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Review

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Microplastics in the cryosphere - a potential time bomb?

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Abstract

Microplastics (MPs) have been detected in many parts of the world in snow, hail, sea ice, glaciers, and permafrost. The ubiquity of microplastic around the globe means that there is a need to focus on its circulation dynamics in the Earth's diverse ecosystems; the prominence of MP fibers, which has been indicated as of human clothing and activities, in high altitude frozen water is explained by their enhanced suspension in the air, allowing them to be transported over long distances from urban centers. The MP particles can act as nucleation centers for ice crystals and, once incorporated, reduce the albedo (reflective capacity) of the frozen mass, causing temperature increases. However, cores have indicated that ice in glaciers may remain frozen for thousands of years. This article reviews the quantities and types of MPs that have been detected in snow, hail, sea ice, and glaciers. The potential for release of these, as well as MPs in the permafrost, following global warming, is discussed. As the global warming process evolves, these sites will act as additional sources of MPs accumulated over the course of recent human history. It is important to be aware of the future entry of microplastic into the global environment from these sources, especially into the already fragile extreme ecosystems of the cryosphere.

Keywords: Ice contamination, pollutants, snow, extremophilic organisms



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INTRODUCTION

Microplastics (MPs) reach aquatic environments from different terrestrial sources and by different pathways^[1,2]. Sources include manufacturers of plastic products used in industry or agriculture, as well as clothing and utensils used domestically or for fishing or aquaculture^[3-8]. Pathways include the physical and chemical degradation of plastic materials in the terrestrial environment^[9] and the release of MPs from sewage treatment plants^[10].

After entering the aquatic environment, MPs pass through several further degradation paths [Figure 1], including physical, chemical and biological action, which may reduce them to nanoparticles (NPs), 1-1,000 nm in size, or even further^[11]. Physical breakdown includes light, thermal and mechanical degradation, while chemical degradation mainly includes hydrolysis and thermal oxidation reactions^[12]. MPs may be degraded more rapidly since plastic molecules are squeezed in the ice and produce an excited state that leads to accelerated oxidation and degradation^[13].

In addition to the mechanical and photodegradation of microplastic in the aquatic environment, microorganisms, for example *Bacillus sp.*, *Rhodococcus sp.*^[14], *Pseudomonas aeruginosa*^[15], *Zalerion maritimum*^[16], and *Aspergillus clavatus*^[17], may use plastics as an energy source, resulting in their degradation and inciting physical and chemical impacts which include alterations in the surface structures of the particles. They may produce chemical bonding structures, such as carbonyl groups, ketones, and aldehydes^[14]. Thus, microorganisms may contribute to polymer breakdown first by producing surface changes and then by releasing extracellular enzymes, resulting in chain cleavage to produce monomers that can be used by the aquatic microbiota^[14,18]. Some microbial species can convert polymers into monomers and, in a few cases, break down them into carbon dioxide and water.

In aqueous environments where temperatures fall below freezing, however, any microbial activities will be slow, if not absent. These regions, which include various forms of frozen water, are collectively known as the cryosphere [Figure 2].

The cryosphere is composed of a series of environments considered of great importance in the global biogeochemical balance and radiative forcing (energy balance) of the Earth. Being controlled by the global climate, the cryosphere is responsible for maintaining the climate balance of the planet^[19,20]. It contains "extremophilic" forms of life, that is, those capable of withstanding extreme environmental conditions. In ecosystems located at the poles of the planet, where mathematical models of global circulation previously projected a more pronounced rise in temperatures^[21], the raised subsurface sea temperatures^[22,23] have already caused increased retraction of the ice shelves^[24,25]. Some benthic invertebrate^[26] and larger vertebrate populations^[27,28] have decreased. The original habitats and the primary production process are being dramatically altered^[29,30], although for other species, the short-term impacts may not yet be significant^[31].

Snow layers are the main element of the cryosphere. They reach around 25 million km², most being present in the northern hemisphere. Obviously, their total size varies according to the season^[32]. Sea ice, on the other hand, is present in most of the polar regions of the seas, covering an average of about 20 million km²^[33].

Except for perennially frozen environments, ice on rivers and lakes during the year is due to seasonal cooling. Like snow cover, the ground freezes depending on the season. Permafrost, the permanently frozen portion of the soil, occupies approximately 24.5% of the Northern Hemisphere. Its maximum thickness reaches 600 m in northeastern Siberia and Alaska^[34].



Figure 1. Plastic degradation processes in aquatic environments.



Figure 2. The various environments that make up the cryosphere.

Finally, about 77% of the global cryosphere is concentrated in ice sheets on land. These total about 64 m, sea level equivalent (or potential sea level rise), and are located mainly in Antarctica and Greenland. The Antarctic and Greenland ice systems have a fundamental impact on atmospheric circulation, the cyclone system and the global energy balance. Large portions of the West Antarctic ice sheet are concentrated below sea level; the main mass, however, rests on bedrock in Antarctica. In the central part of the mantle, due to pressure or geothermal heating, the ice forms subglacial lakes. Ice shelves and outgoing glaciers continuously generate icebergs (about 2,072 km³ of ice in Antarctica and 235 km³ in Greenland)^[35].

MPs have been found in the many forms of frozen water around the world and might be expected to persist unaltered under such conditions. The deterioration rate of MPs may indeed be reduced in continuous permafrost zones, where freezing and thawing do not occur and light, temperature and oxygen levels are low. However, following global warming, the stable permafrost will undergo an alternation of physical states^[36], allowing MP release and degradation. The same may occur with the forms of frozen water.

MPs have been detected in snow and ice samples in many countries using various methods of collection, even manual^[37]. Examples include Italy^[37], Mount Everest^[38], Ecuador^[39], Iceland^[40], Tibet^[41,42], Austria^[43] and Antarctica^[44]. In the polar regions where water occurs predominantly in the frozen state, there is little human influence. Nevertheless, MPs have been found in such locations. The main types of plastics indicated in the literature are polyethylene terephthalate (PET), polyamide (PA), polyethylene (PE), and rubber^[45]. For a brief review of the methods used in detection and identification, see Zhang *et al.* (2022)^[45].

The potential for microbiological degradation of MPs has often been considered, and even ice-derived bacteria have been suggested as candidates^[46-48]. The presence of microorganisms in sea ice has been studied by several groups^[49-51]. It seems clear that these psychrophilic organisms, bacteria, archaea, and algae grow in liquid water at the sea-ice interface during warmer weather and become incorporated into the ice in winter. Thiele *et al.* (2022), collecting ice core samples from the Arctic pack ice north of Svalbard, Norway, studied the changes between the winter and summer communities in Arctic Sea ice, concluding that the winter community used a nitrogen-based metabolism, which switched to microorganisms that used carbon derived from algae and cyanobacteria in the spring and summer^[52]. Although not studied by these workers, it is possible that some of these microorganisms could be plastic-degraders.

The mechanics of freezing represent a survival challenge to living organisms, as ice crystallization can damage cell membranes. Life in the cryosphere is thus particularly difficult and hence scarce; most of the organisms are bacterial and archaeal groups, such as *Pseudomonas*, *Calothrix*^[53], and Bacteroidetes^[54]. To protect themselves, the psychrophilic cells concentrate lipids and antifreeze enzymes to maintain physical plasticity below the freezing limit and to allow cellular membrane homeostasis and biochemical reactions. They produce ice-binding proteins that act via thermal hysteresis and inhibition of ice recrystallization^[55]. Overall, little is known about the potential impacts of microplastics on organisms that live in the cryosphere, especially the microbiota, although substrates that are more difficult to biodegrade (such as plastics) have been suggested to reduce the growth potential of certain psychrophilic organisms^[46]. Research on psychrophilic and plastic-degrading microorganisms continues, but it seems unlikely that the microbiota associated with MPs in the cryosphere will influence plastic degradation either before or after any thawing event. Considering the difficult accessibility of these environments and the impact that global warming will bring, this article seeks to provide more details about the presence of MPs in the cryosphere and potential effects of global climate change on the balance and circulation of microplastics from these environments. The article was written based on the scientific literature available through the platforms ResearchGate, Scientific Electronic Library Online (SciELO), ScienceDirect, and Google Scholar, among others. MPs in the various forms of frozen water that make up the Earth's cryosphere are discussed in the following sections.

SNOW

Snow is a temporal sink for MPs^[45] and a method of aerial transport of these particles, which can act as nucleation centers for ice formation in the atmosphere^[56]. Various types of plastics are found in snow in different places in the world and at different levels of urbanization. In Arongqi city in the inner Mongolian plateau, 86-199 MPs L⁻¹ of freshly fallen snow were detected^[57]. Most were fibers, but the type of plastic varied. In Hokkaido, Japan, MPs found in all deposited snow samples were mainly alkyd, ethylene-vinyl acetate, and PE^[58]. These were attributed to long-distance transport through the atmosphere, whereas the rubber and larger particles found mainly in cities and near highways were considered to be from local sources. A similar situation was found in Arctic snow falling on sea ice^[59]. It contained large amounts of MPs, including road MPs like tyre-wear particles, which would have been transported in snow from North America and Europe, later falling on Northern Greenland and other parts of the Arctic.

Snow samples taken in cities or other conurbations are expected to yield higher MP counts. However, Crosta *et al.* (2022), working in the Italian Alps, hypothesized that the higher levels of MPs on the Ebenferner-Vedretta Piana glacier (0.265 ± 0.027 MPs g⁻¹ dry weight) were higher than those on the Forni and Cedec glaciers (0.033 ± 0.007 and 0.025 ± 0.009 g⁻¹ dry weight, respectively) because of its greater footfall^[60]. In this case, the direct influence of humans was suggested, rather than the transfer of MPs from more distant urban centers. However, most glaciers are not subject to human footfall and long-range transport is the main source of their contamination.

Transport through the air, which can occur over many hundreds of kilometers, can result in MPs being degraded to nanoplastics (NPs), with a resulting increase in the total particle counts. Materić *et al.* (2021) detected 46.5 ng·mL⁻¹ NPs of melted surface snow in the high Austrian Alps, mainly composed of polypropylene (PP) and PET^[61]. It was assumed that these originated as larger particles in European towns and cities and were broken down to NPs during aerial transportation. The authors calculated that more than 2×10^{11} NP particles were deposited per square meter of surface snow per week.

Polymer types in Arctic snow have been found to vary greatly. Bergmann *et al.* (2019) found that varnish (acrylates), plasticized rubber and polyamides (PA) were most common, while in European snow, MP composition was 67% polyamide, varnish, rubber, ethylene vinyl acetate (EVA), and PE^[62]. The Antarctic had been considered a relatively untouched (unpolluted) area until MPs were detected there in 2020^[63]. More recently, MPs (mainly PE fibers) have been detected in fresh snow samples collected near and distant from research stations in the Ross Island region and considered likely to originate either locally, in clothing and equipment around research stations, or, following modeling using the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT)^[64], to have a possible origin up to 6,000 km away^[44].

A rare instance of the almost complete absence of MPs in snow was reported in Dimon Lake, a highmountain lake in the Italian Alps^[37]. No MPs were detected in the lake water, sediment, or biota. The extremely low MP (PET) particle levels in the snow $(0.11 \pm 0.19 \text{ L}^{-1})$ were suggested to be due to particles trapped by massive snow precipitates in the winter. The location obviously influences the types of plastic present in snow, but there is no evidence of any relationship between snowflake formation and the type of particle entrapped.

Napper *et al.* (2020) examined the presence of MPs (above 30 μ m) in snow samples taken from Mt. Everest at 5,300 to 8,400 m above sea level^[38]. They found MPs in all snow samples, with the highest level at the Base Camp (79 particles L⁻¹). The majority were fibers and plastic types were PE > acrylic > nylon > PP. The researchers concluded that the fibers were most likely deposited from the clothes and equipment of climbers, who spend more time at the base camp, and that high levels of MPs in such snow-covered areas are related to tourism activities. The majority of technical clothing worn by trekkers and climbers on Mt. Everest is composed of synthetic fabrics and De Falco *et al.* (2020) estimated that most MP fibers are released into the air as a direct consequence of wearing clothes made of MP^[65]. A recently developed online tool for calculating the "plastic footprint"^[66] determined that, of a distinct group of students living in the mountains, mountain activities had the second largest footprint (after food consumption), and that this was due mainly to synthetic fleeces, followed by special climbing footwear. Although many other workers have detected more MP fibers than fragments in snow^[62,67,68], they have not always attributed this to clothing worn at the site, more often considering fibers transported through the air or water. Owing to the large surface area to volume ratio of MP fibers, the air resistance is increased, and the settling speed is reduced, leading to a high proportion of fibers at high altitudes^[69,70].

HAIL

Hail is produced when a water droplet is raised above the freezing level in the atmosphere. The droplet attracts supercooled vapor that freezes on contact, causing the hailstone to grow [Figure 3A].

The recent increased incidence of giant hailstones has been linked to the presence of MP fibers, which act as nucleation centers^[71]. These authors used micro-FTIR and -Raman spectroscopy to identify over 450 MP fibers in the interior of 10-12 cm diameter hailstones that fell in Slovenia. Felton *et al.* (2021) had previously reported MPs (mainly fibers) in four large hailstones from thunderstorms in Texas; one hailstone contained an MP fragment^[72]. There are very few reports on MPs in hailstones, but their plastic-related content may well be found to be similar to that of snow. Their formation in the atmosphere is similar, but differences are clear. Hail falls in defined paths known as hail swaths. They can range in size from 100,000 - 215,000 ft² to an area 10 miles wide and 100 miles long. Hailstorms normally last from a few minutes up to 15 min in duration, accumulating to a depth of over 5 cm [Figure 3B], and can occur in areas not normally associated with frozen water. The increasing frequency and severity of hailstorms in Europe have been associated with climate change^[73], but the influence of MPs on the size and duration of hailstones has never been considered.

SEA ICE

Sea ice is a highly variable and complex biogeochemical component of the Antarctic marine environment^[74]. Two major sea ice types can be discerned - landfast ice and pack ice. Whereas pack ice is free drifting sea ice, which moves with winds and currents, landfast sea ice is attached to the coast, shallow seafloor, or grounded icebergs^[75]. Landfast ice usually forms and dissipates seasonally, controlled by atmospheric and oceanic conditions.

The first indication that MPs were present in sea ice was in the early 1960s when plastic fragments were found in Canadian seabirds^[76]. In the 1970s, the quantity of beached plastic increased substantially in the Bering Sea^[77], suggesting its deposition from ice. Since this time, MPs have been identified in sea ice in many areas. As long ago as 2014, Obbard *et al.* stated that sea ice at the North Pole is a major historic global sink for MPs^[78]. Von Friesen *et al.* (2020) found that the average number of anthropogenic MPs (> 50 μ m) per liter in Arctic sea ice was 158 ± 155 (221-1,054) and that some of these were derived from pigmented ship paint^[79]. MPs were released during the summer melt and thus became directly available to the marine biota of the summer bloom, increasing the immediate risk of plastic-associated damage to sea life.

Peeken *et al.* (2019) found that most of the MP particles identified in the Central Arctic sea ice cores were smaller than 50 μ m, with 67% being of the smallest detectable size (11 μ m); this suggests that von Friesen's numbers are too low and also indicates the high risk of uptake by and damage to the cells of marine organisms if the ice melts^[80]. Peeken's group found over 12,000 MP particles L⁻¹, a much higher number than previous workers, and attributed this to their methodology allowing the detection of much smaller particles. They deduced that MPs became incorporated into the ice when it was first formed and also as it continued to grow while passing through the water masses. The high levels of PE found were attributed to the remains of the Great Pacific Garbage Patch, now being driven along the Bering Strait into the Arctic Ocean. However, in ice from the shallow seas along the margin of Siberia, paint particles from ships and nylon from shipping nets were predominant. These ice floes take a maximum of 11 years to reach the Fram Strait. Here, they melt, releasing the MP load, which may then become colonized by microorganisms and sink into the sediment^[81].



Figure 3. (A) Image of a 6 cm hailstone [National Severe Storms Laboratory (NSSL) Collection: https://photolib.noaa.gov/Collections/ National-Severe-Storms-Laboratory/Hail/emodule/462/eitem/275]; (B) deposited hail in Colorado, in USA's "Hail Alley", August 2019.

MPs do not affect the growth of sea ice^[82], although they may act as nuclei for ice formation^[56]. High concentrations of microplastics at the ice surface can, however, increase ice salinity and reduce its reflectance properties (albedo)^[82], which can increase melting. Sea ice is a significant sink for MP pollution. MPs will concentrate as the water becomes ice. Drifting ice floes, which can be many square kilometers in size, transport MPs potentially over many kilometers. The melting ice can act as a vector of MPs not only laterally but also vertically^[83].

In the Arctic, the sea ice is dominated by positively buoyant microplastics, transported to the area through surface transport, while the Southern Ocean is dominated by neutrally buoyant plastics, transported to the area through deep water^[84]. These differences in plastic type have not yet been explained; they may have something to do not only with the origin of the particles, but also with their interaction with microorganisms during passage through the water bodies.

GLACIERS

Glaciers are particularly efficient at concentrating small particles from the air^[85]. They provide interesting natural freezing and thawing events that involve the uptake and release of MPs. Materić *et al.* (2020), testing a new detection technique based on thermal desorption - proton transfer reaction - mass spectrometry, analyzed snow collected on a glacier in the Austrian Alps at 3 km above sea level and far from any anthropogenic activity for the presence of MPs and NPs^[43]. Samples from within a snowpit, cores from nearby ice on the glacier, and snow covering the ice were collected. Surface snow and snowpit samples all contained PET, while snowpit samples also contained polypropylene copolymer (PPC) and polyvinyl chloride (PVC). After filtration through 0.2 μ m pore size filters to extract NPs, however, only PET was detected. The PET NPs had the highest concentration of all plastics detected in the snow and snowpit, as well as in recently deposited snow. The authors considered that more work would be needed to determine whether any PS (polystyrene) MPs present might have undergone chemical changes by weathering. PS was not detected in their analyses, although it had been reported in remote parts of the Pyrenees, occurring as sheets and fragments^[86].

Using data previously obtained from the high Austrian Alps in 2020, Materić *et al.* (2021) specifically examined the content and importance of NPs in the samples^[61]. They subjected the data to analysis using the HYSPLIT dispersion model^[64] to track the transit of the NPs over the previous 96 h. The results suggested that NPs had been carried over large distances and principally from highly populated areas in Europe,

although some deposits could have been carried from beyond Europe. It has been suggested that marine sources may contribute to atmospheric MPs^[87] and the HYSPLIT model would indicate that this is certainly possible in this case.

The importance of MP transport in the atmosphere for the spread of MP pollution was emphasized by Stefánsson *et al.* (2021), who, using optical microscopy and Raman spectroscopy, recorded several types of MP particles of a wide range of sizes and materials in the Vatnajökull Ice Cap^[40]. This ice cap, located in southeast Iceland, is, by size, the largest ice cap in Europe. The types of plastic materials identified included polyurethane, polyvinyl chloride, polyamide, and acrylonitrile butadiene styrene.

Despite the scarcity of studies regarding the presence of MPs in glaciers, these ice masses are of significant importance for the global circulation of water. Glaciers occupy a significant part of the planet's surface, representing the largest reservoirs of freshwater. The presence of MPs has a direct impact on glacier balance, influencing their light absorption as well as their structure and general rheological properties^[88,89]. MPs thus potentially contribute to the melting of glaciers, contributing to sea level rise^[90]. It was recently calculated that glaciers worldwide lost 2% of their total volume in the 10 years between 2010 and 2020^[91]; the result of continued global warming will lead to rising sea levels and the release of any MPs previously locked in the ice. The real impact of MPs has not yet been measured, but they will probably act in such a way as to unbalance an already established balance fundamental for the existence of these environments.

PERMAFROST

The International Permafrost Association (IPA) defines permafrost as a ground remaining at or below 0 °C for at least two consecutive years. It comprises an essential percentage of continental Arctic environments^[92]. Some mathematical projections suggest that the temperature at this site may double more rapidly than the global average during the present century, resulting in a non-ignorable permafrost loss^[93]. Such significant permafrost damage may result in a substantial impact on global MP flux. During the melting of stored ground ice, MP migration in the permafrost region will be significantly affected, the permafrost becoming a source of MPs rather than a storage bank.

As stated before, MP degradation may be reduced and their properties may become stable in continuous permafrost zones due to the absence of the freeze-thaw process, the light-shielding effect, low temperature, and the oxygen-deficient environment. However, global warming can change this, with an annual freeze-thaw process occurring in the permafrost, allowing the installation of MP processes such as aging or other kinds of mechanical weathering, working together with biodegradation^[94,95]. Such freezing and thawing events also allow the incorporation of MPs transmitted via the atmosphere into the permafrost. MPs may become chemically transformed, for example, by polymer-chain fracture and the resulting increase in surface functional groups^[96], producing more reactive micro- or nano-plastics that are more readily spread. After such a thaw, the resulting water starts to work as a microplastic diffusion mechanism, carrying it into water bodies around the permafrost, producing a new source of contaminants for the environment.

The impact of MPs on the permafrost soil layer depends on the types of MPs present^[97]. 70% of MPs can significantly change the physicochemical properties of their surroundings, for instance, decreasing soil permeability, resulting in increased water accumulation and future water evaporation^[98]. Freeze-thaw cycles often result in the aggregation of fine particles with fragmented coarse mineral particles, making soil particles more cohesive and homogeneous. Finally, the freeze-thaw events can accentuate particle interaction, resulting in the aggregation of soil particles and MPs^[99].

QUESTIONS FOR THE FUTURE

Many authors have tried to establish correlations between changes in global mean surface temperature and mean sea level^[100-103]. However, the impact of global warming on MP dispersion and resulting circulation has not even been addressed. Difficulties due to the empirical nature of such studies may explain this phenomenon. These difficulties lie not only in those associated with collecting suitable samples, but also in the lack of appropriate methods for identifying MPs, which applies to MP research in all environments. But the truth is that these projections are becoming more and more necessary for the future management of the challenges that will be faced. The main question that remains is: How important is frozen water, in its various forms, as a storage deposit for MPs? Ice cores from glaciers on the Tibetan plateau have been used to determine the changes in the environment over hundreds of years^[104], indicating that MPs could be held in ice for many years after plastics have ceased to be produced. So, is global warming going to release large amounts of MPs? How much and at what speed? Colored MPs, especially, can absorb radiation and increase the melting of snow, the so-called "radiative forcing"^[105]. Thus, recordings of MP colors in the environment (a commonly reported characteristic) can take on a new and important meaning when dealing with icy environments. Perhaps this information is even important in the new sustainability policies of the plastics industry. MPs could be released sooner than expected from other matrices in response to their absorption of energy and consequent increase in temperature due to the color. Other issues related to MPs refer to global balances. What is the potential impact of MPs in the cryosphere on the Earth's biogeochemical cycles? There are no published studies on this. What will be the effect of global warming and the release of MPs previously trapped in the cryosphere on the world's ecosystems and on marine organisms in polar regions?

CONCLUSIONS AND PERSPECTIVES

MPs have been detected in all the types of frozen water on the planet. The majority are present as fibers; this, and the types of polymer mainly identified, have led to the conclusion that MPs in frozen water are the result of transport from areas of human activity, even though such activity may be thousands of miles away. The degradation rate of MPs in frozen environments is low, resulting in accumulation and potential future release to cause pollution of rivers and marine environments. Their increasingly significant presence in the cryosphere reduces the reflection of the sun's rays, increasing the temperature. These small particles thus contribute to the melting of polar environments, affecting not only sites considered borderline, which have a biosphere extremely sensitive to temperature change, but also the oceanic circulation as a whole, increasing the flow of melted ice and potentially unbalancing the global thermohaline fluxes. Even if we manage to solve the current MPs problem by eliminating the production of non-degradable plastics, will the hidden time bomb of MPs in frozen water around the world explode and destroy our environment?

DECLARATIONS

Authors' contributions

Conceptualization, investigation, writing - original draft preparation: Gaylarde CC, Baptista Neto JA, da Fonseca EM

All authors have read and agreed to the published version of the manuscript.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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