

Review

# Coupling between Increased Amounts of Microplastics and Dissolved Organic Compounds in Water

Wengang Yan <sup>1</sup>, Qianjin Wang <sup>1</sup>, Ya Gao <sup>2</sup>, Mengchen Xu <sup>1</sup>, Huiying Li <sup>1</sup>, Yuping Zhou <sup>1</sup>, Changqing Liu <sup>1</sup> and Yihua Xiao <sup>1,\*</sup> 

<sup>1</sup> School of Environmental and Municipal Engineering, Qingdao University of Technology, Qingdao 266520, China

<sup>2</sup> College of Municipal and Ecological Engineering, Shanghai Urban Construction Vocational College, Shanghai 200438, China

\* Correspondence: yihua.xiao@qut.edu.cn

**Abstract:** Microplastic (MP) pollution is a rapidly spreading global problem, threatening the use and sustainability of freshwater resources. MPs in water can act as both a source and sink of dissolved organic compounds. This review summarizes the current knowledge of interactions between MPs and dissolved organic compounds, including the adsorption and release of dissolved organic compounds by MPs and the impacts of MPs on the source and sink of natural dissolved organic matter (DOM) in aquatic ecosystems. The key mechanisms for the adsorption of dissolved organic compounds on MPs are hydrophobic interactions, van der Waals forces, and  $\pi$ - $\pi$  interactions. Particle size, morphological characteristics, density, and environmental factors (pH, ionic strength, and UV radiation) have a great influence on the adsorption of dissolved organic compounds on MPs. Although research on the interactions between dissolved organic compounds and MPs has progressed rapidly, to date, research on the impacts of increasing amounts of MPs on natural DOM cycles (production, transformation, and fate) in aquatic ecosystems has been very limited. Knowledge gaps and future research directions are outlined at the end of this review.

**Keywords:** microplastics; adsorption; release; dissolved organic matter; source; sink



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## 1. Introduction

With the growth of the plastic industry all over the world, plastic pollution in the environment has drawn much attention [1–3]. Currently, plastic debris is widely found in the ocean [4,5], freshwater [1,6], sewage [7], sediments [8], and aquatic organisms [9]. Increasing amounts of plastic in water have pronounced effects on freshwater ecology and societal services, as increasing plastic pollution may have toxic effects on aquatic organisms [10], alter aquatic species composition [11], and increase the cost of drinking water purification [12]. Microplastics (MPs) are defined as plastic debris with a diameter of less than 5 mm [13], characterized by a small size and large specific surface area. Based on their chemical composition, MPs are classified as polyethylene (PE), polypropylene (PP), polyamide (PA), polyvinyl chloride (PVC), polystyrene (PS), polyethylene terephthalate (PET), etc. There are two primary sources of MPs in aquatic systems: (1) fragmentation of plastic litter released into water through solar radiation and microbial degradation [14,15], and (2) direct discharge from municipal wastewater treatment plants, which may contain personal care and cosmetic products or textile fiber residues [7].

MPs in the environment are often hydrophobic, chemically stable, and resistant to degradation [16]. However, studies have shown that MPs can leach polymers or additives into the surrounding environment through biotic and abiotic processes [17–19]. Plastic additives are chemical compounds incorporated into plastic during the manufacturing process, which can be used as plasticizers, foaming agents, flame retardants, antioxidants, stabilizers, and pigments [20]. Most plastic additives are hydrophobic organic compounds

and are recognized as toxic to aquatic organisms [21]. Lithner et al. (2009) tested the acute toxicity of plastic leachates to *Daphnia magna* and found that 9 of 32 plastic leachates had different toxic effects (48 h EC<sub>50</sub>s ranging from 5 to 80 g plastic L<sup>-1</sup>) on *Daphnia* mobility [22]. After losing the protection of additives, the degradation of MPs in water can be accelerated [23]. There is a great possibility that MP leachates (additives or any other organic substrate) released into aquatic systems contribute to carbon cycling in water. However, the effects of MP pollution on carbon cycling in water are not well studied.

Once released into the aquatic ecosystem, MPs can serve as a carrier for various organic pollutants and heavy metals [13,24], affecting the transportation and fate of chemical pollutants. Ziajahromi et al. (2019) studied the effect of PE MPs on the acute toxicity of the synthetic pyrethroid bifenthrin to the invertebrate *Chironomus tepperi* in both synthetic water and river water and found that the presence of PE MPs could reduce the toxicity of bifenthrin to exposed larvae [25]. Studies have shown that PVC, PE, PP, and PS have a high sorption capacity for organic pollutants, such as dichlorodiphenyltrichloroethane (DDT), phenanthrene (Phe), bis-2-Ethylhexyl phthalate (DEHP), and chlorinated benzenes [26–28]. The adsorption by MPs can transfer chemical compounds from water into aquatic organisms. The concentrations of organic pollutants (polychlorinated biphenyls and polybrominated diphenyl ethers) in aquatic organisms have been found to be positively related to the amount of ingested MPs [29,30]. However, the adsorption capacity for organic pollutants on MPs highly depends on the MPs' characteristics, the chemical composition of the organic pollutants, and environmental factors, such as pH and ionic strength [28].

Besides adsorption, MPs can leach organic compounds into water. Most of the plastic additives are not covalently bound to MPs and can be released into the surrounding water. The release process can be assisted by solar radiation and the biological degradation of MPs [31]. DEHP and bisphenol A (BPA) additives have been detected in commercial PVC and PS plastic solutions under UV light [17,32]. Polybrominated diphenyl ethers (PBDEs), phthalates, nonylphenols (NPs), and antioxidant additives have also been found in marine environments [20]. Besides additives, MPs can leach other dissolved organic compounds derived from MP polymers into the aqueous phase. A few published studies have documented that these polymer-derived dissolved organic compounds potentially contribute to dissolved organic matter (DOM) pools in aquatic ecosystems [23,33]. DOM is a complex mixture of organic molecules that can pass through a 0.2–0.7 µm filter [34]. MPs in natural waters can form a “micro-environment”, the chemical composition and microbial activities of which are significantly different from those of the surrounding environment. This “micro-environment” can affect the biogeochemical cycles of natural DOM and microorganic pollutants [23,35–37]. MPs can also serve as a carrier for DOM, which significantly impacts DOM transport along the aquatic continuum [38].

Research on the occurrence and ecological effects of MPs in water has progressed rapidly in recent years. This study aims to review the current research and identify knowledge gaps in the interactions between increasing amounts of MPs and dissolved organic compounds in aquatic systems. In Sections 2 and 3, we summarize the adsorption and release of dissolved organic compounds by MPs and their environmental factors. In Section 4, we explore the current knowledge on the impacts of MPs on the source and sink of natural DOM. Guidance on future study directions in this field is provided at the end of this paper.

## 2. Adsorption of Dissolved Organic Compounds on MPs

Currently, studies on the adsorption of dissolved organic compounds by MPs mainly focus on the following aspects: (1) the adsorption mechanisms of dissolved organic compounds on MPs, and (2) the impact of environmental factors on the adsorption of dissolved organic compounds on MPs. Studies on the adsorption of dissolved organic compounds on MPs are summarized in Table 1.

**Table 1.** The adsorption mechanisms of dissolved organic compounds on MPs and the influencing factors.

Adsorption Mechanisms	Influencing Factors	Specific Process	Literature Source
Hydrophobic interactions	Chemical property	Adsorption increases with increasing hydrophobicity	[27,39–44]
	pH	Increasing pH → promoting dissociation of hydrophobic neutral sorbent molecules into hydrophilic, negatively charged substances → reducing hydrophobic interactions	[42,45]
	Ionic strength	The presence of salt ions → reducing the solubility of the compound in aqueous solution → promoting hydrophobic adsorption of the compound on MPs	[40,42,46,47]
	UV radiation	UV irradiation → leading to the aging process → changing the surface properties (size, surface area, porosity, surface polarity) of MPs → enhancing the adsorption of hydrophilic organic pollutants	[48,49]
Van der Waals force	Temperature	Increasing temperature → increasing the mobility and solubility of the adsorbed molecules → the van der Waals forces decrease → the adsorption capacity decreases	[50]
	Ionic strength	Increasing ion concentrations → ions (Na and Ca) can occupy the adsorption sites of MPs → decreasing absorption capacity	[48]
$\pi$ – $\pi$ interactions	pH	Increasing pH → increasing the $\pi$ donor capacity of the sorbent → enhancing $\pi$ – $\pi$ interactions	[51,52]
	Ionic strength	The stronger the cation → the stronger the binding between organic compounds and other ionic compounds → leading to increased adsorption of organic compounds on MPs	[53]
Electrostatic interactions	pH	Negatively charged MP surface and lower pH → leading to the protonation of MPs → contributing to the electrostatic gravitational force between organic compounds and MPs	[43,48,53–55]
	Ionic strength	Electrolytes can compete with adsorbates for electrostatic sites → decreasing the adsorption capacity	[43,53,56,57]

## 2.1. Adsorption of Dissolved Organic Compounds on MPs: Mechanisms

### 2.1.1. Hydrophobic Interactions

Hydrophobic interactions are of major importance for the adsorption of nonpolar dissolved organic compounds on MPs in aqueous solutions [38]. Hüffer and Hofmann (2016) investigated the sorption behavior of seven aliphatic and aromatic organic compounds on four types of MPs (PA, PE, PVC, and PS). The experimental isotherm results showed that the chemical properties of both the MPs (monomeric composition) and organic compounds (hydrophobicity) had important effects on the sorption behavior [58]. The adsorption of Suwannee River humic acid (SRHA) and Suwannee River fulvic acid (SRFA) on PS in an aquatic environment was investigated using kinetic, isotherm, and site energy distribution analyses [39]. The results showed that hydrophobic interactions were one of the two main adsorption mechanisms of SRHA and SRFA adsorption on PS. The adsorption capacity for different organic compounds on MPs is positively correlated with their octanol–water partition coefficient ( $K_{ow}$  or  $\log K_{ow}$ ), a parameter that is commonly used as a hydrophobic parameter [37,42,59].

### 2.1.2. Van der Waals Force

For nonpolar aliphatic polymers with no specific functional groups, their interactions with organic compounds are mainly van der Waals interactions. For instance, Guo and Wang (2019) demonstrated that the sorption capacity for sulfamethoxazole (SMX) on polystyrene (PS) was higher than that of polypropylene (PP) [41]. This phenomenon is due to the different chemical characteristics of PE and PS. PE and PS are aliphatic and aromatic polymers, respectively. The adsorption of SMX on PE and PS is driven by van der Waals

and  $\pi$ - $\pi$  interactions, respectively, based on their aliphatic and aromatic characteristics. The higher energy of  $\pi$ - $\pi$  interactions than that of van der Waals interactions resulted in a higher adsorption capacity for SMX on PS than on PE [41,43]. Li et al. (2018) also showed that the adsorption affinity of sulfadiazine (SDZ) on PS through both non-specific van der Waals and  $\pi$ - $\pi$  interactions was higher than that on PE through only van der Waals interactions [54].

### 2.1.3. $\pi$ - $\pi$ Interactions

In the summary of the adsorption mechanisms of organic compounds on MPs (Table 1),  $\pi$ - $\pi$  interactions are often discussed together with van der Waals interactions. Through spectroscopic analyses, Chen et al. (2018) investigated the interaction between commercial dissolved organic matter humic acid (HA) and PS. Their results showed that PS mainly interacts with the aromatic structure of dissolved organic compounds via  $\pi$ - $\pi$  interactions and is then entrapped in the organic molecule by carboxyl-group C=O bonds within the DOM [52]. The study by Zhang et al. (2012) showed that, in addition to hydrophobic interactions,  $\pi$ - $\pi$  electron donor-acceptor interactions play an important role in the adsorption of HA and FA on porous PS [53].

## 2.2. Adsorption of Dissolved Organic Compounds on MPs: The Effect of MP Characteristics

The adsorption of dissolved organic compounds on MPs is highly affected by the characteristics of MPs, such as their particle size, porosity, and specific surface area [60]. The chemical composition of a polymer is described based on its chain structure. The polymer chains are arranged and stacked to form an aggregate structure, including crystalline and amorphous components. The influence of the aggregate structure on adsorption is usually more important than that of chain structures. In addition, other structural properties of MPs, such as their density, degree of crystallinity, and abundance of rubbery and glassy states in the amorphous region, can directly lead to different adsorption capacities [54,61].

### 2.2.1. Particle Size

The particle size of MPs is of great importance for the adsorption of dissolved organic compounds on MPs [62,63]. Chen et al. (2018) demonstrated that the affinity of MP and DOM interactions is highly dependent on the particle size of the MPs [52]. Smaller MP particle sizes possess a larger specific surface area and higher porosity, which are favorable for the adsorption of DOM on MPs [42,64,65]. Studies show that MPs' specific surface area and adsorption sites increase with decreasing particle size, which can enhance the adsorption capacity for dissolved organic compounds on MPs [40]. However, Fang et al. (2019) found that the adsorption capacity for triazole fungicide was the highest at a PS particle size of 10  $\mu\text{m}$ , followed by a particle size of 2  $\mu\text{m}$ . The reason for this phenomenon may be due to the agglomeration of MPs with particle sizes that are too small [66].

### 2.2.2. Morphological Effects

Based on molecular chain arrangements, plastic polymers can be classified into crystalline, semi-crystalline, and amorphous structures. Amorphous structures consist of rubber and glass subcomponents. Plastics in a glassy state can transform into a rubbery state at a certain temperature, which can be influenced by a few factors including chain segment fluidity [56]. The morphological transformation of plastics can influence their adsorption of organic compounds [58]. Zhao et al. (2020) found that the adsorption capacity for organic compounds on polar MPs was almost two orders of magnitude higher than that on nonpolar MPs, due to the higher proportion of rubbery states in the amorphous region of the polar MPs [67]. Liu et al. (2019) demonstrated that rubbery PS and PE possess a larger internal cavity volume in the rubbery region compared to their glassy counterparts, which favors the accumulation and adsorption of polycyclic aromatic hydrocarbons (PAHs) [68].

On the other hand, the surface characteristics and crystallinity degree of MPs can determine the adsorption of antibiotics on MPs [54]. Guo et al. (2012) also found that PEs with the same chemical composition but different crystallinities (ranging from 58.7%

to 25.5%) had varying organic carbon content-normalized sorption coefficients ( $K_{oc}$ ) for hydrophobic organic compounds. However, the study by Liu et al. (2019) found no significant relationship between bisphenol A adsorption capacity and MPs' crystallinity. These studies demonstrated that the sorption capacity between organic compounds and MPs is not only affected by the crystallinity factor but also by other factors including surface functional groups and surface roughness, which can influence the hydrophobicity of MPs and regulate the interactions between organic compounds and MPs [46,69].

### 2.2.3. Density

The density of MPs also affects the adsorption of dissolved organic compounds on MPs. For instance, low-density PE showed a higher diffusion rate for PAHs than high-density PE, demonstrating that the adsorption of organic compounds on MPs is inversely related to the density of MPs [70]. When studying the sorption behavior of three non-steroidal anti-inflammatory drugs (NSAIDs) on PE MPs with different densities, Elizalde-Velázquez et al. (2020) found that, in comparison with ultrahigh-density PE and medium-density PE, low-density PE had the highest sorption capacity for NSAIDs [71].

## 2.3. Adsorption of Dissolved Organic Compounds on MPs: The Effect of Environmental Factors

### 2.3.1. pH

The pH of media is an important factor influencing the adsorption of organic compounds on MPs, due to the fact that variations in pH can change the morphology and surface charge of organic compounds [71]. For instance, PE, PS, and PP have a net positive charge at pH values below their respective points of zero charge, i.e., 6.63, 6.69, and 6.76 [54]. The acidic condition favors the partitioning of organic compounds onto MP particles [71]. A few scholars demonstrated a gradual decrease in the adsorption of organic compounds on MPs with increasing pH [54,72,73]. However, studies also showed that the adsorption process of some organic compounds on MPs did not significantly change when the pH was altered [40,48]. For instance, Zhang et al. (2020) proposed that the pH did not significantly affect the adsorption of 9-Nitroanthrene (9NAnt) on PE. This phenomenon can be explained by the sorption of 9NAnt on PE due to the combined effects of hydrophobic interactions and van der Waals forces rather than electrostatic interactions, which are more easily affected by the pH of the medium [48,74].

### 2.3.2. Ionic Strength

The adsorption of dissolved organic compounds on MPs can be affected by the ionic strength level. An increase in ionic strength (including  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  ions) could reduce the adsorption of hydrophilic compounds but increase that of hydrophobic organic compounds on MPs [24,40,75–77]. The presence of salt ions could reduce the solubility of organic compounds and promote their hydrophobic adsorption on MPs, but the adsorption enhancement may reach a plateau when the compound's hydrophobicity no longer changes with increasing ionic strength [40]. Guo et al. (2018) found that the presence of potassium ions ( $\text{K}^+$ ) in the solution can cause competition between  $\text{K}^+$  ions and DOM for MP adsorption sites. This competition increases with the ionic strength of the solution, which results in a decrease in adsorption [78]. However, Tang et al. (2019) found that the sorption isotherms of benzene on HA were not affected by the concentration of  $\text{CaCl}_2$  in the solution, which may be due to the fact that the sorption of benzene on HA does not occur via electrostatic interactions or ion exchange [76].

### 2.3.3. UV Radiation

UV radiation is crucial in the degradation of microplastic particles in the environment [19,79,80]. UV radiation leads to the formation of carbonyl groups in the surface layer of MPs due to the introduction of oxygen. As a result, the polarity of MPs increases, which can lead to a decrease in the adsorption capacity of MPs for nonpolar organic compounds, such as benzene, toluene, ethyl benzene, and xylene [49]. Hüffer et al. (2018) suggested

that UV-induced surface functionalization decreases the adsorption coefficient of organic compounds on PS [80]. The adsorption of hydrophilic organic compounds on artificially aged (UV-accelerated aging) MPs was studied by Liu et al. (2019). Their results showed that the adsorption capacities of dissolved organic compounds on aged PS and PVC were much higher than on pristine MPs. The higher adsorption capacity of the aged MPs was caused by the enhanced hydrogen bonding and electrostatic interactions after UV radiation [68].

### 3. Release of Dissolved Organic Compounds from Microplastics

Although durability and inertness are important characteristics of plastics, studies have shown that plastics can leach additives, such as plasticizers and colorants, when encountering different environmental conditions [81–85]. Mechanical, chemical, and biological processes can cause fragmentation, embrittlement, and modification of MPs in aquatic environments. For instance, Shi et al. (2021) found that the photoaging of polycarbonate MPs could facilitate the fragmentation of PC MPs and enhance bisphenol A release [82]. Romera-Castillo et al. (2018) estimated that, globally, up to 23,600 metric tons of dissolved organic carbon (DOC) can be leached from marine plastics each year. Leached DOC is crucial for the composition and activity of microbe communities in seawater [23]. The environmental modification and weathering processes of MPs in aquatic systems can result in the loss of their surfactants, accelerating the release of organic compounds from MPs into the environment [17].

Besides leaching artificial additives (i.e., plasticizers, colorants, and flame retardants), MPs can also leach absorbed organic compounds into the environment. After irradiation with UV and visible light, Chen et al. (2019) detected the release of organotin compounds (OTCs) from PVC microplastics (MPs) [86]. Four types of OTC, namely dimethyltin (DMT), monomethyltin (MMT), dibutyltin (DBT), and monobutyltin (MBT), were observed to be released from PVC in the dark. However, upon exposure to UV-visible light, only DMT and DBT were detected. This can be attributed to the rapid photodegradation of MMT and MBT [83].

#### 3.1. Effects of MPs' Characteristics

The concentration of organic compounds released from PE is almost four times higher than that released from PP, indicating that the leaching concentration of porous organic matter varies with the type and characteristics of the polymer [23]. Lee et al. (2020) found that the desorption of the MP-derived additive BPA from rubbery PE and PP is usually greater than that from glassy PVC and PS [17]. Research has demonstrated that the molecular chain segments in the glassy subcomponent are denser and more tightly linked than those in the rubbery subcomponent. As a result, the molecules located in the amorphous regions are less densely packed and more prone to decomposition than those in the crystalline regions [87]. The adsorption process in the glass subcomponent is affected by partitioning and space filling [88]. Furthermore, space filling results in a lag in release, primarily due to the conformational changes and distinct physical formation of pores during adsorption and release [89]. It is evident that the release mechanism of MPs can be affected by their distinct morphologies, which alter their conformation.

Organic compounds' release efficiency can be affected by plastic materials such as polymers and additives. Lee et al. (2020) compared the concentration and fluorescence characteristics of DOM released from four different plastic materials (two polymers, PVC and PS, and two additives, DEHP and BPA) under dark and light conditions. Their results showed that even small amounts of additives added to the polymers can increase the possibility of organic compounds being leached from MPs into the aqueous environment [17]. Based on linear model fitting, Zuo et al. (2019) found that the adsorption capacity for phenanthrene (PHEN) was much higher on the biodegradable plastic poly(butylene adipate co-terephthalate) (PBAT) than on conventional plastics, such as PE and PS. The sorption and desorption capacities of MPs are highly dependent on their molecular properties, such as the abundance of rubbery subfractions [90].

### 3.2. Effects of Environmental Factors

Various environmental factors can affect the release of organic compounds from MPs. Liu et al. (2019) found that the release of the MP additive BPA increased significantly as the pH increased from 3.0 to 11.0 [46]. This result can be explained by the fact that under alkaline conditions, BPA becomes ionized and promotes MP hydrolysis, which increases the solubility and release of BPA [46]. Suhrhoff and Scholz-Böttcher (2015) investigated the impact of salinity, UV radiation, and turbulence on the leaching of plastic-derived organic additives (citrate, phthalates, BPA, etc.). A positive relationship between turbulence and the magnitude of plastic-derived additive leaching was found. In contrast to turbulence, salinity has a minor impact on organic additive leaching from MPs. The effect of salinity highly depends on the inherent properties of plastics. The reason for this is that changes in salinity can alter the water and compound chemistry, affecting the pH, ionic strength, polarity, and other parameters [19]. Chen et al. (2019) found that the release of organotin compounds from PVC particles was inhibited under high-salinity conditions, probably due to organotin's re-adsorption on PVC [86].

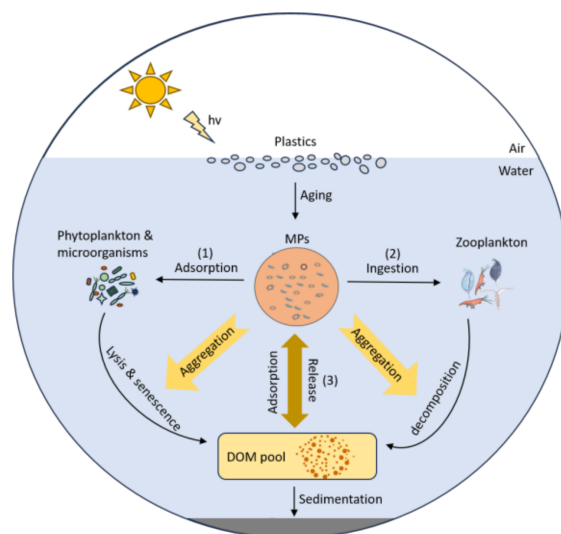
The weathering or aging of MPs can lead to changes in MPs' surface and their release of organic compounds. Lee et al. (2020) investigated the leaching of DOM from additive-free MPs in artificial freshwater under UV radiation and dark conditions. Their results showed that UV radiation facilitated the release of DOM from plastic polymers, and the amount of leached DOM was approximately 3% of the total plastic mass [91]. Lee et al. (2020) explored the fluorescence signature of DOM leached from two plastic polymers (PVC and PS), two additives (diethylhexyl (DEHP) and BPA), and two commercial plastics. They found that UV radiation facilitated the leaching of plastic-derived DOM. Under UV radiation, one humic-like component (Ex/Em = 235(290)/410 nm) and one protein/phenol-like fluorescent component (Ex/Em = 270/309 nm) were found to have strong correlations with the polymer-derived DOM [17].

## 4. Impacts of MPs on Natural DOM in Aquatic Ecosystems

DOM is ubiquitous and plays an essential role in aquatic ecosystems by regulating underwater light and providing an energy source for microorganisms [92,93]. The primary source of autochthonous natural DOM in water is living phytoplankton, which release DOM through lysis, senescence, and grazing [94]. Numerous studies have investigated the toxicity effects of MPs on phytoplankton in water; however, very little is known about the impact of MPs on the phytoplankton production of natural DOM. One recent study by our research group found that light-aged MPs could decrease algal DOM production by 38% and modify the chemical composition of natural DOM by increasing the aromaticity and molecular weight [95]. Compared to direct DOM leaching, the impact of MPs on phytoplankton production of DOM may be more important to natural DOM cycling in water (Figure 1).

Since natural DOM is a heterogeneous organic mixture (ranging from small amino acids to large humic substances) with various functional groups [96], the aforementioned mechanisms (hydrophobic interactions, van der Waals interactions,  $\pi$ - $\pi$  interactions, hydrogen interactions, and electrostatic interactions) can apply to the interactions between MPs and natural DOM in aquatic environments. In addition, as the molecular structure of natural DOM is much more complex than that of a single organic compound, several mechanisms often coexist for the adsorption of natural DOM on MPs.

Firstly, MPs can affect the physicochemical state of natural DOM in water. Natural DOM in the water column can quickly form organic aggregates due to adsorption on MPs via covalent bonding, hydrogen bonding, or other reactive functional groups, which can lead to the co-precipitation of natural DOM with particulate organic matter (POM). Galgani et al. (2018) observed an accumulation of chromophoric DOM (CDOM) in the sea surface microlayer when MPs were present [97]. Chen et al. (2018) found that 10 ppb nanoplastic particles in the water column accelerated DOM-POM aggregation due to the hydrophobic kinetic assembly [38].



**Figure 1.** Schematic diagram of the impacts of microplastics (MPs) on the production and transformation of natural dissolved organic matter (DOM) in water. These processes are as follows: (1) MPs affect the autochthonous production of DOM by interacting with phytoplankton and microorganisms; (2) MPs affect DOM production by interacting with zooplankton; and (3) MPs affect DOM production and transformation by releasing and adsorbing organic molecules.

Secondly, MPs can influence the natural DOM cycle by altering the microorganism community in water [98]. Microorganisms are closely associated with MPs in water and sediments and play a crucial role in aquatic biogeochemical cycles [99]. MPs can move up the food chain and quickly become part of the biogeochemical cycles in the water column. They can act as a carbon source for elemental cycling [100]. Planktonic microorganisms can attach to or aggregate with MPs or actively consume or break down MPs [101]. Environmental factors, such as photo-oxidation, can cause microplastics to age and change their surface morphology, roughness, and chemical properties. These changes can increase microbe adhesion, provide favorable conditions for biofilm formation, and ultimately accelerate the biodegradation of MPs [99]. Studies have shown that microorganisms can actively interact with or passively attach to MPs, using available electron acceptors to break down these polymers. These intermediate degradation products may act as electron donors for microbial utilization [101]. On the other hand, the adsorption and release of DOM by MPs can impact the productivity and structure of microbial communities in natural water bodies [101]. Andres et al. (2019) proposed that DOM released by MPs could explain the different characteristics of carbon substrate utilization by microorganisms attached to MPs compared to microorganisms in the surrounding water [102]. Pinto et al. (2020) demonstrated that certain prokaryotes can survive solely on MPs and are relatively abundant in various water masses of the global ocean [103]. Recent studies have shown that the release of DOM from MPs can stimulate microbial utilization of DOC in water [104,105]. However, the article by Oberbeckmann and Labrenz (2020) reviewed the role of microbial interactions with MPs in marine ecosystems and demonstrated that MPs in the ocean represent recalcitrant substances for microorganisms that probably would not be microbially degraded [105].

Finally, MPs can influence natural DOM cycling by interacting with zooplankton. Fecal pellets excreted by zooplankton are not only a food source for marine organisms but also part of the biological pump that contributes to the marine vertical flux of POM, an important source of DOM in water. Cole et al. (2016) found that zooplankton that ingested marine MPs could reduce the density, structural integrity, and sinking rate of their fecal pellets. This interference can hinder the biological transport of carbon from the ocean surface to the deep sea [106]. This result was also observed by Corsi et al. (2020), who demonstrated that the adsorption of MP particles on the surface or their internalization



in feces reduced their motility and affected their sinking or floating behavior, ultimately affecting the “sink” of natural DOM [107].

## 5. Conclusions and Future Perspectives

The present review on the interactions between MPs and dissolved organic compounds addressed the following research issues: the adsorption mechanism of dissolved organic compounds on MPs and environmental factors; the release of dissolved organic compounds from MPs and environmental factors; and the impact of MPs on natural DOM cycling in aquatic ecosystems. Although researchers have made progress in understanding how organic compounds are absorbed and released by MPs in water, the mechanisms that drive the adsorption and release behaviors of dissolved organic compounds on MPs are still not fully understood. More importantly, there has been little investigation into the direct interactions between MPs and natural DOM in aquatic environments. Specifically, the impacts of MPs on the production and transformation of natural DOM in aquatic ecosystems are unanswered questions. In addition, the interactions between aquatic organisms and MPs are numerous and complex, and the nature of their interactions has not yet been thoroughly investigated. The following knowledge gaps require further studies:

(1) Thus far, studies have concentrated on the adsorption of specific organic pollutants on MPs, and little information is available on the direct interactions between MPs and natural sources of dissolved organic compounds.

(2) A few recent studies reported the magnitude of DOM released from MPs in water; however, the significance and contribution of DOM released by MPs to aquatic carbon cycling require further evaluation.

(3) The topic of “MPs have the potential to become a local hotspot for microbial activity and influence the carbon cycling process in water” has been widely proposed. Nevertheless, to what extent MPs influence microorganism metabolism linked to carbon cycling remains an enigma.

This review highlighted the interactions between MPs and natural DOM, offering a limited understanding of the interactions between MPs and dissolved organic compounds in water. Due to the wide variety of MPs and natural DOM, future advances in understanding the impact of MPs on the magnitude and transformation of dissolved organic compounds are urgently needed.

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