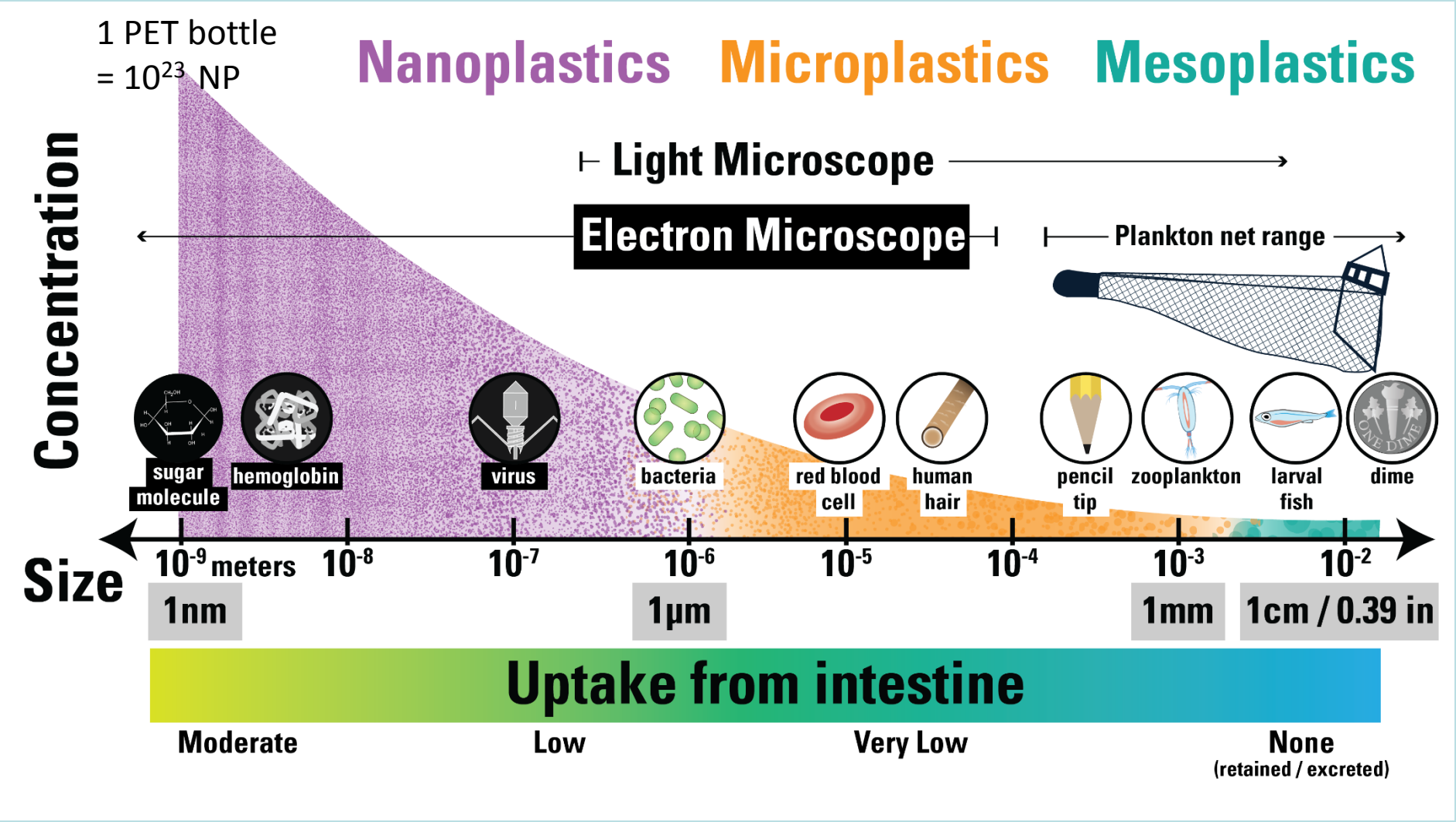
Micro-Plastic Particle Analysis of Hudson River Surface Water Using Flow-Through Imaging Raman Spectroscopy

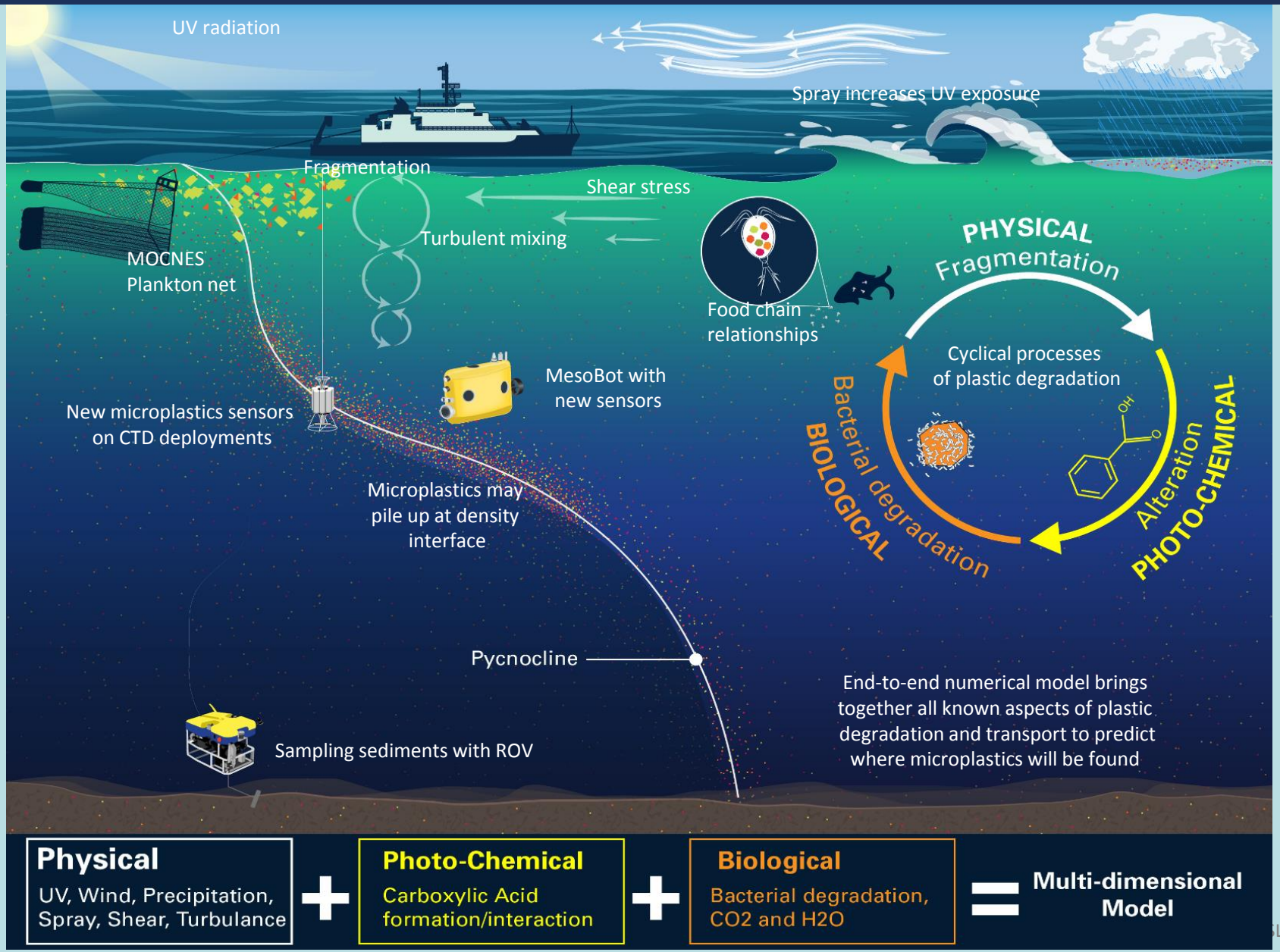
Scott M. Gallager
Woods Hole Oceanographic Institution

Microplastics Workshop October 16, 2019

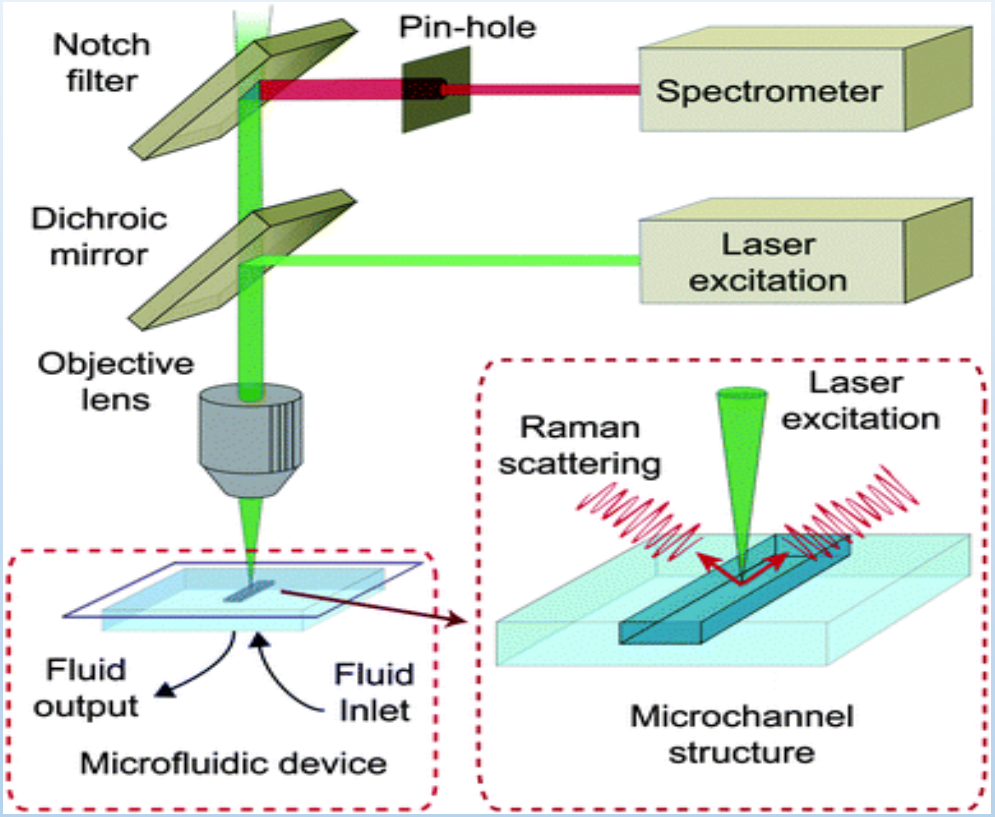
Microplastics: A 10,000,000-fold size range

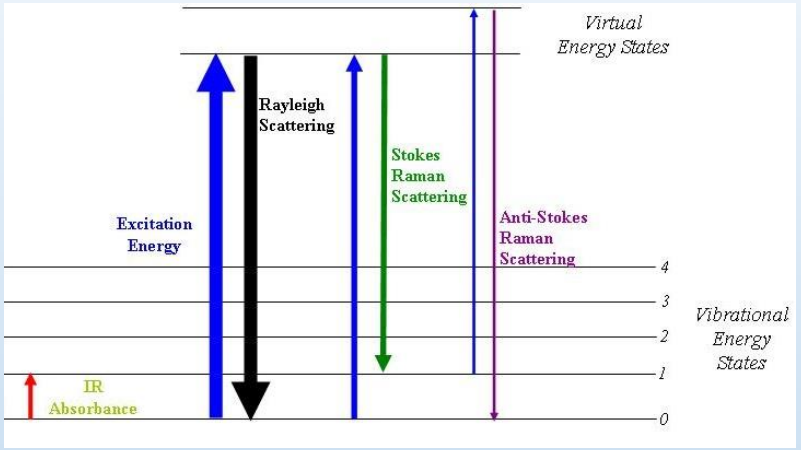


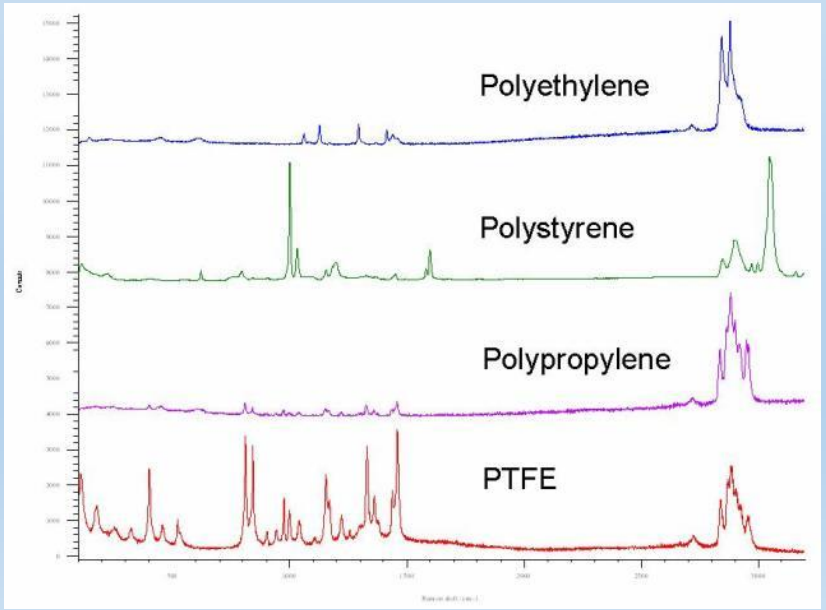
Field Experiment: Surface to Sediment-
Scott Gallager and whole MP team



Raman Spectroscopy to Detect, Classify and Quantify Plastics in the Ocean







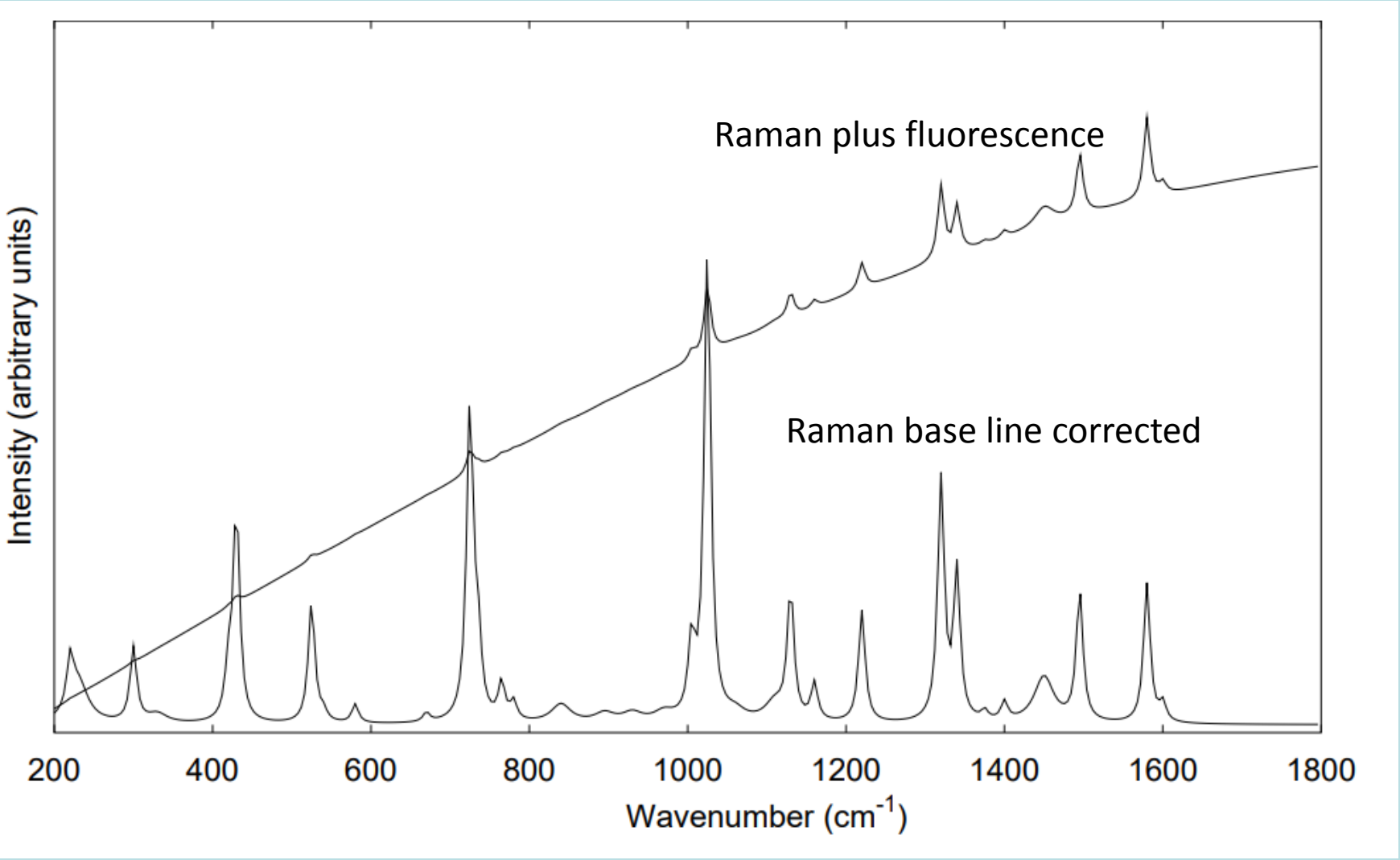
The Raman signal can be a very precise finger print for a given plastic compound.

Characteristics of Raman Scattering

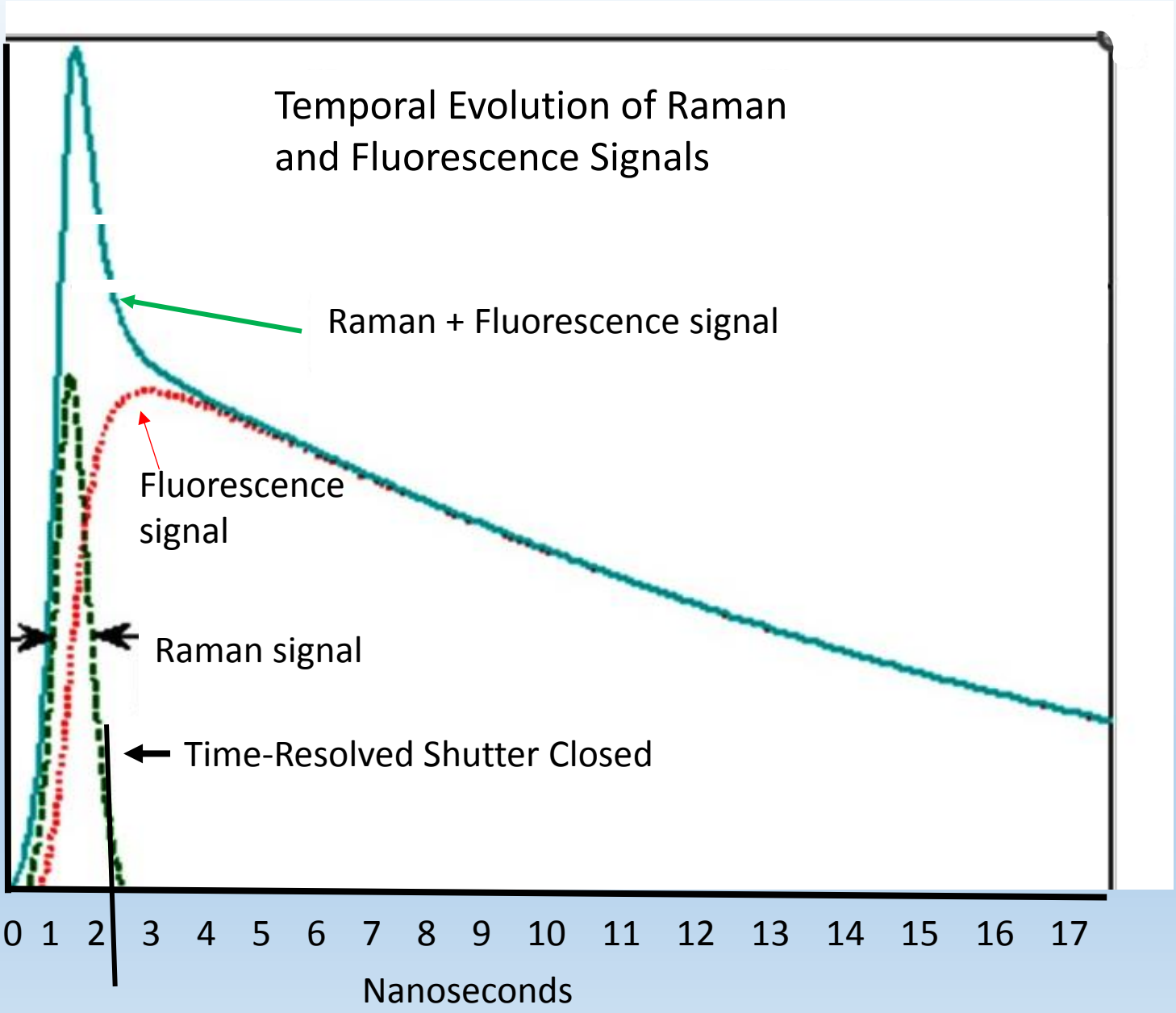
- Very week effect
- Only 1 in 10^7 photons in Raman scattered
- Virtual state in a short-lived distortion of the electron cloud
  which creates molecular vibrations
  $\tau < 10^{-14}$ s ~10 femtoseconds

- Strong Raman scatterers have distributed and overlapping
  electron clouds
  C=C π - bonds

Fluorescence: The Nemesis of Raman



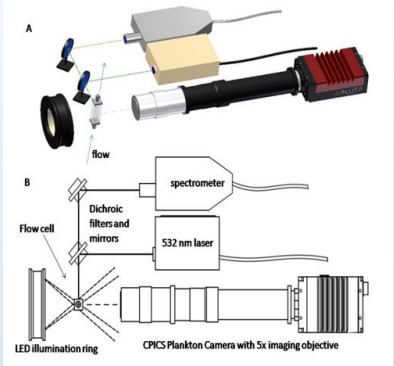
Here's the Problem……Fluorescence contaminates the Raman Signal



Time-Resolved Flow-Through Imaging Raman Spectrometer

Top View

Side View



Dark field illumination array

Piezo electric acoustic focusing element

in

Flow cell

out

Focused particle stream

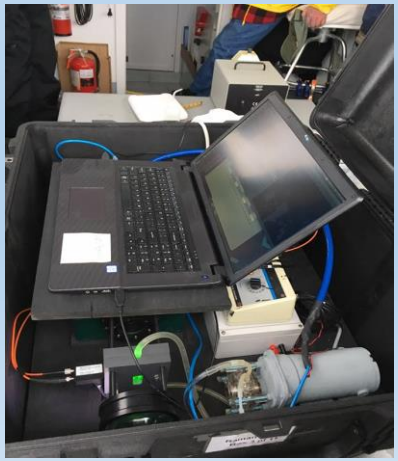
in

out

20x LD objective

Telecentric lens

Color CCD camera



Single Photon Avalanche Detector (SPAD) Spectrometer

Nanosecond 2 W Laser 25 kHz 532 nm

Trigger generator/delay circuit

Albany 42.65

Hudson 42.25

Saugerties

Kingston 41.92

Poughkeepsie 41.70

41.6 Wappingers Falls

Newburg

Bridge 41.51

Peekskill 41.28

Tappan Zee Bridge 41.07

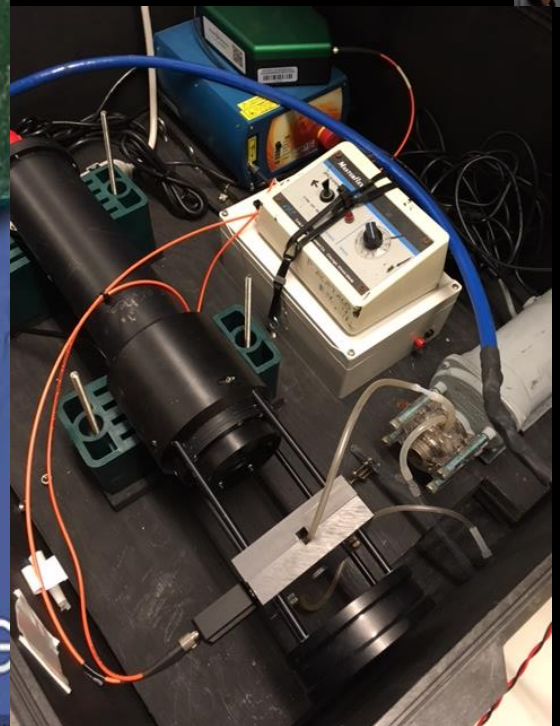
East River

Data SIO, NOAA, U.S. Navy, NGA, GEBCO
Image Landsat / Copernicus
Image U.S. Geological Survey

Riverkeeper.org

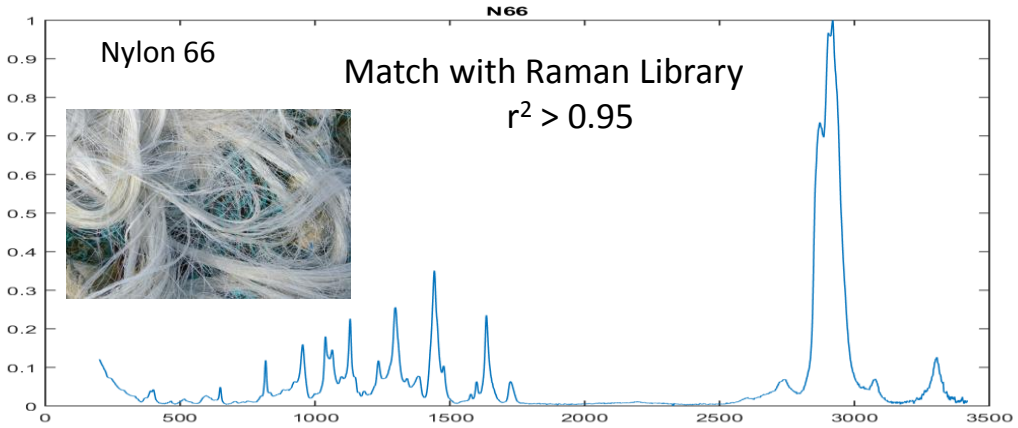
Full river cruises
Monthly April-November

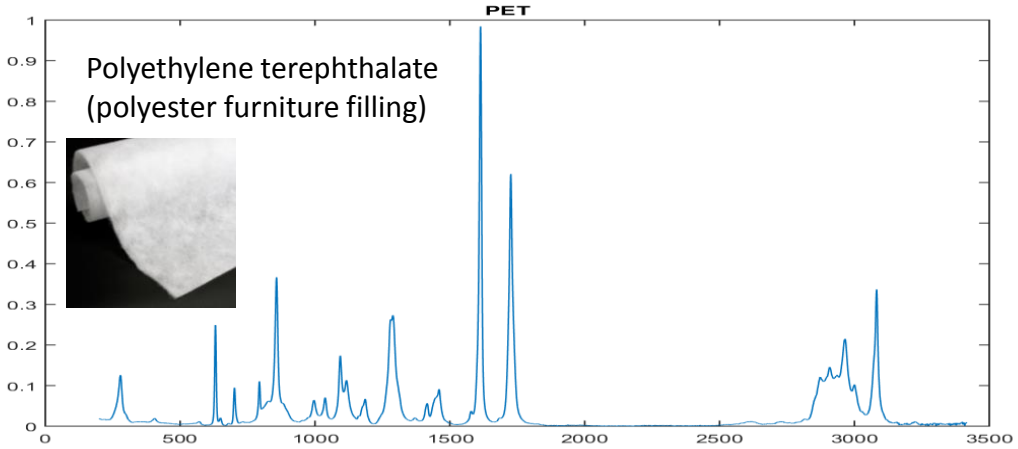
This trip
May 10-18, 2017

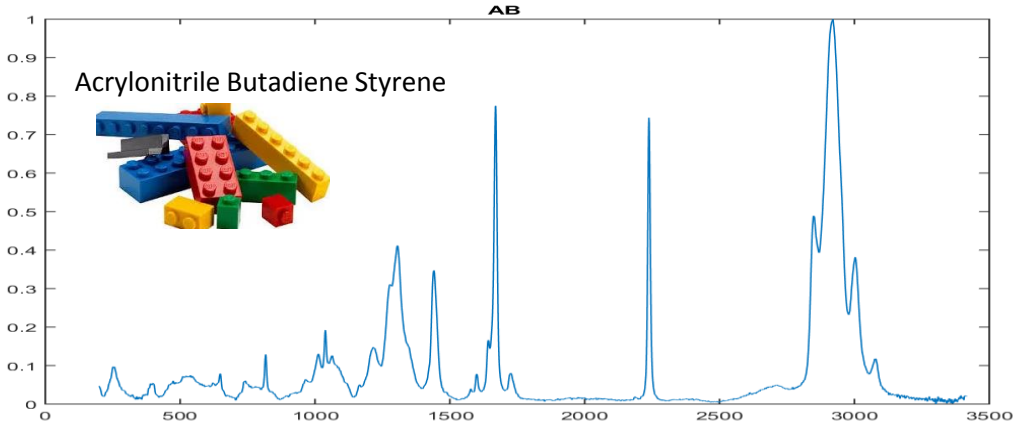


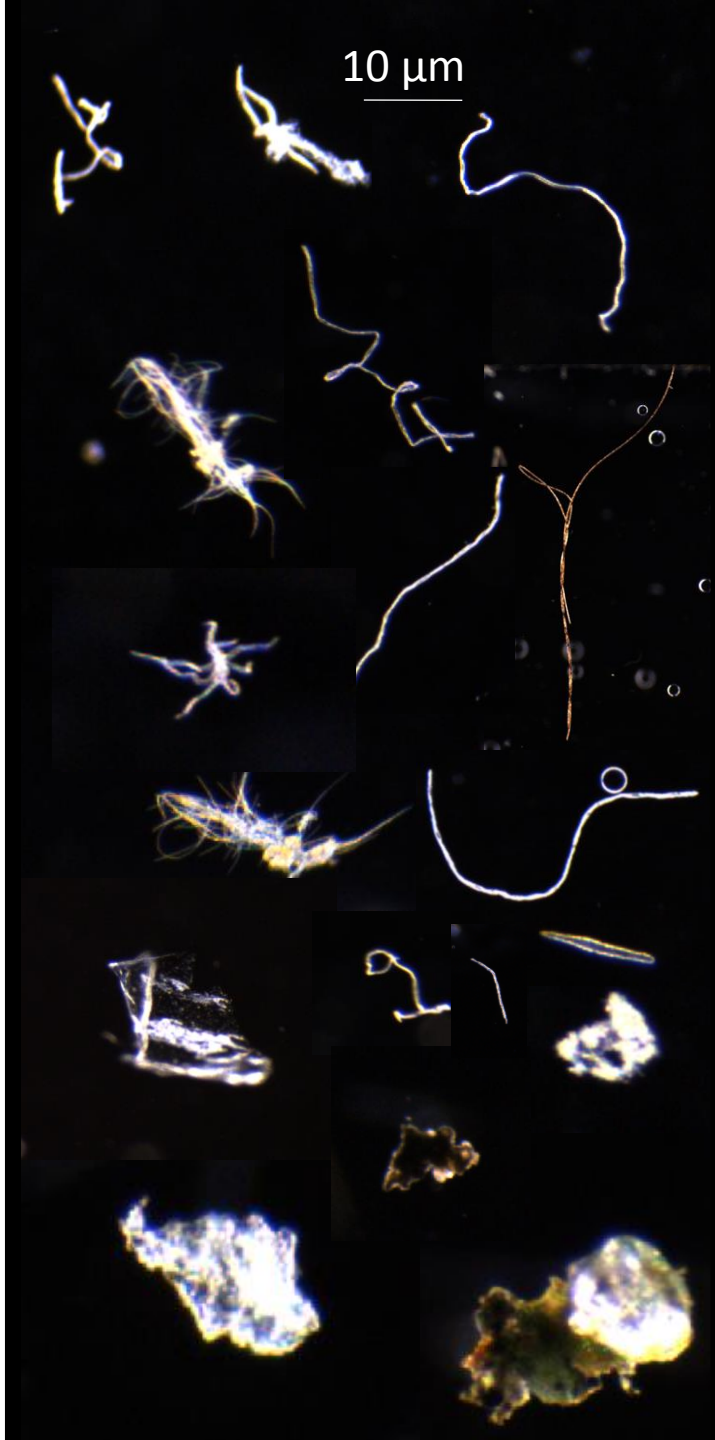
Capt. John Lipscomb

Water intake 1m below hull

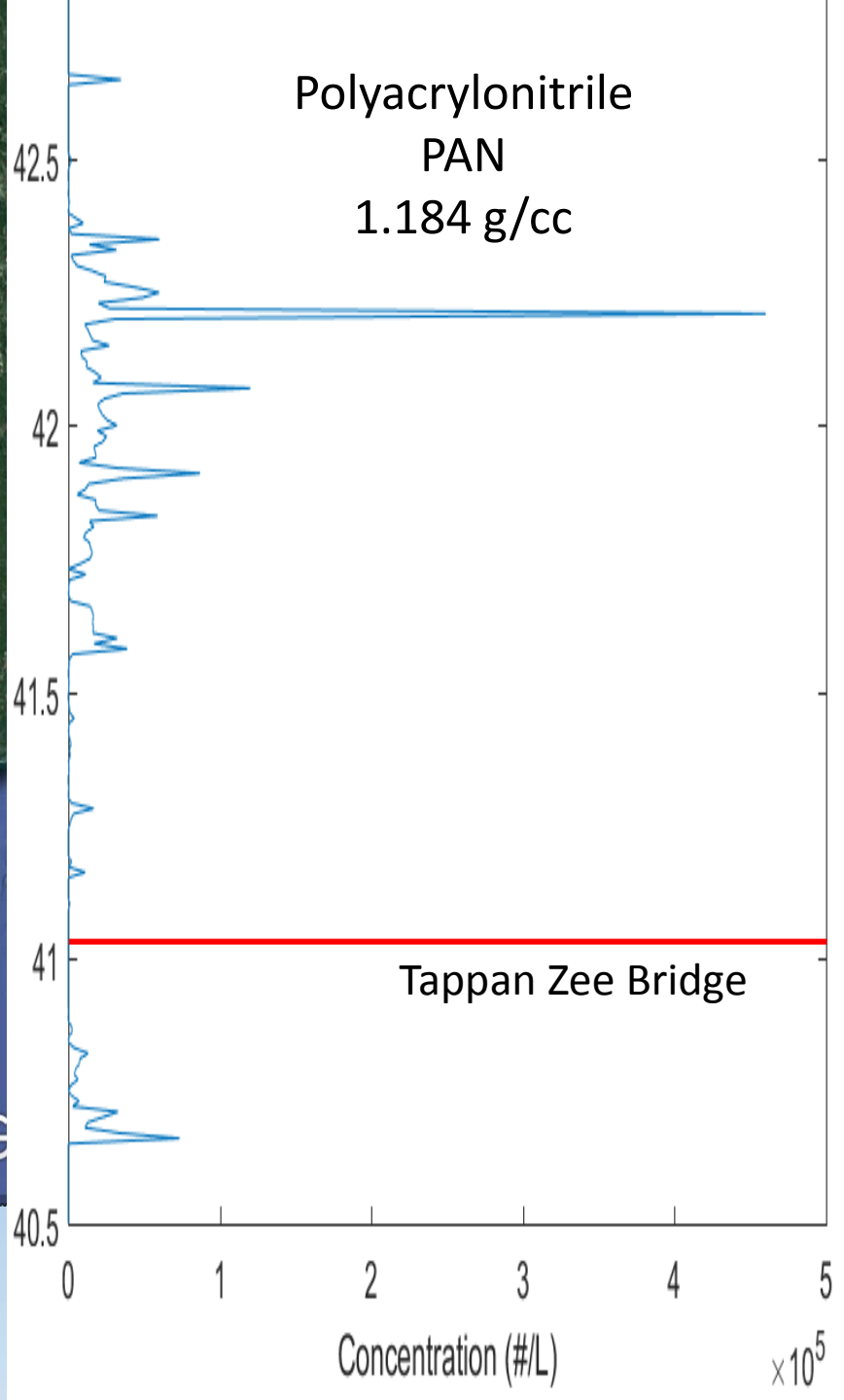

N66
Nylon 66
Match with Raman Library
$r^2 > 0.95$

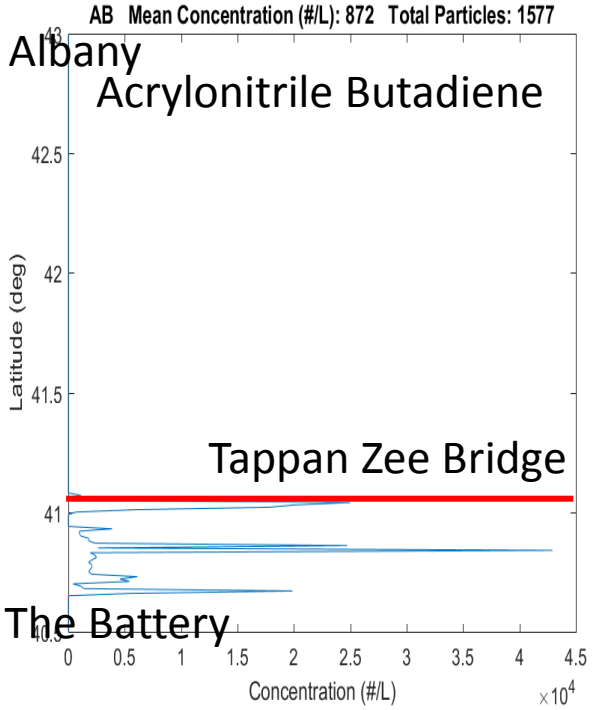

PET
Polyethylene terephthalate
(polyester furniture filling)

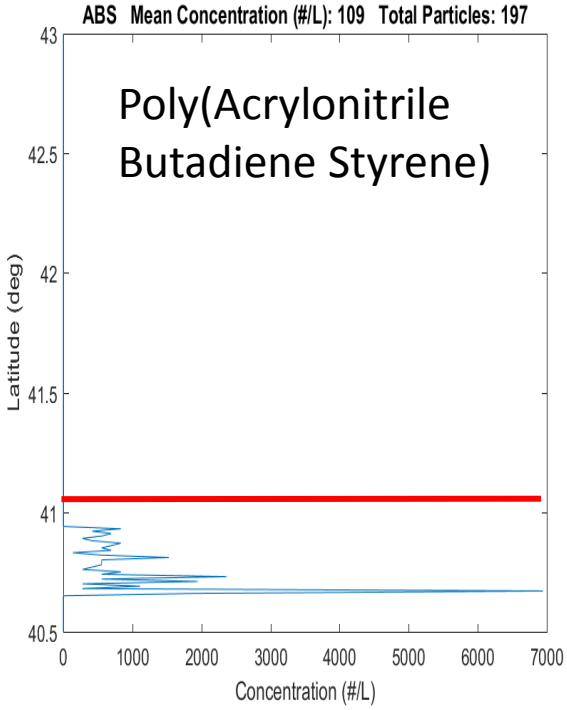

AB
Acrylonitrile Butadiene Styrene

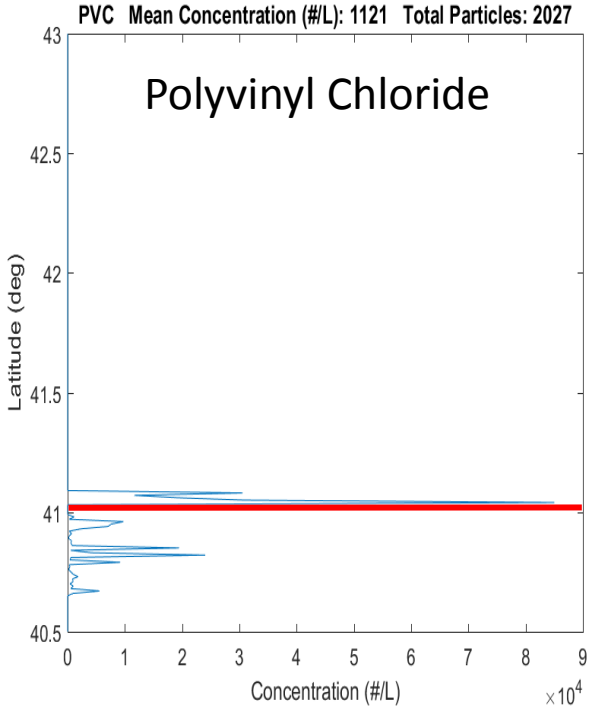

10 µm

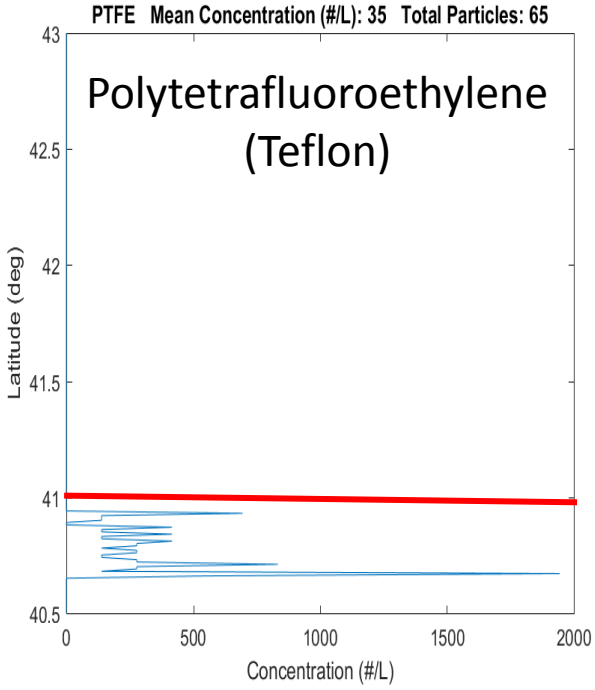
May 10-18, 2017

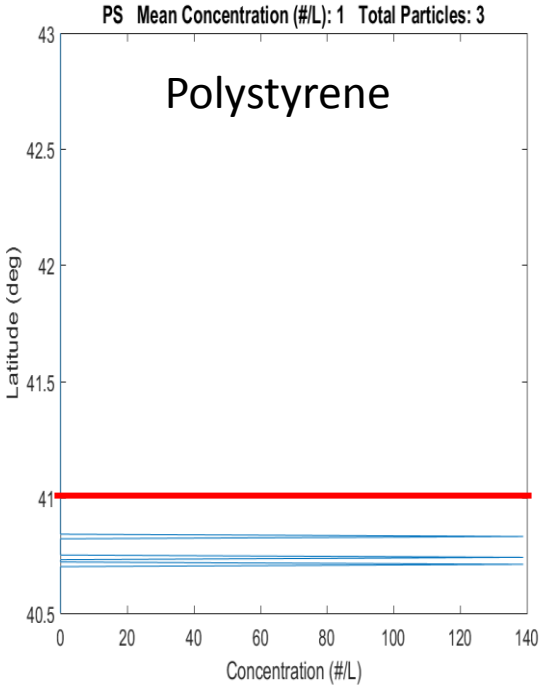


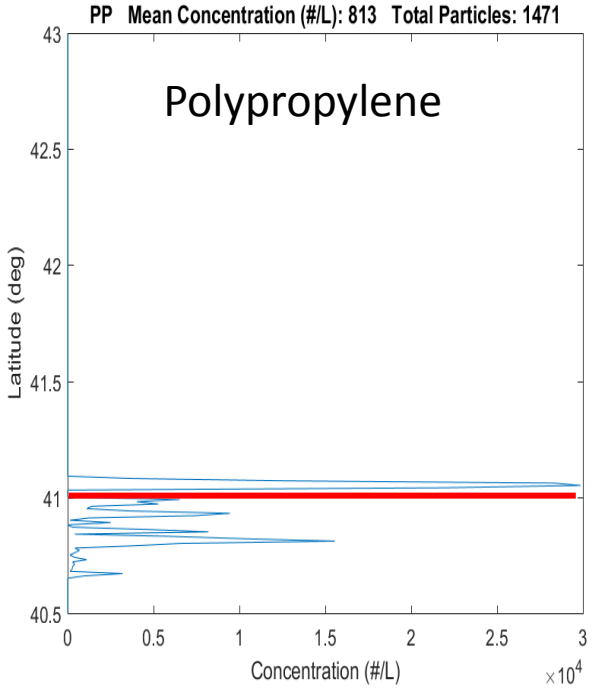

AB Mean Concentration (#/L): 872 Total Particles: 1577
Albany
Acrylonitrile Butadiene
Tappan Zee Bridge
The Battery
Latitude (deg)
Concentration (#/L)
×10^4

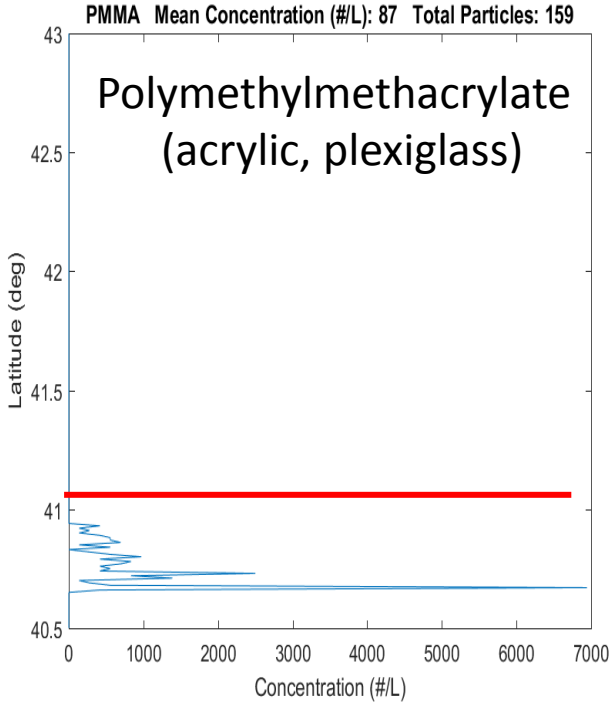

ABS Mean Concentration (#/L): 109 Total Particles: 197
Poly(Acrylonitrile Butadiene Styrene)
Latitude (deg)
Concentration (#/L)

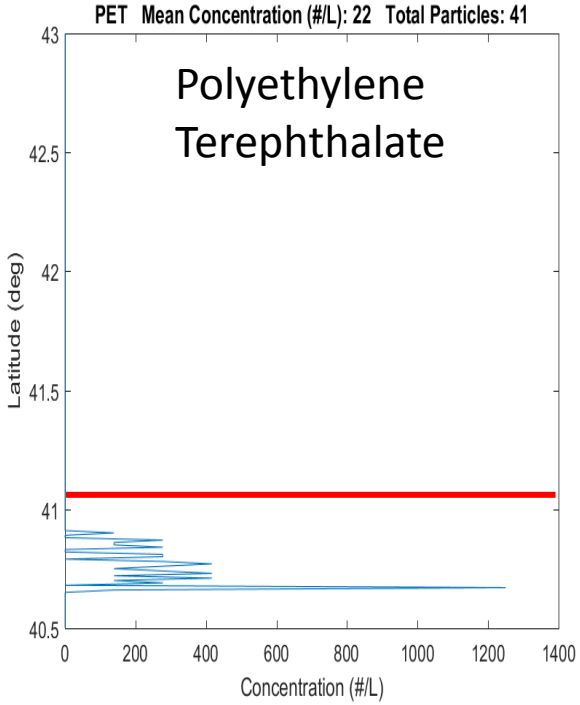

PVC Mean Concentration (#/L): 1121 Total Particles: 2027
Polyvinyl Chloride
Latitude (deg)
Concentration (#/L)
×10^4

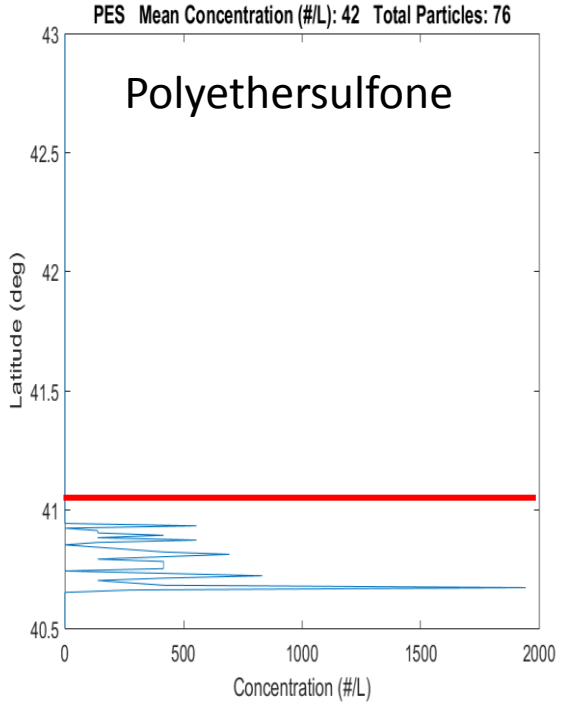

PTFE Mean Concentration (#/L): 35 Total Particles: 65
Polytetrafluoroethylene (Teflon)
Latitude (deg)
Concentration (#/L)

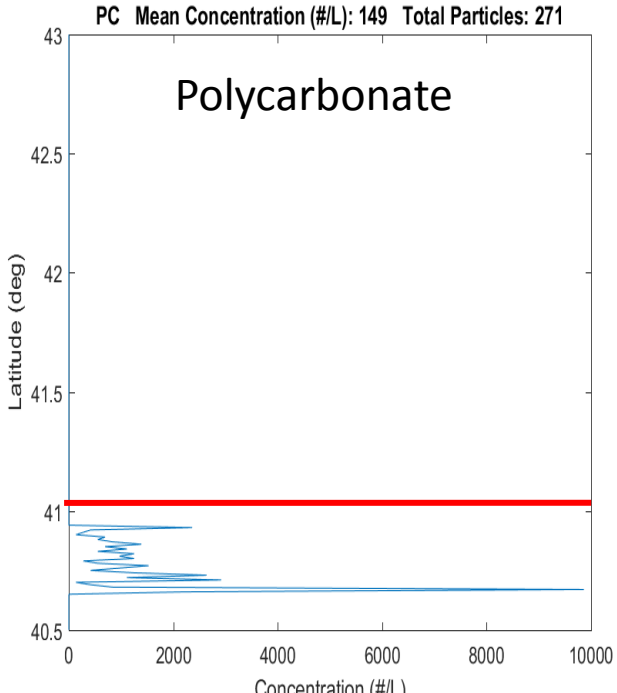

PS Mean Concentration (#/L): 1 Total Particles: 3
Polystyrene
Latitude (deg)
Concentration (#/L)

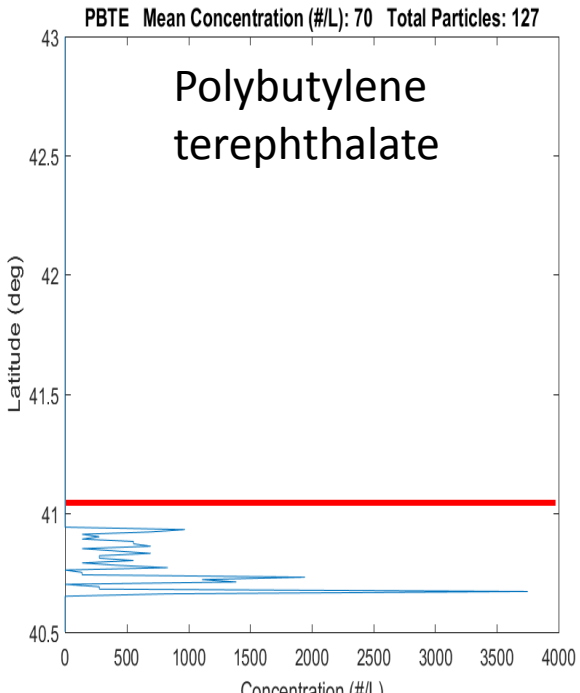

PP Mean Concentration (#/L): 813 Total Particles: 1471
Polypropylene
Latitude (deg)
Concentration (#/L)
×10^4

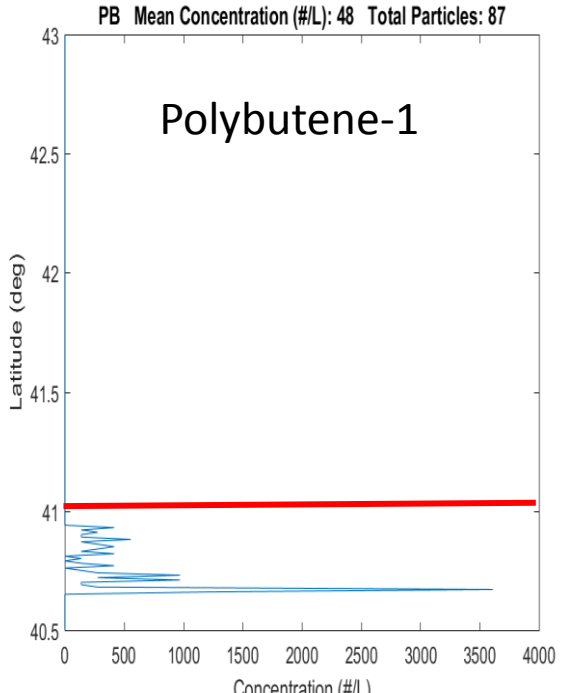

PMMA Mean Concentration (#/L): 87 Total Particles: 159
Polymethylmethacrylate
(acrylic, plexiglass)
Latitude (deg)
Concentration (#/L)


PET Mean Concentration (#/L): 22 Total Particles: 41
Polyethylene
Terephthalate
Latitude (deg)
Concentration (#/L)

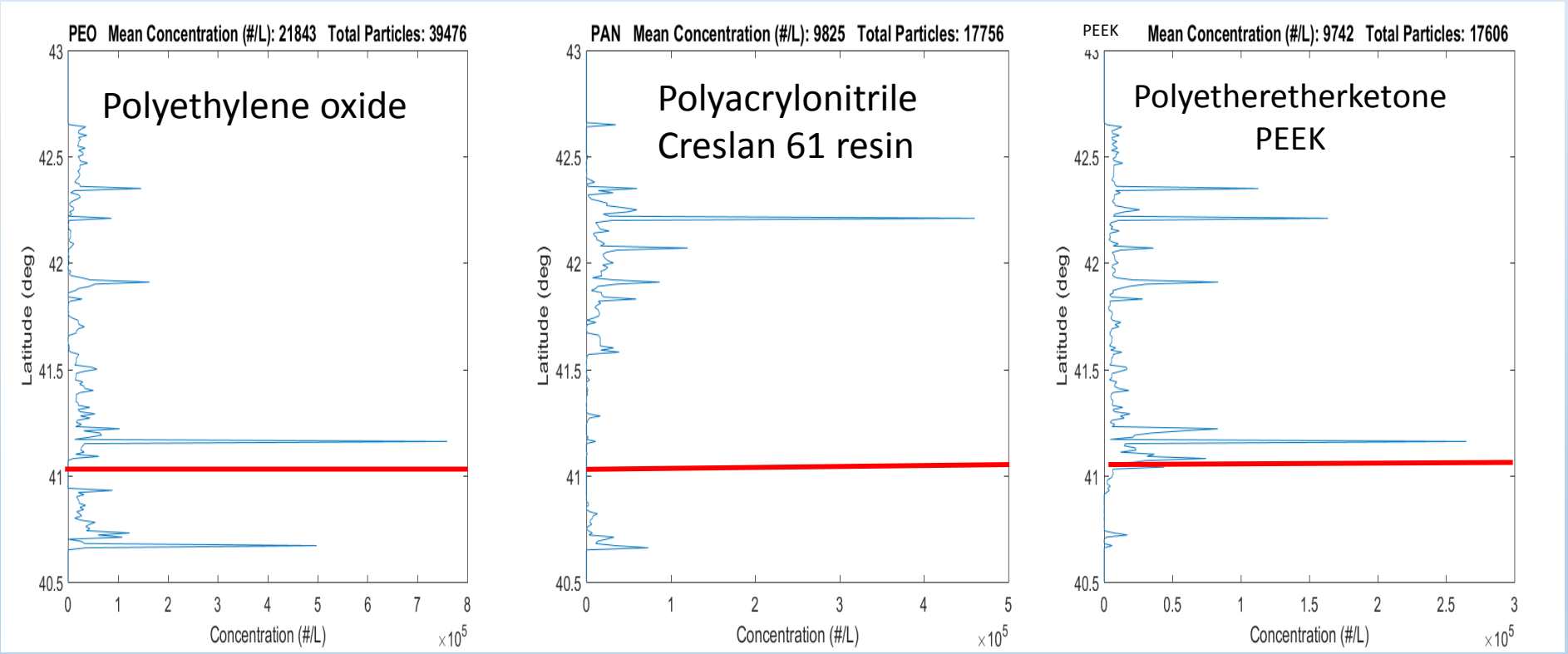

PES Mean Concentration (#/L): 42 Total Particles: 76
Polyethersulfone
Latitude (deg)
Concentration (#/L)


PC Mean Concentration (#/L): 149 Total Particles: 271
Polycarbonate
Latitude (deg)
Concentration (#/L)


PBTE Mean Concentration (#/L): 70 Total Particles: 127
Polybutylene
terephthalate
Latitude (deg)
Concentration (#/L)


PB Mean Concentration (#/L): 48 Total Particles: 87
Polybutene-1
Latitude (deg)
Concentration (#/L)

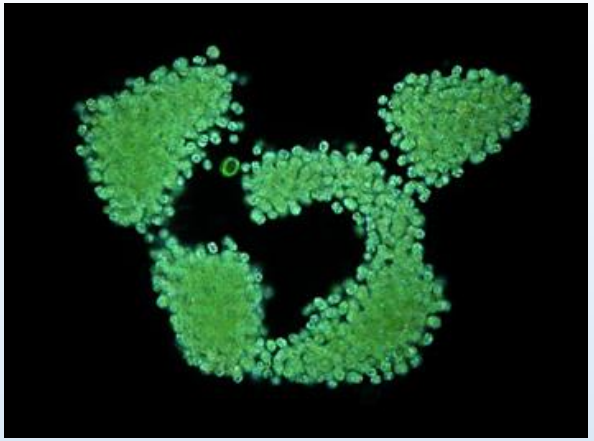
Only a few polymers concentrated throughout river

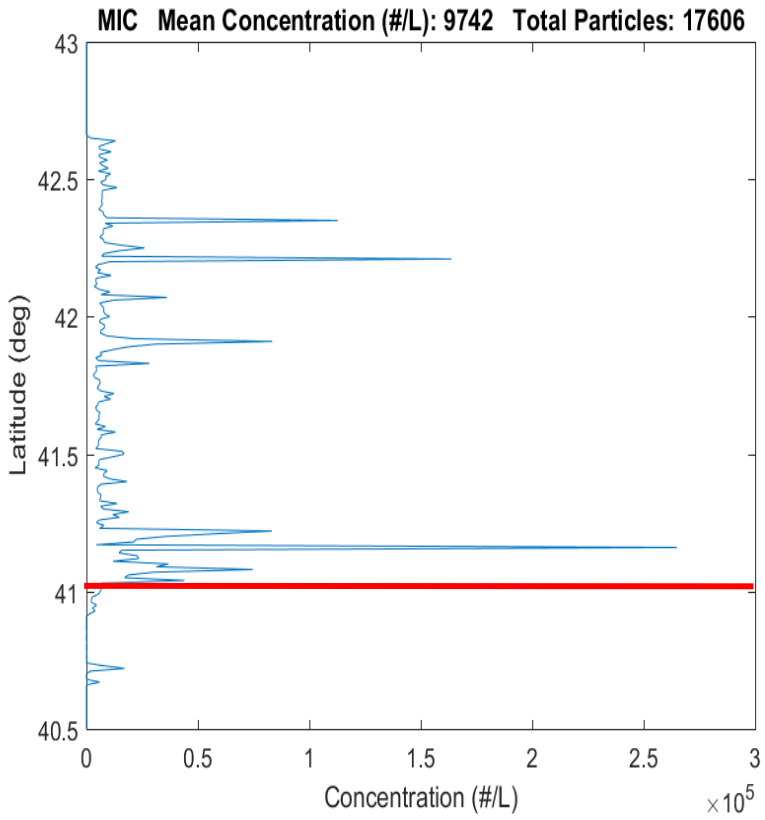


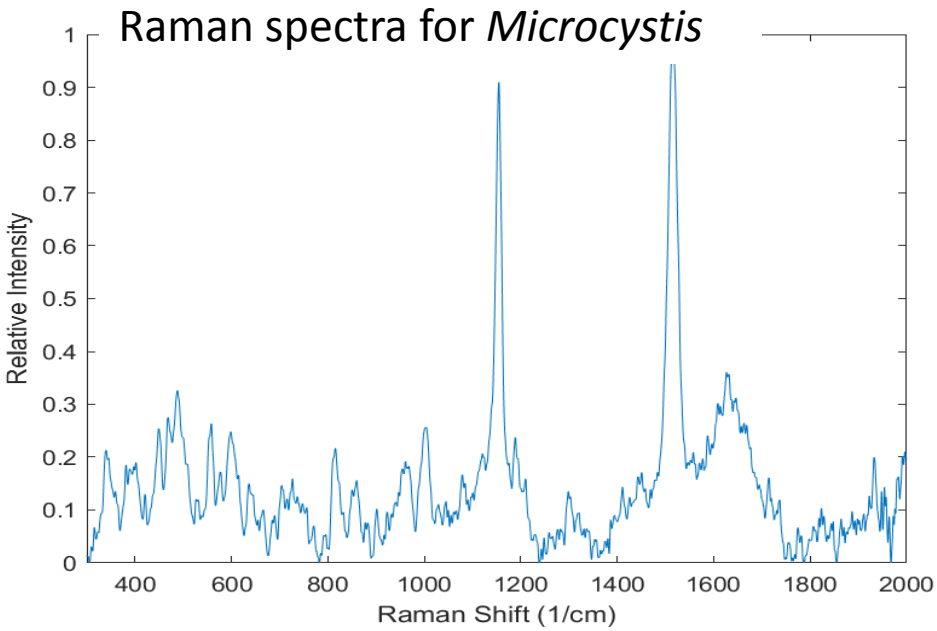
An aside issue:

Microcystis aeruginosa

also in Raman library





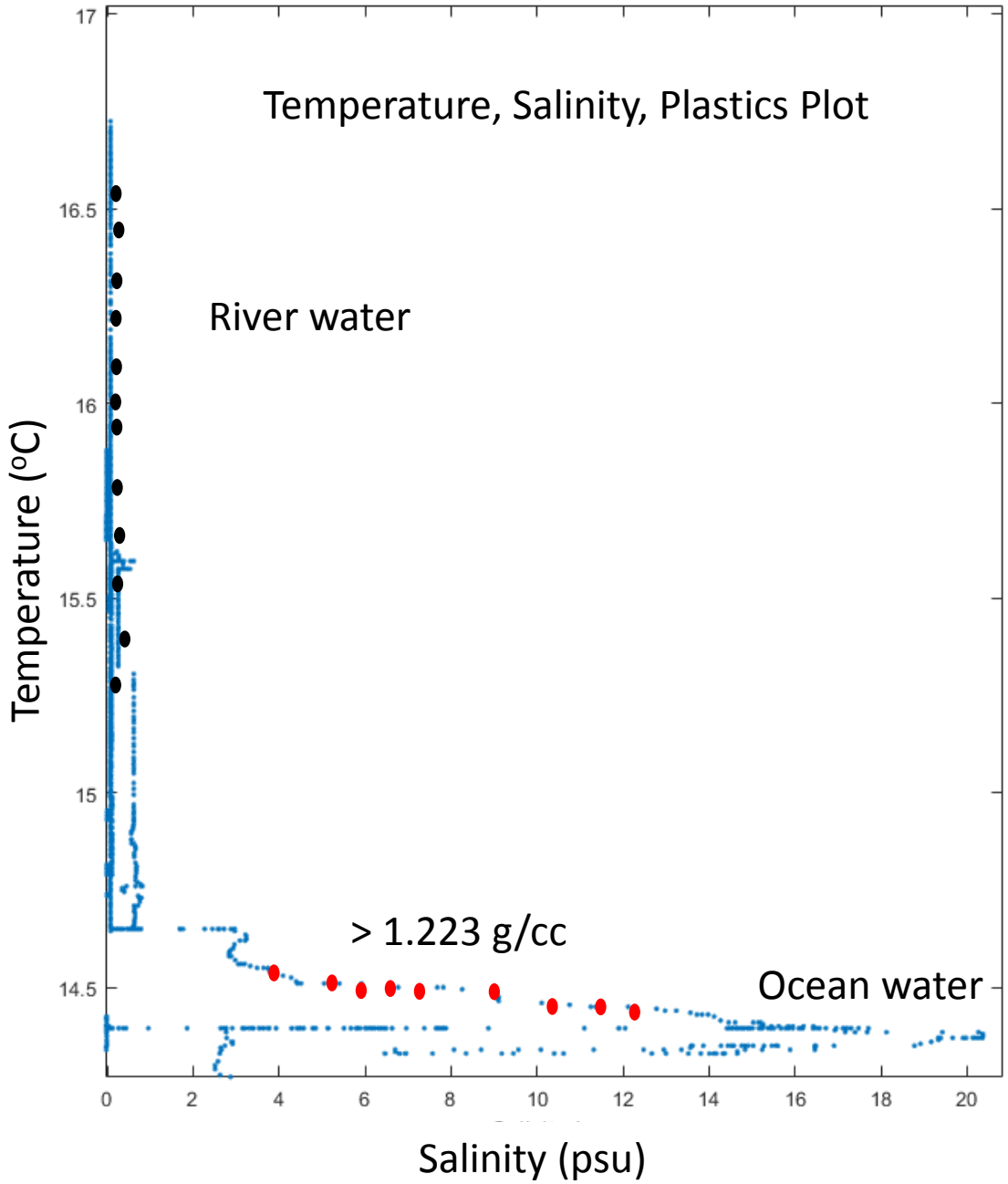


Contains neurotoxin, microcystin

Abv.	Polymer	mean #/L	Total	den g/cc	Location
AB	Acrylonitrile Butadiene	872	1,577	1.080	L
ABS	Poly(Acrylonitrile Butadiene Styrene)	109	197	1.058	L
EVA	Ethylene Vinyl Acetate Copolymer	4	8	0.951	U
HDPE	High Density Polyethylene	Na	1	0.970	U
LDPE	Low Density Polyethylene	Na	2	0.940	U
NY	Nylon 66	2,753	4,977	1.150	L
PAN	Polyacrylonitrile Creslan 61 resin	9,825	17,756	1.184	UL
PB	Polybutene-1	48	87	0.910	L
PBTE	Polybutylene Terephthalate	70	127	1.316	L
PC	Polycarbonate	149	271	1.223	L
PES	Polyethersulfone	42	76	1.376	L
PET	Polyethylene terephthalate	22	41	1.386	L
PEO	Polyethylene oxide			1.211	UL
PMMA	Polymethylmethacrylate (acrylic, plexiglass)	87	159	1.183	L
PP	Polypropylene	813	1,471	0.855	L
PS	Polystyrene	1	3	1.040	L
PTFE	Polytetrafluoroethylene (Teflon)	35	65	2.211	L
PVAL	Poly(Vinyl Alcohol)	4	9	1.192	L
PVC	Polyvinyl Chloride	1,121	2,027	1.452	L
SAN	Poly(Styrene Acrylonitrile)	2	4	1.082	U

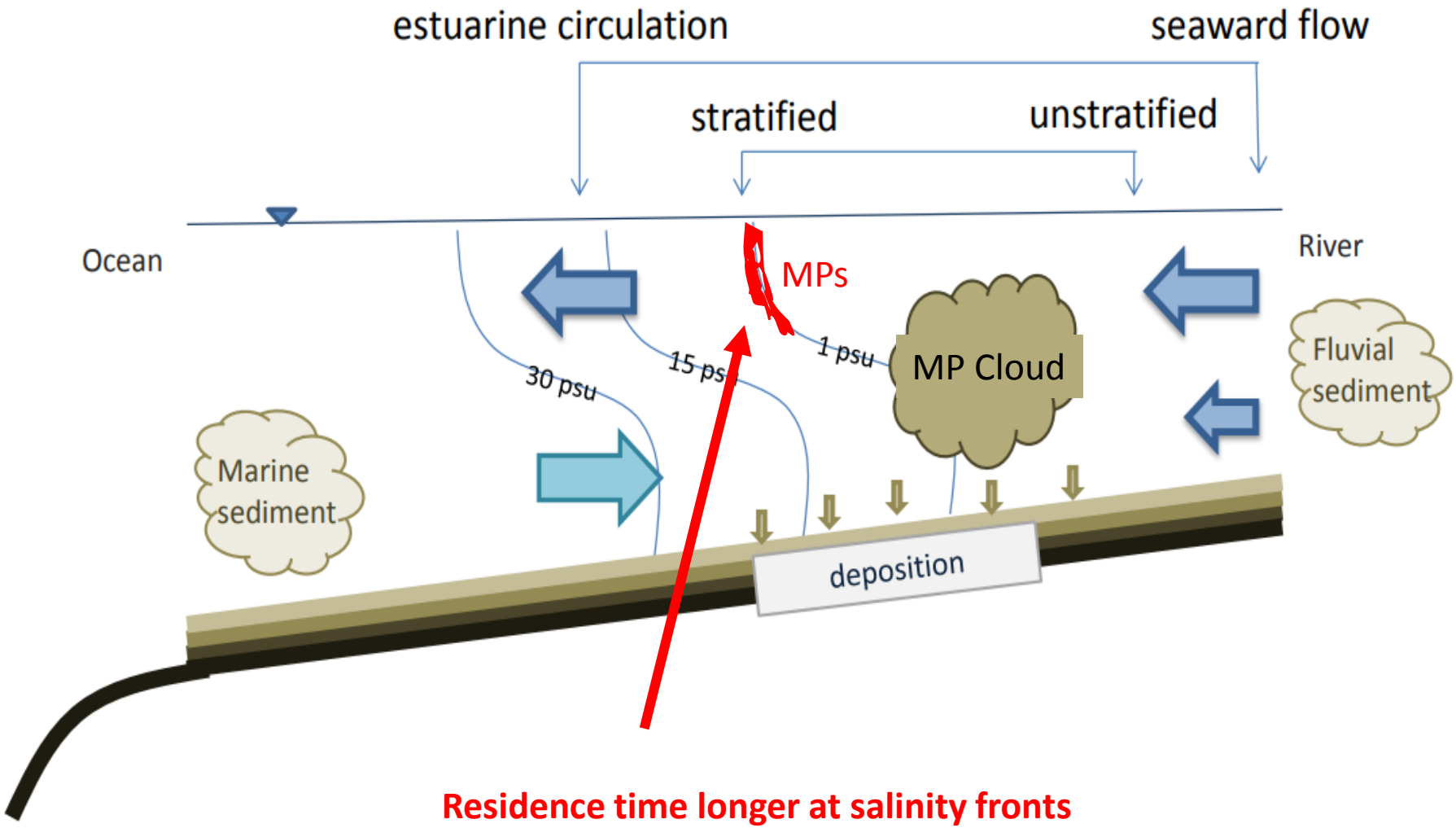
What's in the river?

Lower river: L
Upper river : U
Both: UL



Microplastics > 1.223 g/cc are concentrated at density front

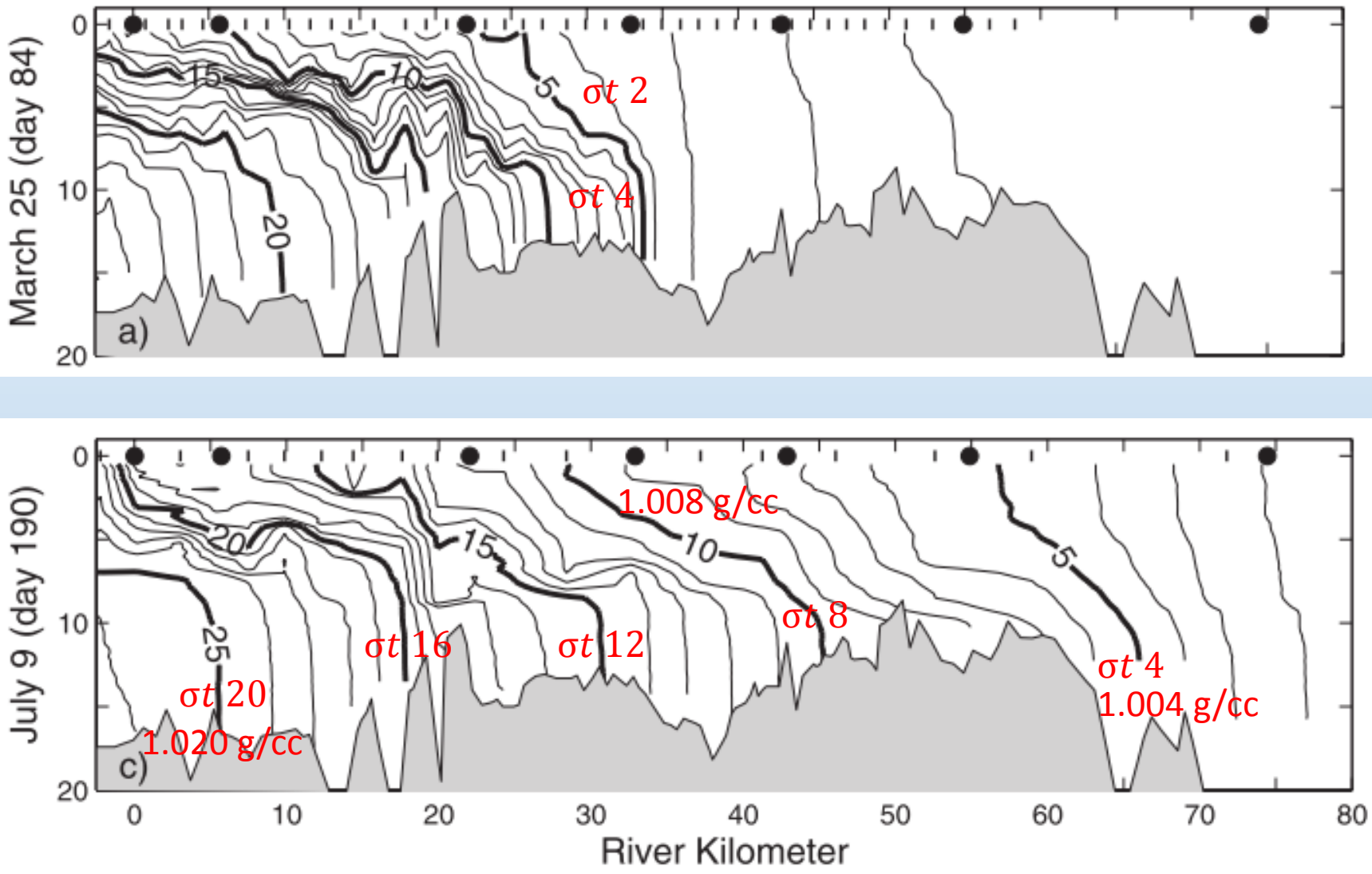
Two Layer Estuarine Flow and Concentration of MPs on Density Front



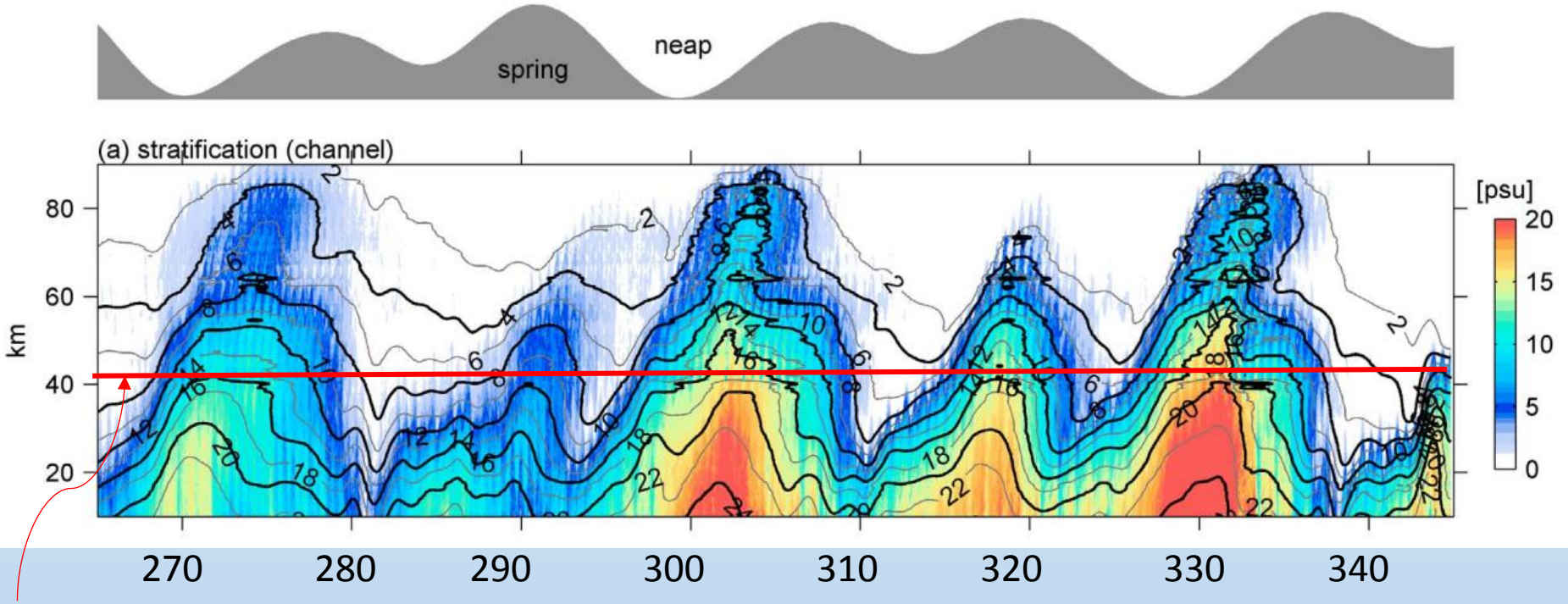
Residence time longer at salinity fronts

Adapted from Ralston et al. 2015

Hudson River Salinity Front in Spring and Summer



Ralston et al. (2009)



Tappan Zee Bridge

Strong stratification extends well beyond the Tappan Zee Bridge on Spring tides depending on season.

Dense microplastics could be tidally pumped on the salinity front in all parts of the water column.

Conclusions

Based on density, MPs were concentrated at density fronts near and below the Tappan Zee Bridge where the salt wedge is known to extend bringing salt water along the river bed.

Some polymers (e.g., Polyacrylonitrile and Polyvinyl Chloride) were scattered in the northern sections of the river. Upriver source?

These results suggest that MPs become distributed as a function of salinity/density in the river.

Next Step: We need to complete rapid vertical profiles while conducting spatial survey along the river.

Density fronts may provide a concentration point where clean up efforts could be focused