Advances and Challenges: Microplastic Sampling and Analysis in Drinking Water

(*What We Know, What We Don't Know, What We Need to Know*)

Michael McKie, Charles Balkenbusch, Husein Almuhtaram & Robert Andrews,
Department of Civil & Mineral Engineering, University of Toronto

Overview:

- Ubiquitous in surface waters (lakes, rivers)
- Removal during drinking water treatment - poorly understood
- Health risk - not well defined:
  - Especially when considering sma


Chemosphere 307 (2022) 135585

Contents lists available at ScienceDirect

Chemosphere

Environmental Science & Technology

pubs.acs.org/est

Article

Defining the Chemical Additives Driving *In Vitro* Toxicities of Plastics

Wanzhen Chen, Yufeng Gong, Michael McKie, Husein Almuhtaram, Jianxian Sun, Holly Barrett, Diwen Yang, Menghong Wu, Robert C. Andrews, and Hui Peng*

Potential Health Impacts (2019 WHO):

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

2) **Chemical** - Identify polymer (plastic) types

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

3) **Toxicological** – Impact on human health

Complex Potential Health Impacts!

Monitoring Objectives:

Drinking water - Human health impacts

- **Ultimately** – need info to quantify an acceptable level of risk (*associated with microplastics*)

What/how do we want to monitor?

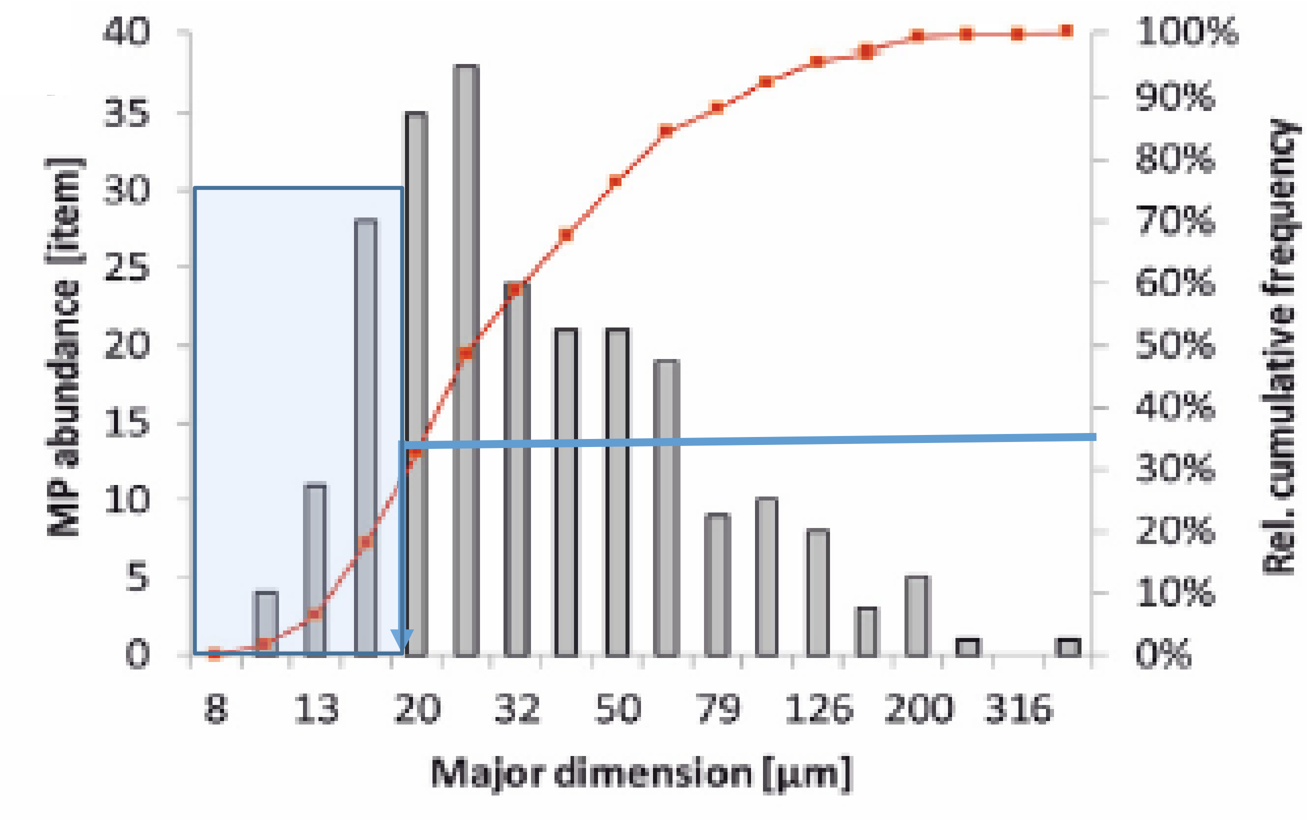
- Influent/finished water?
  (Obtain occurrence, baseline data? assess treatment performance)
- Collect discrete or composite?

What do we want to quantify?

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

Need to define an "***appropriate***" monitoring & analysis strategies

1) Physical Characteristics: (What Particle Sizes to Monitor?)



Previous data - *Kirstein et al. (2021)* - suggests approx 35% of all particles ≤ 20µm

Our recent DWRG data shows:
80 - 90% ≤ 20µm (in treated water)

Important to include smallest particle size possible ≈ 1-2 µm!
(Depends on both particle separation methodology & analytical capabilities)

Jour Water Research (2021) - Kirstein et al. "Quantification and qualification of microplastics"

Sampling and Analytical Studies (Global)

- Microplastic Occurrence in Drinking Water

Our recent DWRG data shows:
80 - 90% ≤ 20μm (in treated water)

Raw and Treated Drinking Water				
Author	Concentration (particles/L)			Lower Size Limit
	Raw Water	Treated Water	Tap Water	
Wang et al. (2020)	6,614±1132	930±72	Not Measured	> 1 μm
Mintenig et al. (2019)	3.7×10^{-3}	0.7×10^{-3}	0	> 20 μm
Ball et al. (2019)	4.9	0.00011	Not Measured	> 25 μm
Pivokonsky et al. (2018)	WTP 1: 1,473±34 WTP 2: 1,812±35 WTP 3: 3,605±497	WTP 1: 443±10 WTP 2: 338±76 WTP 3: 628±82	Not Measured	> 1 μm
Uhl et al. (2018)	< LOQ	< LOQ	< LOQ	> 60 μm

Questions:

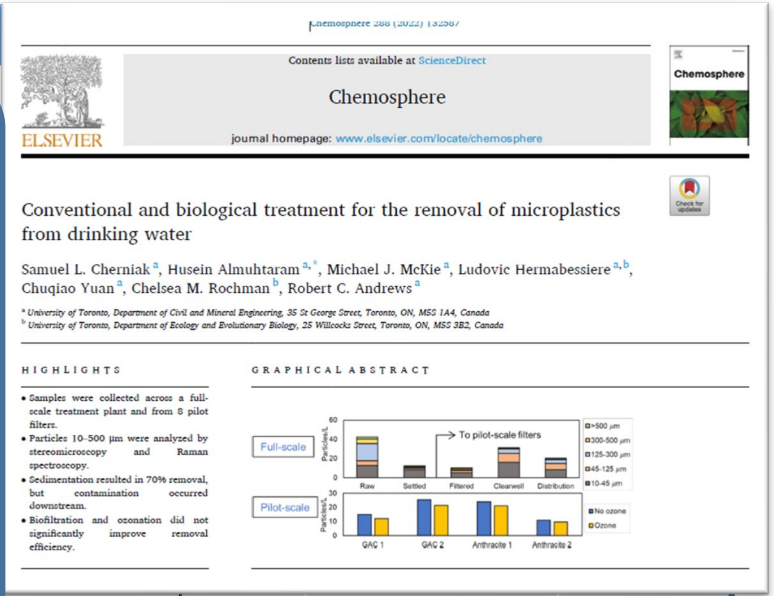
What sampling methods were employed?

- Smallest Size? (collected/analyzed)
- Volume of Water Filtered?

Sampling and Analytical Studies (North America)

- Microplastic Occurrence in Drinking Water

Continent	Country	Reference	Volume Sampled (L)				
			Source Water	Treated Water			
North America	Canada	Cherniak et al., 2022	10	10			
		Yuan et al., 2022	Not Sampled	9			
	Mexico	Shruti et al., 2020	Not Sampled	1	Glass Bottle (In-Lab)	SEM-EDS, Raman	1



Chemosphere 288 (2022) 132587
Contents lists available at ScienceDirect
Chemosphere
journal homepage: www.elsevier.com/locate/chemosphere

Conventional and biological treatment for the removal of microplastics from drinking water

Samuel L. Cherniak [a], Husein Almuhtaram [a,*], Michael J. McKie [a], Ludovic Hermabessiere [a,b], Chuqiao Yuan [a], Chelsea M. Rochman [b], Robert C. Andrews [a]
[a] University of Toronto, Department of Civil and Mineral Engineering, 35 St George Street, Toronto, ON, M5S 1A4, Canada
[b] University of Toronto, Department of Ecology and Evolutionary Biology, 25 Willcocks Street, Toronto, ON, M5S 3B2, Canada

HIGHLIGHTS

- Samples were collected across a full-scale treatment plant and from 8 pilot filters.
- Particles 10–500 µm were analyzed by stereomicroscopy and Raman spectroscopy.
- Sedimentation resulted in 70% removal, but contamination occurred downstream.
- Biofiltration and ozonation did not significantly improve removal efficiency.

GRAPHICAL ABSTRACT

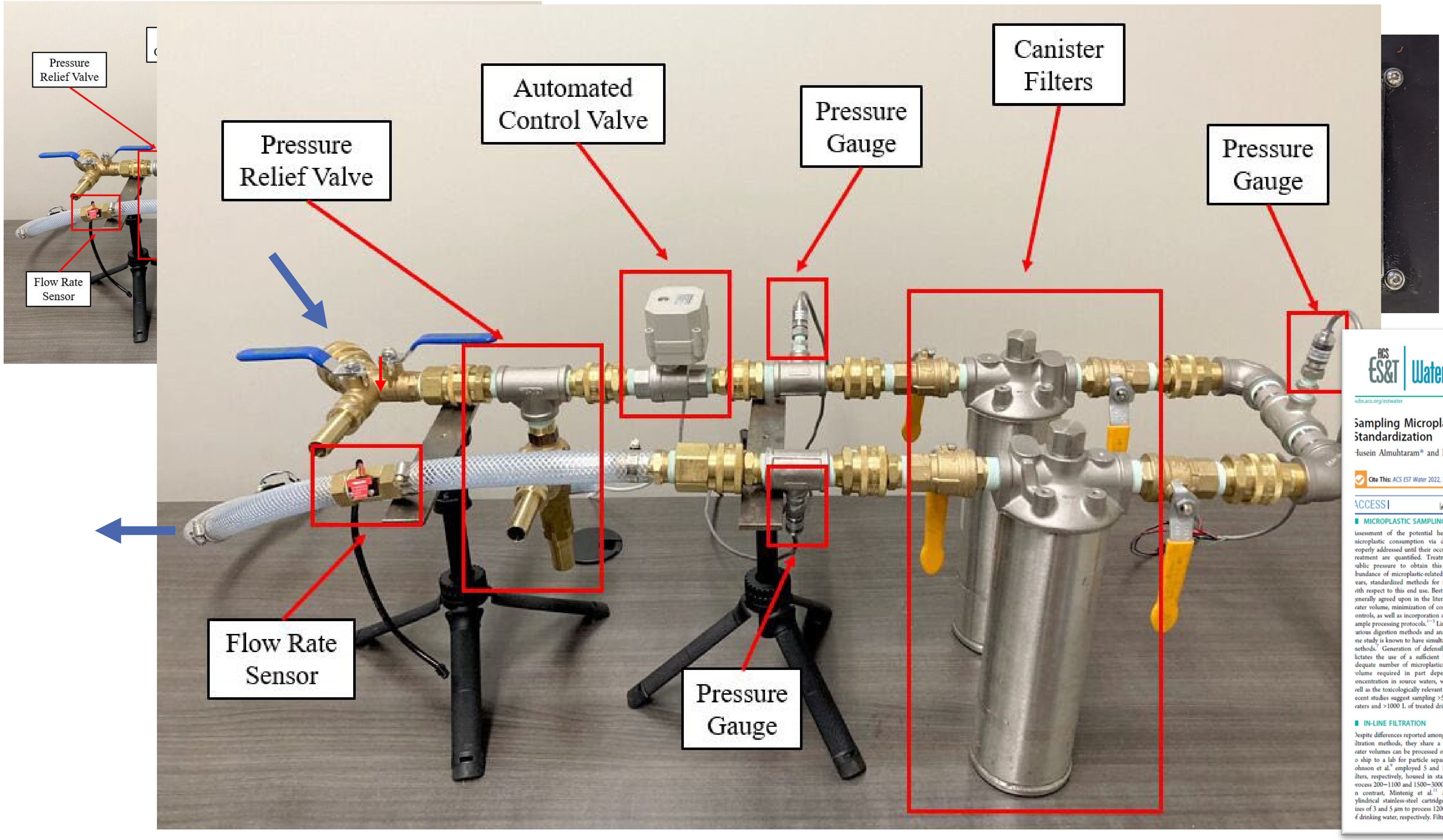
Sampling Volumes: (Surface waters - rivers/lakes, drinking water)

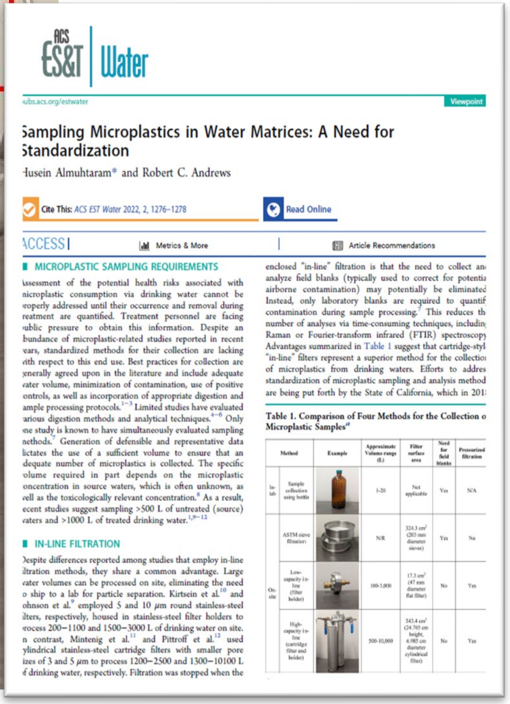
*Koelmans et al.(2019) – **Suggests "500 L as a minimum sample volume for surface water.** However, given the often very low particle number concentrations in some lakes and rivers, a volume > 500 L is recommended".*

*"**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".*

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

High Capacity Sampling – Large Volumes (150 to > 1,000+ L)





ACS ES&T | Water

ubs.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 | Read Online

ACCESS | Metrics & More | Article Recommendations

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

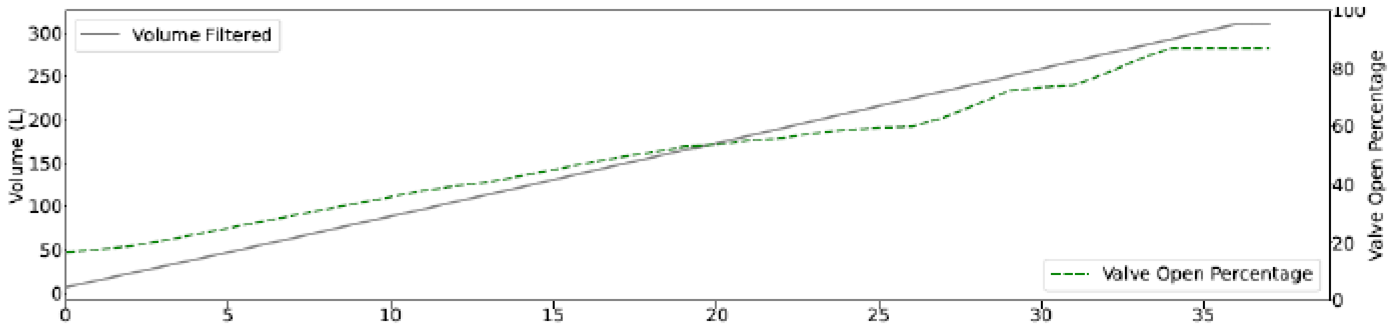
enclosed "in-line" filtration is that the need to collect and analyze field blanks (typically used to correct for potential airborne contamination) may potentially be eliminated. Instead, only laboratory blanks are required to quantify contamination during sample processing.[7] This reduces the number 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 201

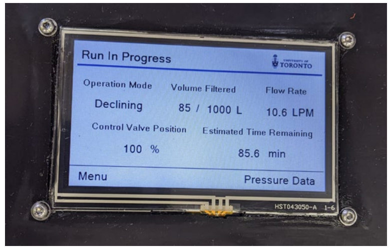
Table 1. Comparison of Four Methods for the Collection of Microplastic Samples[a]

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 cm² (203 mm diameter sieves)	Yes	No
	Low-capacity in-line (filter holder)		100-3,000	17.3 cm² (47 mm diameter flat filter)	No	Yes
	High-capacity in-line (cartridge filter and holder)		500-10,000	543.4 cm² (24.765 cm height, 6.985 cm diameter cylindrical filter)	No	Yes

High Capacity Sampling (≈250L/hr) – Sampling Control & Data Acquisition System

Total Volume Filtered





Control/record sample collection data

2) Chemical Characterization of Polymer types: (Analytical Methods)

Pyrolysis GC/MS

(Particles – all sizes, Measure mass, polymer type, Destructive technique)

Time - A few hours

FTIR Spectroscopy

(**Particles >20um**, size, shape, colour)

Time - A few days

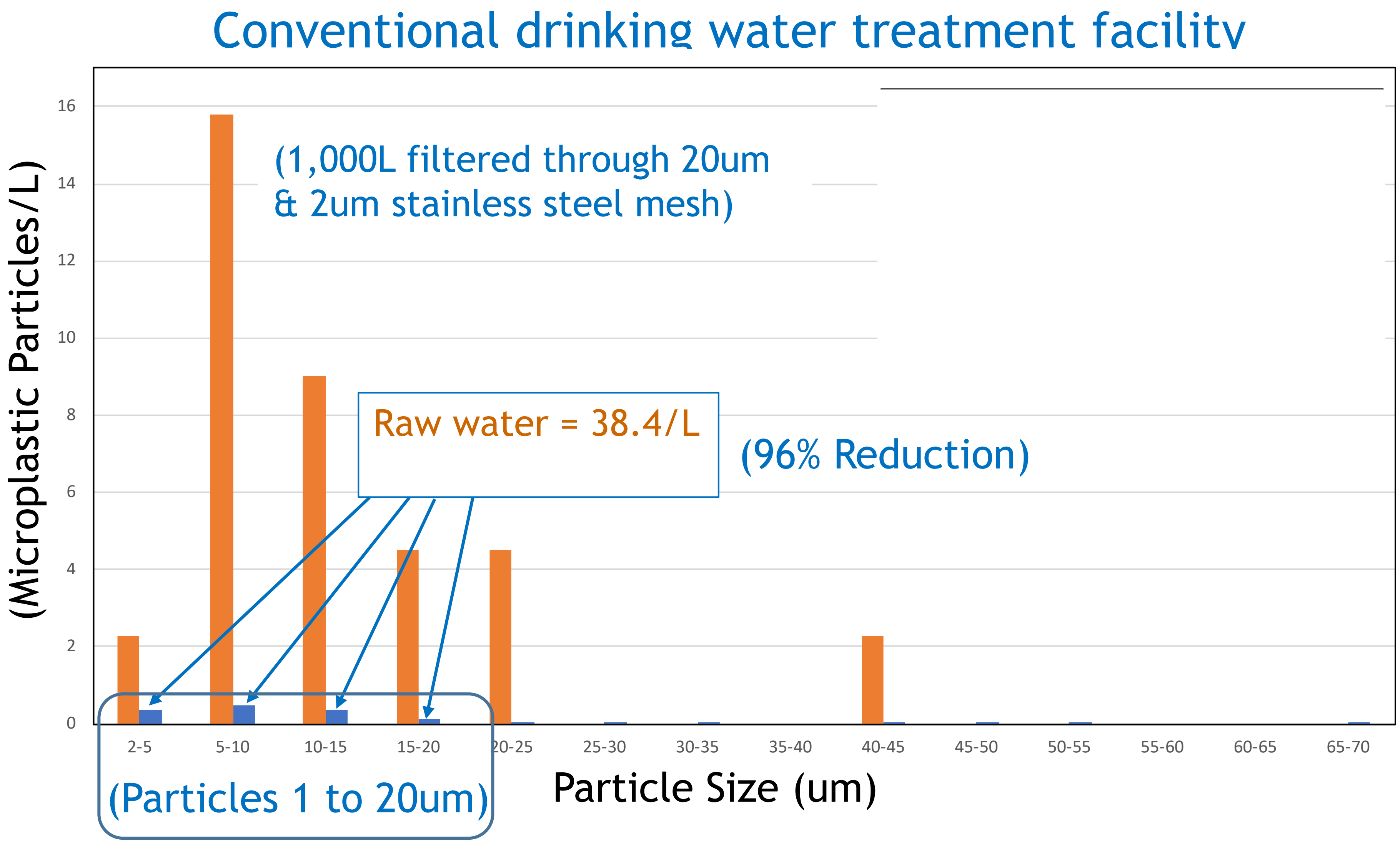
IMPT! -Require sample "clean-up" using digestion step prior to analysis

µ Raman Spectroscopy

(**Particles >1um**, size, shape, colour)

Time - A few days

Combine Sampling (Large Volume) + Analysis (Polymer Size & Type)



Recommendations:

Sampling - High Capacity (closed system) on-site filtration

- High recovery - *reduce particle loss*
- Reduce/eliminate atmospheric contamination
- Efficient procedure – *reduce sampling time*
- On-site - *eliminate need to transport (large volumes) of water to lab*

Microplastic Analysis

- Raman Spectroscopy – *preferred method to identify small MP particles (<20um)*

DWRG
DRINKING WATER RESEARCH GROUP

Summary – Optimal Sampling & Analysis Methods

1) Select appropriate sampling & analysis strategy!

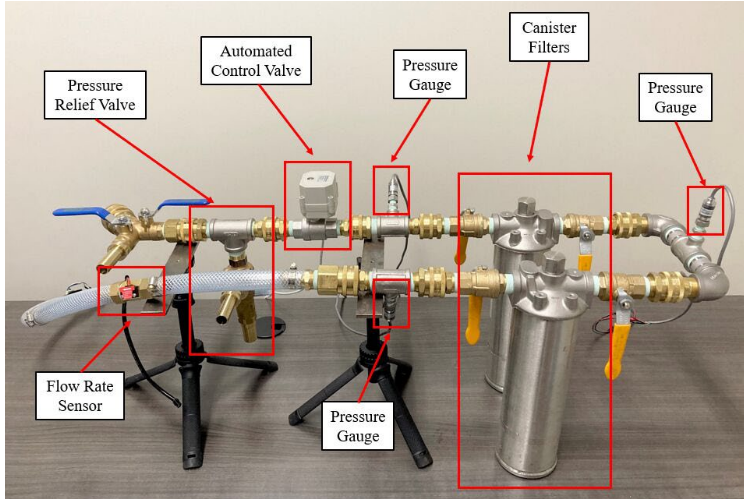
   (Consider microplastic conc. & study objectives),

2) Sampling configuration/mesh size - *depends on source water quality and desired level of microplastic quantification,*

3) Volume filtered – *greatly depends on water quality, applied pressure/flowrate, filter mesh size,*

4) Whenever possible, conduct initial sampling trial!!!

   - *Helps to identify optimal sampling approach*



Summary - What We Know & Don’t Know

What We Know:

- Appropriate volume to be sampled (> 1,000L)
- Appropriate MP size range (1um - 100um) - to be collected and analyzed,
- Appropriate analysis methodology (Raman spectroscopy)
- Occurrence of microplastics in source & drinking waters - Ongoing

What We Don’t Know (Varying levels of uncertainty):

- Removal of microplastics by treatment processes - Ongoing
- Diurnal/seasonal fluctuations in source/treated water – Ongoing
- Presence of chemical additives (in virgin and weathered microplastics) - Ongoing

3) Chemicals Associated with Toxicology (Potential Health Concerns)

- What We Ultimately Need to Know:

- *In addition to Microplastic Occurrence/Removal Data & Polymer Types*
  - Obtain Info for Subsequent Toxicological Assessment – to estimate potential human health impacts

1) Identify specific chemical additives
2) Determine which chemicals contribute to toxicity
3) Quantify concentrations of chemical additives for various polymer types

3) Chemicals Associated with Toxicology (Potential Health Concerns) - What We Ultimately Need to Know:

Microplastic (ingestion) threshold values - to avoid adverse health impacts

(Types? Mass? Concentration? Size distribution?)

- Mode of action of microplastics within tissue (*in-vivo*)
  - To-date, limited *in-vivo* mammalian toxicity studies have only considered PS & PE, (unknown chemical additives)

Ongoing DWRG Microplastic Studies (2023-2025):

Quantify microplastic occurrence & removal at 15 WTPs:

- Varying source water quality/wide range of treatment processes (+ *distribution*)

    Assess using both Raman and Pyro-GC/MS methods

    - obtain water quality data – (particle counts, turbidity, etc.) – to elucidate potential relationships

Continue assessment of microplastics as contaminant vectors:

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

DWRG
DRINKING WATER RESEARCH GROUP

Primary Microplastics Funding:

Natural Sciences and Engineering Research Council (NSERC) - *Alliance Program*

Environment and Climate Change Canada (ECCC) - *Increasing Knowledge on Plastic Pollution Initiative*

+ Municipal & Industry Partners:

City of Barrie
Durham Region
Eugene Water & Electric Board
Lake Huron and Elgin Area Primary Water Supply Systems (London)
Peterborough Utilities Commission
Ontario Clean Water Agency
Regional Municipality of York
Regional Municipality of Peel
Toronto Water
Brown & Caldwell

Questions?

robert.andrews@utoronto.ca

DWRG
DRINKING WATER RESEARCH GROUP