Watershed Modeling for Nanosilver Risk Assessment

Amy Dale
Engineering and Public Policy

Elizabeth Casman, Ph.D.
Engineering and Public Policy

Gregory Lowry, Ph.D.
Civil and Environmental Engineering

Carnegie Mellon University

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Risk Assessment: Nanoparticles

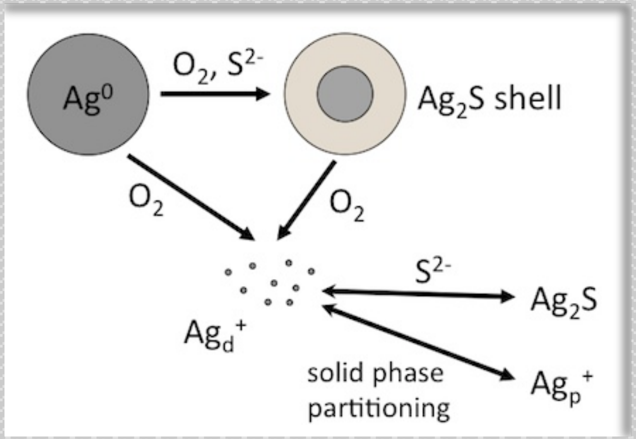
- Nanotechnology is a multi-billion dollar industry
- Nanoparticles
  1. 1-100 nm
  2. Unique size-dependent properties

What are the implications of *2*?

Nanosilver

- Nanosilver is the largest and fastest growing application of nanotechnology in consumer goods[1]

- Broad-spectrum biocide
  - High surface-to-volume ratio → rapid release of toxic Ag^+
- Fate and transport models needed to assess risk

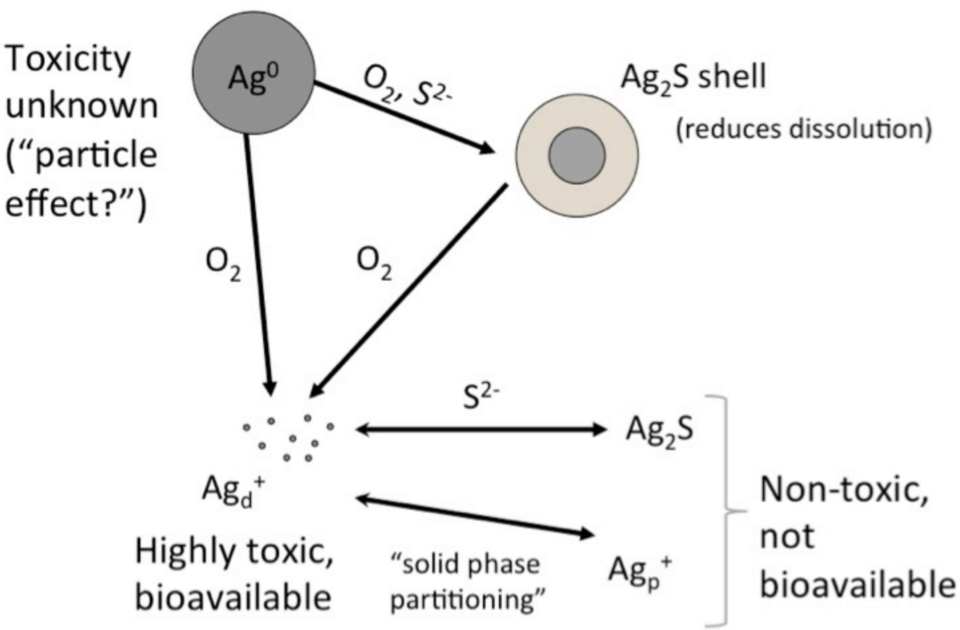


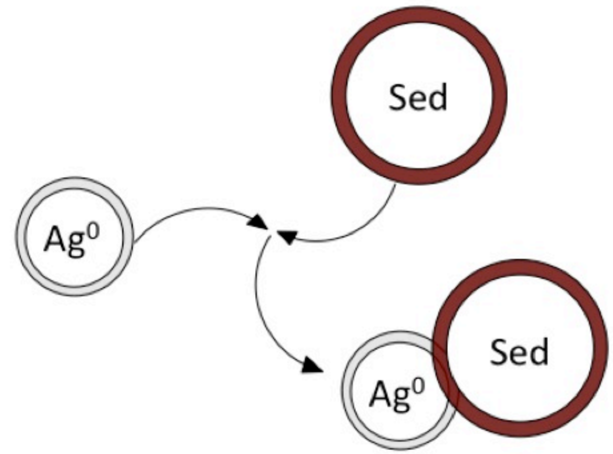
Previous Work

A.L. Dale, G.V. Lowry, E.A. Casman. "Modeling nanosilver transformations in freshwater sediments." (submitted)

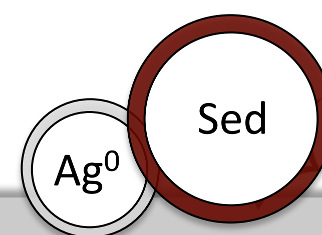
Motivation

1. Environmental transformations determine nanosilver bioavailability and toxicity





2. Nanosilver aggregates with sediments. Sediment co-transport (advection, settling) and bed chemistry are key determinants of fate.



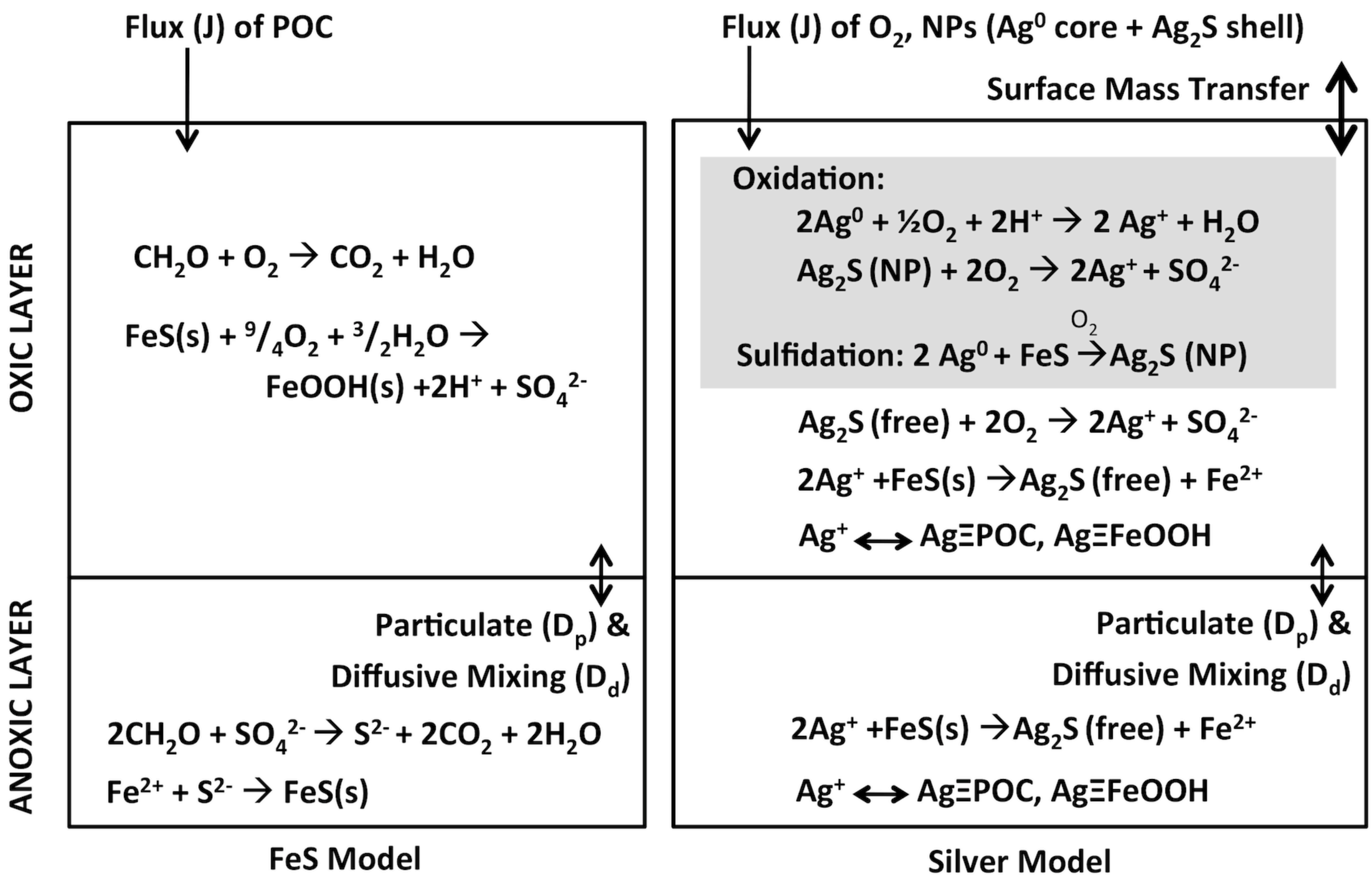
Previous work

Objective

Adapt a conventional metal-sediment chemistry model (Di Toro *et al.*, 1996) to describe chemical transformations of nanosilver in sediments

Di Toro, D. M.; Mahony, J. D.; Hansen, D. J.; Berry, W. J., A model of the oxidation of iron and cadmium sulfide in sediments. *Environmental Toxicology and Chemistry* **1996,** *15*, (12), 2168-2186.

Conceptual Model



Key Findings

- ***Conclusion 1:*** Non-toxic Ag_2S dominates speciation, while toxic Ag^+ is present only at low concentrations (<0.01 wt-%)

- ***Conclusion 2:*** Environmental conditions and seasonal variation are important!
  - Eutrophic systems (e.g., low-lying lakes and wetlands) minimize toxic Ag^+ formation
  - The half-life of typical sulfidized (85% Ag_2S) AgNPs in the sediment may vary from 5 years to over a century depending on redox conditions

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But this model can't tell us …

- Predicted environmental concentrations
- Strengths and weaknesses of alternative risk management strategies

Current Work

Motivation

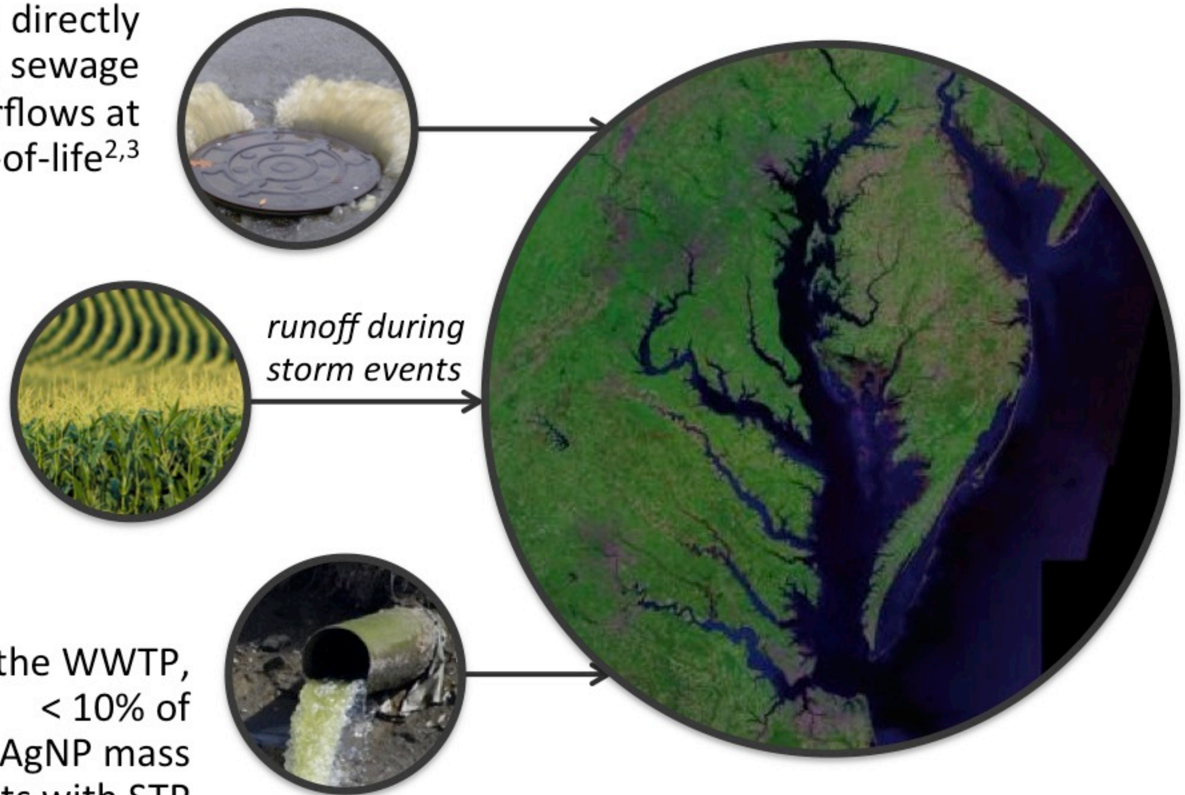
Risk management and policy decisions often require a broader perspective

4-13% of AgNP mass enters the stream directly from sewage overflows at end-of-life[2,3]

In the WWTP, > 90% of AgNP mass exits with STP sludge[4]

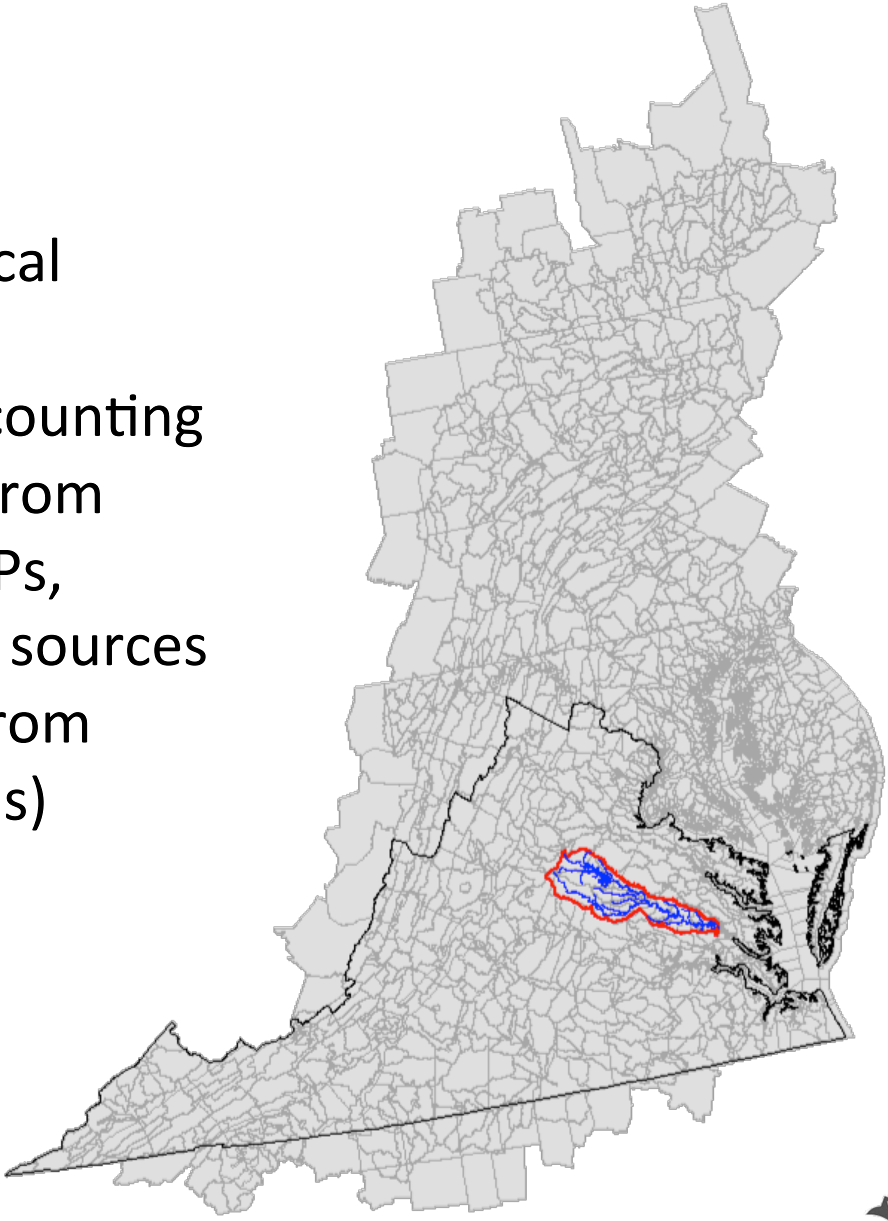
>50% of STP sludge is applied to crops as biosolids (E.U., U.S.)[3]

In the WWTP, < 10% of AgNP mass exits with STP effluent[4]



Objective

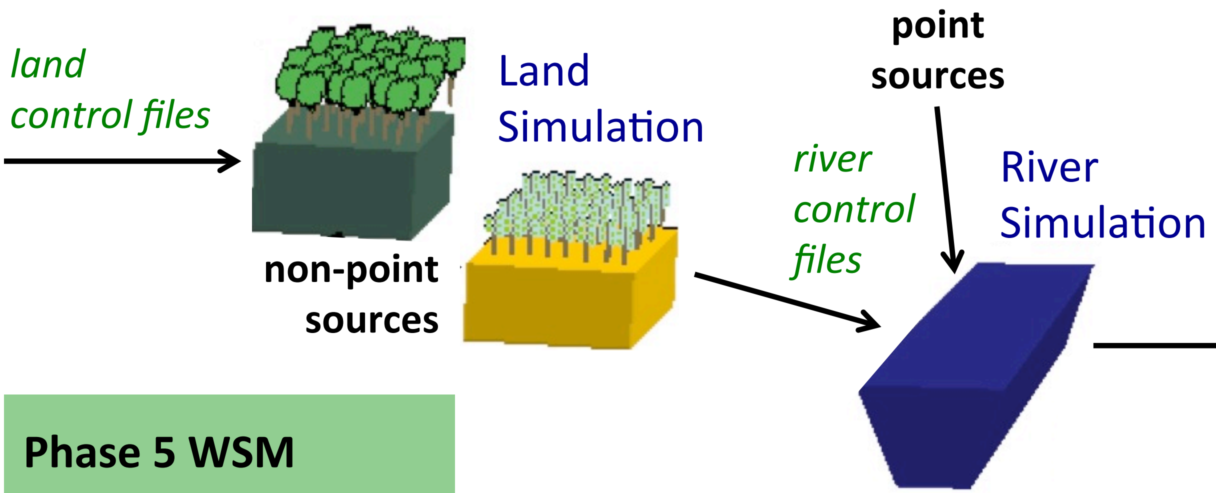
Model nanosilver transport and chemical transformations in a watershed basin, accounting for stream loadings from point sources (WWTPs, CSOs) and non-point sources (agricultural runoff from land-applied biosolids)



Approach

Conceptual Model

Hydrological Model



Phase 5 WSM

Creates HSPF control files from a library of Fortran g77 scripts and ASCII files containing parameter definitions, parameter values, formatting instructions, geographic data, etc.

HSPF control files →

HSPF

Performs the operations specified in the control files for all land and river segments in the basin

- **Hydrology**
- **Annual variation in water quality constituents *(temp, pH, DO)***
- **Stream loadings from NPS, PS**

Contaminant Fate Model

- Sediment transport
- Contaminant transport
- Contaminant chemistry in river and sediment bed

What does this get us?

- Bounds on the predicted environmental concentrations of AgNPs and reaction byproducts
  - Do we exceed water quality standards or toxicity thresholds?
  - What are the expected loadings to the estuary?
- Understanding of the relative impact of point and non-point sources on river and bed concentrations
  - Comparison of alternative land use best management practices on the reduction of stream loadings
  - How does land type (e.g., degree of urbanization) affect loadings?
- Understanding of where AgNPs accumulate and the impact of transient bed storage on fate
- Framework generalizable to other metal and metal oxide NPs (CuO, ZnO)
- Ability to include biouptake and ecotox submodels in the future

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Thank You

Acknowledgements

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References

1. *Analysis of Consumer Products, Nanotechnology Project*; Project on Emerging Nanotechnologies, Woodrow Wilson International Center for Scholars, 2012; www.nanotechproject.org/inventories/consumer/analysis_draft/. **2012**.

2. Mueller, N. C.; Nowack, B., Exposure modeling of engineered nanoparticles in the environment. *Environ Sci Technol* **2008,** *42*, (12), 4447-4453.

3. Gottschalk, F.; Sonderer, T.; Scholz, R. W.; Nowack, B., Modeled environmental concentrations of engineered nanomaterials (TiO2, ZnO, Ag, CNT, fullerenes) for different regions. *Environ Sci Technol* **2009,** *43*, (24), 9216-9222.

4. Kaegi, R.; Voegelin, A.; Sinnet, B.; Zuleeg, S.; Hagendorfer, H.; Burkhardt, M.; Siegrist, H., Behavior of metallic silver nanoparticles in a pilot wastewater treatment plant. *Environ Sci Technol* **2011,** *45*, (9), 3902-3908.