





# Pathways of entry and signatures of weathering for microplastics in surface waters

Nicole L. Fahrenfeld, Ph.D.

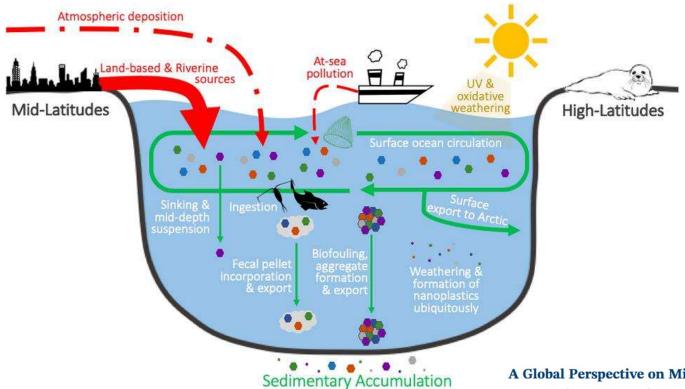
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# Conceptual model of MP fate



A Global Perspective on Microplastics

Robert C. Hale<sup>1</sup>, Meredith E. Seeley<sup>1</sup>, Mark J. La Guardia<sup>1</sup>, Lei Mai<sup>2</sup>, and Eddy Y. Zeng<sup>2</sup>

<sup>1</sup>Virginia Institute of Marine Science, William & Mary, Gloucester Point, VA, USA, <sup>2</sup>Guangdong Key Laboratory of Environmental Pollution and Health, School of Environment, Jinan University, Guangzhou, China

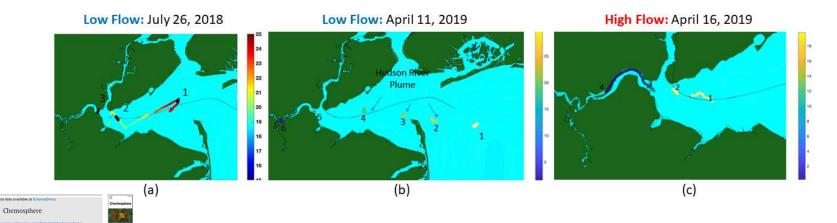
# Comparing surface water & pathways of entry

Bay: nets trawled 20-30min at 1-2 knots

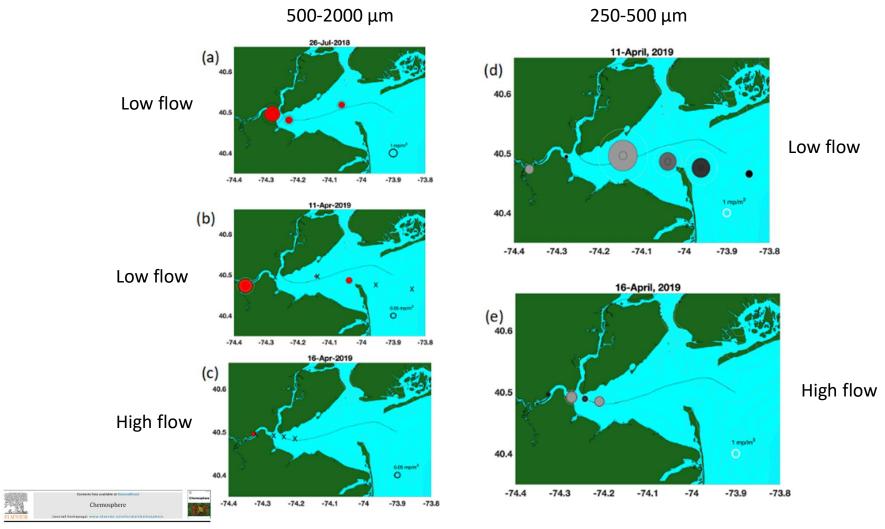
 $16-65 \text{ m}^3$   $80-153 \text{ }\mu\text{m}$  mesh size

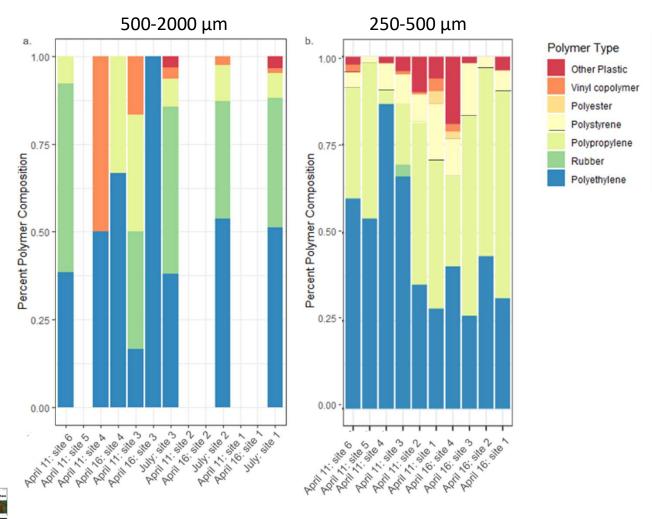
Wastewater influent + effluent (4L)

Stormwater Zooplankton



Quantification and composition of microplastics in the Raritan Hudson Estuary: Comparison to pathways of entry and implications for fate Kendi Balley \*, Karli Sipps \*, Crace K. Saba \*, Georgia Arbuckle-Keil \*, Robert J. Chant \*, N.E. Fahresilde<sup>1</sup>.

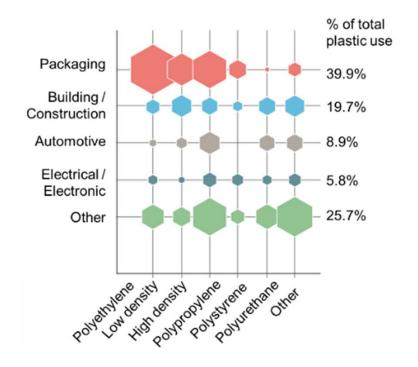






Quantification and composition of microplastics in the Raritan Hudson Estuary: Comparison to pathways of entry and implications for fate Kendi Bailey \*, Karli Sipps  $^b$ , Grace K. Saba \*, Georgia Arbuckle-Keil  $^b$ , Robert J. Chant \*, N.L. Fahrenfeld  $^{h,*}$ 

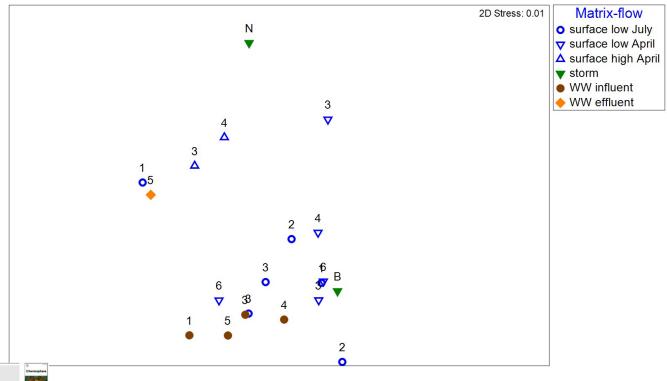
### Linking polymer type to use?



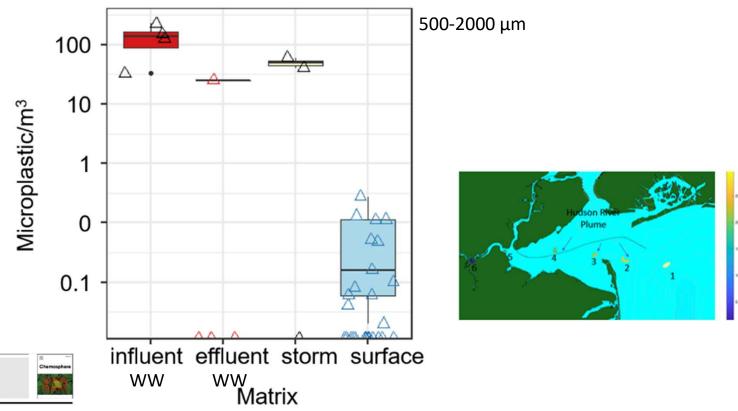
(Plastics Europe, 2016)

.... too much overlap

# Comparing polymer profiles from the estuary to pathways of entry



### Comparing pathways of entry to surface water MP

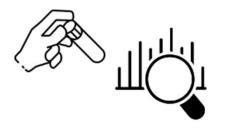


Quantification and composition of microplastics in the Raritan Hudson Estuary: Comparison to pathways of entry and implications for fate

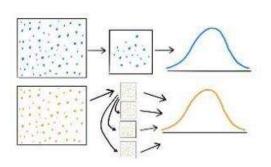
Contents lists available at ScienceDirect

Chemosphere





# Urban wastewater & stormwater MP observations



Impact of methods on polymer diversity and MP count-based concentrations



Signatures of oxidative weathering

# Wastewater sampling

4 WWTP × 3 dates

Influent

6.2L

Pre-filtration

6.8L

Effluent

21L

























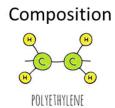


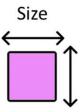




Density separation



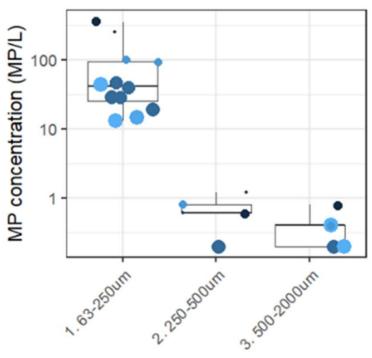




Morphology

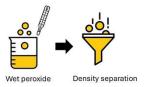


### Stormwater microplastic observations

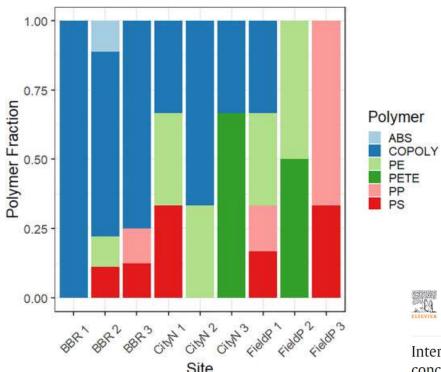


Urban stormwater microplastic size distribution and impact of subsampling on polymer diversity†

Size Range



# Stormwater microplastic polymer types 250-2000 µm





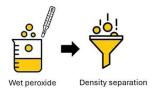


Inter-storm variation in microplastic concentration and polymer type at stormwater outfalls and a bioretention basin

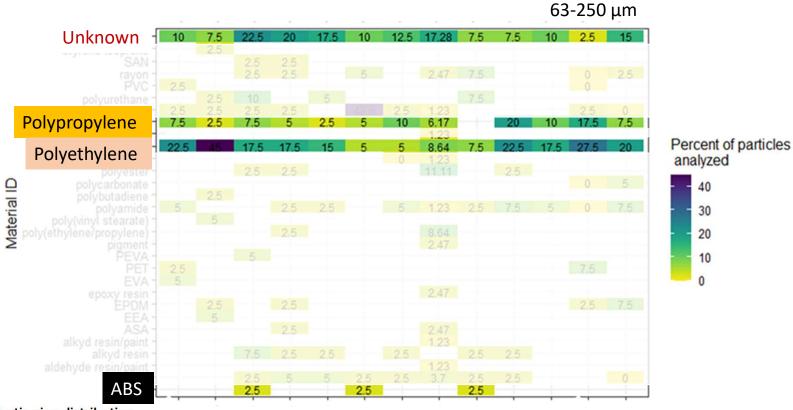
William Boni a, Georgia Arbuckle-Keil b, N.L. Fahrenfeld a ス 🖾

# Example urban stormwater MPs (63-250 µm)

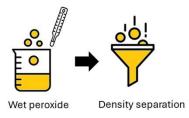




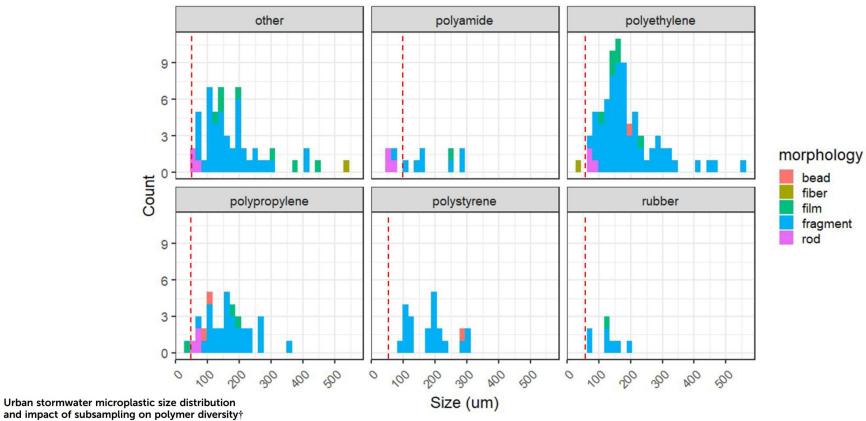
#### Stormwater polymer types



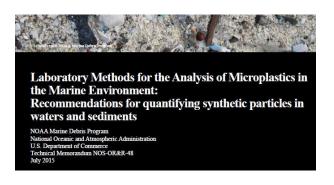
Samples

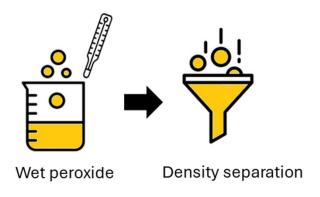


### Moving beyond size bins for MP...



## Evolving extraction methods

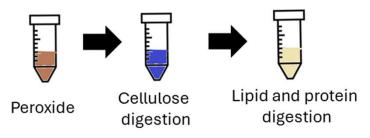




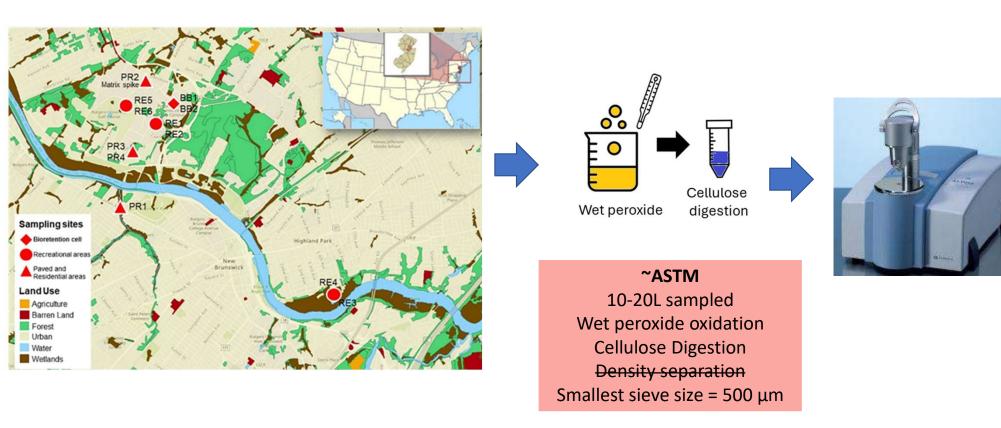
- Losses due to heating?
- Losses of dense polymers?

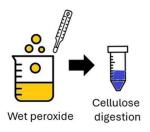


Standard Practice for Preparation of Water Samples with High, Medium, or Low Suspended Solids for Identification and Quantification of Microplastic Particles and Fibers Using Raman Spectroscopy, IR Spectroscopy, or Pyrolysis-GC/MS<sup>1</sup>



 Limited adoption in the literature to date





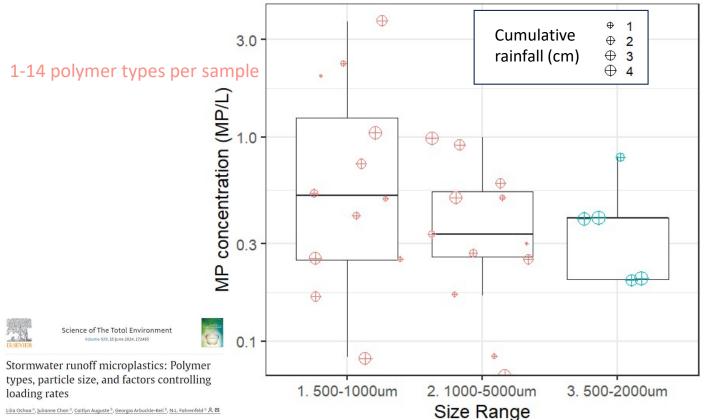
#### ~ASTM

10-20L sampled
Wet peroxide oxidation
Cellulose Digestion
Density separation

#### **NOAA**

5L sampled
Wet peroxide oxidation
Cellulose Digestion
NaCl density separation





1-4 polymer types per sample



Science of The Total Environment



Inter-storm variation in microplastic concentration and polymer type at stormwater outfalls and a bioretention basin

# Estimating MP loading

# Watershed delineation



Curve number (SCS-CN)



#### Runoff

#### **ArcGIS Pro**

- Digital Elevation Model (DEM)
- USGS Water Boundary Data

Flow direction, flow accumulation  $\rightarrow$  Boundaries of the watershed

#### ArcGIS Pro and Arc Hydro

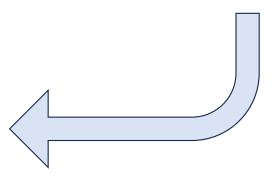
- **Digital Elevation Model**
- Land Use/Land Cover
  - Soil data

$$Q = \frac{(P - I_a)^2}{P - I_a + S}$$



$$L = C * Q$$

Where: L is MP load [MP/m²], C is MP concentration [MP/L], Q is runoff [mm]



<sup>1.</sup> Tahmasebi Nasab, M. (2023). Create curve number CN raster using Archhydro tools in Arcgis Pro. Retrieved from https://www.hydromohsen.com/create-curve-number-cn-raster-for-a-watershed 2. Piñon-Colin, T., Rodriguez-Jimenez, R., Rogel-Hernandez, E., Alvarez-Andrade, A., & Toyohiko-Wakida, F. (2020). Microplastics in stormwater runoff in a semiaria region, Tijuana, Mexico. Science of The Total Environment, 135411.

### Results

#### **Precipitation and Microplastics Loads:**

- Positive correlations with accumulated precipitation and rainfall intensity.
- No significant correlation between MP load and antecedent dry days

#### **Runoff and Microplastic Loads:**

- Dependent on accurate precipitation data.
- MPs loads are influenced by watershed characteristics (land use and soil types).

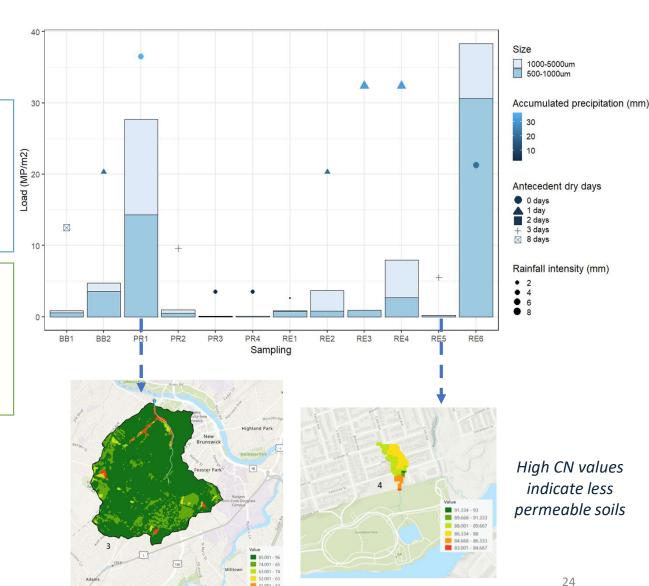


Science of The Total Environment
Volume 929, 15 June 2024, 172485



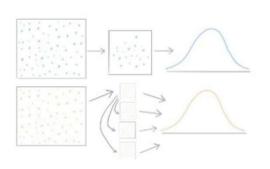
Stormwater runoff microplastics: Polymer types, particle size, and factors controlling loading rates

Lilia Ochoa a, Julianne Chan a, Caitlyn Auguste b, Georgia Arbuckle-Keil b, N.L. Fahrenfeld A 🖰 🖾





# Urban wastewater & stormwater MP observations

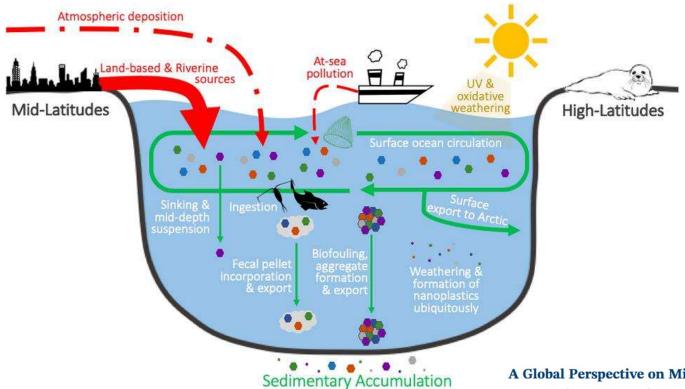


Impact of methods on polymer diversity and MP count-based concentrations in stormwater



Signatures of oxidative weathering

# Conceptual model of MP fate



A Global Perspective on Microplastics

Robert C. Hale<sup>1</sup>, Meredith E. Seeley<sup>1</sup>, Mark J. La Guardia<sup>1</sup>, Lei Mai<sup>2</sup>, and Eddy Y. Zeng<sup>2</sup>

<sup>1</sup>Virginia Institute of Marine Science, William & Mary, Gloucester Point, VA, USA, <sup>2</sup>Guangdong Key Laboratory of Environmental Pollution and Health, School of Environment, Jinan University, Guangzhou, China

### Vibrational spectroscopy can provide insight into weathering

#### **Bond indices**

Reference peak (CH<sub>2</sub>)

#### 1. Hydroxyl Index (HI)

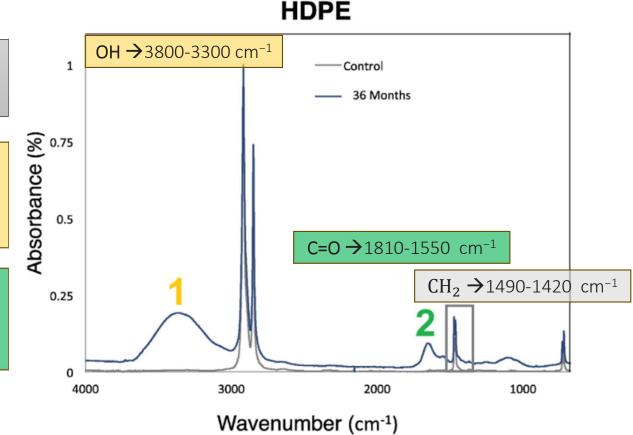
Maximum absorbance of OH

Maximum absorbance of CH<sub>2</sub>

#### 2. Carbonyl Index (CI)

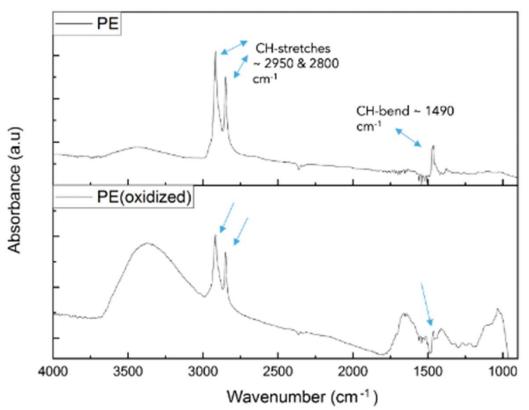
Maximum absorbance of C = 0

Maximum absorbance of CH<sub>2</sub>



Brandon, J., Goldstein, M., & Ohman, M. D. (2016). Long-term aging and degradation of microplastic particles: Comparing in situ oceanic and experimental weathering patterns. Marine Pollution Bulletin, 110(1), 299–308. doi:10.1016/j.marpolbul.2016.06.048

# Many stormwater MP spectra show signs of oxidative weathering

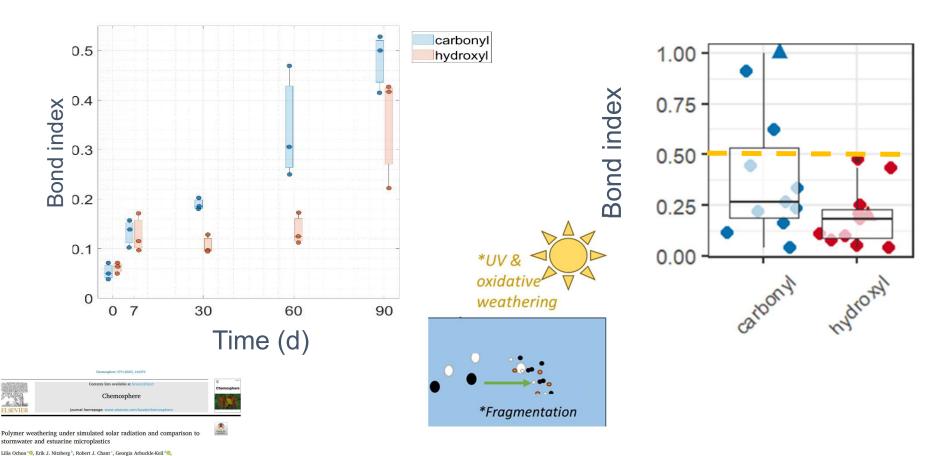


Urban stormwater microplastic size distribution and impact of subsampling on polymer diversity†

Swaraj Parmar, a Georgia Arbuckle-Keil, 🔘 G. Kumia and N. L. Fahrenfeld 🔘 \*b

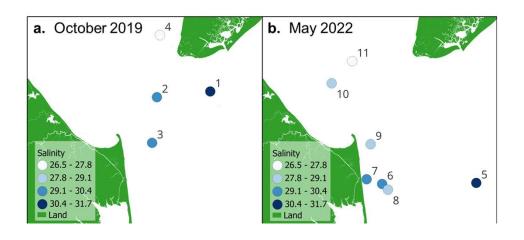
#### Lab weathered polypropylene

#### Stormwater polypropylene



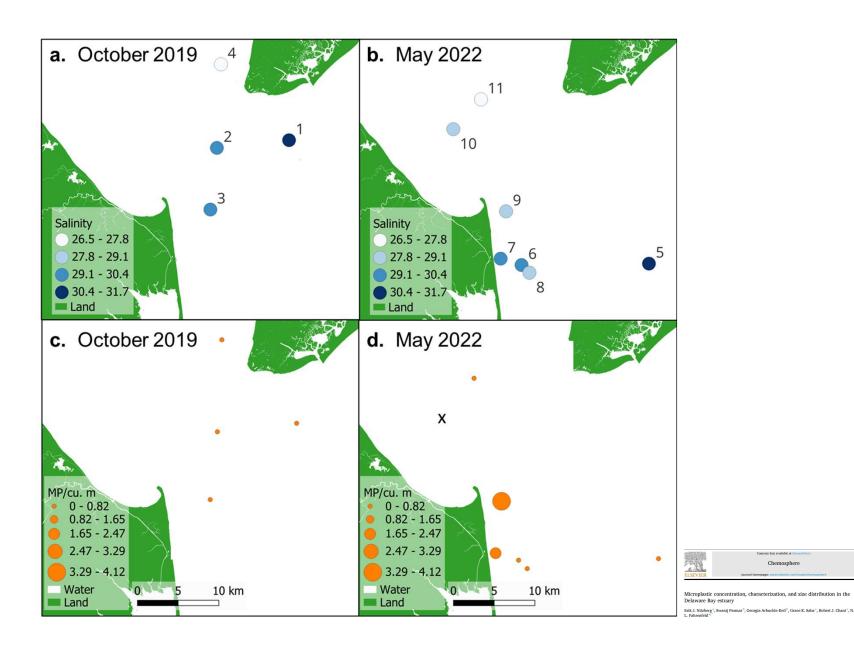
### **Delaware Bay**

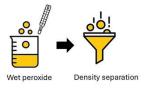
Bay: nets trawled 20-30min at 1-2 knots 4-120  $m^3$  20, 80, 153  $\mu m$  mesh size

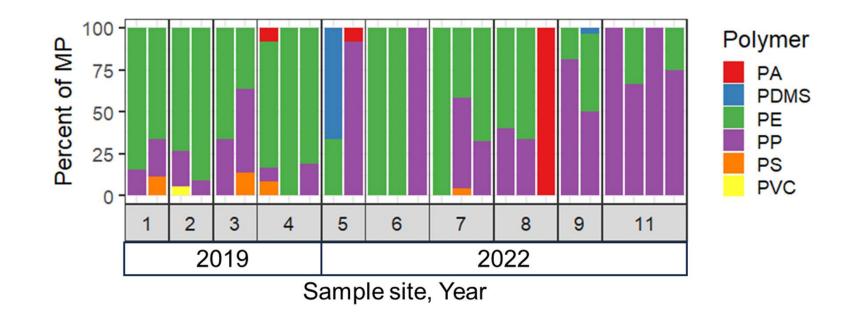










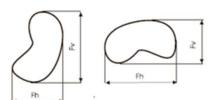


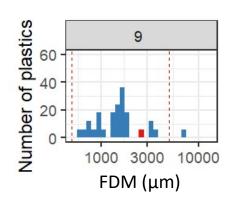


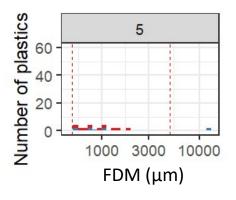
Microplastic concentration, characterization, and size distribution in the Delaware Bay estuary  $\,$ 

Erik J. Nitzberg  $^a$ , Swaraj Parmar  $^b$ , Georgia Arbuckle-Keil  $^b$ , Grace K. Saba  $^c$ , Robert J. Chant  $^c$ , N. L. Fahrenfeld  $^{b_c}$ 

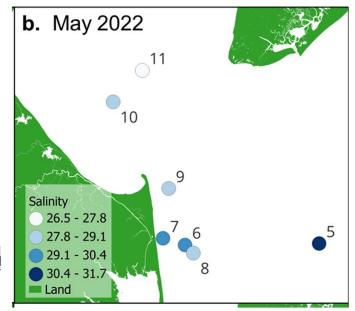


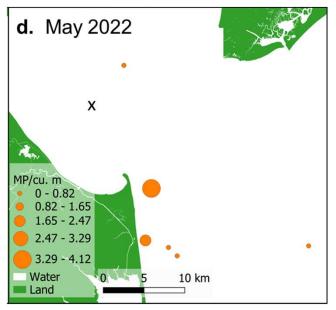






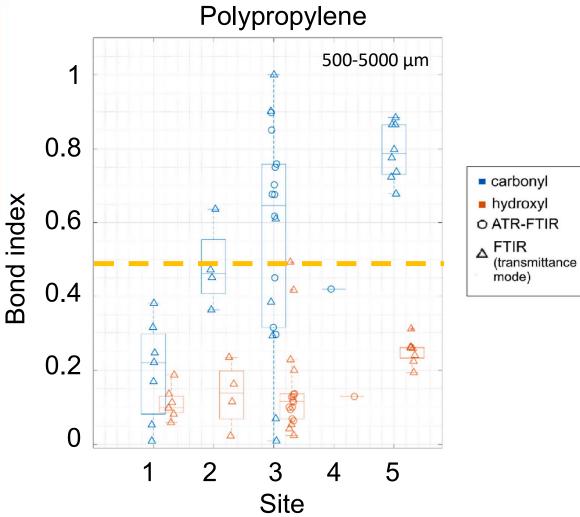
Fiber Fragment Sphere











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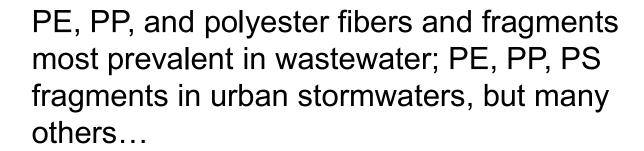
Chemosphere

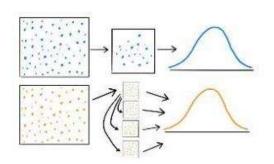
Journal homepage: www.elsevier.com/Jocata/chemosphere

Polymer weathering under simulated solar radiation and comparison to stormwater and estuarine microplastics  $\,$ 

Lilia Ochoa <br/>  $^{\rm a}$  , Erik J. Nitzberg  $^{\rm b}$ , Robert J. Chan<br/>t  $^{\rm c}$ , Georgia Arbuckle-Keil  $^{\rm d}$  , N.L. Fahrenfeld <br/>  $^{\rm a, *}$   $^{\rm o}$ 







Sampling volume, extraction techniques, target size, and subsampling will impact reported polymer diversity!



Range of surface oxidation which impacts other properties...

#### **Acknowledgments**

Kendi Bailey, Will Boni, Karli Sipps, Raj Parmar, Erik Nitzberg, Lilia Ochoa, Julianne Chan, Alexandra Mondzrick, Isabella Dela Cruz



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Georgia Arbuckle-Keil, PhD, Robert Chant, PhD, Grace Saba PhD









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Quantification and composition of microplastics in the Raritan Hudson Estuary: Comparison to pathways of entry and implications for fate



Kendi Bailey <sup>a</sup>, Karli Sipps <sup>b</sup>, Grace K. Saba <sup>c</sup>, Georgia Arbuckle-Keil <sup>b</sup>, Robert J. Chant <sup>c</sup>, N.L. Fahrenfeld <sup>a, a</sup>

#### Quantitative and qualitative impacts of nitric acid digestion on microplastic identification via FTIR and Raman spectroscopy, implications for environmental samples

Karli Sipps<sup>1,2</sup> · Shreya Patil<sup>3,4</sup> · Lilia Ochoa<sup>3</sup> · Julianne Chan<sup>3</sup> · Caitlyn Auguste<sup>1</sup> · Georgia Arbuckle-Keil<sup>1</sup> · N. L. Fahrenfeld<sup>3</sup> ©

#### Chemosphere 379 (2025) 144379



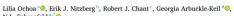
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#### Science of The Total Environment Volume 809, 25 February 2022, 151104



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