

# Microplastics in Potable Water by Pyrolysis-GC/MS: A Global Survey


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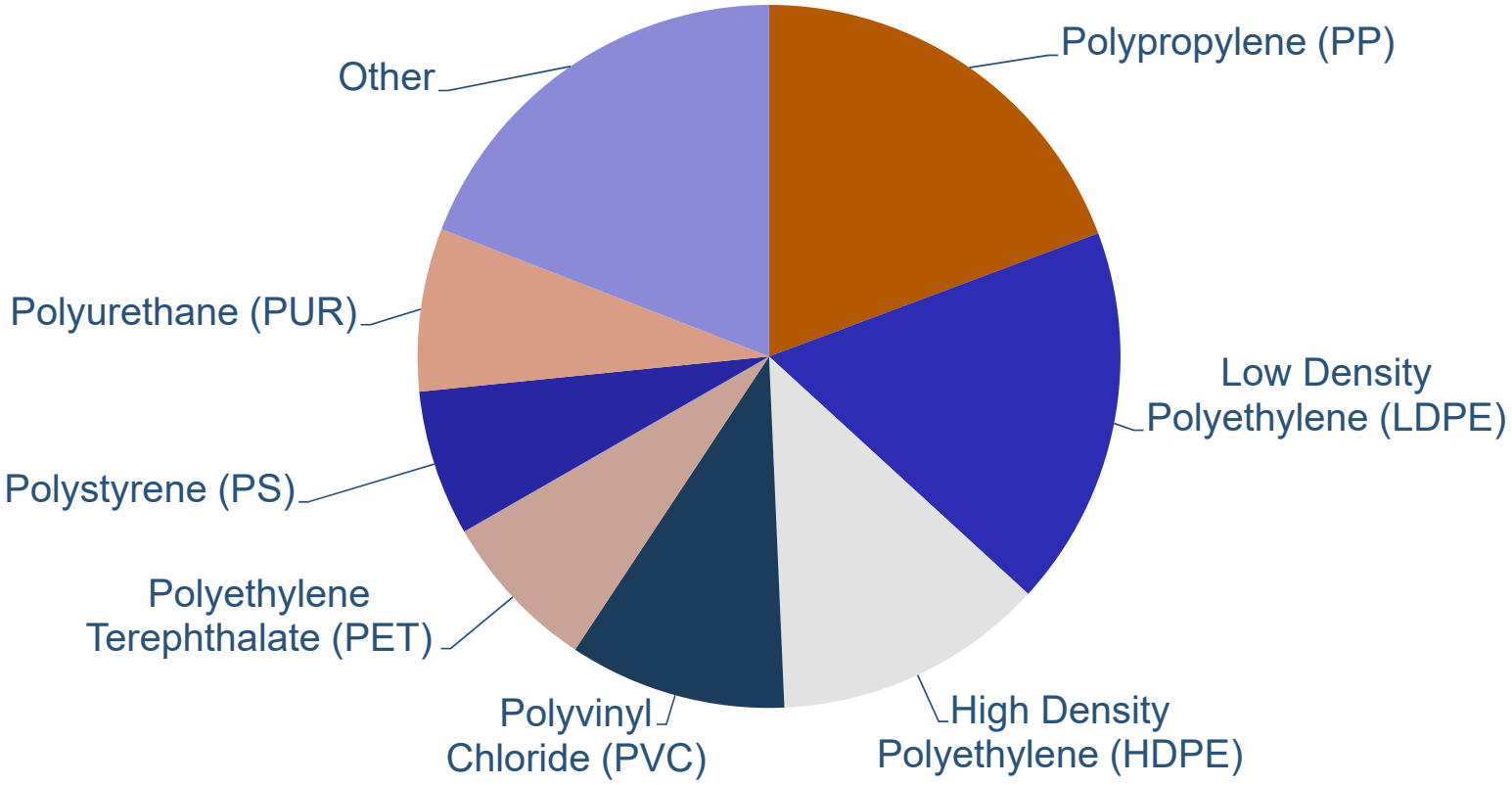
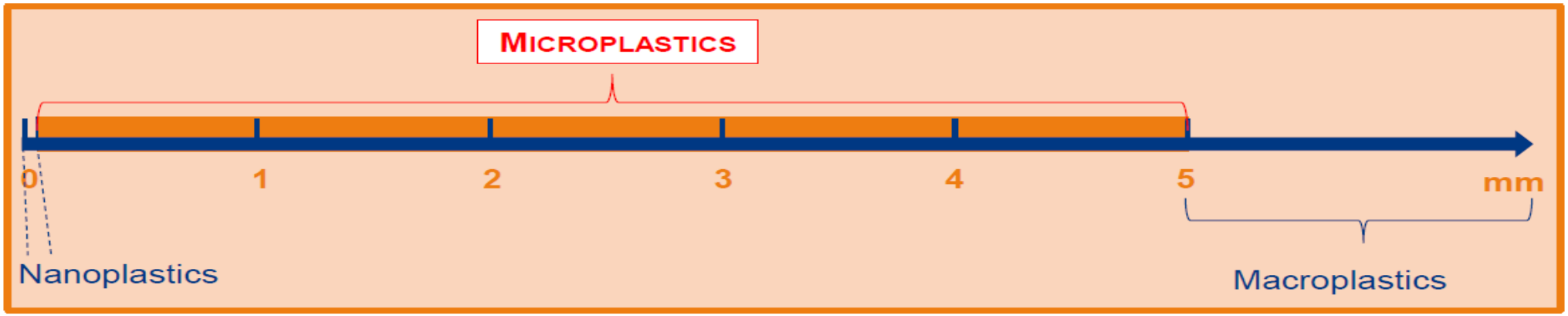
# There Are About 322 Million Tons Of Plastic Manufactured Per Year



# What Are Microplastics?




**Definition: Microplastics are small particles, pieces and fibers of any kind of plastic, defined by their size: Generally 1 um <size< 5,000 um.**
**But even the definition for size range is not standardized and may be method defined.**

# Where Do Micro-plastics Come From?



- **Primary (used directly)**
  - Health and beauty products
  - Toothpaste
  - Spills
- **Secondary (Larger products become smaller)**
  - Bottles
  - Bags
  - Carpet
- **Size < 5 mm**

# The More We Look the More We Find Microplastics

**Microplastics have been found everywhere in the environment:**

- In water (marine, freshwater)
- In soils
- In the air (as dust)

**As a result of environmental contamination, microplastics are also present in the food chain:**

- Drinking water and bottled water
- Marine life: shellfish, fishes, etc.
- Sea salt
- In larger animals which are contaminated as a result of consumption of smaller ones.

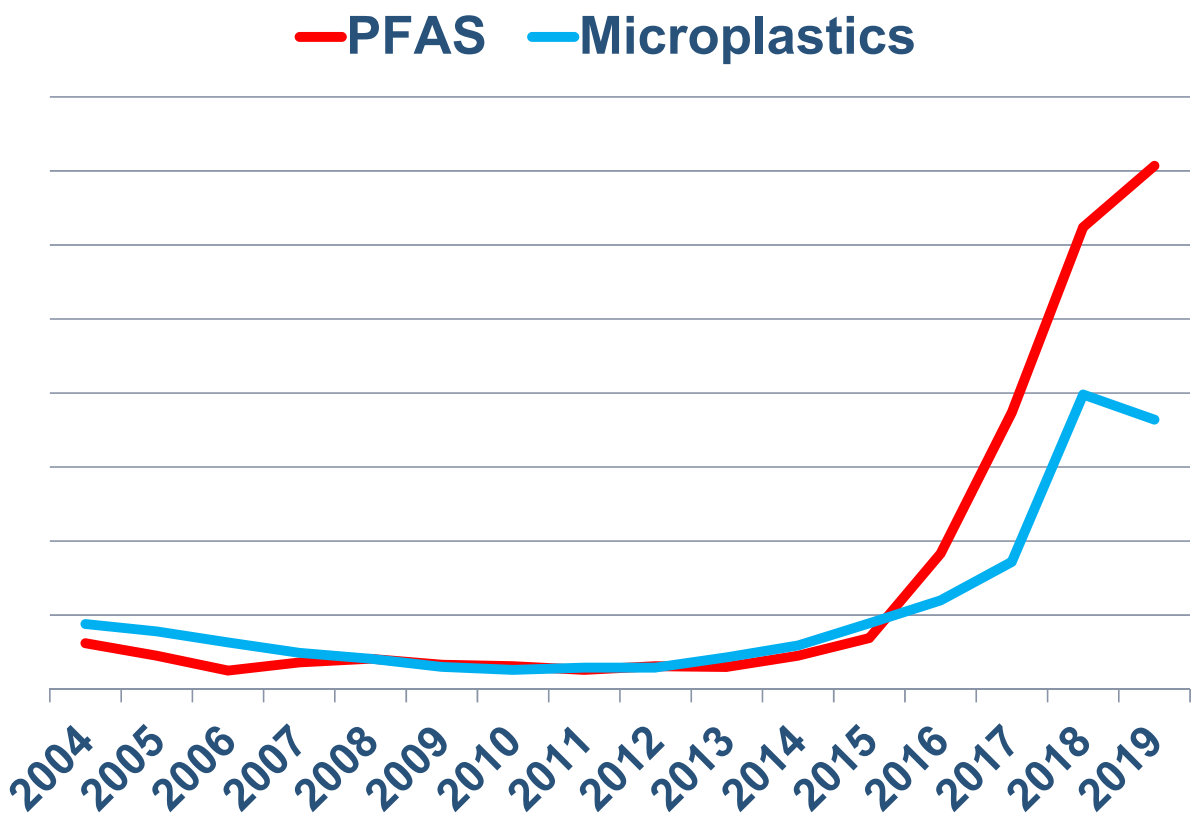
# Microplastics In Water, And What It Could Mean



- Plastics debris and microplastics occur worldwide (much more prevalent outside the US)
  - Beaches
  - Surface water
  - Wastewater
  - Drinking water
  - Food
  - Inside fish, birds, mammals

# Microplastics Are A Growing Concern For Consumers, Often Due to News Reports

# Google Trends (Web Search) Microplastics vs PFAS



# Review Articles in Major Journals are Now Common



Environmental Science & Technology

Article

Cite This: *Environ. Sci. Technol.* XXXX, XXX, XXX−XXX

pubs.acs.org/est

## Human Consumption of Microplastics

Kieran D. Cox,[*,†,‡] Garth A. Covernton,[†] Hailey L. Davies,[†] John F. Dower,[†] Francis Juanes,[†] and Sarah E. Dudas[†,‡,§]

[†]Department of Biology, University of Victoria, Victoria, British Columbia V8P 5C2 Canada
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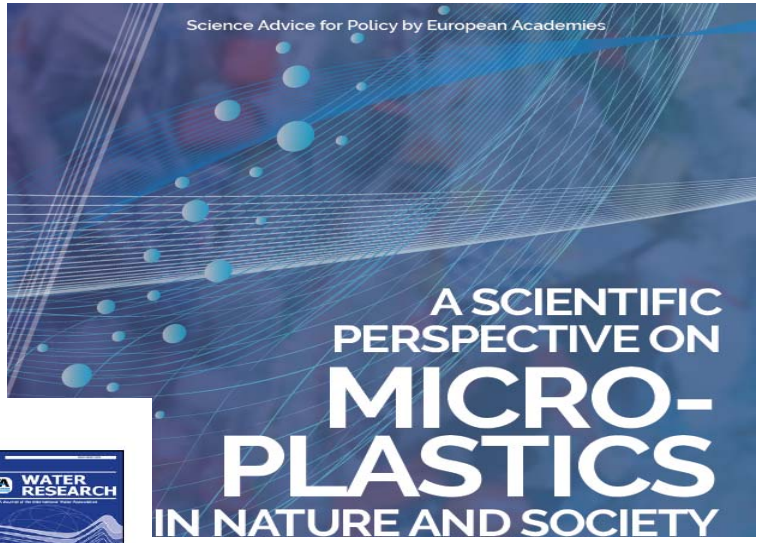


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Water Research

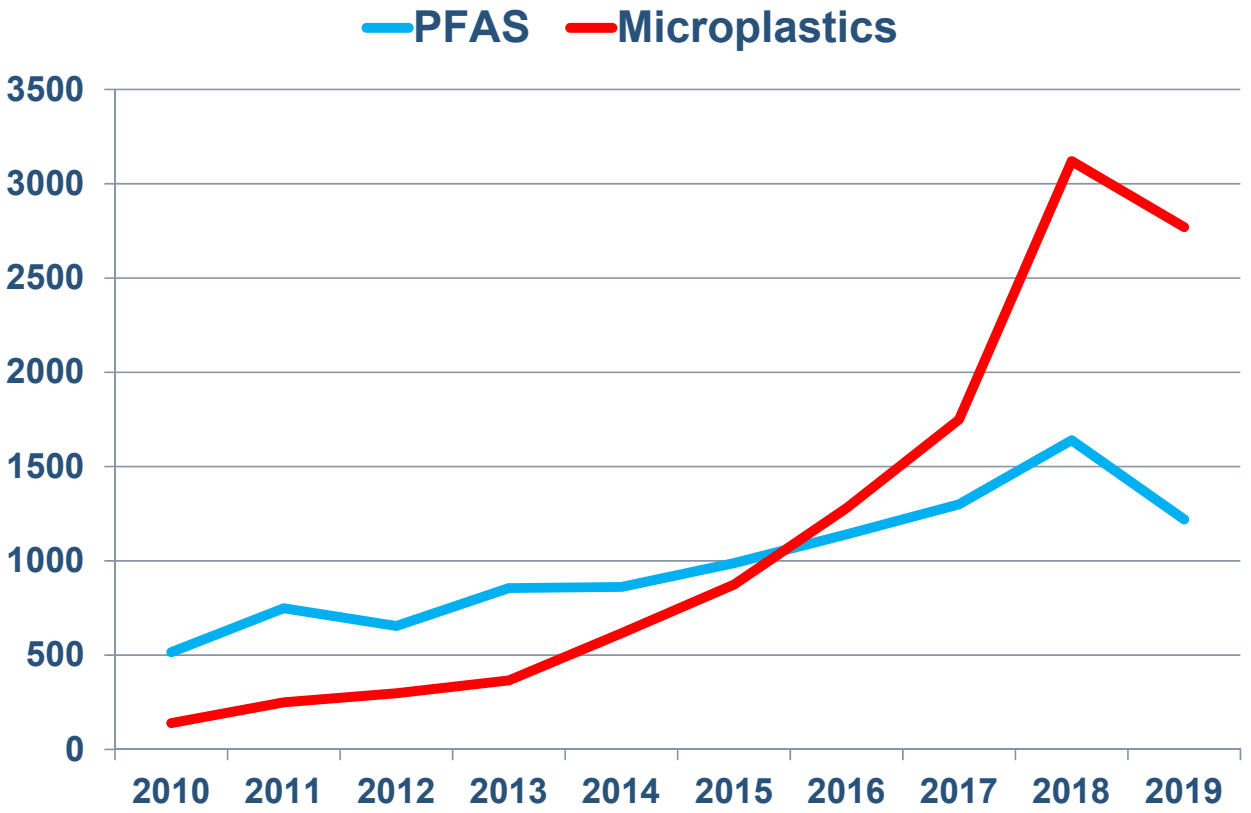
journal homepage: www.elsevier.com/locate/watres

Review

## Microplastics in freshwaters and drinking water: Critical review and assessment of data quality

Albert A. Koelmans [a, *], Nur Hazimah Mohamed Nor [a], Enya Hermsen [a], Merel Kooi [a], Svenja M. Mintenig [b, c], Jennifer De France [d, **]

# Google Scholar Citations Microplastics vs PFAS



# EPA Has Convened Expert Workshops on Microplastics



**Microplastics Expert Workshop Report**

*Trash Free Waters Dialogue Meeting*

*Convened June 28-29, 2017*

*EPA Office of Wetlands, Oceans and Watersheds*

*Primary Author: Margaret Murphy, AAAS S&TP Fellow*

*Report Date: December 4, 2017*

…the workshop participants echoed the conclusion of many microplastics review papers and reports that the **development of reliable, reproducible and high-quality methods for microplastics quantification and characterization is fundamental and of paramount importance** for understanding microplastics risks.

**Lack of standardized methods is identified as a critical issue!**

# 3 Main Approaches Have Been Used for Analysis of Microplastics



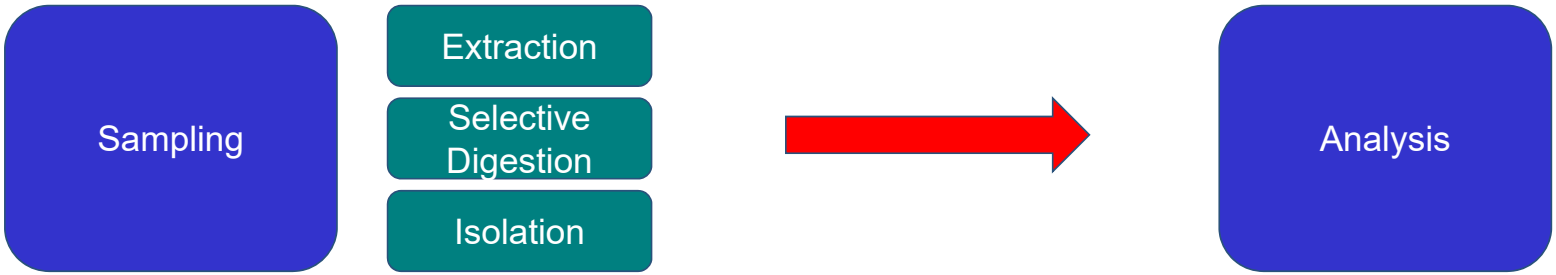
- **Micro-FTIR**

- **Micro-Raman Spectroscopy**

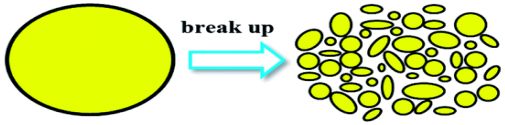
- **Pyrolysis GC-MS**

**Each of these methods has pros and cons. All share the same challenges in getting reliable samples.**

# One of the Most Challenging Aspects Of Microplastic Analysis Is Sampling

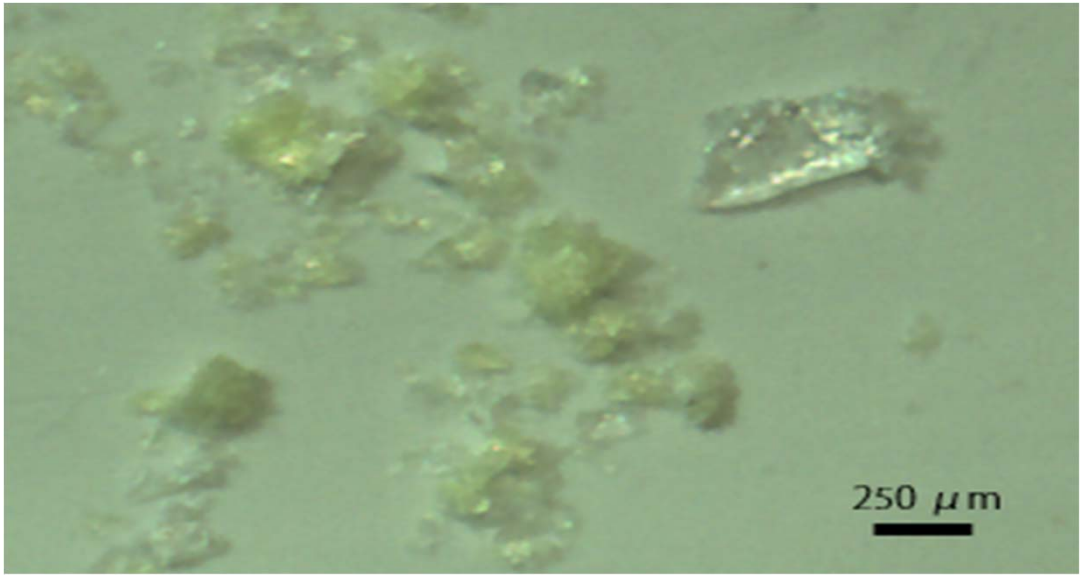


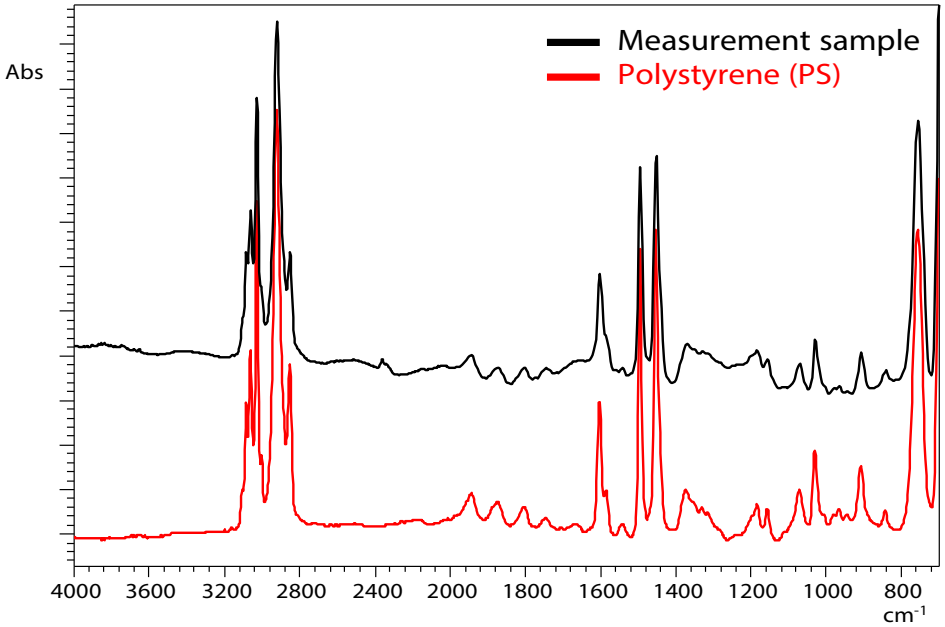

- Sample preparation "breaks" particles
- What's the size of interest?




- Size has implications!

# Analysis of Micro-plastics, Using an IR-Microscope

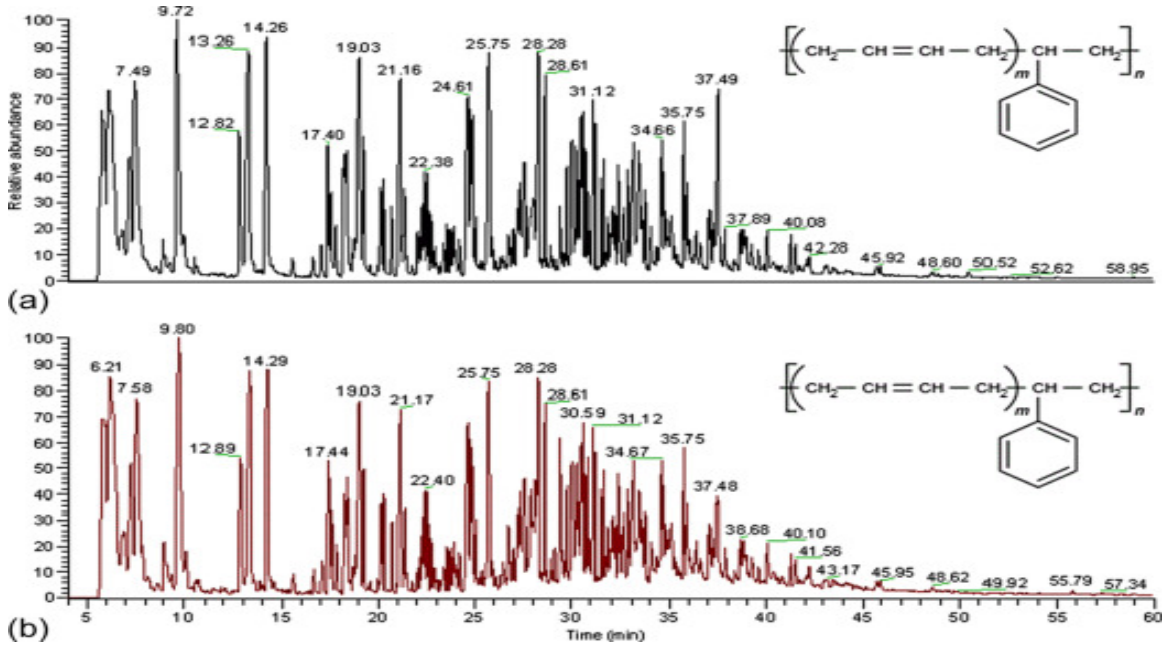



## Count particles, determine ID, Size and shape

## Can only estimate mass

# Analysis of Micro-plastics, Using Pyrolysis GCMS




https://doi.org/10.1016/B978-0-08-100116-5.00017-X

## Mass / Volume measurement

## ID polymer

## Don't know:

- # particles
- Size
- Shape

# Why Pyrolysis GC-MS?

- Eurofins Bergen Norway Lab has been running the method for a year.
- Being used in research projects across Europe
- Relatively quick analytical method, especially compared to FTIR and Raman methods
- Has high sensitivity and can detect not only microplastics, but also rubber.

# Sample Preparation



**Method** | Sample preparation | Instrument | Analytical run

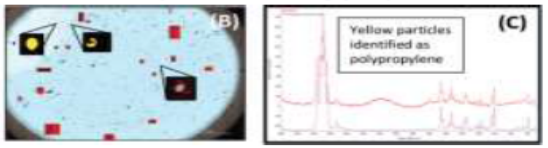
**FTIR**

Sample prep and Filtration

Filter

FTIR

Quantitative
(#, Size, Type)




Particle size >10 µm

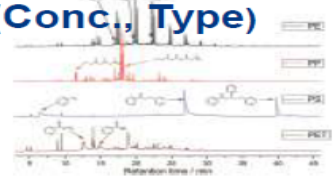
**Method** | FTIR filter quatitative introduced in Pyr-GC-MS cup | Instrument | Analytical run

**Pyr-GC-MS**

Pyr-Cup

Pyrolytic GC-MS


Quantitative
(Conc., Type)



Particle size >0.2

Eurofins Environment Testing Norway

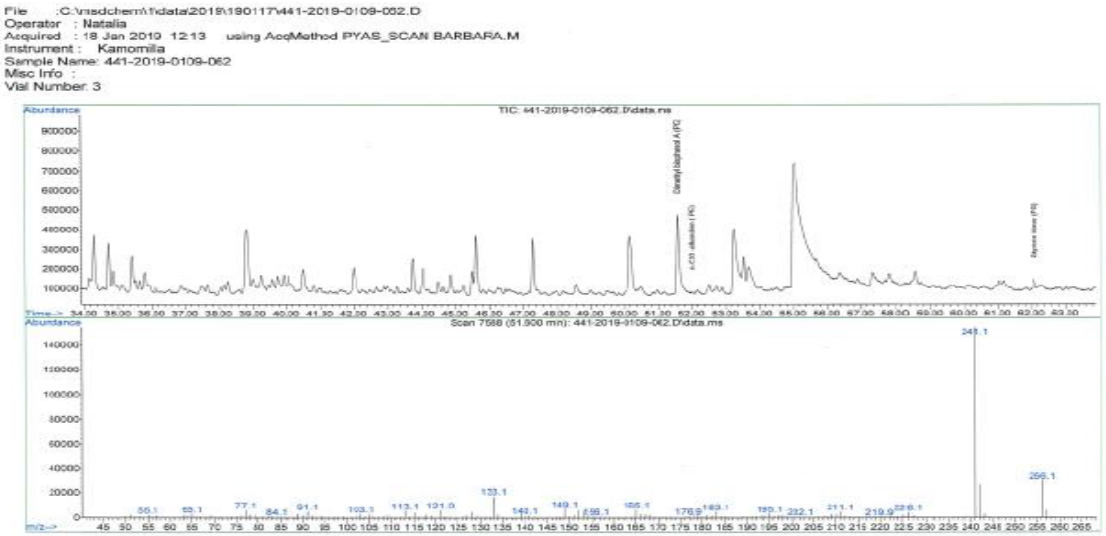
# Avoiding Contamination is Important



- Special filtration setup in polymer dust free lab facility.
- Specially designed stainless steel filtration apparatus
- Filtered to 0.2 um in size to capture small particles (much smaller than FTIR or Raman methods normally measure).

# Pyrolysis GC-MS Equipment and Example Chromatogram & Detections





# Sample Processing

- Samples received in glass bottles (1L min)
- Filtered through 0.2 um 13 mm anodisc filters
  - Can take hours to filter  (but can batch)
- Add tetramethylammonium hydroxide (TMAH) as derivatization agent
- Frontier EGA/PY 3030D coupled with an Agilent 6390 GC and Agilent 5975 single quadrupole MS.
- Pyrolysis temp of 600°C.  MS run in full scan

# Characteristics of Pyrolysis GC-MS

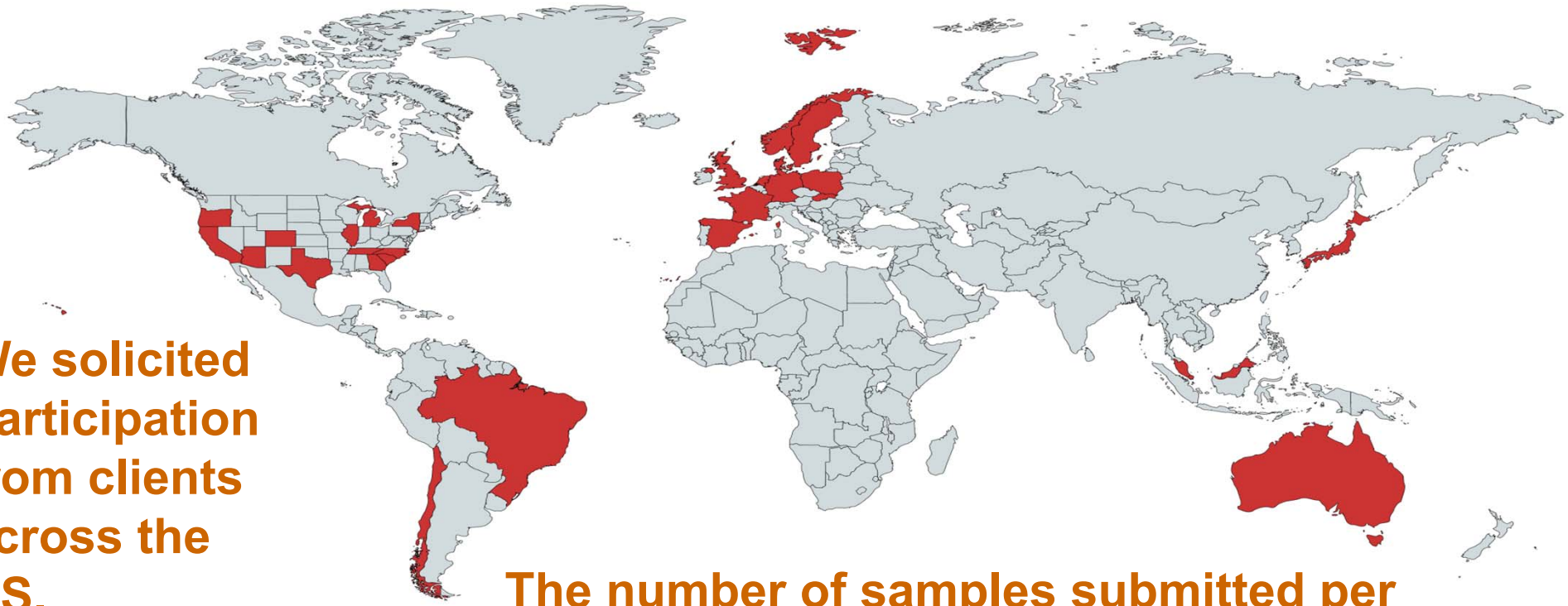
- The primary polymers that are produced globally: PE, PP, PS, PVC, PET, PC, PMMA, and PA6 are individually quantified with PYR-GC-MS.
- Method covers the size range from 0.2 um to 5 mm (again, much smaller particles than FTIR)
- Sensitivity is 0.1 to 1 ug/L, depending on the polymer. What is more important? Total mass or total count?

# Leveraged Eurofins Global Footprint



- Eurofins has labs on 5 continents
- Sent general request to all labs to solicit participation by obtaining tap water samples
- Definitely not a fully random sample
  - Reminiscent of early oceanography trace metals sampling!
- Ultimately ended up with 244 samples
- Sample volumes generally > 1L

# 17 Countries Submitted Samples for Microplastics in Tap Water

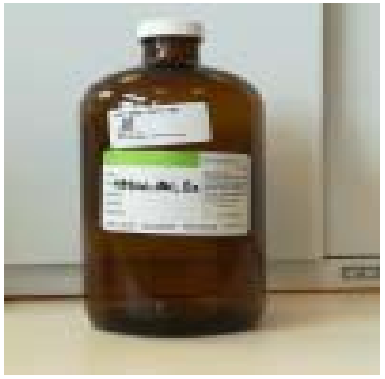


**We solicited participation from clients across the US.**

**The number of samples submitted per country varied from 2 to 20.**

# Everyone Used Their Own Bottles: Different Cap Types









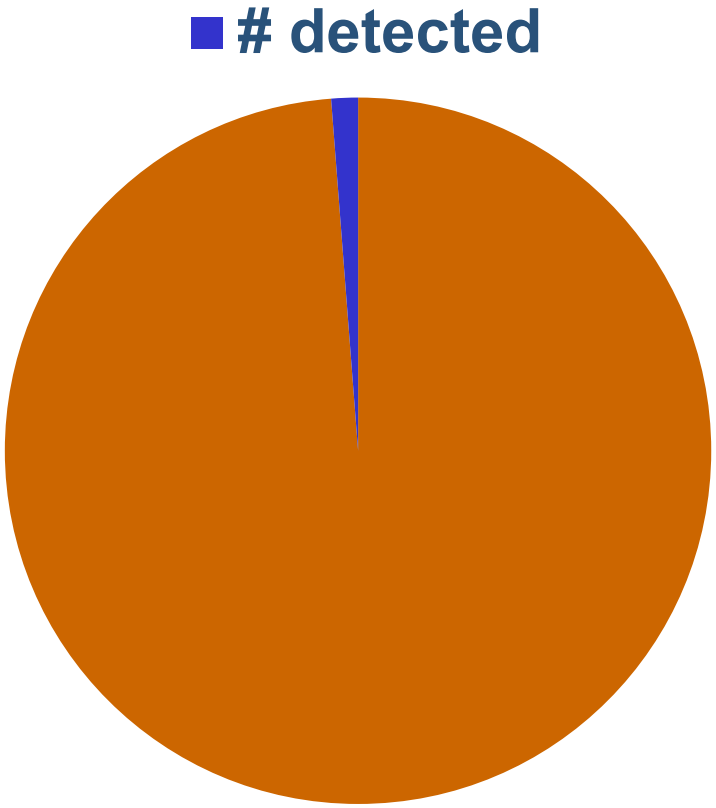


# Instructions to Participants

- Participants were asked to use glass bottles of at least 1L in size.
- They were asked to rinse bottles with sample prior to filling.
- They were also asked to provide material or method blanks (not all did).
- The variety of bottles used reflects what is commonly available in individual countries.

# Results Indicate That Microplastics Are NOT Ubiquitous in Tap Water






**Only about 1% of samples had detectable microplastics .**

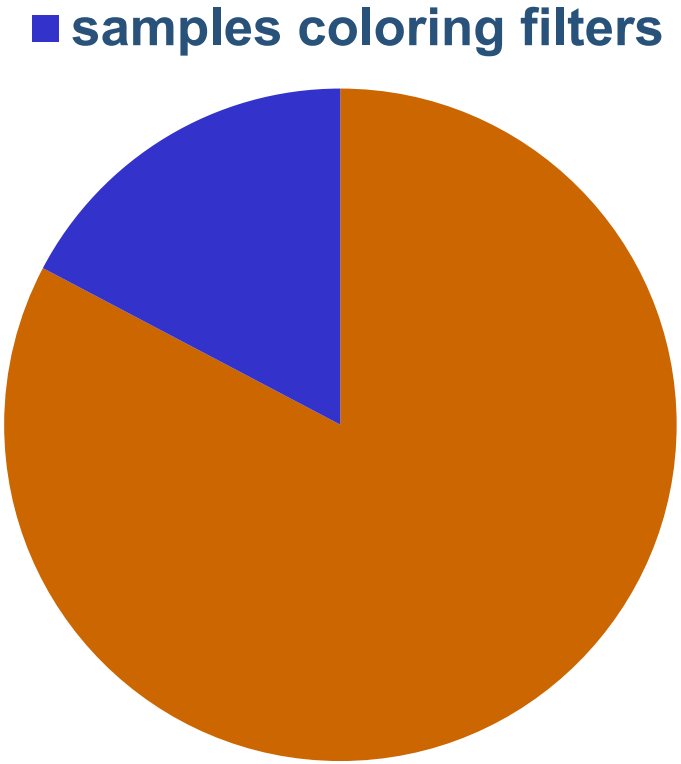
# When MPs Were Detected, the Concentrations Were Low



- Polystyrene and Polycarbonate were detected above the 0.1 ug/L LOQ in 3 samples.
- All < 0.25 ug/L.
- One major exception: ALMOST ALL samples from Spain had detections of polypropylene, as did the material blank. This was linked to the bottle caps, and confirmed through analysis of caps.
- Critical to rinse bottles!


# There Were However Other Interesting Observations

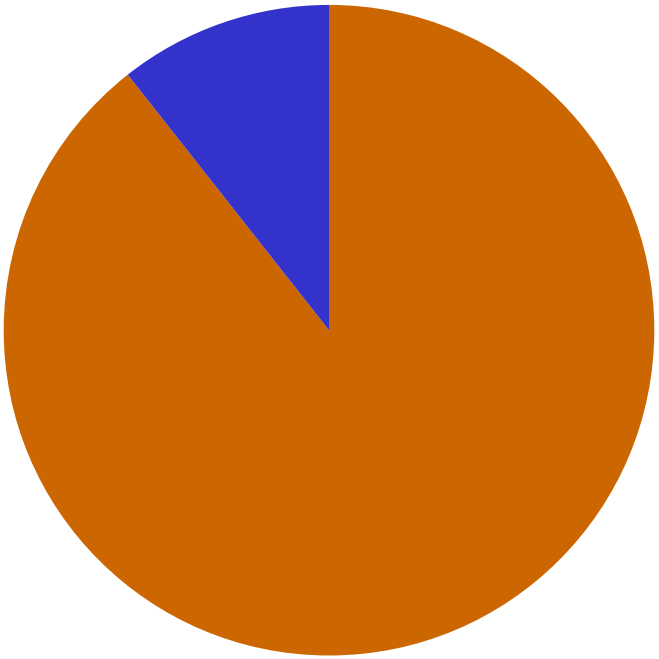





**21% of samples resulted in colored filters. Occurred in most countries.**

# Additionally Some Samples Actually Clogged Filters

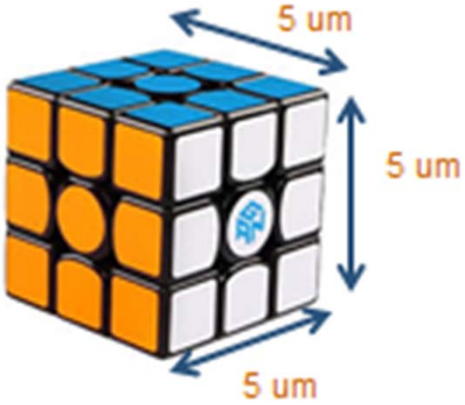
12% of samples resulted in clogged filters (<1L could be filtered). Most common in Australia and Malaysia.




Did not have a major impact on detection (some increase in LOQs).

# What Does ND Actually Mean in This Case?






Consider a plastic cube 5 um per side.

What would it weigh?

Density of most plastics is about 1.4


Volume of such a cube = 125 um3 = 125 x $10^{-9}$ mm3

Density of 1.4 g/cc = 1400 ug/mm3

=1400 x 125 x $10^{-9}$ ug = 0.000175 ug = 0.175 ng

So if the pyrolysis results < 100 ng/L you could still have >500 particles of microplastic of 5 um cube size.

So we are actually back to the challenge of deciding what is more significant and what is the relevant "standard".

Count?
Mass?
Surface area?

# Conclusions

- Although it's a small sample size (244), MPs were infrequently detected in tap water, even for very small particle sizes.
- Consistent with ES&T article (Cox et al, 2019) which estimated 4 MP particles per liter for tap water (count vs mass…), but there could still be a lot more….
- Sample collection protocols are critical, and there is potential for false positives.

# Any Questions?

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