Microplastics in Drinking Water:
What we Know, What we Don't Know, What we Need to Know

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Overview:

- Microplastics ubiquitous in surface waters
- Removal during drinking water treatment – require site specific data
- Health risk - not well defined:
  - Especially when considering sma

ACS ES&T Water

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Leaching of Dibutyltin from Virgin Polyvinyl Chloride Pipe Material

Menghong Wu, Wanzhen Chen, Hui Peng, Husein Almuhtaram,* and Robert C. Andrews

Cite This: https://doi.org/10.1021/acsestwater.3c00003 Read Online

Potential Health Impacts (2019 WHO):

1) **Physical** (especially <20 µm particles)

2) **Chemical** - Identify range of ***polymer types***

- ***"Adsorption"*** *of chemicals of concern (CECs),*
- ***"Leaching"*** *of chemical additives,*

3) **Toxicological** – Potential impact on human health

Complex Potential Health Impacts!

Monitoring Objectives: Why are we monitoring?

Drinking water – Identify/mitigate human health impacts
– Quantify an acceptable level of risk (*associated with microplastics*)

What/how do we want to monitor?

- Influent/finished water?
  (Obtain occurrence, baseline data?
  - assess treatment?)
- Discrete or composite samples?

What do we want to quantify?

- Particle *size* (minimum size? size distribution?)
- Polymer *types*? (Analyze using Raman or FTIR?)
- Total polymer *mass*? (Analyze using Pyro-GC/MS?)
- Polymer-associated chemical additives?

Answers help identify ***"appropriate" monitoring & analytical*** strategies!

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1) Sampling Issues: (Surface waters - rivers/lakes, treated drinking water)

Koelmans et al.(2019) – Suggests "500 L as a minimum sample volume for **surface water.** *However, given the often very low particle number concentrations in some lakes and rivers, a volume > 500 L is recommended"*

(Assuming particles > 300μm)

*"**For tap water*** *(range 1 × 10^{-4} to 100 particles per litre), a greater sample volume is proposed compared to surface water. Advise a minimum volume of 1,000 L, because concentrations can be very low"*

(Assuming particles > 20μm)

Koelmans et al., 2019. Microplastics in freshwaters and drinking water: Critical review and assessment of data quality.

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1) Sampling Issues: (Surface waters - rivers/lakes, treated drinking water)

Specific issues to consider:

1) Number of microplastics/L in water,
2) Number of “other” particles/L in water,
   - microplastics typically only represent 1/100 to 1/1,000 particles
3) Turbidity, NOM
4) Ease of filterability

Always recommend - “pre-sampling” trial!

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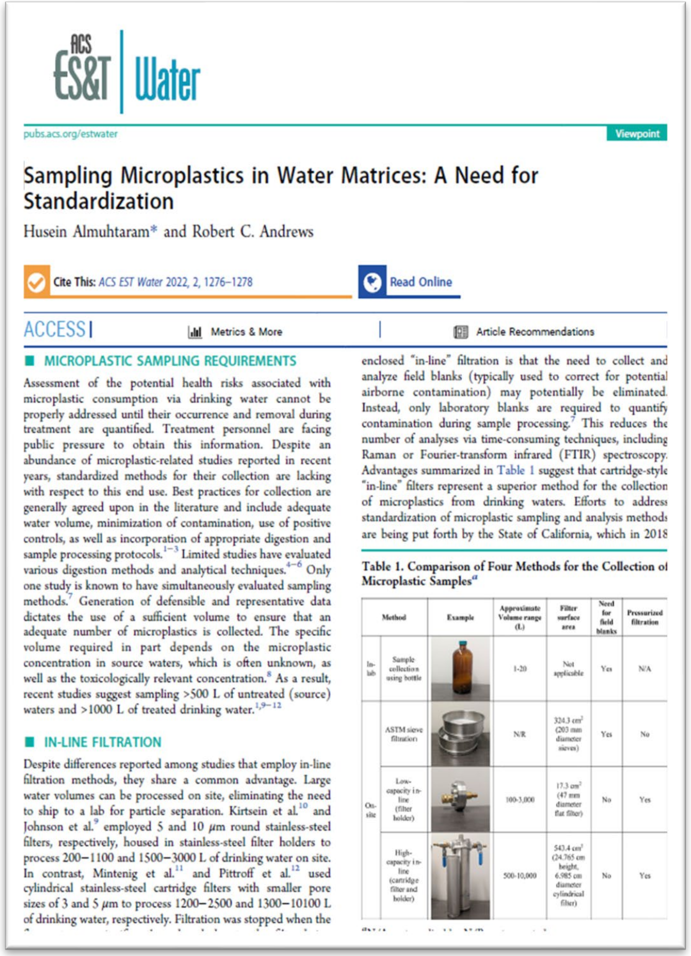
Comparison of Potential Sampling Methods

Method		Example	Approximate Volume range (L)	Filter surface area	Need for field blanks	Pressurized filtration
In-lab	Sample collection using bottle		1-20	Not applicable	Yes	N/A



ACS ES&T Water

pubs.acs.org/estwater Viewpoint

Sampling Microplastics in Water Matrices: A Need for Standardization

Husein Almuhtaram* and Robert C. Andrews

Cite This: ACS EST Water 2022, 2, 1276–1278

MICROPLASTIC SAMPLING REQUIREMENTS

Assessment of the potential health risks associated with microplastic consumption via drinking water cannot be properly addressed until their occurrence and removal during treatment are quantified. Treatment personnel are facing public pressure to obtain this information. Despite an abundance of microplastic-related studies reported in recent years, standardized methods for their collection are lacking with respect to this end use. Best practices for collection are generally agreed upon in the literature and include adequate water volume, minimization of contamination, use of positive controls, as well as incorporation of appropriate digestion and sample processing protocols.[1−3] Limited studies have evaluated various digestion methods and analytical techniques.[4−6] Only one study is known to have simultaneously evaluated sampling methods.[7] Generation of defensible and representative data dictates the use of a sufficient volume to ensure that an adequate number of microplastics is collected. The specific volume required in part depends on the microplastic concentration in source waters, which is often unknown, as well as the toxicologically relevant concentration.[8] As a result, recent studies suggest sampling >500 L of untreated (source) waters and >1000 L of treated drinking water.[1,9−12]

IN-LINE FILTRATION

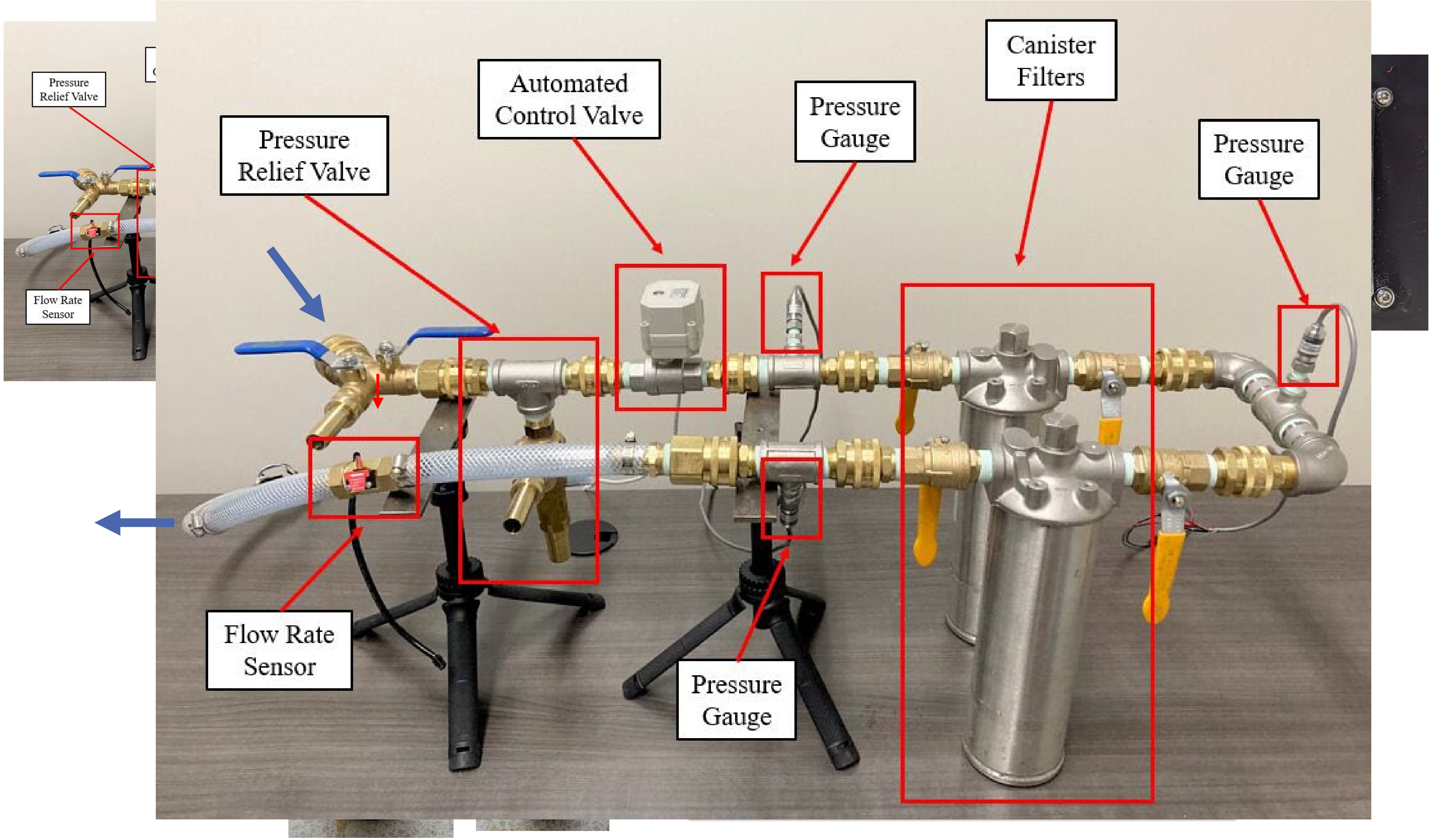
Despite differences reported among studies that employ in-line filtration methods, they share a common advantage. Large water volumes can be processed on site, eliminating the need to ship to a lab for particle separation. Kirtsein et al.[10] and Johnson et al.[9] employed 5 and 10 μm round stainless-steel filters, respectively, housed in stainless-steel filter holders to process 200−1100 and 1500−3000 L of drinking water on site. In contrast, Mintenig et al.[11] and Pittroff et al.[12] used cylindrical stainless-steel cartridge filters with smaller pore sizes of 3 and 5 μm to process 1200−2500 and 1300−10100 L of drinking water, respectively. Filtration was stopped when the

enclosed "in-line" filtration is that the need to collect and analyze field blanks (typically used to correct for potential airborne contamination) may potentially be eliminated. Instead, only laboratory blanks are required to quantify contamination during sample processing.[7] This reduces the number of analyses via time-consuming techniques, including Raman or Fourier-transform infrared (FTIR) spectroscopy. Advantages summarized in Table 1 suggest that cartridge-style "in-line" filters represent a superior method for the collection of microplastics from drinking waters. Efforts to address standardization of microplastic sampling and analysis methods are being put forth by the State of California, which in 2018

Table 1. Comparison of Four Methods for the Collection of Microplastic Samples[a]

Method		Example	Approximate Volume range (L)	Filter surface area	Need for field blanks	Pressurized filtration
In-lab	Sample collection using bottle		1-20	Not applicable	Yes	N/A
On-site	ASTM sieve filtration		N/R	324.3 cm^2 (203 mm diameter sieves)	Yes	No
	Low-capacity in-line (filter holder)		100-3,000	17.3 cm^2 (47 mm diameter flat filter)	No	Yes
	High-capacity in-line (cartridge filter and holder)		500-10,000	543.4 cm^2 (24.765 cm height, 6.985 cm diameter cylindrical filter)	No	Yes

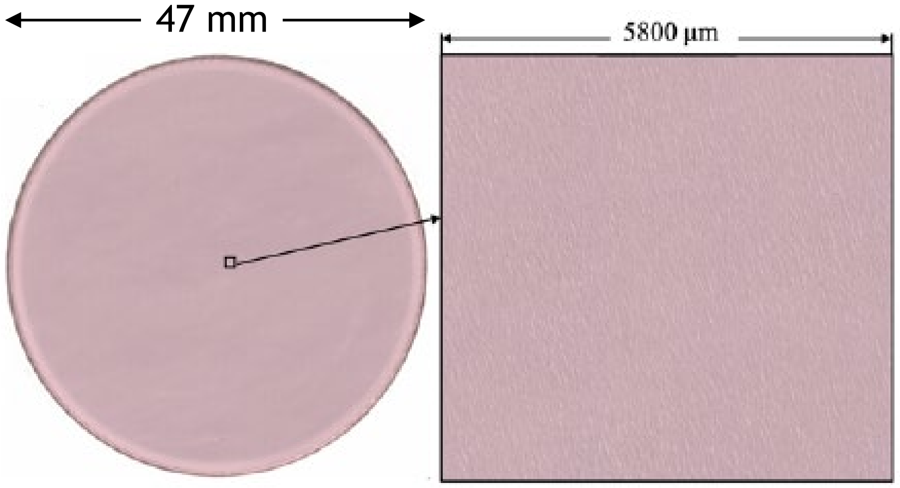
Example (High Volume) Sampling Equipment – 500 to 10,000L



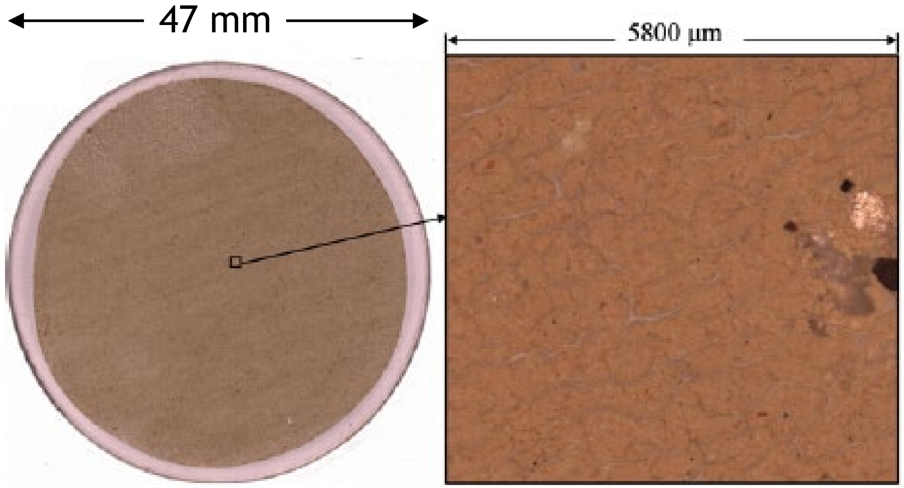
Sample Preparation - Prior to Analysis (Using Raman or FTIR)

Majority of particles in raw and treated waters *non-microplastics*

Must "clean up" (digest) filtered material – reduce extraneous (non-microplastic) particles prior to Raman/FTIR analysis



Clean, "blank filter"



1,000 L filtered tap water

(particles >2 µm)

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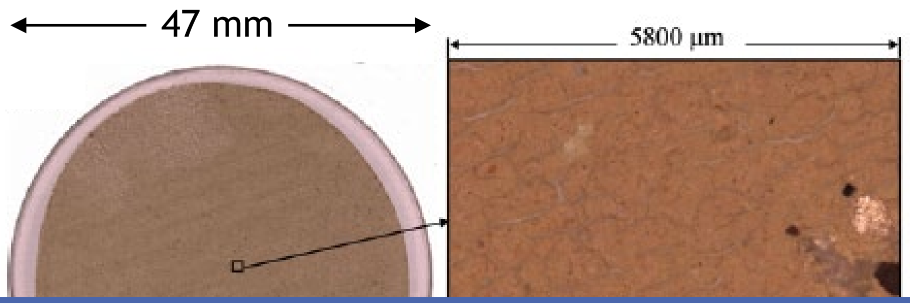
Wide Range of Published Sample Preparation (Digestion) Methods

1,000 L tap water filtered through 2 µm, (47 mm filters)



Selection of appropriate digestion method – *depends on: i) minimum particle size collected, ii) volume of water filtered, iii) characteristics of filtered material*

No digestion

2) Characterization of Polymer Types: (Analytical Methods)

A) Pyrolysis GC/MS

(Particles – **all sizes**, Quantify mass, polymer type, NOTE: Destructive technique)

Time - A few hours/sample

Need to decide "acceptable" analysis time!

B) FTIR Spectroscopy

(Particles >20µm, Quantify polymer type + size, shape, colour)

Time - A few days/sample

IMPT! -Require sample "clean-up" using digestion step prior to analysis

C) Raman Spectroscopy

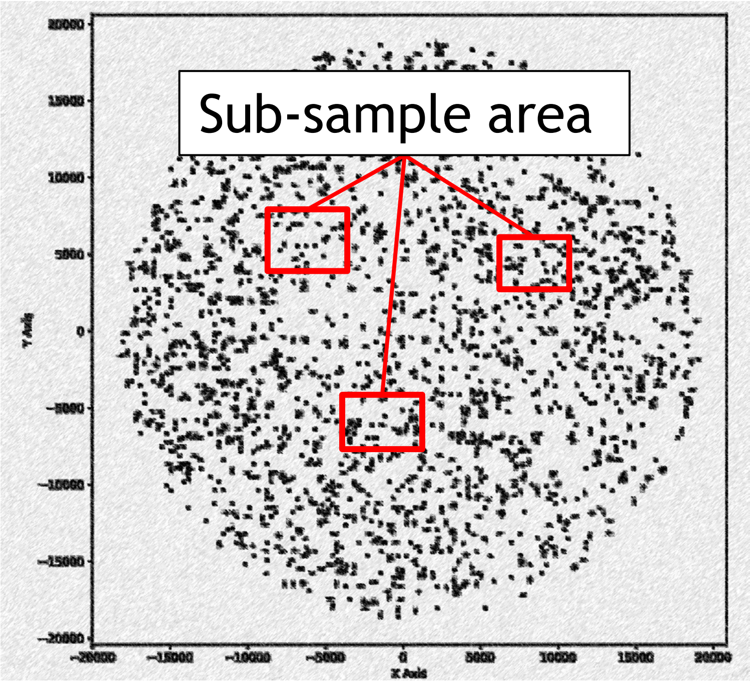
(Particles >1µm, Quantify polymer type + size size, shape, colour)

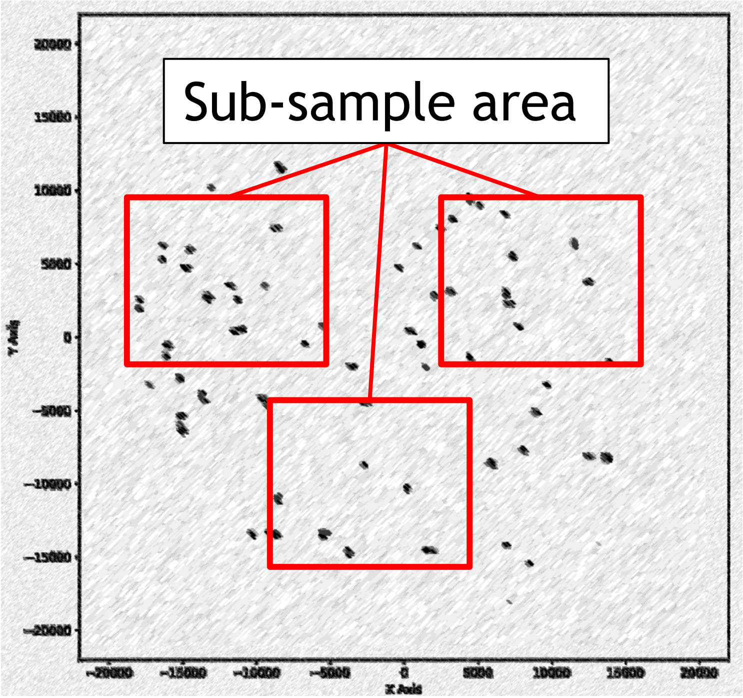
Time - A few days/sample

Analytical Detection Limitations – FTIR (>20µm), Raman (>1µm)

Total Sample Volume – *directly impacts number of particles (& microplastics)*

- Unrealistically large amount of time to analyze complete filter area - require "sub-sampling" of filter area *(may need larger sub-sampling area if low microplastic conc)*





From practical standpoint, suggest maximum instrumentation time – *approx 2 days/sample*

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Important Sampling & Analysis Method Considerations!

Sample Volume

↓

Selection of "Appropriate" Digestion Method

↓

Sub-sampling area (size + number of areas on filter)

↓

Raman or FTIR Analysis Time

More water volume - more extraneous particles & NOM

More particles & NOM – dictates more intensive digestion method

Higher particle numbers – smaller or fewer sub-sampling areas?

(Typically analyze 7,000 - 12,000 particles per 1% area)

Higher particle numbers – longer analysis time to "laser" all individual particles + match individual spectra to library

Application of Methods: Occurrence & Removal of MPs

Recent advances in sample collection, clean up, and analysis

- allow accurate characterization/quantification of >1um MP occurrence & removal (during drinking water treatment)

Quantify:

- Overall removal: raw, treated, & distribution system

  + removal associated with individual treatment processes

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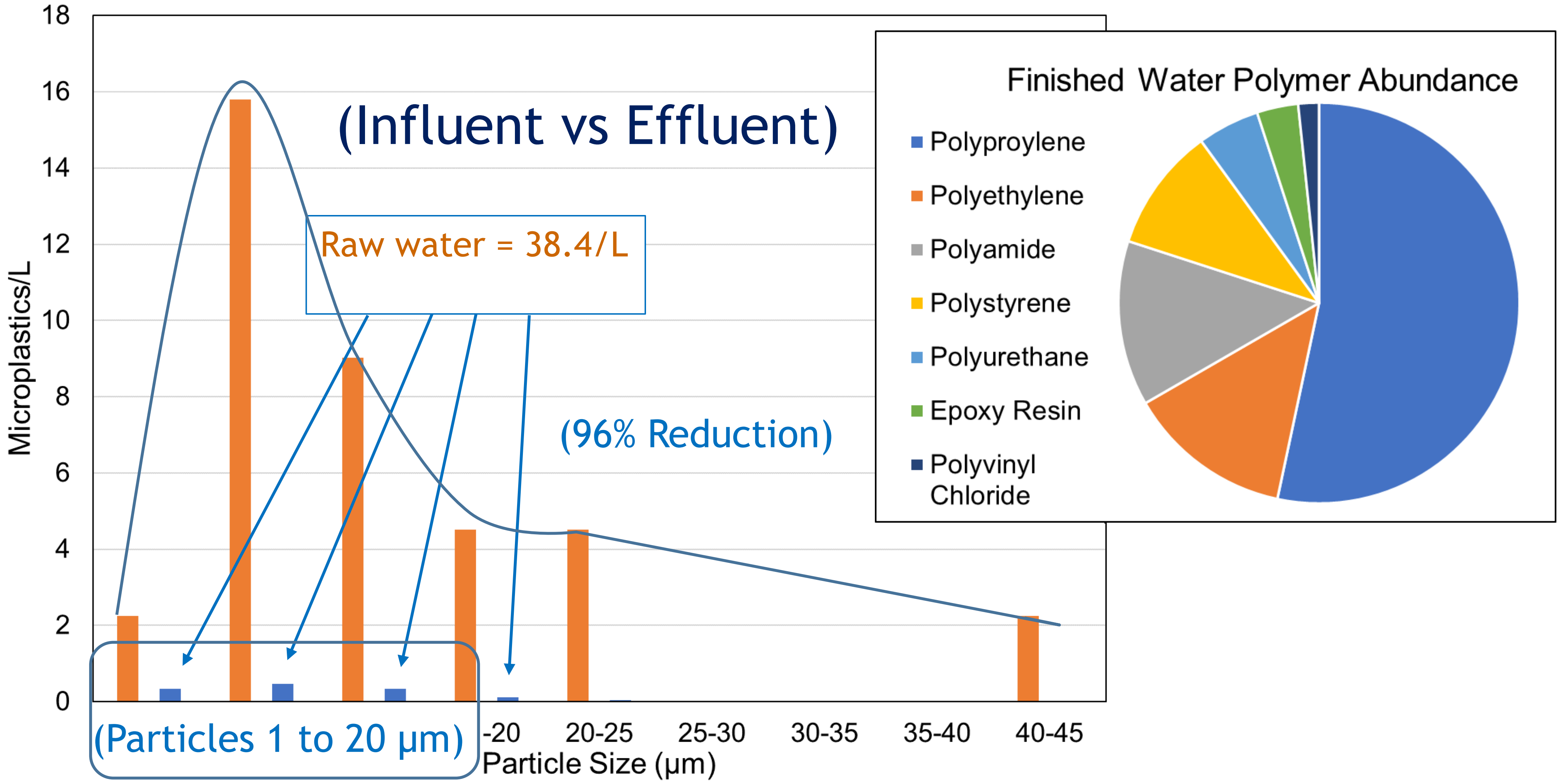
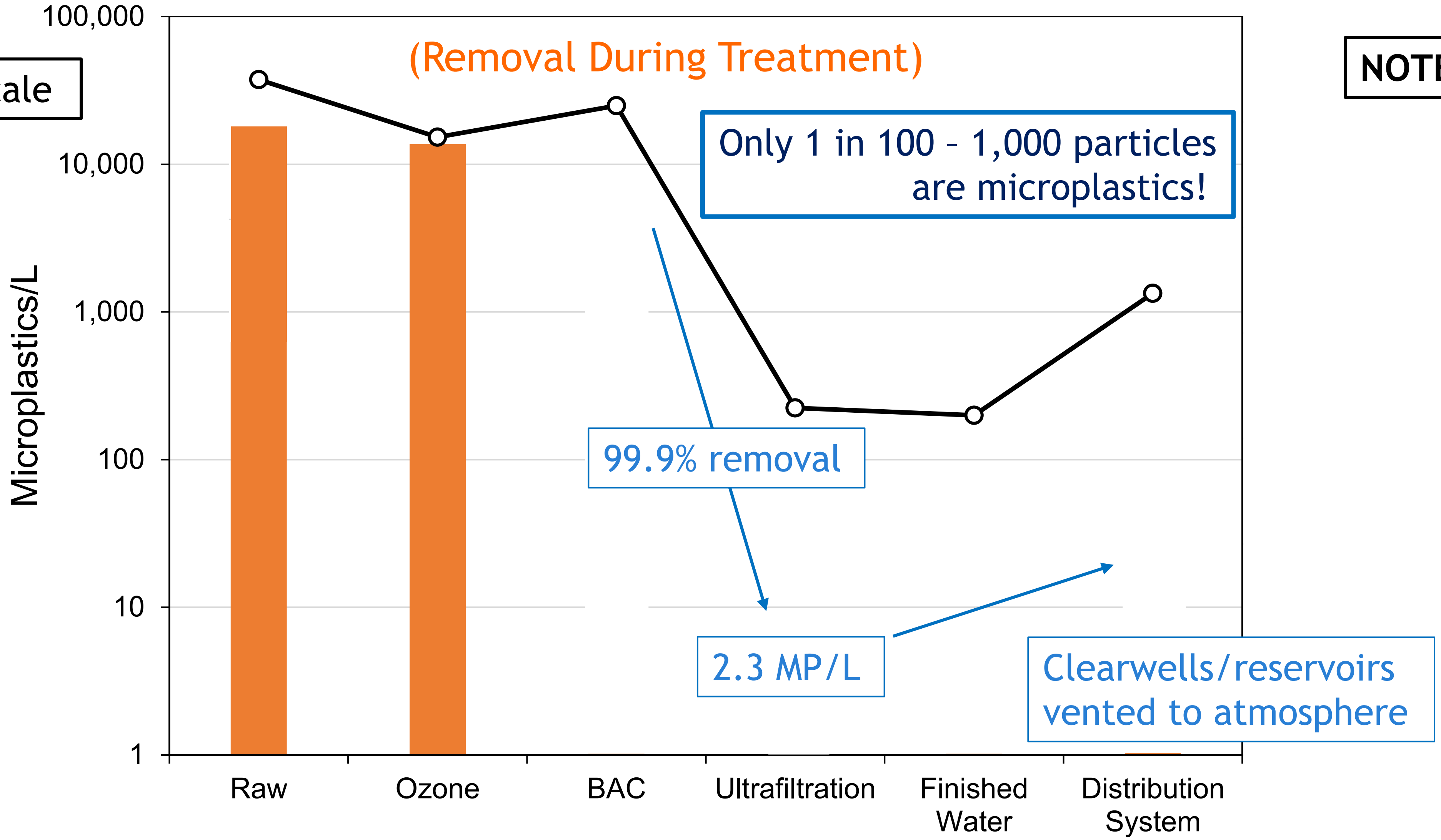
Example Microplastic Results (Raman) – Conventional Treatment

(1,000L filtered through 20 µm & 2 µm stainless steel mesh)



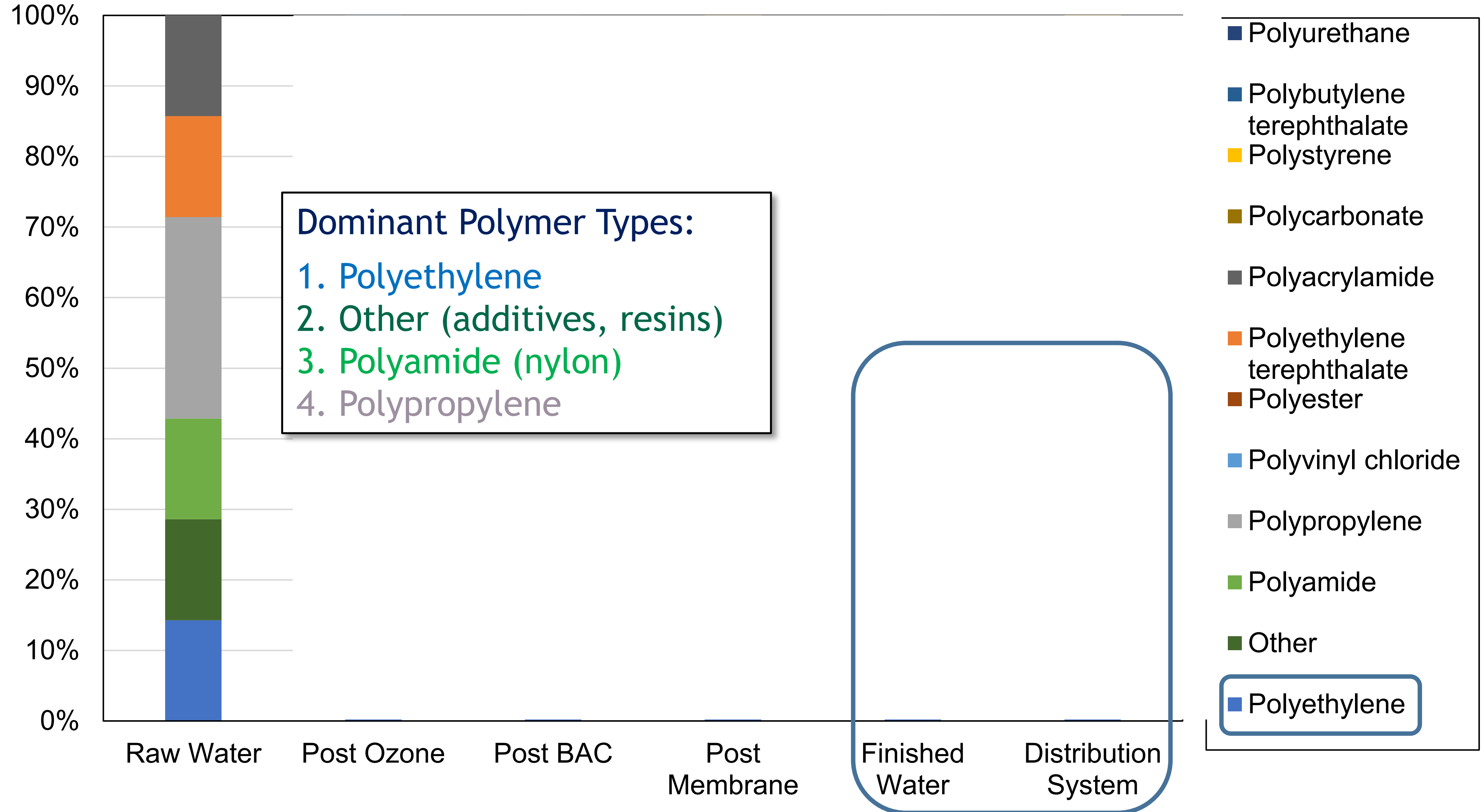
Example Microplastic Results (Raman)– Advanced Treatment

NOTE: LOG Scale



NOTE: LOG Scale

Example Polymer Abundance (Raman) - Advanced Treatment



Dominant Polymer Types:

1. Polyethylene
2. Other (additives, resins)
3. Polyamide (nylon)
4. Polypropylene

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Summary - What We Currently Know & Don’t Know

What We Know:

- Appropriate volume to be sampled - likely varies for source vs post-filtered waters
- Appropriate MP size range (1um - 100um) – for sampling and analysis
- Appropriate analysis methodology (Raman spectroscopy (>1µm) – likely preferred)
- Quantification of microplastics in source & drinking waters – new data emerging

What We Don’t Know:

Presence of Chemical Additives (in virgin and weathered microplastics)

3) Toxicology - What We Need to Know:

In addition to Microplastic Occurrence/Removal Data (for specific polymer types)

Obtain Data for Subsequent Toxicological Assessment *(to estimate potential human health impacts)*

- Identify specific *chemical additives*
- Quantify *concentrations of chemical additives* *(for various polymer types)*
- Determine *which chemical additives contribute to toxicity*
- Compile polymer types - *typically associated with toxic chemical additives*

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Ongoing DWRG Microplastic Studies:

2023 - 2024

Quantify microplastic occurrence & removal at WTPs in Canada & USA

Compare source water quality & wide range of treatment processes (+ *distribution*)

- Quantify using ***both*** Raman and Pyro-GC/MS methods
- Assess water quality data (particle counts, turbidity, etc.) – *to elucidate potential relationships*

2023-2025

Continue toxicological assessment of microplastics:

- Strong focus on identification of chemical additives (*in weathered microplastics*)
- Quantify toxicological impacts (*in-vitro & in-vivo*)

Develop methods to identify nano-plastic polymer types

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NSERC Alliance - Water Industry Partners

- Brown and Caldwell
- City of Barrie
- City of London
- De Nora
- Durham Region
- Eugene Water and Electric Board (EWEB)
- Niagara Region
- Ontario Clean Water Agency (OCWA)
- Peel Region
- Peterborough Utilities Group
- Toronto Water
- York Region

Questions?

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