Abstract

The abundance of microplastics in natural systems is a concern even in relatively pristine areas such as Lake Superior, on the border between the United States and Canada. In this study, beach sand and surface water were sampled in the Apostle Islands National Lakeshore (APIS) in May and July 2018. Additional sand samples were collected at non-APIS beaches in western Lake Superior in May 2018. Microlitter particles (<4 mm), consisting of microplastics and other low-density particles, were enumerated. Microplastics in sand samples, as identified by melt test, exhibited low abundances (0 to 55 particles/kg dry weight) and were mainly fibers. Microplastics in water samples were also low in abundance (9000 to 40,000 particles/km^2) and were mostly fibers. Pyrolysis gas chromatography (pyGCMS) analysis was performed on a subset of microplastics from the sand and water samples. All particles with identifiable mass spectra were polyethylene. When beach sands were processed by density fractionation and filtration, the resulting microlitter samples also contained 260 to 2630 non-plastic particles per kg dry weight. A subset of these non-melting particles was analyzed by Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS). Results indicated that both organic and inorganic particles were included within non-plastic microlitter. Re-analysis of additional aliquots of the same sand samples using oxidation in addition to density fractionation reduced the number of non-plastic particles by roughly half, further highlighting that many of these were organic. Post-oxidation surface-water microlitter (333 µm to 4 mm) also contained non-plastic low-density particles, which comprised 29 to 47 % of the total microlitter particle counts. Based upon color distributions, non-plastic microlitter particles in sand and water samples include a small portion of particles identifiable as anthropogenic. The sources for many microlitter particles cannot be distinguished at present and may be natural in origin.

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1. Introduction

Since the introduction of large-scale plastic production around 1950, plastics have become an important presence in human habitats and the open environment. Of the plastics produced since 1950 (estimated at 8300 $x10^6$ metric tons by 2015), 79 % is now waste present in landfills or the open environment (Geyer et al., 2017). As plastics are so prevalent and are relatively inert, there is the potential for them to be spread from population centers and other areas of input to remote regions of the earth by water currents and wind currents (Bergmann et al., 2019; Liss, 2020; Wichmann et al., 2019).

Microplastics, 0.001 to 5 mm (Lippiatt et al., 2013), in the environment overlap the size range of food sources for many aquatic biota or can become incorporated within particles acting as food sources. Plastic particles in the environment have also been found to contain additives and sorbed toxins (León et al., 2019; Zhang et al., 2018) and such chemicals could also impact the health of aquatic organisms ingesting these particles (Jovanović, 2017). Thus the prevalence of microplastics in aquatic environments is of concern for biological and ecological reasons.

This study was developed to investigate the prevalence of microplastics in beaches bordering western Lake Superior. We also wished to compare the abundances of microplastic particles in waters and beaches within a national park relative to nearby lake and beach locations. Located along the border between the United States and Canada, Lake Superior is the largest freshwater lake on Earth by area (Herdendorf, 1982) and contains approximately 10 % of our planet's liquid surface freshwater (http://www.seagrant.umn.edu/superior/facts). It is a relatively pristine and remote aquatic system with an average of 5.3 people per km^2 living within its watershed (Sterner et al., 2020). The highest population centers are Duluth, MN, USA and Superior, WI, USA, which are located at the far western shoreline of the lake and Thunder Bay, ON, CA located

49 midway along the northwestern shoreline (http://www.globalgreatlakes.org/lgl/superior/,
50 accessed February 13, 2020). Despite the lake's remoteness, it is a popular destination for
51 tourists (Sterner et al., 2020), many of whom visit the Apostle Islands National Lakeshore (US
52 National Park Service), which is within western Lake Superior.
53 Previous microplastic studies in Lake Superior have focused on surface water concentrations
54 in the lake (Eriksen et al., 2013; Hendrickson et al., 2018) and in two of its tributary systems, the
55 St. Louis and Nemadji Rivers (Baldwin et al., 2016). In these studies of microplastics ranging
56 from 0.333 to 5 mm in size, open lake waters exhibited concentrations somewhat lower than
57 (Eriksen et al., 2013) or somewhat larger than (Hendrickson et al., 2018) those found in the
58 North Atlantic Ocean gyre system (where annual averages for 2005 through 2008 ranged from
59 7000 to 19,000 counts/km^2, (Law, 2010)). The study by Ericksen and co-workers (2013), which
60 did not include fibers as microplastic particles, found primarily pellets and fragments in lake
61 samples. Hendrickson and co-workers (2018) found that 39 % of microplastic particles in
62 western Lake Superior were fibers, 34 % were fragments, and 21 % were films. Baldwin and co-
63 workers (2016) do not report the morphology of the Lake Superior tributary microplastics
64 separate from those of the other Great Lakes rivers but do find that 71 % of summed tributary
65 microplastics were fibers. Whether the differences between studies are due to variations in
66 plastic loadings (e.g., microbeads were banned in U.S. cosmetics in 2015,
67 https://www.fda.gov/cosmetics/cosmetics-laws-regulations/microbead-free-waters-act-faqs) or
68 due to differences in analytical procedure is difficult to determine.
69 There have been few studies of plastics in Lake Superior beach sediments. Previous studies
70 have focused primarily on macroplastics as part of beach clean-up projects (Driedger et al.,
71 2015). These have found fewer plastic particles and a larger proportion of non-plastic debris

(wood and metal storage and building materials, glass beverage containers, paper bags, batteries, clothes, tires, fireworks debris, condoms, etc) in Lake Superior relative to the other Laurentian Great Lakes. Note, however, that counts were not normalized to the area of beach in each lake that was surveyed and that the plastic vs non-plastic categories were somewhat arbitrary.

One existing study addresses microplastic particle abundance in Lake Superior beach sand. A beach on York Island, in the Apostle Islands National Lakeshore (APIS) was included in a survey of microplastics at 37 sites in US National Parks throughout the country (Whitmire et al., 2017) and was found to have the highest microplastic loading (in particles per dry kg of sample) of all the locations studied. York Island is a remote site, far from population centers and requiring a boat for access, so this result was surprising. As it was based upon one sampling event, there was considerable interest in seeing if high microplastic loadings occurred throughout western Lake Superior beaches. In addition, the microplastic abundances reported for the National Park samples (Whitmire et al., 2017) were technically microlitter (low-density particles from unoxidized samples identified only by microscopy) rather than confirmed microplastics. Initial follow-up sampling to identify microplastics (as determined by melt test and pyrolysis gas chromatography mass spectrometry) within APIS beaches did not yield high plastic abundances (Minor et al., unpubl data).

The study presented here investigates both microlitter and its component microplastic concentrations within beaches in western Lake Superior. We include beaches on the north and south shore of the lake, in APIS and on one of the world's longest freshwater sandbars (Park Point in Duluth, MN). We also measure microlitter and its component microplastics in surface waters within APIS for comparison with western and eastern lake non-park sites.

2. Material and Methods

2.1.Sampling

2.1.1. Sand

In May 2018, beach sand samples were taken from 7 sites in the Apostle Islands National Lakeshore and 4 sites outside the Lakeshore (Fig. 1 and Supplemental, Table A1). Sites 8 and 11 (see Fig. 1) are "upstream" of currents entering the lakeshore (Weber et al., 2020), and Site 11 is within the major population center (the "Twin Ports" of Duluth, MN and Superior, WI) for western Lake Superior. Sites 10 and 12 give context for beaches not impacted by currents flowing from Duluth and Superior via the St. Louis/Nemadji River entrance along the Wisconsin South Shore. Note that these rivers drain portions of Superior and Duluth, including areas occupied by an oil refinery, an active port area that receives lake and ocean-going vessels, and regional and municipal wastewater treatment plants.

In May, for each beach sampling event, 5 field replicates were obtained every 10 m along a horizontal transect midway between the waterline and the highest zone of storm wrack material (Fig. 2), (Whitmire et al., 2017). A field blank was taken during each sampling event by placing an open sampling container at the mid-point of the transect and leaving it open for the duration of sampling (Fig. 2). For each field replicate, a metal ring that has an area of 481cm^2 and a depth of 1.4 cm was placed into the sand. A metal spoon was used to move the sand from inside the ring (to a depth of 1.4 cm) into a clean ~ 1 L glass sampling jar. After each jar was filled, aluminum foil was placed between the jar and its lid to prevent the plastic-coated lid from potentially contaminating the sample.

In late July 2018, three beach sites (Sites 1, 3, and 7) were sampled using the same metal ring and spoon protocol. For these sites, samples were taken in a cross sampling pattern, with the vertical samples being between the upper storm line and the water, and the horizontal five samples being the same horizontal pattern as in the May sampling (Fig. 2). The field blank sampling container was placed next to the midpoint sample in these two transects.

2.1.2 Water

In May 2018, surface water samples were collected via Manta net tow on transects offshore of sites 7 and 9 and at a midpoint location within APIS (Fig. 1 and Supplemental, Table A2). In July 2018, Manta net tows were again taken offshore of sites 7 and 9. Net tows were performed using a 3m-long Manta net with a 333-µm mesh size. Net tow distance was determined via flowmeter and the width of the net opening was used to determine the area of water sampled. Prior to each sample collection, the net was rinsed with water near the collection site but without a cod end in place. Then, after adding a clean cod end, the manta net was towed for 500 to 1000 meters for each sample. The contents collected in the cod end were immediately sieved through a cascade consisting of 4 mm and 250 µm metal sieves. The material on the top sieve was removed and archived into ~ 1 L glass jars using a pair of forceps. The material on the 250 µm sieve was collected into separate 1-L glass jars using Milli-Q water to resuspend the particles and a pair of metal forceps to aid in particle transfer. The particles collected on the 250 µm sieve constitute the surface-water microplastics processed for this study. It should be noted that due to sample collection via Manta net, the size range for surface-water microplastics is different from that of the sand samples. However, it is consistent with previously measured surface water samples in Lake Superior (Eriksen et al., 2013; Hendrickson et al., 2018).

2.2. Sample processing

2.2.1. Sand

Sand processing followed previous protocols (Whitmire et al., 2017) with slight modifications in the upper sieving size range and in the choice of replicate samples to process. For the May 2018 sampling, two to three replicates from each sampling event (generally the two end points from the transect and the mid-point, Fig 2) were processed and analyzed. Each jar of sand was oven dried at 90 °C (Masura et al., 2015), usually overnight though sometimes longer. Dry mass of sample ranged from 821 g to 1665 g (average 1084 g). Each dried sample was sieved (twice) through a 4 mm metal sieve into a metal catch pan to remove larger particles such as rocks and sticks. The >4 mm particles were archived. 200 g of sieved material was processed for analysis (Whitmire et al., 2017). This aliquot of sand was removed from the catch pan under the sieve after the second sieving and sample homogenization with a metal spoon. It was density extracted in a 1-L glass jar with an aluminum foil seal and a metal lid. The remainder of the sieved material was returned to the original sample container. For density fractionation, NaCl solution (5 M, density 1.18 g/L) was chosen; the density of this solution was sufficient to float many plastics (though not PVC or PET) without floating much of the clay that also occurs along Lake Superior beaches. NaCl solution is also more environmentally friendly that other density extraction solutions. 250 mL of 5M NaCl solution, (certified ACS grade NaCl from Fisher Scientific) was added to each 200 g aliquot of sample. The sample plus salt solution was shaken for three minutes then left to settle for 2 hours. The supernatant was removed using a metal turkey baster with a rubber bulb and placed into a 1000-mL KIMAX bottle, sealed with a foil liner and then its plastic cap. The density-extraction process was performed a total of three times.

The pooled supernatant was filtered through a 0.45-µm gridded filter (MF-Millipore membrane filter) via vacuum using an all-glass filter rig capped loosely with aluminum foil. After the entire sample was filtered, Milli-Q water (~250 mL) was used to rinse away remaining salt. The filter plus sample was dried in a clean petri dish either at room temperature or at 90 °C for 5 to 10 minutes. The dried filter was then analyzed by microscopy as described below.

Partway through applying this method to May samples, we began filtering the NaCl solution through a 0.45 µm filter before using in the density separation process (e.g., Besley et al., 2017). Samples processed with unfiltered solution are marked in Table A3; blank data for both unfiltered and filtered solution are presented in Table A3 as well.

July samples were processed using the laboratory procedure described above with filtered NaCl solution. Samples processed were the end points from both horizontal and vertical transects and the midpoint sample (see Fig. 2).

For selected samples from both May and July sampling campaigns (marked with an asterisk in Tables A3 and A4), we performed an oxidation step after density extraction (Masura et al., 2015). The density fractionation was performed as described above. The sample was then resuspended from the membrane filter using ~ 10 mL of MilliQ water, transferred to a clean (previously combusted) glass beaker and was dried in an oven at 90°C. This dried sample was oxidized with Fenton's reagent at 75 °C (Hendrickson et al., 2018). At the end of the oxidation, the reaction was quenched by adding previously combusted NaCl in a ratio of 6 g salt to 20 mL of liquid. The sample was then filtered onto a MF-Millipore Membrane Filter (mixed cellulose esters filter, 0.45-µm pore size, gridded), rinsed with MilliQ water, and either allowed to dry at room temperature or dried in an oven at 90 °C for 5 to 10 minutes. This filter was then ready for microscopic analyses.

2.2.2. Water

Water sample processing followed previously published protocols (Hendrickson et al., 2018). Collected samples were transferred to separate pre-weighed beakers, loosely covered with aluminum foil and dried in an oven at ~ 90 ℃. The dried samples were then oxidized using Fenton's reagent at 75 °C. After oxidation, density separation was performed by adding solid sodium chloride to the oxidizing solution (6 g of previously combusted sodium chloride per 20 mL of liquid). After settling, each sample was filtered onto either a MF-Millipore Membrane Filter (mixed cellulose esters filter, 0.45-µm pore size, gridded) or a 250-µm Nylon filter (note: all particles from water samples should be >333 µm due to net mesh size and were further collected onto a 250 µm sieve prior to the oxidation step). The microlitter within the samples was then analyzed by microscopy with hot needle testing.

2.3.**Microscopy**

Microscopy was performed at 25X magnification using either an Olympus SZH10 Research Stereo Microscope or an AMSCOPE 3.5x-90x Stereo Zoom Microscope (SM-2TZ-10M) and particles were characterized morphologically as in Fig. 3. When scanning a sample filter, particles that were suspected to be plastic were moved to the side and tested with a hot needle (De Witte et al., 2014). If such a particle melted, it was deemed plastic and placed into a new sample vial. Note that this gives a conservative approach to plastics identification as it minimizes false positives but is subject to false negative responses (some materials considered plastic may burn or remain unresponsive upon application of a hot needle). Beach sand sample filters were scanned twice via microscopy to ensure complete particle counting.

2.4. Pyrolysis–gas chromatography/mass spectrometry (PyGCMS)

Plastic particles from both sand and water samples were characterized for their polymer composition using pyrolysis-gas chromatography/mass spectrometry (PyGCMS) following previously published protocols (Hendrickson et al., 2018). PyGCMS was also performed on empty clean quartz pyrolysis tubes handled only via metal forceps and on a tube handled directly with sampling gloves (glove blank). The instrumentation used was a pyrolysis and thermal desorption unit (TDU) by Gerstel GmbH & Co. KG, Germany coupled to an Agilent 7890B Gas Chromatograph and an Agilent 5977A mass-selective detector (MSD). In most cases, individual particles were analyzed; in two cases, two small particles from the same beach sand sample were analyzed together. The TDU was ramped from 50 ℃ to 300 ℃ at 720 ℃/minute and held at 300 ℃ for one minute prior to pyrolysis. Pulsed pyrolysis was performed for 20 seconds beginning at 550 ℃, ending at 500 ℃. A cooled-injection system liner (CIS) was used between the pyrolyzer and the GC inlet, which was operated in splitless mode. The CIS was set at 300 ℃ and increased to 320 ℃ at 12 ℃ per minute and was held at the final temperature for one minute. Gas chromatography was performed using a 30-meter Agilent HP-5MS column with the following temperature program: initial temperature 50 ℃ with a temperature ramp of 10 ℃ per minute to 320 ℃, which was held for 3 minutes. Mass spectrometry ionization was electron impact (EI^+, 70 eV, source temperature 230 ℃), and ions from m/z 10 to 550 were scanned.

The qualitative analysis program, MassHunter, was used to evaluate the pyrograms (total ion chromatograms resulting from pyrolysis) and the mass spectra resulting from this method. Mass spectra from individual peaks were compared with results from NIST and F-search (Frontier Laboratories, Ltd) library searches. Mass spectra integrated over the whole total ion

chromatogram (TIC) or a large portion of the TIC were compared with spectra from the PyGC-MS14.Demo portion of the F-search library. Mass spectra were also compared with PyGCMS analysis of standards reported in the literature (Hendrickson et al., 2018; Tsuge et al., 2011). Positive identification was defined as one of the following: 1. a match of >80 % in the F-search library with the mass spectrum summed over the entire TIC; 2. >85 % match in F-search for the mass spectrum over 3.3 to 17 minutes; 3. a match of the significant characteristics in the TIC along with the major m/z values for at least 3 of the key peaks described in the literature. A tentative match consisted of an 80 to 85 % match within F-search for mass spectra over 3.3 to 17 minutes. The peaks within the glove blank were individually identified by comparison with the NIST library.

2.5. SEM/EDS analysis

To further determine the chemical composition of both plastic and non-plastic particles, scanning electron microscopy (SEM) was used on two plastic particles from Station 2, May sampling campaign, and eight non-plastic particles from Station 5, May sampling. Selected particles for SEM analysis were individually mounted onto aluminum stubs with double-sided carbon tape. Samples were analyzed on a Jeol JSM-6490LV scanning electron microscope equipped with an INCAx-act energy dispersive x-ray detector for elemental analysis. A 15 kV electron accelerating voltage was used for imaging in high vacuum mode. Samples were imaged at 230x – 4,000x using the microscope's backscattered electron (BSE) detector. After imaging, all samples underwent electron dispersive x-ray spectroscopy (EDS) analysis for determination of elemental composition.

2.6. QA/QC

Clothing that was 100 % cotton or wool was worn during the collection of samples and cotton was worn during processing of samples, blanks, and positive controls to avoid contamination. All non-metal materials were cleaned with soap and water, acid-leached in 10 % HCl, and rinsed copiously with deionized water prior to use. In addition to these cleaning steps, glass supplies were then combusted 4 hours at 450 °C. Metal materials (sieves, forceps, turkey baster) were rinsed copiously with deionized water prior to use and between each sample processed. All solutions were made with reagent grade (or higher grade) chemicals and MilliQ water in glass containers cleaned as described above.

As a field blank, an empty jar identical to those used for beach sand sample collection was opened for as long as the sampling took place for each site. Field blanks gathered with the beach samples were processed alongside beach samples using the same density separation method. A method blank was also processed to determine the possible microplastic contribution from the salt solution, hydrogen peroxide, ferrous iron reagents and other possible sources in the lab. All blanks were filtered and analyzed using the microscopy methods described above. Field blank data was not used to correct sample counts as it was difficult to correct for varying morphology and color between plastics found in the blanks and the samples. Instead, field blank data is presented in the results section (and shown in Tables A3 and A4) along with the sample data. Method blank data is presented in Table A4.

In addition to field blanks, we instituted count blanks to monitor in-lab contamination. Count blanks consisted of clean petri dishes open to the lab environment while sample processing was conducted. Count blank results are shown in Table A4.

As a positive control, sand from Park Point, MN (near Site 11) was collected, sieved through a 4 mm metal sieve and ashed in a combustion oven at 450 °C for four hours to remove any previous microplastic burden. Thermogravimetric analysis has shown that onset of plastic loss occurs just above 200 °C and that 450 °C efficiently removes polystyrene, polymethyl methacrylate, PVC and PE (Zhou et al., 2019). The ashed sand was then split into two equal aliquots, which were each spiked with ten polyethylene (PE) spheres (Cospheric CPB-0.96, 600-710 µm) and ten polypropylene (PP) fragments, created with a lab grinder and approximately 3 mm in length. These spiked sand aliquots (Controls A and B) and a blank without sand but spiked with the same number of PE and PP particles were then subjected to density extraction, filtration, and microscopy as described above for the spring 2018 samples. Recoveries in each of the spiked sand samples were 9/10 PE and 10/10 PP particles. The recovery in the spiked blank was also 9/10 PE and 10/10 PP particles.

To expand the positive control to include oxidation, we resuspended the particles from the density positive control samples described above. In the spiked blank out of the original 10 PE and 10 PP particles, 5 PE whole spheres and 5 (probable, identified by microscopy and melt testing) PE fragments were found along with 10/10 PP particles. In Control A, 7 PE spheres and 6 probable PE fragments out of 10 original particles were found along with 11 PP particles. In Control B, 9/10 PE spheres and 10/10 PP particles were found. The results from the spiked blank and control A indicate that in some cases, the oxidation step appears to fragment the original plastic particles.

Positive controls for combined oxidation-density extraction of water samples have been performed using spiked MilliQ water samples and have been reported previously (Hendrickson et al., 2018). Briefly, mass recoveries were 93 % for PE, 77 % for PP, 78 % for PS, 81 % for

PET, and 12 % for PVC. The low recovery for PVC was likely due to its high density relative to the NaCl solution used for the density extraction. Mean count recoveries via microscopy were similar to the mass recoveries. Count recoveries were: PE (93.0 %), PET (80.8 %), PS (78.5 %), PP (76.6 %) and PVC (11.6 %).

2.7.Statistics

Statistical tests (F-tests, t-tests) were performed in Excel 2016 using the Analysis ToolPak. Type 1 linear regressions were also performed in Excel 2016 with the Analysis ToolPak and are reported relative to α=0.1 and α=0.05.

3. Results

3.1 Microscopy

3.1.1. Sand

Of the eleven beach sites sampled in May , melt testing showed that eight were positive for microplastics (Table A3), but at very low levels (5 to 55 microplastics per kg dry weight of sediment). The highest number of microplastics per kg dry weight was found at Meyers Beach (Site 7). All of the samples processed had a much larger number of microlitter particles that failed the melt test (250 to 2630 particles per kg). These low-density microlitter particles were visually indistinguishable from microplastic particles via microscopy.

To determine if there was a statistical difference between beach sands inside APIS vs those outside APIS, F-tests were first performed on park vs non-park abundances for non-plastic and plastic microlitter. Non-plastic microlitter particles had unequal variance at α=0.05 between park

and non-park samples and thus a t-test assuming unequal variances was performed. The microplastics did not exhibit unequal variance at α=0.05 and thus a t-test assuming equal variance was performed. The t-test results (two-tail, $\alpha = 0.10$) show that in May 2018 there was no statistical difference in the average values for park vs non-park samples for both non-plastic microlitter and microplastic abundances.

Sampling in July 2018 was performed on only three beaches (all within APIS). July samples came from both horizontal transects at the midpoint of the beach and vertical sampling from the waterline and the high wrack line. Of the 14 sand aliquots processed from the three beaches, 10 had plastic particles present (Table A4). As in May, the highest abundance of microplastics was at Meyers Beach (Site 7), where one of the wrack line samples had 35 particles/kg dry weight (7 particles/200g). While the number of vertical transect samples is small, the wrack line samples had generally higher abundances of plastic than the waterline or mid-beach samples.

The microplastics found in the beach sand samples ranged in size from 0.1 to 5 mm for their longest dimension. The majority (52 %) of these microplastics were fibers with films as the second most abundant morphology (28 %, Fig. 4 and Tables A3 and A4). In terms of color, 49 % were translucent or transparent and 25 % were blue.

The morphological distribution of microplastics in the sand samples differed from the that of the field blanks. Field blank microplastics were almost evenly split between fibers (46 %) and fragments (54 %) in May and exhibited no plastic particles in July (Tables A3 & A4). Note that the sources of these plastics in the May blanks may have included our earlier NaCl solutions. Two of these blanks were processed using unfiltered NaCl solutions and three blanks were processed using a filtered NaCl solution. Plastic particles were found in the blanks when

348 unfiltered NaCl solution was used. No plastics were found in the field blanks that were processed
349 using filtered NaCl solution (Tables A3 and A4).

350 For both May and July, samples isolated by density extraction (without oxidation)
351 contained a large number of non-plastic low-density particles, which were mainly fibers (97 %
352 fibers in May and 99.6 % fibers in July).

353 Oxidation of replicate sample aliquots reduced the number of non-plastic microlitter
354 particles. A one-tailed t-test was used to compare replicate aliquots of unoxidized vs oxidized
355 sand samples (n=3, from 3 different samplings, Tables A3 and A4) from the same homogenized
356 starting samples. There was no significant difference in the number of microplastic particles at
357 α=0.10. There was a significant difference in the number of non-plastic microlitter particles at
358 the same criterion ($p = 0.071$). It is likely that many of these microlitter particles sensitive to
359 oxidation were from natural materials in the Lake Superior region, such as catkins or plant
360 trichomes. The morphology and color distributions within oxidized beach sand samples relative
361 to unoxidized samples had a lower proportion of fibers and translucent particles (Figures 4B&C
362 and 5B&C).

363 To determine if the number of non-plastic microlitter and plastic microlitter particles
364 were related, a simple or type 1 linear regression with plastic particles as the explanatory variable
365 was performed (Fig. A1). When the y-variable was non-plastic microlitter from unoxidized
366 samples, there was no significant linear relationship with the number of plastic particles (at
367 α=0.10). When non-plastic microlitter from oxidized samples was used as the y-variable, the
368 resulting linear relationship was significant at α=0.10 (but not at α=0.05). This linear
369 relationship indicates that the non-plastic microlitter resistant to oxidation may have similar

source and transport processes to that of the microplastics, perhaps being more anthropogenic in nature.

3.1.2. Water

The water samples in APIS had microplastic abundances ranging from 9000 to 40,000 particles per km^2 (Table A5). These counts per area are good to only one to two significant figures due to the need for shorter net tows and thus the capturing of fewer microplastic particles per sample. Shorter tows were necessary because of loading from organic particles (especially in July) and because of the spacing between islands and the depth of water. The site with the most microplastics (40,000 particles/km^2) was MB, offshore of beach site 7, in July 2018. The second highest abundance of microplastics (19,000 particles/km^2) was for site LI in July. The July samples (ranging from 18,000 to 40,000 counts/km^2) were higher in microplastic abundances per area than the May samples (ranging from 9000 to 11,000 particles/km^2).

Particle size range differs between beach sand samples and water samples. The water sample microlitter particles are nominally <4 mm and >333 µm in size due to net tow collection while the beach sands (<4 mm) are density extracted and collected onto a 0.45-µm filter, with the lower size limit imposed by microscopic visibility. In terms of microplastic morphology, the water samples had a somewhat higher percentage of fibers (70 %) than did the beach sand samples (52 %). As in the beach sands, the second most abundant microplastic morphology in the surface water was film (Fig. 4D). The microplastics in the water samples had a wider range of colors than beach sand microplastics did (Fig. 5). The dominant microplastic colors in the water samples were blue and pink.

Non-plastic particles comprised between 29 and 47 % of the total microlitter particles in our water samples. Note that, unlike the sand samples, the oxidation step was applied to all water samples. The highest abundance of non-plastic microlitter (27,000 counts/km^2) was at the same site (MB) and sampling time (July) as the highest abundance of microplastic litter. However, likely in part due to the small number of water samples, there is not a statistically significant relationship between the non-plastic and plastic microlitter abundances for the oxidized water samples (Fig. A1.C)

The non-plastics in surface water were primarily fragments (55 %) and fibers (21 %) (Fig. 4E). The main colors of the non-plastic microlitter particles were white (27 %) and translucent (27 %).

3.2. SEM/EDS

We analyzed a sub-set of plastic and non-plastic particles from our density separations using SEM/EDS. Two plastic particles and eight non-plastic particles from beach sand samples collected in May 2018 were analyzed using this method. Melt testing had shown that the fiber in Figure 6A was plastic, and the EDS spectra are consistent with this, showing a high carbon (C) content. The non-plastic fibers tested by SEM and EDS show a mixture of carbon containing particles (e.g., Fig 6B) and non-carbon mineral particles (Fig. 6C). Additional particles tested are shown in the Supplemental (Figure A2). The inorganic particles appear to be mainly silicates or aluminosilicates, based upon amounts of aluminum, silicate, and oxygen, although one (Fig A2D) has high iron content as well.

3.3.PyGCMS

24 individual plastic particles and 2 sets of combined particles (2 per sample tube) out of the 94 total microplastics identified in beach sands were analyzed by pyGCMS. These included particles from oxidized and unoxidized samples and both sampling periods. Of these, 4 samples were identified as polyethylene with 2 additional particles tentatively identified as polyethylene. The rest (18) were unidentified and appeared in many cases to be mixtures of polymers.

35 plastic particles out of the 50 total microplastics identified in surface water samples were analyzed by pyGCMS. These included particles from both May and July sampling events and were all from oxidized samples. Of these, 4 were identified as polyethylene (PE), 4 exhibited carryover problems from previously measured standards, 16 had very low signal, and 11 were unidentified based upon current standards and available libraries. Many of these appeared to contain mixtures from multiple polymer types.

PyGCMS analysis was complicated by the small size of many of the fiber particles and by a contaminant signal (see Supplemental, Fig A6) that occurred because the mass spectrometry operator handled the pyrolysis sample tubes directly (rather than using metal forceps) while wearing nitrile gloves. In splitless mode (necessary because of the small sample sizes) such direct handling of the sample tubes led to a signal primarily of C16:0 and C18:0 methyl esters derived from the gloves. This was determined by comparing tube blanks handled only by contact with metal forceps (which yielded essentially no signal) with a tube blank handled with gloves (Supplemental Fig A6).

4. Discussion

4.1. Sand

Western Lake Superior beaches exhibited low abundances of microplastics, ranging from 0 to 55 microplastic particles per kg sediment. These abundances are similar to those found in beaches in Auckland, New Zealand and in northern France, Portugal and Slovenia (Table 1). The main morphology for Lake Superior's beach microplastics across all samples (oxidized and unoxidized) was fibers (52 %), followed by films (28 %) and then fragments (18 %). The main colors were translucent (33 %) and blue (25 %). In a brief survey of recent microlitter/microplastic studies on beaches across six continents (Table 1), 13 out of 20 studies (including ours) found fibers as the dominant morphology. Only a small subset of Lake Superior beach sand microplastic particles were successfully identified by pyGCMS; these were all polyethylene. Polyethylene has been identified as a dominant identifiable polymer in analysis of microplastics in other beach studies (Doyen et al., 2019; Pannetier et al., 2019; Yu et al., 2016)

When compared to microplastic abundances, Lake Superior's beach sands showed a much higher abundance of non-plastic, low-density microlitter particles. The ratio of non-plastic microlitter to microplastic particles in unoxidized samples ranged from 21:1 to 454:1 for those samples that contained microplastics. The total microlitter counts (plastic plus non-plastic) in our unoxidized samples (260 to 2635 particles per kg) are consistent with previous beach microlitter studies using density extraction without an oxidation step and relying on microscopic identification of particles (range 80 to 2300 particles/kg, Table 1). The abundances we find in APIS beaches are generally higher than previously reported for an APIS beach site where the same microlitter isolation protocol was performed (155-285 particles/kg, (Whitmire et al., 2017)). The previous study reported results as "microplastic" although they performed no analyses to further confirm their microscopic identifications. We found that few of our microlitter particles appeared plastic when tested via hot needle. Further work, however, needs

461 to be done to better classify microlitter particles as microscopy alone yields false positives and
462 yet melt testing can yield false negatives when certain plastic types are tested.
463 Some recent studies have coupled microlitter abundance data with further compositional
464 information on what proportion appears to be microplastic (Bayo et al., 2019; Korez et al., 2019;
465 Robin et al., 2020). Bayo and coworkers (2019) found that 50 % of their microlitter particles (<5
466 mm, >45 um) were plastic when FTIR was applied. Korez at al (2019) report that 11 % of their
467 beach microlitter particles (<5 mm, >100 µm) were found to be plastic via FTIR. In our study,
468 the maximum percentage of microplastic within microlitter from density extracted, unoxidized
469 sand samples was 4.5 % and was found at Meyers Beach in May 2018.
470 Consistent with previous findings (Table 1), the microlitter particles isolated by density
471 extraction from Lake Superior beach sands were mainly fibers. These fibers were predominantly
472 translucent. A predominance of "uncolored" fibers (mainly translucent but including black,
473 brown, and beige as well) has been found in remote beach sands from Saxony's Wadden Sea
474 National Park and was attributed to "probable natural origin" (Nuelle et al., 2014). Natural origin
475 is likely for many of the Lake Superior beach sand fibers as well.
476 Investigation of a subset of non-plastic particles by SEM/EDS showed that both organic and
477 inorganic (silicate and aluminosilicate) particles were included within microlitter in Lake
478 Superior beach sands. Oxidation, which is used to remove natural organic particles in samples,
479 was applied to replicate aliquots of beach samples from both May and July. There was a
480 reduction in microlitter counts in the oxidized aliquots relative to matching unoxidized aliquots,
481 further confirming initial SEM/EDS results indicating organic content in selected non-melting
482 microlitter particles. Previous studies that have investigated the composition of non-plastic
483 microlitter in beach sands have reported calcium carbonate, chipboard (a wood fiber product),

484 silica dioxide, and cellulose (Bayo et al., 2019) and wool, cashmere, and dog fur (Korez et al.,
485 2019). Studies of microplastics in Great Lakes water, sediment and beaches have reported the
486 presence of shell material, cellulose and rayon/cotton (Dean et al., 2018) and, in Great Lakes
487 water samples, coal ash and fly ash. While one of our particles analyzed by SEM/EDS could be
488 coal ash/fly ash (see Supplemental, Fig. A5), the predominantly fiber morphology in most of our
489 samples indicates that coal ash and fly ash are not a major component of the microlitter on Lake
490 Superior beaches. Instead, Lake Superior beach microlitter particles appear to be mainly organic
491 fibers (which could include cellulose, wool, dog fur, natural plant fibers, etc.) and fibrous
492 inorganic material (which could be natural or anthropogenic).
493 There was no significant relationship between microplastic abundance and non-plastic
494 microlitter abundance in unoxidized samples. However, upon oxidation, there is a linear
495 correlation ($p=0.058$). This, in conjunction with the shift in color distributions (the reduction in
496 percentage of translucent materials), indicates that the anthropogenic proportion has been
497 increased upon oxidation. It remains unknown at the present time, how much of the oxidized
498 microlitter is, in fact, anthropogenic.
499 The relationships between location and microplastic and non-plastic microlitter abundances
500 were investigated in May beach sand samples. The highest concentration of microplastics was
501 found at Meyers Beach. This is the most easily accessible of the APIS beaches in this study and
502 is a popular launching spot for kayaking tours. Unoxidized beach sand samples from park vs
503 non-park sites were compared by t-test, with one test comparing microplastics within and outside
504 of the park and the second comparing non-plastic microlitter within and outside the park. No
505 statistically significant difference was found in the abundance of either microplastic or non-
506 microplastic microlitter particles in park vs non-park sampling sites. The microplastic result may

be due in part to the low human population density, which reduces point sources for the plastics, in the Lake Superior watershed. The long water residence time in Lake Superior, coupled with long lifetimes for microplastic particles, could also be contributing factors. These would allow microplastic particles to be mixed through the lake, thus masking source effects within abundance distributions. The non-plastic microlitter result could be a function of some of the same factors as for microplastics or due to natural sources for a majority of these particles.

In July, when vertical beach transects were included in the sampling scheme, the high wrack samples were generally higher in microplastic abundance than the mid-beach or waterline samples. The highest abundance of microplastics was found at Meyers Beach in the wrack line sample. The higher plastic abundance at the wrack line, coupled with the higher abundance of microplastic particles at the most popular beach for tourism, indicates that the plastics probably have more of a land-based source than a water source. The role of storm transport, however, cannot be discounted with the available evidence.

4.2.Water

Microplastics in water samples from APIS ranged from 9000 to 40,000 particles/km^2, averaging 19,000 particles/ km^2, generally higher than seen in Lake Huron waters, similar to the average value for Lake Michigan, and lower than the average for Lake Erie (Hendrickson et al., 2018). The highest abundance was seen at site MB in July 2018. This site is on the western side of APIS and is the most likely APIS site to be affected by currents coming from the Duluth/Superior urban area (Weber et al., 2020). It is also the site most likely affected by local tourist activity as it is offshore of the most easily accessible and popular APIS beach.

The average microplastic abundance seen in APIS, 19,000 particles/km^2, is between the average areal abundances seen for eastern and western Lake Superior, 5400 and 37,000

particles/km^2, respectively (Table A5, Eriksen et al., 2013; Hendrickson et al., 2018). Note that the eastern lake study (Eriksen et al., 2013) did not include fibers, while the western lake study (Hendrickson et al., 2018) found 39 % of identified microplastic particles to be fibers. However, even adjusting the western lake figures downward by 39 %; the eastern lake average remains 4 times lower that the western lake average. Eastern Lake Superior has a considerably lower human population in its watershed area than western Lake Superior does, which might explain the difference in microplastic-particle abundances for these two regions. Microplastics within APIS were more strongly dominated by fibers (70 %) relative to microplastics from non-APIS locations in western Lake Superior (39 % fibers, (Hendrickson et al., 2018)). The only identifiable polymer in the APIS water samples was polyethylene, while in non-APIS locations PVC, polypropylene and polyethylene were found to be the most dominant polymers (Hendrickson et al., 2018)

Non-plastic particles comprised between 30 and 47 % of the total microlitter particles in our western Lake Superior water samples. These particles were resistant to the oxidation step applied to all of these samples. They consisted primarily of fragments (53 %) and fibers (23 %) and were predominantly colors that could be ascribed to natural sources (translucent, white, blank, transparent, brown, grey). Only 10% were an unambiguously anthropogenic color (blue). A previous survey of surface waters in three Laurentian Great Lakes found coal ash and fly ash (both consist of aluminosilicate) in 38 % of their samples (size range 0.355 to 1 mm); the aluminosilicates comprised an average of 20 % of the particles in these samples (Eriksen et al., 2013). Coal ash might be characterized visually as fragments. Non-plastic fibers have been found previously in Lake Superior surface waters (Hendrickson et al., 2018); a subset of these was identified as cotton based upon pyGCMS analysis.

5. Conclusions

Microplastic abundances in sand from Lake Superior's beaches (n=12) were highest at the most popular tourist beach within the Apostle Islands National Lakeshore (APIS), though still low relative to beach sand studies from throughout the world. Microplastic abundances in water samples from APIS were generally lower than found in non-park western Lake Superior and higher than found in the more remote eastern Lake Superior region. Both beach sand (unoxidized) and water samples (oxidized) contained a large proportion of microlitter particles that were not plastic as determined by melt testing. For unoxidized beach sand samples, the dominant non-plastic particle morphology was fiber (99 %) and the dominant color (93 %) was translucent. These non-plastic microlitter particles included both organic and inorganic particles. Non-plastic particles in oxidized water samples were mainly fragments (53%) and fibers (23%) with white and translucent as the most prevalent colors. Microplastics in unoxidized beach sands were approximately two orders of magnitude lower in abundance than the non-plastic microlitter; oxidation of replicate samples roughly halved the non-plastic microlitter abundances. The dominant morphology for beach sand and surface-water microplastics was fiber (52 % and 70 %, respectively). PyGCMS analysis of beach sand microplastic particles was complicated by the small size of these particles and by results indicating a mix of plastic polymers. However, 23 % of the tested particles appeared to be polyethylene. PyGCMS analysis identified 11% of tested microplastics from water samples as polyethylene. Our results show that visual microscopy is insufficient for identifying microplastics in environmental samples. Additional tests to strengthen microplastics identification could include hot needle tests, FTIR, Raman, PyGCMS,

and SEM/EDS. The sources and roles of non-plastic microlitter within the environment remain an open question.

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744 Table Captions:

745

746 Table 1. A comparison of this study's findings with those of previous microlitter and

747 microplastic studies. Y=yes, N=no, NR=not reported in these units (or units easily convertible to

748 these units).

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751 Figure Captions:

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753 Figure 1: Map of the beach sand sampling sites (numbers) and the water sampling sites (MB, ST,

754 and LI). For further site information see Supplemental: Tables A1 & A2.

755

756 Figure 2. The sampling scheme used in May 2018 (horizontal transect only, samples A through

757 E) and July 2018 (both horizontal and vertical transects, samples A through E and 1 and 4). FB is

758 the field blank. Note that horizontal samples are separated by 10 m; vertical samples were closer

759 together and determined by the distance between the water line and the high wrack line at each

760 beach sampled in July.

761

762 Figure 3: Visual morphology classification of both plastic and non-plastic particles used for all

763 the samples. Note that the "other" category is usually a combination of two categories (i.e., long

764 fragment). The pictured particles are from known materials found around the lab; fibers were

765 pulled from a winter hat, the fragment was from a soda bottle, the film was from bubble wrap,

766 the foam was from a packing peanut, the bead was from a polyethylene standard, the "other" is

767 from the same soda bottle as the fragment. Microscopy was 25X using an AMSCOPE 3.5x-90x
768 Stereo Zoom Microscope (SM-2TZ-10M).
769
770 Figure 4. The summed morphology distributions for May and July samples. A. Beach sand
771 microplastics; B. Non-plastic microlitter in unoxidized beach sand samples; C. Non-plastic
772 microlitter in oxidized beach sand samples; D. Microplastics in water samples, E. Non-plastic
773 microlitter in the water samples, which were all oxidized prior to analyses. The total number of
774 particles of each morphology are included in each pie chart. Data are not blank corrected (see
775 Supplemental, Tables A3-A5 for blank information). Note: there were no microplastics found in
776 the counting blanks for the water samples.
777
778 Figure 5. The summed color distributions for May and July samples. A. Beach sand
779 microplastics; B. Non-plastic microlitter in unoxidized beach sand samples; C. Non-plastic
780 microlitter in oxidized beach sand samples; D. Microplastics in water samples, E. Non-plastic
781 microlitter in the water samples, which were all oxidized prior to analyses. The total number of
782 particles of each color are included in each pie chart. Data are not blank corrected (see
783 Supplemental, Tables A3-A5 for blank information). Note: there were no microplastics found in
784 the counting blanks for the water samples.
785
786 Figure 6. SEM/EDS data for the following particles from beach sands sampled in May 2018: A.
787 A particle from Site 2 found to be plastic by melt test. B and C. Particles that did not melt, thus
788 considered non-plastic, from Site 5. Sites analyzed by each EDS spectrum are labeled, with the
789 resulting elemental data for each spectrum given in percentages.

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