Elucidating the Physicochemistry of NP Attachment to Surfaces: Implications for Environmental Transport

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What is Transport?

Porous Media
- Sand Filters
- Groundwater
- Soil & Sediment

Cross Media
- Deposition
- Aggregation state

All transport is affected by Aggregation state & Deposition

Membranes
Carboxylic Acids Dissaggregate nC$_{60}$ and Stabilize Smaller nC$_{60}$ Clusters

Implication:
Organic acids can lead to small nC$_{60}$ clusters whose mobility, toxicity, and physicochemical properties could differ from aq/nC$_{60}$

X. Chang and P.J. Vikesland, Virginia Tech
Factors Affecting Aggregation & Deposition

- **Physical Factors**
  - Size of NP and media (collector)
  - Energy input (e.g. mixing or porewater velocity)
  - Heterogeneity (physical and chemical)

- **Chemical Factors**
  - pH
  - Ionic strength and composition
  - NOM and organic acids
    - type, concentration, conditions of exposure
  - Engineered surface coatings
    - Surfactants, polymers, and polyelectrolytes
  - Biological modifications by EPS

Colloid Science

Less Understood
“Compartments” Approach to Determining Distribution of Environmental Contaminants
Properties needed to Assess the Distribution of Organic Pollutants

<table>
<thead>
<tr>
<th>Chemical Properties</th>
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# Properties needed to Assess the Distribution of Environmental Pollutants

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## Environment Properties

| $f_{oc}$, compartment volumes | ? |
## Properties needed to Assess the Distribution of Environmental Pollutants

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<th>Chemical Properties</th>
<th>Nanomaterials (e.g. C\textsubscript{60})</th>
<th>Nanomaterials (proposed)</th>
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<tr>
<td>Vapor Pressure ((P_{\text{sat}}))</td>
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</tr>
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<td>Agglomeration state, Dispersion stability</td>
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<tr>
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<td>Interfacial behavior (deposition)</td>
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<td>(f_{\text{oc}}), compartment volumes</td>
<td>?</td>
<td>Ionic strength, ionic composition, pH, mixing, (f_{\text{oc}}), mineral surface</td>
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To predict transport we need to know:

- Attachment efficiency ($\alpha$) and how this varies with:
  - pH, Ionic strength, ionic composition, size
  - Adsorbed NOM and other organic macromolecules
  - NP surface chemical composition, i.e., mineral phases and organic matter
  - Biological surface (collector) composition
Current State-of-the-Art

• Aggregation
   Widely studied (1000’s+ papers)
   Colloid and flocculation science

\[ \alpha = \frac{1}{W} = \frac{k_a}{k_{a,\text{fast}}} \]

 Chemistry of the problem \( \alpha \) is handled empirically or stochastically
 Predicting the effects of NOM and adsorbed macromolecules on \( \alpha \) and \( D_f \) is not possible
Aggregation state-of-the-art

• Measure
  ○ Particle size and aggregation kinetics by light scattering
  ○ Electrophoretic mobility
  ○ All as a function of [salt]

• Model attachment efficiency with DLVO
  ○ Hydrodynamic model *assumed*

Chen and Elimelech, 
*Langmuir* 22 10994, 1996
Models for particle aggregation

Collision rate constants

Rectilinear Model

Intermediate model

Curvilinear Model

Smoluchowski, 1917

Veerapaneni and Wiesner, 1997

Han and Lawler, 1992

Coalescing spheres

Porous aggregates
Deposition State-of-the-art

Glass beads
Sand
Model Soil
Soil

\[ \alpha = \frac{\eta}{\eta_o} - \ln\left( \frac{C_e}{C_o} \right) \left( \frac{4a_c}{3(1 - n)\eta_o} \right) \]

Saleh et al., 2008 Environ. Sci. Technol. 42 3349.
Deposition State-of-the-art

- **QCM-D**
  - Quartz Crystal Micro-balance with Dissipation
  - Change in frequency of crystal oscillation indicates adsorbed mass
  - Energy dissipation indicates structural properties of adsorbed layer
    - Determined from time for energy dissipation after power is shut off
  - Many metal-oxide coated quartz crystals now available
    - Highly idealized systems

Most Nanomaterials are Coated

Coatings provide...
- Dispersion stability
- Functionality
- Targeting capabilities
- Biocompatibility
Coatings Dominate the Interaction
Energies between Particles

Attraction due to $V_{vdw} + V_M$

Repulsion due to $V_{ES} + V_{osm} + V_{elas}$

$V_{osm}$ is strong repulsive force and results in agglomeration

Need to consider:
$V_{elas}, V_{osm}$
due to polyelectrolyte

Deposition Predictions need to include chemistry of surface coatings

\[ \alpha_{pre} = 2.53 \times 10^{-3} N_{Lo}^{0.70} N_{E1}^{-0.31} N_{E2}^{3.51} N_{DL}^{1.35} \]  

(J. Colloid Interface Sci. 1999, 218, 488-499)

\[ N_{LEK1} = \frac{d_p d_m^2 \mu \Gamma N \alpha \rho_p}{\mu M_w} \]

Dimensionless number accounting for NP coating properties

\[ \alpha_{pre} = 10^{-1.35} N_{LO}^{0.39} N_{E1}^{-1.17} N_{LEK1}^{-0.10} \]
What is needed for success?

• Understand fate, then transport
  ⊟ Partitioning behavior first
    Show that $\alpha$ is predictive of partitioning
  ⊟ Rates of transfer between phases second

• Get some chemistry into $\alpha$ for NPs coated with organic macromolecules
  ⊟ Understand interface (2 to 3 nm)
  ⊟ Effect of pH, ionic strength, ionic composition, surface properties (e.g. charge), NP size
  ⊟ Need models that include polydispersity and disaggregation
What is needed for success?

• Understand attachment to biological surfaces
  - Bacteria, plant roots, etc.
  - May strongly affect bioavailability
• Understand transformations that affect NP aggregation and deposition
  - Redox reactions, biological reactions, condensation of organic matter
  - Numerical models for NP-macromolecule interactions
    Kinetic rather than thermodynamic
Questions?
Objective: Determine the effect secondary organic acid coatings on nanoparticles emitted into the lower atmosphere

• Results:
  - Measured PSL particle growth in presence of a-pinene and ozone
  - Model predicts 5 to 10-nm growth of SOA per hour

• Implication:
  - NP properties in soil and water determined by coating properties

Neil Donahue and Erica Trump-CMU
NP Attachment and Deposition

\[ \alpha = -\ln \left( \frac{C_e}{C_o} \right) \left( \frac{4a_c}{3(1-n)\eta_o} \right) = \frac{\eta}{\eta_o} \]

- Objectives:
  - Develop models for NP attachment linear combination of surfaces
  - Include chemistry of adsorbed macromolecules
  - Determine benchmarks for mobility based on measureable NP properties
Research Activities

Transport (Mobility Index) (Models)

Aggregation (size effect) (Models)

Reactivity (e.g. ROS)

NP-Macromolecule Interactions (NOM, polyelectrolytes, DNA, proteins)

NP-contaminant Interactions (metals, organics)

Environmental Transformations

Abiotic Physico-chemical (Photolysis, oxidation, reduction, dissolution)

Biological (microbial and higher trophic level organisms)

(Bioavailability and Toxicity) (Ecological Response)
Surface Coatings Affect Attachment

- Inhibits Aggregation
- Charge Stabilization
- Steric Stabilization

Inhibits Deposition

- Water
- Mineral surface

- Lowers Reactivity
- Decreases Toxicity

Phenrat et al., 2008
ES&T 43 1507
Empirical correlations developed to estimate $\alpha$ from particle and collector properties

Elimelech’s correlation (Water Res. 1992, 26, (1), 1-8)

$$\alpha = 2.57 \times 10^{-2} \, N_{col}^{1.19}$$

$N_{col}$ represents a force balance between van der Waals attraction and electrostatic repulsion.

Bai and Tien’s correlation (J. Colloid Interface Sci. 1999, 218, 488-499)

$$\alpha = 2.53 \times 10^{-3} \, N_{Lo}^{0.70} \, N_{E1}^{-0.31} \, N_{E2}^{3.51} \, N_{DL}^{1.35}$$

Also van der Waals attraction and electrostatic repulsion but includes velocity term.
Predicted deposition of electrostatically stabilized colloids

Additional Dimensionless Parameter

Determined from Buckingham-Pi Theory

\[ N_{LEK1} = \frac{d_p d_M^2 u_s \Gamma N a \rho_p}{\mu M_W} \]

Correction for [salt] on layer confirmation

\[ d_M = d_M^0 \left[ \frac{I}{I_{ave}} \right]^{-2/3} \]

Predicted \( \alpha \) for Coated NPs

\[ \alpha_{pre} = 10^{-1.35} N_{LO}^{0.39} N_{E1}^{-1.17} N_{LEK1}^{-0.10} \]

*Refs. for the relationship between \( d \) and \( I \)