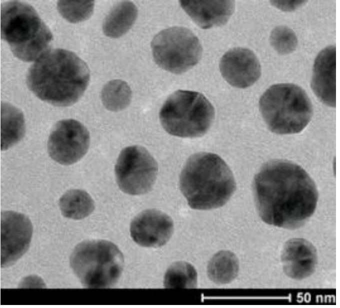
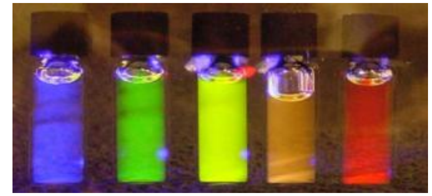
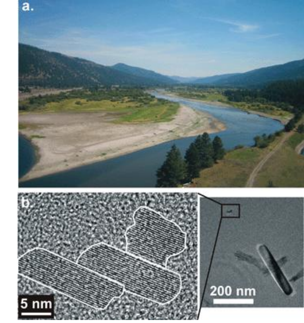




Nanomaterials in the Aquatic Environment:

Persistence, Transformations, and Bioavailability

Heileen (Helen) Hsu-Kim

Duke University

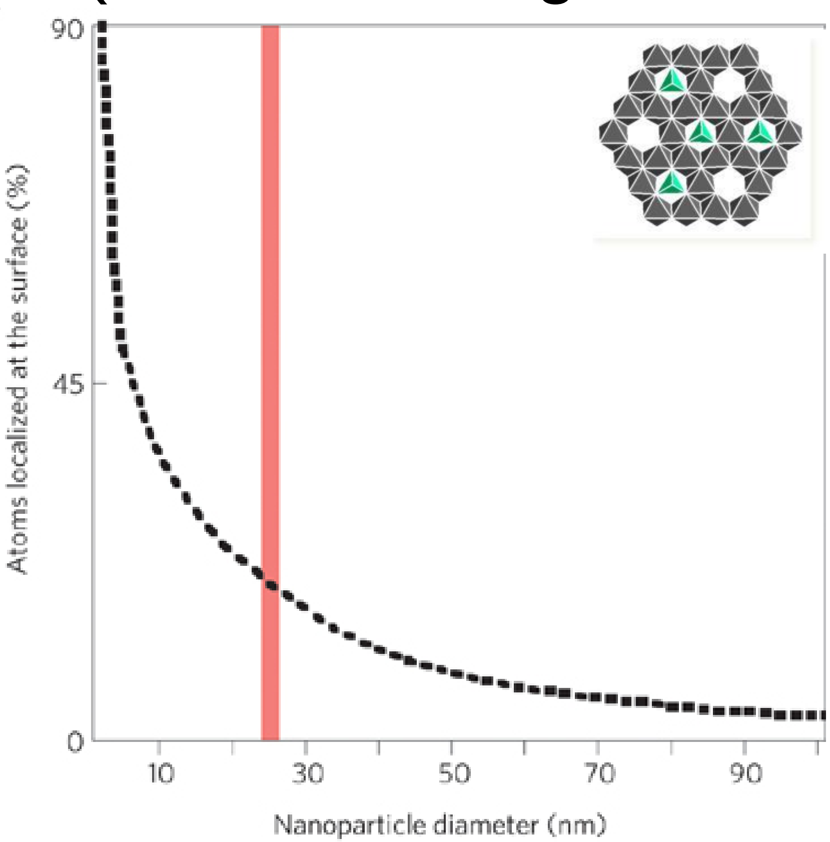
Civil & Environmental Engineering

DUKE
EDMUND T. PRATT, JR. SCHOOL OF ENGINEERING

CEINT
Center for the Environmental Implications of NanoTechnology

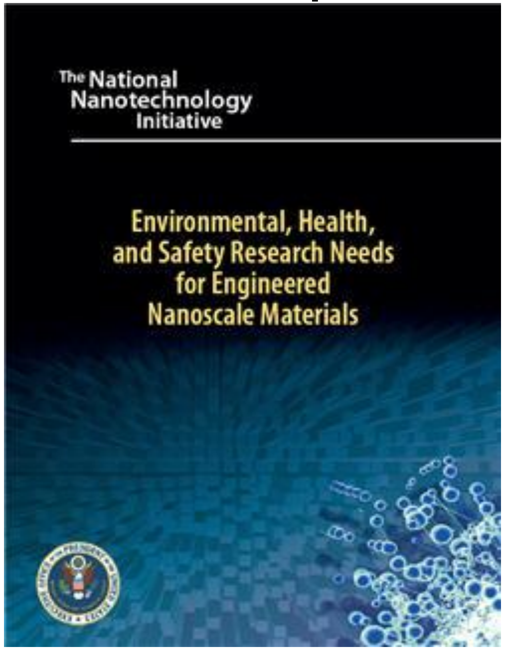
What are engineered nanomaterials?

- Materials manufactured to ~1-100 nm in size
- Exhibit unique properties due to their small size (relative to larger materials)



Auffan et al., *Nature Nano*, 2009

Concerns for their safety and environmental impacts:

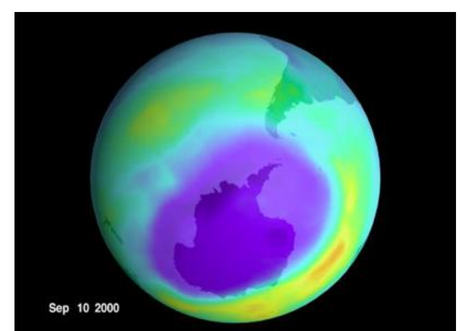


Breaking the Cycle of Unintended Consequences

Mercury amalgamation for precious metals mining

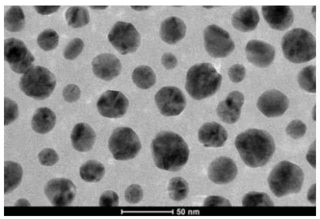
Pesticides for control of disease

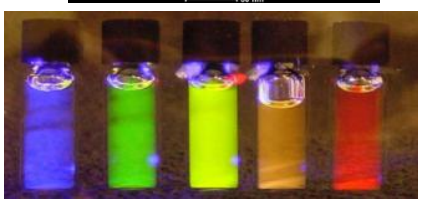
Chloroflurocarbons (CFCs)



Environmental health and safety of nanomaterials

<u>Life cycle of a material:</u>
Raw materials, Fabrication
Products use, Disposal





unintended release

Exposures and Effects?

Environmental exposure to nanomaterials:

Key Questions:

What are the main processes controlling exposures of nanomaterials to ecosystems?

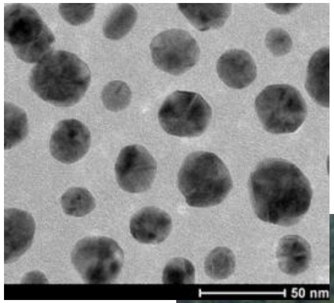
How do other water constituents alter nanomaterial surfaces, speciation, and persistence?

Do nanomaterials naturally occur in these settings?

Presentation Outline

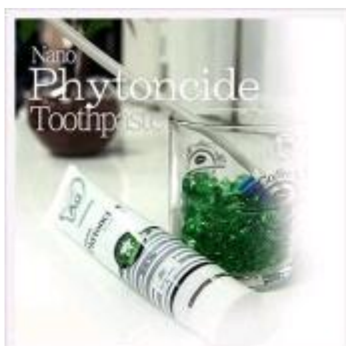
1. Exposure of metal-based nanomaterials in the aquatic environment
2. How other water constituents alter nanomaterial reactivity
3. Naturally-occurring nanomaterials

Example:
Silver nanomaterials in public wastewater treatment systems



Ag^0 NPs in commercial products

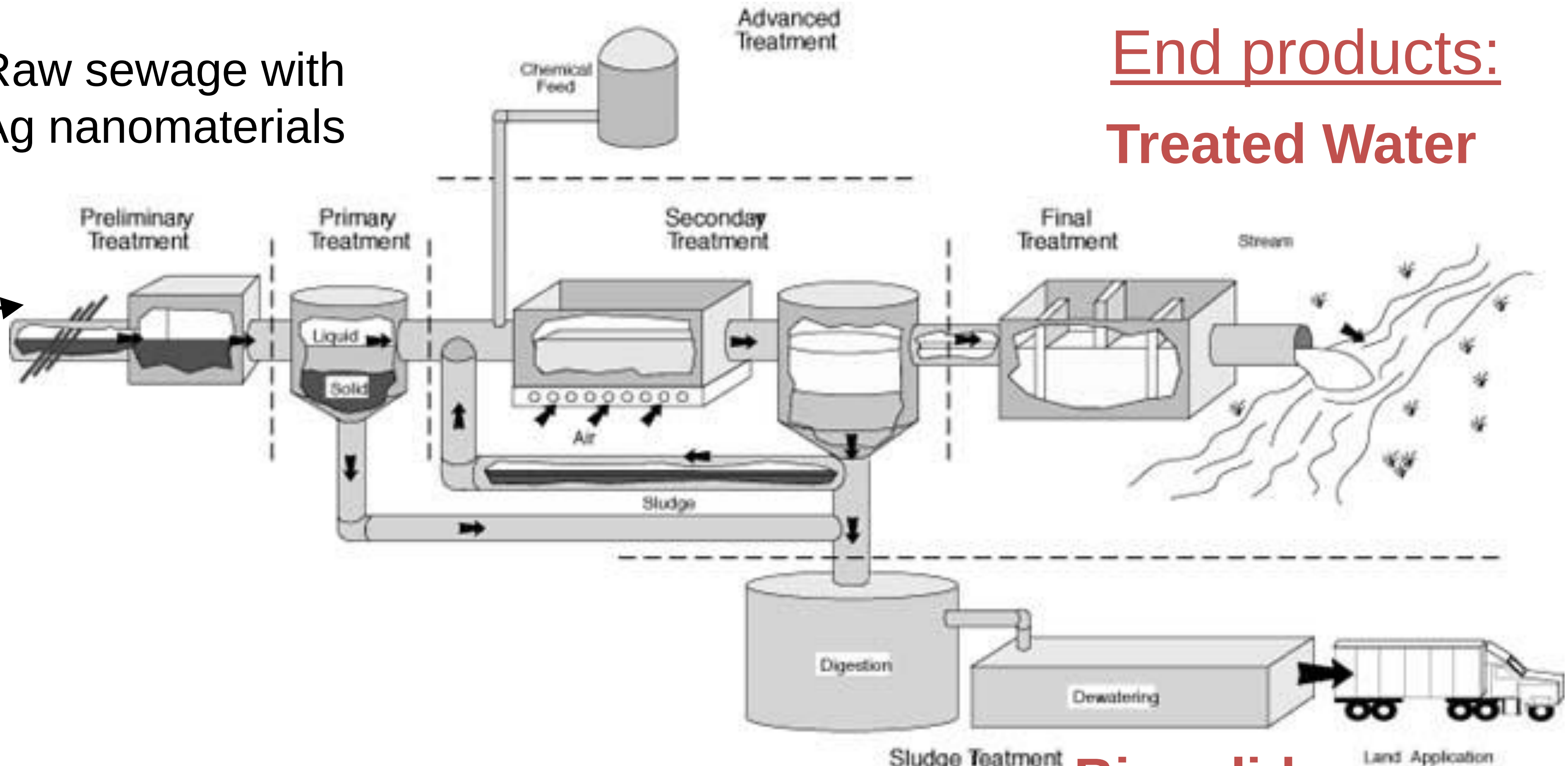
Purpose: antimicrobial coating in household goods



Ref: Project on Emerging Nanotechnologies

Release of silver nanomaterials into domestic wastewater

Raw sewage with Ag nanomaterials



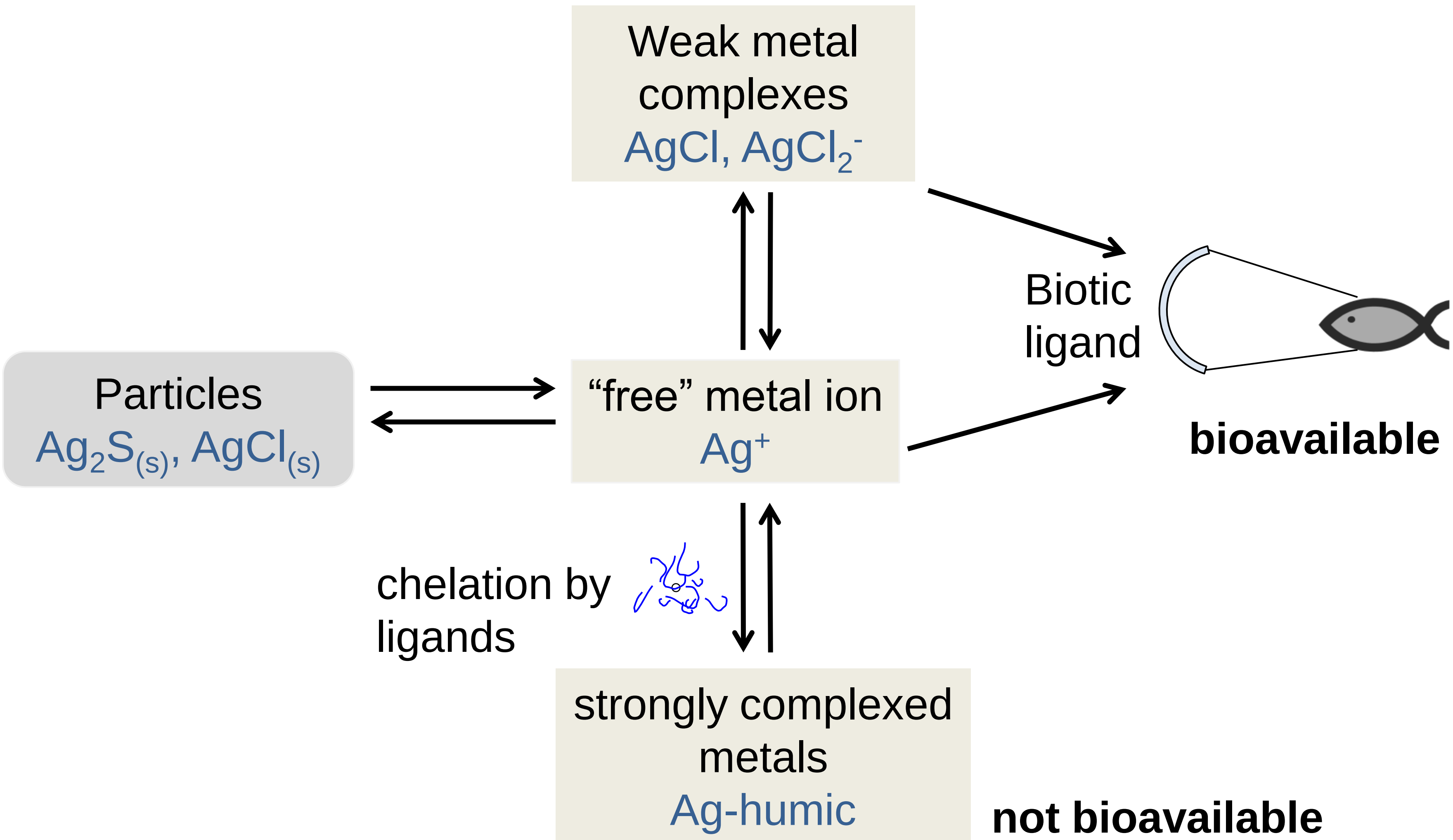
<u>End products:</u>

Treated Water

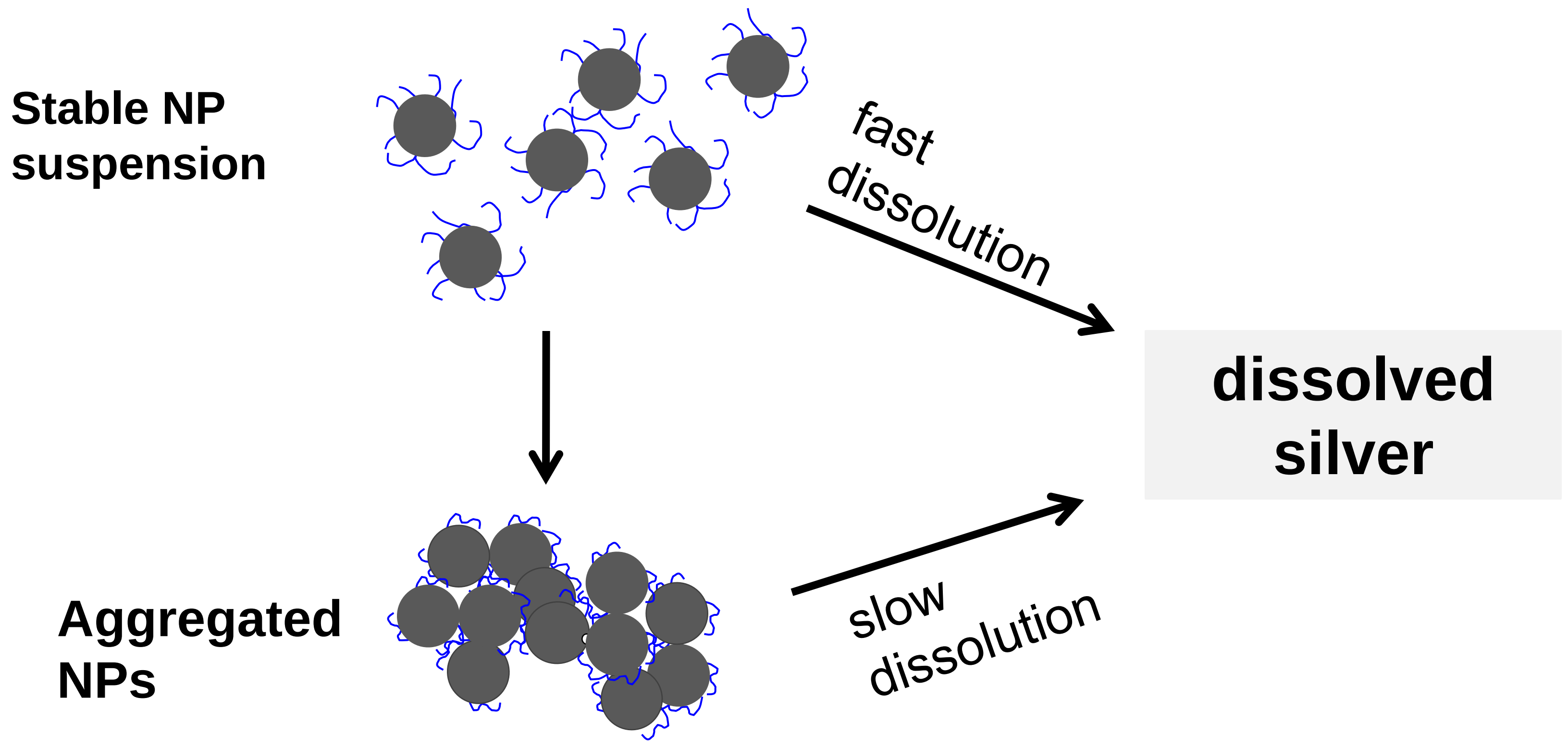
Biosolids

Geochemistry and Toxicity of Trace Metal Pollutants

The Conventional View: Biotic Ligand Model

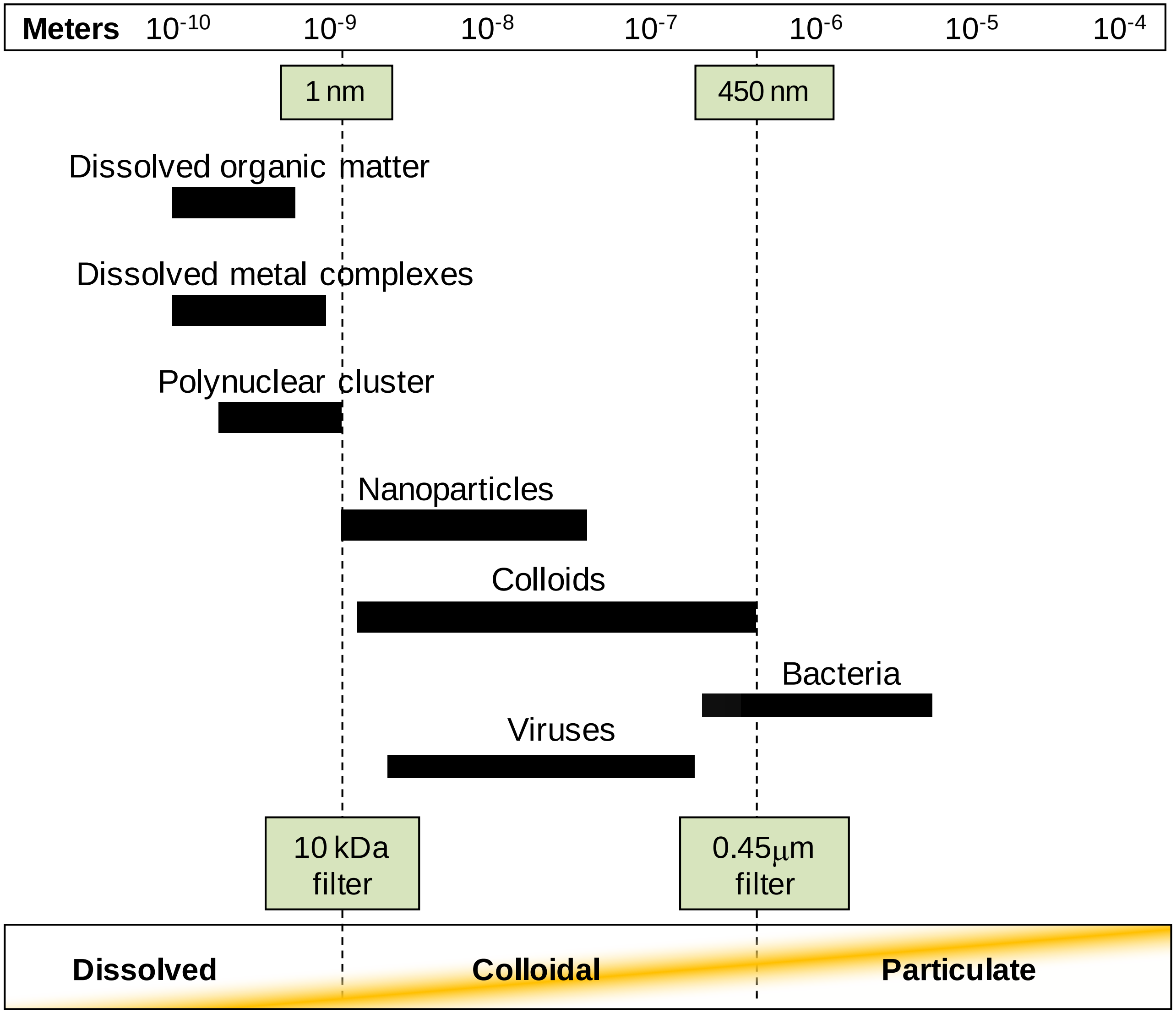


Ag^0 persistence and bioavailability



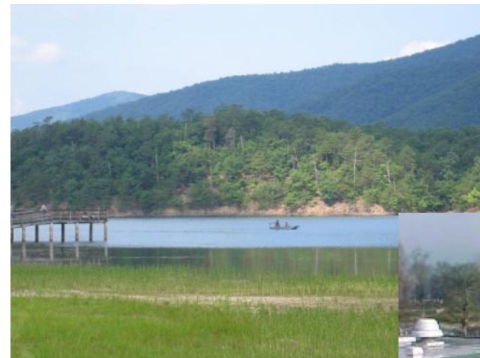
What is the influence of other water constituents for nanoparticle reactivity?

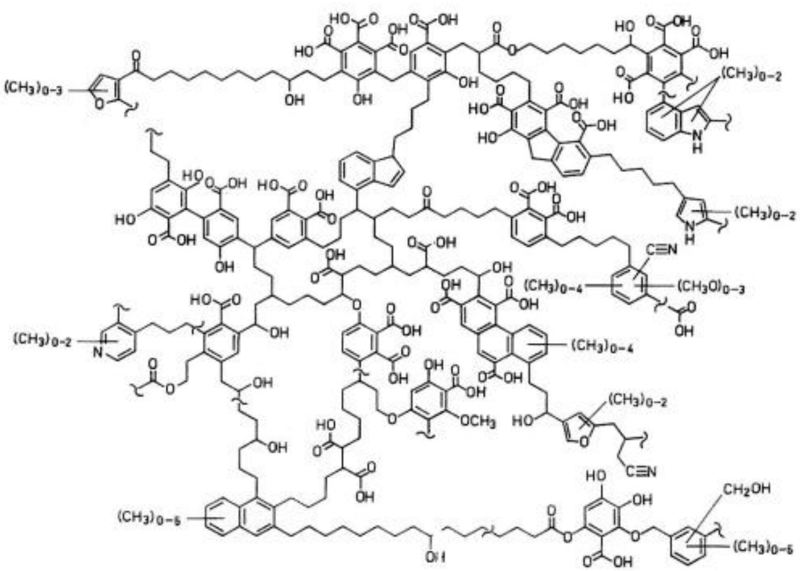
Other constituents in natural waters



Other constituents in environmental media

Dissolved Organic Matter





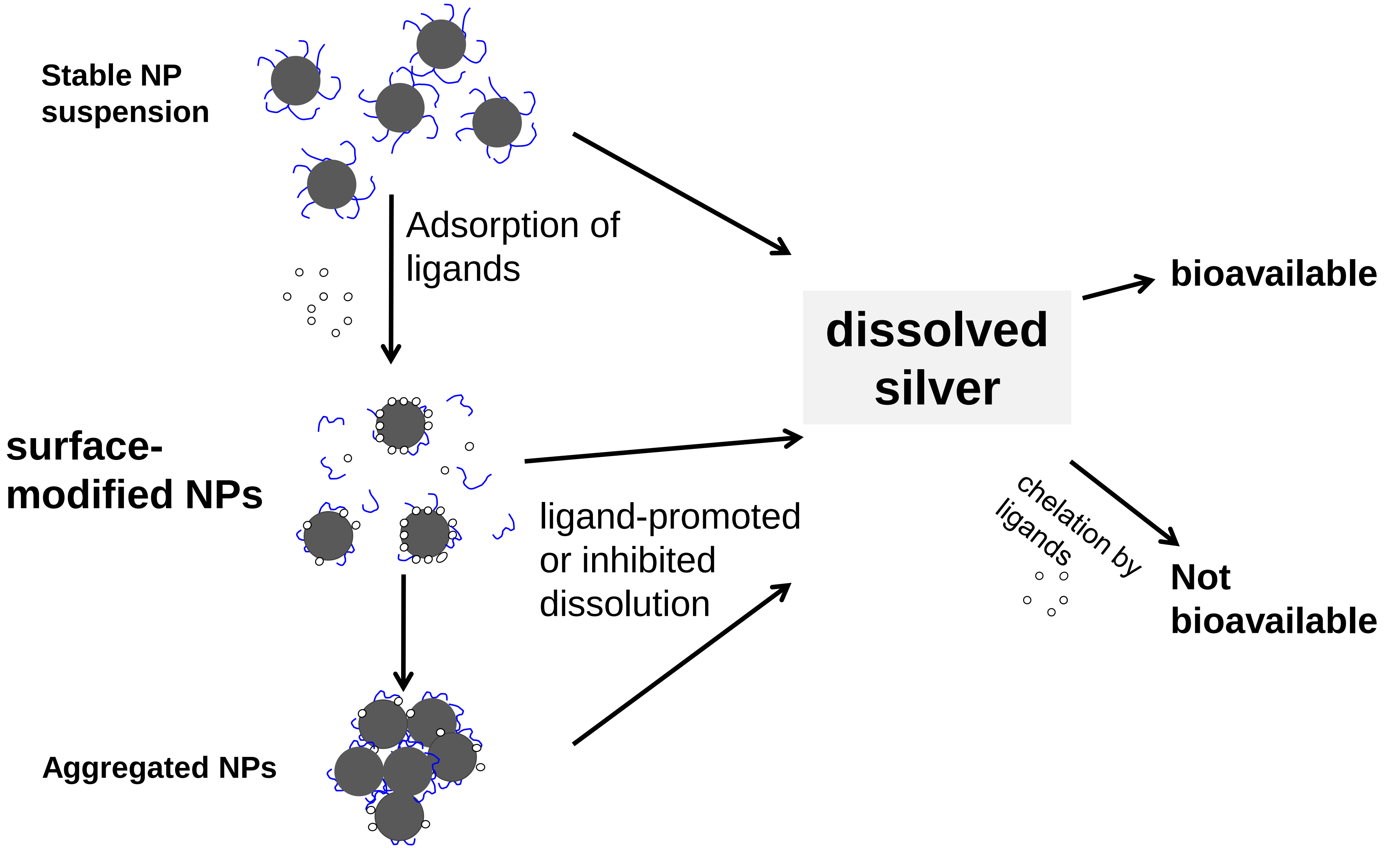
<u>Interactions with nanoparticles</u>:

Macromolecular surfactant

Hydrophilic and hydrophobic moieties

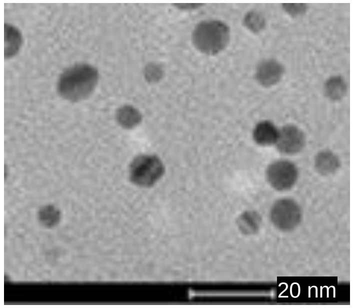
Potential to bind Ag^{+} ions

Ag^0 persistence and bioavailability



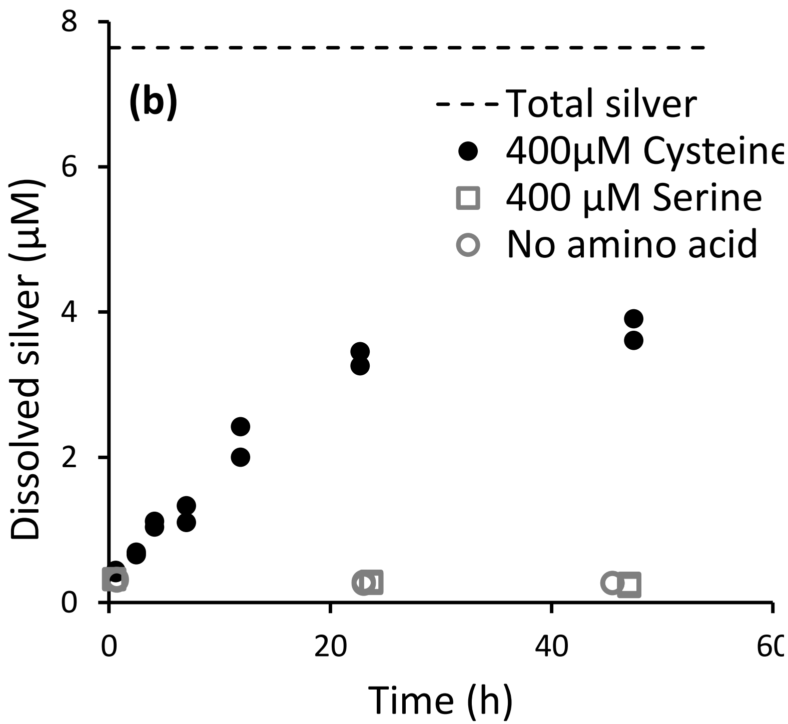
Nanomaterial reactivity in wastewater

PVP-coated Ag nanoparticles

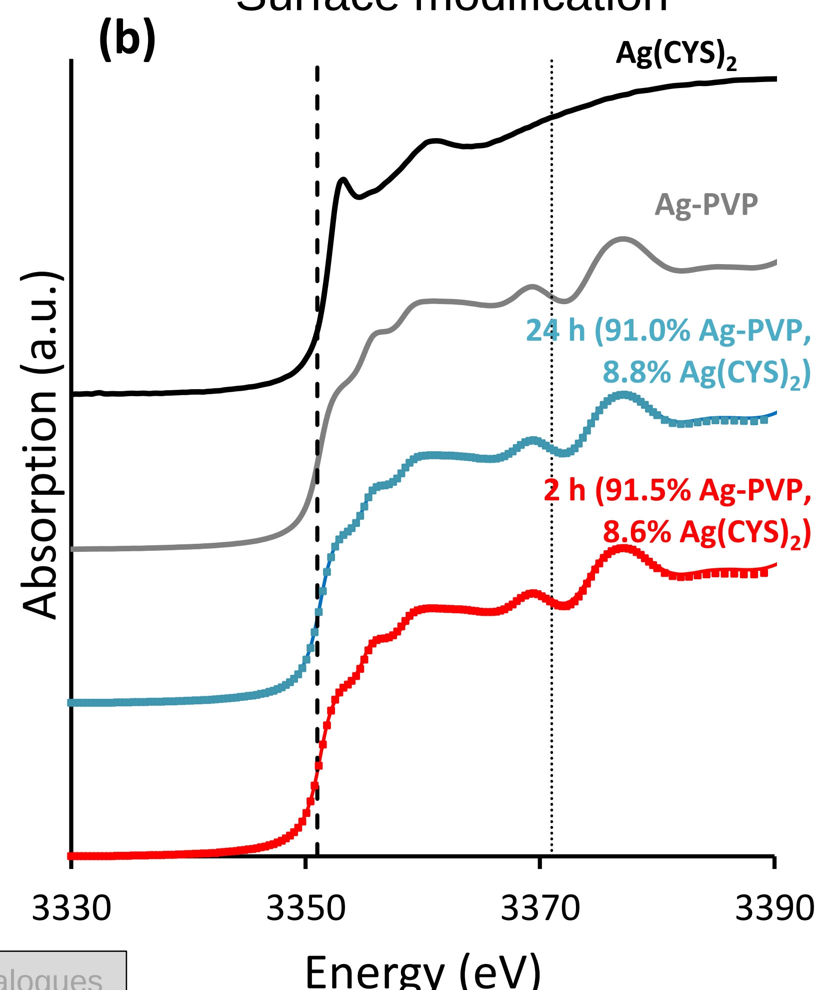


Transformations after exposure to cysteine

Dissolution

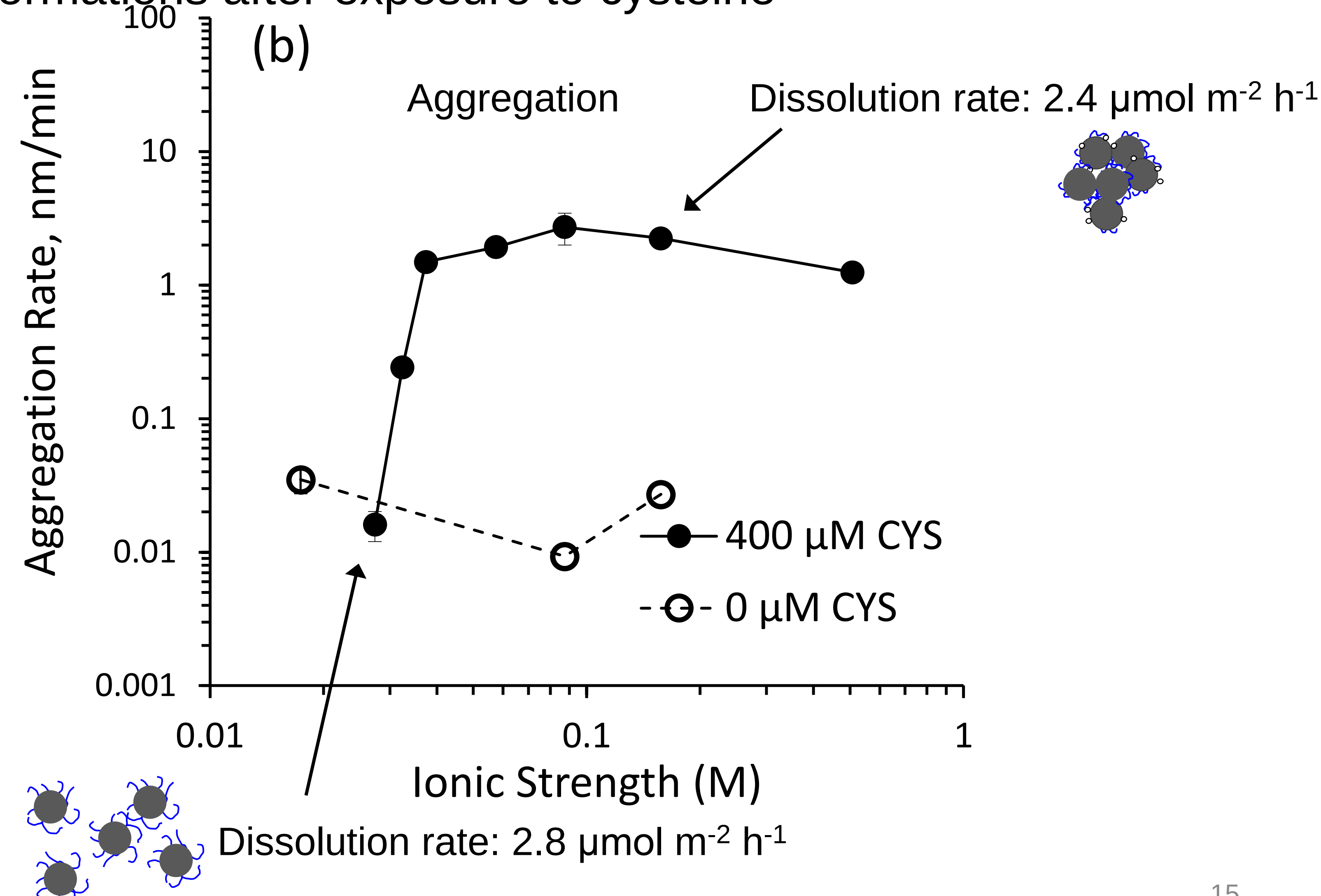


Surface modification



Nanomaterial reactivity in wastewater

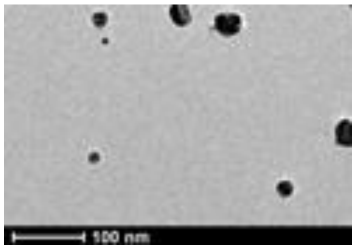
Transformations after exposure to cysteine



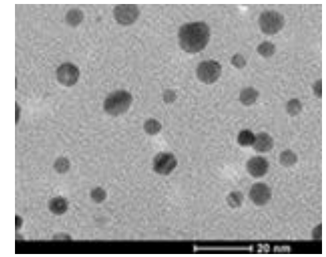
Nanomaterial reactivity in wastewater

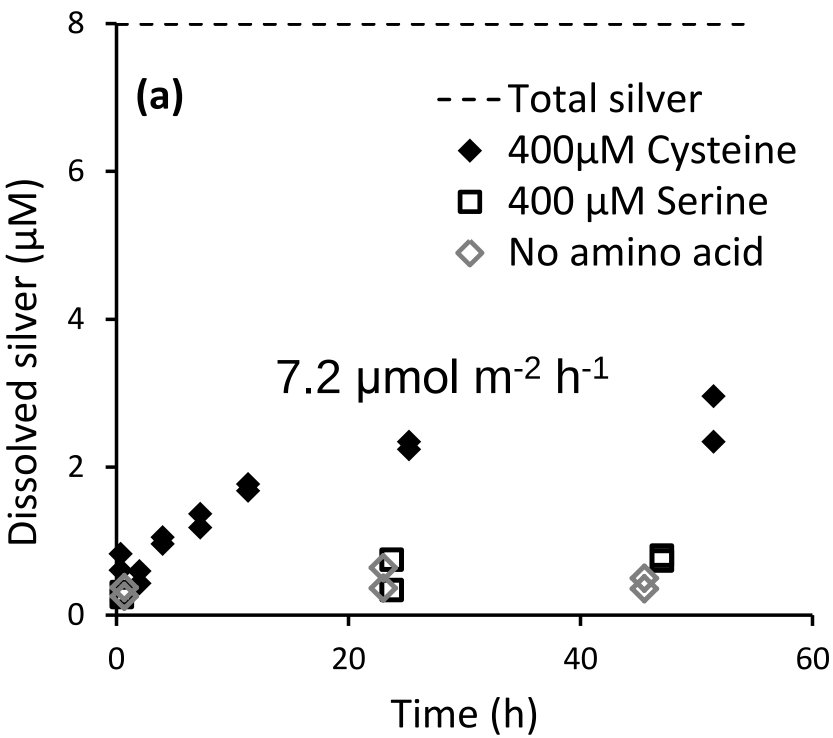
Transformations induced by cysteine

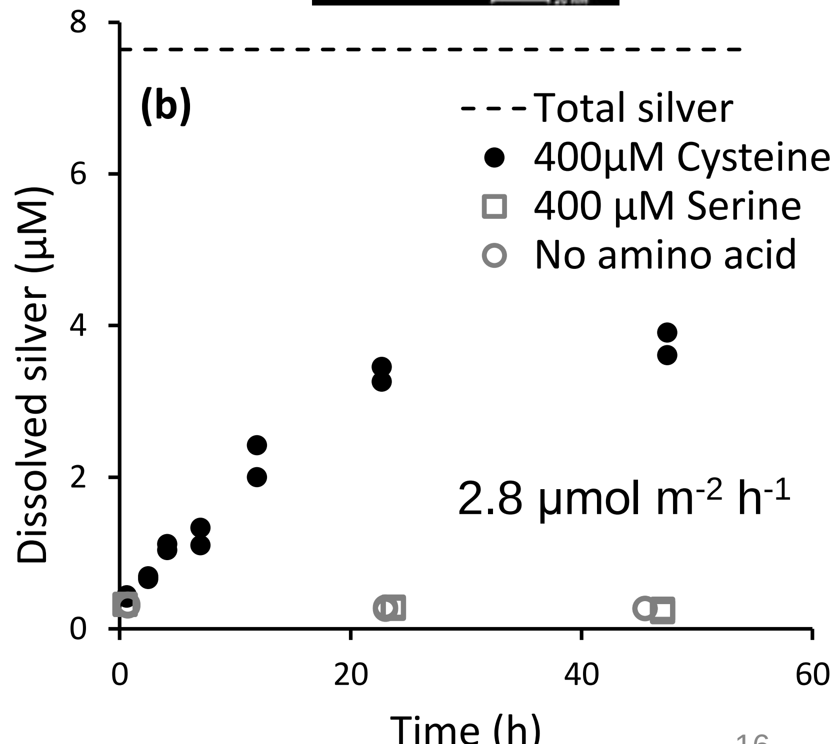
Citrate-coated Ag NPs



PVP-coated Ag NPs



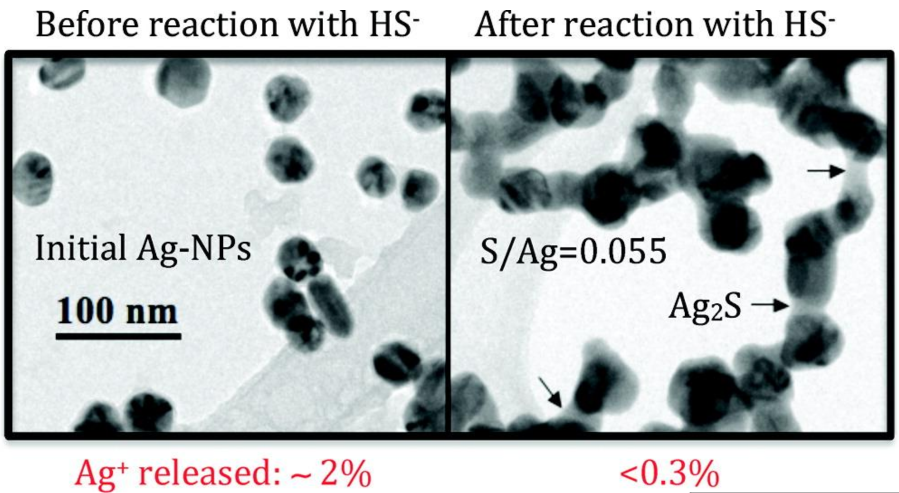


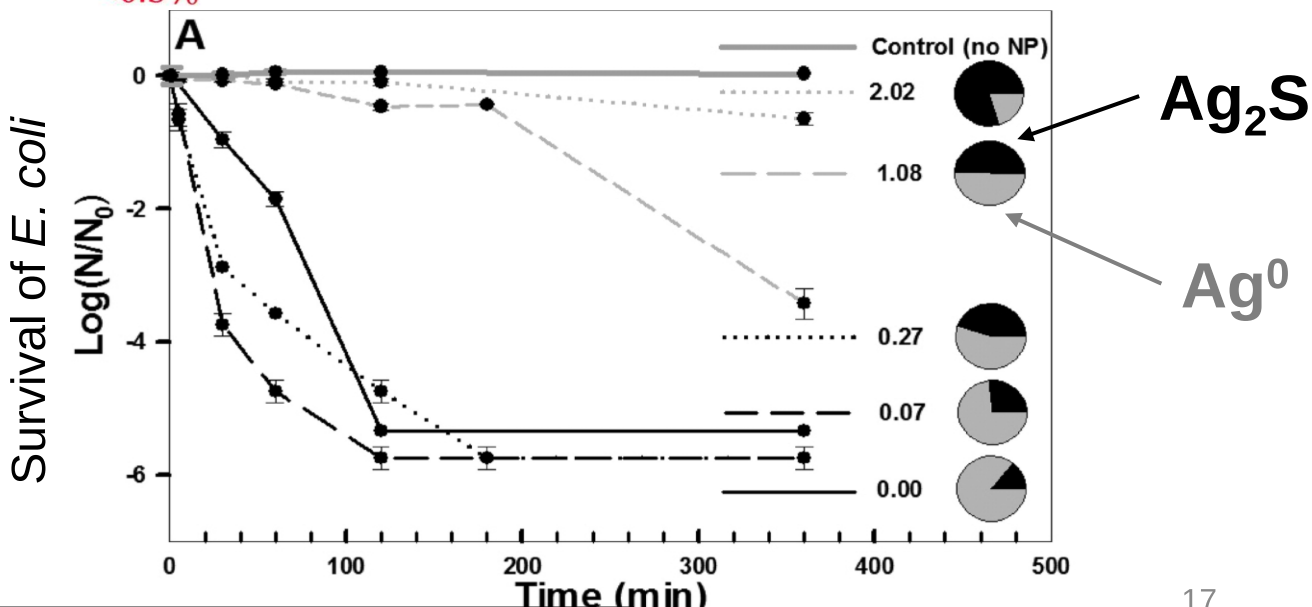


Nanomaterial reactivity in wastewater

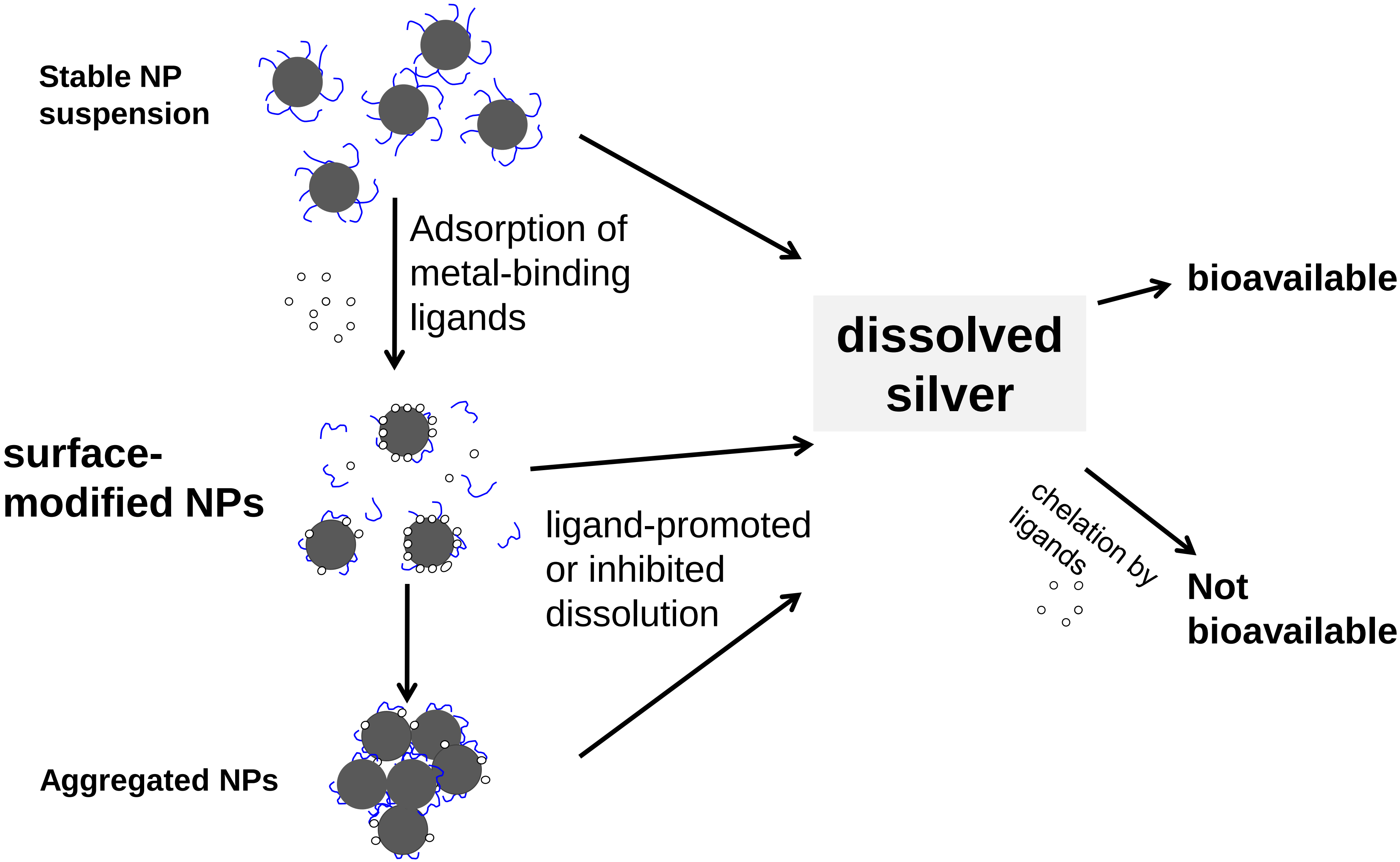
Reaction with sulfide

Levard *et al.* 2011
Reinsch *et al.* 2012



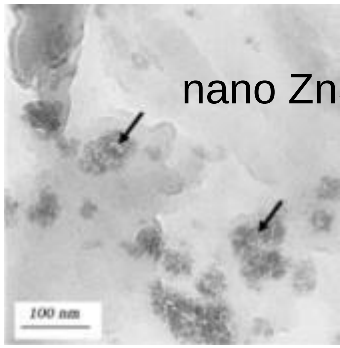


Ag^0 persistence and bioavailability

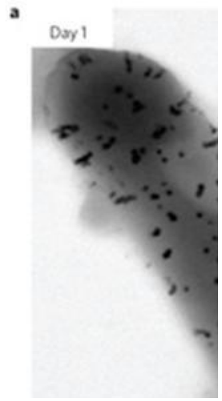


Naturally-Occurring Nanomaterials

Contaminated soil and sediments

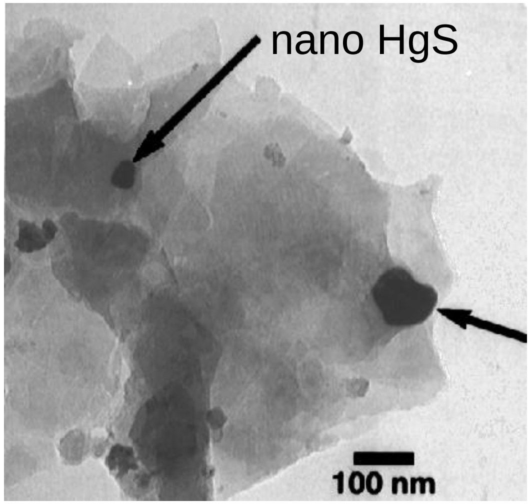


nano ZnS



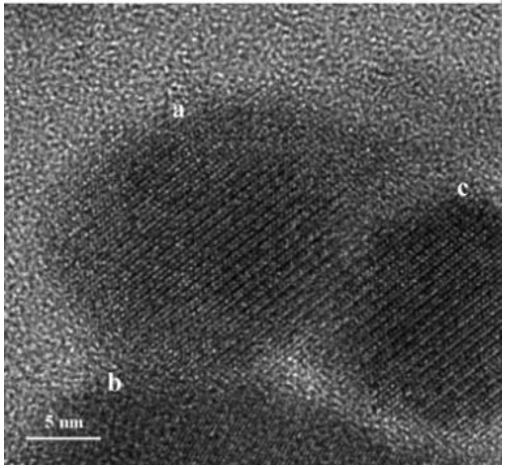
nano-FeS/CuS
on sediment
bacteria

nano HgS



Oak Ridge, TN

Treated Sewage Effluent and Biosolids



nano Ag_2S

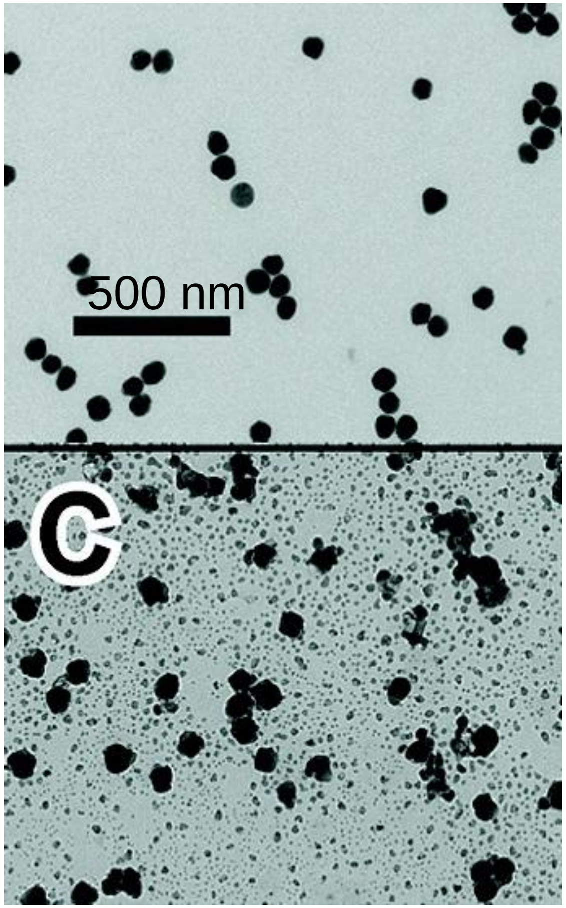
Originally from silver nanomaterials?

Kim *et al.* (2010)

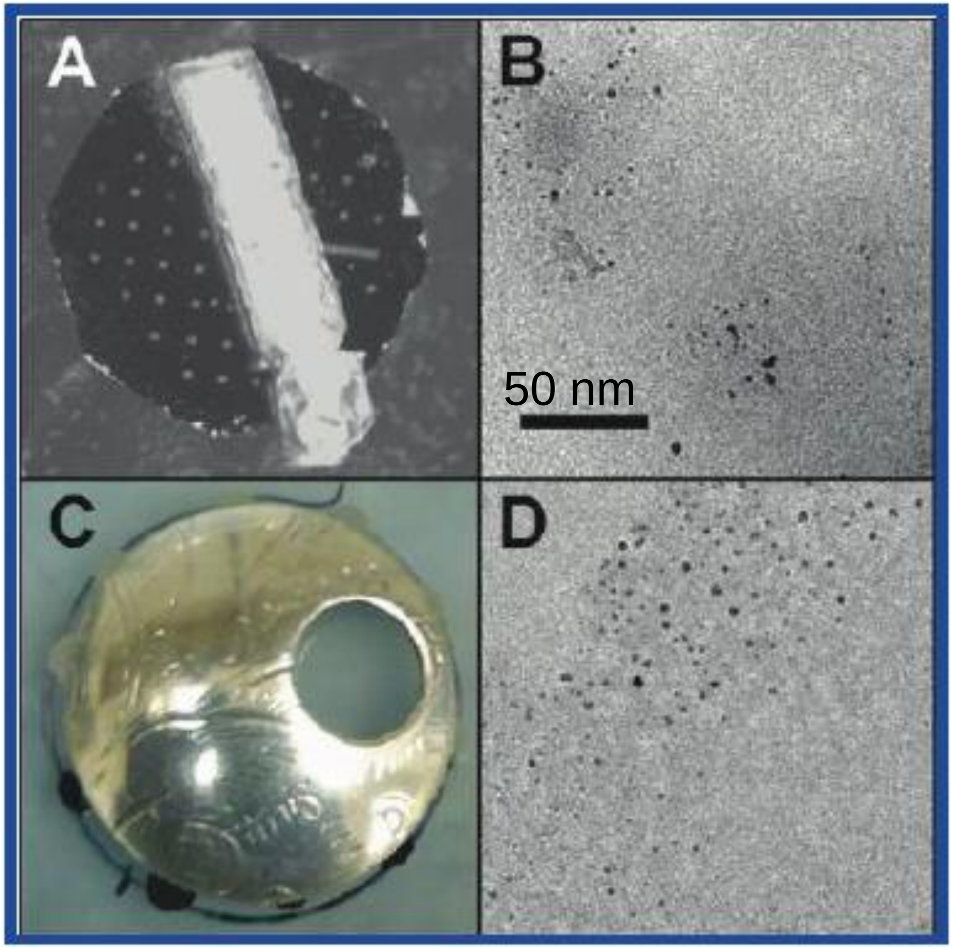
Naturally-Occurring Nanomaterials

New nanoparticles formed from silver objects

Silver nanoparticles



Silver wire



Glover *et al.* ACS Nano (2011)

Silver earring

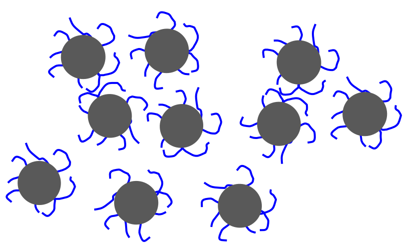
Manufactured vs. Naturally-Occurring Nanomaterials

Similarities

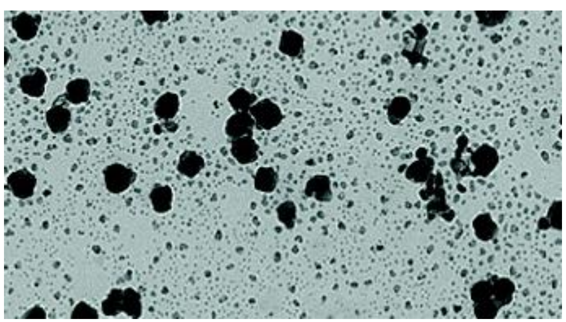
Shared core composition:

- TiO_2
- SiO_2
- ZnO
- Fullerenes (C_{60})
- Metallic Ag^0, Au^0, Cu^0
- ZnS, CuS, CdS
- CeO_2
- (?) carbon nanotubes
- (?) quantum dots (e.g. CdSe, CdTe)

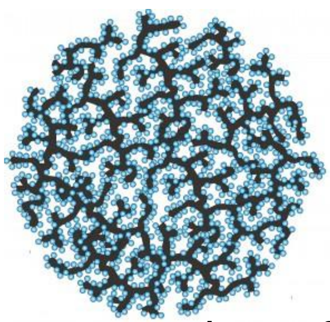
Differences



Surface coatings (synthetic vs. natural)



Polydispersivity & Crystallinity



Composites of nanomaterials

Summary and Challenges

- Increasing use of nanomaterials → Increase of exposure
- Transformations in the environment
  (example: natural organic matter)
  Dissolution, Surface Chemistry, Aggregation
- Naturally-occurring nanomaterials:
  Can they provide lessons for engineered nanomaterials?