Watershed Modeling for Nanosilver Risk Assessment

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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 is the largest and fastest growing application of nanotechnology in consumer goods\(^1\)

- Broad-spectrum biocide
  - High surface-to-volume ratio $\rightarrow$ rapid release of toxic Ag\(^+\)

- Fate and transport models needed to assess risk
Previous Work

Motivation

1. Environmental transformations determine nanosilver bioavailability and toxicity

Toxicity unknown ("particle effect?")

\[
\begin{align*}
\text{Ag}^0 & \xrightarrow{O_2, S_2} \text{Ag}_2S \text{ shell} \\
& \quad \text{(reduces dissolution)} \\
\text{O}_2 & \xrightarrow{S^{2-}} \text{Ag}_2S \\
\text{Ag}_{d^+} & \quad \text{Highly toxic, bioavailable} \\
\text{Ag}_{p^+} & \quad \text{"solid phase partitioning"} \\
& \quad \text{Non-toxic, not bioavailable}
\end{align*}
\]

2. Nanosilver aggregates with sediments. Sediment co-transport (advection, settling) and bed chemistry are key determinants of fate.
Adapt a conventional metal-sediment chemistry model (Di Toro et al., 1996) to describe chemical transformations of nanosilver in sediments.

**Conceptual Model**

**Previous work**

**Conceptual Model**

**FeS Model**

- Flux (J) of POC
  
  \[ \text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]
  
  \[ \text{FeS(s)} + \frac{9}{4}\text{O}_2 + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{FeOOH(s)} + 2\text{H}^+ + \text{SO}_4^{2-} \]

**Anoxic Layer**

- Particulate (Dₚ) & Diffusive Mixing (Dₐ)
  
  \[ 2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{S}^{2-} + 2\text{CO}_2 + 2\text{H}_2\text{O} \]
  
  \[ \text{Fe}^{2+} + \text{S}^{2-} \rightarrow \text{FeS(s)} \]

**Oxic Layer**

- Flux (J) of O₂, NPs (Ag⁰ core + Ag₂S shell)
  
  \[ \text{Oxidation:} \quad 2\text{Ag}^{0} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Ag}^{+} + \text{H}_2\text{O} \]
  
  \[ \text{Ag}_2\text{S (NP)} + 2\text{O}_2 \rightarrow 2\text{Ag}^{+} + \text{SO}_4^{2-} \]

  \[
  \text{Ag}_2\text{S (free)} + 2\text{O}_2 \rightarrow 2\text{Ag}^{+} + \text{SO}_4^{2-}
  \]

  \[
  2\text{Ag}^{+} + \text{FeS(s)} \rightarrow \text{Ag}_2\text{S (free)} + \text{Fe}^{2+}
  \]

  \[
  \text{Ag}^{+} \leftrightarrow \text{Ag} \equiv \text{POC, Ag} \equiv \text{FeOOH}
  \]

**Silver Model**

- Particulate (Dₚ) & Diffusive Mixing (Dₐ)
  
  \[ 2\text{Ag}^{+} + \text{FeS(s)} \rightarrow \text{Ag}_2\text{S (free)} + \text{Fe}^{2+} \]

  \[
  \text{Ag}^{+} \leftrightarrow \text{Ag} \equiv \text{POC, Ag} \equiv \text{FeOOH}
  \]

*Previous Work: Motivation | Objective | **Approach** | Key Findings*
**Conclusion 1:** Non-toxic Ag$_2$S 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$_2$S) AgNPs in the sediment may vary from 5 years to over a century depending on redox conditions

But this model can’t tell us ...

- Predicted environmental concentrations
- Strengths and weaknesses of alternative risk management strategies
Current Work
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.²³

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

runoff during storm events
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)
Modeling Nanosilver Transformations in Freshwater Sediments

Approach
**Conceptual Model**

**Hydrological Model**

- *land control files*
- *non-point sources*
- *Land Simulation*
- *river control files*
- *point sources*
- *River Simulation*

**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**

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

**Contaminant Fate Model**

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

**Approach**

- 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

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