Heteroaggregation, surface affinity and implications for nanomaterial fate

Mark R. Wiesner, Niall O'Brian, Nick Geitner

Director

Center for the Environmental Implications of NanoTechnology

Duke University

Center for the Environmental Implications of NanoTechnology

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Heteroäggregation and importance in aquatic systems

1. Removal of viruses

2. Fate of abrasion and weathering products

1. Fate trace particulate contaminants

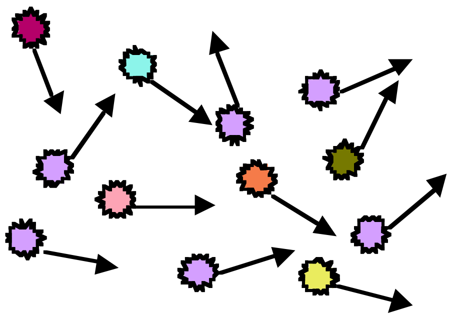
2. Micro/nano plastics

3. Colloids in wastewater discharge

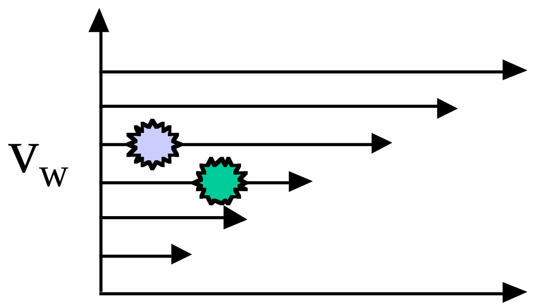
4. Bacterial inactivation using bacteriophages

5. Fate of adsorbed contaminants

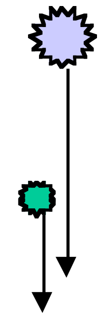
Transport: Particle collision mechanisms



Brownian Diffusion



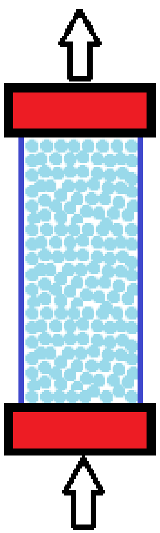
Velocity gradients (shear)

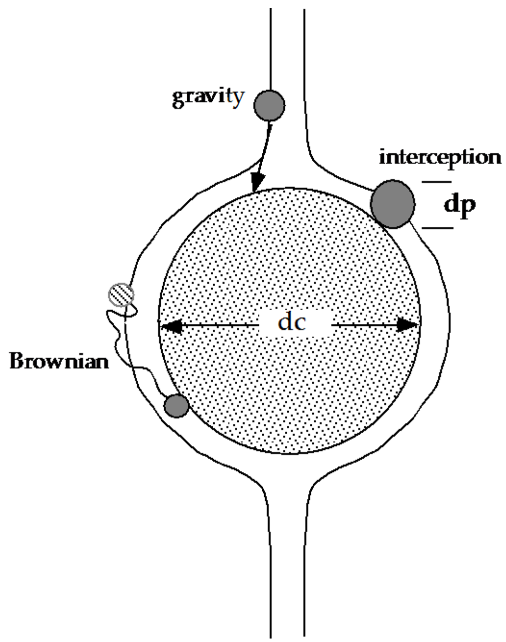


Differential Sedimentation

Aggregation

β





Deposition

η_0

(Hetero)aggregation and deposition both depend on surface affinity

	Chemistry	Physics
Aggregation	α	β
Deposition	α	η

Aggregation rate proportional to $\alpha\beta$

Surface affinity

Deposition rate proportional to $\alpha\eta$

Settling rate dependent on (hetero)aggregation rate

Surface affinity includes effects from:

- Nanoparticle composition, composition of surface, intervening fluid
- Adsorbed macromolecules
  - Proteins
  - Engineered surface treatments/ stabilizers
  - Humic materials, polysaccharides…
- Ionic composition
  - Ionic strength, charge screening
  - Specific adsorption of ions (e.g., Ca, PO4…)
  - pH
- Surface modifications due to redox transformations, dissolution…
- Electro-steric interactions (interface between macromolecules and ionic environment)
- Surface reactions/ electron sharing / protein binding

Challenges in calculating surface affinity from theory (and intrinsic nanoparticle properties)

1. DLVO- role of ionic strength, ionic composition…
2. Role of macromolecules, electro-steric stabilization, and hydrophobicity
3. Complex geometry of aggregates and surfaces

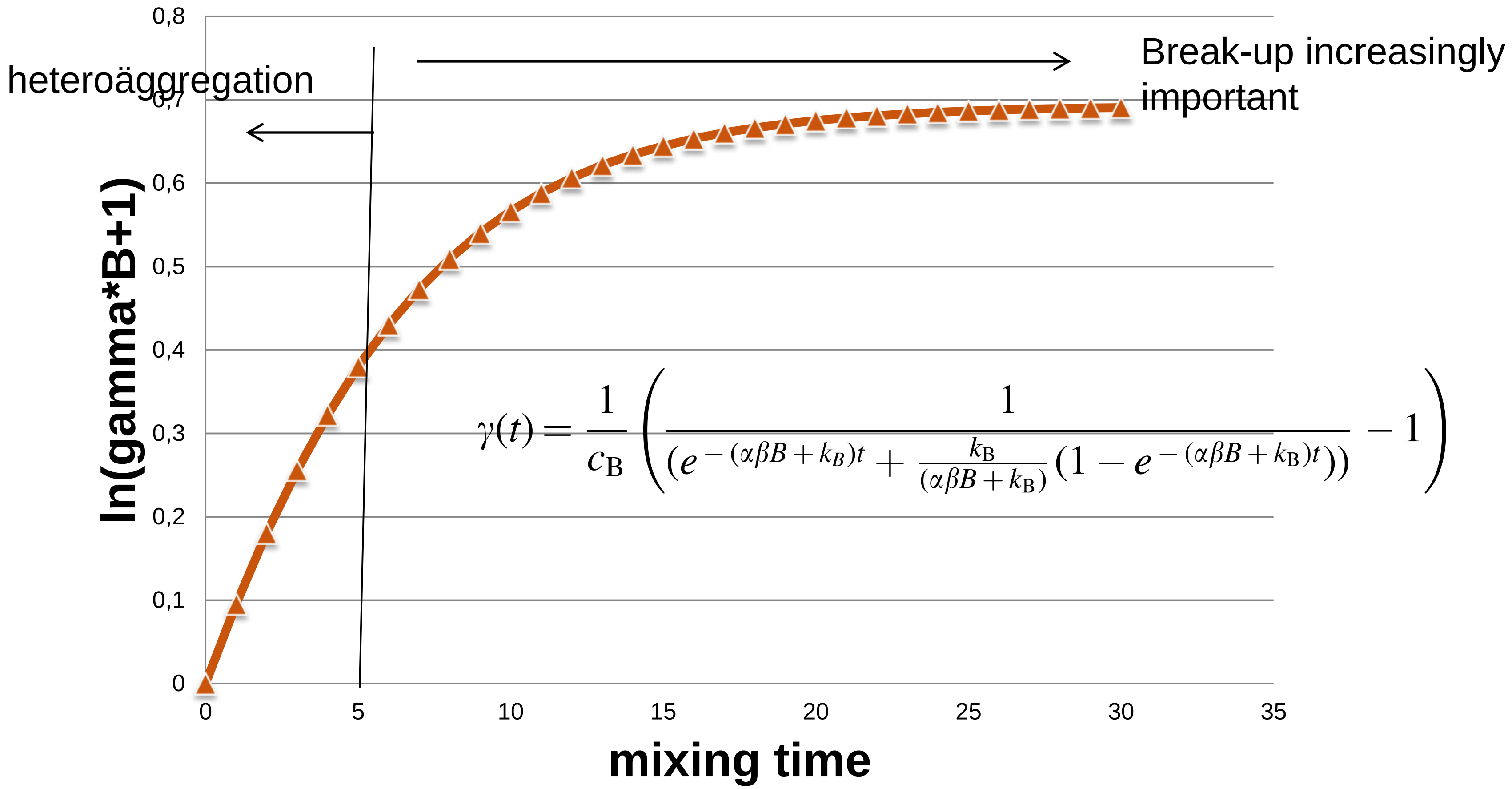
qualitatively useful but, not quantitatively predictive in real systems

Measuring surface affinity in complex systems

$$\frac{dn_k}{dt} = \frac{1}{2} a \sum_{i+j \to k} b(i,j) n_i n_j - a n_k \sum_i b(i,k) n_i - breakup$$

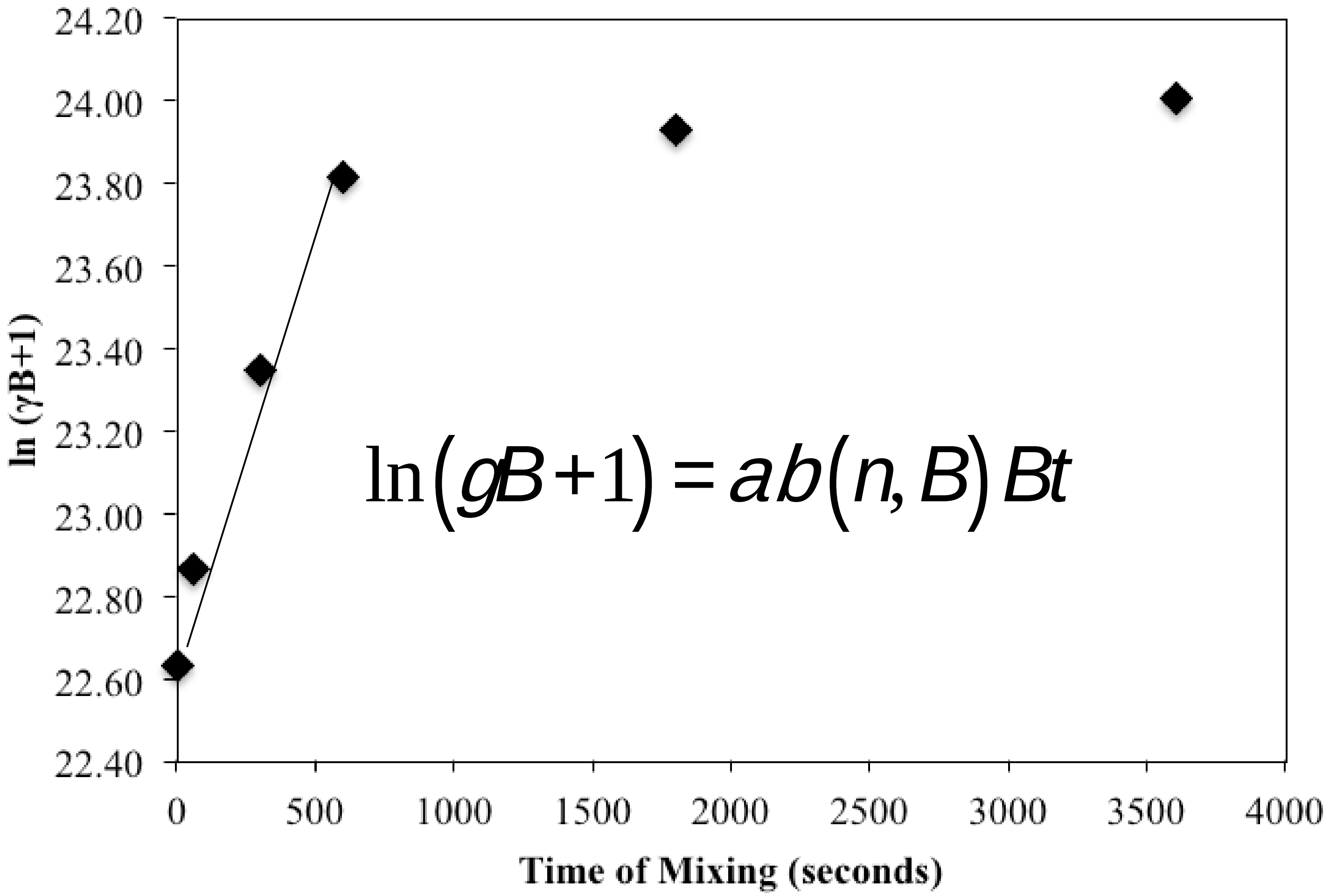
$$\frac{dn}{dt} = -\alpha\beta(n,B)nB + k_B(n_0 - n)$$

Predicted trend for heteroäggregation



$$\gamma(t) = \frac{1}{c_{\mathrm{B}}}\left(\frac{1}{(e^{-(\alpha\beta B + k_B)t} + \frac{k_{\mathrm{B}}}{(\alpha\beta B + k_{\mathrm{B}})}(1 - e^{-(\alpha\beta B + k_{\mathrm{B}})t}))} - 1\right)$$

Time dependent distribution coefficient vs. aggregation time



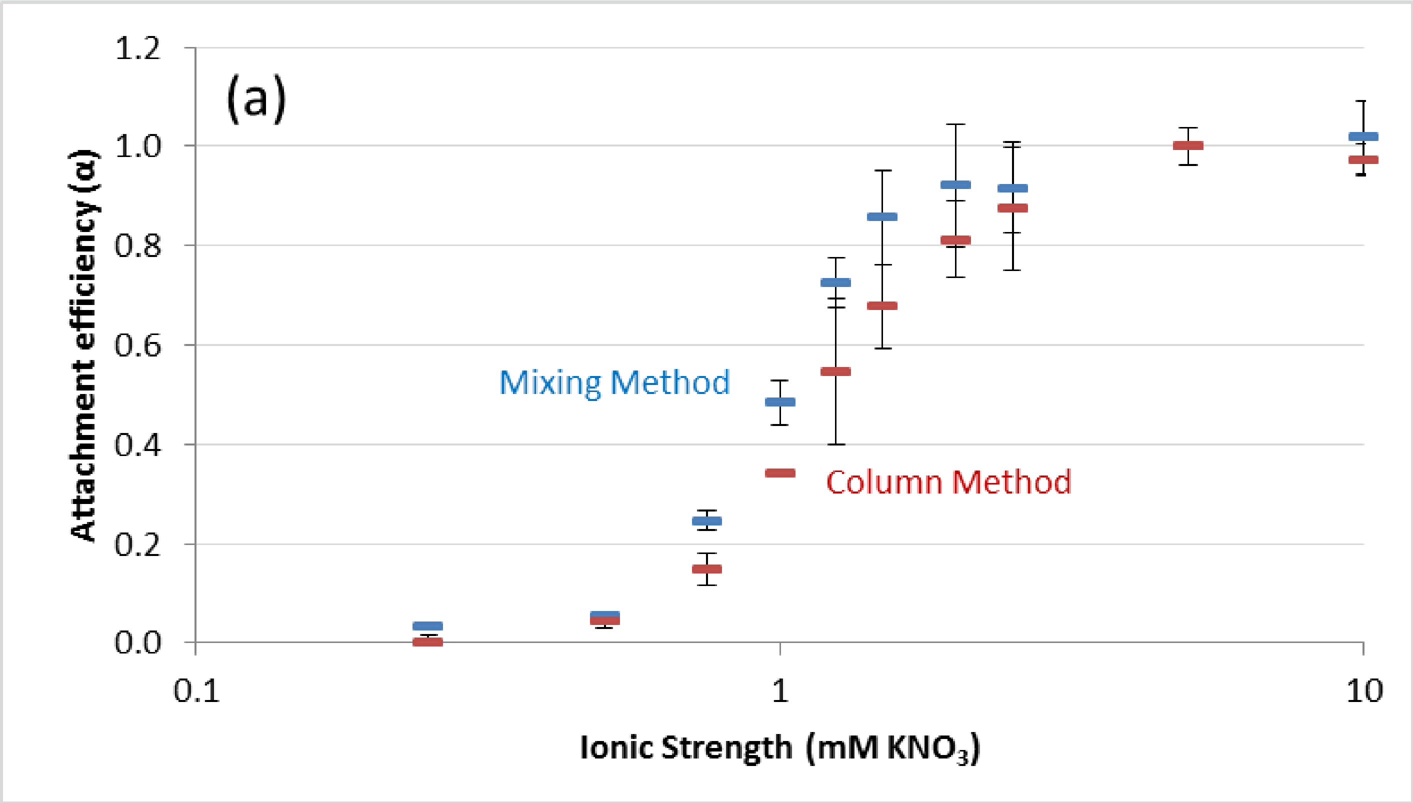
Barton et al., ENVIRONMENTAL ENGINEERING SCIENCE
Volume 31, Number 7, 2014

Comparison of column and suspension surface affinities

Matrix Conditions

pH3: α assumed to be close to 1, homoaggregation minimized

☞ SiO_2 ZP ≈ -20 mV; CeO_2 ZP ≈ +28 mV



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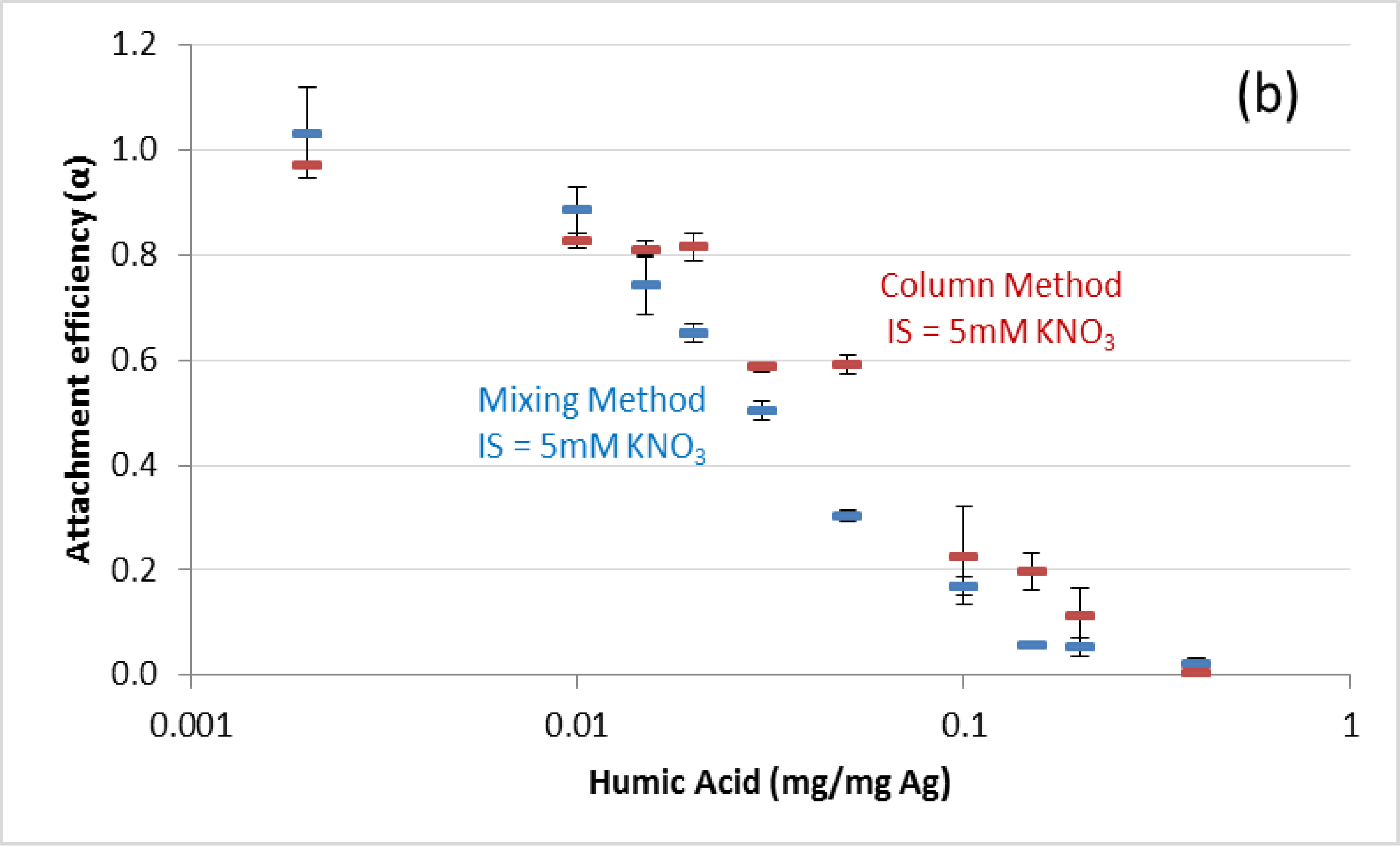
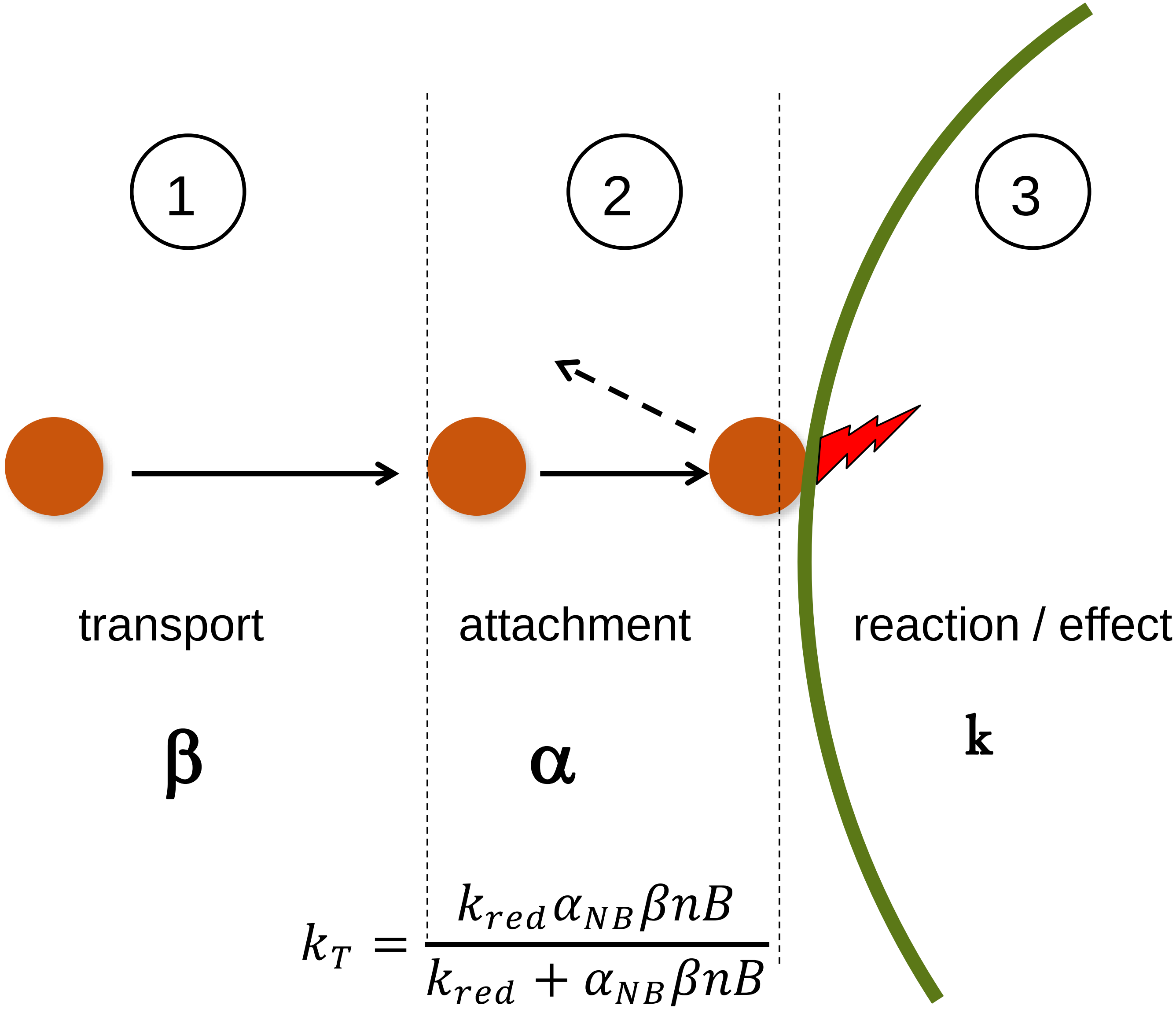
Column vs. mixing
Effect of humic acid



Conceptual model for nanoparticle reactivity

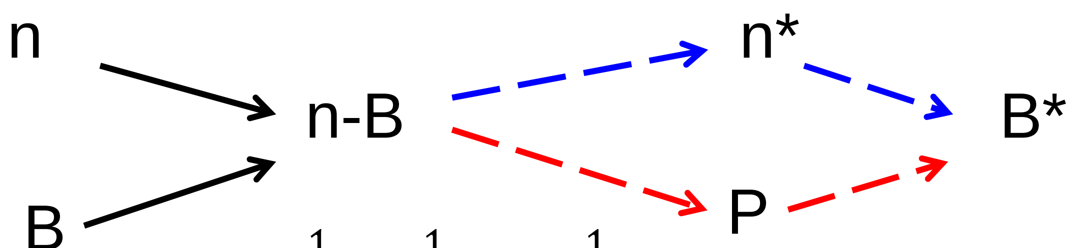


$$k_T = \frac{k_{red}\alpha_{NB}\beta nB}{k_{red} + \alpha_{NB}\beta nB}$$

Examples of nanoparticle reactivity

Effect	Underlying reaction
Toxicity to plants and fish by nano Ag	Nano silver dissolution
Viral inactivation by fullerol	Singlet oxygen generation
Bacterial inactivation by CeO2	Ce reduction
Toxicity of herbicide on NP	Herbicide desorption

heteroäggregation reaction

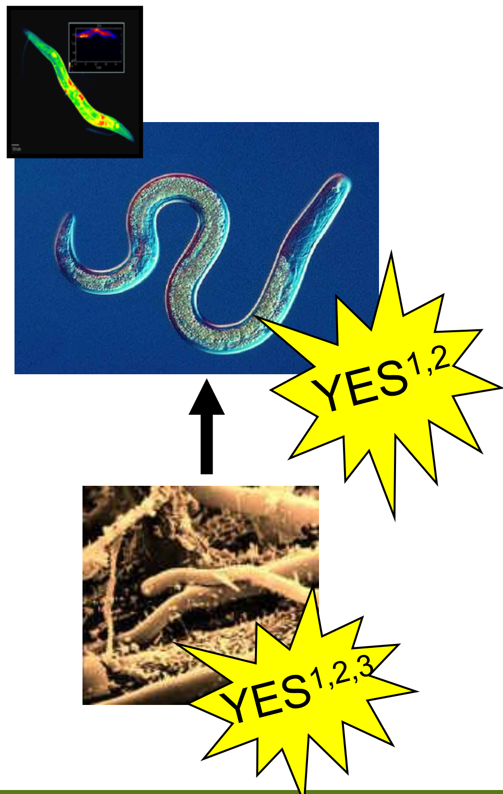


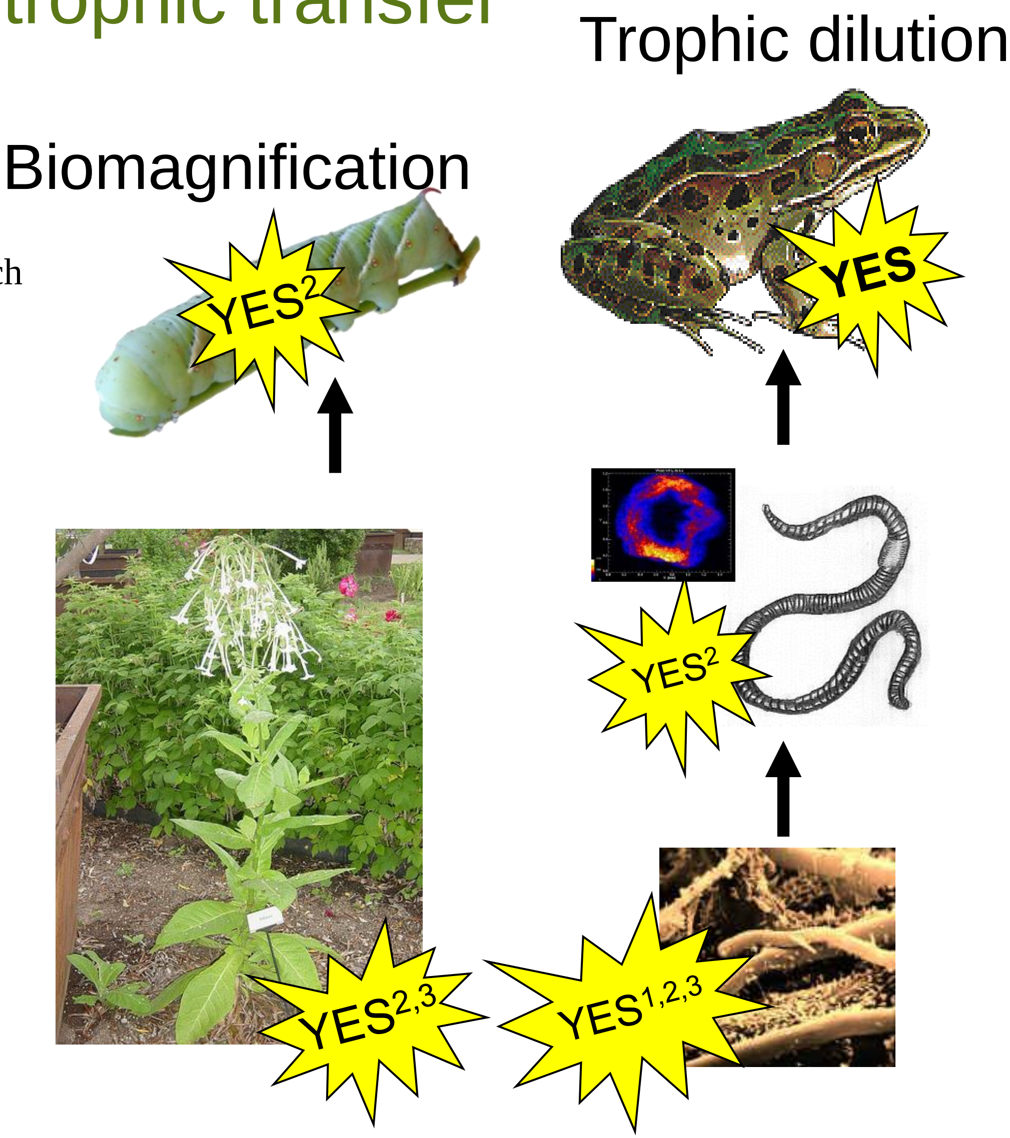
$$\frac{1}{k_T} = \frac{1}{k_{red}} + \frac{1}{\alpha_{NB}\beta n B}$$

$$k_T = \frac{k_{red}\alpha_{NB}\beta n B}{k_{red} + \alpha_{NB}\beta n B}$$

Observations of trophic transfer

[1]Joel Meyer
[2]Paul Bertsch and Jason Unrine
[3]Emily Bernhardt, Curt Richardson & Claudia Gunsch
[4]Dana Hunt





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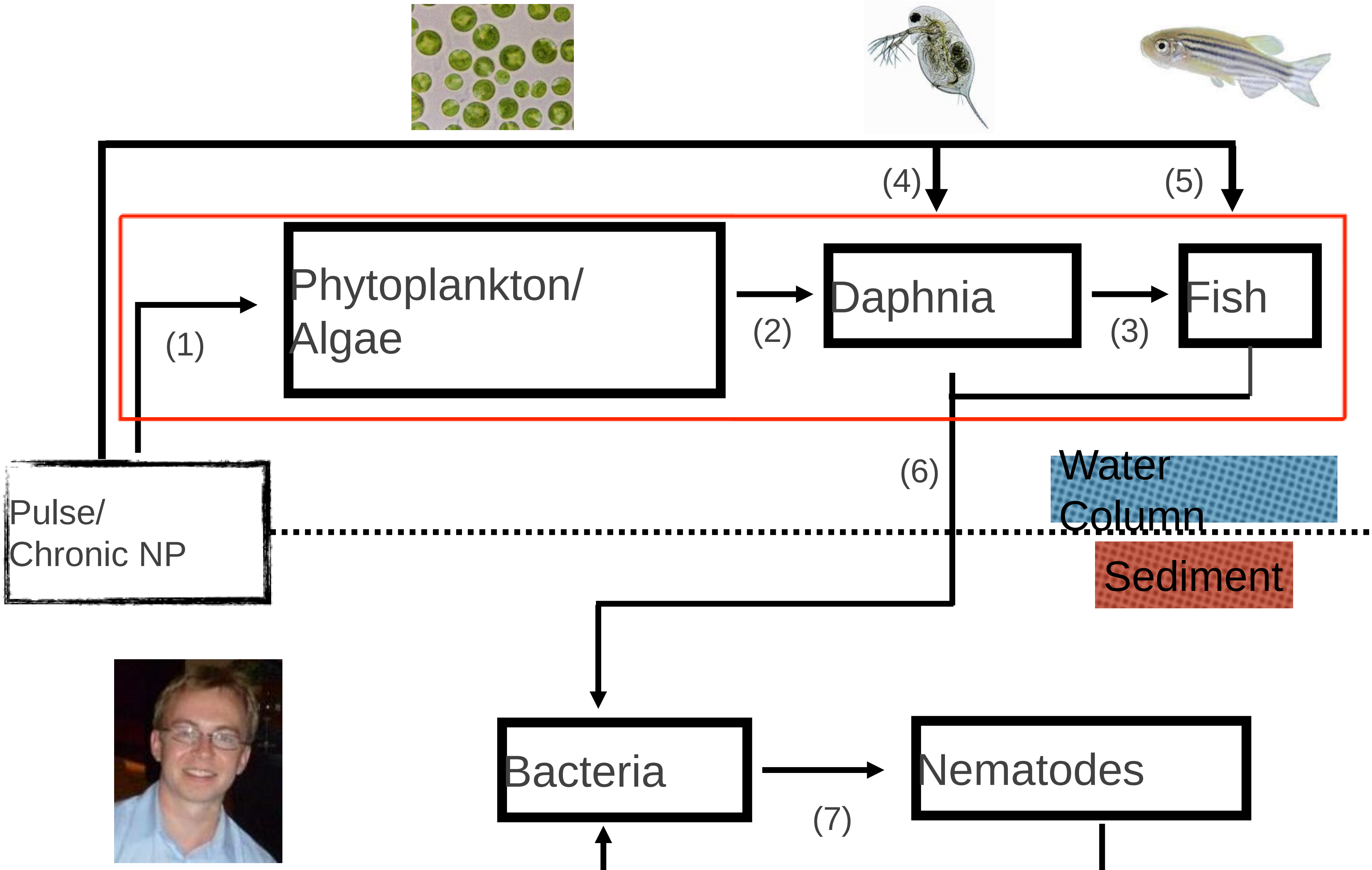
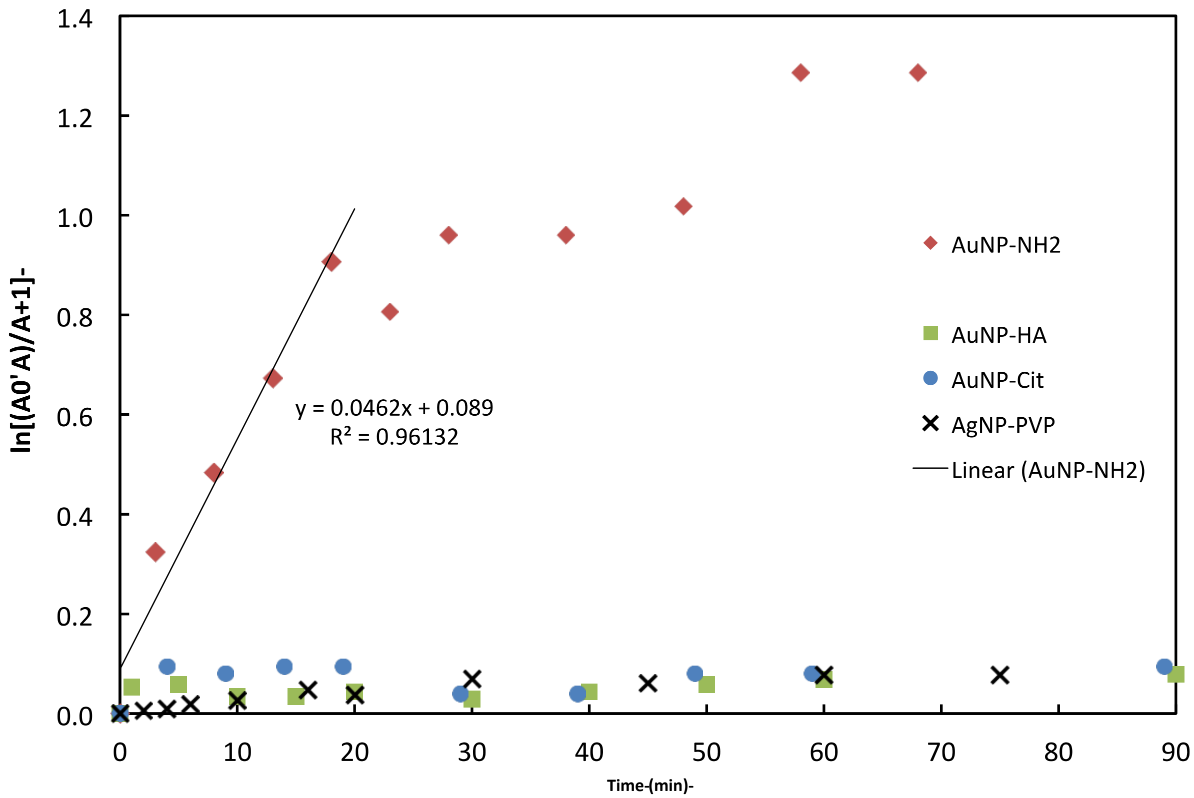


Nick Geitner

Positively charged NPs have much greater potential for association with algae



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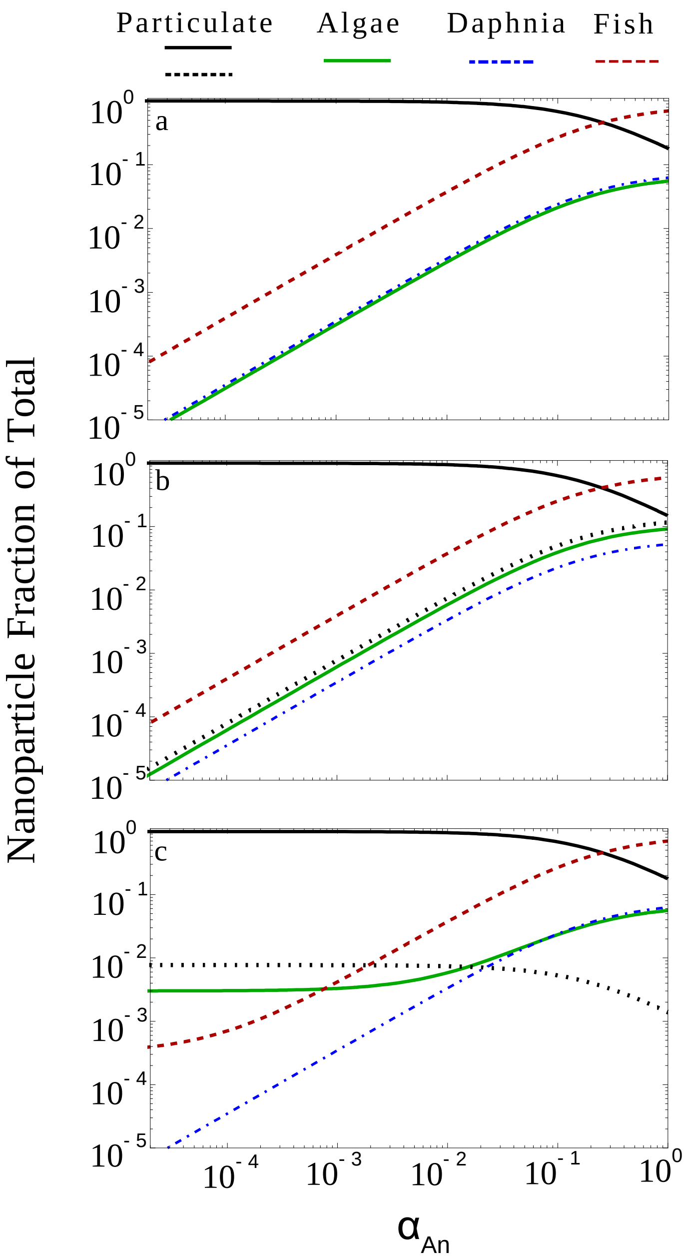
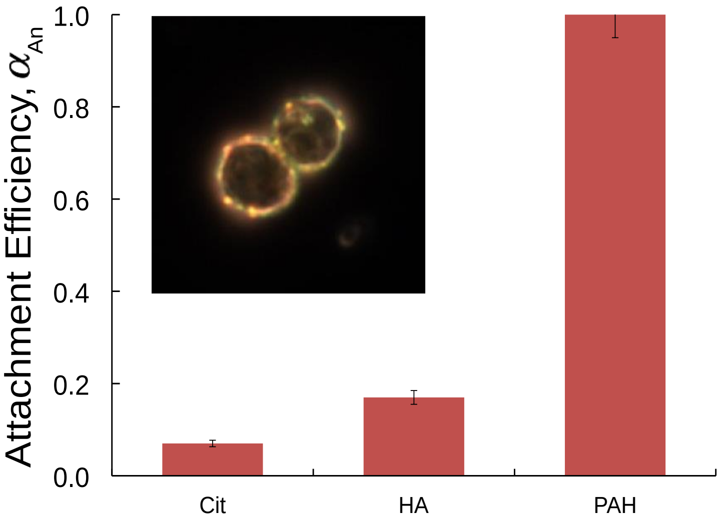
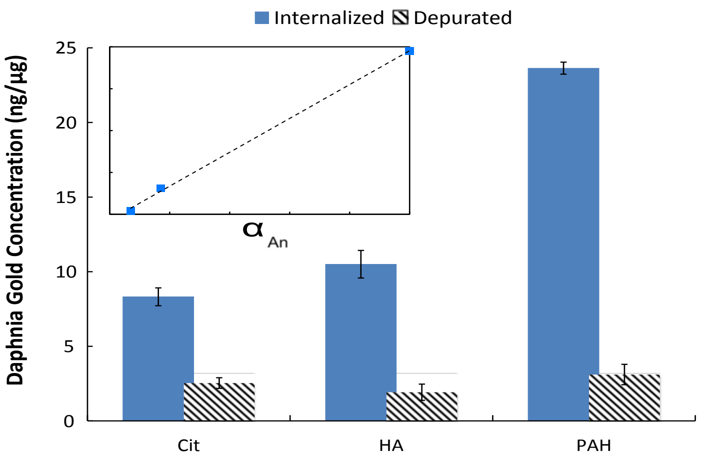
Surface affinity predicts bioäccumulation

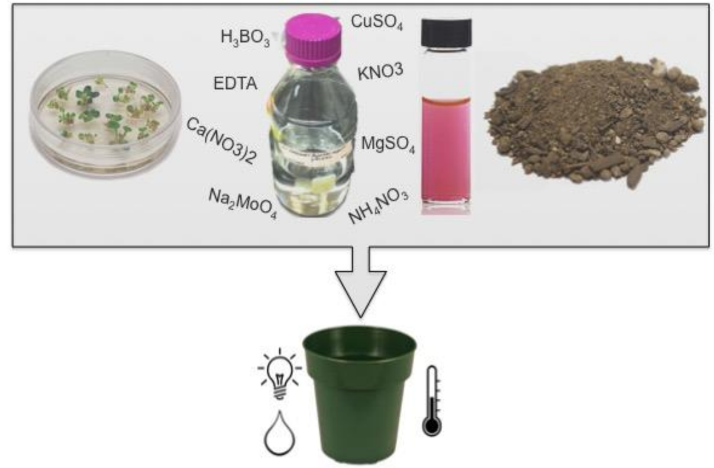


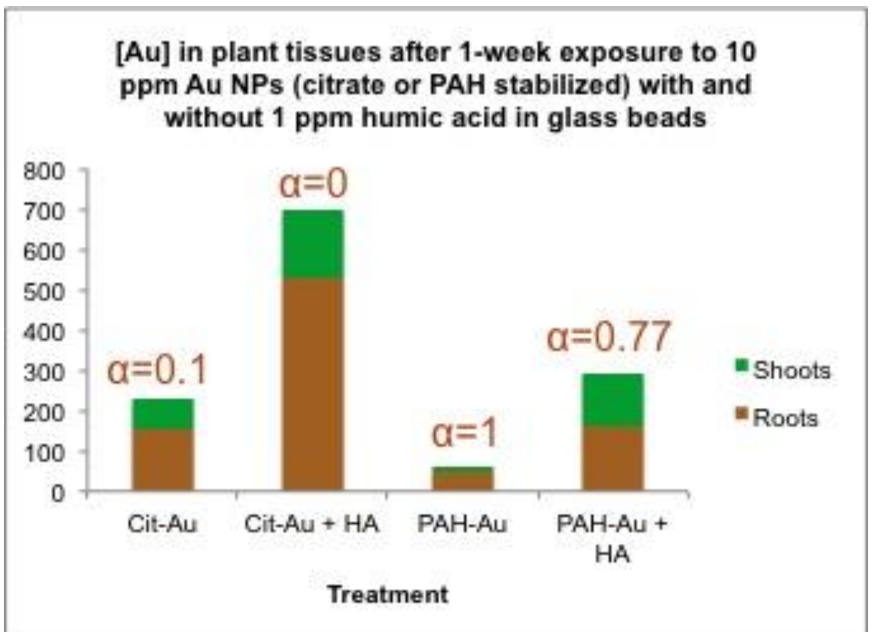


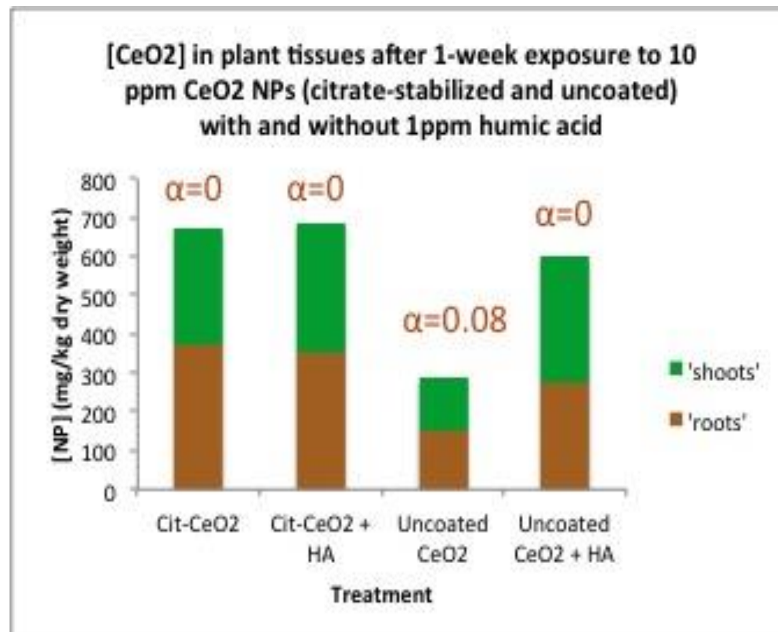


Plant uptake

Amalia Turner







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Conclusions

1. Heteroäggregation/ deposition is a key fate process

1. Surface Affinity in complex media can be measured using programmed mixing procedure

2. Applications to predicting bioüptake and trophic transfer

3. Surface affinity also plays a role in determining nanoparticle effects

Thank you

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