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Quantification of microplastics in sediments from Narragansett Bay, Rhode Island USA using a novel isolation and extraction method *,**

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ABSTRACT

Microplastics are small plastic particles found ubiquitously in marine environments. In this study, a hybridized method was developed for the extraction of microplastics (45–1000 μ m) from sediments using sodium bromide solution for density separation. Method development was tested using spiked microplastics as internal standards. The method was then used to extract microplastics from sediments in Narragansett Bay, Rhode Island, USA. Suspect microplastics were analyzed with Raman spectroscopy. Microplastic abundance ranged from 40 particles/100 g sediment to 4.6 million particles/100 g sediment (wet weight). Cellulose acetate fibers were the most abundant microplastic. These results are some of the first data for microplastics in Rhode Island sediments.

1. Introduction

Microplastics (MPs) are small plastic particles (1 nm-5 mm) commonly identified as a marine pollutant (Thompson et al., 2004). Many MPs entering the oceans will ultimately end up in sediments (Andrady, 2011; Browne et al., 2011; Cózar et al., 2014; Hidalgo-Ruz et al., 2012; Kowalski et al., 2016). Understanding the distribution and abundance of MPs in sediments is the first step to determine their potential risks to marine environments. However, there are many technical challenges associated with extracting and identifying MPs from marine sediments.

The wide diversity of their physical properties makes MPs a particularly challenging class of contaminants to extract, quantify, and identify in environmental media. While there are dozens of published methods for the extraction of MPs from sediments, procedural differences, sediment characteristics, and MP physical properties can all affect the efficacy of MP extraction and types of MPs reported in environmental samples (Burgess et al., 2017; Rochman et al., 2019). Our prior

research compared the extraction efficacy of 5 types of MPs from two sediment types using a range of different extraction procedures from the scientific literature (Cashman et al., 2020). The findings and recommendations from these data were used to develop a new isolation and extraction method to more efficiently capture a wider range of MPs from environmental sediments. Referred to as the "hybrid method", this new method combines recommendations from Cashman et al. (2020) with characteristics from the methods evaluated in the comparison study (Coppock et al., 2017; Fries et al., 2013; Gilbreath et al., 2019; Nuelle et al., 2014; Zobkov and Esiukova, 2017) to develop a method that is cost efficient, generates minimal hazardous waste, doesn't require equipment fabrication, and successfully extracts MPs from a range of sediments. The research herein uses the hybrid method for the extraction of MPs from marine sediments from Narragansett Bay (NB), Rhode Island.

NB is located on the northeast Atlantic coast of the United States (Fig. 1). The greater NB watershed area (4081 km^2) is densely populated with an estimated 1.9 million people from both Rhode Island and

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Massachusetts (NBEP, 2017; Vadeboncoeur et al., 2010). Twenty percent of the watershed's population resides in urbanized coastal land. Classified as a coastal plain estuary, NB has an area of 342km^2 and an average depth of 9 m (Raposa, 2009). Plastics have been reported in NB surface waters and coastlines for decades (Carpenter and Smith, 1972; Colton et al., 1974; Cundell, 1973; Kraimer et al., 2018; STB, 2019). While many of these reports confirm MPs through visual observation, advanced analysis of MPs in environmental matrices are often too cost-prohibitive for small-scale research initiatives.

Many studies focus on MP particles composed of conventional plastic polymers, but anthropogenically modified and semi-synthetic particles such as regenerated celluloses can have physical similar properties to conventional petroleum-based particles (Athey and Erdle, 2021). Organizations such as the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) limit their MP definition strictly to particles made from polymers (Kershaw, 2015). But other researchers now include semi-synthetics in their definition of MPs. Semi-synthetic particles are considered MPs according to the legal definition adopted by the State of California and are becoming more commonly

recognized as MPs in other research (Coffin, 2020). Although semisynthetic particles are derived from natural materials, during production or use they are often modified with chemical additives, dyes, and finishing agents that can include toxic compounds, such as per and polyfluoroalkyl substances (PFAS), formaldehyde, and azo dyes (Remy et al., 2015; Zambrano et al., 2021). Such particles have shown adverse effects to aquatic organisms (Kim et al., 2021), like microfiber pollution from smoked cigarette filters producing leachates toxic to Daphnia magna ($EC_{50} = 0.017$ smoked filters) (Belzagui et al., 2021). The additives in semi-synthetic particles may also contribute to their persistence in the environment, which can range from months to decades in aquatic systems (Sait et al., 2021) and are found ubiquitously in the marine environment (Grbić et al., 2020). For this study, we use the definition of microplastics adopted by the State of California Code of Regulations on Microplastic Materials, which includes modified cellulose and semisynthetic particles (Board, 2020).

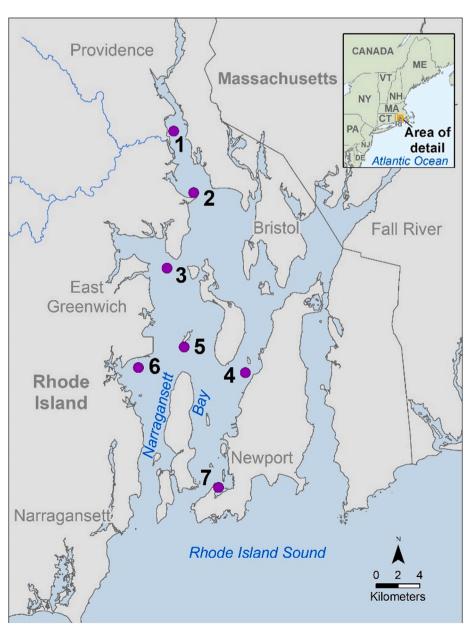


Fig. 1. A map of sampling locations in Narragansett Bay, RI, USA.

2. Methods

2.1. Method development & validation

A key aspect of the present study was development of a hybrid method for the extraction of MPs from marine and estuarine sediments. Previous research showed MP extraction efficacy is impacted by the type of extraction method, as well as the physical properties of the sediment and MPs (Cashman et al., 2020). Lessons learned from that method comparison study guided the development of a hybrid method for MPs 45-1000 μm from sediments with different grain sizes and organic carbon content. This methods section gives a brief overview of the procedure, but detailed step-by-step instructions and quality assurance practices are available in the Supplemental Information.

The hybrid extraction procedure efficacy was assessed using two model sediments, silty sediment from Long Island Sound (LIS), New York (USA) (n = 5) and beach sand from the coastline of Narragansett Beach (NAR), Rhode Island (USA) (n = 5) (Supplemental Information (SI) Table 1) (Cashman et al., 2020). Both sediments were press-sieved through a 2 mm sieve prior to analysis to remove any coarse fragments. The NAR sand was heated in a muffle oven at 550 °C for 6 h to remove natural organic material and existing plastics. Each sediment was homogenized using a metal spatula and split into 100 g (wet) samples in glass jars. Each sediment sample was spiked with known quantities of five representative conventional MP types (polyethylene (PE), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC) and polypropylene (PP)), with various fragment shapes (sphere, fragment, fiber), particle sizes (45 - 710 µm), and densities (0.91–1.38 g/cm³) (SI Table 2). Plastics were chosen to represent a range of polymers, sizes, shapes and colors of microplastics to more accurately represent environmental microplastics. A minimum of 20 plastic pieces per polymer type were carefully transferred to each sediment sample (20 MP pieces * 5 plastic types = 100 pieces of MP/sample). The plastic-amended sediments were then mixed on a roller mill (4 RPM) at 4 °C for a minimum of 48 h in the dark (Cashman et al., 2020).

Detailed instructions for MP extraction can be found in the SI. Briefly, pre-weighed (100 g, wet) sediment samples were passed through a series of stacked sieves (1 mm, 250 μm , and 45 μm) using deionized (DI) water (Fig. 2a) (Gilbreath et al., 2019). Debris >1 mm and <45 μm were discarded. Retained sediments were of two size classes: 251-1000 μm and 45-250 μm (Fig. 2b & c). MPs were extracted from both sieve size classes using a two-step density separation technique. For this technique, two sodium bromide (NaBr) solutions with known densities ($\varrho=1.3$ & 1.5 g/mL) were prepared by dissolving anhydrous NaBr (95%, Honeywell Fluka, Fisher Scientific) in DI water. Densities were checked using a Baum hydrometer and filtered through a 0.45 μm PCTE membrane filter to remove suspended solids.

Sediment samples were then transferred to 1-L glass separatory funnels using 300 mL of the low density (1.3 g/cm³) NaBr solution (Fig. 2b & c). Separatory funnels containing the NaBr solution and sediments were capped, tipped at a 90° angle, and vigorously shaken for 2 min. Separatory funnels were then returned to their upright position and rinsed with the low density NaBr solution to ensure no particles adhered to the walls of the separatory funnel. The funnel contents were left to settle until the supernatant was clear and sediment had resettled to the bottom (a minimum of 2 h). Sediment that had settled out of each separatory funnel were transferred to a second 1-L separatory funnel by opening the funnel stopcock and allowing the settled sediment to flow out. The remaining supernatant and floating debris were filtered onto a 20 µm PCTE membrane filter and retained for analysis (Fig. 2D & F). The separatory funnel was rinsed thoroughly to ensure all particles were removed from the walls of the funnel. Sediment that was transferred to the secondary separatory funnels underwent a second round of shaking and settling with the higher density (1.5 g/cm³) NaBr solution. After another settling period, supernatant and floating debris were filtered onto a second 20 μm PCTE filter (Fig. 2E & G). Sediment that settled to the bottom of this separatory funnel was discarded.

After extraction, each sediment sample produced four filters representing the two sieve size classes and two density separation steps. Each filter was oxidized with 30% hydrogen peroxide for 2 h at 60 $^{\circ}$ C to

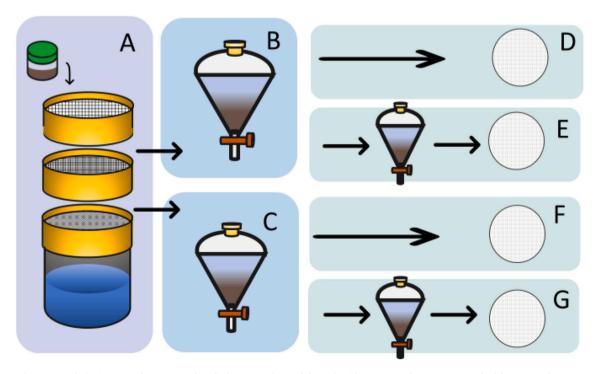


Fig. 2. A wet sediment sample (2a) is poured over a set of stacked sieves and rinsed through with DI water. The sieves are stacked from top to bottom, 1000, 250, and 45 μ m. Sediment that passes through all three sieves or is retained on 1000um sieve is discarded. Materials retained on the 250 μ m sieve are retained as size class 250-1000 μ m (2b). Materials retained on the 45 μ m sieve are retained as size class 250-45 μ m (2c). Each size class undergoes two density separations. MPs are retained on 4 filters for each sample (2d, 2e, 2f, 2g).

remove natural organic material and then filtered onto new PCTE filters (Masura et al., 2015; Zhao et al., 2018). All filters were stored at room temperature in covered petri dishes to prevent airborne contamination. Filters containing spiked MPs from method development were analyzed (i.e., counted) for MP recovery using a Nikon SMZ-45 t stereoscope.

2.2. Identification of internal standard MPs

Filters containing spiked MPs were visually inspected with a Nikon microscope at $2\times$ magnification count spiked MPs retained on the filters. Two analysts verified each MP count using both normal light and cyan excitation with a NightSea (Lexington, MA, USA) fluorescence filter (excitation 490–515 nm, emission 550 nm long pass). Spiked internal standard MPs were counted on each filter and tallied by polymer type. Recovered MPs were compared to initial spiked values to determine percent recovery. Samples used for method development did not undergo further analysis with Raman spectroscopy.

2.3. Narragansett Bay sediments

2.3.1. Collection

Seven locations within NB were analyzed for MPs (Table 1). Sampling locations were chosen based on prior knowledge of proximal land use and geomorphology. All sampling equipment was rinsed with DI water prior to use and in-between sampling events. Sediment samples were collected in July of 2019 using a Van Veen sediment grab with a 0.1 m² surface area. The top 5 cm of sediment from each sediment grab sample was collected using a metal spade and transferred to clean, muffled glass jars with foil-lined lids. Upon returning to the laboratory, each sediment sample was homogenized with a metal spatula. Sediment grainsize was determined with triplicate analysis using a grainsize MasterSizer 3000. Remaining sediment was split into sediment samples weighing 100 g (wet) each. All samples were stored in glass jars at 4 °C in the dark until extraction. Quality assurance (QA) procedures for collection are detailed in the SI.

2.3.2. MP extraction process

NB sediments were extracted using the hybrid method described above. To account for MP loss during extraction, one sediment sample from each sampling location was spiked with known quantities of 3 types of MPs as described above to serve as internal standards. The plastics used as internal standards included PS spheres, PET fibers, and PE films ranging from 45 to 500 μm (SI Table 2). All sediments samples were stored at 4 $^{\circ}C$ in the dark until the time of extraction. Detailed description of QA practices, including air blanks, process blanks, and

Table 1 Sampling Station Locations of Sediments collected from Narragansett Bay in July 2019. Sediment sizes classified using grainsize diameter (μ m) 10% (D₁₀), 50% (D₅₀), and 90% (D₉₀) cumulative percentile value.

Station number	Location (decimal degrees)	Description	Water depth (m)	D ₁₀	D ₅₀	D ₉₀
1	41.772233, -71.381617	Fields Point	3.3	6.57	27.9	127
2	41.721517, -71.359733	Conimicut Point Reach	4	6.68	51.7	340
3	41.659233, -71.389233	Rocky Point	3.8	78.1	240	556
4	41.572983, -71.303400	Arnold Point	5	5.14	22.3	494
5	41.594250, -71.370500	Hope Island	7.3	6.77	31.4	129
6	41.577283, -71.420767	Wickford Harbor	4.5	13.8	99.5	288
7	41.478333, -71.332950	Fort Adams State Park	6.5	6.64	56.9	339

sediment spiking with internal standards can be found in the SI. The spiked sediment samples from NB underwent the same recovery as described above. Alternatively, sediments extracted for environmental MP analysis were examined using Raman spectroscopy.

3. Raman analysis

Environmental MPs extracted from NB sediments were identified and quantified with a Renishaw Qontor Confocal Raman spectrometer with Renishaw Wire software (Renishaw PLC, Wotton-Under-Edge, United Kingdom). All data were post-processed with Wire 5.2 Software. The Raman spectrometer was calibrated each day prior to use with a preloaded silicon sample. All samples were analyzed using a 785 nm laser at a power of 1%, an integration time of 10s, 1 accumulation, a spectral range of 100 to 3200 Raman shift/cm⁻¹ and an objective with $20 \times 50 \times$, and 100× magnifications. The Raman spectral libraries used to identify materials included the Renishaw spectral libraries for polymers and inorganics, as well as the SLoPP and SLoPP-E spectral libraries (Munno et al., 2020) and Open Specy (Cowger et al., 2021). Particle analysis parameters were optimized for each sample. All suspected MPs retained on the 251-1000 um size class filters were picked using fine forceps (Excelta 5SA) and placed on a piece of double-sided tape adhered to a slide. Each picked particle was circled with permanent marker, numbered, and had their physical properties (e.g., size, color, and shape) recorded (SI Table 7). Single point analysis was used for the picked particles (i.e., $251-1000 \mu m$) whereas automated maps were used for the filters' subsections. Information on each spectrum including instrument parameters, spectral library, and quality index can be found in SI Table 7. Particles retained on the 45-250 µm size class filters were too small to pick using forceps. Therefore, a 1/4 wedge-shaped subsection from each filter was analyzed using the scanning feature to maximize efficiency and reduce the amount of time required to analyze each sample. Prior to analysis, filters containing 45-250 μm particles were refiltered onto new PCTE filters with SkinTac adhesive as described by Thaysen et al. (2020) to prevent particle movement on the filter. All MPs identified from the 1/4 filter sections were multiplied by 4 to extrapolate the total particle number per filter.

4. Evaluation of Raman data

Particles with a confirmed polymer match and hit quality index (HQI) >0.4 were accepted as a MP particle. All confirmed MP particles were analyzed further for their size, shape, and color. The extraction method was designed for MPs 40–1000 μm in diameter. However, some MP particles with smaller diameters, such as fibers, were identified during extraction. These particles were still reported in the data. Many non-anthropogenic particles were also identified, such as cotton, wool, and silk fibers. These are reported in SI Table 7, but ultimately not presented in our data due to a lack of laboratory controls for these types of particles. Spectra identified as polycarbonate (PC) were also omitted from our data due to background interference resulting from the use of PCTE filters in the extraction procedure.

5. Results

5.1. Assessing extraction efficiency using internal standards

The hybrid method was assessed by recovering known quantities of internal standard MPs from five replicates for both LIS and NAR sediment samples (SI Fig. 1, SI Tables 3 & 4). Mean recovery for MPs was >70% for nearly all polymers and both sediment types (i.e., silty and beach sand). The one exception to this was the mean recovery of PET fibers from LIS sediment (mean = 45.14%, RSD = 62.1%). The PET fibers used in percent recovery tests had a length of 250-500 μm , but a fiber diameter of roughly 20 μm . We suspect PET fiber loss most likely occurred in the initial sieving steps (Fig. 2a). Several mean recoveries

were >100%. This was due to fragmentation of MPs during the extraction process and is further explained in the discussion.

For the spiked environmental samples from NB, mean recoveries across all types of spiked MPs ranged from 40 to 100% (Table 2, SI Table 5). The lowest recoveries were observed at Station 1, with a mean recovery of 40%. This was largely due to poor recovery of PS MPs (19%). With the exception of Station 1, PET fibers had the lowest recovery. Station 1 had the poorest overall MP recoveries (i.e., 40% PE, 19% PS, 63% PET), and Station 3 had the highest overall spiked MP recoveries (i.e., 115% PE, 53% PS, 93% PET). The number of particles found in water and air blanks was below 5 particles per filter (SI Table 6). Particle abundance in the water and air blanks are reported in the SI but are not used to make any baseline subtractions from the data presented.

5.2. MPs in Narragansett Bay sediments

Each station contained a total of 40 to 4.6 million MPs per 100 g (wet) sediment sample (Fig. 3). Station 4 had the highest number of total MPs (4.6 million), followed by Station 3 (293), Station 2 (269), Station 7 (189), Station 6 (67), Station 1 (45), and Station 5 (40). Stations 3 and 4 had high abundances of cellulose acetate fibers with 146 and 4.6 million fibers per 100 g sample, respectively. A total of 38 different polymer types (semi-synthetic and synthetic) were identified across all stations (Fig. 3; SI Table 7). When looking at the summation of MPs across all stations, cellulose acetate was the most commonly identified particle polymer (4.6 million particles), followed by polyester PEY (297 particles), PP (186 particles), methyl cellulose (148 particles), polyurethane (93 particles), PS (33 particles), PE (26 particles), ethyl cellulose (20 particles), and PVC (20 particles) (Fig. 4). These nine polymer types accounted for 45 - > 99% of all particles found at each station (Station 1 (84%), Station 2 (75%), Station 3 (83%), Station 4 (99%), Station 5 (70%), Station 6 (45%), and Station 7 (81%) (Fig. 4)). All other identified polymers can be found in SI Table 7. The top five polymer types are mapped separately in Fig. 5 to show spatial distribution.

MP color was observed under the stereomicroscope, or by analyzing pictures from the Raman imaging software (SI Table 7). Inconsistencies in nomenclature and technique can result in large discrepancies in reporting MP physical characteristics such as particle color (Lusher et al., 2020). Therefore, colors were reported in broad classes to account for observation variability. A breakdown of MP physical characteristics showed that most MPs were achromatic in color (Fig. 6a). Achromatic MPs (black, white, brown, transparent & gray) made up 68-99% of the MPs at each station. MPs were also characterized by shape (Fig. 6b) and size (Fig. 6c), when possible. Fibers were the dominant MP found at Stations 3 (77%), 4 (>99%), and 5 (45%). Whereas fragments were the dominant MP at Stations 2 (49%), 6 (45%), and 7 (54%). Foams were the most common shape at Station 1 (32%). MPs were measured by their longest length to the nearest $100 \mu m$. Fig. 6c shows these size classes grouped into larger subcategories (45-200, 201-400, 401-600, 601-800, and $801-1000 \mu m$). MPs in the $45-200 \mu m$ size range were the most identified MP size at Stations 3 (89%), 5 (53%), 6 (43%), and 7 (72%). Station 1 had an equal percentage of MPs in the 45-200 and 201-400 μm size range (32%). Most MPs found at Station 2 were 201-400 μm

Table 2Percent recovery of internal spiked MPs from environmental samples.

Station	% Recovery					
	PE	PS	PET	Mean recovery (PE, PS & PET)		
1	37.9	18.8	62.5	39.7		
2	114.7	53.3	43.5	70.5		
3	93.9	113.5	93.3	100.2		
4	80.0	50.0	28.6	52.9		
5	115.0	81.3	26.7	74.3		
6	43.9	80.0	23.8	49.2		
7	85.7	86.8	42.9	71.8		

(51%). Due to the large abundance of cellulose acetate fibers found at Station 4, the majority of the MPs at this station were in the 601-800 μm size range (>99%).

6. Discussion

6.1. Extraction method effectiveness

The isolation, extraction and identification of MPs from environmental sediments are challenging. Physical characteristics of sediments and MPs, as well as the selected extraction method can greatly affect results of MP extraction and identification. Many existing MP extraction methods focus on MPs >300 µm (Cai et al., 2020; Kowalski et al., 2016; Masura et al., 2015), despite acknowledgement that small ($<300 \mu m$) are prevalent in the environment (Corami et al., 2021). This is most likely because the 333 μm neuston net was standard for marine MP trawls for many years (Lindeque et al., 2020). This study aimed to extract and characterize smaller MPs (45–1000 µm) to better understand their presence in marine sediments. Recovery of spiked MPs from NAR and LIS sediments extracted with hybrid method development had >80% mean recovery for all MPs except PET fibers (SI Fig. 1). PET fiber recovery was 40% (LIS sediment) and 70% (NAR sediment) during method development. Fibers can be very difficult to recover from sediments due to their small diameter. Many fibers were noted to pass through sieving steps in the spiked MP recovery tests. The spiked MP recoveries from environmental samples ranged from 18 to 114% for the polymer types and sediments investigated herein (Table 2). One possible explanation for the large variations is the different physical characteristics of each sediment. Station 1 had the smallest grainsize distribution (Table 1) and the lowest mean percent recovery of spiked MPs (SI Table 5). Station 3 had the largest grainsize distribution and the best mean recovery of spiked MPs. However, it is more difficult to sieve and process finer grained sediments, which in turn may result in lower MP recovery. A regression analysis showed no significant relationship between the grainsize and MP recovery, indicating that grainsize is not the only influence on extraction efficacy. The use of the internal standards suggests strongly that some of the environmental MPs were lost or unidentified during the extraction process, and reported MP values for NB sediments are under-representations of true MP quantities. In addition, this method did not analyze MPs below and above the range 45-1000 μm. The PVC fragments used as spiking material were fragile and were fragmented during the extraction process. This explains why their % recoveries were >100%. These PVC fragments were not ideal, and therefore not used as spiking materials for the environmental samples. But this does point to the likelihood of MP fragmentation during the extraction process.

6.2. Presence of cellulose acetate

Perhaps the biggest surprise in analyzing NB sediments was the high abundance of cellulose acetate fibers. The reporting units for MPs in sediment vary by study, but the concentration of MPs found in NB are substantially higher than many existing sediment studies. Some of the highest reported MP concentrations in sediment include 27,606 MPs/m² in South Korea (Lee et al., 2013), 8000 MPs/kg in Nova Scotia (Mathalon and Hill, 2014), 5000-7000 MPs/m³ in Portugal (Ballent et al., 2012), and 4205 MPs/kg in China (Wang et al., 2019). Our data are reported in MP/100 g wet weight or 0.03m² surface area. Extrapolating our results from Station 4 would results in 46 million MPs/kg sediment, or 153 million MPs/ m^2 . Other studies note that cellulose acetate and other regenerated cellulose fibers make up a large portion of recovered MPs (Bridson et al., 2020; Lusher et al., 2013). The cellulose acetate fibers from NB were uniform in size, shape, and color (SI Fig. 2). Their uniformity and high abundance lead us to believe that they likely entered NB from a proximal source.

This study was unable to determine the exact source or transport

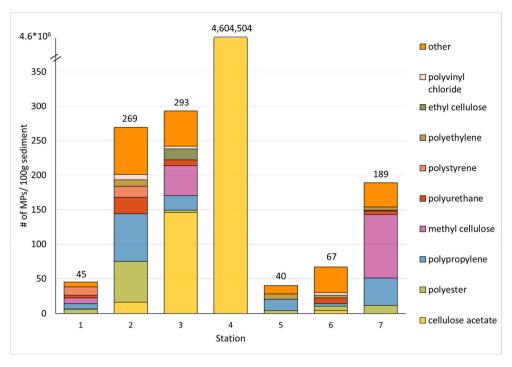


Fig. 3. Number of Microplastics (MPs) per 100 g sediment sample at each station. Total number of MPs per sediment displayed in text above bars.

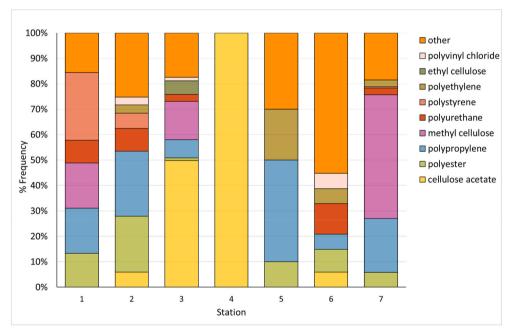


Fig. 4. Percent frequency of Microplastics (MPs) by polymer type at each station.

mechanism of the cellulose acetate MPs into NB. Most plastic pollution enters the marine environment from land through rivers (Jambeck et al., 2015). Sediment transported by rivers is often deposited in estuarine and deltaic sedimentary environments (Coleman and Wright, 1975), which may explain why coastal environments exhibit such high MP concentrations (Harris, 2020). Semi-enclosed marine regions can result in high sequestration of MPs (Alosairi et al., 2020). For these reasons, there is strong evidence observed MPs likely came from nearby land sources. Station 2's sampling location was chosen for its proximity to NB's largest WWTP discharge, and we had originally hypothesized the highest number of MPs would be observed at this station. High fiber

abundances are often associated with sewage discharge (Browne et al., 2011). However, very few cellulose acetate fibers were detected at this station. This leads us to believe that these fibers did not come from NB's major WWTP. Cellulose acetate fibers have many industrial uses, including fiberglass for boats (Spaulding, 1966), cigarette filters (Shen et al., 2021), and textiles (Law, 2004). The collected cellulose acetate fibers were visually compared against weathered and pristine cigarette filters to establish visual similarities. The size and texture of the cellulose acetate fibers did not match the cigarette filters, leading us to believe these fibers did not come from cigarette filters. Narragansett Bay supports many services, including recreational and commercial boating,

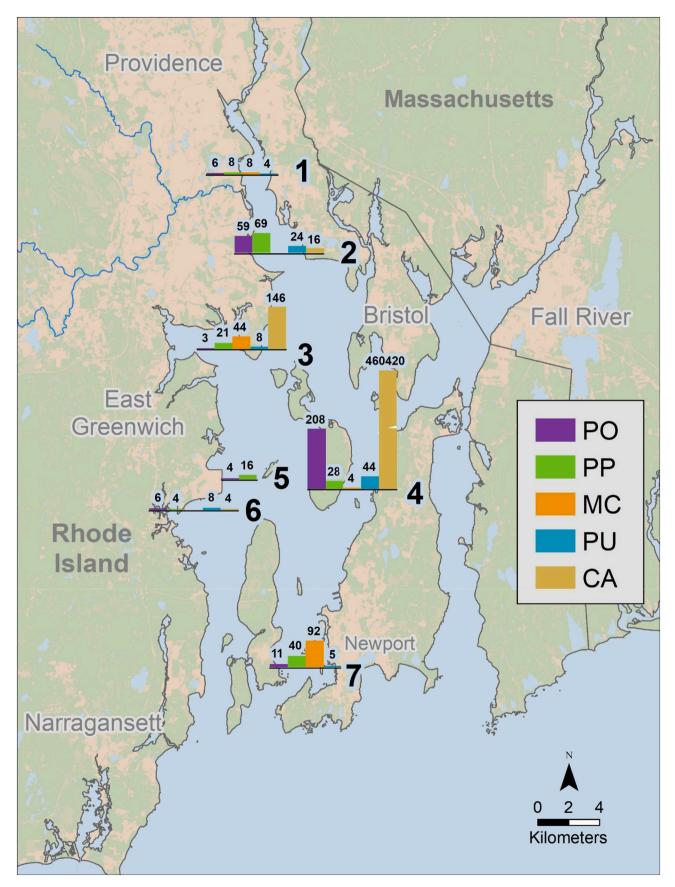


Fig. 5. Select Microplastics (MPs) displayed as number of MPs by the five most frequently occurring plastic types: cellulose acetate (CA) gold, polyurethane (PU) blue, Methyl cellulose (MC) orange, polypropylene (PP) green, and polyester (PO) purple. CA, PU, MC, PP, and PO non-detects are not shown on this figure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

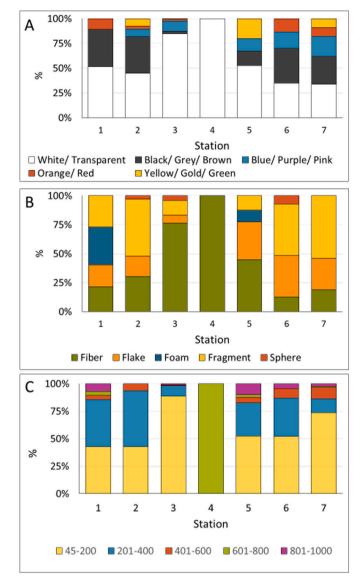


Fig. 6. Breakdown of Microplastics (MPs) by physical characteristics: percent frequency of MP by color (6A), shape (6B), and size (6C).

beaches, small-scale industry, commercial fishing, and residential housing (Dalton et al., 2010). Numerous textile manufacturers and processing companies within NB are known to have worked with cellulose fibers over the past century. The station with the highest MP abundance was Station 4, Arnold Point (Fig. 5). This sampling station is on the northwestern point of Aquidneck Island and south of Mount Hope Bay. Geographically this region has a strong history of textile production and boating industry. We believe these fibers could be from the manufacturing of cellulose acetate textiles used in marine industries.

6.3. Challenges with microfibers

Microfibers are often the dominant shape of MPs found in environmental samples (Claessens et al., 2011; Cole and Strawhecker, 2014; Lusher et al., 2014; Nel and Froneman, 2015; Nor and Obbard, 2014; Sanchez-Vidal et al., 2018; Willis et al., 2017; Woodall et al., 2014). Due to the high loss of microfibers in QA recovery samples, we believe our estimates of microfibers underestimate of microfiber occurrence in these sediments. Microplastic research techniques are constantly advancing capabilities to extract and identify MPs from sediments. Earlier studies that focused on MPs >300 μ m may have missed many of the fibers that

were caught in finer sieves or filters. This investigation was a survey of sediments across Narragansett Bay. To better understand the variability associated with the measurements reported here, a more intensive and expensive study would be required. However, despite this, these results are some of first to identify MPs in marine sediments from the North Atlantic Region. Further, these results show the wide variability of MP abundance, polymer type, size, shape, and color.

Modified cellulose particles are increasingly noted as one of the most commonly identified MP morphologies in environmental samples (Lenaker et al., 2020; Lusher et al., 2013; Remy et al., 2015), but the toxicity and effects of these fibers are not well understood (Athey and Erdle, 2021). Semisynthetic particles were previously thought to readily degrade and be less concerning than their synthetic counterparts. However, several studies have shown MPs often are ingested by benthic organisms including polychaetes (Wright et al., 2013), crustaceans (Watts et al., 2014), and bivalves (Von Moos et al., 2012) and studies by Bour et al. (2018) and Kim et al. (2021) demonstrated acute toxicity to benthic organisms. In addition, more recent studies note that semisynthetic fibers are digested and cause negative impacts in brine shrimp (Kim et al., 2021). The data emerging about the toxicity of modified cellulose fibers and other semisynthetic particles clearly demonstrates the need for further research. The stress of ingestion, retention, and exposure of associated chemicals are of great concern given the high MP concentrations (Andrady, 2011; Remy et al., 2015; Wright et al., 2013). This is especially true for particles with additional additives such as dyes and finishing additives (Athey and Erdle, 2021). The concentrations of MPs are particularly concerning to benthic deposit feeders (Morét-Ferguson et al., 2010).

7. Conclusion

Advancing methodologies for the extraction and identification of MPs from sediment is vital for predicting their impacts in the marine environment. The hybrid method presented here represents a harmonization of existing methods to extract a broad range of MPs from sediments. While no singular method can ensure complete recovery of all MPs from sediment, we believe the hybrid method is advantageous for its low cost, minimal waste generation, and favorable MP recovery. Using the hybrid method to extract MPs from Narragansett Bay sediments revealed very high concentrations of MPs, particularly cellulose acetate fibers. With the exception of Station 4, MPs 45-200 µm in size accounted for 42-88% of all MPs (Fig. 6c). This size class is not often reported in traditional extraction methods. We expect that higher MP abundances will continue to be reported as extraction methods advance. This suggests studies evaluating the toxicity of MPs may need to reassess the thresholds for environmental relevance in order to select spiking concentrations which realistically represent potential threats. These results signify the importance of adequately assessing MP abundance in sediments to better understand their risk and effects.

CRediT authorship contribution statement

Michaela A. Cashman: Conceptualization, Methodology, Investigation, Visualization, Validation, Writing – original draft. Troy Langknecht: Validation, Investigation, Writing – review & editing. Dounia El Khatib: Validation, Investigation, Writing – review & editing. Robert M. Burgess: Conceptualization, Validation, Formal analysis, Data curation, Writing – review & editing, Visualization, Project administration, Funding acquisition. Thomas B. Boving: Validation, Formal analysis, Resources, Data curation, Writing – review & editing. Sandra Robinson: Validation, Investigation, Data curation, Writing – review & editing. Kay T. Ho: Conceptualization, Investigation, Validation, Resources, Writing – review & editing, Visualization, Project administration, Funding acquisition.

Declaration of competing interest

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

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Appendix A. Supplementary data

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