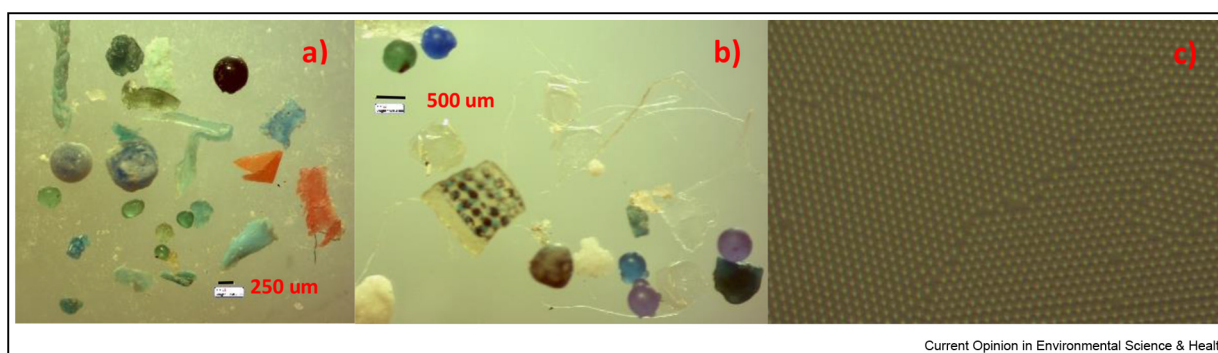
For the third source and one of the main sources of NP (beads and fibers) to the marine environment are the biosolids and effluent waters from wastewater treatment plants to ocean, rivers, and lakes. The most relevant nanoplastic particle is the synthetic fibers made from different polymers. Washing synthetic cloths can result into more than 1900 fibers per item per wash in the sewage [27]. Because synthetic fibers are not readily decomposed, they concentrate in sewage sludge and are also discharged in effluents [28].

Two main techniques are currently used to determine the presence of nanoparticles in water solutions. Coulter counter is a conductivity based technique that can identify particles from 0.4 to 1200 μm diameter. Nanoparticles tracking analysis (NTA) is a laser beam based technique that can identify particles from 30 to 2000 nm diameter [24]. Maes and collaborators (2017) [29] detected MP and microfibers, in sediments, using Nile Red dye and compare the identification with Raman analysis. However, it is obvious the absence of studies of MP and NP in deep-sea sediments [3,30].

Known impacts of Micro(nanoplastics)

There is a big number of studies of MP ingested by fish [9,31–33]. However, there are others species that are affected such as the birds (blockage of digestive enzymes, lower steroid hormone levels and decrease reproductive function) turtles (nutrient deficiency), and whales (starvation) [34,35]. Microalgal growth was negatively affected (up to 45%) by uncharged

Fig. 1



Photomicrographs of Micro(nano) plastics from St. Louis River Estuary: a) and b) pictures showing micropellets and microfragment of plastics (bar sizes, a) 250 μm and b) 500 μm). c) polystyrene particles of 10 μm size.

polystyrene MP and NP, but these negative effects were only observed for the smaller size (50 nm) and at high particle concentration (250 mg/L) [36]. The research results for MP collected for first time, in the Great Lakes during summer 2012 (Abstract ACS L. Rios and [37]) attracted the attention of the scientific community located around of these lakes. And as result Canada added MP as toxic compounds under Canadian Environmental Protection Act (CEPA) and USA banned the use of MP in some personal care products (2017) [38].

The NP ingestion by zebrafish larvae showed neurotoxicity in its locomotor activity [39]. NP has been shown to cross cell membranes, under laboratory conditions, causing tissue damage [17]. On the other hand, even carboxylated (–COOH) PS NP that are partly hydrophobic highly sorb organic pollutants such as PAHs [29]. The combination of these two observations can lead to a conclusion for increased hazard due to polluted NP entering an organism body. When different diameter NP having phenanthrene sorbed on them were tested for their toxicity on *Daphnia magna*, the smaller ones (50 nm) showed the highest toxicity and physical damage. Thus, they showed an additive effect in terms of toxicity [15].

Knowledge gaps

There is a massive number of studies about microplastic impacts and lately about nanoplastics, for e.g., identification of NP sources [40,41], ingestion [42]; fibers in the Baltic Sea [43]. However, there is not any conclusive data about their impacts [44]. One of the main obstacles in the advance of knowledge in MP and NP ecological and human health consequences is the absence of harmonization of assessment methodologies (sampling and analysis). There are inconsistencies among the research results because there are limits in the accuracy of the sizes and possible concentrations in the environment due to the analytical instrumentation. Nevertheless, there are no papers in marine plastic pollution literature that do not mention at least one plastic particle in the marine environment or an organism, which reinforces its ubiquity. Although the formation of nanoplastics is studied in detail, only the parent material was characterized before and after degradation [24]. The formed nanoparticles were not characterized and thus, the chemistry of the NP formed from the degradation of larger plastic and thus, their chemical behaviour is not known.

The potential effect of MP and NP including synthetic fibers on marine life is uncertain, these nanosynthetic particles has toxic chemical associated with its production and its adsorption from the environment [45]. It is not clear the role and threat of these micro (nanoplastics) in the organisms and human. Researchers have been studying the concentrations and

type of NP ingested from the lowest to the highest organisms in the trophic chain, but their results are still limited [35,46–50].

To understand the potential, fate and accumulation of NP in the environment as well as its sorption and accumulation of toxic compounds, one needs to know the effects of its composition (kind of polymer), size, density, shape, surface charge, and dynamic fragmentation.

Without consensus in a standardisation of analytical methods for collection, identification and quantification of micro(nanoplastics) in the environment, their concentrations, spatial and temporal changes, and risks will be unknown.

It is recognised that MP and NP can adsorb POPs and become an important source of these toxic compounds, that can produce cancer and some of them are endocrine disruptors [11,51]. These MP and NP with POPs adsorbed onto their surface can be ingested by organisms and be introduced to the food web with unknown consequences to human health, for e.g., if a fish ingested these particles, the endocrine disruptor will affect only the fish system or when the fish is consumed by humans they will be affected as well: this is a question with an unknown answer. MP and NP can carry microbes and other pathogens from the natural waters and from Wastewater Treatment Plants [52–54] with unknown effects in the marine biota. Several works have reported pathogenic bacteria [55]. For example, McCormick *et al.* [56], compares the bacterial assemblage composition on microplastic particles and natural debris in rivers. Fungi were detected on plastic bottles [57] and it was demonstrated that MP are new substrate where fungal communities differed from the communities from surrounding water of different natural substrate [58].

Conclusion

There is no doubt of the presence of micro and nanoplastic debris in all oceanic environment compartments and its intrusion in marine species. Future studies focusing on the harmonization of the methodology to collect and analyse NP are necessary as well as more controlled feeding experimentation with concentrations of NP closed to the natural marine environment. These studies will allow us to understand the real scale of the impacts and threats of NP to the food web and then to humans. The connection of results under controlled laboratory conditions with the impact of NP in natural marine environment is necessary. To study the effect of the pH, salinity, temperature on the NP to adsorb toxic compounds in the ocean and its role as carrier of invasive species (bacteria, virus and other pathogens).

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