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Transport of persistent organic pollutants: Another effect of microplastic pollution?

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Abstract

Over the past decade, the number of studies examining the presence and effects of microplastics in the environment has drastically increased. Works seeking to identify these particles have proven beyond doubt that microplastics constitute a generalized pollution affecting all environmental compartments, from inside air to arctic snows. Studies on their potential ecotoxicological impacts were more nuanced but many have shown deleterious effects when these microplastics were associated with persistent organic pollutants. This primer mainly focuses on POP sorption and transport by microplastics in the aquatic environment and the possible toxic effects that result from it. Indeed, the associations between microplastics and persistent organic pollutants are very common in the environment. If the mechanisms of interactions are well known, they depend on many factors and their significance in the environment can be very variable in time and space. Indeed, these interactions depend on both the plastic particle (polymer type, crystallinity, particle size, shape, specific area, and functional groups/ polarity) and the pollutant (hydrophobicity, functional groups) but also environmental factors (microorganism population, salinity/ionic strength, pH, dissolved organic matter concentration, and temperature). Changes in the interactions between pollutants and microplastics can result in pollutant release in the aquatic environment and potential toxic effects. However, apart from specific situations, the role of microplastics as local source of exogenous molecules (PAHs, PCBs, etc.) is rarely significant because the limited amounts of involved pollutants. It is much less negligible for endogenous chemicals that enter into the initial composition of the plastic (phthalates, biocides, etc.).

This article is categorized under:

- Water and Life > Stresses and Pressures on Ecosystems
- Science of Water > Water Quality

K E Y W O R D S

aquatic ecosystems, ecotoxicological effects, interaction, microplastics, persistent organic pollutant

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1 | INTRODUCTION

Plastic items with small sizes (<5 mm) are currently named "microplastics" (MPs). Primary microplastics (plastic specifically manufactured to be of this size) and secondary microplastics (plastic items broken down in the environment) are both transported within the marine and freshwaters (Horton & Dixon, 2018). (Micro)plastics are made of long polymer chains with different composition depending on the desired properties of the manufactured plastic (acrylonitrile butadiene styrene [ABS], polycarbonate [PC], polyethylene [PE], polyethylene terephthalate [PET], polytetrafluoroethylene [PTFE], polyvinyl chloride [PVC], polymethyl methacrylate (PMMA), polypropylene [PP], polystyrene [PS], etc.). All commercial plastics also contain monomeric additives (plasticizers, colorants, antioxidants, ultraviolet absorbers, flame retardants, etc.). If the polymers used in plastics are generally harmless, some of their additives are toxic to organisms. For example, the unfortunately popular Di-2-ethylhexyl phthalate (DEHP) is an endocrine disruptor that also leads to embryo mortality and toxicity symptoms, such as necrosis, cardiac oedema, and no-touch response, in zebrafish (Rowdhwal & Chen, 2018). Microplastics are therefore a carrier of endogenous toxic additives that can be released to the aquatic environment during material aging. Through different disposal routes, the plastic particles will also encounter environmental contaminants present in, for example, wastewater or landfill leachate. Consequently, mixing of the particles with other chemicals takes place after their intended use. At the same time, hydrophobic pollutants with a low water solubility become more mobile when sorbed to plastic particles, which may increase their transport and consequently impact their distribution and bioavailability (Li, Wang, et al., 2021). By this process, plastic items potentially become a carrier of exogenous toxic compounds.

Microplastics are then a vector of numerous chemicals to the aquatic environment. From all the substances, persistent organic pollutants (POPs) are of particular concern because of their long-term durability and their harmful properties for most of the living organisms. POPs are regulated since 2001 under the Stockholm Convention. Initially, 12 POPs have been recognized for their adverse effects on humans and the ecosystem. This dirty dozen were pesticides (aldrin, chlordane, dichlorodiphenyltrichloroethane [DDT], dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, and toxaphene), industrial chemicals (polychlorinated biphenyls PCBs) and by-products (hexachlorobenzene, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans PCDD/PCDF). The list of POPs unfortunately increases from year to year. It currently includes (i) intentionally produced chemicals that are or that have been used in agriculture, disease control (such as DDT, which is still in use to control mosquitoes and prevent malaria in some parts of the world), manufacturing, or industrial processes (such as PCBs, which have been namely useful in electrical transformers and large capacitors) and (ii) unintentionally produced chemicals, such as dioxins or Polycyclic Aromatic Hydrocarbons (PAHs), that result from some industrial processes and from combustion.

This primer mainly focuses on POP sorption and transport by microplastics in the aquatic environment and the possible toxic effects that result from it. Thus, the organic pollutants commonly associated with microplastics and their interactions in aquatic environments are listed in Box 1. The analytical methods used to study the pollutants sorbed on plastics and their limits are detailed. The possible transfer pathways to aquatic organisms as well as their potential toxic effects are summarized. Finally, we discussed whether or not the microplastic are likely to act as secondary sources of organic pollutants in aquatic environment.

BOX 1 List of POPs according to the Stockholm Convention.

Aldrin¹, Chlordane¹, Chlordecone¹, DDT¹, Decabromodiphenyl ether², Dicofol¹, Dieldrin¹, Endrin¹, Heptachlor¹, Hexabromobiphenyl², Hexabromocyclododecane², Hexabromodiphenyl ether and heptabromodiphenyl ether², Hexachlorobenzene¹²³, Hexachlorobutadiene²³, Alpha hexachlorocyclohexane, Beta hexachlorocyclohexane¹, Lindane¹, Mirex¹, Pentachlorobenzene¹²³, Pentachlorophenol and its salts and esters¹, Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride¹, Polychlorinated biphenyls²³, Polychlorinated dibenzo-p-dioxins (PCDD) ³, Polychlorinated dibenzofurans (PCDF) ³, Polychlorinated naphthalenes²³, Perfluorooctanoic acid (PFOA) its salts and PFOA-related compounds², Short-chain chlorinated paraffins², Technical endosulfan and its related isomers¹, Tetrabromodiphenyl ether and pentabromodiphenyl ether², Toxaphene¹, ¹Pesticide, ²Industrial chemical, ³Unintentional Production.

2 | MICROPLASTIC-ASSOCIATED ORGANIC POLLUTANTS IN AQUATIC ECOSYSTEMS

Microplastic samples contained additive derived chemicals to prevent oxidation, UV degradation or combustion of polymeric structure and to improve mechanical properties of plastics (Table 1). These additives (radical scavengers, UV absorbers, or antioxidants, depending on the mechanism of degradation to prevent) improve the polymer stability and duration.

Some of these additives such as PBDEs, DEHP, or Nonylphenols have the properties of POPs. Part of them degrade during plastic aging. As an example, the primary antioxidant Tris(2,4-di-terbutylphenyl) phosphite (Irgafos 168) is degraded under UV irradiation in the two more soluble and toxic products 2,4-di-tert-butylphenol and tris (2,4-di-tert-butylphenyl) phosphate (Yan et al., 2018).

Plastics may also adsorb organic contaminants present in environmental media because of their hydrophobicity. Due to their high specific surface area (SSA), small particles are known to enhance adsorption of contaminants. Hydrophobic contaminants such as PAHs, PCBs, per-/poly-fluoroalkyl substances (PFAS) and PBDEs in aqueous media could well be adsorbed on MPs. The occurrence of PCBs and PAHs in MPs is indeed reported in different regions (Bouhroum et al., 2019; Chen et al., 2020). The hydrophobicity of the contaminant, often evaluated by its K_{OW} (the ratio of concentrations of a not ionized compound between a water-saturated octanolic phase and an octanol-saturated aqueous phase at equilibrium), is identified as a driving factor of adsorption on MPs (Wang et al., 2018). However, hydrophobic interactions are only one of the many sorption mechanisms that can bind POPs onto MPs and that depend on the pollutant chemical structure (Table 2).

POPs concentrate on the hydrophobic surface of plastics, with environmental concentrations recorded in the ng/g to μ g/g range (Barnes et al., 2009; Teuten et al., 2007, 2009). For example, virgin plastics (PE, PP, & PET) incubated for few months in Muskegon Lake and displayed detectable PAH concentrations (PET: <0.20 ng/g, PP: <0.20-0.24 ng/g, LDPE: 0.21-0.35 ng/g) or PCB concentrations (PET: 1.40 ± 0.71 ng/g, PP: 0.89 ± 0.04 ng/g, LDPE: 0.86 ± 0.19 ng/g) on the three polymer types (Steinman et al., 2020).

3 | INTERACTIONS BETWEEN ORGANIC POLLUTANTS AND MICROPLASTICS IN THE AQUATIC ENVIRONMENT

The sorption mechanisms are namely hydrophobic interactions, electrostatic interactions, pore-filling, Van der Waals forces, hydrogen bonding, and π - π interactions (Torres et al., 2021). However, London interaction forces (physisorption), hydrogen or halogen bonding and Pi stacking of aromatic rings (chemisorption) are prevalent for POPs-MPs interactions (Hüffer & Hofmann, 2016). Despite low interaction energy, the neutral hydrophobic solutes are efficiently sorbed to MPs in aqueous media (Figure 1). The sorption isotherms in the low loading limit are linear, reversible, and can be characterized by a partition coefficient, K_d . This partition coefficient is generally correlated with the K_{OW} of the contaminant (Ziccardi et al., 2016) but also depends on other factors that can be classified as MP (polymer type, crystallinity, particle size, shape, SSA, and functional groups/polarity) and micropollutant characteristics (hydrophobicity, functional groups/*p*Ka) or environmental factors (salinity/ionic strength, pH, dissolved organic matter concentration, and temperature). Plastic weathering (due to some combination of sunlight, heat, and moisture) or colonization by biofilm may also significantly influence the sorption equilibria.

3.1 | Microplastic/pollutant characteristics

The first parameter influencing the sorption of pollutants is obviously the composition of the plastic, including both the polymer chain and the additives, which conditions the type of interactions between MPs and POPs. For example, results suggest that strobilurin fungicides have stronger affinity for PS-MPs than PE-MPs as the presence of aromatic rings in PS could allow π - π interactions (Hai et al., 2020). Similarly, halogenated additives such as some biocides (chlorinated) or some flame retardants (brominated) allow halogen bonding with some polutants (Wu et al., 2019). Endo et al., (2011) also reported strong sorption of pharmaceuticals and biocides onto PA thanks to hydrogen bonds between the pollutants and the polymer amide groups. The crystallinity of MPs also greatly affects their sorption capacity and lead to significant difference in pollutant concentrations between semi-crystalline (HDPE, LDPE, and PP) and

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TABLE 1 Examples of additives according to their use in plastic production.

| Additive categories | Example of compounds | Example of chemical structure |
|---------------------|---|--|
| UV stabilizers | Benzotriazoles (e.g., UV 328), Benzophenones (e.g., BP12), derivatives of tetramethylpiperidine (also named HALS for hindered amine stabilizers) | UV 328 |
| Antioxidants | Nonylphenol, Organophosphites (e.g., Irgafos168) | $(CH_3)_3C \xrightarrow{C(CH_3)_3} C(CH$ |
| Flame retardants | Hexabromocyclododecanes, Polybromodiphenylethers (PBDE) | $Br \qquad Br \qquad Br \\ Br \\$ |
| Plasticizers | Phthalates (e.g., DEHP), Bisphenol A | CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ DEHP |
| Biocides | Oxybisphenoxarsine, Isothiazalones | |

Oxybisphenoxarsine

TABLE 2 Main physicochemical properties of some POPs in relation with the MP sorption capacity.

| POPs | Log Kow | Number of aromatic rings | Halogen group | Ionisable under environmental conditions |
|---------------------|---------|-----------------------------|---------------|---|
| PAHs | 3.4–6.7 | >2 | _ | No |
| PCBs | 4.6-8.2 | 2 | Cl | No |
| PBDEs | 5.7-8.3 | 2 | Br | No |
| PFAS (in acid form) | 2.8–7.7 | 0 | F | Yes |
| Chlordecone | 3.45 | 0 | Cl | No |
| Heptachlor | 6.1 | 0 | Cl | No |
| Lindane | 3.6-3.7 | 0 | Cl | No |
| DDT | 6.36 | 2 | Cl | No |

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FIGURE 1 Fate of microplastic-associated pollutants in aquatic ecosystems.

amorphous (PVC, PS) plastics after long-term environmental exposition (Rochman et al., 2013) or laboratory experiments (Song et al., 2021). The crystallinity modifies the sorption capacity by influencing the pollutant diffusion through the plastic matrix (Černá et al., 2021; Teuten et al., 2007). The dimension of the MP is also a decisive factor as the sorption capacity usually increases with the decrease in MP size (Munoz et al., 2021) due to the rise in SSA and the concomitant increase in the number of adsorption sites (Fan et al., 2021). However, in some cases, aggregation of small particles may also occur therefore resulting in a decrease of the SSA (Wang et al., 2019).

Contrasting results were reported about the weathering/aging effect on the MP adsorption capacity due to different processes with opposite effects occurring during the aging (Černá et al., 2021; You et al., 2021). The first process is the fragmentation and physical alteration of the surface of the particles which results in an increase in the SSA and consequently, in the adsorption capacity (Fan et al., 2021). A second process is the chemical alteration of the surface which results in the breakage of polymer chain and in the addition of hydroxyl or other functional groups to the MP surface resulting in a decrease of the hydrophobicity (Yao et al., 2022; You et al., 2021). Similar changes may also occur with the

colonization by a periphytic biofilm (Hanun et al., 2021). As more hydrophilic functional groups are added to the MP surface, hydrophobic interaction may decrease while new electrostatic interactions or hydrogen/halogen bonds may appear. This change in sorption capacity of hydrophobic compounds can lead to their desorption into the aqueous phase (Bao et al., 2021). On the contrary, the sorption capacity of POPs that contain hydrophilic/ionisable functional groups such as biocides may increase during weathering/aging (Fan et al., 2021; Munoz et al., 2021). Finally, another aspect related to the presence of a biofilm is the enhanced biotransformation of some compounds which results in less diffusion of pollutants from the particles to the aqueous phase or in a biotransformation of the diffused pollutant (Wu et al., 2017).

3.2 | Environmental factors

Some interactions between pollutants and microplastics are due to electrostatic forces. In this case, changes in pH may influence the charges of the functional groups and therefore affect either positively or negatively the sorption capacity. For example, adsorption of perfluorooctanesulfonic acid (PFOS) onto PE and PS-MPs is higher in acidic conditions due to the appearance of complementary charges (Wang et al., 2015) while pH <5 leads to electrostatic repulsion between oxytetracycline and PS-MPs (Zhang et al., 2018). Ionic strength and therefore salinity can have opposite effects on the sorption of pollutants. On the one hand, it will tend to reduce electrostatic interactions as the ions compete for the sorption sites therefore reducing the ability of some compounds to bound to MPs (Chen et al., 2021). On the other hand, hydrophobic interactions may be promoted by the "salting out" effect as the great concentrations of ions reduce the solubility of organic compounds (Endo et al., 2012). Thus, changes in salinity at the river-ocean interface can lead to shifts in the partition balance between MPs and the aqueous phase and consequently enhance either their sorption or their release of pollutants, depending on their chemical properties. The water temperature also influences the sorption capacity of POPs onto MPs. Indeed, the surface tension decreases with the rise in temperature while the solubility of some chemicals decreases with temperature. These two processes lead to an increased sorption with decreasing temperature (Zhan et al., 2016). Nevertheless, laboratory experiments showed that the effect of temperature is rather limited and that a maximum absorption could sometimes be observed around 15-20°C (Qiu et al., 2019) depending on the involved sorption processes. Finally, the abundance of natural organic matter (OM) in water has a strong influence on the sorption capacity of pollutants. The competition between OM and pollutants for the sorption sites led to a decrease in the pollutant sorption capacity (Lara et al., 2021; Munoz et al., 2021). The presence of dissolved organic matter (DOM) can even induce release of additives such as phthalates initially present in the plastic matrix by increasing their solubility in water (Yan et al., 2021).

4 | METHODS FOR THE QUANTIFICATION OF POLLUTANTS ASSOCIATED WITH MICROPLASTICS

Due to the limited masses of MPs that can be sampled during field work, the quantification of MP-associated POPs can be challenging. Several methods are possible to overcome this issue:

- Some authors have been working on both MPs and macroplastics to increase the mass available for analyses (Hirai et al., 2011). This approach makes it possible to study the differences in pollutant concentrations in relation with the polymer types. However, information on the effects of particle size related to the surface alteration that occurred during fragmentation or to the change in SSA, is lost.
- Rather than directly determining the POP quantities on the surface of MPs, some works focused on the correlation between POP and MP levels in water, sediment or biota (Fraser et al., 2020; Garcia-Garin et al., 2020). The problems associated with the mass of samples available are thus overcome, but this method does not constitute a direct measurement of the quantities of pollutants absorbed on plastics and can therefore lead to interpretation bias.
- Another method is to combine samples or to work on large volumes of water or sediment to obtain sufficient masses of plastic. Nevertheless, the masses thus obtained are small and analytical techniques require low limits of quantification (Chen et al., 2020). In addition, working on large samples often requires a pre-treatment step to separate the plastics from the organic and mineral fractions. Previous works compared the different possible pre-treatments (Stock et al., 2019) that constitute an essential step for the correct determination of plastic concentrations, in particular in continental samples. However, the use of some reagents (e.g., hydrogen peroxide) could modify the pollutant concentrations (Mai, Bao, Shi, Wong, & Zeng, 2018) either directly by degrading them or by altering the biofilm

present on the MP surface (Wu et al., 2017). Similar issue may occur when working on MP-associated pollutants in wastewater treatment plants.

• Finally, some authors worked on sites where microplastics are abundant or where the matrices are easy to process, such as beaches (Lozoya et al., 2016) or oceanic gyres (Chen et al., 2018). This approach is interesting to investigate the effect of the polymer type or the particle size but it is limited to specific location.

Conventional analytical techniques are then used. In most cases, a GC–MS is used since this technique allows the assay of many compounds in a single run (Frias et al., 2010; Zhang et al., 2015). Occasionally, other techniques are used to target specific compounds such as LC–MS/MS for pharmaceutical compounds (Magadini et al., 2020; Santana-Viera et al., 2021), GC-ECD for halogenated compounds (Antunes et al., 2013) or HPLC-DAD for pesticides (Šunta et al., 2020). Specific technic can also be used to lower the limits of quantification such as UPLC-Fluo for PAHs (Bouhroum et al., 2019). The quantification of the endogenous additives is less restrictive since their contents are usually much higher even if desorption or solubilization in adequate organic solvent is necessary before analysis.

5 | ECOTOXICOLOGICAL EFFECT OF MICROPLASTIC-ASSOCIATED POLLUTANTS

5.1 | Microplastics as a source of pollutants for aquatic biota: Indirect pathway

MPs can induce toxic effects on aquatic organisms by releasing pollutants from their surface to the water. Indeed, the sorption of pollutants is partly reversible (Song et al., 2021) and in some situations the aqueous - particulate phase balance is not reached (Chen et al., 2018). Consequently, microplastics can be a source of pollutants for aquatic environments. However, under environmental conditions, the levels of exogenous POPs associated with MPs are similar to those measured in natural organic matrices (wood, sedimentary organic matter, charcoal; Beckingham & Ghosh, 2017). Thus, the limited amounts of MPs in the environment do not constitute a significant source of contamination (Mai, Bao, Shi, Liu, & Zeng, 2018). While this hypothesis may be true in general, it should not mask the possibility of a significant impact for certain compounds (especially endogenous toxics) or specific locations such as the outlets of wastewater treatment plants where both pollutants and MPs are present in large quantities (Mason et al., 2016). For example, MPs can promote transfers of biocides such as triclosan from highly contaminated area and have a deleterious impact on the development of primary producers in aquatic ecosystems (González-Pleiter et al., 2021; Verdú et al., 2021). Similarly, MPs were found to be the main source of PAE and PBDE in sediments of the Yangtze River leading to significant ecotoxicological risk (Deng et al., 2021). The reverse situation is also possible and the presence of MPs can reduce the toxicity of compounds such as DDT or ibuprofen by reducing their dissolved phase concentrations (Liu et al., 2021; Wang et al., 2020). Thus, MPs may also impact aquatic ecosystems not as a source of pollutants but because they can change the distribution of POPs between the environmental compartments.

5.2 | Microplastics as a source of pollutants for aquatic biota: Ingestion pathway

Microplastic can be ingested and introduced to the biological systems of a wide range of organisms from herbivores and secondary consumers to the predators of higher trophic levels, such as invertebrates and fish (Markic et al., 2020; Setälä et al., 2014). This phenomenon could be filled by the aging of the MPs and their colonization by biofilm which makes them more likely to be ingested (Wang et al., 2021). It is still unknown if, under environmental conditions, the sorbed contaminants have the potential to be transferred from ingested plastics to aquatic organisms at concentrations that could cause harm or the importance of dietary uptake in comparison with other pathways of exposure. The physicochemical conditions in the digestive systems of aquatic organisms are likely to modify the interactions of pollutants and microplastics and therefore their distributions. For example, the chemical alteration of PVC-MPs in simulated gastric conditions lead to the desorption of anthracene (Bao et al., 2021). Likewise, tire microparticles are more likely to release antibiotics in gastric fluids than in ultrapure water (Fan et al., 2021). However, the effects of MPs on organisms can be deleterious or beneficial as two different situations can occur: (i) An increased bioaccumulation by ingestion of polluted MPs and a subsequent release or (ii) a decreased bioaccumulation by sorption of POPs present in the gastric fluids onto MPs and an excretion of the polluted MPs. (Bakir et al., 2014) have quantified faster desorption rates of POPs with gut

surfactant than in seawater, with a further substantial increase under conditions simulating warm blooded organisms. On the contrary, (Koelmans et al., 2013) predicted a decreased bioaccumulation in marine ecosystems due to a cleaning mechanism that counteracted biomagnification. However, they considered the differences too small to be relevant from a risk assessment perspective. The difference between the two situations comes mainly from the physicochemical properties of the pollutants and especially their hydrophobicity. Thus, PE-MPs can cause an accumulation of PFAS in mussels and, at the same time, have a beneficial effect on the presence of pharmaceutical and personal care products and pesticides in the tissues (Álvarez-Ruiz et al., 2021).

Pollutants may follow different pathways through the organisms. In addition to ingestion and desorption, (Lin et al., 2021) reported that PS-MPs lead to the contamination of *Daphnia Magna* by aqueous pyrene through endocytose. Microplastics can also fragment into nano-sized plastics and then translocate from digestive tract to cells in the living organisms. Thus, nanoplastics facilitate the transport and uptake of phenanthrene and increase both its bioavailability and potential toxicity to zebrafish embryos (Zhang & Goss, 2020). Similarly, the influence of MP on the bioaccumulation of PBDEs was found negligible except in the case of fragmentation in the organism (Sun & Zeng, 2022). The deleterious effects of MP-associated pollutants can also be due to a change in gut biota rather than a direct toxicity (Montero et al., 2022). The role of MPs is therefore major, by shifting the partition equilibrium, they promote the accumulation of pollutants in the digestive system.

6 | CONCLUSION

Environmental systems are complex and it is difficult to definitively conclude about the role that microplastics play in the transfer of persistent organic pollutants and in their impacts on aquatic ecosystems. Generally, the associations between MPs and POPs are very common in the environment since most of these pollutants are hydrophobic and therefore have an affinity for plastics. The main sorption mechanisms are the Van der Waals-London forces, hydrogen bounding, halogen bounding, and π - π interactions. They are variable in time and space and depends on both the MP and the pollutant properties but also on environmental factors. As time passes and the particle travels, several processes occur including MP aging, colonization by biofilm and changes in environmental factors (potentially due to ingestion of the MPs by aquatic organisms). These changes are likely to shift the partition equilibria between POPs and MPs. Usually, the MP aging leads to a lower sorption capacity for hydrophobic compounds and to a greater sorption of "hydrophilic" pollutants. The distribution of pollutants between dissolved phase and particles depends mainly on the K_{OW} of the compounds. For plastic exogenous pollutants, levels in microplastics are of the same order of magnitude as those in natural organic matter. Considering the limited amounts of plastic particles in regard with the organic matter, the MPs are unlikely to constitute a significant source of pollutants in aquatic environment except for some specific location (Lohmann, 2017). However, the role of MPs in freshwater and marine ecosystems is not negligible. Indeed, many studies have shown that MPs can carry pollutants over long distances. Their presence in the soil is likely to increase the transfer of pollutants to aquatic ecosystems because MPs have sorption capacity similar to soil particles but higher transferability (Li, Guo, et al., 2021) and because MPs may modify the soil sorption capacity (Hüffer et al., 2019). Furthermore, the levels of plastic endogenous compounds (chemicals that are part of the manufacturing processes of plastics) in MPs are very substantial. These compounds are not linked by covalent bonds to the polymeric structure of plastics. Therefore, the fragmentation of plastics is likely to lead to a continuous and long-term release of these pollutants. MPs constitute the main source of phthalates (plasticizer) in certain rivers. Despite the fact that MPs are likely to carry pollutants across aquatic ecosystems, the impacts of these pollutions on ecosystems remain poorly understood. Laboratory works showed that synergies between pollutants and microplastics can be harmful for aquatic organisms. However, many studies were based on pollutant concentrations exceeding usual environmental concentrations. Furthermore, few studies compare the effects of MPs and natural organic matter as pollutants carrier under similar contamination levels. Regarding the indirect effects of MP-associated pollutants by contamination of water, the hydrophobic nature of POPs as well as the relatively small quantities involved suggest a limited effect except for specific situations (WWTP effluents) where the concentrations of pollutants and MPs are high or for certain compounds (biocides) that have a strong impact on primary producers. Due to the potentially large amount of particulate organic matter, the bed sediment can also be significantly impacted by the pollutants released from MPs. Regarding the direct effects by ingestion by organisms, changes in physicochemical conditions in gastric fluids can cause shifts in the distribution of pollutants between the particulate and dissolved phases. These changes can be harmful or beneficial depending on the chemical properties of the pollutants. Thus, the ingestion of MPs can be both a source of contamination or an easier way to excrete

contaminants already present in the organism. Regarding the ingestion of contaminated particles, the data currently available do not allow a comparison of the harmfulness between MPs and natural organic particles with comparable levels of contamination. However, if natural particles turn out to be more fragmentable in a digestive system, they could generate a greater ecotoxicological risk than MPs. The MPs stay long in organisms and aquatic ecosystems and, in doing so, they alter the distribution of pollutants creating locally more contaminated areas. In organisms, this can result in an accumulation of pollutants in the digestive system and changes in gut biota, leading to deleterious effects.

The previous works carried out on microplastic-pollutant associations showed that MPs can effectively act as carrier of pollution but the impacts of these pollutants are generally limited. Nevertheless, certain knowledge gaps are still to be filled. They mainly concern the role of MPs (i) in pollution emissions from soils to aquatic systems, (ii) in pollutant transfers through and at the outlet of WWTPs, (iii) as a source of endogenous pollutants (plastic additives) for ecosystems and aquatic organisms. In addition, future studies will face two challenges: (iv) investigating MP-associate pollutants in the field to better understand the complex processes that occur in situ and that involved pollutions from contrasting sources and (v) reducing the size of investigated particles to nanoplastics which are more able to translocate within organisms and therefore cause adverse effects.

AUTHOR CONTRIBUTIONS

David Gateuille: Conceptualization (equal); supervision (equal); visualization (lead); writing – original draft (lead); writing – review and editing (equal). **emmanuel naffrechoux:** Conceptualization (equal); supervision (equal); writing – original draft (supporting); writing – review and editing (equal).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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RELATED WIRES ARTICLES

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FURTHER READING

The current article is a quick overview of the potential interaction between MPs and POPs. For the interested reader, we recommend reading some more specific reviews on:

The POP-MP interactions and their drivers: Fu et al., (2001 and Yu et al., (2021)

The ecotoxicological effects: Huang et al., (2021) and Xiang et al., (2022).

The toxicity of plastic additives: Beiras et al., (2021).

The technical and scientific obstacles to overcome about MP-POP effects in freshwater: Eder et al., (2021).

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