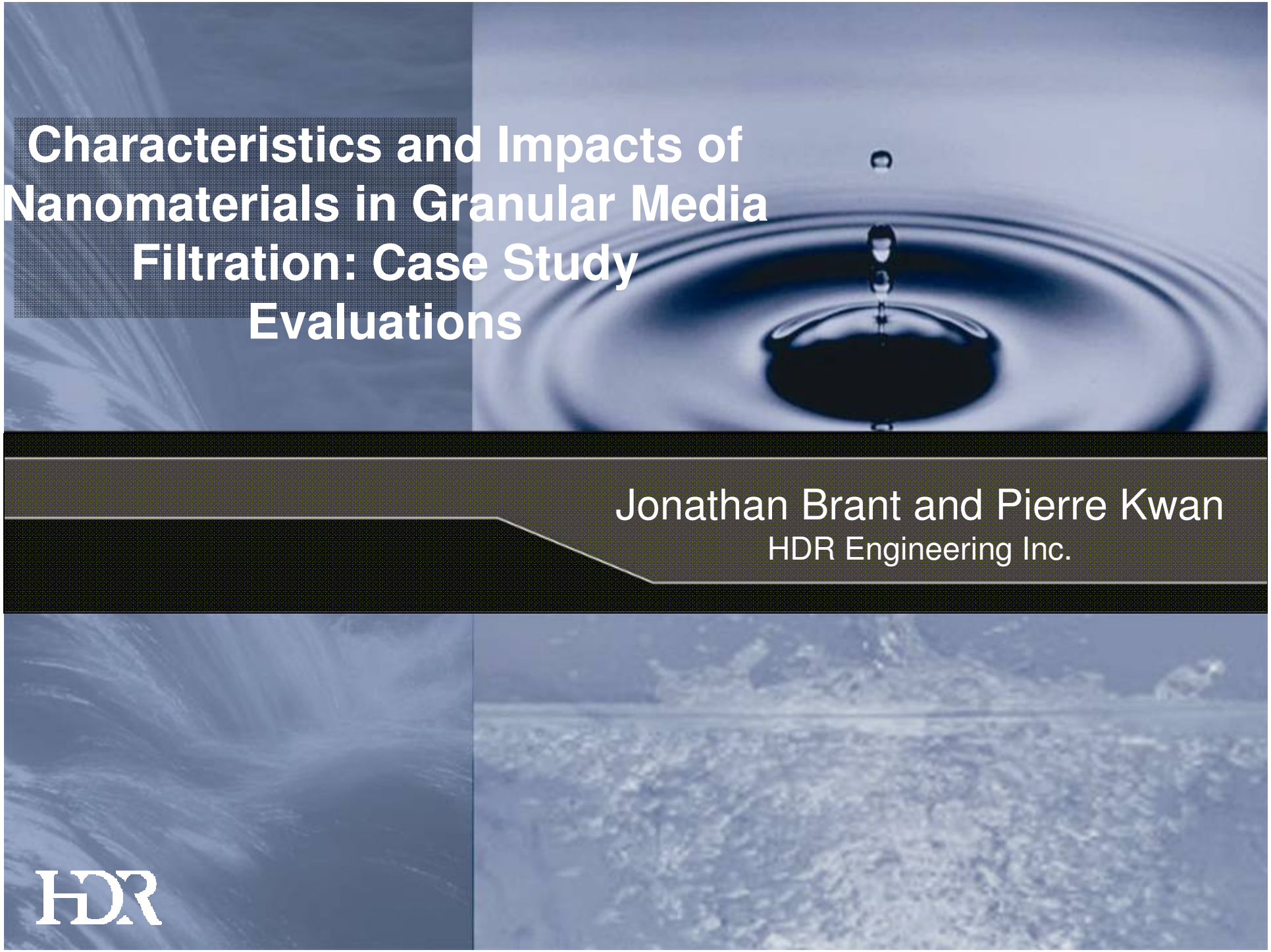

Characteristics and Impacts of Nanomaterials in Granular Media Filtration: Case Study Evaluations

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HDR Engineering Inc.

Presentation Outline

- **Background**
  - Granular media filtration
  - Colloids and nanoparticles
- **Current results and understanding**
  - Filtrate composition
  - Origins
- **Summary and conclusions**
- **Questions**

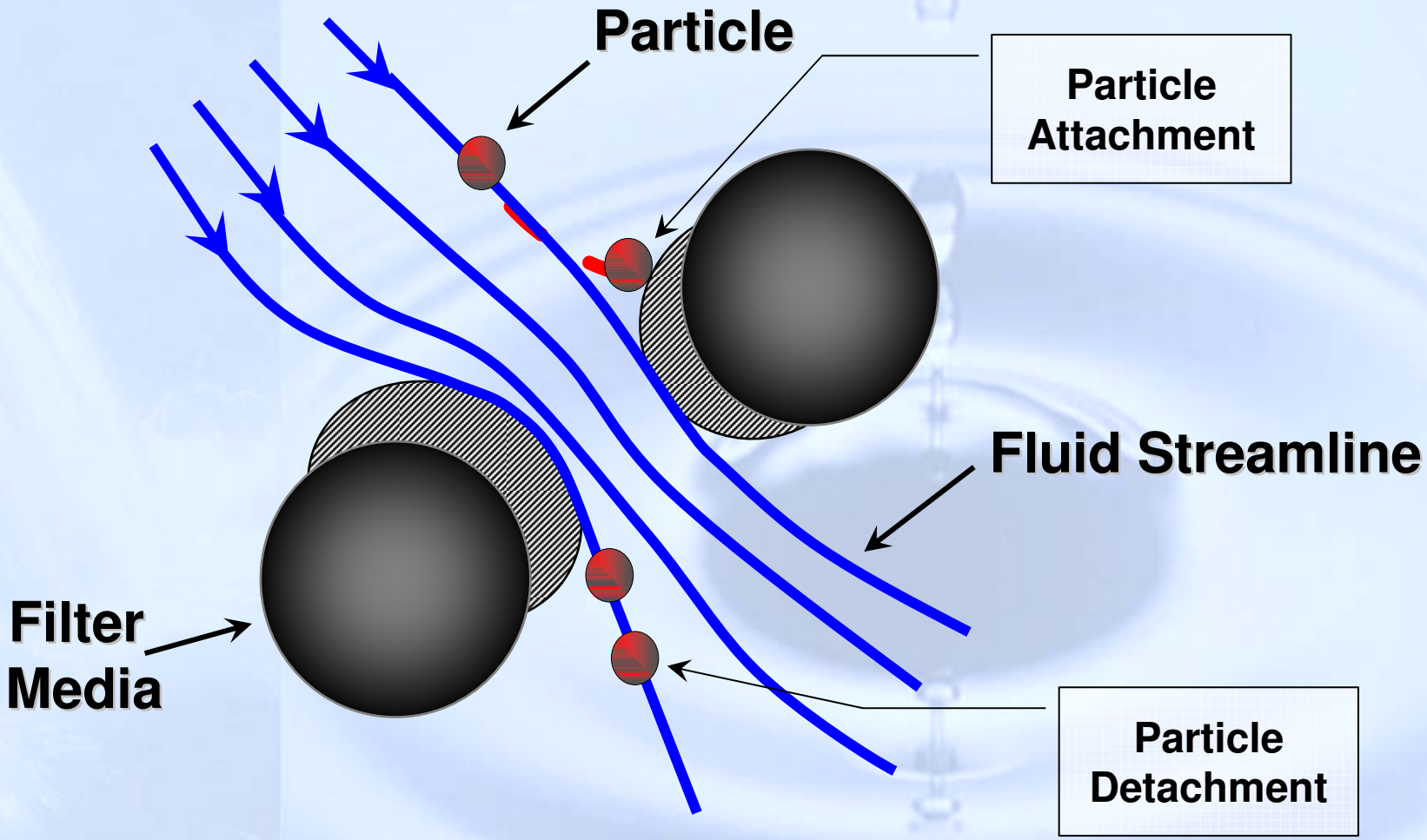
Granular Media Filtration

- **Introduced in 1807, granular media filtration remains one of the most highly used processes for potable water treatment**
- **Little data exists on occurrence of ultrafine (*d* < 450 nm) particles in filter influent / effluent**
  - Interpretation of turbidity / particle count data
  - Increasing focus on “nanoparticles”
- **Particle impacts on down-stream processes**
  - Silica fouling of membranes
  - Disinfection efficiency
  - Vectors for contaminant transport

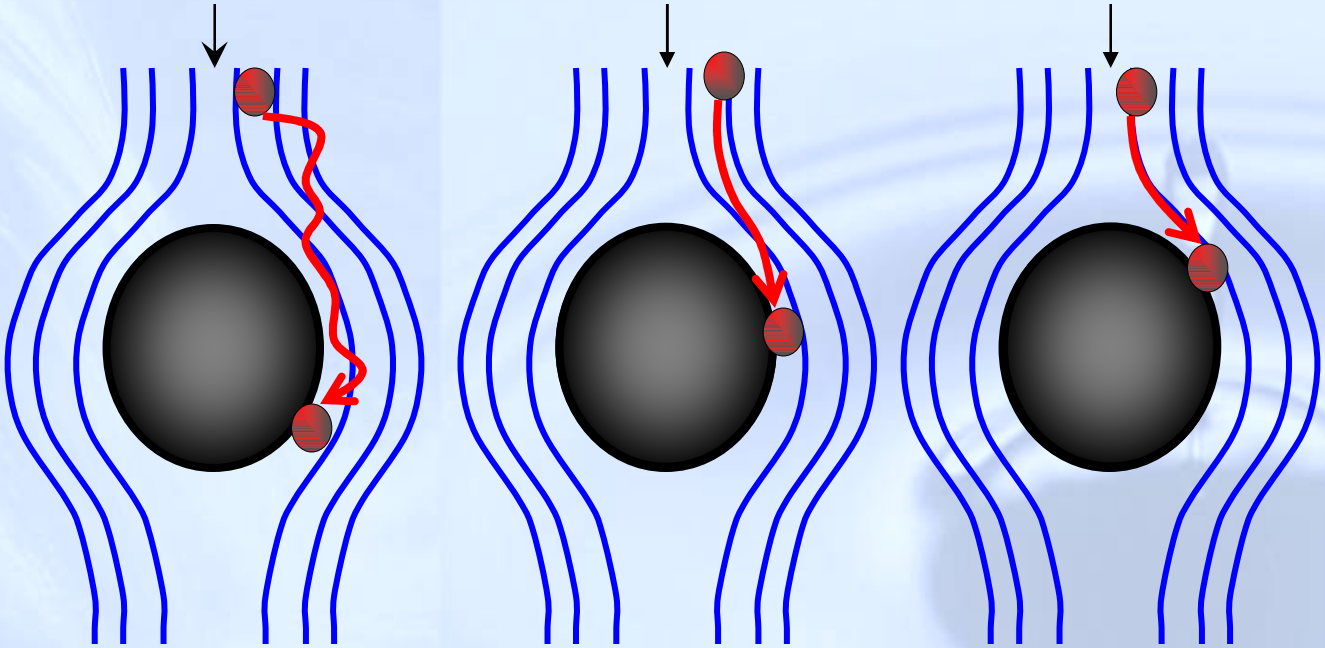
Colloids and Nanoparticles

- **Nanoparticles = colloids**
  - At least one dimension between 0.1 and 100 nm
  - High surface area / mass ratio
  - Highly surface reactive
- **Naturally occurring nanoparticles**
  - Minerals/metals
  - Biopolymers
  - Organic acids/bases from degradation of bio-materials
- **Engineered nanoparticles**
  - Carbon nanotubes
  - Quantum dots

Filtration Mechanisms



Trajectory Theory



Diffusion

$d_p < 1\ \mu m$

Gravity

$d_p > 1\ \mu m$

Interception

$d_p > 1\ \mu m$

Viruses

0.01 -0.025 µm

Bacteria

0.2 - 1 µm

Cryptosporidium

3 - 5 µm

Giardia

6 - 10 µm

Motivating Questions

- **What is the composition and size distribution of particles in the effluents from conventional filters?**
  - Focus on colloidal/ nano-scale particles (ultrafine particles)
  - What is the relative importance of the ultrafine fraction to the total particle load?
- **Are there differences in ultrafine particle composition before and after filtration?**
- **How does pretreatment and filter operation affect the characteristics of filtrate particles?**
- **Do conventional measurements of turbidity and particle concentrations track changes in ultrafine particle concentrations?**

Case Study Participants

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Plant Overviews

Municipality	Raw Water Source	Pretreatment	Filter Design
Milwaukee Water Works	Lake Michigan	Pre-ozonation Alum + Polymer aid	Anthracite / Sand
Southern Nevada Water Authority	Lake Mead	Pre-ozonation Ferric	Anthracite / Sand / Garnet
Johnson County Water District No. 1	Missouri/Kansas Rivers + Groundwater	Lime softening Ferrous chloride + Alum	Anthracite / Sand
City of Salem	Santiam River	Alum	Slow sand filter Sand / Gravel Support

Plant Overviews

Municipality	Raw Water Source	Pretreatment	Filter Design
Buffalo Pound Water Administration	Buffalo Pound Reservoir	Pre-chlorination Alum	Anthracite / Sand
City of Cincinnati Dept. Water Works	Ohio River	Alum, PAC, ferric sulfate, polymer aid	Rapid Sand Filtration Torpedo sand / filter sand
City of Houston	Trinity River	Alum	Anthracite
Modesto Irrigation District	Modesto Reservoir	Pre-ozonation Alum, polymer aid	Anthracite
Northern Kentucky Water District	Ohio River	Pre-oxidation ($KMnO_4$) Ferric, PAC, polymer aid	Anthracite / Sand

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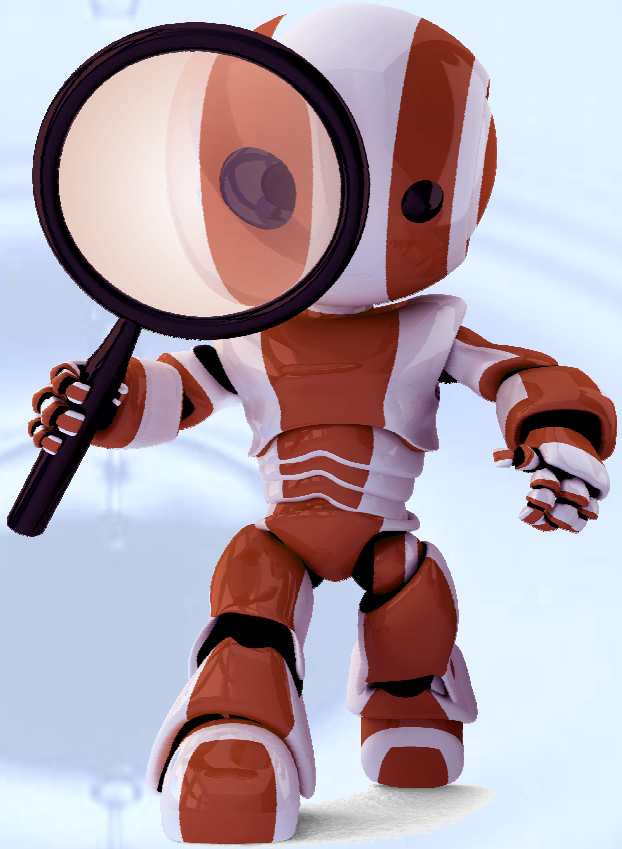
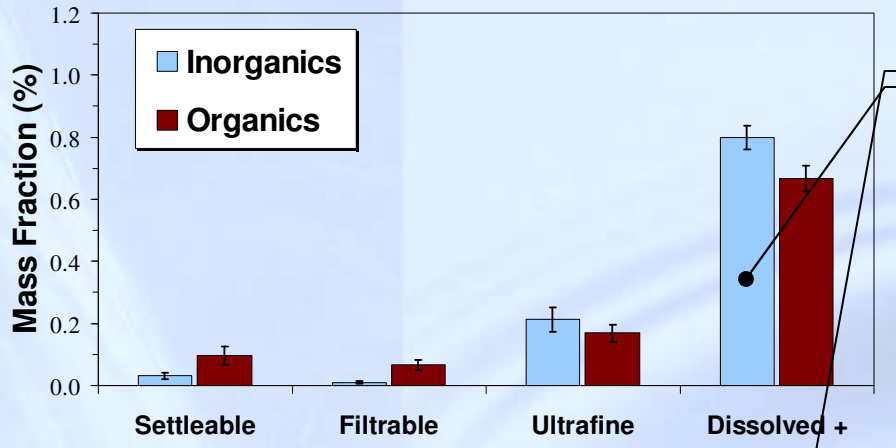
Sample Analysis

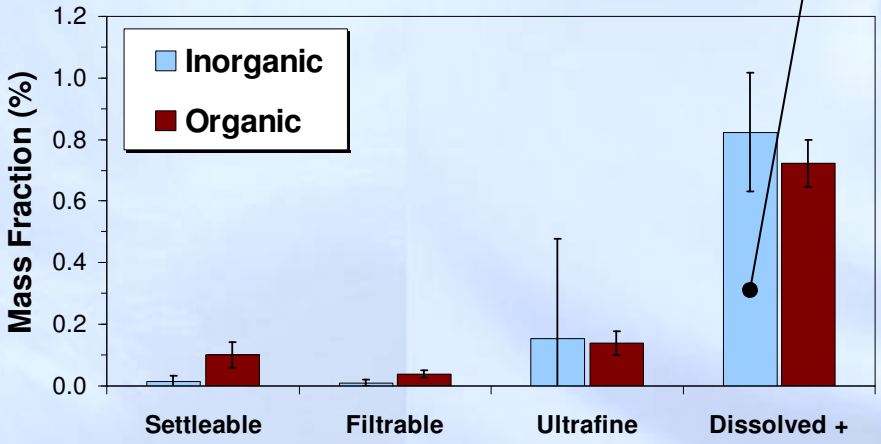
- **Samples collected during 3 stages of a filter run**
  - Ripening
  - Stable operation
  - Just prior to backwash
- **Four particle size fractions**
  - Settleable $d \geq 260\ \mu m$
  - Filtrable $450\ nm \leq d \leq 260\ \mu m$
  - Ultrafine $30\ nm \leq d \leq 450\ nm$
  - Dissolved + nano $d \leq 30\ nm$

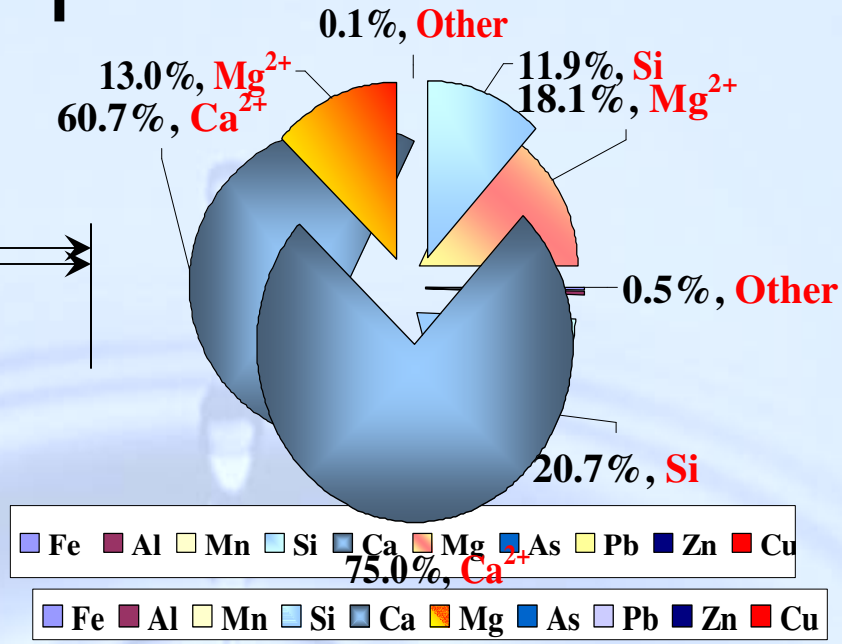


Results and Discussion

Filtrate Composition





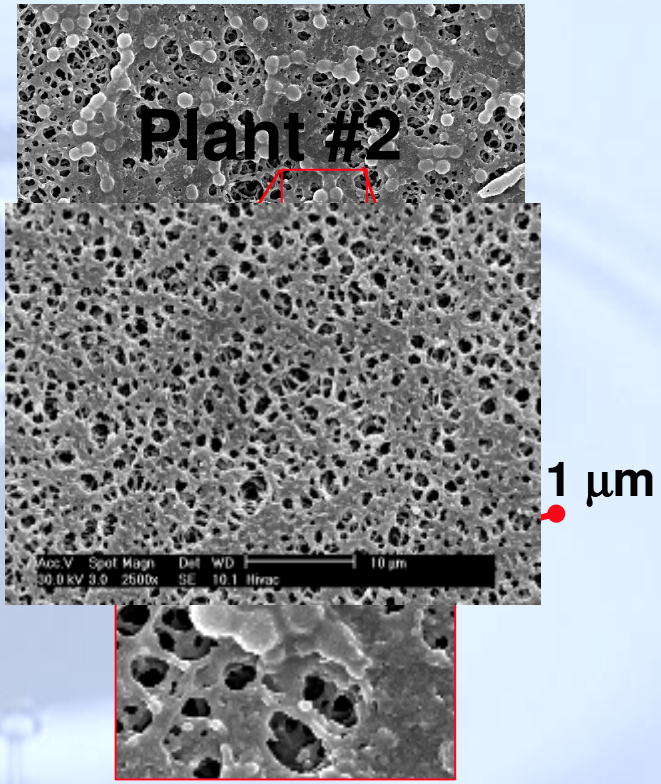


- **Influent**
  - Inorganic = 50 mg/L
  - Organic = 2.9 mg/L
- **Effluent**
  - Inorganic = 47.5 mg/L
  - Organic = 1.9 mg/L

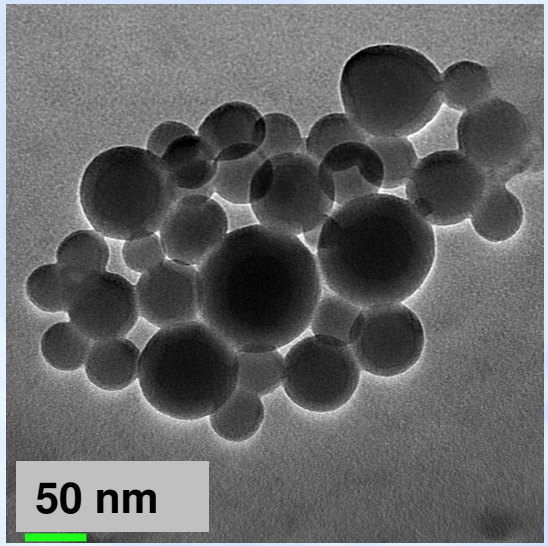
SEM Imagery of Effluent Materials

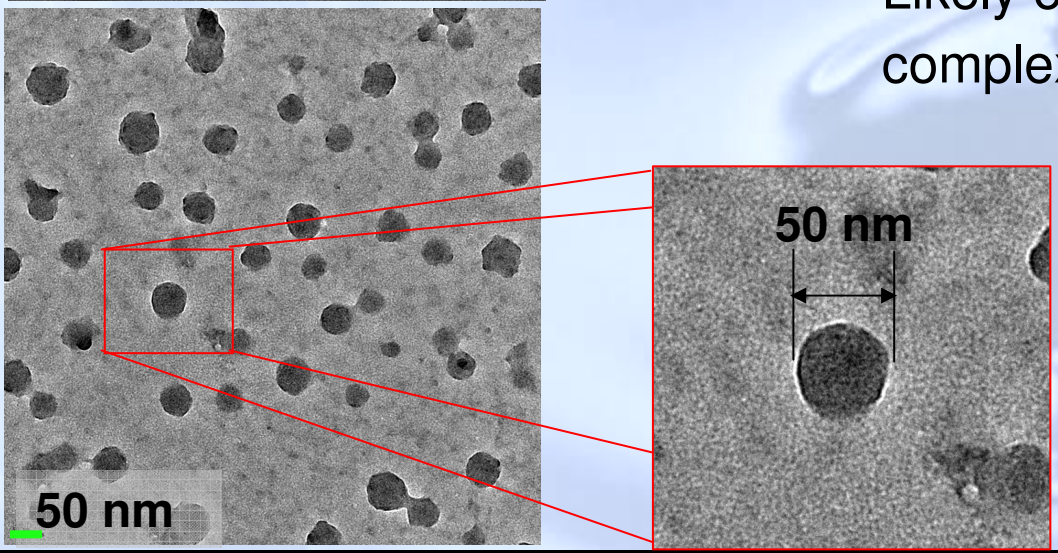
- **Variable effluent quality between plants**
- **Plant #1**
  - Cake-like residue deposited on filter pad
    - 7% effluent particles d > 0.45 µm
  - Spherical particles embedded in filter matrix
  - EDX analysis of particles: 25% Al; 10% Fe; 55% Si; some Na, Ca, and Mn
- **Plant #2**
  - Filtered effluent resulted in little detectable residue
    - 3% effluent particles d > 0.45 µm

Plant #1



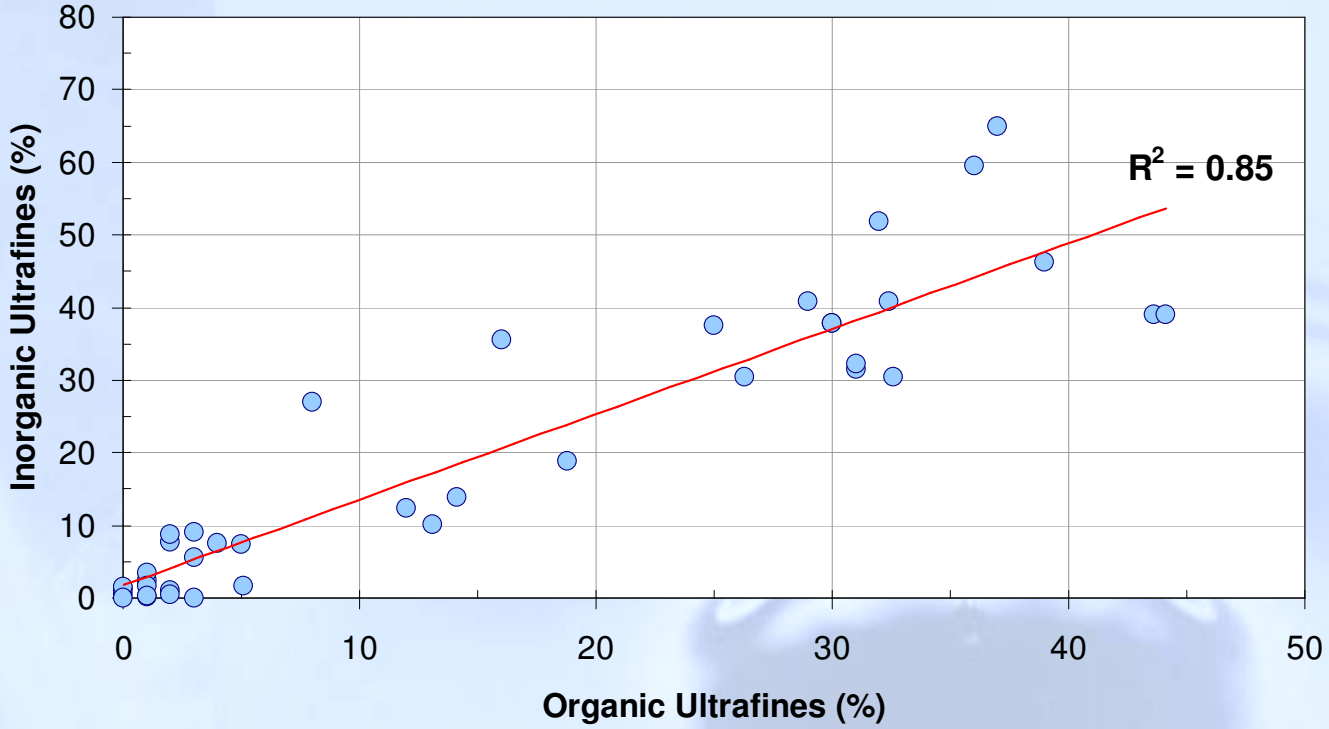
Effluent Nanoparticles





- **Nanoparticles (d < 100 nm) found in 100% of filtrate samples**
  - Variable structure and geometry
- **Unknown composition**
  - Likely organic/inorganic complexes

Organic - Inorganic Complexation

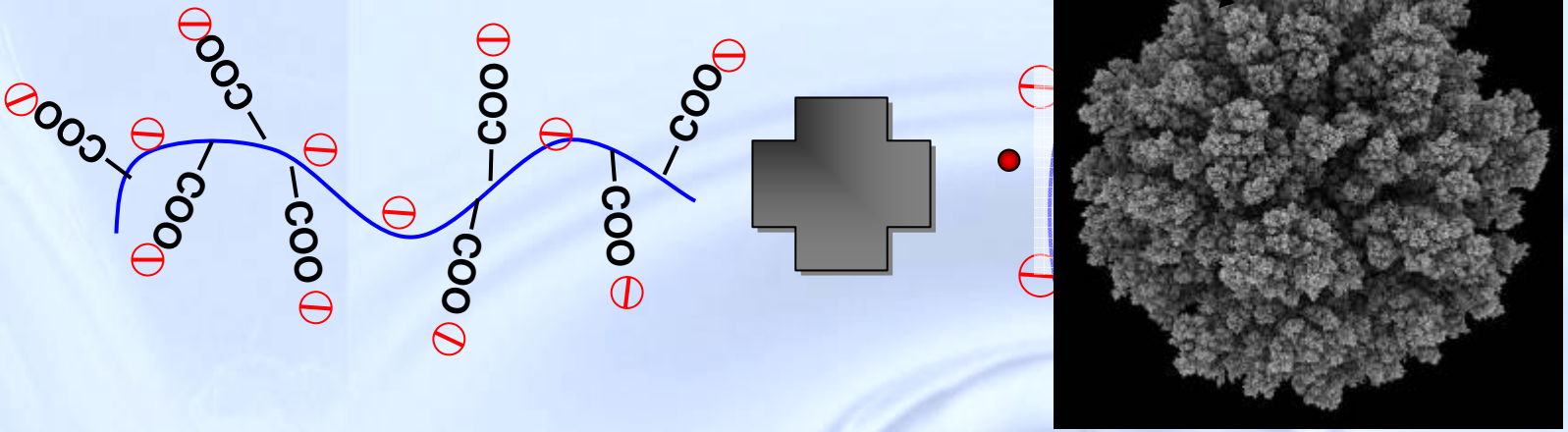


- **Ultrafines may originate from complexation between organic and inorganic materials**
- **Principle inorganics of concern:**
  - Residual coagulants (Fe, Al)
  - Calcium and magnesium

Formation of Ultrafines

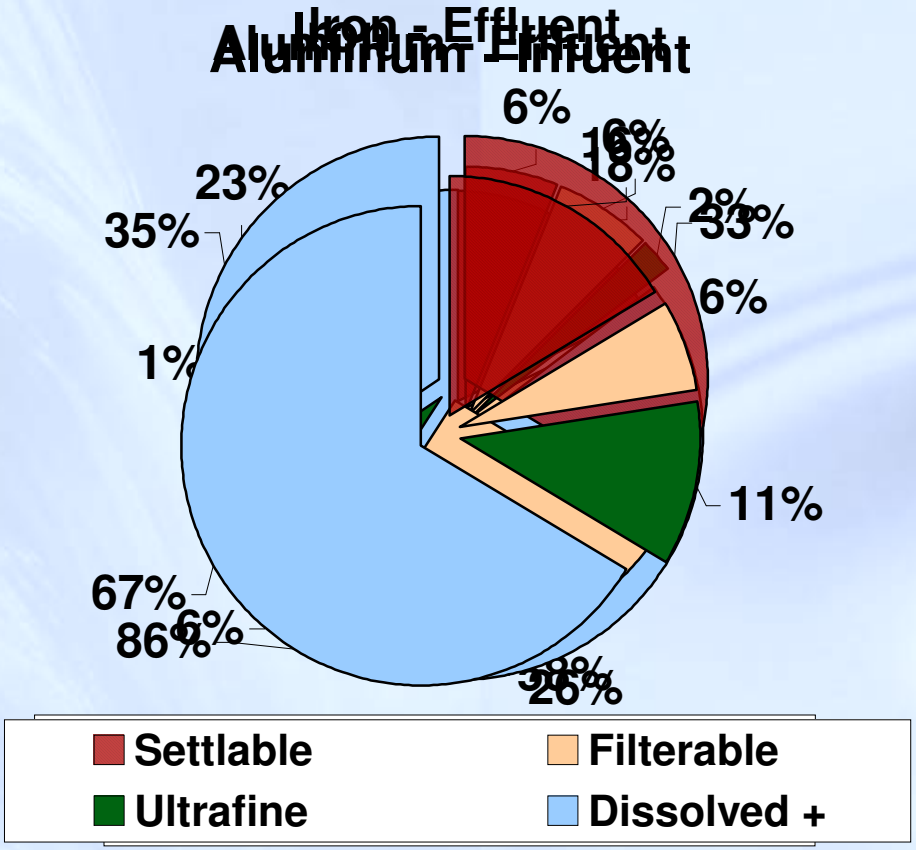
Organic Matter

Molecular Restructuring



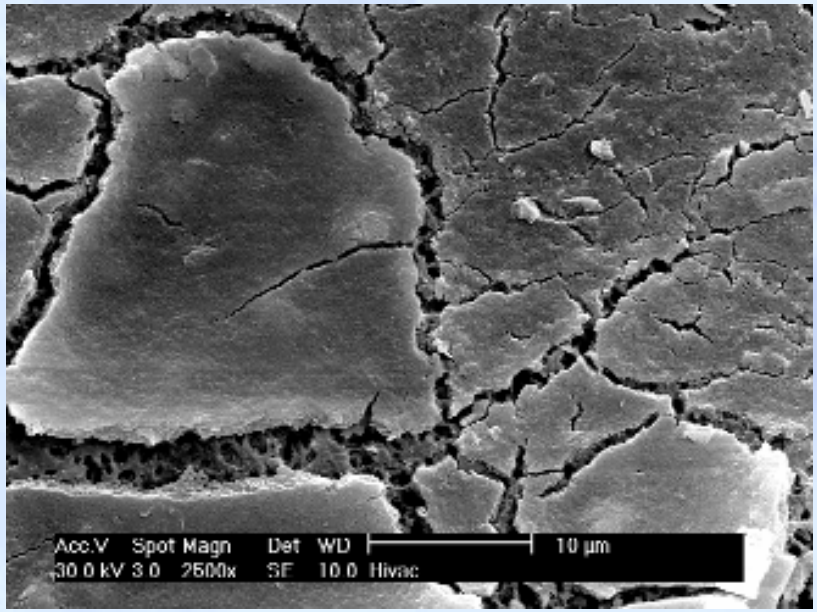
Organic matter and multivalent salts and metals can form ultrafine and nanoparticles before, during and / or after filtration!

Residual Coagulants



- **Shift from larger to smaller size fractions across the filters**
- **Reformation of larger particles may be occurring**

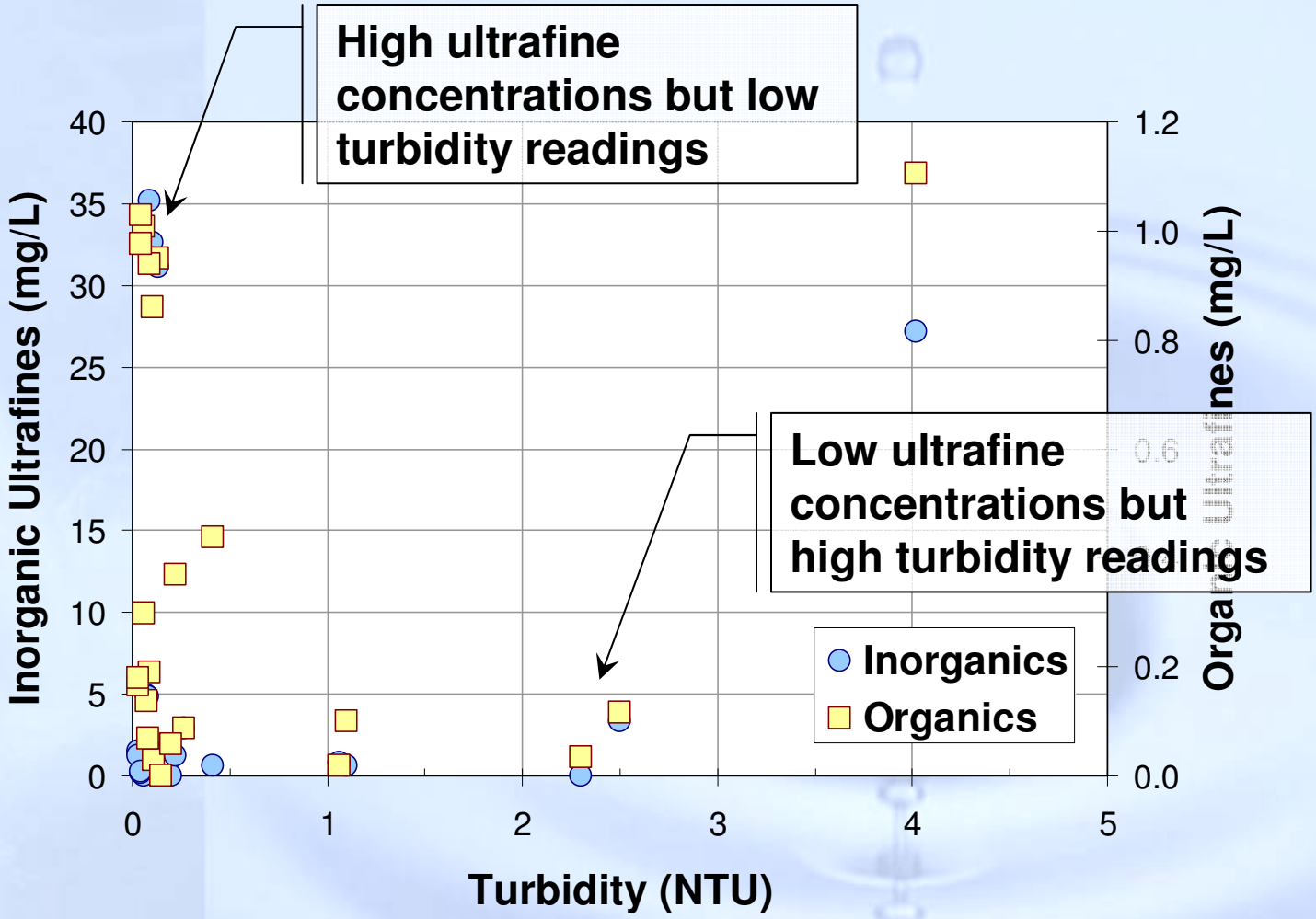
SEM Imagery of Influent Material



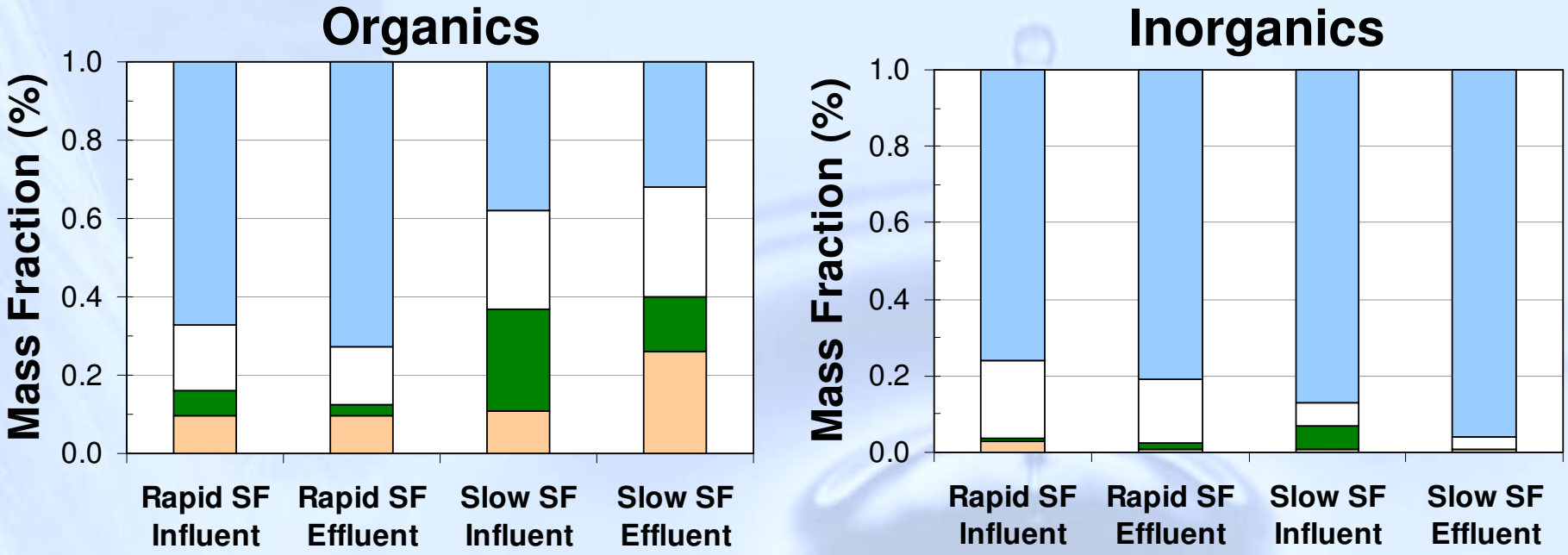
Plant #1
Plant #2

- **Plant #1**
  - Cake-like residue on 0.45 µm filter
  - EDAX analysis: **35% Al; 10% Fe; 50% Si**
- **Plant #2**
  - Cake-like residue on 0.45 µm filter
  - EDX analysis: **94% Al; 4% Ca; 2% Fe**

Turbidity and Ultrafines



Filtration Rate



- **Higher amounts of organics in larger size fractions for slow sand filters**
  - Detachment of bio-materials
- **Inorganics mostly present in ultrafine and dissolved + size fractions for slow and rapid sand filters**

Filtrate Characterization Summary

- **Bulk (70%) of material mass present in dissolved + nano size fraction**
  - Mostly calcium, magnesium, silica and organics
  - Residual coagulant (Fe and Al) present in significant quantities (influent and effluent)
  - Variable composition for different plant conditions
- **Nanoparticles and nanomaterials prevalent in all filter effluent samples**
- **There is a shift from "dissolved"/nano- to ultrafine-scale nanoparticles during filtration**
  - Generation of ultrafine organic / inorganic complexes across filter
- **The composition of the ultrafine fraction may change across filter**

Acknowledgements

Participating Utilities

- City of Cincinnati, Department of Water Works, OH
- Buffalo Pound Water Administration Board, Canada
- Southern Nevada Water Authority, NV
- Johnson County Water District, KS
- Northern Kentucky Water District, KY
- Modesto District Irrigation , CA
- Milwaukee Water Works, WI
- Salem Public Water Works Department, OR
- City of Houston, East Water Plant, TX

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Thank you.

Any Questions?