

Global warming releases microplastic legacy frozen in Arctic Sea ice

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INDEX TERMS

Sea ice; Contaminants

KEY WORDS

Microplastics; sea ice; Arctic; pollution

KEY POINTS

Arctic sea ice from remote locations contains tiny particles of microplastics

Polymers in microplastics were identified using Fourier Transform Infrared Spectroscopy

Concentrations of microplastics in Arctic sea ice are higher than those in water

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ABSTRACT

When sea ice forms it scavenges and concentrates particulates from the water column, which then become trapped until the ice melts. In recent years, melting has led to record lows in Arctic sea ice extent, the most recent in September 2012. Global climate models, such as that of *Gregory et al.* [2002], suggest that the decline in Arctic sea ice volume (3.4% per decade), will actually exceed the decline in sea ice extent, something that *Laxon et al.* [2013] have shown supported by satellite data. The extent to which melting ice could release anthropogenic particulates back to the open ocean has not yet been examined. Here we show that Arctic sea ice from remote locations contains concentrations of microplastics at least two orders of magnitude greater than those that have been previously reported in highly contaminated surface waters, such as those of the Pacific Gyre. Our findings indicate that microplastics have accumulated far from population centers and that polar sea ice represents a major historic global sink of man-made particulates. The potential for substantial quantities of legacy microplastic contamination to be released to the ocean as the ice melts therefore needs to be evaluated, as do the physical and toxicological effects of plastics on marine life.

1. INTRODUCTION

Sea ice regulates the exchange of heat and chemical compounds between the oceans and the polar troposphere and has a substantial influence on our climate. Over the past several decades, multiyear sea ice, which lasts through melt seasons, is rapidly being replaced by thinner first year ice, leading to an overall a decrease in Arctic sea ice volume [*Reimnitz et al., 1993; Stroeve et al., 2012; Laxon et al., 2013*]. As it forms, sea ice scavenges and concentrates natural particulates from the water column [*Gregory et al., 2002*]. Here we

examine the extent to which this mechanism has led to accumulation of man-made microplastic particles in polar sea ice.

Small fragments of plastic (<5mm diameter) known as ‘microplastics’ have accumulated in the oceans through direct release of particles from cosmetics (also known as microbeads), release of fibres from washing machines and probably most substantially from the fragmentation of larger items of plastic debris [Thompson *et al.*, 2004; Barnes *et al.*, 2009; Browne, *et al.*, 2011]. Microplastics are now widespread in the environment and have been reported in surface waters and on shorelines at a global scale [e.g. Law *et al.*, 2010; Browne, *et al.*, 2011]. In the North Atlantic and North Pacific there is evidence that the abundance of microplastics has increased in recent decades [Thompson *et al.*, 2004; Goldstein *et al.*, 2012]. Microplastics are ingested by a wide range of organisms and there are concerns this could lead to physical [Wright *et al.*, 2013] or toxicological harm [Teuten *et al.*, 2007; Browne *et al.*, 2013; Rochman *et al.* 2013], but there is controversy about the extent of any such effects [Koelmans *et al.*, 2013]. Understanding about the dynamics, rates and locations of microplastic accumulation are very limited, but are essential in order to assess the potential for microplastics to cause harm [Barnes *et al.*, 2009; Andrady, 2011; Browne *et al.*, 2011]. The potential for microplastics to transport organic pollutants to the Arctic has been considered from a theoretical perspective [Zarfl *et al.*, 2010], however, there are no previous reports on the presence of microplastics in polar waters or sea ice.

Sea ice forms by the segregation of nearly fresh water ice crystals from saltier seawater, and thickens primarily by downward growth (accretion). In the initial stages, small (<1 mm) ice crystals called frazil gather at the surface, aggregate, and grow. As they do, they tend to scavenge particulates in the water column, a process that can lead to particle enrichment in the ice [Gregory *et al.*, 2002]. It has been suggested that irregularly shaped

particles and particles less dense than water are more effectively trapped than silt and sand, which can be trapped and later released [Gregory *et al.*, 2002].

In order to determine the extent to which microplastics may have become trapped in sea ice we examined sea ice cores collected from locations hundreds of kilometers apart during two separate Arctic expeditions: the 2005 NSF-funded Healy-Oden Trans-Arctic Expedition (HOTRAX) and the 2010 NASA-funded Impacts of Climate change on the Eco-Systems and Chemistry of the Arctic Pacific Environment (ICESCAPE) in the Beaufort and Chukchi Seas (Figure 1).

2. MATERIALS AND METHODS

The discoveries described in this paper were made in the course of investigating sea ice as a habitat for diatomaceous life. We were provided with sea ice cores collected during the 2005 NSF-funded Healy-Oden Trans-Arctic Expedition (HOTRAX) and the 2010 NASA-funded Impacts of Climate change on the Eco-Systems and Chemistry of the Arctic Pacific Environment (ICESCAPE). The 1 m to 3.5 m sea ice cores from which the samples were taken were from the following locations: HOTRAX Site 11 84°18.772N, 149°03.533W (sample depth 135 cm); HOTRAX Site 3 78°17.493N, 176°40.739W (sample depths: 83 cm and 107 cm), HOTRAX Site 26 88°03.333' N, 58°44.9 E (sample depths: 252 cm and 347 cm). ICESCAPE Site I2, 68°18.19N, 166°58.86W (sample depths: 95 cm, 105 cm, and 115 cm). Sample depths are measured from the top of the ice core.

The first sample we cut, melted and filtered was from HOTRAX Site 11, the bottommost layer of which was turbid (sediment-laden). It was during examination of this sample that we discovered 24 brightly colored particles in addition to sediment and diatoms. Ten were pieces of plastic (7 identified with > 70% confidence) and 14 were pieces of rayon.

This prompted formal examination of the prevalence of these foreign particles in Arctic sea ice cores from other locations, and a stringent handling protocol that would eliminate the possibility that the microplastics were being introduced during coring, handling, or sample preparation. The data reported in this paper and shown in Figure 2 are all from these subsequent samples. New syringes and filters were used each time. All other tools and containers were cleaned prior to each use with first acetone, then methanol, then three rinses of deionized water. Extreme care was taken to avoid introduction of any contamination with synthetic material during cutting, melting or cutting. Cotton laboratory coats and latex gloves were worn and samples were sealed in pre-cleaned petri dishes. Such steps are essential order to minimize contamination (see *Nuelle et al., 2014* for discussion).

We cut 50-100 cm³ interior sections from each core, by first using a band saw and then removing the exposed faces with razor blades. We then melted these remaining interior samples directly in pre-cleaned glass bottles and filtered the meltwater through new 0.22 µm Millipore nitrocellulose membranes that were attached to new 50 mL plastic syringes. The filters were allowed to air dry, then the residue was photographed using a Leica EZ4D optical microscope and camera.

Particles that were suspected to be synthetic based on their shape and color were removed and identified using FT-IR stereoscopy following the methods in Thompson *et al.* 2004 and refined as follows. A Specac DC2 Diamond compression cell (2 mm in diameter) was used to allow adequate transmission of IR beam to the detector. Identification of fragments used a Bruker Hyperion 1000 microscope and a Bruker IFS66 Fourier transform infrared (FTIR) spectrometer with a MCT detector operating in the 4000-600 cm⁻¹ wave number range. Bruker's Opus 5.5 spectroscopy software was used for measurement, processing and evaluation of the spectra. Matches with quality index ≥ 0.7 were accepted. Any matches with quality index < 0.7 but ≥ 0.6 were individually inspected and interpreted

based on the closeness of their absorption frequencies to those of chemical bonds in the known polymers. Matches with quality index < 0.6 were rejected. We added the spectra of the latex gloves used during sample processing to our FTIR library in order to eliminate any fragments from our data, but no matches with this material were found in any of our samples.

3. RESULTS

Submillimeter synthetic pieces, mostly blue, black, green or red, were found in all four cores analyzed. These included including fibers up to 2 mm in length, blue nodules approximately 0.02 mm in diameter, orange chips < 0.2 mm in the largest dimension, and various other shapes. Rayon was the most prevalent synthetic microparticle (54%), followed by polyester (21%) and nylon (polyamide) (16%), polypropylene (3%), then by 2% each of polystyrene, acrylic and polyethylene (Figure 2).

Rayon is not a plastic, but we have included it in our results because it is a manmade semi-synthetic that makes up a significant proportion of synthetic microparticles found in the marine environment [Lusher *et al.*, 2013]. Rayon is used in cigarette filters, personal hygiene products and clothing, and introduced to the marine environment through sewage, including from the washing of clothes [Barnes *et al.*, 2009]. Lusher *et al.* [2013] were the first to identify it in fish samples, and interestingly the proportions they found (57.8% of synthetic particles ingested by fish) are very similar to the proportions we report in sea ice (54% of microparticles found).

4. DISCUSSION

The abundance of microplastics was substantial, ranging from 38 to 234 particles per cubic meter of ice. Although litter has been reported in northern Europe including the Arctic [Galgani and Lecornu, 2004; Bergman *et al.*, 2012] this is the first report of microplastic in the Arctic and the microplastic concentrations we found are at least two orders of magnitude greater than those reported in Atlantic waters north of Scotland or in waters of the North Pacific Subtropical Gyre [0.34 and 0.12 particles per cubic meter of water, respectively] [Thompson *et al.*, 2004; Goldstein *et al.*, 2012]. Similar relative proportions, but lower quantities, have been reported in intertidal sediments [Browne *et al.*, 2011]. This can be explained by the scavenging phenomenon that accompanies ice growth and is supported by data showing that the levels of suspended organic carbon in Arctic sea ice may also be two orders of magnitude greater than those in seawater [Mel'nikov and Pavlov, 1978; Gregory *et al.*, 2002]. It would therefore appear that the Arctic sea ice represents a major global sink for microplastic particles.

The polymers we identified from the sea ice have a wide range of domestic and industrial uses. The quantities of microplastics in our samples were higher than those reported in studies from temperate regions. However, the relative proportions of different polymer types were similar to those reported elsewhere in sediment and biota, including polyester, acrylic, poly-propylene, polyethylene and polyamide [Browne *et al.*, 2010, 2011; Lusher *et al.*, 2013]. As with other studies the relative proportions of different polymers found as microplastics debris did not closely match the relative proportions found as larger items of debris (see Browne *et al.* 2010 for comparison) or in the water column [Sadri and Thompson, 2014], where polystyrene, polyethylene and polypropylene are the dominant materials. The cause of this difference is not clear but is likely to result from differential transport of the various size fractions. We were not able to conclusively identify the origins of the microplastics we found. We did run back trajectories on the turbid ice from HOTRAX Site 3,

and found that it may have been formed on the Alaskan coast and transported by the Beaufort Gyre, but without further tests we cannot confirm this. The fact that cores from other locations in the Arctic contained microplastics but no sediment suggests that this is not a coastal phenomenon.

However, differences in sea level cause a net flow of water from the Pacific across the Bering and Chukchi shelves [Stigebrandt, 1984], where it mixes with flows from the East Siberian Sea and discharges into the Atlantic [Stigebrandt, 1984; Macdonald and Carmack, 1991; Weingartner *et al.*, 1999]. The Arctic Ocean also receives some water from the Atlantic Ocean, through the Fram Strait and Barents Sea [Rudels *et al.*, 2004] but inflowing Atlantic Water is denser than Arctic water and tends to sink as it enters the Arctic Ocean basin. Seabed topography, mixing, and surface conditions produce the Arctic thermocline and halocline with a layer of colder, less saline water at the surface (0-100 m); this is stable until the fall and winter, when seasonal ice forms. While there are riverine inputs to the Arctic Ocean, especially from several large Siberian rivers (i.e., Ob, Yenisei, and Lena) and Canada's Mackenzie River, the surrounding regions are sparsely populated and unlikely to be the source of large quantities of plastic debris. Hence, we hypothesize that the microplastics entered the region primarily from the Pacific, where substantial quantities of microplastic have been reported [Goldstein *et al.*, 2012; Maximenko *et al.*, 2012] and remained afloat until they were entrained in sea ice. This process is likely to have occurred for as long as there has been plastic in the oceans. However the recent shift from thick, multiyear sea ice to thinner, annual ice cover will likely result in substantial net release of trapped microplastic.

There are about 6 million square kilometers of multiyear Arctic sea ice, mostly >2 meters thick [Comiso, 2012], but thickness and extent have shown a dramatic decline in recent years [Reimnitz *et al.*, 1993]. If current trends continue, in the next decade 2,040 trillion cubic meters of ice will melt [Comiso, 2012]. If all of this were to contain the lowest

quantity we report here (38 particles/m³), this could release over one trillion pieces of plastic. In the Southern hemisphere, microplastic debris has been found on shorelines as far south as Punta Arenas, Chile (53°08S, 70°53W) [Browne *et al.*, 2011]. While multiyear sea ice makes up a smaller proportion of annual sea ice cover in the Southern Ocean, and perennial sea ice cover around Antarctica is following different trends [Comiso and Nishio, 2008], our findings indicate the importance of sampling ice from the Antarctic to see if it too contains microplastics. The environmental consequences of microplastic fragments are not fully understood, but they are clearly ingested by a wide range of marine organisms including commercially important species [Murray *et al.*, 2011; Lusher *et al.*, 2013] they can be retained in tissues [Browne *et al.*, 2011] and there are concerns they may present a physical or toxicological challenge as hydrophobic organic compounds such as polychlorinated biphenyls and polycyclic aromatic hydrocarbons may be released upon ingestion [Teuten *et al.*, 2009; Browne *et al.*, 2013; Wright *et al.*, 2013].

Our findings go some way to help clarify one of the most puzzling aspects of current understanding on the quantities of plastic debris reported in the oceans. Despite exponential increases in production and associated increases in discharges to the environment the vast majority of monitoring data from the environment show no associated temporal trends in abundance e.g. extensive data collected from surface waters in the Atlantic between 1986 and 2008 show neither increases nor decreases over time [Law *et al.*, 2010]. It has been suggested that there may be substantial, but as yet un-quantified, sinks of marine debris [Thompson *et al.*, 2004]; our calculations indicate sea ice represents such a sink. It is therefore important to conduct more detailed assessment of the quantities that have become trapped in the ice. This will inform our understanding of the dynamics and accumulation of microplastic contamination in relation to their potential environmental consequences as this material is released back to the oceans.

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Accepted Article

Figure 1. (A) Location of sea ice cores where microplastics, identified by Fourier transform infrared spectrometry (FTIR), were found. (B) Sea ice core being collected during the NASA ICESCAPE expedition in July 2010.

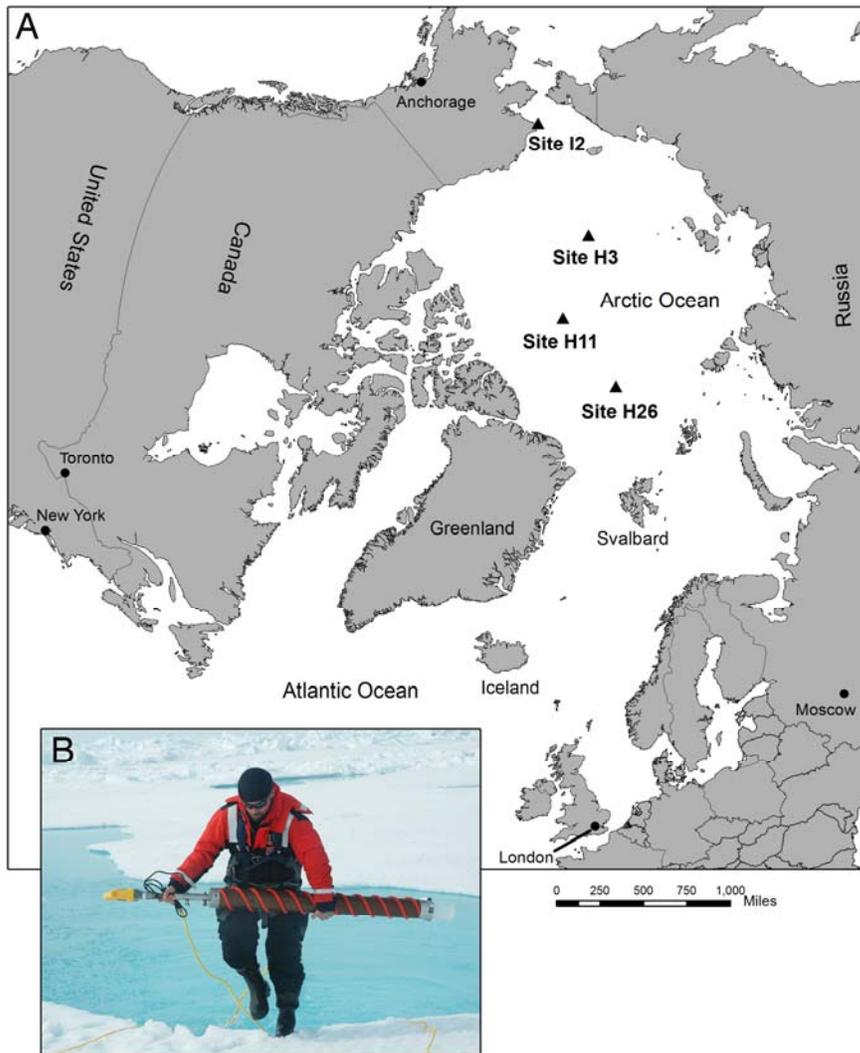


Figure 2. (A) Total number of microplastic pieces presented as values per cubic meter of seawater (scaled up from sample volumes examined which were typically 50-100 cm³), by polymer type, according to the location of sea ice cores. Photographs of microplastic fragments, identified using FT-IR: (B) HOTRAX Site 3, polyethylene terephthalate (polyester), (C) HOTRAX Site 11, polypropylene, (D) HOTRAX Site 26, polyester, (E) ICESCAPE Site 2, nylon, (F) HOTRAX Site 11, polyethylene. Scale bars represent 1 mm.

