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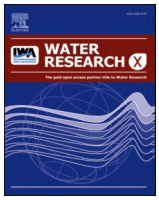

Nanoplastics are significantly different from microplastics in urban waters

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ABSTRACT

Microplastics (MPs) and nanoplastics (NPs) are ubiquitous and intractable in urban waters. Compared with MPs, the smaller NPs have shown distinct physicochemical features, such as Brownian motion, higher specific surface area, and stronger interaction with other pollutants. Therefore, the qualitative and quantitative analysis of NPs is more challenging than that of MPs. Moreover, these characteristics endow NPs with significantly different environmental fate, interactions with pollutants, and eco-impacts from those of MPs in urban waters. Herein, we critically analyze the current advances in the difference between MPs and NPs in urban waters. Analytical challenges, fate, interactions with surrounding pollutants, and eco-impacts of MPs and NPs are comparably discussed., The characterizations and fate studies of NPs are more challenging compared to MPs. Furthermore, NPs in most cases exhibit stronger interactions with other pollutants and more adverse eco-impacts on living things than MPs. Subsequently, perspective in this field is proposed to stimulate further size-dependent studies on MPs and NPs. This review would benefit the understanding of the role of NPs in the urban water ecosystem and guide future studies on plastic pollution management.

1. Introduction

The wide application of plastics in our lives has resulted in a huge amount of waste plastic debris in the environment, and it was estimated that about 400 Mt of plastic wastes were generated globally in 2019 (Liu et al., 2023; Yuan et al., 2021). Worse still, the recent COVID-19 pandemic has largely exacerbated global plastic pollution due to a sharp increase in the use of single-use plastic products (Adyel, 2020). Currently, plastic wastes have been identified in various environmental matrixes, including water, ambient air, soil, sediment, and biota (Lai et al., 2021). Among these, plastic wastes in urban waters (e.g., drinking water, freshwater, receiving water, stormwater, sludges, and wastewater) are of growing concern as they are closely linked with human quality of life. Small plastic debris in urban waters, especially microplastics (MPs, 100 nm - 5 mm) and nanoplastics (NPs, $<$ 100 nm), are considered as troublesome pollutants due to their difficult removal and accumulation in human bodies through the food chain (Luo et al., 2023; Xu et al., 2021). The management of MPs and NPs in urban waters is thus an urgent and challenging environmental problem, and a good understanding of the formation, occurrence, fate, interactions with other pollutants, and eco-impacts of MPs and NPs in urban waters is a prerequisite.

Naturally, MPs and NPs are generated from large plastic debris through various processes, such as mechanical wear, weathering/aging, photolysis, hydrolysis, heat, and biological fragmentation (Arpia et al., 2021; Shi et al., 2022). MPs and NPs can also originate directly from plastic products (e.g., industrial abrasives, exfoliants in personal care products, and accidental spills) (Chen et al., 2022c). In earlier studies, NPs have largely been treated as an extension of MPs, and have not been analyzed separately. The main reason for this is their similar origin and composition. However, an avalanche of investigations shows that NPs in urban waters differ from MPs in terms of their analytical challenges, transport properties, interactions with pollutants, bio-effects, and removal behavior (Gigault et al., 2021). Theoretically, a 2 mm polyvinyl chloride (PVC, a density of $\sim$ 1.4 g/cm^3) bead is determined to settle in water at a rate of about 87 cm/s according to Stokes' law (for ideal conditions), while the settling rate of a 100 nm PVC bead would be $\sim$6.9 cm/year. Thus, NPs and MPs would show distinct transport and fate behavior in urban waters, due to their different physicochemical properties (Fig. 1). NPs appear to remain homogeneously dispersed in water systems for quite a long time, which would lead to analytical and removal difficulties. Also, the higher toxicity of NPs compared to MPs to eco-systems has been identified (Ma et al., 2016) and reviewed (Yin et al., 2021a). To this end, clarifying the differences in the analysis, fate, interactions with pollutants, and eco-impacts of NPs and MPs is vital for gaining a full picture of pressing plastic pollution in urban water

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systems. Currently, a handful of informative reviews have analyzed the MPs and/or NPs pollution in terms of their origin, analysis, removal, transport, and eco-impacts (Chen et al., 2022a; Dong et al., 2023; Gaylarde et al., 2021; Huang et al., 2022, 2021a; Ivleva, 2021; Larue et al., 2021; Roy et al., 2022; Zhao et al., 2022), in most cases, MPs and NPs are discussed as a whole pollutant and the differential features have not been thoroughly analyzed. Therefore, a comprehensive review on the different analytical challenges, fate, interactions with pollutants, and eco-impacts of MPs and NPs is still highly needed to guide guiding further precise plastic pollution control in terms of developing advanced analytical techniques, understanding fate, designing efficient removal strategies, etc.

In this Review, we examine the current understanding of the differential characteristics of MPs and NPs in urban waters. Analytical challenges, fate, interactions with pollutants, and eco-impacts of MPs and NPs are discussed. With these analyses, we aim to provide a clear cognitive profile of MPs and NPs in urban waters. Finally, perspective in this field is proposed to stimulate further studies on MPs and NPs, especially the more challenging NPs.

2. Analysis of NPs is more challenging than MPs

The accurate characterization, chemical identification, and quantification of MPs and NPs in urban waters is critical for assessing actual risks associated with these tiny plastics. To date, various mass-based and particle-based qualitative and quantitative analyses of MPs and NPs have been developed. Prior to quantification, chemical identification of polymer types is suggested to ensure the reliability of analytical results, especially when analyzing complex samples (Cai et al., 2021).

2.1. Mass-based methods

Some sophisticated mass-based methods allow effective analysis of MPs, such as thermal degradation-GC/MS (gas chromatography/mass spectrometry) (El Hayany et al., 2020; Hendrickson et al., 2018), TD-PTR/MS (thermal desorption-proton transfer reaction-mass spectrometry) (Materić et al., 2020), TGA-MS (thermogravimetric analysis/mass spectrometry) (David et al., 2018), TGA-DSC (thermogravimetric analysis/differential scanning calorimetry) (Majewsky et al., 2016), and inductively coupled plasma (ICP)-based methods (Klöckner et al., 2019; Wang et al., 2017). Among these methods, thermal-related methods focus on analyzing MPs' conversion products generated under typical temperatures and atmospheres, while ICP-based methods are performed to detect and quantify MPs' typical chemical components (e.g., trace elements) (Wang et al., 2017). Overall, these mass-based methods can also be used for NPs characterization owing to the common analytical mechanism (Blancho et al., 2021; Sullivan et al., 2020), while fewer attempts have been reported. However, the sampling/pretreatment processes for NPs are more complex than the dead-end filtration process for MPs. Generally, digestion (acid/hydrogen peroxide/alkali treatment) (Schwaferts et al., 2019), preconcentration (ultrafiltration, continuous flow centrifugation, cloud point extraction, and ultracentrifugation) (Shi et al., 2023; Zhou et al., 2018), and separation treatments (asymmetrical flow field-flow fractionation, size-exclusion chromatography) (Correia and Loeschner, 2018) of NPs are required to ensure the quality of subsequent analytical methods.

2.2. Particle-based methods

Particle-based methods, mainly microscopic and spectroscopic techniques, have been widely used for the characterization of organic polymers. Based on the interaction of plastics' molecular vibrations with typical radiation, Raman spectroscopy and Fourier transform infrared (FTIR) are widely used to determine the type, number, size distribution, and shape of polymers in plastics (Ivleva, 2021). For MPs analysis, FTIR and Raman spectroscopy as well as optical microscopy can provide meaningful identification and quantification information. However, the smaller size of NPs makes the far-field geometric optics-based chemical analysis and imaging inaccurate. Specifically, when the size of particles (NPs) is smaller than the wavelength of infrared (700–1000 nm) or visible (400–700 nm) lights, the optical diffraction would be significant, leading to an Abbe diffraction resolution limit (approximately 200 nm) for analytical techniques that depend on transmitted/reflected light (bright-field microscopy and micro-FTIR) or laser spot sizes (micro-Raman spectroscopy) (Gigault et al., 2021). Accordingly, diffraction-unlimited optical microscopy (e.g., stimulated emission depletion microscopy, nonlinear structured illumination microscopy) (Dedecker et al., 2008) or electron microscopy (Wang et al., 2020) is demanded to precisely image NPs. Compared to far-field light techniques which are incompatible with the full characterization of NPs, near-field techniques can evade the diffraction resolution limitation by confining the light to an evanescent field (Bouloumis and Nic Chormaic, 2020; Jakubowicz et al., 2021).

2.3. Integrated methods

The development of integrated techniques that combine the advantages of different methods is becoming a trend in the analysis of NPs and MPs. The scanning electron microscopy (SEM)-Raman spectroscopy combination has been demonstrated for the identification and visualization of 100 nm polystyrene (PS) particles (Fang et al., 2020). Atomic force microscopy (AFM)-spectroscopy techniques (AFM-IR, AFM-Raman) can achieve a better spatial resolution at the nanoscale

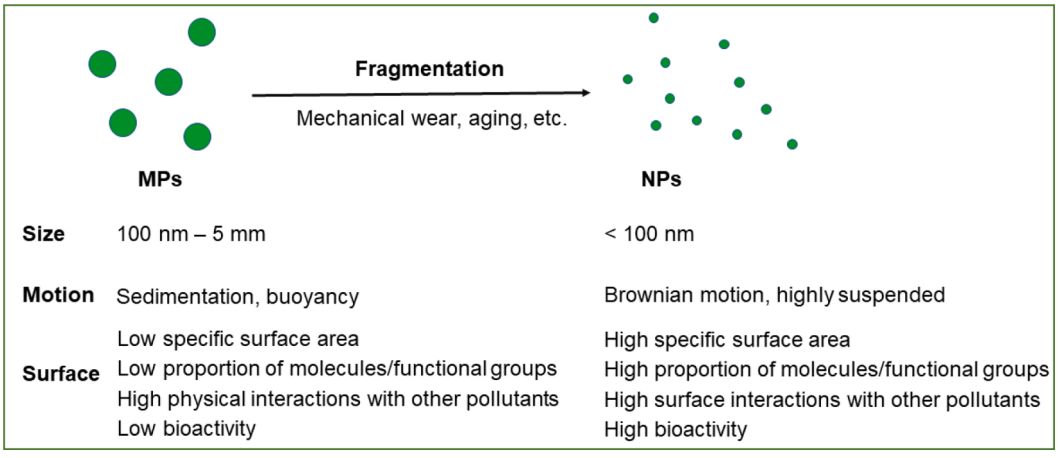

Fig. 1. The highly different physicochemical properties of MPs and NPs in urban water systems.

(approximately 20–50 nm) (Dazzi and Prater, 2017). By online coupling of Raman microspectroscopy and field-flow fractionation enabled by optical tweezers, Schwaferts et al. realized tiny particle separation and characterization in the size range of 5 to 0.2 μm (Schwaferts et al., 2020). These demonstrations highlight the cooperation of diverse methods in the analysis of NPs and MPs, and the optimal technique depends on the properties of plastics (e.g., size, concentration, shape) and the associated water matrix (e.g., (in)organic pollutants, pH) for real sample analysis.

3. Fate of NPs is more complex than that of MPs

The different physicochemical characteristics of MPs and NPs influence their fate in urban waters. The colloidal nature and dominant Brownian motion of small and light NPs would severely limit their buoyancy/sedimentation-driven vertical transport, compared to MPs made from the same material. Therefore, NPs tend to remain homogeneously dispersed in urban waters, while MPs will sink or float. Such differences lead to different environmental fates of MPs and NPs.

3.1. Transport

Urban waters are important sources and sinks of MPs and NPs. When MPs and NPs enter the urban water system, they can transport with the water flow or deposit in the sediment. Plastic size, density, shape, surface chemical properties, surrounding substances (e.g., clay, natural organic matter (NOM)), and hydrodynamic and hydrometeorological factors largely govern the transport of MPs and NPs (Huang et al., 2022). Notably, although we have mentioned that NPs will be in a highly dispersed state in urban waters, aggregation of NPs would result in larger particles that are likely to deposit in the sediment (Gigault et al., 2021). NPs can homo-aggregate with NPs and hetero-aggregate with colloids (clays, algae, anthropogenic materials, and dissolved organic matter (DOM)) in urban waters (Alimi et al., 2018). The aggregation of NPs is controlled by their size, surface chemical properties, ionic strength of water, and surrounding chemicals/colloids. According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, particles with larger sizes are less likely to aggregate with surrounding substances, leading to higher stability and mobility in urban waters. As evidenced by Song et al., MPs with a size of 200 nm size were more stable and did not form aggregates, while the 50 nm NPs could efficiently aggregate with organic matter and metal ions in the same aqueous condition (Song et al., 2019). This study also highlighted the importance of surface functional groups in the hetero-aggregation of NPs. In addition, the concentration, valence, and hydration ability of cations (e.g., Ca^{2+}, Mg^{2+}, Na^{+}) jointly affect the aggregation rate and aggregate structure of NPs (Mao et al., 2020; Sun et al., 2021), and high salinity and high valence of cations promote the aggregation of NPs (Hou et al., 2022). Interestingly, extracellular polymeric substances (EPS) have been shown to negatively affect NPs aggregation due to steric effects (Mao et al., 2020). Such environmental factors have a disproportionate effect on the aggregate/attachment efficiency of NPs compared to MPs because of the leading role of plastic particles' surface properties. In addition, the collision rate for NP aggregation is controlled by Brownian diffusion and structural layer force (Sun et al., 2021) rather than by fluid motion, settling, and sedimentation. Therefore, the fate of NPs in urban waters could not be directly deduced from that of MPs, and is more complex than that of NPs.

3.2. Aging and decomposition

In urban waters, the natural aging and decomposition of MPs and NPs regulate their physicochemical properties and thus their fate. For MPs, degradation/aging through natural abiotic and/or biotic processes (such as biodegradation, photodegradation, photolysis, mechanical, chemical, and thermal routes) leads to the destruction of structural and mechanical characteristics (da Costa et al., 2016). Thus, the specific surface area of aged MPs is increased, and the surface of aged MPs has a high proportion of organic molecules (functional groups, especially -OH and -COOH), which enhances plastic surface interactions with microbial and other contaminants (Ali et al., 2021a). At present, the natural aging and decomposition of NPs in urban waters is less explored, as MPs and NPs are in most cases co-occurring. However, it is reasonable to assume that aging could influence the colloidal stability and transport of NPs by regulating the surface chemistry (surface functional groups, surface charge), which is an important factor in controlling aggregation. In addition, compared to MPs, NPs with smaller size and weight are less likely to be destroyed by a mechanical process. Also, NPs dispersed in the water body and deposited in the sediment are less likely to be affected by light-induced oxidation processes.

3.3. Removal

In urban water systems, wastewater treatment plants (WWTPs) play a critical role in the removal of MPs and NPs. It is suggested that the overall removal efficiency of MPs reaches 94–99% with the primary, secondary, and tertiary units (Ali et al., 2021a; Sun et al., 2019). For the removal of NPs, the tertiary unit can make a large contribution (Mohana et al., 2021). Nevertheless, it should be noted that none of the current studies provides a definitive removal efficiency of NPs in WWTPs, as most of the detected plastic debris has a size larger than 1 μm and the detection of NPs remains a major challenge (Ali et al., 2021a). Therefore, the fate of NPs in WWTPs needs further investigation based on precise quantification.

4. Interactions of NPs with other pollutants are stronger than MPs

In real urban water conditions, MPs and NPs coexist with different substances. Compared to MPs, the high surface-to-volume ratio and rich surface functional groups of NPs allow more contact with other pollutants in urban waters, including inorganic metal ions and clays, organics, microbes, etc. The interaction of MPs and NPs with surrounding pollutants leads to the formation of composite pollutants, which can affect the analysis, fate, toxicity, and removal of plastics (Ali et al., 2021a; Yu et al., 2021).

4.1. Abiotic pollutants

The interaction of MPs and NPs with abiotic pollutants is mainly driven by van-der-Waals force, hydrophobic/hydrophilic interaction, pore-filling interaction, hydrogen bonding, surface complexation, electrostatic interaction, and π-π interaction (Chen et al., 2022b; Yu et al., 2021). Thus, plastics' size, surface area, and surface chemistry (functional groups) are principal factors influencing the interaction between surrounding abiotic pollutants and plastic particles. Theoretically, reducing the particle size can increase the interaction strength and frequency due to the increased surface area-to-volume ratio, specific surface area, and exposed functional groups (Yu et al., 2021). For example, Velzeboer and co-workers studied the adsorption behavior of typical organic contaminants (polychlorinated biphenyls (PCBs)) on polyethylene (PE) MPs (10–180 μm) and PS NPs (70 nm) and unveiled that the adsorption capacity of PS NPs was 1–2 orders of magnitude higher than that of PE MPs (Velzeboer et al., 2014). This study also suggested that the interaction of MPs and NPs with pollutants was influenced by NOM, pH value, metal ions, etc. Similarly, Wang et al., suggested that the aggregation of NPs would reduce the adsorption capacity (Wang et al., 2019).

Aside from artificial organic contaminants, the interaction of metal ions with MPs and NPs should also be investigated. The oxygen-containing functional groups on MPs and NPs lead to an affinity between metal ions and plastic debris. For MPs, the metal ions will adsorb

on the surface and settle or flow with the MPs, and MPs' porosity, surface area, and morphology are key factors affecting the sorption capacity (Ali et al., 2021a). Differently, the interaction of metal ions with NPs results in the aggregation of NPs by compressing the electric double layer on the particle surface (Xiong et al., 2020), and high-valence metal ions (e.g., Fe^{3+}) are more likely to induce NPs aggregation than low-valence counterparts (e.g., Na^{+}) (Cai et al., 2018). The interaction between metal ions and NPs can be regulated by aging. The ultraviolet irradiation aging process can inhibit the aggregation of PS NPs in a NaCl solution by increasing the negative charge on the surface of PS NPs and the organic matter content in the solution, while it can promote PS NPs aggregation in $CaCl_2$ solutions due to the interactions between Ca^{2+} and carboxyl groups formed on the surface of PS NPs (Liu et al., 2019).

NOM, which is ubiquitous in natural waters, with different chemical groups (e.g., -OH, -COOH, and phenolic groups) is expected to adsorb onto the plastic surface and further regulate the surface properties of plastic particles (Chen et al., 2018; Wei et al., 2022). Current studies suggest that the adsorption of NOM on MPs and NPs will form a protein layer (Ali et al., 2022). Several reports indicated that the adsorption of humic acid (HA) and sodium alginate could improve the aggregation of PE MPs (Li et al., 2019) and PS MPs (Pradel et al., 2021), respectively. However, Li and co-authors found that NOM had a negligible effect on MPs and coexisting clay, at low ionic strength (Li et al., 2021a). For the study of NPs, NOM (e.g., HA) showed an insignificant effect on the heteroaggregation of PS NPs because of the steric hindrance according to the DLVO theory (Li et al., 2019). However, the addition of NaCl could regulate the interaction among HA, PS NPs, and suspended sediment, thereby facilitating the heteroaggregation and co-settling of NPs, suspended sediment, and HA mixture (Fig. 2a) by reducing the electrostatic repulsion between PS NPs and large suspended sediment. In general, the interaction of NOM with NPs has little effect on dispersed NPs by boosting particles' steric hindrance and electrostatic repulsion. However, NOM could increase or decrease the aggregation of PS NPs in Fe^{3+} solutions at different ion concentrations (Cai et al., 2018). To this end, the interaction of NPs with NOM is greatly affected by other coexisting substances in urban waters, and it is necessary to include NPs,

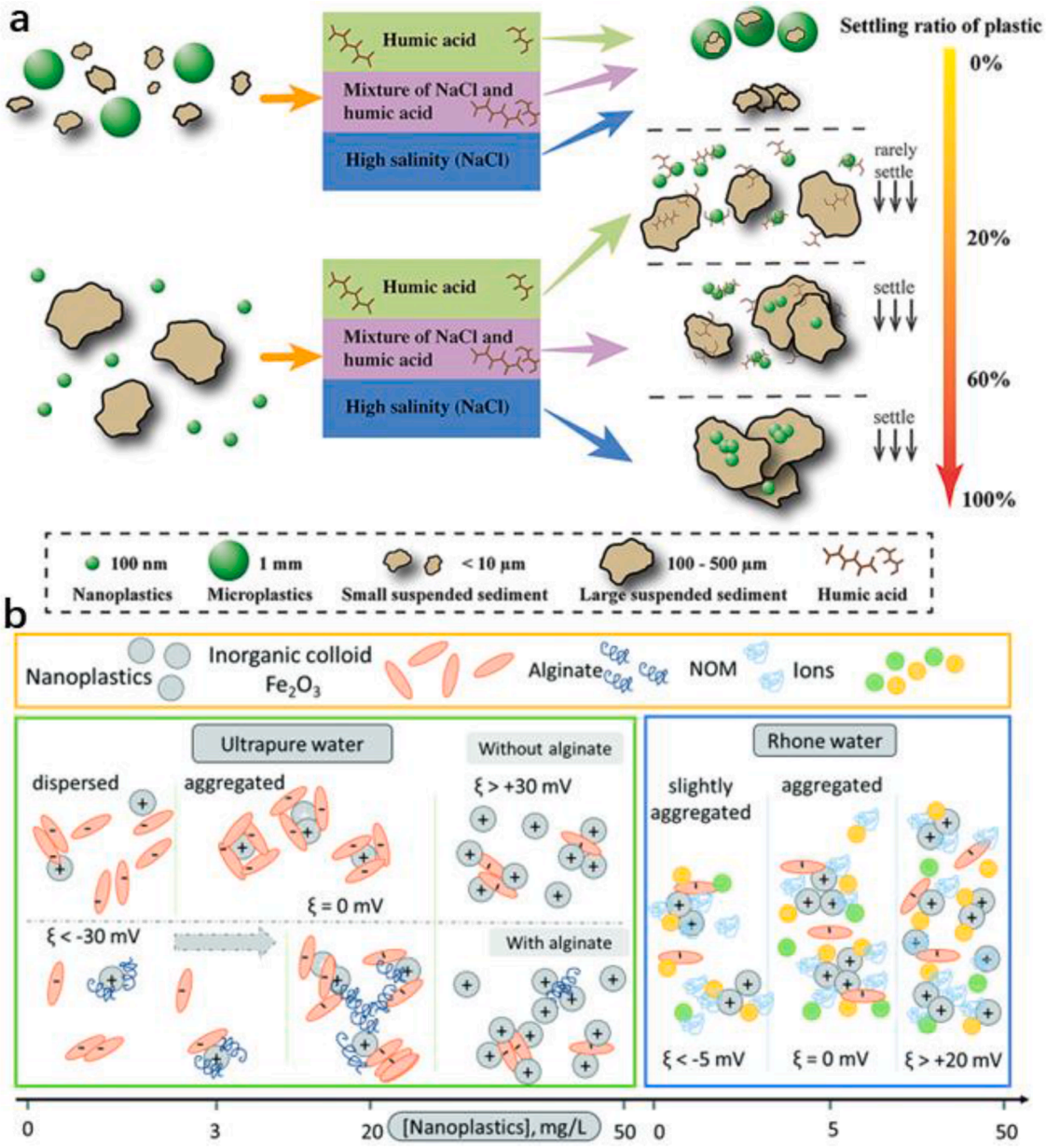

Fig. 2. (a) Interactions of PS MPs and NPs with suspended sediment in water (Li et al., 2019); and (b) Heteroaggregation of PS NPs in various waters and in the presence of different abiotic pollutants (Oriekhova and Stoll, 2018).

NOM, ions (ionic strength), and suspended matter when discussing the interaction between NPs and abiotic pollutants (Song et al., 2019). In 2018, Oriekhova et al. examined the interaction of NPs with Fe_2O_3 particles, ions, and alginate mixtures, at different concentration ratios. As depicted in Fig. 2b, the electrostatic effect was found to play a critical role and the maximum heteroaggregation was observed at the isoelectric point of heteroaggregate. Furthermore, the addition of alginate caused the shift of the maximum heteroaggregation to higher NP concentrations because of the neutralization of excess negative charges (Oriekhova and Stoll, 2018). Naturally, the components and concentrations of NOM, MPs, NPs, suspended colloids, and ions/ionic strengths in urban water vary regionally and seasonally, which would make it quite challenging to understand their interaction. Hence, it is too early to conclude and differentiate the interaction of MPs and NPs with abiotic pollutants.

4.2. Biotic pollutants

Compared to most microbes, NPs have a smaller size, indicating potential differences in microbial interaction with MPs and NPs. MPs are large enough to serve as a substrate for microbial colonization and the development of biofilms (Miri et al., 2022). The involved microbes form a large part of the microbe-MPs heteroaggregates and would influence the distribution and fate of MPs by changing the effective density, but the whole heteroaggregate particle remains primarily MPs (He et al., 2022). Differently, NPs may be a minor portion of the large NP-microbe complex and represent a small proportion of the mass of the formed microbes-NPs heteroaggregates (Gigault et al., 2021). In this case, the properties of NPs would have a relatively small effect on the fate of the microbes-NPs complex, and some coexisting pollutants (e.g., NOM, heavy metals) may have a large effect. Apart from the composition of plastic-microbe heteroaggregates, another issue related to the plastic-microbe interaction is the biodegradation of MPs and NPs. The biodegradation process generally involves the attachment of microbes on MPs and NPs, biofilm formation, exoenzymes-driven biodeterioration, depolymerization/fragmentation, assimilation, and final mineralization (Ali et al., 2021b). Although the difference in the biodegradation between MPs and NPs remains unclear, recent results have provided some interesting information. Wu et al. found that PS MPs with a smaller particle size (75 μm) were more easily colonized by biofilms than the 4 mm counterparts. On the 4 mm MPs surface, a thin layer of biofilm was noticed, while the 75 μm MPs formed heteroaggregates with biofilms (Wu et al., 2022). Accordingly, when the size is further reduced to 100 nm, the interaction between biofilms and NPs would further intensify the colonization process and modify NPs' properties. In another study, PS NPs (100 nm) showed a more significant negative effect on the nitrogen and carbon cycling of freshwater biofilms than MPs (0.5 μm, 1 μm, and 9 μm) (Miao et al., 2019).

5. Eco-impacts of NPs are higher than those of MPs

MPs and NPs, together with their associated chemical additives, heavy metals, and organic pollutants, form a complex pollutant system in urban waters. These pollutants have shown ecotoxicological effects on aquatic organisms and even humans (Lehner et al., 2019). Compared to MPs, a remarkably higher proportion of the additives/molecules/adsorbed pollutants on NPs surface leads to much higher surface reactivity and bioavailability. More importantly, the size of NPs is closer to that of natural proteins, making it easier for NPs to cross biological membranes via passive diffusion and endocytosis pathways (Huang et al., 2021b; Liu et al., 2021). This section discusses the current understanding of the different eco-impacts of MPs and NPs in urban water systems.

5.1. Biological wastewater treatment processes

In biological wastewater treatment systems, MPs and NPs can have an impact on microbes and regulate the associated water treatment processes. Generally, NPs play a more prominent role than MPs. Zhou et al. found that nitrogen removal by activated sludge was limited by PS NPs (100 nm) but not influenced by MPs (100 μm). This was because NPs could cause acute toxicity to activated sludge via induced reactive oxygen species (ROS) production and lactate dehydrogenase (LDH) release, decrease nitrifiers and denitrifiers, and suppress nitrification and denitrification genes (Fig. 3) (Zhou et al., 2022). The more significant inhibitory effect of PS NPs (50 nm) on nitrification was also reported by Lee et al., who found that the observed effects of PS NPs on nitrification should be owing to the disruption of the membrane potential of the cells (Lee et al., 2022). Similar results also suggested the more significant effect of NPs than MPs on the production of fuels (e.g., hydrogen, methane), in anaerobic digestion processes (Wang et al., 2022, 2023; Zhang et al., 2020).

5.2. Aquatic plants

NPs and MPs have different effects on plants (plankton, macrophytes) in urban water systems. As reported, nearly 90% of studies investigating the effects of NPs on phytoplankton suggested NPs had toxic effects, while 90% of concerned studies indicated that MPs (1–10 μm) had no toxicity (Larue et al., 2021). In general, MPs only influence plants by clogging the nutrient transport channel (Li et al., 2021b). Differently, NPs, which can be absorbed and migrated through plants, show more complicated phytotoxicity. Furthermore, NPs can internalize into plant tissues and cause damage to plant tissues via the regulation of cell membranes/endomolecules, and ROS-induced genotoxicity and cytotoxicity (Maity and Pramanick, 2020; Yin et al., 2021b). Germination, elongation growth, biomass, and photosynthesis are the most frequently studied parameters of plant stress responses to MPs and NPs (Mateos-Cárdenas et al., 2021). Compared to PS MPs (100 μm), PS NPs (100 nm) show more significant adverse effects on algal (*Chlamydomonas reinhardtii*) growth and reproduction over a wide concentration range of 50–500 mg/L (Yan et al., 2021). Weert and co-authors studied the influence of PS MPs and NPs on the growth of two macrophytes (*Myriophyllum spicatum* and *Elodea* sp.). The negative effect of NPs on the two types of macrophytes was more prominent than that of MPs, in terms of the relative growth rate, root and shoot dry weight, shoot/root ratio, and shoot length. Interestingly, a dose-dependent negative effect was witnessed in all tests related to NPs. Nevertheless, for the MPs, this dose-dependent phenomenon was only observed in the main shoot length of *Myriophyllum spicatum* (van Weert et al., 2019).

Notably, although most studies suggest that NPs are more toxic to plants than MPs, there are some exceptions. Jiang and co-authors examined the effect of 5 μm PS MPs and 100 nm PS NPs on *Vicia faba*. The PS MPs entered the root tissue of *Vicia faba* and exhibited higher toxicity than the smaller NPs on plant weight (Jiang et al., 2019). In another study, the vascular plant *Lepidium sativum* exposed to 4.8 μm, 500 nm, and 50 nm plastics for 8 h showed germination rates of 21%, 46%, and 56%, respectively. The reason for this was that larger MPs led to a more severe blocking effect and thus a more significant delay in germination (Bosker et al., 2019). In this context, the effects of MPs and MPs on plants need to be studied in detail, and the plastic dose, exposure time, and plant type should receive more attention (Agathokleous et al., 2021).

5.3. Aquatic animals

The size-dependent effects of plastic debris on aquatic animals (e.g., zooplankton, fish) are also significant. NPs enter body tissues and cells more easily, and it is extremely challenging to remove these tiny particles from animal bodies. Therefore, NPs exhibit increased exposure period, bioavailability, and risks to aquatic animals, compared to MPs (Jeong et al., 2016; Shen et al., 2019; Shin and Jeong, 2022). When investigating the effect of PS on the brackish water flea *Diaphanosoma*

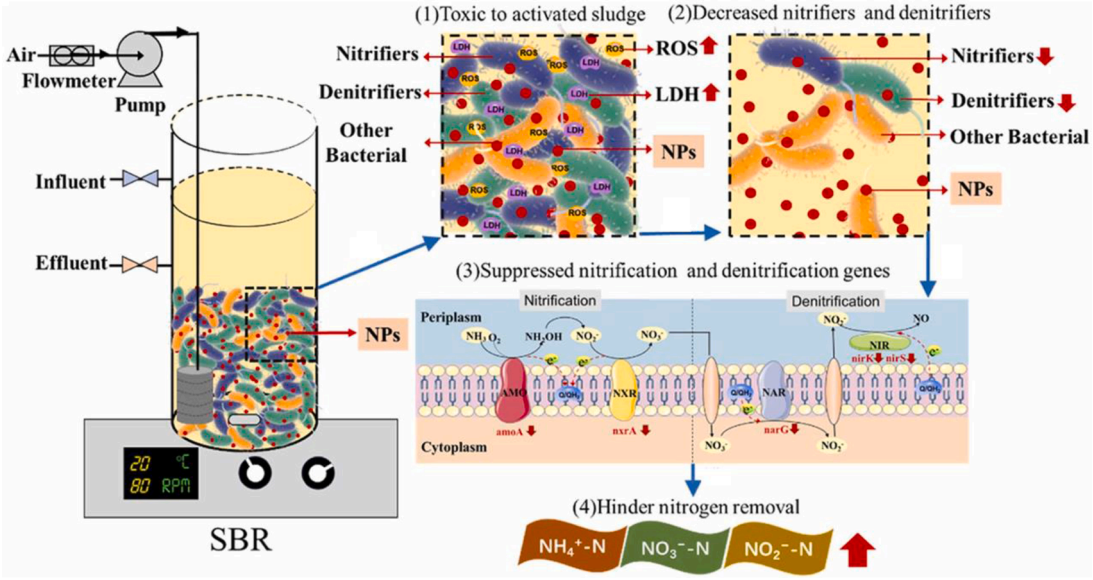

Fig. 3. The inhibition mechanism of NPs on nitrogen removal in sequence batch reactors (SBR) (Zhou et al., 2022).

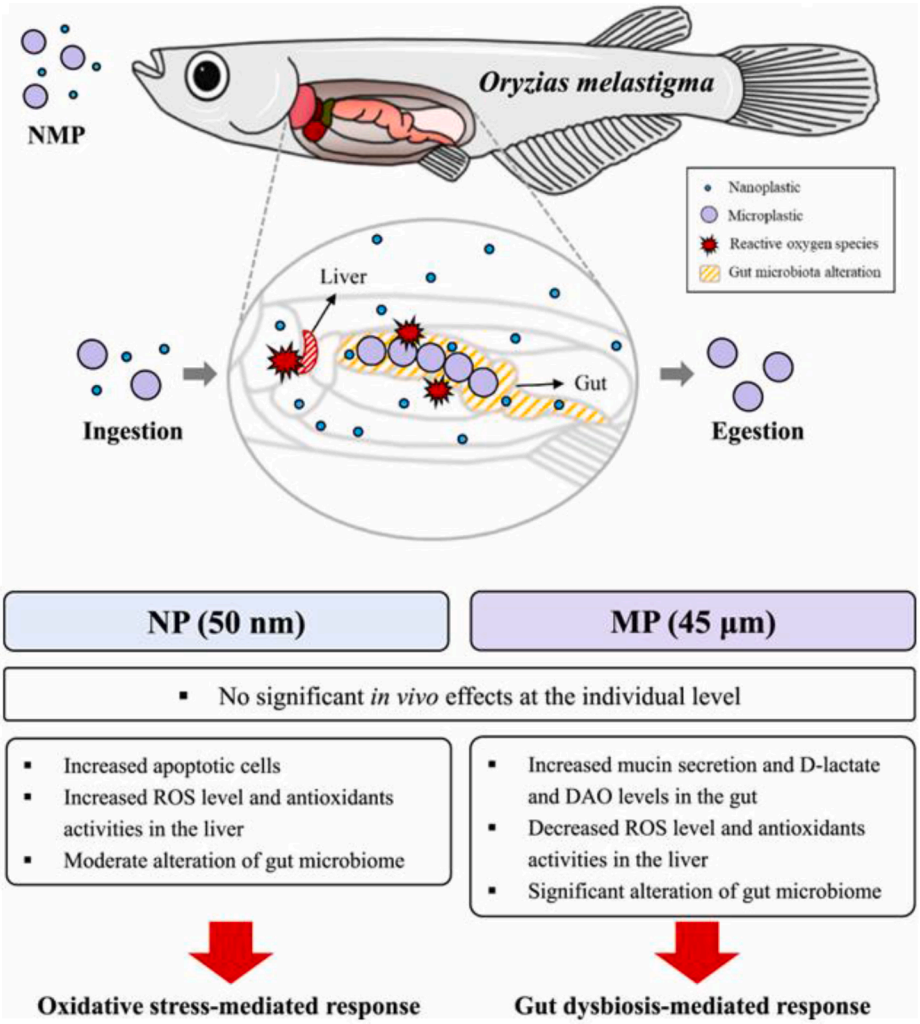

Fig. 4. Impacts of MPs and NPs on the oxidative status and gut microbiota in *Oryzias melastigma* (Kang et al., 2021).

celebensis, a size-dependent oxidative stress response was found. The smaller PS NPs had a longer retention time and higher acute toxicity than micro-sized ones (Yoo et al., 2021). Ma et al. found that 50 nm NPs caused physical damage and significant toxicity to *D. magna*, while 10 μm MPs did not. The presence of NPs largely improved the bioaccumulation of phenanthrene-derived residues in the daphnid body and hindered the dissipation/transformation of phenanthrene, while 10 μm MPs showed insignificant effects on the bioaccumulation, and dissipation/transformation of phenanthrene (Ma et al., 2016). In general, exposure to MPs and NPs would lead to obvious size-dependent effects on zooplankton, with smaller NPs being more hazardous than MPs, NPs could cause reduced growth rate, increased mortality, longer reproduction time, and reduced fecundity, etc. (Besseling et al., 2014).

Apart from zooplankton, fish are an important part of aquatic ecosystems and the food chain, and some studies have examined the negative effects of MPs and NPs on fish. In the study of plastics' effect on zebrafish larvae' locomotor activity, MPs (45 μm) exhibited insignificant effects except for the upregulated *zfrho* visual gene expression. However, NPs (50 nm) showed more pronounced harmful effects, including inhibition of acetylcholinesterase activity (40%), reduction of larvae body length (6%), inhibition of larval locomotion (22%), and significant upregulation of *zfrho, gfap, zfblue*, and *α1-tubulin* gene expression (Chen et al., 2017). In another study, both PS MPs (8 μm) and NPs (80 nm) induced microbiota dysbiosis in the gut of zebrafish, whereas only NPs increased the mRNA levels of *tnfα, il8, il10*, and *il1β* in the gut (Xie et al., 2021). Hence, NPs had a more negative effect on the zebrafish gut than MPs, causing inflammation and microbiota dysbiosis. Interestingly, Kang et al. uncovered distinct toxicity pathways of NPs and MPs on *Oryzias melastigma*. They found that NPs induced oxidative stress-mediated responses, while MPs regulated microbiota composition and resulted in dysbiosis (Fig. 4) (Kang et al., 2021). Qin et al. also found that PS NPs could induce high oxidative stress in the Cd-treated zebrafish larvae, which promoted taurine metabolism and unsaturated fatty acid biosynthesis (Qin et al., 2021). These studies highlight the importance of separately examining the eco-impact of MPs and NPs.

5.4. Human

The omnipresent NPs and MPs in urban waters (especially drinking water, bottled water, and aquatic fish) render human exposure to tiny plastic particles inevitable, and recent reports have indicated the accumulation of different MPs and NPs particles in human bodies (Amato-Lourenço et al., 2021; Jenner et al., 2022; Kannan and Vimalkumar, 2021). In vitro investigations have also revealed diverse toxicological effects of highly permeable MPs and NPs particles on human cells (e.g., oxidative stress, necrosis, genotoxicity, neurotoxicity, cytotoxicity, reproductive toxicity, and inflammation) (Huang et al., 2021a; Rahman et al., 2021; Schwabl et al., 2019). For instance, exposure to PS NPs (60 nm) induced oxidative destruction of the epithelial cells (Inkielewicz-Stepniak et al., 2018). Recently, Grodzicki and coworkers summarized the effects of NPs on the gut-brain axis, as shown in Fig. 5 (Grodzicki et al., 2021). Generally, the persistence of MPs and NPs, together with their chemical additives, and adsorbed toxic pollutants would pose serious health risks to human bodies.

Compared to MPs, NPs can more easily cross the gastrointestinal barrier in human bodies and enter the capillary blood system and be further transported throughout the whole body (Lehner et al., 2019). NPs can also accumulate in tissues and cells, leading to local inflammation and metabolic disorders. As suggested by Forte et al., smaller PS NPs (44 nm) accumulated more efficiently in the cytoplasm of gastric adenocarcinoma cells compared to the larger counterpart (100 nm). In addition, the smaller NPs strongly induced the upregulation of IL-6 and

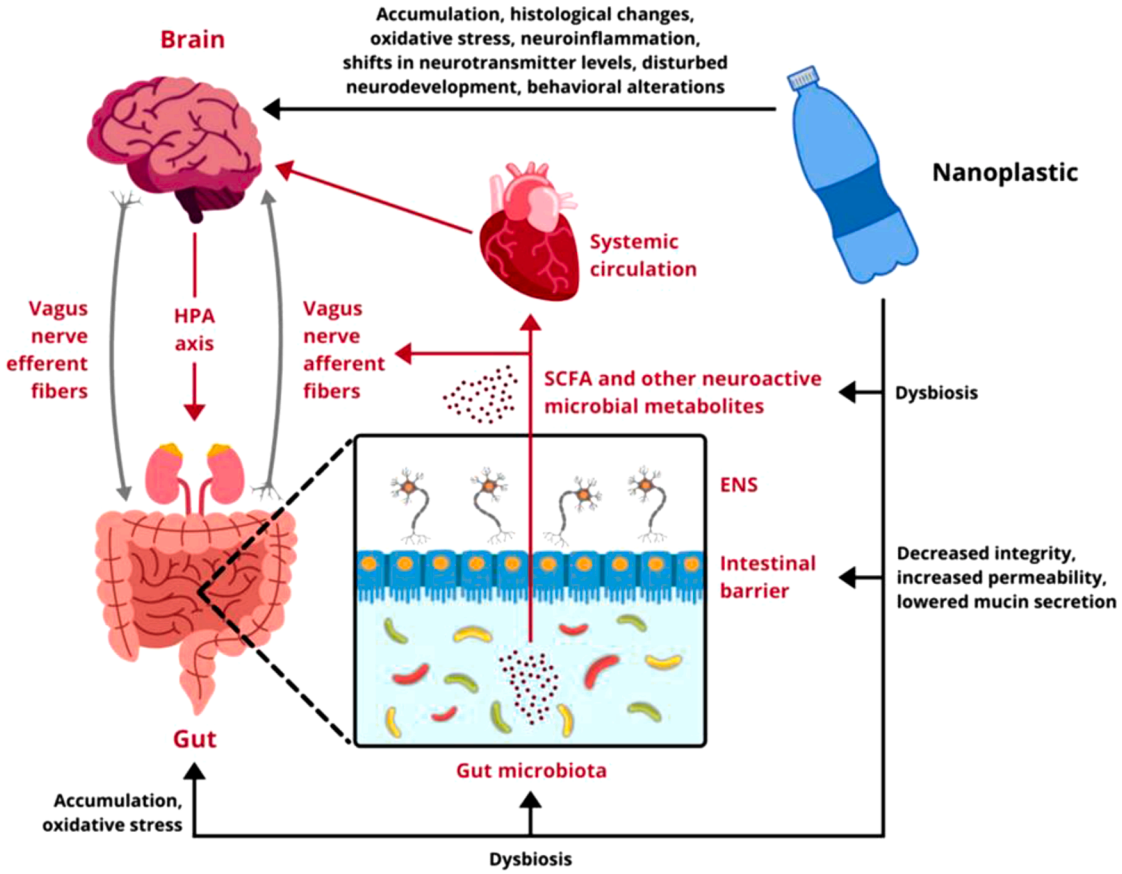

Fig. 5. The impacts of NPs on the gut-brain axis. SCFA: short-chain fatty acids; ENS: enteric nervous system; and HPA axis: hypothalamic-pituitary-adrenal axis (Grodzicki et al., 2021).

IL-8 genes, two critical cytokines involved in gastric pathologies (Forte et al., 2016). A previous study also suggested that the smaller 40 nm NPs could penetrate cells through the follicular epithelium, but the larger MPs (750 and 1500 nm) were blocked by the skin (Vogt et al., 2006). Current studies are mainly based on model MPs and NPs and real environmental samples are rarely investigated, and the study of the size-dependent toxicological effect of environmental MPs and NPs on human health is still in its infancy.

6. Conclusions and perspective

Due to their smaller size, NPs differ significantly from MPs in terms of analytical challenges, fate, interactions with pollutants, and eco-impacts. Compared to MPs, the analysis of NPs with sizes below the geometric optical resolution requires more complicated techniques and equipment. In addition, NPs tend to remain homogeneously dispersed in urban waters, whereas MPs mainly undergo vertical transport driven by buoyancy and sedimentation. The higher surface area and surface functional group content of NPs makes them easier to aggregate and regulate their fate, and also gives them high adsorption capacities towards surrounding pollutants. Such characteristics further provide NPs with higher hazardous effects on microbes, plants, animals, and even humans in the urban water systems than MPs, although some exceptions do not follow the size-dependent effect. Further studies should focus on the following points:

(1) Accurate analysis. Analytical challenges have substantially impeded the acquisition of accurate data on the fate, interaction with surrounding pollutants, and eco-impacts of MPs and NPs. Since the size of NPs is below the geometric optical resolution, many existing analytical techniques for MPs fail to detect NPs. Accordingly, the establishment of new analytical theories, methods, and facilities for the analysis of NPs is an important research direction. It should be noted that organic pollutants that are attached to the MPs and NPs would interfere with the identification of MPs and NPs. In this context, it is necessary to separate plastic particles from the associated organics during the sampling process. In addition, a standard procedure/protocol for MPs and NPs analysis should be established to make results from different studies more reliable and comparable.

(2) Real environmental samples. In real urban waters, MPs and NPs samples generally show high inhomogeneity in size, shape, and type, and experience long-term aging. Therefore, it is necessary to perform the size-dependent study with real environmental samples, instead of the purchased plastic debris with similar size, density, and shape. Another issue of concern is the concentration of MPs/NPs. Current studies generally use high concentrations of MPs and NPs to investigate their effect within a short exposure period, which will not occur in the real urban water system. Further research is needed to explore the behavior/long-term effects of MPs and NPs at environmental doses.

(3) Efficient removal strategies. Current strategies applied in WWTPs can deal well with the problem of MPs, but the removal of NPs is still in its infancy and membrane-based techniques may hold the promise for efficient removal of NPs. In addition to the extraction of NPs from water, the development of efficient degradation methods is also highly recommended. Catalytic degradation (photocatalysis, electrocatalysis) and biodegradation could mineralize these polymers in water or valorize plastics into value-added chemicals and fuels.

(4) MPs/NPs combined environmental contaminants. In urban waters, MPs/NPs are associated with various pollutants, such as heavy metal ions, persistent organic pollutants, pathogens, and antibiotic resistance genes. MPs/NPs act as vectors for these contaminants and alter the overall toxicity to ecosystems. Current studies on the combined toxic effects of MPs/NPs and other environmental contaminants remain mainly at the phenomenological level, while the underlying molecular mechanisms causing the regulated toxicity remain unclear. The transport of MPs/NPs and combined pollutants in organisms, the interaction between MPs/NPs and the combined pollutants, and the in-depth analysis of the biological effects of MPs/NPs and combined pollutants need to be further investigated.

Declaration of Competing Interest

None.

Data availability

Data will be made available on request.

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