

# TiO<sub>2</sub> 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*

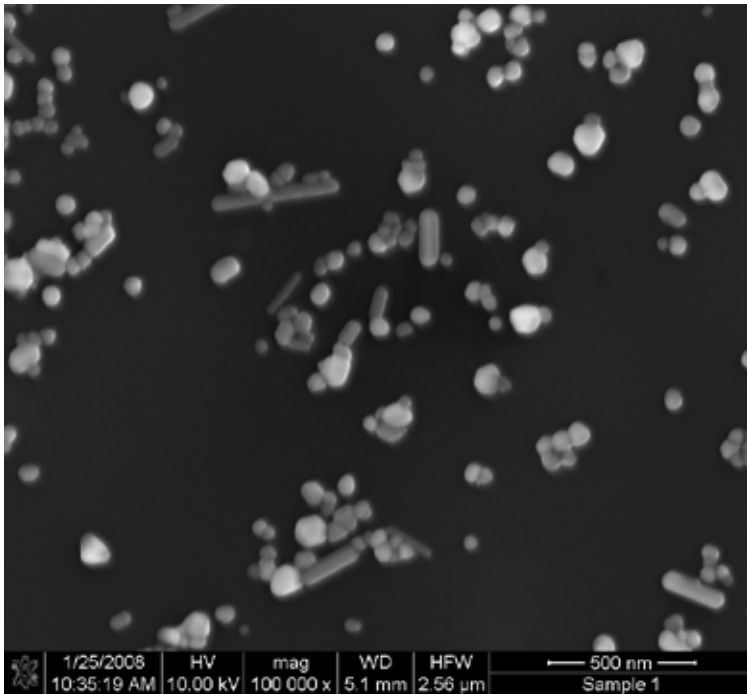
*October 7, 2009*

*Ann Miracle, Ph.D.*

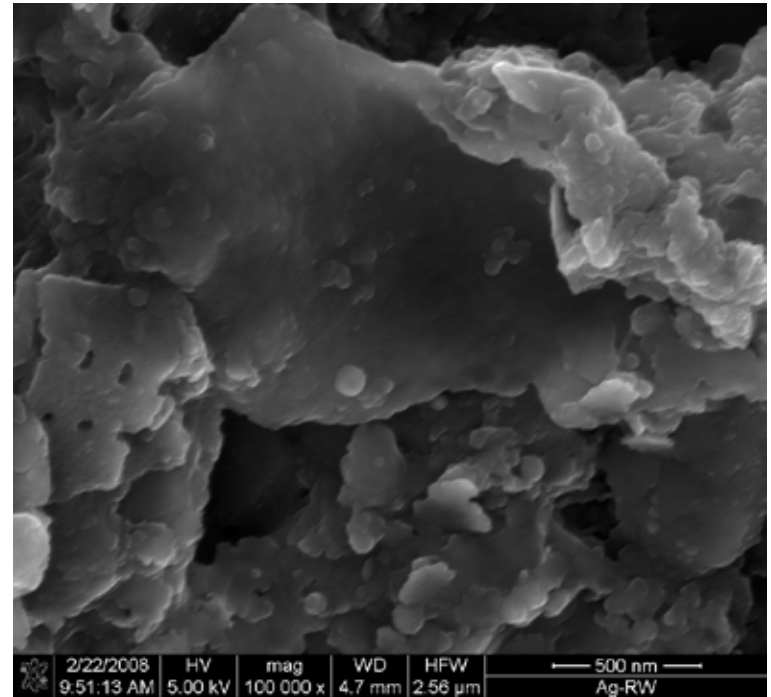
# Understand the transformation of nanomaterials under different environmental conditions

- ▶ 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 CaCO<sub>3</sub>)
  - 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



→  
CRW



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):

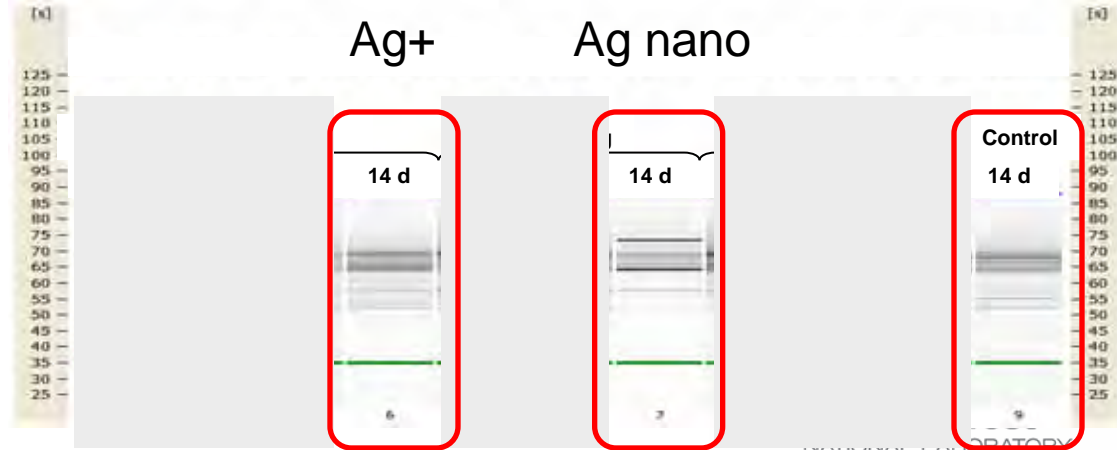
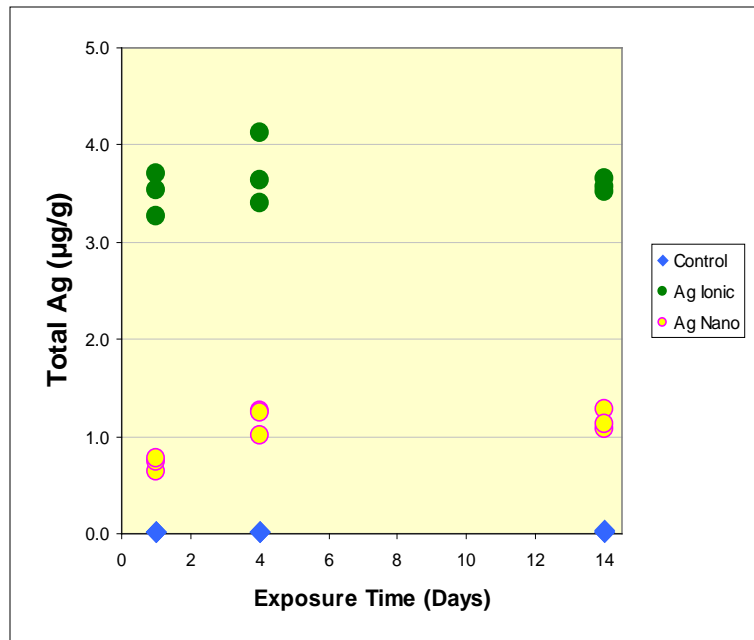
1 ug/g Ag nano

4 ug/g Ag+

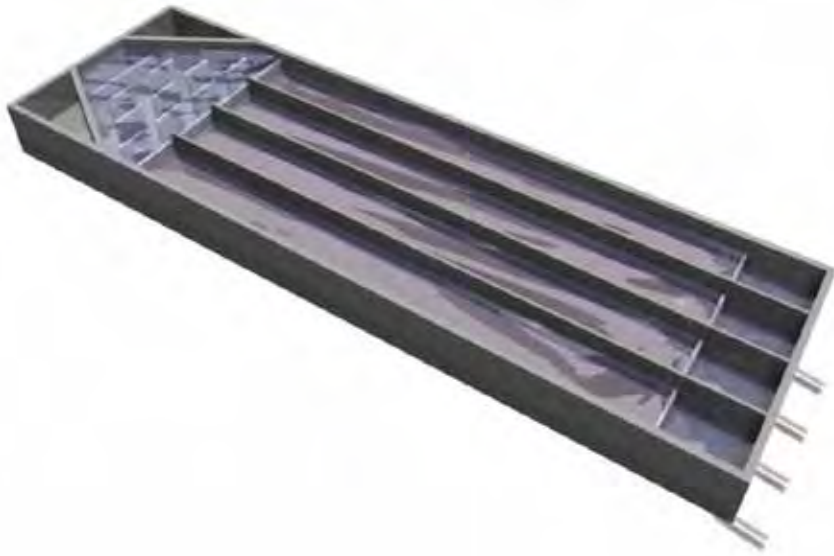
Controls

- Shift in dominant microbial species at 14 days

- Ag nano had greater community shift than Ag+



# Silver Mesocosm Exposure



24 hr exposure, 24 hr depuration

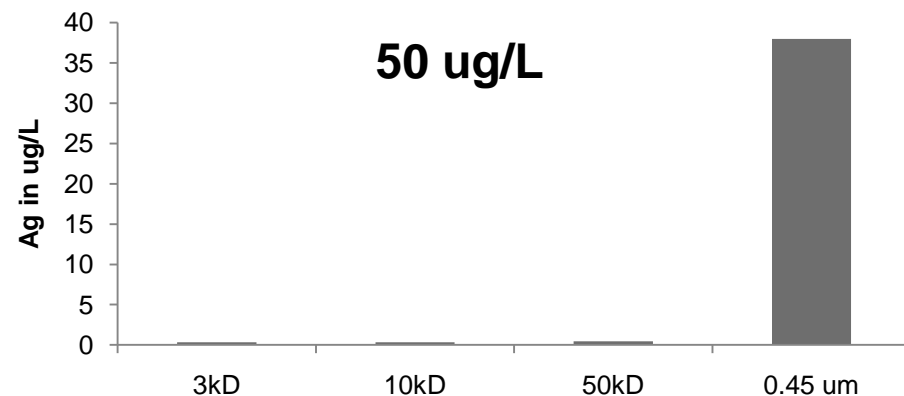
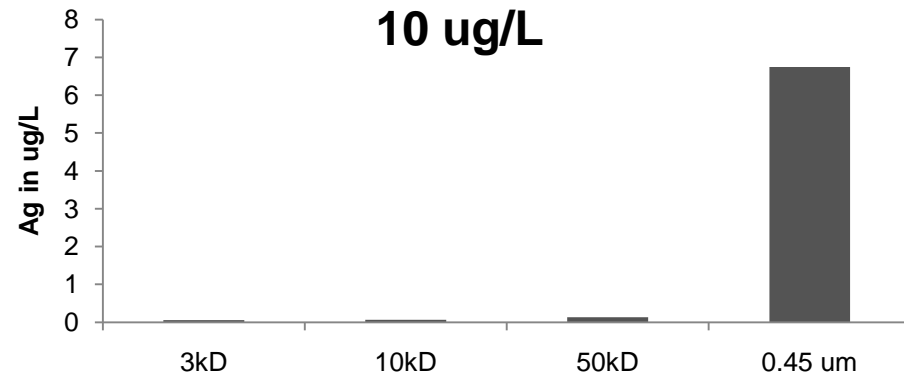
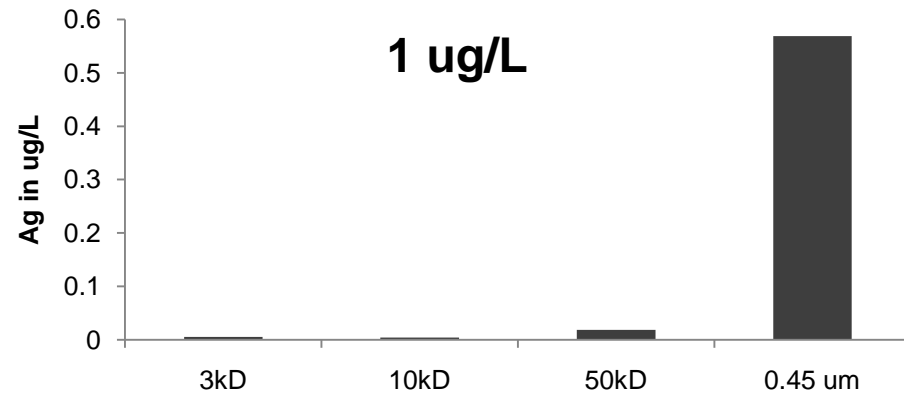
- Columbia River water (CRW)
- Clams
- Amphipods
- Microbial community in sand sediments

Control, 1  $\mu\text{g/L}$ , 10  $\mu\text{g/L}$ , 50  $\mu\text{g/L}$

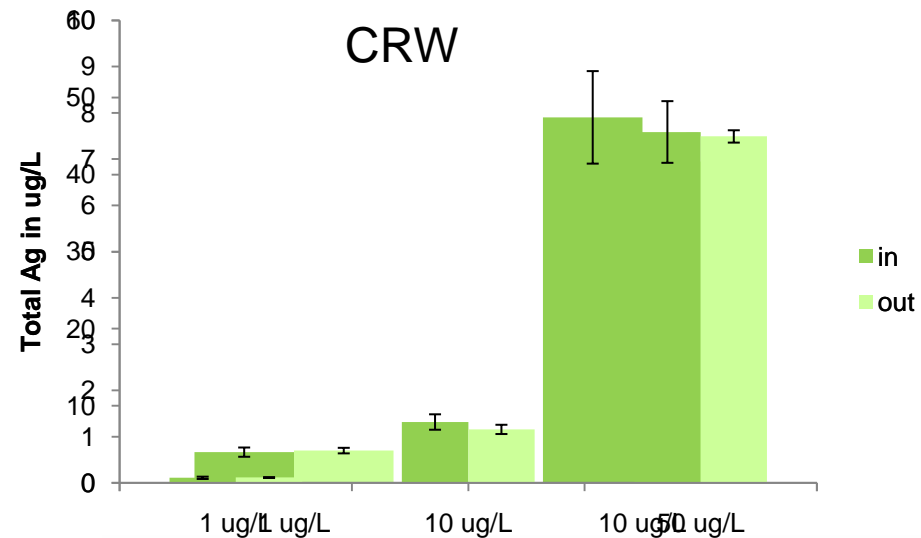
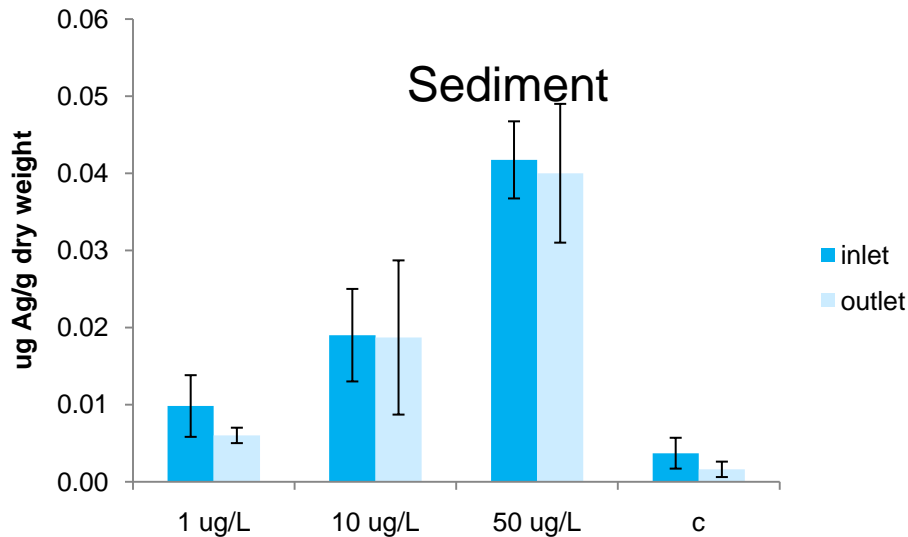
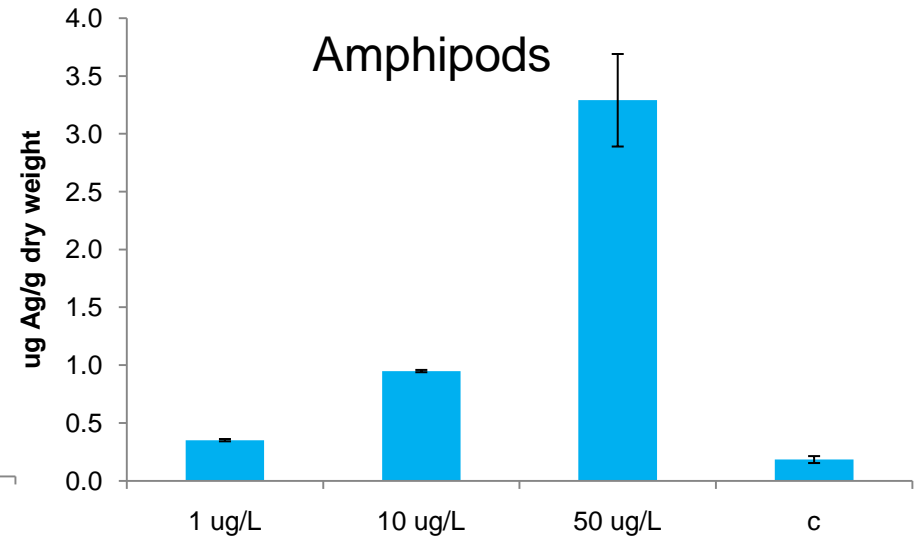
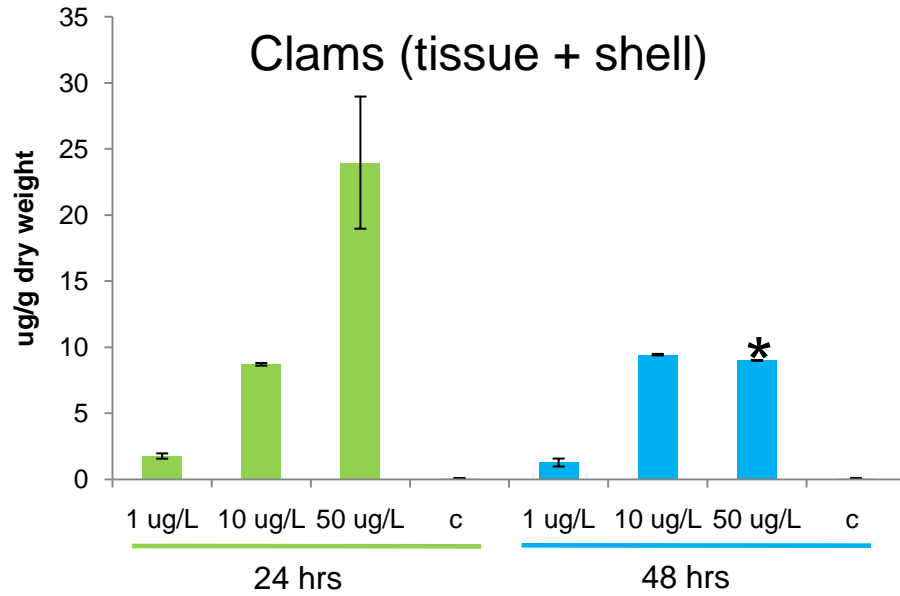


# Ag particle size in CRW

- ▶ 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

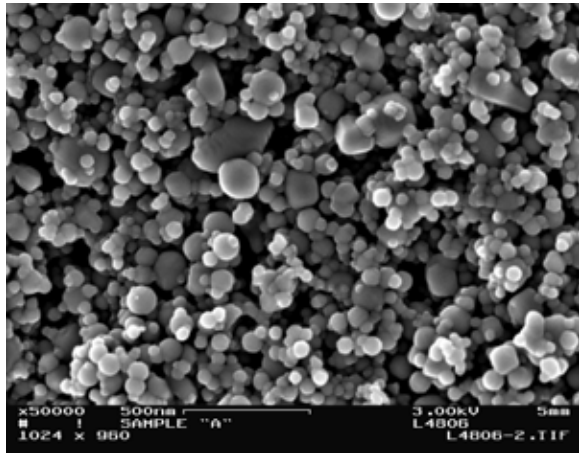


# Accumulation of Silver



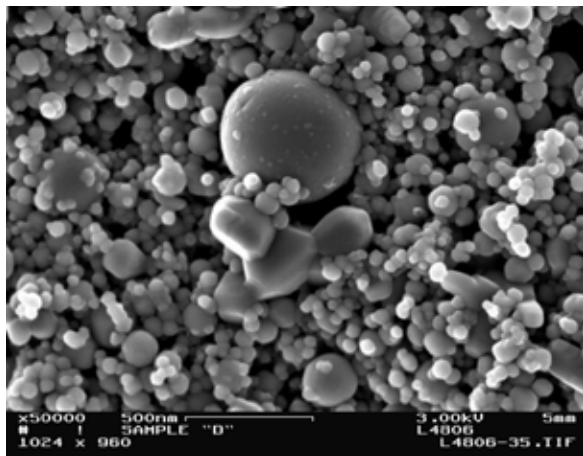
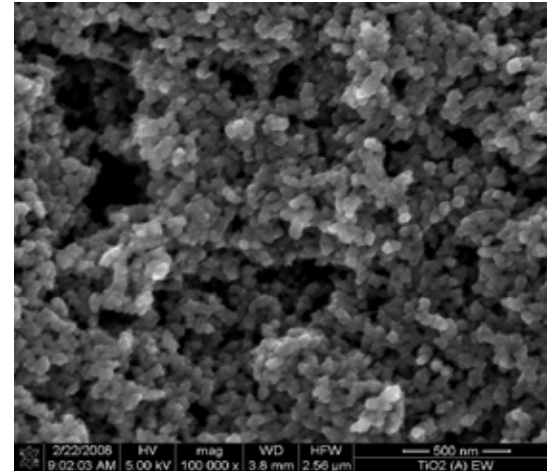


# Titanium Oxide Materials



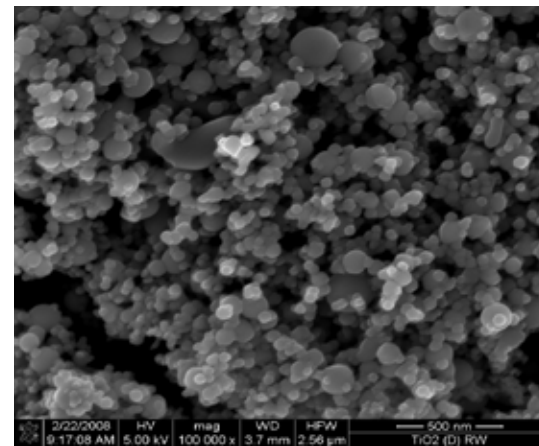
5-30 nm anatase

→  
CRW



<75 nm rutile/anatase

→  
CRW





# Titania Mesocosm Exposures



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



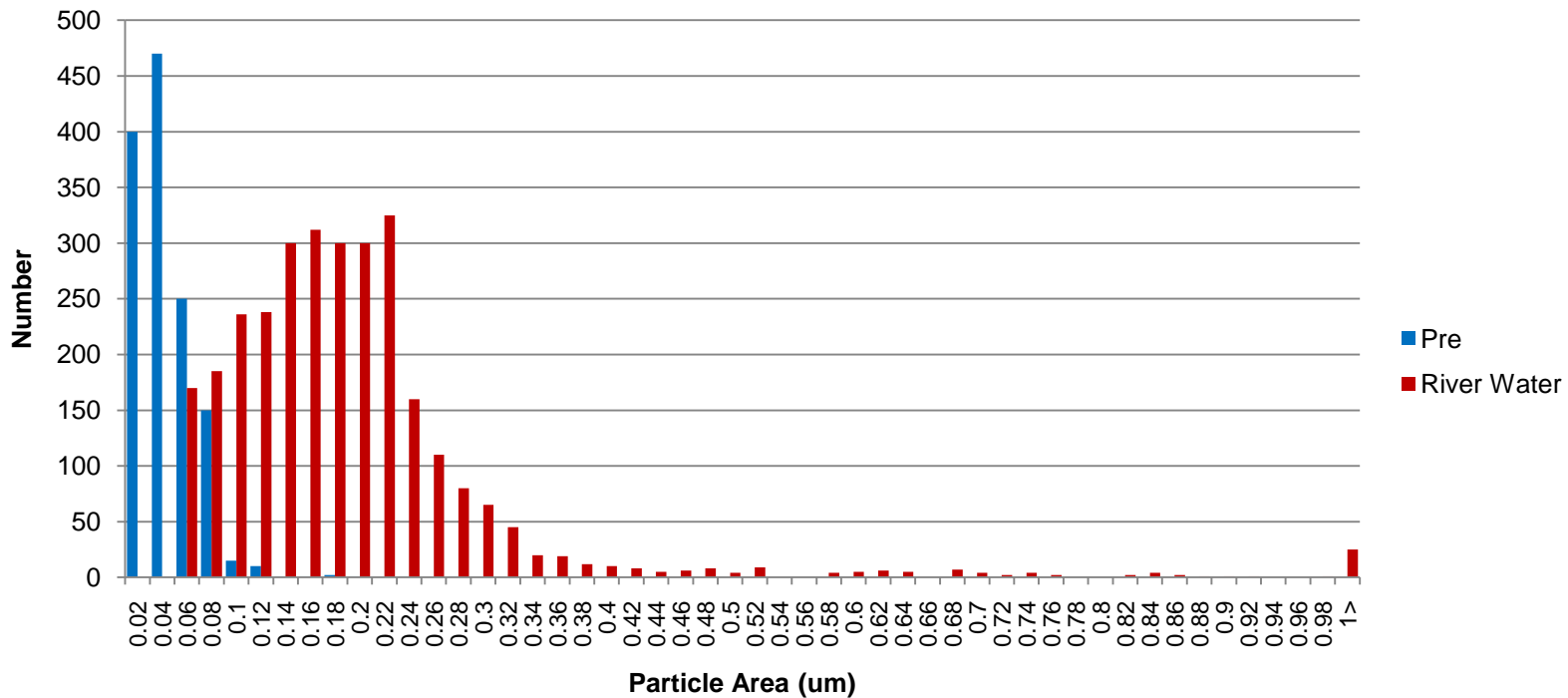
# Titania exposures



Variable	TiO <sub>2</sub> (mg/g dry weight) or % total dose (5 mg/L)		
	Flow - Through	Static*	
	A	A/R	A
amphipods	47.9	64.8	2.1
clams	0.55	1.04	0.03
sediment	66%	13%	34%

Clam : Amphipod uptake ratio ~1:70

# TiO<sub>2</sub> Size Distribution from SEM



- ▶ 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



# Acknowledgements

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