Surface affinity: a functional assay for quantifying nanoparticle behavior in complex systems

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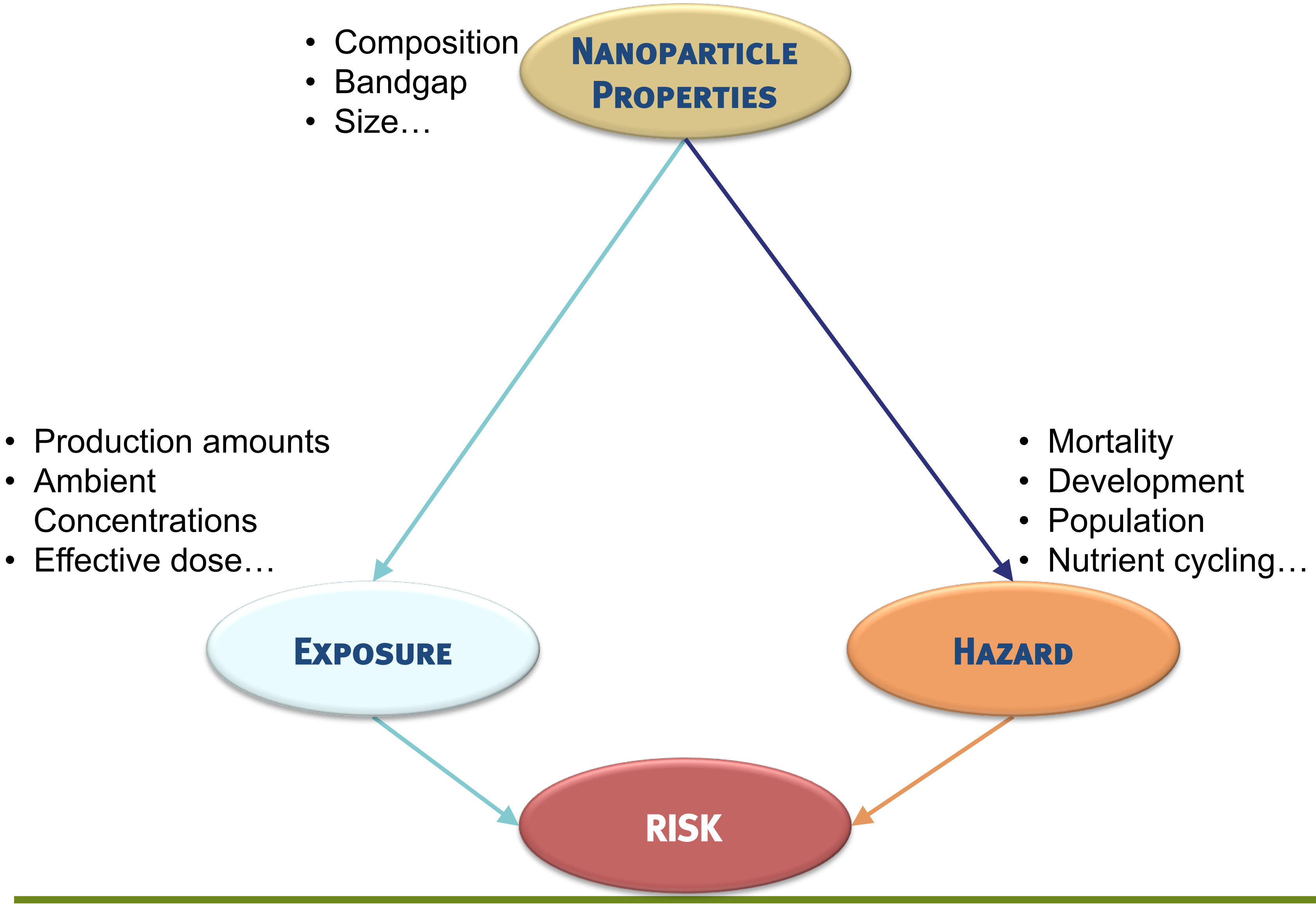
KEY MESSAGES

1. *HETEROÄGGREGATION AND DEPOSITION ARE A KEY FATE PROCESS*

2. *SURFACE AFFINITY IS A USEFUL, EASILY MEASURED, CHARACTERIZATION PARAMETER FOR PREDICTING FATE AND REACTIVITY AND PERHAPS BIOLOGICAL INTERACTIONS*



- Composition
- Bandgap
- Size…

NANOPARTICLE PROPERTIES

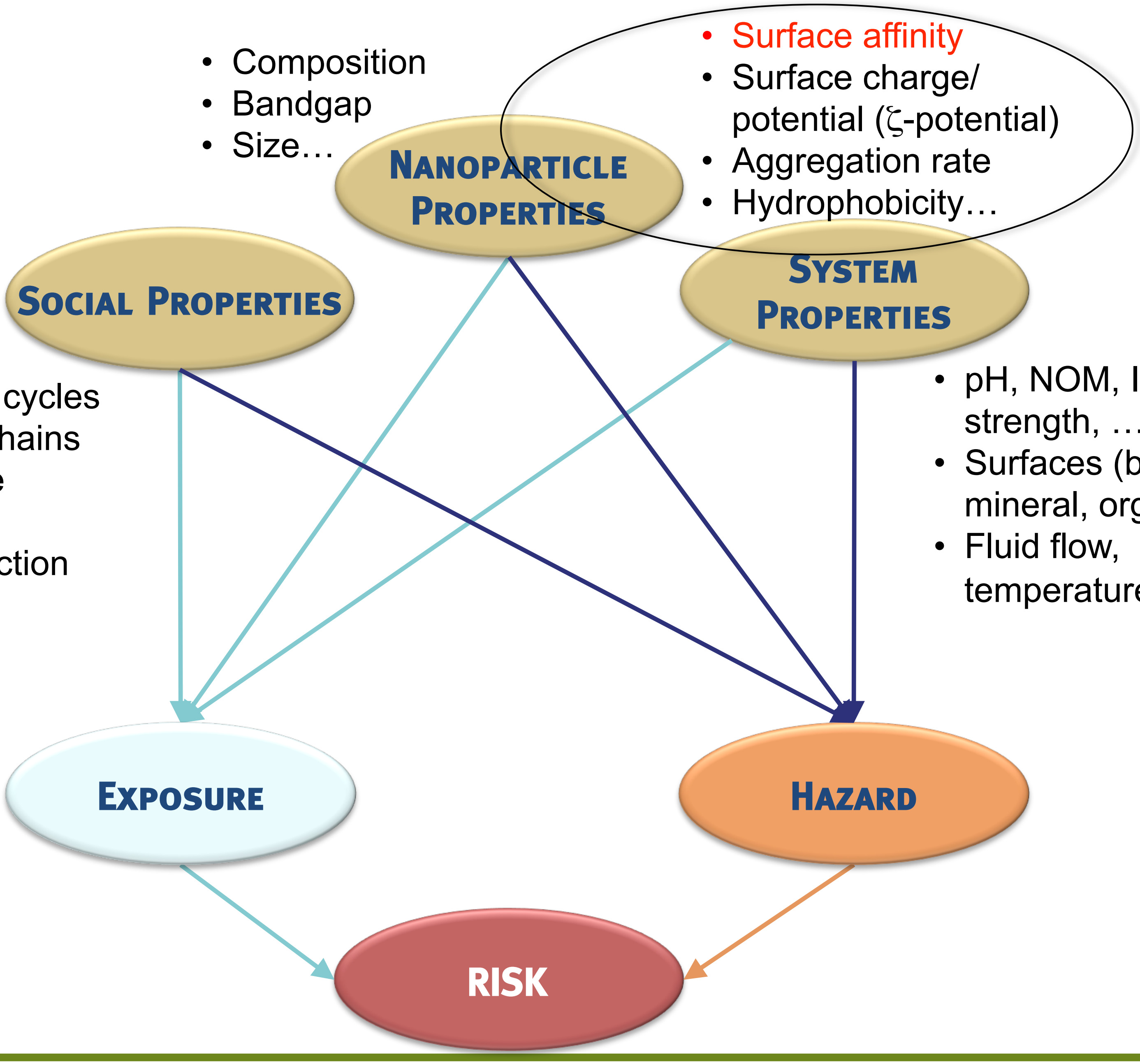
- Production amounts
- Ambient Concentrations
- Effective dose…

- Mortality
- Development
- Population
- Nutrient cycling…

EXPOSURE

HAZARD

RISK

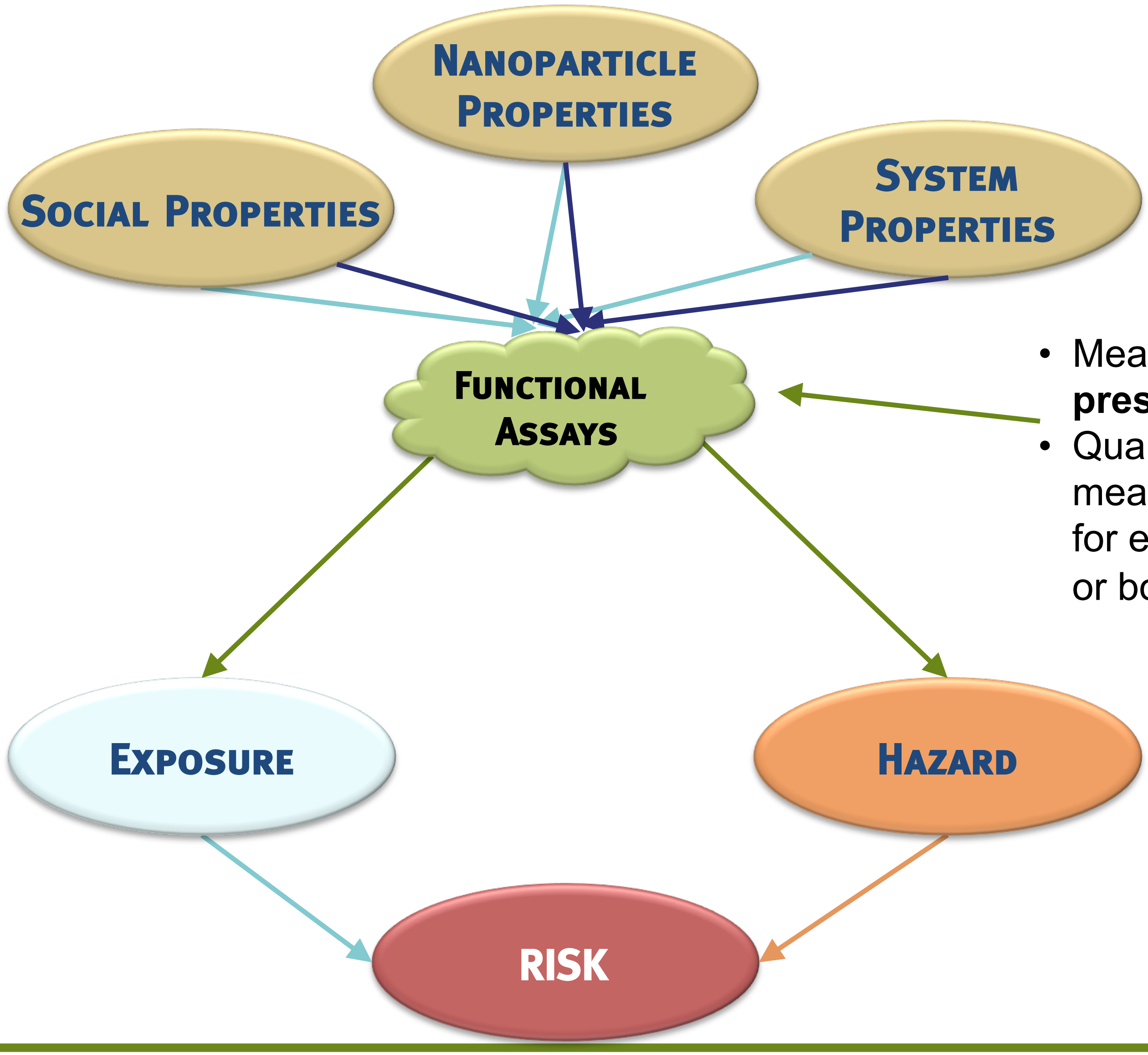


- Composition
- Bandgap
- Size…

- Surface affinity
- Surface charge/ potential (ζ-potential)
- Aggregation rate
- Hydrophobicity…

- Product life cycles and value chains
- Product use behaviors
- ENM production magnitudes

- pH, NOM, Ionic strength, …
- Surfaces (biotic, mineral, organic…)
- Fluid flow, temperature…



- Measurement in **prescribed system**
- Quantifies a meaningful process for exposure, hazard or both

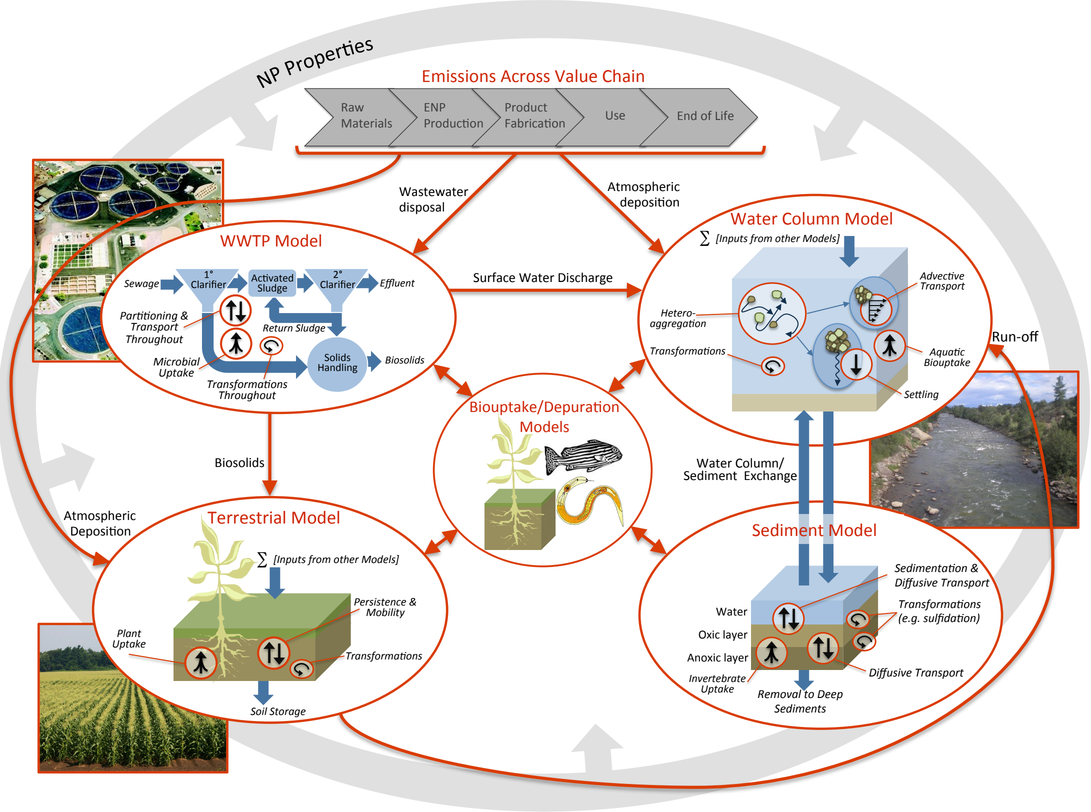
FUNCTIONAL ASSAY FOCUS – FATE & TRANSPORT EXAMPLE

$$\frac{dn_{k_i}}{dt} = \pm\alpha\beta n_i\gamma_j - k_{dissolution} n_k + k_{formation} n_k + k_{transformation} n_k + k_{biouptake} n_k + k_{depuration} n_k$$

- Settling
- Aggregation
- Deposition

- Precipitation
- Bioproduction

- Sulfidation
- Complexation
- Hydroxylation
- Oxidation/ Reduction …



Key functional Assays:

- Surface affinity
- Dissolution rate
- Transformation rates
- Bioüptake/ depuration

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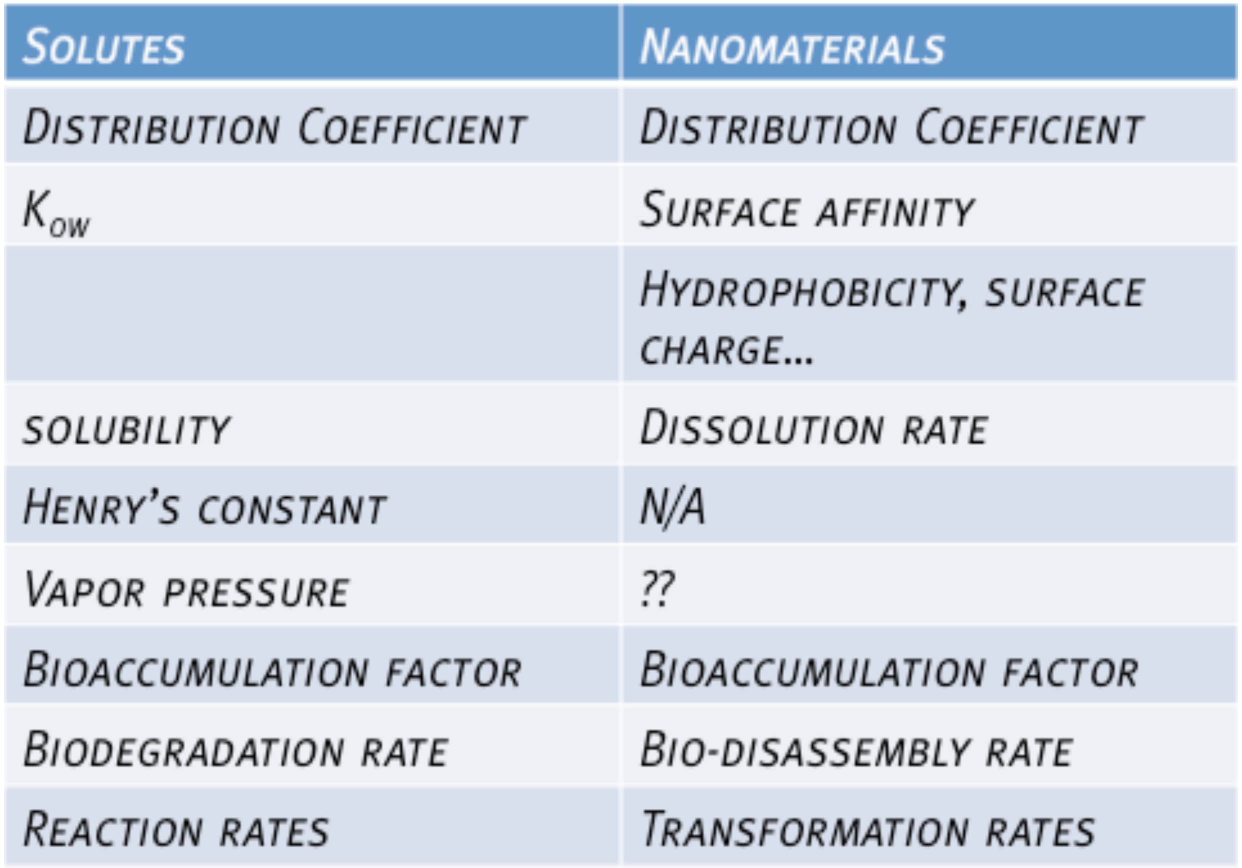
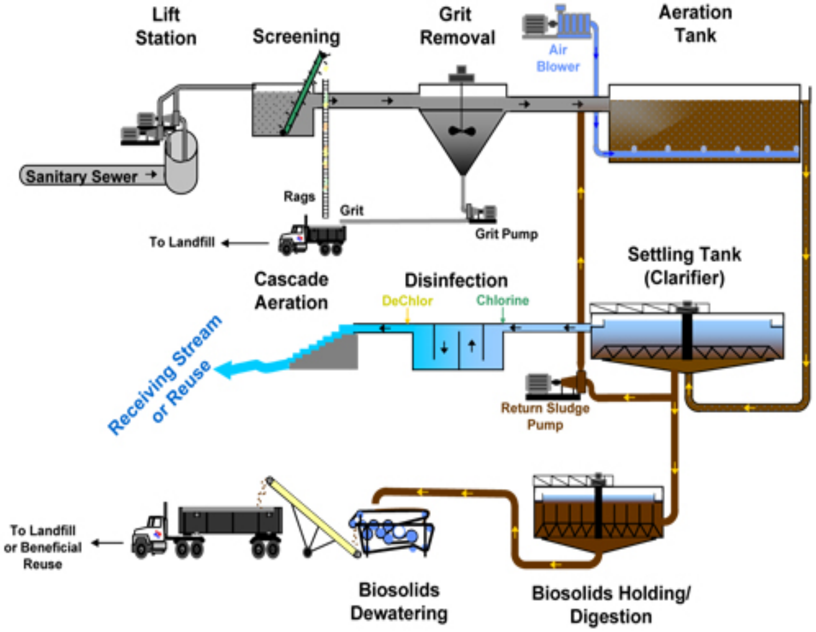
WHAT PARAMETERS ARE NEEDED TO PREDICT TRANSPORT AND FATE OF NANOPARTICLES/



Solutes	Nanomaterials
Distribution Coefficient	Distribution Coefficient
K_{ow}	Surface affinity
	Hydrophobicity, surface charge…
solubility	Dissolution rate
Henry’s constant	N/A
Vapor pressure	??
Bioaccumulation factor	Bioaccumulation factor
Biodegradation rate	Bio-disassembly rate
Reaction rates	Transformation rates

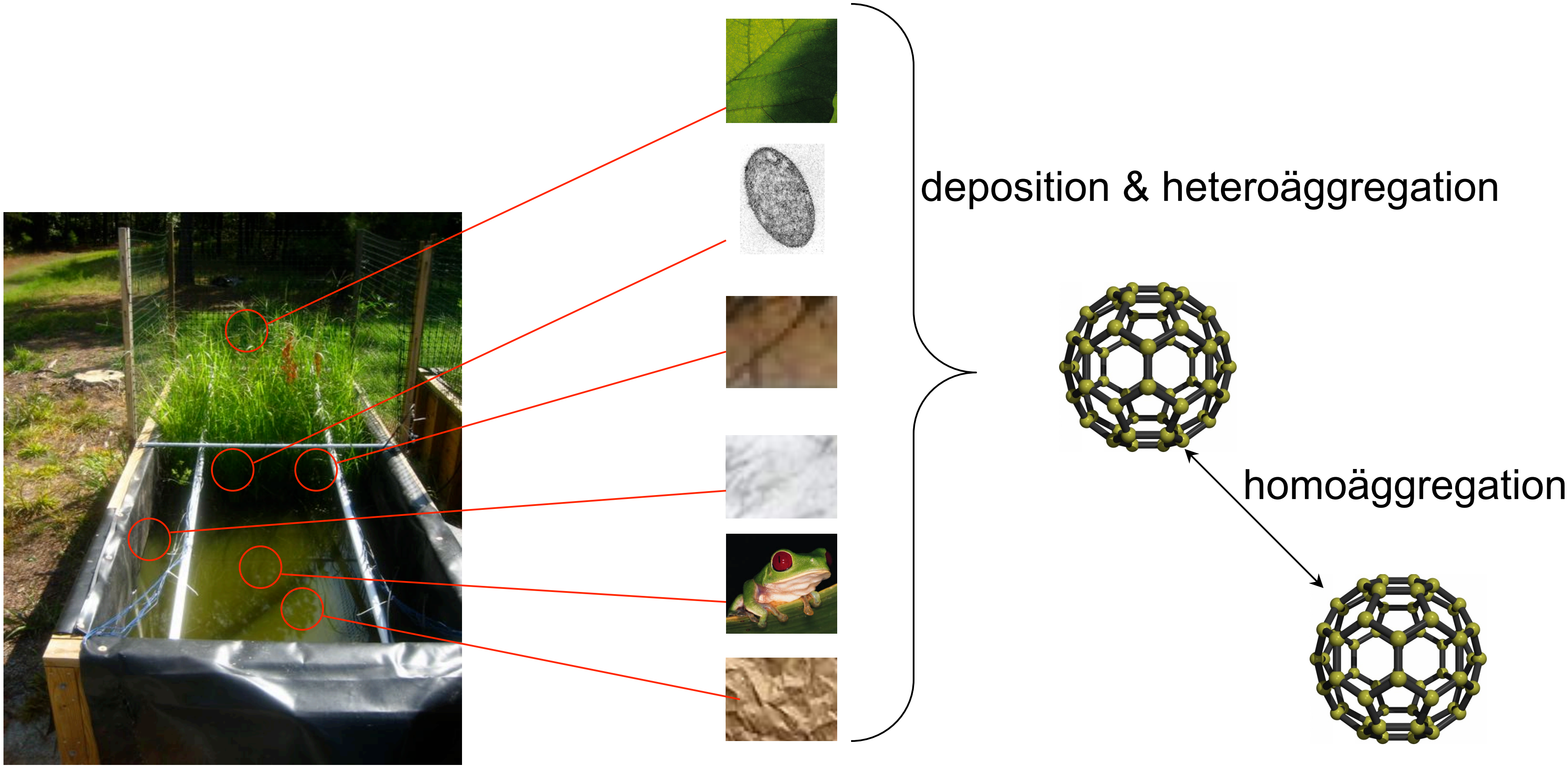
“REAL WORLD” TRANSFORMATIONS

Wastewater Treatment Plant



Freshwater Wetland

AFFINITY OF NANOPARTICLES FOR VARIOUS SURFACES



deposition & heteroäggregation

homoäggregation

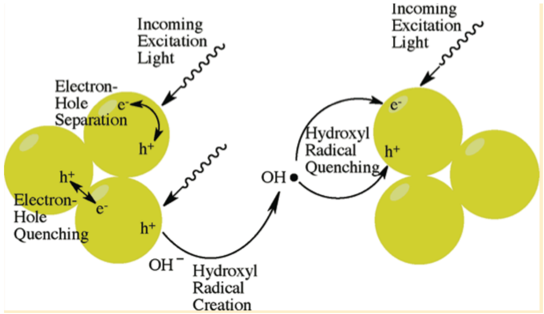
AGGREGATION, TRANSPORT AND SURFACE AFFINITY

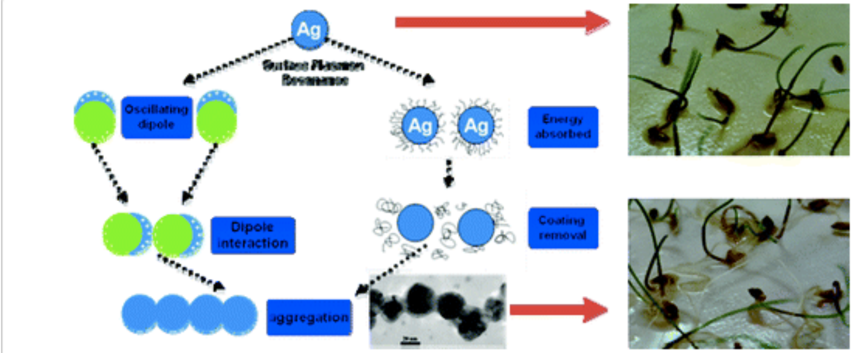
$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j\rightarrow k} \alpha_{ij}\beta_{ij}n_i n_j - n_k \sum_{i=1}^{\infty} \alpha_{ik}\beta_{ik}n_i$$

Depends on
Aggregate size

+/- breakup –settling – dissolution…

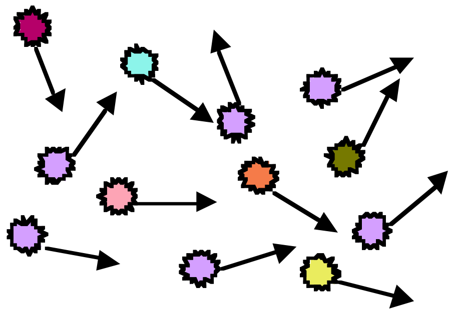
- *AGGREGATION:*
  - *DISSOLUTION*
  - *REACTIVITY*
    - *PHOTO-CATALYSIS*
    - *MOLECULAR ADSORPTION*
  - *TRANSPORT (SETTLING)*
- *DEPOSITION:*
  - *ENVIRONMENTAL DISPERSAL*
  - *BIOUPTAKE*
  - *TRANSLOCATION IN ORGANISMS*



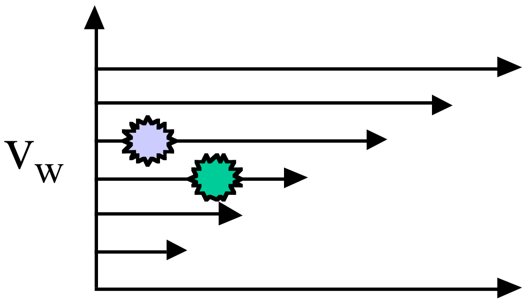


Hotze et al., *Langmuir* 2010, 26(13), 11170–11175
Jassby et al*., Environ. Sci. Technol*. 2012, 46, 6934−6941

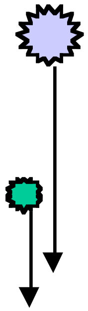
TRANSPORT: PARTICLE COLLISION MECHANISMS



Brownian Diffusion



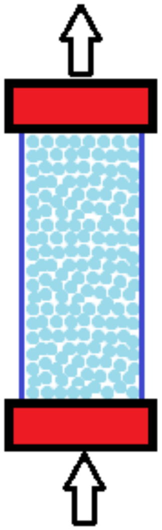
Velocity gradients (shear)

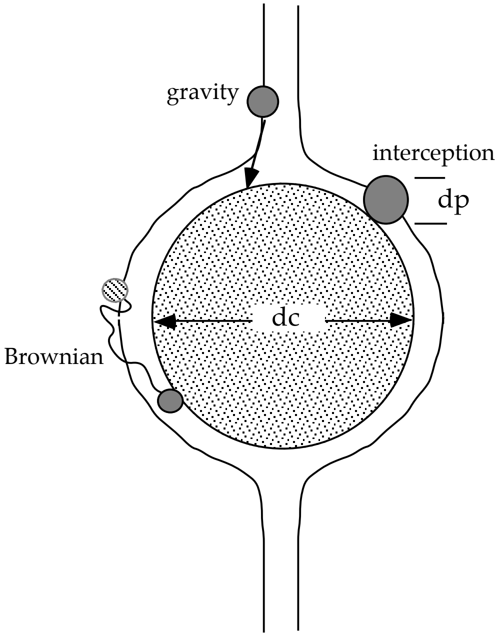


Differential Sedimentation

Aggregation

β





Deposition

η_0

AGGREGATION AND DEPOSITION BOTH DEPEND ON SURFACE AFFINITY

Aggregation rate proportional to $\alpha\beta$

Deposition rate proportional to $\alpha\eta$

Settling rate dependent on (hetero)aggregation rate

SIMULATING HETEROÄGGREGATION

$$\frac{dn_{\mathrm{k}}}{dt} = \frac{1}{2}\sum_{\mathrm{i+j\to k}} \alpha_{\mathrm{ij}}\beta_{\mathrm{ij}} n_{\mathrm{i}} n_{\mathrm{j}} - n_{\mathrm{k}} \sum_{\mathrm{i=1}}^{\infty} \alpha_{\mathrm{ik}}\beta_{\mathrm{ik}} n_{\mathrm{i}}$$

$$\begin{aligned}\frac{dn_{T2\mathrm{k}}}{dt} = \frac{1}{2}\sum_{\mathrm{i+j=k}} &\begin{pmatrix} \alpha\left(f_{\mathrm{i}},f_{\mathrm{j}}\right)\beta\left(r_{\mathrm{i}},r_{\mathrm{j}},f_{\mathrm{i}},f_{\mathrm{j}}\right)n_{T2\mathrm{i}}n_{T2\mathrm{j}} \\ +\alpha(f_{\mathrm{i}},0)\beta\left(r_{\mathrm{i}},r_{\mathrm{j}},f_{\mathrm{i}},0\right)n_{T2\mathrm{i}}n_{T3\mathrm{j}} + \alpha\left(0,f_{\mathrm{j}}\right)\beta\left(r_{\mathrm{i}},r_{\mathrm{j}},0,f_{\mathrm{j}}\right)n_{T3\mathrm{i}}n_{T2\mathrm{j}} \\ +\alpha(f_{\mathrm{i}},1)\beta\left(r_{\mathrm{i}},r_{\mathrm{j}},f_{\mathrm{i}},1\right)n_{T2\mathrm{i}}n_{T4\mathrm{j}} + \alpha\left(1,f_{\mathrm{j}}\right)\beta\left(r_{\mathrm{i}},r_{\mathrm{j}},1,f_{\mathrm{j}}\right)n_{T4\mathrm{i}}n_{T2\mathrm{j}} \\ +\alpha(0,1)\beta\left(r_{\mathrm{i}},r_{\mathrm{j}},0_{\mathrm{i}},1\right)n_{T3\mathrm{i}}n_{T4\mathrm{j}} + \alpha(1,0)\beta\left(r_{\mathrm{i}},r_{\mathrm{j}},1,0\right)n_{T4\mathrm{i}}n_{T3\mathrm{j}} \end{pmatrix} \\ &- n_{T2\mathrm{k}}\sum_{\mathrm{i}} \alpha(f_{\mathrm{k}},f_{\mathrm{i}})\beta(r_{\mathrm{k}},r_{\mathrm{i}},f_{\mathrm{k}},f_{\mathrm{i}})n_{T2\mathrm{i}} + \alpha(f_{\mathrm{k}},0)\beta(r_{\mathrm{k}},r_{\mathrm{i}},f_{\mathrm{k}},0)n_{T3\mathrm{i}} \\ &+ \alpha(f_{\mathrm{k}},1)\beta(r_{\mathrm{k}},r_{\mathrm{i}},f_{\mathrm{k}},1)n_{T4\mathrm{i}} - n_{T2\mathrm{k}}\frac{U(r_{\mathrm{k}},f_{\mathrm{k}})}{h} \end{aligned} \tag{18}$$

Mixed aggregates

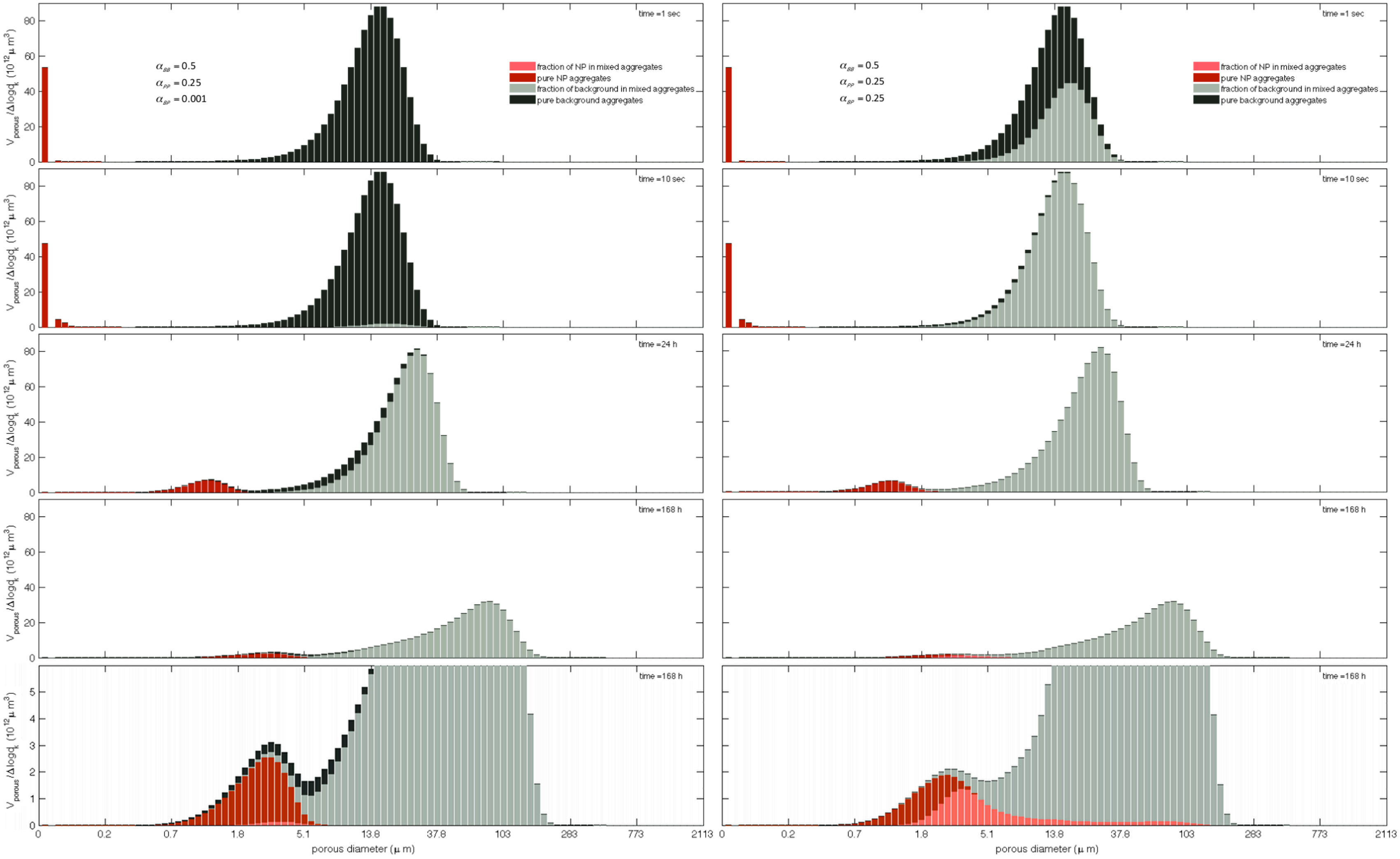
$$\begin{aligned}\frac{dn_{T3\mathrm{k}}}{dt} = \frac{1}{2}\sum_{\mathrm{i+j=k}} &\alpha_{BB}\beta\left(r_{\mathrm{i}},r_{\mathrm{j}},0,0\right)n_{T3\mathrm{i}}n_{T3\mathrm{j}} \\ &- n_{T3\mathrm{k}}\sum_{\mathrm{i}} \alpha(0,f_{\mathrm{i}})\beta(r_{\mathrm{k}},r_{\mathrm{i}},0,f_{\mathrm{i}})n_{T2\mathrm{i}} + \alpha_{BB}\beta(r_{\mathrm{k}},r_{\mathrm{i}},0,0)n_{T3\mathrm{i}} \\ &+ \alpha_{NB}\beta(r_{\mathrm{k}},r_{\mathrm{i}},0,1)n_{T4\mathrm{i}} - n_{T3\mathrm{k}}\frac{U(r_{\mathrm{k}},0)}{h} \end{aligned} \tag{19}$$

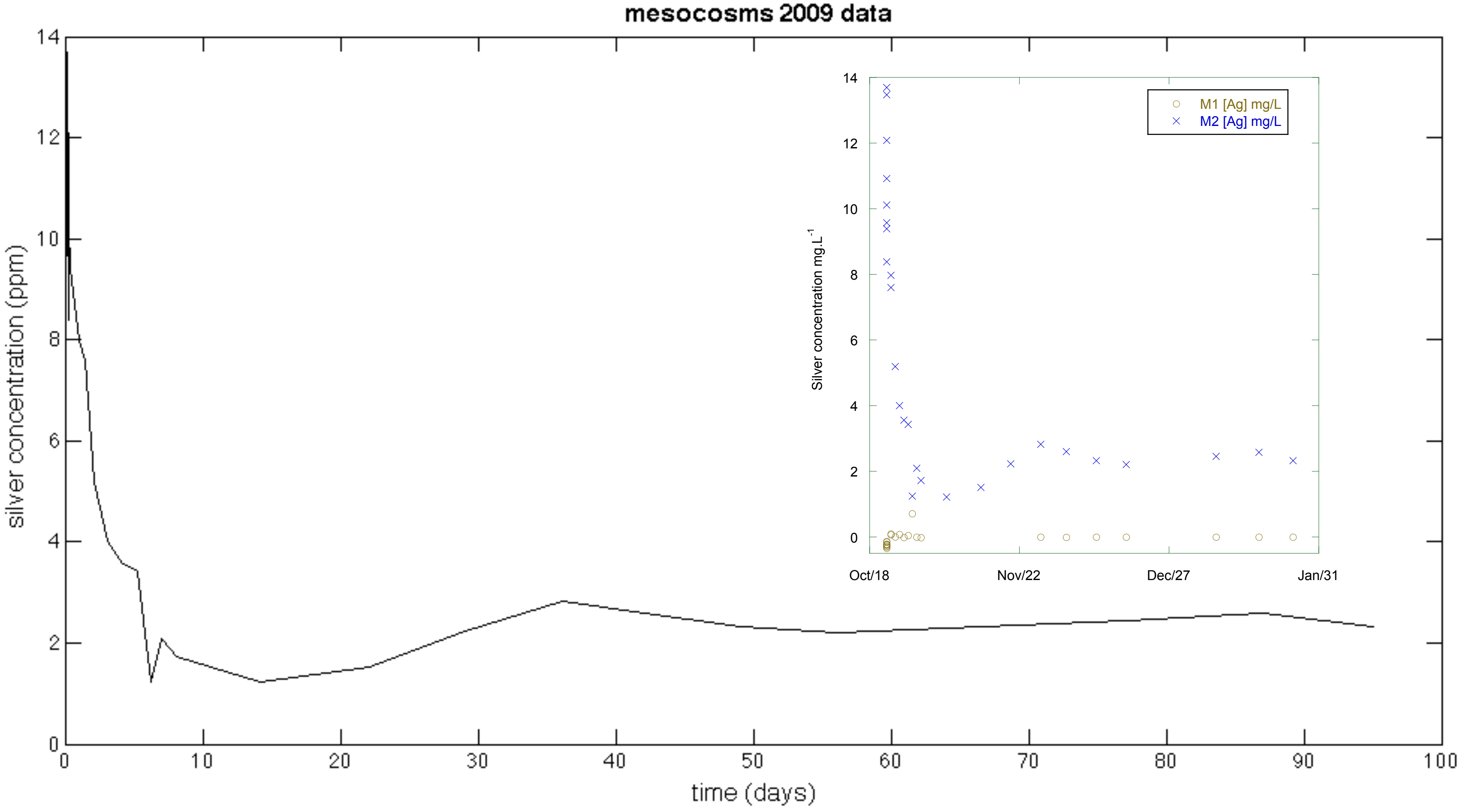
Aggregates of
“background” particles

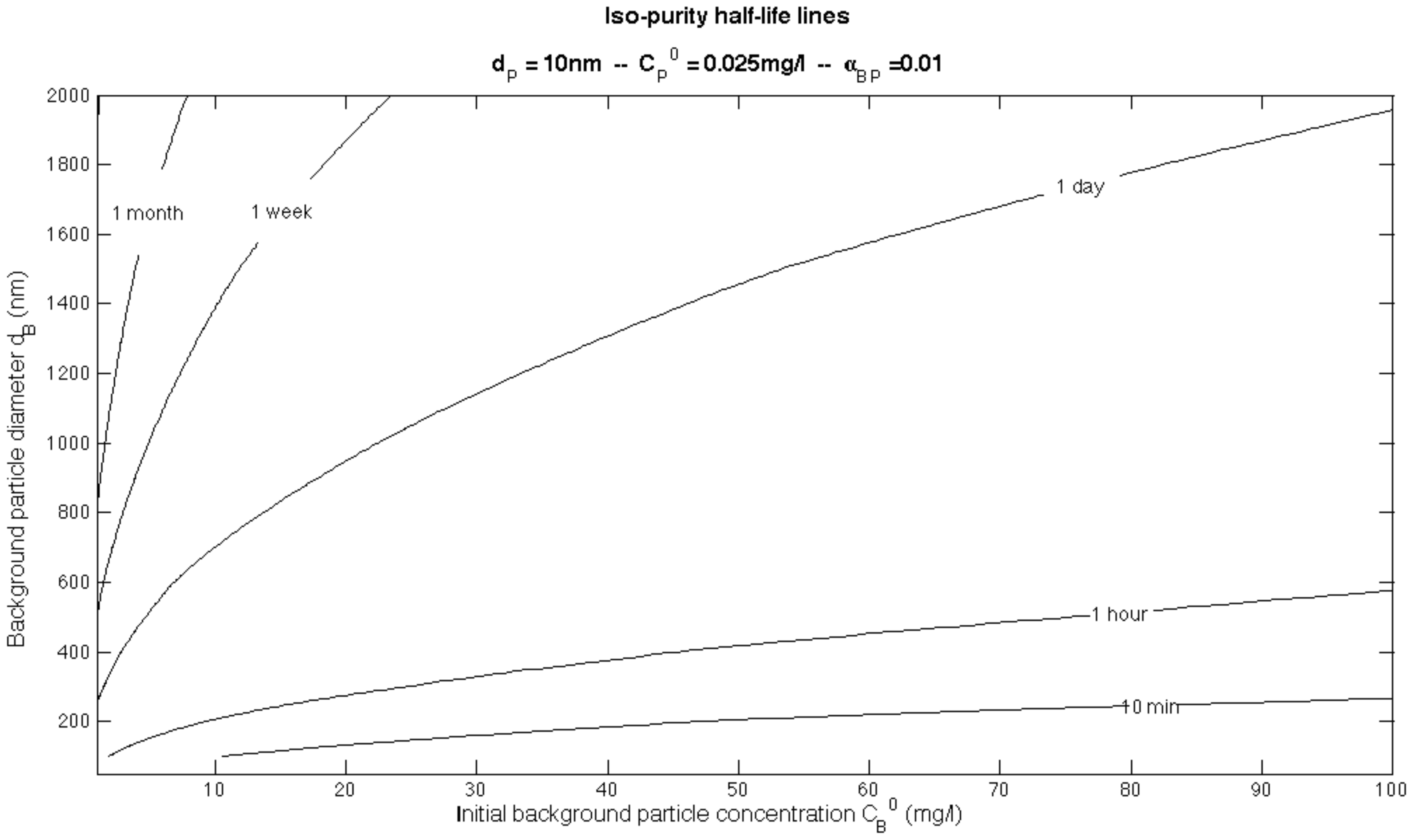
$$\begin{aligned}\frac{dn_{T4\mathrm{k}}}{dt} = \frac{1}{2}\sum_{\mathrm{i+j=k}} &\alpha_{NN}\beta\left(r_{\mathrm{i}},r_{\mathrm{j}},1,1\right)n_{T4\mathrm{i}}n_{T4\mathrm{j}} \\ &- n_{T4\mathrm{k}}\sum_{\mathrm{i}} \alpha(1,f_{\mathrm{i}})\beta(r_{\mathrm{k}},r_{\mathrm{i}},1,f_{\mathrm{i}})n_{T2\mathrm{i}} + \alpha_{NB}\beta(r_{\mathrm{k}},r_{\mathrm{i}},1,0)n_{T3\mathrm{i}} \\ &+ \alpha_{NN}\beta(r_{\mathrm{k}},r_{\mathrm{i}},1,1)n_{T4\mathrm{i}} - n_{T4\mathrm{k}}\frac{U(r_{\mathrm{k}},1)}{h}. \end{aligned} \tag{20}$$

Homoäggregates of
nanoparticles

SIMULATIONS OF HETEROÄGGREGATION




mesocosms 2009 data
silver concentration (ppm)
time (days)
0
2
4
6
8
10
12
14
0
10
20
30
40
50
60
70
80
90
100
Silver concentration mg.L^{-1}
M1 [Ag] mg/L
M2 [Ag] mg/L
Oct/18
Nov/22
Dec/27
Jan/31


Iso-purity half-life lines
d_P = 10nm -- C_P^0 = 0.025mg/l -- α_{BP} = 0.01
Background particle diameter d_B (nm)
2000
1800
1600
1400
1200
1000
800
600
400
200
Initial background particle concentration C_B^0 (mg/l)
10
20
30
40
50
60
70
80
90
100
1 month
1 week
1 day
1 hour
10 min

SURFACE AFFINITY INCLUDES EFFECTS FROM:

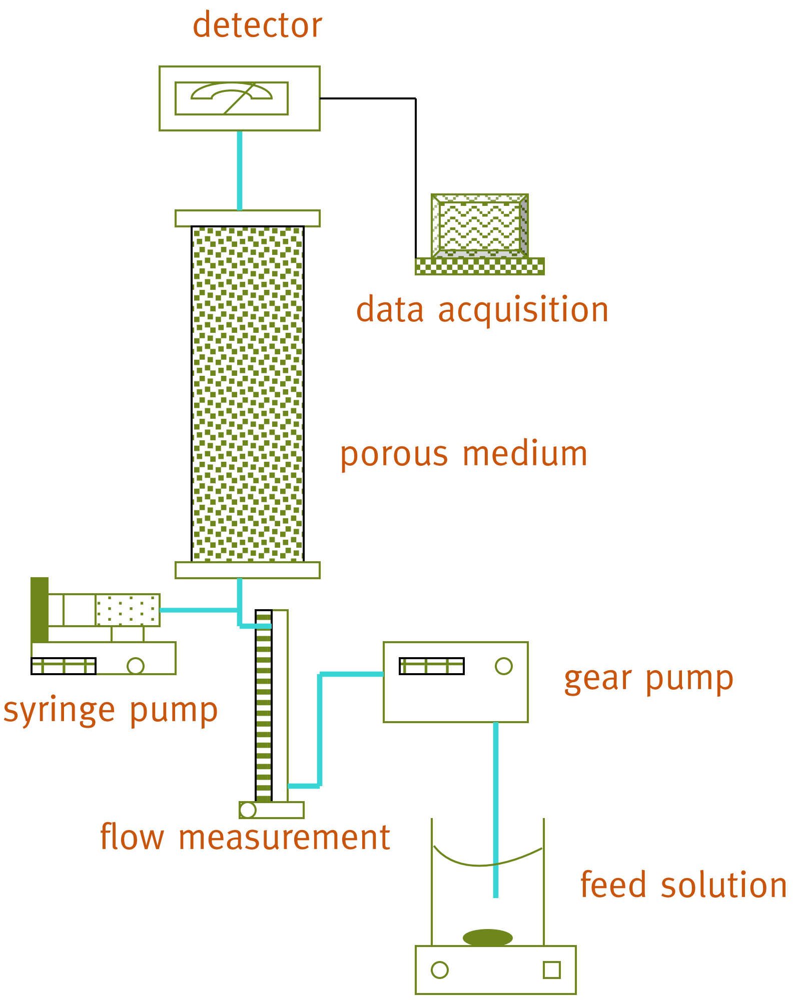
- *NANOPARTICLE COMPOSITION, COMPOSITION OF SURFACE, INTERVENING FLUID*
- *ADSORBED MACROMOLECULES*
  - Proteins
  - Engineered surface treatments/ stabilizers
  - Humic materials, polysaccharides…
- *IONIC COMPOSITION*
  - Ionic strength, charge screening
  - Specific adsorption of ions (e.g., Ca, PO4…)
  - 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 (ALPHA)


detector

data acquisition

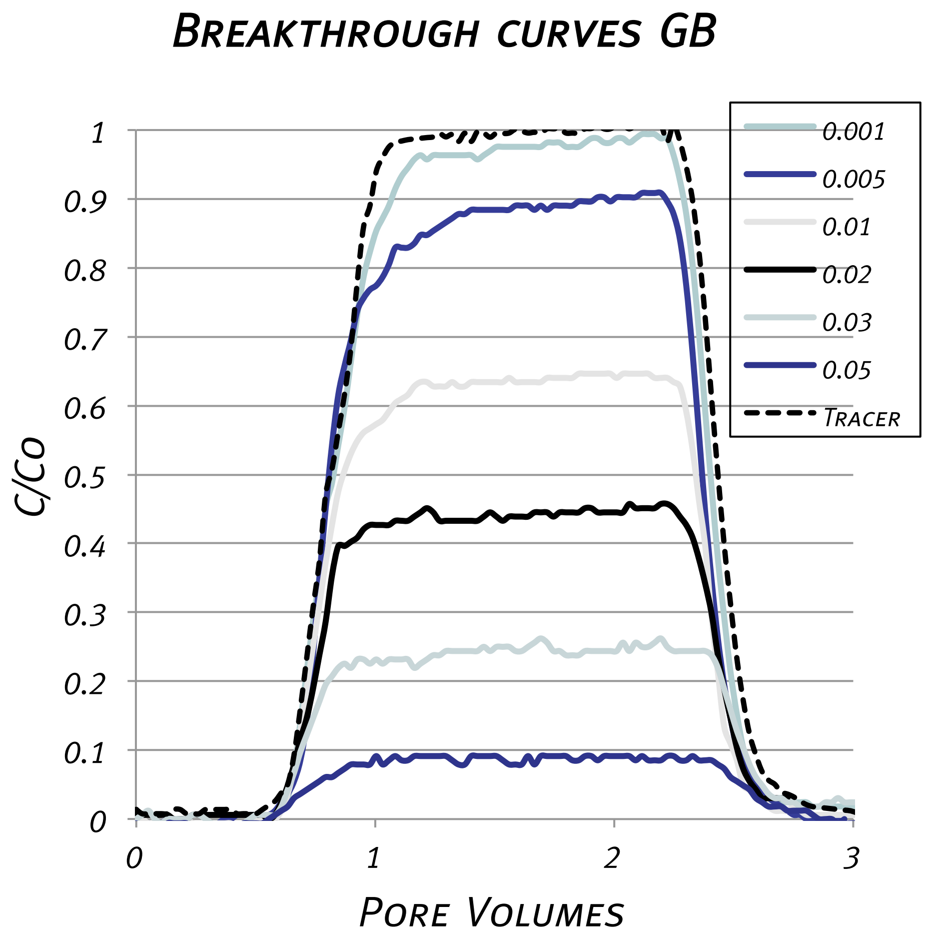
porous medium

syringe pump

gear pump

flow measurement

feed solution


BREAKTHROUGH CURVES GB

MEASURING SURFACE AFFINITY IN COMPLEX SYSTEMS

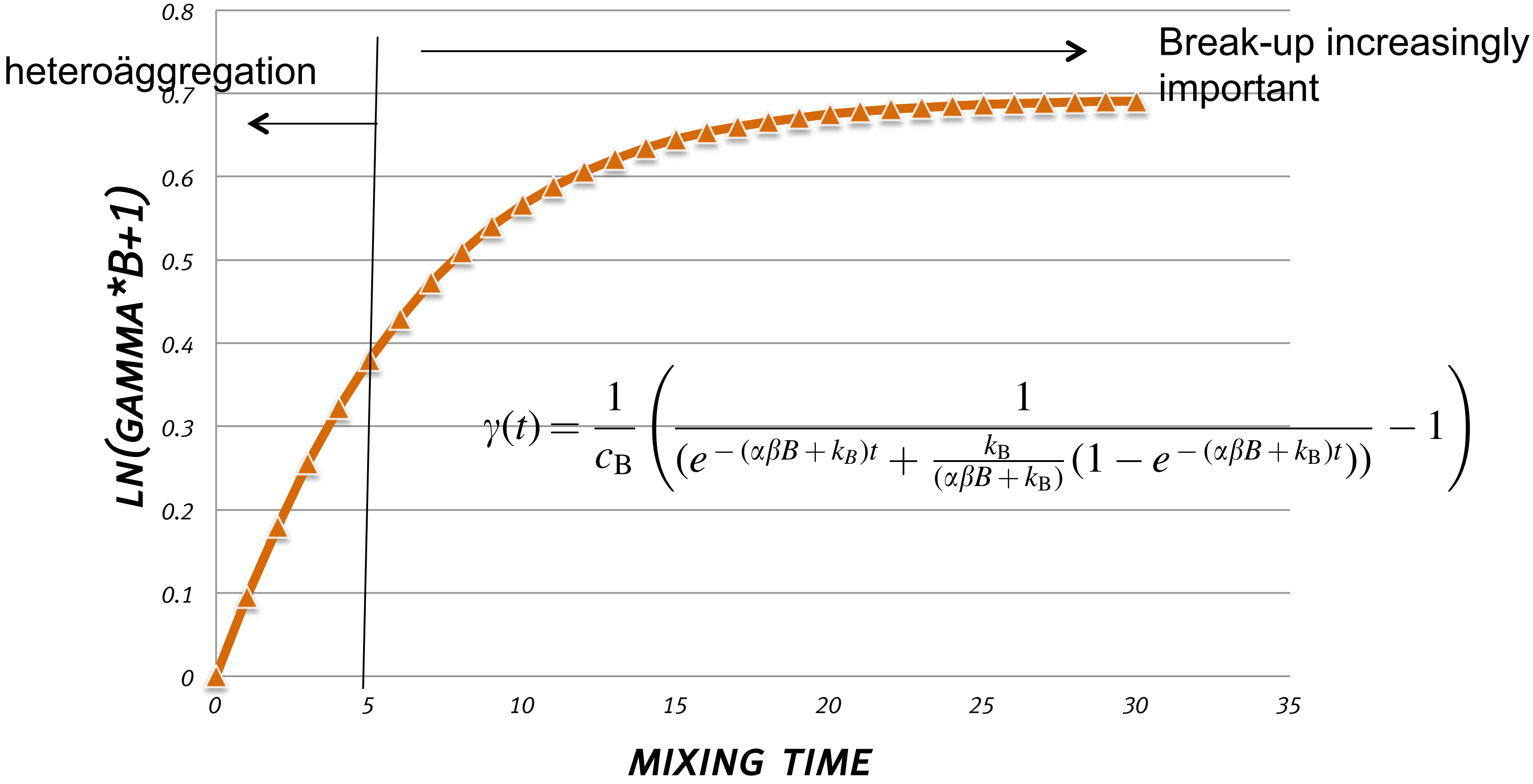
$$\frac{dn_k}{dt} = \frac{1}{2}\alpha \sum_{i+j\rightarrow k} \beta(i,j) n_i n_j - \alpha n_k \sum_i \beta(i,k) n_i - breakup$$

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

$$\ln(\gamma B + 1) = \alpha\beta(n,B)Bt$$

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

PREDICTED TREND FOR HETEROÄGGREGATION

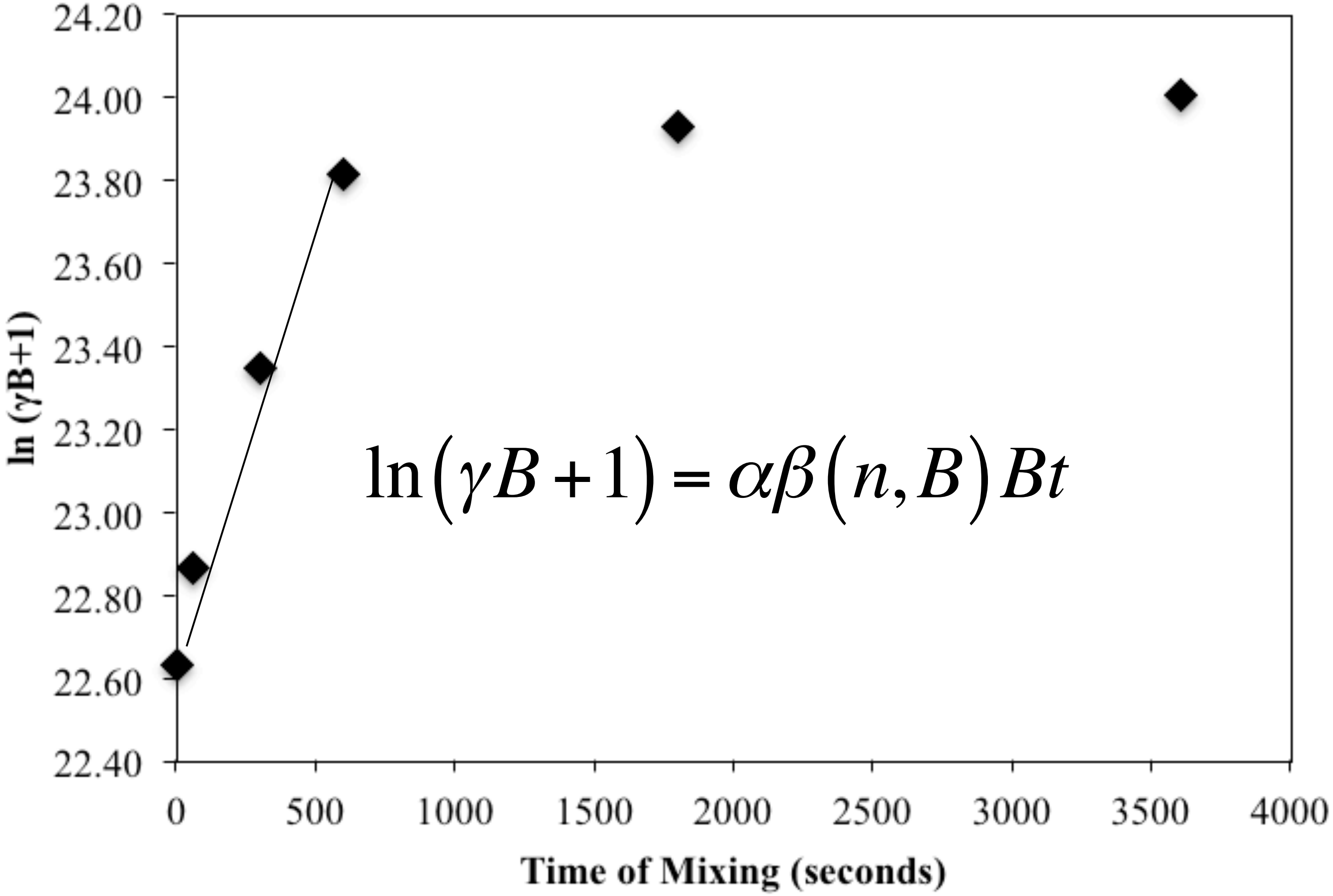


heteroäggregation

Break-up increasingly important

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

Time dependent distribution coefficient vs. aggregation time



$$\ln\left(\gamma B+1\right)=\alpha\beta\left(n,B\right)Bt$$

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

TYPICAL TRENDS FOR α (COLUMN EXPERIMENTS) REPORTED IN THE LITERATURE

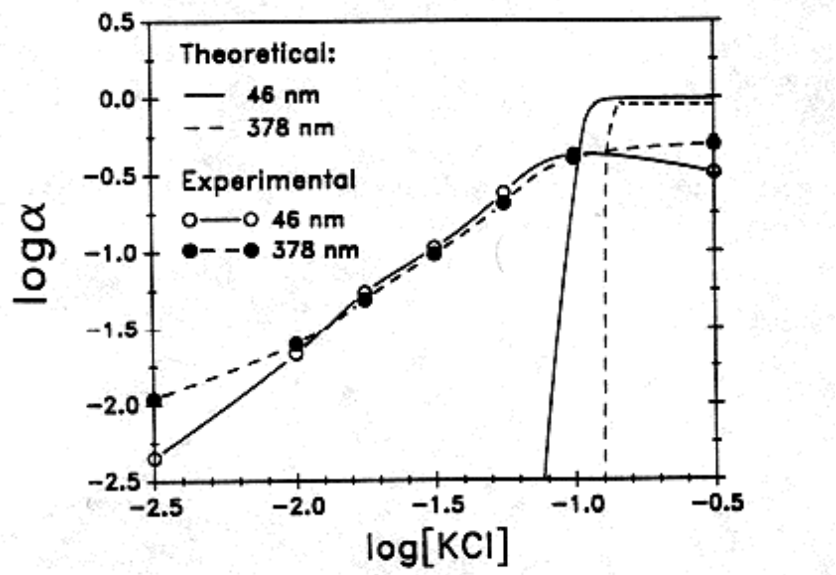
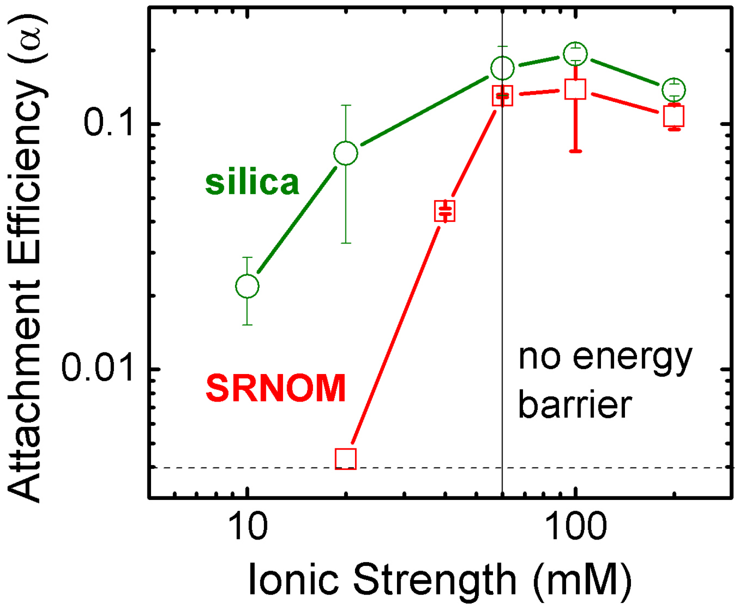


Fig. 2. Comparison of theoretical and experimental collision efficiencies of two different suspensions of Brownian (submicron) latex particles.

M. Elimelech

Wat. Res. Vol. 26, No. 1, pp. 1–8, 1992

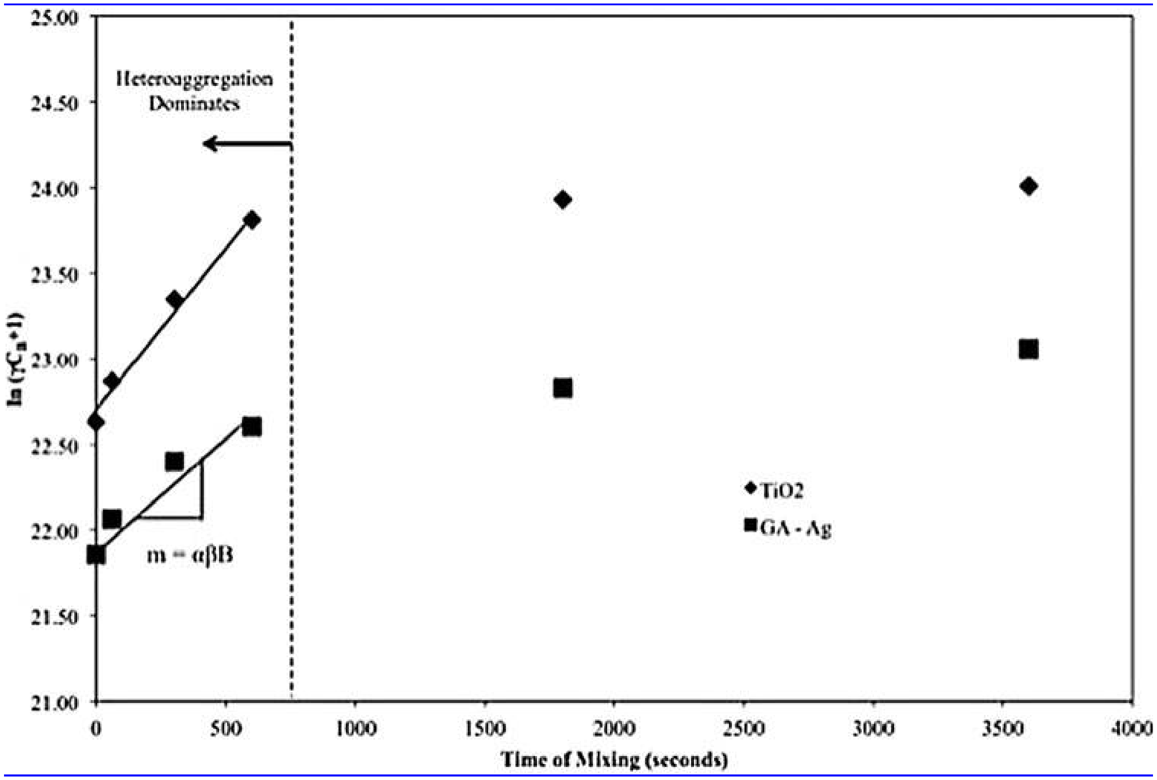


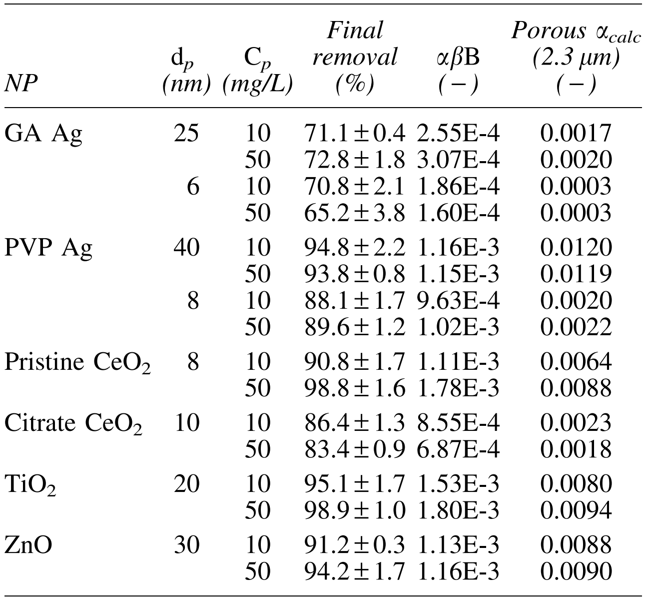
MS2 virus deposition

B. Yuan et al.

Environ. Sci. Technol., **2008**, *42* (20), pp 7628–7633

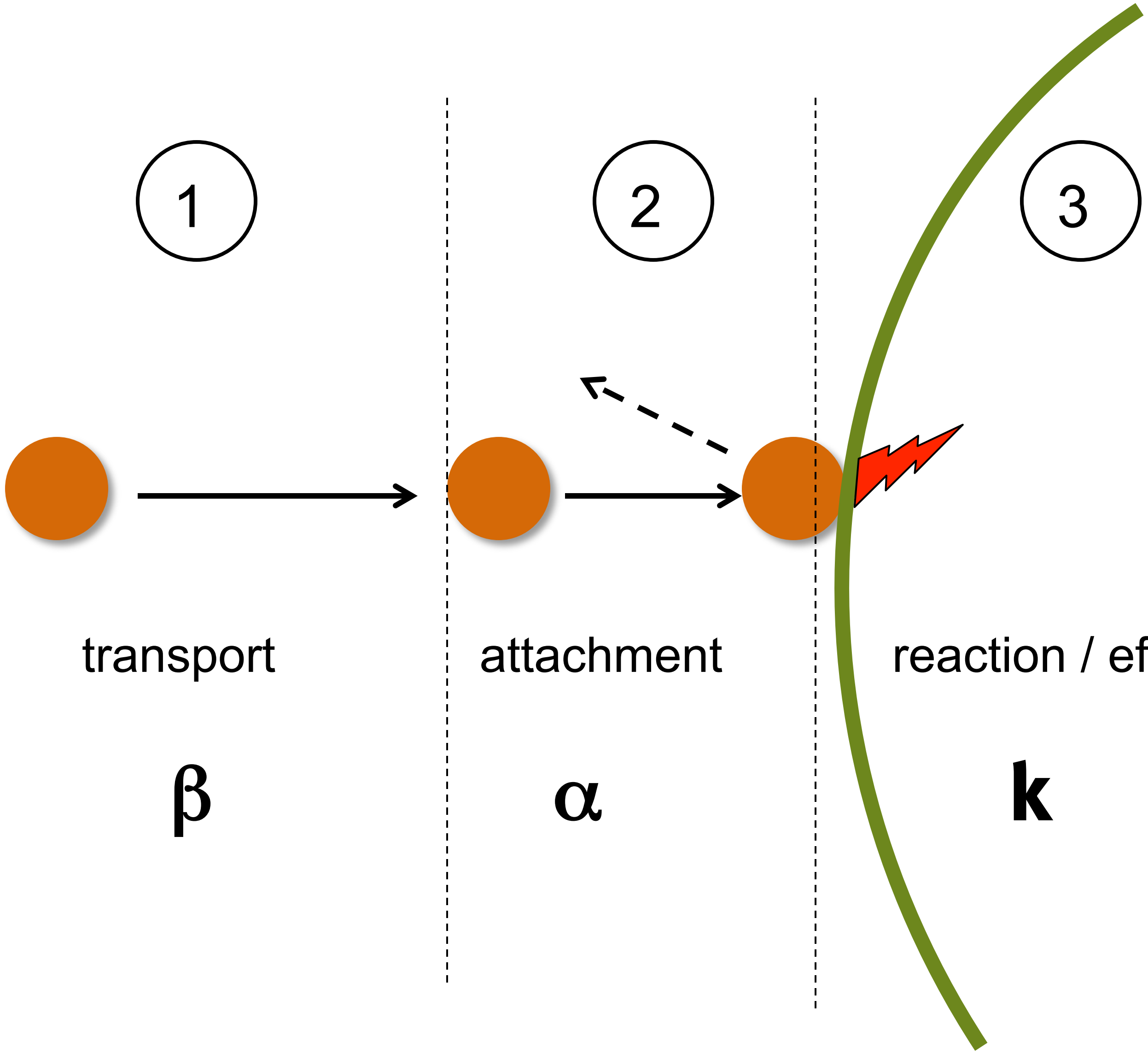
SURFACE AFFINITIES FOR SEVERAL NANOMATERIALS AND ACTIVATED SLUDGE



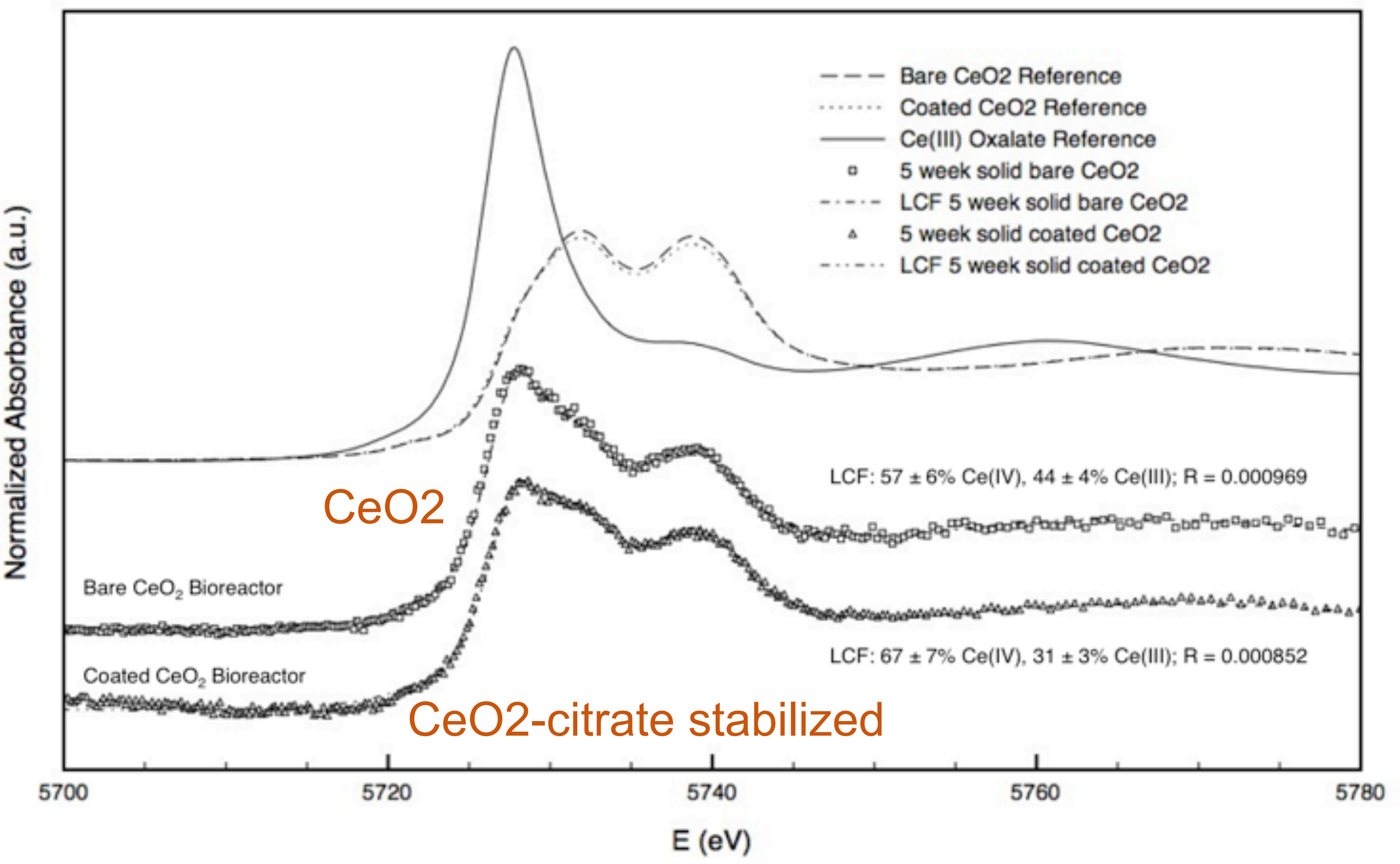


NP	d_p *(nm)*	C_p *(mg/L)*	*Final removal (%)*	$\alpha\beta$B *(−)*	*Porous* α_{calc} *(2.3 μm) (−)*
GA Ag	25	10	71.1 ± 0.4	2.55E-4	0.0017
		50	72.8 ± 1.8	3.07E-4	0.0020
	6	10	70.8 ± 2.1	1.86E-4	0.0003
		50	65.2 ± 3.8	1.60E-4	0.0003
PVP Ag	40	10	94.8 ± 2.2	1.16E-3	0.0120
		50	93.8 ± 0.8	1.15E-3	0.0119
	8	10	88.1 ± 1.7	9.63E-4	0.0020
		50	89.6 ± 1.2	1.02E-3	0.0022
Pristine CeO_2	8	10	90.8 ± 1.7	1.11E-3	0.0064
		50	98.8 ± 1.6	1.78E-3	0.0088
Citrate CeO_2	10	10	86.4 ± 1.3	8.55E-4	0.0023
		50	83.4 ± 0.9	6.87E-4	0.0018
TiO_2	20	10	95.1 ± 1.7	1.53E-3	0.0080
		50	98.9 ± 1.0	1.80E-3	0.0094
ZnO	30	10	91.2 ± 0.3	1.13E-3	0.0088
		50	94.2 ± 1.7	1.16E-3	0.0090

CONCEPTUAL MODEL FOR NANOPARTICLE REACTIVITY



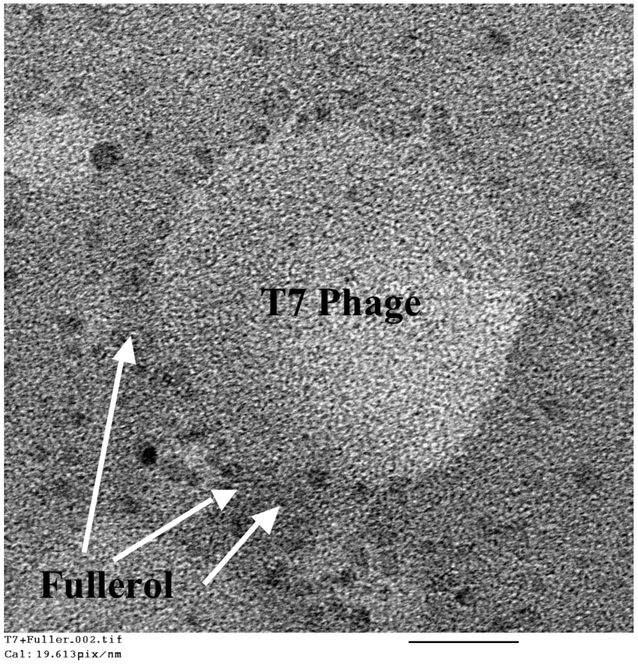
Importance of surface affinity for transformtion: CeO2

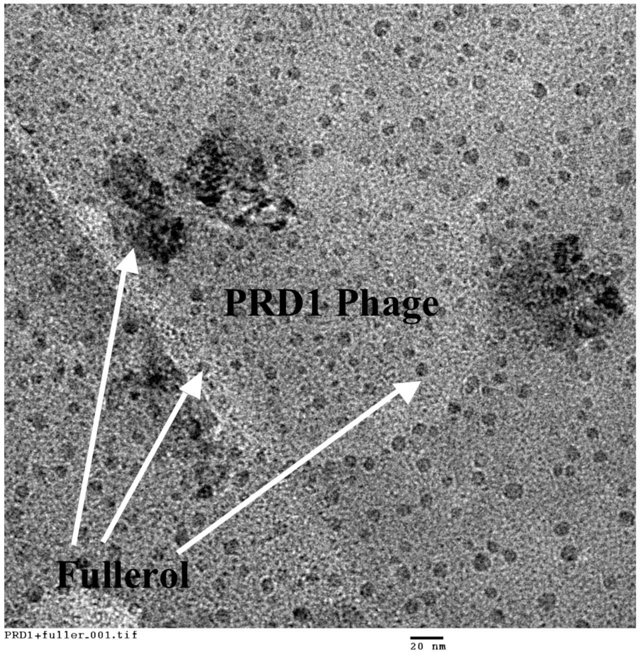


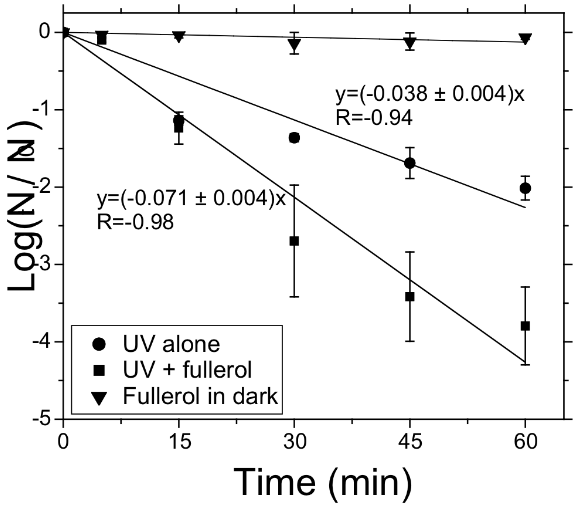
CeO2

CeO2-citrate stabilized

Barton et al. 2014 (in review)

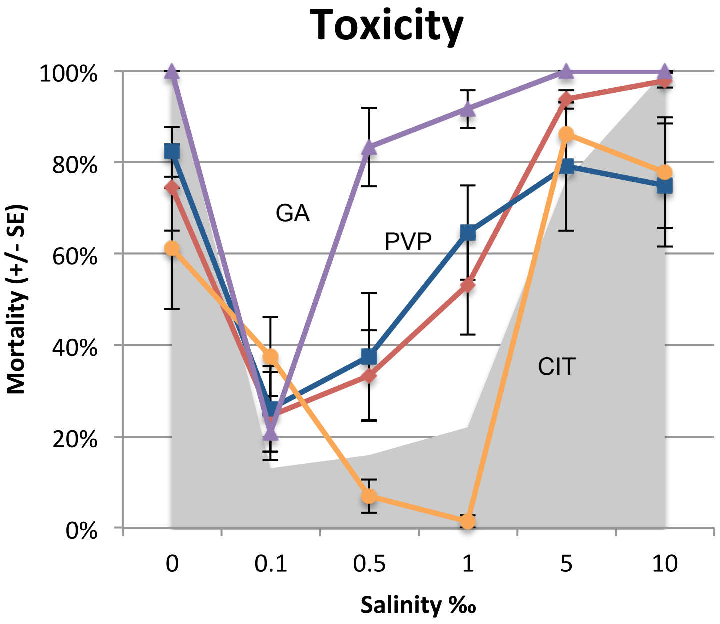


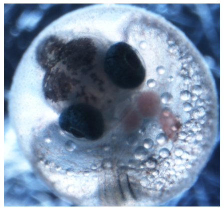




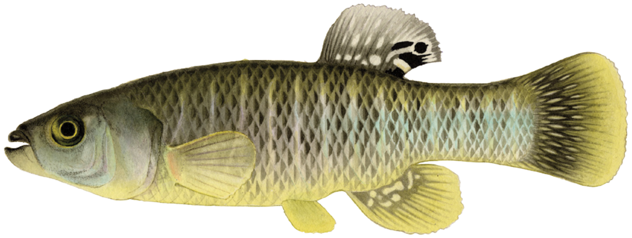
Badireddy et al., *Environ. Sci. Technol.* VOL. 43, NO. 17, 2009

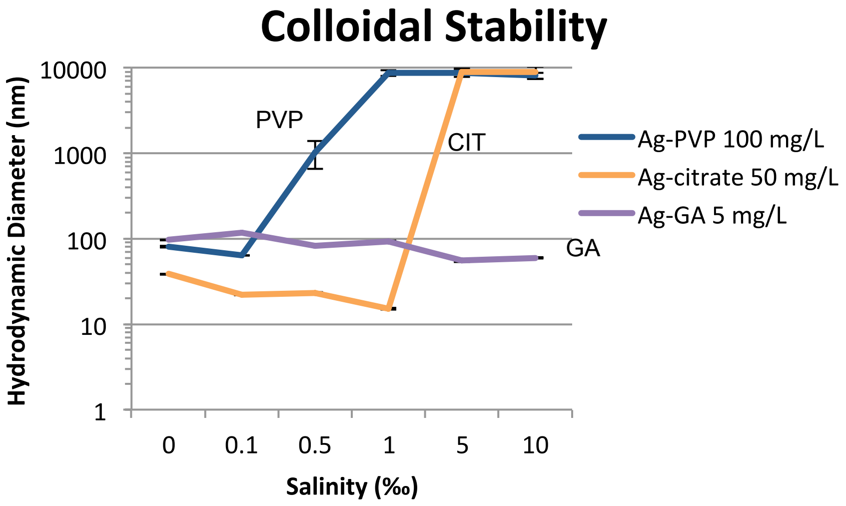
Ag NP Embryotoxicity across a Salinity Gradient – The Role of Coatings and Dissolved Silver





Atlantic killifish
Fundulus heteroclitus





- Ag NP coatings significantly affect particle behavior
  - Stability/Aggregation (Ag-gum arabic most stable)
  - Toxicity (Ag-gum arabic most toxic)
- Dissolved silver and silver speciation play a significant role in toxicity
  - Toxicity curve shape related to silver speciation (total dissolved Ag, not Ag^+)

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AUFFAN ET AL., *NANOTOXICOLOGY*, 2013, BONE ET AL, *ES&T* 2012

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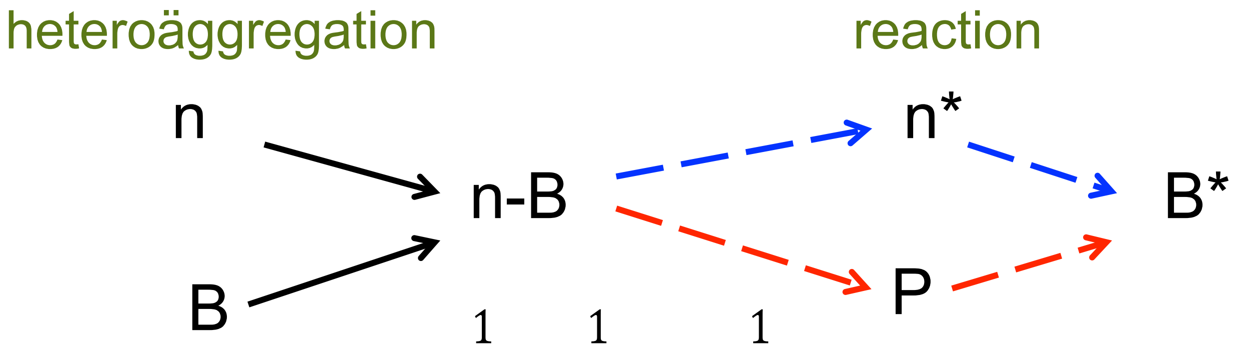
EXAMPLES OF NANOPARTICLE REACTIVITY

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



heteroäggregation

reaction

n

B

n-B

n*

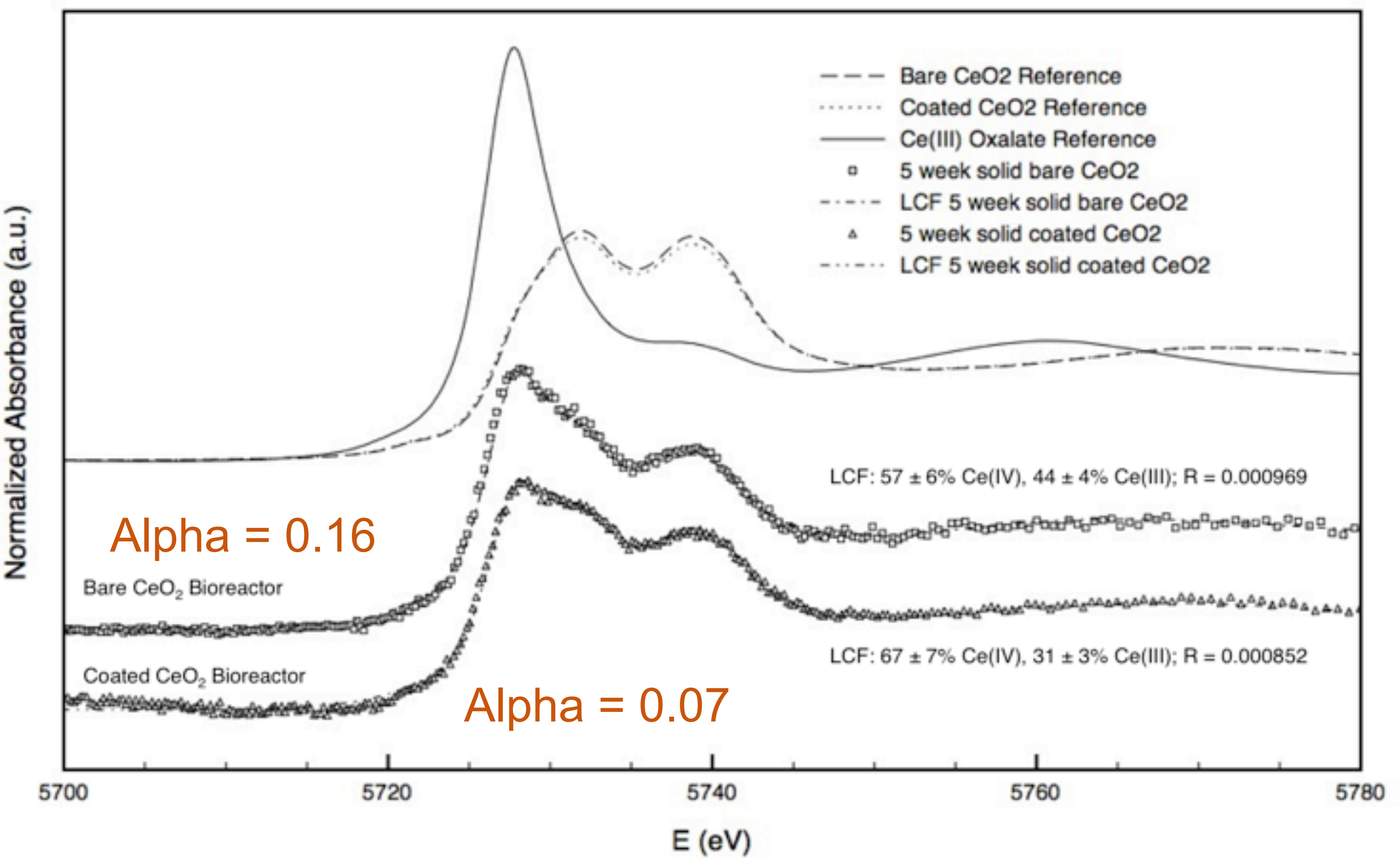
P

B*

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

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

Importance of surface affinity for transformtion: CeO2



Alpha = 0.16

Alpha = 0.07

Barton et al. 2014 (in review)

Conclusions

1. Heteroäggregation/ deposition is a key fate process
2. Surface Affinity in complex media can be measured using programmed mixing procedure
3. Limitation- for practical purposes, only varies over 4 orders of magnitude
4. Surface affinity appears to be important for some aspects of nanoparticle reactivity and perhaps bioavailability
5. Need reference systems