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Microplastic contamination in east Antarctic sea ice

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ABSTRACT

The durability of plastics in the marine environment has led to concerns regarding the pervasiveness of this debris in remote polar habitats. Microplastic (MP) enrichment in East Antarctic sea ice was measured in one ice core sampled from coastal land-fast sea ice. The core was processed and filtered material was analyzed using micro Fourier-Transform Infrared (μFTIR) spectroscopy. 96 MP particles were identified, averaging 11.71 particles L^{-1}. The most common MP polymers (polyethylene, polypropylene, and polyamide) were consistent with those most frequently represented in the majority of marine MP studies. Sea-ice MP concentrations were positively related with chlorophyll *a*, suggesting living biomass could assist in incorporating MPs in sea ice. Our preliminary results indicate that sea ice has the potential to serve as a reservoir for MP debris in the Southern Ocean, which may have consequences for Southern Ocean food webs and biogeochemistry.

1. Introduction

Despite their small size, microplastics (MP, plastic particles < 5 mm) have become pervasive even in the most remote marine habitats. Within the past few years a wealth of MP research has been performed in many mediums with high particle concentrations reported (Isobe et al., 2017; Jiang, 2018). Ocean surface waters, deep-sea sediments, and even marine organisms themselves have been analyzed for the presence, quantity, size, and polymer types of MP particles (Andrady, 2011; Bergmann et al., 2017; Germanov et al., 2018; Jiang, 2018). Studies suggest that high MP concentrations in the ocean environment have far reaching implications for biogeochemical processes, biota, and marine ecosystems (Arthur and Baker, 2011; Cole et al., 2011; Koelmans et al., 2014).

MP research remains a relatively young field, evidenced by the fact that particles in polar regions have been discovered only within the last six years (Lusher et al., 2015; Obbard et al., 2014). The possibility of plastic accumulation in polar regions was widely overlooked due to the lack of nearby urban populations and local pollution sources. Yet, while polar seas are more remote, MP concentrations have been found to rival those of more urbanized and heavily populated areas (Cózar et al., 2017; Jiang, 2018). In the Antarctic, dense concentrations of MPs were recently reported in the surface waters of the Pacific and Indian Ocean sectors of the Southern Ocean, with levels comparable to those in Northern Hemisphere oceans at 3.1×10^{-5} particles L^{-1} (Isobe et al., 2017). The highest concentrations (9.9×10^{-5} particles L^{-1}) were those found nearest the Antarctic coastline and accounted for 86% of all MPs recorded during the survey (Isobe et al., 2017). Similarly, sediment samples from the region have revealed MP contamination levels comparable to those found in sea beds worldwide (Munari et al., 2017; Waller et al., 2017), indicating that ocean currents as well as sea ice may be providing means of transport for MP particles (Obbard, 2018).

Annually, sea ice covers roughly 35 million km^2 of Earth's surface throughout the seasons (approx. 8% of global oceans), making it one of the largest biomes on the planet (Parkinson and DiGirolamo, 2016). In the Southern Ocean, sea ice extends outward from the continent, covering roughly 17–20 million km^2 in austral winter through spring (NSIDC, 2018). Both land-fast ice (sea ice fastened to a coastline or ice shelf) and pack ice (free-drifting in response to winds and currents) can be found in the Southern Ocean. As opposed to multi-year ice common in the Arctic, the majority of ice in the Antarctic is first-year ice, with about 80% of the sea-ice melting each season (Thomas and Dieckmann, 2003). To date there are three studies identifying MPs in sea ice, all conducted in the Arctic. Initially, MPs were discovered unintentionally in archived ice cores dating as far back as 2005 (Obbard et al., 2014). Recently, Arctic sea ice was confirmed as a primary sink for MP litter after mean concentrations of 2.3×10^4 particles L^{-1} were detected in pack ice and 6.3×10^3 particles L^{-1} in fast ice (Peeken et al., 2018),

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Table 1
Vertical distribution of measured sea-ice parameters (temperature (°C), salinity, particulate organic carbon POC (μg L^{-1}), dissolved iron dFe (nmol L^{-1}), particulate iron pFe (nmol L^{-1}), and Chl*a* (μgL^{-1})).

Depth (cm)	Salinity	Temperature (°C)	POC (μg C L^{-1})	dFe (nmol L^{-1})	pFe (nmol L^{-1})	Chl*a* (μg L^{-1})
0–6	2.90	−4.9	328.7	2.94	80.18	0.05
30–36	5.20	−2.6	336.7	3.37	662.36	0.05
70–76	4.00	−1.3	267.1	4.01	1284.90	0.05
103–109	5.90	−1.8	726.6	10.98	460.82	0.53
109–115	11.50	−2.0	12,549.9	22.17	3795.95	94.50

respectively. An additional field study in the Baltic Sea showed sea-ice MP concentrations ranged from 8 to 41 particles L^{-1} of melted ice (Geilfus et al., 2019). To our knowledge, the current study is the first to determine MP concentrations in Antarctic sea ice.

MPs remain a new and emerging field of study in the marine environment, and as a result, there is a lack of consistency in sampling techniques for particle extraction and quantification. MP particles are pervasive in all marine realms, and sample processing remains heavily dependent upon the medium analyzed (e.g. sediments, animal tissues, or sea water samples). Hydrogen peroxide treatments, density separations, acid or alkaline digestions, enzymatic treatments, mesh sieving and pre-filtrations have all been used to reduce biological material prior to spectroscopic analysis of MP samples (Bergmann et al., 2017; Valeria Hidalgo-Ruz et al., 2012; Masura et al., 2015). Known methods for MP isolation can be time-consuming, costly, or lead to MP loss. After sample processing is complete, Fourier-Transform Infrared (FTIR) spectroscopy remains one of the best techniques for accurate polymer identification and quantification (Käppler et al., 2016). This spectroscopic method uses infrared light to measure light absorption through particles, leading to spectral fingerprints characteristic of individual polymeric chemical structures (Berthomieu and Hienerwadel, 2009). However, even with the use of focal plane array detector (FPA)-based μFTIR the identification and quantification of MP particles can be laborious and time consuming, as several data management and analysis steps may be needed (Primpke et al., 2017).

With so few studies performed, there are currently no robust or universal methods for analyzing MPs in seawater, let alone sea-ice cores. Of those performed on sea ice, one study used visual sorting to identify plastic particles (Obbard et al., 2014), the second processed samples with hydrogen peroxide (H_2O_2) and filtration (Peeken et al., 2018) prior to FTIR analysis, and the third used the Nile Red technique to visually inspect particles that were suspected to be MPs (Geilfus et al., 2019). However, Antarctic sea ice harbors some of the highest accumulations of biological material anywhere in the marine environment (Iida and Odate, 2014), with sea ice contributing a small but significant portion of total Southern Ocean productivity (Arrigo, 2014). While diatoms dominate these communities, sea ice also hosts other algae, bacteria, heterotrophic protozoans, small metazoans, and high concentrations of extracellular polymeric substances (EPS), also known as exopolysaccharides (Garrison, 1991; Krembs and Deming, 2008). Micro-organisms, such as bacteria and algae, excrete these high-molecular weight compounds in the ice (Meiners et al., 2004) which we hypothesize may bind with MP particles in the same manner as they bind with trace metals and particulate materials (Lannuzel et al., 2014; van der Merwe et al., 2009). Therefore, productive biological communities and dense chlorophyll concentrations in Antarctic sea ice could make MP analysis with FTIR more difficult. Overlapping particles covering the filter can cause complicated spectral profiles due to overlapping spectra of mixture, making an automated analysis approach nearly impossible.

Sea ice could provide an important temporal reservoir for retaining MPs in the surface layers of the Southern Ocean, allowing them to remain bio-available for consumption. This study provides methods for comprehensive sea-ice MP isolation prior to μFTIR analysis, aims to determine whether MP litter is present in Antarctic sea ice, and opens up questions surrounding the impacts of MP debris in Antarctic sea ice. An archived ice core sampled off Casey Station was analyzed to assess the quantity and composition of MPs in East-Antarctic fast ice. In the absence of standard procedures, two methods (hydrogen peroxide treatment, HP; pre-filtration, PF) were performed to compare effectiveness of sample processing and accuracy with polymer identification using FTIR (Primpke et al., 2017). Here we present a workflow for sea ice associated MP analyses and the first data on MP contamination in East-Antarctic sea ice.

2. Methods and materials

2.1. Sea-ice coring and sample preparation

One archived ice core from Casey station from November (late austral spring) 2009 was analyzed. The core was collected from East Antarctic coastal fast ice at 66° S/110°E, 12 km north of Casey Station using trace metal and organic carbon clean-sampling methods (van der Merwe et al., 2011). A Tyvek clean suit (Bioclean-D non-sterile coverall with hood, manufactured by Clean Room Garments) was worn over expedition gear for all sea-ice fieldwork. An electro-polished stainless-steel corer was used for drilling, and parameters such as particulate organic carbon, chlorophyll *a*, salinity, and temperature were measured as described by van der Merwe et al. (2011) (Table 1). The collected ice core was triple-bagged in acid-cleaned plastic bags (200 mm × 100 μm low density PE, manufactured by QIS packaging) for transport and freezer storage. The core was stored at −18 °C until analysis in the home lab.

To avoid additional confounding sources of contamination a Tyvek clean suit was worn for all ice-core processing and stored in a bag when not in use to avoid atmospheric particle contamination. All ice-core handling in the lab was performed in a laminar flow cabinet. A 100% cotton lab coat was worn for all filtrations to protect samples from potentially confounding synthetic fibers. Nitrile gloves were worn for all processing procedures to ensure no organic matter from human contact could taint sample readings. All chemicals used throughout the experiments were pre-filtered through 0.7 μm glass microfiber filters (Whatman GF/F). All sample vessels and filtration apparatuses were glassware, and container openings were covered with aluminum foil to prevent atmospheric contamination. No other plastic was used during sample processing.

This core exhibited typical land-fast ice texture, with a thin layer of granular ice in the top section of the core, and the remainder was columnar ice. The core was cut into vertical horizons with a Japanese pull saw (Gyokucho, 240 mm) with this ice profile in mind. The top section of the core was cut from 0 to 10 cm, followed by 10–105 cm for the middle section, and 105–115 cm for the bottom, most biologically-dense section of the ice. As a precautionary approach, to remove potential atmospheric contamination during ice-core storage and handling, the surface of the ice core was removed with a stainless steel knife, and the remainder rinsed with MilliQ™ water. Each ice core section was weighed and melted in a 2 L glass cylinder (pre-cleaned with isopropyl alcohol and washed in a glassware-only dishwasher) at room

temperature and covered with aluminum foil.

2.2. Filtrations

After melting each ice section, the resulting meltwater volume was measured and split equally in half. One portion was set aside for later processing. The half samples were then filtered onto 0.2 μm Whatman Anodisc (aluminum oxide) 25 mm filters. For these samples (HP), 10 mL of hydrogen peroxide (35% H_2O_2, Chem-Supply) were added per 100 mL sample to help solubilize biological material. Following filtration, filters were overlaid with 40 mL H_2O_2 at room temperature and incubated overnight. The H_2O_2 was drained, filtration funnels were rinsed with MilliQ™ water, and flushed with 5 mL of ethanol (Ethanol absolute, ExpertQ, ACS, ISO Scharlau S.L.) to reduce surface tension and ensure all particles were on the filter. Each filter was placed in a glass Petri dish and dried at 40 °C in a drying cabinet. After initial filtrations, a heavy biomass load was noted on each filter, which made micro Fourier-transform infrared spectroscopy (μFTIR) analysis difficult. Therefore, the remaining half sample that had previously been set aside was used to investigate pre-filtration as a means for removing heavy biomass. The pre-filtered sample (PF) was filtered through 5 μm silver membrane filters (Sterlitech, 25 mm) and otherwise processed identically to HP samples (Fig. 1).

2.3. Blank tests

To ensure no outside sources of contamination (such as laboratory personal protective equipment) were added during processing of the ice core, three blank cores were created. Blanks were created using MilliQ™ water, Reverse Osmosis water, and pre-filtered samples from the Derwent River (Hobart, Tasmania) in identical PE storage bags, stored for one week at −20 °C, and then filtered and processed whole (identical to HP samples) as laid out above.

2.4. FTIR spectroscopy

FTIR hyper-spectral imaging was performed following previously established methods for image analysis data (Primpke et al., 2017) for characterizing MP quantities and polymer types in the environment (Hidalgo-Ruz et al., 2012; Rocha-Santos and Duarte, 2015). Baseman automated IR spectral library (Primpke et al., 2017) was used in order to compare unknown spectra of particles with those of known polymers.

A Hyperion 3000 microscope (Bruker Optics) attached to a Vertex 70 (Bruker Optics) spectrometer was used. The instrument and microscope compartment were flushed with dry air, at an airflow rate of approximately 200 L h^{-1}. An optical overview image was taken of the entire filter using x4 magnification and IR measurements were performed with two x15 magnification lenses. An FPA 64 × 64 detector was used (binning of 4) and scans were run in transmission mode (6 co-added scans, 8 cm^{-1} resolution). Either one 62 × 62 or 70 × 70 FPA image was taken per sample. Analysis was conducted with OPUS 7.5 software (Bruker).

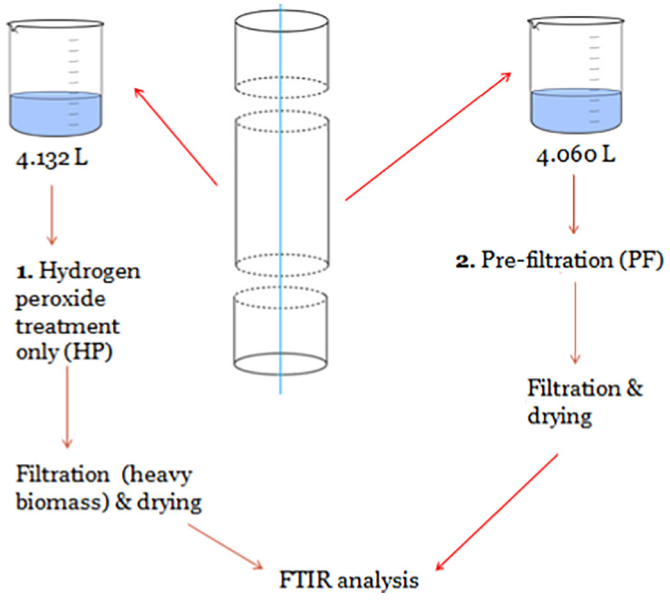

Fig. 1. Schematic of sample processing procedure.

2.5. Data analysis

False color images produced were integrated (3000–2800 cm^{-1}) specific to CH bonds, indicating the presence of any organic material. HP and PF treatments did not sufficiently solubilize enough biological material to allow for a fully automated data analysis approach following μFTIR spectroscopy. As sample spectra overlapped, on screen analysis was performed by visually inspecting areas of high intensity integration values and numbering them.

In order to confirm polymeric composition of suspected MP particles, suspected MP spectra were manually extracted. If needed, following manual extraction, the overlapping biological spectra were subtracted. The resultant spectra were then individually compared to polymer libraries by following established methodology (Primpke et al., 2017). The spectral data was pre-processed by means of vector normalization of the original spectrum and the first derivative and the baseline hit quality was set at 300. ImageJ (Schneider et al., 2012) image analysis software was used to calculate equivalent spherical diameters of all MPs.

3. Results

Through the analysis of one fast ice core, 96 MP particles were detected with a total concentration of 11.71 particles L^{-1}. Across all horizon samples concentrations ranged from 6 particles L^{-1} to 33.3 particles L^{-1}, with a mean of 20.38 particles L^{-1}. In total, 14 polymer types (Fig. 2) were identified in the ice core. PE, PP, PA, and varnish accounted for nearly two-thirds (63%; 60 particles) of all polymers identified. In our study, PE, PP, and PE copolymers constituted 49% (47 particles) of identified MPs.

HP samples had a higher yield at 56 particles (1.35 × 10^1 particles L^{-1}), while PF samples were slightly lower with 40 total particles identified (0.99 × 10^1 particles L^{-1}). The highest particle concentration was found in the bottom 10 cm of the core (3.16 × 10^1 particles L^{-1}) where chl *a* (95.03 μg L^{-1}) and salinity (8.7 ppm average) peaked sharply (Table 1, Fig. 3). This was followed by 2.24 × 10^1 particles L^{-1} in the top 10 cm of the ice core, and 0.71 × 10^1 particles L^{-1} in the middle ice-core section (10–105 cm).

All polymers detected were < 0.35 mm in size (Fig. 4). MP particles varied from 20 to 325 μm in diameter, with a mean diameter of 56.7 μm and standard deviation of 43.37 μm. Overall, 60% of MP particles were ≤50 μm, with a majority (90%) of particles measuring ≤100 μm. The four most frequent MPs (PE, PP, PA, and varnish) also maintained the greatest variety in size distribution.

4. Discussion

Our preliminary study suggests that MP concentrations in East-Antarctic fast ice may be significant and indicates that sea ice has the potential to be an important reservoir for MP particles in the Southern Ocean. The concentration in our ice core is extremely high in relation to Antarctic surface waters (average 3.1 × 10^{-5} particles L^{-1}), including the sample taken nearest the continental coastline (9.9 × 10^{-5} particles L^{-1}) (Isobe et al., 2017), and similar to

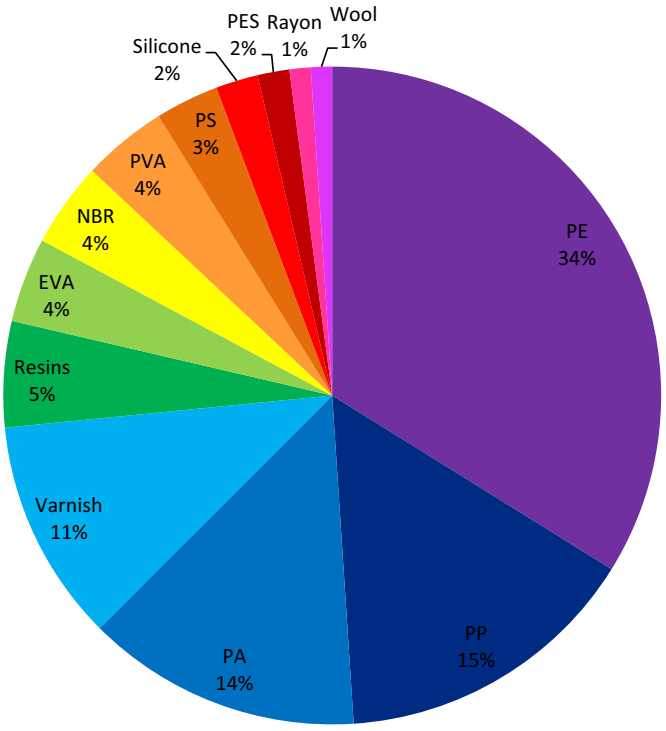

Fig. 2. Total percent composition of polymers in the land-fast sea-ice core using both HP and PF methods. Polyethylene (PE; including low density polyethylene LDPE), polypropylene (PP), polyamide (PA; includes nylon), varnish (including polyurethanes and polyacrylates), ethylene vinyl acetate (EVA), resins (including phenoxy and epoxy), nitrile rubber (NBR), polystyrene (PS), poly vinyl alcohol (80–100% hydrolyzed), rayon, wool, polyester (PES), and silicone.

concentrations reported from the Baltic Sea (Geilfus et al., 2019) but is much lower than recent reports in Arctic sea ice (33–75,143 particles L^{-1}) (Peeken et al., 2018). Yet, we identified 14 polymer types in our ice core, only slightly less than the 17 polymer varieties identified across 9 Arctic ice cores (Peeken et al., 2018). It has been hypothesized that in general, concentrations observed in Antarctic sea ice may be lower than those observed in the Arctic (Obbard, 2018). The Southern Ocean is farther away from major sources of plastic production and use, and experiences less ship traffic around the continent than Arctic waters. Surrounded by land masses, the Arctic Ocean also experiences high levels of terrestrial input from river run-off, whereas the Southern Ocean is completely open to surrounding global oceans, but isolated from other continents and urbanized cities, and experiences very little terrestrial input. Yet, while there may be greater overall pollution in the Arctic, we speculate that the rate of particle release and entrapment in sea ice is higher in Antarctic waters, as about 80% of Antarctic sea ice melts and reforms anew each year. Consequently, rather than being exported to the deep ocean, MPs may be held in the surface realm longer due their seasonal entrapment into and release from the ice, in accordance with sea-ice formation and melt-cycles. As a result, these particles would be made bio-available longer for consumption by marine organisms such as *Euphasia superba* (Antarctic krill), which are a keystone species in Southern Ocean food webs. Research has shown that Antarctic krill are capable of ingesting MPs and breaking them down into nanoplastics during digestion (Dawson et al., 2018). Combined, these phenomena could broaden complications of plastics in Antarctic marine ecosystems, and the role of ice-associated pelagic herbivores in Southern Ocean biogeochemical cycles. In conjunction, global plastic production has steadily increased in recent years, therefore it may be expected that contamination levels in sea ice may be increasing into the future. Comparisons between recently collected and older, archived ice cores may show trends of steadily increasing particle abundance in Antarctic sea ice.

The similarity between the vertical distributions for chlorophyll *a* concentration, particulate organic carbon concentration, and ice core bulk salinity with respect to particle abundance illustrates that sea ice does not have uniform MP concentrations throughout the whole ice cover. We hypothesize that plastics could be incorporated via physical or biological processes or, depending on the time of year and location, a combination of the two. Physical incorporation of MP into newly-forming sea ice could be mediated by means of frazil ice formation. This process has been suggested for incorporation of Fe and particulate organic matter (Janssens et al., 2016; Meese et al., 1997; Reimnitz et al., 1993). As with detritus and micro-organisms, MPs may also act as nucleation sites for ice crystals (Knopf et al., 2011; Weeks and Ackley, 1982). As frazil ice rises through the water column during sea-ice formation in autumn and winter, MPs may be scavenged or adhere to ice crystals, therefore leading to their accumulation in newly formed sea ice. Microcosm experiments performed by Geilfus et al. (2019) similarly suggest that higher MP levels in the surface of the ice could result from particle inclusion within the ice during early phases of sea-ice growth, depleting the underlying seawater of MP particles. As a result, sea-ice growth rate may have some bearing on the incorporation of MP particles within the ice (Geilfus et al., 2019). The Southern Ocean greatly favors frazil ice formation (60–80%) as opposed to the Arctic Ocean which favors congelation ice growth (60–80%) (Thomas and Dieckmann, 2003), meaning MP physical incorporation mechanisms may differ between the two regions. Accumulation of MPs through

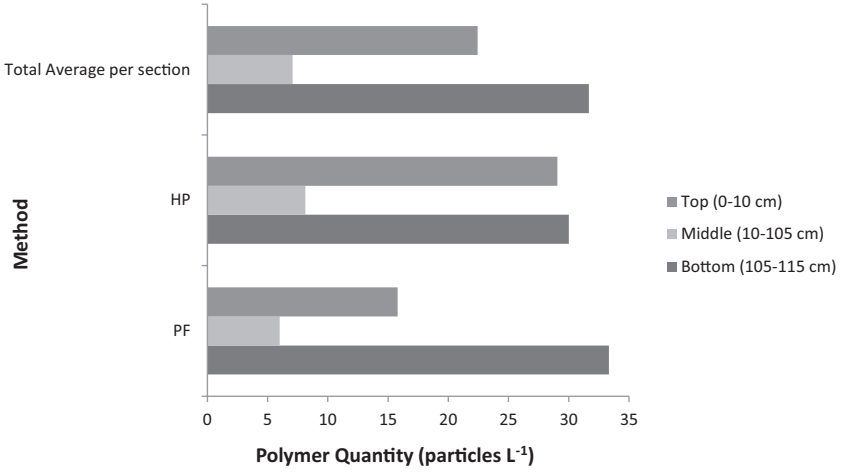

Fig. 3. Bar graph of MP counts (particles L^{-1}) by method and vertical resolution.

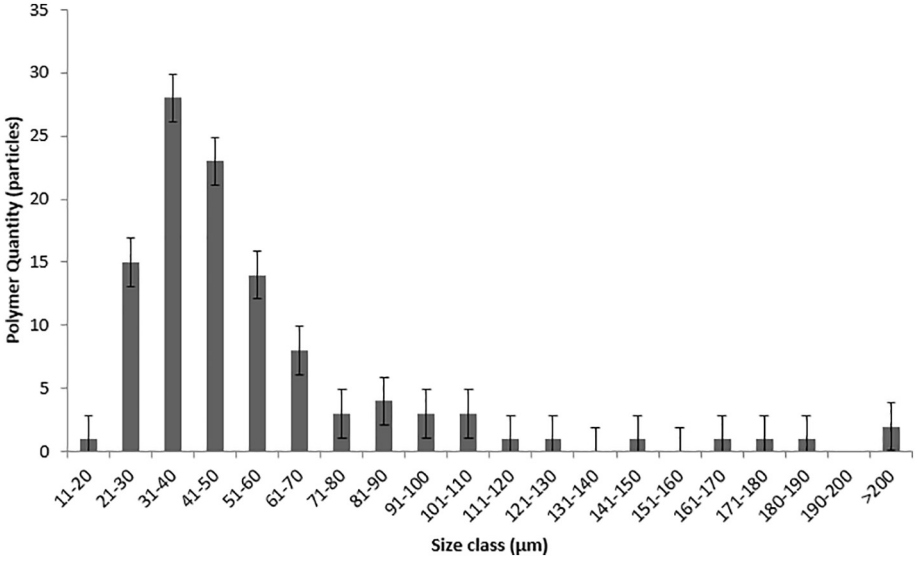

Fig. 4. Bar graph of polymer size distribution (equivalent spherical diameter, µm) in coastal fast-ice core.

frazil ice formation is however more likely to occur in pack ice than fast ice (Thomas and Dieckmann, 2003), thus further research is needed to determine MP abundance and polymer diversity differences between these two types of sea ice. Physical processes associated with congelation ice growth could also explain the similar vertical profiles between sea-ice salinity and polymer abundance. Frazil and columnar ice growth experiments conducted under controlled conditions could be beneficial in order to address further questions surrounding MP incorporation.

Biological processes, e.g. via the production of EPS, could also mediate MP incorporation into forming sea ice. In situ experiments have shown that particulate matter is enriched into newly-forming sea ice and particle enrichment began with the initial phases of sea-ice growth (Janssens et al., 2016). This may hold true for MP particles as well, as MP concentrations in sea ice, including in the surface layer, were higher than seawater samples. If MPs are entrapped in EPS similarly to trace metals, it would be expected that the majority of plastic particles would be found in the bottom 15 to 20 cm of the ice core where EPS and biomass are generally the densest (Meiners et al., 2003). We found high MP concentrations within the bottom section of our core, alongside high POC and chl*a* concentrations in the bottom of the ice (Table 1, Fig. 3). However a significant, negative correlation was observed between chl*a* content and MP particle abundance in the Arctic (Peeken et al., 2018). Yet, both studies do indicate the distribution of MP particles in sea ice is not homogenous. A significant positive correlation has been noted between chl*a*, POC, and EPS concentrations in sea ice (Meiners et al., 2004), suggesting that while there could be a relationship between chl*a* and MP abundance, MP counts may actually be more strongly correlated with EPS quantities.

In the case of our fast ice core, a slight increase in POC and particulate Fe (Table 1), Mn and Al concentrations were observed in the middle of the core at 73 cm depth (Lannuzel, Personal Communication, May 2019). As the site had a water depth of only 17 m, we hypothesize that plastic-laden marine sediments could have been re-suspended during storms in autumn/winter, and become attached to the bottom of the growing ice floe. The sea ice would have continued to form, retaining the MP signal within the ice. The process may have been aided by EPS. This theory, previously put forward in the case of Fe (Lannuzel et al., 2010), evidently needs further investigation.

The differences noted between the HP and PF methods need further exploration. However, we believe both these methods have significant disadvantages for processing plastics within sea-ice cores and for the subsequent data analysis needed to determine polymer sizes and chemical composition. We found hydrogen peroxide treatments did not sufficiently solubilize enough biological material to allow for a fully automated data analysis approach following FTIR spectroscopy. Sample spectra overlapped, and in order to confirm polymeric composition suspected MP spectra had to be manually extracted, and overlapping biological spectra were subtracted. This approach could lead to misidentification of MP, however in our case the biological signal was definitive and easily identifiable (either cellulose or zein purified). Sharp spectral peaks in the C—H region provided strong indications when plastic polymers were present, and are not present in biological material found within Antarctic sea ice. Additionally, difficult spectra were run through multiple libraries for a spectral match, and visually confirmed by experienced researchers. Therefore, while we can remain confident we accurately interpreted spectral data, this method was laborious and time consuming and is not viable for a robust sea-ice study. Additionally, the HP method had a higher yield in the top horizon compared to the PF method. We suspect fewer MPs, particularly larger particles, may have been noted in PF top section due to error associated with a double filtration. Prior to using these methods further, an estimate of MP particles unaccounted for during the sampling process should be considered as a primary step forward.

It has been suspected that due to its seclusion, pollution may take longer to reach the Antarctic, resulting in smaller particle sizes on average (Obbard, 2018). In the present study, that was not the case, as the majority of particles detected were slightly larger than those found in Arctic sea ice (Peeken et al., 2018). In the Baltic Sea MPs < 63 µm were not collected as a result of experimental constraints, but of those suspected particles analyzed a majority fell between 63 and 125 µm. Importantly though, with all MP particles being < 0.5 mm in size, these particles are small and therefore readily bio-available for many marine organisms. However, the larger sizes of MP polymers in the Antarctic may indicate local pollution sources, contrasting long-range transport mechanisms which play a role for MP contamination in Arctic sea ice (Obbard, 2018). Tourists and scientific researchers who visit the continent may contribute to MP pollution from clothing fibers and other equipment. 35% of all primary MPs in the marine environment are estimated to be fibers originating from synthetic clothing (Boucher and Friot, 2017). Identified polymers such as wool, PES, PE, and nylon may be a result of contamination from researchers and field workers in the Antarctic, as these polymers are present in their expedition and cold-weather gear. In addition, the proximity of our sampling site to Casey Research Station may have some bearing on MP pollution in local sea ice.

The occurrences of varnish and EVA could be related with ship

traffic around the continent, as both polymers have industrial uses and are often associated with paints for vessels (Doganci et al., 2012; FAO, 2017). It is important to note that western Antarctica may experience higher levels of MP pollution due to the presence of more scientific research stations, heavier marine traffic, and the majority of Antarctic tourism operations.

MPs could also result from commercial activities in the Southern Ocean, as fishing debris has been reported in the region for nearly 30 years (Slip and Burton, 1991). Studies have shown approximately 18% of all marine plastic debris can be attributed to the fishing industry (Andrady, 2011). Globally, fisheries employ plastic gear primarily made of PE and PP, some of which is invariably lost, discarded, or broken down at sea (Andrady, 2011; FAO, 2017). In our study, nearly 75% of all polymers identified were those most notably used in maritime industries (PE, PP, PA, and varnish). In Southern Ocean surface-water samples, 66% of all recorded MPs were PE, PP, and PE copolymers (Isobe et al., 2017). In our study, these polymers constituted 49% of identified MPs. PA, which is also heavily associated with fishing gear (GESAMP, 2016) was found frequently in all sections of the sea-ice core.

Our preliminary findings indicate the crucial need for stringent methods, able to fully recover MP particles from sea-ice samples in order to accurately measure MP particles in polar marine environments. Future work is needed to compare MP distributions in sea ice around Antarctica. Pack ice versus fast ice, as well as a range of pan-Antarctic ice cores (in the proximity of densely and lightly populated research stations) should be sampled and compared to better elucidate sources and MP distribution around the continent. Laboratory-based and modeling approaches would be beneficial for determining the role of physical versus biological processes in MP particle incorporation in newly-forming sea ice. Connections between MP concentration regarding seasonality and decadal changes may also produce significant findings.

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Data availability

Data can be made available upon request.

CRediT authorship contribution statement

A. Kelly:Data curation, Writing - original draft, Investigation, Formal analysis.**D. Lannuzel**:Supervision, Conceptualization, Methodology, Writing - review & editing.**T. Rodemann**:Supervision, Conceptualization, Methodology, Data curation, Formal analysis, Software.**K.M. Meiners**:Supervision, Conceptualization, Writing - review & editing.**H.J. Auman**:Supervision, Conceptualization, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Andrady, A.L., 2011. Microplastics in the marine environment. Mar. Pollut. Bull. 62 (8), 1596–1605. https://doi.org/10.1016/j.marpolbul.2011.05.030.
Arrigo, K.R., 2014. Sea ice ecosystems. Annu. Rev. Mar. Sci. 6 (1), 439–467. https://doi.org/10.1146/annurev-marine-010213-135103.
Arthur, C., Baker, J., 2011. Proceedings of the Second Research Workshop on Microplastic Debris. (Retrieved from).
Bergmann, M., Wirzberger, V., Krumpen, T., Lorenz, C., Primpke, S., Tekman, M.B., Gerdts, G., 2017. High quantities of microplastic in Arctic deep-sea sediments from the HAUSGARTEN observatory. Environ Sci Technol 51 (19), 11000–11010. https://doi.org/10.1021/acs.est.7b03331.
Berthomieu, C., Hienerwadel, R., 2009. Fourier transform infrared (FTIR) spectroscopy. Photosynth. Res. 101 (2), 157–170. https://doi.org/10.1007/s11120-009-9439-x.
Boucher, J., Friot, D., 2017. Primary Microplastics in the Oceans: A Global Evaluation of Sources. (Retrieved from Gland, Switzerland).
Cole, M., Lindeque, P., Halsband, C., Galloway, T.S., 2011. Microplastics as contaminants in the marine environment: a review. Mar. Pollut. Bull. 62 (12), 2588–2597. https://doi.org/10.1016/j.marpolbul.2011.09.025.
Cózar, A., Martí, E., Duarte, C.M., García-de-Lomas, J., van Sebille, E., Ballatore, T.J., Eguíluz, V.M., Gonzalez-Gordillo, J.I., Pedrotti, M.L., Echevarría, F., Trouble, R., Irigoien, X., 2017. The Arctic Ocean as a dead end for floating plastics in the North Atlantic branch of the thermohaline circulation. Sci. Adv. 3 (4). https://doi.org/10.1126/sciadv.1600582.
Dawson, A.L., Kawaguchi, S., King, C.K., Townsend, K., King, R., Huston, W.M., Nash, S.M., 2018. Turning microplastics into nanoplastics through digestive fragmentation by Antarctic Krill. Nat. Commun. 9, 1001. https://doi.org/10.1038/s41467-018-03465-9.
Doganci, M.D., Cansoy, C.E., Ucar, I.O., Erbil, H.Y., Mielczarski, E., Mielczarski, J.A., 2012. Combined XPS and contact angle studies of flat and rough ethylene-vinyl acetate copolymer films. J. Appl. Polym. Sci. 124 (3), 2100–2109. https://doi.org/10.1002/app.35189.
FAO, 2017. Microplastics in Fisheries and Aquaculture: Status of Knowledge on Their Occurrence and Implications for Aquatic Organisms and Food Safety. pp. 615.
Garrison, D.L., 1991. Antarctic Sea Ice Biota. American Zoology 31, 17–33.
Geilfus, N.X., Munson, K.M., Sousa, J., Germanov, Y., Bhugaloo, S., Babb, D., Wang, F., 2019. Distribution and impacts of microplastic incorporation within sea ice. Mar Poll Bull 145, 463–473. https://doi.org/10.1016/j.marpollbul.2019.06.029.
Germanov, E.S., Marshall, A.D., Bejder, L., Fossi, M.C., Loneragan, N.R., 2018. Microplastics: no small problem for filter-feeding megafauna. Trends Ecol. Evol. 33 (4), 227–232. https://doi.org/10.1016/j.tree.2018.01.005.
GESAMP, 2016. Sources, fate, and effects of microplastics in the marine environment: part 2 of a global assessment. GESAMP Reports and Studies 1–221.
Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M., 2012. Microplastics in the marine environment: a review of the methods used for identification and quantification. Environ Sci Technol 46 (6), 3060–3075. https://doi.org/10.1021/es2031505.
Iida, T., Odate, T., 2014. Seasonal variability of phytoplankton biomass and composition in the major water masses of the Indian Ocean sector of the Southern Ocean. Polar Science 8 (3), 283–297. https://doi.org/10.1016/j.polar.2014.03.003.
Isobe, A., Uchiyama-Matsumoto, K., Uchida, K., Tokai, T., 2017. Microplastics in the Southern Ocean. Mar. Pollut. Bull. 114 (1), 623–626. https://doi.org/10.1016/j.marpolbul.2016.09.037.
Janssens, J., Meiners, K.M., Tison, J.-L., Dieckmann, G., Delille, B., Lannuzel, D., 2016. Incorporation of iron and organic matter into young Antarctic sea ice during its initial growth stages. Elementa: Science of the Anthropocene 4. https://doi.org/10.12952/journal.elementa.000123.
Jiang, J.-Q., 2018. Occurrence of microplastics and its pollution in the environment: a review. Sustainable Production and Consumption 13, 16–23. https://doi.org/10.1016/j.spc.2017.11.003.
Käppler, A., Fischer, D., Oberbeckmann, S., Schernewski, G., Labrenz, M., Eichhorn, K.-J., Voit, B., 2016. Analysis of environmental microplastics by vibrational microspectroscopy: FTIR, Raman or both? Anal. Bioanal. Chem. 408 (29), 8377–8391. https://doi.org/10.1007/s00216-016-9956-3.
Knopf, D.A., Alpert, P.A., Wang, B., Aller, J.Y., 2011. Stimulation of ice nucleation by marine diatoms. Nature 4, 88–90. https://doi.org/10.1038/NGEO1037.
Koelmans, A.A., Besseling, E., Foekema, E.M., 2014. Leaching of plastic additives to marine organisms. Environ. Pollut. 187, 49–54. https://doi.org/10.1016/j.envpol.2013.12.013.
Krembs, C., Deming, J.W., 2008. The role of exopolymers in microbial adaptation to sea ice. In: Margesin, R., Schinner, F., Marx, J.-C., Gerday, C. (Eds.), Psychrophiles: From Biodiversity to Biotechnology. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 247–264.
Lannuzel, D., Schoemann, V., de Jong, J., Pasquer, B., van der Merwe, P., Masson, F., Tison, J., Bowie, A., 2010. Distribution of dissolved iron in Antarctic sea ice: Spatial, seasonal, and inter-annual variability. J. Geophys. Res. 115.
Lannuzel, D., van der Merwe, P.C., Townsend, A.T., Bowie, A.R., 2014. Size fractionation of iron, manganese and aluminium in Antarctic fast ice reveals a lithogenic origin and low iron solubility. Mar. Chem. 161, 47–56. https://doi.org/10.1016/j.marchem.2014.02.006.
Lusher, A.L., Tirelli, V., O'Connor, I., Officer, R., 2015. Microplastics in Arctic polar waters: the first reported values of particles in surface and sub-surface samples. Sci. Rep. 5, 14947. https://doi.org/10.1038/srep14947.
Masura, J., Baker, J., Foster, G., Arthur, C., 2015. Laboratory Methods for the Analysis of Microplastics in the Marine Environment: Recommendations for Quantifying Synthetic Particles in Waters and Sediments.
Meese, D.A., Reimnitz, E., Tucker, W.B., Gow, A.J., Bischof, J., Darby, D., 1997. Evidence for radionuclide transport by sea ice. Sci. Total Environ. 202 (1), 267–278. https://doi.org/10.1016/S0048-9697(97)00121-6.
Meiners, K., Gradinger, R., Fehling, J., Civitarese, G., Spindler, M., 2003. Vertical distribution of exopolymer particles in sea ice of the Fram Strait (Arctic) during autumn. Mar. Ecol. Prog. Ser. 248, 1–13.
Meiners, K., Brinkmeyer, R., Granskog, M., Lindfors, A., 2004. Abundance, Size Distribution and Bacterial Colonization of Exopolymer Particles in Antarctic Sea Ice

(Bellingshausen Sea). 35.
van der Merwe, P., Lannuzel, D., Nichols, C.A.M., Meiners, K., Heil, P., Norman, L., Thomas, D.N., Bowie, A.R., 2009. Biogeochemical observations during the winter–spring transition in East Antarctic sea ice: evidence of iron and exopolysaccharide controls. Mar. Chem. 115 (3–4), 163–175. https://doi.org/10.1016/j.marchem.2009.08.001.
van der Merwe, P., Lannuzel, D., Bowie, A.R., Meiners, K.M., 2011. High temporal resolution observations of spring fast ice melt and seawater iron enrichment in East Antarctica. J. Geophys. Res. 116 (G3). https://doi.org/10.1029/2010jg001628.
Munari, C., Infantini, V., Scoponi, M., Rastelli, E., Corinaldesi, C., Mistri, M., 2017. Microplastics in the sediments of Terra Nova Bay (Ross Sea, Antarctica). Mar. Pollut. Bull. 122 (1–2), 161–165. https://doi.org/10.1016/j.marpolbul.2017.06.039.
NSIDC, 2018. SOTC: sea ice. Retrieved from. https://nsidc.org/cryosphere/sotc/sea_ice.html.
Obbard, R.W., 2018. Microplastics in polar regions: the role of long range transport. Current Opinion in Environmental Science & Health 1, 24–29. https://doi.org/10.1016/j.coesh.2017.10.004.
Obbard, R.W., Sadri, S., Wong, Y.Q., Khitun, A.A., Baker, I., Thompson, R.C., 2014. Global warming releases microplastic legacy frozen in Arctic Sea ice. Earth's Future 2 (6), 315–320. https://doi.org/10.1002/2014ef000240.
Parkinson, C.L., DiGirolamo, N.E., 2016. New visualizations highlight new information on the contrasting Arctic and Antarctic sea-ice trends since the late 1970s. Remote Sens. Environ. 183, 198–204. https://doi.org/10.1016/j.rse.2016.05.020.
Peeken, I., Primpke, S., Gutermann, J., Beyer, B., Katlein, C., Krumpen, T., Bergmann, M., Hehemann, L., Gerdts, G., 2018. Arctic sea ice is an important temporal sink and means of transport for microplastic. Nat. Commun. 9 (1505). https://doi.org/10.1038/s41467-018-03825-5.
Primpke, S., Lorenz, C., Rascher-Friesenhausen, R., Gerdts, G., 2017. An automated approach for microplastics analysis using focal plane array (FPA) FTIR microscopy and image analysis. Anal. Methods 9, 1499. https://doi.org/10.1039/C6AY02476A.
Reimnitz, E., McCormick, M., McDougall, K., Brouwers, E., 1993. Sediment export by ice rafting from a coastal polynya. Arct. Alp. Res. 25 (2), 83–98.
Rocha-Santos, T., Duarte, A.C., 2015. A critical overview of the analytical approaches to the occurrence, the fate and the behavior of microplastics in the environment. TrAC Trends Anal. Chem. 65, 47–53. https://doi.org/10.1016/j.trac.2014.10.011.
Schneider, C.A., Rasband, W.S., Eliceiri, K.W., 2012. NIH image to ImageJ: 25 years of image analysis. Nat. Methods 9, 671. https://doi.org/10.1038/nmeth.2089.
Slip, D., Burton, H., 1991. Accumulation of fishing debris, plastic litter, and other artefacts, on heard and Macquarie Islands in the Southern Ocean. Environ. Conserv. 18 (3), 249–254. https://doi.org/10.1017/S0376892900022177.
Thomas, D.N., Dieckmann, G.S., 2003. Sea Ice: An Introduction to Its Physics, Chemistry, Biology, and Geology. Wiley-Blackwell.
Waller, C.L., Griffiths, H.J., Waluda, C.M., Thorpe, S.E., Loaiza, I., Moreno, B., Pacherres, C.O., Hughes, K.A., 2017. Microplastics in the Antarctic marine system: an emerging area of research. Sci. Total Environ. 598, 220–227. https://doi.org/10.1016/j.scitotenv.2017.03.283.
Weeks, W.F., Ackley, S.F., 1982. The Growth, Structure, and Properties of Sea Ice. Hanover N.H. US Army Corps of Engineers, Cold Regions Research & Engineering Laboratory.