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Review

Micro- and Nano-Plastics Induced Release of Protein-Enriched Microbial Exopolymeric Substances (EPSs) in Marine Environments

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Abstract: Plastics are produced, consumed, and disposed of worldwide, with more than eight million tons of plastic litter entering the ocean each year. Plastic litter accumulates in marine and terrestrial environments through a variety of pathways. Large plastic debris can be broken down into micro- and nano-plastic particles through physical/mechanical mechanisms and biologically or chemically mediated degradation. Their toxicity to aquatic organisms includes the scavenging of pollutant compounds and the production of reactive oxygen species (ROS). Higher levels of ROS cause oxidative damages to microalgae and bacteria; this triggers the release of large amounts of exopolymeric substances (EPSs) with distinct molecular characteristics. This review will address what is known about the molecular mechanisms phytoplankton and bacteria use to regulate the fate and transport of plastic particles and identify the knowledge gaps, which should be considered in future research. In particular, the microbial communities react to plastic pollution through the production of EPSs that can reduce the plastic impacts via marine plastic snow (MPS) formation, allowing plastics to settle into sediments and facilitating their removal from the water column to lessen the plastic burden to ecosystems.

Keywords: micro- and nano-plastics; exopolymeric substances (EPSs); marine plastic snow (MPS); biological control of sedimentation

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1. Introduction

Plastics, ubiquitous in modern society, are produced in vast quantities and serve as essential synthetic polymeric materials across various industries and households. The global production of plastic soared to an estimated 367 million tons in 2020, with projections indicating a climb to 600 million tons by 2025 [1,2]. However, the disposal and mismanagement of plastic waste have resulted in a substantial accumulation of litter in diverse aquatic ecosystems.

Plastic waste has been accumulating through a variety of pathways, including treatment plant effluents, river discharge, urban runoff, and air–water exchange [3–5]. Fresh plastics and debris of aged materials that enter the environment are slowly broken down into smaller fragments, referred to as micro- and nano-plastics, through the processes of mechanical fragmentation, chemical degradation (oxidative, photo, and thermal), and biodegradation [4,6–8]. Nano-plastic particles, due to their nano-size, exhibit more intricate ecological and toxicological impacts on the environment [9,10]. Defined as plastic debris

with sizes < 5 mm and <100 nm [11], micro- and nano-plastics disperse rapidly and can be transferred along the food webs, ranging from 0 to 50 mg/L in aquatic environments [12,13].

Extensive studies have demonstrated that plastic fragments as fibers and beads are present in polluted environments such as wastewater effluents, lakes, rivers, and coastal oceans, but they are also found in remote locations such as deep-sea sediments, polar seas, and ice cores. These findings provide evidence that plastic is present in a wide variety of environments [14–20]. Further, a diverse number of organisms, including bivalves, mussels, shrimp, oysters, zooplankton, copepods, and lugworms, have been found to take up microplastics [21–24], including the associated microbial cells, thus providing additional routes for transferring plastics into food chains of marine and freshwater environments [25].

Haye et al. [26] demonstrated that the filter-feeding Eastern Oyster (*Crassostrea virginica*) is capable of effectively filtering suspended particles, including negatively charged colloidal-sized nano-plastics (40 nm) at ambient concentrations of approximately 1 mg/L, possibly in the form of marine plastic snow (MPS). The results from subsequent laboratory research suggested that plastic intake can directly and indirectly lead to negative toxicological and/or physical effects [27]. Due to the unique characteristics that these plastic particles possess (e.g., high surface area, porosity, buoyancy), they have also been suggested to play a role as vectors of harmful algae species, microorganisms (potential pathogens), and persistent organic pollutants (POPs) [28,29]. Additionally, plastics found in marine environments can serve as potential reservoirs for genes that confer resistance to antibiotics and toxic metals [30].

Nano-plastics have high surface area to volume (S/V) ratios, which makes them very reactive. Thus, they are of great interest, given how difficult it is to document their presence in complex matrices. The high S/V ratios cause their properties to be fundamentally different from those of the same polymer type in bulk form [31]. Although many new technologies that are directly applicable to nanoscale particles have recently been developed, the environmental behavior, transport, and distribution of nano-plastics have received significantly less research attention than those of micro-plastics. This is due to the fact that the majority of separation and analytical techniques in aquatic sciences are not directly applicable for micro- and nano-plastic investigations [32,33]. New tool developments are critically needed for aquatic science applications to deepen our understanding of nano-plastics' impact and reduce plastic-derived stress.

Various aquatic microbes can reduce plastic stress by producing exopolymeric substances (EPSs) with distinctive characteristics that promote aggregation and production of MPS and aid in the removal of plastics from the water. This review will focus on the molecular mechanisms activated by microbes in response to plastic pollution, for example by the release of protein-rich EPSs, which facilitate efficient removal from the water column. Most importantly, this review highlights the areas of uncertainty that should be taken into account in future research efforts designed to promote the self-cleaning capacity of aquatic ecosystems.

2. Aggregates and Plastics

2.1. Formation of Aggregates Consisting of Micro- and Nano-Plastics, Natural Organic Matter, and Mineral Particles (Marine Plastic Snow—MPS)

In 1955, the presence of microorganisms embedded in suspended natural organic matter in the ocean, known today as marine snow, was described for the first time [34]. In subsequent years, research established that marine snow consists of phytoplankton, small zooplankton, fecal material, and other particles in a matrix of organic material (see recent reviews by [35–37]). Silver et al. [38] measured the abundance of marine snow and its contribution to the total microbial community in situ, demonstrating that marine snow aggregates are "metabolic hotspots", with levels of microbes three to four orders of magnitude higher than those in the surrounding seawater. Rapidly sinking marine snow is important in the marine carbon cycle, given its critical role in vertical (re)distribution and remineralization of organic carbon as well as the biogeochemical cycling of various elements (e.g., [39,40]) and contaminants e.g., oil, dispersants, and

micro- and nano-plastics [36,41,42]. Recent publications have demonstrated that plastics entering aquatic systems can be rapidly colonized by microbial biofilms [43,44]. Marine natural organic matter and organic aggregates such as microgels, EPSs, and transparent exopolymeric particles (TEPs) have been found to contain micro- and nano-plastics [45–48].

Interactions of plastic particles with natural colloids, such as biopolymers released from microbes and colloidal-sized inorganic particles, will result in modifications to the degradation pathways of micro- and nano-plastics, as well as aggregation, disaggregation, and consequent settling (scavenging) processes (Figure 1). Further studies to gain new insights into the probable environmental fate and potential ecological risks of plastic particles are needed [49,50]. For example, de Haan et al. [51] reported from field and laboratory studies that, on average, 40% of microplastics are incorporated with sinking aggregates, that is, MPS, and this material might potentially settle on sediments. Their evidence supports the hypothesis that marine aggregates can promote ingestion of micro- and nano-plastics by suspension-feeding bivalves, zooplankton, and other marine species. It has also been hypothesized that marine snow and fecal pellets have the capability of removing the vast majority of micro- and nano-plastics from the surface of the ocean. As a result, they are regarded as a major vector as well as a significant sink for micro- and nano-plastics [52]. The studies presented above suggest that micro- and nano-plastics are increasingly becoming an essential component of marine snow, which could transform the snow's fate as well as its chemical and biological properties. Despite the significance of this research topic, comparatively little research has been conducted to understand the interactions that occur between micro- and nano-plastics and marine snow, as well as the mechanisms that explain the formation of MPS and the factors that drive its sinking and transport. Figure 1 was developed in an effort to capture the major variables that may act on micro- and nano-plastic materials in the ocean as they interact with microbes. Most of the evidence was obtained through controlled laboratory experiments with elevated plastics concentrations but with ratios of microplastics to microbial cells and produced EPSs similar to those in the natural environment.

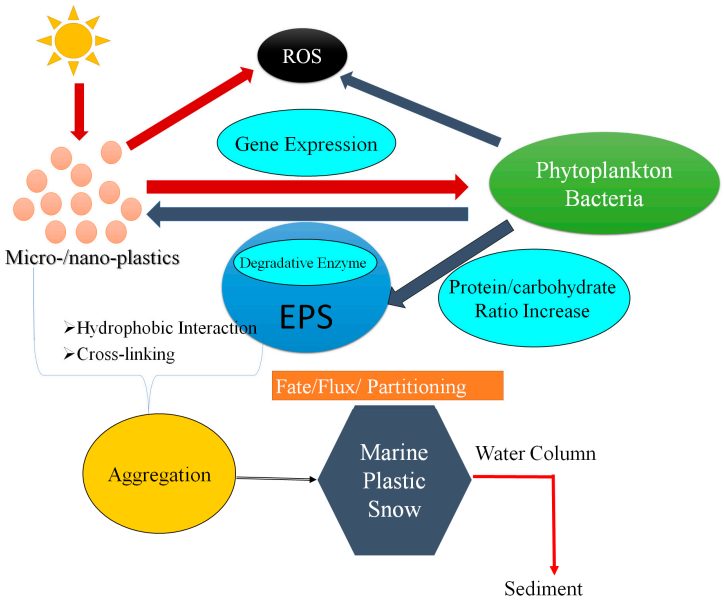

Figure 1. Model of hypothetical pathways and processes for micro- and nano-plastic interactions with aquatic microbes in the environment. Plastic particles, when contacting microbes, induce the generation of radical oxygen species (ROS), which themselves induce changes in the expression of genes to produce more protein-enriched EPSs with higher protein-to-carbohydrate (P/C) ratios, making EPS aggregates more hydrophobic. Such EPSs are stickier and tend to promote aggregation with other particles, including denser mineral particles (scavenging), producing larger agglomerates that allow the lighter plastic particles to sink to sediments without disaggregation.

2.2. A Major Component of MPS: Exopolymeric Substances (EPSs)

Marine microbes are capable of producing high-molecular-weight exudates [35]. EPSs (also called extracellular substances, exopolysaccharides, and exopolymeric substances) describe a heterogeneous variety of organic materials released from microbes, existing in a size continuum from dissolved to colloidal phases and including gels. EPSs may be attached to cell surface coatings and biofilms or produced as coronas [53,54], or may be colony matrices or free floating. These polymeric substances have diverse functional roles (e.g., protecting microbes, aiding their attachment), chemical and physical characteristics [55–59], and appearance. The synthesis and release of EPSs by planktonic microbes can facilitate the formation of aggregates [60,61], and/or MPS [48,62,63] and impact the fate of pollutants (e.g., oil, dispersants, nanomaterials) in the ocean through emulsification, degradation, dispersion, aggregation, and/or sedimentation [35,64–66]. On the other hand, the concentration and chemical composition of the pollutant materials have an effect on the structure and function of the microbial community, which includes the production and release of EPSs and their properties (e.g., [67,68]). Exposure to micro- and nano-plastics has been shown to induce EPS secretion in various species of microalgae [65,69–73], which might serve as a way of detoxifying from environmental stresses. Nevertheless, the secretion of EPSs can, in turn, result in the creation of marine aggregates (i.e., MPS). A similar EPS secretion has been described for bacteria in response to exposure to plastics [74,75].

Ding et al. [76,77] previously demonstrated that nano-plastic particles can facilitate dissolved organic matter (DOM) and EPS microgel formation through hydrophobic interactions without Ca^{2+} crosslinking. In Chen et al. [45] and Shiu et al. [48], phytoplankton EPS microgel formation was found to be accelerated by nano-plastics in seawater, likely due to a higher protein content of the EPSs produced. Shiu et al. [48] demonstrated that EPS microgel formation was significantly enhanced by nano-plastics in different river and lake waters as well as seawater. Aggregates of algal cells with 1 µm polystyrene microplastics encased in an EPS matrix have also been observed (Figure 2), suggesting that plastic particles could be incorporated into the phytoplankton EPS matrix when forming MPS.

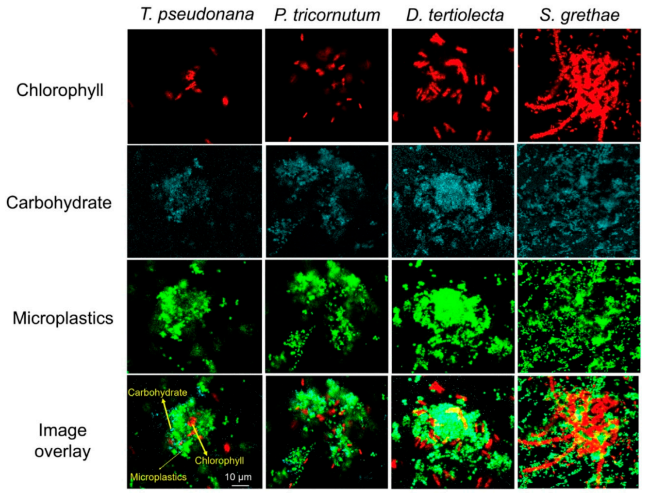

Figure 2. Micro-plastics and laboratory-formed aggregates (MPS) consisting of marine phytoplankton (*Thalassiosira pseudonana*) and micro-plastics (1 µm polystyrene). Red, chlorophyll-containing structures; blue, carbohydrate-containing structures (e.g., EPSs); green, polystyrene microparticles ([48,63], with permission of the publisher).

2.3. The Key Aspects of Marine Plastic Snow (MPS)

2.3.1. Reactive Oxygen Species and Plastics

Ultraviolet ray exposure (UVA) (near UV, 315–400 nm) is the key environmental factor that enhances free radical formation on micro- and nano-plastic surfaces via subtraction of a hydrogen atom from the macromolecular chain, or their addition to an unsaturated carbon

chain group (chemical crosslinking reaction) [78]. The resulting free radicals continue to react with atmospheric oxygen and produce per-oxy radicals with further generation of secondary polymer alkyl radicals, which further modify the plastic surface and have toxicity effects to microbes either extracellularly or intracellularly [79]. The combined effects of these processes irreversibly alter both the surface of plastic particles [80] and the DOM concentration in the water [81].

Micro- and nano-plastics have recently been shown to directly generate ROS in various aquatic environments [82–85]. Furthermore, it is well-known that micro- and nano-plastics have the ability to boost the production of ROS in cells, such as superoxide, hydrogen peroxide, and hydroxyl radicals from electron accumulation in cells, by reducing the electron transfer and the reactivity of the photosynthesis reaction centers, and improving the efficiency of the oxygen-evolving complex [86,87]. Overproduction of ROS can result in cellular damage, which can manifest as DNA, lipids, and proteins that are damaged. In order to lower the levels of ROS and lessen the amount of damage that occurs within them, cells have a number of antioxidant defensive enzymes, such as superoxide dismutase (SOD), catalase (CAT) [88], and peroxidase (POD) [89,90]. As a result of the presence of nano/micro-plastics [91] and nanoparticles in general [92,93], it has been demonstrated that the enzyme activities of SOD, CAT, and POD in microbes can be activated to reduce the negative impacts of ROS.

Creating a buffer zone with secreted EPSs between the living cell and the surrounding environment in order to chemically mitigate the effects of ROS is yet another defense tactic that can be implemented [94]. Many cyanobacteria [95], e.g., *Nostoc commune* [96,97] and *Microcoleus vaginatus* [98,99], produce EPSs under UV-induced oxidative conditions. Sun et al. [100] showed that ROS were produced by irradiation of seawater and ROS were responsible for chemically crosslinking proteins. This research also found that the greater the protein-to-carbohydrate ratio of EPSs, the greater the increase in the size of the microgel aggregates formed [100]. In addition, there is a reciprocal interaction between ROS production and intracellular Ca^{2+} [101], which is closely related to the release of EPS. It is well known that increased levels of free Ca^{2+} within the cell can result in the activation of protein kinase C, which is an enzyme involved in a variety of intracellular signaling pathways. The Ca^{2+}-mediated secretion pathway is responsible for controlling the release of EPSs from phytoplankton cells. Chin et al. [102] provided direct evidence for Ca^{2+} signaling related to exocytosis in phytoplankton cells. Other studies have also demonstrated that unfavorable or stressful environmental factors can induce intracellular Ca^{2+} changes, leading to EPS secretion [102,103]. Therefore, the increased production of ROS caused by micro- and nano-plastic challenge can in turn trigger EPS secretion and contribute to MPS formation. In order to draw a final conclusion regarding the interrelationships between these processes, additional research is certainly required.

2.3.2. EPS-Producing Gene Expression Altered under Environmental Stress

As discussed in the above examples, exposure to micro- and nano-plastics stimulates EPS secretion. Many observations reporting EPS secretions in response to plastic exposure highlight the important cellular and ecological role of this process (Figure 1). Several studies have found expression of genes associated with EPSs in response to external/environmental stress, including antibiotics [104], salt stress [105], and oxidative stress [106,107]. Evidence suggests that cellular contact with plastic surfaces can stimulate the transcription of the EPS genes, including expression of alginate biosynthesis promoter algC, which was observed when the bacteria *Pseudomonas aeruginosa* was exposed to a Teflon mesh substratum [108]. As gene expression precedes synthesis and secretion of cellular organics, a good correlation between EPS production and the expression of associated genes has been reported in a few scenarios. For example, homologous overexpression of a complete EPS gene cluster in the bacterium *Lactococcus lactis* led to increased EPS production levels [109]. Other studies have suggested the presence of micro-plastics can induce the overexpression of sugar synthesis genes, thus resulting in a different EPS composition [110,111], or alter the gene expression

for producing extracellular lipids and fatty acids in microalgae cells [112]. Although several cellular and environmental functions of EPSs have been proposed, including symbiosis, nutrient trapping, signaling, antibiotic protection, genetic exchange, as a carbon source, etc. [113], much remains unknown at the genetic and molecular levels. That which is known has largely been focused on bacteria in industrial settings; there is still a paucity of information on microbial communities or individuals in natural settings. Therefore, experiments examining the time-course gene expression for EPS synthesis in response to plastic exposure are needed to provide cues to the role of EPSs in the context of oxidative stress consequent to microbial exposure to micro- and nano-plastics and in the formation of MPS.

2.3.3. Protein/Carbohydrate (P/C) Ratios and Hydrophobic Interactions

The secretion of microbial EPSs is initiated by environmental conditions; its composition in turn can be driven by various factor(s) (Figure 1). Proteins are the dominant hydrophobic component in EPSs, whereas carbohydrate moieties are considered as hydrophilic, thus their ratio, after being normalized to carbon, is used as a proxy for the biochemical and physical properties of the EPSs, and this ratio has been related to their interactions with many contaminants, like micro- and nano-plastics. The protein-C/carbohydrate-C (P/C) ratio is calculated by Equation (1):

$$\mathrm{P/C} = \frac{neutral\ sugar \times 0.4 + uronic\ acid \times 0.37}{protein \times 0.52} \quad (1)$$

For example, EPSs with higher protein to carbohydrate (P/C) ratios are induced by unfavorable growth conditions, including nutrient limitation, toxins (nanoparticles, oil, and dispersants), and light exposure [2,100,102,114–116]. Shiu et al. [48] showed that the P/C ratio of loosely bound EPSs, which accounts for >80–90% of total microbial produced EPSs, increased in the presence of nano-plastics. In another study, the P/C ratios of the loosely bound EPSs produced by *Microcystis aeruginosa* consistently increased when this alga was exposed to micro-plastics; attached EPSs (i.e., EPSs tightly bound to cells, a minor fraction of total EPSs) had a decreasing P/C ratio [65]. EPSs with high P/C ratios are more hydrophobic and stickier (Table 1) and thus easily aggregate, forming a natural barrier against the hazardous agents [117] and reducing the entrance of toxins into microbial cells.

Table 1. The relative stickiness of EPSs (experimentally determined with magnetic tweezers) in relation to P/C ratios. EPSs were extracted from the diatom *Amphora* sp., the coccolithophore *Emiliana huxleyi*, and the bacteria *Sagittula stellata*. Each value is the mean ± SD of replicate measurements (N ≧ 4) [118].

Species	Protein/Carbohydrate Ratio (P/C)	Stickiness Value *
Amphora sp.	0.14	0.09
Emiliana huxleyi	0.30	0.31
Sagittula stellata	0.63	0.92

* Relative values between 0 and 1 [118].

Furthermore, EPSs rich in proteins have the ability to allow faster assembly rates of marine aggregates, resulting in larger aggregates [45,116]. As a result, the P/C ratio of EPSs can be utilized to estimate stickiness, attachment, and aggregation tendency [63]. This relationship between P/C ratio and stickiness was comprehensively demonstrated by Chen et al. [118]. The interactions between the growth and survival of microorganisms and the key features of EPSs in the presence of micro- and nano-plastics have, however, attracted much less research attention. In light of this, gaining an understanding of the intricate biochemical interactions that take place between three essential components (microbes, plastics, and EPSs) during the exposure of natural microbial communities to nano/micro-plastics will be of great significance in elucidating the mechanisms of plastics' incorporation into MPS, particularly with regard to their aggregation and scavenging processes in aquatic

environments, which can aid in their rapid transfer from the water to sediments (e.g., [119]). The lack of detailed understanding of these processes prevents the determination of the fate of pollutants such as micro- and nano-plastics and the development of measures for their removal from aquatic ecosystems.

3. Open Questions and Suggestions for Future Research

EPSs are produced by microbes under a variety of conditions. A review of the literature suggests that micro-/nano-plastics affect microbes producing EPSs via pathways such as ROS upregulation-induced intracellular Ca^{2+} signaling, reflected in EPS amounts and composition changes (i.e., protein-to-carbohydrate ratio), the latter of which has been shown to be a critical factor in regulating EPS–microbes–plastics aggregation and disaggregation (Figure 1). Intracellularly, a variety of genes are activated both to produce EPSs and increase toxicity of these materials. Plastic-induced changes in turn lead to aggregation (after microgel formation) and incorporation of micro- and nano-plastics into aggregates, i.e., forming MPS, which is necessary for their settling to sediments. This ternary EPS–microbes–plastic system ultimately affects the flux/fate of micro-/nano-plastics and organic carbon (Figure 1).

The first question may be how do plastic particles (micro- and nano-plastics) induce biosynthesis and the release of protein-rich exopolymeric substances in aquatic microbes (phytoplankton and bacteria)? Would the released protein-rich EPSs lead to the aggregation of plastics, facilitating the vertical transport of plastic pollutants to the deeper ocean and the sediments? Representative phytoplankton and bacteria species could be selected for the purpose of demonstrating (1) ROS production induced by the presence of micro- and nano-plastics triggering EPS production; (2) a general response of phytoplankton and bacteria to micro- and nano-plastics in producing more EPSs, and/or with increased P/C ratios; (3) EPS genes that are being regulated by this process; (4) EPSs produced by the marine algae and bacteria that have the potential of forming MPS. One way to address this question is to use both commercial and field-collected aged plastic particles (with greater oxidized surface) to reveal the role of micro- and nano-plastics in the nature of released EPSs and the governing mechanisms to form MPS.

Experimental tests could include using plastic particles that are of (1) different sizes (nano- and micro-plastics); (2) various concentrations; (3) various types, including commercially available micro- and nano-plastics (e.g., polystyrene, polymethylmethacrylate), as well as field-collected aged plastics from heavily plastic polluted regions; and/or (4) exposed to selected environmental conditions (e.g., with and without photoirradiation) (Figure 3).

In addition, one could quantify and select conditions under which the individual species (i.e., microalgae or bacteria) have the greatest responses in terms of producing high ROS concentrations. For example, the generation of ROS likely will be more evident for microbes exposed to nano-plastics than micro-plastics due to their higher specific surface area. ROS likely will be produced in proportion to plastic particle surface area (determined by imaging or BET (Brunauer–Emmett–Teller) techniques) under identical conditions. In addition, one could examine how the presence of micro- and nano-plastics leads to changes in EPS-related gene expression in phytoplankton and bacteria, the latter of which regulates EPS production and composition, specifically higher P/C ratios, as part of the cellular antioxidant pathways. The abundance and composition of EPSs, which are produced as part of the cellular protective mechanisms under environmental stress, will in turn, change with different ROS levels, related to the types, concentrations, and sizes of micro- and nano-plastics [120,121]. Hence, higher levels of ROS can trigger gene expression changes, leading to greater EPS release [122,123]. Those conditions that produce the most ROS and/or EPSs can then be scaled up for RNA sequencing, with an emphasis on genes associated with EPS synthesis processes. After such experiments, EPSs may be separated from the medium by filtration and ultrafiltration and then analyzed to determine the total carbohydrate, protein, and uronic acid content, which is needed to calculate the P/C ratio of EPSs.

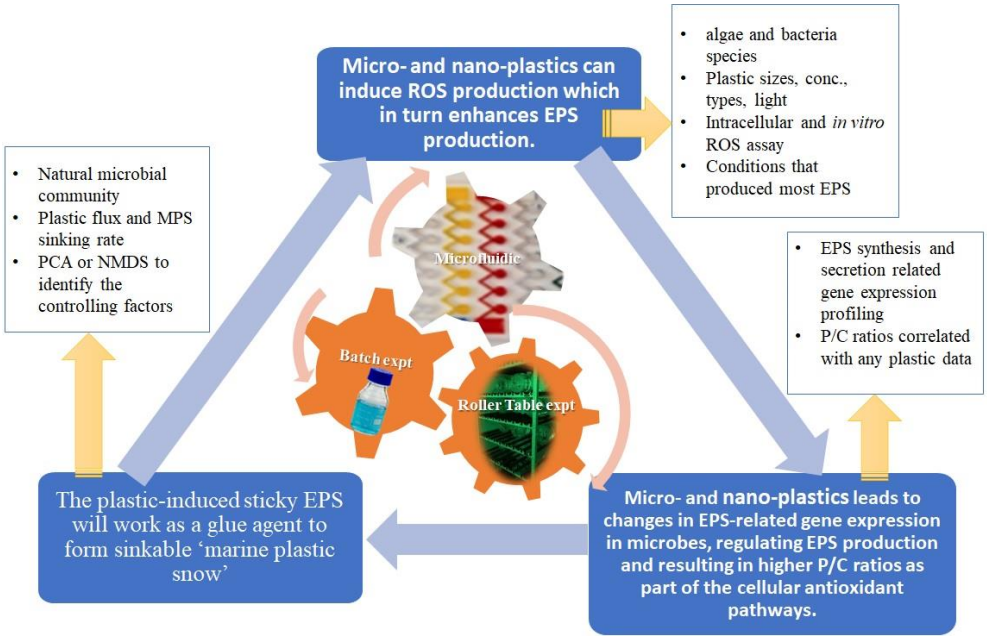

Figure 3. Diagram of interrelated aggregation steps (marked in blue) and questions, suggestions and tests for future research (marked in white), and experimental approaches (marked in orange).

Once the above details are understood, additional effort could be directed at determining how plastic-induced sticky EPSs (i.e., with higher P/C ratio) facilitate the formation of "marine plastic snow", with relatively faster sinking rates. It would be expected that nano-plastics induce higher ROS concentrations and therefore higher EPS production, likely with higher P/C ratios, which results in better aggregation of MPS and faster sinking of MPS compared to micro-plastics. The MPS at the end of the experiment should then be collected and analyzed for its chemical composition (incorporated plastic concentrations, aggregate EPS concentration and composition). MPS sinking rates can then be calculated [124].

While in the sections above we have focused on the influence of micro- and nano-plastics on ROS and EPS production, there are other known developmental, reproductive, and genotoxic effects of these materials on microalgae, though more research is needed. For example, Zheng et al. [125] examined the harmful algal bloom-forming cyanobacteria *Microcystis aeruginosa* and found that while exposure to up to 100 mg L^{-1} micro- and nano-plastics inhibits its growth, it resulted in a decrease in malondialdehyde (MDA) and SOD contents over time (enzymes in the ROS pathway) and also promoted the release of the toxin microcystins. These potent liver toxins are thought to be possible human carcinogens and are also known to kill fish as well as livestock and pets that drink affected waters. Previous studies have shown the polyaromatic hydrocarbons released during oil spills can trigger toxin release in other microalgal species, including the cosmopolitan diatom *Pseudo-nitzschia* sp. found in coastal environments, which produces domoic acid [126]. That these introduced materials can trigger toxin production in microorganisms that are known to produce harmful algal blooms needs further investigation.

Other studies have shown that after an initial growth inhibition, microalgae begin to grow positively despite continued exposures to micro- and nano-plastics. *Chlorella pyrenoidosa* (green algae) growth increased despite exposure to 1–5 mg L^{-1} nano-particles for 15–21 days [127]. Yang et al. [127] reported that after an initial negative growth period, which led to the inhibition of gene expression of aminoacyl-tRNA synthetase, the following period of positive growth was associated with cell proliferation, cellular regulation of intracellular osmotic pressure, and acceleration of the degradation of damaged proteins. For the marine diatom *Phaeodactylum tricomutum*, the presence of EPSs was found to provide an antioxidant scavenging activity that protected cells in the presence of 1–100 mg L^{-1} polystyrene-COOH [128]. With the delayed positive and differential responses to micro-

and nano-plastics, one critical issue to address in the future is the role of the "shell" on some species of microalgae, which may act as a critical barrier to these materials and their toxic effects, while those species that lack a shell may be more susceptible.

Future efforts will need to focus on if the above route is the dominant pathway for micro- and nano-plastics to accumulate throughout the water column and eventually in the sediments, leading to their enhanced long-term accumulation into the oceans. The sizes, polymers, and concentrations of micro- and nano-plastics may impact their interaction with EPSs and the associated toxicological outcomes. The aggregation, flocculation, and sedimentation of micro- and nano-plastics associated with EPSs may follow similar pathways to that observed for "marine oil snow" [41,129], but given the difference in their chemical characteristics to oil, they may follow pathways yet to be determined. For example, when plastics are associated with a high density of particles (e.g., the abundant phytoplankton group known as diatoms or suspended mineral grains) via EPS, aggregation processes may increase effective plastic sinking rates. This may explain not only why concentrations of plastics in the surface ocean are lower than expected [124] but also why more are being found at great depth. When these materials are ingested (because marine organisms are unable to discriminate between target food sources and plastic aggregates), they enter the food chain [21] and may become associated with fecal pellets, thereby increasing not only the biomass of micro- and nano-plastic sedimenting but also the rate at which this occurs. The latter means that they are less likely to be modified by microbes as they sink, and so more intact materials may be found on the ocean floor. Indeed, there is a greater abundance of these materials in sediments than in the overlying water column [130,131]. Despite some of these details, there remains a large knowledge gap on the specific pathways and related mechanisms that lead to the ultimate accumulation of micro- and nano-plastics in the ocean; given their potential toxicity to all parts of the food web, these areas should be investigated in the future.

4. Summary and Conclusions

Plastic litter that accumulates in marine and terrestrial environments through a variety of pathways is only slowly broken down into micro- and nano-sized particles in marine and freshwater systems. Plastics also accumulate potentially toxic pollutants through sorption processes that exert toxicity on aquatic ecosystems by overproduction of ROS and oxidative damage to microalgae and bacteria. The role of microbial responses is not well known, as some of these responses are able to reduce the plastic stress by producing more sticky protein-rich EPSs with unique features that undergo aggregation, formation of denser marine plastic snow, MPS, and subsequent sedimentation.

This review summarizes what is known currently about the molecular mechanisms microbes use to regulate the fate and transport of this material and identify the knowledge gaps that should be considered in future research endeavors. In particular, this review highlights the following topics: (1) EPS gene expression regulated by exposure to micro- and/or nano-plastic-inducing ROS production; (2) EPS composition, protein-to-carbohydrate (P/C) ratio, molecular weight, and hydrophobicity changes in response to plastic exposures; (3) mechanisms for microplastics, nano-plastics, microbes, and EPS change to form MPS; (4) sinking velocity of MPS compared to marine snow.

The importance of this review thus lies in revealing the connections between the physical-chemical processes and the molecular mechanisms of microbes in response to exposure to micro- and nano-plastic particles. Another novel focus is on the relationship between exposure to pollutants, ROS generation, the extent and speed of self-assembly of microgels, the stickiness of EPSs, their hydrophobicity, and the protein-to-carbohydrate ratio.

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