

Using single particle ICP-MS to track plastic particles through soils: A new way of quantifying the transport of nano- and micro-plastics in terrestrial environments

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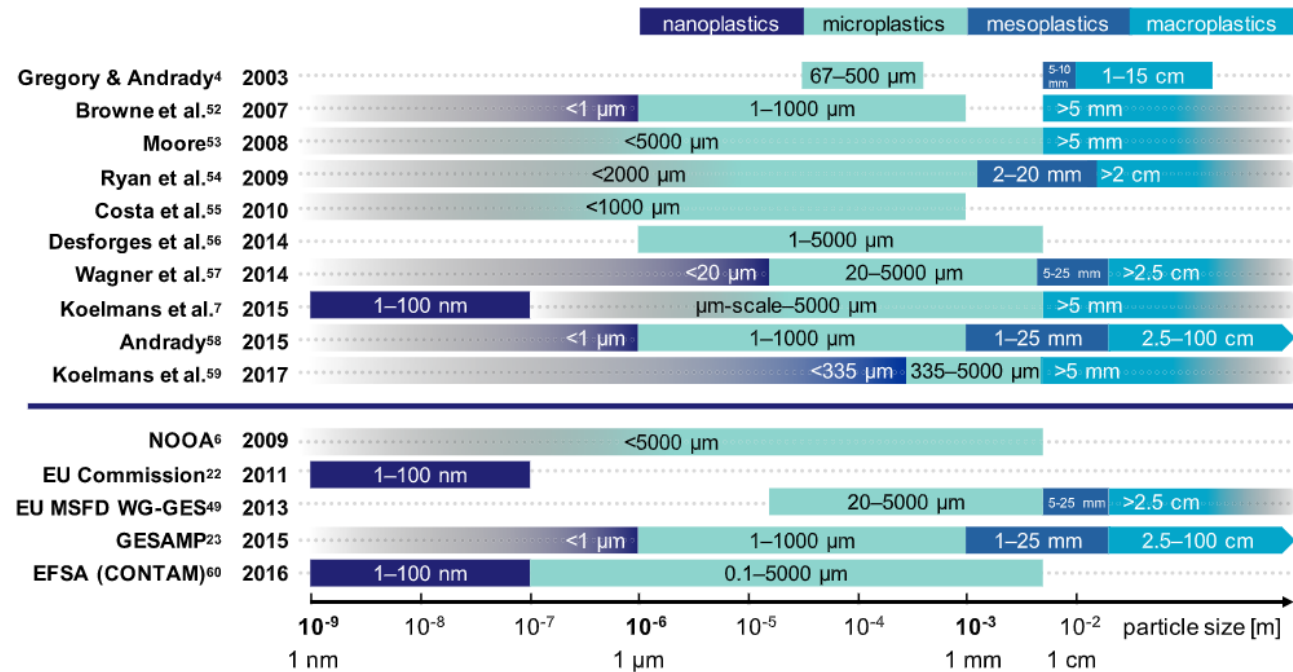
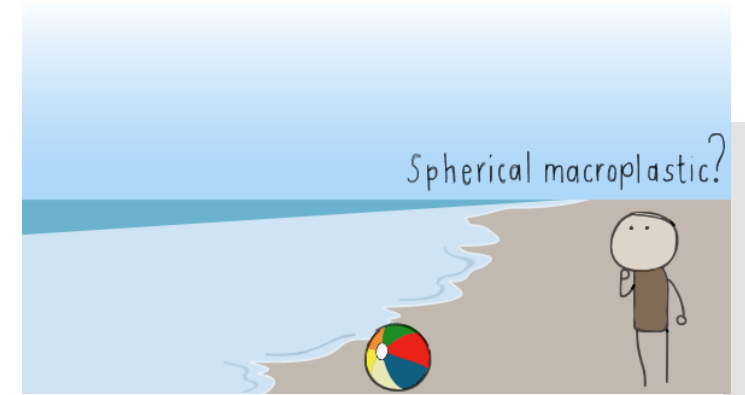


Microplastics in the Environment

A quick overview...

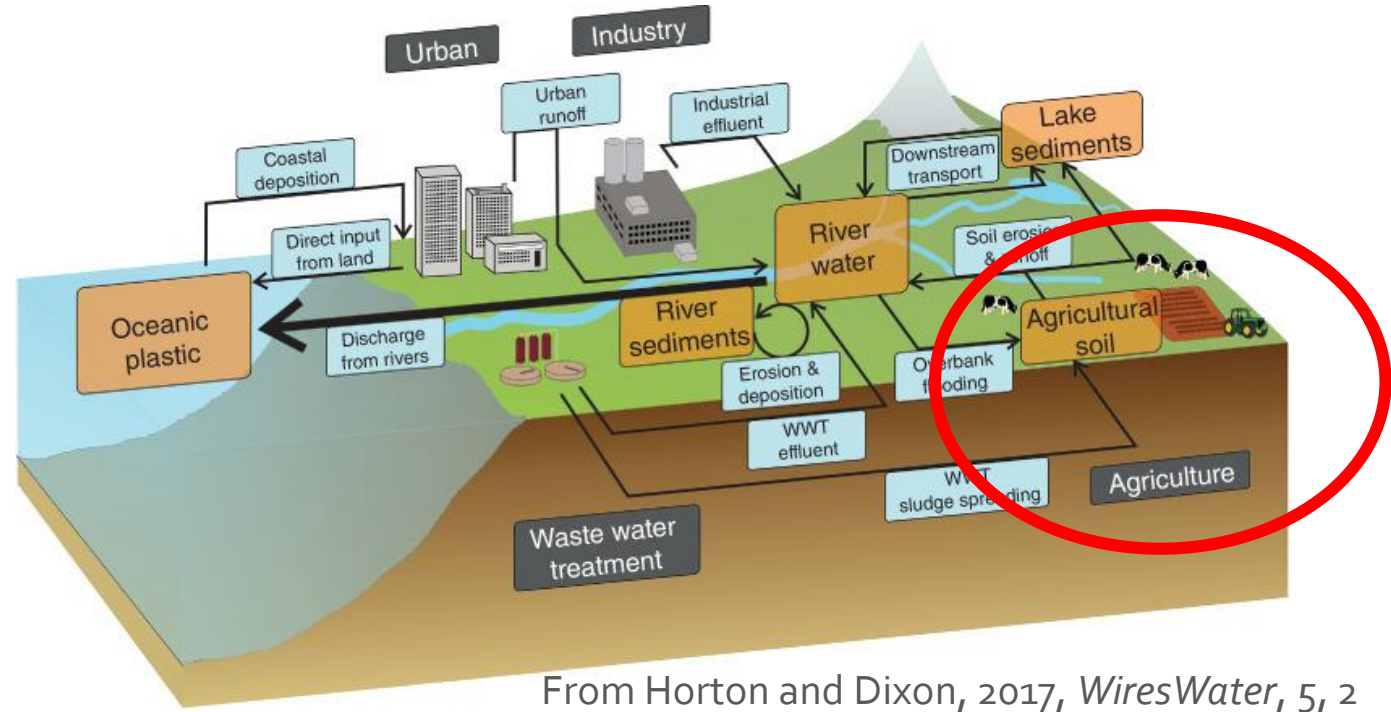
Let's start with some definitions...

- Microplastic (MP) is in the 1-1000 μm range
- Nanoplastic is in the 1-1000 nm range



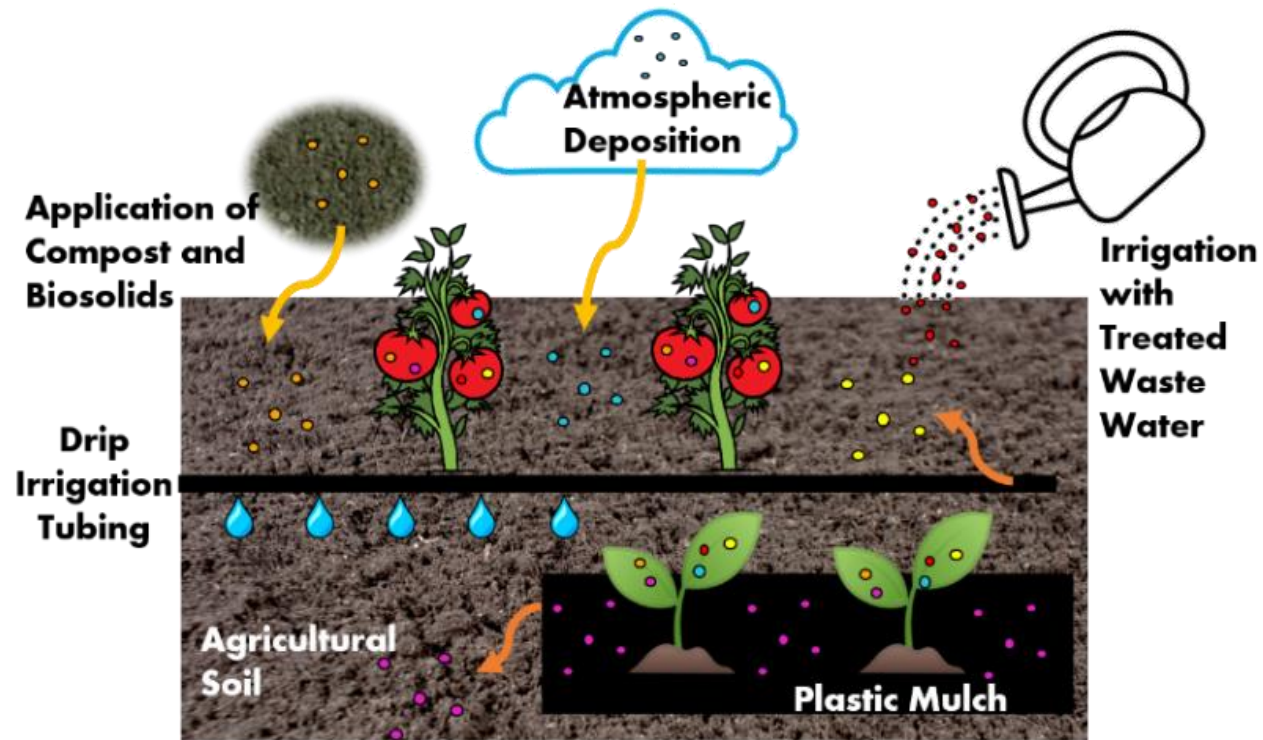
From Hartmann et al. (2019) Environ. Sci. Technol. 2019, 53, 1039–1047

...And in terrestrial environments



- Even more plastic is input onto land than into the ocean (perhaps 4-23 times more, says Horton et al. 2017) of macroplastic waste...
- Input coming from tire erosion, irrigation with MP-containing treated wastewater, atmospheric deposition, decomposition
- Agricultural soils are a particular problem due to the breakdown of plastic mulch, irrigation of fields with TWW, and application of MP-containing biosolids

Why exactly is plastic in the soil a problem for agriculture?



- Changes soil physical attributes, including soil hydrophobicity, moisture content, bulk density, and hydraulic conductivity
- Impacts soil microbiome
- Leaches toxic secondary contaminants (additives)
- Serves as a vector for heavy metals
- Can migrate through soils and redistribute sorbed soil nutrients
- Uptake of plastic particles by plants, affecting plant health and resulting in bioaccumulation

Really a problem at the nano-scale!

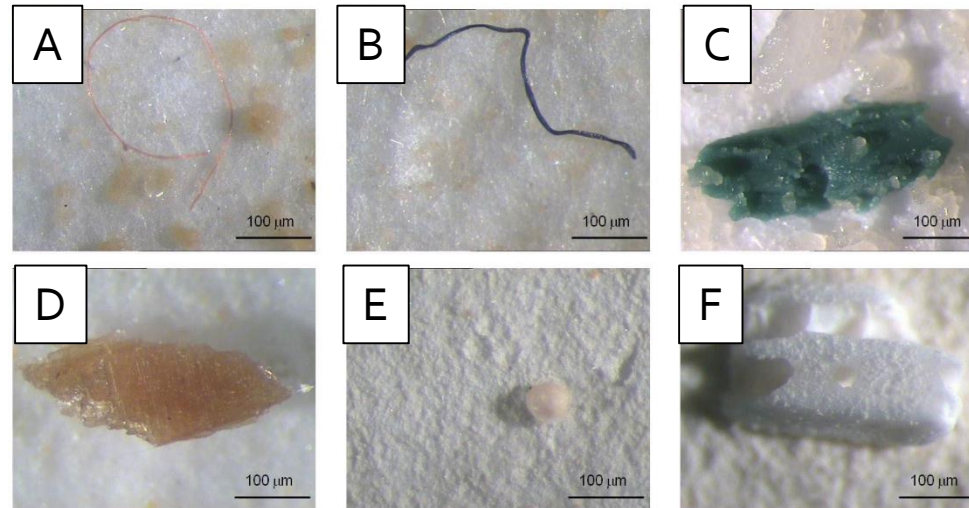


Analytical Challenges for Nano-scale plastics

How do we know what's really there?

Barriers to monitoring plastic in the environment

- Plastic is mostly carbon and inert- which makes it difficult to detect analytically
- It is so DIVERSE- it ranges by:
 - ✓ polymer
 - ✓ size
 - ✓ shape (film, foam, fragment, sphere)



(A,B) fibers
(C,D) fragments
(E) Granule
(F) Foam

Pizzuro et al. 2022,
Microplastics, 1(2)

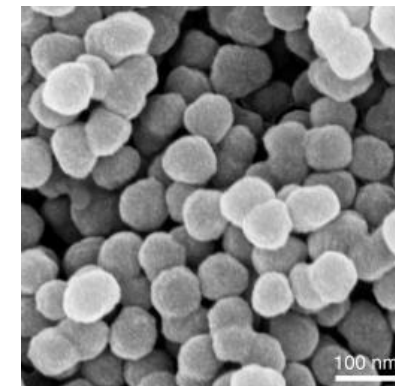
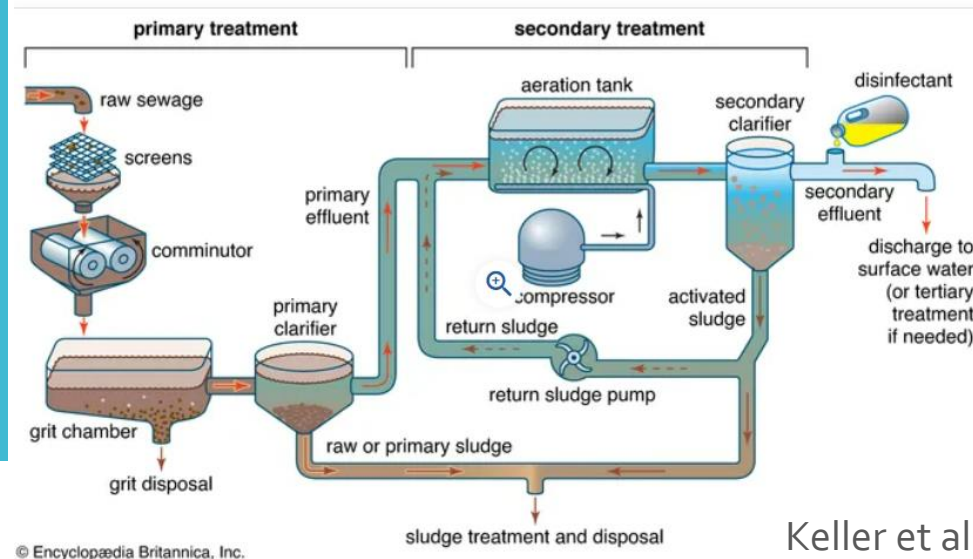
Issues unique to nanoplastics

Problems:

- Nanoplastics are notoriously difficult to detect because of their small size
- Difficult to separate from environmental matrices
- Generally not large enough to see optically

Current Analytical Techniques:

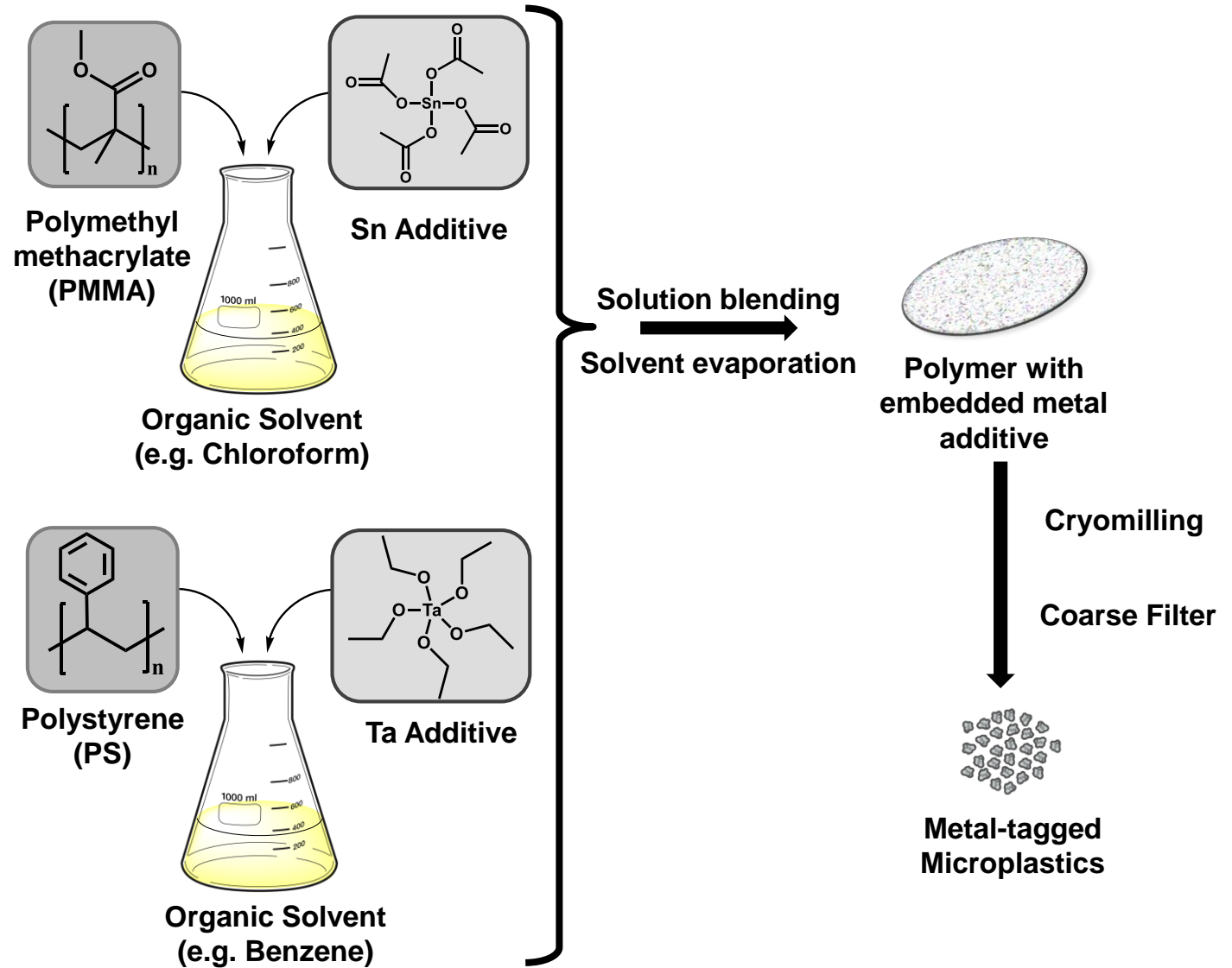
- Visual identification with electron microscopy
- Light scattering techniques
- SPOS
- Fluorescence spectroscopy with labelled beads
- Metal-labelling and detection with ICP-MS



Keller et al. 2020, ES&T, 54(2)

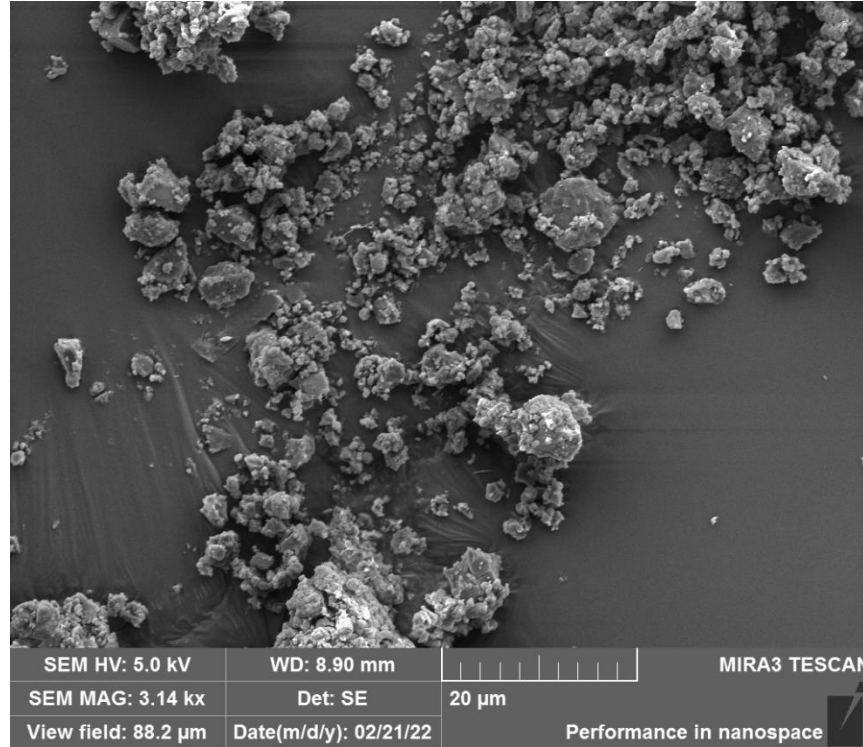
Mitrano et al. 2019, Nature Nanotechnology, 14(4)

Manufacturing of metal-doped plastics

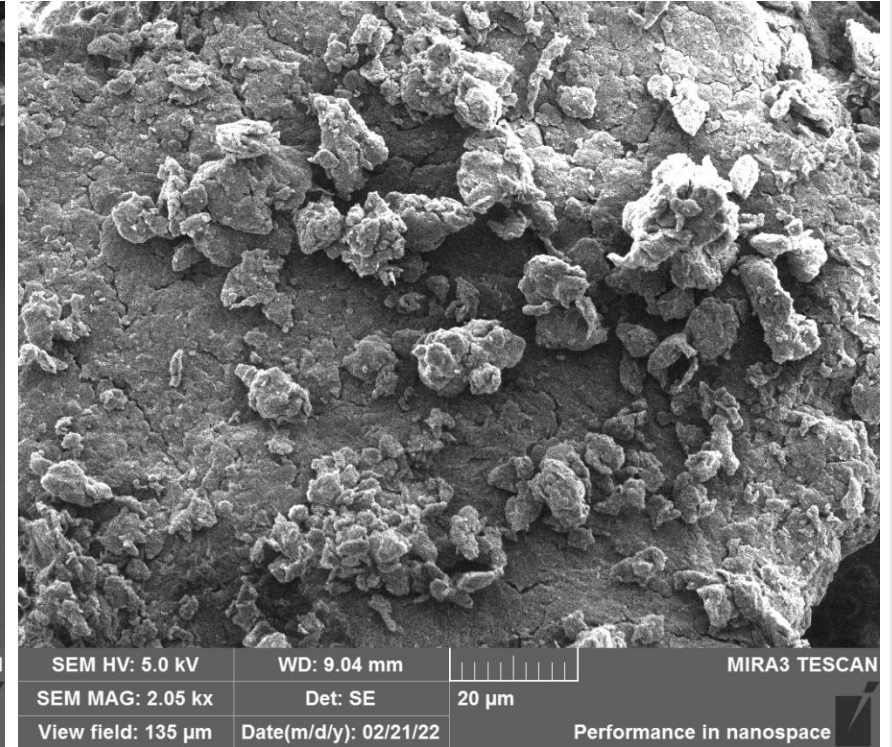


Credit: Shaun Bevers

Metal-doped microplastics



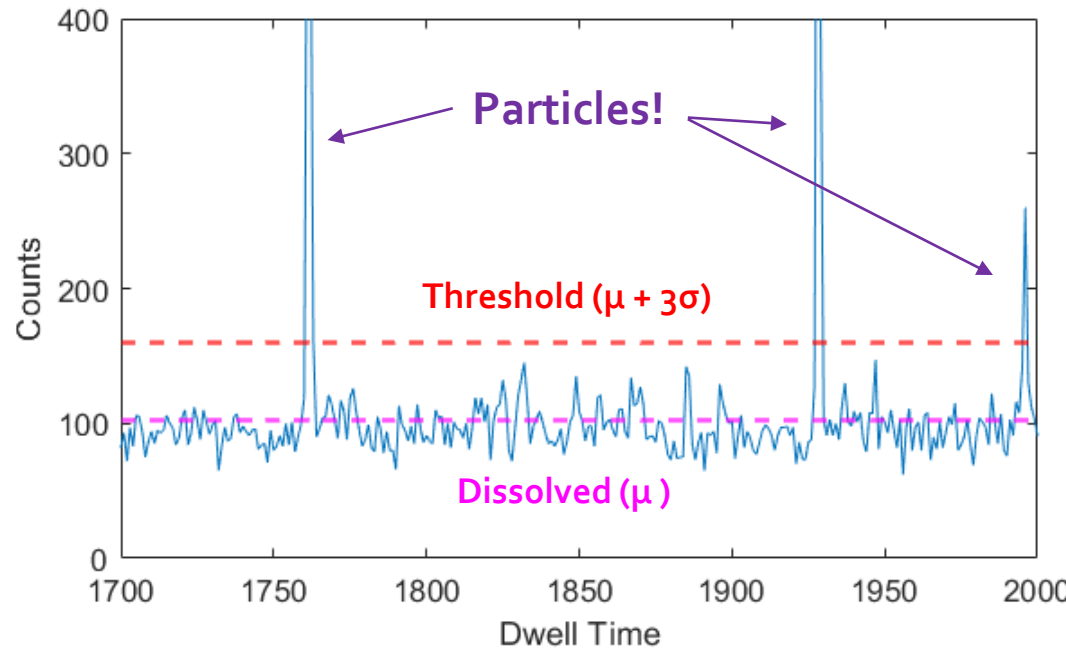
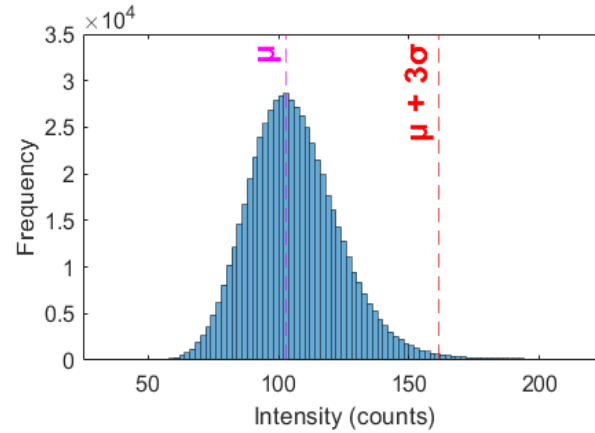
Tantalum-Polyvinylpyrrolidone (Ta-PVP)



Tin-Polystyrene (Sn-PS)

spICP-MS: How it works

How does spICP-MS differ from traditional ICP-MS?

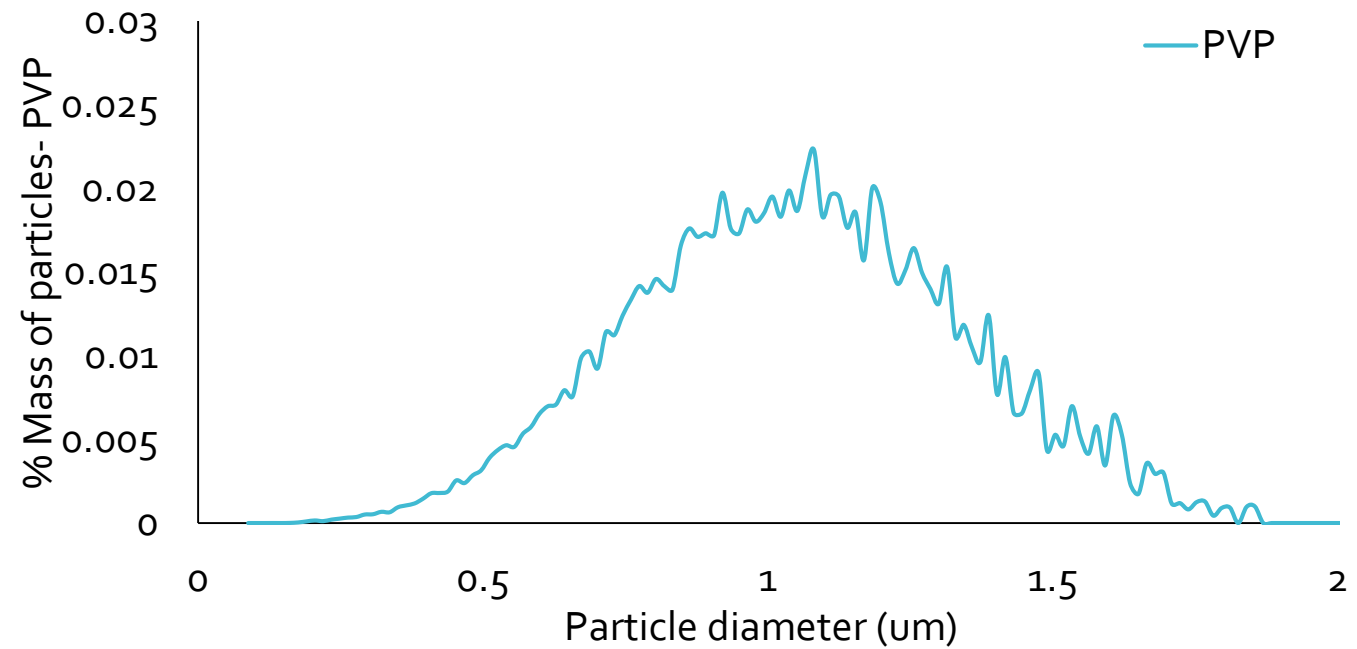


Spikes which are normally considered noise are now your data

Credit: Shaun Bevers

spICP-MS: What it does

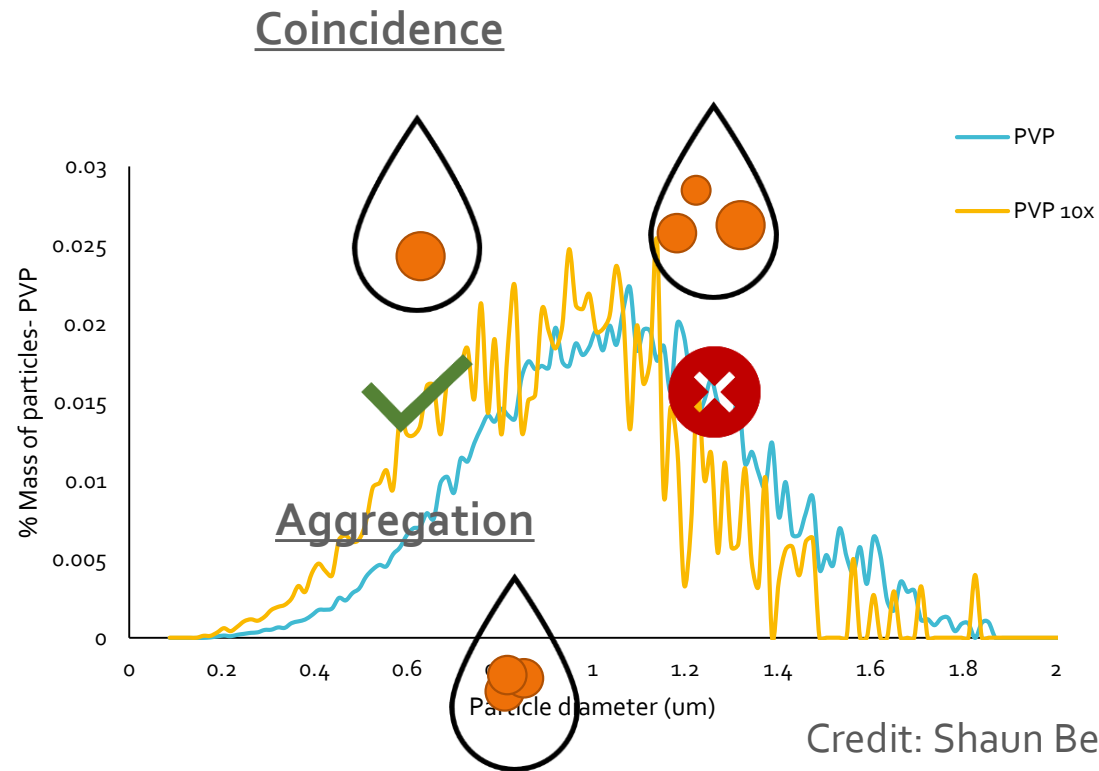
Particle size distribution



PVP=Polyvinylpyrrolidone

Particle Size Distributions

Particle size distribution in your sample



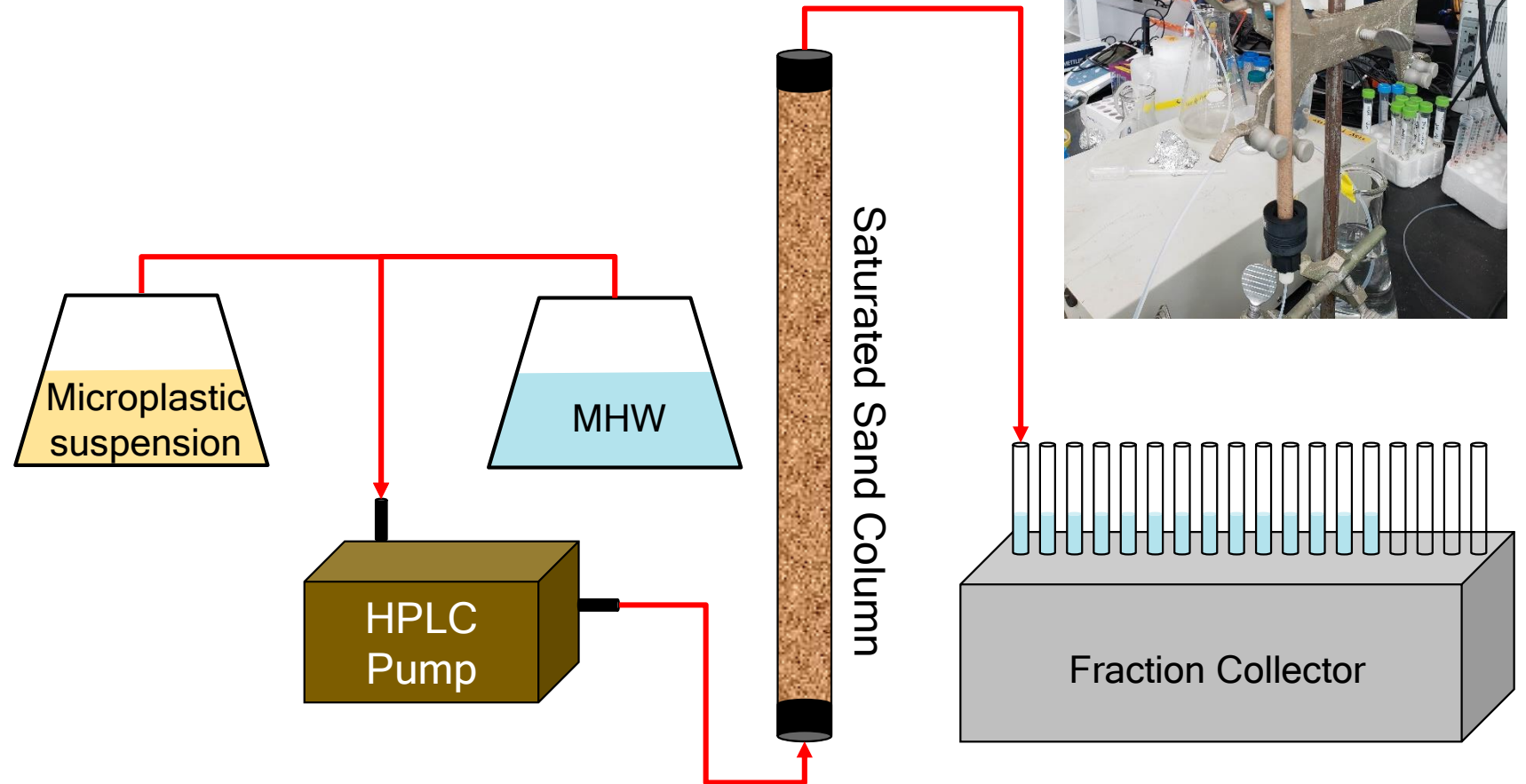
Because of coincidence, dilution can lead to a “shift” in particle size distribution, where more smaller particles are revealed, and larger particles are diluted out

Transport Experiments

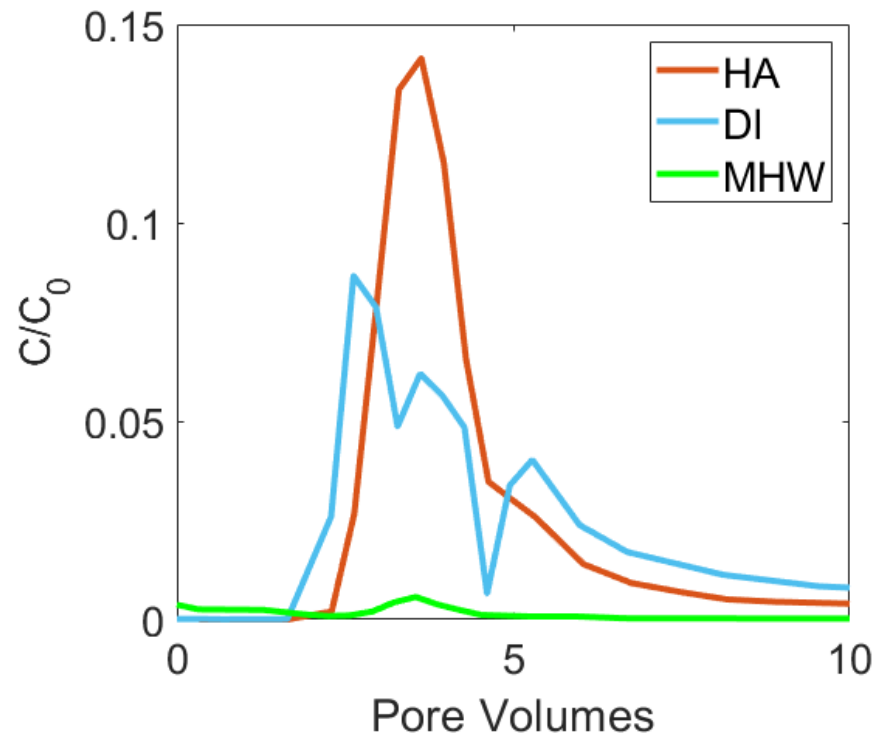
Demonstrating splCP-MS on a laboratory scale

spICP-MS:
What can we
do with it?

Column Experiments



Determine particle transport by background solution chemistry

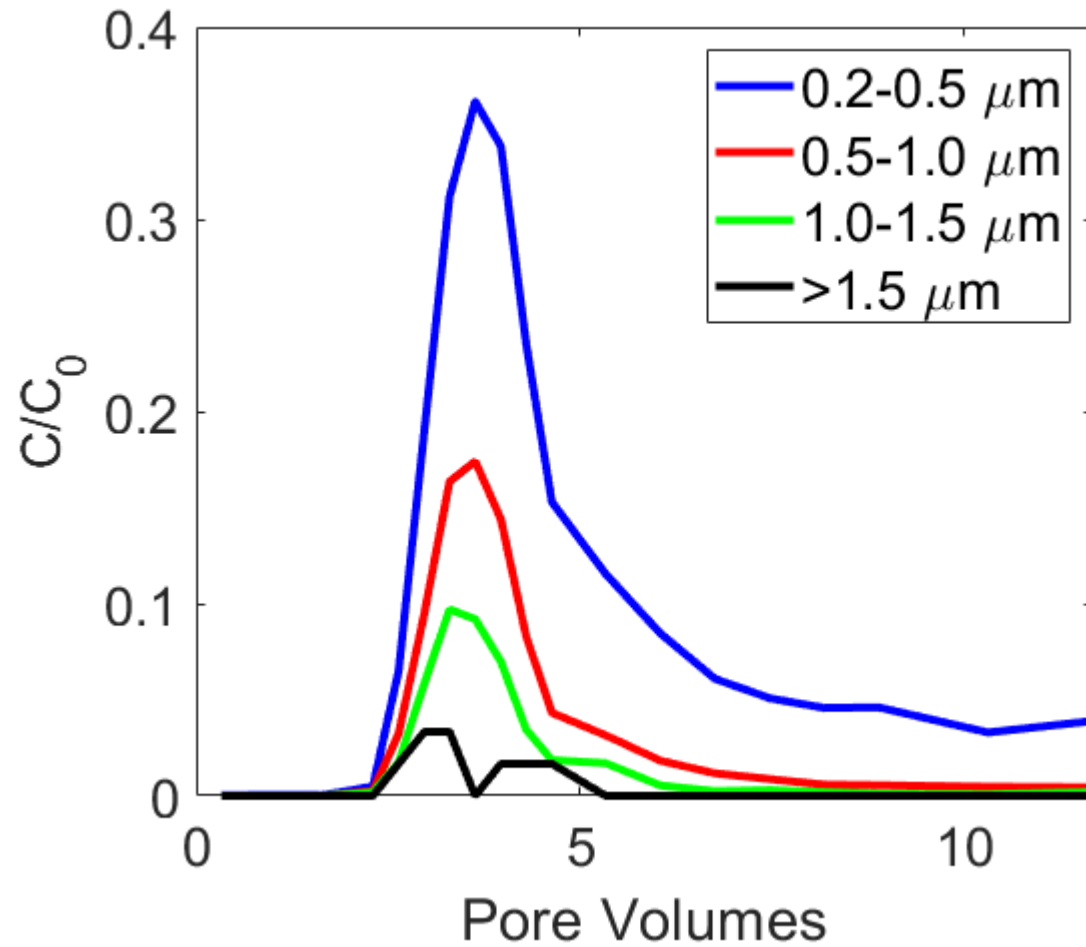


- In different experiments, we can use total intensity of the metal signal to determine overall transport of a particular particle type by mass
- Here we compare the impact of solution chemistries
- This shows suspensions of PVP particles (as total mass) in either 5 mg/L humic acid, deionized water, or modified hard water (~5 mM)



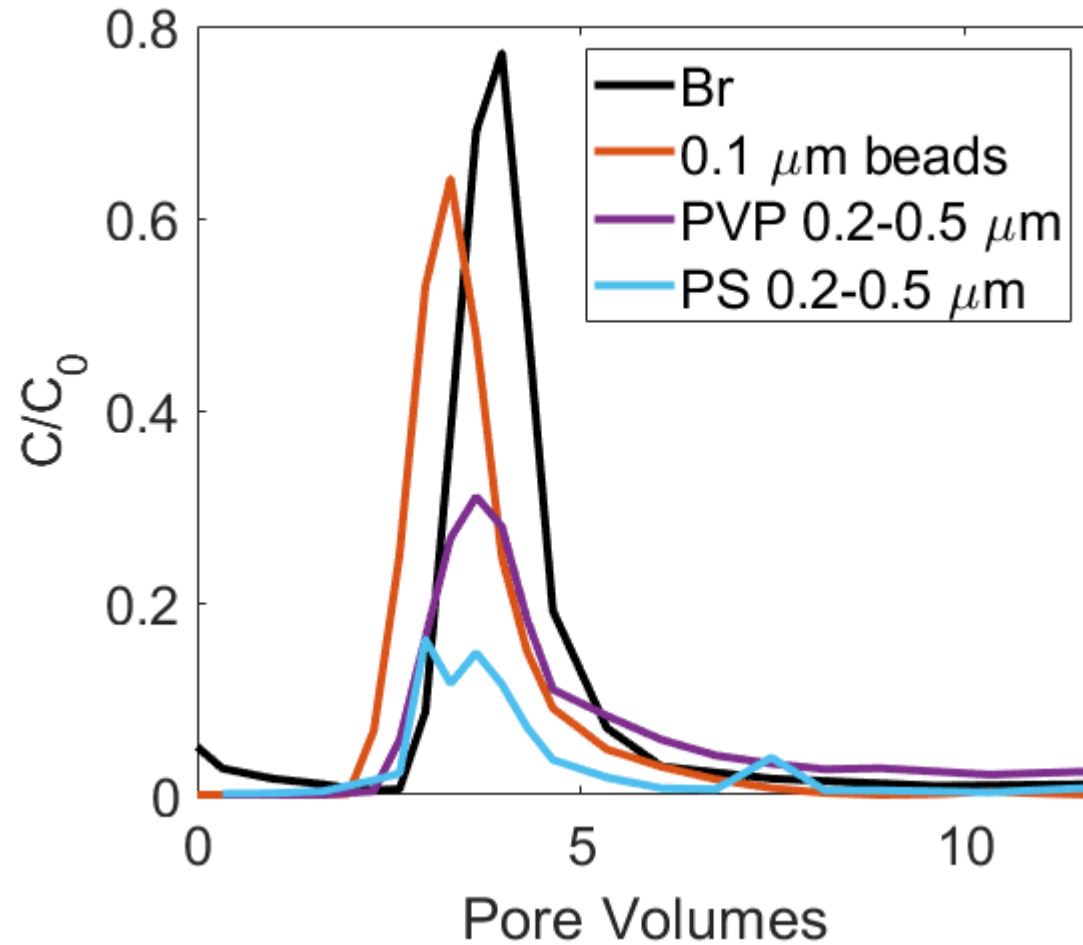
Side note: What do you think that means for plastics in composted agricultural fields?

Determine
particle
transport by
particle size



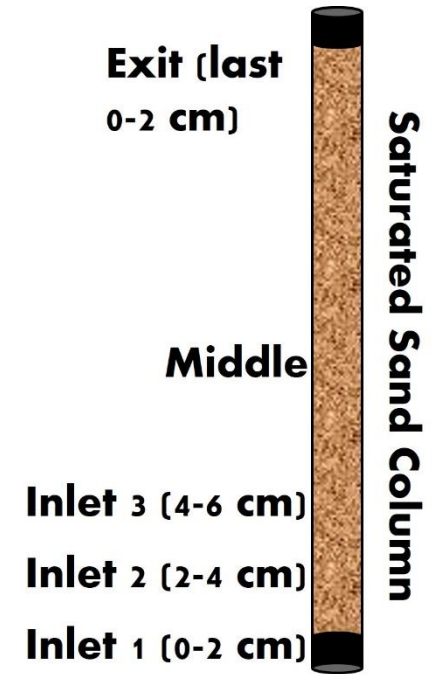
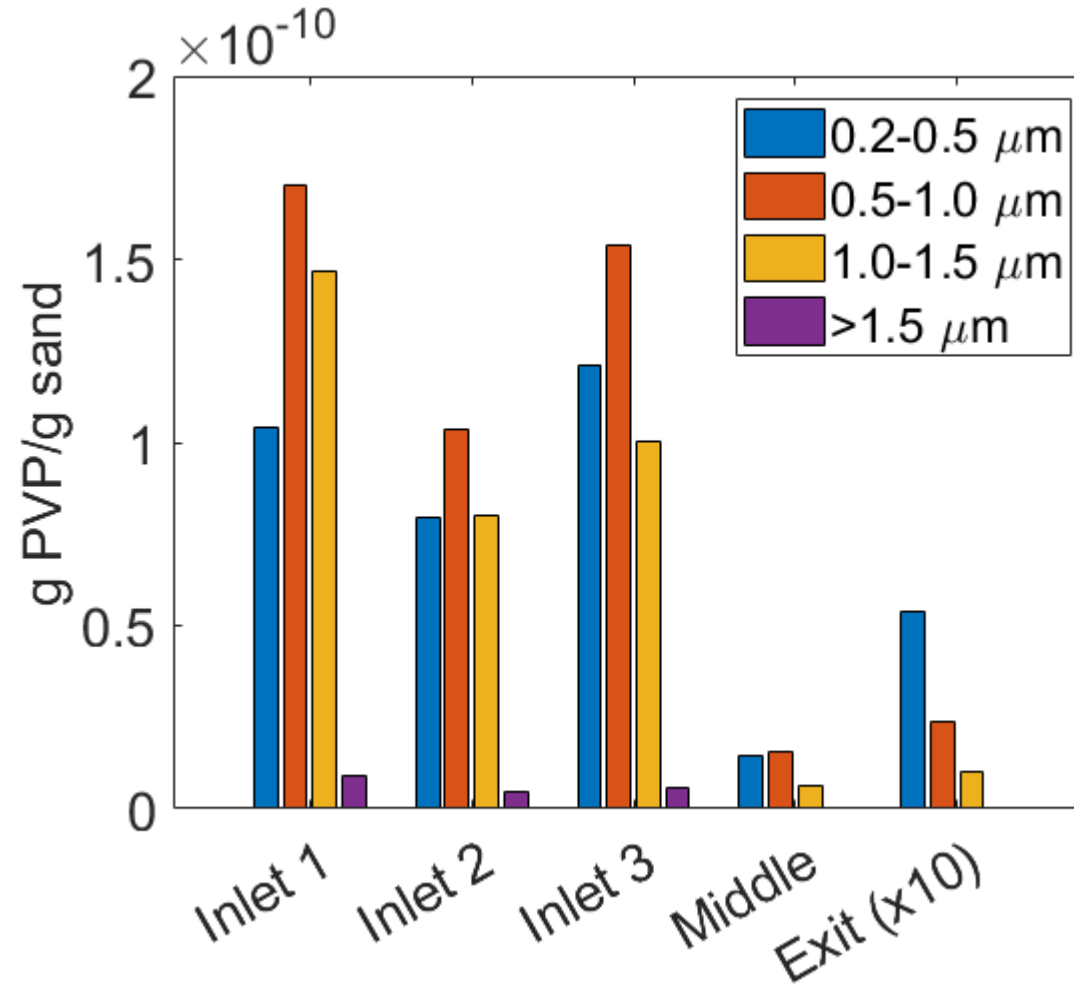
We can compare transport of different size bins of the same polymer (PVP as an example)

Determine
particle
transport by
polymer or
shape



We can compare transport of similar size ranges of different polymers (PVP vs PS) or different shapes (ie, fragment vs sphere)

Deposition of particles in sand column: PVP



The majority of the plastic mass originates from particles of increasingly smaller sizes as it moves through the column



Potential Applications

Ok, so now how would we use this new technique?

Soil Transport and Plant Uptake

- How does particle size impact transport in soils?
- How does particle size impact uptake by plants?
- How does chemical makeup of the soil impact mobility of nano-sized plastics through soils?
- How does polymer type and its associated characteristics (i.e. hydrophobicity) impact mobility through soils?

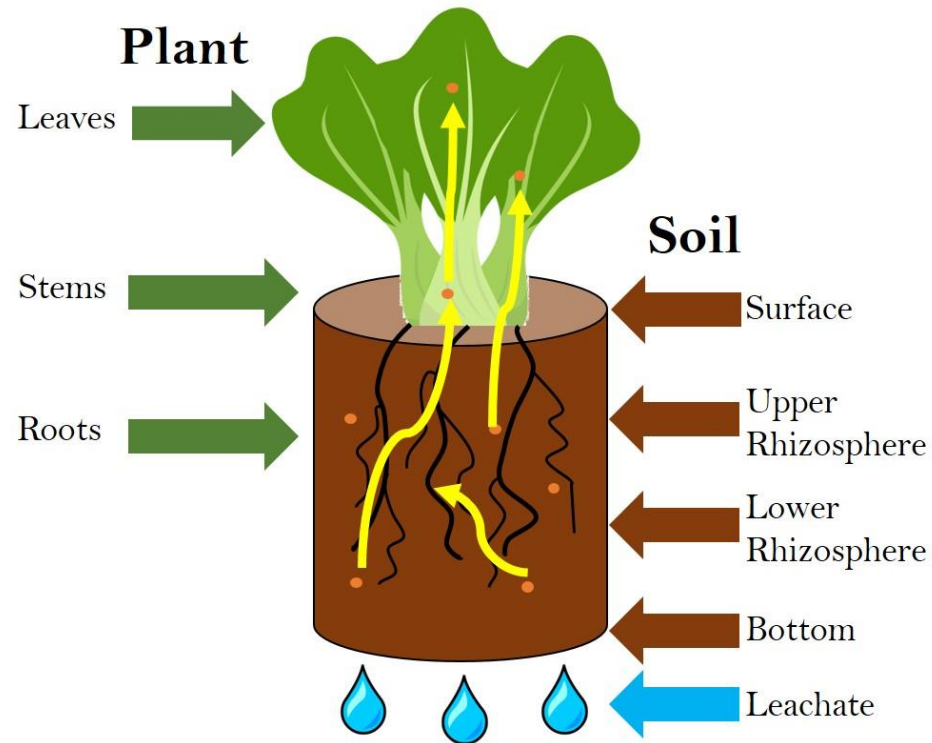
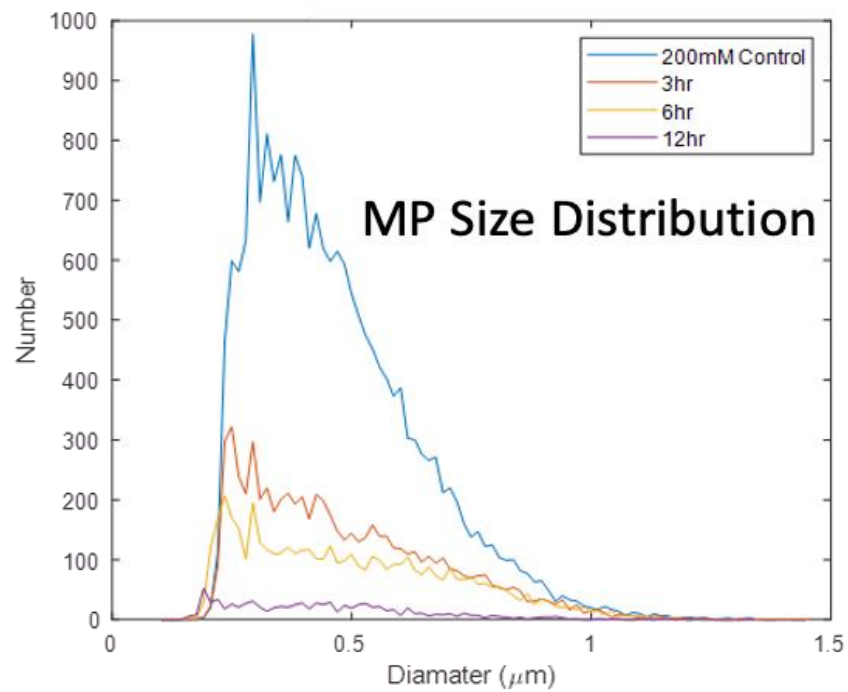
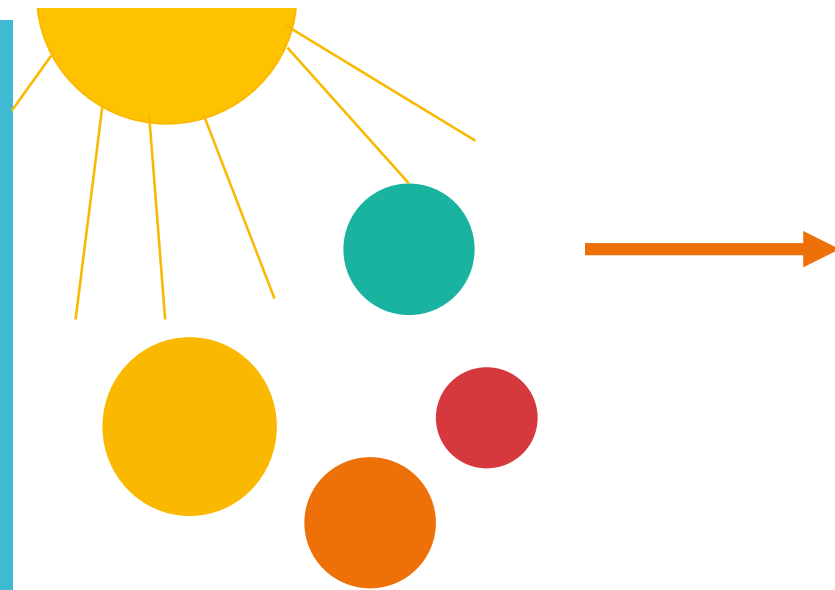


Photo- or bio- degradation of particles



- Single particle ICP-MS has been used to track particle distributions and concentrations already in engineered NPs.
- Currently, this is being used for photodegradation of particles by our group in CO
- Potentially can be used to track biodegradation

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