Environmental Multimedia Distribution of Nanomaerials

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Fate & Transport Analysis

http://www.nanoinfo.org
Is this Engineered Nanomaterial Environmentally Safe?

Hazard Identification

Physicochemical Characterization

Exposure Assessment

In Vitro In Vivo Toxicity

In Silico Toxicity

Transport and Fate studies/Modeling

Monitoring

Environmental Concenrations

In Silico Toxicity

Mechanistic Conceptual

Quantitative Nano-SAR

Environmental Impact Assessment

Decision Analysis

• Dose-Response
• Hazard Thresholds

HT Exp. LT Exp.

Information/Data Management

Experimental Studies / Models

Environmental Impact Assessment

Product manufacturing & use approval

Product/process redesign

Exposure control
Engineered nanomaterials (ENMs) do not respect environmental phase boundaries

Range of exposure concentrations and releases of ENMs

Fate & transport (F&T) analysis (estimate environmental exposure concentrations):
  • Single medium models
  • Is the particle size distribution important?

Deterministic F&T models specific to ENMs

F&T exposure model selection: Complexity vs Uncertainty

Model validation
Environmental Intermedia Transport in a Multimedia System

- Wind Resuspension

Dry/Wet Deposition

Vegetation

Soil Matrix

Groundwater

Atmosphere

Particles

Aerosolization

Dry/Wet Deposition

Suspended Solids

Biota

Water

Runoff

Flooding
Intermedia Transport of ENMs is Governed by their PSD

Precipitation scavenging

Sedimentation

Dry deposition/collection

Wind resuspension

Aerosolization

Rain Collection Efficiency

Particle Diameter (µm)

Rain Collection Efficiency

Single Collector Efficiency

Soil Particle Collector Efficiency

Particle Diameter (µm)

Actual data (Radke et al., 1980)

Slinn (1984) -- t=0 s

River and Cohen (1986)

Slinn (1984) -- t=2000 s
Intermedia Transport of ENMs is Governed by their PSD

Precipitation scavenging

Sedimentation

Rain Collection Efficiency

Soil Particle Collector Efficiency

Nanoparticles:
- Transport processes are not constrained by phase equilibria
- Intermedia transport is affected by particle size
- Possible interfacial/interphase accumulation?
Exposure Concentrations: Modeling and Measurements (Review of State-of-the-Art in 2013)


Concentrations in surface water

Model predictions vs. Measured Concentrations

<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration (µg/L)</th>
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<tbody>
<tr>
<td>nano-TiO₂</td>
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Sediment

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Two Current Approaches:

- Material flow analysis to track ENM emissions & assess exposure concentration ranges
  - Heuristic estimates of transport rates

Deterministic Fate & Transport Models

Information on NP Releases is critical to assessing the potential environmental distribution of ENMs


http://www.nanoinfo.org
Lifecycle Environmental Assessment of the Releases of ENMs (LearNano Simulation Tool)

Information on NP Releases is critical to assessing the potential environmental distribution of ENMs

There is significant uncertainty/range in estimates of releases. Therefore → It is imperative to assess potential exposures due to low and high release rates.
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Caution: Would using an average or median values or upper/lower estimates be acceptable from regulatory or other applications?
Contribution of various ENMs use applications to environmental mass distribution in Los Angeles

Major contributions:
(i) Coatings, paints & pigments
(ii) Energy, environment
(iii) Cosmetics

Simulation using LearNano/ MendNano: 1-year simulation

Contribution of various ENMs use applications to environmental mass distribution in Los Angeles

Estimation of Releases requires compilation of data from multiples sources and where there may exist significant degree of data uncertainty & variability of various conditions (e.g., env., manufact., lifecycle)

Simulation using LearNano/ MendNano: 1-year simulation

Environmental Fate & Transport Analysis: 
Single-Medium Models

Atmospheric dispersion

- Extensive collection of models (analytical and numerical from box models to 3-D (some consider deposition)

Sediment transport in flowing streams

- Analytical and numerical models (typically consider a single size or a few size bins; recent models consider both homoaggregation, heteroaggregation and sedimentation)

\[
\frac{\partial C_i}{\partial t} + u \nabla C_i = \nabla \left( K_{ij} (\nabla C_i) \right) - R_i + S_i
\]

Agricultural drainage canal (SJV, CA) → Surface water

\[
\frac{\partial C_i}{\partial t} + u_j \frac{\partial C_i}{\partial x_j} = \frac{\partial}{\partial x_j} \left[ D_{E,i} \frac{\partial C_i}{\partial x_j} \right] + \frac{\partial}{\partial x_j} \left[ (\delta_j \nu_{s,i}) C_i \right]
\]
Single-Medium F & T Models

Contaminant transport in lakes

• Mostly numerical models (consider the impact of currents and waves, typically do not consider the complete PSD)

Colloidal/particle transport in soil

• Analytical and numerical models of colloidal filtration theories (bed/porous filter, colloid deposition/filtration)
Dispersion and Sedimentation in a Flowing Stream
(Continuous Discharge: A Simple 1-D model for a single species)

\[ \frac{C}{C_0} = \frac{V_{\text{sed}}}{V_{\text{river}}} \frac{L}{h} = \frac{t_{\text{conv}}}{t_{\text{sed}}} \]

\[ Pec = \frac{V_{\text{river}} L}{D_E} = \frac{t_D}{t_{\text{conv}}} \]

\( V_{\text{sed}} \) – sedimentation velocity
\( V_{\text{river}} \) – average current speed
\( L \) – length of stream
\( h \) – river depth
\( D_E \) – longitudinal dispersion coefficient

Concentration varies significantly downstream from the release point.

(Generalized solution in terms of dimensionless parameters)

Increasing Da

Lower Pec

(1,1)

(10,1)

(10,10)

(10,100)

(1,10)

(1,100)

\( \infty \)
Spatial Explicit F&T Modeling of Nanoparticles in a Flowing Stream

  - Integration of the Smoluchowski Coagulation Equation with the DUFLOW Modeling Studio for 1-D simulation of hydrology + solute F&T in an open channel.

Simulations: River Dommel

Initial Conc: 10 ng/L

**Heterogeneous Channel Flow**

**Homogenous Channel Flow**

5 Particle bins
Aquatic Stream Model for ENMs (Water, Sediment, NPs, SPM)

Rhine river model: TiO₂ Case study

- Series of linked aquatic compartments (approximates finite-difference approach)
- Considers NP particle size distribution (PSD)
- Suspended particulate matter (SPM) PSD: log-normal distribution
- Use of attachment efficiency ($\alpha_{\text{het-agg}}$)

Approach can in principle be extended to include additional compartment and transport processes

_Praetorius et al., 2012, 46 (12), 6705–6713_2012
Aquatic Stream Model for ENMs (Water, Sediment, NPs, SPM)

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Stream Dynamics Fate & Transport Model for Silver and ZnO NPs (James River Basin, Virginia)


“Coupled the James River Basin (VA) portion of the Phase 5.3.2 Chesapeake Bay Watershed Model (WSM) to the USEPA’s water quality modeling suite WASP”

(a) “Agricultural runoff accounted for 23% of total metal stream loads from NPs.”

(b) “Average NP-derived metal concentrations in the sediment varied spatially up to 9 orders of magnitude, highlighting the need for high-resolution models.”
Examples of single Medium & Multimedia Model Equations for Particulate Matter

- **Convection-Diffusion-Reaction with Surface Collection**

\[
\frac{\partial C_i}{\partial t} + u \nabla C_i = \nabla \left( D_{E,i} \left( \nabla C_i \right) \right) - \nabla \left( \frac{D_{E,i} \cdot F_i}{k_B T} C_i \right) - R_i + S_i
\]

- **Transport of suspended solids (in water)**

\[
\frac{\partial C_i}{\partial t} + u_j \frac{\partial C_i}{\partial x_j} = \frac{\partial}{\partial x_j} \left[ D_{E,i} \frac{\partial C_i}{\partial x_j} \right] + \frac{\partial}{\partial x_j} \left[ (\delta_{j3} v_{s,i}) C_i \right] + R_i + S_i
\]

- **Compartmental Model:**

\[
\frac{d}{dt} [V_i C_{i,k}] = \left\{ \begin{array}{l}
\text{Adective flow} \\
\text{Reaction}
\end{array} \right\} U + \sum_{n=1}^{M} R_{i,k}^n + \sum_{j=1}^{P} \sum_{l=1}^{M} I_{i,j,k}^l + S_{i,k}
\]

\[
\text{Intermedia transport}
\]

- **Increased Complexity**

- **Ordinary Differential Equations**

- **Partial Differential Equations**
Homoaggregation and Heteroaggregation

Smoluchowski Coagulation Theory

\[ \frac{\partial n_k}{\partial t} = \frac{1}{2} \sum_{i=k-1}^{i=k-1} K_{ij} n_i n_j - n_k \sum_{i=1}^{\infty} K_{ik} n_i \]

Classical DLVO Theory + Extensions

\[ \Phi_{\text{Total}} = \Phi_{\text{vdW}} + \Phi_{\text{EDL}} + \Phi_{\text{HR}} + \Phi_{\text{ST}} \]

- \( n \) – particle number conc.
- \( K_{ij} \) – agglomeration frequency
- \( \Phi \) – interaction energy
- \( K_{ij} = \frac{\beta_{ij}}{W_{ij}} = \alpha_{ij} \beta_{ij} \)
- \( \beta_{ij} \) - collision frequency = \( f(\text{particle sizes}) \)
- \( \alpha_{ij} \) - sticking coefficient (attachment efficiency)
- \( W_{ij} \) – stability ratio = \( 1/\alpha_{ij} = f(\text{interaction energy}) \)

The Smoluchowski equation can in principle be used to model both homoaggregation and heteroaggregation by tracking the population balance.

- Direct time dependency.
- Suitable for integration with F&T models (time scales?)

Dynamic MC requiring time step calibration. Difficult to integrate with F&T models

Solution of the coagulation equation without having to assume constant \( \alpha \) can be accomplished via a Constant-Number Direct Simulation Monte Carlo (DSMC) Method.

\( \alpha_{ij} \) - the attachment efficiency is a function of particle size; however, studies that solve the Smoluchowski equations directly are forced to assume a constant value for \( \alpha \) (data-derived).
Homoaggregation and Heteroaggregation

Smoluchowski Coagulation Theory

\[ \frac{\partial n_k}{\partial t} = \frac{1}{2} \sum_{i=k}^{i-k-1} K_{ij} n_i n_j - n_k \sum_{i=1}^{\infty} K_{ik} n_i \]

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Illustration of Simulation Results for NP Agglomeration

The Constant Number/Concentration Monte Carlo Simulation Approach can accommodate non-DLVO interactions
- The challenge is in developing/defining fundamental analytic expressions for such interactions

$pseudo R^2 = 0.96$
MAPE = 10.8%

primary diameter = 30 nm (SiO₂)
Monte Carlo Simulations of NP Aggregation

Example: \( \text{CeO}_2 \) (20 ppm; 24 h) Aqueous suspension

For the relatively narrow primary size range (8-40 nm):

NP primary size ↑ → PSD tail of small aggregates ↑
Average NP aggregate size (in suspension) ↓

Which exposure/dose metrics are most relevant?

- Number concentration (specific sizes), mass/volume, area/volume

Deterministic F&T Models and their Resource Requirements

- Spatial Models $[C=C(x,t)]$
- Hybrid Compartmental-Spatial Models $[C=C(x,t) \text{ and } C=C(t)]$
- Compartmental Models $[C=C(t)]$

- Dependence of concentrations on position/location
- Site-specific scenarios

Steady-State Models $[C \neq C(t)]$  Dynamic Models $[C=C(t)]$
Deterministic F&T Models and their Resource Requirements

- Spatial Models \[ C = C(x,t) \]
- Hybrid Compartmental-Spatial Models \[ C = C(x,t) \text{ and } C = C(t) \]
- Compartmental Models \[ C = C(t) \]

- Spatially averaged concentrations (primarily regional scale)
- First tier analysis
- Provide source input to media-specific spatial models
- Integrate with lifecycle analysis

Steady-State Models \[ C \neq C(t) \]  Dynamic Models \[ C = C(t) \]
Deterministic F&T Models
and their Resource Requirements

- Spatial Models \([C=C(x,t)]\)
- Hybrid Compartmental-Spatial Models \([C=C(x,t)\text{ and } C=C(t)]\)
- Compartmental Models \([C=C(t)]\)

Fundamental spatial transport models exist, but need to be adapted to account for NPs agglomeration, association with ambient matter and their potential unique physical, chemical and bio-transformations

<table>
<thead>
<tr>
<th>No. Parameters</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increasing Number</td>
<td>Regional/global/local (( &gt;0.1 \text{ km}^2 ))</td>
</tr>
<tr>
<td></td>
<td>Regional/global (( &gt;1-10 \text{ km}^2 ))</td>
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Steady-State Models \([C\neq C(t)]\)
Dynamic Models \([C=C(t)]\)
Modeling the Environmental Distribution of Manufactured Nanomaterials (MNM)

MNM properties: (e.g., Particle size distribution, reactivity, solubility)

Transport Processes (Intermedia and within environmental media)

MNM Fate & Transport Model

MNM Source Release Rates

MNM Environmental Distribution, Concentrations, intermedia transport rates
Compartmental Aquatic Model (NP Persistence)

- USETox model adapted to NPs to estimate impact on aquatic environments
- Accounts for PSD
- Utilizes attachment efficiency
- Assess persistence of NPs
- Partially empirical
- Requires calibration for specific NPs

Multimedia F&T Models for ENMs

MendNano/LearNano
- Considers SPM and complete PSD
- Self-preserving SPM PSD
- Unsteady-state
- Episodic processes (wet scavenging, wind-resuspension, runoff)
- Time-variable intermedia transport parameters
- Expandable web-based modeling platform (e.g., biota, vegetation)

SimpleBox4nano
- Considers SPM and coarse NP PSD
- Steady-state concentrations
- Episodic processes (i.e., rain scavenging) modeled as continuous processes
- Some intermedia parameters values are assumed constant

Meesters, et al., 2014
Liu et al., 2013/2014
Comparison of MendNano Predictions with Field and Measurements of PAH Concentrations and PCB Fluxes


Intermedia transport fluxes of particle-bound PCBs in Lake Michigan

Near Source
Regional Average

[BAP] Southeast Ohio

[PAHs]air Birmingham, UK

[BAP] in SoCAB
Multimedia Analysis of Environmental Release & Distribution of ENMs

Temporal concentration profiles for TiO$_2$ in LA

Major Contributors

Simulations for a large number of NPs in various regions suggest that exposures concentrations are likely to be in the ranges of:
- 0.0003 - 30 ng/m³ (air)
- 0.0058 - 150 ng/L (water)
- 0.0095 - 40 µg/kg (soil)
- 0.0054 - 100 mg/kg (sediment)
Estimates of the Range of Potential CeO$_2$ Multimedia Concentrations in Different Countries
Estimates of the Range of Potential CeO$_2$ Multimedia Concentrations in Different Countries

- Air: < ~ 0.1 ng/m$^3$
- Water: < ~ 3 ng/L
- Soil: < ~ 0.8 µg/kg
- Sediment: <~ 0.3 mg/kg
Example of Ranking of Environmental Impact Based on Exposure Concentrations and Probability of Being Identified as Toxic

- Exposure concentrations obtained via MendNano
- Toxicity probability obtained via QSAR analysis

\[ EI_i = \frac{\beta_i}{\max(\beta)} \]

\[ \beta_i = C_i \times P_i \]

\( P_i \) – probability of having an adverse biological response

EI can also be defined based on EC\( \lambda \)

\[ EI_{EC\lambda} = \frac{c_i}{EC\lambda} \]

MendNano simulations based on regional parameters for the Los Angeles

Selecting the Appropriate Fate & Transport Model

What is the purpose of the analysis?
e.g., regulatory compliance, priority settings, industrial, research, material design

What are the questions that need to be answered?

What is the required model resolution?
- Spatial: Site-specific? Regional?
- Temporal: Unsteady state? Steady state? Episodic scenarios?

What is the required level of accuracy w.r.t estimated exposure concentrations?

Was the model validated? Calibrated?
Model Complexity Trade-Off Diagram

- Risk of improper system representation
- Cost of obtaining a solution

Increased Cost

Increased Uncertainty

Increased Model Complexity

Decisions

Simple

Complex
Model Validation Pyramid

Integrated model

Sub-modules

Module components

Units/parameters

Face validity

Comparison with other models

Applicability domain

Event validity

Comparison with data

Sensitivity analysis & statistical validation

Parameter validation & model sensitivity

Mechanistic/empirical validity

Fundamental validity
Categories of Models and Validations

- **Increased understanding**
- **Increased data availability**

**Empirical (Data-driven) Models**
- **Statistical validation**
- **Exploratory Models/ Theoretical Developments**
  - **Conceptual validation** (partial validation of mechanisms)

**Detailed Mechanistic/ Deterministic Models**
- **Quantitative validation**
- **Theoretical / Deterministic Models**
  - **Qualitative validation** (component validation)
Exposure Modeling: Issues of Concern

- Uncertainties in release rates lead to uncertainties in exposure estimates.
- Reliable mechanistic models of intermedia transport are necessary.
- Parameter requirements, even for simple compartmental models, can be excessive and parameter values may not be readily available.
- Time scales for different processes can span several orders of magnitude.
- Comprehensive integration of all media is desirable (but represent a major challenge) to ensure proper mass conservation and system dynamics.
- Reusable model components will be required to respond to rapid changes in scientific approaches, computational needs and knowledge accumulation.
- Validation of models is a formidable task, particularly for multimedia assessment.
Exposure Modeling: Issues of Concern

Are uncertainties in exposure estimates significant relative to uncertainties in toxicity information?
\[
\frac{d}{dt} [V_i C_{i,k}] = (Q_i^{\text{in}} C_{i,k}^{\text{in}} - Q_i^{\text{out}} C_{i,k}) + \sum_{j=1}^{M} \sum_{l=1}^{P} I_{i,j,k}^l + \zeta_i K_{i,k}^r C_{i,k} V_{i,k} + \quad m_i \alpha(r_k, r_n) \frac{f(r_k) w(r_k)}{\int_0^\infty f(r) w(r) dr}
\]

\[
- K_{i,k}^s (C_s - C_{\text{dis}}) A_{i,k}^T + S_{i,k}
\]

\[
v_s = \frac{(\rho_p - \rho_f)(1 - \phi_i) \cdot g \cdot d_i^2}{18 \mu}
\]

\[
m_b(t) = m_b^o + (m_b^\infty - m_b^o) \left(1 - e^{-t/\tau}\right)
\]

\[
D = 0.1 \cdot h_{\text{mix}}^4 (-\kappa \cdot L_{\text{MO}})^{\frac{1}{3}} \cdot u^*
\]

\[
\vec{U} \cdot \nabla C = \nabla \cdot \vec{D} \nabla C
\]

\[
\vec{U} \cdot \nabla (\rho \vec{U}) = -\nabla p + \nabla \cdot \eta \nabla \vec{U}
\]

\[
\frac{d}{dt} m_i = 12 D (C_s - C_{\text{dis}}) \left(\frac{m_i}{\rho d_i^2}\right) \left(\frac{d_i}{d_{\text{pri}}}\right)^{\frac{df}{2}}
\]

\[
\tau = \frac{(V + P) T}{(1 - b) P + RT}
\]

\[
\frac{d}{dt} m_s = \sum_k I_{\text{dry,a,s,k}} + \sum_k I_{\text{wet,a,s,k}} + I_{\text{washoff,f,s}} - I_{\text{s,a}}^{\text{resusp}} - I_{\text{s,w}}^{\text{runoff}} + \zeta_s K_s^r C_s m_s + S_s
\]

\[
\frac{d}{dt} m_{\text{sed}} = I_{\text{w,sed}}^{\text{sedimentation}} - I_{\text{sed,sw}}^{\text{resusp}} + \zeta_{\text{sed}} K_{\text{sed}}^r C_{\text{sed}} m_{\text{sed}} + S_{\text{sed}}
\]