UNIVERSITY OF CALIFORNIA

UC CEIN Center for Environmental Implications of Nanotechnology

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Environmental Multimedia Distribution of Nanomaerials

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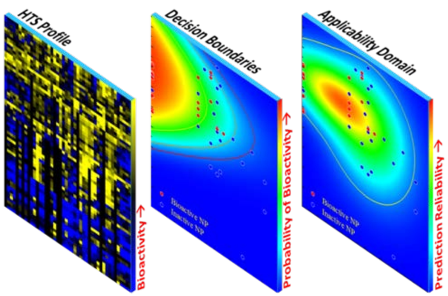
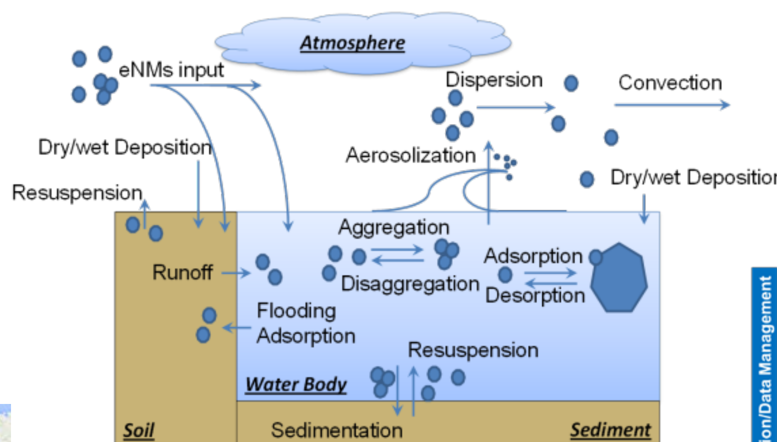
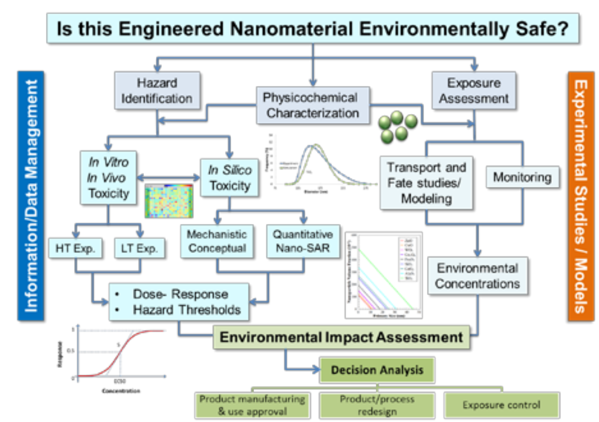


Models of ENM Toxicity

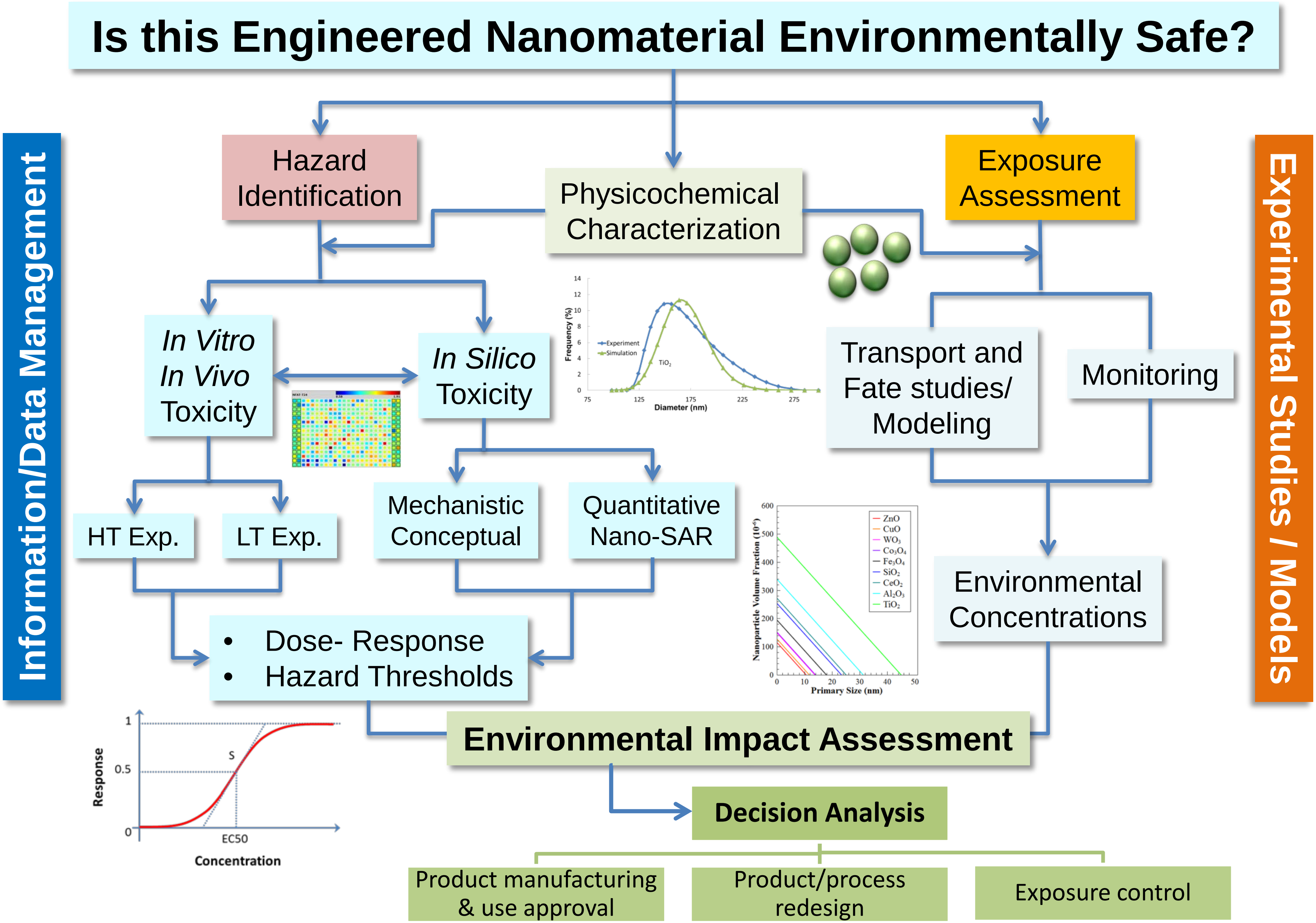


Fate & Transport Analysis



Environmental Impact Assessment

http://www.nanoinfo.org


Is this Engineered Nanomaterial Environmentally Safe?
Information/Data Management
Experimental Studies / Models
Hazard Identification
Physicochemical Characterization
Exposure Assessment
In Vitro In Vivo Toxicity
In Silico Toxicity
Frequency (%)
Experiment
Simulation
TiO2
Diameter (nm)
Transport and Fate studies/ Modeling
Monitoring
HT Exp.
LT Exp.
Mechanistic Conceptual
Quantitative Nano-SAR
Nanoparticle Volume Fraction (10⁻⁶)
ZnO
CuO
WO3
Co3O4
Fe3O4
SiO2
CeO2
Al2O3
TiO2
Primary Size (nm)
Environmental Concentrations
• Dose- Response
• Hazard Thresholds
Response
S
EC50
Concentration
Environmental Impact Assessment
Decision Analysis
Product manufacturing & use approval
Product/process redesign
Exposure control

Outline

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):

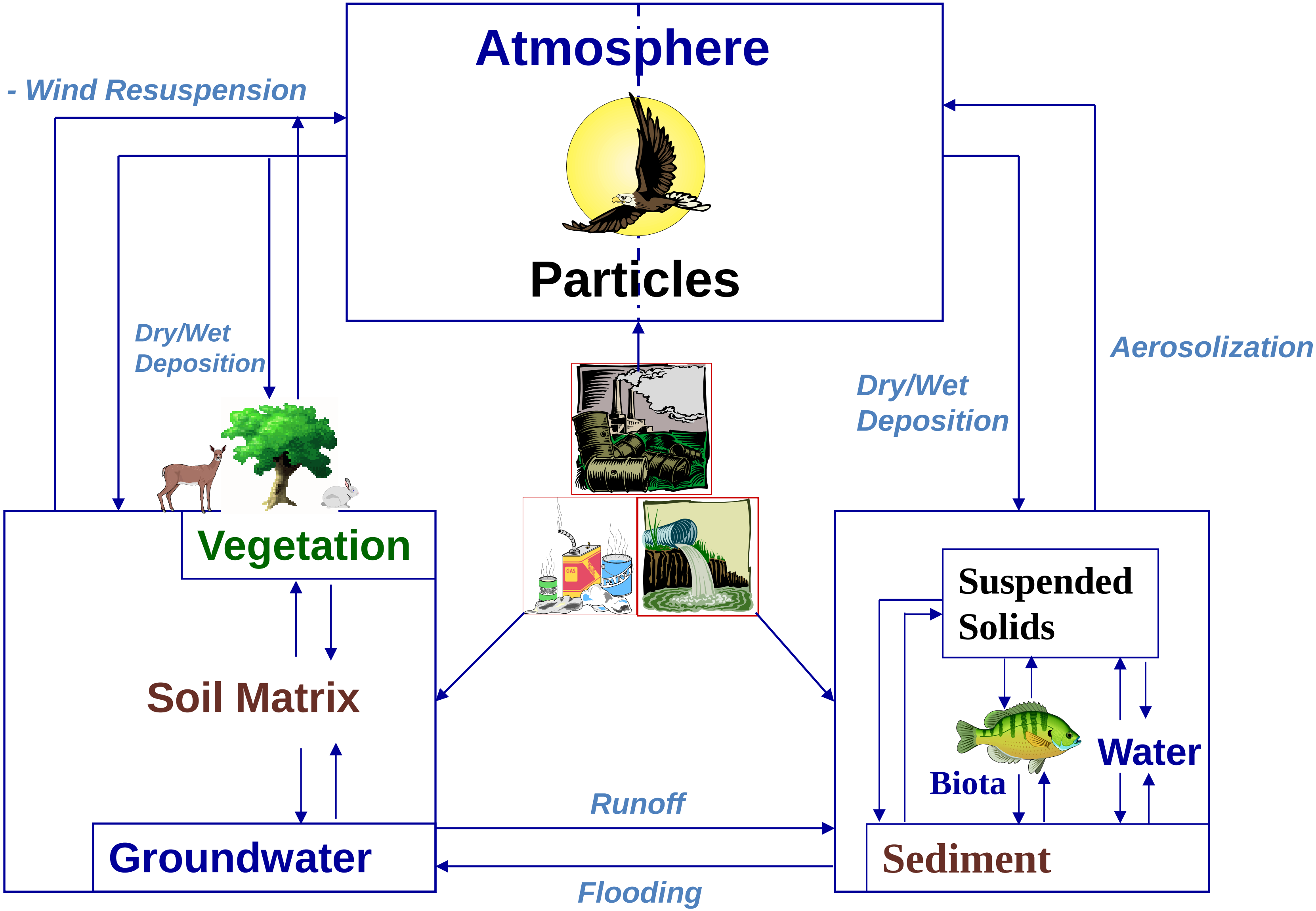
- Single medium models
- Is the particle size distribution important?

Deterministic F&T models specific to ENMs

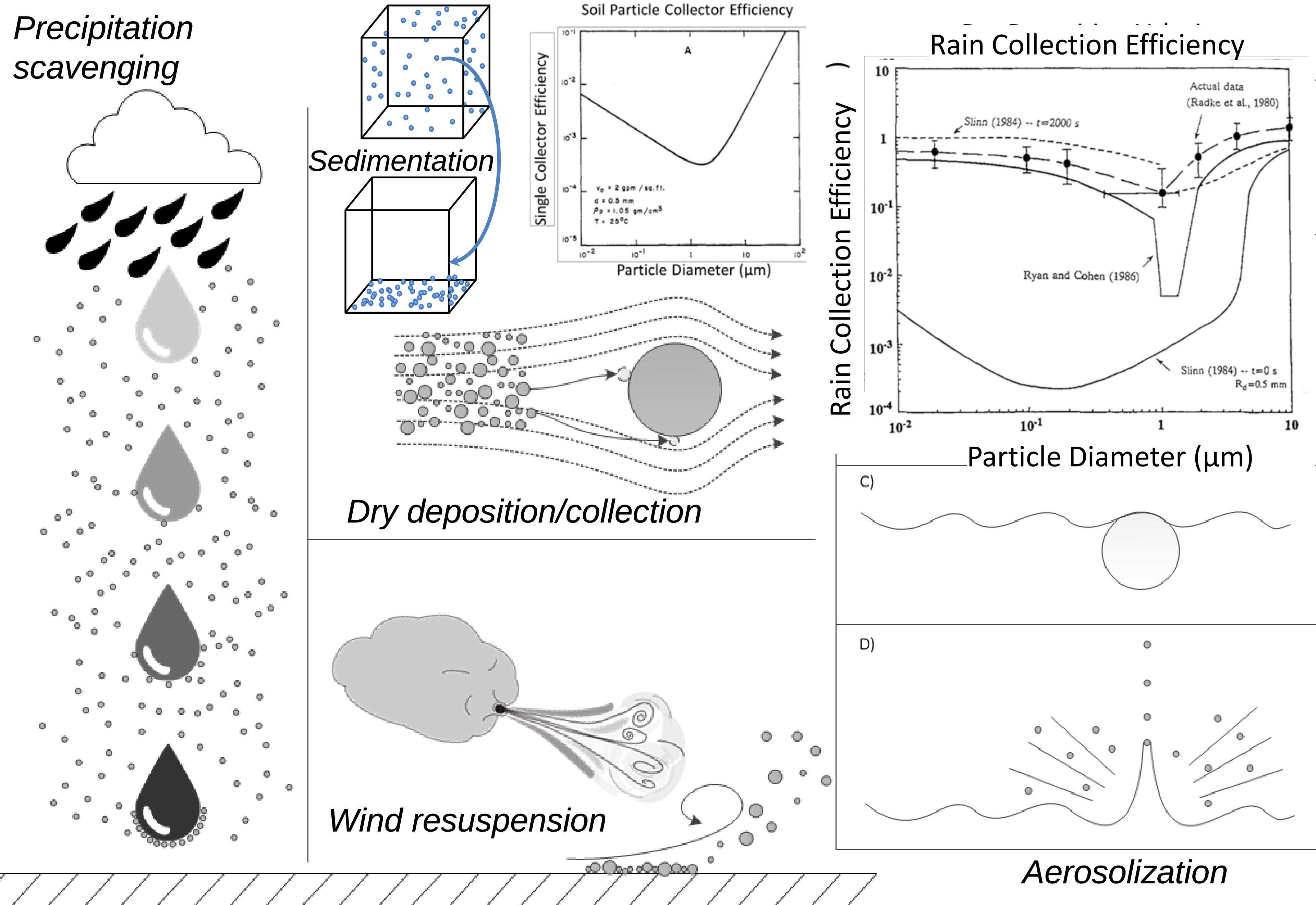
F&T exposure model selection: Complexity vs Uncertainty

Model validation

Environmental Intermedia Transport in a Multimedia System



Intermedia Transport of ENMs is Governed by their PSD



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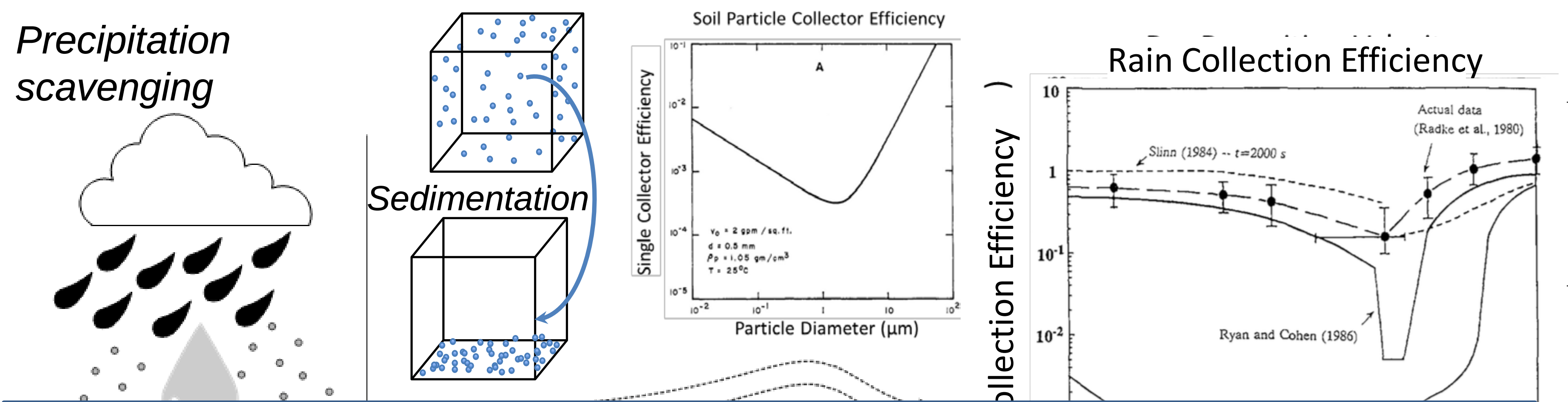
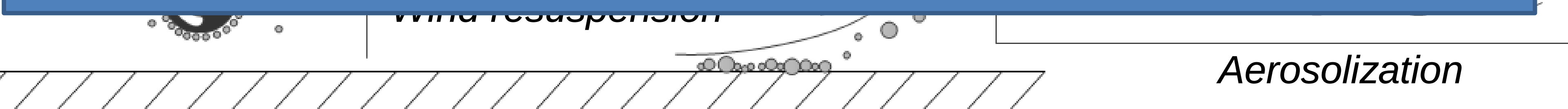


Nanoparticles:

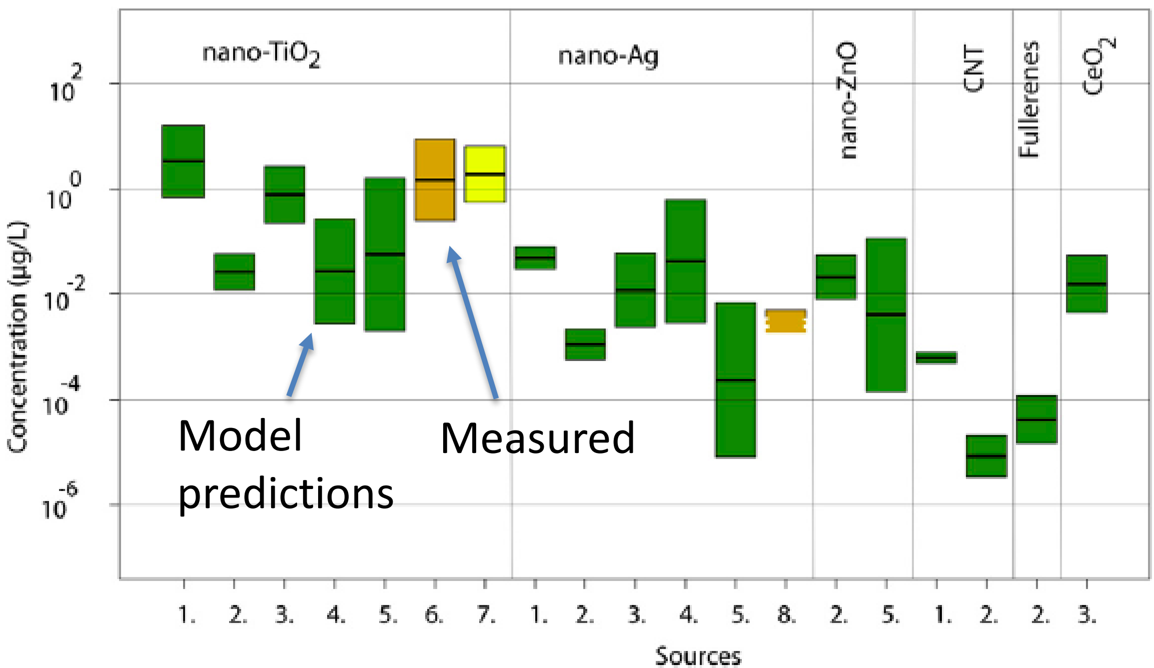
- Transport processes are not constrained by phase equilibria
- Intermedia transport is affected by particle size
- Possible interfacial/interphase accumulation?



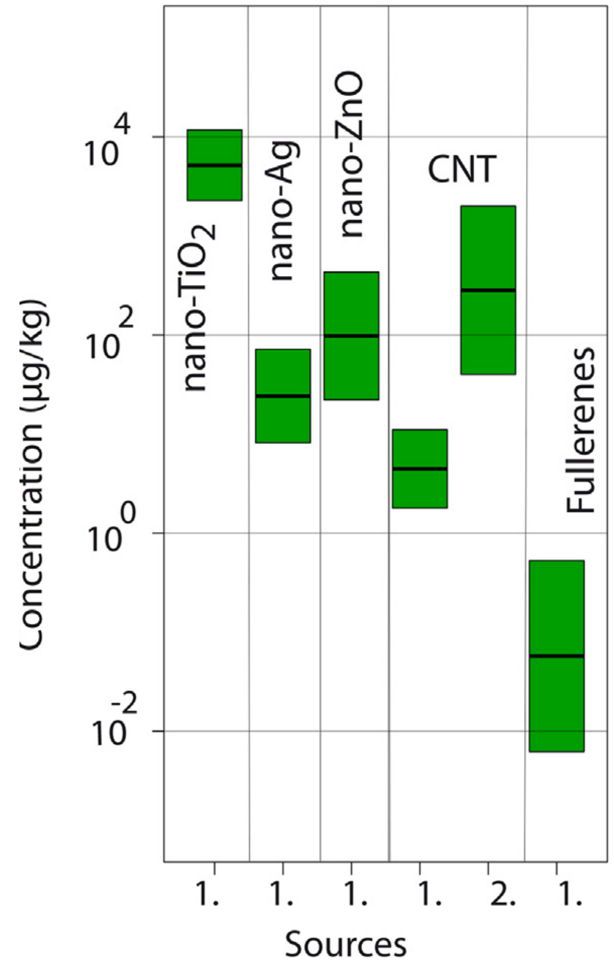
Exposure Concentrations: Modeling and Measurements (Review of State-of-the-Art in 2013)

<u>Review</u>: Gottschalk et al., Env. Poll., 181 (2013) 287-300

Concentrations in sur face water



Sediment



Gottschalk et al.,Env. Sci. Technol, 2009, 43, 9216-9222; ibid, Int.J.Env.Res. Public Health, 2015, 12, 5581-5602. (nine ENMs)

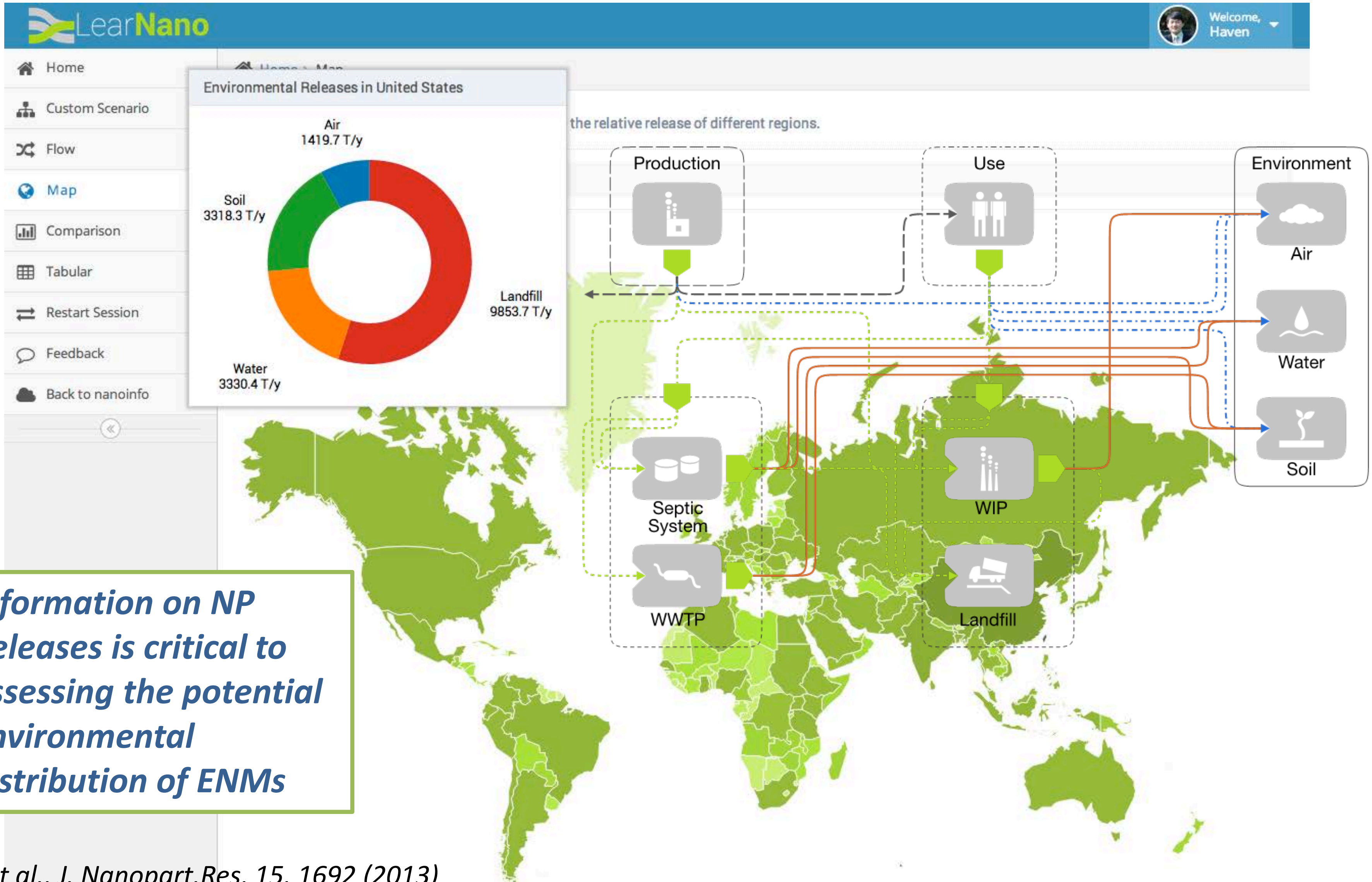
Two Current Approaches:

Material flow analysis to track ENM emissions & assess exposure concentration ranges

- Heuristic estimates of transport rates

Deterministic Fate & Transport Models

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

Keller et al., J. Nanopart.Res, 15, 1692 (2013)
Liu, et al., Beilstein J. Nanotech., 6, 930-951 (2015)

http://www.nanoinfo.org

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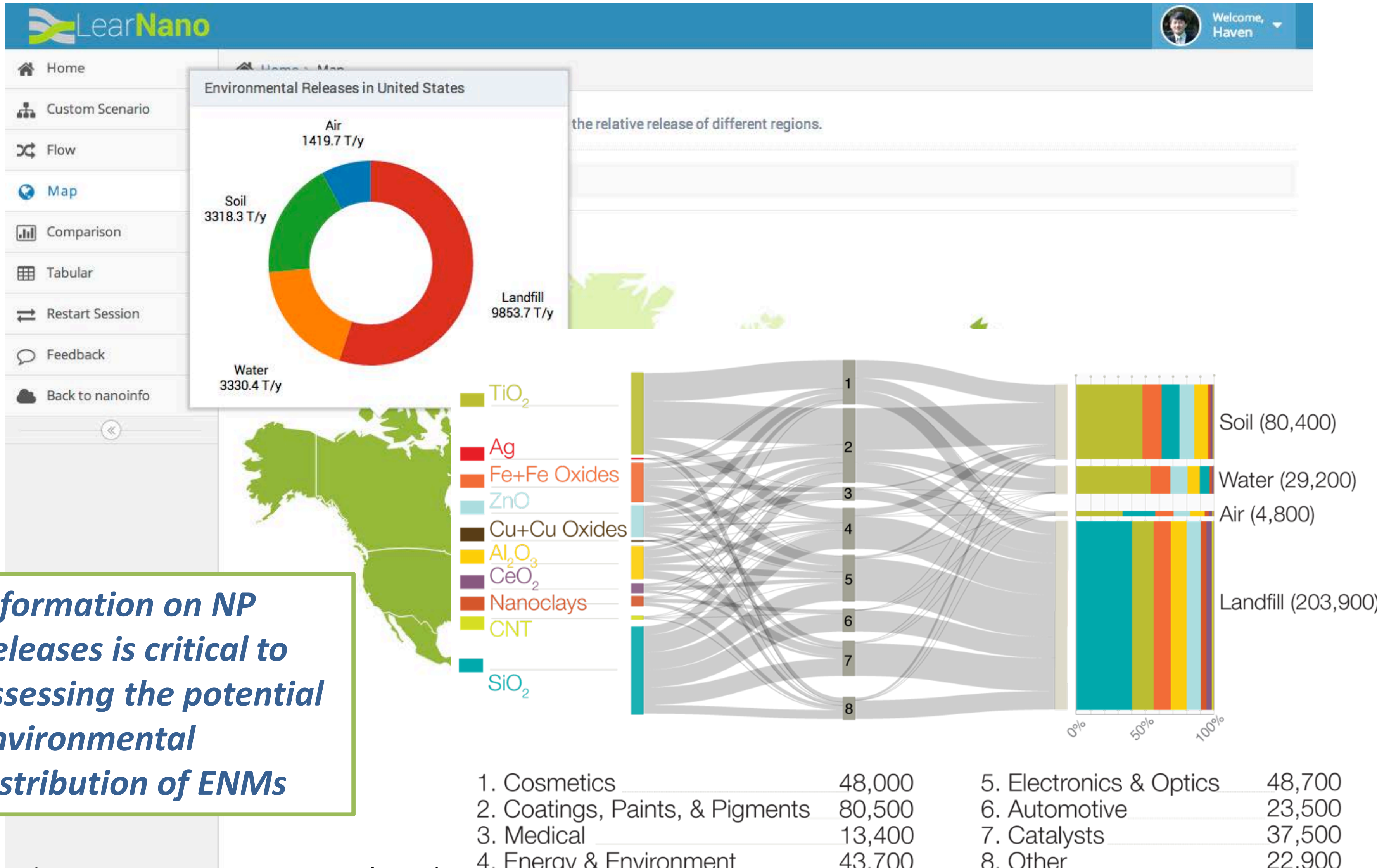

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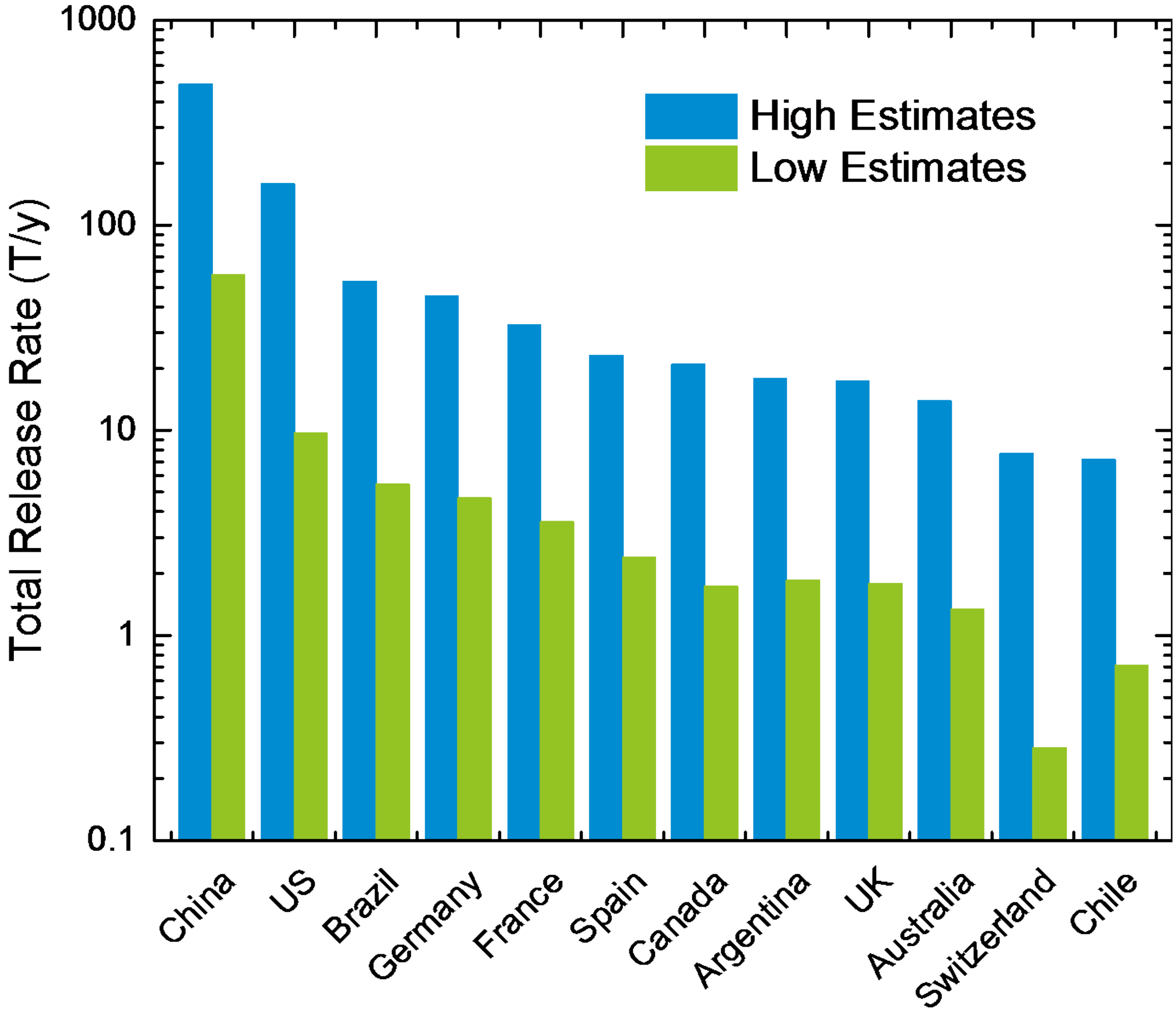
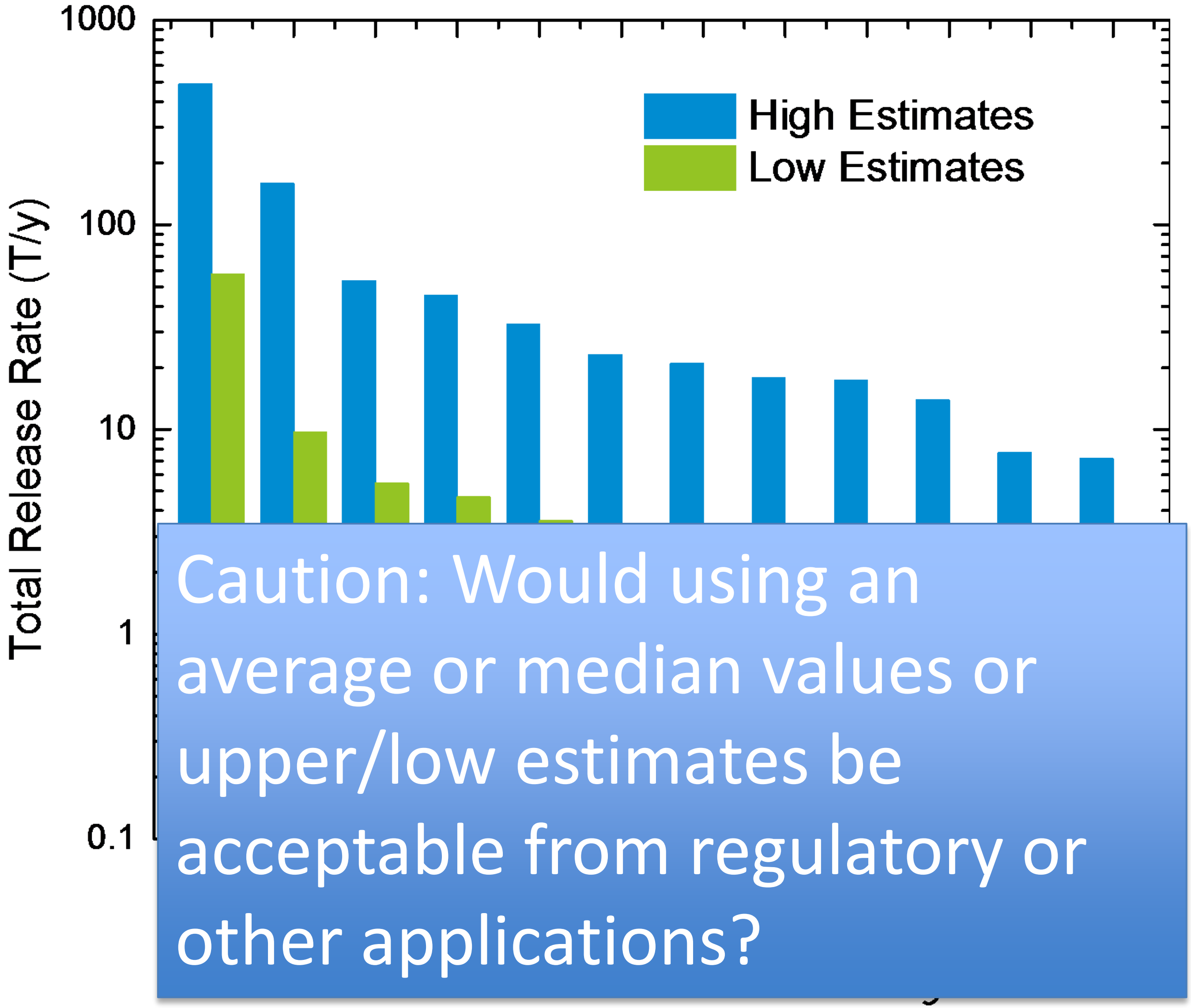
Illustration of LearNano Analysis: CeO_2 release rates in various countries



There is significant uncertainty/ range in estimates of releases

Therefore → It is imperative to assess potential exposures due to low and high release rates

Illustration of LearNano Analysis: CeO_2 release rates in various countries

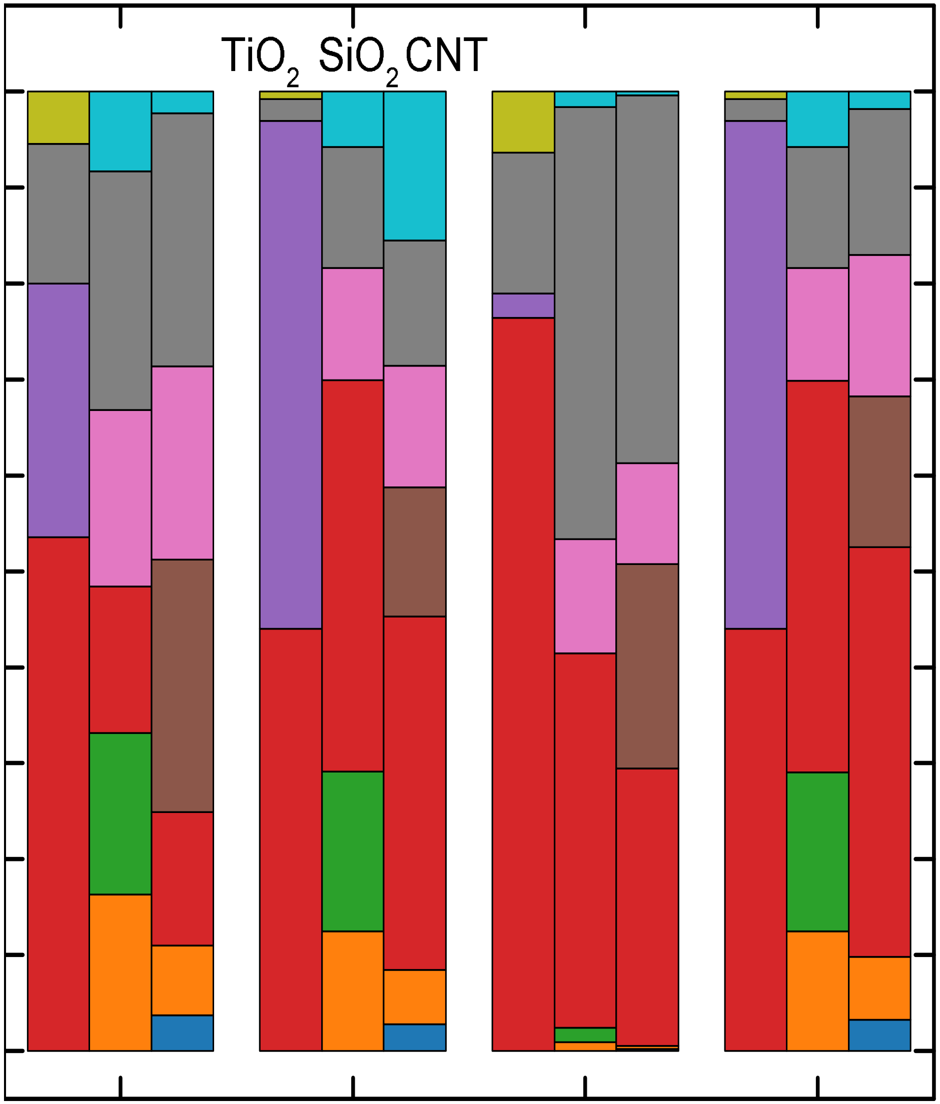


Caution: Would using an average or median values or upper/low estimates be acceptable from regulatory or other applications?

There is significant uncertainty/ range in estimates of releases

Therefore → It is imperative to assess potential exposures due to low and high release rates

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

Liu, et al., Beilstein J. Nanotech., 6, 930-951 (2015); ibid, Environ. Sci. Tech. , 48, 3281-3292 (2014).

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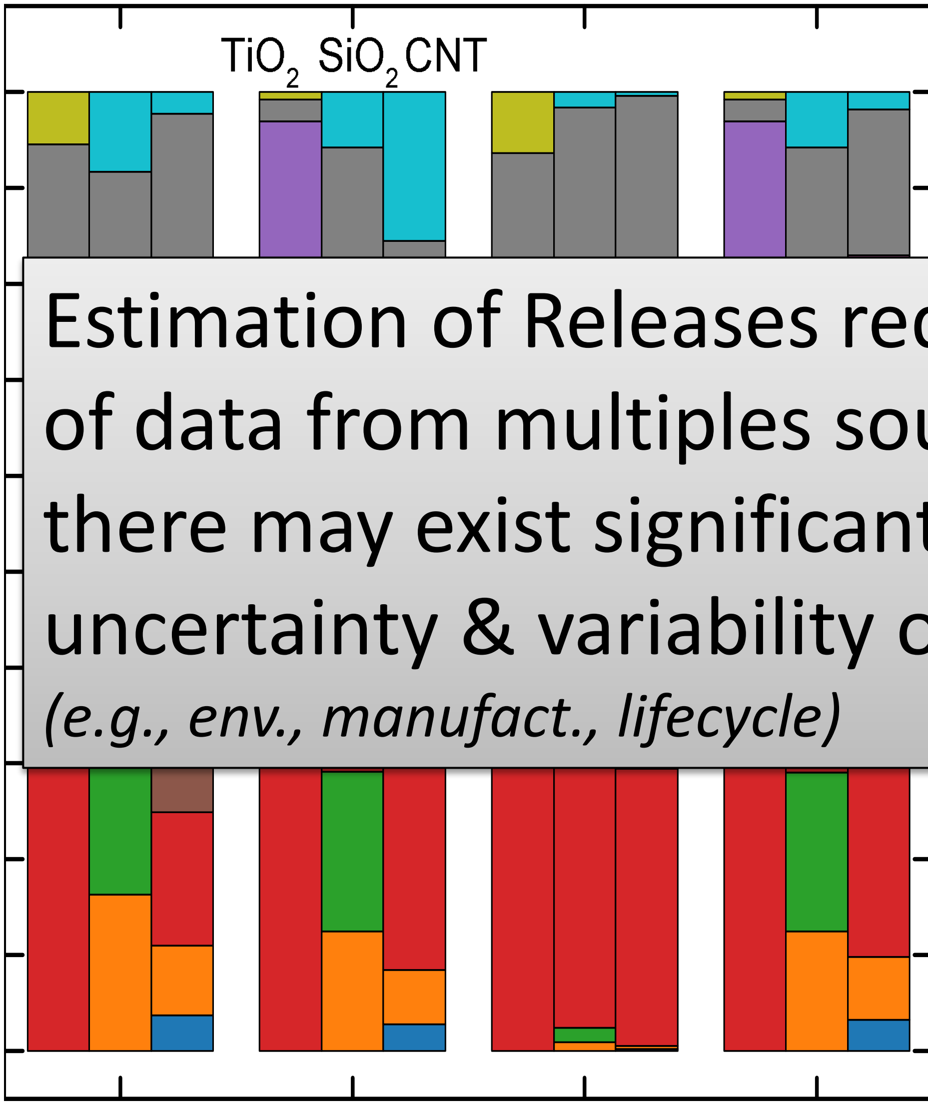

Estimation of Releases requires compilation of data from multiples sources and where there may exist significant degree of data uncertainty & variability of various conditions *(e.g., env., manufact., lifecycle)*

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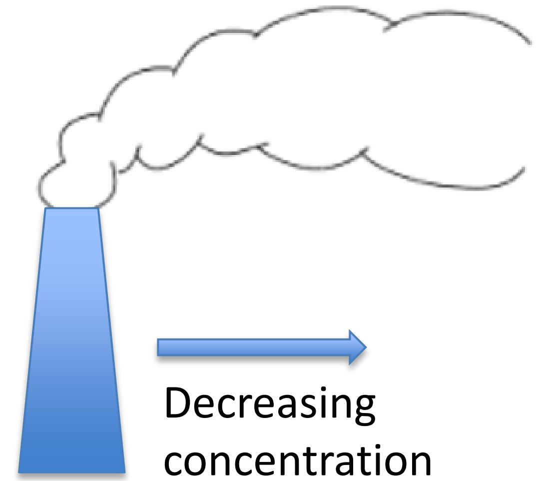
Environmental Fate & Transport Analysis: Single-Medium Models

Atmospheric dispersion

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



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

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)

$$\frac{\partial C_i}{\partial t} + u_j\frac{\partial C_i}{\partial x_j} = \frac{\partial}{\partial x_j}\left[D_{E,i}\frac{\partial C_i}{\partial x_j}\right] + \frac{\partial}{\partial x_j}\left[(\delta_{j3}\mathrm{v}_{s,i})C_i\right]$$

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)

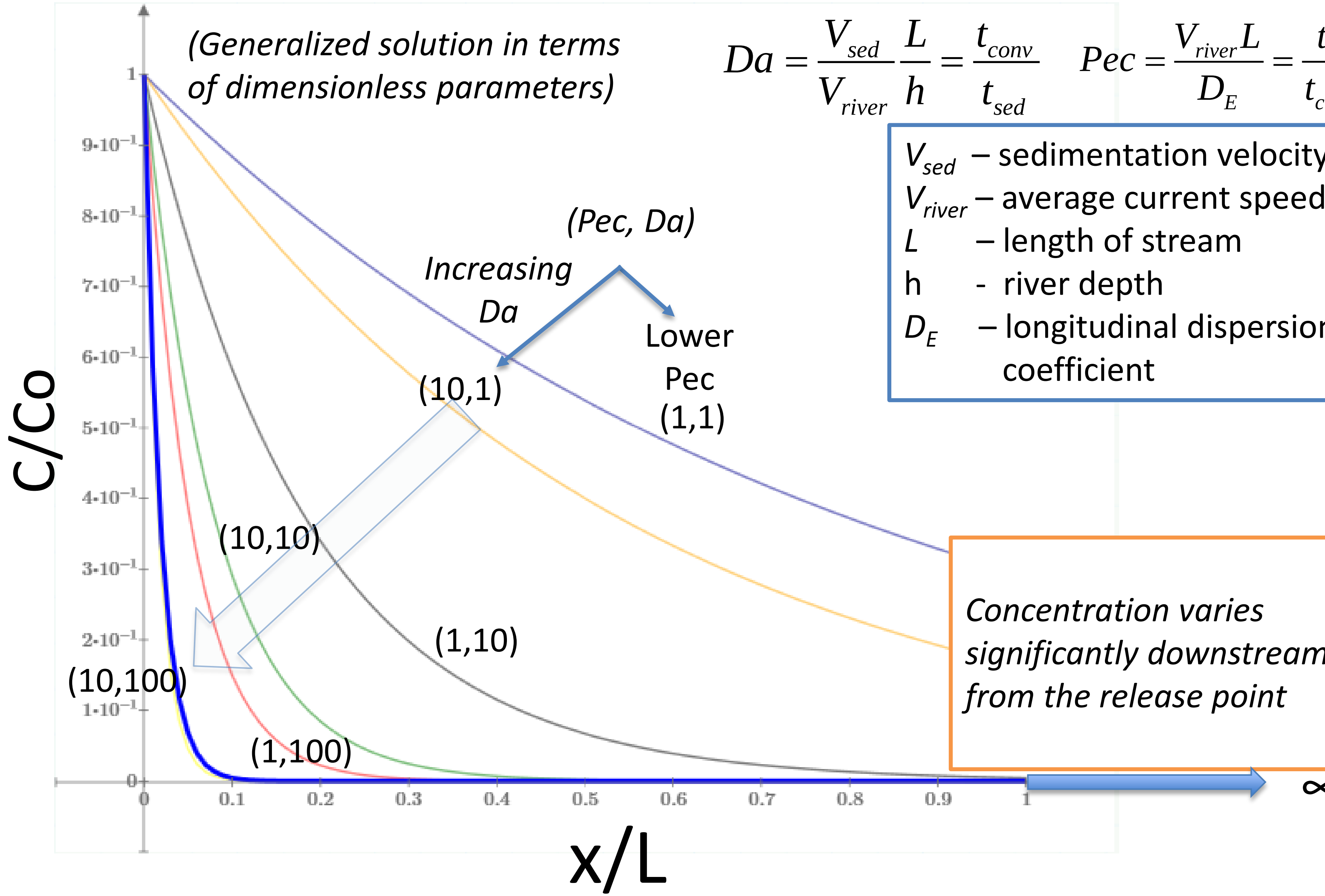
Dispersion and Sedimentation in a Flowing Stream

(Continuous Discharge: A Simple 1-D model for a single species)

(Generalized solution in terms of dimensionless parameters)

$$Da = \frac{V_{sed}}{V_{river}}\frac{L}{h} = \frac{t_{conv}}{t_{sed}} \qquad Pec = \frac{V_{river}L}{D_E} = \frac{t_D}{t_{conv}}$$

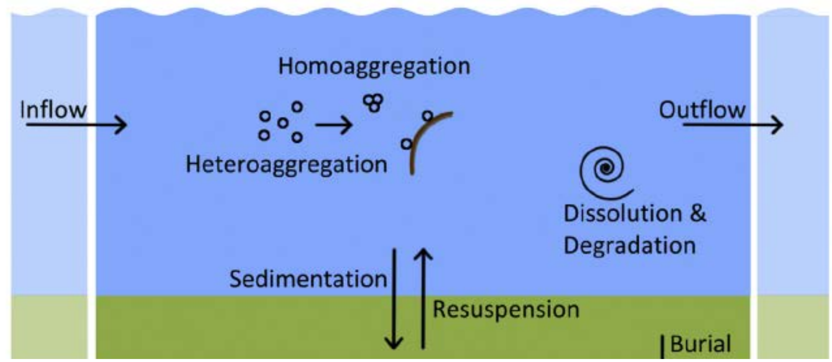
V_{sed} – sedimentation velocity
V_{river} – average current speed
L – length of stream
h - river depth
D_E – longitudinal dispersion coefficient



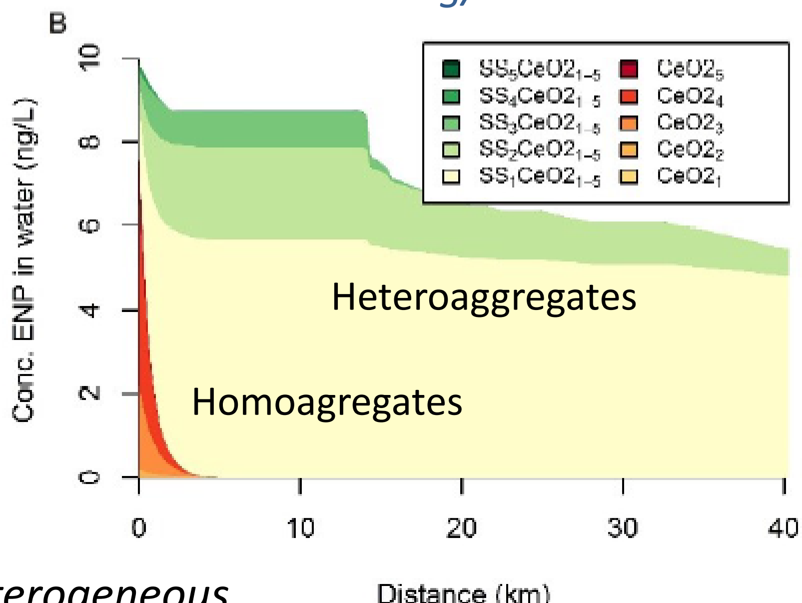
Concentration varies significantly downstream from the release point

Spatial Explicit F&T Modeling of Nanoparticles in a Flowing Stream

- *Quik, de Klein and Koelmans, Water Research, 80, 200-208 (2015)*:
  - 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



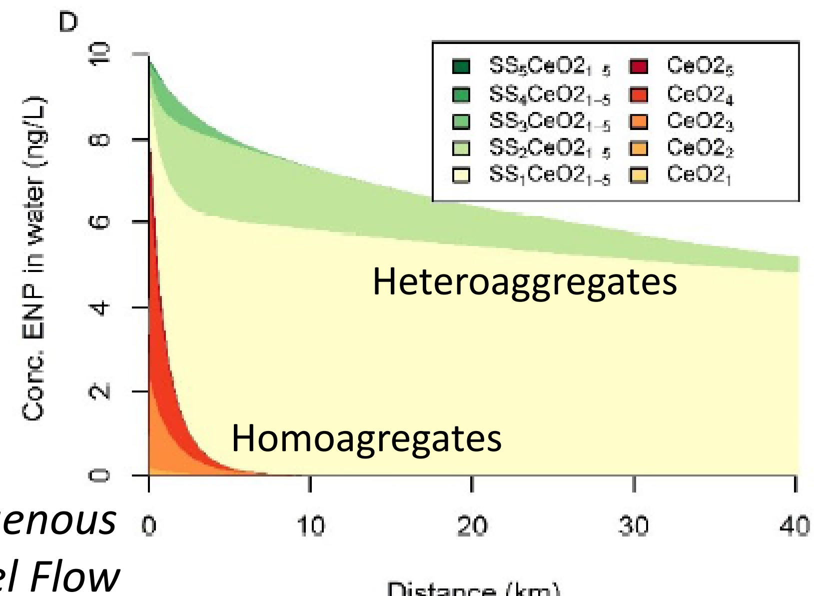
Initial Conc: 10 ng/L



Heterogeneous Channel Flow

5 Particle bins

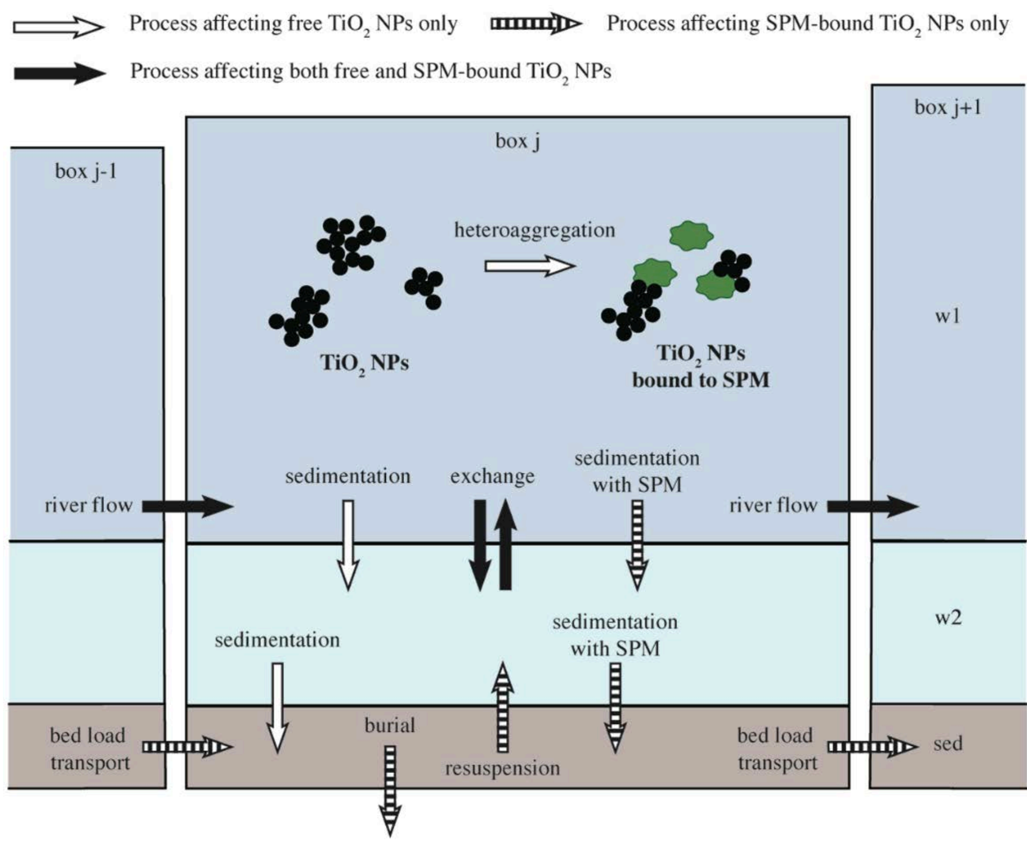
Homogenous Channel Flow



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

Rhine river model: TiO_2 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 ($\alpha_{het\text{-}agg}$)



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

Praetorius et al., 2012, 46 (12), 6705–67132012

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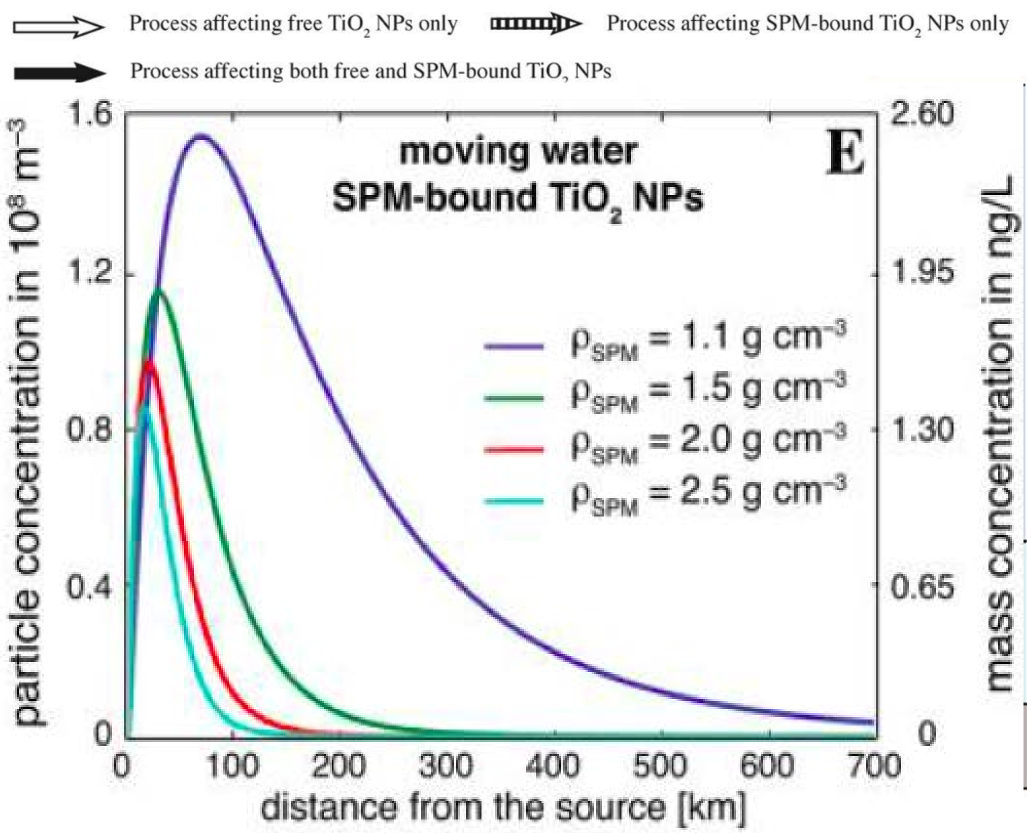

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Stream Dynamics Fate & Transport Model for Silver and ZnO NPs (James River Basin, Virginia)

Dale et al., Env.Sci. Technol., (2015), 49, 7285-7293)

"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*

$$\frac{\partial C_i}{\partial t} + \boldsymbol{u}\nabla C_i = \nabla\left(\boldsymbol{D_{E,i}}\left(\nabla C_i\right)\right) - \nabla\left(\frac{\boldsymbol{D_{E,i}} \cdot \boldsymbol{F}_i}{k_B T} C_i\right) \underbrace{-R_i}_{\text{Degradation}} + \underbrace{S_i}_{\text{Source}}$$

- *Transport of suspended solids (in water)*

$$\frac{\partial C_i}{\partial t} + u_j \frac{\partial C_i}{\partial x_j} = \frac{\partial}{\partial x_j}\left[D_{E,i} \frac{\partial C_i}{\partial x_j}\right] + \frac{\partial}{\partial x_j}\left[(\delta_{j\mathbf{3}} \mathrm{v}_{\mathrm{s,i}}) C_i\right] + R_i + S_i$$

Sedimentation
(3 – vertical Direction)

Partial Differential Equations

Increased Complexity

- *Compartmental Model:*

$$\frac{d}{dt}[V_i C_{i,k}] = \overbrace{(Q_i^{in} C_{i,k}^{in} - Q_i^{out} C_{i,k}^{out})}^{\text{Advective flow}} + \overbrace{\sum_{n=1}^{U} R_{i,k}^{n}}^{\text{Reaction}}$$

$$+ \underbrace{\sum_{\substack{j=1 \\ j\neq l}}^{M} \sum_{l=1}^{P} I_{i,j,k}^{l}}_{\text{Intermedia transport}} + \underbrace{S_{i,k}}_{\text{Source release}}$$

i – compartment
k - particle size bin

Ordinary Differential Equations

Homoaggregation and Heteroaggregation

Smoluchowski Coagulation Theory

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

Classical DLVO Theory + Extensions

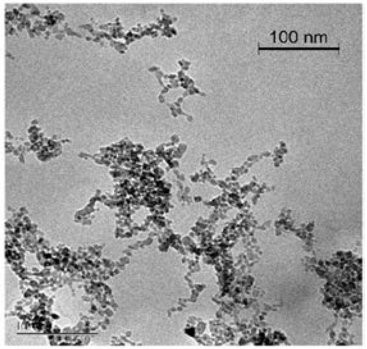
$$\Phi_{\text{Total}} = \Phi_{\text{vdW}} + \Phi_{\text{EDL}} + \Phi_{\text{HR}} + \Phi_{\text{ST}}$$

n – particle number conc.

K_{ij} – agglomeration frequency

Φ – interaction energy

$$K_{ij} = \frac{\beta_{ij}}{W_{ij}} = \alpha_{ij}\beta_{ij}$$



β_{ij} - collision frequency =f(particle sizes)

α_{ij} - sticking coefficient (attachment efficiency)

W_{ij} – stability ratio = $1/\alpha_{ij}$=f(interaction energy)

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

α_{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 α (data-derived)

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 α can be accomplished via a Constant-Number Direct Simulation Monte Carlo (DSMC) Method.

Homoaggregation and Heteroaggregation

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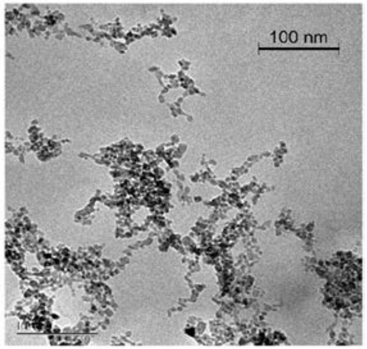

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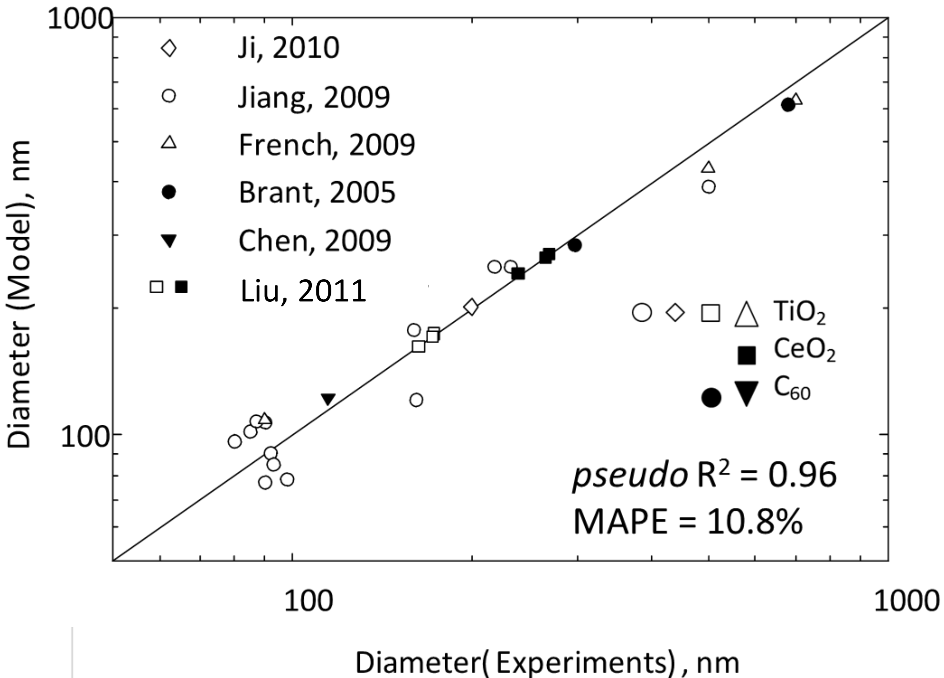
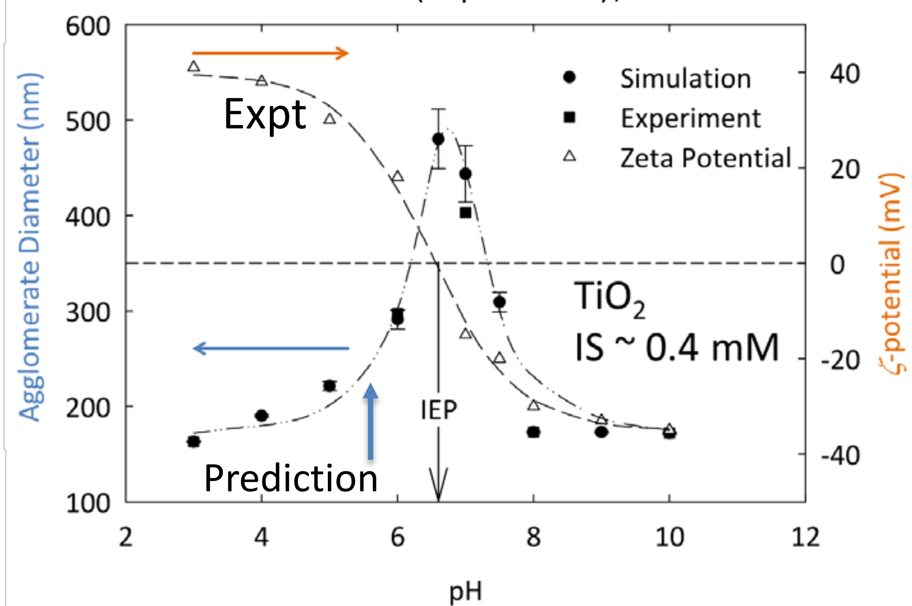
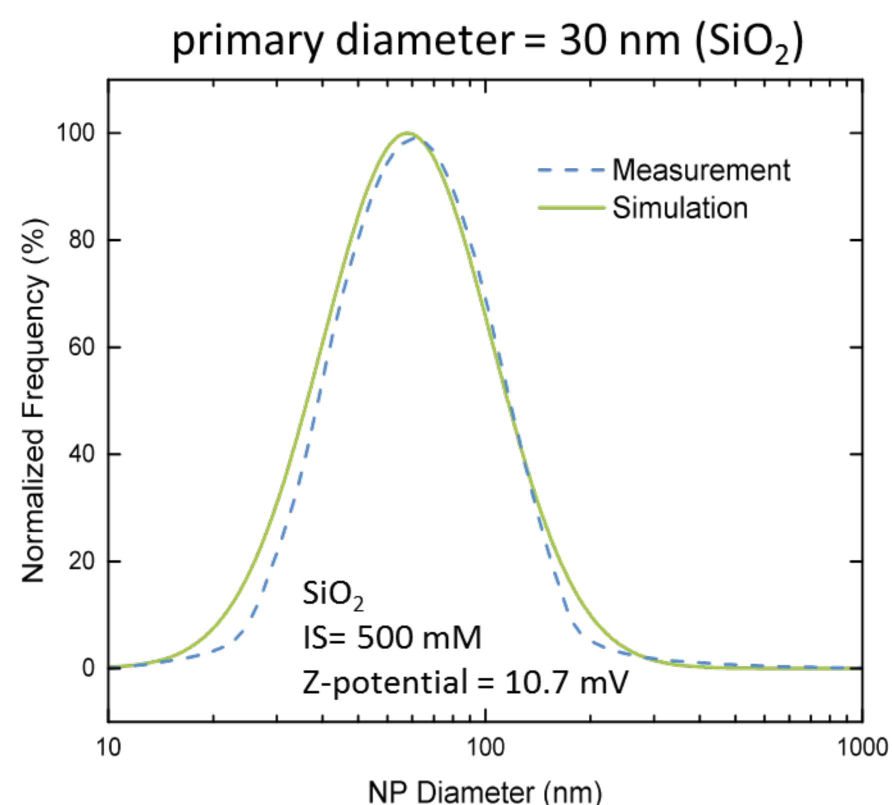
Illustration of Simulation Results for NP Agglomeration



The Constant Number/Concentration Monte Carlo Simulation Approach can accommodate non-DLVO interactions

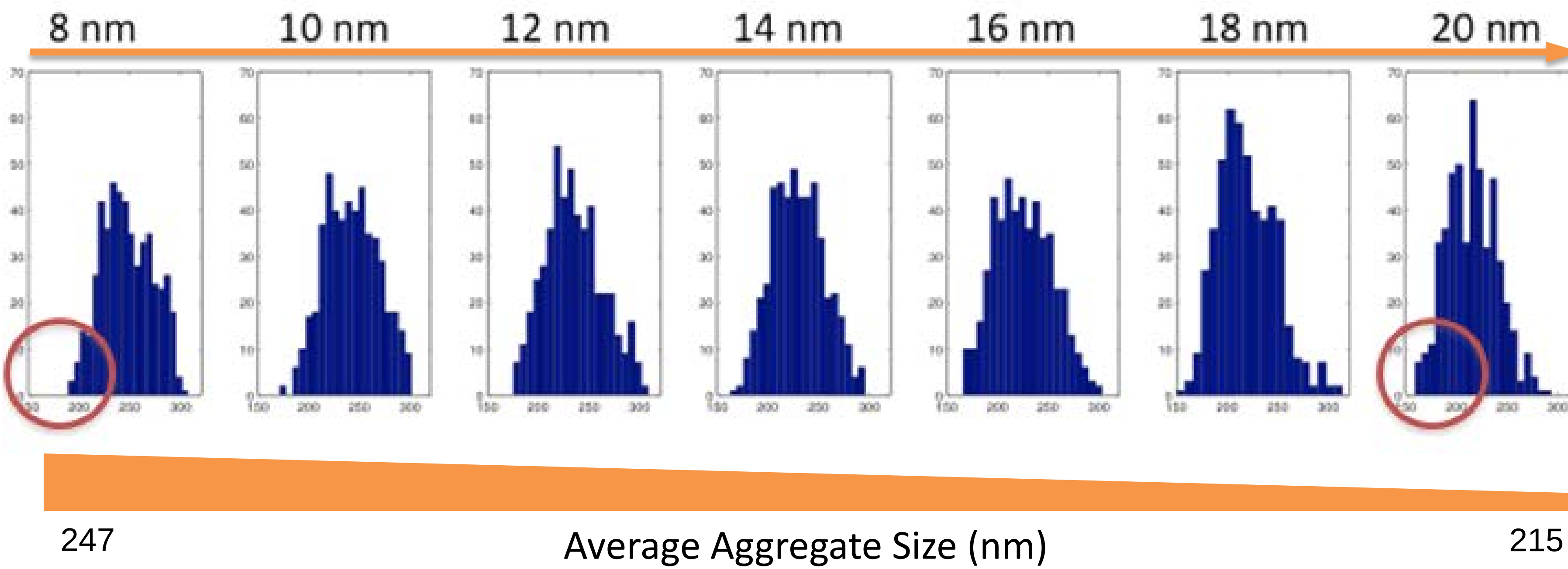
- The challenge is in developing/defining fundamental analytic expressions for such interactions





Monte Carlo Simulations of NP Aggregation

Example: **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

Liu et al., ES&T, 2011, 45 (21): 9284–9292.

Deterministic F&T Models and their Resource Requirements

- Spatial Models [C=C(**x**,t)]
- Hybrid Compartmental-Spatial Models [C=C(**x**,t) and C=C(t)]
- Compartmental Models [C=C(t)]

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

Steady-State Models [C≠ C(t)]

Dynamic Models [C=C(t)]

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- Spatial Models [C=C(**x**,t)]
- Hybrid Compartmental-Spatial Models [C=C(**x**,t) 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≠ C(t)]

Dynamic Models [C=C(t)]

Deterministic F&T Models and their Resource Requirements

No. Parameters | **Scale**

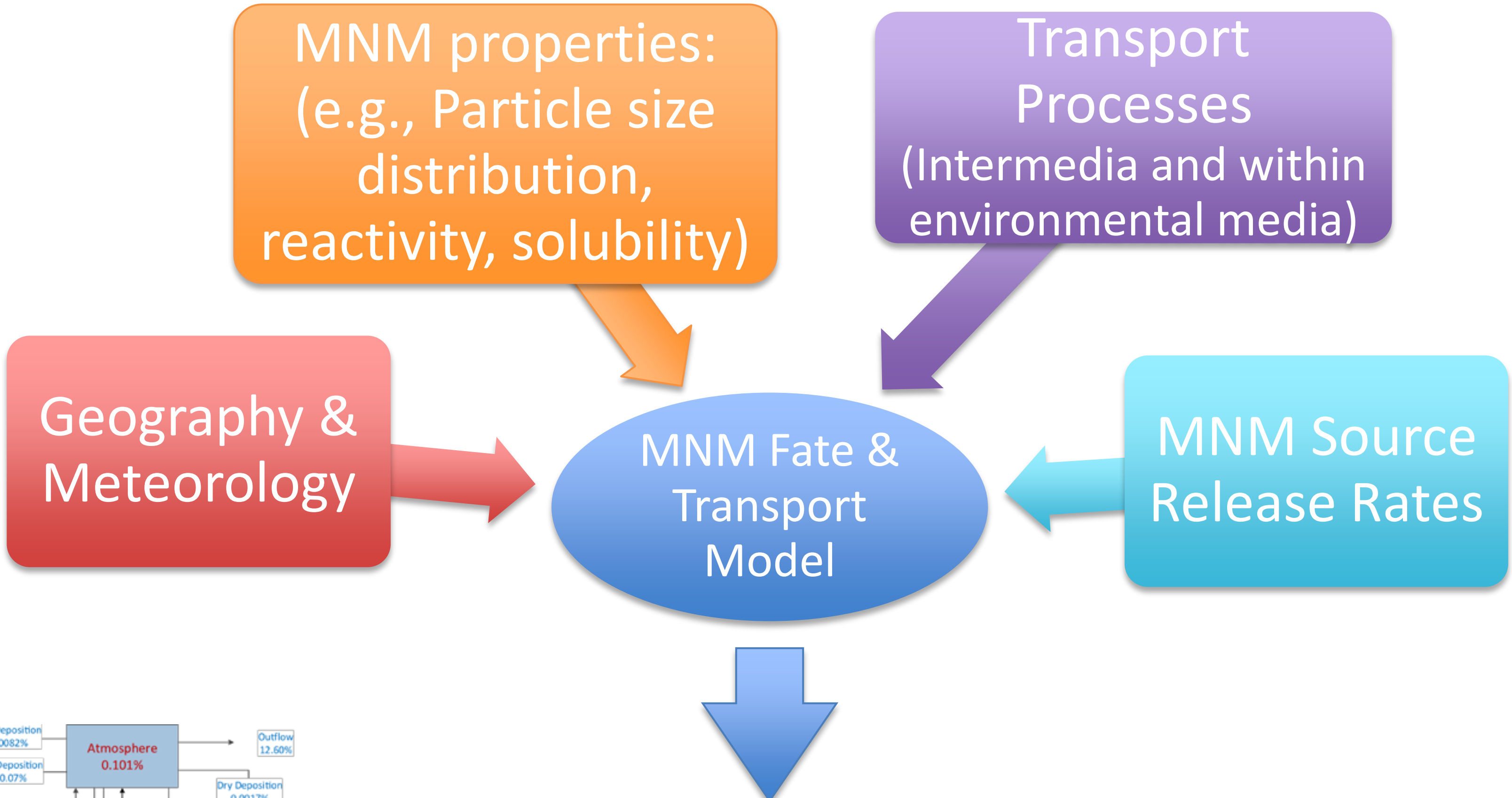
Increasing Number

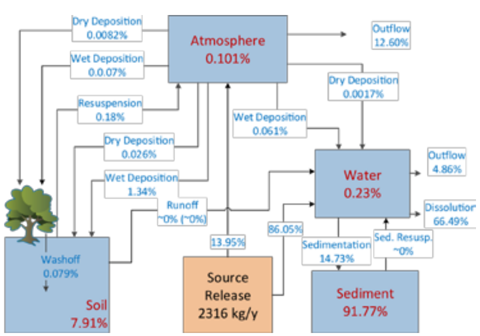
- Spatial Models [C=C(**x**,t)] — Regional/global/local (>0.1 km^2)
- Hybrid Compartmental-Spatial Models [C=C(**x**,t) and C=C(t)] — Regional/global (>1-10 km^2)
- Compartmental Models [C=C(t)] — Global/regional/local (> 1-10 km^2)

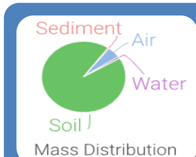
Steady-State Models [C$\neq$ C(t)] — Dynamic Models [C=C(t)]

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

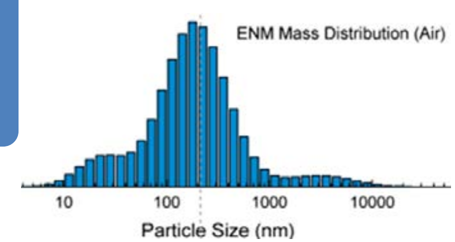
Modeling the Environmental Distribution of Manufactured Nanomaterials (MNM)







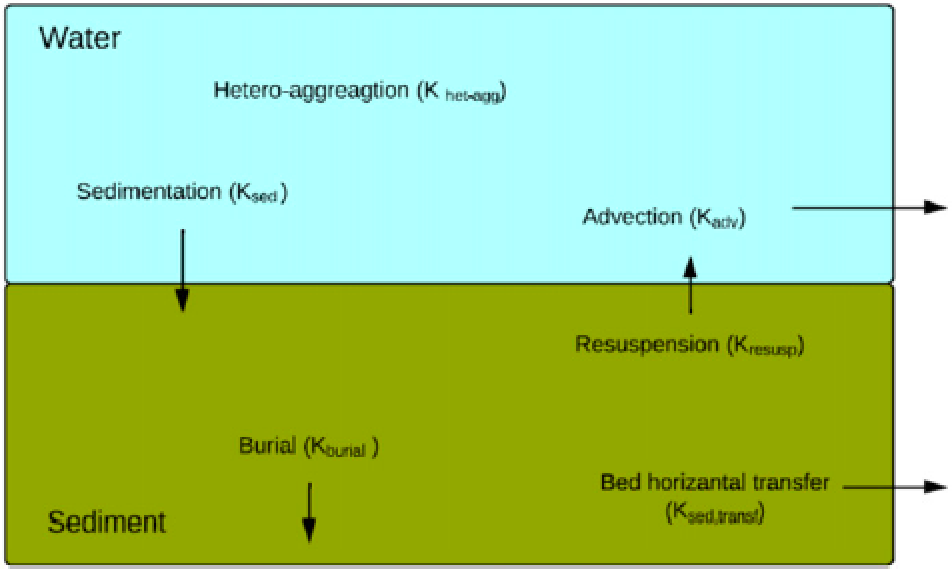
MNM Environmental Distribution, Concentrations, intermedia transport rates



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



Box Model

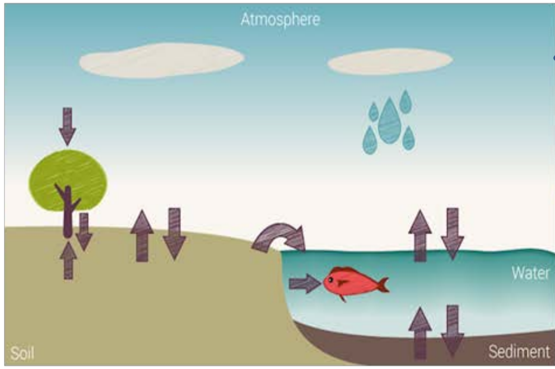
$n^{TiO2}_{sizes\ class}$	1	2	3	4	5
Radius	8 nm	106 nm	204 nm	302 nm	400 nm
$FF_{w,w,i}$	$5.9 \cdot 10^{-1}$	$5.3 \cdot 10^{-1}$	$3.6 \cdot 10^{-2}$	$4.7 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$
$FF_{w,sed,i}$	$4.5 \cdot 10^{-1}$	$4.0 \cdot 10^{-1}$	$2.7 \cdot 10^{-2}$	$3.5 \cdot 10^{-3}$	$8.0 \cdot 10^{-4}$
$FF_{sed,w,i}$	$8.0 \cdot 10^{3}$	$1.0 \cdot 10^{3}$	$1.8 \cdot 10^{3}$	$1.7 \cdot 10^{3}$	$1.6 \cdot 10^{3}$
$FF_{sed,sed,i}$	$9.8 \cdot 10^{2}$	$1.8 \cdot 10^{3}$	$2.4 \cdot 10^{3}$	$2.3 \cdot 10^{3}$	$2.1 \cdot 10^{3}$

Compartmental Residence Time (days)

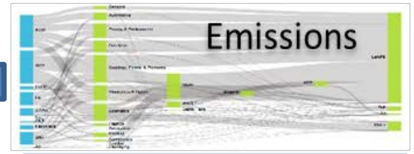
Salieri, Righi, Pasteris and Olsen, Sci. Total Env., (2015), 505, 494-502

Multimedia F&T Models for ENMs

MendNano

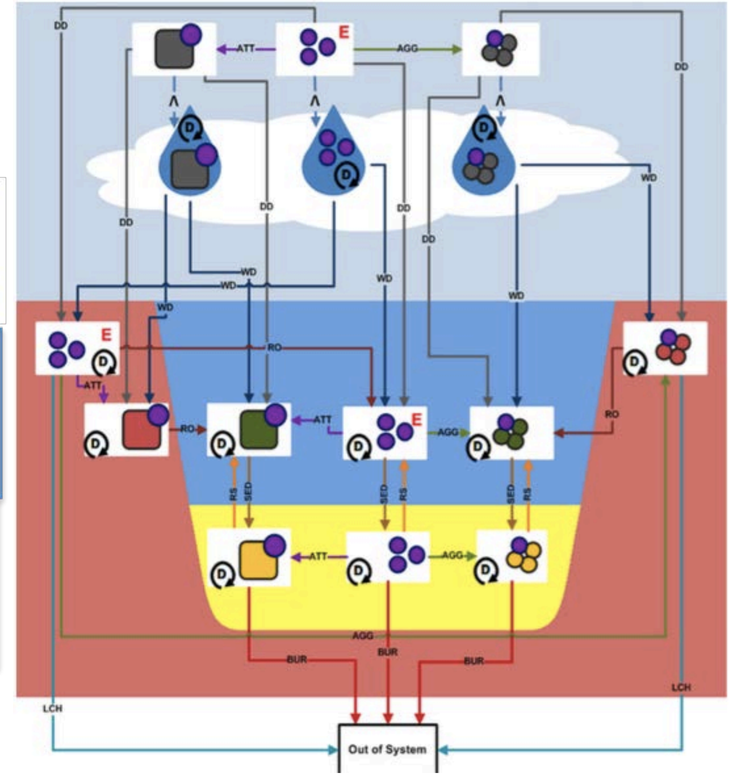


Multimedia Analysis



- ENMs F&T prop.
- Geographical & meteorological info.

ENMs biota/ vegetation uptake parameters



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)

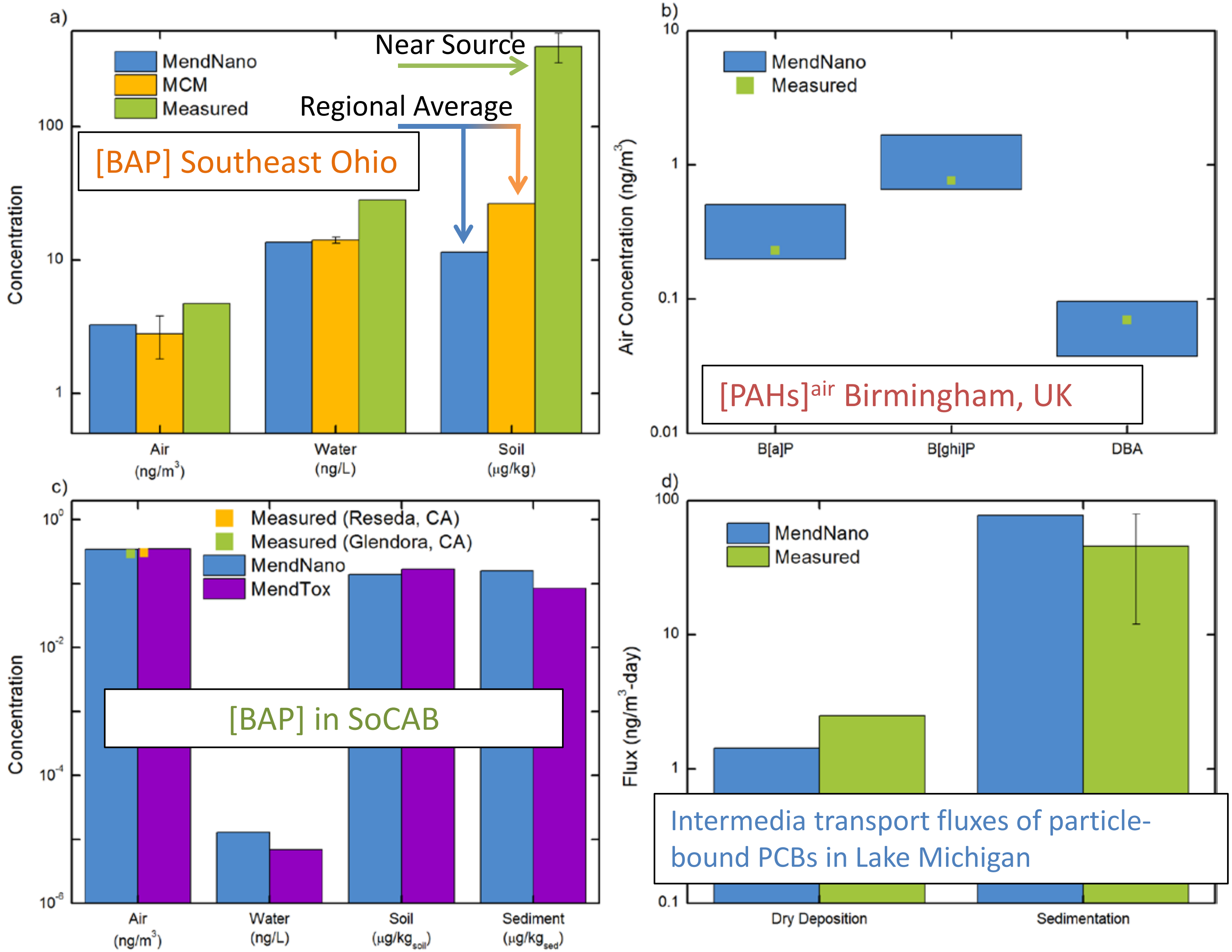
Liu et al., 2013/2014

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

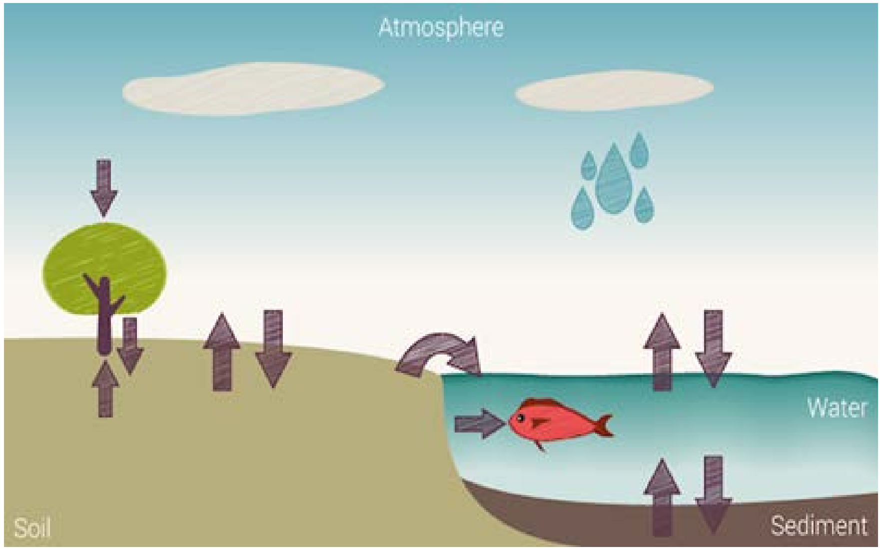
Meesters, et al., 2014

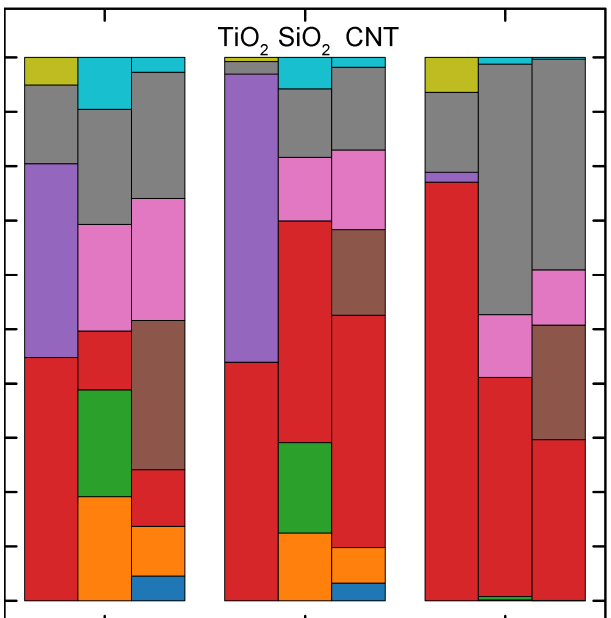
Comparison of MendNano Predictions with Field and Measurements of PAH Concentrations and PCB Fluxes



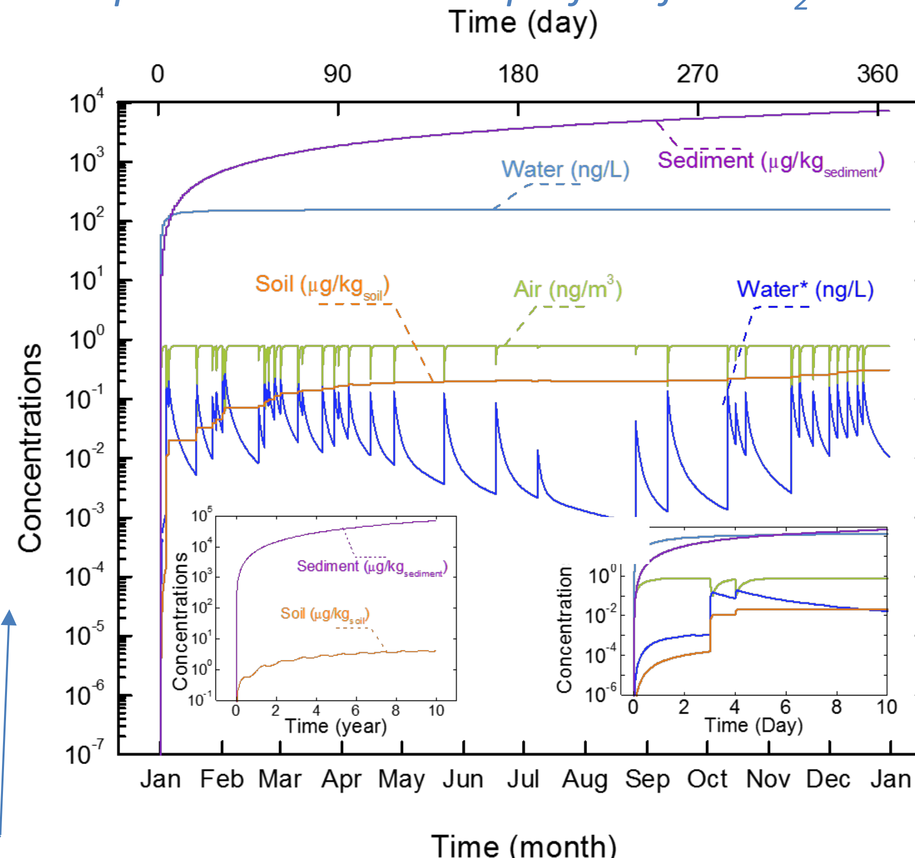
a) Ryan and Cohen, 1986; b) Harrison, et al., 1996; c) Yaffe, et al., 2001; d) Cohen and Cooter, 2002

Multimedia Analysis of Environmental Release & Distribution of ENMs



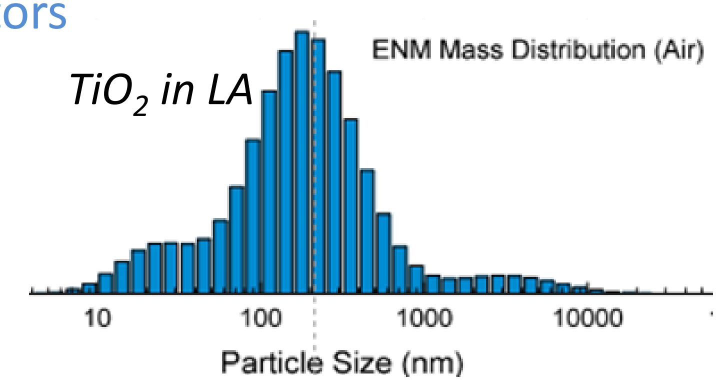


Temporal concentration profiles for TiO_2 in LA



Major Contributors

TiO_2 in LA



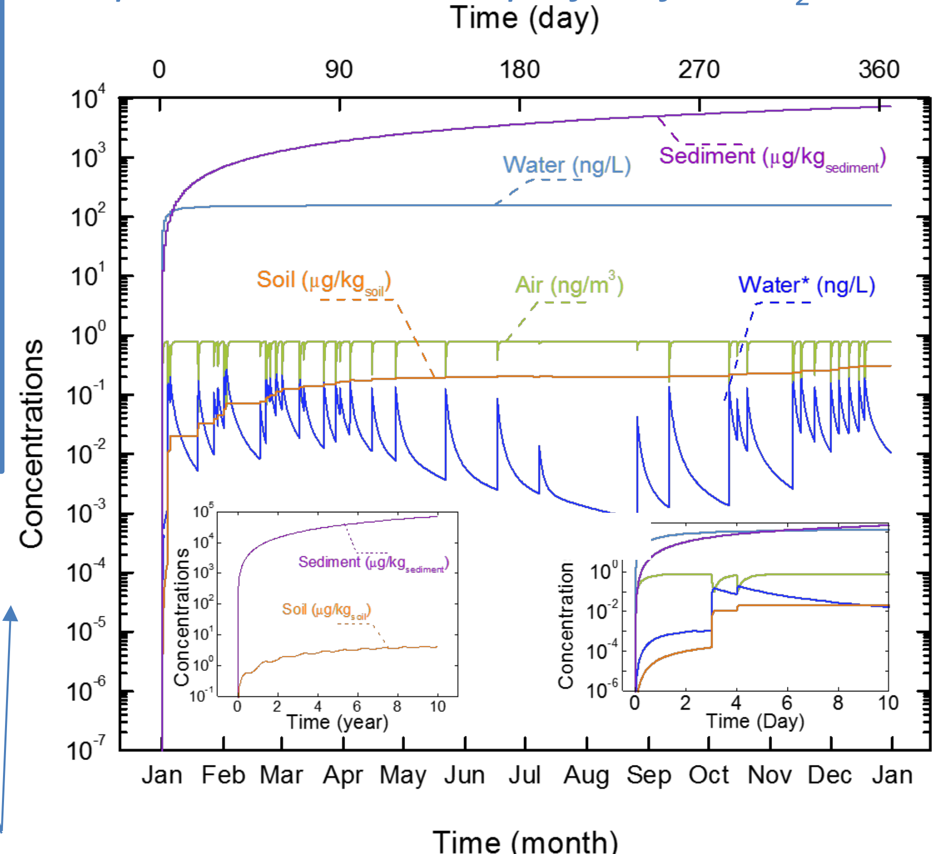
Liu, et al., Environ. Sci. Tech. , 48, 3281-3292 (2014); Beilstein J. Nanotech., 6, 930-951 (2015)

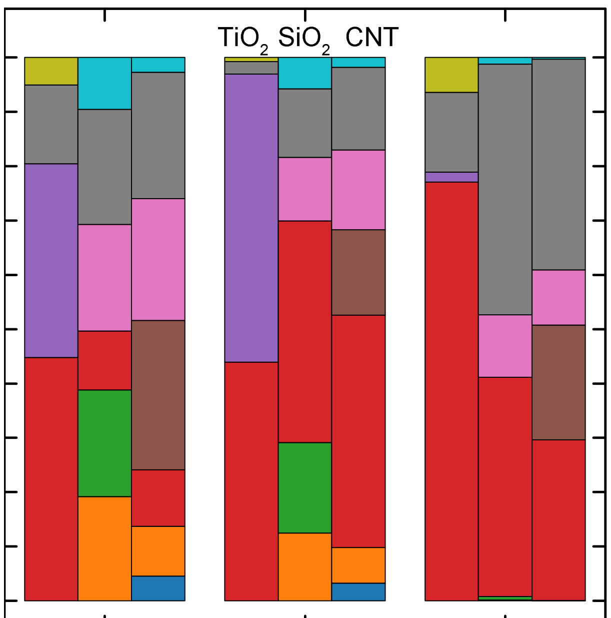
Multimedia Analysis of Environmental Release & Distribution of ENMs

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)

Temporal concentration profiles for TiO_2 in LA





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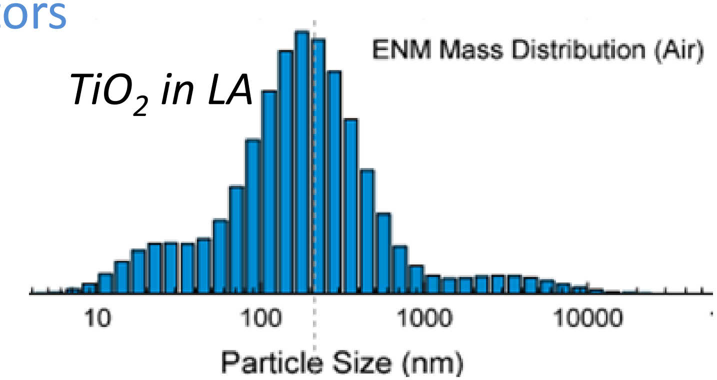

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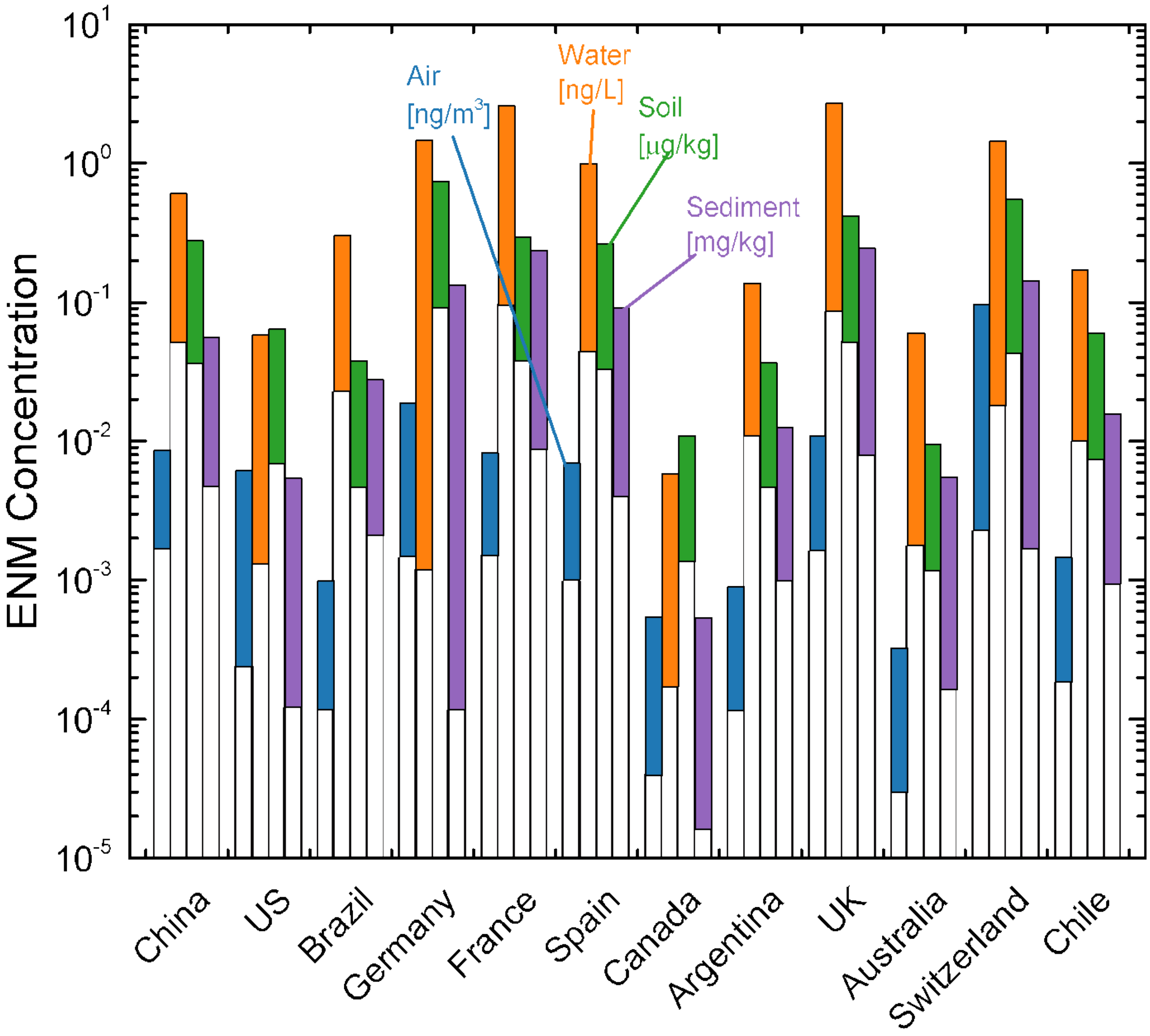
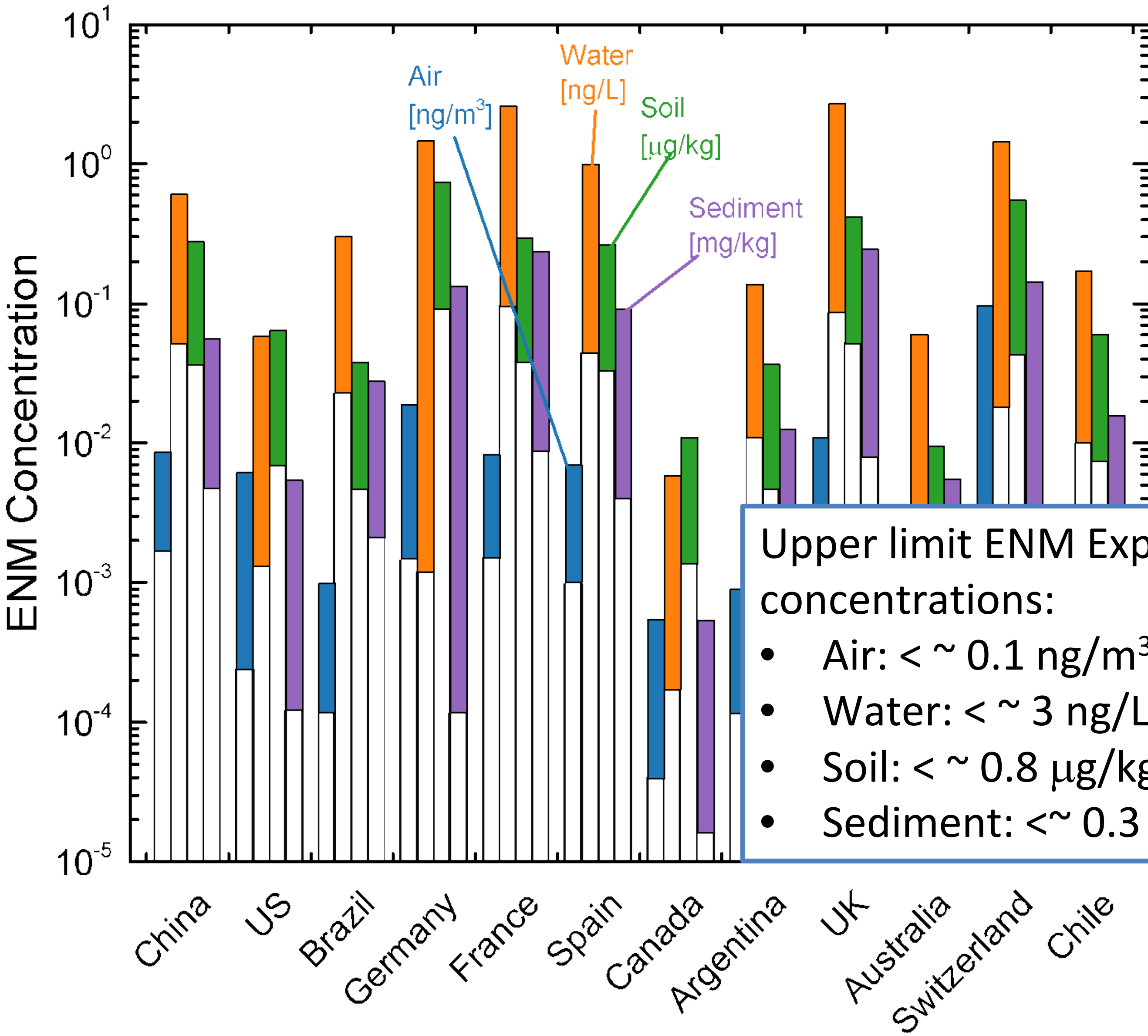
Estimates of the Range of Potential CeO_2 Multimedia Concentrations in Different Countries



Estimates of the Range of Potential CeO_2 Multimedia Concentrations in Different Countries

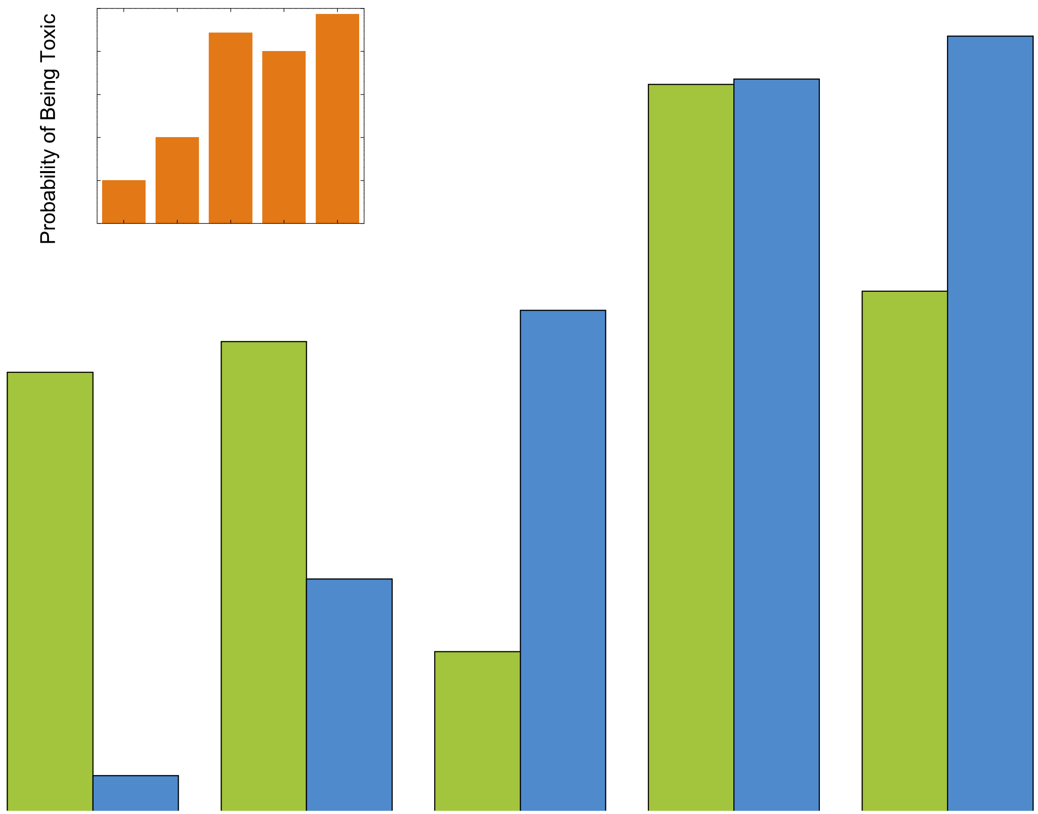


Upper limit ENM Exposure concentrations:

- 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*

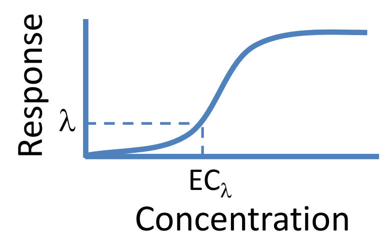


$$EI_i = \frac{\beta_i}{max(\beta)}$$

$$\beta_i = C_i \times P_i$$

P_i – probability of having an adverse biological response

EI can also be defined based on EC_λ



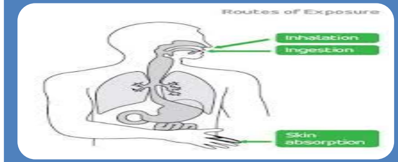
$$EI_{EC_\lambda} = \frac{c_i}{EC_\lambda}$$

MendNano simulations based on regional parameters for the Los Angeles

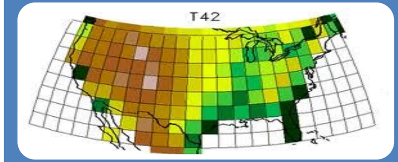
QSAR: R. Liu, et al., Nanoscale, 2013, 5, 5644

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?



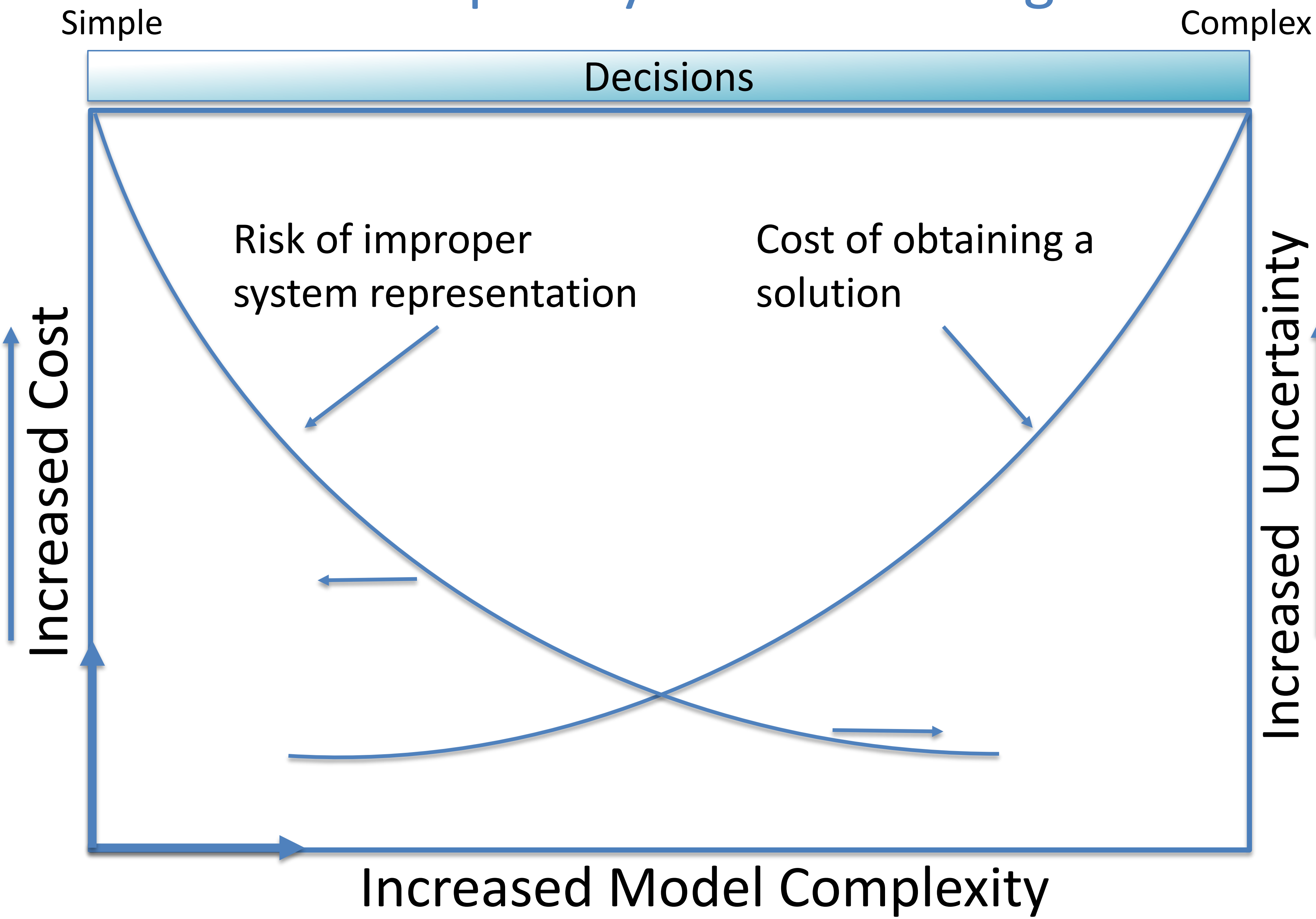
What is the required model resolution?

- Spatial: Site-specific? Regional?
- Temporal: Unsteady state? Steady state? Episodic scenarios?

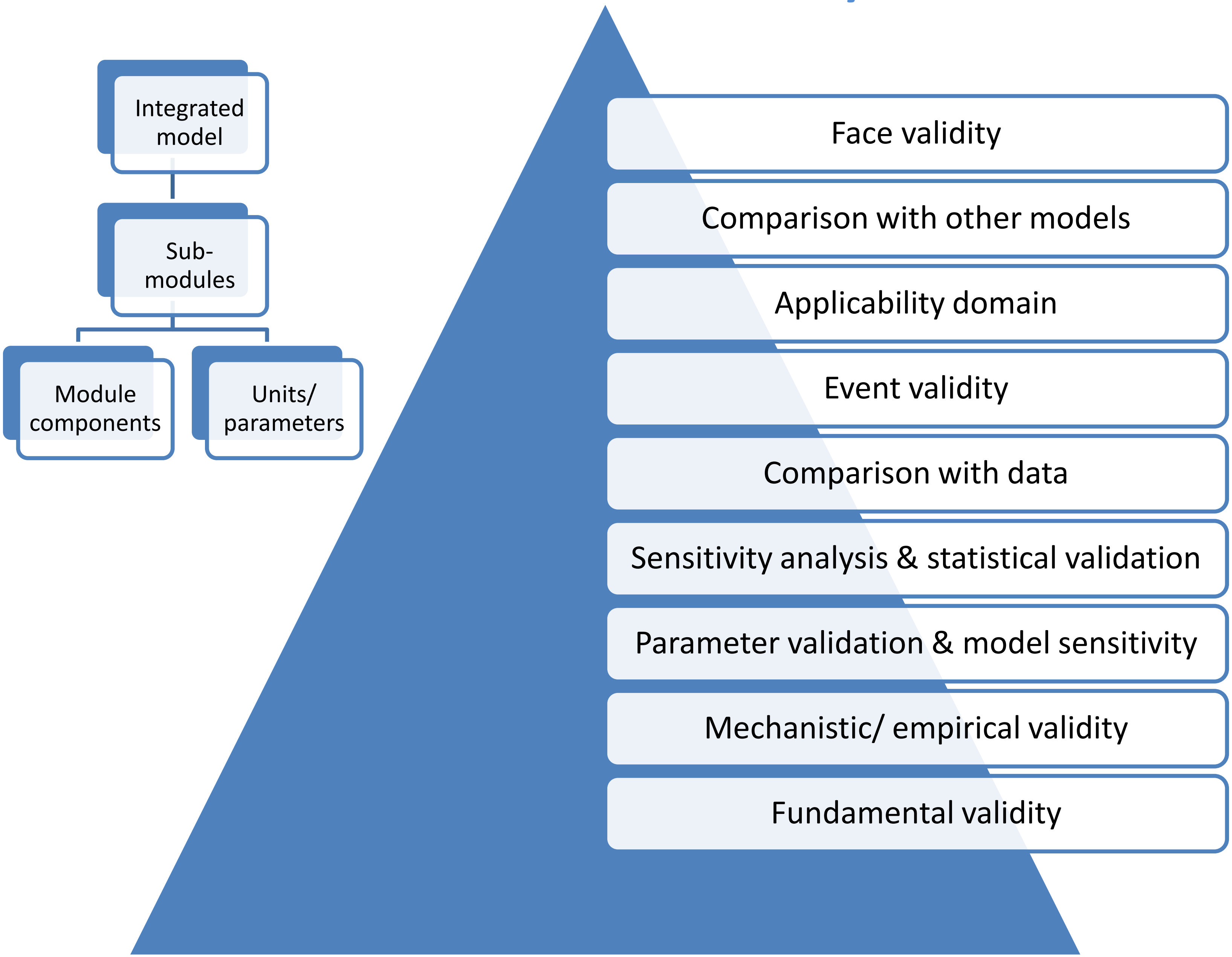
What is the required level of accuracy w.r.t estimated exposure concentrations?

Was the model validated? Calibrated?

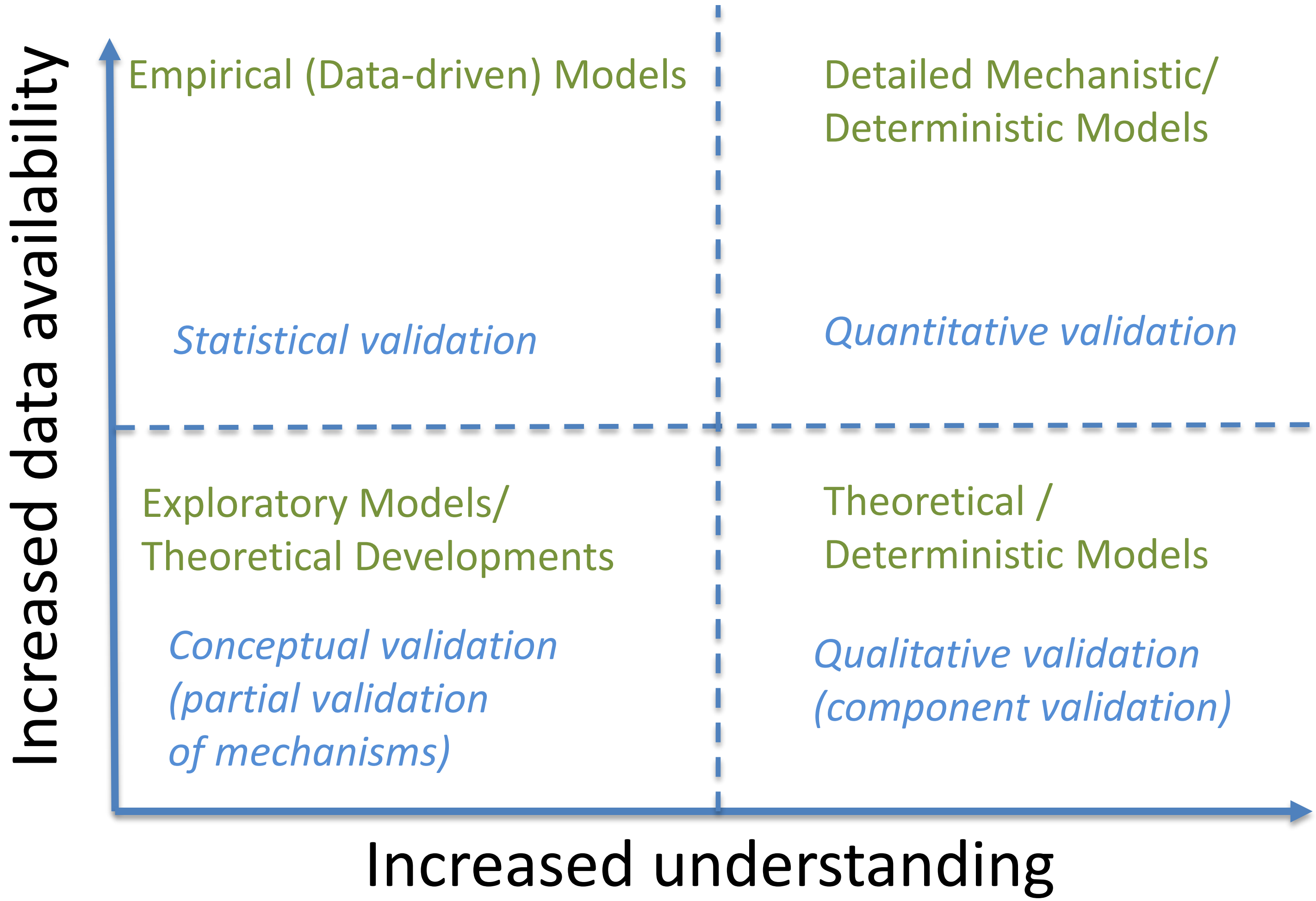
Model Complexity Trade-Off Diagram



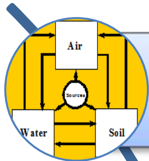
Model Validation Pyramid



Categories of Models and Validations

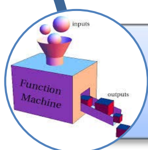


Exposure Modeling: Issues of Concern



Uncertainties in release rates lead to uncertainties in exposure estimates

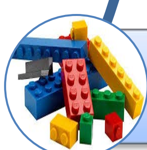
Reliable mechanistic models of intermedia transport are necessary



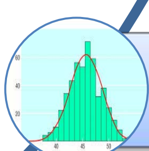
Parameter requirements, even for simple compartmental models, can be excessive and parameter values may not be readily available

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?

$$\frac{d}{dt}[V_i C_{i,k}] = (Q_i^{in} C_{i,k}^{in} - Q_i^{out} C_{i,k}) + \sum_{\substack{j=1 \\ j \neq i}}^{M} \sum_{l=1}^{P} I_{i,j,k}^{l} + \zeta_i K_{i,k}^{r} C_{i,k} V_{i,k}$$

$$-K_{i,k}^{s}(C_s - C_{dis}) A_{i,k}^{T} + S_{i,k}$$

$$\dot{m}_{i,k} = \dot{m}_i \alpha(r_k, r_n) \frac{f(r_k) w(r_k)}{\int_0^\infty f(r) w(r)\, dr}$$

Rong Liu

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

$$m_b(t) = m_b^o + (m_b^\infty - m_b^o)\left(1 - e^{-\frac{t}{\tau}}\right)$$

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

Dennis Bacsafra

Michelle Romero

QUESTIONS?

$$\bar{U} \cdot \nabla C = \nabla \cdot D \nabla C$$

$$I_{i,adj} = I_i \cdot \frac{R}{\sum_i t_i \cdot I\_i}$$

$$\bar{U} \cdot \nabla \left(\rho \bar{U}\right) = -\nabla p + \nabla \cdot \eta \nabla \bar{U}$$

Muhammad Bilal

Haven Liu

$$\frac{dm_i}{dt} = 12D(C_s - C_{dis}) \left(\frac{m_i}{\rho d_i^2}\right) \left(\frac{d_i}{d_{pri}}\right)^{\frac{d_f}{2}}$$

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

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

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