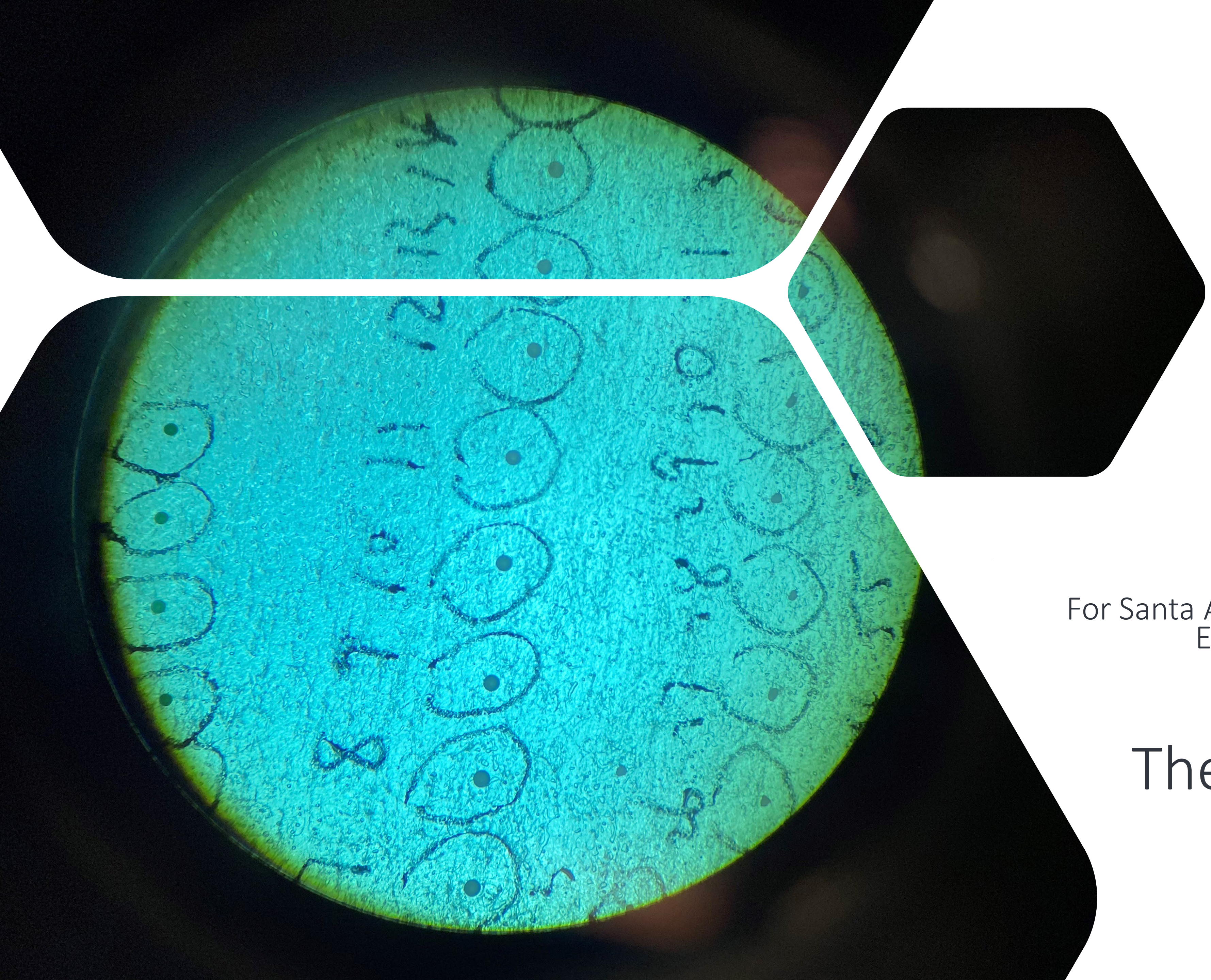


Microplastics

For Santa Ana Watershed Project Authority
Emerging Constituents Task Force

Monday, August 10, 2024

Theresa Slifko, Ph.D.

Metropolitan Water District
of Southern California

Addressing Microplastics Inquiries

What are microplastics?

How are microplastics detected?

Are microplastics in drinking water?

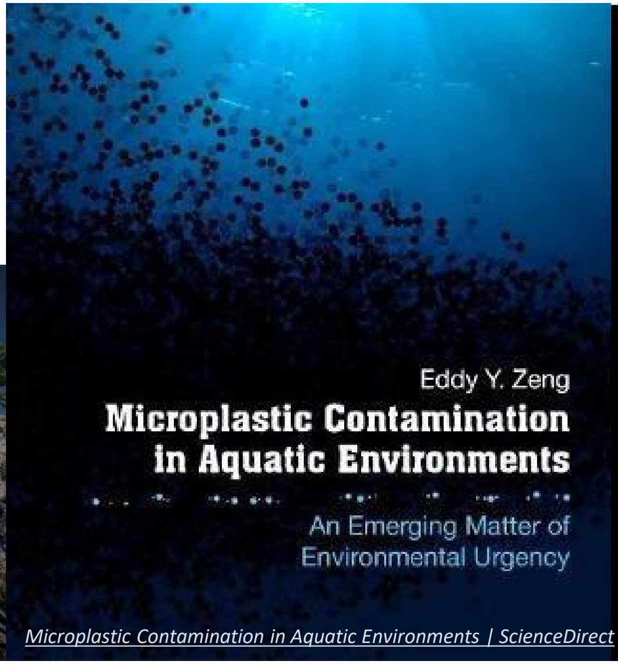
Does water treatment remove microplastics?

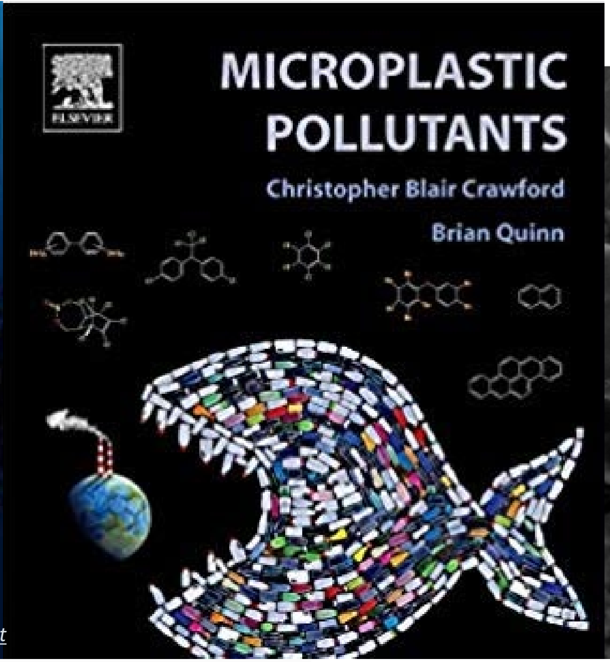
HUMANS HAVE PRODUCED THE PLASTIC EQUIVALENT OF "ABOUT ONE BILLION ELEPHANTS"

https://www.usatoday.com/story/tech/science/2017/07/19/humans-have-produced-18-2-trillion-pounds-plastic-thats-equal-size-1-billion-elephants/491529001/

IAEA
International Atomic Energy Agency

More Plastic Than Fish by 2050 – IAEA Event Gathers Experts Working Together to Save Marine Environments from Plastic Pollution





Today: ~100 BILLION plastic bags are used by Americans every year.

Tied together, they would circle the Earth's 773 times!

http://www.earth-policy.org/press_room/C68/plastic_bags_fact_sheet

Microplastics in air and rain

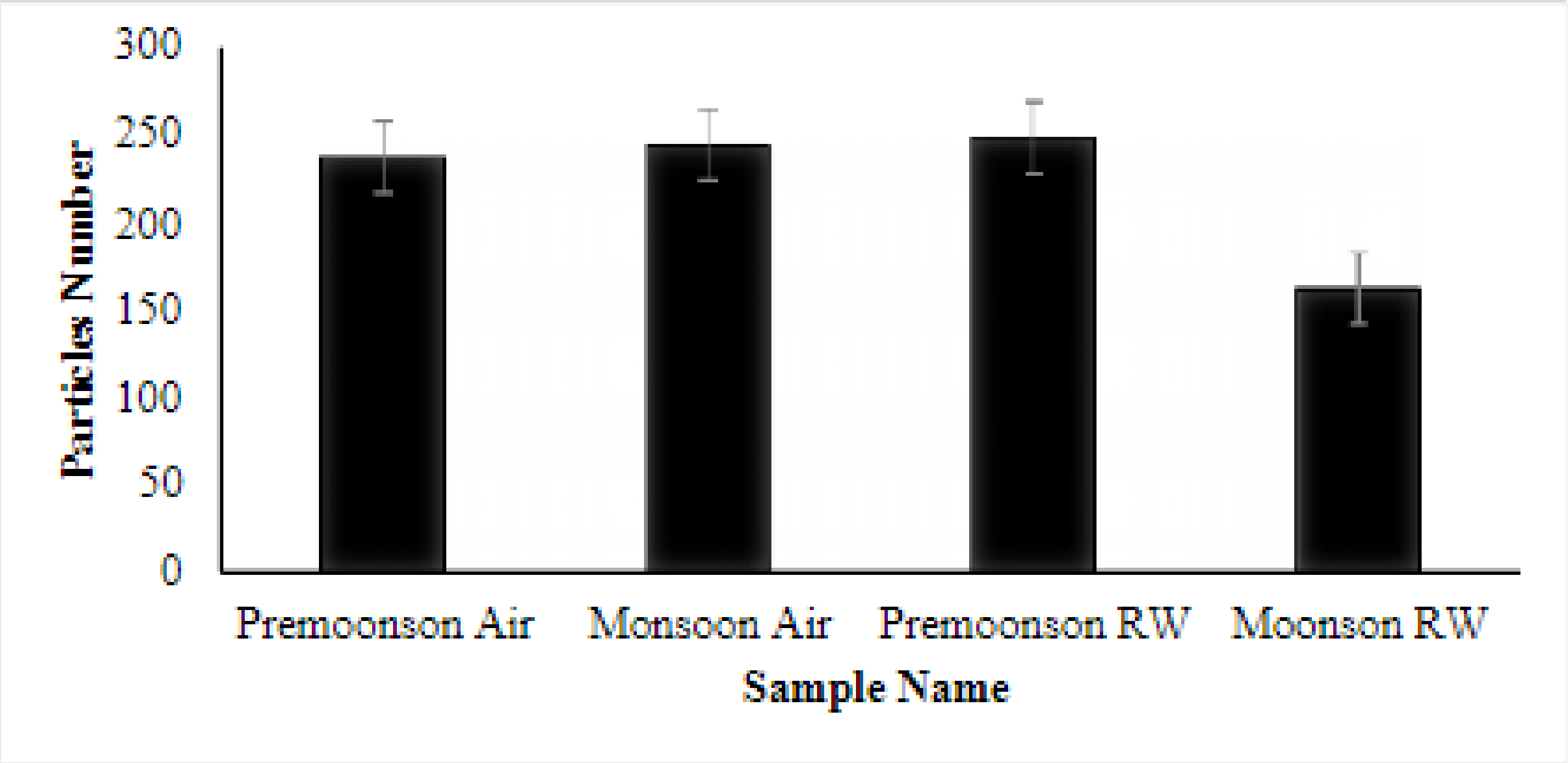


Figure 2: Number of Identified MPs in Sampling Locations with seasonal variation between premonsoon and monsoon season. Particles were highest in Premonsoon RW and lowest in Monsoon RW.

Jahan et. al. 2024. *PA baseline study on identifying and characterizing microplastics in air and rainwater of Dhaka City, Bangladesh.* 7th International Conference on Civil Engineering for Sustainable Development, Bangladesh.

Microplastics in urban waters (Amsterdam)

µ-FTIR: Concentration (number/m³)

Py-GC-MS: Mass (µg/m³)

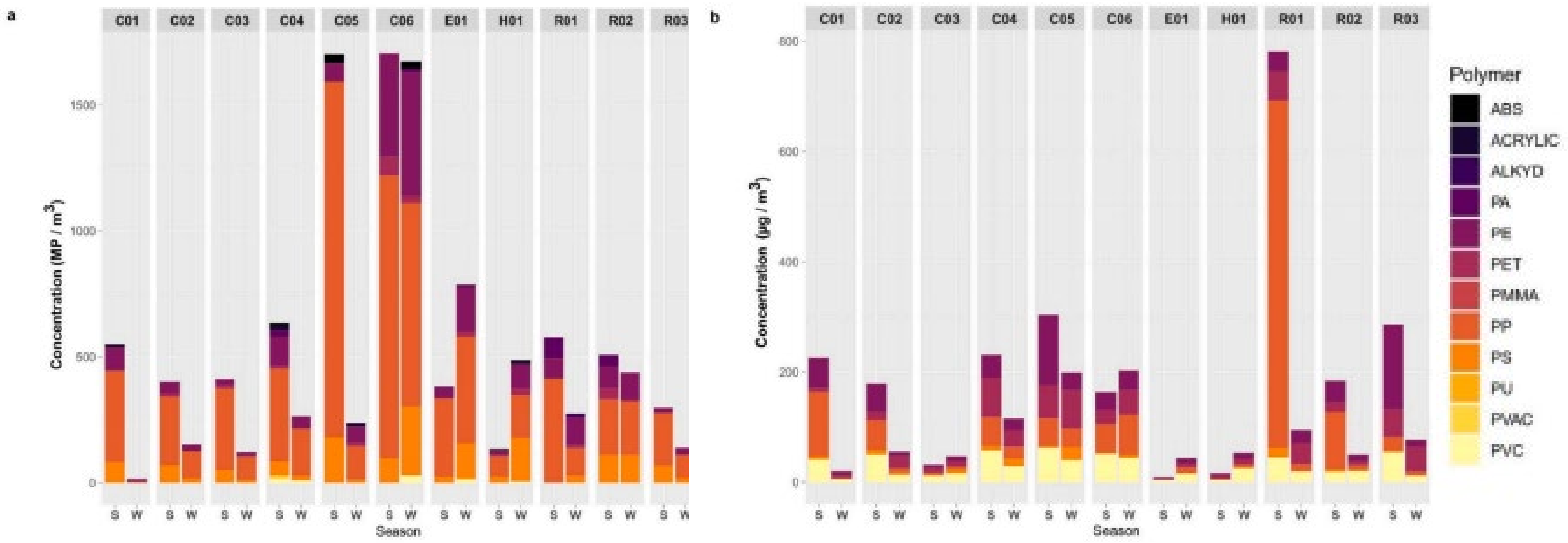


Fig. 4. Polymer concentrations monitored per sampling site at each sampling campaign based on two analysis methods: (a) µ-FTIR imaging, (b) Py-GC-MS mass analysis, seasons: S = summer, W = winter. *From:* Oyku Sefiloglu et. al. 2024. *Comparative microplastic analysis in urban waters using µ-FTIR and Py-GC-MS: A case study in Amsterdam.* Environmental Pollution.

University of Toronto Chelsea Rochman's *Perspectives* Article in Science Magazine, 2018

"Microplastics everywhere"

POLLUTION

Microplastics research–from sink to source

Microplastics are ubiquitous not just in the ocean but also on land and in freshwater systems

By Chelsea M. Rochman

Research on microplastic pollution (small particles of plastic <5 mm in size) has long focused on their largest sink: the ocean. More recently, however, researchers have expanded their focus to include freshwater and terrestrial environments. This is a welcome development, given that an estimated 80% of microplastic pollution in the ocean comes from land (*1*) and that rivers are one of the dominant pathways for microplastics to reach the oceans (*2*). Like other persistent pollutants, such as polychlorinated biphenyls (PCBs), microplastics are now recognized as being distributed across the globe. Detailed understanding of the fate and impacts of this ubiquitous environmental contaminant will thus require a concerted effort among scientists with expertise beyond the marine sciences.

Scientists sporadically reported the presence of small plastic particles in the ocean as early as the 1970s, but research into their distribution and impacts effectively began in 2004 with a pioneering study led by marine ecologist Richard Thompson (*3*). To describe small plastic particles and differentiate them from large plastic debris such as fishing nets, bottles, and bags, the authors dubbed them "microplastics." Recognizing that microplastics were both widespread and potentially unique in their impact on the environment, they encouraged scientists to include the fate, contamination, and effects of microplastics on Earth's natural cycles, ecosystems, and organisms in their studies of plastic pollution.

Department of Ecology and Evolutionary Biology, University of Toronto, Toronto, ON M5S 3B2, Canada. Email: chelsea.rochman@utoronto.ca

Plastic fragments, including microplastics, are now ubiquitous on land, in freshwaters, and in the ocean.

What resulted was a scientific explosion. Over the past 14 years, researchers have documented and studied microplastics across the globe, resulting in tremendous advances regarding the sources, fate, and effects of microplastics and their associated chemicals. Several hundred scientific publications now show that microplastics contaminate the world's oceans, including marine species at every level of the food chain, from pole to pole and from the surface to the seafloor. Yet, scientists have only just begun to document and study microplastics in freshwater and terrestrial systems.

Microplastics were first reported in freshwater lakes in 2013 (*4*). Since then, microplastics have been reported on freshwater beaches, in lakes, or in rivers in Africa, Europe, Asia, North America, and South America (*5*). Just like in the marine realm, microplastics are common in freshwater systems at a global scale. Although contamination tends to be greater near large population centers, microplastics—often in the form of microfibers—have also been found in remote locations (*6*), perhaps as a result of atmospheric deposition (*7*). Microplastic concentrations in freshwater ecosystems are highly variable, and even though these systems are less dilute than oceans, concentrations reported thus far appear to be in a range similar to those in the marine environment (*5*). Microplastic contamination, as seen in marine animals, has also been reported in freshwater animals, including insects, worms, clams, fish, and birds.

Researchers generally seem to expect the effects of microplastics on freshwater organisms to be similar to those on marine organisms. In fact, scientists have been testing impacts of microplastics on freshwater animals for many years because several of them—such as Japanese medaka, zebrafish, *Daphnia*, and *Ceriodaphnia*—are standard toxicity test species. As a result, impacts from exposure to microplastics have been demonstrated in freshwater plants, invertebrates, and several species of fish (*5*). Still, the research remains young, and most studies of freshwater systems and organisms aim to better understand the sources of microplastics to the environment and their effects on animals in general. Given that freshwater ecosystems are highly diverse, with roughly as many fish species as in the oceans, researchers must also ask questions about the unique fate and effects of microplastics in

Published by AAAS

Microplastics

California SB 1422 (September 28, 2018)

SWRCB Deadlines & Requirements

By July 1, 2020

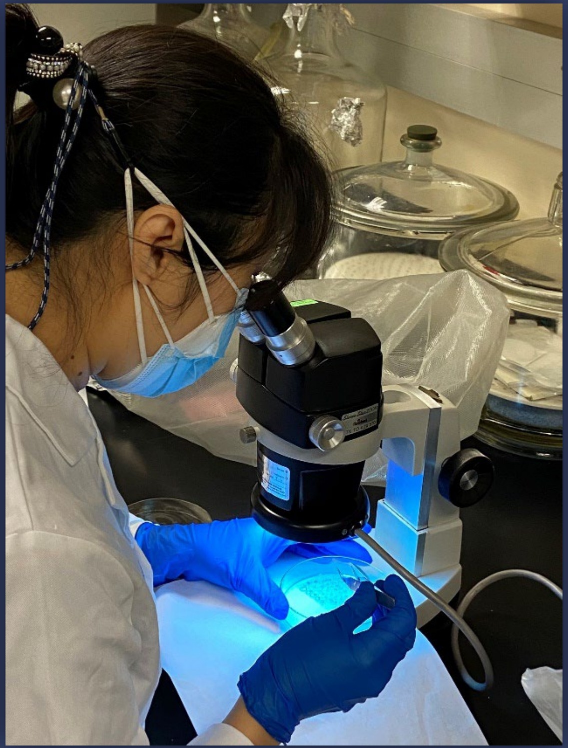
- Definition of microplastics in drinking water

By July 1, 2021*

- Standard microplastics methodology
- Accredit laboratories
- If appropriate, consider issuing a NL or other health guidance
- Requirements for four years of testing & reporting results

**May adopt Policy Handbook to meet these requirements*

California's "Inter-Lab Validation Study"



- Started in October 2019
- Five identification methods
- Four Matrices
  - Ocean water
  - Fish tissue
  - Sediment
  - Clean water
- 26 Laboratories
- At least three labs processing three reps for each matrix/method

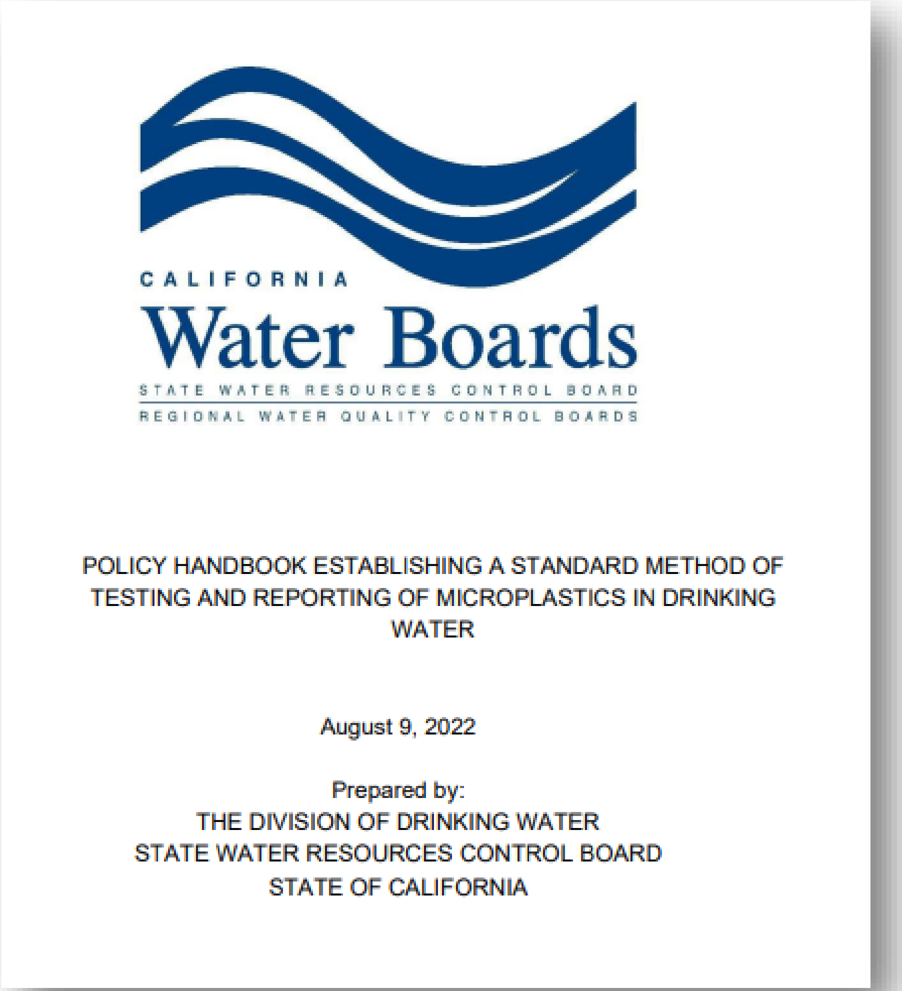
Study Goal: Assess and compare methods for accuracy, repeatability, & resources

SWRCB ‘Microplastics in Drinking Water’ Definition*

“‘Microplastics in Drinking Water’ are defined as solid[1] polymeric materials[2] to which chemical additives or other substances may have been added, which are particles[2] which have at least three dimensions that are greater than 1 nm and less than 5,000 micrometers (µm)[3]. Polymers that are derived in nature that have not been chemically modified (other than by hydrolysis) are excluded.”

*Evidence concerning the toxicity and exposure of humans to microplastics is nascent and rapidly evolving, and the proposed definition of ‘Microplastics in Drinking Water’ is subject to change in response to new information. The definition may also change in response to advances in analytical techniques and/or the standardization of analytical methods.

Formal definition adopted on June 16, 2020


CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

POLICY HANDBOOK ESTABLISHING A STANDARD METHOD OF TESTING AND REPORTING OF MICROPLASTICS IN DRINKING WATER

August 9, 2022

Prepared by:
THE DIVISION OF DRINKING WATER
STATE WATER RESOURCES CONTROL BOARD
STATE OF CALIFORNIA

Handbook adopted September 7, 2022

Microplastics

California SB 1422 (Portantino, 2018)

SWRCB Deadlines & Requirements

By July 1, 2020	✓ Definition of microplastics in drinking water	Published June 16, 2020
By July 1, 2021*	✓ Standard microplastics methodology	Published Sept. 7, 2022
	✓ Accredit laboratories	No approved labs, yet
	✓ **Requirements for four years of testing & reporting results**	No PWS monitored, yet
	▪ If appropriate, consider issuing a NL or other health guidance	No health guidance, yet

**May adopt Policy Handbook to meet these requirements*

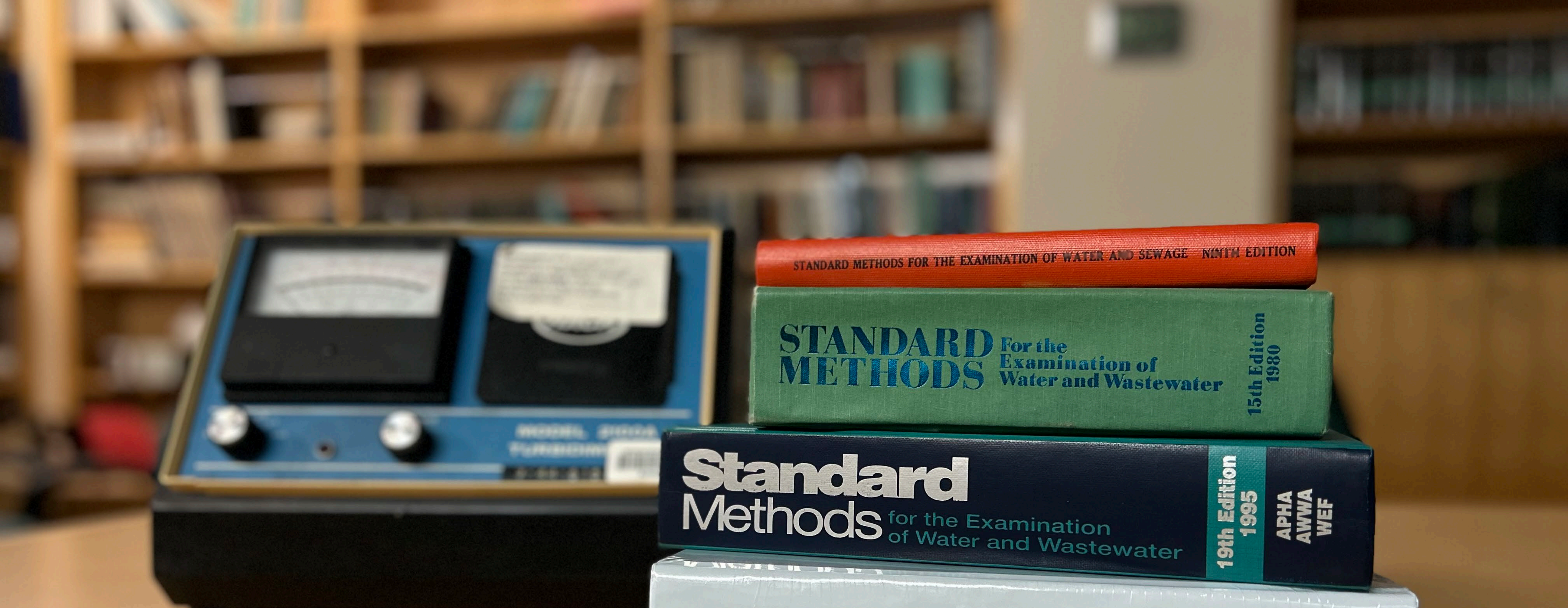
MWD Member Agencies Included in Microplastics Monitoring Handbook

bit.ly/CASystemMap

Microplastics Webinar and Workshop

April 12, 2023

- In-person workshop at MWD Water Quality Laboratory
- ~20 participants from member and retail agencies identified in the Handbook for upcoming monitoring
- Coordination with Dr. Coffin on monitoring plans and sampling locations
- Webinar and workshop were well received, providing valuable information for Metropolitan, member agencies and the State with pathways forward for microplastics monitoring.



Analytical Methods for Detecting Microplastics in Drinking Water

"Why hasn't monitoring started yet?"

The Evolution of Environmental Methods

- 1974-75 - Rome, NY waterborne giardiasis outbreak

Photo courtesy of Walter Jakubowski

U.S. EPA ICR Method for Detecting *Giardia* and *Cryptosporidium* in water (June 1995)

- 25.4 cm (10 inch) long 1 um nominal porosity, yarn-wound polypropylene cartridge

Source: US EPA ICR Protozoan Method for Detecting *Giardia* Cysts and *Cryptosporidium* Oocysts in Water by a Fluorescent Antibody Procedure (EPA/814-B-95-003)
https://www.epa.gov/dwlabcert/methods-1623-and-16231-technical-training-material

It took 30 years to develop, optimize, & validate usable method

U.S. EPA Method 1623: *Cryptosporidium* and *Giardia* in Water by Filtration/IMS/FA (December 2005)

Method is still time consuming and expensive

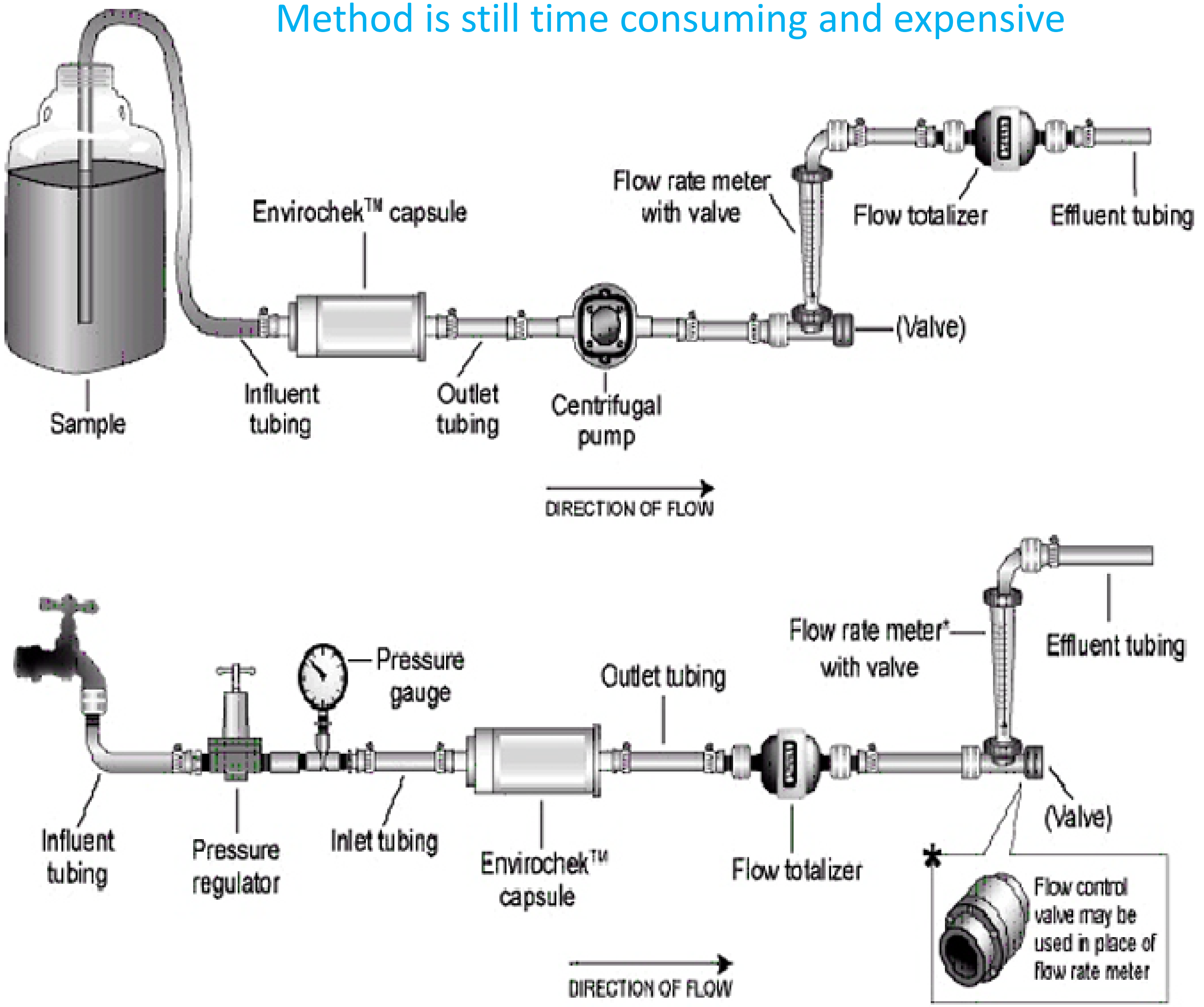


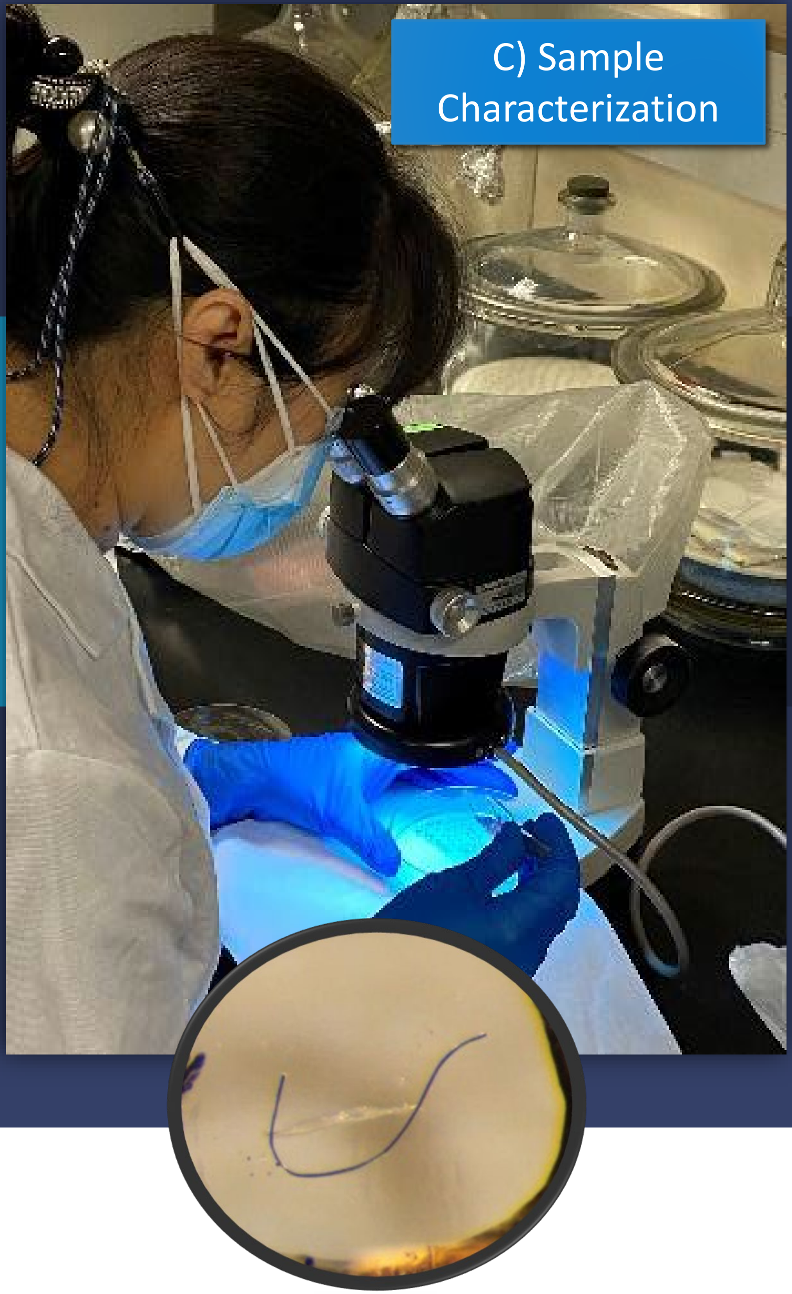
Figure 1. Filtration Systems for Envirochek® HV Capsule (unpressurized source - top, pressurized source - bottom)

Source: https://www.epa.gov/dwlabcert/methods-1623-and-16231-technical-training-material

Developing an Analytical Method to Detect Microplastics in Drinking Water

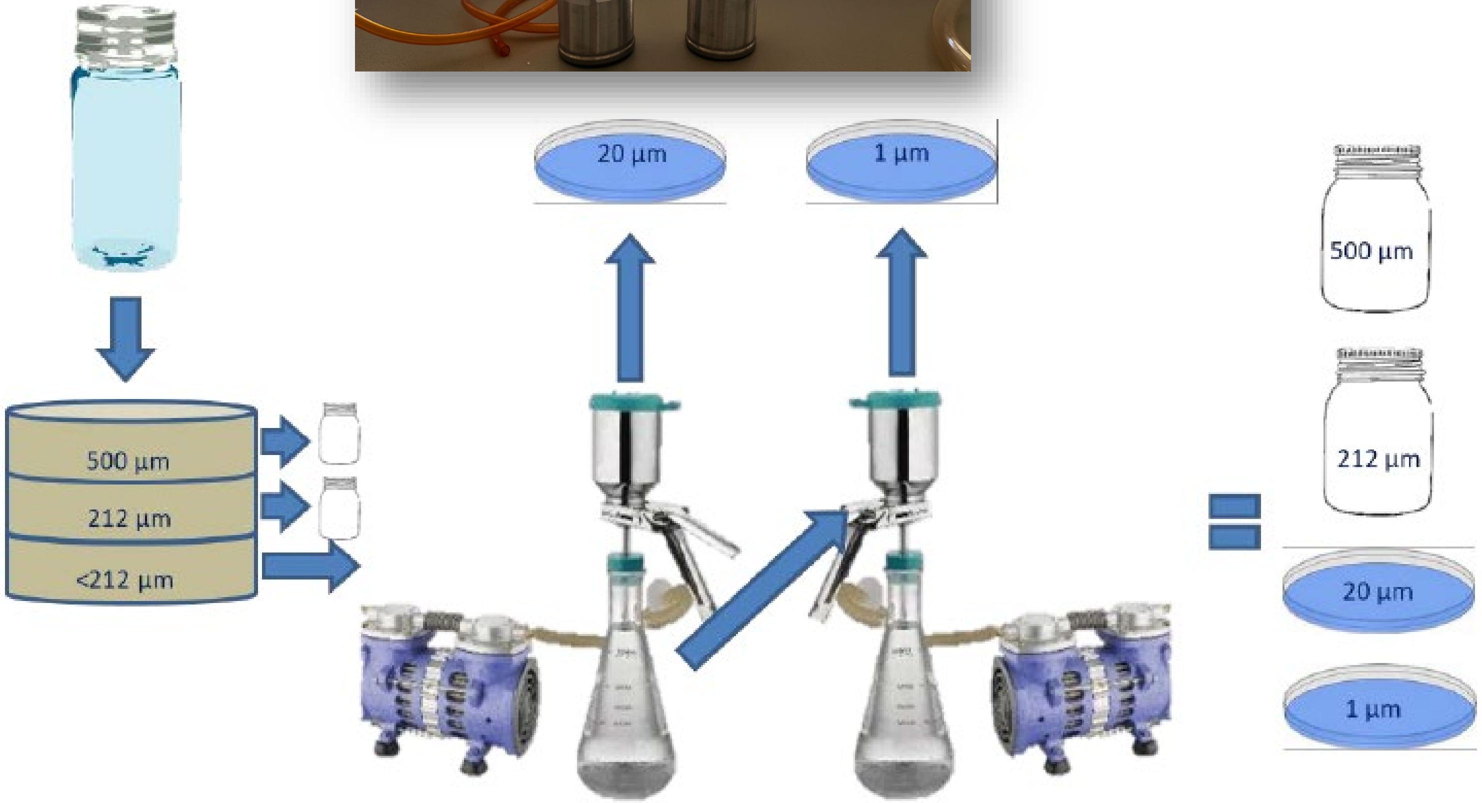
Dr. Lucy Li (MWD) using microscopy to characterize microplastics spiked in samples for microplastics method evaluation study (2020-2021)

C) Sample Characterization



B) Sample Preparation

A1) Sample Collection: “Large Volume” Inline Cartridge Method



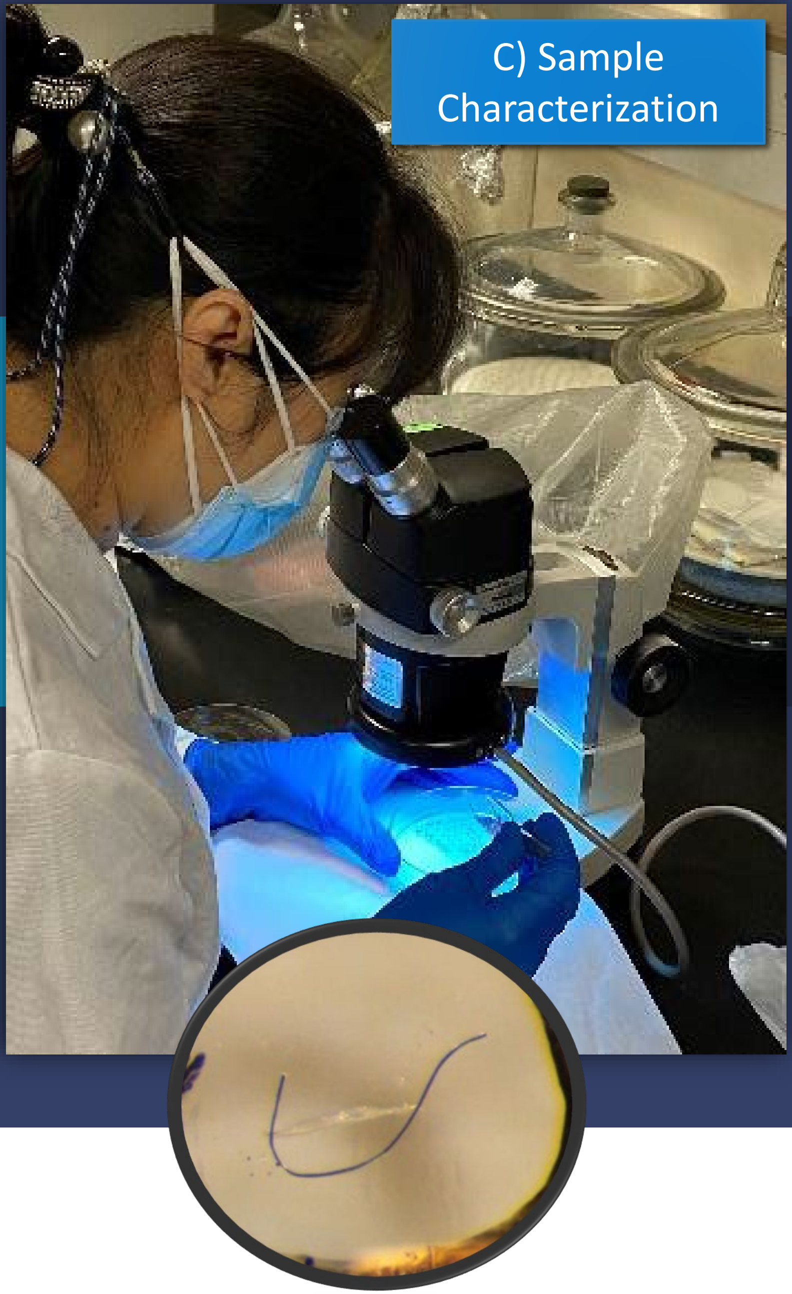
Standard Operating Procedures for Extraction and Measurement by Infrared/Raman Spectroscopy of Microplastics Particles in Drinking Water, May 27th 2022

Sampling Device Challenges – Sample Elution

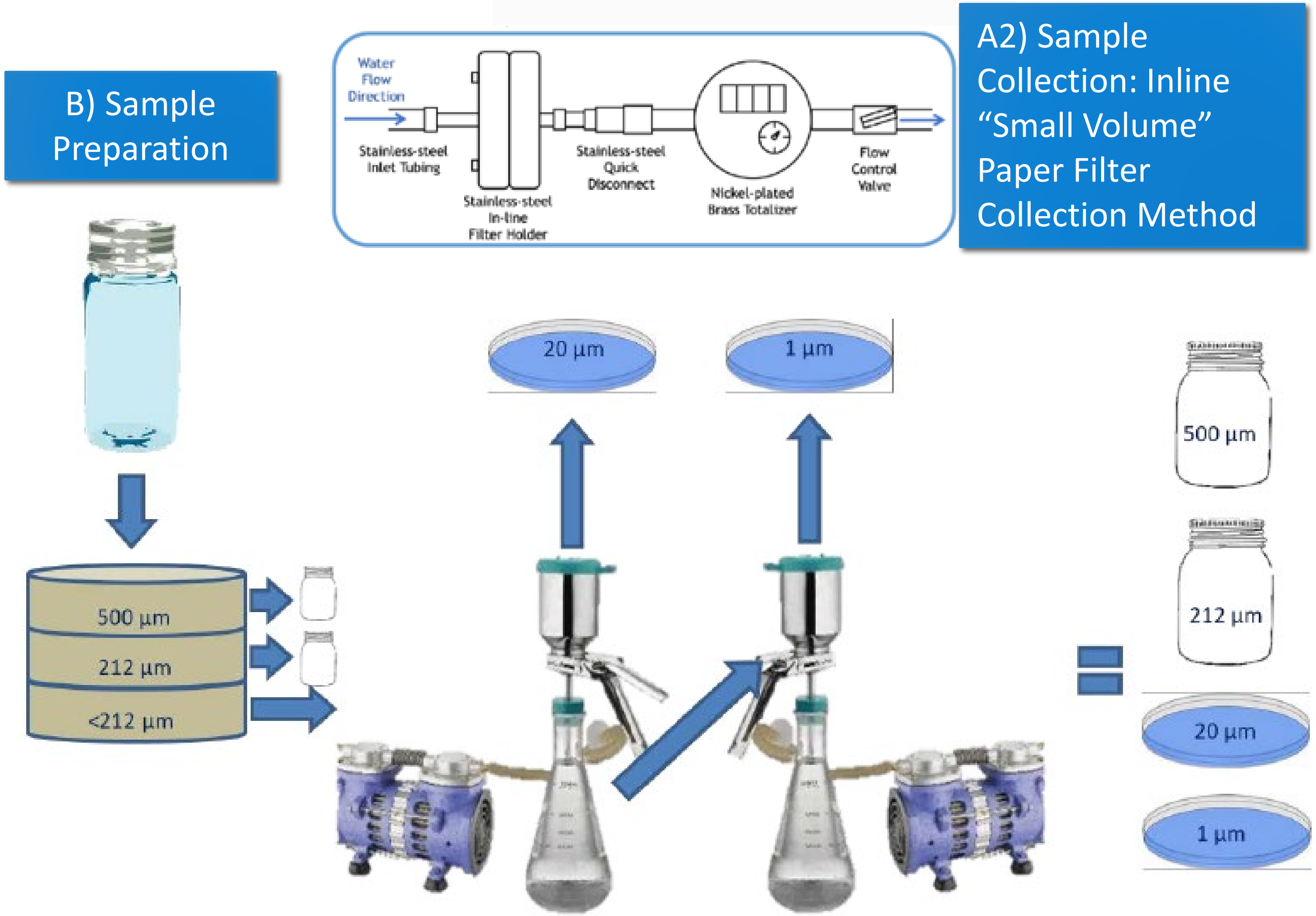
- "High volume" cartridge filter sampling device abandoned
- Cannot fully clean after use
- Cannot reuse cartridges
- Univ. Toronto team experienced similar issue

Cartridge filters coated with sand, soil and other materials, particularly on smaller pore size filters

Dr. Lucy Li (MWD) using microscopy to characterize microplastics spiked in samples for microplastics method evaluation study (2020-2021)

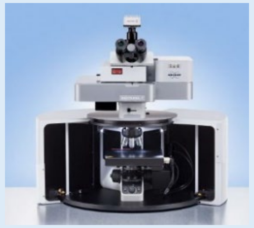


Developing an Analytical Method to Detect Microplastics in Drinking Water



Standard Operating Procedures for Extraction and Measurement by Infrared/Raman Spectroscopy of Microplastics Particles in Drinking Water, May 27th 2022

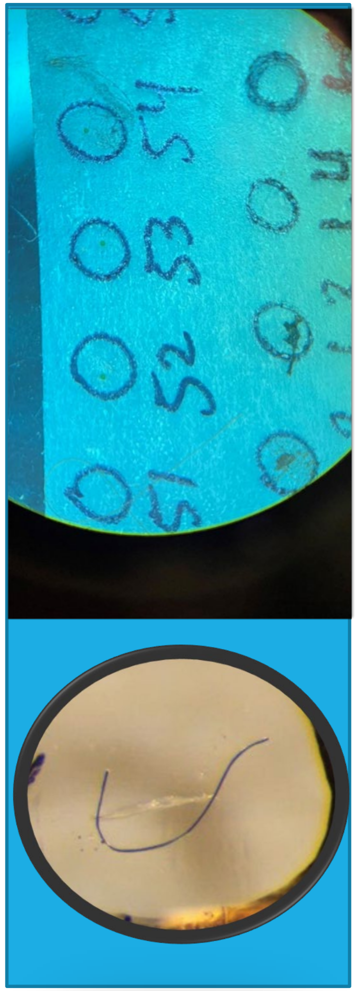
MICROPLASTICS/POLYMER IDENTIFICATION INSTRUMENTS

	Optical Microscopy	micro-FTIR	micro-Raman	LDIR	O-PTIR	Pyr/TD-GC/MS
						
Particle Number	✓	✓	✓	✓	✓	✗
Chemical ID	✗	✓	✓	✓	✓	✓ **
Area (Shape)	✓	✓	✓	✓	✓	✗
Color	✓	✗	✗	✗	✗	✗
Cost*	$5,000-$60,000	$100,000-$250,000	$200,000-$300,000	$400,000	$250,000?	$250,000
Spatial Resolution	>1 µm	20-50 µm	1 - 10 µm	20-50 µm	< 1 µm	N/A
Sample scanning speed	Days	Days	Days	A few minutes ?	?	A few hours

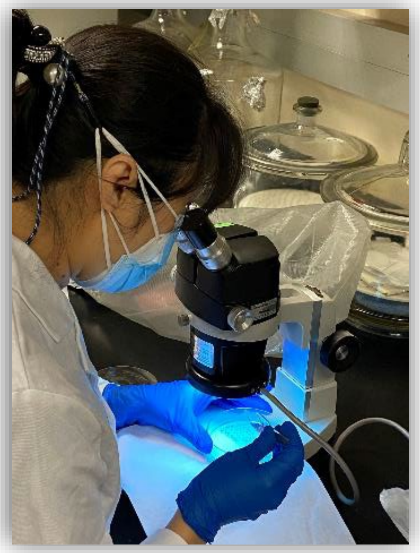
**   Based on manufacturer estimates (September 2022).*
*** Currently has a limited range for polymer identification.*
N/A = Not applicable.

FTIR = Fourier-transform infrared spectroscopy
LDIR = Laser Direct Infrared spectroscopy
O-PTIR = Optical photothermal infrared spectroscopy (simultaneous IR and Raman spectra)
Pyr/TD-GC/MS = Pyrolysis thermal desorption gas chromatography/mass spectrometry

Particle-based analytical methods: Comparison of microplastics method with *Cryptosporidium* & *Giardia* method

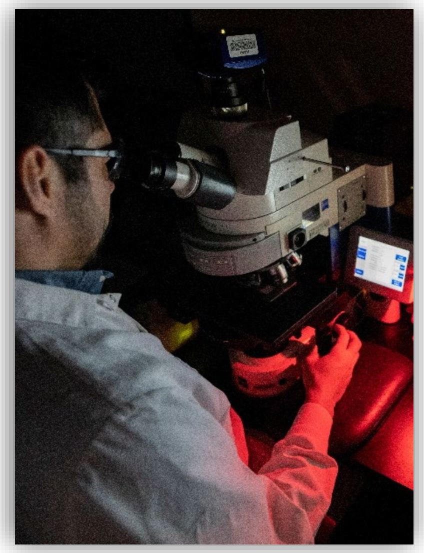


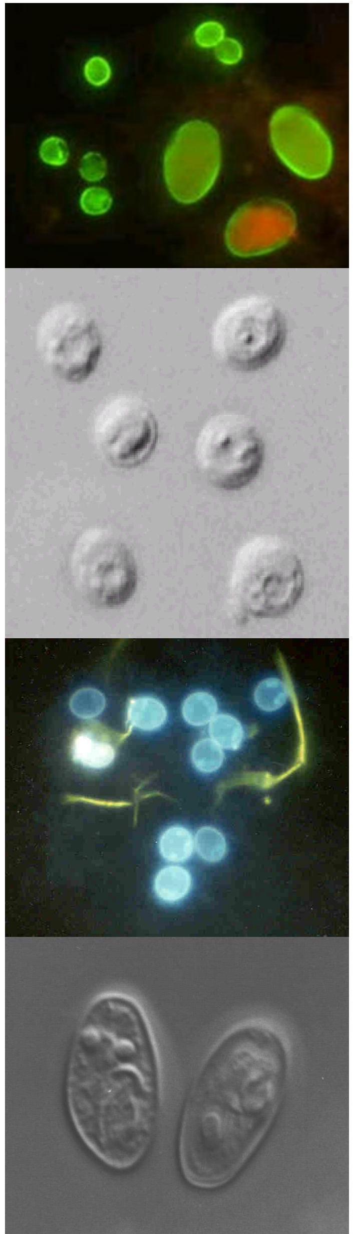
Microplastics



- **Sampling:** High volume filtration
- **Sample prep:** Filter elution & extraction
- **Characterization:** Microscopy
  - Size
  - Shape
  - Color
- **Confirmation:** Chemical ID
- **Water treatment:** Physical removal

Crypto & Giardia





#1 Problem with Microplastics Analysis: It's extremely time consuming!!!

TIME = $$$

Contract lab cost is

~$9,000 per sample

#2 Problem: Pervasive Contamination

- Blanks not analyzed and/or not reported
- Sample contamination control included any or all of the following preventive measures:
  - Minimized use of plastics
  - Sonicated glassware cleaned with ultrapure water
  - All glass materials heated in 525 °C oven
  - Stainless steel filters precleaned with pure water and treated in 525 °C oven
  - Solvents filtered through 0.7 um glass filter
  - Cotton clothing
  - Nitrile gloves
  - Pre-filtered (0.45 um) purified water
  - Processing materials consistently covered
  - "Clean rooms"
  - Laminar flow hoods

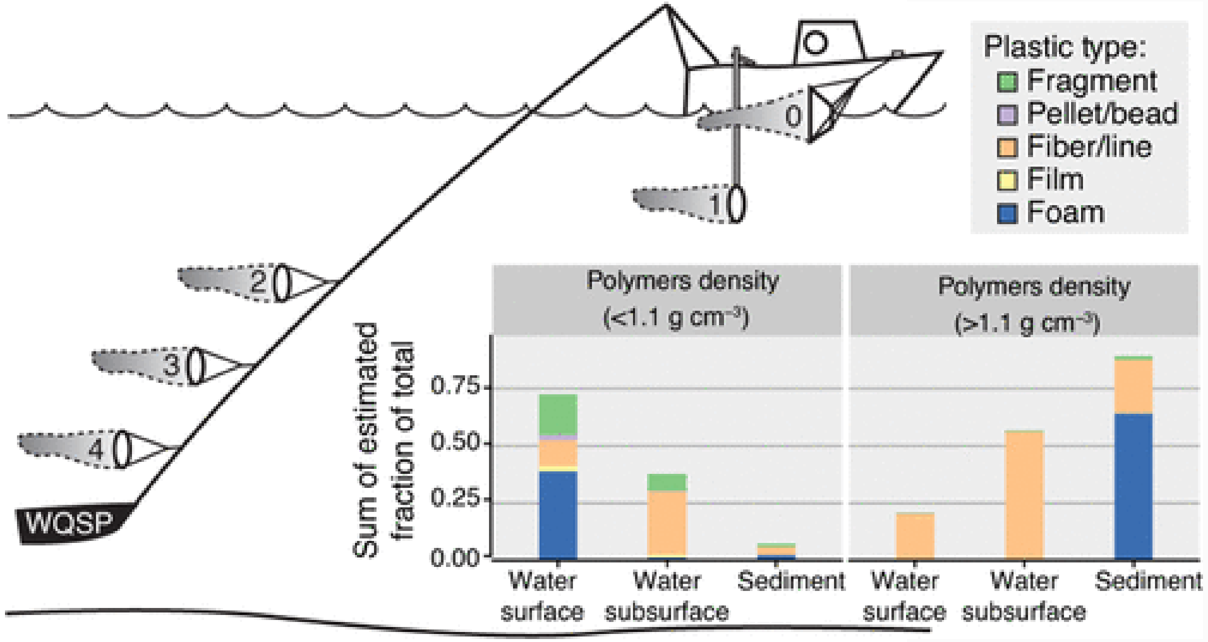
- *"Although microplastics were found in all blank samples, the background contamination was negligible since the number in blank sample was <5% of the abundance of microplastics detected in any water samples" ~Wang et al., 2020*

- *"Important concentrations of fibres (such as cotton, viscose and cellulose) were found all along the drinking water treatment and in blanks, even if several measures were taken to prevent contamination." ~Negrete et al. 2023*

- *"However, between 12 and 64 non-synthetic fibres (av. 36 fibres) and between 0 and 2 synthetic fibres (av. 0.67 synthetic fibres) were found per blank despite the rigorous rinsing of all material with filtered ultrapure water." ~Negrete et al., 2023*

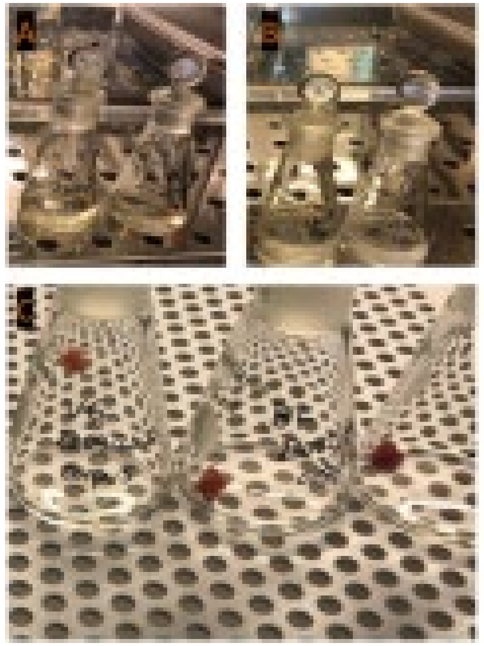
- *While PMMA and PET were detected only in some blanks, an interfering signal of PS, PP, PE, and PVC was present in all blanks. Hence, a blank correction has been applied by subtracting the average blank value from the data." ~Sefiloglu et al. 2024*

#3 Problem: Sample matrix



a) Ambient water

b) Sediments



c) Tissue

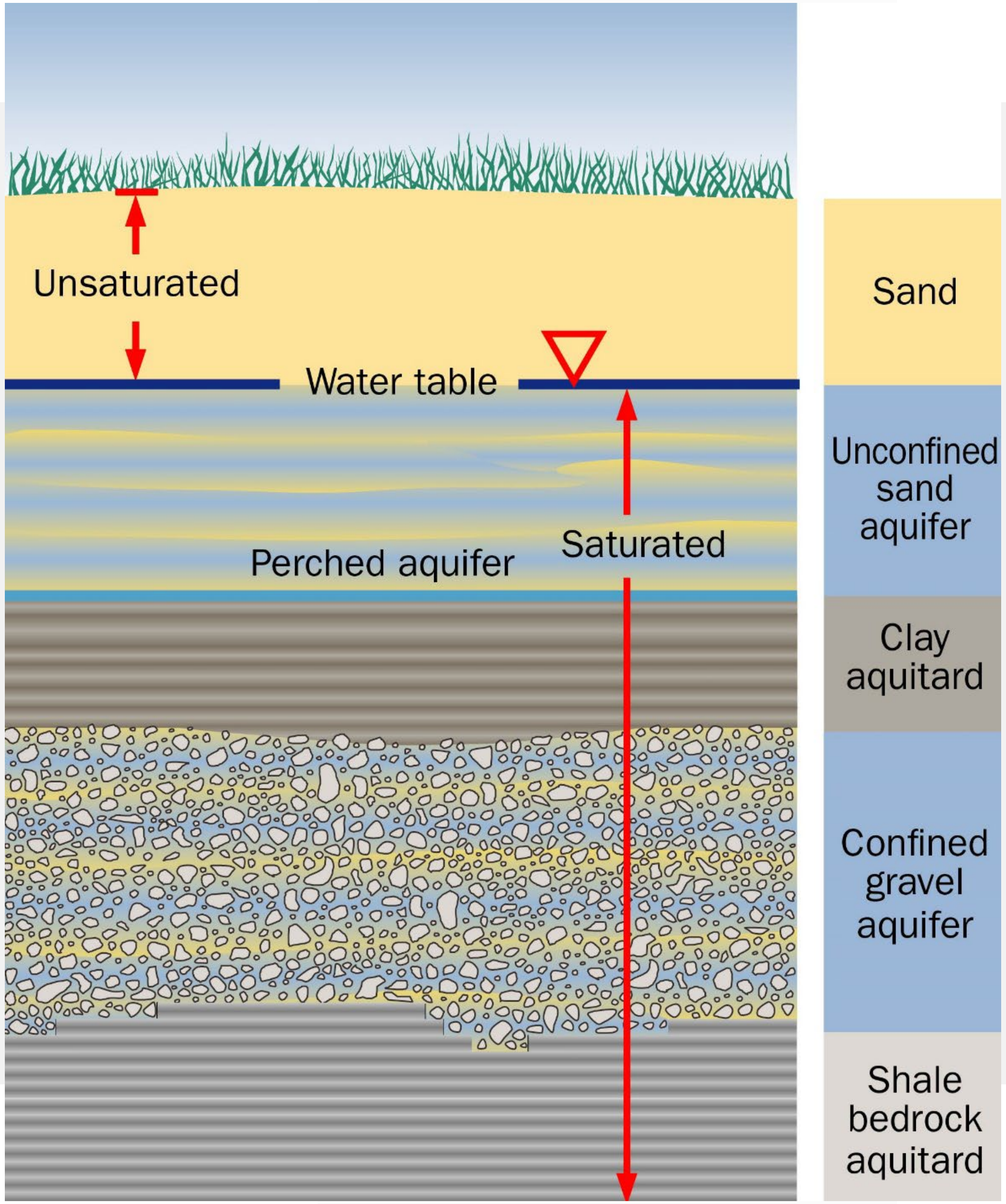
a) Lenaker et al. 2019. Vertical Distribution of Microplastics in the Water Column and Surficial Sediment from the Milwaukee River Basin to Lake Michigan. Environ. Sci. Tech.
b) Rochelle 2023. Manhattan beach after a storm.
c) Codrington et. al. 2024. Detection of microplastics in the human penis. Int. Journal of Impotence Research.

Fate of microplastics in conventional drinking water treatment

- Preliminary research is promising
- Microplastics are removed
- Removal varies with level of treatment (40 to 95%)
- Slow sand filters remove ~99.9% of nanoplastics
- Treatment plant operational parameters correlate with microplastics

Bench-scale sand column filter.

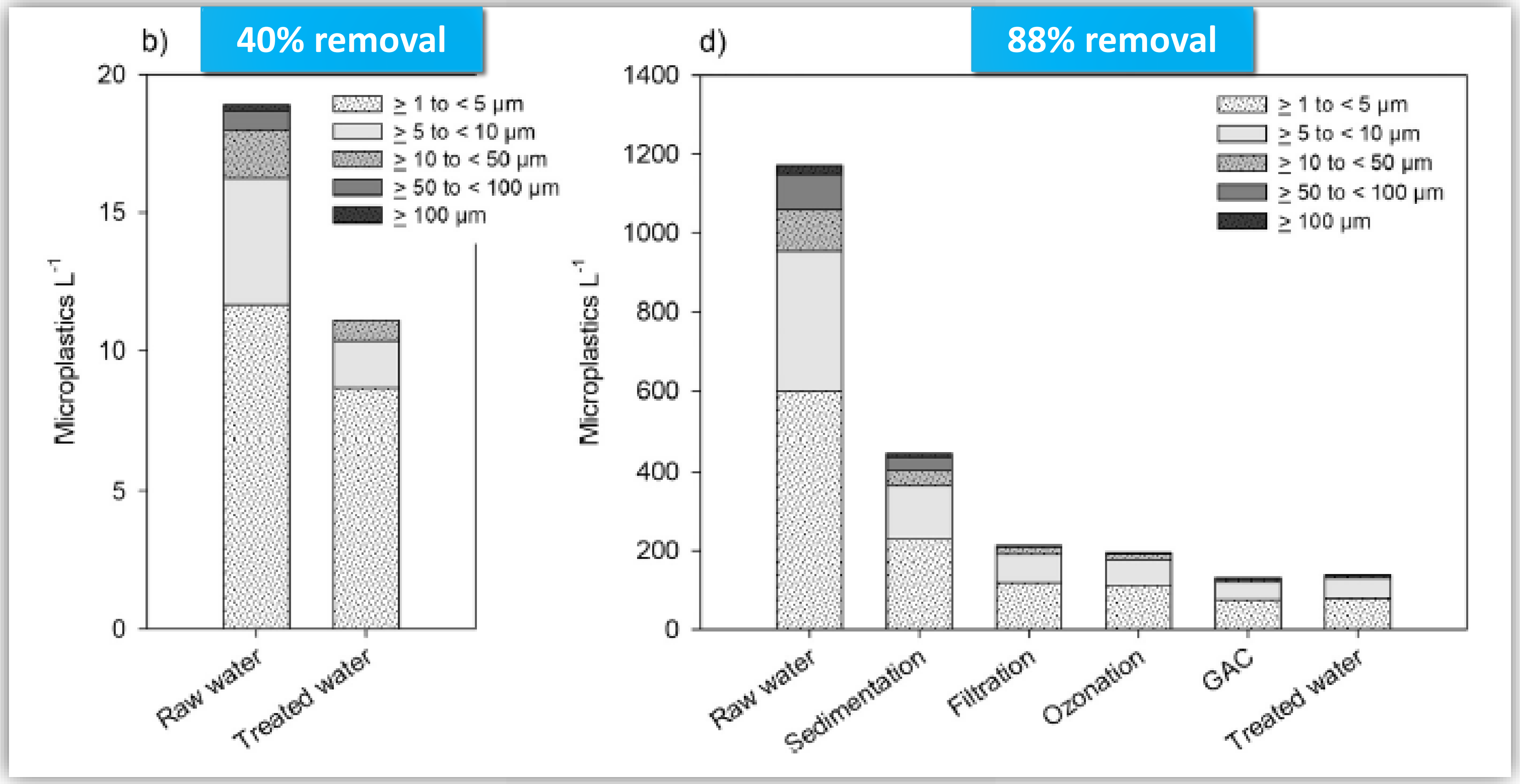
Figure S5, Pulido-Reyes et al. 2022. *Nanoplastics removal during drinking water treatment: Laboratory- and pilot-scale experiments and modeling.* J. Hazardous Materials 436: 129011



Subsurface view of various aquifers.

Figure 3, https://www.ontario.ca/page/understanding-groundwater

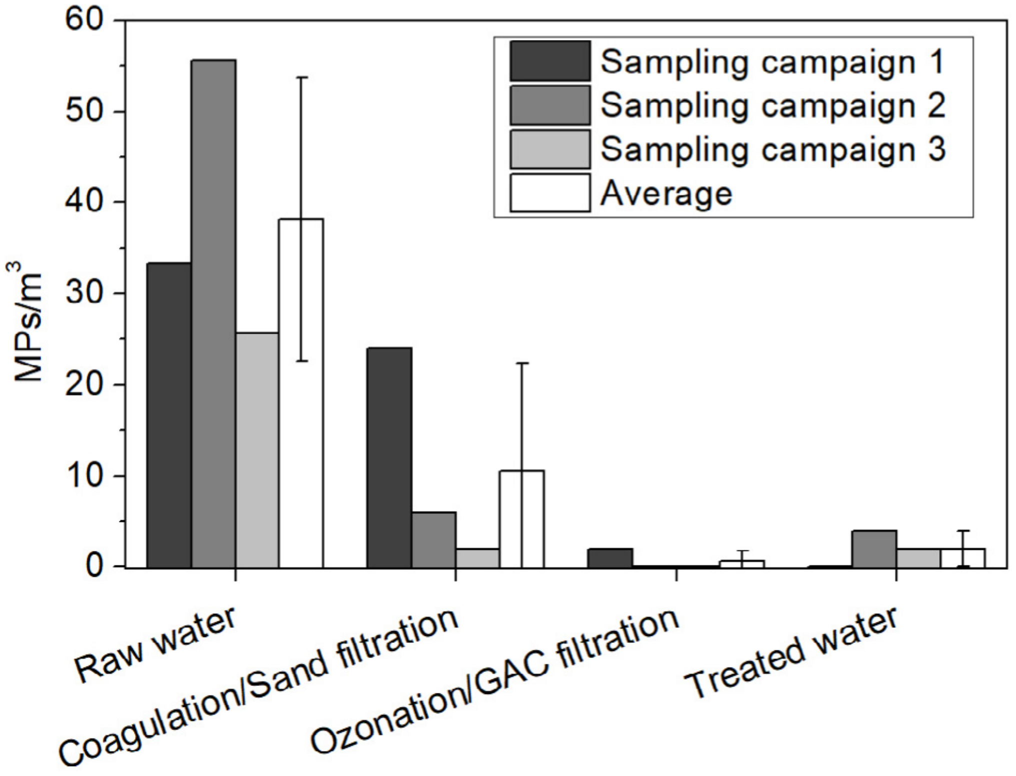
Drinking water treatment removes microplastics fragments (Czech Republic)



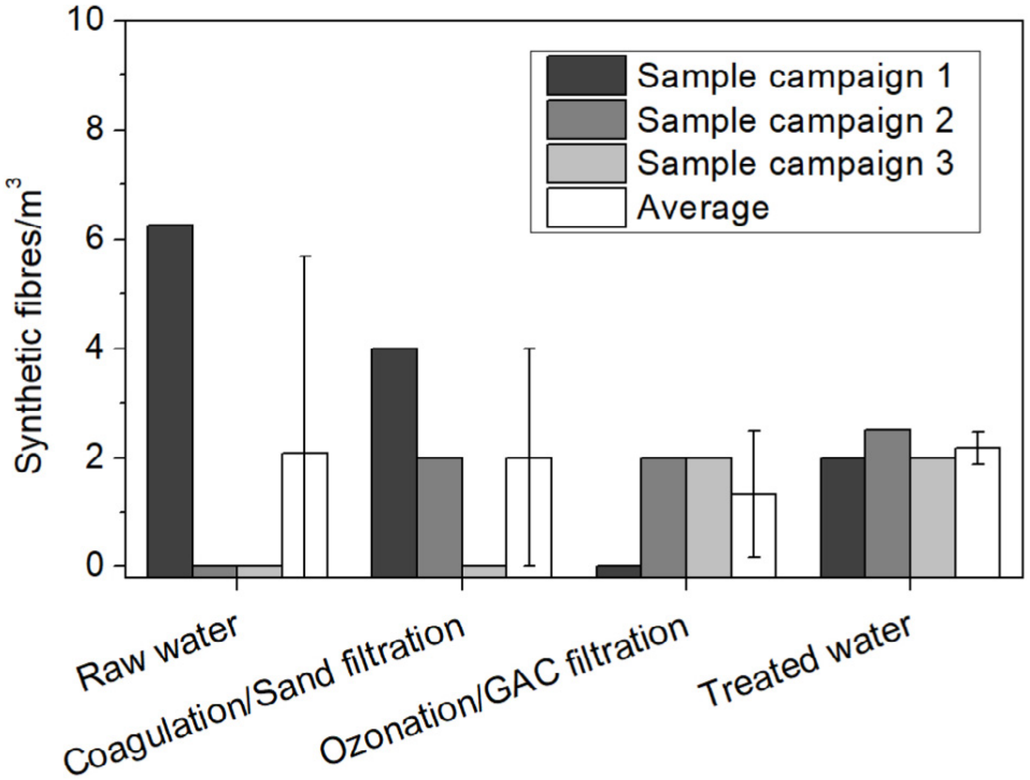
Pivokonsky et. al. 2020. *Occurrence and fate of microplastics at two different drinking water treatment plants within a river catchment.* Science of the Total Environment

Drinking water treatment removes microplastics fragments (Switzerland)

Synthetic particles **95% removal**



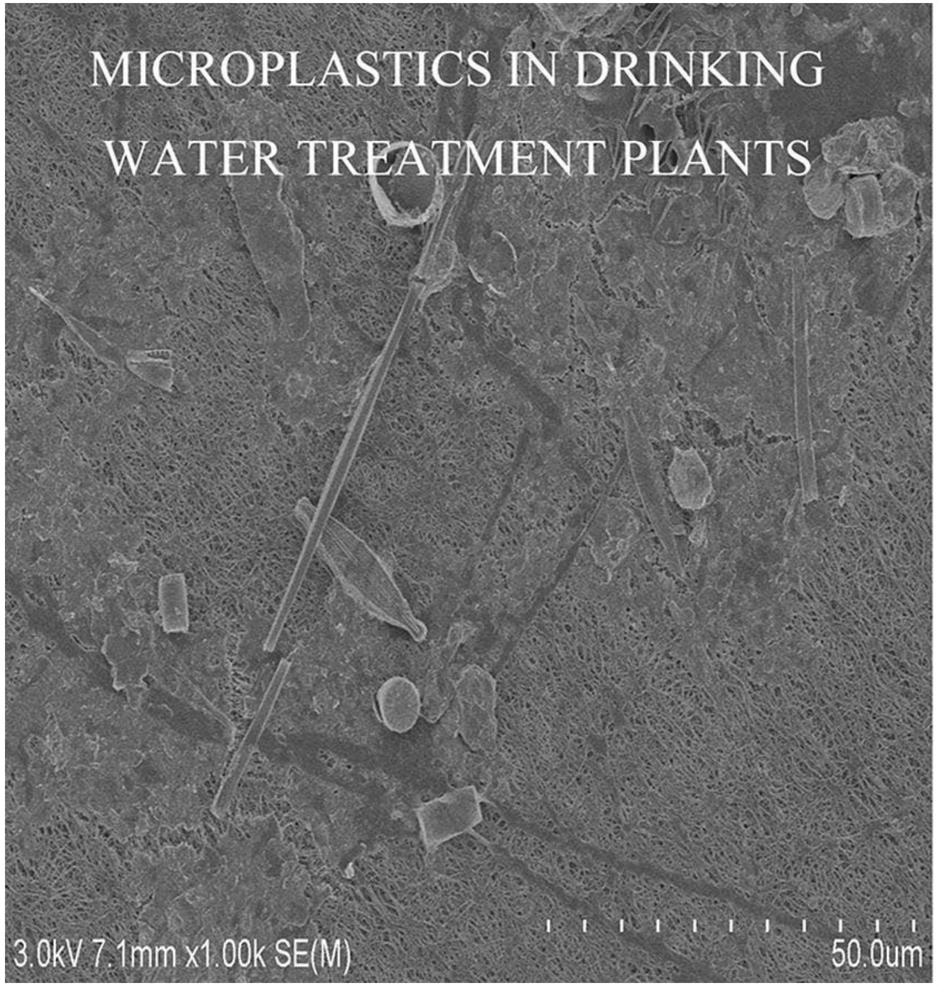
Synthetic fibers **Negligible removal**

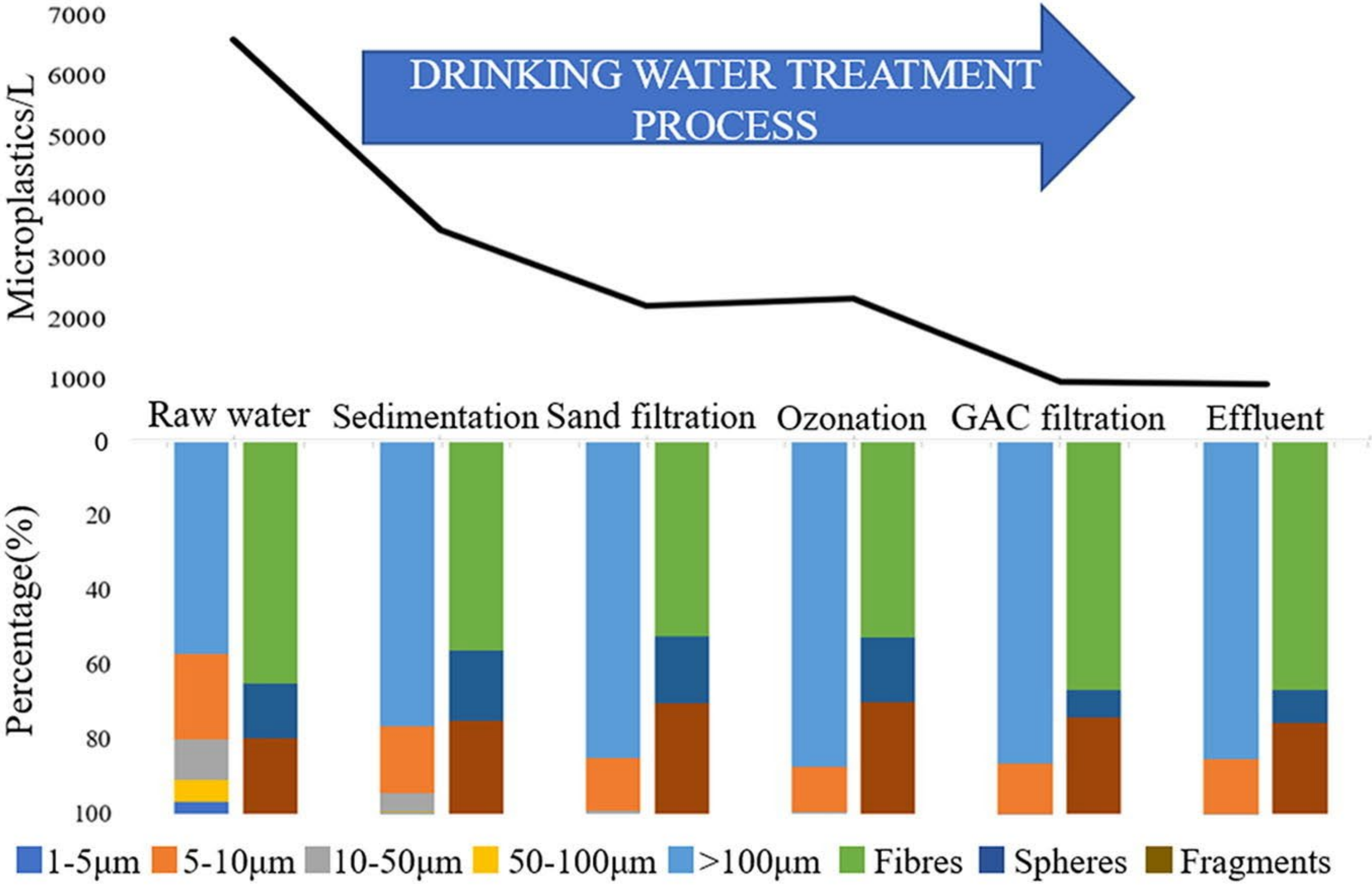


Velasco et. al. 2023. *Contamination and removal efficiency of microplastics and synthetic fibres in a conventional drinking water treatment plant in Geneva, Switzerland.* Science of the Total Environment.

Drinking water treatment removes microplastics particles (China)

>10 um: ND after sand
< 10 um: Up to 71% Removal





Wang et al. 2020. *Occurrence and removal of microplastics in an advanced drinking water treatment plant (ADWTP).* Science of the Total Environment

Drinking water treatment removes nanoplastic particles (Switzerland)

Slow sand filtration
Bench: 99.5% removal
Pilot: >99.9% removal

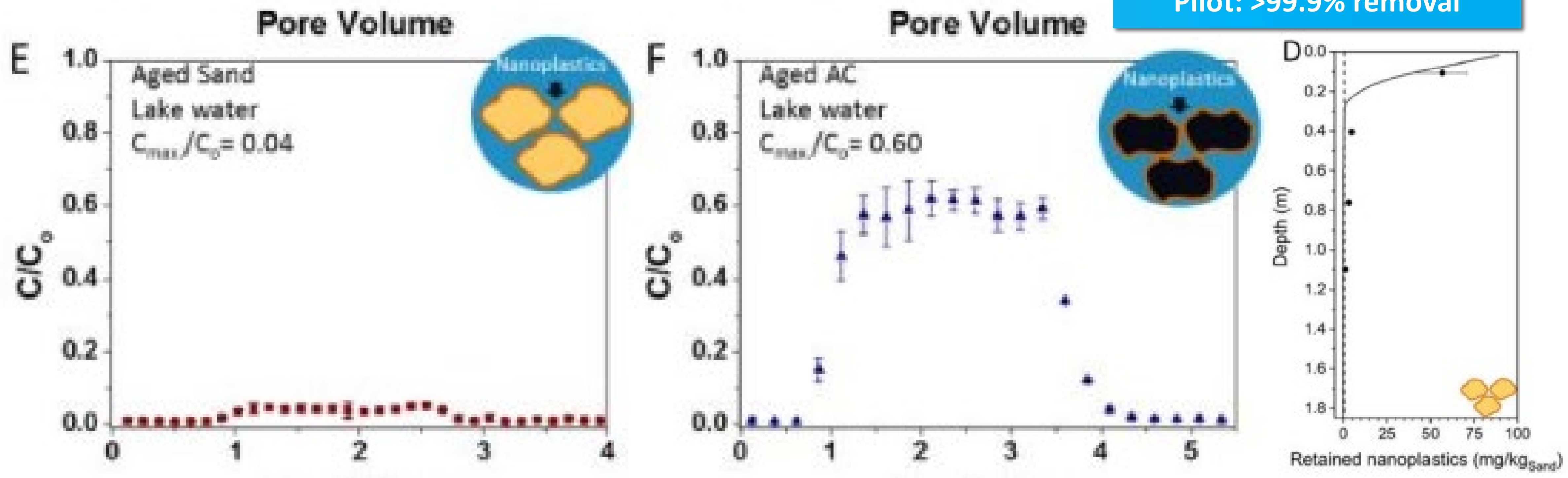
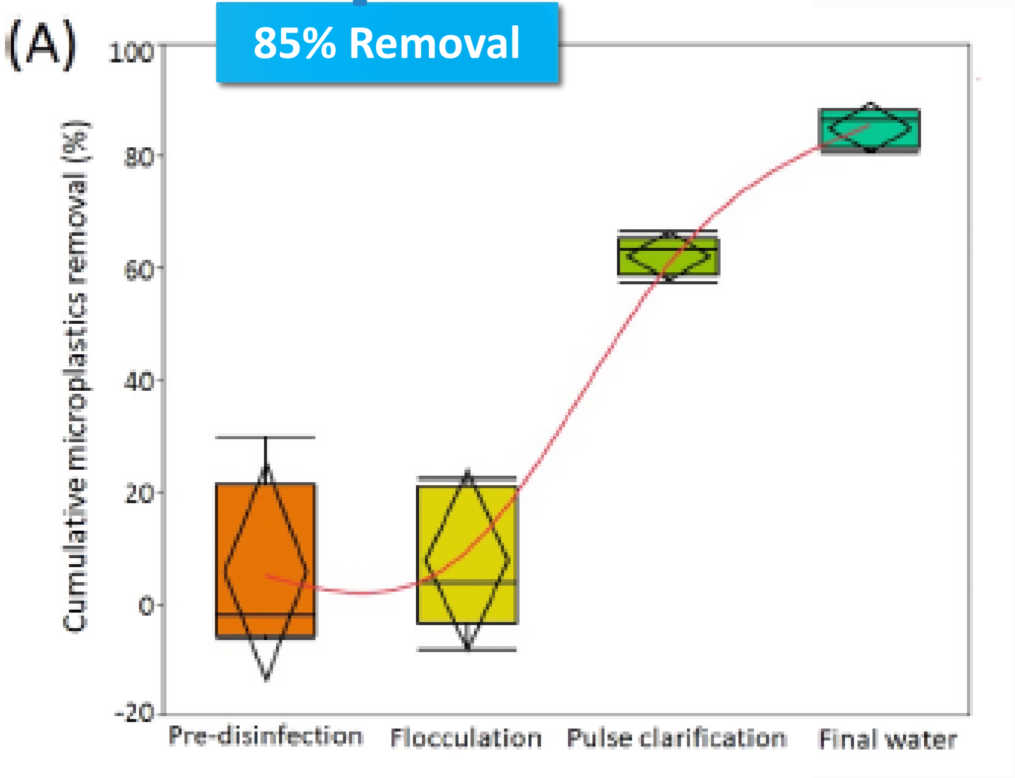


Fig. 3E & F: Influence of the surface characteristics of aged filtration media on the transport/retention of nanoplastic particles. Fig. 4 D: Pilot scale sand filter nanoplastics deposition profile. Aged sand - AC – activated carbon

Pulido-Reyes et al. 2022. *Nanoplastics removal during drinking water treatment: Laboratory- and pilot-scale experiments and modeling.* J. Hazardous Materials 436: 129011

Drinking water treatment operational parameters are correlated with microplastics removal (India)



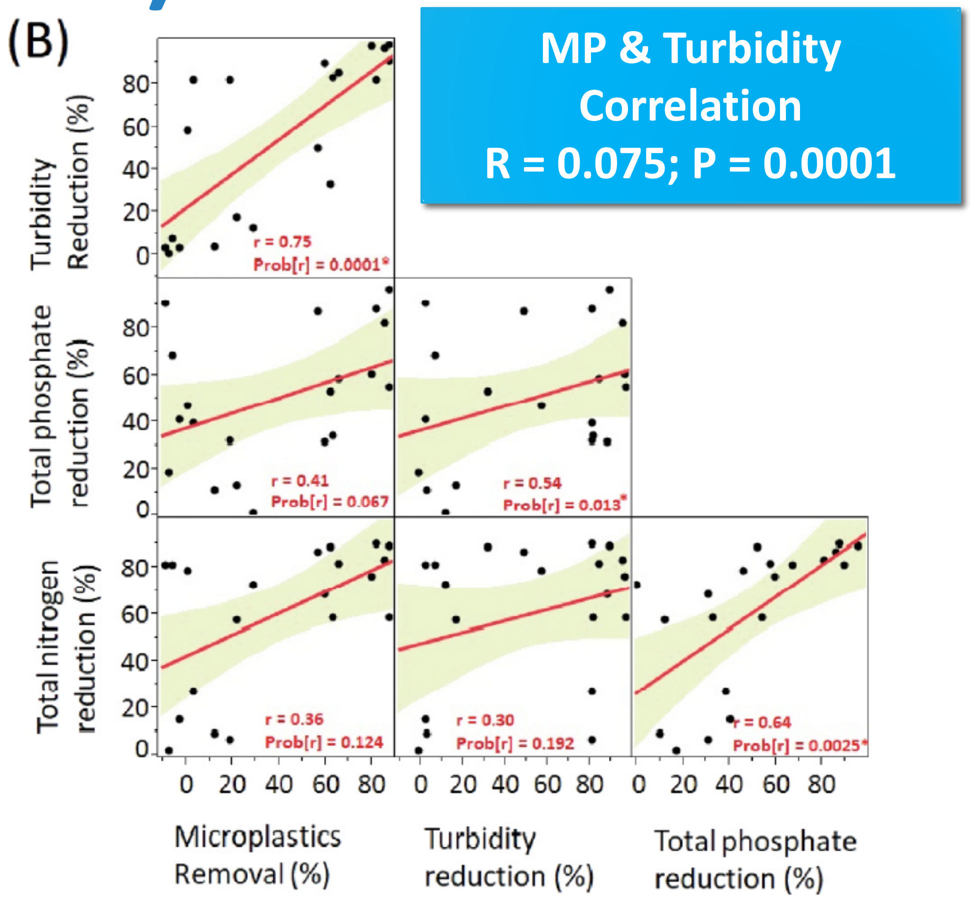
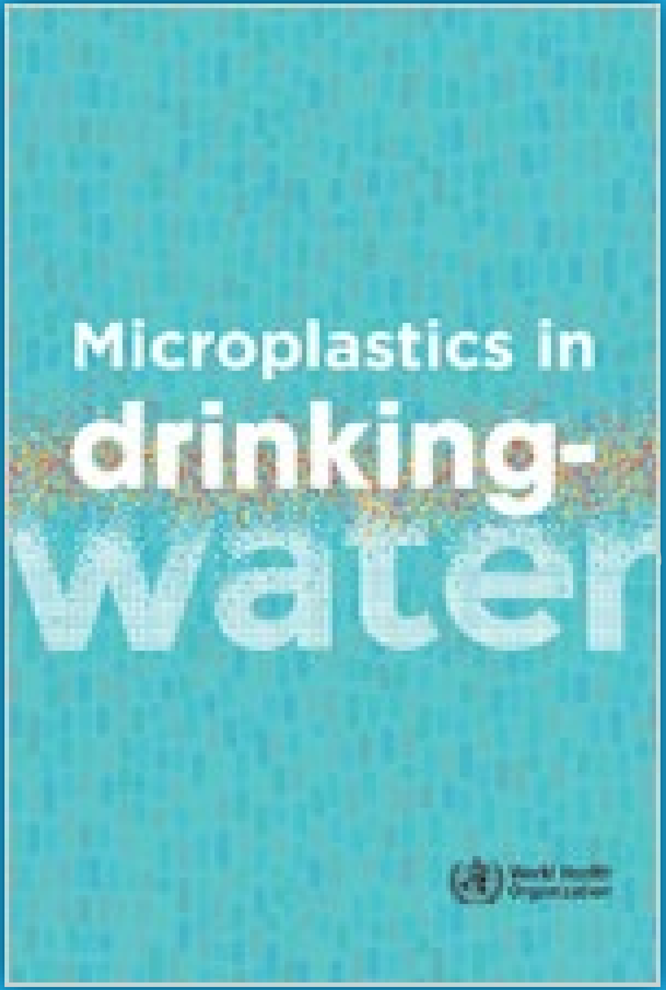


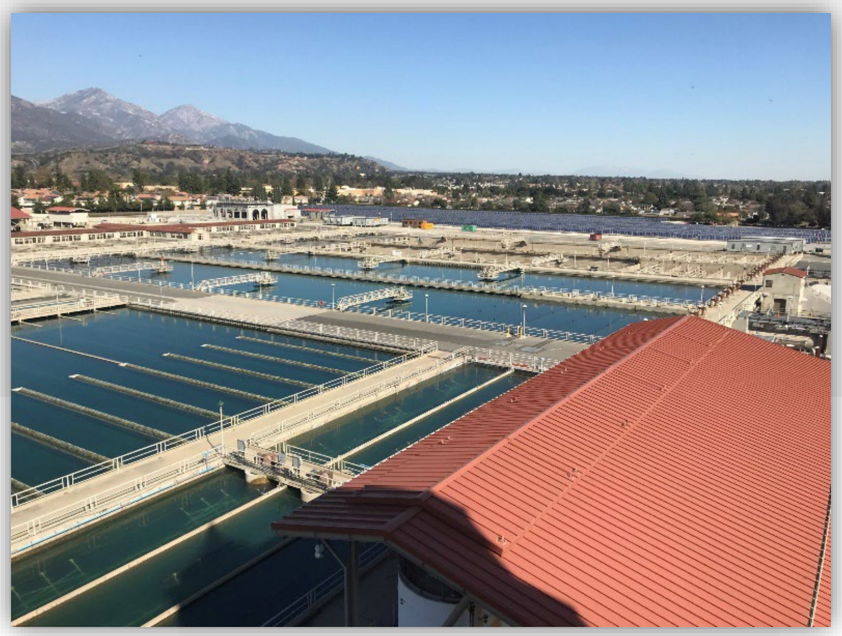
Fig. 5 (A) Cumulative removal of microplastics after distinct treatment steps at the test DWTP. (B) Regression analysis showing correlation between microplastics removal and removal of turbidity, total phosphate, and total nitrate nitrogen.

Sarkar et al. 2021. *Microplastics removal efficiency of drinking water treatment plant with pulse clarifier.* J. of Hazardous Materials



"Water suppliers should optimize water treatment processes for particle removal and microbial safety, which will incidentally improve the removal of microplastic particles."

~ WHO 2019

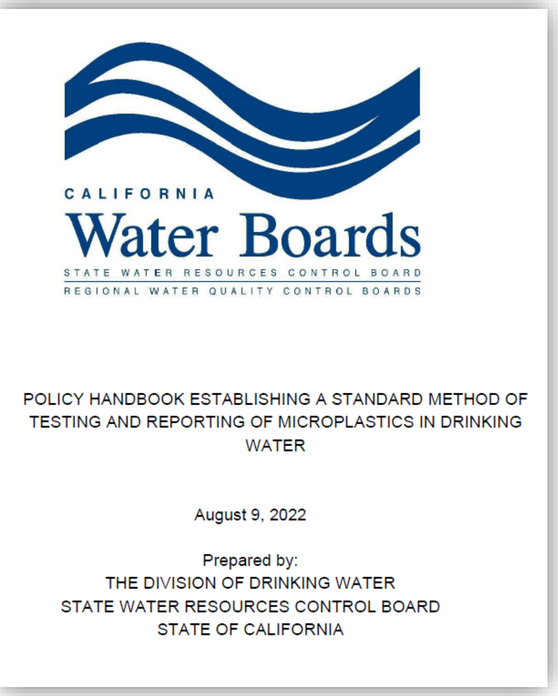


WHO 2019. Microplastics in drinking-water.

Near-term microplastics challenges for purveyors

- Sampling
- Analysis
- Sample contamination
- Costs
- Results communication

Microplastics Monitoring


CALIFORNIA
Water Boards
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POLICY HANDBOOK ESTABLISHING A STANDARD METHOD OF TESTING AND REPORTING OF MICROPLASTICS IN DRINKING WATER

August 9, 2022

Prepared by:
THE DIVISION OF DRINKING WATER
STATE WATER RESOURCES CONTROL BOARD
STATE OF CALIFORNIA

Upcoming Monitoring Requirements*

Pending:

- Phase 1 (“Fall 2023 – Fall 2025”): Source water monitoring for 2 years plus surrogate development
- Phase 2 (“Fall 2026 – Fall 2028”): Treated drinking water monitoring for 2 years

***Missing* from Handbook**:

- Sampling and sample preparation procedures
  - Pilot phase: Standardized and validated SOPs are still being developed

Next steps: *Not sure* - State Water Board has much work to do prior to issuing monitoring orders. They need support (and time) to complete research prior to monitoring.

**Valid as of August 2024*

Acknowledgements

Carrie Guo, Ph.D. - MWD Emerging Chemical Constituents Team Manager

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