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Reducing Uncertainty and Confronting Ignorance about the Possible Impacts of Weathering Plastic in the Marine Environment

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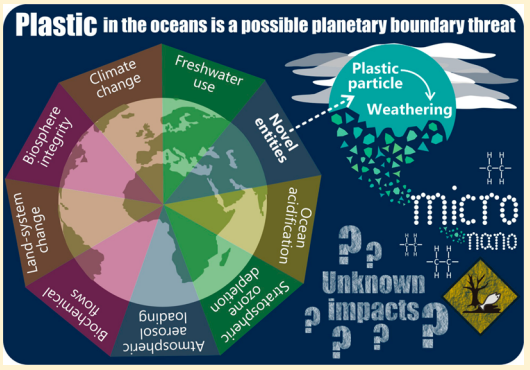
ABSTRACT: Plastic in the global oceans fulfills two of the three conditions for pollution to pose a planetary boundary threat because it is causing planetary-scale exposure that is not readily reversible. Plastic is a planetary boundary threat if it is having a currently unrecognized disruptive effect on a vital Earth system process. Discovering possible unknown effects is likely to be aided by achieving a fuller understanding of the environmental fate of plastic. Weathering of plastic generates microplastic, releases chemical additives, and likely also produces nanoplastic and chemical fragments cleaved from the polymer backbone. However, weathering of plastic in the marine environment is not well understood in terms of time scales for fragmentation and degradation, the evolution of particle morphology and properties, and hazards of the chemical mixture liberated by weathering. Biofilms that form and grow on plastic affect weathering, vertical transport, toxicity, and uptake of plastic by marine organisms and have been underinvestigated. Laboratory studies, field monitoring, and models of the impact of weathering on plastic debris are needed to reduce uncertainty in hazard and risk assessments for known and suspected adverse effects. However, scientists and decision makers must also recognize that plastic in the oceans may have unanticipated effects about which we are currently ignorant. Possible impacts that are currently unknown can be confronted by vigilant monitoring of plastic in the oceans and discovery-oriented research related to the possible effects of weathering plastic.



INTRODUCTION

Plastic debris is ubiquitous in the world's oceans, where it is subjected to physical stress, ultraviolet (UV) radiation, fluctuating temperatures, salinity, oxidizing conditions, and colonization by a range of microorganisms, including phytoplankton, bacteria, and fungi. Plastic in the environment is known to fragment into progressively smaller particles. Particles of "microplastic" in environmental samples are typically defined as having a diameter of <5 mm[1] and may originate from a range of plastic materials. Recently, fragmentation into "nanoplastic" (<100 nm in size) has been observed in laboratory systems, and similar fragmentation is also expected to occur in the environment.[2−5] Plastic usually contains chemical additives and reversibly sorbs chemicals from the environment, and there are several possible degradation pathways for plastic polymers in the marine environment that produce a mixture of chemicals that are chain-scission products from the polymer backbone.[6] Weathering plastic is thus causing global-scale exposure of the world's oceans to tiny plastic particles and to the mixture of chemical additives and polymer degradation products that leach from plastic.

The potential impacts of weathering plastic in the oceans pose assessment challenges that are characterized by both uncertainty and ignorance.[7] It is clear that we must assess the risk of impacts that are known or that can be anticipated on the basis of our experience with other pollution problems. The challenge in this context is to conduct scientific studies to reduce uncertainty in risk assessment of the known or anticipated impacts of plastic in the oceans and eventually to

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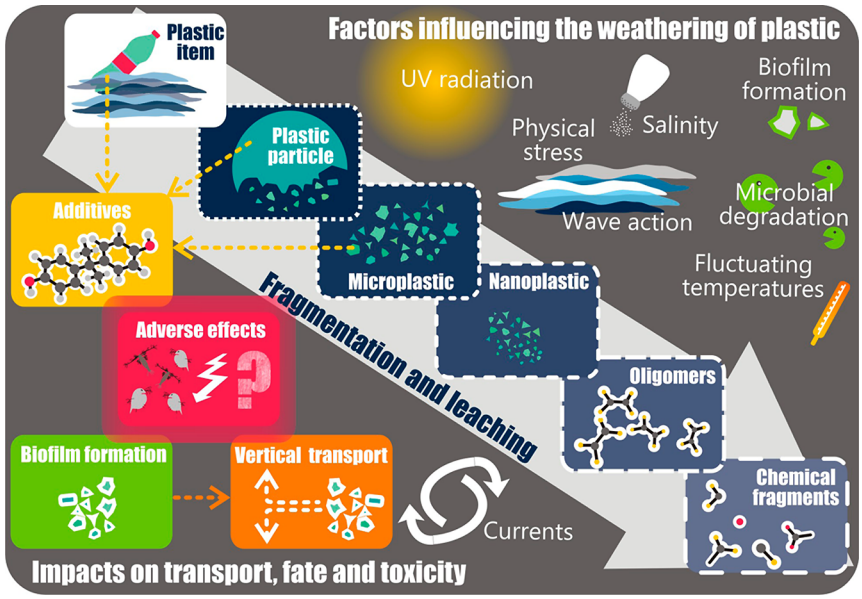

Figure 1. Summary of the factors that influence the weathering of plastic in the marine environment with resulting impacts on transport and fate processes and possible adverse effects.

develop appropriate tools to manage the risks. In the case of weathering plastic debris, the known and anticipated impacts are mostly related to toxicological effects at the individual and ecosystem levels. However, we must also confront the possibility that weathering plastic in the marine environment is having harmful effects about which we are currently ignorant.

The potential for unknown effects of pollutants to have catastrophic consequences has recently been discussed within the planetary boundary framework. The planetary boundary concept introduced by Rockström et al.[8] aimed to define a set of limits within which humanity could operate without disrupting vital Earth system processes that regulate the planet. Chemical agents govern five of the nine planetary boundaries originally defined by Rockström et al., i.e., ozone depletion (halocarbons), climate change (CO_2, CH_4, and other climate-forcing agents), ocean acidification (CO_2), the nitrogen and phosphorus cycles, and chemical pollution.

Recognizing that chemicals defined several of the identified boundaries, Persson et al.[9] proposed that there are more planetary boundaries governed by chemical pollution but that we are currently ignorant of their existence. They defined a set of three conditions that must be simultaneously met for chemical pollution to pose a planetary boundary threat. (1) The pollution must be having an unknown disruptive effect on a vital Earth system process. (2) The disruptive effect must not be discovered until it is a problem on a planetary scale. (3) The disruptive effect must be poorly reversible.

MacLeod et al.[10] defined profiles for pollutants that meet each of these three conditions. Weathering plastic debris is already known to meet two of the three conditions because it is causing global-scale exposure of the oceans (profile 4 for condition 2)[10] and because the exposure is not readily reversible (profile 1 for condition 3).[10] Therefore, plastic in the oceans would fulfill all three conditions to be a planetary boundary threat if it also meets condition 1 because it is causing a currently unknown disruptive effect on a vital Earth system process (profile 1 for condition 1).[10]

Fortunately, no serious disruptive effects of plastic have so far been observed. However, the quantity of plastic waste available to enter the oceans could increase by up to an order of magnitude between 2015 and 2025.[11] Therefore, there is a need to study the fragmentation, biofilm growth, and sedimentation processes that plastic undergoes to improve our understanding of the ultimate fate and effects, in terms of distribution, persistence, ingestion, trophic transfer, and adverse effects and toxicity. An overview of these processes is presented in Figure 1, which depicts the fragmentation and leaching of a plastic item to macroscopic plastic particles, microplastic, nanoplastic, oligomers, and chemical fragments, as a result of diverse stresses from weathering in the marine environment, e.g., UV radiation, biofilm formation, and physical stress through turbulence. The same environmental exposure processes, together with ocean currents, determine the geographical distribution and sinking behavior of plastic, and thus the location and timing of environmental and ecological exposure to weathering plastic. Improving our understanding of these processes will contribute to reducing uncertainty in risk assessment of plastic debris for known or suspected end points. At the same time, however, we must be conscious that plastic in the oceans is a potential planetary boundary threat and be vigilant about searching to discover effects. Below, we review the current understanding of exposure and effects of weathering plastic in the world's oceans and identify research priorities.

EXPOSURE OF THE GLOBAL OCEANS TO WEATHERING PLASTIC

Current research on plastic particles in estuarine, harbor, and sea environments is focused on their origin and distribution patterns on shorelines,[12,13] in subtidal sediments,[14] and in surface waters.[15] Only recently has more focus been directed toward the water column and open sea sediments.[16−19] Generally, it is expected that plastic becomes more brittle with physical aging and weathering[20−22] and thus is more prone to fragmentation over time.

Weathering by physical stress caused by wave action, abrasion by other particles, stones, and sediment, temperature fluctuations, UV-initiated degradation, microbial degradation, and biofilm formation will change the surface and structural

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properties of plastic material.[23−26] Some of these processes are responsible for creating "secondary microplastic" from large plastic debris, such as bottles and other plastic litter. Biofouling has been found to increase the effective density of floating microplastics, which is one of the mechanisms through which plastic debris with a density lower than that of seawater sinks and eventually is deposited on the seabed.[27,28] Particles formed by weathering processes may also aggregate with phytoplankton[29] and natural inorganic particles such as clays that have higher sedimentation rates.[16] Plastic particles consumed by copepods and other zooplankton that produce fast-sinking fecal pellets would have higher rates of sedimentation and burial.[19,30] The spatial variability and seasonality in plankton communities can thus affect the horizontal and vertical distribution of small plastic particles.[19] However, research on these weathering processes is still scant, as highlighted in the conclusions of a recent "State of the Science" report published by the U.S. Environmental Protection Agency.[31]

A few modeling studies have simulated the dispersion of microplastic particles at sea using three-dimensional (3D) hydrodynamic software,[32,33] and there have been modeling studies of the fate of microplastic in rivers.[34,35] The 3D modeling studies conducted to date treat plastic particles as inert tracers without considering changes in their size distribution, shape, and density due to weathering, aggregation with suspended clays, and biofilm formation. Published data for microplastic particles indicate that their size distribution is approximately log-normal,[36] though information about <300 μm particles in the water column is scarce.[37] However, changes in particle size distribution are not the only important parameters affecting transport that are influenced by weathering. Changes in density, particle shape distribution, surface charge properties, surface roughness, and particle brittleness may also play a role. Therefore, modeling the fate and transport of plastic with high fidelity to the real system cannot be achieved if plastic particles are assumed to be inert tracers.

As a part of weathering processes, biofouling can also enhance the uptake of plastic particles into the food web and slow both leaching of chemicals from the plastic and sorption of chemicals from the ambient water. Moreover, biofouling can affect the density and thus sinking rate of plastic particles, potentially determining the exposure of deep sea and benthic organisms. In the water column or when buried in sediment, plastic particles are not exposed to UV light. Hence plastic degradation in these environments is expected to occur only as a result of microbial degradation.[25] Therefore, to predict the fate and impact of plastic in the whole ocean environment, we need to understand the multiple interactions between weathering and biofilm growth and composition, and their joint effects on plastic density, sinking rate, and the consumption of plastic by filter-, suspension-, and deposit-feeding organisms.

Studying weathering plastic collected from the marine environment requires analytical techniques for identifying the plastic polymer and assessing the degree of weathering it has undergone. The two current state-of-the-art approaches to characterize the polymer type of plastic particles found in environmental samples are Fourier transform infrared spectroscopy and Raman spectroscopy.[37,38] The relative intensity of infrared or Raman signals from carbonyl groups (the "carbonyl index"), tensile properties, and average molecular weight are useful measures of molecular changes that accompany weathering processes.[39] Innovative alternative methods in the literature include pyrolysis coupled to gas chromatography and mass spectrometry (GC/MS),[40] GC/MS analysis of Soxhlet extracts of environmental microplastic particles,[41] and scanning electron microscopy coupled to energy-dispersive X-ray spectroscopy, which recently has been shown to be useful in characterizing microplastic surfaces and providing information about a material's elemental composition as a means of distinguishing microplastic from inorganic materials and biological material.[42]

KNOWN AND SUSPECTED EFFECTS OF WEATHERING PLASTIC IN THE OCEANS

The long-term effect of weathering, on the scale of decades or centuries, is expected to be beneficial because it will ultimately remove plastic from the marine environment by mineralization and transfer to deep, inaccessible sediments. However, there are concerns about the short- and medium-term effects, like leaching of chemical additives from the plastic debris, sorption and subsequent release of organic pollutants, and chemical degradation of plastic polymers into oligomers and chemical fragments that may be persistent, bioaccumulative, and/or toxic. For example, the extent of endocrine disruption effects in fish feeding on polyethylene naturally weathered for three months in San Diego Bay, CA, was higher than that in fish feeding on virgin polyethylene,[43] which was likely due to chemicals that had sorbed to the plastic. Another study using the marine crustacean *Nitocra spinipes* found that the toxicity of the leachate from ground plastic materials obtained mostly from consumer items could either increase, decrease, or remain the same after simulated weathering under a UV lamp.[44]

The size and shape of plastic particles have been shown to modulate their effects in feeding experiments. For example, irregular polyethylene fragments (~1−10 μm) that were produced to resemble weathered plastic showed potential to be more harmful to daphnids than commercially produced microplastic spheres of a similar size.[45] Size-dependent effects of microplastic fed to zooplankton have been observed, with the effects differing among the test species and the physiological responses that were monitored.[46,47] Thus, analytical methods and bioassays that can account for how the size distribution and morphology of plastic change over time and in different environments are required to fully understand and anticipate toxic effects.

The ingestion of microplastic by various animals has been demonstrated, and the potential adverse effects on marine biota have become a cause for concern. It has been proposed that microplastic could physically block the gut, gills, or feeding appendages in fish, zooplankton, and other invertebrates, causing decreased rates of growth and possibly starvation and death.[48] However, the majority of feeding studies have employed unrealistically high microplastic concentrations and used virgin microplastic. Another concern with many published studies is the lack of appropriate controls that measure effects of exposure to naturally occurring particles of a similar size, including inorganic particles and natural polymers (e.g., cellulose or chitin), in addition to the effects of exposure to plastic particles. Therefore, the relevance of many published studies to environmental settings is unclear. Although fragmented microplastic has been shown to be more harmful than virgin microplastic or natural clay to daphnids,[45] experimental studies employing weathered plastic at environmentally realistic concentrations and in combination with the mixture of organisms and detritus commonly encountered in aquatic environments are entirely lacking.

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The presence of organic chemicals sorbed to plastic particles raised concerns about their potential to be a vector for transfer of chemicals into the food web.[49] Plastic has a high sorptive capacity for hydrophobic organic chemicals, and it may contain chemical additives, some of which have been shown to cause endocrine-disrupting effects.[50] However, when the effect of ingestion of plastic on the bioaccumulation of organic chemicals is considered along with other sources of accumulation from passive uptake, respiration, and feeding on natural diet items, it is expected to be negligible.[51,52] Considering that high-trophic level organisms are known to biomagnify persistent hydrophobic organic chemicals from their food, it is plausible that ingested and subsequently egested plastic could even be a sink for these pollutants.[53] However, this proposed "cleaning" mechanism was not large enough to be observable in a laboratory study of elimination of polychlorinated biphenyls from rainbow trout fed a diet that included 40% by weight polyethylene microspheres.[54] Two recent critical reviews conducted by different groups of authors summarized the available scientific evidence and concluded that ingestion of microplastic was not likely to significantly influence the exposure of organisms in the marine environment to hydrophobic organic chemicals.[55,56]

One caveat is that most experiments and modeling to date have been based on partition ratios and kinetic parameters for virgin plastics. Karapanagioti and Klontza[57] compared the partitioning of phenanthrene between saltwater and beached, weathered plastic to the partitioning between saltwater and unweathered polyethylene and polypropylene and found higher partition ratios for the weathered plastic. More studies of the effects of weathering on the sorption and desorption of chemicals should be conducted.

RESEARCH PRIORITIES

More knowledge of the following topics is needed: (i) improved understanding of the multiple abiotic and biotic factors influencing the weathering process (Figure 1) by characterization of plastic particles over time, including morphology, particle size distribution, and surface properties, and their degradation products; (ii) elucidation of the role of weathering on sorption and desorption kinetics and the capacity of plastic to sorb chemicals; (iii) characterization of how weathering affects the spatial and temporal distribution of plastic debris, including microplastic and nanoplastic particles; (iv) identification of the adverse effects and mechanisms by which plastic particles and their degradation products affect biological systems (cell-based, organism, population, and community assays, including different trophic levels); (v) development and validation of standardized test methods suitable for assessing biological effects of plastic particles and chemicals that leach from weathering plastic in model organisms; (vi) elucidation of the role of biofilms in fate processes such as aggregation, sedimentation, and burial, and also on uptake and effects of plastic particles in marine organisms; and (vii) assessing risks related to weathering plastic in the marine environment by combining exposure assessment with effect assessment.

The development of a numerical model for predicting the 3D transport, dispersion, and fate of microplastic particles will facilitate a better understanding of plastic degradation and distribution in the marine environment, from the surface to the sediment bed. This requires the coupling of a particulate transport model (similar to a sediment transport model) with a hydrodynamic model to predict transport pathways and turbulence intensity levels. Missing currently is a model that predicts the evolution of microplastic particle transport properties, mean size or size distribution, and density. These properties could be described with a kinetic model that explicitly accounts for the fragmentation−aggregation−sedimentation processes, which in turn partially determine the persistence and fate of plastic particles, and can be derived in analogy to flocculation models for cohesive sediments (e.g., ref 58). The models should predict where plastic can accumulate below the surface by accounting for underwater currents, sediment resuspension, and other turbulence that may lead to either dilution or enrichment of plastic particles. They should also consider the "biological pump" that affects the sinking and burial of plastic particles that is affected by variability in the abundance of plankton that either colonize the plastic particles or transport them in fecal pellets to the seabed. This information is crucial for designing monitoring programs, identifying vulnerable ecosystem compartments, and developing risk assessment methodology for this emerging class of contaminants. In addition, such models will improve our scientific understanding of the distribution of microplastic by providing a platform for scenario analysis of alternative hypotheses about sources and fate processes that can be compared against field monitoring data.[59]

Research on weathering plastic is needed not only to improve our understanding of the current and potential future threats from marine litter but also to develop solutions. Understanding the degradation of plastic in the marine environment, and how it affects transport and fate, can assist in the design of "green" plastic materials. Furthermore, it can also help in the design of more sustainable management and recycling strategies, by identifying thresholds and providing guidance to avoid the risks from excessive use and emissions of harmful chemicals and plastic materials. By considering the fate of plastic debris in the environment, we can start to address the issues of plastic pollution more holistically from scientific, regulatory, and design perspectives.

Plastic debris in the oceans fits the profile of a planetary boundary threat in at least two of the three categories defined by MacLeod et al.,[10] in that it is causing planetary-scale exposure that is not readily reversible. Thus, plastic products should be candidates for precautionary substitution or phase-out with more benign alternatives, for example, by substituting paper packaging or glass when possible. Plastic waste should be minimized by improving recycling infrastructure and closing material flow cycles. Plastic debris is a planetary boundary threat if it additionally causes a currently unknown disruptive effect on the Earth system. There is no systematic way to overcome our ignorance and discover such an unknown effect, but vigilance through environmental monitoring and scientific study of processes related to weathering of plastic debris may contribute to avoiding transgressing a currently unknown planetary boundary.

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Notes

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