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Review

Microbial Interactions with Particulate and Floating Pollutants in the Oceans: A Review

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Abstract: The Earth's oceans are the final resting place of anthropogenic wastes, mainly plastics, metals, rubber, and fabrics, in order of decreasing abundance. On reaching the sea and the benthos, most of these have assumed fragmented or particulate forms. They become colonized by marine microorganisms and later interact with macroorganisms, leading to potential problems with marine life and the ecosystem. Rapid biodegradation of the polluting materials is a possible, and desirable, result if harmful by-products are not produced or toxic constituents are released. Negative effects are the transport of organisms to other ecosystems, with possible disturbance of the natural biological balance, or transfer of pathogenic organisms. A microbial biofilm can mask unattractive anthropogenic materials, increasing ingestion by marine life, with potentially dangerous results. This article seeks to provide a synthesis of the interactions occurring between oceanic anthropogenic polluting matter in solid and particulate form, and the microbiota present in our seas. It discusses the most important solid and particulate pollutants in the oceans, their sources, adverse effects, interactions with living organisms, mainly microorganisms, and future research for their control. Pollutants included are marine litter (macrodebris), microplastics, engineered nanoparticles, metallic particles, and, finally, sinking particles ("marine snow") as a potential biodegradation "hot spot".

Keywords: marine pollution; plastics; marine litter; nanoparticles; metallic particles; sinking particles; biodegradation; anthropogenic pollutants

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Citation: da Fonseca, E.M.; Gaylarde, C.; Baptista Neto, J.A.; Camacho Chab, J.C.; Ortega-Morales, O. Microbial Interactions with Particulate and Floating Pollutants in the Oceans: A Review. *Micro* **2022**, *2*, 257–276. https://doi.org/10.3390/micro2020017

Academic Editor: Ewa Kowalska

Received: 1 April 2022
Accepted: 18 April 2022
Published: 27 April 2022

1. Introduction

Oceans face global natural and anthropogenic challenges. The United Nations has declared 2021 to 2030 the decade of restoration, promoting, among others, resilience to anthropogenic changes, especially in the oceans [1], which are considered the main sink of anthropogenic contaminants [2].

Detectable only with specific equipment, there is an abundant world of microorganisms inhabiting the oceanic ecosystem with a complexity and diversity that competes with all other forms of life on Earth. This group includes bacteria, viruses, fungi, and other microscopic organisms. Of all the living organisms in the ocean, about 50 percent of the biomass weight consists of microbes [3].

Microorganisms are responsible for the food and nutrient cycling that, in their absence, would not be bioaccessible in the ecosystems [4]. Many are also the guardians of ocean water balance and resulting in healthy ecosystems, cleaning the ocean environments of waste, and preventing the proliferation of opportunistic disease-causing beings. Microorganisms inhabit some of the environments considered extreme, such as scalding hydrothermal vents and even underground glacial lakes in Antarctica [5,6]. These were the first organisms to inhabit planet Earth, living in an anoxic environment in a pristine ocean [7].

Several types of surfaces with particular physicochemical and biological characteristics are offered by marine ecosystems; they include living organisms, among them animal and vegetal species. These substrata include many kinds of particles and aggregates, both inert and reactive mineral substrata.

A huge group of aquatic microorganisms shows the capacity to colonize surfaces, resulting in the formation of biofilms and the development of specialized processes within these structures [8,9]. As a survival mechanism, the surface colonization process in aquatic environments has a fundamental role for the microscopic species, since it represents greater access to nutritional resources, higher colony stability, and stronger specimen interactions, in a dynamic environment of low nutrient concentration. Sessile microorganisms (those attached to surfaces in biofilms) have advantages over the planktonic cells in their resistance to adverse conditions and antimicrobial substances, as well as possessing an increased metabolic rate.

Aquatic solid substrates are ideal environments for important biogeochemical activities [10]. Surface colonization and biofilm production protect from predators, viruses, antibiotics, chemical toxins, and other deleterious environmental elements [11–13]. Polluting anthropogenic particles can serve as niches for the survival and replication of marine microorganisms.

Nowadays, however, marine litter is considered a worldwide issue alongside other key environmental threats, such as climate change, ocean acidification, and the loss of biodiversity [14,15]. It is regarded as one of the most significant problems for the marine environment and a major threat to biodiversity [16]. Over the last decades, it has become clear that litter particle pollution presents a global environmental challenge of increasing presence in the oceans. The scientific community has studied the microbial life colonizing particle surfaces of these pollutants, but the general concepts of microbial ecotoxicology have only rarely been involved in the studies [17].

Marine litter results in aesthetically detrimental effects represent a threat to commercial shipping and fishing vessels, can intensify the diffusion of organic and inorganic contaminants, and is harmful to marine higher species and potentially also humans [18]. 30–75% of all marine debris consists of plastic, which pollutes environments from the poles to the equator and from shorelines to the deep-sea [19,20]. Apart from the problems caused when microplastics are ingested by marine animals, the plastics themselves can be degraded under the influence of UV to become toxic and release toxic components such as bisphenols. Marine debris is negatively affecting the global economy, wildlife, and the environment; there is global agreement that it needs to be addressed urgently [21].

Petroleum hydrocarbons resulting from oil spills, shipping disasters, etc. are widely recognized and important marine pollutants. There has been much written about the effects of such contamination on marine ecosystems [22,23] and the potential for its bioremediation using microorganisms [24–26]. The current article will not add to the available information in this area, focussing on less well-studied marine solid particulate pollution of growing importance. The aim is to review the more recent literature that documents the interactions of marine microorganisms with particulate pollutants.

2. Macrodebris

Marine litter, or macrodebris, is one of the sources of microcontaminants. Macrodebris not removed by other means will be broken down by mechanical, chemical, and biological activities in the oceans to add to the already present levels of polluting microparticles. Its vast distribution around the globe and long-life durability make marine litter a critical environmental issue [21,27]. This type of pollutant is present worldwide, from shallow water to the deep sea and from the poles to the equator. The most direct impact of marine litter on marine biota is the mechanical effect resulting from the entanglement of animals, which potentially harms their mobility, feeding, breathing, and reproduction capacities [28], affecting, most of the time, wandering species like fish, marine mammals, sea turtles and seabirds [29]. Sessile species are also potential targets; they are subject to mechanical impacts resulting from the movement of waste, which can affect their body structure [30,31].

In the deeper layers of the sea, larger-sized anthropogenic litter, which may be composed of plastic, metal, glass, rubber, and fabrics such as rope and clothing, is becoming increasingly common as human beings expand their oceanic activities.

These materials can become colonized by microorganisms within a few days [32], producing biofilms that differ not only according to the physical and chemical environment but also to the man-made substratum. It has been suggested that the main anthropogenic plastic litter in the oceans is associated with fishing activity [30,33–36]. 12.2 million tonnes of plastic are discarded into marine ecosystems per year, 80% being from coastal, 9.4% from fishing, and 4.9% from shipping origin [37,38].

The major type of marine debris affecting the worlds' reefs is derived from fishing activities [39], while in the deep seas most litter is from ships offshore [38]. Plastics are the most frequent materials, followed by metals [40] (Figure 1). *Plastics*, in both macro and micro form, become colonized by cyanobacteria and diatoms within hours of immersion in the sea, these microorganisms later becoming superseded by proteobacteria and, later, by rare fungi (mainly dothideomycetes [41]). The initial adhesion of diatoms and cyanobacteria on polyethylene has been confirmed using the new technique of CLASI-FISH [42]. Diatoms were shown to be associated with surface bacteria of the Bacteroidetes, Rhodobacteriaceae, and Gammaproteobacteria groups. Main colonizers subsequently were found to be members of the Rhodobacteriaceae, which remained predominant over the whole 5 weeks of immersion in the North Atlantic. In the Tropical Atlantic Ocean, the picture was a little different and the microflora more diverse, but Rhodobacteriaceae remained the major colonizers after one week.

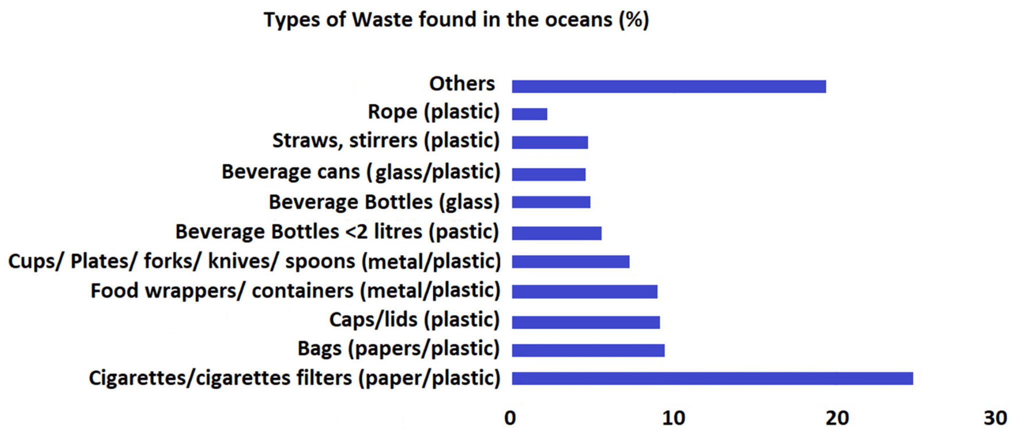

Figure 1. Types of waste (macrodebris) found in the oceans (%). Adapted from UNEP [43] and compiled from [44].

The majority (80%) of litter in coastal areas of the oceans is considered to be land-based in origin [45]. *Metal* litter has been thought to be relatively unimportant in coastal areas of the Mediterranean Sea, since aquatic circulation and meteorological dynamics ensure no permanent impairment of planktonic populations, leading to rapid correction of anthropogenic perturbations in these areas [46]. However, some marine invertebrates have been found rafting on metals, thereby invading other geographical areas [47,48], indicating the importance of this type of litter in ecosystem disturbances. Woodall et al. [49] found that, of all the types of litter collected from the deep waters of the equatorial Atlantic Ocean, metal showed the lowest biofilm diversity compared with the plastic, rubber, glass, and fabric litter investigated and was the only material on which zetaproteobacteria were detected. This is particularly interesting since zetaproteobacteria are iron-oxidizing bacteria that are associated with corroding steel structures [50–52]. Corrosion-associated bacteria had not previously been reported on metallic ocean litter, but in 2019 Muthukrishnan et al. [53] detected higher levels of the anaerobic, heterotrophic sulfate-reducing bacterial genus, *Desulfovibrio*, along with *Pseudomonas*, in steel biofilms from the Sea of Oman, while the main colonizer in wood biofilms was *Corynebacterium*. The application of antifouling coatings to metallic surfaces may be another reason for the smaller contribution of waste composed of metals to the colonization and transport of microorganisms. These antifouling coatings can stop or at least reduce the propagation of microorganisms on various surfaces [54]. The use of antimicrobial coatings on metal surfaces is based on the presence of compounds toxic to microorganisms, for example, pigments, solvents, metals, and organic and organometallic biocides [55,56]. Antifouling paints may also, themselves, become pollutants; the release of paint particles during use and cleaning of the vessels thus protected is a threat to aquatic life [57,58], Researchers have pointed to the increasing biocide (antifoulant) concentrations in water and sediment samples collected near boat maintenance areas, posing a threat to aquatic life [59–61]. Hence there is considerable effort being expended to discover and develop antifouling surfaces that are ecologically acceptable [62,63].

Rubber is not commonly considered one of the most important marine pollutants, but it can be significant because of its refractory character. In 2007, a shipload of rubber ducks completed a 15-year-long journey, which began in January 1992 when a cargo ship named Ever Laurel, traveling from Hong Kong to the United States, lost some of its cargo during an ocean storm [64]. The load consisted of approximately 29,000 toys, some of which had reached the Australian and the east coast of the United States by 2007. Others went through the Bering Strait and the Arctic Ocean until arriving in Greenland, the United Kingdom, and Nova Scotia. This represents the considerable potential for the transfer of rafting organisms. Car tire rubber is a major contributor to terrestrial wastes, and its leachates can be found in the oceans. These include cobalt and zinc, both of which inhibit algal growth and mussel reproduction [65]. Most tires are made of polyisoprene rubber and several bacteria and fungi have been shown to degrade isoprene [66], actinomycetes being considered to be the most important [67–69]. Carrión et al. [70] used an isoprene-degrading gene probe (*IsoA*) to detect degrading microorganisms from various habitats. They found that, in coastal sediments, the gene was associated with the genera *Rhodococcus* and *Variovorax*, while in freshwater sediments *Rhodococcus* and *Sphingopyxis* were prevalent. Isoprene degraders had previously been identified in estuarine waters [71].

Textiles also constitute part of marine litter. Microparticles of synthetic and natural fibers are one of the most abundant marine pollutants [72,73]. The increased emphasis on the environmental effects of textiles is linked to an escalation in public focus on plastic pollution [74], of which a significant part is thought to be composed of textile microfibers. Textiles can be produced from various types of plastic polymers, mainly PET, and microfibers can be released during manufacture and normal laundry activities [75,76]. Natural textile polymers, such as silk, cotton, and wool, are less problematic since they are biodegradable and less persistent in the ocean. The pollution associated with textile laundering has recently been reviewed by Gaylarde et al. [75].

The international textile industry is a major booster of global environmental contamination. Global fiber manufacturing exceeded 105 million metric tons in 2018 [77] and it has been estimated that 0.19 million tonnes of microfibers from the production, disposal, and laundering of textiles enter the marine environment annually [76]; indeed, it has been calculated that, for a city of 100,000 inhabitants, approximately 1.02 kg of microfibers will be released into the wastewater treatment system per day from the washing of polyester fleece jackets alone [78].

Fibers can release bioavailable contaminants, like toxic metals and other substances, that have been used during textile production [79]. The Industrievereinigung Chemiefaser [77] has emphasized that the negative environmental influence of the textile industry is centered around the amounts of industrial compounds used during the manufacturing process, as well as the liberation of a variety of pollutants into ecosystems [80–84], including textile fibers [74,78,85–88]. Many are not degraded by any biochemical and/or natural photochemical process and this may result in bioaccumulation and/or biomagnification.

Even though natural fibers are relatively biodegradable in the marine environment, degradation may release other pollutants, such as dyes, which can carry risks to marine life. Stanton et al. [89] question whether natural fibers are better for the environment than microplastic fibers; in their study, microplastic textile fibers such as polyester and nylon were absent from 82.8% of samples, whereas 'natural' textile fibers were absent from just 9.7% of samples. Nevertheless, it cannot be denied that the resistance of plastic fibers to biodegradation makes them potentially more important pollutants.

Harmful chemical compounds and pollutants can be released from various plastics through UV-linked or biodegradation [31,79,90]. Endocrine disruptors, for example, have negative effects on marine biota even at the extremely low levels produced during the transportation and degradation of the polymer matrix. These pollutants have been identified as major contaminating compounds in wastewater effluents [91] that will be released into the Earth's waters. Endocrine disruptors consist of chemical compounds able to mimic endogenous hormones, as they have a very similar chemical constitution. So a hormone receptor can mistakenly recognize these compounds, activating or blocking the normal functioning of the endocrine system [92,93]. Sex change of organisms exposed to contaminants that mimic estrogen compounds has been recorded in marine ecosystems, with all the specimens becoming female. Imposex (sexual impotence) has also been detected in several marine gastropod groups exposed to TBT (tributyltin).

Girard et al. [94] performed in vitro colonization experiments with mixed textile fibers extracted from intertidal sediments in Indonesia and with HDPE microbeads. They used seawater from a coral reef aquarium as the suspending medium, with its natural microbial populations. The colonizing bacteria (identified by DNA sequencing) differed substantially between the two substrata. HDPE beads became colonized by a community enriched in Alcanivoracaceae, while the bacterial populations on textile fibers (40% cotton, mainly dyed black or blue) became enriched in Kordiimonadaceae and Cellvibrionaceae. According to the authors, oxygen consumption and specific colonization patterns suggested that the fiber and plastic substrata were being biodegraded. They did not consider any possible negative effects of the degradation products on the biota, simply considering that degradation was a positive process removing the fibers from the environment.

3. Microplastics

The increased use of plastic materials over the last years has led to millions of tonnes per year of these recalcitrants being released into our seas. It is acknowledged that they are one of the most important anthropogenic influences on our waters and are even found in the Arctic Sea, arriving there from as far away as the Asian coast [95]. They cause problems through their ingestion by aquatic life [96,97] and references therein. Microplastics also provide a surface on which pollutant molecules and potentially dangerous microorganisms can become concentrated and carried to other locations 18, 19. Once the plastic becomes modified by oceanic organics, a completely new surface, much more attractive as a food source, is presented to living creatures.

There are five plastic accumulation zones in our oceans (Figure 2) [98], perhaps the best known of which is the Great Pacific Garbage Patch, in the north-central Pacific Ocean [41]. However, not all ocean gyres have been equally studied and, indeed, difficulties in standardizing sampling procedures make this a very problematic area [99].

Initially, plastics are broken down in the seas into small fragments by abiotic forces such as u-v and wave action; when these fragments are less than 5 mm in size they are known as microplastics. They rapidly become covered by a thin film of organics present in the water and then by marine microorganisms (Figure 3), forming a surface population known as the plastisphere [100]. This contains a wide variety of prokaryotes and eukaryotes and the exact makeup may depend on the type of plastic, as well as the local environment [101,102], although it has been suggested that the plastisphere is only specific to plastic-type in conditions of low nutrients and low salinity [103]. A survey of plastisphere biofilms from around the world, and of various degrees of maturity, indicated that the most abundant phyla are Proteobacteria, Cyanobacteria, and Bacteroidetes [42].

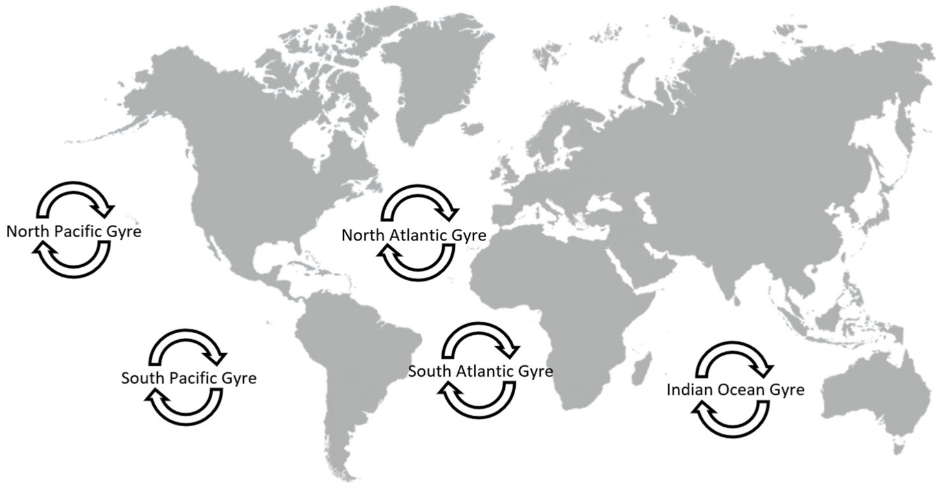

Figure 2. The five swirling ocean garbage patches are called "gyres".

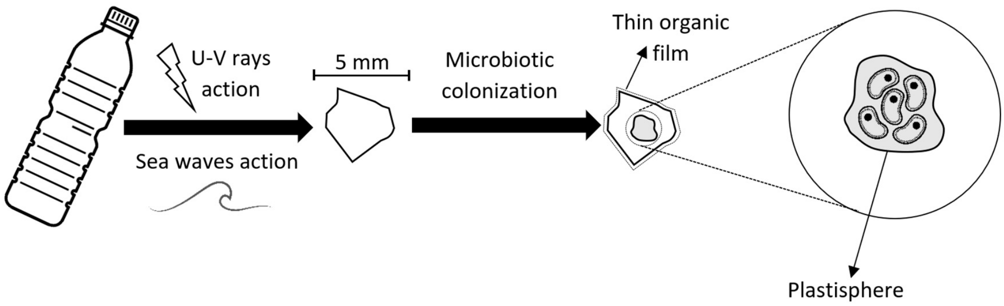

Figure 3. Microplastic colonization.

Colonized microplastics are carried on ocean currents and in spray and so transported to other regions, where the result may be prejudicial to the environment and its biota. It has been suggested that this may be one of the routes whereby metal- and antibiotic-resistant genes are spread around the world [104,105], but pathogenic microorganisms themselves may be transported in this way. For example, opportunistic invasive bacterial populations can enhance coral bleaching [106] and the biofilm in most plastic pools in the Bay of Brest has been shown to contain species related to the potential oyster pathogen, *Vibrio splendidus* [107].

Even if not directly harmful, the introduction of a new microbial population may alter the oceanic ecosystem in unknown ways [108]. Such transfers of local biota are known to occur; plastic debris carrying invasive corals and other living forms can be responsible for the persistence of new species in the ecosystem [109,110]. If such introduced species survive, they may alter the local ecosystems in undesirable ways [111]. In the Antarctic Peninsula Region, 13 species, mainly marine invertebrates, have been identified as presenting a major risk to the native biota [112]. Although these are considered to be transported mainly on ships, the authors point out that the role of floating plastics should not be discounted. Yet another potential problem associated with the biofilm on microplastics is its ability to adsorb contaminants, and potentially toxic, molecules. Biofilms on LDPE have been shown to adsorb Ba, Cs, Fe, Ga, Ni, and Rb and to facilitate the uptake of Cu, Pb, Al, K, U, Co, Mg, and Mn [113].

On the other hand, microorganisms transported on anthropogenic particles may have desirable effects. The surface-associated genus *Phaeobacter*, for example, produces antibiotics, including tropodithietic acid, which inhibit a variety of bacteria, including pathogenic *Vibrio* species, and may have protective effects in pisciculture [114] and references therein.

Another positive result of the microbial colonization of plastics is the potential for biodegradation of the material by the adherent organisms. Debroas et al. [115] found that there was an overrepresentation of microorganisms capable of xenobiotics degradation in the plastisphere. Some of the microorganisms that have been detected in the plastisphere are known hydrocarbon-degraders and may be involved in the breakdown of the plastic substrate [115,116]. Enzymes involved in such degradation include lipases, proteinases, cutinases, and dehydrogenases [117]. Table 1 lists some of the plastic-degrading microorganisms that have been identified in the plastisphere and elsewhere, using culture or molecular techniques. Although several fungal species are listed, and, indeed, were among the earliest microorganisms to be demonstrated to have a plastic-degrading ability, few of these plastilytic eukaryotes have been detected in the plastisphere and even less have been assessed for activity under marine conditions. Indeed, fungi are rarely detected in biofilms on benthic marine plastic debris [118,119].

Table 1. Plastic-degrading microorganisms.

Plastic	Microorganism	Reference
PE/PET	*Achromobacter xylosoxidans*	[120]
	Rhodococcus ruber	[42,121]
	Brevibacillus borstelensis	[122]
	Bacillus spp.	[123–125]
	Thermobifida fusca	[126]
	Thermobifida halotolerans	[127]
	Alcanivorax	[119,128]
	Marinobacter	[119]
	Arenibacter	[119]
	Ideonella sakaiensis	[100]
	Kocuria palustris	[78]
	Clostridium thermocellum	[129]
	Saccharomonospora viridis	[130]
	Thermomonospora curvata	[131]
	Streptomyces sp.	[132,133]
	Streptomyces albogriseolus	[134]
	Aspergillus sp.	[135]
	Penicillium simplicissimum	[105,136]
	Zalerion maritimu	[137]
	Anabaena spiroides	[138]
PHA	*Pseudomonas stutzeri*	[139]
	Alkaligenes faecalis	[140]
	Streptomyces sp.	[141]
PCL	*Alkaligenes faecalis*	[142]
	Alcanivorax	[143]
	Tenacibaculum	[143]
	Pseudomonas spp.	[143,144]
	Clostridium botulinum	[139]
	Streptomyces thermoviolaceus	[145]
	Fusarium sp.	[53,102]
	Brevundimonas sp.	[146]
PLA	*Bacillus brevis*	[147]
	Fusarium moniliforme	[148]
	Penicillium roqueforti	[139]

Table 1. *Cont.*

Plastic	Microorganism	Reference
Polyurethane/PE-PU	*Comamonas acidovorans*	[149]
	Pseudomonas chlororaphis	[150]
	Pseudomonas putida	[151]
	Acinetobacter gerneri	[152]
	Aureobasidium pullulans	[153]
	Fusarium solani	[140]
	Alternaria sp.	[154]
PVC	*Pseudomonas putida*	[155–157]
Polystyrene	*Rhodococcus ruber*	[158]
	Azotobacter beijerinckii	[159]

Abbreviations: PCL—polycaprolactone, PE—polyethylene, PET—polyethylene terephthalate, PHA—polyhydroxyalkanoate, PU—polyurethane, PVC—polyvinylchloride.

Some plastics may become accessible to microbial metabolism only after partial breakdown or modification by non-biotic factors, such as u-v or heat. Such non-hydrolyzable polymers include polyethylene, polypropylene, and polystyrene. Many modern plastics, such as PET, however, are directly susceptible to hydrolysis. Two enzymes jointly capable of degrading PET into environmentally benign monomers have been isolated from the bacterium *Ideonella sakaiensis* in a PET bottle recycling site [160]. [161] has produced a more efficient engineered PET-hydrolase that could form the basis of a bioremediation treatment for environments contaminated with plastics.

Delacuvellerie et al. [116] found that plastic-enriched populations of bacteria from plastispheres contained hydrocarbon-degrading bacteria. These included *Alcanivorax*, *Marinobacter*, and *Arenibacter* on LD (low density) PE and PET. *Alcanivorax borkumensis* from thick biofilms on LDPE was shown, by weight loss, scanning electron microscopy, and ATR-FTIR analysis, to degrade the plastic substratum. Although there was only 3.4% degradation after 80 days, this is worthy of further investigation, since LDPE is a very hydrophobic plastic and thus rather resistant to biodegradation. PET has also been shown, by SEM and FTIR, to degrade and develop surface cracks on exposure to marine biofilms in the Arabian Gulf, while polypropylene and PVC showed cracking under biofilms formed in Chinese coastal waters. Despite the considerable amount of research effort that has been applied to the microbial degradation of plastics, Oberbeckmann and Labrenz [146], in a recent review, conclude that microplastics are recalcitrant substrates for microorganisms and will probably not be biodegraded within a reasonable timescale.

The colonization of microplastics in the oceans leads to an increase in their weight and, because of the production of extracellular polymeric substances (EPS) within the plastisphere, to their agglomeration, resulting in their eventual deposition in the benthos [118], and references therein, where the vast majority of oceanic plastic wastes are deposited [162,163]. Floating microplastic particles have a 50% chance of sinking between 17 and 66 days after they arrive in the water [164] and it is considered that very large amounts of microplastics are removed from surface waters by attachment to organic sinking particles (q.v.) [138]. Once incorporated into the sea-bottom sediments, the final fate and distribution of the plastics are strongly controlled by sea-bed currents [165]. Even here, problems can result from ingestion by benthic organisms [166,167]. Plastic waste has been registered at a depth of almost 11,000 m and plastics have been detected in the hind guts of amphipods from deep ocean trenches of depths 7000 to 10,890 m from the Pacific rim [166]. In order to more accurately assess the degree of plastic contamination in our oceans, more measurements need to be made on this specific ecosystem. Here, any degradation processes must be primarily anaerobic or microaerophilic, given that only low amounts of oxygen will reach the benthos via thermohaline (bottom) currents [165]; the lack of sunlight and low temperature at these depths also drastically reduces non-biological degradation [43]. Very little is known about these biodegradation processes, although several plastic degraders have been detected in cold marine habitats [168], and the sulfate-reducer *Desulfatitalea tepidiphilia* has been found attached to plastic surfaces in marine sediments in Germany [169]. Since sulfate reduction is the dominant type of bacterial respiration in sediments, this could be important in any biodegradation process. There are no accepted standard tests to assess anaerobic biodegradability in the marine environment. The elucidation of mechanisms for the biodegradation of plastics in the benthos is an important objective for future research.

Upon further breakdown, microplastic particles become nanoplastics, with a size of below 1000 nm according to Gigault et al. [139]. This group of marine pollutants overlaps with the so-called "primary nanoparticles", which are manufactured by industry, and are discussed in the next section (Engineered Nanoparticles). They are subject to the same degradation forces as microplastics but are more readily taken up by marine organisms and have been shown to have adverse effects on a variety of marine species [139,170]. Although it is assumed that nanoplastics will be subject to the same degradation mechanisms as microplastics, there is little direct evidence for this, mainly because of the challenges of isolating and analyzing them [57] and references therein. Gigault et al. [170] discuss these methods in some detail and point out the inherent problems. They consider that innovative tools, such as chemometrics, and newly developed instrumentation will be required for future studies on nanoplastics.

4. Engineered Nanoparticles

Particles of up to 100 nm in diameter are known as nanoparticles. The European Union defines a suspension of nanoparticles as that in which 50% or more particles have one or more external dimensions of 1–100 nm. These suspensions exist in nature (e.g., nanoclays), but in the recent past, they have been manufactured for specific human purposes. Such engineered nanoparticles (ENPs) may be used, for example, in coatings, insulating and magnetic materials, and as antimicrobial additives, principally nanometal oxides, such as TiO_2, which become increasingly antimicrobial under the action of UV In fact, metal and metal oxide nanoparticles are those most produced worldwide, with TiO_2 having the highest produced mass [171], and many, along with silica nanoparticles, are used as antifouling materials for protection of marine and seawater-associated structures [172–174]. The antifouling materials can, of course, also affect the non-target biota in the sea, especially when liberated from the protected structures by sloughing or friction. Toxic effects of the principal metal oxide ENPs in the marine environment decrease in the order Au > Zn > Ag > Cu > Ti > Carbon60 [175].

At some stage in their lifetime, even if not utilized directly in the marine environment, ENPs will be released into their surroundings and end up entering the oceans, where they can exert negative effects on the biota [176,177], including inhibition of movement and metabolic processes, oxidative stress and dysfunctional DNA replication [178]. NanoZnO particles ranging from 30 nm to 2 µm have been shown to be highly toxic to flounder cells in culture and zebrafish embryos [179]. ENPs can readily pass from terrestrial waters into the ocean and thence into the marine food web [180]. It has been suggested that the main effects of ENPs on coastal marine life forms will be in sediments [181], where they have been shown to have toxic effects on foraminifera [182].

There has been little empirical study of the fate of ENPs in the aquatic environment [183], although it has been suggested that they can cause significant harm to the marine ecosystem [184] and references therein and that they have significant toxic effects on marine phytoplankton [185]. The release of silver NPs has been shown to alter the functioning of the marine food web by hampering important viral and bacterial processes [186]. In a mesocosm experiment, the addition of silver NPs, even at a low dose, affected planktonic communities, especially reducing the growth of the cyanobacterium *Synechococcus.* Viral auxiliary metabolic genes involved in cyanobacterial photosynthesis were also decreased.

It has, however, been suggested recently that ENPs may not be found at sufficiently high concentrations in the natural environment to pose a current problem [187]. More data on the effects and fate of nanoparticles released into the environment are necessary.

Life cycle and ecological risk assessments of ENPs in our oceans are essential to stimulate remediation processes and protect the marine environment.

5. Metallic Particles

Mining of polymetallic nodules, found on the surface of abyssal plains at around 4000 m depth, results in the release into the benthos of sediment plumes and nodule debris. These can be rich in Mn, Ni, Cu, and Co [188]. Fazey and Ryan [164] examined the aerobically grown bacteria present on the surface of nodules and in the overlying sediment, identifying *Halomonas aquamarina*, *H. meridiana,* and *Erythrobacter citreus* in both, but the genera *Arthrobacter*, *Kocuria*, *Loktanella*, *Marinobacter* and *Pseudoalteromonas* only in sediment within 4 cm of the nodule surface. Cho et al. [189] confirmed that the microbiome of nodules differs from the microbial population in the surrounding sediment, but their use of NGS technology led to the detection of a different set of bacteria and Archaea. Thaumarchaeota were found in both sediment and nodule, Mn-oxidizing bacteria (*Hyphomycrobium, Aurantimonas,* and *Marinobacter*) were predominant in nodules, and *Idiomarina*, *Erythrobacter,* and *Sulfitobacter* in sediments. Gillard et al. [188], based on their analyses, suggest the use of standard cultivation techniques for monitoring plume propagation; indicator organisms for sediment would be *Diezia maris* and *Pseudoalteromonas shioyasakiensis*, for nodules *Rhodococcus erythropolis* and water *Marinobacter flavimaris*.

Much of the iron found in aerosols over the oceans is anthropogenic in origin, resulting from the burning of fossil and biofuels and fires on land (biomass burning), a situation that is probably mirrored by zinc [190]. Conway et al. [191], using iron-isotope ratios, showed that deposition of anthropogenic Fe could reach almost 100% of the total Fe near highly populated areas. Their model suggested that this effect would be greatest in the Southern and Pacific Oceans, and this was echoed by Hamilton et al. in 2020 [192]. Much of the iron, and, indeed, many metals found in marine particles may be linked to the presence of microorganisms that produce metal-chelating siderophores. Chuang et al. [193] found that hydroxamate siderophores comprised a large part of the sinking particles ("marine snow" q.v.) collected in the Sargasso Sea. One of the important ecological functions of the siderophores produced by microorganisms is the release of iron from sinking particles to supply dissolved iron to the water column [194]. The export of iron from hydrothermal vents in the Southern East Pacific has likewise been linked to particles containing microorganisms [195].

Pollution by mercuric ions is a potential risk to human health, principally through the consumption of fish [196]. The main anthropogenic source of this metal is artisanal and small-scale gold mining, followed by the burning of fossil fuels [197]. The metal is converted to toxic methylmercury and dimethylmercury by microbial activity in the seas [198] and is largely associated with marine particulate matter [199]. The latter authors identified the sulfate-reducing bacterium, *Desulfovibrio desulfuricans*, as important for the uptake or exchange of Hg^{2+} in anaerobic environments. Marine Group II (MGII) archaeal genes associated with assimilatory sulfate reduction have been detected, along with MGII genes involved in surface adhesion, in samples collected from around the world during the Tara Oceans' circumnavigation trip [156]. The authors suggested that archaea MGII could be implicated in the degradation of marine particles, a more positive role for microbial biofilms in our oceans.

Marine microorganisms are also important in the production of metallic compounds. The mineral barite (or baryte), used principally in drilling muds, is produced in the oceans by barium binding initially to phosphate groups in bacterial cells or EPS; the thus concentrated barium is then converted in the marine environment to barite [200].

6. Sinking Particles ("Marine Snow") and Pollution

Marine snow is considered to be composed of heterogeneous agglomerates of living and dead organic matter of >500 um in size, formed by the attachment of organisms to the so-called "transparent exopolymer particles" (TEPs) that consist mainly of acidic polysaccharides previously produced by phytoplankton and heterotrophic prokaryotes [201] and references therein. The particles contain diverse groups of eukaryotes, which may somewhat resemble, but certainly do not equal, the plankton in the local environment [202]. They have a highly variable composition and there are fundamental differences in particle composition between oligotrophic and eutrophic environments [202]. The microbial taxa associated with the particles are very different from those in the surrounding seawater and may contain increased oil degraders in oil-polluted environments [203,204] or methylmercury genes in saline waters in the North Sea [205]. Hence the particles may be "hot spots" for the degradative activity of surrounding pollutants [206].

Such sinking particles differ from floating particles in the oceans in carrying a changing population of prokaryotic species. Duret et al. [207] identified the prokaryotic populations on both types of particles in the Scotia Sea (Southern Ocean) and suggested that *r*-strategists, with generalized metabolic activities and rapid substrate consumption, were better adapted to sinking particles, with their changing environment, while *K*-strategists, specialized for complex organic material degradation, were better adapted to the more stable environment of semi-labile floating particles. So, for instance, pseudomonads and Rhodobacteriales were enriched on sinking particles, Flavobacteriales on floating. Datta et al. [208] had previously shown, using model polysaccharide particles, that the attached bacterial communities underwent rapid metabolic successions, driven by the environment. They suggested that there are 3 phases of colonization: attachment of a highly diverse community, selection of specific metabolic activities by the environment (reducing diversity) and replacement by secondary consumers, metabolizing the products of the second phase cells, and increasing diversity somewhat once more. Liu et al. [209], investigating differences between the two types of particles at low and high pressures in the New Britain Trench, Solomon Sea (Pacific), found that, although there were differences in prokaryotic populations on floating and sinking particles, similar groups participated in the degradation of diatom debris.

Even if similar organisms are involved in degradation, the physical act of sinking, whereby water flows past the particle surface, increases the rate of biodegradation simply by aiding the removal of the degradation products, driving the reaction to the right. This increase in microbiodegradation in sinking, as opposed to static, particles was elegantly demonstrated in a mathematical model developed by Alcolombri et al. [210].

The presence of eukaryotes in marine snow has been less frequently investigated. Bochdansky et al. [211] showed the presence of a fungal biomass equal to that of prokaryotes in bathypelagic particles from the North Atlantic and Arctic seas. Fungi and labyrinthulomycetes (the latter mainly labyrinthulids and thraustochytrids) dominated the biomass. These eukaryotes are tolerant of low temperatures and high pressures and were considered to be potentially important biodegraders in the particles. Schultz et al. [212], using metaproteomics and functional analyses of marine particles, showed that eukaryotes were more abundant in the particles than in the surrounding seawater. Those detected in particles were phytoplankton, Oomycetes, and Fungi. Greater amounts of viral proteins were also found in the particles. They reported rather small differences between bacterial proteins on particles and in the planktonic phase. The relative abundance of eukaryotes and viruses confirmed the results of López-Pérez et al. [213], who investigated the coastal waters off Alicante, Spain. They also found that there was an overrepresentation in the particle-associated microbiome of alpha, delta, and gamma proteobacteria, bacteroidetes (Flavobacteria), Planktomycetes, and Actinobacteria.

Gregson et al. [214] discuss the problems involved in studying oil degradation associated with marine snow. Most experiments have been performed using relatively high concentrations of oil in static or rotating vessels in the laboratory, although decreasing hydrocarbon concentrations as the particles sink from the contaminated site have been well demonstrated in loco. Their excellent review discusses not only the need to employ more relevant conditions in degradation studies but also the influence of dispersants. More research is necessary to determine the structure and function of the sinking, as well as the floating, particle microbiome and its relation to biodegradation activities.

7. Perspectives

A greater understanding of microbial responses to anthropogenic changes in our oceans is required to protect the marine environment. Recently, the number of studies on the biodegradation of synthetic plastics by microorganisms or enzymes has grown exponentially, representing a possibility to develop biological treatment technology for these wastes, of which most are in the public eye at this time.

There is a great need for the development of standard methods for the analysis of the chemistry and environmental effects of particles in the oceans. Much of the research carried out at present use unproven or non-standard methods, and many of the accepted effects of pollutant particles on the environment are based on laboratory experiments, often using simulated particles and conditions, or even using pure cultures of microorganisms. The changes that the particles undergo when exposed to the real environment are insufficiently understood. Life cycle and ecological risk assessments of ENPs and other particulate pollutants in our oceans are essential to stimulate and develop remediation processes. Research into the structure and function of the sinking, as well as floating, particle microbiome and its relation to biodegradation activities, could indicate potential ways of manipulating such activities for a natural "clean-up" of the environment.

Changes in traditional materials and practices to protect materials exposed to the marine environment, such as ships and marine constructions, are necessary to reduce anthropogenic pollution and these are under investigation, in the development of ecologically acceptable antifoulants and non-adhesive surfaces, for example.

Governments can accelerate these activities by introducing relevant legislation aimed at reducing polluting materials and activities, as has been done, for example, in Europe, Thailand, and some of the U.S. states, to combat plastics pollution. As part of the attributions of world managers, there are a series of measures that governments can use to protect the oceans from the harm caused by pollution. Among them can be cited fisheries management, conservation, and restoration of marine ecosystems, investments in research aimed at the environment sector, and effective inspection of the respective coastal areas. But the responsibility should not lie with the government sector alone. The awareness of the population must be used as a tool to maintain the quality of ecosystems. For this, effective educational policies must be applied in the most diverse strata of society and the information collected by the scientific community must be translated to other sectors as a way to mobilize independent and joint initiatives.

Funding: This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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