Open Horizon Scientific Review

Vol. 03 No.04 2025

Microplastic Interactions with Dissolved Organic Matter in Aquatic Systems

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ABSTRACT

Microplastics are now found in rivers, lakes, estuaries and oceans, where they meet dissolved organic matter, a complex mixture of humic, fulvic and protein-like compounds that is present in all natural waters. The interaction between these two components changes the surface properties, aggregation, transport, transformation and ecological effects of microplastics, and it also changes how dissolved organic matter itself behaves. This article reviews the occurrence and properties of microplastics, the composition of dissolved organic matter, the mechanisms of sorption, the formation of organic coatings known as eco-coronas, and the consequences for aggregation, settling, photochemical ageing, biological colonisation and pollutant binding. Analytical methods for studying these interactions are summarised, and research gaps are identified. A representative example shows how increasing organic matter concentration shifts the surface charge of common plastics toward similar negative values, and the numbers shown are illustrative. The article concludes that organic matter is a central factor controlling the fate and risk of microplastics in aquatic systems, and that realistic studies must include it.

Key words: *Microplastics, Dissolved organic matter, Aquatic systems, Eco-corona, Contaminant transport*

Introduction:

Plastic production has risen steadily for decades, and a large share of plastic waste reaches the environment through poor waste management, runoff, wastewater and the fragmentation of larger items. Particles smaller than five millimetres, called microplastics, include fragments, fibres, films and beads from cosmetics, textiles, tyres and packaging. They have been detected in surface waters, sediments and organisms from polar regions to the deepest ocean trenches, and in the Indus and other major river systems that carry waste from densely populated catchments.

In natural waters, microplastics never exist alone. They are immersed in a medium containing dissolved organic matter, which makes up the largest pool of organic carbon in most aquatic systems and arises from plant and algal decay, microbial activity and human inputs. This matter is rich in functional groups and reactive with surfaces, so it rapidly adsorbs to submerged particles, forming a coating that defines how the particle interacts with its surroundings.

Understanding these interactions is vital because laboratory tests with pristine plastics in clean water may not reflect behaviour in the environment. The organic coating can alter buoyancy, stability against aggregation, binding of toxic chemicals, uptake by organisms and rates of degradation. This article examines these aspects in order, from the nature of the materials involved to the methods and open questions that will guide future research.

1. Occurrence and Properties of Microplastics in Aquatic Systems

Microplastics are classified as primary, manufactured at small size, or secondary, formed by breakdown of larger debris through sunlight, mechanical abrasion and biological action. Polyethylene, polypropylene, polystyrene, polyvinyl chloride and polyethylene terephthalate dominate in the environment, and polyester and nylon fibres from laundering are widespread in wastewater. Concentrations vary by orders of magnitude depending on proximity to sources, hydrology and sampling methods.

The physical and chemical properties of microplastics determine how they behave. Density controls whether particles float, as polyethylene and polypropylene do, or sink, as polyvinyl chloride and polyethylene terephthalate do. Hydrophobicity, crystallinity, surface roughness and the presence of additives such as plasticisers and flame retardants influence interaction with other substances, and particle size and shape affect settling, transport and ingestion.

Over time, weathering changes the surface. Ultraviolet light and oxygen create carbonyl and hydroxyl groups that make the surface more polar and rougher, and cracks and pits increase the area available for sorption. A weathered particle can therefore behave very differently from a new one, which is an important consideration when comparing laboratory and field results.

2. Composition and Sources of Dissolved Organic Matter

Dissolved organic matter is operationally defined as organic compounds that pass through a filter of about 0.45 micrometres. It is a complex mixture of thousands of molecules, including humic and fulvic acids derived from the decay of terrestrial plants, protein-like and carbohydrate compounds released by algae and bacteria, and anthropogenic compounds from wastewater and agriculture.

Its properties vary widely. Terrestrial material tends to be aromatic, high in molecular weight and rich in carboxyl and phenolic groups, while microbially derived material is more aliphatic and nitrogen-rich. Specific ultraviolet absorbance gives a measure

of aromaticity, and spectral indices reveal source and degree of processing. Concentrations range from below one milligram of carbon per litre in clear oceans to tens of milligrams in wetlands, humic lakes and polluted rivers.

These characteristics determine how dissolved organic matter interacts with surfaces. Aromatic and hydrophobic fractions adsorb most strongly to nonpolar plastics, while polar and charged fractions affect colloidal stability through electrostatic and steric effects. Water chemistry, particularly pH, ionic strength and the concentration of calcium and magnesium, further modifies the behaviour of the matter.

3. Sorption Mechanisms Between Microplastics and Dissolved Organic Matter

Adsorption of dissolved organic matter on microplastics is governed by several mechanisms acting together. Hydrophobic interaction draws aromatic and aliphatic components toward nonpolar polymer surfaces such as polyethylene and polystyrene. Pi-pi interactions occur between aromatic rings of humic molecules and polystyrene, and hydrogen bonding is important on polar surfaces, including aged plastics and polyamides.

Electrostatic forces act between charged groups of the organic matter and the plastic surface. Most dissolved organic matter is negatively charged at environmental pH, so adsorption on negatively charged plastics is limited unless cations such as calcium bridge the two surfaces. Cation bridging and complexation explain why increases in hardness enhance sorption in many experiments, and why pH changes that alter charge strongly affect uptake.

The extent and kinetics of sorption are described by isotherm and rate models, and results often show fast initial uptake followed by slow approach to equilibrium. Molecular size matters because larger molecules preferentially adsorb but may be unable to enter pores and cracks, and competitive adsorption leads to fractionation, with the plastic selectively retaining the most hydrophobic and aromatic compounds from the mixture.

4. Formation of the Eco-Corona and Surface Property Changes

When a particle enters natural water, it rapidly acquires a layer of adsorbed biomolecules and organic matter called an eco-corona, by analogy with the protein corona formed on nanoparticles in biological fluids. The corona forms within minutes to hours and continues to evolve over days as additional components adsorb, exchange and are transformed by microorganisms.

The corona changes the surface in ways that matter for behaviour. It adds negative charge through carboxyl and phenolic groups, increases

hydrophilicity, and creates a steric layer that affects how particles approach one another. Particles that were hydrophobic and weakly charged therefore become more hydrophilic and more strongly charged. The figure below shows an illustrative example in which surface charge of three common plastics shifts toward similar negative values as organic carbon concentration increases.

The tendency of different plastics to converge toward a similar surface character after coating has an important consequence. Their initial differences in polymer chemistry, which dominate in laboratory tests with clean particles, may partly give way to the properties of the organic layer, so that behaviour in natural waters depends on water chemistry as well as on polymer type. The thickness and composition of the corona also depend on the source of the organic matter, with humic-rich waters giving different coatings from algal-dominated waters.

5. Influence on Aggregation, Transport and Settling

Colloidal stability of microplastics depends on the balance of attractive van der Waals forces and repulsive electrostatic and steric forces between particles. Organic coatings usually increase negative surface charge and add a steric barrier, so that particles in freshwater with low ionic strength remain dispersed for longer periods. This stabilisation can extend transport distance, increase the time that particles stay in the water column and raise the chance of encountering organisms.

In waters of higher ionic strength or in the presence of divalent cations, charge screening and cation bridging promote aggregation. Estuaries are especially important because mixing of fresh and salt water produces rapid changes in ionic strength, and organic matter can promote flocculation and formation of larger aggregates that settle. Heteroaggregation with natural colloids, clay minerals, algal cells and organic detritus produces dense aggregates that sink even if the plastic itself is buoyant.

Biofouling, the growth of microbial biofilms on the surface, works together with organic coatings. Colonised particles gain density and can sink, then rise again if biofilm is grazed or degraded, which contributes to vertical transport. As a result, the burial of microplastics in sediments, and their redistribution during floods and storms, depend on the interplay of organic matter, ionic conditions and biological activity.

6. Photochemical and Biological Transformations

Sunlight drives transformation of both microplastics and dissolved organic matter. Chromophoric organic matter absorbs light and produces reactive species, including singlet oxygen,

hydroxyl radicals and excited triplet states, which can attack plastic surfaces and accelerate their oxidation and fragmentation. At the same time, dissolved organic matter can screen light and scavenge radicals, so its net effect on plastic degradation can be either acceleration or protection depending on concentration and composition.

Photodegradation of plastics also releases organic compounds into the water. Leachates of dissolved organic carbon, additives and monomers from weathered plastics add a new and labile fraction to the natural pool, and they can stimulate microbial growth and alter the composition of the community. Studies have shown that plastic-derived organic matter is often readily bioavailable, with potential consequences for carbon cycling.

Microbial communities that colonise plastics, sometimes called the plastisphere, differ from those in surrounding water and use dissolved organic matter as a source of nutrients. Enzymatic activity may slowly alter polymer surfaces, although complete biodegradation of most common plastics is extremely slow. The coating of organic matter influences which organisms attach first and therefore the direction of community development.

7. Effects on Pollutant Binding and Toxicity

Microplastics can adsorb hydrophobic organic pollutants, such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons and pesticides, and may bind metals through surface groups, and they have been described as vectors for chemicals. The importance of this role is debated, because in many settings the amount of contaminant carried by plastic is small compared with that in water, sediment and natural particles, and model analysis suggests that the effect on bioaccumulation is often modest.

Dissolved organic matter modifies pollutant binding in several ways. It may compete with pollutants for sorption sites, form complexes with pollutants in solution and thereby reduce the freely dissolved fraction, or increase sorption by building a coating that provides additional binding domains for metals and polar compounds. The net effect depends on the compound, the polymer and the type of organic matter, and published results sometimes conflict.

The coating also changes biological interactions. Particles with organic corona may be more or less readily ingested by zooplankton, filter feeders and fish, may adhere differently to cell membranes, and may show altered toxicity. Some studies report reduced toxicity because organic matter

binds additives and reduces particle contact with cells, while others report increased uptake because the coating makes particles resemble food. Realistic exposure studies must therefore include organic matter.

8. Analytical Methods for Studying Interactions

Studying these interactions requires methods that characterise both the particle surface and the organic matter. Batch sorption experiments with defined particles and organic matter solutions provide isotherms and kinetics, and dissolved organic carbon analysers and ultraviolet absorbance measure how much is removed from solution. Fluorescence excitation-emission matrices, interpreted by regional integration or parallel factor analysis, reveal which fractions adsorb and how composition changes.

Surface characterisation uses zeta potential measurement for charge, contact angle for wettability, and dynamic light scattering for particle size and aggregation. Fourier transform infrared and Raman spectroscopy detect functional groups on the surface, X-ray photoelectron spectroscopy gives elemental composition of the outer nanometres, and atomic force microscopy and electron microscopy show topography and coating thickness. Quartz crystal microbalance with dissipation monitoring follows adsorption in real time and indicates the softness of the layer.

Advanced chemical analysis, including high resolution mass spectrometry, identifies molecular formulae of adsorbed and leached compounds. Field studies add complexity because particles must be separated from sample matrices without altering the coating, so gentle digestion and density separation methods are needed. Standard protocols and reference materials would allow results from different studies to be compared more reliably.

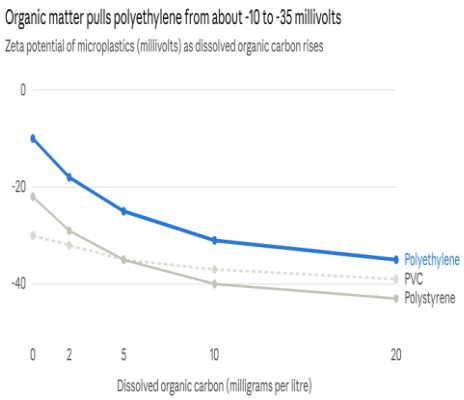
9. Environmental Implications, Research Gaps and Future Directions

The interaction between microplastics and dissolved organic matter has broad implications. By controlling aggregation and settling, it influences where plastic accumulates, whether in surface waters, sediments or organisms. By altering surface chemistry and bioavailability, it shapes exposure and risk to aquatic life, and by affecting photochemistry and microbial activity, it connects plastic pollution to the carbon cycle and to water treatment performance.

Several gaps remain. Most experiments use spherical, pristine polystyrene particles at high concentrations, while the environment contains irregular, weathered mixtures at low concentrations. Long-term ageing,

the role of specific organic fractions and the interplay with biofilms are poorly understood, and the toxicity of coated particles is inadequately tested. Little data exist for regions such as South Asia, where high loads of organic matter and plastic from rivers raise particular concerns.

Future research should use environmentally relevant particles, concentrations and waters, combine laboratory and field work, and integrate chemical characterisation with ecological endpoints. Modelling approaches that couple sorption, aggregation and transport can then predict fate across catchments. Reducing plastic input at source, improving wastewater treatment and managing waste remain essential, but a better understanding of organic matter interactions will improve risk assessment and guide effective policy.



Summary

This article reviewed the interactions between microplastics and dissolved organic matter in aquatic systems. Organic matter adsorbs to plastic surfaces through hydrophobic, pi-pi, hydrogen bonding and electrostatic mechanisms, forming an eco-corona that raises negative charge and hydrophilicity. This coating influences colloidal stability, aggregation and settling, interacts with biofilm formation and sunlight-driven transformation, and modifies the binding of pollutants and the biological effects of particles. Organic matter and plastics also change each other, with sorption removing aromatic fractions and weathering releasing new organic compounds. A range of spectroscopic, microscopic and chemical methods is available to study the processes, although standardisation is needed. Including dissolved organic matter in experiments and models is essential for realistic prediction of the fate and risk of microplastics in natural waters.

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