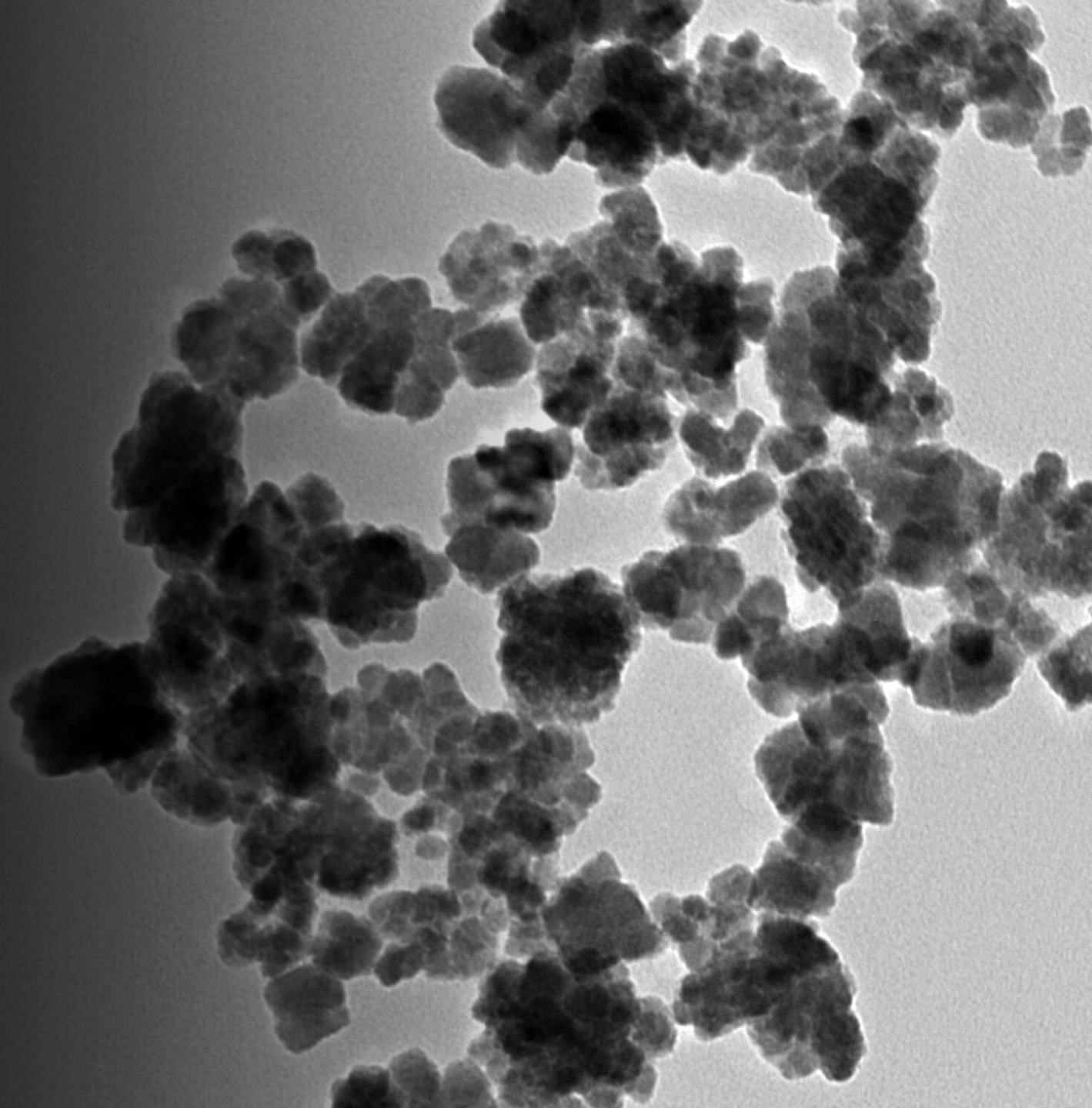




Lead Particulate Release

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- Cincinnati, Ohio, United States
- 2020 EPA Drinking Water Workshop
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**Christy
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Who we are - Acknowledgments



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Formal**



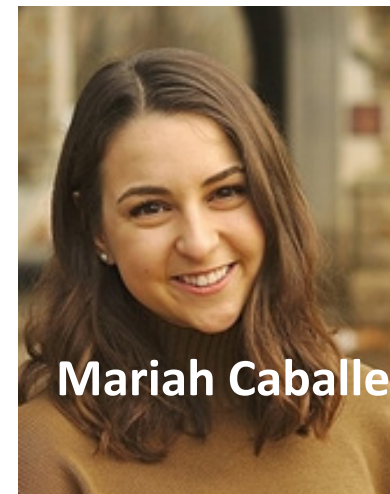
**Regan
Murray**



**Steve
Harmon**



**Evelyn
Doré**



Mariah Caballe



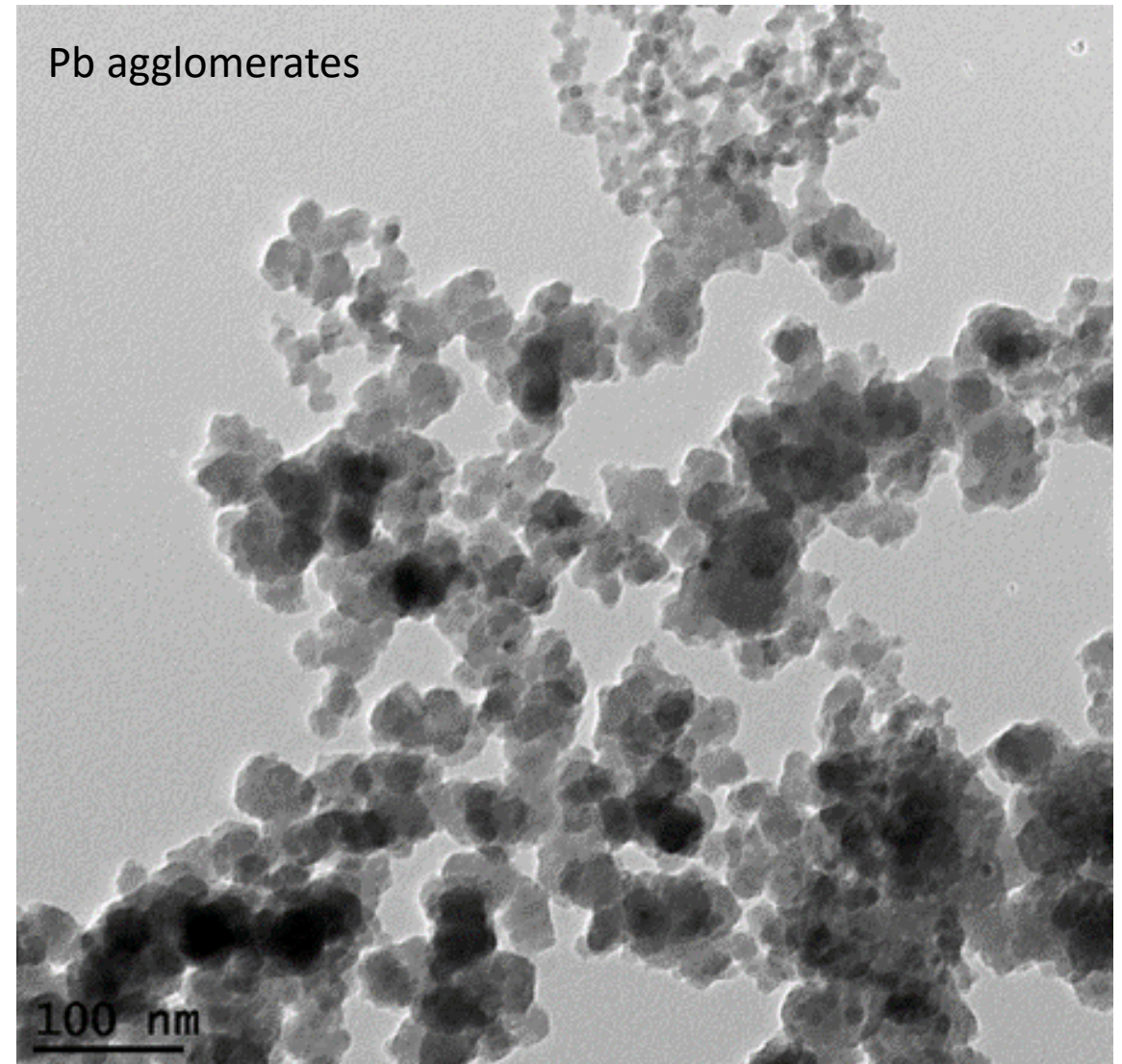
Reasons to Understand Lead Particles

- Lead particles pose a health risk (total lead)
- May contribute large and unpredictable lead spikes
- Understand tap water lead source(s)
- Understand mechanism(s) of lead release
- Treatment approaches may differ from soluble lead
- Presence may indicate state of corrosion control
- Reflect the robustness of lead scale
- Be a signal of an underlying issue

Lead (Pb) in Drinking Water

Relevant Definitions

- Pb^{2+} (Pb[II]) and Pb^{4+} (Pb[IV])
- Soluble (dissolved) and particulate (particles)
- **Soluble** Pb refers to the fraction that passes a pre-identified filter (e.g., $0.45\ \mu\text{m}$, $0.2\ \mu\text{m}$)
- **Particulate** Pb is defined as the difference between the “total” Pb (unfiltered) and soluble Pb
 - *Colloidal particle*- 1 to 1000 nm in diameter
 - *Nanoparticle*- 1 to 100 nm in diameter
- **Agglomeration** refers to the joining together of colloidal particles into larger assemblages
 - van der Waals forces of attraction
 - Electrophoretic mobility (zeta potential) repulsive forces
 - Dispersed particles are spread uniformly across the suspension



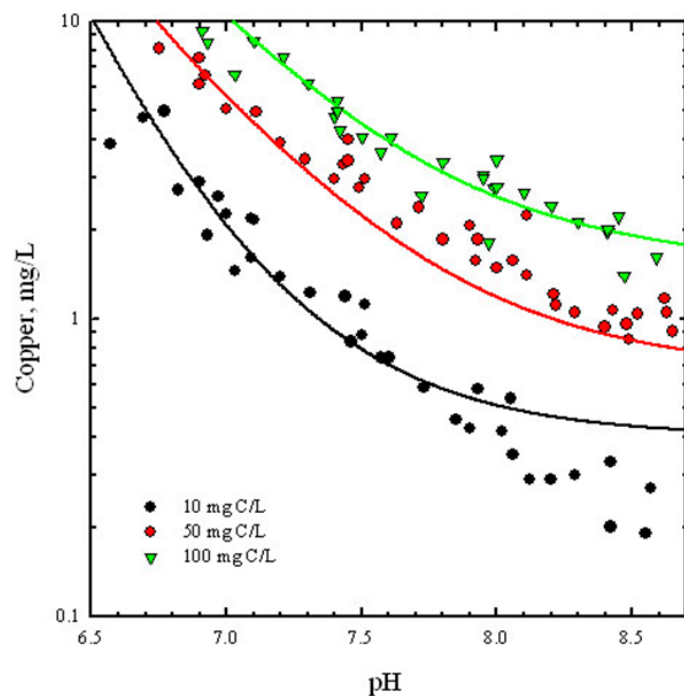


Sources of Lead Particles

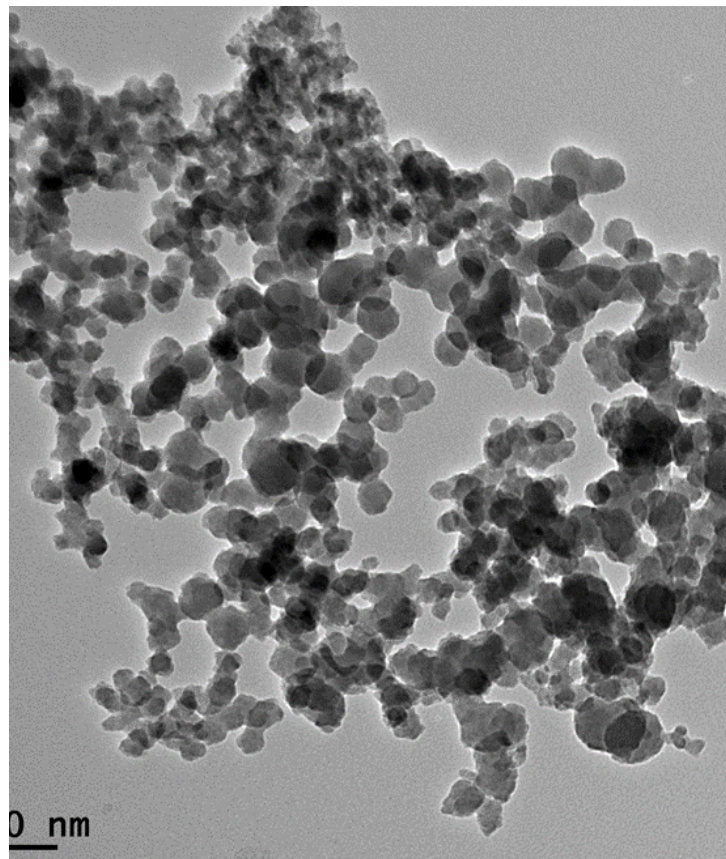
- Lead service line pipe scale
- Pipe scale associated with other lead sources- brasses and leaded solder
- Galvanized pipe- lead associated with iron corrosion by-products
- Other scale or sediment where lead may have sorbed or deposited
- Precipitated lead in bulk water



“Corrosion Control” Refers to Minimizing Metal Release from Distribution System Materials



Copper solubility



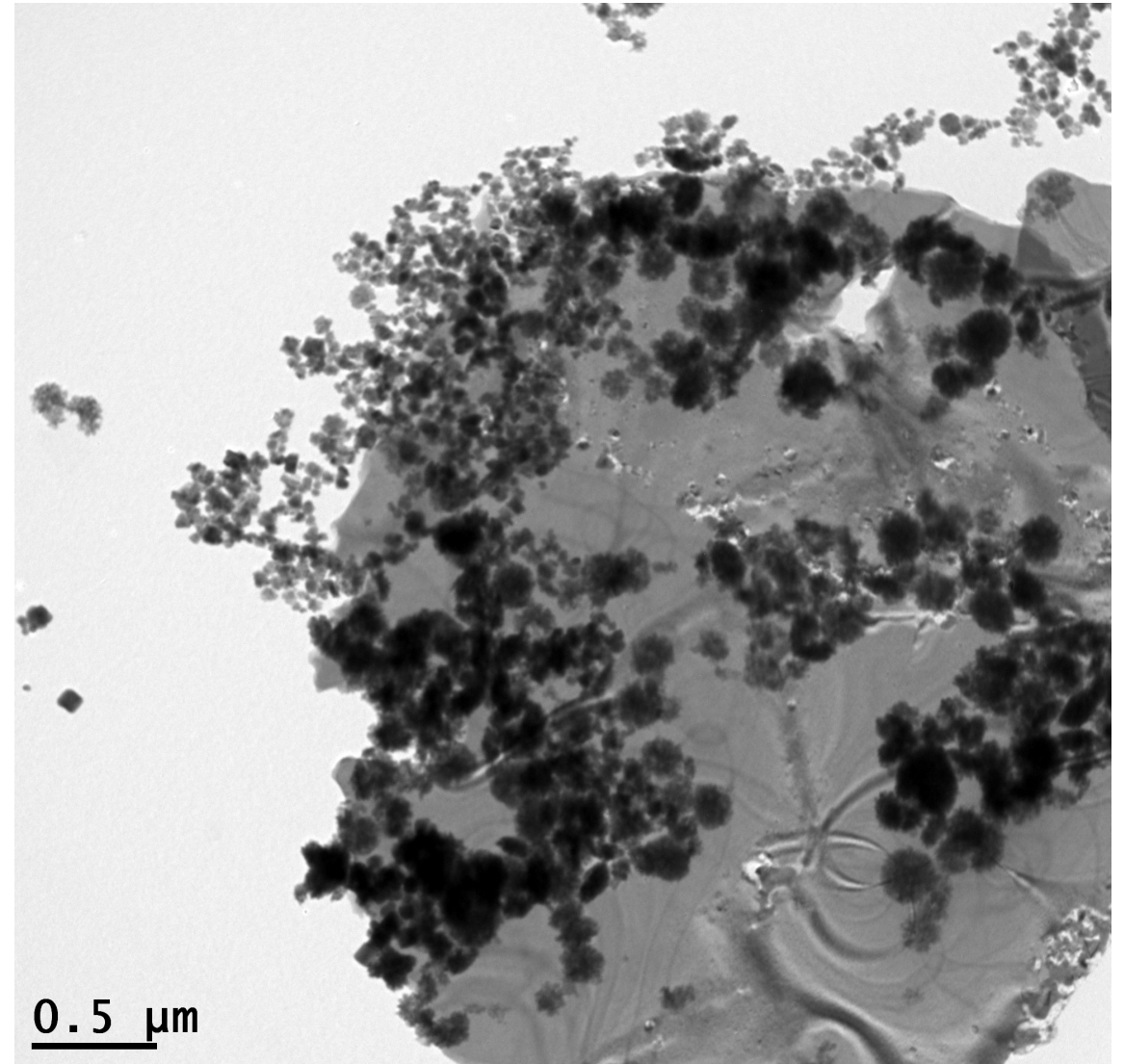
Lead particles

Metal release control involves:

- Corrosion control (galvanic, uniform, localized)- electron transfer
- Adjusting water quality to minimize the solubility of minerals on pipes
 - Orthophosphate addition to form Cu- and Pb-phosphate minerals
 - pH adjustment
- Pipe scale integrity
- Biofilm
- Stable water quality
- *Minimize particle release*

Particle Properties

- Size
- Shape or morphology
- Elemental make-up
- Mineralogy
- Charge
- Clustering





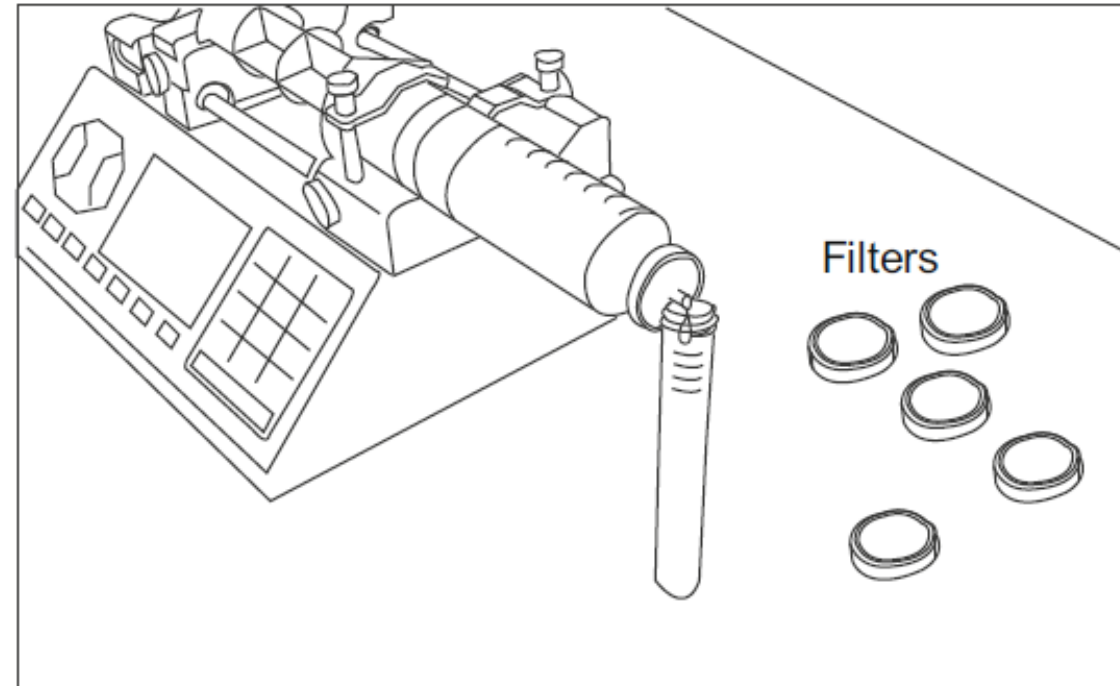
Particle Sample Preparation

- Ideally, prepare solids samples immediately after sampling to minimize artifacts
 - Mineralogical aging transformations
 - Particle agglomeration
 - Sorption losses



Defining the Particle Fraction

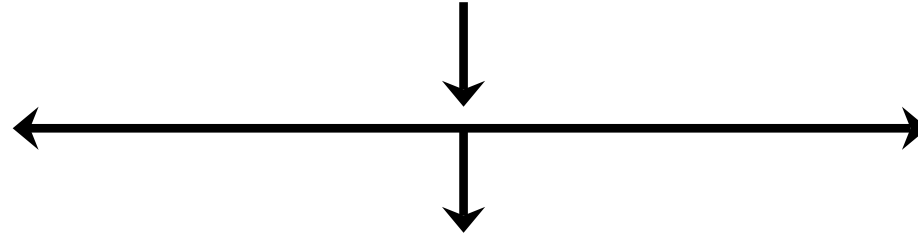
- Defined by the difference between a filtered Pb and the total lead analyses. Traditionally a 0.45 μm filtration has been considered the standard but much smaller particles can be present
- Others use smaller filter separations (0.1 or 0.2 μm filters, ultrafiltration)
- Filter material selection must be considered as some materials adsorb dissolved lead*. Recommended materials: **polypropylene and mixed cellulose esters**



*Minning, T., Lytle, D.A., Pham, M., and K. Kelty. Systematic Evaluation of Dissolved Lead Sorption Losses to Particulate Syringe Filter Materials. Environ. Monitor. Assess. 187(6):383. doi: 10.1007/s10661-015-4610-7 (2015).

Lead Speciation by Filtration

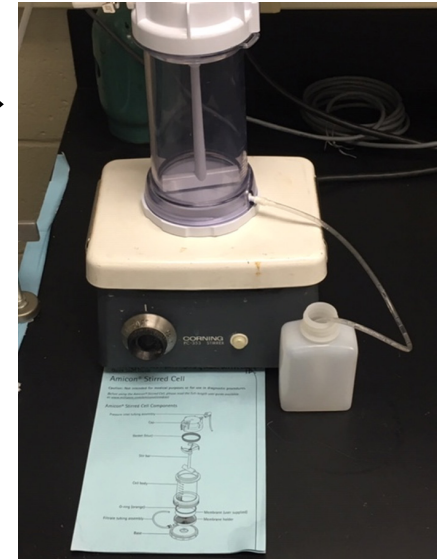
Size Separations Performed in the Field



No filter (total lead)



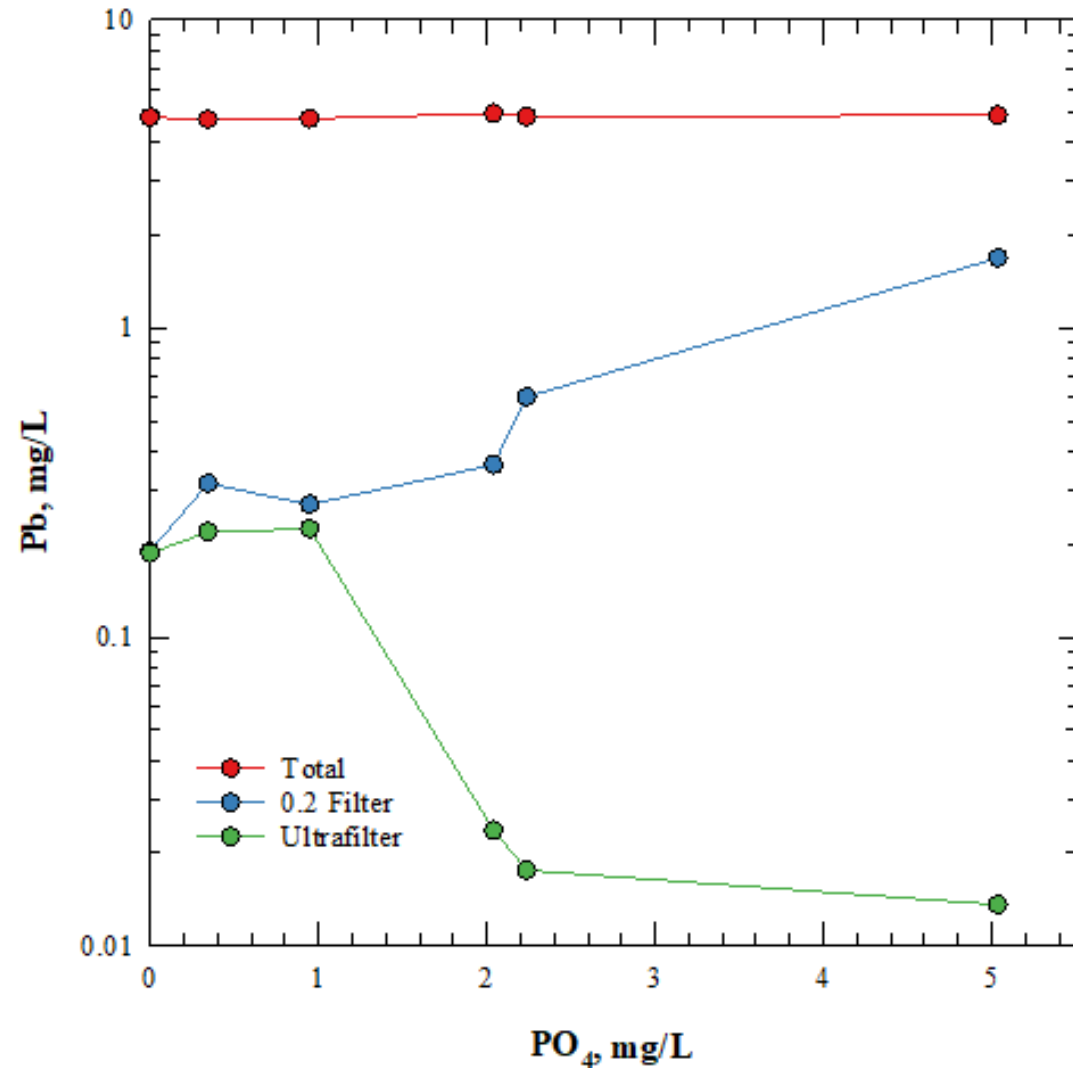
0.45 and 0.2 μm syringe filters



Ultrafiltration (lead passing the filter is defined as “soluble” lead)

Example: Particles pass 0.2 μm filter

Lead precipitation in presence
of orthophosphate (pH=8, 50
mg C/L DIC)

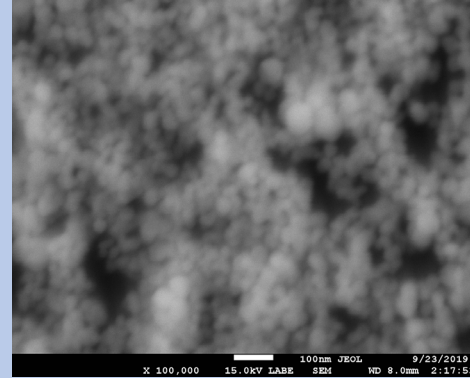
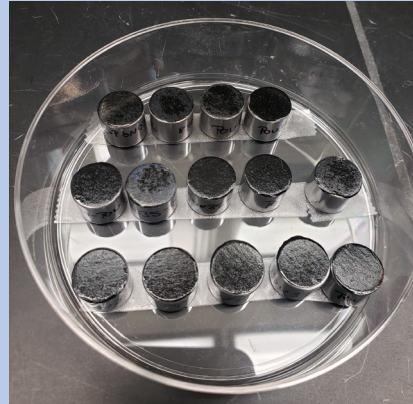


Size Measurements and the Methodology

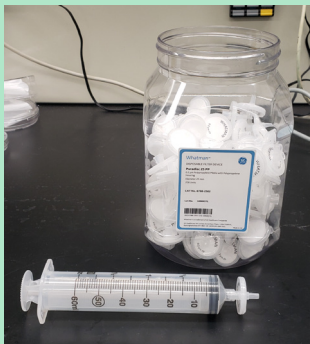
Results Differ by Method for Same Lead Particles



Zetasizer ZS90: **103 nm**



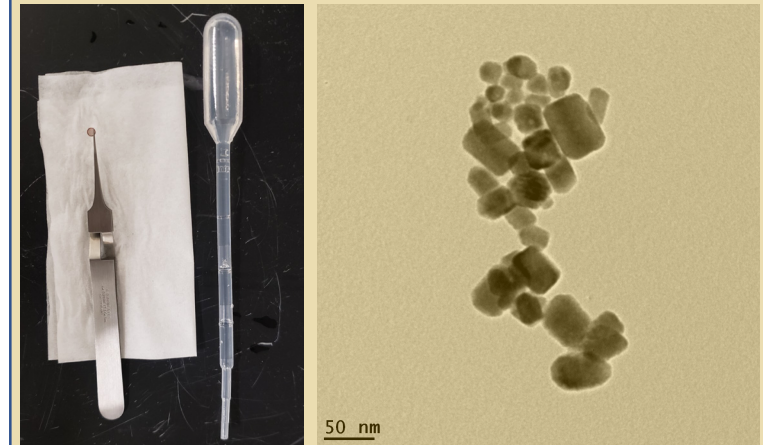
- Image quality was not high enough to get specific size measurements
- **Particles are observed well below 100 nm in diameter**



0.2 µm Syringe Filter

30 kDa Ultrafilter

- 97% of Pb passed through the 0.2 µm filter, but not the ultrafilter.
- **97% of particles are between 10 nm and 200 nm in diameter**



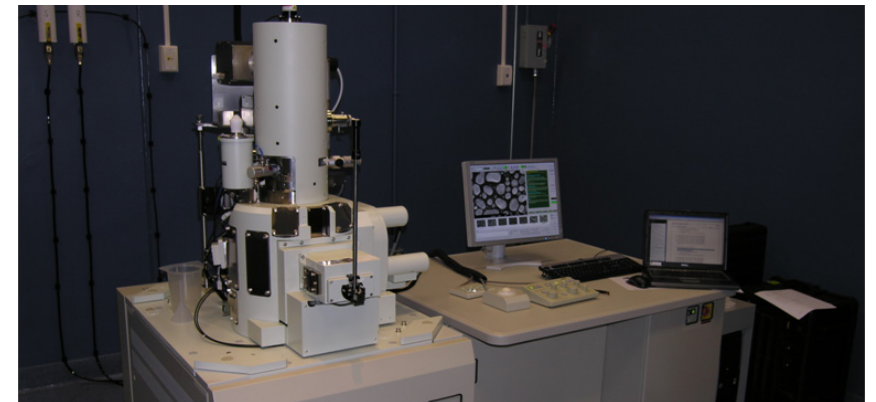
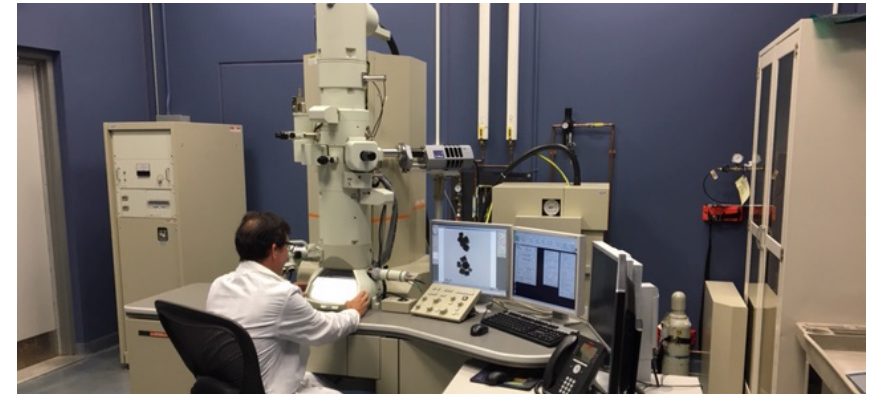
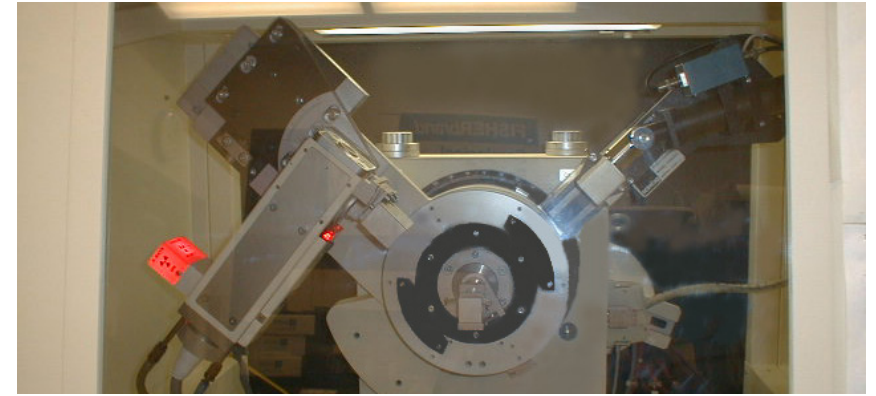
TEM: Average observed particle size: **32 nm**



X'Pert Pro X-ray diffractometer: **16 nm**

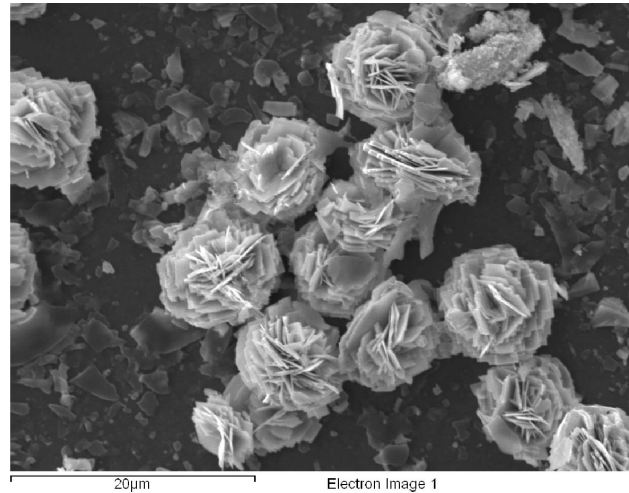
Other Important Solids Analysis Tools

- EPA ORD Advanced Materials Solids Analysis Research Core (AMSARC)
- Examine particles trapped on ultrafilters
- *Scanning Electron Microscopy (SEM)*: size ($> 1\ \mu\text{m}$), shape, feature
- Transmission Electron Microscope (TEM): size ($< 1\ \mu\text{m}$), shape, feature
- *Energy Dispersive Spectroscopy (EDS)*: elemental composition
- *X-ray diffraction (XRD)*: crystalline mineral phase identification
- Electrophoretic mobility (EPM): suspended particles

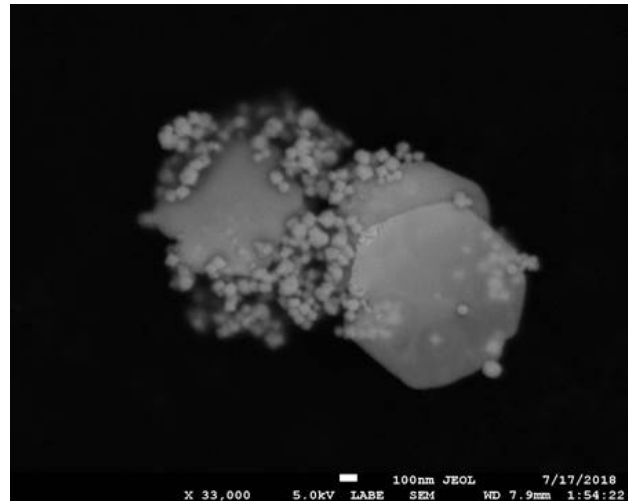
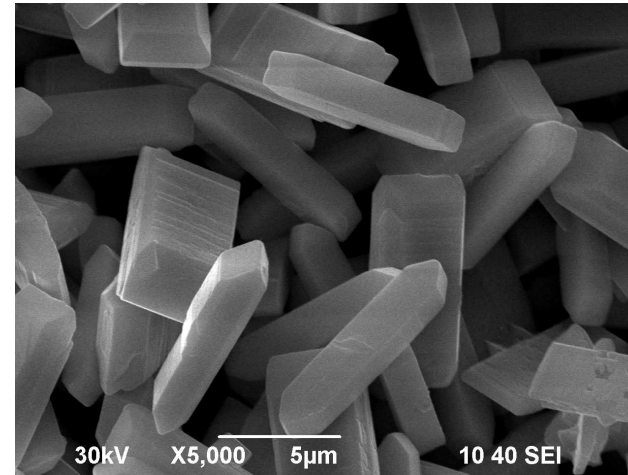


Lead Mineral Particles Come in Different Shapes and Sizes

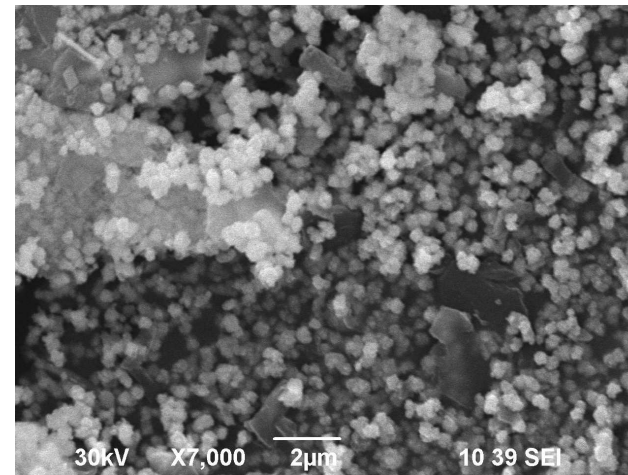
Pb-pyrophosphate



Anglesite, PbSO_4



Pb-orthophosphate and carbonate



Pb(IV)-oxide, PbO_2

Lead Particle Release Mechanisms

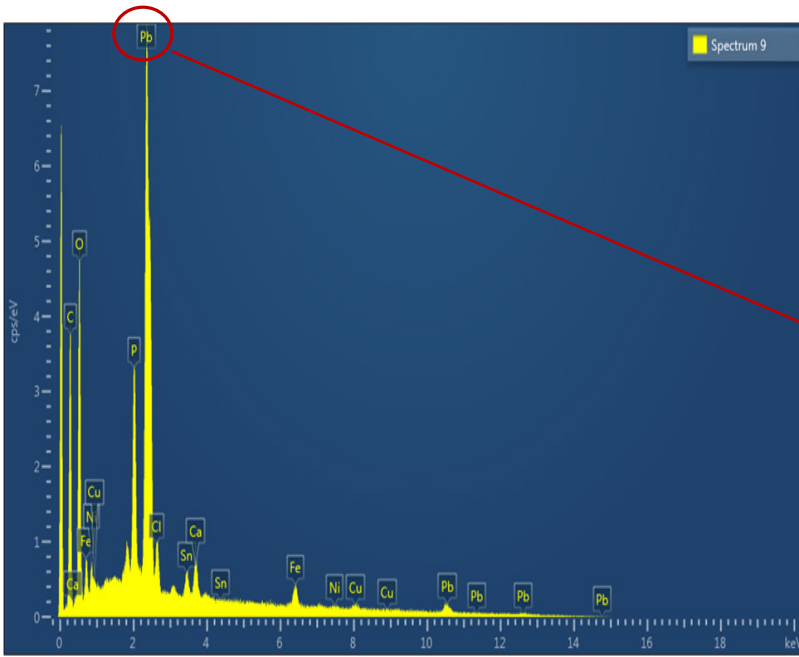
Physical release

- Water flow changes (direction, velocity)
- Vibrations resulting from construction or other physical disturbances
- Water hammer

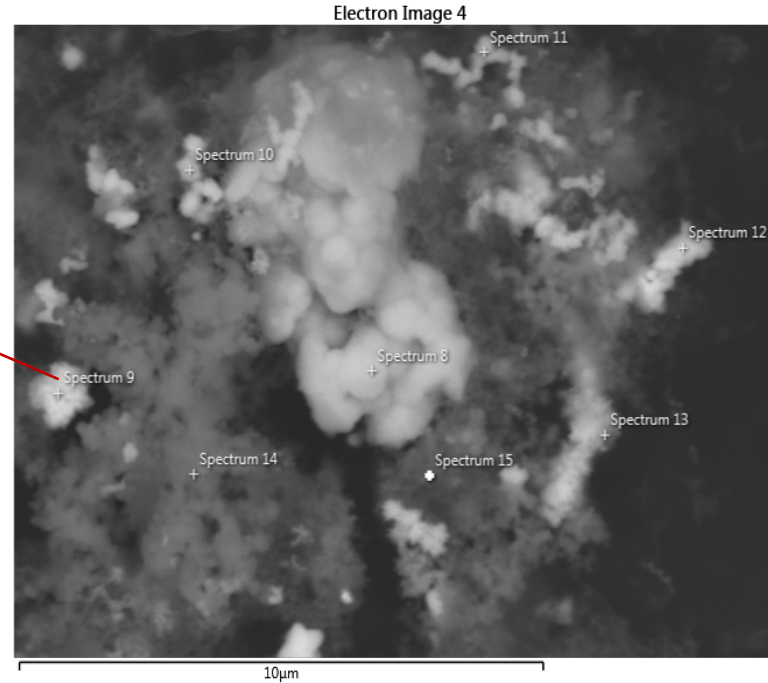
Chemically or biologically induced release

- Direct water quality changes dissolve scale components that hold scale together
- Biologically-associated local water quality changes
- Changes in scale incorporated particle properties (e.g., EPM)
- Local corrosion related chemistry changes
- Biofilm sloughing
- Long stagnation

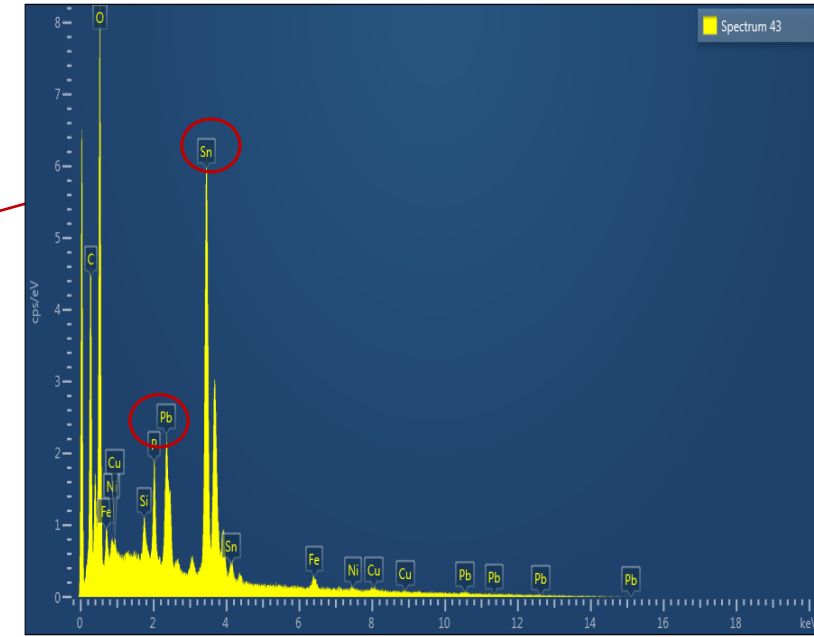
Lead, phosphate, chlorine and calcium



Mass of mixed solids of different sizes and structure



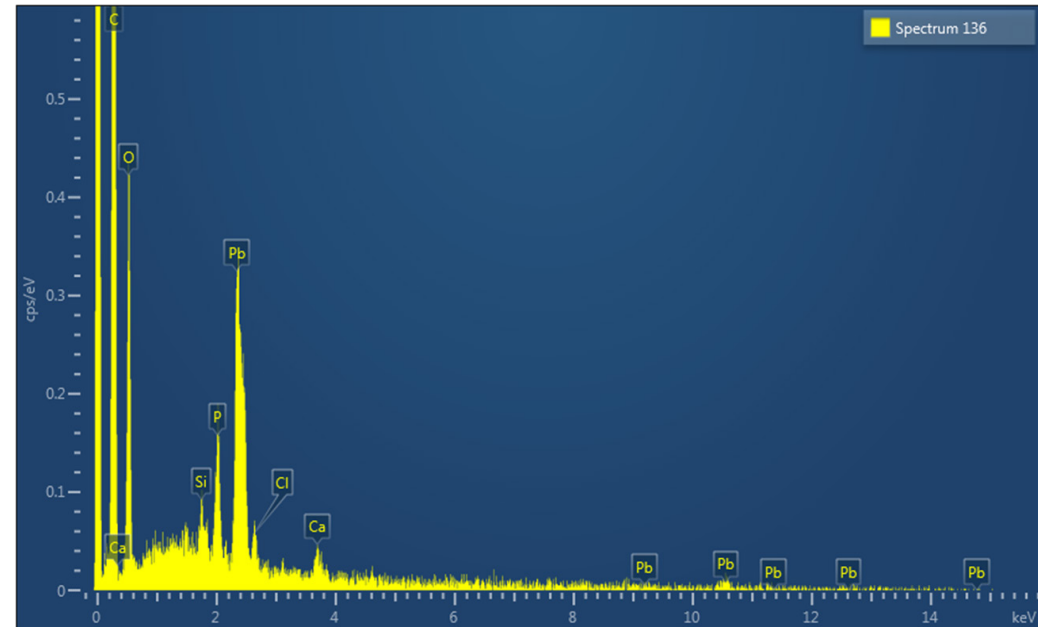
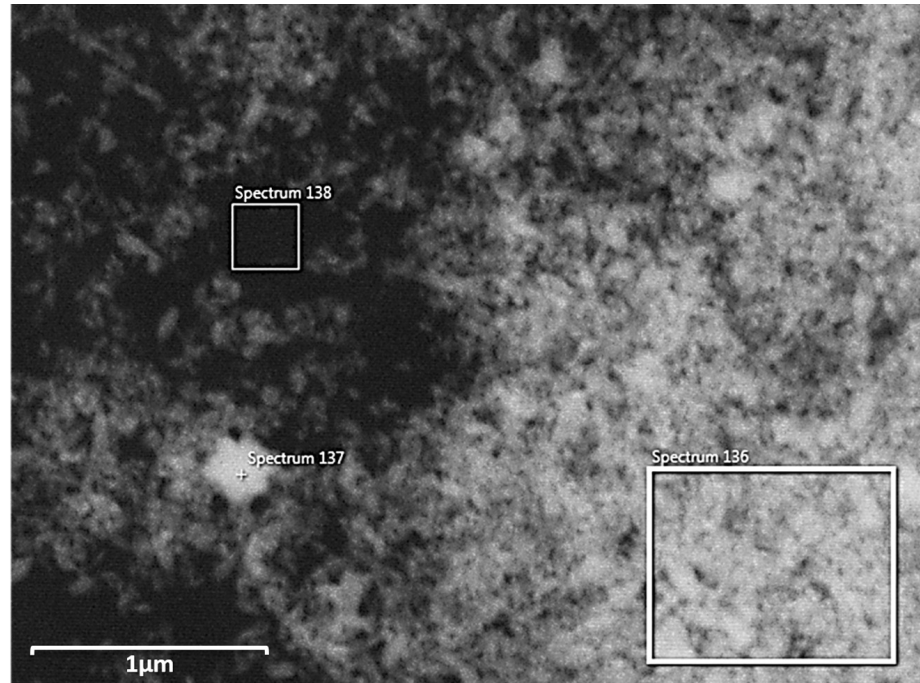
Tin, lead, phosphorus, calcium, chlorine, iron



Particle Analyses and the Source of Lead: Case 1

- Particles removed from lead contaminated drinking water
- Pb-Cl-Ca-P particles present with tin-, iron- and calcium-rich particles
- Observation suggests that lead:tin solder is likely an important lead source
- Observations also suggest that pipe scale may be breaking down and/or sloughing off
- Pipe scale analysis will help with assessment

Particle Analyses and the Source of Lead: Case 2



- Particles removed from lead contaminated drinking water
- Pb-Cl-Ca-P particles present without coexisting particles
- Observation suggests that lead particles were formed near the pipe scale:water interface or in bulk water
- Pipe scale analysis will help with assessment

Conclusions

- Particles can be an important form of lead in drinking water
- Presence of particles indicates ineffective “corrosion control”
- Sample preparation is important and several tools for particle characterization are available
- Particle size determination varies with method used
- Examination of particles can help identify the source of lead issues and inform on a solution



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Thank-you

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