ACS ES&T Water

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Article

Microplastics in the Water Column of Western Lake Superior

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Cite This: https://doi.org/10.1021/acsestwater.2c00169

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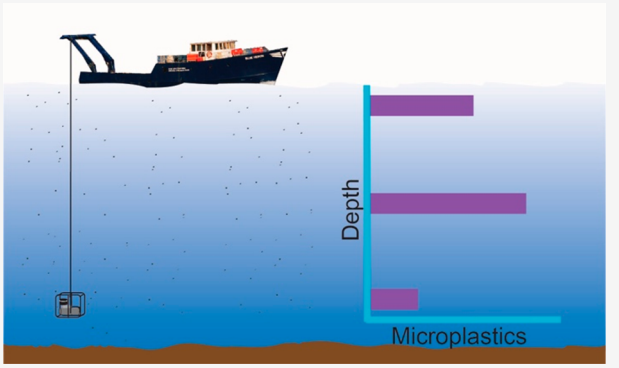
ABSTRACT: Microplastic contamination of surface waters, sediments, and shorelines of the Laurentian Great Lakes has received substantial attention. However, little is known regarding the presence of microplastics in the pelagic water column within these freshwater systems. We sampled the water column and the air−water interface at four locations in western Lake Superior. Our results show that microplastics are present in the Lake Superior water column under both stratified and unstratified conditions. The depth distributions found at the Lake Superior sites suggest that, to understand the total load of microplastics, it is insufficient to extrapolate from surface water concentrations alone. Additionally, we investigated the relationships between microplastic abundance and water column characteristics (e.g., temperature or clarity); no significant correlations were found across all sample sites. Finally, we developed an automated computational pipeline to detect microplastics based on hyperspectral data gathered via FTIR microscopy. The automated approach was capable of accurately detecting relative differences in microplastic abundances but consistently overpredicted particle abundance as compared to manual analysis of both natural and control samples. This research extends our understanding of the distributions of microplastics within large lake systems and develops a new tool for automatic detection of microplastics in natural samples.



KEYWORDS: *plastic pollution, natural samples, FTIR microscopy, Great Lakes*

INTRODUCTION

The formal characterization of microplastics in 2004 by Thompson et al.[1] was brought about by the realization that small plastic fragments were not accounted for by standard surveys of larger littoral plastic waste. In this seminal paper, a call was made for the development of techniques to quantify the amount of microplastic present in the environment.[1] Since that time, thousands of studies have addressed the issue of anthropogenic microplastics and their entry into and movement through the environment (September 2021 Scifinder search: microplastics). A significant portion of this research has focused on the transportation dynamics,[2] accumulation,[3] and breakdown[4] of environmental microplastics in aquatic systems. Attending the rise in microplastic research activity has been the development of a suite of commonly used sampling methods, such as manta nets for sampling the air−water interface[5,6] and grab samplers for bulk sediment sampling.[6−8] Although far from uniformly standard, the use of manta nets with 333 μm mesh has become common enough[5] to enable the facile comparison of results between studies, allowing for a better understanding of relative microplastic abundances across aquatic systems where such sampling has occurred.

Recently, however, it has been suggested that the number of microplastics in the water column may not correlate well with the number of microplastics sampled from the air−water interface, and therefore total microplastic loads based on manta net sampling alone may be inaccurate.[9] This has brought about a situation similar to the one originally encountered in 2004, whereby standard sampling techniques do not account for the total amount of microplastics in the environment. Specifically, surveys of microplastic waste at the air−water interface and in surface sediments do not accurately account for the total load of microplastics in aquatic systems. Published examples of water column sampling in the ocean remain limited due to the increased difficulty of deep-water sampling, and methodologies remain disparate. Several promising water column sampling techniques have included in situ filtering using McLane pumps[10] or custom in situ pumps[11−13] and volume-sampling using Niskin bottles.[14,15]

Received: April 15, 2022
Revised: August 15, 2022
Accepted: September 7, 2022

Despite making headway toward an improved understanding of microplastics in the marine water column, to our knowledge, no research has attempted to characterize the vertical distribution of microplastics throughout the water column in any freshwater lentic system, including the Laurentian Great Lakes. Although a significant amount of research has been conducted regarding microplastics in the surface waters,[16−19] sediments,[20−22] and tributaries[9,23] of the Great Lakes, the water column itself remains conspicuously undersampled and uncharacterized.

In 2019, Lenaker et al. characterized the vertical distribution of microplastics in the lotic environment of the Milwaukee River Basin.[9] This study also included one shallow (15 m) lentic sampling location in Lake Michigan, outside the Port of Milwaukee, that was sampled by towing 333 μm mesh neuston nets fixed at five depths including the surface. At this location, the average concentration of >333 μm microplastics in the water column over four sampling trips was 0.42 particles m^{-3}, and the distribution of microplastics did not vary significantly with depth.[9] The depth-invariant microplastic concentration may be expected at this shallow near-shore location, which is more likely to be mixed by storm events, winds, and currents than a stratified water column in the open lake. Nonetheless, characterizing the vertical distribution of microplastics in the water column of Lake Michigan was not the objective of that research, and the nearshore lentic sampling location was included only for comparison to riverine sampling locations.

The objective of this study was to perform the first characterization of the vertical distribution of microplastics in a lentic water column. Herein, we sample multiple locations in Lake Superior using in situ pumping, a technique that has not previously been used within the Great Lakes for microplastic research. While there exists a growing body of data regarding the concentration of microplastics in the surface waters of Lake Superior,[16−19] in order to better estimate the total load of microplastics in the lake, it is important to understand concentrations of microplastics in the water column and how they relate to surface water concentrations. To compare surface water concentrations to water column concentrations, we performed manta net sampling along with in situ pumping at various depths at each location.

To further extend our understanding of microplastic distributions, this work also sought to develop an effective methodology for the quantification and characterization of smaller microplastics (<333 μm) by collecting particles >100 μm using in situ McLane pumping and filtering followed by analysis using FTIR microscopy (μFTIR). Although the use of μFTIR to count and characterize microplastics has received extensive attention in the literature,[24−28] it remains a challenge to obtain quality IR spectra with this technique. In the literature, approaches to IR spectral acquisition and analysis have so far been ad hoc, time-intensive, or reliant upon highly advanced instrumentation that is not widely available. Using μFTIR to obtain quality IR spectra from microplastics in environmental samples (which include organic and inorganic matrices) is a substantially greater challenge than spectrally identifying known microplastics placed on an otherwise clean filter. While the use of focal-plane array FTIR spectroscopy with automated analysis has led to impressive breakthroughs in microplastic characterization,[27,29,30] such an approach is often unavailable to research groups and remains subject to the challenges of working in complex environmental matrices. By way of several simplifying assumptions, our work provides an automated approach for environmental samples available to laboratories that do not have access to these specialized instruments. In this research, we present an automated data analysis pipeline for μFTIR spectra, written in Python and enabling the automatic detection of microplastic particles in natural samples. Because excellent quality IR spectra are difficult to obtain using reflectance μFTIR spectroscopy, our efforts herein focus on microplastic identification and enumeration rather than identifying the polymer macromolecule. To the best of our knowledge, this is the first study using μFTIR spectroscopy to quantify, rather than solely characterize, microplastic particles in the Laurentian Great Lakes.

MATERIALS AND METHODS

Water Sampling. Four sites in Western Lake Superior (Figure S1) were sampled in August 2020, when the water column exhibits temperature-driven density stratification. Site A is closest to the largest population center in the region, and site B is a deep-water location; site C is located along the shallow South Shore, and site D, also along the South Shore, is near the mouth of the Nemadji River. Site B was resampled in May 2021, when the water column was well-mixed.

The air−water interface at each location was sampled with an NQS-45-60 manta net (333 μm mesh) following previous protocols.[16] Water-column sampling was by in situ filtering using WTS-LV McLane pumps (McLane Research Laboratories, East Falmouth, MA). At each site, prior to McLane pump deployment, water column characteristics were measured using a conductivity−temperature−depth (CTD) sensor (SBE 911plus CTD, Sea-Bird Scientific, Bellevue, WA), a Wetlab CStar transmissometer, and a WetStar Chl a fluorometer, (Sea-Bird Scientific, Philomath, OR). For August 2020 sampling, a 100 μm nylon mesh filter (McMaster-Carr, Elmhurst, IL) was placed in the McLane pump filtration manifold. During May 2021 sampling, 300 and 100 μm nylon mesh filters were placed serially in the filtration manifold. After pumping, filters were placed in combusted glass storage jars with Milli-Q (MQ) water to prevent drying of collected material before further processing. The pump was backflushed and primed with MQ water, and the filter housing was rinsed with MQ water between each sampling deployment.

Processing. Particles were resuspended from the mesh filters by placing sample jars in an ultrasonic bath (Ultrasonic Cleaner, Branson Cleaning Equipment Company, Shelton, CT) for 5 min. Each filter was then thoroughly rinsed with MQ water and removed; the resuspended sample was dried in an oven at 90 °C. Nonplastic organic and inorganic material was removed by oxidation followed by density separation using saturated NaCl solution, similar to the protocol of Hendrickson et al.[16] Supernatants from the 300 μm McLane pump samples (May) and the 333 μm manta net samples were filtered onto 47 mm diameter, gridded, 0.45 μm mixed cellulose ester (MCE) filters (MF-Millipore membrane filter, MilliporeSigma, Burlington, MA) for analysis via optical microscopy. Supernatants from the 100 μm McLane pump samples were filtered onto 25 mm diameter, 0.2 μm aluminum oxide filters (Anodisc, MilliporeSigma, Burlington, MA) for analysis via FTIR microscopy. Filters were stored in clean, previously combusted glass Petri dishes for subsequent analysis.

Optical Microscopy. Optical microscopy was performed using a 3.5−90× LED trinocular zoom stereo microscope with

https://doi.org/10.1021/acsestwater.2c00169
ACS EST Water XXXX, XXX, XXX−XXX

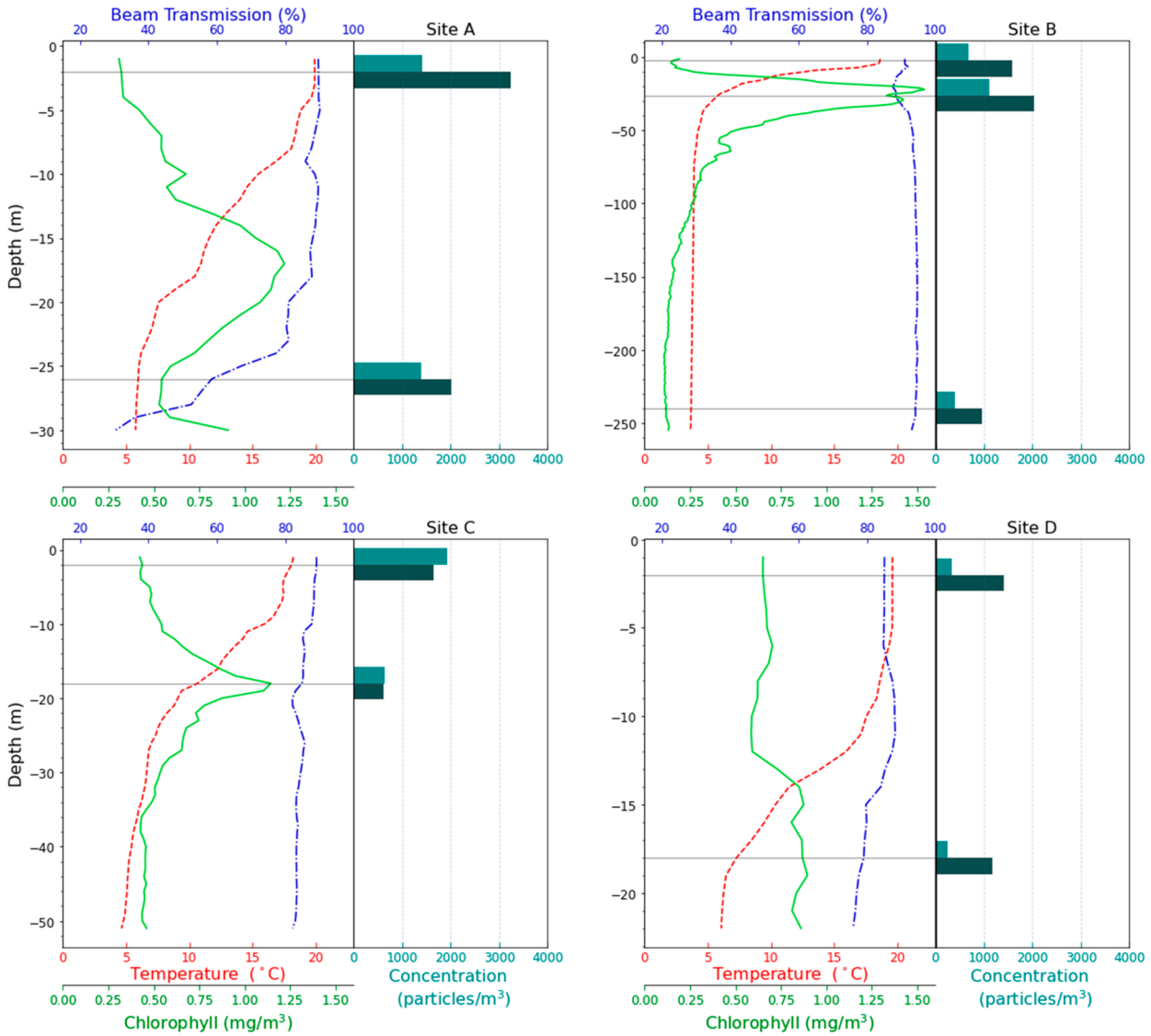


Figure 1. Water column characteristics and microplastic particle concentrations (>100 μm, collected via McLane pump) for sites A–D in August 2020. Gray horizontal lines show the depths of microplastics sampling. Chlorophyll concentration is shown in green (solid line), water temperature in red (dashed line), and beam transmission percent in blue (dot-dashed line). Dark teal bars correspond to computationally detected particle concentrations that were normalized by an empirically determined correction factor of 1.785 and light teal bars to manually detected microplastic particle concentrations, based on μFTIR spectral data.

a 10 megapixel digital camera (Amscope, Irvine, CA). Potential microplastic particles (see Figure S2 for example particles) were subjected to a hot needle test.[16] Particles identified as plastic and large enough to be handled with metal forceps (~200 μm) were placed in labeled vials for validation via ATR-FTIR.

ATR-FTIR was performed using a diamond crystal on a Nicolet iS50 FTIR instrument (Thermo Fisher Scientific, Waltham, MA). Each background-corrected sample was chemically interrogated with 64 scans at a resolution of 4 cm^{-1}. Microplastics in sample spectra were identified by comparison with standard spectra from the Hummel Polymer Library preloaded in OMNIC Series software (Thermo Fisher Scientific, Waltham, MA).

FTIR Microscopy. FTIR mapping of the 100 μm McLane pump samples was performed using a Nicolet continuum infrared microscope in reflectance mode coupled to a Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA) after optimization of instrument settings (Figures S3 and S4); see the SI for setting details. The same aluminum oxide filter background was used to correct spectra in all mapping experiments. Because scanning an entire sample filter was prohibitively time-consuming, ten randomly chosen 2.05 mm × 2.05 mm fields of view (chemical maps) were acquired from each filter, which together constituted ~21% of the effective filter surface area. The resulting chemical maps were both manually and computationally analyzed using the C–H signal at 2850 cm^{-1} to identify plastic particles. A strong signal in this region is characteristic of most plastic polymers, and the minimal signal in this region from natural organic matter (NOM) should be further minimized by the removal of most of this NOM via the Fenton oxidation step used in sample processing.

More details about the materials and methods, including details on method validation, computational analysis, and blanks/controls, can be found in the Supporting Information.

https://doi.org/10.1021/acsestwater.2c00169
ACS EST Water XXXX, XXX, XXX–XXX

RESULTS AND DISCUSSION

Quantification of Water Column Microplastics. Microplastics (>100 μm) were detected at every sampled depth at all locations sampled (Figure 1). This is the first data to confirm that microplastics are present throughout the water column of Lake Superior, as prior work in the lake focused on sampling shorelines,[31−33] sediments,[16] and surface waters.[16−18,34] The highest concentration of microplastics in the water column as detected by manual analysis of the μFTIR spectral data was 1900 particles m^{-3} from a depth of 2 m at site C and the lowest concentration was 250 particles m^{-3} from a depth of 18 m at site D. Relatively high concentrations at the surface at each site may be due to the sources of microplastics to the lakes, which include aerial deposition, riverine inputs, and runoff,[16,17] which tend to deliver particles to surface waters, or due to the buoyancy of microplastics, which are generally less dense than water. Nonetheless, in the absence of replicate samples at each site and depth, and due to the demonstrated variability of microplastic concentrations between manta trawls,[34] it is not possible to make definitive conclusions about the specific vertical or horizontal distributions of microplastics determined in our study. Note that all sites showed evidence of a stratified water column during sampling in August 2020, indicating that surface water and deep water (generally below 20−25 m) were not in exchange at this time. By manual analysis, microplastic concentrations did not appear to be higher near the population center, though processing of more than four sampling sites would be needed to definitively determine distributions relative to anthropogenic stressors.

To further evaluate the relationship between depth, water column characteristics, and microplastic counts, the deepest-water site (B) was resampled in May 2021. Counts of 100−300 μm microplastics, determined by manual analysis of μFTIR spectral data, were added to counts of >300 μm microplastics, determined by visual microscopy analysis for comparison to the August data that consisted of all particles >100 μm and less than 4 mm. The May data yielded uniformly lower concentrations (Figure 2, panel 2) than in August 2020 (Figure 1, site B), at times by an order of magnitude. In May, the majority of the microplastics particles at all depths was in the smaller size fraction (100−300 μm).

Because the water columns in August vs May had different physical characteristics (stratified in August; well-mixed in May), in order to estimate the total number of microplastics in the water column in August relative to the total number in May, stratification had to be accounted for. We estimated the total load of microplastics contained in a hypothetical column with a 1 m × 1 m cross section extending from the water surface to the lakebed in each sampling month. For the stratified August column, depths from 0 to 10 m were assigned the concentration detected at 2 m, depths from 10 to 40 m the concentration detected at 40 m, and depths from 40 to 250 m the concentration detected at 240 m. For the well-mixed May column, the average of these three sampling depths was assigned to the entire water column. The microplastic abundances in these hypothetical water columns were then summed. It was estimated that the total load of microplastics in the 1 m × 1 m column in August 2020 was 124 000 particles whereas in May of 2021 it was only 51 000 particles. These integrated estimates indicate that the difference in total water column concentrations between the two sampling times was not simply due to differences in water column stability. In other words, surface water concentrations in August do not appear higher merely because a larger proportion of the total particles are trapped in the surface layer by water column stratification. Instead, additional environmental and anthropogenic factors must also be affecting the surface water concentrations of microplastics between the two sampling times.

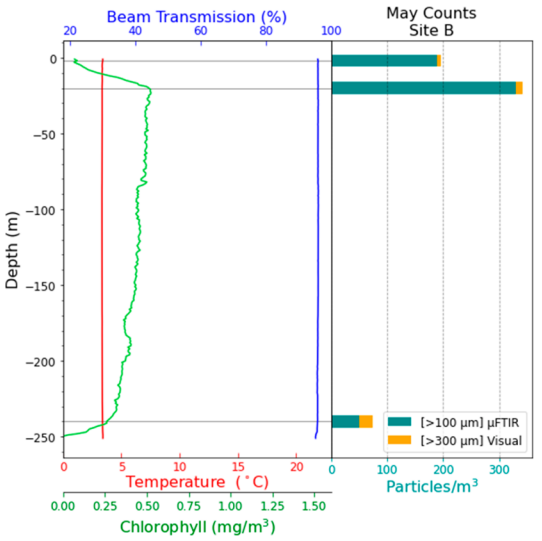


Figure 2. Water column characteristics and microplastic concentrations (>100 μm, collected via McLane pump) for site B in May 2021. Horizontal gray lines indicate sampling depths. Chlorophyll concentration is shown in green, water temperature in red, and beam transmission percent in blue. Dark teal bars correspond to manually detected microplastic particle concentrations, based on analysis of μFTIR spectral data (100−300 μm). Orange bars correspond to >300 μm particle concentrations, determined by optical microscopy analysis.

Manta Net Quantification. To benchmark our sampling technique to standard methods within the microplastics community, manta net sampling was performed at every site. This allowed microplastic concentrations at the air−water interface to be compared to concentrations in the water column. To facilitate this comparison, during the May 2021 cruise, a 300 μm filter was placed above the 100 μm filter in the filtration manifold of the McLane pump. This yielded water column concentrations for >300 μm microplastics that could be more appropriately compared to the >333 μm size fraction collected at the surface by the manta net. This comparison of manta net and McLane pump samples allowed us to explore the relationship between concentrations at the air−water interface and in the water column.

Exploring the manta net results, we observed areal concentrations for 0.333−4 mm microplastics to range between 7000 and 118 000 particles km^{-2} (x^{-} = 41 000 ± 46 000) (Figure 3). These results are the same order of magnitude as those from previous studies of Lake Superior surface waters. In 2018, Hendrickson et al. reported open water microplastic concentrations of 25 000−54 000 particles km^{-2} in Western Lake Superior collected by a 333 μm manta net.[16] In 2013, Eriksen et al. reported an average microplastic concentration of 5397 ± 4547 particles km^{-2} at five locations in Eastern Lake Superior and an average concentration of 43 157 ± 115 519 particles km^{-2} for all 21 study locations throughout Lakes Superior, Huron, and Erie.[17] In 2021, Cox et al. reported an average microplastic concentration of 29 948

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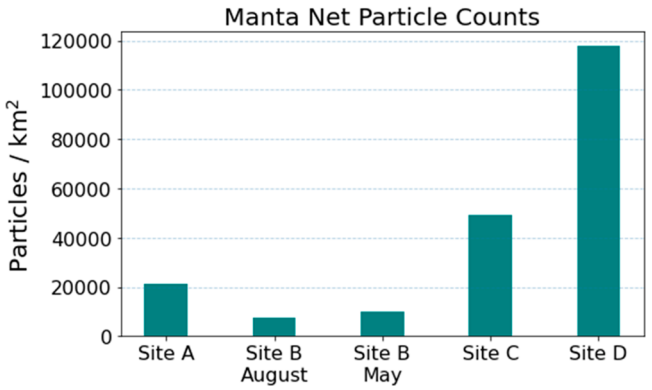

Figure 3. Areal microplastic concentrations (333−4000 μm) for Lake Superior surface waters.

particles km^{-2} in the 0.5−4.75 mm size class for 187 sites in Lake Superior sampled by neuston net.[19]

Of the 129 manta net particles that were visually detected as microplastics via optical microscopy in this study, 25 were large enough to be extracted for ATR-FTIR analysis (Table S9). Of all polymer types detected by ATR-FTIR, the predominance of polyethylene (PE) (44%), polypropylene (PP) (20%), and polyethylene terephthalate (PET) (28%) (Figure S10 and Table S9) in Western Lake Superior is in agreement with the fact that the majority of plastic in production is PE, PP, and PET.[35] These results are also in agreement with a previous manta net survey in Western Lake Superior that found PE, PP, and PET to be abundant,[16] in addition to other studies throughout the Laurentian Great Lakes.[32] Two of the 25 particles evaluated by ATR-FTIR were unknown to the sample Hummel Polymer Library and were uploaded to openspecy.org which suggested they were likely cellulose and therefore nonplastic. The ATR-FTIR results suggest that 8% of the 129 particles identified as microplastics by visual microscopy are in fact nonplastic, making 8% the false positive rate by visual microscopy. Accordingly, it is likely that the total number of true microplastic particles captured by manta net (333−4000 μm) was closer to 119.

To compare the concentrations between manta net and McLane pumps, manta net concentrations were converted to volumetric values using the below-water draft of the net (14 cm). At site B, concentrations of >300 μm microplastics in the water column, as sampled by the McLane pump at 2 m depth (Figure 2), were between 2 and 3 orders of magnitude greater than the concentration of >333 μm microplastics at the air−water interface, as sampled by the manta net (0.0352 particles m^{-3}, Table S10). The difference in mesh sizes used for each technique was likely a factor contributing to the difference in concentration between surface water and water column. Specifically, environmental plastic concentrations have been observed to be inversely proportional to microplastic particle size,[23] so it is an anticipated result that a 300 μm filter will yield higher concentrations than a 333 μm filter. For example, it has been found that microplastic fibers are 250 times more likely to be captured by an 80 μm filter than with a 330 μm filter.[36] However, assuming an inverse third order power law relationship between abundance and size,[37] the concentration of >300 μm microplastics in the water column would be expected to be only ∼1.4 times greater than the concentration of >333 μm microplastics at the air−water interface. In this research, our water column concentrations were 167 times greater (Table S10).

It is therefore likely that functional differences between manta net sampling and McLane pump sampling strongly contributed to the difference in detected microplastic concentrations between surface waters and the water column. These functional differences include the area of the respective mesh filters, the total volume of water sampled, the angle and speed of water through the mesh, the ability to rinse the mesh thoroughly (which is easier to do with pump samples than the entire manta net), the depth of sampling (15 cm vs 2 m), and the inclusion of a postsampling sieving step for the manta net samples. Previous research has compared the relative effectiveness of in situ filtration pumping and manta net trawling in terms of their ability to recover microplastic particles.[11] In that research, it was concluded that high volumes should be sampled, and a minimum of 26 particles per sample should be recovered to avoid statistical counting errors. The asymmetry between the large volumes of water sampled in Lake Superior by the manta net trawl and the relatively small volumes sampled by the McLane pump may limit the comparability of our samples. Nonetheless, it was the >100 μm McLane pump samples that easily surpassed the 26-particle statistical threshold, though some >300 μm May 2021 samples fell short of this value, whereas the manta net samples did not all pass this threshold.

Our data suggest that making assumptions about total microplastic abundance based solely on surface water concentrations from manta net samples could lead to a dramatic underestimation of the total load of microplastics in a given freshwater system. When comparing the concentration of water column microplastics in Western Lake Superior to the concentrations from the water column near the Port of Milwaukee, there are notable differences. Outside the Milwaukee harbor, at five depths (0−13.7 m), sampled with a 333 μm neuston net, and across four different sampling excursions, concentrations were consistently less than 3 microplastics m^{-3}.[9] While subsurface microplastic concentrations in this study were more than 2 orders of magnitude larger (720 ± 600 particles m^{-3}) than the concentrations outside the Port of Milwaukee, it is important to note that concentrations in this study were for particles >100 μm as opposed to >333 μm. In fact, the average subsurface microplastic concentration calculated from samples collected with the 300 μm filters during the May cruise was 14 ± 13 particles m^{-3}, which is in much better agreement with the concentrations reported near Milwaukee.

Water Column Characteristics May Contribute to Observed Seasonal Differences in Microplastic Counts. Seasonality is another factor likely contributing to the difference in concentrations between August 2020 and May 2021 (Figures 1 and 2). During August 2020 at site B, the water column was completely stratified whereas during May 2021 the water temperature was 3 °C at all depths. Other seasonally mediated factors such as the presence and magnitude of open water currents are likely to have a significant influence on the spatiotemporal variability of microplastics in the Lake Superior water column. As an illustration of this, in the Atlantic Ocean near the Canary Islands, >100 μm microplastic fragments and fibers in the water column down to 1150 m were found to be present in concentrations from 0 to 3000 particles m^{-3} in the winter and from 1000 to >90 000 particles m^{-3} in the autumn. This

https://doi.org/10.1021/acsestwater.2c00169
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variability was hypothesized to be driven by changes in mesoscale convective structures. These >100 μm oceanic microplastic concentrations are also notable as they are similar in magnitude to the concentrations detected in this study.[14]

To investigate the relationship between microplastic concentrations and water column characteristics, data from both May and August were considered. In the ocean, microplastic abundance in the water column has previously been found to have a linear relationship with zooplankton abundance.[14] In other studies of marginal marine water columns, microplastics were determined to be most abundant just below the mixed-layer in Monterey Bay,[13] and between 5 and 15 m in the Bohai Sea.[15] In order to interrogate the ability of water column characteristics to predict microplastic abundance, we plotted microplastic particle counts versus water column characteristics (Figure 4 and Figures S11−S14)

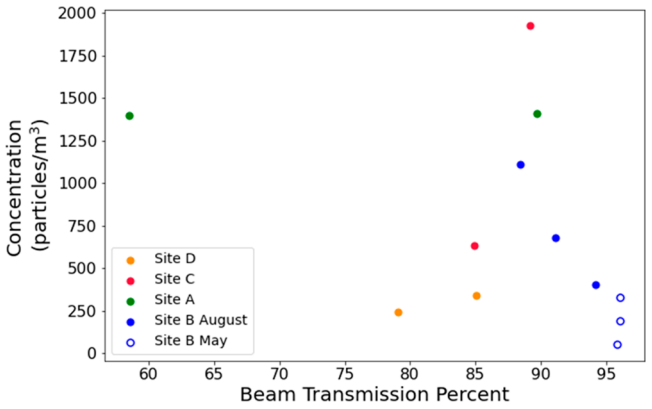

Figure 4. Microplastic particle count versus beam transmission percent for all sampling depths and locations.

and performed a linear regression (Model I). Beam transmission, a measure of water column clarity, and microplastic abundance (Figure 4) show a slight negative relationship, although the trend is not significant (p-value = 0.219, R^2 = 0.147, F-statistic = 0.859; degrees freedom = 12) across all samples. Nonetheless, the negative slope of the predicted line is what we would intuitively expect (Figure S11); lower percent beam transmission corresponds to higher microplastic particle counts and vice versa. In a similar vein, if samples from the same site (site B) are compared, there is again an inverse relationship between microplastic concentration and transmission, and this linear relationship does have predictive power, with x explaining 92% of the variance in y (r = −0.96, p = 0.002, n = 6).

Assessment of Automated Pipeline. An important objective of this research was the development of an analytical pipeline for the automatic quantification of small microplastics (>100 μm) in oxidized samples using FTIR microscopy. Comparing the results of this automatic analytical pipeline with results obtained from the manual analysis of the μFTIR data allowed us to assess the performance of the computational approach. Computational analysis of the μFTIR spectral data yielded consistently higher microplastic concentrations than the manual analysis of the data. Comparison of manual and computational μFTIR analyses of known microplastics samples (Table S8) showed that manual μFTIR yielded estimated concentrations of 101−116% of the known values as determined by visual microscopy. The computational μFTIR estimates were considerably higher and suggested that these estimates should be divided by a correction factor of 1.785, which was done for the Lake Superior data presented here. Through corrected computational analysis of the μFTIR data, the highest concentration of microplastics in the water column was 3230 particles m^{-3} from a depth of 2 m at site A, and the lowest concentration was 610 particles m^{-3} from a depth of 18 m at site C. It should be noted that site C computational values were lower than the manual abundances after applying the correction factor. The intrasite computational trends are notable for being similar to the intrasite trends detected by the manual analysis of the same data. The only exceptions were the results for site A, where the manual analysis detected equal microplastic concentrations (1400 particles m^{-3}) at 2 and 26 m while the computational analysis detected a greater concentration at 2 m (3230 particles m^{-3}) than at 26 m (2010 particles m^{-3}). The general agreement between the trends of the manual analysis and the computational analysis (Figure S15) is notable as it shows that the computational procedure is capable of distinguishing real differences in microplastic concentrations between samples that have been shown to differ in concentration by manual analysis. Whether these sample concentration differences are indicative of true concentration differences in the lacustrine water column is a question that would benefit from repeat sampling at each location and depth. A likely cause of the higher number of microplastic particles detected by computational analysis can be traced back to the formula that is used to calculate the cutoff between plastic spectra and nonplastic spectra. The current formula is likely too liberal in its determination of outliers, even with the applied correction term as determined with the positive controls. Determining an optimized empirical threshold for outlier detection with a representative training spectral data set could be a fruitful area for further research. Replacing the current algorithm with a more robust spectral matching function, however, would be the best way to improve the results of the program. This approach would require the attainment of high-quality reflectance spectra for comparison with reference spectral libraries. Our spectra did not meet such quality standards as spectral acquisition was hampered by the heterogeneity of natural samples, even after oxidation and density extraction. Nonetheless, the computational analysis in this research is notable for being one of the few completely automatic pipelines[13,29,30] capable of successfully analyzing natural samples collected from the environment.

CONCLUSIONS

Overall, this research shows that microplastic particles are present throughout the water column of Western Lake Superior. By comparing water column microplastic concentrations determined by in situ pumping to concentrations at the air−water interface from manta net sampling, we showed that relying only on surface net towing to estimate the total amount of microplastics in a freshwater system will likely lead to a significant underestimation of the total load of microplastics in that system. Lately, this is a consideration that has been receiving more attention in the literature,[9,14] yet there remains significant work to be done before a full understanding of the relationship between surface water and water column microplastic concentrations is obtained. This is a particularly important relationship to understand within the Laurentian Great Lakes where significant sampling at the air−water interface has occurred, yet very little water column sampling has been undertaken.

https://doi.org/10.1021/acsestwater.2c00169
ACS EST Water XXXX, XXX, XXX−XXX

By developing and testing an automatic analytical pipeline designed to reduce researcher bias and enhance sample throughput, this research takes an important step toward the standardization of microplastic identification and quantification methodologies. As most FTIR instruments can export hyperspectral data in CSV format, our approach is highly accessible as it does not rely on sophisticated hardware or software configurations. While the computational approach was highly sensitive to microplastics, it was not highly specific. This research would stand to benefit from improved μFTIR spectral quality, which would enable the characterization of exact polymer type and likely make possible the implementation of a more sophisticated spectral matching algorithm. However, obtaining excellent quality spectra from messy natural samples remains a challenge. As microplastic researchers have already identified effective processing methods for the isolation of microplastics from heterogeneous natural matrices, it is now necessary to identify the most effective approaches for spectral acquisition, including the fine details of spectrometer settings. When these problems are comprehensively solved, computational pipelines will enable reproducibility and rapid throughput. Our research herein is one of the first studies to apply a computational method to natural samples and thus is an important step toward the automation of reliable, long-term microplastic monitoring programs in Lake Superior and other lentic aquatic systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.2c00169.

Expanded materials and methods, details on FTIR microscopy data analysis, details on automated computational approach, blanks and controls methods and results, polymer identification results, correlation plots with water column characteristics, and Python script (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was prepared by J.M.F., G.D.S., K.M.S., E.C.M., and M.A.M.-J. using federal funds under award NA18OAR4170101 from Minnesota Sea Grant, National Sea Grant College Program, National Oceanic and Atmospheric Administration, U.S. Department of Commerce. The statements, findings, conclusions, and recommendations are those of the authors and do not necessarily reflect the views of NOAA, the Sea Grant College Program, or the U.S. Department of Commerce. The authors wish to acknowledge Irene van Baalen for her help with sample processing and the captain and crew of the R/V *Blue Heron* for sampling assistance.

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https://doi.org/10.1021/acsestwater.2c00169
ACS EST Water XXXX, XXX, XXX−XXX