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A potpourri of microplastics in the sea surface and water column of the Mediterranean Sea

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ABSTRACT

This review provides insight into the abundance, origin, distribution and composition of MPs in the sea surface and water column of the Mediterranean Sea. Literature data on MP particles on the sea surface showed an evident heterogeneous distribution and composition, with marked geographical differences between Mediterranean sub-basins. A standardized protocol for water sampling, extraction and detection of plastic debris is strongly recommended. The heterogenicity of MPs distribution and its concentration levels could be related to several factors, such as the different methodological approaches. In addition, the influence of hydrodynamic features such as currents, up and down-welling, gyres and fronts could also be responsible for this heterogeneity in concentrations. Marine litter modelling studies have been applied to understand litter sources, fate, transport and accumulation in oceans. Recent studies focused on the "plastisphere" in order to better understand the potential risk of pathogen dispersion with plastic transport in the Mediterranean Sea.

1. Introduction

The Mediterranean Sea has recently been described as one of the most affected marine environments with regards to marine litter [1]. Intense navigation, highly developed tourism and important industrial and fishing activities are responsible for this trend. In some countries, lack of proper waste water treatment and densely populated coastline, home to about 150 million inhabitants, have contributed to the issue of marine litter. Concerns about marine litter in the Mediterranean Sea were first expressed in 1976, when its coastal countries, within the framework of the Barcelona Convention, adopted a protocol (amended in 1995) to protect this environment against marine and land-based sources. In 2008, the European Union developed the Marine Strategy Framework Directive (2008/56/EC) to monitor the marine environment and related activities. This was made to achieve "Good Environmental Status (GES)" by 2020, according to the directive 2010/477/EU. This included marine litter and its impact on the marine environment and biota as one of the eleven key descriptors (Descriptor #10) of marine environmental status quality. In 2013, contracting Parties of the Barcelona Convention developed a Regional Action Plan for preventing, reducing and removing marine litter from the Mediterranean through management measures, programs, thus reducing knowledge gaps and providing financial resources at a regional and national level.

The Mediterranean Sea is one of the most investigated maritime regions of the world but knowledge on marine litter is still limited and fragmented. Although the type of litter found is highly heterogeneous, plastics are the most abundant material recorded, as evidenced in extensive visual surveys conducted in the central part of the basin, where plastic floating particles reached sometimes up to 100% of the debris observed. Recently, it has been demonstrated that the total annual input of plastic inside the Mediterranean Sea equates to 100,000 tons; of these 100,000 tons, 50% are likely to originate from land-based sources, 30% from riverine systems and 20% from maritime navigation [2]. Plastics accumulate in the marine environment, ultimately degrading after several centuries or millennia in the water [3]. This leads to the fragmentation of plastic

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debris due to synergistic effects into four main categories: macroplastics (≥1 cm), mesoplastics (≥5 mm to 1 cm), microplastics (≤5 mm) and nanoplastics (≤100 μm) [4,5].

MPs can occur in the marine environment either by primary or secondary sources. Primary microplastics may directly enter the ocean in the form in which they are originally manufactured, as industrial and cosmetic abrasive, pre-production pellets or acrylic textile fibres entering wastewater circuits from clothes washing machines; whereas, secondary microplastics are derived from the breakdown of larger plastics debris due to combined chemical, physical, biological, photic and thermal actions, resulting in fragmentation of the original plastic items [6].

To date, little is known about the plastic degradation in seawater, including its time scale and ultimate sinks [7]. MPs have been recognized to be persistent in the marine environment and have also been found in the surface water of remote areas, such as Arctic and Antarctic [8]. The ingestion of plastic debris by invertebrates, fishes, seabirds, turtles, and mammals has been extensively proved [9–12]; marine organisms may confuse MPs with food or indirectly ingest MPs through prey already contaminated. MPs ingestion by marine biota presents a variety of consequences, such as reducing stomach storage capacity, impaired satiation feeling ultimately biasing feeding behaviour. Ingestion may also cause internal wounds in gastrointestinal tracts (e.g. perforated gut or gastric rupture), leading to death [13]. In addition, due to their chemical composition and large surface to volume ratio, MPs can easily adsorb hydrophobic Persistent, Bioaccumulative and Toxic (PBT) chemicals and trace metals from the surrounding seawater at concentration ranging from ng/g to μg/g [14,15]. The leakage of added plasticizers and stabilizers is also attested. This review provides insight into the occurrence and distribution of MPs in the sea surface and water column of the Mediterranean Sea, and identifies the challenges that should be investigated.

2. Discussion

In the past decade, the number of published studies on surface MPs in the marine environment has significantly increased and results show that MPs are now ubiquitous in the marine environment. The composition of MPs varies depending on the type of monomers used as building blocks; however, the most common polymers found in the marine environments (in no particular order) are polyethylene (PE), high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC) and polyamide (PA). Once released in the oceans, their environmental fate primarily depends on their physio-chemical properties, in particular polymer density, shape, position in the water column and possible interaction with different organisms [16], which influence plastic buoyancy or sink.

Polymers with lower density (e.g. PE and PP) predominantly float at the surface, while those denser than seawater (like PVC) tend to sink, with their position varying in the water column due to water fronts or biofouling. The latter increases the weight of particles, influencing buoyancy and accelerating their sinking on bottom sediments [4,17]. Moreover, degradation, fragmentation and the leaching of additives can affect the density of objects and their distribution along the water column.

2.1. MPs in sea surface waters of the Mediterranean Sea

A summary of MP concentrations found in the Mediterranean Sea together with investigated areas, number of samples, year of sampling, sampling net and instrumental methods to use for detection of MPs is reported in Table 1. The absence of a standardized sampling protocol for the identification and quantification levels of floating MPs complicates their comparison. This is mainly due to differences in extraction and detection methods, number of replicates, gear and mesh sizes. The most common methods for MPs identification consist in visual inspection of possible plastics on optical microscope (typically a stereomicroscope), which could bring potential bias depending on various factors such as the sensitivity of the examiner, the particle shape and size, the sample matrix and the microscope used [18]. Thus, it is fundamental that these measurements are followed by chemical analysis of the polymeric composition (i.e Fourier Transform Infrared Spectroscopy (FTIR), (μ)-Raman, scanning electron microscope (SEM) to exclude that some non-plastic items are estimated as MPs. The quantity of MPs trapped in the net has been expressed in different units, divided by the towed area (e.g., items/km^2) or volume of sampled water (items/m^3) or weight by sampled area (g dry weight/km^2). Moreover, Kulkulka et al. [19] evidenced that the concentration of MPs in the sea can be strongly affected by the presence of winds prior to sampling, thus, in recent studies, the effect of wind mixing has been evaluated to correct concentration data [20–24].

The first study on the abundance of floating plastic debris in the Mediterranean Sea was conducted by Morris et al. [25], who reported a concentration of about 1300 plastic items per km^2 at 50 miles SW of Malta in 1979. In 1998, Kornilios et al. [26] found an average weight concentration of 119 ± 250 g d.w./km^2 in the Cretan Sea. Literature on the topic has been steadily increasing in the last decade, showing a heterogeneous spatial and temporal distribution of MPs concentrations in the Mediterranean's surface waters. Location of literature sampling stations is displayed in Fig. 1. Taking into consideration that MPs tend to accumulate at the sea surface, mainly in the neustonic layer [27], neustonic microplastic abundances were determined in the Northwestern (NW) Mediterranean Sea during a cruise in the summer of 2010. A 90% of the 40 sampling stations contained MPs (size 0.3–5 mm) of various compositions, their abundances showed wide fluctuation between the sampling stations, with an average particle concentration of 116,000 particles/km^2 over all the investigated area, and the highest concentrations (>360,000 particles/km^2) observed in shelf stations [28]. In the following studies, 0.15 particles/m^3 were found in the same area, with an average concentration of 62,000 particles/km^2 observed in the Bay of Calvi (Corsica), between August 2011 and August 2012 [29], with neustonic plastic particles observed in 74% of the 38 samples [3].

NW Mediterranean coasts were also characterized with the presence of high accumulation zones in the near-shore region [20], whereas, Baini et al. [22] evidenced that seasonality and distance from the coast did not affect MPs abundance, showing high MPs levels at 10 and 20 km from the coast and lower values in the stations closer to the coast of Tuscany (Italy). Moreover, same authors [22] suggested the fragmentation of larger PE and PP items as the main source of MPs, having predominantly found fragments and sheets of 1–2.5 mm size.

Schmidt et al. [30] found an average MPs concentration of 112,000 items/km^2 (range 6000–1,000,000 items/km^2) in the Gulf of Lion between 2014 and 2016 evidencing that a high spatial heterogeneity for MPs distribution can also be observed on a small scale for samples taken at a distance of 10 km from one another. The same study confirmed that the Rhone River, densely populated areas (e.g. Marseille) and industrialized coastlines act as inputs of MPs in the NW Mediterranean Sea. In addition, the Northern Current (NC) acts as a transport pathway for the dispersion of MPs from the input areas to wider regions.

In a recent paper [31], the abundance and distribution of MPs were also evaluated in two areas close to the mouth of Po and Tevere

Table 1
Literatura data on microplastic abundance in Mediterranean surface waters and instrumental analysis methods used for detection of MPs.

Mediterranena sub-region	Number of samples	Year of sampling	Average Particle Concentration	Units	Average Weight Concentration g d.w./km^2	Sampling nets	Net mesh μm	Instrumental Analysis Method	References
Central Mediterranean Sea		1980	1300	Items/Km^2					[25]
Cretan Sea	25	1995			119 ± 250	net Mesh	500		[26]
NW Mediterranean	40	2010	0.116	Items/m^2	2020	net Mesh	333	Binocular microscope	[28]
Western Mediterranean (Ligurian Sea and Sardinian Sea)	23	2011	0.62 ± 2.00	Items/m^3		WP2	200	Stereomicroscope	[9]
Whole Mediterranean Sea	71	2011	147,500	Items/Km^2	579.3	Manta trawl	333	Optical microscope	[32]
Western Mediterranean Sea (Bay of Calvi)	38	2011–2012	62,000	Items/m^2			200	Binocular microscope	[29]
Western Mediterranean Sea (Ligurian Sea)	70	2012	0.31 ± 1.17	Items/m^3		WP2	200	Stereomicroscope	[11]
Western Mediterranean Sea (W Sardinia)	27	2012–2013	0.17 ± 0.32	Items/m^3		WP2	200	Stereomicroscope	[10]
Whole Mediterranean Sea	39	2013	243,853	Items/Km^2		Neuston net	200	Stereomicroscope	[34]
Western Mediterranean Sea (W Sardinia)	30	2012–2013	0.15 ± 0.11	Items/m^3		Manta trawl	500	Binocular stereomicroscope	[3]
Western Mediterranean Sea (Ligurian Sea)	33	2013	125,930 ± 132,485	Items/Km^2		Neuston net	200	Zooscan digital scanner/FTIR	[20]
Western Mediterranean Sea	24	2013–2014	69,161 ± 83,244 0.26 ± 0.33	Items/Km^2 Items/m^3		Manta trawl	333	Stereomicroscope/FTIR	[22]
Western Mediterranean Sea	6	2014	112,000	Items/Km^2		Manta trawl	780	Zooscan digital scanner	[30]
Western Mediterranean Sea	21	2014	82,000 ± 79,000	Items/Km^2		High Speed Manta Trawl	333	Stereomicroscope/FTIR	[24]
Aegean-Levantine Sea	108	2013–2015	7.68 ± 2.38	Items/m^3		Manta trawl	333	Stereomicroscope/FTIR	[38]
Adriatic Sea	17	2014	472,000 ± 201,000	Items/Km^2		Neuston net	300	Digital microscope/ near-Infrared spectrometer	[40]
Aegean-Levantine Sea	17	2015	140,418 ± 120,671	Items/Km^2		Manta trawl	330	Stereomicroscope/FTIR	[39]
Aegean-Levantine Sea	7	2016	37,600	Items/m^2		Manta trawl	333	Microscope	[35]
Italian minor Islands	8	2017	0.3 ± 0.04	Items/m^3		WP2	333	Binocular stereomicroscope mFTIR	[31]
Northeastern Levantine coast of Turkey	14	2017	1,067,120	Items/Km^2		Manta trawl	333	Microscope/FTIR	[23]

rivers, and in six Italian minor islands (Eolie, Ventotene, Asinara, Elba Tremiti, Ischia), together with the concentrations of polychlorobiphenyls (PCBs) and organochlorines (OCs). Results showed that the average microplastic density of 0.3 ± 0.04 items/m^3 (values ranged from 0.119 to 0.641 items/m^3) did not correlate with the levels of organic contaminants, evidencing that the concentrations of contaminants in water bodies is the result of multiple sources.

Studies on MPs debris in Specially Protected Areas of Mediterranean Importance (SPAMI) also play a key role in the understanding of MP impacts on biota and their potential toxicological effects on the large filter-feeding species that inhabit these environments (i.e. *Balaenoptera physalus*), due to the leaching of plastic additives or presence of other toxic chemicals. The study of Fossi et al. [9] provided the concentrations and spatial distribution of MPs in the Pelagos Sanctuary area, which is located in the NW Mediterranean Sea and encompasses about 87,500 km^2. They detected the presence of MP particles in the 56% of the total surface neustonic/planktonic samples and found a MPs abundance seven times higher in the samples collected in the Ligurian Sea (mean value 0.94 items/m^3) than in the samples from the Sardinian Sea (mean value 0.13 items/m^3), with a mean abundance of 0.62 ± 2.00 items/m^3, similar to those found by Panti et al. [10] (0.17 ± 0.31 items/m^3) in the same area. Few years later, Fossi et al. [11] detected a mean particle concentration in the same marine protected area, in the section of the Ligurian Sea, with 0.31 ± 1.17 items/km^2. Authors [10] also measured phthalates concentrations as tracers of MPs amount, and found a significant correlation between these organic contaminants and microplastic density. Both papers [9,10] evidenced high levels of MPs in the Pelagos Sanctuary, similar to those measured in the North Pacific Gyre. This highlights the possible exposure to MPs ingestion by fin whales in this area.

An assessment of floating plastic debris in the Mediterranean Sea was provided in 2011 by Ruiz-Orejon et al. [32], reporting an average weight concentration of 579.3 g d.w./km^2 and an average particle concentration of 147,500 items/km^2, mainly characterized by a <5 mm plastic size distribution.

The Mediterranean is a semi-enclosed sea, with inputs of Atlantic water originating from the Strait of Gibraltar and numerous large rivers (i. e. Po, Ebro, Nile), and characterized by high variability of surface currents and diverse instabilities [33]. Thus, it has been regarded as a great accumulation region of microplastic debris, sometimes comparable to average concentrations of five subtropical gyres [34], even if the estimates on MPs load show high variability.

The heterogenicity of the MPs distribution and of its concentration levels could be related not only to the above mentioned different methodological approaches but also to the influence of ocean circulation (currents, wave action, and wind-driven turbulences), biofouling, salinity and temperature, shape of the coast line, different land litter sources (i.e. river inputs) and coastal activities, together with hydrodynamic features, such as up-welling, down-welling gyres or fronts [30].

A recent paper [35] has evidenced the effects of multiple flood events in MPs abundance in the Mersin Bay (Turkey), in the north eastern Mediterranean region, between December 2016 and January 2017. The sampling showed a dramatic 14-fold increase of MPs pollution, ranging from 539,189 items/Km^2 before the flood period to 7,699,716 items/km^2 post-flood, and a predominance of PE both pre- and post-flood. Same authors evidenced an average quantity of 225,400 items/km^2 in the surface samples collected in the North sector of the Iskenderun Bay, while in a following survey in the same area [23] the average level was 1,067,120 items/km^2.

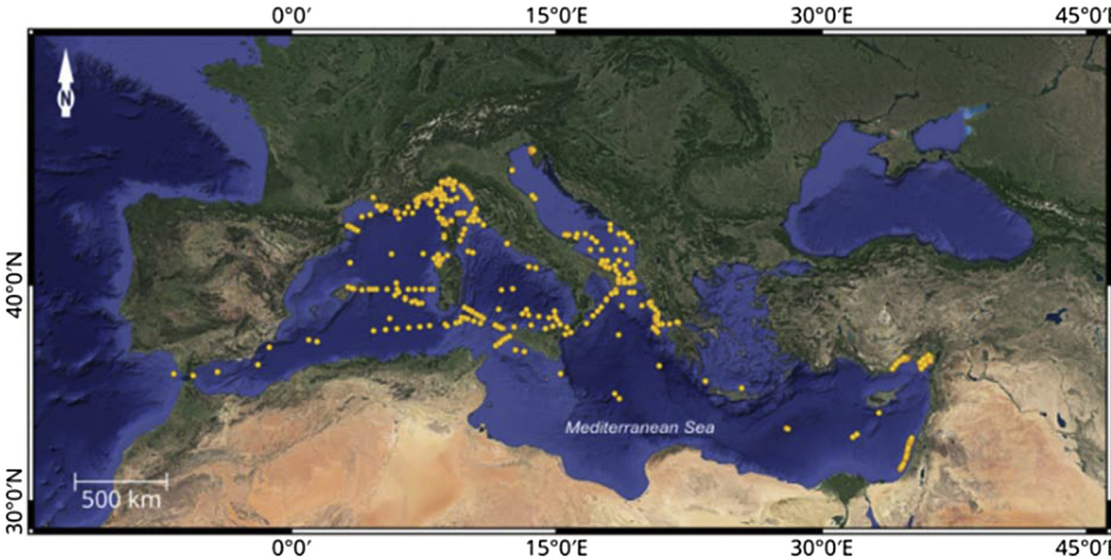

Fig. 1. Map of the Mediterranean Sea showing the location of literature sampling stations.

Marine litter modelling is a growing field aiming at understanding litter sources, fate, transport and accumulation in oceans. Current circulation is considered the principal driver of marine litter transport, as it plays a key role in the advection of items of every size, at all depths. Recently, modelling studies have evidenced potential sites of floating litter accumulation in open sea and coastal areas in the Mediterranean Sea [1,2,33]. Mansui et al. [33] evidenced that the formation of transitory open sea MPs aggregation zones is caused by the periodic strong wind stress associated with the complex local circulation patterns that result in different concentrations of MPs. Taking into consideration the formation of these plastic aggregation areas, Fossi et al. [24] proposed an interesting and promising approach, in which the overlap of micro-meso and macroplastics convergences areas (MPs mean concentration: 82,000 ± 79,000 items/km^2) with the fin whale feeding grounds could be useful for modelling and estimating potential hazards to marine biota in the Pelagos Sanctuary and other pelagic Specially Protected Areas of Mediterranean.

The mass of MP particles in the basin estimated by Van Sebille et al. [7], using the largest data set and comparing three different ocean circulation models [1,36,37], varied from 4800 to 30,300 MT, and predicted that 21–54% of all global microplastic particles (equating to 5–10% of global mass) are in the Mediterranean Sea. However, the previous result contrasted with Cozar et al. [34], who performed an extensive survey throughout the basin and found an average surface concentration of 243,853 items/km^2, comparable to the average concentration measured in the Pacific Ocean gyres. The averaged plastic concentration measured into the basin allowed to estimate the surface load of plastic in the Mediterranean (range 1000 and 3000 T), which was one order of magnitude lower than Lebreton's estimate considering both total and microplastic loads.

In strong contrast to the western basin, the Ionian and Adriatic Seas were not extensively studied until the first survey of Van der Hal et al. [38], which presented the first data on the abundance and other characteristics of MP particles along the Israeli Mediterranean coast between 2013 and 2015. Researchers found microplastics (0.3–5 mm) in all the investigated samples, with a mean abundance of 7.68 ± 2.38 items/m^3 or 1,518,340 items/km^2.

A high average concentration of floating MPs debris (PE representing 80% of analysed particles) was also recorded on the surface of the Slovenia section of the Adriatic Sea (472,000 ± 201,000 items/km^2) [40], which is a land-locked sea collecting a third of the fresh water flowing in the Mediterranean, mainly due to the Po River. Significant spatial and temporal variations in MPs pollution were strictly linked to surface currents in the area. The results confirmed the prediction of the numerical model studies, which, respectively, estimated the highest debris concentrations in the northern part of the basin and the Northern Adriatic coast of Italy [2] and identified the Mediterranean Sea as one of the basin with the highest small floating particle debris [1,2,7].

In the samples collected along the Mediterranean coast of Turkey [39] the MPs size predominantly ranged between 0.1 and 2.5 mm, with rare presence of the other sizes, whereas the quantity of floating MPs in surface water samples varied from 16,339 to 520,213 items/km^2. These results were in accordance with the estimated values resulting from the Maximenko et al. [36] rather than van Sebille et al. and Labreton et al. [1,7] oceanographic models.

More recently, Politikos et al. [40] linked a circulation model with a particle-tracking model to simulate, for the first time, the transport of floating litter particles in the Aegean Sea (Greece), evidencing a major tendency of floating litter particles to accumulate in the North Aegean Sea, in the Saronika Gulf and Evia and Crete islands, and a tendency of the Aegean Sea to act as a source rather than receptor of floating litter pollution in the Eastern Mediterranean Sea.

2.2. MPs in the water column of the Mediterranean Sea

To the extent of our knowledge, a limited number of studies have focused on the levels of MPs in the water column (see Table 1) [9,22,39,41]. Fossi et al. [9] did not detect microplastic particles in water column samples (items/m^3) collected in the Pelagos Sanctuary; while Guven et al. [39] reported only the absence of Styrofoam in the water column in the Turkish territorial water columns, even if this material was detected on the surface water. Bagaev et al. [41] investigated the distribution of MPs debris in the water column at different depths in the Baltic Sea in 2015–2016, observing 3 to 5 times higher concentrations in the near-surface and near-bottom layers with respect to intermediate layers, with fibres as predominant shape category. Baini et al. [22] observed an average concentration of 0.26 items/m^3 in the Tuscany coast (Italy), with a predominance of fragments (62%) and filaments (29%), and 82% of the total microplastic items were in the size range < 1 mm. The abundance of smaller particles into deeper waters and the importance to study the vertical transport of ocean microplastics for improving the plastic load estimation methods was also stated by Reissner et al. [42].

More recently, researchers have started to focus their studies on the characterization, formation, composition and spatio-temporal distribution of a new ecosystem of marine microorganisms and bacteria, which colonise and live on microplastic degraded particles ("plastisphere") and can transform themselves into microbial barriers distinct from surrounding biological communities. Plastisphere has been suggested to play significant roles as a vector for distinct microbial assemblages, modulation of particle buoyancy and biodegradation of plastic polymers [43].

3. Conclusions

Plastic marine debris not only represents a serious risk for the ecosystem, involving a wide array of marina taxa, but has also serious socioecological implications in the coastal communities (i.e. tourism, maritime transport, aquaculture, fishing industry).

Long-term extensive monitoring programmes should be carried out on a regular basis to increase the *in situ* data, better quantify the occurrence of MPs in spatial and vertical profiles and sediments in a broader range of Mediterranean sub-regions, and translate these observations into predictive models. In fact, it is fundamental to improve the existing models simulating a 3-dimensional circulation in the Mediterranean Sea, that take into consideration not only wind mixing effects, but also ocean particle properties, in particular particle size, and other types of vertical transport processes, as, for example, the Langmuir circulation.

The existing data on MP particles on the sea surface showed not only an evident heterogeneous distribution but also marked geographical differences between Mediterranean sub-basins. However, there are few *bias* that do not allow a reliable and comparable quantitative data analysis in order to characterize the marine environmental status with respect to marine litter. To date, a standardized protocol for water sampling, extraction and detection of plastic debris is lacking and thus the comparison between size class categories, sampling procedures and unit values (weight, volume or area) is limited to a little number of published data. A harmonization of sampling protocols for surface and column waters is thus strongly recommended.

Other fundamental challenges rely on the analytical characterization of plastic particles, increasingly more difficult for smaller particles, and the identification of sources and sinks of MPs. This last aspect would be fundamental to better understand the fate and impacts of these polymers in the marine environments, and effectively implement knowledge-based reduction and prevention and/or mitigation measures to achieve the GES in the Mediterranean Sea. Management strategies for reducing plastic waste at source, as well as reducing the amount of plastic used, giving incentives for recycling and improving landfill facilities, need to be stimulated and implemented to protect the marine environment.

A key aspect that should be further deepened in future studies is the ecology of microbial life on the "plastisphere", in order to better understand the potential risk of pathogen dispersion with plastic transport all around the Mediterranean Sea, the fate of toxic chemicals adsorbed to plastics that may be degraded by microorganisms and the potential for microbial degradation of synthetic plastics.

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