

Weathering processes of microplastics in the sea ice and ocean environment: an 18-month- long mesocosm study

By

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Abstract

The persistence and impact of microplastics (MPs) in marine ecosystems are of increasing concern. In recent years, sea ice has been recognized as an effective temporary reservoir for MPs in polar oceans. While many studies have reported the presence of MPs, the weathering processes of MPs and their interactions with other contaminants remain largely unknown, especially in polar oceans with a dynamic sea ice environment. This study conducted an extensive 18-month-long, outdoor mesocosm experiment to investigate the weathering processes of MPs in the marine cryosphere that involved two complete cycles of sea ice growth and melt under natural ambient conditions. Microplastics of different size, color and chemical composition were used in the study to examine the weathering processes and the interactions between microplastics with other trace metal species (e.g., mercury). By simulating a polar marine cryosphere dominated by a seasonal sea ice cover at a mesocosm scale, the study captures complex interactions between MPs and the surrounding environment. Key findings reveal that prolonged exposure to natural weathering processes, primarily due to photodegradation, biofilm formation, and seasonal sea ice dynamics, significantly alters MP surface properties and Hg accumulation efficiency in ways not observed in laboratory scale experiments. Photodegradation of MPs occurred, but to a much lesser degree than reported from laboratory studies; instead, seasonal changes in temperature, and sea ice and biofilm dynamics had a much more prominent role in the weathering and Hg accumulation. The unique natural weathering patterns found in the mesocosm study indicate that such a process cannot be easily reproduced in lab-based, short-term, single-factor studies. The study also reveals the role of weathered MPs as a medium for toxic substances such as Hg, which might present additional ecological risks when ingested by marine biota. This work promotes the understanding of the long-term fate of MPs in marine ecosystems and informs mitigation strategies, advocating for policies grounded in realistic environmental conditions. By bridging the gap between laboratory experimentation and real-world complexity, the study shows the value of the employed mesocosm approach for future research on plastic pollution, especially on its implications in the polar marine cryosphere under a rapidly changing climate.

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List of Abbreviations and Acronyms

AMX - Amoxicillin

ANOVA - Analysis of Variance

A_{oc} - Absorption Intensity of Carbonyl Group

A_{ref} - Absorption Intensity of Methylene Group

ATR - Attenuated Total Reflection

BPA - Bisphenol A

CRM - Certified Reference Material

CVAFS - Cold Vapor Atomic Fluorescence Spectroscopy

EDX - Energy Dispersive X-ray Spectroscopy

EPA - Environmental Protection Agency

EPS - Extracellular Polymeric Substances

FTIR - Fourier Transform Infrared Microscopy

ICP-MS - inductively coupled plasma mass spectrometry

IQR - interquartile range

MPs - Microplastics

PA - Polyamide

PAHs - Polycyclic Aromatic Hydrocarbons

PBDEs - Polybrominated Diphenyl Ethers

PCA – Principal Component Analysis

PCBs - Polychlorinated Biphenyls

PE - Polyethylene

PE-B - Polyethylene-Black

PET - Polyethylene Terephthalate

PE-W - Polyethylene-White

PFAS – Per- and polyfluoroalkyl Substances

PFOS - Perfluorooctanesulfonate

POPs - Persistent Organic Pollutants

PP - Polypropylene

PS - Polystyrene

PUR - Polyurethane

PVC - Polyvinyl Chloride

QA/QC – Quality assurance and quality control

SEM - Scanning Electron Microscopy

SERF - Sea-ice Environmental Research Facility

TCS – Triclosan

UV - Ultraviolet

Chapter 1. Introduction

This chapter serves as an introduction to my thesis research. It starts with a brief scientific background, key knowledge gaps, and my research hypotheses. This is followed by a literature review on the current research on microplastics (MPs), the weathering processes of MPs with a special focus on the sea ice and marine environment, and the general research methodology. The chapter ends with a summary of the organization of the thesis.

1.1 Background and Objectives

My research focuses on MPs in the sea ice and marine environment. The term "microplastic" was introduced by Richard Thompson to describe the pervasive small plastic particles, measuring less than 5 mm in size, that were present in ocean sediments and surface waters (Thompson et al., 2004). Microplastics in the ocean originate from direct human inputs and fragmentation of larger plastic items delivered from terrestrial, marine, and atmospheric sources (Liu et al., 2019; Lusher et al., 2015). Evidence is mounting that MPs in the marine environment are a global concern due to their ubiquitous presence, exceptionally long lifetimes, and potential risks to ecosystem and human health (Ahrendt et al., 2020; Bergami et al., 2019; Luo et al., 2019; Jung et al., 2022). For example, MPs can interfere with the growth and reproduction of phytoplankton and zooplankton in the ocean, and the oceanic carbon sequestration by affecting the atmosphere-ocean CO₂ exchange (Shen et al., 2020). The ingestion of MPs can lead to adverse effects on the immune system of sea urchins (Bergami et al., 2019), intestinal function in fish (Ahrendt et al., 2020), gut microbiomes of wild seabirds (Fackelmann et al., 2023) and marine mammals such as dolphin and seals (Nabi et al., 2022; Wang et al., 2021). Since the manufacturing of plastics usually involves a mixture of chemicals, fragmentation of MPs can release toxic contaminants that may become more bioavailable (Luo et al., 2019; Boyle et al., 2020). Additionally, once in the marine environment, MPs are recognized as a potential carrier of various contaminants (e.g., metals and organic compounds), as they tend to accumulate these contaminants during weathering, facilitating their uptake by the marine food web (Kinigopoulou et al., 2022).

Of particular interest to my PhD research is that over the past 10 years, MPs have been found in the Earth's cryosphere including sea ice, snow, and glaciers (Kanhai et al., 2020; González-Pleiter et al., 2021; Obbard et al., 2014). Sea ice has been recognized as an effective temporal reservoir and transporter of MPs since it can scavenge the floating MPs during ice formation and growth, redistributing them over long distances (Bergmann et al., 2023; von Friesen et al., 2020; Geilfus et al., 2019; Kelly et al., 2020; Peeken et al., 2018). While most of the studies reported the presence and abundance of MPs in sea ice, few of them studied the interactions between MPs and sea ice. Geilfus et al. (2019) reported the first dataset collected from a mesocosm experiment to examine the ice-water partitioning of MPs and its impact on ice formation, growth, and melting. The results showed that the majority of MPs were scavenged into the surface layer of sea ice at highly elevated concentrations, and the surface enrichment could impact sea ice salinity and albedo. Another study by Chubarenko et al. (2022) attributed the redistribution of MPs during sea ice formation to the hydrophobicity and density of MPs and to the disparities in thermal properties between MPs and ice, which agreed well with the observations of Geilfus et al. (2019). However, both studies employed virgin MPs during ice formation for a short period, which are less common in the natural environments; and none have considered the weathering of MPs.

After entering the marine environment, plastics including MPs go through natural weathering processes including physical, chemical, and biological processes that could greatly alter their physicochemical properties (Jahnke et al., 2017). The increase in specific surface area and changes in chemical properties could make weathered MPs a much more effective vector for carrying contaminants and microorganisms, assisting their uptake and trophic transfer through food webs (Caruso et al., 2019). Weathered MPs have been reported to have higher capability of accumulating contaminants including organic contaminants (e.g., polycyclic aromatic hydrocarbons and polychlorinated biphenyls) and trace metals (e.g., cadmium, chromium, mercury, nickel), which can lead to secondary hazards to marine ecosystems (Gao et al., 2019; Liu et al., 2020; Wang et al., 2018). Of particular concern is mercury (Hg), which is a pollutant of global health concern whose anthropogenic emissions are being regulated by the Minamata Convention (Selin and Selin, 2022). Despite being away from primary sources, Hg is redistributed

via long-range atmospheric, oceanic and biological transport to polar regions and the methylated species undergoes bioaccumulation and biomagnification in the marine ecosystem (AMAP, 2021; AMAP/UN Environment, 2019). Yet the role of MPs in Hg biogeochemical cycling in polar regions remains less understood and could be of particular importance, especially due to the enrichment of MPs in sea ice. In addition, biological weathering processes could affect the properties and fate of MPs by forming biofilms and by enhancing biological degradation of MPs (Bergmann et al., 2023; Nguyen et al., 2020). In a laboratory study, Hoffmann et al. (2020) found that sea ice algae can produce extracellular polymeric substances (EPS) which promoted the attachment of MPs on different surfaces. Kelly et al. (2020) reported a positive association between MPs and biomass in Antarctic sea ice. However, no studies have investigated the weathering of MPs in the marine environment in the presence of sea ice and sea ice biota.

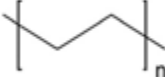
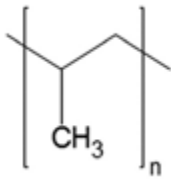
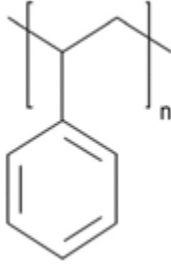
Therefore, the goal of my PhD thesis research was to examine the weathering processes of MPs in the marine environment in the presence of seasonal sea ice and how the weathering processes would affect the interaction between MPs and Hg. This was done by an 18-month-long mesocosm experiment in the Sea-ice Environmental Research Facility (SERF) at the University of Manitoba. Specifically, the objectives of the study were to address the following knowledge gaps regarding the MPs in the polar marine environment:

- (a) How do the weathering processes affect the morphology and chemical structure of MPs in seawater with the presence of seasonal sea ice?
- (b) What are the interactions between MPs and sea ice and how do they change as the MPs weather?
- (c) How does the interaction between Hg on MPs change as the MPs undergo various stages of weathering in the presence of seasonal sea ice? And,
- (d) How do different types, colours, and sizes of MPs affect the aforementioned processes?

1.2 Overview of Plastics and Microplastics in the Environment

Plastics are materials characterized by high molecular weight, consisting of synthetic or semi-synthetic organic compounds. Plastics are typically classified based on the chemical composition of their polymer backbone and the nature of their side chains. Among the most commercially used are polyethylene (PE), polypropylene (PP), polystyrene (PS), polycarbonate (PC), polyamide (PA), polyester (PES), polyvinyl chloride (PVC), and acrylic. This thesis deals with three of them - PE, PP, and PS; their chemical and physical properties are shown in Table 1-1.

Table 1-1. Three types of most commonly used commodity plastics (Ram, 1997; Ward and Reddy, 2020)

Polymer name	Polyethylene (PE)	Polypropylene (PP)	Polystyrene (PS)
Chemical formula			
Molecular weight (of repeating unit)	28 g · mol ⁻¹	42 g · mol ⁻¹	104 g · mol ⁻¹
Density	0.88–0.96 g · cm ⁻³	0.85–0.95 g · cm ⁻³	0.96–1.06 g · cm ⁻³
Melting point	115–135 °C	130–171 °C	240–260 °C
Solubility in water	Not soluble	Not soluble	Not soluble
Approximate lifetime in the environment	Hundreds to thousands of years	Decades to centuries	Hundreds to thousands of years

Since the advent of synthetic polymers in the early 20th century, plastics have become one of the most transformative materials in modern history, shaping industries, economies, and daily life (Geyer, 2020). The first fully synthetic plastic, Bakelite, was invented in 1907 by the Belgian chemist Leo Baekeland, marking the beginning of the modern plastics era (Bijker, 1987). Bakelite, a phenol-formaldehyde resin, was heralded for its electrical non-conductivity and heat resistance, finding immediate application in electronics and consumer goods.

The surge of innovation and growth of plastics were around the World War II, where the development of PE, PVC, and PS, rapidly expanded the use of plastics into packaging, construction, and manufacturing sectors (Hyltoft, 1990). Nylon, introduced by DuPont in 1935, further cemented plastic's role as a versatile, cost-effective material, and it was applied in military use such as parachutes and ropes. The post-war boom of the 1950s and 1960s witnessed the rise of PP and PET, which revolutionized consumer packaging, including bottles, films, and food containers. These lightweight, durable polymers underpinned a culture of convenience and disposability. By the 1970s, plastic had become ubiquitous in global trade, and annual production volumes skyrocketed. So far, the worldwide annual plastic production was about 400 million tons, and this number is projected to be tripled by 2060 if current trends continue (Joshi and Vashishth, 2024).

However, with the benefits of plastic came with unforeseen environmental costs. Since the first reported discovery of plastic fragments found within the stomachs of albatrosses during the late 1960s (Kenyon and Kridler, 1969), researchers began to document plastic's persistence in natural ecosystems, raising concerns about its long-term ecological impact. The durability that made plastic useful in industry was also responsible for its resistance to degradation in nature. It is estimated that 8-12 million metric tons of plastic waste enter the ocean annually (Saha et al., 2024; Shams et al., 2021).

Meanwhile, the proliferation of MPs, fragments resulting from the breakdown of larger plastics, was highlighted in marine environments and has been identified as a global environmental challenge since the early 2000s (Thompson et al., 2004; Vivekanand et al., 2021). Microplastics are broadly categorized into primary and secondary types. Primary MPs are intentionally produced and incorporated into various consumer and commercial goods, including

cosmetics, personal care items, pharmaceuticals, detergents, and pesticides. In contrast, secondary MPs arise inadvertently from the degradation of larger plastic products, such as fishing gear, bottles, bags, and food containers, through physical, chemical, or biological mechanisms (Osman et al., 2023). It has been estimated that there are approximately 171 trillion pieces of microplastic floating at the ocean's surface, a significant increase from earlier estimates of 80 trillion pieces around 2010 (Eriksen et al., 2023). And surveys have reported concentrations of MPs ranging from zero to hundreds of particles per cubic meter, with significant spatial heterogeneity across the sampling area (Brander et al., 2020; Prata et al., 2021; Tanhua et al., 2020).

Today, global regulatory strategies addressing MPs focus on reducing plastic waste and improving environmental management practices. In 2022, the UN Environment Assembly initiated negotiations for a legally binding global treaty on plastic pollution, with a focus on mitigating both macroplastics and MPs pollution (UNEP, 2022). The EU introduced its plastics strategy in 2018, aiming to ban certain single-use plastics and address the release of microplastics into the environment. Regulations have targeted sources like microbeads in cosmetics and tire wear (European Commission, 2018). Canada has been proactive in addressing microplastic pollution through national regulations and partnerships. In 2018, Canada banned the manufacture, sale, and import of toiletries containing plastic microbeads under the Microbeads in Toiletries Regulations (Government of Canada, 2017). This was one of the country's first major actions to combat MPs in consumer products. These strategies illustrated a growing global and national focus on reducing microplastic pollution.

1.3 Weathering of Microplastics in the Marine Environment

Weathering of plastic refers to the gradual breakdown and alteration of plastic materials when exposed to environmental factors such as sunlight, temperature, moisture, mechanical forces, and biological activity. After entering the marine environment from various sources, plastics and MPs undergo physical, chemical, and biological weathering processes (Jahnke et al., 2017; Wayman and Niemann, 2021) (Figure 1-1). In the meanwhile, interactions with other

substances such as aggregation with aquatic particles and accumulation of other contaminants, biofouling, and ingestion by biota, take place in the water column (Zhang et al., 2024). The distribution and persistence of MPs in marine environments are also influenced by dynamic physical processes, including flotation, sedimentation, resurfacing, oscillation, deposition, resuspension, and bioturbation.

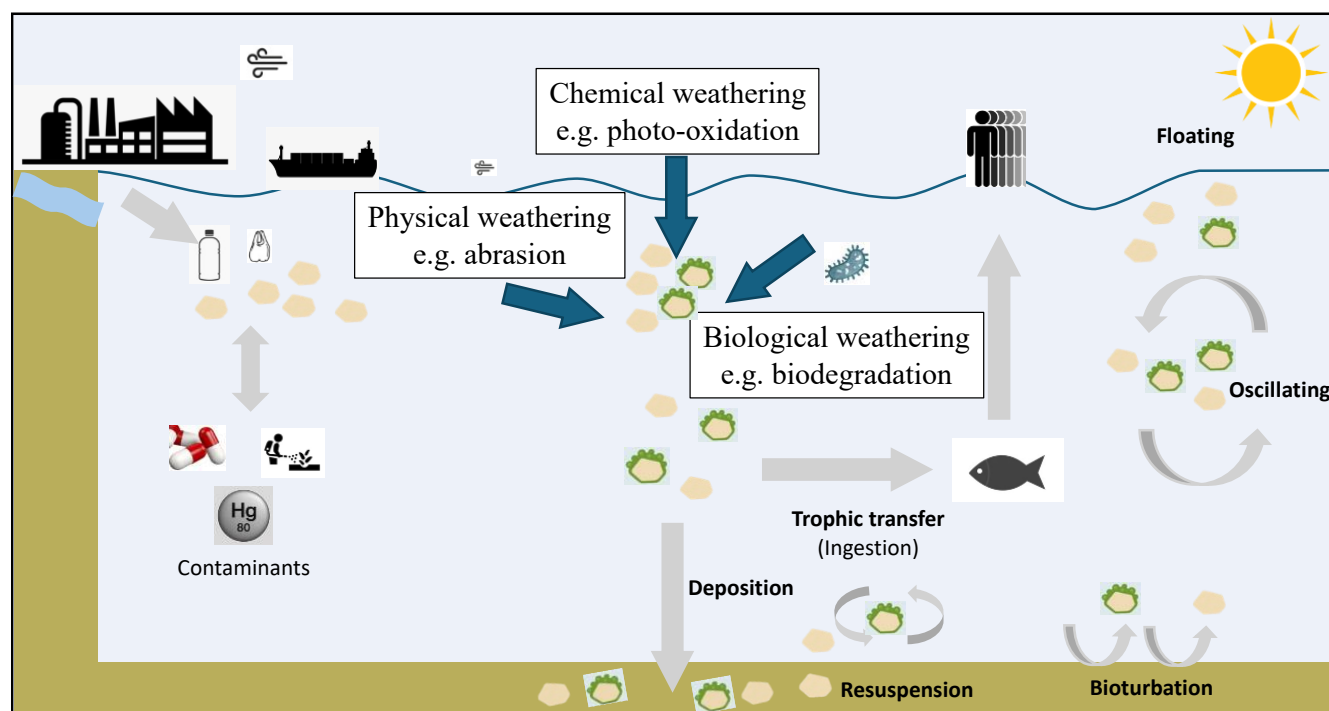


Figure 1-1. A schematic showing the transport and weathering of plastics and microplastics in the marine environment (modified from Wayman and Niemann, 2021)

1.3.1 Key environmental factors affecting microplastics weathering

Among the key environmental factors affecting MP weathering are mechanical stress, solar radiation, and biological activities.

Mechanical stress

Mechanical stress such as wind, waves, tides, and abrasion with rocks and sediments play a major role in physical weathering of MPs in the marine environment. For example, the shearing force from waves and tides, the friction with sediments and the resuspension induced by shipping

activities and bioturbation over a long period of time can facilitate the fragmentation of plastics into MPs and even smaller nanoplastics (size < 100 nm) (Song et al., 2017; Arp et al., 2022). As mentioned below, after photooxidation, the polymers become more brittle and easier to be fractured. Hence, the mechanical weathering process shows combined effects with photooxidation.

Solar radiation

Plastics were introduced commercially primarily because of their chemical inertness that leads to durability and long lifetimes. However, most plastics are susceptible to photodegradation in the presence of solar radiation, especially ultraviolet (UV) radiation (wavelength ranging from 100 – 400 nm). UV is divided into three wavelength ranges: UVA (315-400 nm) accounting for about 95% of the UV at the Earth's surface, UVB (280-315 nm) which is mostly removed by the stratospheric ozone layer, and UVC (100-280 nm) which is essentially all removed by molecular oxygen, ozone and other atmospheric molecules before reaching the surface. It has been widely accepted that UV photooxidation is one of the most significant weathering processes that MPs go through in the marine environment (Jahnke et al., 2017; Masry et al., 2021).

The UV photooxidation of MPs occurs via free radical reactions with oxygen (Gewert et al., 2015; Mao et al., 2020). In general, a chemical bond (e.g., C-H bond) in a plastic molecule absorbs UV photons and free alkyl radicals are generated during chain scission. The produced alkyl radicals then react with molecular oxygen to form peroxy radicals that are strong oxidizing agents. The adjacent hydrogens can be abstracted, producing hydroperoxide groups and new free radicals. Upon further UV irradiation, aldehyde or ketone or carboxyl acid including carbonyl groups (C=O), and the alcohol (C-OH) are formed in different media including air and water, separately. The newly formed compounds such as aldehyde and alcohol can be subject to further oxidation. The resulting oxidation products are more polar and reactive than the parent polymer. Figure 1-2 shows an example of the weathering scheme of PS under UV irradiation (Mao et al., 2020). Generally, the susceptibility to photooxidation follows the order of PS > PP > PE (Min et al., 2020). This is because PS has phenyl rings containing unsaturated bonds, which are more effective and efficient in absorbing UV radiation. For saturated polymers, PP is more susceptible to photooxidation because it has tertiary carbons that are more reactive than the secondary carbons

in PE. Photooxidation of saturated polymers such as PE and PP can also be enhanced by chromophoric impurities from the environment such as pigments, humic substances, and PAHs (Gijssman et al., 1999).

In addition to the chemical structure change, the surface properties and colours are also altered by photooxidation. Research has shown the surface roughness of MPs is increased after UV photooxidation (Cooper and Corcoran, 2010; Gong et al., 2019; Turner et al., 2020). The cracks of the surface found after photooxidation were attributed to the chain scission of MPs. Photo-oxidized MPs are also more susceptible to fragmentation into smaller pieces and with decreased polymer molecular weight (Shi et al., 2021).

Regarding the colour changes of ocean plastics, Marti et al. (2020) characterized the colour of plastics sampled from the ocean and found that discoloration and yellowing were intensified as the exposure extent increased, which was correlated with the downsizing of plastics. The yellowing or tanning effect was due to the aggregation of photo-oxidized products in the plastic, which might serve as more chromophores and provoke further photooxidation processes (Andrady, 2017).

The extent of UV photooxidation of MPs is subject to the intensity of UV irradiation and the exposure time. In addition, plastic properties such as colour (as mentioned above), density, shape can affect the process. For example, MPs with density less than seawater such as PE ($0.88\text{--}0.96\text{ g}\cdot\text{cm}^{-3}$) usually is more exposed to UV irradiation than those with density larger than seawater such as PVC ($1.38\text{--}1.39\text{ g}\cdot\text{cm}^{-3}$) because denser particles tend sink in the water body. Ter Halle et al. (2016) conducted a study on how the shape of MPs affects the fragmentation patterns in the North Atlantic. They showed that flat MPs had unsymmetrical photooxidation with one side more oxidized whereas the other more colonized by microorganisms. In contrast, for smaller cubic pieces, all the surface area was evenly oxidized due to its easier rotation in the water body.

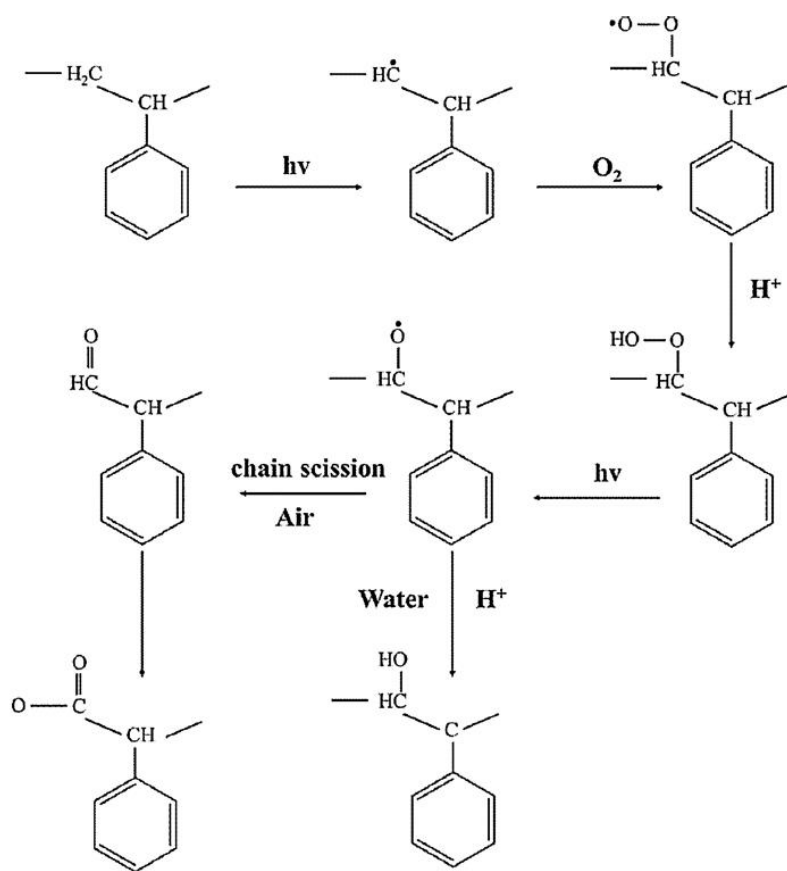


Figure 1-2. One of the weathering schemes of PS under UV irradiation (Mao et al., 2020)

Biological weathering

In the marine environment, MPs can also undergo the biological weathering process. The degradation of MPs with the involvement of microorganisms is usually referred to as biodegradation. Biodegradation can be divided into two types: 1) polymers are hydrolyzed into smaller organic molecules by enzymes; 2) polymers are mineralized to inorganic products by enzymes. Yoshida et al. (2016) succeeded in isolating an indigenous bacterium that can utilize PET as carbon source in sediment samples collected from a PET bottle recycling site. The bacterium yields enzymes to hydrolyze PET into its monomers, terephthalic acid and ethylene glycol. Tian et al. (2017) employed carbon isotope to trace the mineralization of PS. The PS films were mineralized to CO₂ by a fungus, and weathered PS greatly reinforced the mineralization process.

The mineralization process of plastic is influenced by many factors including exposure time, thickness of the plastic, types of plastic, and additives in the plastic such as antioxidants.

In addition to hydrolysis and mineralization, the formation of biofilm on MPs is another critical factor. Once MPs enter the ocean, marine microorganisms will start to colonize on them, which is the fundamental cause of biofouling. The surface microbial layer is termed as biofilm (Oberbeckmann et al., 2015). In the early-stage formation of biofilm, biofilm was able to reduce the hydrophobicity and buoyancy of MPs (Lobelle & Cunliffe, 2011). This facilitated the development of aggregates and biofouling which accelerate the sinking of MPs in the water (Nguyen et al., 2020). Marine snow refers to a continuous shower of organic material falling from the upper layers of the ocean to the deep sea. It was reported that marine snow could accelerate the sinking of MPs and increase the bioavailability to benthic organisms (Porter et al., 2018). The nature of substrate, surface roughness, and hydrophobicity have been recognized as influential to the forming of biofilms. While weathering process such as photooxidation increases the surface roughness and polarity of the MPs, the attachment of microorganisms is enhanced. The downsized plastic particles from weathering process have more specific surface area, which provide more colonization sites for microbials (Kerr & Cowling, 2003).

1.3.2 Impact of weathering on the fate and transport of microplastics

Plastic waste, including MPs, in the ocean can be floating at the ocean surface, suspended in the sea water column, and settled at the sea floor (Figure 1-1). Due to their small sizes and relatively low density, most MPs are subject to buoyancy and ocean waves and currents. However, models on the budget of plastic waste in the ocean (Koelmans et al., 2017; Van Sebille et al., 2015) show that the floating MPs in the ocean surface account for only 1% of the total plastics in the ocean. The rest resides in the deeper water column and ocean floor due to aggregation and sinking, much of which is enhanced by the weathering processes.

First, UV photooxidation changes the molecular structure of the MPs so that tensile strength is reduced. For example, Garvey et al. (2020) found PE in the marine environment could be embrittled after exposed to UV irradiation because the molecular lamellar structure of this

semicrystalline plastic was damaged. So, the UV oxidized plastic can be more brittle and prone to be fragmented. Mechanical force can break down the plastic particles with decreased plastic particle size and deformed shape. On the other hand, the produced hydrophilic functional groups after UV weathering increases the hydrophilicity of MPs. Combined with reduced particle size from fragmentation, MPs tend to be suspended in the water body before further settling processes happen (Arp & Knutsen, 2019). Song et al. (2017) studied the combined effects of photooxidation and mechanical stress on breaking down three types of plastics including PE, PP, and PS. They found for PE and PP, neither UV irradiation nor mechanical abrasion can fragment the plastics alone. While for PS, one of the two weathering processes alone can achieve fragmentation because of the unsaturated double bonds of PS were more readily to be photooxidized.

Waldschläger and Schüttrumpf (2019) modeled the settling and rise velocities of virgin MPs in freshwater in lab-scale where density was one of the major factors. While another study found for weathered MPs, both velocities became slower due to the biofouling (Waldschläger et al., 2020). Uneven biofilm coverage could cause unstable motion, leading to reduced settling speeds of plastic pieces, even though their overall density increases. Furthermore, turbidity current was revealed as another driving force for MPs to settle and be buried in the marine sediments (Pohl et al., 2020). Although MPs are ultimately deposited at the bottom of sea, the redistribution processes such as bottom currents and flows, biological activities of marine organisms of the depositional MPs have not been well studied.

The nature of substrate, surface roughness, and hydrophobicity have been recognized as influential to the forming of biofilms. While the weathering process such as photooxidation increases the surface roughness and polarity of the MPs, the attachment of microorganisms is enhanced. The downsized plastic particles from weathering process have more specific surface area that provide more colonization sites for microbes (Kerr & Cowling, 2003). From this perspective, weathering processes accelerate the formation of biofilms and reinforce the sinking trend.

However, the presence of biofilm can in return affect the weathering processes. The shields of biofilm prevent MPs from being exposed to UV irradiation. After sinking into deeper

column, MPs become less exposed to UV radiation, oxygen, and surface mechanical forces (e.g., wind and waves) (Rummel et al., 2017). Therefore, weathering is lessened and biofilms begin to disintegrate, in a process termed as de-fouling. The de-fouling increases the buoyancy of MPs, to obtain buoyancy again, resulting in sinking-resurfacing cycle or suspension of MPs (Ye & Andrady, 1991). A model was developed to evaluate the effects of biofouling on the sinking of MPs in the marine environment (Kooi et al., 2017). The results found that both biofouling and de-fouling lead to a major concentration of MPs oscillating at mid depths, which was in accordance with the observations (Cózar et al., 2014). Similarly, Choy et al. (2019) reported the MPs were primarily distributed between 200m and 600m in the offshore environment of Monterey Bay, California. In terms of the interactions between MPs and other marine organisms, it was manifested that the fragmentation of MPs was enhanced by crustacean digestion and released to the ocean, which produced secondary MPs (Cau et al., 2020; Dawson et al., 2018). Meanwhile, weathered MPs were found to be more favorable to be ingested by organisms such as marine zooplankton (Vroom et al., 2017), mussels (Brate et al., 2018).

In summary, the weathering significantly influences the fate and transport of MPs in the ocean, yet a comprehensive understanding is lacking due to the complexity and entangling factors affecting the weathering process. Despite the fact that lab-scale experiments may shed light on such a process, studies in a dynamic natural environment are much needed.

1.3.3 Impact of weathering on the hazards of microplastics

The hazardous impact of MPs in the marine environment is usually due to their ingestion by marine organisms, which might further affect human health through trophic transfer. MP particles can physically impair the organisms after being ingested. In addition, the hazards of MPs on marine organisms and human health are mainly of concern by two aspects: 1) release of secondary chemicals contained in parent plastic materials; and 2) MPs as carrier of other contaminants. Since the weathering changes the physiochemical properties of MPs, the hazards of weathered MPs have been increasingly recognized as a knowledge gap.

Release of secondary chemicals contained in parent plastic materials

Monomers and oligomers

In polymer chemistry, a monomer refers to a molecule that can undergo polymerization with other monomer molecules, and an oligomer refers to a polymer with comparatively few repeating units. Since weathering such as UV photooxidation can cause chain scission reactions, secondary compounds such as monomers and oligomers are generated (Gewert et al., 2015). Hazardous oligomers have been proposed as an indicator of plastic pollution in the marine environment (Barboza et al., 2020; De Rooij et al., 2004; Kwon et al., 2015). For example, styrene oligomers from weathering of PS, which are persistent in the environment to various extents (Kwon et al., 2015), have been recognized as one of the new global contaminants (Amamiya et al., 2019; Kwon et al., 2017, 2018). Higher concentrations of styrene have been found in more populated regions than in remote regions, as expected from their anthropogenic origin (Kwon et al., 2015). The presence of styrene monomers and oligomers has also been reported from precipitation to overland flow and ultimately to the ocean (Amamiya et al., 2019), with the concentration of styrene trimers being the highest, following by styrene dimers and monomer. Other plastic oligomers such as Bisphenol A (BPA) as main monomer in PC and vinyl chloride from PVC have also been detected in seawater and marine organisms (Barboza et al., 2020; De Rooij et al., 2004).

Additives

In the production process of plastics, additives are often incorporated to achieve certain functions or properties and to extend the lifespan (Hahladakis et al., 2018). The common additives used are plasticizers that enhance the flexibility and stretchability, flame retardants that prevent or slow ignition, slip agents that reduce friction, and stabilizers that delay degradation. These additives can be released to the environment as plastics and MPs weather when they are subject to physical fragmentation, UV radiation, and biological activities (Gewert et al., 2018; Rani et al., 2017; Paluselli et al., 2018).

The additives of major concern include polybrominated diphenyl ethers (PBDEs) as flame retardants, Hg as a biocide, among others, as they can harm and disrupt the endocrine, immune,

reproductive and nervous systems in biota including humans (Campanale et al., 2020). These hazardous compounds have been found in the ocean. For example, PBDEs were observed from the open ocean and beaches in remote areas of America and Europe (Hirai et al., 2011). From fragments of PE and PVC in the ocean, phthalates were migrated to seawater and taken up by marine microorganisms within a few months (Paluselli et al., 2018). Among them, some of the hazardous compounds such as brominated flame retardants and Hg can be bioaccumulated and biomagnified (Bowman et al., 2021; Guo et al., 2017; Hahladakis et al., 2018). In addition, the released additives might be attached to other particles and be transferred to the food web. The desorption of persistent organic contaminants from MPs has been shown to accelerate in the gut condition with gut surfactants and low pH (Bakir et al., 2014). Meanwhile, MPs can function as a two-way transporter for PBDEs as well (Scopetani et al., 2018). The results suggested that MPs acted more effectively as scavengers (7.4%) than as carriers (3.9%) of contaminants. However, additional factors were mentioned to be considered to evaluate the results.

In addition, little is known about the fate and effects of secondary compounds generated from chemical and biological weathering processes, such as oxygenated substances that are more water-soluble and reactive (see Section 1.3.1). Comparing with monomers, oligomers and additives, the identification of intermediate and potentially more toxic compounds from the weathering process is much more convoluted and poorly studied. Furthermore, the pathways of these secondary chemicals from the environment to marine organisms remain to be investigated.

Carrier of other contaminants

Due to the large surface area to volume ratio, MPs have been shown to be ideal substrates for accumulation of other contaminants in the environment (Wang et al., 2020a) and act as a carrier for transport and biological uptake. This is especially the case with weathered MPs that usually have altered surface properties with more reactive oxygenated functional groups (Liu et al., 2019b). For example, a rougher surface morphology provides an even larger specific surface area for contaminant accumulation (Ter Halle et al., 2017).

Due to their high hydrophobicity, MPs, especially virgin MPs, can effectively accumulate hydrophobic organic contaminants including persistent organic pollutants (POPs) and others such

as PAHs. For instance, weathered PP in the ocean was found to concentrate polychlorinated biphenyls (PCBs) about 100 to 1 million times than the adjacent seawater (Mato et al., 2001). Lee et al. (2014) studied the accumulation of PAHs and three types of MPs including PE, PS, and PVC in seawater. They showed a strong correlation between partitioning coefficients and the hydrophobicity of the materials. Similarly, Fang et al. (2019) reported accumulation of three fungicides on PS and attributed the main mechanism to hydrophobic sorption and micropore filling. In addition to the surface properties of materials, density and particle size also affect the accumulation capacity (Fries & Zarfl, 2012; Velzeboer et al., 2014).

Once in the environment, weathering processes such as UV photooxidation and hydrolysis result in the formation of oxygen-containing functional groups. These functional groups are more hydrophilic, which increase the polarity of the MPs and affinity to hydrophilic contaminants including trace metals.

The accumulation of hydrophilic organic compounds such as per- and polyfluoroalkyl Substances (PFAS) and perfluorooctanesulfonate (PFOS) (Wang et al., 2015, Llorca et al., 2018), and antibiotics such as amoxicillin (AMX) (Li et al., 2018) on weathered MPs has been reported. In addition, weathered MPs have been reported to accumulate a variety of trace metals such as Cd, Co, Cr, Pb, Ag, Cu, Sb, Hg, Fe, Ni, Zn, and Mn (Godoy et al., 2019; Zhou et al., 2019; Turner et al., 2020). Particularly, the accumulation capacity of weathered MPs has been shown to be significantly enhanced than that of the virgin ones (Holmes et al., 2014; Turner and Holmes, 2015, Mao et al., 2020).

Factors that influence contaminants accumulation on MPs in the ocean

There are various factors that influence the capability of MPs on accumulating contaminants. Understanding the accumulation mechanism under different environment conditions can provide more insights for environmental risk assessment.

Particle size of MPs can influence contaminants accumulation. The specific surface area is increased by decreased particle size of plastic particles as they weather. The increased surface area to volume ratio improves the sorption capacity of MPs. Ma et al. (2019) observed that smaller sizes of PVC had better accumulation extent of triclosan than larger ones due to the

increased specific surface area. Davranche et al. (2019) performed a Pb binding experiment that showed that Pb was largely bound with smaller fragments. Similar results were found by Chen et al. (2019) on the sorption capability of dioxin-like persistent organic pollutants on PP.

The pH of water is another parameter affecting the capability of MPs on accumulating contaminants. Seawater is slightly basic with a pH around 8 – 8.3, that reduces hydrophobic interactions because of the high electrostatic repulsion. Studies have shown that for pH higher than 8, the surfaces of MPs tend to have negative charges (Xu et al., 2018). This implicates less accumulation of hydrophobic compounds on MPs, which might lead to promoted accumulation of metal ions. Ma et al. (2019) found the adsorption of TCS on PVCs decreased significantly with the increase of pH values within 3-11, which was related to surface charge of PVCs under different pH values. Turner and Holmes (2015) reported the accumulation of trace metals by MP pellets in freshwater. When the pH value of the tested water was adjusted to approximately 8, the accumulation of Cd, Co, Ni, Pb, and Zn was increased compared to at pH of 6.5. This suggests that MPs in the ocean environment might be more effective in accumulating trace metals than in freshwater.

Salinity is also an important factor that affects the contaminant accumulation on. Liu et al. (2019a) reported that higher concentrations of NaCl and CaCl₂ can lead to increased accumulation of two hydrophobic phthalate esters (PAEs). Similarly, the sorption of PFOS on PE was also found with increasing Na²⁺ and Ca²⁺ concentrations (Wang et al., 2015; Wang et al., 2018). The authors attributed this to the salting-out effect, since the solubility of the organic compounds decreases as the concentration of salts increases. However, increasing seawater salinity can reduce metal accumulation on the MPs, as abundant major ions in seawater compete with metal ions on the surface of MPs. Xiao et al. (2017) found higher ionic strength can lead to lower accumulation of Pb on crayfish shells. In a different study, the accumulation of metals on weathered plastics in freshwater was found to be higher than that in seawater (Holmes et al., 2014).

Biofilms formed on the surface of MPs can be another significant factor for accumulation of contaminants due to the presence of an organic layer containing water, proteins, lipids, and humic acids (Rummel et al., 2017). Humic acids have been reported to abate the accumulation of PCBs by taking up the accumulation sites on charcoal (Koelmans et al., 2009). Wicke et al. (2008)

investigated the effect of biofilms on the accumulation of PAHs on glass beads and found the diffusion efficiency was significantly decreased with the shielding of biofilm. In lab-scale research, the impact of biofilms is often neglected. In a natural environment, the formation of biofilms is inevitable and many factors during weathering processes can enhance the microbial growth. For example, the additives released from MPs can be a carbon source for certain microbials (Fawcett et al., 2021). The aldehydes and ketones containing carbonyl group produced due to UV photooxidation can enhance the growth of biofilm (Min et al., 2020).

1.4 Microplastics in Sea Ice

1.4.1 Abundance of microplastics in sea ice

There have been about 10 studies reporting the abundance of MPs in sea ice from different polar regions, which are summarized in Table 1-2. The abundance of MPs in sea ice from these studies varied over several orders of magnitude, with no clear nor consistent patterns, potentially due to inconsistent methods used in sampling and analysis (see Section 1.5). The most common polymer types identified in sea ice include PE, PP, PVC, polyurethane (PUR), PS, PET, acrylic, PA, and polyester.

Arctic has been identified as a critical sink of MPs and several possible pathways have been proposed. Oceanic currents play a crucial role in the dispersal of floating MPs. In the west Arctic Ocean, MPs are mainly drifted from the Pacific Ocean via the Bering Strait by the ocean surface circulation (D'Angelo et al., 2023; Kim et al., 2021). In the east Arctic Ocean, MPs are imported from the North Atlantic under the influence of the warm segment of thermohaline circulation (Cózar et al., 2017; Lima et al., 2021). Other major pathway of MPs to the Arctic is via riverine and atmospheric transport. It has been estimated that automotive tire-wear and brake-wear particles can be transported to Arctic via the atmosphere with similar levels of that from river discharge (Evangelidou et al., 2020). Additionally, economic development and resource exploitation in the Arctic region can also lead to increasing MPs from local sources.

Since the formation of sea ice in these regions could encapsulate MPs from seawater (Chen et al., 2024), sea ice functions as both a temporal reservoir and an effective transport vector

for MPs. Concentrations of MPs in sea ice are generally higher than the underlying water by a factor of 10 to 100 (Friesen et al., 2020; Kanhai et al., 2020; Bergmann et al., 2023). In a study in the Svalbard near shore area, Friesen et al. (2020) reported that summer sea ice melt released concentrated MPs to the water, making sea ice transport and wastewater as two localized and diffusive sources of MPs in the area. A recent assessment estimates that Arctic sea ice has accumulated a total of 6.1×10^{18} pieces of MPs, more than 80% of which is in the first year sea ice (Zhang et al., 2023). Consequently, climate change induced acceleration of sea ice melting can significantly influence the fate and mobility of MPs not only within the polar regions but globally.

So far, MPs in the Antarctic sea ice has only been reported by Kelly et al. (2020). They found that the majority of MPs in the Antarctic sea ice were slightly larger than those found in the Arctic but the concentration was much lower than that in the Arctic sea ice. Since most of the Antarctic sea ice is first year ice, the types of MPs identified matched with commonly used plastic materials in maritime industries, suggesting important contributions from local sources such as shipping, fishing, and tourism activities.

Table 1-2. Summary of abundance of microplastics in sea ice (updated from Chubarenko et al., 2022b)

Location	Ice type	Size range and major types of MPs	Abundance, bulk mean, items L ⁻¹	Reference
Central Arctic	Multiyear ice	<5 mm; including PS, Acrylic, PE, Nylon, Polyester	38 - 234	Obbard et al., 2014.
Fram Strait Nansen Basin North of Svalbard	Pack ice	11 µm–5 mm; including PE, PP, PVC, PS, PET	12,000 ± 14,000 2900 ± 2400 2400 ± 1000 1100 ± 800	Peeken et al., 2018
Fram Strait	Landfast ice	11 µm–5 mm; including PE, PP, PVC, PS, PET, PUR	4100 ± 2000	Peeken et al., 2018
Gulf of Bothnia, the Baltic Sea	Landfast ice	<5 mm; including PP, PVC, PET	8–41	Geilfus et al., 2019
Central Arctic	Multiyear ice	<5 mm; including PVC, PP, PE, PA, PUR, polyester	2–17	Kanhai et al., 2020

Location	Ice type	Size range and major types of MPs	Abundance, bulk mean, items L ⁻¹	Reference
North of Svalbard	Free floating sea ice	50 µm–5 mm; including PS, PUR, PET, PE, PA	158 ± 155	Friesen et al., 2020
East Antarctic	First year ice	20 – 325 µm; including PE, PP, PA	6–33.3	Kelly et al., 2020
Chukchi Sea	Ice floes	>100 µm >20 µm; Including PE, PP, PVC, PUR, PS, PET	11.4 ± 9.12 43.2 ± 32.0	Kim et al., 2021
Novik Bay, Sea of Japan	First year ice	25 µm–5 mm; including PS, PET, PA, PP, PE	428	Chubarenko et al., 2022b
Northwest Passage	Multiyear ice	10 µm to 1 mm; Including PVC, PET	23 ± 11	D'Angelo et al., 2023

1.4.2 Interactions between and sea ice

Geilfus et al. (2019) was the first to examine the partitioning of MPs between seawater and sea ice and the impact of MPs on sea ice properties and processes. By carrying out a mesocosm experiment in an outdoor pool with experimental seawater, the authors showed that the majority of MPs were distributed in the topmost layer of the sea ice. Incorporation of MPs in sea ice did not significantly influence the sea ice formation process. However, at highly elevated levels, MPs accumulated at the sea ice surface led to an increase in ice salinity and albedo. They further compared the levels of MPs in the Baltic Sea with the concentrations used in the mesocosm study. They concluded that, at the present levels, MPs in the Baltic Sea or the Arctic Ocean are not expected to affect sea ice formation or properties.

Chubarenko et al. (2022a) explored the mechanisms of MP interaction with sea ice, and attributed the observed distribution patterns of MPs in sea ice to hydrophobicity, density, and the pronounced disparities in thermal properties between MPs and ice. First, the hydrophobicity of MPs leads to icephobicity, which facilitates the migration of MPs through brine channels and to the upper/lower interfaces of the ice as ice forms and grows. Microplastics tend to be more enriched in the surface layer of the ice due primarily to the density difference, as MPs generally have a lower density than water. Second, the specific heat capacity of plastics is significantly lower than that of ice and water. Therefore, quicker thermal responsive properties of MPs causes them to be the first to melt when the heat is introduced. Third, MPs become more brittle under cold temperature in the polar areas, which explains why larger plastic pieces are less found floating than fragmented ones. In addition, sea ice porosity and permeability may also influence the re-distribution of small MPs via brine tunnels, although the process is not well studied.

1.4.3 Biological processes related to microplastics in sea ice

Sea ice algae have been reported to interact with MPs in the sea ice environment. Hoffmann et al. (2020) found that sea ice alga *Fragillariopsis cylindrus* can produce extracellular polymeric substances (EPS), which promoted the attachment features of MPs on different surfaces such as walls in a lab-scale study. Sea ice algae usually produce relatively high EPS to be

adapted to the cold environments. While algae did not substantially affect the distribution of MPs, the presence of MPs can significantly diminish the settlement of ice algae on the sea ice (Aslam et al., 2018). Instead, biofilms exhibited improved interactions with MPs. Bergmann et al. (2023) demonstrated that the Arctic sea ice alga *Melosira arctica* had the capability to sequester MPs from both melting ice and the surrounding marine environment.

These studies implicate algae functions both as a carrier to trophic networks and as an agent facilitating the sedimentation of MPs to the ocean floor. In the deep-sea sediments of the Arctic, a positive correlation was observed between the accumulation of elevated concentrations of MPs and chlorophyll a levels, which might be due to an aggregation effect (Bergmann et al., 2022). In Antarctic sea ice, Kelly et al. (2020) identified the positive association between MPs and biomass. With the presence of MPs, algal photosynthesis can be prohibited due to their adherence to the surface, leading to reduced sunlight exposure and potential harm to the cell's chloroplast after penetration. Since sea ice algae are primary producers in polar oceans, the increasing interaction of MPs with algae might impact carbon sequestration, therefore the oceanic biological pump, and disturb the food web in the ocean.

1.5 Methodologies in Microplastics Research

MP pollution has been recognized as a global environmental concern. As a result, the studies on MPs have increased dramatically in the past decades, especially in the marine system (Zhang et al., 2020). Accompanied with the booming research, numerous and diversified methodologies of sampling, separation, and characterization are employed, which have introduced uncertainties and ambiguities in interpretation of the results (Hartmann et al., 2019; Rist et al., 2021). Thus, there is a critical need to build a consensus in the research framework to improve the reproducibility and comparability of the results.

1.5.1 Sampling

Seawater

To sample MPs from seawater, a variety of tools including nets, pumps, containers, and even the ship's water intake lines have been employed (Hidalgo-Ruz et al., 2012). The sampling techniques can be divided into volume-reducing sampling and bulk sampling.

Carpenter and Smith (1972) reported the first volume-reducing sampling method of ocean MPs using a neuston net from the surface water of the Sargasso Sea with reported concentration of 3500 pieces (pcs)·km². Since then, more than 50% of the studies have used net sampling as the major volume-reducing sampling technique (Rist et al., 2021). Nets sampling provided the freedom of large-scale sampling without the need of a large storage space. The nets can be trawled in the ocean vertically, horizontally or both at the same time to obtain MPs (Isobe et al., 2017). The size of MPs collected by this method is operationally defined by the mesh size of the net and is a critical parameter associated with the reported MPs abundance. For example, in a comparative study of nets sampling with three different mesh sizes simultaneously, MP abundance using a 100-μm net was found to be 2.5 times higher than using a 333-μm net and 10 times higher than using a 500-μm net (Lindeque et al., 2020). Therefore, a standardization of the net mesh size is essential. Currently, the widely adopted mesh size for net sampling of MPs is 333 μm, which is known to underestimate the MPs abundance (Tokai et al., 2021; Lindeque et al., 2020).

Another volume-reducing sampling technique is pump sampling, by which a large volume of water can be withdrawn and filtered in situ. However, the operation depth is usually limited by the length of tubing (Schönlau et al., 2020). If filter is installed on the pump, the mesh size of filter can affect the sample size as well and once the filter gets blocked by certain particles, the efficiency will be hampered.

Bulk sampling is the second dominating sampling technique for MPs in the ocean (Rist et al., 2021). Bulk sampling refers to collection of the entirety of the sample without discarding any fraction (Cutroneo et al., 2020). It is usually a simple and cost-efficient sampling strategy in the field because further treatment of samples can be accomplished in the labs. Additionally, there is

more flexibility of the sampling depths. Bulk water sampling devices such as Niskin bottles have been widely used in scientific cruises (Dai et al., 2018; La Daana et al., 2018). Compared to the net sampling, bulk sampling is not limited by the mesh size which enables the access to smaller MPs (Whitaker et al., 2019). However, insufficient sample volumes can be a concern when using bulk sampling, which may lead to variation of reported abundance (Tamminga et al., 2018). Furthermore, there are some tailored approaches for sampling in the specific area. For example, Lusher et al. (2015) employed the ship's water intake line for sub-surface MPs sampling in the Arctic. For sea surface covered with ice, this enabled sample collection directly from under the ice without extra work requirements. However, the sampling is only limited to a certain depth of water.

Sea ice

To sample MPs from sea ice, the most common method is sampling with ice cores. Ice cores were obtained by a specific coring system such as the Kovacs ice coring system with a diameter of 9 cm (D'Angelo et al., 2023; Chubarenko et al., 2022b; Peeken et al., 2018) and Nordic ice drill with motor and core barrel with a diameter of 12 cm (Kanhai et al., 2020). After retrieval, ice cores are cut into sections of various vertical resolution and then wrapped with aluminum foil and sealed in clean bags. For floating sea ice, the ice packs may be captured by a metal hook into a plastic basket following protocols to avoid cross-contamination (Friesen et al., 2020). Then the ice cores or packs can be stored at a freezer until further analysis in the lab (Kanhai et al., 2020; Kelly et al., 2020; Kim et al., 2021; Obbard et al., 2014). Usually, sampling of the seawater via the drilled hole would follow after the ice core is retrieved.

1.5.2 Separation

After MPs are sampled from the field, the next step is to separate MPs from water or sea ice for further characterization. The common separation processes include filtration/sieving and density separation.

Filtration/sieving

Filtration or sieving are the most common approaches to extract MPs from water because of the insolubility of MPs. By passing the water sample through a filtration membrane or sieve, MPs of a certain size range are obtained. The pore sizes of filters range widely from less than 1 μm to 500 μm (Hidalgo-Ruz et al., 2012; Pico et al., 2019), which affect the reported concentration of MPs. Covernton et al. (2019) summarized more than 40 literature studies that employed diverse pore sizes ranging from 0.45 μm to 500 μm and found the pore size was negative exponentially correlated with the abundance of MPs. Although using smaller pore sizes tends to capture more MPs, it may also lead to the clog of the filters and decrease the processing efficiency. Therefore, adoption of an appropriate pore size is important. Cai et al. (2020) performed a study comparing the effect of pore sizes on the quantification of MPs. The results showed that the inflection point of the pore size was around 20 μm in terms of MPs abundance and filtration duration. The inflection point of the pore size is identified as the size where the number of MPs becomes steady, happening once the pore size surpasses this limit. Based on the maximum magnification of a stereomicroscope, it is difficult to identify particles smaller than 20 μm (Simon et al., 2018; Song et al., 2015). Considering the above factors, the authors recommended a 20 μm pore size for the filtration in field sampling. However, the materials of filters available at this pore size are limited to nylon, PE, and stainless-steel. To avoid secondary contamination of polymer, stainless-steel mesh filter was recommended to use. In summary, MPs collected in different studies are generally operational defined without a standardized sample filtration protocol, it is thus difficult to evaluate and compare the reported MPs concentration. Therefore, standardization on filtration procedure should be established in consideration of the sample volume, the turbidity of water, filtration time.

Density separation

The density of plastics can range from 0.8 g cm^{-3} to 1.4 g cm^{-3} . For most plastic with density less than 1 g cm^{-3} in seawater, the gravity-based separation can easily obtain the buoyant MPs such as PP and PE from the supernatant of the seawater. This is the simplest separation based on the difference of densities (Nuelle et al., 2014). However, it is not applicable for all the polymers such as polyvinyl chloride (PVC) and PS whose densities are larger than water. Thus, solutions

with higher density were required. To increase the density of solution, NaCl has been adopted to produce a saturated solution with density around 1.2 g cm^{-3} since 2006 (Ng and Obbard, 2006). NaCl is widely used because it is cost efficient and environment friendly with easy accessibility. However, for polymers with higher density than 1.2 g cm^{-3} such as PVC and PET, there is need for solution with even higher density. In addition, weathering might increase the density of MPs with other attachment or aggregates. Studies have shown NaI (density 1.6 g cm^{-3}) and ZnCl_2 (density $1.5\text{-}1.7 \text{ g cm}^{-3}$) had better MPs separation capability with increased recovery rate than NaCl (Quinn et al., 2017). Since the density of sediment is typically around 2.7 g cm^{-3} , it is generally recommended the density of solutions for higher than 1.4 g cm^{-3} and less than 2 g cm^{-3} for separation between MPs and sediments. Therefore, the combination of NaCl and NaI can be an ideal reagent to the eco-friendly and recyclable properties (Cutroneo et al., 2021).

1.5.3 Identification of microplastics

Microplastics (MPs) are usually identified and characterized by visual examination and selection, and characterization by instrumental methods.

Visual examination and selection

Visual selection exists every step from sampling to separation to identification. It selects the particles as a preliminary sorting process as suspected MPs with naked eyes or with the aid of a stereoscope or microscope. Lusher et al. (2020) summarized the merits of visual selection before further characterization. For some equipment like Fourier transform infrared spectroscopy and Raman imaging system, large particles can be disruptive since the imaging system usually work best with small size fractions. Visually pick-up can decrease the non-essential works for imaging. In addition, the morphology of MPs can be obtained directly from visual selection. For example, if some research aims at intensively weathered MPs to evaluate the potential environment risks, it will improve the effectiveness to have a generate visual sorting as a fast examination (Hidalgo-Ruz et al., 2012). But the visual selection is subjective and can lead to discrepancy of researchers. Consequently, visual selection cannot be a substitute for the physical and chemical analysis.

Characterization by instrumental methods

Various characterization approaches have been used to identify and characterize MPs. The non-destructive methods are universally adopted since the integrity of MPs are protected for other analysis.

Scanning electron microscopy (SEM). Being more advanced than conventional microscopy, SEM can provide images of samples with higher magnification and resolution. For investigation of weathered MPs, it provides details of the surface morphology including roughness and cracks. When combined with energy dispersive X-ray spectroscopy (EDS), the elemental composition can be analyzed, which is useful to differentiate the polymers from the inorganic matters (Gniadek & Dąbrowska, 2019). Despite the excellent surface properties and elemental composition analysis, SEM has strict requirements on the preparation of the sample since conductive coatings and surface charges will interfere the results. Additionally, it is time consuming and has limited capability on large quantities of samples (Zhu & Wang, 2020).

Fourier Transform Infrared (FTIR) Spectroscopy and Raman Spectroscopy. FTIR has been the dominant method to identify and characterize MPs. FTIR utilizes the absorption of infrared light by certain chemical bond to identify certain composition via comparison with reference spectrum. With the automated system, FTIR can either scan all the suspected MPs or focus on a specific particle. There are three modes of FTIR for analyzing different types of MPs (Olesen et al., 2017). Transmission mode is for thin and translucent samples since the radiation can penetrate the sample while reflection mode is conversely for thick and non-transparent samples. Attenuated total reflection mode is usually for MPs with larger size ($>300\text{ }\mu\text{m}$) and irregular shape. Cheng et al. (2021) managed to qualify and quantify MPs in sediments using FTIR combined with laser direct infrared spectroscopy, with higher resolution and faster speed compared the traditional FTIR. However, FTIR has weak capability of analyzing mixtures due to the interference of other organic matter. Hence, it requires samples to be separated well to get optimal results. In addition, FTIR can only effectively examine samples with particle size larger than $20\text{ }\mu\text{m}$ (Chen et al., 2020). For samples less than $20\text{ }\mu\text{m}$, Raman microscopy is regularly used which is a reliable technology as well. Compared to FTIR, Raman microcopy has advantages in higher spatial

resolution and less disruption by moisture. But it can be greatly affected by the impurities such as additives, pigments, and environmental attached compounds (Huppertsberg & Knepper, 2018).

1.5.4 Quantification of microplastics

Quantification of microplastics is performed using various techniques, primarily focusing on visual and spectroscopic methods.

Visual Counting refers to use optical microscopes to visually identify and count microplastic particles. Nile red dyeing was usually employed to stain the MPs and then imaging processing software such as Image J was used for quantification using the images (Geilfus et al., 2019; Hanvey et al., 2017; Prata et al., 2019). This method is common while labor-intensive and sometimes subject to human error.

Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) is also robust technique that involves the thermal degradation of a substance to analyze the volatile organic compounds produced. This method provides both qualitative and quantitative information about MPs. Jung (2021) quantification of microplastics using Pyro-GC/MS with selected representative indicator chemicals and ions. However, quantitative analysis involved the use of calibration curves constructed with representative indicator ions for each polymer. This method offers detailed chemical characterization but is more complex and expensive.

FTIR Spectroscopy is used to identify the polymer type of microplastics by analyzing their infrared absorption spectra. FTIR can differentiate between various plastic types based on their unique spectral signatures. To date, a newly developed Laser Direct Infrared (LDIR) technique for analyzing MPs has been widely evaluated (Primpke et al., 2020; Ourgaud et al., 2022). LDIR uses a quantum cascade laser to generate a mid-infrared light, which interacts with the sample. This technique is automatic, rapid, and provides detailed information on MP composition and size with minimization of sample preparation. It allows for large sample volumes, improving the representativeness of MP detection. While LDIR offers several advantages, it also has some limitations such as high cost and the interpretation of LDIR spectra can be complex, especially

when dealing with mixed environmental samples containing various types of microplastics and organic matter (Ghanadi et al., 2024).

1.5.5 Units of concentration used in quantification research

For the reported concentration of MPs from water and sediments, different units were used across studies. For example, for MPs from water, $\text{particles}\cdot\text{m}^{-3}$ and $\text{particles}\cdot\text{m}^{-2}$ were both used. For MPs from sediments, $\text{particles}\cdot\text{g}$ and $\text{particles}\cdot\text{ml}^{-2}$ were both used. These can lead to the inconsistencies of the data and disintegrate the comparability across studies (Lu et al., 2021). Therefore, using a unified unit such as $\text{particles}\cdot\text{m}^{-3}$ for water samples and $\text{particles}\cdot\text{g}^{-1}$ for sediment samples may enhance the comparability from different studies. In addition, sampling volume can lead to great ambiguity in reported MPs concentration (Liu et al., 2019a). For water sampling, the sampling volume of current works can range from as low as 5 L to more than 10000 L (Prata et al., 2019). The quantification of microplastics using limited sample volumes may lead to a significant overestimation of their abundance. For example, Zheng et al. (2019) reported the MPs abundance in Jiaozhou Bay of $46 \pm 28 \text{ particles}\cdot\text{m}^{-3}$. The employed sampling approach was bulk sampling with volume of 50 L. In contrast, another study adopted net sampling in the same area reported the MPs abundance of only $0.18 \pm 0.05 \text{ particles}\cdot\text{m}^{-3}$ (Zheng et al., 2021). Although bulk volume will be more representative than small volume, it is difficult to realize due to a lot of restrictions. For instance, for bulk sampling, it is impossible to hold a large volume of sample for further analysis. But for net sampling, despite the sampling volume can be very large, the entrapment of particles finer than mesh size would be missed (Karlsson et al., 2020). The sampling depth is another factor that can contribute to the variations of the data (Lu et al., 2021). To date, there has been no standardized sampling volume for MPs sample in the marine environment. Thus, it is crucial to justify and find a balance between the sampling approaches and sampling volume.

Contamination is also a challenge in MPs research since plastic pollution is ubiquitous. During sampling processes, field blanks are essential to determine the cleanliness of sampling. Plastic equipment and containers should be avoided for sampling and storage because the

polymer might go through degradation, introducing potential contamination to the samples (Brander et al., 2020; Prata et al., 2021). Furthermore, replicates can enhance the reliability and reproducibility of the data.

1.6 Organization of the Thesis

The thesis follows a traditional structure. Chapter 1 provides an overall introduction, setting the context and objectives of the research. Chapter 2 focuses on the methodology, detailing the approaches and techniques used in the study. Chapter 3 focuses on environmental conditions and the distribution of MPs in sea ice. Chapter 4 explores the weathering processes of MPs including surface morphology and other qualitative characterization, while Chapter 5 examines the interactions between weathered MPs and mercury, along with other metals. Chapter 6 is the conclusion section, summarizing the key findings and implications of the research.

Chapter 2. Methodology

This chapter outlines the preparation of MPs and the experimental design employed to investigate their behaviour in an outdoor sea ice mesocosm environment. The study employed a diverse array of MPs, including PE in both white and black variants, PP, and PS and a large outdoor seawater pool facility. The pool was filled with artificial seawater at a salinity and major ion composition resembling those of Arctic seawater, creating a (semi-)controlled environment for studying the dynamics of MPs across the seawater-sea ice-atmosphere interface.

The experiment spanned 18 months to study the weathering processes of MPs, covering two annual cycles of sea ice formation and melting and one open-water season in between. Sampling involved monthly collection of water and ice samples, with subsequent filtration and characterization of MPs using advanced techniques such as Fourier Transform Infrared Microscopy (FTIR) and Scanning Electron Microscopy (SEM). Additionally, the retention of mercury (Hg) on MPs was analyzed using cold-vapour atomic fluorescence spectroscopy, providing insights into the potential for weathered MPs to act as a vector for contaminants in the marine environment.

2.1 Preparation of Microplastics

The MPs in this study included the following combinations of type, size, and colour: white PE (PE-W, 1 mm in diameter), black PE (PE-B, 1 mm in diameter), white PP (3 mm), and white PS (1 mm). They were prepared from the corresponding 5 mm granular pellets (Goodfellow Cambridge LTD, Injection Moulding Grade; ET316305, ET316311, PP306320, ST316311) by freezing in liquid nitrogen, grinding in a coffee grinder for 1 min with about 5 g at a time and sieving through standard test sieves (2.0 mm/1.4 mm/1.0 mm/0.6mm/0.3 mm, ThermoFisher Scientific). The 1-mm nominal size refers to a diameter range from 1 to 1.4 mm, and the 3-mm nominal size refers to a diameter range from 3 to 3.4 mm. About 30 g to 50g of each MPs were prepared in this process.

2.2 Mesocosm Experimental Set-Up

The mesocosm experiment was conducted at the Sea-ice Environmental Research Facility (SERF; 49.80° N, 97.14° W; Figure 2-1) on the campus of the University of Manitoba, Winnipeg, Canada. With air temperatures ranging from -30°C in winter to $+30^{\circ}\text{C}$ in summer, SERF's outdoor seawater pool (18.3 m long, 9.1 m wide, and 2.6 m deep) provides a unique mesocosm to support process-oriented studies on the dynamics of the ocean-sea ice-atmosphere interface (Geilfus et al., 2019; Gao et al., 2022b).

For this study, the pool was filled with artificial seawater in September 2020, formulated by mixing groundwater with concentrated NaCl brine ($\sim 23\%$) and secondary salts including $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, CaCl_2 , and NaBr, with major-ion composition resembling that of the Standard Seawater with a salinity (S) of 30 to 31, which fell in the normal range of Arctic seawater from 30 to 34 (NSIDC, n.d.). The water was continuously mixed using circulation pumps until the start of the experiment in November 2020.

The experiment involved 15 microcosms placed inside the SERF pool, consisting of five treatments, each with three replicates: control (no MP additions), PE-W, PE-B, PS, and PP, as summarized in Table 2-1. Based on the results from Table 1-2 of 12 research, 5 research work reported average concentrations more than $100 \text{ pcs} \cdot \text{L}^{-1}$. In the previous mesocosm study of MPs, $120 \text{ particles L}^{-1}$ was used as low-level concentration (Geilfus et al., 2019). To ensure the recovery of MPs during the 18 months experiment period as well, $100 \text{ pcs} \cdot \text{L}^{-1}$ was selected in this study. This concentration ensures robustness in detecting MPs over an 18-month period while reflecting real-world pollution scenarios to some extent. All the 15 microcosms were randomly assigned as shown in Figure 2-1. Each microcosm measured 0.9 m long $\times$ 0.9 m wide $\times$ 0.75 m deep with a volume of $\sim 600 \text{ L}$. The microcosms were built from white PVC pipes as supporting frames and enclosed by a 100% cotton bed sheet (thread counts: 46 cm^{-2} ; mesh size: $\sim 63 \mu\text{m}$) that was permeable to seawater but not to the MPs used in the study.

The experiment lasted for 18 months from November 2020 until April 2022, during which time the seawater in the pool went through two annual cycles of sea ice formation and melting (December 2020 to April 2021, and December 2021 to April 2022) and one open water season in

between (April to December 2021). A one-time groundwater addition to the pool was done in June 2021 to compensate the evaporative water loss and to keep the salinity of the water at around 30. Following a heavy snowfall event in December 2021, the excessive amount of snow was shovelled off to allow sampling of the microcosms. Other than that, the pool was left essentially undisturbed.

Table 2-1. Summary of microplastics used in the mesocosm experiment

MPs	Size	Density	Color	Concentration	Replicates
PE	1 mm	0.92 g·cm ⁻³	Black	100 pcs·L ⁻¹	3
PE	1 mm	0.92 g·cm ⁻³	White	100 pcs·L ⁻¹	3
PP	3 mm	0.88 g·cm ⁻³	White	11 pcs·L ⁻¹	3
PS	1 mm	1.06 g·cm ⁻³	White	100 pcs·L ⁻¹	3



Figure 2-1. The set-up of the mesocosm experiment with 15 microcosms at the Sea-ice Environmental Research Facility (SERF) of the University of Manitoba, Winnipeg, Canada. PE-W: white color polyethylene; PE-B: black color polyethylene; PS: polystyrene; PP: polypropylene; A: weather station.

2.3 Sampling and Sample Processing

Figure 2-2 shows photos of the mesocosms taken at various times during the 18-month experiment period. Water and ice samples (when present) were collected from each microcosm monthly from November 2020 to October 2021, and every three months after that until the end of the experiment in April 2022. Approximately 1 L of water was taken by a submersible hydroponic sump ($750 \text{ L}\cdot\text{h}^{-1}$) at three different depths from the surface: 0-10 cm, 30-40 cm, and 60-75 cm. The samples were filtered through Whatman glass fibre filters ($0.7 \mu\text{m}$ pore size, Cole-Parmer Canada). The MPs retained on the filter were manually picked up by clean stainless-steel tweezers for characterization. They were rinsed three times with Milli-Q water, before being covered with an aluminum foil to avoid cross-contamination and stored in a glass desiccator for drying under room temperature. The filtrate was collected in new 50-mL clean polypropylene tubes (Falcon tubes, ThermoFisher Scientific) for chemical analysis.

For ice sampling, the ice cores (one core from each microcosm) were obtained by a Kovacs Mark II coring system (internal diameter: 9 cm). To measure the temperature within the sea ice, holes were drilled, perpendicular to the core length, by a cordless power drill with 1/8-inch drill bit at a vertical resolution of 3 cm. A calibrated temperature probe (Testo 720, $\pm 0.1 \text{ }^{\circ}\text{C}$ precision) was inserted into each hole for the measurement. Then, ice cores were evenly cut into three equal-length sections (top, middle, bottom) and then melted in clean glass beakers for sea ice bulk salinity analysis. The MPs in the meltwater were collected following filtration, rinsing, and drying as described above.

For cross-contamination prevention and control, all containers and tools were thoroughly pre-rinsed with ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$) prior to use. Filters were baked at $450 \text{ }^{\circ}\text{C}$ for 4 hours (where applicable) to remove organic residues. During sampling and filtration, all equipment was covered with aluminum foil or sealed immediately after use to minimize airborne contamination. Laboratory work was conducted in clean environments, and all working surfaces were regularly wiped with ethanol and ultrapure water. To prevent MP cross-contamination from the air, only cotton lab coats were worn during packing, and synthetic clothing was avoided.

Procedural blanks were included in every sampling event and laboratory batch to monitor potential cross-contamination from the environment, materials, or procedural steps. These blanks involved filtering ultrapure water through the same setup and use sea ice core that generated in a 4-liter beaker frozen in cold lab (-20°C) without any sample addition, then analyzing the filters in the same way as the samples. No MPs were found in blanks.

A designated “clean area” in the lab was maintained for sample filtration and processing, where there was limited personnel entry and movement. Field-collected samples were stored in pre-cleaned, tightly sealed glass containers to avoid cross-contamination from plastic containers. Filtration was performed using stainless steel sieves and glass vacuum filtration setups. All filters were inspected under a stereomicroscope to ensure that no external particles were introduced before use. All field blanks and transport blanks were processed and analyzed alongside real samples.

Nov 2020



Dec 2020



Feb 2021



Apr 2021



May 2021



Jul 2021





Figure 2-2. Photos of the mesocosm at various times during the 18-month experimental period

2.4 Measurement of Environmental Parameters

The ambient air temperature and wind speed during the experiment was measured by a weather station (Vaisala HMP45C sensor) located 1.5m above the SERF water surface (see Figure 2-2) at a resolution of every 10 minutes. The UV index was imported from the weather data section of Environment and Climate Change Canada.

Salinity of the water and ice was calculated from the temperature and conductivity that was measured by a conductivity benchtop meter kit (STAR A212, Thermo Scientific) with a 4-cell conductivity probe (Orion 013005MD, Thermo Scientific). The pH of the water samples was measured by a pH glass electrode (Orion 420A, Thermo Scientific). The composition of major ions in water samples were analyzed by a DIONEX 5000+ ion chromatography (IC) system. The major cations measured included sodium (Na^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}). The major anions included chloride (Cl^-) and sulfate (SO_4^{2-}). The certified reference material (CRM) used for major ions analysis was from Environment and Climate Change Canada including Burtap-14 (drinking water) and Mississippi-14 (River Water).

2.5 Characterization of Microplastics

The MPs collected from various time intervals during the experiment were characterized by FTIR and SEM. The FTIR analysis was done on a PerkinElmer Spotlight 200i under the attenuated total reflection (ATR) mode. A single MP particle was selected and placed on top of the diamond center of the ATR system. Then the sample was pressed by clamps, adjusted to an 80% gauge pressure, and scanned across the wavenumber range from 4000 to 450 cm^{-1} , with a resolution of 4 cm^{-1} and a rate of 30 scans per analysis. For each sample, at least three individual MP particles were analyzed. The spectra were processed by the PerkinElmer Spectrum IR software. Each spectrum was evaluated by assessing the peaks within the wavenumber range, characterized by the library analysis tool and compared with the spectrum of respective original, virgin MPs. The repeatability was checked as well. If there were abnormal spectra such as low match where the percentage of correspondence was less than 70% representative of the targeted type of MP, another MP sample would be selected and scanned.

The SEM analysis was done on a FEI Quanta 650 FEG Environmental SEM. Microplastics were analyzed under a vacuum pressure of 10^{-4} to 10^{-3} bar with an accelerated electron beam. To improve the quality of images of the MP surface, a platinum coating was applied before the SEM analysis. Microplastics was attached to the SEM pin stub mount by a double-sided tape and then placed in the Denton vacuum sputter coater (Capovani Brothers) for a platinum coating for about 5 min. Elemental compositional analysis was also done by an octane super energy dispersive X-ray spectroscopy (EDX) detector on multiple spots of a sample.

2.6 Analysis of Hg and Other Trace Metals Retained on Microplastics

The analysis of Hg retained on the MPs was done by cold-vapour atomic fluorescence spectroscopy (CVAFS) following microwave digestion. The microwave digestion was carried out on a Mars 6 microwave digestion system. About 0.1 g MP samples were weighed on an analytical balance and then placed into a MARS Xpress 50 ml vessel, followed by addition of 5 ml 70% HNO_3 (Trace Metal Grade, Fisher Scientific). The digestion was done at a microwave power of 1600 W, with a ramp time of 25 min for heating to 200°C and a holding time of 15 min at that temperature to ensure complete digestion; the solution after digestion was clear and light yellow. For quality assurance and quality control (QA/QC), a CRM, ERM-EC680m Polyethylene from the European Commission Joint Research Centre (Germany), was used to assure the Hg recovery was within 95% $\pm$ 5%.

The digested solution was analyzed for total Hg by CVAFS following the U.S. EPA Method 1631 (U.S. EPA, 2002). Briefly, the solution was added with 0.5% bromine monochloride (BrCl) for overnight to oxidize all forms of Hg to divalent Hg or Hg (II). To prepare the BrCl solution, HCl (CMOS grade, JT Baker) was incrementally added into a highly concentrated mixture comprising KBr ($50 \text{ g}\cdot\text{L}^{-1}$, A.C.S. Reagent grade, JT Baker) and KBrO_3 ($50 \text{ g}\cdot\text{L}^{-1}$, A.C.S. Reagent grade, JT Baker), which resulted in a BrCl solution where the volume fraction of HCl was 96% of the total volume. Then, 3% SnCl_2 (Fisher) solution was added to the mixture as a reducing agent to reduce Hg(II) to Hg^0 , which was first concentrated on a gold trap, then released by heating the gold trap, before being analyzed on a Tekran 2600 CVAFS total mercury analyzer. The method detection limit for Hg

was $0.1 \text{ ng}\cdot\text{L}^{-1}$. For QA/QC, a CRM, BCR-579 coastal seawater from the Institute for Reference Materials and Measurements - Joint Research Centre), was analyzed following the same procedure. The measured concentrations were $2.0 \pm 0.3 \text{ ng}\cdot\text{L}^{-1}$ ($n = 10$), which agreed very well with the certified value of $1.9 \pm 0.5 \text{ ng}\cdot\text{L}^{-1}$.

Trace metals analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS) to determine the concentrations of target metals in the samples. Calibration standards were prepared by serial dilution of a $10 \text{ ug}\cdot\text{mL}^{-1}$ multi-element stock solution (Li, Be, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Cd, Ba, Pb) in a matrix-matched solution of 2% HNO_3 . Internal standards (^{45}Sc , ^{89}Y , and ^{209}Bi) were added to both samples and standards to correct for instrumental drift and matrix effects. The ICP-MS operating conditions were optimized daily to ensure maximum sensitivity and stability. The collision/reaction cell was operated in helium mode to minimize polyatomic interferences.

Quantification was performed using external calibration with internal standardization. The limit of detection for each metal (Li, Be, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Cd, Ba, Pb) were, 0.87, 1.39, 1.57, 1.13, 1.66, 1.29, 2.78, 1.23, 1.38, 1.23, 1.22, 1.43, 1.26, 1.61, 0.82, 1.23, 1.15, $1.40 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ respectively. Analytical accuracy and precision were validated using CRMs with known metal concentrations. Recoveries of the target metals ranged from 92% to 108%, and the relative standard deviations were typically less than 5%, demonstrating the repeatability of the method. All samples were analyzed in triplicate to determine an uncertainty, and blank samples were included in each batch to monitor potential contamination.

2.7 Statistical Analysis

For all statistical analyses performed in this study, hypotheses were formally stated to clarify the inferential framework. The significance level was set at $\alpha = 0.05$, and results with $p < 0.05$ were considered statistically significant unless otherwise noted. The statistical method and related hypotheses were summarized as below:

(a) Comparisons between groups

To assess differences among treatment groups (e.g., CI, roughness, Hg accumulation), statistical comparisons were conducted using one-way or two-way Analysis of Variance (ANOVA), where applicable. The hypotheses are as following:

Null hypothesis (H_0): There is no significant difference in the mean response variable across the groups being compared.

Alternative hypothesis (H_1): At least one group mean is significantly different from the others.

(b) Correlation Analysis

Correlation analyses were performed to determine whether two variables (e.g., CI and Hg accumulation) co-vary linearly or monotonically. Pearson correlation was used for normally distributed data.

Null hypothesis (H_0): There is no correlation between variable X and variable Y ($r = 0$).

Alternative hypothesis (H_1): There is a significant correlation between variable X and variable Y ($r \neq 0$).

(c) Regression Analysis

Simple and multiple linear regression analyses were used to investigate whether surface properties (e.g., roughness, CI) could predict contaminant accumulation (e.g., Hg concentration). Linear regression was applied to predict the value of a variable (dependent variable) based on the value of another variable (independent variable) between different values such as CI values and Hg accumulation, hypothesizing that CI increases Hg-binding potential.

Null hypothesis (H_0): The slope of the regression line is zero ($\beta = 0$), indicating no relationship between the predictor and response variable.

Alternative hypothesis (H_1): The slope is significantly different from zero ($\beta \neq 0$), indicating a linear relationship.

Model fit was assessed using R^2 values, and regression assumptions (linearity, homoscedasticity, normality of residuals) were tested prior to interpretation.

(d) Principal Component Analysis (PCA)

PCA was used as an exploratory tool to reduce dimensionality and identify key patterns in normalized, multivariate data (e.g., pH, temperature, major ions concentration, Cl, roughness, etc). No explicit hypothesis testing was conducted for PCA, but variable loadings and scree plots were interpreted to inform the grouping and correlation structure of variables.

Statistical analysis was conducted by Microsoft Excel and SigmaPlot 13. This statistical framework ensured consistent and rigorous evaluation of the experimental data, enabling robust interpretation of treatment effects, correlations, and multivariate patterns throughout the study.

Chapter 3. Environmental Conditions and MP

Distribution in Sea Ice

3.1 Environmental Conditions During the 18-month Experiment

3.1.1 Air temperature, UV index, and wind speed

Air temperature: Figure 3-1A shows the variability of ambient air temperature, measured at 0.5 m above the SERF pool surface, throughout the 18-month experiment. For reference, the average temperature profile of Arctic Bay (73°N), Nunavut, is also shown in Figure 3-1A (WeatherStats, n.d.). The air temperature of SERF shows a clear seasonal pattern, rising from as low as -30°C in January/February to as high as +30°C in July/August.

For SERF, the average temperature (yellow dots) aligned well with the median temperature (50th percentile, the black line within the box) for each month. From November 2020 through March 2021 and again in November 2021 to March 2022, the median air temperatures were generally negative, representing winter conditions. There is a consistency in the overall seasonal trends across the two consecutive winter periods (2020-2021 and 2021-2022). However, slight variations in the amplitude of the temperature fluctuations were observed, with the winter of 2021-2022 showing more extreme cold than the previous year. Of the two winter periods covered in this study, January 2021 was about 10°C warmer than January 2022, but air temperatures in February 2021 and February 2022 were similar, showing particularly low temperatures, with the median air temperature reaching below -20°C, highlighting an extreme cold period. During the summer months (June 2021 to September 2021), temperatures peak, with median temperatures reaching above 20°C in July and August.

A longer interquartile range (IQR), represented by a longer box, implies that the middle 50% of the data points are more spread out, showing that there is more variation in the air temperatures during that month. Specifically, winter months such as February 2021 to March 2021 and January 2022 to March 2022 indicated greater spread and variability, possibly due to diurnal temperature changes. The greater variability could result from larger day-to-day or even hour-to-hour changes in temperature. Months with a shorter IQR (such as January 2021 and

December 2021) experienced more consistent temperatures within that middle 50% range, meaning the temperatures were more stable and did not fluctuate as much.

The lines extending from the top and bottom of the box represent the range of the data. The presence of longer whiskers during transitional months, such as March and November, indicated greater variability in temperature during these periods, likely due to changing seasonal conditions. The presence of shorter whiskers such as April in 2021 and 2022, indicated that the temperature was more consistent.

In comparison with Arctic Bay's temperature profile (WeatherStats, n.d.) in the same temporal scale, this enormous seasonal temperature variability provides a good seasonal pattern of the temperature regime in the Arctic while temperatures at SERF are generally warmer across all months. The average air temperature of the southern Arctic Ocean should be higher than the blue line in the figure. In the winter months (December to February), the temperatures at SERF drop significantly, with values ranging from -10°C to -25°C . For sea ice formation, the critical temperature is below the freezing point of seawater, which is around -1.8°C . Although the central Arctic is colder, with temperatures ranging from -20°C to -35°C , the SERF conditions are cold enough to simulate ice formation and freezing conditions. This range closely approximates the sub-zero conditions of the Arctic Ocean during winter, where sea ice forms and is maintained. It is sufficient to study sea ice dynamics, as ice forms and persists at these sub-zero temperatures.

The winter months at SERF provided cold conditions necessary for freezing, while the spring and summer months showed temperatures rising above freezing, similar to what happened in the Arctic during the melt season. This cyclical pattern allowed for studying the freeze-thaw cycles that were critical to understanding sea ice dynamics in the Arctic. The fact that the temperature at SERF rose above freezing in summer also enabled studying processes related to sea ice melting, which occurred when Arctic sea ice retreated during the warmer months. During transitional months (between summer and winter), SERF temperatures fluctuated around 0°C , similar to conditions near the Arctic ice edge, where sea ice was actively forming and melting. This aspect is vital because the ice edge is where many significant processes occur, including nutrient exchanges, brine rejection, and biological productivity associated with ice-algal growth.

In summary, SERF offers a semi-controlled environment where temperatures can simulate the Arctic's freeze-melt cycle without the extreme cold of the high Arctic. This allows us to replicate freeze-up conditions and sea ice dynamics in a setting where logistical challenges (such as those faced in the Arctic) are reduced.

UV intensity: The UV index is commonly used to represent UV intensity because it provides a standardized and simple way to represent the daily UV radiation at the Earth's surface and a UV Index of 1 corresponds to a UV intensity of $25 \text{ mW} \cdot \text{m}^{-2}$. UV radiation at the Earth's surface consists of UVA (longer wavelength, deeper penetration) and UVB (shorter wavelength, more energy, and potential for skin burns). The UV index reflects a weighted consideration of both.

Figure 3-1B provides the variability in UV index values. The UV index at SERF shows a clear seasonal pattern, with UV index values increasing from a low of around 1 in the winter (November 2020 to February 2021) to a peak around June 2021, reaching values as high as 8 or 9. During the peak summer months, the UV index is consistently higher, with some variability as indicated by the error bars. In contrast to SERF, Arctic Bay exhibits much lower UV index values overall, peaking at around 4 in the middle of the summer (June 2021). The increase in UV index is more gradual compared to SERF, and the values remain relatively low throughout the months of polar night (September to March), with the UV index close to 0.

Overall, SERF shows greater variability during the summer months (April to September), where the whiskers extend significantly, while Arctic Bay's values are more consistent and less variable overall. SERF has overall higher UV intensity than the High Arctic due to the low latitude. So photochemical weathering at SERF is expected to be more than in the Arctic locations.

Wind speed: Figure 3-1C provides the variability in wind speed of SERF and Arctic Bay. The profile of SERF shows a relatively stable wind speed over the period, with moderate variation, as evidenced by the width of the IQR in the boxplots. Most wind speeds range between approximately 10 to $40 \text{ km} \cdot \text{h}^{-1}$ with average around $20 \text{ km} \cdot \text{h}^{-1}$. The profile of Arctic Bay shows general lower and more variable wind speeds when compared with SERF (blue line). The average wind speed ranges from 5 to $20 \text{ km} \cdot \text{h}^{-1}$, which fluctuates more compared to SERF.

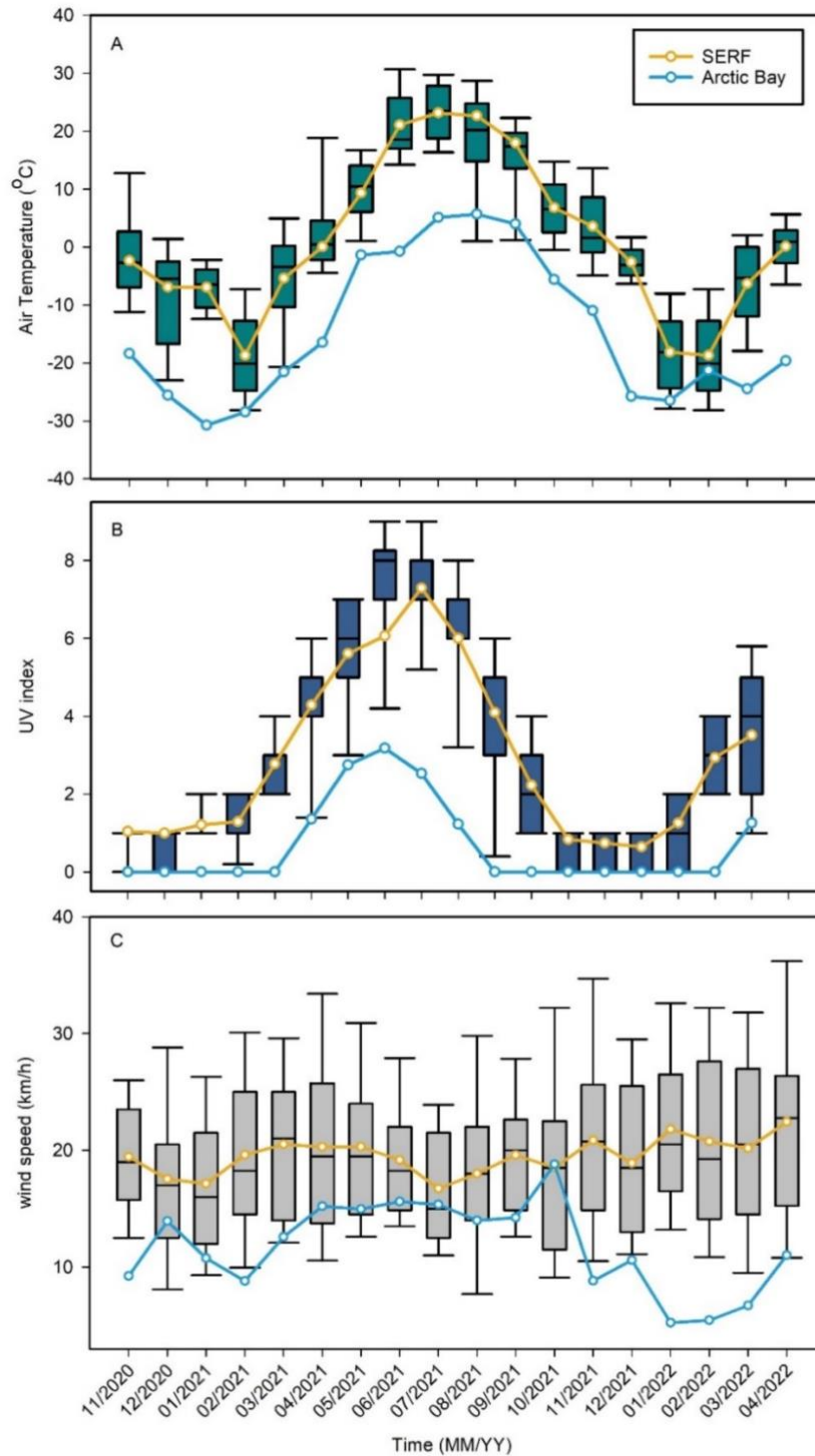


Figure 3-1. Variability of (A) ambient air temperatures (green box); (B) UV index (dark blue box); (C) wind speed (grey box) during the 18-month mesocosm experiment and respective mean at SERF (yellow line) and at Arctic Bay (blue line) (data of SERF was collected by weather station and data of Arctic Bay was from WeatherStats, n.d.)

3.1.2 Seawater properties

Throughout the 18-month experiment, the pH of the experimental seawater at SERF remained nearly constant at 7.9 ± 0.2 (mean $\pm$ standard deviation) (Figure 3-2A), well within the pH range of Arctic surface water from 7.5 to 8.4 (Steiner et al., 2021). The stability in pH suggests that carbonate buffering systems are likely maintaining equilibrium despite environmental changes.

Over the same period, salinity of the experimental seawater was more variable at 30.3 ± 1.2 (Figure 3-2B), with notable peaks and dips. The increase in salinity to 32 around June 2021 was due to evaporative water loss as temperature increased, which was adjusted to ~ 30 by the addition of groundwater to compensate the volume change and the compensation of water was kept across the summer. The slight increases in salinity during winter months were consistent with the formation of sea ice, which expelled sea salts into the water column. The depression of salinity and major ions in April 2021 was an indicator of sea ice melting while that in October 2021 was possibly attributed to the rainy season.

As expected, the concentrations of major ions (Cl^- , Na^+ , Mg^{2+} , SO_4^{2-} , Ca^{2+} ; Figure 3-2C) in the experimental seawater followed the general trend of salinity. Chloride and sodium ions, being the most abundant in seawater, showed closely aligned trends with concentrations fluctuating between 400 and 550 mM. The similarity in their behaviour of the sea ice environment reflected their common origin from salt rejection during sea ice formation. The other major ions (Mg^{2+} , SO_4^{2-} , and Ca^{2+}) exhibited lower concentrations and remained stable (around 40 mM, 20 mM, and 10 mM, respectively).

This figure highlighted the interplay between physical processes, such as sea ice formation and melting, and the chemical properties of seawater. The observed fluctuations in salinity and major ion concentrations suggested that brine rejection during ice formation plays a critical role in driving these changes. Additionally, the relatively stable pH implies a well-buffered marine environment, maintained by carbonate chemistry, even as ion concentrations and salinity fluctuate in response to seasonal changes.

The consistent pH values, dynamic but controlled salinity adjustments, and stable ion compositions provide a robust framework for interpreting the broader MPs implications of microplastic pollution in polar regions, ensuring that the findings from this study were both reliable and applicable to natural environments. These detailed environment parameter profiles provided a foundational context for the subsequent analysis within the mesocosm experiment.

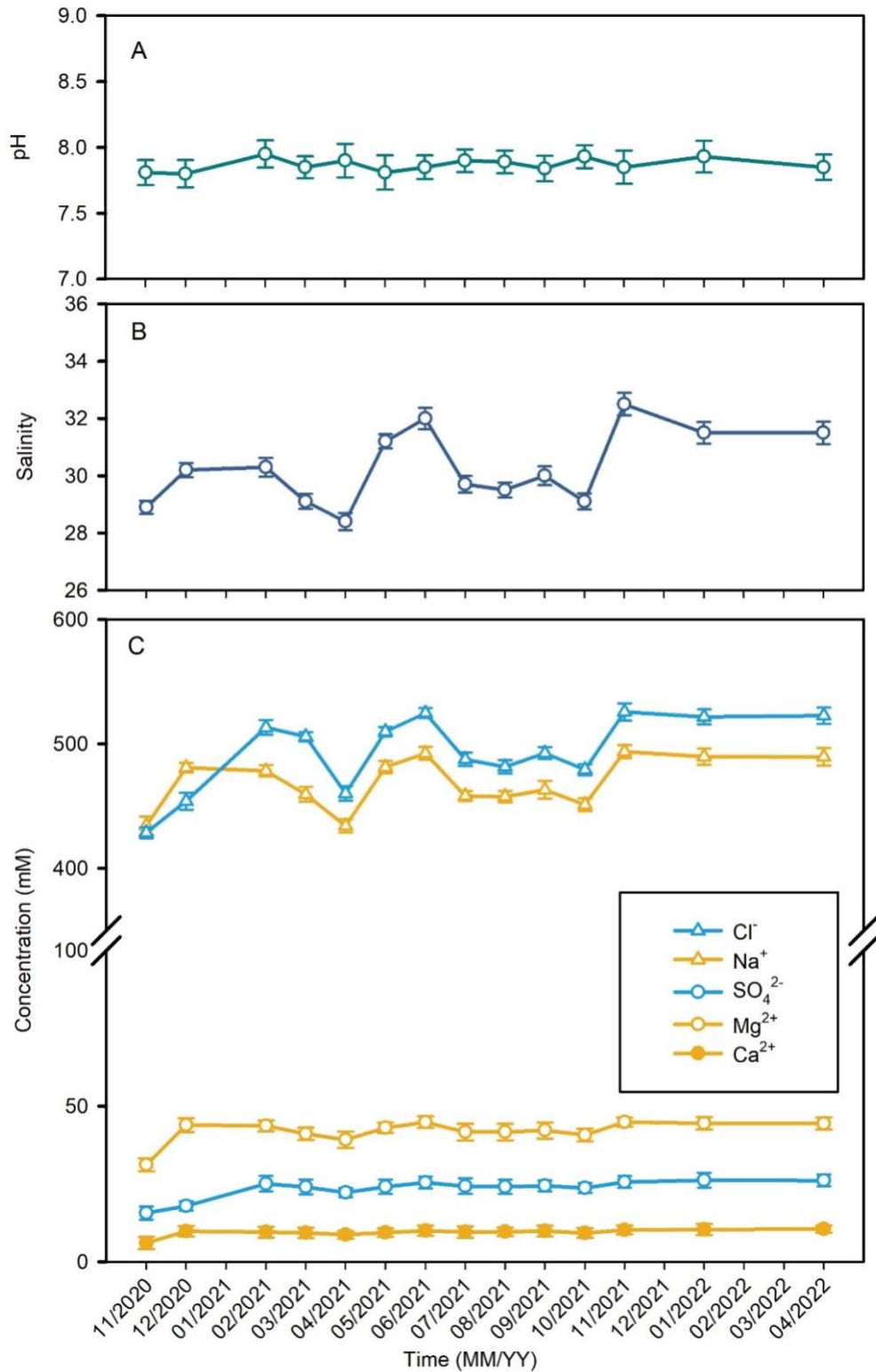


Figure 3-2. Variation of the properties of the experimental seawater during the 18-month mesocosm experiment, including (A) pH, (B) salinity, and (C) major ions composition

3.1.3 Sea ice dynamics

Thickness: Starting from November 2020, the sea ice started to form. In December 2020, the sea ice depth was relatively shallow, around 6 cm. The ice thickness started to increase and peaked at 40 cm by February 2021. By March 2021, the sea ice began to thin slightly, though it still remained near 30–40 cm in depth, suggesting the onset of melting as the season progresses. The ice was completely melted by the beginning of April 2021. For the second winter cycle, the peak of thickness was about 46 cm in February, the melting processes begun after mid-April. Through two winter cycles, the sea ice showed a pattern of seasonal thickening and subsequent thinning, with the maximum thickness observed in February.

Temperature: Sea ice temperature profiles are shown in Figure 3-3A for December 2020, February 2021, January 2022, and April 2022 for microcosms with (in yellow) or without (in blue) the addition of MPs.

Across all time points, temperature profiles show a gradient where surface ice (at 0–10 cm depth) is colder than deeper ice (10–40 cm depth). This is consistent with expected patterns in sea ice formation, where surface layers are more exposed to colder air temperatures.

All the vertical temperature profiles exhibit a nearly linear increase from the surface (ranging from -4°C ~ -10°C), which was controlled by the air temperature at the time of the sampling, to the bottom, which was nearly constant at -2°C , which was controlled by seawater salinity. This suggests increasing heat retention at deeper depths as ice thickens.

Variations among treatments are minimal, with average temperature differences of less than 1°C between the treatments at any given depth or time point. The different treatments exhibit minor deviations, indicating the presence of MPs do not significantly alter the temperature profiles compared to the blanks ($p > 0.05$).

Salinity: Figure 3-3B presents the vertical profiles of bulk ice salinity in sea ice samples with and without the presence of MPs across two winters including four time points: first winter with December 2020, February 2021 and second winter with January 2022, and April 2022. The bulk salinity follows a characteristic C-shaped profile, typical of first-year sea ice (Thomas, 2017),

with elevated salinity levels at both the surface and base of the ice, reflecting salt expulsion during ice formation.

According to statistical analysis, for the first winter, the presence of MPs did not significantly alter bulk salinity ($p > 0.05$). For the second winter, microcosms containing PP and PS also showed no significant impact ($p > 0.05$) on bulk salinity. However, in the second winter, microcosms with PE (both PE-W and PE-B) led to an increase of approximately 2 (from 7 to 9 and 5 to 7) in bulk salinity at the surface layer of the sea ice ($p < 0.05$).

Figure 3-4 shows the difference in bulk ice salinity of the topmost section of sea ice in January 2022 and April 2022, for five different treatments including PE-W, PE-B, PP, PS, and Blank. For January 2022, PE-W and PE-B treatments exhibit the highest salinity levels, both averaging close to 9 in January 2022 and 7 in April 2022, which is significantly higher than the other treatments ($p < 0.05$). The PP, PS, and Blank treatments show lower salinity values, around 6 in January 2022 and less than 5 in April 2022, and are not statistically different from one another but significantly lower than PE-W and PE-B.

The statistically significant differences between the treatments suggest that PE-W and PE-B have an influence on bulk ice salinity compared to PP, PS, and Blank after one year of weathering. Geilfus et al. (2019) proposed that MPs could concentrate impurities within the brine channels of sea ice, facilitating brine migration through the ice matrix, especially in early growth stages. The salinity changes observed were mainly limited to the upper layers of the ice, indicating that the presence of MPs has its greatest effect near the surface. As shown in Figure 3-5, PS was minimally incorporated into the ice, resulting in bulk salinity levels similar to the control group.

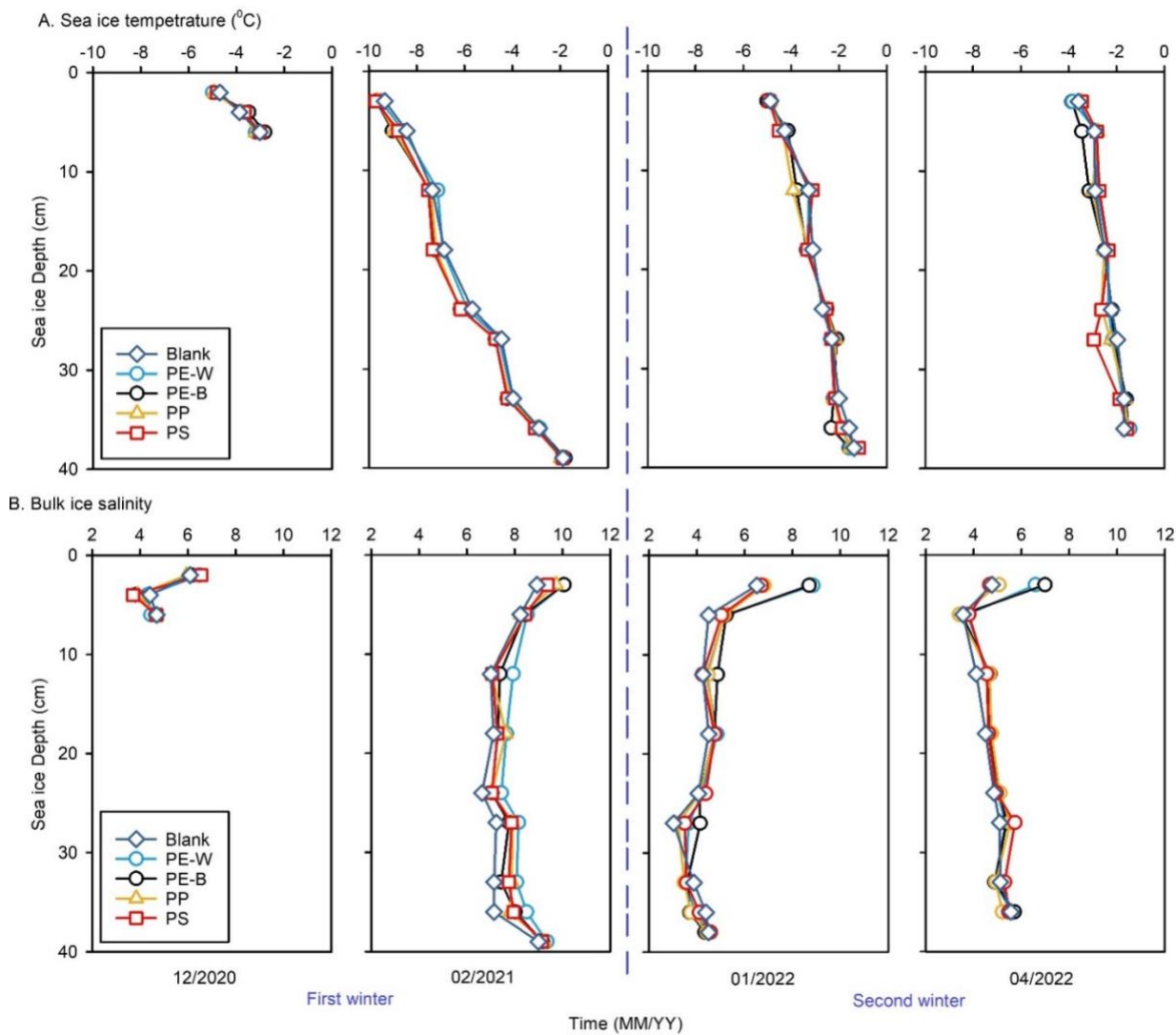


Figure 3-3. (A) Sea ice temperature (top) and (B) bulk salinity (bottom) with or without MPs during 4 different sea ice freezing months

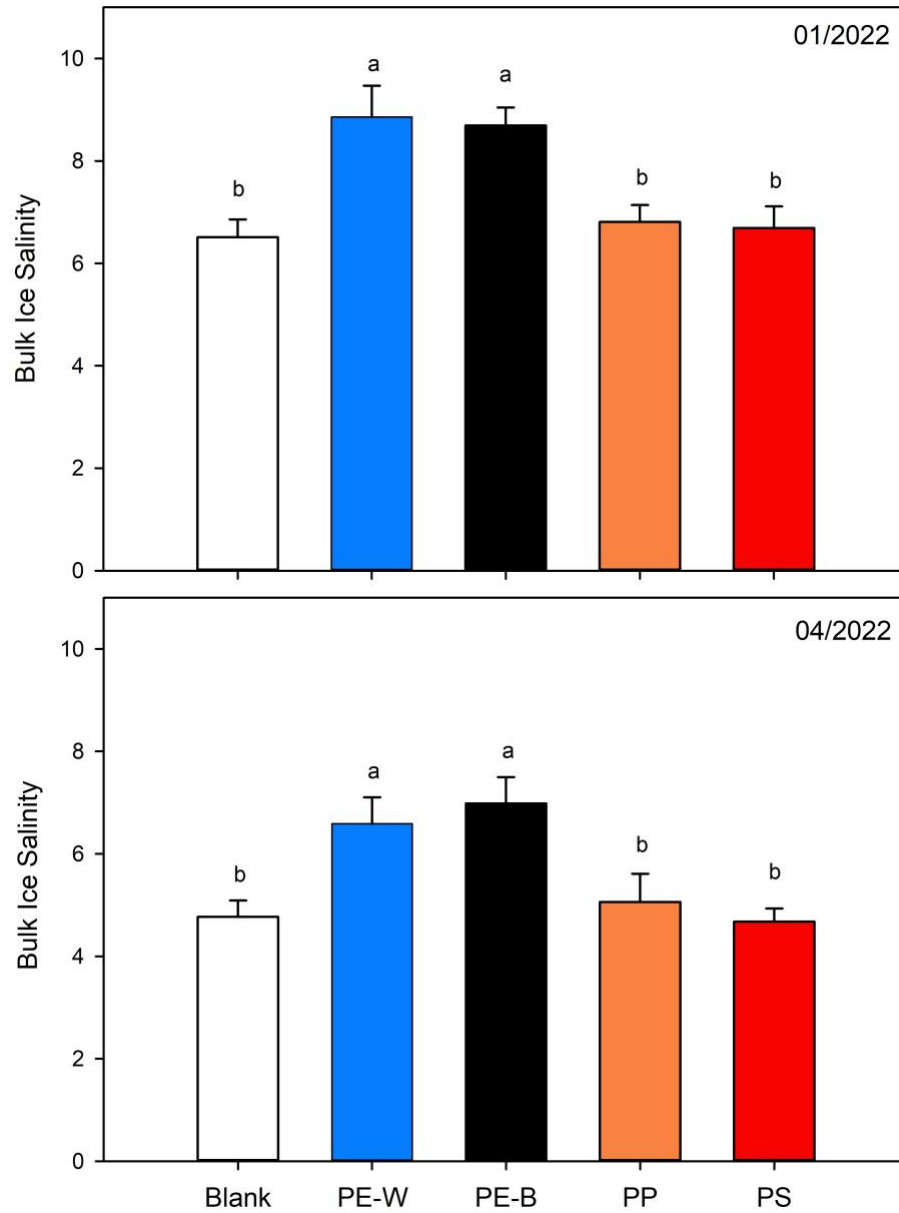


Figure 3-4. One-way ANOVA test of bulk salinity of topmost ice section among different types of MPs in January 2022 and April 2022. Different letters (a, b) indicated statistical significance ($p < 0.05$) between the groups, with groups sharing the same letter indicating no significant statistical difference ($p > 0.05$).

3.2 Distribution of Microplastics between Seawater and Sea Ice

Figure 3-5 shows the vertical distribution of microplastic particles (MPs) per liter within sea ice at different depths (0 to 40 cm) across two winters including four time points: first winter with December 2020, February 2021 and second winter with January 2022, and April 2022.

The MPs used in this experiment were mostly larger than 1 mm in diameters, the size of which did not change much during the 18-month experiment; no smaller pieces were found under microscope. The concentrations of MPs in the ice are reported as the number of MPs per liter of meltwater of the ice (p L^{-1}).

Across all four time points, PE-W and PE-B exhibit similar overall vertical patterns in MP distribution. Among the total MPs trapped in the ice, more than 95% were trapped in the top 0-5 cm of the sea ice (about 140 p L^{-1}) and about 5% remained in 5-10 cm in sea ice (about $10\text{-}15 \text{ p L}^{-1}$). For PP, the vertical profile is similar to that of PE, with about 90% of MP particles being trapped in the top 0-5 cm of the sea ice (about $30\text{-}40 \text{ p L}^{-1}$) and around 10% remained in 5-10 cm in sea ice (about $5\text{-}15 \text{ p L}^{-1}$).

The concentration of PE and PP in the surface ice was about 1.5 times higher than the initial concentration in the water. On the other hand, few PE and PP were found in the water under the sea ice. As sea ice grew thicker, the concentration of MPs decreased rapidly with increasing depth, which agrees well with the observations for the distribution of virgin MPs (Geilfus et al., 2019). No MPs were found in ice deeper than 15 cm, which indicated MPs were trapped in the upper layers of sea ice during its formation. This could be due to the lower density of PE and PP than seawater and the carrier effect by brine expulsion during sea ice formation.

In contrast, PS exhibited a different distribution profile. Few PS was found in most of the ice cores, with the exception that 12 p L^{-1} were found in the bottommost section of a core sampled during February 2021 when the ice reached its maximum thickness of around 40 cm. This could be attributed to its higher density than water and thus its incorporation in ice only became possible when the ice grew the deeper into the microcosm.

In terms of temporal evolution, the distribution patterns of MPs are relatively stable over time, suggesting that once incorporated into the ice, the MPs were trapped there with minimal

vertical migration. After one year of exposure to the environment, weathering alters the physical and chemical properties of MPs. These changes have no significant effect on the vertical distribution of MPs.

The distribution of MPs in sea ice shows clear patterns of depth-dependent accumulation, with higher concentrations at deeper layers for all MP types. PE-B, PE-W, and PP consistently show the higher concentrations in the top layer (0-10cm) of sea ice, which enhances their interaction with brine. PS exhibit lower concentrations in the ice, but high concentrations in the water body under the ice. The one-year weathering does not have significant effects on the distribution of MPs in the sea ice.

The higher surface concentrations of PE-W, PE-B, and PP contrasted with the deeper entrapment of PS, suggesting different behaviours influenced by physical properties such as buoyancy and density. The observed temporal stability of MP concentrations further underscored the persistence of these pollutants once they are incorporated into the ice structure.

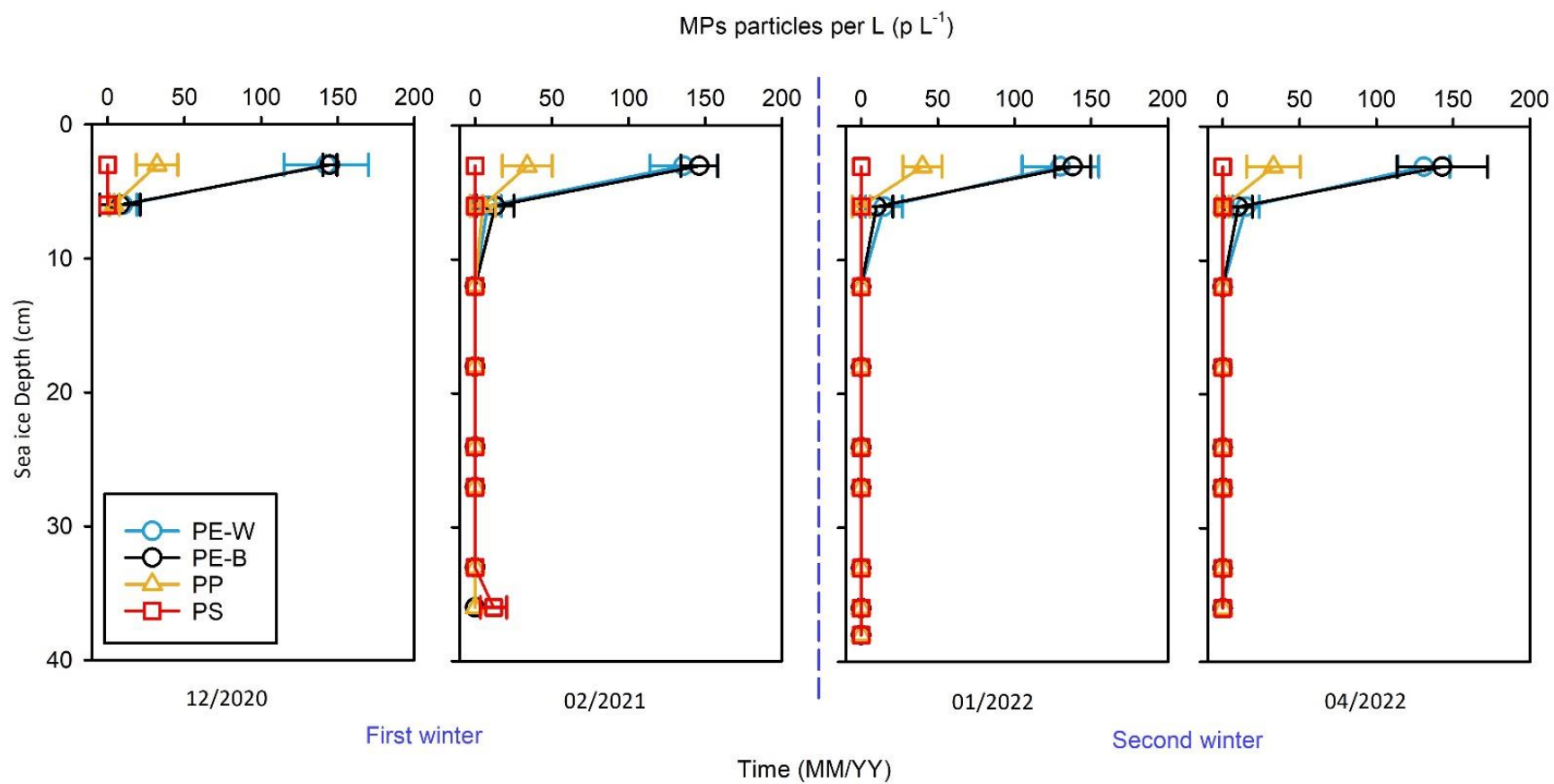


Figure 3-5. Distribution of MPs in the sea ice during the two consecutive winters

3.3 Discussion

In this section, the figures collectively provided a comprehensive understanding of how environmental parameters and MPs interact in a controlled mesocosm setup. These detailed environment parameter profiles provided a foundational context for the subsequent analysis within the mesocosm experiment.

The detailed comparison of the vertical profiles of sea ice temperature and bulk salinity in the presence of both virgin and weathered MPs revealed that MPs did not significantly affect the temperature profiles of sea ice. However, they did impact the bulk salinity distribution, with MPs leading to higher salinity levels, particularly at the surface. In contrast to the finding of Geilfus et al. (2019) that virgin MPs affected surface bulk ice salinity over the first winter, the incorporation of MPs into the ice matrix in this study did not significantly alter the properties of sea ice until the second winter, specifically for systems containing PE. Ice samples containing weathered PE (second winter) displayed 50% higher surface bulk ice salinity compared to control group without MPs, which indicated that weathered PE promoted the increase of surface bulk ice salinity. After prolonged exposure to environmental conditions, especially over the span of one year, the surface properties of PE can undergo significant changes due to weathering. These changes can influence its interaction with brine and ice in the polar environment, potentially affecting the bulk ice salinity observed in the PE-B and PE-W treatments. There might be several factors lead to these changes of ice properties.

Firstly, Figure 3-5 shows that PE-W and PE-B are predominantly distributed near the surface of the sea ice when compared with PP and PS. This distribution reinforces the idea that PE MPs are more likely to interact with surface processes, such as salt entrapment and release, directly affecting surface salinity. The close surface concentration of PE means these MPs are exposed to greater UV radiation and environmental interactions, as described in Chapter 4. This exposure enhances their weathering and the likelihood of salt accumulation, which is released during freeze-thaw cycles, influencing salinity. Conversely, PS, located deeper, have less opportunity to influence surface salinity, explaining their negligible impact.

Second, the small size of PE (1 mm in diameter, compared to PP of 3 mm) with more specific surface area are susceptible to more fragmentation due to the combined effects of photodegradation, thermal cycling, and mechanical forces such as ice movement or abrasion (Pfohl et al., 2022). The smaller particle size plays a role in the retention of brine within the sea ice. Therefore, smaller particles can fill the pores of forming ice more effectively, reducing the permeability of the ice. This smaller size can hinder the natural brine drainage process by blocking the brine channels within the ice matrix, thereby trapping more saline water. In contrast, larger particles of PP might not occupy the brine channels as effectively, allowing for better drainage and thus lower bulk ice salinity. In addition, PP has low initial concentration, which provides less participation as particles.

Third, weathering over time can result in increased surface roughness (Figure 4-7). A rougher surface with more micro-structures can trap water more effectively than a smooth surface, contributing to the higher retention of saline water in the PE-treated ice samples.

Fourth, the biological weathering cannot be neglected in the natural environment. The formation of biofilms can lead to the surface changes of MPs as well. For example, the formation of biofilms on PE surfaces can further enhance the surface roughness and hydrophilicity of the material (He et al., 2022, Vu et al., 2009). Biofilms are typically composed of water-retentive polysaccharides, proteins, and lipids, which increase the ability of the material to bind and retain water. This increased water retention may prevent the effective drainage of brine from the ice matrix, contributing to the higher bulk ice salinity observed in the PE-B and PE-W treatments.

Last, the formation or presence of oxygen-containing functional groups such as carbonyl ($-C=O$), hydroxyl ($-OH$) on the surface of PE makes the surface of PE more hydrophilic (the CI increase in Figure 4-9). As a result, weathered PE may interact more strongly with the water and brine in the ice matrix. This can lead to enhanced water retention, as the weathered PE may now have a higher affinity for binding water molecules, preventing efficient brine expulsion.

Chapter 4. Weathering of MPs

4.1 Changes in Surface Morphology and Roughness

This section presents changes in the surface morphology of MPs, as revealed by SEM imaging, as they weathered during the 18-month experiment at SERF. The sequential images provide insight into the distinct stages of surface degradation and morphological transformation during the weathering.

The SEM images are shown in Figures 4-1 to 4-4 at Months 1, 4, 6, 7, 9, 10, 11, 12, 15, and 18. At each time interval, two images are shown: one showing an entire MP particle (at about 50x to 75x magnification), and the other showing detailed surface morphology of part of a particle (at around 500x magnification).

4.1.1 SEM images - Qualification

Overall, the surface changes of MPs can be divided into three stages: Initial phase, mid-stage weathering, and late-stage stabilization.

PE-W

Initial Phase (November 2020 to February 2021, month 1 to 4)

In the initial stage (Months 1 to 4), the SEM images (Figure 4-1) reveal relatively smooth and intact surfaces, with only minor imperfections and occasional shallow indentations. The detailed views display fine surface textures with slight grooves and occasional scratches. At higher magnification, the surface appears uniformly textured with some mechanical stress lines from preparation processes. This period reflects the initial weathering phase, where the material remained largely resistant to substantial structural breakdown.

By February 2021 (Month 4) and in the presence of sea ice, the surface began to show early signs of weathering, with slightly increased appearance of visible attachments. These changes suggest initial interactions with the natural environment.

Mid-stage weathering (May 2021 to October 2021, month 7 to 12)

During the mid-stage, from May 2021 (Months 7) when the sea ice melted away, inorganic and organic aggregates began to accumulate on the surface of the MPs, indicating a progressive increase in their presence over time. SEM-EDX analysis showed the cubic substances were NaCl crystals deposited from the seawater (Fig. 4-5) and the pennate-shaped substances were diatom cells (Fig. 4-6) suggesting the presence of biofilm due to biological activity in the pool.

By July 2021 (Month 9), the surface textures became markedly coarse and there was a noticeable increase in surface complexity. The NaCl crystal accumulation continued. Substantial biological growth became evident, suggesting significant biofilm formation during the summer months.

Late-stage stabilization (January 2022 to April 2022, month 15 to 18)

In the late-stage (after month 12 to 18), the degradation process appeared to stabilize. Detailed views showed a reduction in the density of cracks and grooves, with a more uniform surface texture. In January 2022 (Month 15), there was a reduction in surface deposits compared to the previous months. The surface still showed weathering effects, but the biofilm presence appeared less pronounced, which was in agreement with reduced biological activity in cold, ice-covered water.

By April 2022 (Month 18), the MPs exhibited continued weathering with a mix of residual salt crystals and biological cells. The biological cells began to appear again, indicating continuous physical, chemical, and biological interactions with the environment as the season transited. This phase suggested a potential increase in surface roughness, which suggested the presence of sea ice have influence on the microbial activities.

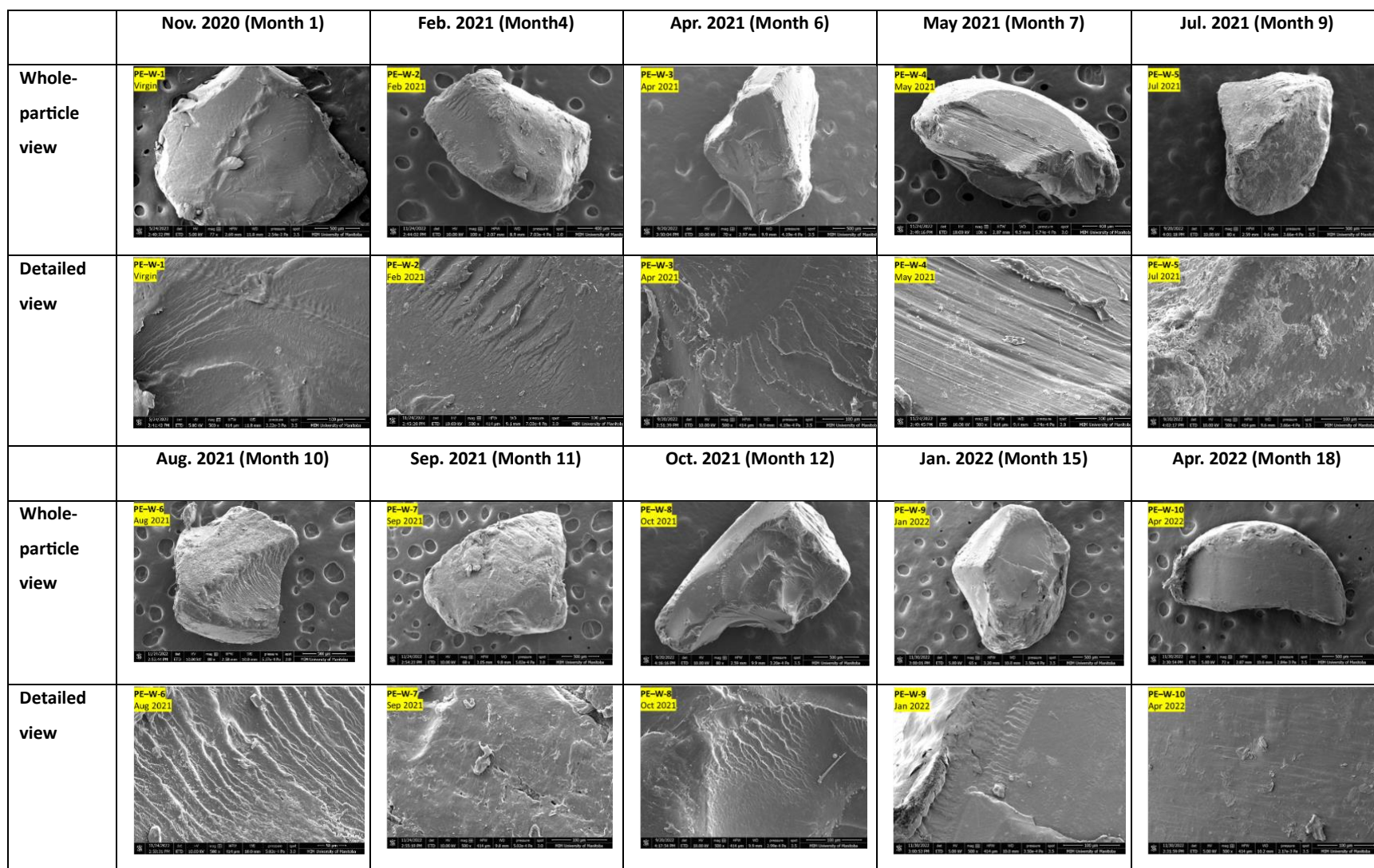


Figure 4-1. SEM images of polyethylene - white (PE-W) microplastics as they weathered through the 18-month study period at the Sea-ice Environmental Research Facility. For each time interval, a whole particle view (~50x to 75x magnification) and a detailed view (500x magnification) are shown.

PE-B

Initial Phase (November 2020 to February 2021, month 1 to 4)

In the initial months (Months 1 to 4), PE-B exhibited relatively smooth surfaces (Figure 4-2). The detailed views revealed faint scratches and minor surface roughness, which might be attributed to slight mechanical abrasion. The particle structure remained largely intact.

Mid-stage weathering (Apr 2021 to October 2021, month 6 to 12)

By Month 6, significant transformations began to manifest. The whole-particle views started to show a rougher surface. Detailed views revealed substantial development of surface textures, including pronounced roughness across the particle surface. During this period, faint crystalline structures became visible on some surfaces, especially in the detailed views. These features were characteristic of salt crystallization. These features suggested that the MPs might have entered an accelerated weathering phase, potentially driven by UV oxidation, biological weathering and mechanical stress.

Started from Month 9 to Month 12, diatoms began to dominate the surface area. The visible pennate shape indicated these microbials start to colonize on the surface of the MPs. This increased surface complexity likely resulted from continued environmental stress. The particles appeared more rugged, marking a distinct departure from the smoother textures observed in the earlier months.

Late-stage stabilization (January 2022 to April 2022, month 15 to 18)

As the study neared its last stage (Months 15 to 18), the surface morphology of PE-B stabilized, showing fewer new signs of attachments but still irregular stripes. Whole-particle views depicted clean surface, indicating the MPs undergo a relative stable period. The detailed views in this phase displayed a mix of worn textures and residual cracks, suggesting that the surface had reached a form of plateau where additional weathering progresses at a slower rate. This plateau in transformation might be due to the depletion of biofilms, resulting in reduced susceptibility to further environmental weathering.

PP

Initial Phase (November 2020 to February 2021, month 1 to 4)

In the first few months (Months 1 to 4), PP maintained a smooth and even in the whole surface (Figure 4-3). At higher magnification, the surface appeared uniformly textured from the manufacture process. The detailed views reinforced this observation, showing relatively unblemished textures. These initial images indicate that PP remains largely unaffected by early environmental exposure.

After Month 4, subtle changes started to appear on the surface of the PP, with clusters of irregularities beginning to form. These changes suggested early stages of environmental interaction.

Mid-stage weathering (Apr 2021 to October 2021, month 6 to 10)

From Month 9 to Month 10, the surfaces underwent more pronounced changes. The surface roughness increases significantly, with more pronounced irregularities and more substantial biological material, indicating significant biofilm formation during the summer months. This can also be shown in Figure 4-7, which exhibited high surface roughness by quantification methods. Detailed views revealed clusters of biological cells, mainly composed of silica, characteristic of diatom attachment. After Month 10, the signs of diatoms began to disappear gradually.

Late-stage stabilization (January 2022 to April 2022, month 15 to 18)

During the late-stage period (Months 15 to 18), the PP showed a stabilization in surface morphology. There was a noticeable reduction in biological attachments compared to previous months, likely due to gradually reduced biological activity. However, the surface remained slight roughness, with mostly signs of salts deposition. By April 2022, the PP surface showed a layer of residual salt crystals and few biological cells, maintaining a level of surface attachments. These observations suggested continuous interactions with the marine environment, which might lead to next cycle of biological weathering of PP.

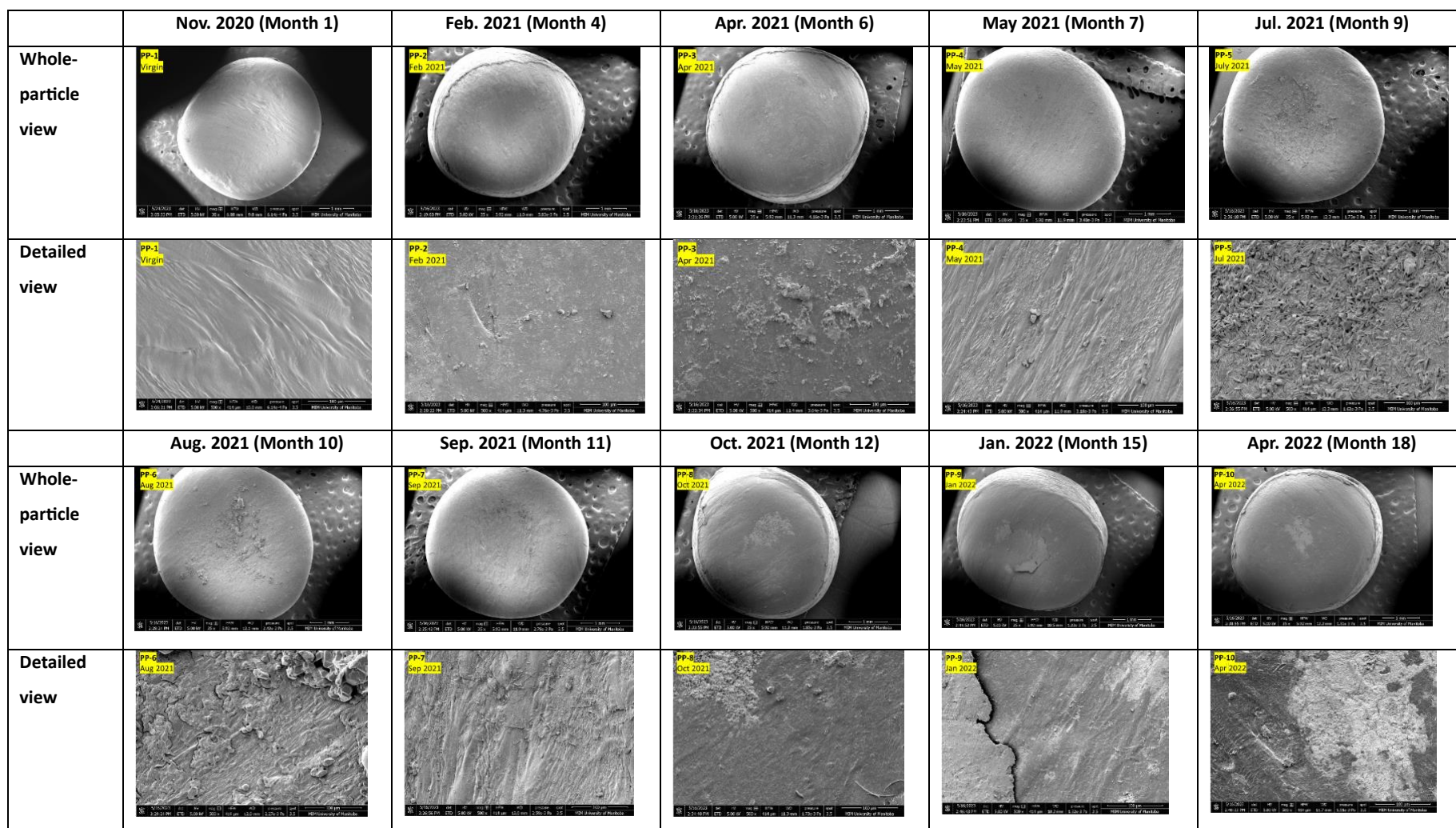


Figure 4-3. SEM images of polypropylene (PP) microplastics as they weathered through the 18-month study period at the Sea-ice Environmental Research Facility. For each time interval, a whole particle view (~50x to 75x magnification) and a detailed view (500x magnification) are shown.

PS

Initial Phase (November 2020 to February 2021, month 1 to 4)

Initially, the virgin PS exhibited surfaces with minimal irregularities (Figure 4-4). The higher magnification images displayed a relative uniform texture but less mechanical stress scratches from the preparation process. The absence of significant surface alterations indicated that environmental conditions have not yet induced substantial weathering.

Mid-stage weathering (Apr 2021 to July 2021, month 6 to 9)

The surface showed minor increases in roughness, with the formation of small particulate attachments, mostly salt precipitation like sodium chloride. This mid-stage period suggested a slight shift in the weathering pattern, as the PS surface became slowly responsive to the environment.

Late-stage stabilization (August 2021 to April 2022, month 10 to 18)

Starting from Month 10, the surface roughness continued to increase, and more biological growth was evident but still in a low state. However, by contrast with PE and PP, the crystals and cells remained after August 2021, were sparsely distributed on the surface and did not significantly change over the remaining period.

From Month 10 to Month 18, no dramatic increase in roughness or additional cracking was observed, indicating that the weathering process may be in a slowly changing state. This final phase suggested that while PS undergo surface changes, the weathering rate was slow over time, likely due to PS stayed in the water with continuous interactions water environment but less activities. The material's structural integrity, while altered, remained relatively preserved.

Overall Summary

In summary, with SEM images, combined with EDX analysis of elements, the combination of Na, Cl, Si, and other elements supported the hypothesis that the MPs surface were undergoing complex interactions with seawater and biological entities, leading to the observed surface changes.

The SEM images demonstrated clear seasonal variations in the surface properties of MPs. During summer months (April to October), there was a significant increase in salt and biological attachments, driven by higher biological activity and salt crystallization due to evaporation and seawater exposure. In contrast, winter months (January) showed reduced biological activity, with fewer cells attached to the MP surfaces, indicating that temperature and seasonal biological cycles play critical roles in the weathering process.

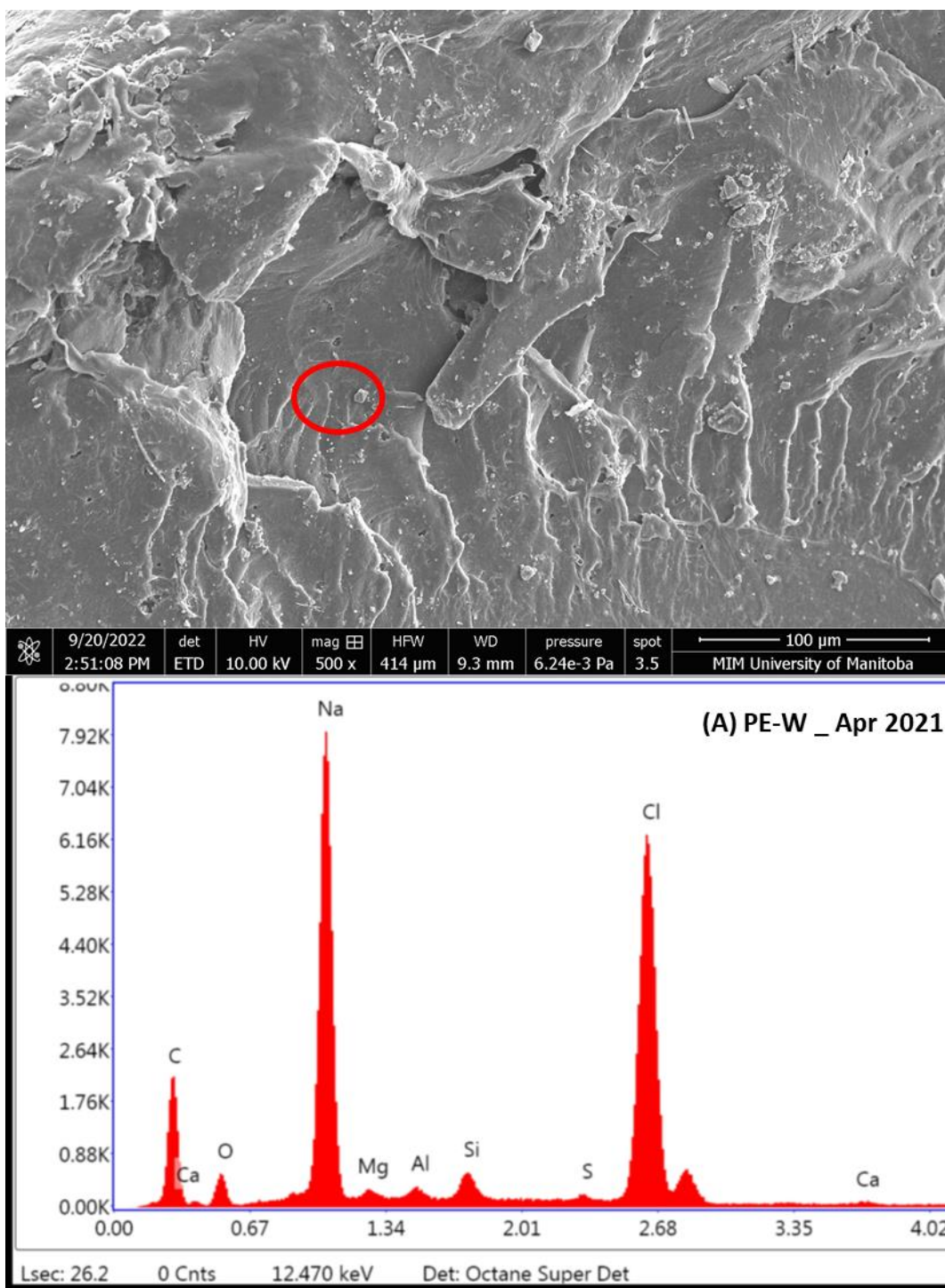


Figure 4-5. SEM-EDX analysis of a cubic substance (identified inside the red oval) accumulated on the surface of a polyethylene-white (PE-W) MP in April 2021 (suggesting it was NaCl deposited from the seawater)

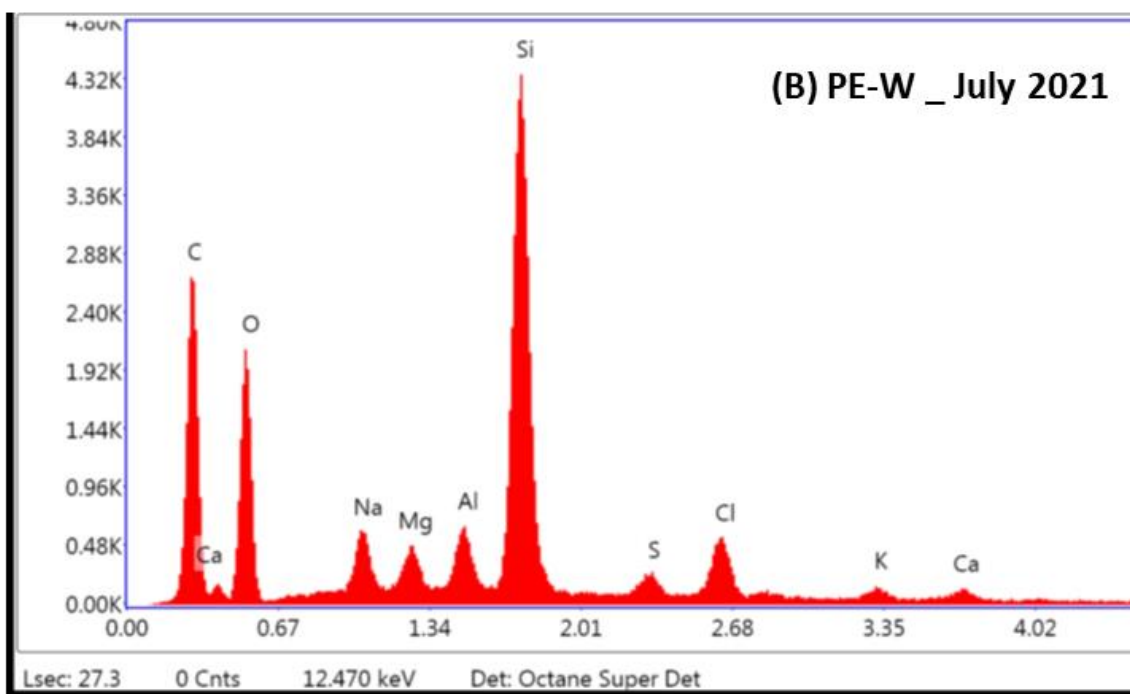
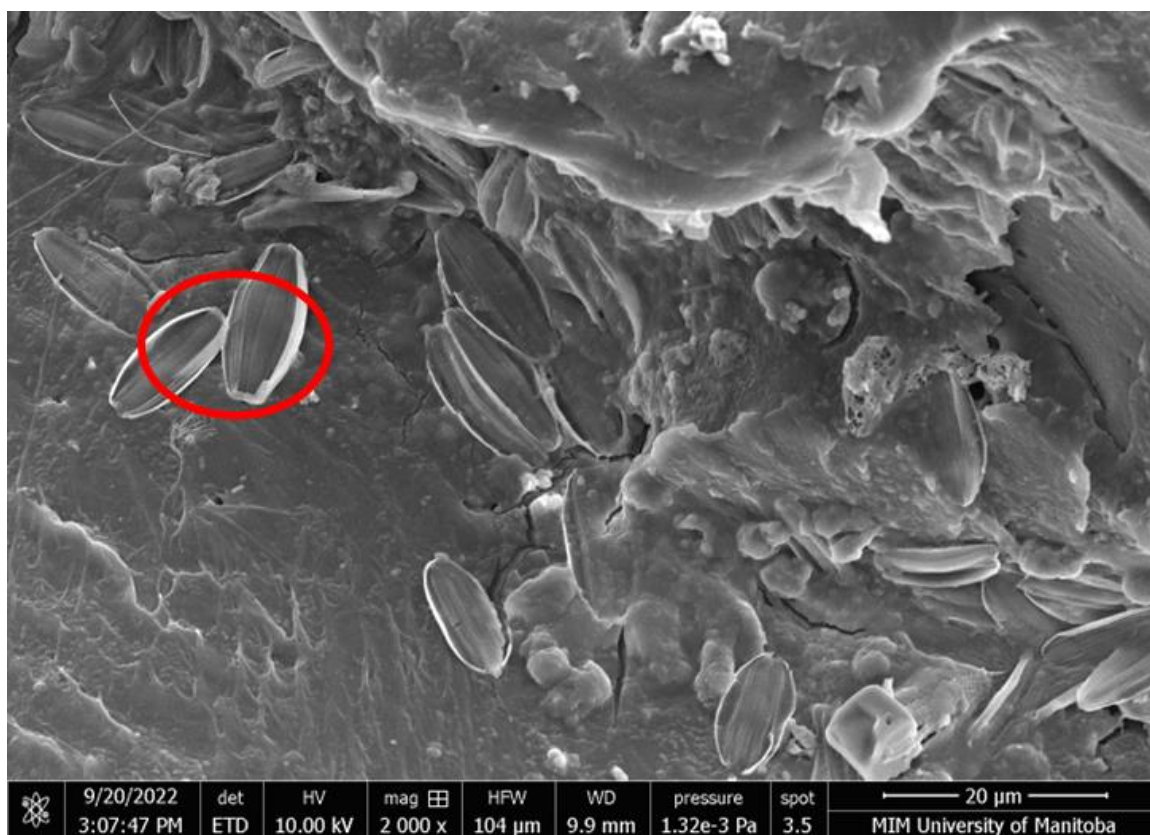


Figure 4-6. SEM-EDX analysis of a pennate-shaped substance accumulated on the surface of a Polyethylene-white (PE-W) MP in July 2021 (suggesting it was a pennate diatom)

4.1.2 SEM images – Quantification

The quantification of surface roughness of MPs was achieved by Python using the Gray Level Co-occurrence Matrix (GLCM) methodology. GLCM can help quantify the extent of surface roughness (Valentino et al., 2022). It is a powerful image processing technique for quantifying surface roughness of materials. GLCM analyzes the spatial relationship between pixels in a greyscale image, providing statistical measures of texture that can be directly associated with surface roughness. Surface roughness information can be effectively represented in greyscale images, where GLCM thrives. No color information is necessary, making it easier to analyze images obtained from standard microscopes or other imaging tools, which often produce high-resolution grayscale images suitable for texture analysis.

Surface roughness in images manifests as variations in texture. When a surface is rough, there are rapid changes in light intensity in the image, creating distinct textures. GLCM captures these textures by analyzing how often pairs of pixels with specific greyscale intensities appear in a certain spatial relationship (distance and direction). By examining these pixel pairs, GLCM provides a measure of local intensity variations that represent surface irregularities, which correlate with the roughness of the material.

As MPs get weathered, their surfaces become increasingly uneven and textured. GLCM can capture these minute roughness levels by analyzing greyscale images at the pixel level, making it highly sensitive to the kinds of surface changes associated with environmental weathering. Using GLCM is a non-destructive way to quantify surface roughness from images, which is beneficial when studying MPs (Lin et al., 2024).

Figure 4-7 illustrates the temporal changes in quantified surface roughness of four types of MPs over an 18-month weathering period. In general, all MPs show seasonal or periodic peaks with peaks in mid-2021, specifically around summer months, suggesting possible environmental factors contributing to increased roughness during these months.

Initially, all MPs exhibit relatively moderate roughness values between 400 and 500 units, indicating a similar baseline surface texture across polymers, which align with the previous observations that all MPs exhibit relatively smooth, intact surfaces with minimal roughness.

As the weathering progresses, however, each polymer shows unique variability in surface roughness, especially with PE-W reaching peak roughness levels of more than 700 units around mid-2021. This corresponds with the findings of salt crystals and diatom cells mentioned in the previous section. The seasonal increase in biological and inorganic attachments, particularly in warmer months, aligns with heightened biological activity, as demonstrated by the presence of diatom cells. These observations highlight the role of summer conditions in accelerating weathering, with biological activity intensifying surface roughness, likely due to increased biofilm growth and salt crystallization.

In contrast, there is not much change to PS with some fluctuations (ranging between 400 to 500 units), and PP experiences a sharp decline in roughness after October 2021. PE-B has a fluctuated surface roughness. Towards the end of the experiment, all MPs converge towards lower roughness levels. The SEM image observations reveal fewer new attachments, and roughness values begin to converge at lower levels for all MPs. The reduction in biofilm presence was likely due to colder temperatures that slowed down biological activities. PE-B and PP exhibit fewer diatoms and salt crystals, indicating a reduced rate of surface alteration as the environmental conditions shift towards winter, when biological activity is minimized. These results indicated a reversible process that might be related to biofilm rather than irreversible weathering processes, which agreed well with Hg trends described in Section 5.1. This might be related to the lower density of PE than seawater, which exposed more to the air and sunlight. And smaller size of PE leads to more specific surface area, which provides more sites for formation of biofilms.

However, there are limitations on surface morphology. Since SEM captures a 2D representation of the surface from a single angle, making it challenging to fully assess complex 3D structures or features like pits, cracks that may exist around the entire particle.

This restricted perspective can lead to an incomplete understanding of the MPs' overall morphology. For example, cracks that are visible from one direction may appear different or may be hidden when viewed from another angle, potentially leading to underestimation of surface roughness or damage extent. A lack of 3D data limits the ability to accurately quantify surface area, which is crucial for understanding the potential adsorption sites for pollutants or

microorganisms. Important internal changes, like pore formation or degradation beneath the surface layer, may go undetected. This can result in an incomplete picture of the degradation mechanisms affecting microplastics, especially if the weathering process involves internal structural breakdown as well as surface erosion.

In addition, observing surface features from a single angle can create ambiguity, as certain structures may appear differently depending on the angle of view. For instance, small particles attached to the surface or biofilms may look like artefacts rather than real features, or vice versa, depending on how they reflect or absorb the electron beam. Misinterpretation of features, especially in complex MPs samples, can lead to inaccurate conclusions about biofilm presence, or surface roughness. This is particularly problematic for studies that rely on surface feature identification to infer environmental exposure or microbial colonization. But the general trend of increased surface roughness and a decline after can still be found from both qualification and quantification results. Therefore, the examination of chemical structural changes needs to be conducted.

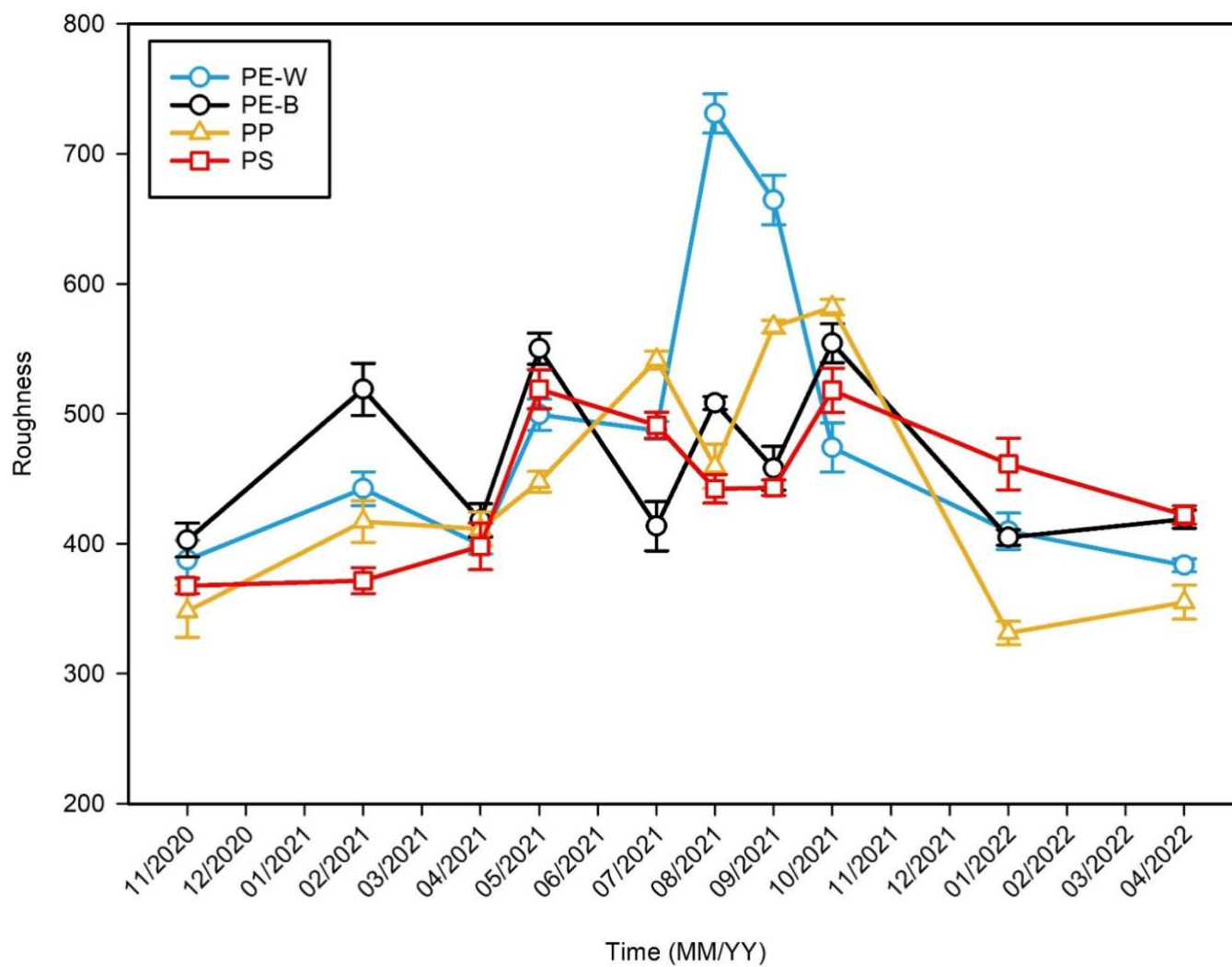


Figure 4-7. Change of surface roughness of four types of MPs during the study period

4.2 Changes in chemical properties

Figure 4-8 shows example FTIR spectra of four types of MPs across the entire experiments by months. The spectra were collected at various time points from November 2020 to April 2022, illustrating the temporal evolution of chemical properties due to weathering. Table 4-1 summarizes characteristic peaks of three types of MPs for virgin and weathered characterization (Ercan et al., 2023; Fang et al., 2012).

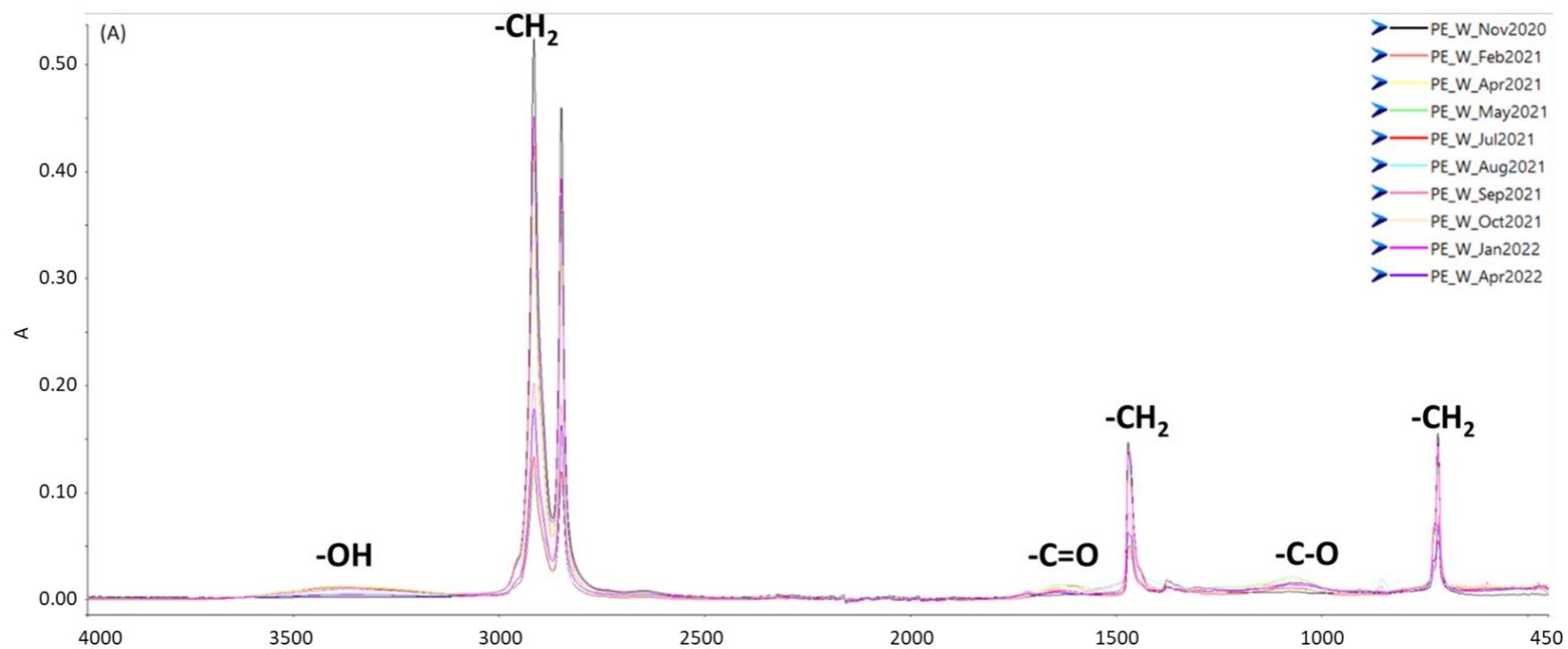
For each type of MPs, the spectra reveal characteristic peaks associated with the virgin materials. The wave numbers of each characteristic peak for each type of functional groups are listed in the table below. These consistent peaks, with a matching accuracy of over 90% compared to known reference spectra, confirm the initial identity and integrity of the MPs prior to weathering.

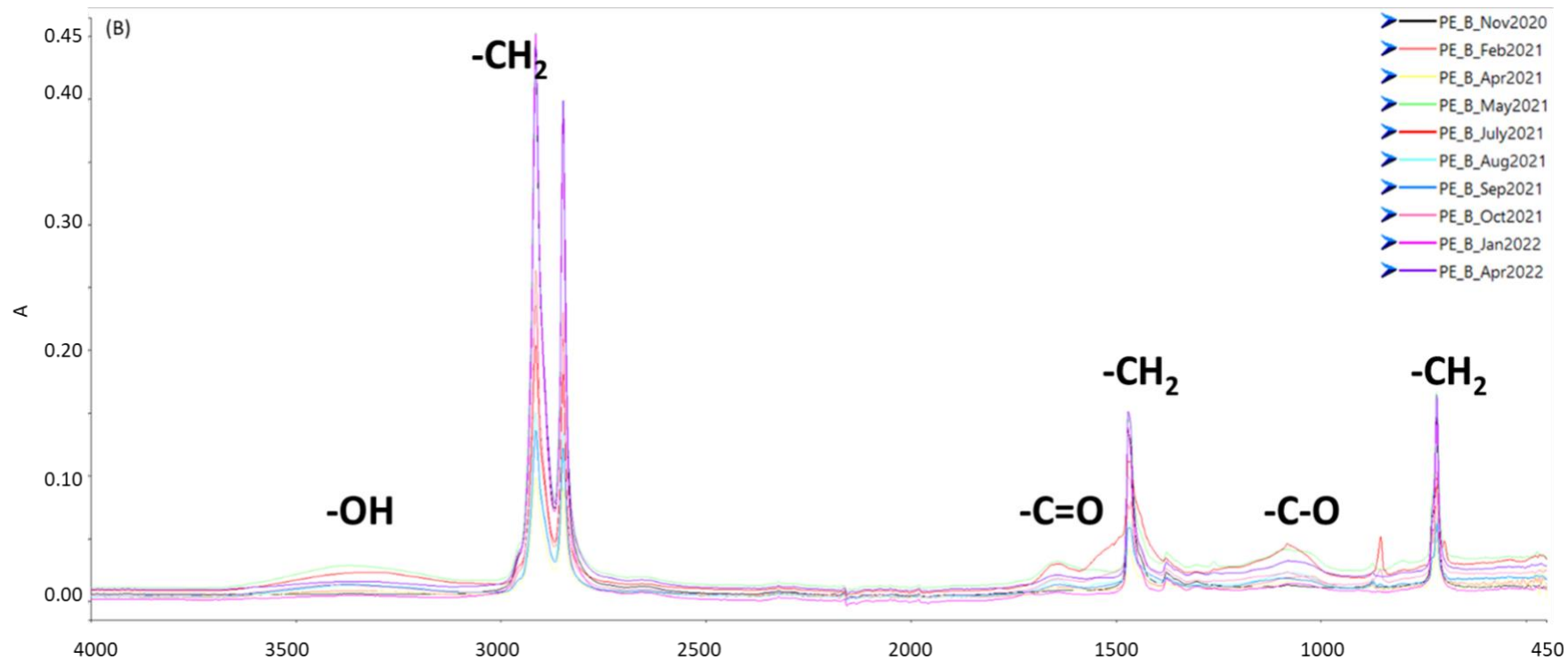
For the weathered PE-W and PE-B, new peaks appeared representing hydroxyl groups (-OH) and carbonyl groups (-C=O), and alkoxy groups (-O-), signifying the occurrence of weathering. In the case of PP and PS MPs, only new peaks appeared corresponding to hydroxyl groups (-OH), and carbonyl groups, yet without additional alterations in the other fingerprint region. This observation implies that, although weathering affects all polymers to some degree, PP and PS experienced less chemical structural change than PE under similar environmental conditions, with less evidence of secondary oxidative degradation groups.

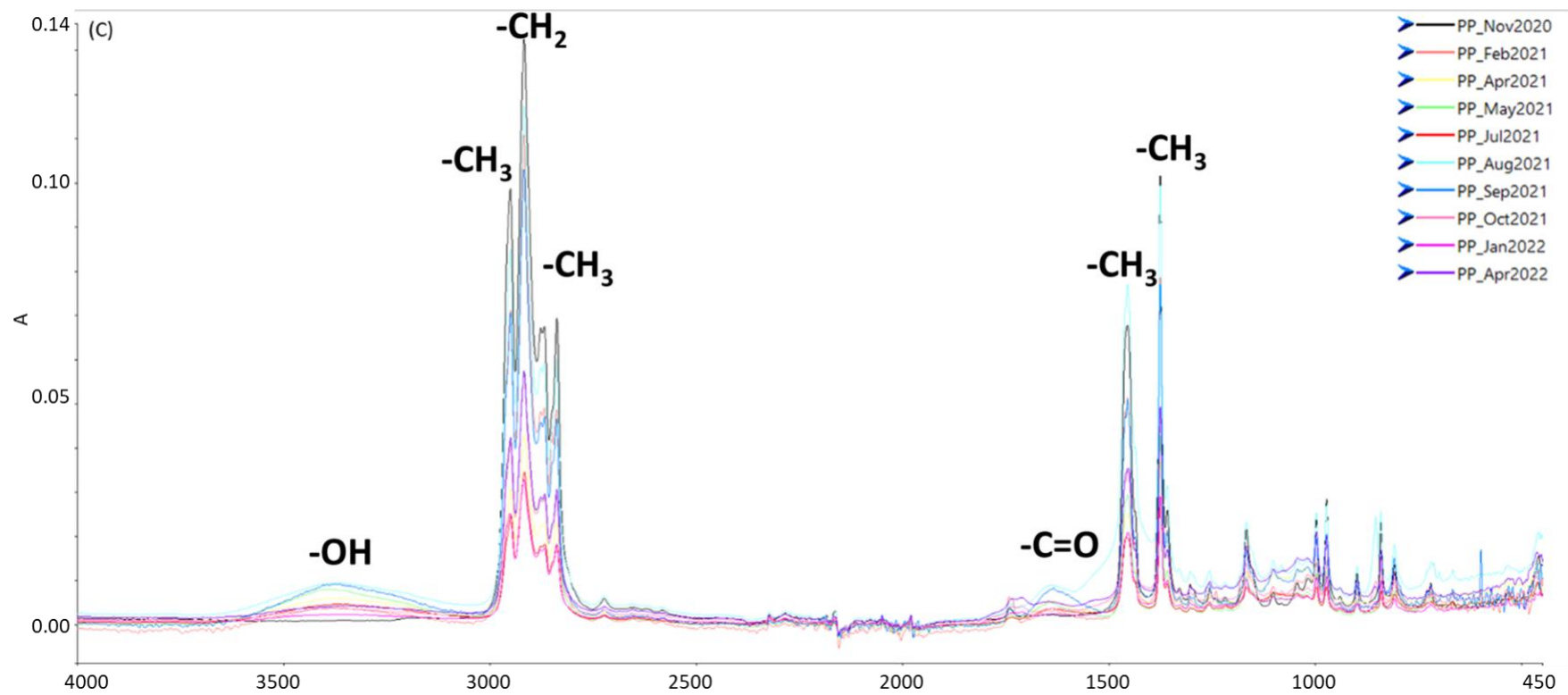
The consistent presence of primary -CH₂ peaks across all MP types suggests that while surface-level oxidation occurs, the core polymer backbone remains largely intact. However, the recurrent appearance of -OH and -C=O groups across all materials underscores that weathering-induced oxidation is a common degradation pathway, driven by factors such as UV exposure, oxygen infiltration, and possibly microbial interactions. The degree and nature of this oxidative degradation vary between polymer types, with PE showing the most substantial chemical transformation, PP demonstrating moderate changes, and PS remaining the most chemically resilient.

Table 4-1. Characteristic peaks of three types of microplastics for virgin and weathered characterization (Ercan et al., 2023; Fang et al., 2012)

MPs	Virgin		Weathered	
	Functional group	Wave number (cm ⁻¹)	Functional group	Wave number (cm ⁻¹)
PE	-CH ₂	2947, 1470, 730	-OH	3500 - 3000
			-C=O	1700 - 1500
			-C-O	1200 - 800
PP	-CH ₂	2920	-OH	3500 - 3000
	-CH ₃	2950, 1456	-C=O	1700 - 1500
PS	-CH	3081, 3059, 3025, 756	-OH	3500 - 3000
	-CH ₂	2921, 2848	-C=O	1700 - 1500
	-C=C	1600, 1491, 1451		







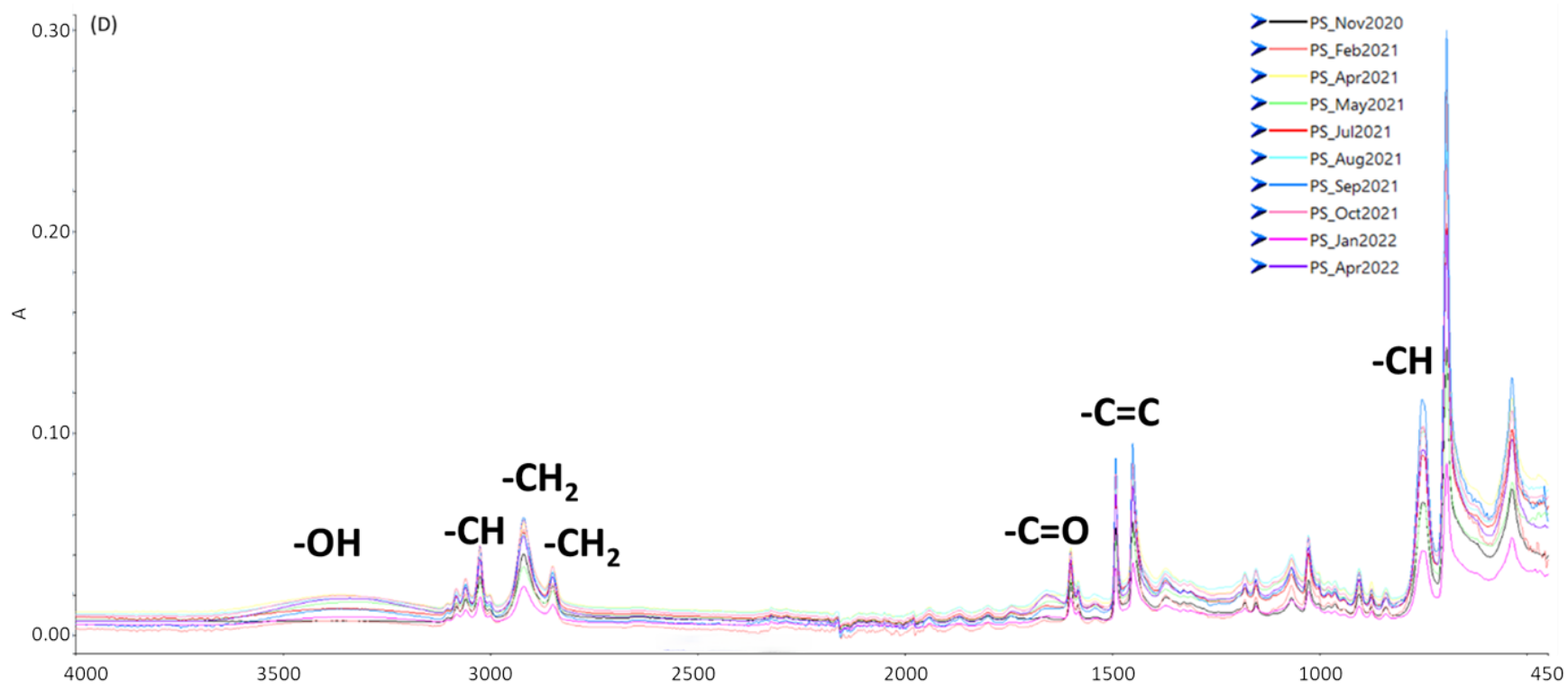


Figure 4-8. FTIR spectrum of (A) Polyethylene - white (PE-W), (B) Polyethylene – black (PE-B), (C) Polypropylene (PP), (D) Polystyrene (PS) across the entire experiment

4.3 Degree of Weathering

For the virgin MPs, no peaks were observed around 1800 cm⁻¹ to 1500 cm⁻¹ and 3500 cm⁻¹ to 3000 cm⁻¹. When compared with virgin MPs, carbonyl group (C=O) in the range of 1800 - 1500 cm⁻¹ and hydroxyl (-OH) in the range of 3500 cm⁻¹ to 3000 cm⁻¹ groups was founded in weathered MPs samples, which might indicate the oxidation of MPs in the water.

To estimate the degree of weathering, carbonyl index (CI) index was calculated as the ratio between the absorption intensity of carbonyl group (around 1650 cm⁻¹), A_{OC} , and the absorption intensity of methylene group (-CH₂ group at 2915 cm⁻¹), A_{ref} , which serves as a stable reference during weathering processes (Chen et al., 2021; Gomes et al., 2024; Liu et al., 2019):

$$CI = \frac{A_{OC}}{A_{ref}} \quad (1)$$

Figure 4-9 showed the CI index of four types of MPs over 18 months. The zero CI index of the initial MPs (virgin) indicates no carbonyl groups found on the MPs.

Across the observation period, PE-B (black circles) and PP (yellow triangles) exhibit the highest CI, peaking around mid-2021. Both materials show a rapid increase in the CI from early 2021, reaching maxima around July 2021. This sharp rise indicates an accelerated weathering phase likely induced by increased temperature during summer months, which could facilitate oxidative processes. Interestingly, after peaking, both PE-B and PP exhibit a gradual decline in CI, suggesting a reversible effect where the extent of carbonyl formation reaches a threshold and diminish.

PE-W (blue circles) demonstrates a more restrained increase in CI relative to PE-B, but remains a similar trend across the experimental period. The CI for PE-W remains lower throughout, with a modest peak in mid-2021 followed by a sharp decrease towards the end of the year. This trend implies that the aquatic environment might mitigate some weathering effects, possibly due to reduced biofilm attachment described in previous section. Experimental study (Dobretsov et al., 2013) has demonstrated that found that biofilm communities, tended to accumulate more on darker surfaces in marine environments due to enhanced radiant energy and favourable light conditions.

In contrast, PS (green squares) displays the most stable and consistent CI across the entire experimental timeline, with minimal fluctuations compared to the other polymers. This stability highlights the relative stable environment condition that PS had. Unlike PE and PP, PS shows only slight increases in general, combined with the observation that PS were mostly existing in the bottom layer of the microcosms, suggesting that PS is considerably more resilient to weathering-induced surface changes under aquatic conditions.

Overall, these data reveal distinct weathering profiles among the MP types. The significantly higher CI for PE-B and PP indicates a greater susceptibility to weathering processes. In contrast, the lower and more stable index for PS underscores its stability to environmental weathering.

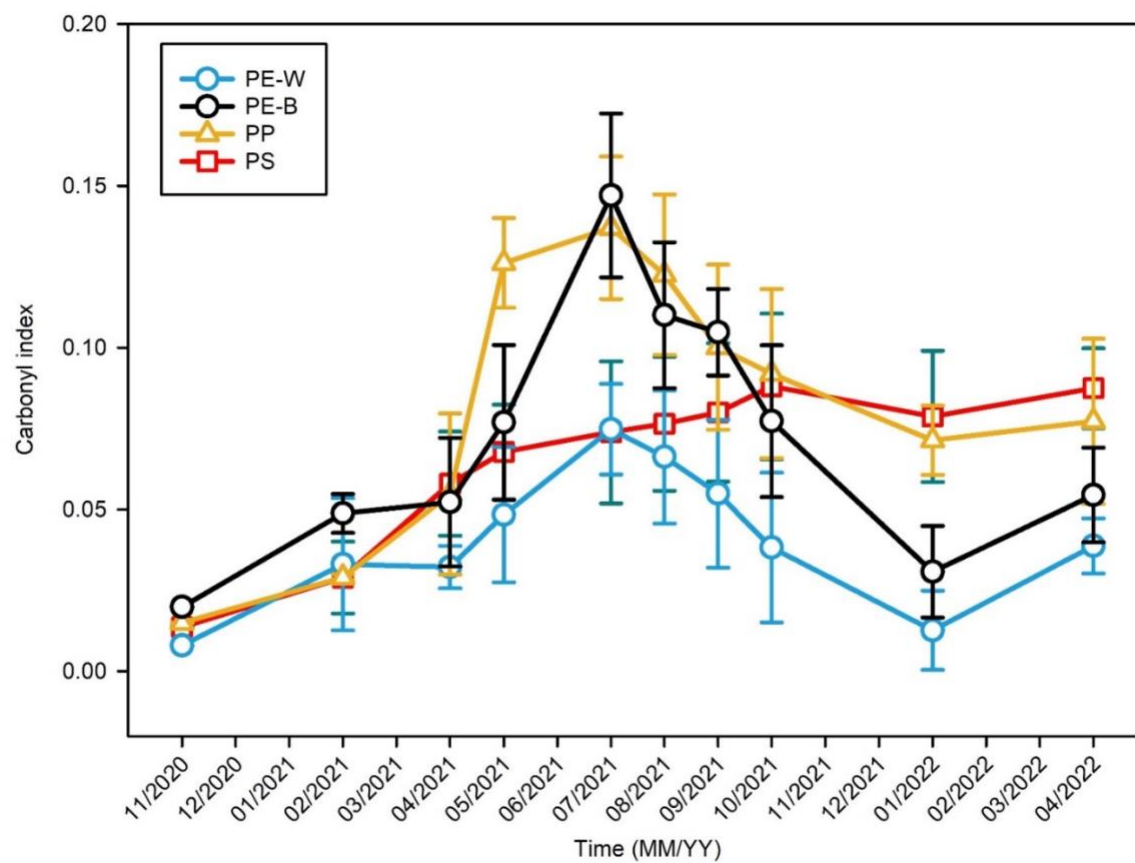


Figure 4-9. Change of carbonyl index (CI) of four types of MPs during the study period (MPs from Nov 2020 referred to virgin MPs).

4.4 Statistical Analysis

Correlation between surface roughness and carbonyl index

Pearson correlation analysis was conducted between surface roughness and CI. The data in Table 4-2 shows correlation coefficients and p-values for the relationship between surface roughness and CI for the four types of MPs.

PE-W is the only material with a statistically significant correlation ($p < 0.05$) between surface roughness and CI. The moderate positive correlation suggests that as surface roughness and CI tends to increase together. The other three types (PE-B, PP, PS) show very weak correlations ($p > 0.05$), and none are statistically significant.

Table 4-2. Correlation between surface roughness and CI for four types of microplastics

	PE-W	PE-B	PP	PS
Correlation coefficient (r)	0.511	0.0265	0.112	0.0355
p value ($\alpha = 0.05$)	0.0214	0.912	0.640	0.882

Linear regression between surface roughness and carbonyl index

The coefficient of determination between surface roughness and CI across different MP types are illustrated in Figure 4-10. This analysis offers a quantitative examination of the relationship between physical surface characteristics and degree of weathering, providing insights into how weathering manifests as morphological changes.

PE-W and PP have coefficient of determination (R^2 is about 0.3), which is more than PE-B and PS (R^2 less than 0.1). However, for four types of MPs, the coefficient of determination between surface roughness and CI are all positive but weak (R^2 less than 0.4), which means most of the variability (larger than 60%) of surface roughness cannot be explained by the linear model. This implies that the increase chemical changes do not directly lead to significant changes in surface roughness.

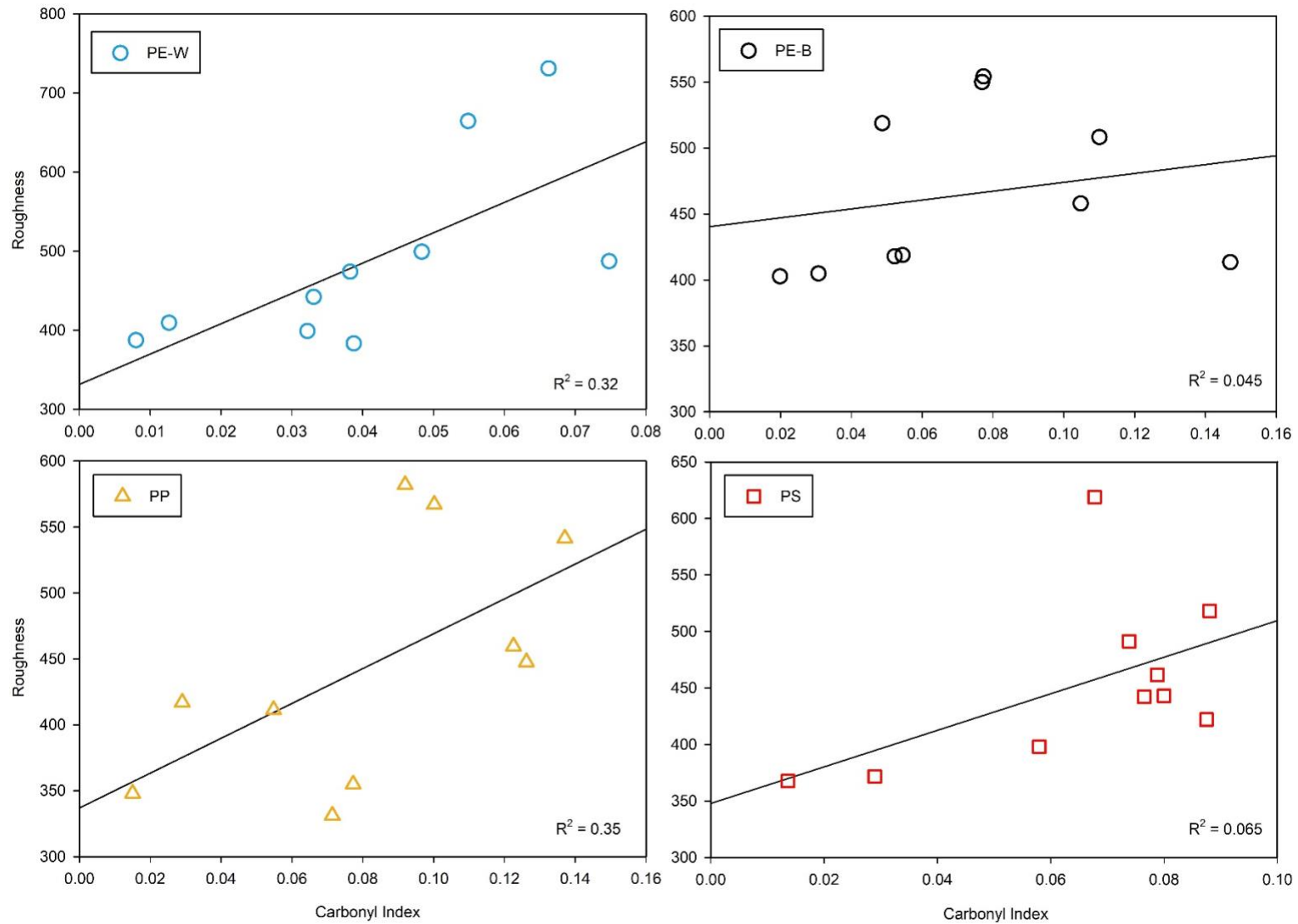


Figure 4-10. Correlation analysis between surface roughness and carbonyl index (CI)

Principal component analysis for multiple linear regression analysis

To pick the appropriate independent variables for multi-linear regression analysis, principal component analysis (PCA) is conducted. Three standards are adopted in this analysis.

First, the contributions of each variable to the principal components (PC1 and PC2) are considered. Variables with long arrows (vectors) in this PCA plot contribute more significantly to the principal components. This indicates that they capture more variance in the data and may be more informative for regression analysis. In this plot, UV index, temperature, and pH have relatively high contributions. UV and temperature point in similar directions, suggesting they are positively correlated and may represent similarly in PC2. The other variable, pH, pointing downward, is distinct from others and may provide unique information.

Second, multicollinearity needs to be avoided by figuring out relationships among them. Variables that are close together and point in the same direction are highly correlated. Including too many correlated variables in a regression model can lead to multicollinearity issues. Salinity, Mg^{2+} , Ca^{2+} , Na^+ , Cl^- , and SO_4^{2-} cluster closely together along PC1, indicating they are highly correlated. To avoid multicollinearity, one representative variable is selected from this cluster.

Third, information obtained needs to be unique. Variables pointing in different directions capture unique aspects of the variance. Including variables with unique orientations may provide a more balanced set of predictors. And wind speed is not selected due to multicollinearity with pH based on the actual analysis.

Based on these criteria for a balanced multi-linear regression model with minimal multicollinearity, temperature (high on PC1 and PC2), pH (high negative on PC2 but low on PC 1), and salinity (high on PC 1, moderate on PC2) in distinct directions and might serve as useful independent variables.

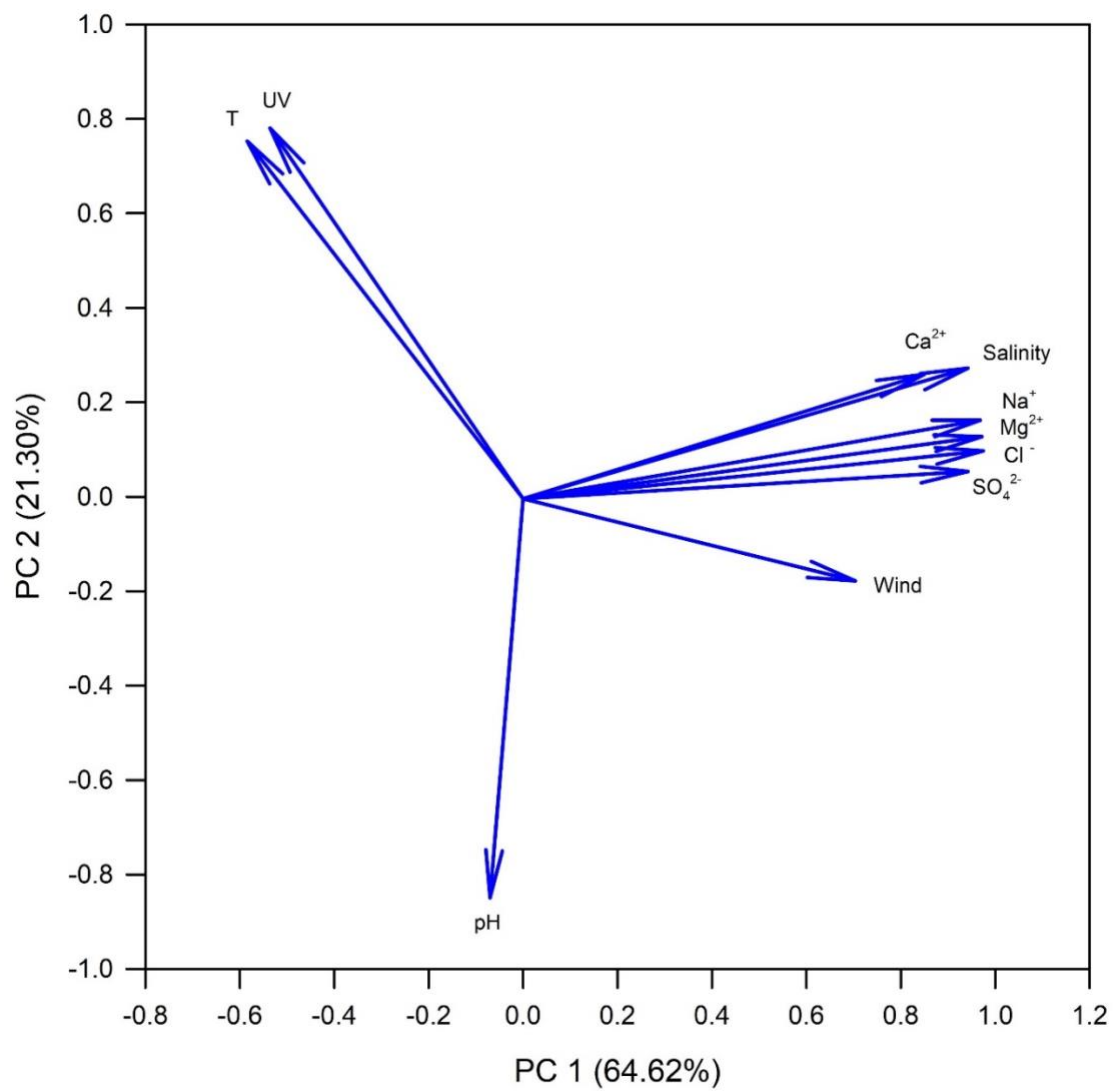


Figure 4-11. Principal component analysis for selection of independent variables

Multiple linear regression analysis

Multiple linear regression analysis is employed to explore the environmental factors (independent variables, X) that contribute to the surface roughness and CI (dependent variables, Y), respectively. Microplastics in months with (full season) and without presence of sea ice were analyzed separately.

Carbonyl index (Y) vs temperature, salinity, and pH (X)

A multiple linear regression analysis of the CI as a dependent variable (Y) with temperature, salinity, and pH as independent variables (X) was conducted for four types of MPs.

Based on the results, temperature is significantly correlated with CI for PE-W and PE-B ($p < 0.05$), suggesting the CI of these MPs are sensitive to temperature changes across the year. Temperature has no significant influence on CI for PP and PS ($p > 0.05$), regardless of ice presence. While salinity does not appear to have a significant effect ($p > 0.05$) on CI for any type of MP in either condition, indicating that variations in salinity may not strongly influence the weathering represented by CI. In addition, pH shows no significant effect ($p > 0.05$) on CI across all types of MPs and conditions.

In summary, temperature is the only factor with a notable impact ($p < 0.05$) on CI, specifically for PE-W and PE-B across a year. This suggests that these types of PE are more susceptible to changes under lower temperatures or possibly related stress conditions associated with ice. Salinity and pH show no significant effects ($p > 0.05$) on CI for any MP type or condition, suggesting that these variables are less influential in driving the weathering measured by CI.

The significant response of PE-W and PE-B to temperature, particularly with presence of ice, indicates that these materials might undergo temperature-sensitive weathering processes. PP and PS appear less reactive to environmental changes, as none of the factors had significant impacts on their CI in either condition.

Surface roughness (Y) vs temperature, salinity, and pH (X)

A multiple linear regression analysis of the surface roughness as a dependent variable (Y) with temperature, salinity, and pH as independent variables (X) across four types of MPs.

According to the results, temperature does not have a statistically significant effect ($p > 0.05$) on surface roughness for most MPs under both conditions, except for PS under no-ice conditions, where it shows a significant impact ($p < 0.05$). This suggests that temperature may play a role in affecting the surface of PS when not constrained by ice, possibly due to increased exposure to environmental factors. Salinity and pH generally do not have a significant effect on surface roughness for most MPs under both conditions ($p > 0.05$).

To summarize, the surface roughness PS under open water conditions demonstrates a higher sensitivity to temperature than other MPs. The other MPs (PE-W, PE-B, and PP) exhibit minimal response to these variables, suggesting that their oxidative weathering is less influenced by these factors in both ice-covered and ice-free environments.

4.4 Discussion on Microplastics Weathering

Laboratory-scale experiments using artificial accelerated UV-weathering have demonstrated a positive linear correlation between the CI and the duration of UV irradiation, suggesting that prolonged UV irradiation directly drives oxidation in MPs (Liu et al., 2019; Feng et al., 2022; Syranidou et al., 2023). However, our study revealed a different trend for PE and PP, where CI initially rises, peaks, and subsequently declines over time. Given the generally irreversible nature of oxidation, this trend suggests additional, seasonally variable factors influencing CI fluctuations beyond direct UV-driven oxidation. Since this research also focuses the metal binding ability of MPs, the MP samples with the biofilms were considered as a whole system, which was first proposed as *plastisphere* by Zettler et al. (2013).

The SEM analysis on MPs (Figure 4-6) highlights that pennate diatoms, identified through EDX as silica-bearing cells, dominate the microbial communities attached to MP surfaces, corroborating findings from Salimon et al. (2020). With regards to the results of SEM-EDX, the presence of putative diatoms indicated the formation of biofilm. Diatoms are single-celled algae that contain photosynthesis pigments including chlorophyll and carotenoid that have peaks of carbonyl group (around 1600 cm^{-1} - 1700 cm^{-1}) in their IR spectra (Wang et al., 2007; Wilson et al., 2008), likely contribute to seasonal variations in CI. The periodic intensity shifts in the FTIR

spectrum's carbonyl group (around 1638 cm^{-1} in FTIR spectrum) and C-O (between 1000 to 1100 cm^{-1}) reflect this biological influence (Tu et al., 2020), suggesting that biofilm formation plays a crucial role in modulating CI alongside chemical weathering.

Our seasonal experimental results of CI index pattern over time aligned with the study of marine plankton (Zingone et al., 2019). Zingone et al. (2019) reported that the seasonal patterns and life cycles of chlorophyll with higher concentrations in summer from April to October and lower concentrations in the remaining months, which is the sign for the seasonal presence of biofilm. Further verification through bleaching treatments showed a significant decrease in the CI index for PE and PS, suggesting that biofilm formation primarily influences their CI index. In contrast, PP exhibited less reduction, suggesting a dual role of biofilm and intrinsic chemical weathering in PP's CI trends. This dual influence may be attributed to the methyl groups in PP, which enhance its susceptibility to biodegradation compared to PE (Arutchelvi et al., 2008). The high density of diatoms on PP during summer months further suggests that PP provides a more favorable substrate for microbial colonization, resulting in a biofilm-driven seasonal CI pattern.

These observations during the experiment also highlight differences in the physical behaviour of each MP type within the water column. PE and PP primarily float, while PS, with a density of approximately $1.06\text{ g}\cdot\text{cm}^{-3}$, sinks and stabilizes at mid-depth before the onset of winter. As biofilms experience seasonal life cycles (He et al., 2022), the floating behaviour of PE and PP limits biofilm growth during ice formation, curtailing biological activity. Conversely, the sinking behaviour of PS minimizes its UV exposure, resulting in a distinct weathering pattern. Initially, PS accumulates biofilm upon entering the water, increasing in buoyancy until biofilm decay, driven by reduced sunlight at greater depths, gradually decreases its CI. Over time, PS reaches an equilibrium between buoyancy and biofilm density, maintaining a relatively stable CI.

The effect of sea ice on biofilm dynamics is also notable. For PE and PP, sea ice formation restricts biological activity, limiting biofilm growth. In contrast, PS's buoyancy fluctuations due to biofilm loss may allow it to resurface beneath the ice, re-exposing it to diatoms and other microorganisms. SEM images of PS support this, showing a sparse yet steady diatom presence throughout the year, indicating a persistent but low-level biofilm activity even under ice.

While all MP types show evidence of weathering, their distinct surface morphologies and spectral profiles underscore inherent chemical differences. PE and PP, with aliphatic structures, display similar oxidation and roughness patterns, whereas PS, with its aromatic structure, exhibits unique spectral features and a different degradation pathway. These findings further show the influence of environmental conditions—temperature, sunlight, and biological cycles—on MP degradation, with warmer months accelerating biofilm formation and oxidation and winter months promoting stabilization and retreat. The cyclical pattern observed in CI and surface roughness emphasizes the dynamic interaction between physical, chemical, and biological weathering processes in shaping the long-term environmental fate of MPs.

Chapter 5. Interactions of Weathered Microplastics with Mercury and Other Metals

MPs in the marine environment can act as a carrier of other chemical substances including contaminants in the system. This chapter focuses on the interaction of MPs with Hg because of its bioaccumulation and biomagnification in the marine environment. Interactions with some other major ions and trace metals were also examined.

5.1 Hg Accumulation on Microplastics

Hg concentration in the water

Figure 5-1 shows the Hg concentration in seawater from various microcosms containing different types of polymers as well as a blank control, over the 18-month period from November 2021 to April 2022. Hg concentrations in seawater of all microcosms, including the blank control, remained relatively stable throughout the experiment, ranging between approximately $0.20 \text{ ng}\cdot\text{L}^{-3}$ and $0.40 \text{ ng}\cdot\text{L}^{-3}$ ($0.32 \pm 0.04 \text{ ng}\cdot\text{L}^{-3}$). The blank microcosm, which did not contain MPs, shows a similar Hg concentration trend to those that contained MPs, which is to be expected as the water moved freely across microcosms.

The results demonstrate that Hg concentration remained nearly constant throughout the experiment. As the water moved freely among microcosms, MPs could have some impact on Hg retention or transformation, but the variability is small due to changes in water such as evaporation and groundwater addition mentioned in chapter 2.

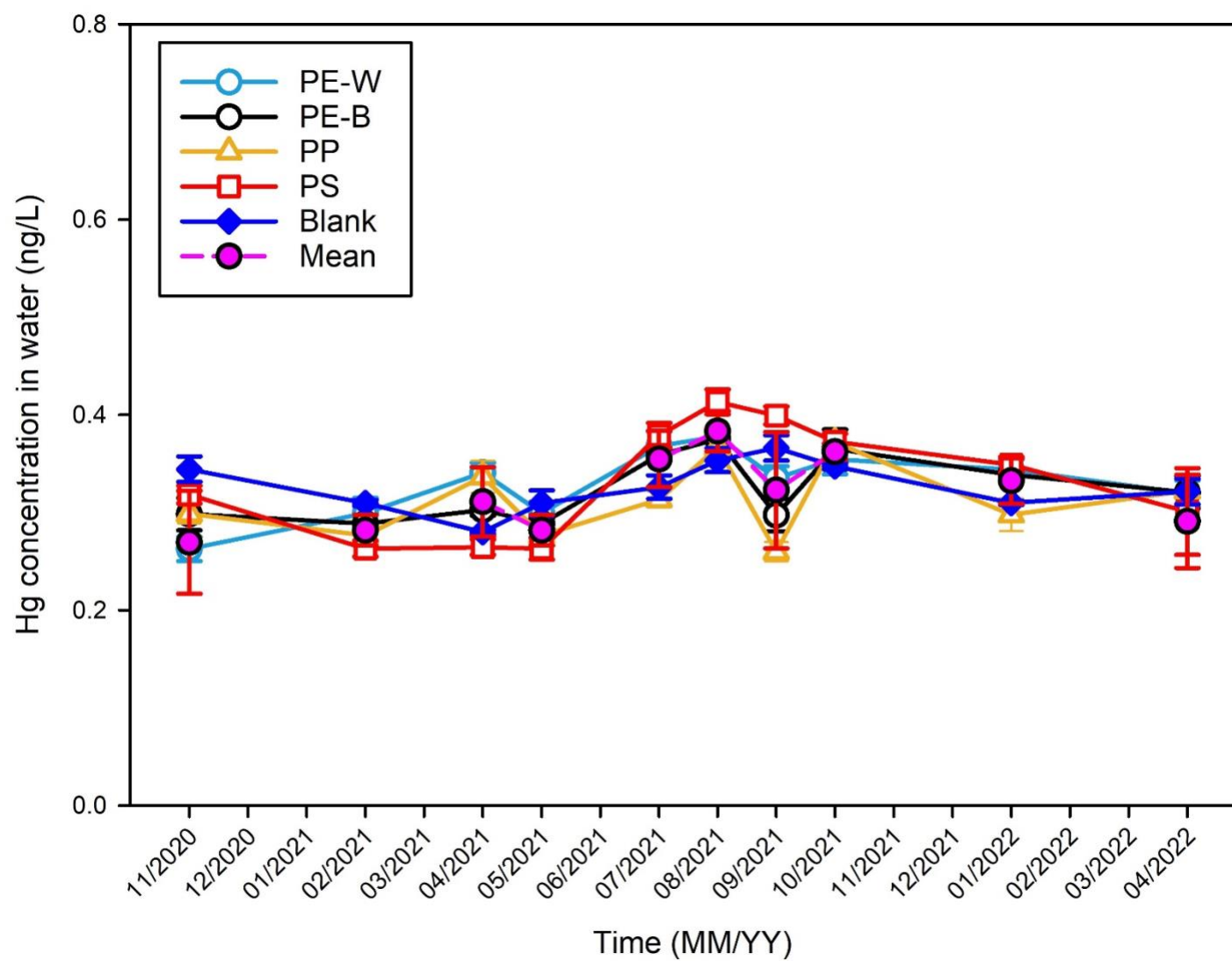


Figure 5-1. Variability of the Total Hg concentration in water as measured in different microcosms during the 18-month experiment

Hg accumulation on microplastics

Figure 5-2 shows distinct seasonal patterns of Hg accumulation across different types of MPs, with varying peak concentrations and decline rates as the MPs weathered over 18 months, covering two winters. Throughout the period, the concentrations of Hg on the different microplastic surfaces demonstrated nonlinear dynamics, potentially driven by environmental and physicochemical changes that affected Hg binding affinity. At the start point of the experiment, all four types of virgin MPs have less than $0.01 \text{ ng}\cdot\text{g}^{-1}$ of Hg.

For all types of MPs, it can be divided into three phases including the initial phase, the peak and decline phase, and stabilization phase.

During the initial phase of the experiment, all MP types show a relatively gradual increase in Hg concentrations. By February 2021, accumulated Hg concentrations rose to approximately 0.60 , 0.68 , 0.85 , and $0.38 \text{ ng}\cdot\text{g}^{-1}$ for PE-W, PE-B, PP, and PS, respectively. This possibly reflecting the early stages of exposure and weathering where surface oxidation and biofilm formation start to influence Hg accumulation.

For PE-W and PE-B, the second phase from April 2021 to July 2021 represents the peak of Hg accumulation, with both showing highly elevated concentrations, peaking in July 2021 at around $3.98 \text{ ng}\cdot\text{g}^{-1}$ and $4.48 \text{ ng}\cdot\text{g}^{-1}$, respectively. The sharp rise suggests that PE may have undergone significant surface weathering (including the formation of biofilms) after the first winter passed, enhancing their Hg-binding capacity. Following the peak accumulation, PE exhibits a gradual decline in Hg concentrations until Oct 2021, which falls back to about $1 \text{ ng}\cdot\text{g}^{-1}$. By the third phase from Oct 2021 to April 2024, Hg levels stabilized around $1 \text{ ng}\cdot\text{g}^{-1}$.

PP exhibits an increase from February 2021 to May 2021, reaching a peak concentration of approximately $2.3 \text{ ng}\cdot\text{g}^{-1}$. The peak was followed by a 24% decline by July 2021 and remained plateau for the following three months. The decline continues after Oct 2021 and stabilizes for the early 2024, which is around $0.68 \text{ ng}\cdot\text{g}^{-1}$.

PS displays a delayed and lower peak, reaching approximately $1.8 \text{ ng}\cdot\text{g}^{-1}$ from May 2021 to July 2021. This delay could be attributed to the slower weathering processes than the other types of MPs. And the Hg concentrations remain relative stable after, which is confirmed by the

One-way ANOVA analysis in Figure 5-3D. Notably, PS maintains the highest Hg levels during the stabilization phase, whereas PE-B and PP showed the most significant reduction in Hg concentrations ($p < 0.05$).

Throughout the 18-month experiment, the two PE types (PE-W and PE-B) consistently demonstrated higher Hg accumulation compared to PP and PS until Oct 2021. This could be attributed to the smaller size (around 1 mm in diameter, less than PP with 3 mm in diameter) and structural properties of PE, such as its greater surface area and higher susceptibility to weathering, which might enhance its capacity for Hg accumulation. The seasonal trends in Hg accumulation on MPs align with variations in biofilm activity and the CI observed during the 18-month weathering period. The mid-stage weathering phase, particularly during summer months, exhibited heightened Hg retention, corresponding to increased biofilm growth as evidenced by diatom colonization and elevated CI levels on the MPs' surfaces. The presence of biofilms likely enhanced Hg accumulation by providing additional active sites and altering the surface chemistry of MPs. Conversely, during late-stage stabilization, reduced biofilm activity due to colder temperatures and ice formation coincided with a decline in Hg accumulation and CI values, suggesting that biofilms play a critical role in modulating Hg retention.

PP and PS, on the other hand, show lower peak Hg concentrations and reach stabilization earlier. PP exhibits moderate biofilm formation and weathering (Figure 4-3), which contribute to its limited Hg accumulation. PS, with its higher density than sea water, remained at the bottom of the microcosms and had limited access to the light, thereby the biofilm development is limited and stable. This resulting in a slower and lower accumulation rate overall.

These findings highlight the complex and dynamic nature of Hg accumulation on MPs, driven by both polymer characteristics and environmental factors. The distinct phases of accumulation, peak, and stabilization underscore the importance of seasonal changes, particularly temperature and light, which impact oxidative processes and biofilm formation. The sharp decline following peak accumulation suggests that environmental conditions, including temperature fluctuations and biofilm dynamics, play a critical role in Hg retention and release on MP surfaces. This seasonal variation aligns well with reversible biofilm dynamics observed in Chapter 4. Even though the Hg accumulation on some of MPs (PE and PP) have declined after 18

months, the final Hg concentrations in the MPs are still much higher ($\sim 1 \text{ ng}\cdot\text{g}^{-1}$ for PE, $\sim 0.8 \text{ ng}\cdot\text{g}^{-1}$ for PP) than in the initial virgin MPs.

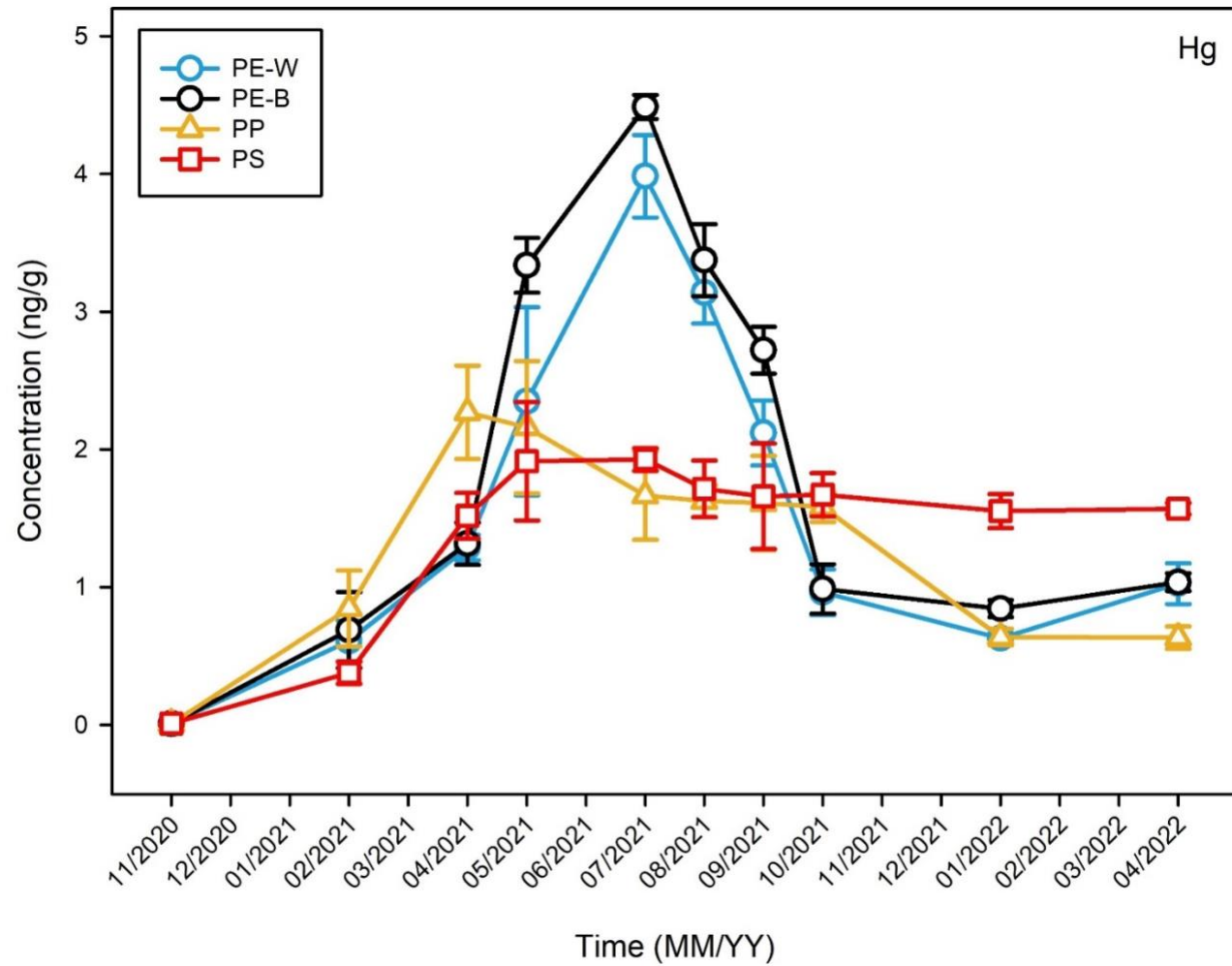


Figure 5-2. Temporal changes of Hg accumulation on MPs as they weathered during the 18-month experiment

5.1.2 Statistical Analysis

One-way ANOVA test for Hg accumulation

Figure 5-3 shows the statistical tests of the differences across different months for each type of MPs.

For both PE-W and PE-B, Hg accumulation is highest in July 2021, which is significantly higher than August 2021 and May 2021. For November 2020, the concentration reaches its lowest point, which is significantly different from the higher concentrations observed in earlier months. Except October 2021, the winter months with presence of ice have significant lower Hg accumulation including November 2020, February 2021, January 2022, and April 2022.

For PP, the highest Hg accumulation is observed in April 2021 and May 2021. The winter months with presence of ice have significant lower Hg accumulation than the ice-free months including November 2020, February 2021, January 2022, and April 2022.

For PS, Hg concentration peaks in July 2021 with no significant difference in May 2021, August 2021, and October 2021. Next significantly lower Hg accumulation is found in September 2021, April 2022, January 2022, and April 2021. The significant lowest concentration is found in the initial stage of the experiment, which is February 2021 and November 2020.

The one-way ANOVA results underscore the seasonal and environmental influences on Hg accumulation on MPs. Both PE-W and PE-B show significant seasonal fluctuations, with peak Hg accumulation in summer months (July 2021) and significantly lower levels during winter months with ice cover. This trend suggests that environmental factors like temperature and UV exposure, which are reduced during winter months, strongly influence the chemical and biological processes that facilitate Hg accumulation.

For PP, the peak Hg accumulation in April and May 2021 suggests a slightly earlier response to environmental changes than PE, possibly due to differences in its susceptibility to biological colonization and oxidation. The significant reduction in Hg accumulation during winter months further supports the impact of seasonal variations, indicating that PP's surface

characteristics are also affected by temperature and light exposure, albeit with a distinct seasonal timing compared to PE.

PS shows less pronounced seasonal variability, with Hg concentrations remaining relatively stable across warmer months (May to October 2021). However, the lowest Hg levels observed in the initial winter months (February 2021 and November 2020) still suggest that PS adsorption is influenced by environmental conditions, albeit less dynamically than PE and PP.

Overall, this analysis reveals that Hg accumulation on MPs is highly influenced by seasonal variations, with summer months facilitating higher accumulation likely due to increased biological activity and oxidative weathering, and winter months limiting Hg uptake characterized by ice cover and reduced environmental exposure. These findings emphasize the complex interplay between polymer structure, environmental conditions, and seasonal variations.

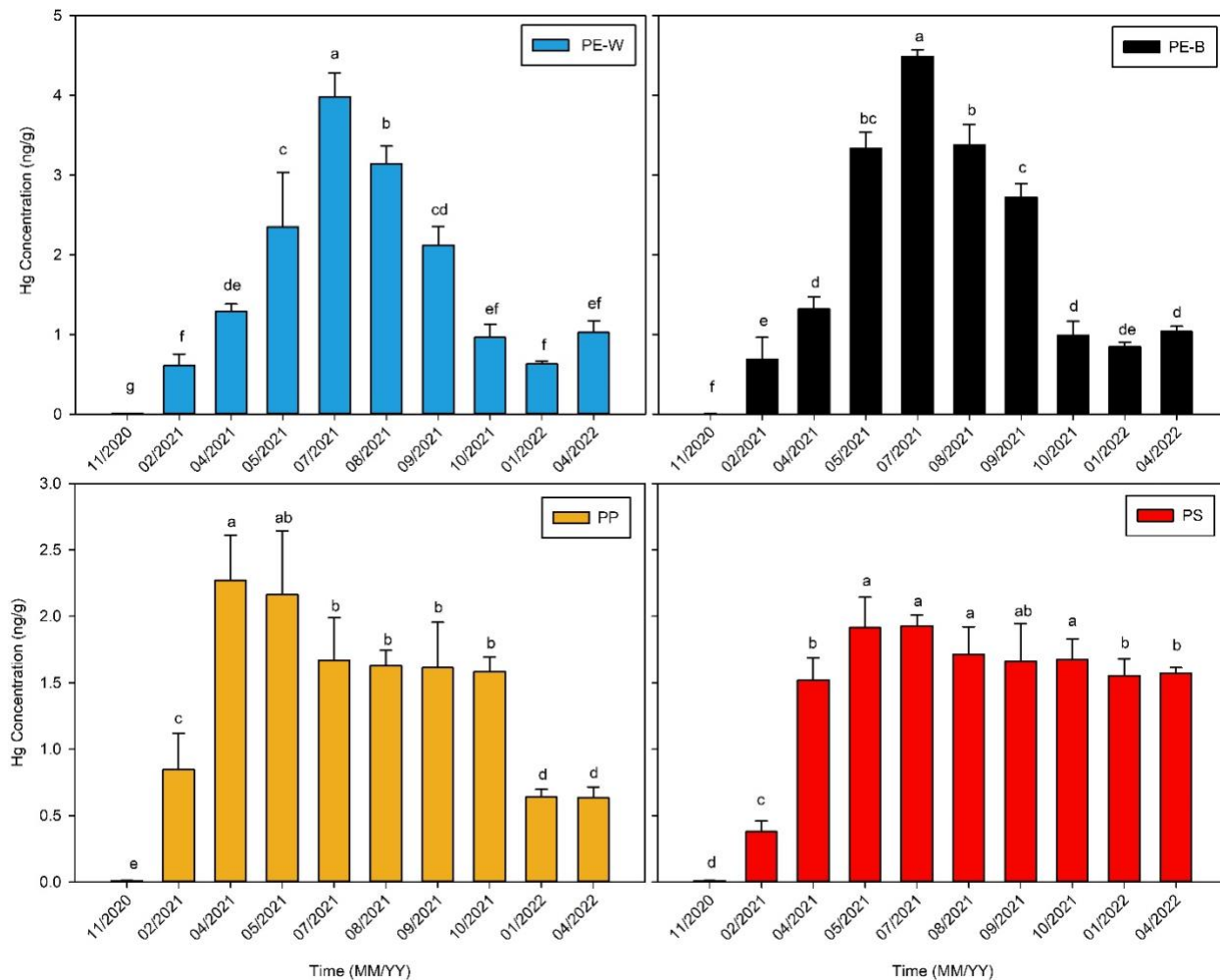


Figure 5-3. One-way ANOVA test for statistical difference of Hg accumulation among four types of MPs for the experiment period. (The letters above each bar represent groupings determined by one-way ANOVA test, with different letters indicating statistically significant differences at a significance level (usually $p < 0.05$). Bars sharing the same letter are not significantly different, while bars with different letters are significantly different.)

Correlation analysis between Hg accumulation and carbonyl index

The data in Table 4-2 shows correlation coefficients and p-values for the relationship between Hg accumulation and surface roughness for the four types of MPs. PE-W and PP displayed moderate positive correlation with statistical significance ($p < 0.05$), tending to increase together. The other three types (PE-B, PS) show very weak correlations ($p > 0.05$), and none are statistically significant.

Table 4-3 shows correlation coefficients and p-values for the relationship between Hg accumulation and CI for the four types of MPs. All four types of MPs displayed positive correlation with statistical significance ($p < 0.05$), tending to increase together. This positive correlation implies that the weathering of MPs in marine environments makes it more conducive to Hg accumulation. Specifically, PE-W and PE-B show strong positive correlation (correlation coefficient > 0.9) between Hg accumulation and CI. This suggests that chemical characteristics, represented by the CI, play a significant role in Hg accumulation, particularly for PE-based MPs.

Table 5-1. Correlation between Hg accumulation and Roughness for four types of microplastics

	PE-W	PE-B	PP	PS
Correlation coefficient (r)	0.632	0.181	0.640	0.273
p value ($\alpha = 0.05$)	0.0498	0.618	0.0463	0.259

Table 5-2. Correlation between Hg accumulation and Carbonyl Index for four types of microplastics

	PE-W	PE-B	PP	PS
Correlation coefficient (r)	0.940	0.912	0.636	0.459
p value ($\alpha = 0.05$)	<0.0010	<0.0010	0.0483	0.0481

Linear regression analysis for Hg accumulation

Figure 5-4 shows the relationship between Hg concentration and CI of four types of MPs. For all types of MPs, more than 60% of the variation in Hg concentration can be explained by the CI.

For PE-W and PE-B, 89% and 79% of the variation in Hg concentration can be explained by the CI, respectively. The high R^2 value further indicates that CI is a strong predictor of Hg accumulation on PE.

In the case of PP, about 67 % of the variation in Hg concentration can be explained by the CI. This indicates that while weathering contributes to Hg accumulation on PP, the effect is less pronounced compared to PE. However, the positive relationship still implies that weathering plays a role in enhancing PP's Hg accumulation, possibly through microbial colonization or biofilm development, which can further increase sites on the surface.

For PS, about 81 % of the variation in Hg concentration can be explained by the CI. This result suggests that despite PS's Hg accumulation pattern is not similar to PE and PP, the relatively high R^2 value still indicates that CI remains a reliable predictor of Hg concentration for PS.

Figure 5-5 shows the linear regression analysis between Hg concentration and surface roughness of four types of MPs. For all four types of MPs, the coefficient of determination between Hg concentration and surface roughness are all below 0.5, with an R^2 value of 0.29, 0.0043, 0.41, and 0.48 for PE-W, PE-B, PP, and PS, respectively. This means less than 50% of the variation in Hg concentration can be explained by the CI. This suggests that roughness has less impact on Hg accumulation than CI.

Overall, the analysis reveals that surface roughness contributes less than CI to Hg accumulation to varying degrees across different MPs. For PE-W and PE-B, surface roughness has a weaker impact on Hg accumulation, indicating that CI or other factors may play a larger role than morphological changes alone. PP and PS have dependency on both surface roughness and CI for Hg accumulation.

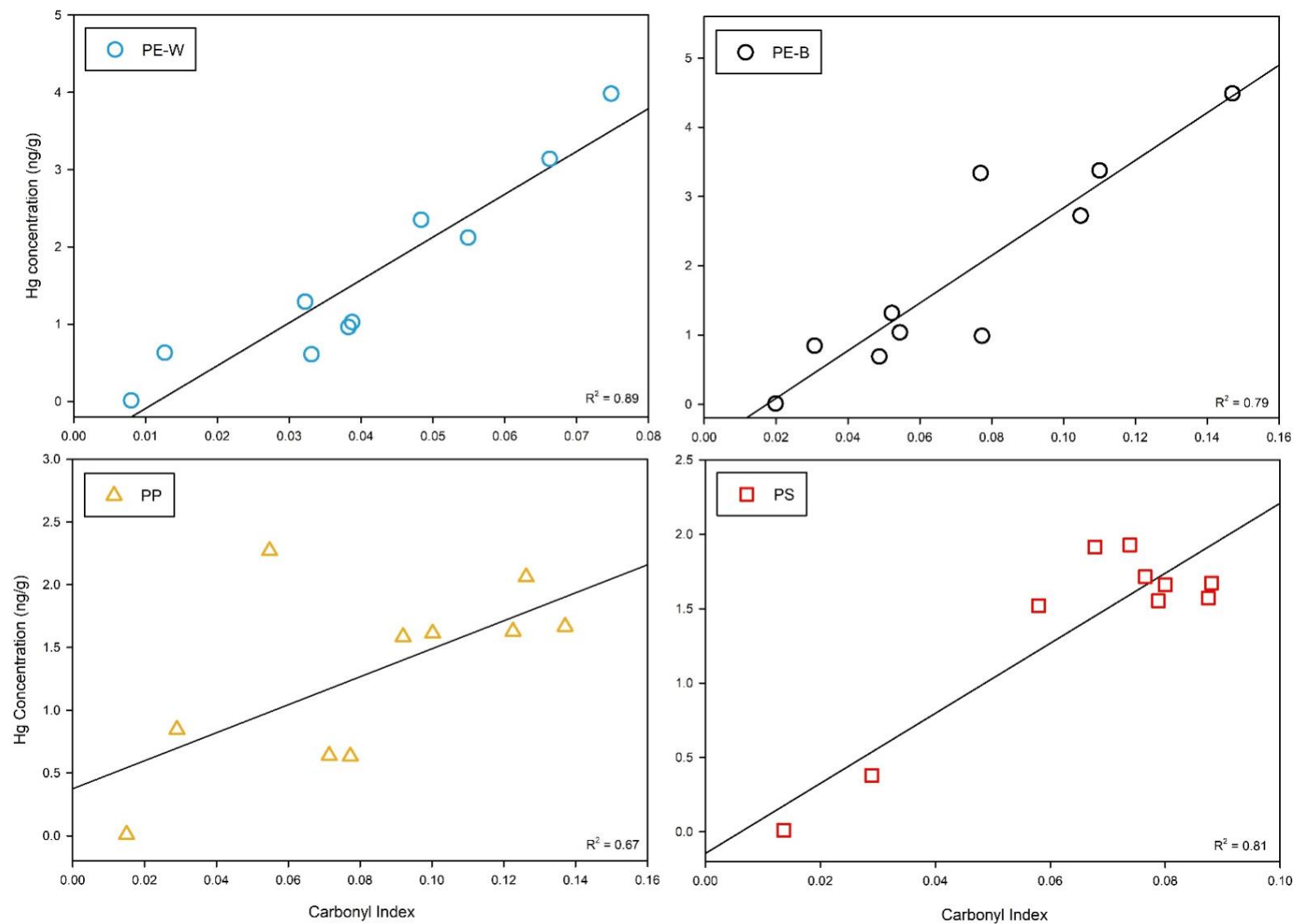


Figure 5-4. The linear regression analysis between Hg concentration and Carbonyl Index of four types of MPs

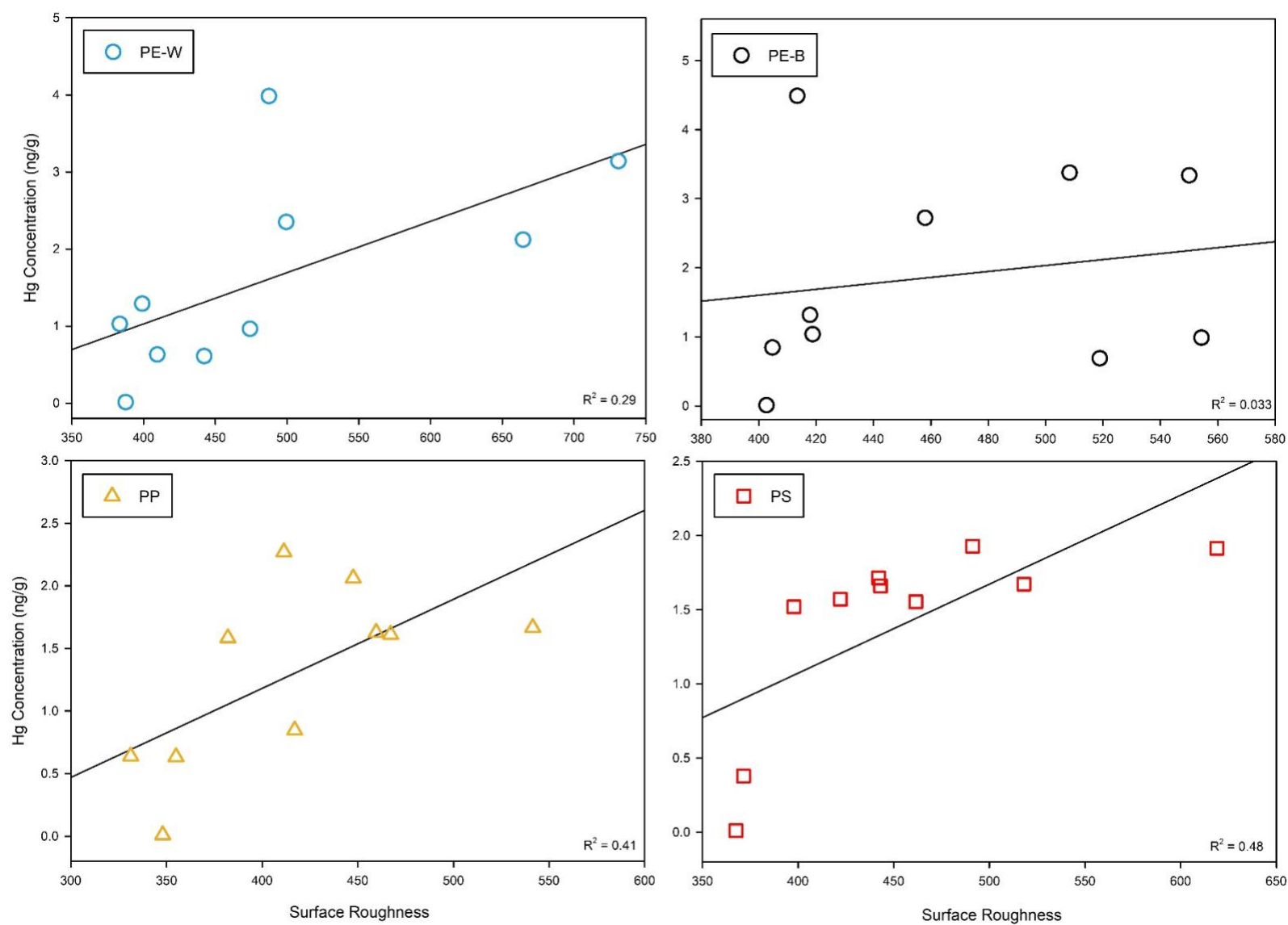


Figure 5-5. The linear regression analysis between Hg concentration and Surface Roughness of four types of MPs

Principal component analysis for Hg accumulation

Similar to the PCA in section 4.4, surface roughness is added as another independent variable. Based on these criteria for a balanced multi-linear regression model with minimal multicollinearity, temperature (high on PC1 and PC2), pH (high negative on PC2 but low on PC 1), salinity (high on PC 1, moderate on PC2), and surface roughness (no multicollinearity with temperature) in distinct directions are finally selected as useful independent variables.

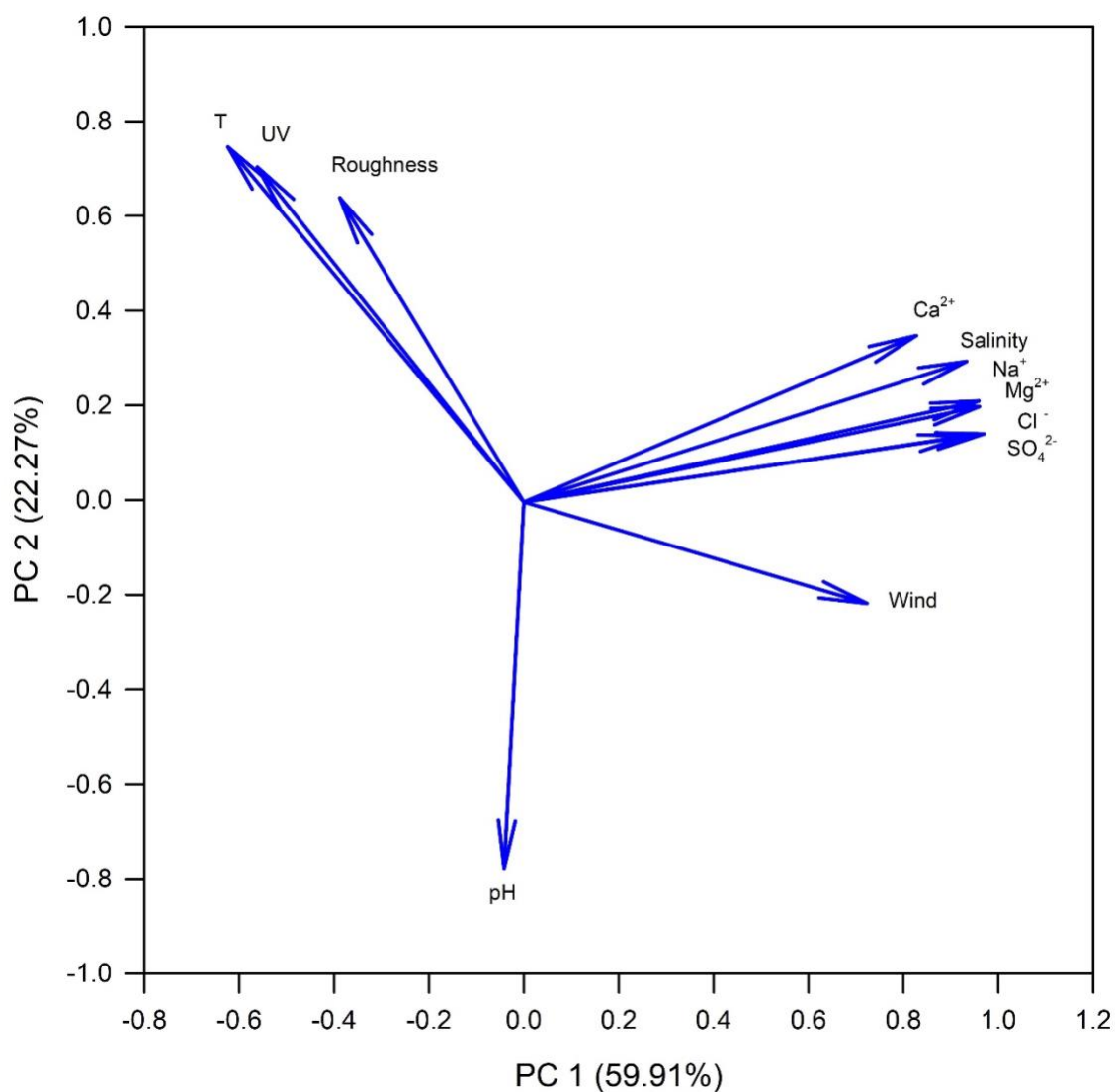


Figure 5-6. Principal component analysis for selection of independent variables

Multiple linear regression analysis for Hg accumulation

Hg concentration on MPs (Y) vs Temperature, Salinity, pH, and surface roughness (X)

A multiple linear regression analysis of the Hg concentration on MPs as a dependent variable (Y) with temperature, salinity, pH, and surface roughness as independent variables (X) was conducted for four types of MPs. Microplastics in months with (full season) and without presence of sea ice were analyzed separately.

Temperature has a statistically significant impact on surface roughness only for PE-W under ice conditions ($p < 0.05$). This suggests that temperature may play a role in Hg accumulation of PE-W across the year. For the other MPs, temperature does not significantly impact Hg concentrations under both conditions.

Salinity has a statistically significant effect on surface roughness only for PP under ice conditions ($p < 0.05$). This suggests that salinity may influence the Hg accumulation of PP in ice environments, potentially due to changes in ionic concentration that impact the binding capacity on the surface of MPs. Salinity does not have a significant effect on the Hg concentrations of PE-W, PE-B, or PS in either condition ($p > 0.05$).

pH does not have a statistically significant effect on surface roughness for any of the MPs in both conditions ($p > 0.05$). This suggests that pH is not a major factor influencing Hg concentrations across the different types of MPs in both conditions.

In conclusion, PE-W and PP are more responsive to temperature and salinity, respectively, suggesting that these environmental factors may contribute to Hg retention in colder environments for these specific types of MPs. The other MPs appear less influenced by temperature, salinity, or pH under both ice and no-ice conditions, indicating a general stability in response to these factors.

5.2 Other metals accumulation on MPs

The concentrations of major cations in the water (Na, Mg, Ca) were shown in Figure 3-2. The concentrations of Fe in the water were below limit of detection. Therefore, it was not shown. For Figure 5-7 to Figure 5-12 present the temporal pattern of Na, Mg, Ca, and Fe concentrations ($\text{ng}\cdot\text{g}^{-1}$) on four types of polymer samples measured over several time points from November 2020 to April 2022.

Na

Figure 5-7 shows temporal pattern of Na accumulation on four types of MPs. For PE-W, Na accumulation began at a low level ($< 20 \text{ ng}\cdot\text{g}^{-1}$) in November 2020, rising and peaking in July 2021 at around $150 \text{ ng}\cdot\text{g}^{-1}$, after which Na levels decreased to about $110 \text{ ng}\cdot\text{g}^{-1}$ by October 2021. Following this decline, there was a secondary increase, reaching $137 \text{ ng}\cdot\text{g}^{-1}$ in February 2022, before dropping again to approximately $48 \text{ ng}\cdot\text{g}^{-1}$ by April 2022. The initial rapid increase and subsequent fluctuation suggested that PE-W's Na accumulation might be influenced by environmental factors such as seasonal salinity changes, surface weathering, and biofilm formation.

PE-B and PP displayed a similar initial accumulation trend, with Na concentrations rising from a low baseline ($<20 \text{ ng}\cdot\text{g}^{-1}$) to a peak around $150 \text{ ng}\cdot\text{g}^{-1}$ by July 2021, followed by a pronounced decrease to nearly $33 \text{ ng}\cdot\text{g}^{-1}$ and $55 \text{ ng}\cdot\text{g}^{-1}$ by January 2022, before a subsequent rise to around $70 \text{ ng}\cdot\text{g}^{-1}$ in April 2022. The sharp fluctuations in PE-B and PP, particularly the significant decrease after July 2021, were potentially due to reduced biofilm activity and limited environmental interactions.

PS exhibited a slower initial rate of Na accumulation compared to the other MP types, reaching around $70 \text{ ng}\cdot\text{g}^{-1}$ by February 2021. Its Na concentration peaked at approximately $95 \text{ ng}\cdot\text{g}^{-1}$ in July 2021, similar to the trend observed in the other MPs. Following this peak, PS maintained relatively stable Na levels, with only minor fluctuations, at about $\text{ng}\cdot\text{g}^{-1}$ by April 2022. The stable pattern in PS, with fewer pronounced fluctuations, may be due to its higher density and lower susceptibility to weathering, which could limit its interaction with Na and reduce the influence of seasonal changes on its surface chemistry.

Across all MP types, Na accumulation generally increased during the initial months, peaking in mid-2021 (July), and subsequently declined towards the end of the study period. The July peak may correspond to seasonal factors such as increased biofilm formation, higher salinity levels, or enhanced surface oxidation during warmer months, which facilitated Na adsorption. The decline in Na concentrations observed in late 2021 and early 2022 may reflect biofilm die-off, reduced environmental exposure, or desorption processes in colder months.

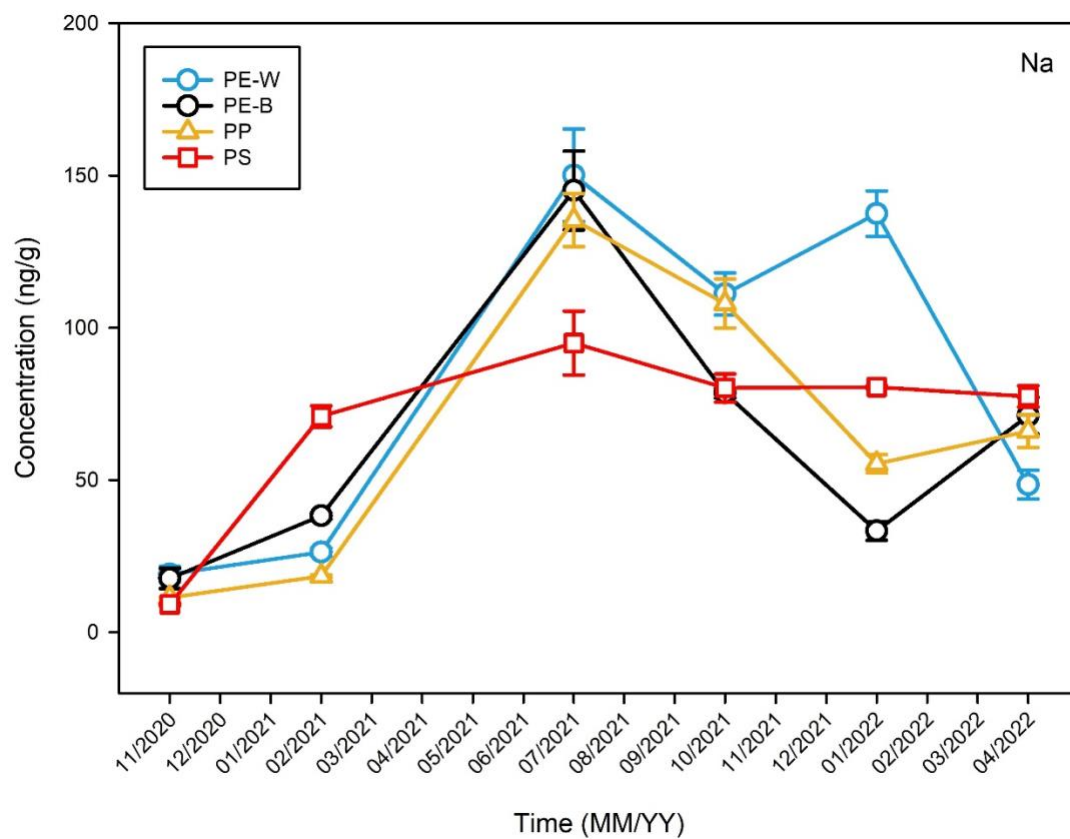


Figure 5-7. The change of Na accumulation on four types of MPs

Mg

Figure 5-8 shows temporal pattern of Mg accumulation on four types of MPs.

Initially, all four types of MPs exhibited low Mg concentrations at the beginning of the study, around $1\text{--}2\text{ ng}\cdot\text{g}^{-1}$. From the beginning of the study, Mg accumulation increased and peaked at around $15\text{ ng}\cdot\text{g}^{-1}$, $15\text{ ng}\cdot\text{g}^{-1}$, $14\text{ ng}\cdot\text{g}^{-1}$, and $18\text{ ng}\cdot\text{g}^{-1}$ for PE-W, PE-B, PP, and PS in July 2021, respectively. This peak in Mg accumulation might correspond to increased environmental interactions during warmer months, where biofilm growth, temperature, or salinity could enhance the Mg accumulation capacity of the MPs. After reaching peak levels, Mg concentrations fluctuated across MPs, showing no consistent upward or downward trend.

PE-W and PP showed a decline in Mg concentrations by October 2021, with levels stabilizing around $5\text{ ng}\cdot\text{g}^{-1}$ and $10\text{ ng}\cdot\text{g}^{-1}$, respectively. PS also exhibited slight variability but generally stabilizes around $13\text{ ng}\cdot\text{g}^{-1}$ through early 2022. PE-B maintained relatively stable Mg levels with minor fluctuations at around $17\text{ ng}\cdot\text{g}^{-1}$ until the end of the study period.

The absence of a clear seasonal pattern in Mg accumulation after July 2021 suggested that factors promoting Mg accumulation may be less active or that Mg reached an equilibrium state on the MP surfaces over time. Overall, the patterns suggested that MPs may serve as transient reservoirs for Mg, with the initial environmental exposure phase having the most significant impact on Mg accumulation, after which equilibrium or saturation limits further increases.

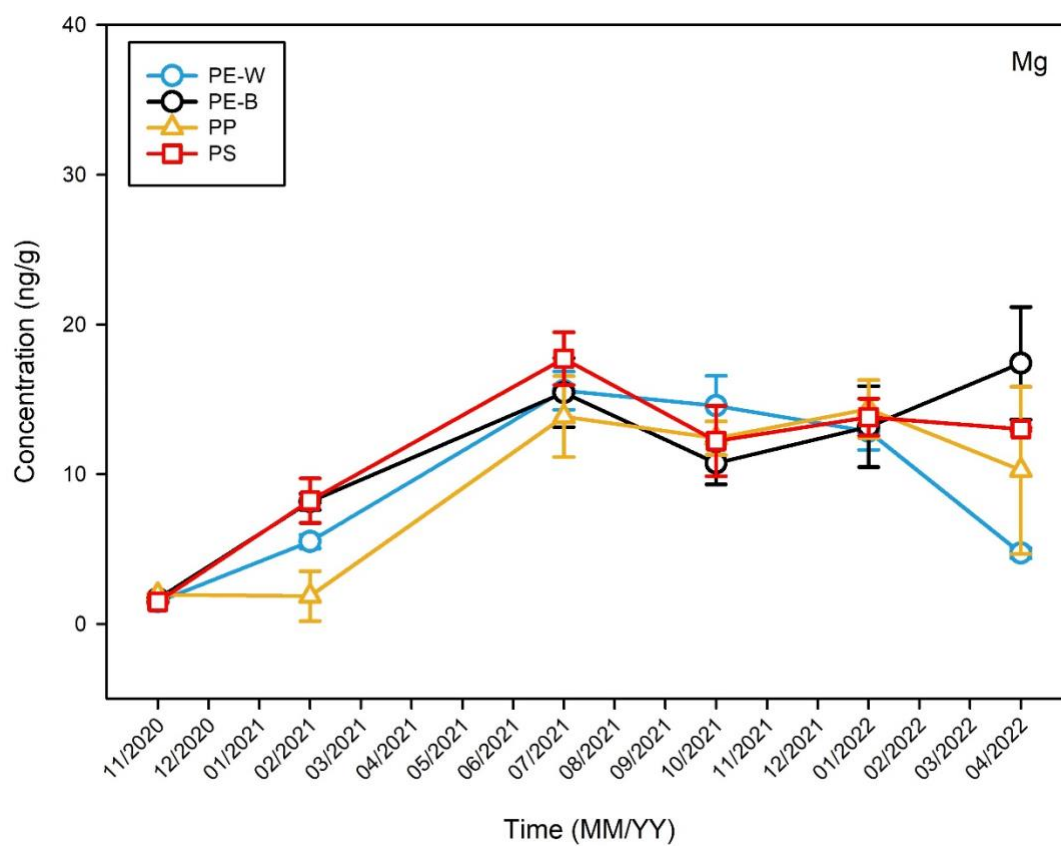


Figure 5-8. The change of Mg accumulation on four types of MPs

Ca

Figure 5-9 shows temporal pattern of Ca accumulation on four types of MPs.

All four types of MPs began with low Ca concentrations, ranging from approximately 5 to 10 $\text{ng}\cdot\text{g}^{-1}$ in November 2020. By February 2021, Ca concentrations increased across all MPs, reaching around 16-19 $\text{ng}\cdot\text{g}^{-1}$. PP exhibited peak Ca levels at this stage (around 20 $\text{ng}\cdot\text{g}^{-1}$) and maintained moderately high levels until October, indicating a slightly earlier peak compared to the other MPs.

Start from July 2021 to October 2021, PS showed the highest Ca accumulation during this period, peaking around 25 $\text{ng}\cdot\text{g}^{-1}$ in April 2021, maintaining elevated levels until October 2021. After October 2021, Ca levels declined in all MPs except PS. PE-W, PE-B, and PP stabilize at lower concentrations (less than 20 $\text{ng}\cdot\text{g}^{-1}$). PP showed the most substantial decline, with Ca concentrations dropping around 12 $\text{ng}\cdot\text{g}^{-1}$ by January 2022 and remaining relatively low through April 2022.

The Ca accumulation on MPs showed an initial increase, peaking around mid-2021, followed by stabilization or fluctuations. PS exhibited the highest Ca retention, consistently maintaining elevated levels, while PE-W, PE-B, and PP showed lower and more stable Ca levels after an early rise. This pattern suggested that initial environmental exposure had the most substantial impact on Ca accumulation, followed by equilibrium or saturation effects that limit further adsorption.

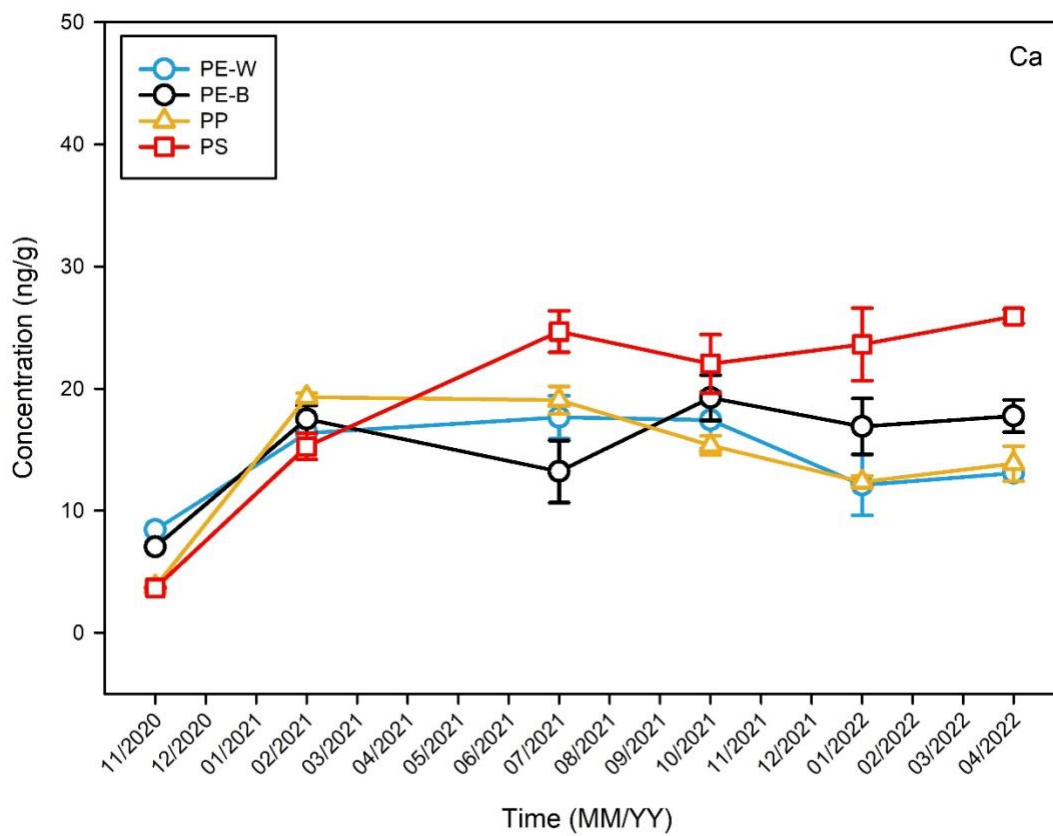


Figure 5-9. The change of Ca accumulation on four types of MPs

Fe

Figure 5-10 shows temporal pattern of Fe accumulation on four types of MPs.

At the start of the study, all four types of MPs exhibited very low Fe concentrations, close to $0 \text{ ng}\cdot\text{g}^{-1}$ in November 2020. By February 2021, Fe concentrations increased across all MP types, with PE-B showing a notable rise to approximately $12 \text{ ng}\cdot\text{g}^{-1}$. The other MPs (PE-W, PP, and PS) exhibit a more modest increase, reaching around $2\text{-}6 \text{ ng}\cdot\text{g}^{-1}$. PE-B showed a pronounced increase in Fe concentration, reaching a peak of around $30 \text{ ng}\cdot\text{g}^{-1}$ by October 2021, which was substantially higher than any other MP type. PP, and PE-W maintained lower Fe levels throughout mid 2021, with concentrations generally fluctuating between 2 and $7 \text{ ng}\cdot\text{g}^{-1}$. PS reached its peak in October 2021, with a concentration of around $11 \text{ ng}\cdot\text{g}^{-1}$. These MPs did not exhibit a strong upward trend like PE-B, suggesting they have lower Fe retention capacity or that environmental conditions affecting them were less conducive to Fe accumulation.

The Fe accumulation patterns show that PE-B consistently retained higher Fe levels than the other MPs. The stabilization or mild decline in Fe levels in PE-B toward the end of the study suggested that it may have reached an equilibrium in Fe retention. In contrast, PS showed moderate but steady Fe accumulation, while PP and PE-W displayed minimal Fe retention throughout the study period, suggesting that they interact less effectively with Fe in their environments.

Summary of the regression analysis on the other metals

Multiple linear regression analysis was employed to explore the environmental factors temperature, salinity (or metal concentrations in water), pH, and roughness as independent variables (X) that contribute to the metal concentrations (dependent variables, Y), respectively. Microplastics in months with (full season) and without presence of sea ice were analyzed separately. The multiple linear regression analysis revealed that environmental factors (temperature, salinity, pH, and surface roughness) exhibit a limited influence on metal accumulation across most microplastic types, with no statistically significant relationships ($p > 0.05$) observed for the majority of metals analyzed.

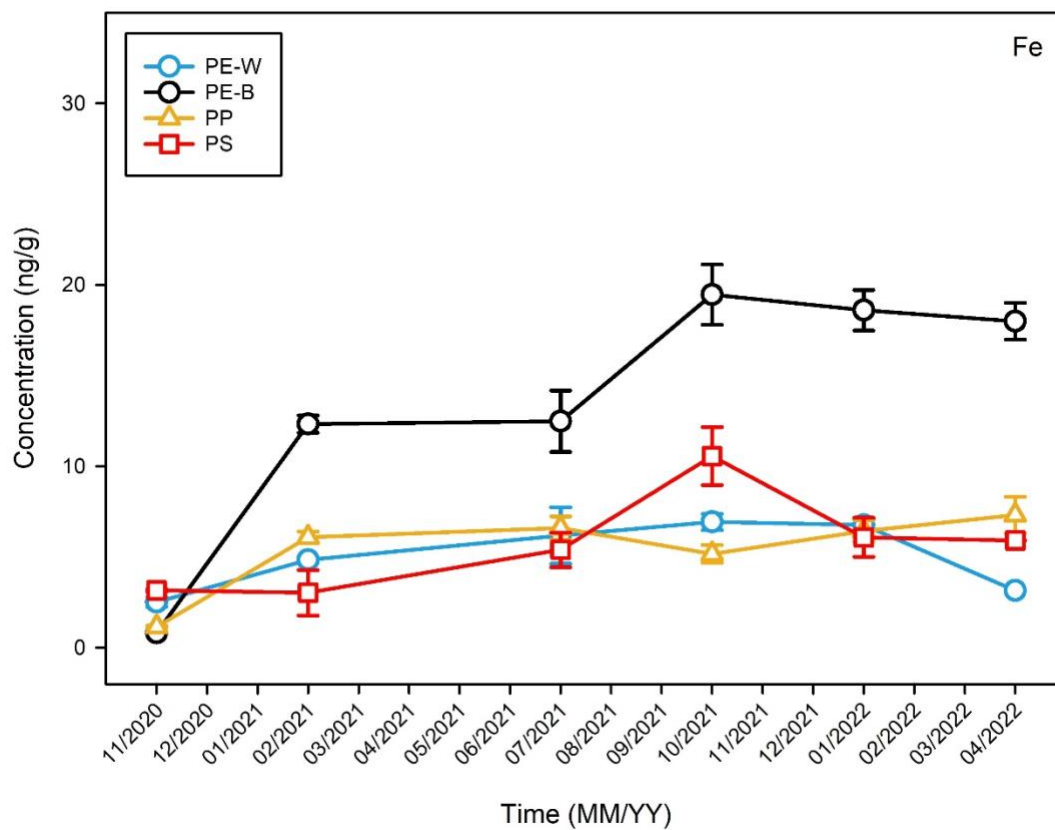


Figure 5-10. The change of Fe accumulation on four types of MPs

5.3 Discussion

Building on the results from Section 4.4, the seasonal patterns of Hg accumulation on MPs and CI suggest a link between Hg binding and biofilm dynamics, with Hg concentrations rising during biofilm growth and declining as biofilms die off. Previous research has shown that algae can sequester Hg, thereby introducing it into trophic transfer pathways (Bełdowska et al., 2015; Le Faucheur et al., 2014; Mangal et al., 2018). Additionally, diatoms have been identified as vectors for Hg (Mason et al., 1996; Zaferani et al., 2018; Zhong and Wang, 2009), providing further support for the observed alignment between Hg accumulation and biofilm patterns in this study.

In the case of PP, the size of 3 mm led to different results including less but moderate correlation between Hg accumulation and CI index. Observations throughout the experiment revealed that most PP particles floated on the water surface with limited exposure to water circulation, resulting in less rotation and uneven biofilm distribution. SEM images confirmed that biofilms were patchy on PP surfaces, leading to localized density increases rather than uniform coverage. Some regions of PP accumulated biofilm, while others remained exposed to sunlight, undergoing chemical weathering. This uneven biofilm coverage may be due to PP's larger particle size (3 mm in diameter) and lower density ($0.89 \text{ g}\cdot\text{cm}^{-3}$) compared to PE ($0.92 \text{ g}\cdot\text{cm}^{-3}$) and PS ($1.06 \text{ g}\cdot\text{cm}^{-3}$). These characteristics may also have introduced bias during FTIR-ATR measurements. Due to limited water movement, Hg accumulation in PP followed the general pattern of biofilm presence, with levels declining earlier than PE.

For PS, Hg accumulation initially increased upon entering the water, then stabilized at a relatively constant level. As PS particles tended to sink and remain at the bottom, they were colonized by biofilms with limited seasonal fluctuation, which corresponds with the stable CI pattern observed. During the ice-covered months, both PE and PP became trapped in the sea ice, resulting in reduced Hg accumulation. Consequently, Hg accumulation in PE shows a pattern of increasing with phytoplankton blooms and decreasing as biofilm communities die off.

PE, in both white and black forms, demonstrated the highest Hg accumulation levels with weathering, indicating that these polymers may serve as significant reservoirs for Hg in aquatic environments. Given the widespread presence of PE in natural waters, its capacity to accumulate

Hg as it weathers may increase environmental risks, especially in areas with Hg contamination. The findings suggest that the weathering of PE and PP in particular could contribute to the persistence and mobility of Hg in marine ecosystems with the presence of sea ice, underscoring the potential ecological risks associated with these common plastics.

These results reveal that seasonal biofilm dynamics significantly influence Hg accumulation on MPs, with Hg levels rising during biofilm growth and declining as biofilms die off. Algae including diatoms that are known to sequester Hg, likely contribute to these patterns. For PE, Hg accumulation is closely linked to biofilm presence, peaking with phytoplankton blooms and declining with biofilm degradation. PP, which floats with less rotation and uneven biofilm coverage, shows a weaker correlation between Hg and surface oxidation, while PS accumulates Hg initially before stabilizing at lower levels due to its tendency to sink and attract stable biofilms. Overall, PE showed the highest Hg accumulation, indicating its potential role as a significant Hg reservoir in aquatic systems. These results highlight the ecological risks associated with microplastics, particularly PE and PP, as they weather and interact with contaminants in natural waters.

Seasonal variations emerged as a pivotal factor, with summer months showing higher accumulation for most metals, likely due to increased temperature, UV exposure, and biological activity. For example, Hg accumulation on PE and PP peaked during warmer months, coinciding with biofilm proliferation and oxidative weathering. Conversely, winter months with ice cover limited metal adsorption due to reduced light and temperature, highlighting the role of environmental exposure in metal dynamics.

The study underscores the complex interactions between weathered MPs and metals in marine environments, driven by both material properties and external conditions. PE types exhibit the highest propensity for Hg and other metal retention, posing significant environmental risks as carriers of pollutants. The distinct seasonal patterns emphasize the importance of considering temporal variations and polymer-specific behaviors in assessing the ecological impacts of MPs. It highlights the importance of considering both material properties and seasonal conditions in assessing the pollutant-carrying potential of MPs in natural ecosystems, providing insights into the long-term environmental impacts of different MPs' types.

Chapter 6. Conclusion

6.1 Uniqueness of the Mesocosm/Microcosm Approach

This research provides comprehensive investigation into the weathering processes of MPs under cold marine environments, by using a mesocosm/microcosm approach and with a focus on the dynamics of sea ice growth and melting. The interactions between MPs and sea ice, the morphological and chemical changes of MPs, as well as their role in contaminant cycling were investigated.

This research spans the longest weathering study of its kind, incorporating two full cycles of sea ice growth and melting, providing much-needed insight into the natural weathering processes that might occur in polar oceans. Previous studies on MPs weathering have mostly relied on short-term, laboratory experiments under unrealistic environmental conditions such as intense UV radiation and unrepresentative temperature, wind, and relative humidity conditions. In comparison, this study employed a real-world outdoor mesocosm environment for 18 months to study MPs weathering. One of the key contributions of this research is its direct application to understanding weathering processes in the polar ocean environment, especially for those mediated by seasonal sea ice dynamics.

This extended mesocosm/microcosm approach is crucial because it simulates seasonal variations in the polar ecosystems. The experimental design to carry out the study outdoors, in mesocosm settings with sea ice formation and decay, results in data that more accurately reflect the complex interactions between MPs and their polar environment. By collecting data across multiple seasons, including two complete ice growth and melt cycles, this study provides a deeper understanding of the long-term impacts of such cycles on MPs weathering. The results from this field-based investigation greatly expanded current understanding of MPs weathering into cold, harsh conditions. The seasonal changes were shown to play a pivotal role in weathering patterns, contributing to the surface changes with presence of biofilms in ways not captured in shorter-term lab-scale studies. This long-term exposure to natural environmental stresses provides a

better understanding on the behaviour of MPs, with bounded contaminants and biofilms, as a result of seasonal sea ice dynamics.

The main advantage of the mesocosm/microcosm approach is that it provides a controlled or semi-controlled environment where key variables like temperature, light, and chemical concentrations can be manipulated, allowing for precise experiments and easier isolation of factors. Compared to field studies, mesocosms and microcosms are less expensive, time-consuming, and logistically feasible, as researchers do not need to monitor large, natural ecosystems directly. Using a mesocosm or a microcosm reduces the risk of disturbing natural ecosystems and allows experiments that would otherwise not be applicable in the field. This enables researchers to carry out process-oriented studies, especially those with a focus on climate change, in a contained and ethical way. In addition, replicate experiments under similar conditions allows for more reliable data.

Despite mimicking natural ecosystems, it should be noted that mesocosms and microcosms are much smaller in scale and may not fully capture all dynamics of natural environments. The complexity of interactions in the dynamic natural environments may be oversimplified, such as the limited biodiversity or variability employed in the mesocosm. Artificial boundaries (such as tanks or enclosures) can influence organism behaviour or environmental factors like water circulation and nutrient input in ways that would not occur in the open environment. High levels of control can sometimes lead to results that are too specific or unrealistic when compared to highly dynamic natural environments.

In summary, the mesocosm and microcosm approach used in this study is valuable for providing controlled and realistic simulations of environmental systems, but the findings must always be considered in light of the limitations imposed by the scale and complexity of the artificial environment. Specifically, it is designed to represent ecosystems in a more natural way than lab-scale beaker studies, offering insights closer to what might occur in the real world. This makes them ideal for studying the effects of pollutants, the behaviour of organisms, and interactions between them. The results can be used as a valuable dataset to bridge the gap between laboratory experiments and field research campaigns.

6.2 Major Scientific Contributions

This 18-month polar mesocosm study reveals three critical dimensions of MPs dynamics in marine environments: sea ice was an effective density-driven temporary MPs reservoir and weathered MPs affected the properties of sea ice; biofilm-driven weathering exhibited seasonal variability; and Hg accumulation was related to polymer-specific interactions with seasonal variability.

Interaction between MPs and sea ice

This 18-month mesocosm study revealed that sea ice functioned as a temporary reservoir for MPs in the polar marine environment, with a notable pattern of particle distribution driven primarily by density differences during ice growth. The majority of MPs—particularly lower-density polymers such as PE and PP—were concentrated near the upper layers of the sea ice. The vertical distribution of MPs indicated significant enrichment in the surface layers, with particle densities in the upper 0 - 5 cm being more than 95% of the MPs instead of in deeper ice layers. This pattern aligns with previous findings by Geilfus et al. (2019) and Chubarenko et al. (2022), which reported similar surface accumulation driven by the lower density and hydrophobic nature of PE and PP, which resist incorporation into deeper ice layers.

In contrast to the finding of Geilfus et al. (2019) that virgin MPs affected surface bulk ice salinity over the first winter, the incorporation of MPs into the ice matrix in this study did not significantly alter the overall properties of sea ice during the first winter. However, notable changes were observed in surface bulk ice salinity in systems containing PE for the second winter. Ice samples containing weathered PE (second winter) displayed 50% higher surface bulk ice salinity compared to control group without MPs, which indicated that weathered PE promoted the increase of surface bulk ice salinity. Geilfus et al. (2019) focused on higher concentrations of MPs and more smaller particles, which increased the likelihood of deeper incorporation and greater influence on brine rejection and ice formation. This study, however, employed MPs at lower concentrations and revealed cumulative weathering effects on PE during the second winter, highlighting how prolonged exposure can influence bulk ice salinity and brine dynamics differently over time. These findings emphasize the importance of considering particle size, initial

concentration of MPs, weathering stage, and polymer type when assessing the environmental impacts of MPs in sea ice.

Weathering of MPs

Over the 18-month outdoor mesocosm study, MPs exposed to natural weathering conditions experienced notable morphological and chemical alterations. The surface of the MPs got roughened due to the attachments. SEM images revealed a progressive development across the surface of MPs, with the extent of roughness varying by polymer type with PE exhibiting the most pronounced alterations, followed by PP and PS.

The study showed that chemical alterations were significant. In the laboratory-scale experiments utilizing artificial weathering protocols, the CI generally increased and eventually reached a plateau, suggesting that the chemical weathering process is irreversible (Campanale et al., 2023; Syranidou et al., 2023). Since this research consider the weathered MPs with their attachment as a whole component, FTIR analysis showed a seasonal variability in the CI that deviated from laboratory findings based solely on chemical weathering only. Specifically, the CI increased substantially for PE-B and PP, rising from below 0.03 to approximately 0.14, while PS and PE-W exhibited CI values of 0.08 and 0.07, respectively, indicating heightened chemical heterogeneity that peaked during the summer months. During the subsequent winter period (January 2021 to April 2021), the CI for PE and PP decreased to less than half of their summer peaks, whereas PS maintained its summer levels. Seasonal variations played a crucial role in shaping the weathering dynamics of chemical alterations. SEM images captured during summer months showed extensive colonization by diatoms. In contrast, colder months led to stabilization of weathering processes, with reduced chemical alterations and biofilm activities. The presence of biofilms, primarily composed of diatoms, contributed substantially to the observed increases in CI and surface roughness. Therefore, these findings expand on those observations by demonstrating the influence of polymer type and seasonal cycles on weathering dynamics in a simulated polar environment.

Accumulation of Hg

Hg accumulation on MPs showed distinct seasonal patterns over 18 months, with varying peak concentrations in summer months and decline in winter months. During the peak phase (April - July 2021), PE-W and PE-B reached Hg concentrations of $\sim 4.0 \text{ ng}\cdot\text{g}^{-1}$ and $\sim 4.5 \text{ ng}\cdot\text{g}^{-1}$, respectively, while PP peaked at $\sim 2.3 \text{ ng}\cdot\text{g}^{-1}$ and PS at $\sim 1.8 \text{ ng}\cdot\text{g}^{-1}$. Following the peaks, Hg concentrations declined, with PE types stabilizing at $\sim 1 \text{ ng}\cdot\text{g}^{-1}$ by October 2021, and PP and PS at $\sim 0.7 \text{ ng}\cdot\text{g}^{-1}$ and $\sim 1.6 \text{ ng}\cdot\text{g}^{-1}$, respectively, by early 2022.

The PE types exhibited higher Hg accumulation due to their smaller size with greater surface area, promoting greater biofilm growth and weathering. In contrast, PP and PS showed lower accumulation due to slower weathering with limited biofilm activities but lower decline due to larger size and higher density, respectively. Despite declines, final Hg concentrations remained significantly higher than initial levels, highlighting the role of MPs in long-term Hg retention in aquatic environments.

Seasonal variations were found in both CI changes and accumulation of Hg. According to statistical analysis, PE-W and PE-B have strong positive correlation (correlation coefficient > 0.9) between Hg accumulation and CI. And 89% and 79% of the variation in Hg concentration can be explained by the CI, respectively. The high R^2 value further indicates that CI is a strong predictor of Hg accumulation on PE. Seasonal variations strongly influenced weathering dynamics, with warmer months accelerating surface alterations and biofilm formation, while colder months conditions provide a temporary reprieve, slowing down the weathering transformation processes.

Previous studies have demonstrated that artificial weathering, such as UV irradiation, enhances the binding of trace metals to MPs (Gao et al., 2021; Liu et al., 2022). Under controlled laboratory conditions, Hg accumulation on MPs has been reported by Zhou et al. (2024) to reach $1\text{--}4 \text{ }\mu\text{g}\cdot\text{g}^{-1}$ within just four hours of exposure to a $10 \text{ }\mu\text{g}\cdot\text{L}^{-1} \text{ Hg}(\text{NO}_3)_2$ solution; this Hg concentration of the stock solution is about 50,000 times higher than in Hg levels in natural seawater ($\sim 0.2 \text{ ng}\cdot\text{L}^{-1}$). In contrast, this mesocosm study reveals a fundamentally different mechanism governing Hg accumulation under natural conditions at Hg levels close to that in natural seawater. Rather than direct photochemical weathering, biofilm formation emerged as

the primary driver of Hg retention on MPs, particularly in cold marine environments. Even within a single summer, Hg concentrations on MPs were found to reach as high as 4.5 ng·g⁻¹. According to the previous research, the Hg concentrations in surface sediments of the Arctic Ocean range from 5 to 100 ng·g⁻¹ (Fox et al., 2014). This suggests that MPs, particularly weathered ones with biofilm, may act as effective carriers for toxic contaminants like Hg. When ingested by marine biota, these MPs could transfer organic form of Hg such as methylmercury up the food chain, increasing the potential for biomagnification and subsequent ecological and human health risks. As a result, the ability of MPs to transport hazardous materials like Hg means that their environmental and ecological risks could be different than the current understanding. Moreover, this study uniquely captures the influence of seasonal freeze-thaw cycles, which modulate both biofilm activities and chemical alterations, ultimately shaping contaminant dynamics. Consequently, the risk posed by MPs to ecosystems and human populations may be underestimated, requiring a rethinking of pollution mitigation strategies in these sensitive regions. By integrating long-term natural weathering processes, this research advances the understanding of MP–Hg interactions beyond short-term laboratory experiments, providing novel insights into the environmental fate of MPs in real-world aquatic systems.

In summary, unlike previous short-term laboratory weathering studies that emphasized rapid, strong photochemical reactions, this long-term mesocosm study demonstrates that natural weathering processes in polar marine environments are dominated by biofilm formation and seasonal freeze-thaw cycles, which are determining factors in alterations in MP behavior and contaminant interactions while the photodegradation of MPs was not as significant as observed from lab studies with enhanced UV radiation. This combination of physical, chemical, and biological weathering processes increases the environmental risk associated with MPs, as weathered particles are more effective vectors for contaminant transport, potentially impacting marine food webs and biogeochemical cycles. Collectively, these results not only highlight the critical roles of polymer type, particle size, and weathering stages in contaminant uptake but also extend our understanding of MP - sea ice - metal interactions beyond artificial weathering scenarios. It also highlights the complex interplay of environmental factors influencing the

weathering of MPs and underscores the need for further quantitative assessments to fully understand their long-term ecological implications.

6.3 Implications for Communities, Governments, and Industries

This research on the weathering processes of MPs in polar environments has several important implications for various sectors, including communities, governments, and industries. It highlights the urgency of understanding how MPs behave in cold ecosystems, such as polar regions, where environmental changes are accelerating.

First, the findings of this research are timely to the communities, especially those living in the Arctic or coastal regions, because MPs directly impact the health and sustainability of the environment, which people rely on for country food, resources, cultural practices, and recreational activities. For example, local fish populations and marine mammals, which may ingest contaminated MPs, could face health issues that also affect local fishing and hunting practices. By understanding how MPs interact with pollutants such as Hg, local residents will be more aware of both direct and indirect risks posed by plastic pollution, including contaminant bioaccumulation and potential human health consequences. As climate change accelerates the melting of sea ice and exposes more MPs into the environment, these risks will become more widespread. The deep understanding of local ecosystems can play a key role in contributing to research that combines traditional ecological knowledge with modern scientific methods. Furthermore, many communities have an emotional and cultural connection to natural landscapes, including polar environments. These communities have historically been stewards of the land and waters, and their involvement in addressing MP pollution can foster more holistic, sustainable solutions to environmental issues. Protecting these ecosystems from the escalating risks of pollution directly benefits the long-term well-being of the community.

Second, the findings of this research will inform governments, particularly those in countries with polar regions or coastal areas, on regulations around pollution monitoring, environmental protection laws, and international cooperation, particularly given the shared nature of ocean ecosystems. Traditional efforts to reduce plastic waste are vital but may not be

enough since the ocean has already accumulated large amounts of MPs, which are subject to weathering processes and interactions with contaminants. Governments, particularly those with polar regions or coastal areas, need to recognize the role of sea ice as both a reservoir and transporter of MPs. As this study shows, MPs are incorporated into sea ice during freezing and released back into the environment as the ice melts. This creates a mechanism for the long-range transport of MPs between different marine ecosystems. With the accelerated melting of sea ice due to climate change, the release and redistribution of MPs in the polar regions will likely intensify. Governments need to revise their climate change mitigation and adaptation plans to incorporate the impacts of MP pollution. For example, governments should prioritize monitoring not only the concentrations of MPs in the sea ice but also track their distribution patterns, especially as sea ice dynamics are altered by climate change. This will help identify potential hotspots for MPs and related contaminants accumulation and release, which could pose threats to marine life and ecosystems. Increased monitoring of MPs in both sea ice and surrounding waters should be integrated into national and regional environmental surveillance programs. International agreements and frameworks should be strengthened or developed to create joint monitoring programs, shared data, and coordinated response strategies for MPs and other contaminants that traverse national borders. In addition, understanding the pathways through which MPs and their contaminants enter human diets (such as through seafood consumption) is critical for developing health advisories, preventive measures, and public education. As more research highlights the potential bioaccumulation of harmful chemicals through the food web, these organizations can work to inform policy changes to protect public health. By integrating these findings into policy development and international agreements, governments can better mitigate the risks posed by MPs and ensure the protection of marine and polar ecosystems for future generations.

Third, as global awareness around plastic pollution grows, industries may face increased regulations, operational impact and consumer demand for more sustainable products. The movement of MPs through sea ice and the resulting global contamination underscores the importance of industries worldwide acknowledging their role in plastic pollution. The widespread nature of the issue calls for a coordinated, international approach to tackling plastic waste. Global

industries, no matter their location, must engage in adhering to and promoting policies and practices that reduce plastic production, enhance recycling efforts, and minimize plastic waste to protect both marine ecosystems and public health across the globe. This is no longer a local issue but a shared global responsibility. There is also operational impact for industries. Industries involved in resource extraction (such as oil, gas, and mining) and shipping may be affected by the ecological shifts caused by MPs. As MPs interact with sea ice, they may influence environmental conditions like bulk ice salinity and albedo, potentially impacting operations and weather patterns in these regions. For example, increased bulk ice salinity lead by trapped MPs may lead to softer, weaker ice, potentially disrupting offshore drilling operations. Additionally, MPs, particularly those with black coloration, tend to absorb more heat in the surface layer of sea ice, further accelerating ice melt. These changes in ice dynamics can lead to unpredictable environmental conditions, impacting operational stability, scheduling, and infrastructure integrity in polar regions. In addition, this research underscores the impact of MP weathering, including changes in surface roughness and chemical composition. Industries could invest in developing new materials that degrade more efficiently or recycle more effectively to minimize the environmental footprint of plastic products as vectors for contaminants. This research can provide industries with valuable insights into how their actions contribute to larger environmental problems, empowering them to adopt more sustainable practices and develop strategies to reduce plastic pollution. Furthermore, with the increasing likelihood of policies targeting plastic production and disposal, industry stakeholders should act now to stay ahead of potential legislation aimed at reducing the impact of MPs on the environment.

6.4 Future Directions

The results of this study suggest that the weathering processes of MPs in the real environment could be slower and more complex than what is typically assumed from laboratory studies, especially in polar regions. Based on the current findings, the weathering processes are influenced not only by chemical factors such as UV radiation and physical factors such as mechanical stress but also by biological factors such as biofilm formation. In future studies,

several avenues can be explored to extend the understanding of MPs behavior, fate, and ecological impacts in cold marine environments, especially those influenced by seasonal sea ice dynamics. This section elaborates on potential future research directions, addresses what could be done differently in a re-experimentation of this study, and offers insights into bridging microcosm results to real-world scenarios, enhancing both environmental policy-making and scientific understanding.

1. Long-term fate of weathered MPs: The weathering process in this study appears to be more dynamic than previously thought. The study observed that the weathering of MPs in cold marine environments, particularly in the presence of sea ice, exhibits seasonal variability. If this study were to be repeated, a key improvement would be to extend the investigation into the long-term transport and breakdown of MPs post-release from melting sea ice. Extended and spatial scales with longer-term monitoring (e.g., 5–10 years) could capture slower weathering processes and cumulative ecological effects. Although the study captures the weathering of MPs during their exposure to sea ice, their fate after being released into the oceanic environment could be more closely monitored. Long-term field observations of how MPs continue to degrade or interact with other environmental components, such as sediment and marine life, would provide a more holistic picture of their role in global pollutant transport and ecosystem disruption. Additionally, better tracking of their movement and distribution in the open ocean could provide valuable insights into their global circulation patterns.

2. Interactions between MPs and other contaminants: One of the significant findings in this study was the accumulation of Hg on weathered MPs, with potential implications for contaminant cycling. However, it suggests that more attention should be paid to the interactions of MPs with contaminants and biofilms. These interactions significantly alter MPs' surface properties and their capacity to accumulate contaminants, which in turn impacts their environmental behavior and toxicity. Weathering processes, such as biofilm-driven weathering, play a vital role in transforming MPs, making them more hazardous, especially given their potential to bioaccumulate and biomagnify in Arctic food webs. PE, due to its widespread presence and high weathering susceptibility, may pose a greater risk as a transport medium for toxic metals compared to other polymers. Seasonal variations further complicate this risk, with

warmer months acting as periods of heightened metal aggregation, followed by potential redistribution during colder periods. Thus, focusing on both weathering and interactions with contaminants, particularly in dynamic environments like sea ice, should be prioritized.

Future research could aim to broaden this scope by investigating the interactions between MPs and other contaminants like PCBs, PFAS, and pesticides, etc. A detailed understanding of how MPs act as vectors for these toxicants under various environmental conditions (e.g., temperature, salinity, UV radiation) will help assess the ecological and human health risks associated with their bioaccumulation and biomagnification. Experimental setups that explore varying levels of pollutant exposure, possibly integrating mesocosm models or field data, could provide clearer insights into these complex interactions.

3. Ecological impacts of MPs on marine food webs: This study focused on MPs' weathering properties and contaminant interactions but did not deeply explore the ecological consequences of MPs in marine food webs. With biofilm formation and increased surface roughness enhancing their potential for contaminant uptake, MPs could potentially increase the risks associated with MPs in marine ecosystems. The biofilm not only enhances the surface properties of MPs, making them more attractive to metals due to increased hydrophilicity, but it may also facilitate the ingestion of MPs by these organisms. Future work should involve examining how different types of MPs, particularly those weathered and biofilm-laden, affect primary producers (e.g., phytoplankton), higher trophic levels, and species such as fish and marine mammals that ingest them. Given the increasing presence of MPs in the Arctic and Antarctic ecosystems, assessing the effects of MPs on species' health, reproductive success, and behavior in these fragile environments should be prioritized. Meanwhile, it is essential to understand how organisms interact with MPs that carry contaminants, particularly in terms of ingestion, digestion, and assimilation. By better understanding how organisms digest, absorb, or expel MPs and the contaminants they carry, future research can help clarify the risks posed to marine food webs. These interactions are crucial in predicting the spread of contaminants across trophic levels and potential effects on biodiversity and ecosystem function, with an emphasis on polar regions where MPs are accumulating at alarming rates.

4. Quantifying factors affecting risk of MPs: Understanding the risk of MPs in marine environments involves quantifying numerous factors that influence their environmental behaviour and toxicity. Future studies should focus on developing standardized metrics to quantify the risk posed by MPs based on their size, weathering state, biofilm presence, and contaminant load. The study could also examine the role of environmental factors such as ocean currents, temperature fluctuations, and light exposure in the transformation, and transport of MPs. Additionally, exploring how the biofilm and microbial communities on MPs evolve in different environments could be key in understanding their toxicity and persistence in marine ecosystems. Incorporating these factors into risk models would provide more accurate projections of the long-term effects of MPs.

5. Bridging microcosm and mesocosm experiments with the real environment: As global plastic pollution continues to grow, this research directly informs management strategies for preventing further degradation of fragile polar ecosystems. Understanding this seasonal cycle is crucial for predicting the behavior and ecological impact of MPs in polar and temperate marine environments, especially in light of climate change, which is expected to extend the duration and intensity of warmer periods in these regions. As polar ice sheets and sea ice continue to respond to warming temperatures, understanding how materials weather in these environments becomes critical for predicting future environmental shifts.

One of the challenges in extrapolating results from controlled experiments to real-world conditions lies in the simplification of environmental complexities. In future studies, there should be a focused effort to integrate microcosm and mesocosm data with large-scale field experiments, especially by comparing lab-based results with data collected from actual polar environments. This would help validate the findings and ensure they are representative of natural conditions. Furthermore, linking field observations with modeling studies could improve our understanding of the dynamics of MPs in polar marine environments and their potential to impact global oceanic systems. This could involve simulating the long-range transport of MPs, their interactions with ocean, and their eventual deposition or ingestion by marine organisms.

6. Informing policy and advancing MPs management: The results from this study have the potential to inform policymaking by highlighting the need for more rigorous monitoring of

MPs in polar marine ecosystems. Given the risks MPs pose as vectors for contaminants, policy recommendations should focus on reducing plastic pollution at its source, preventing the accumulation of MPs in sea ice, and mitigating their release during melting events. Additionally, improving regulations related to plastic waste management, promoting sustainable alternatives, and encouraging international cooperation on addressing plastic pollution in polar regions could be important outcomes of this research. By integrating these findings into policy frameworks, future research can directly contribute to global efforts to reduce the environmental impact of MPs.

In summary, this study opens new opportunities to advance future research on the environmental impacts of MPs, particularly in cold marine ecosystems. The unique, long-term nature of this study provides a benchmark for assessing how ongoing changes in the polar climate will influence not just local ecosystems, but also the broader global climate system. By offering a more naturalistic picture of weathering processes, this study helps to better assess the long-term impacts of human activities in these fragile ecosystems, guiding future policy and management strategies for polar conservation. By addressing these research gaps and enhancing our understanding of the fate, transport, and ecological consequences of MPs, we can better predict their long-term impacts and develop effective mitigation strategies.

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