TiO₂ and Ag Nanoparticles in a River Environment

Transformation in the organism and in the environment:
What do we measure and how do we develop testing strategies to measure impacts of transformed particles in the environment

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Understand the transformation of nanomaterials under different environmental conditions

- Titania and Silver nanoparticles in a simulated river/sediment system
  - Columbia River water (TSS=7 mg/L; pH=7.65; hardness=77 mg/L as CaCO₃)
  - Sand sediments

- Titania and Silver citrate in static cells and flow through river mesocosms
  - Microbial community changes (static only)
  - Uptake by clams and amphipods
  - Deposition on sediments
  - Aggregation in flowing water
Silver Citrate Materials

30 – 200 nm for spheres

80 – 400 nm x 30 – 50 nm for rods
Microbial Community Silver Exposures

Static Exposure Study
- Homogenized sediment from surface water mesocosm
- Exposures (1, 4 and 14 d):
  - Doses in CRW (detection limit 3 ng/L):
    1 ug/g Ag nano
    4 ug/g Ag+
- Controls

- Shift in dominant microbial species at 14 days
- Ag nano had greater community shift than Ag+

![Graph showing exposure times and Ag concentrations](image)
Silver Mesocosm Exposure

24 hr exposure, 24 hr depuration
- Columbia River water (CRW)
- Clams
- Amphipods
- Microbial community in sand sediments

Control, 1 µg/L, 10 µg/L, 50 µg/L
Ag particle size in CRW

- Low concentrations of dosed Ag nanoparticles fractionated to larger particle sizes

- Degree of fractionation occurs over 24 hours

- Prior studies show dissolved fractions at doses > 100 ug/L
Accumulation of Silver

Clams (tissue + shell)

Amphipods

Sediment

CRW

Total Ag in ug/L
Titanium Oxide Materials

5-30 nm anatase

<75 nm rutile/anatase
Titania Mesocosm Exposures

-5 mg/L over 12 hour flow-through
-36 hr flow-through depuration
Titania exposures

<table>
<thead>
<tr>
<th>Variable</th>
<th>TiO$_2$ (mg/g dry weight)</th>
<th>% total dose (5 mg/L)</th>
<th>Clam : Amphipod uptake ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Flow - Through Static*</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>A/R</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>amphipods</td>
<td>47.9</td>
<td>64.8</td>
<td>2.1</td>
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<tr>
<td>clams</td>
<td>0.55</td>
<td>1.04</td>
<td>0.03</td>
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<tr>
<td>sediment</td>
<td>66%</td>
<td>13%</td>
<td>34%</td>
</tr>
</tbody>
</table>

Clam : Amphipod uptake ratio ~1:70
Mean equivalent diameter*

- Distilled Water – 30 nm
- CRW – 200 nm
Two Materials – One Exposure Scenario
Abiotic and Ecosystem-Wide Effects

- NP size affected by environmental characteristics

- Specific properties of NP material may affect bioaccumulation and downstream ecosystem impacts
  - Silver uptake higher in clams; stays in water column
  - Titania uptake higher in amphipods; settling out greater

- Acute toxicity not observed in Columbia River water
Research Gaps Remain

- NP toxicity/effect may be different in a complex environmental setting compared with single variable/static lab exposures.

- Chronic (long-term) studies under complex environmental conditions need to be matched with ability to measure and characterize NPs in complex environmental samples:
  - absorption, distribution, metabolism, excretion
  - recycled NPs
  - route(s) of exposure – absorption, dietary
Case Study

Seeing changes that reflect ecosystem scale disturbance
- Birds, fish dead
- Deformed frogs
- Selective flora die-offs

Relevance of materials in complex matrix
- New paradigm vs. a standard tier-testing approach?
- Choice of organisms for toxicity endpoints
- Transformation of materials in complex media
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