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Dissolution and retention of nanoparticles in soils

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GUIDE *nano* 

NANOFASE

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Dissolution

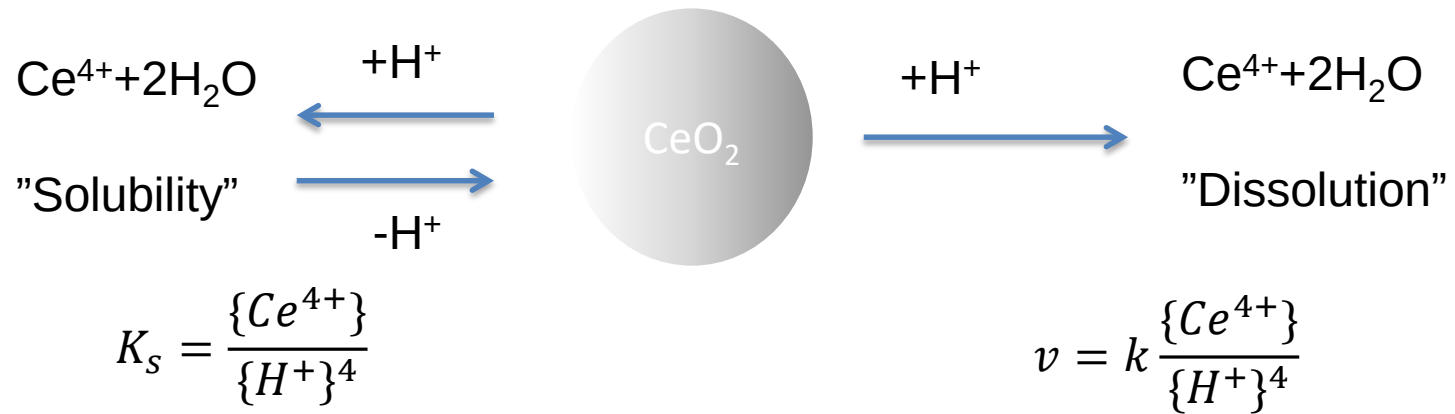
- Intro
- Methods
 - Ultrafiltration
 - (Ultra)centrifugation
 - Dialysis
 - spICP-MS
- Parameters affecting AgNP dissolution
- Dissolution



Dissolution: relevance

- Toxic mode of action often through ion, not NP (e.g. Ag)
- Fate of ions is vastly different from NP
- Risk assessment tools for metals are well developed for dissolved ions, much less so for NP

Dissolution vs. solubility



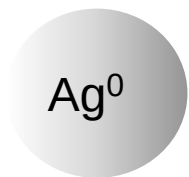


Dissolution

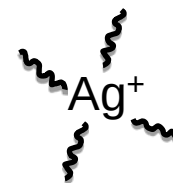
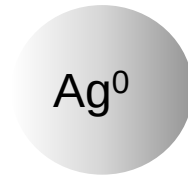
What is the "*dissolved*" phase

- Ionic
- Molecular
- $< 0.45 \text{ } \mu\text{m}$
- "not centrifugeable"
- $< 1 \text{ nm}$
- $< 1 \text{ kDa}$

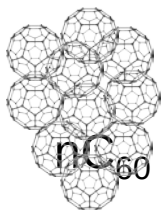
Dissolved or not?



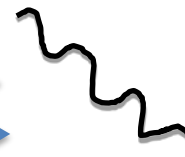
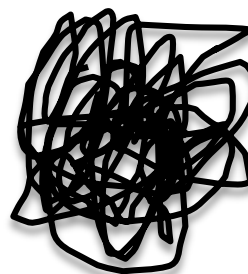
1 nm



1 nm



1 nm



1 nm



Dissolution: methods

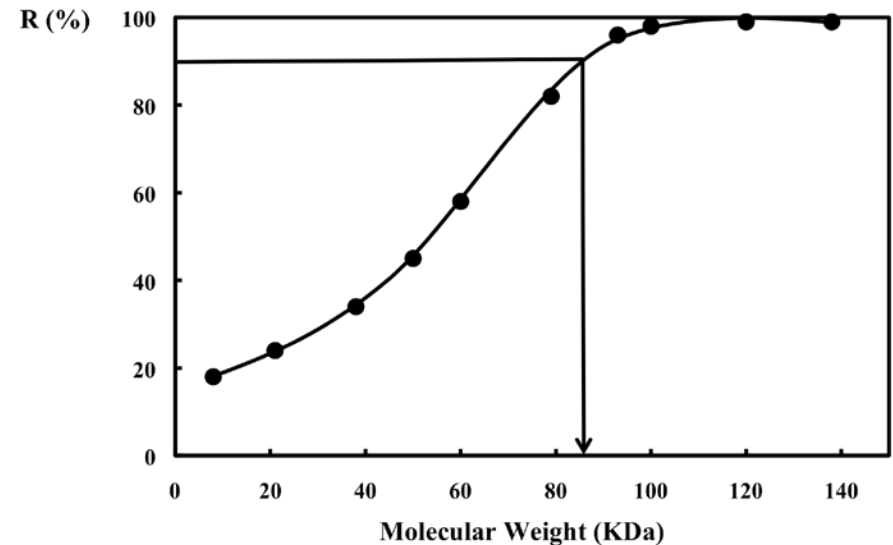
Available techniques

- Ultrafiltration
- Ultra-centrifugation
- Dialysis bags
- spICP-MS

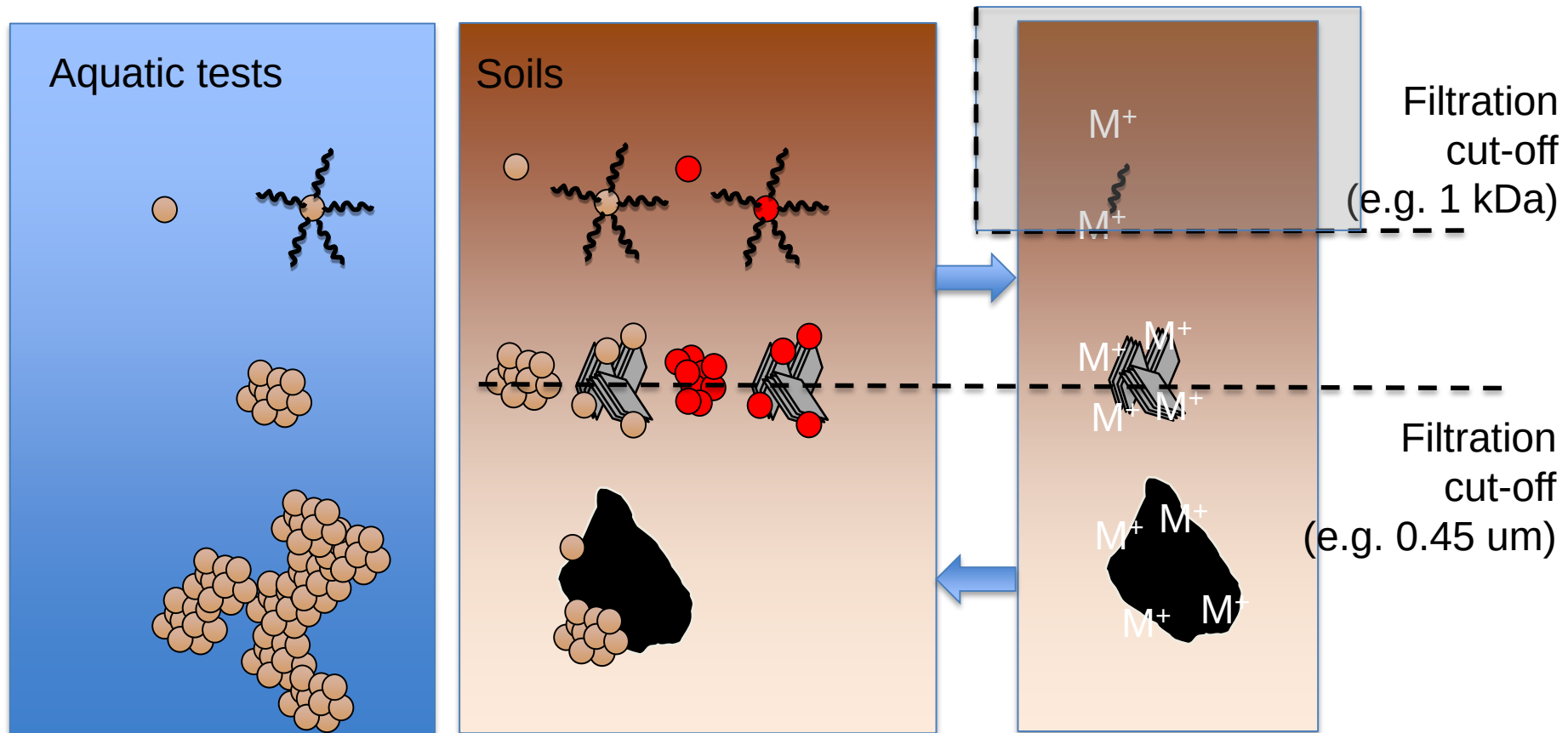


Ultrafiltration

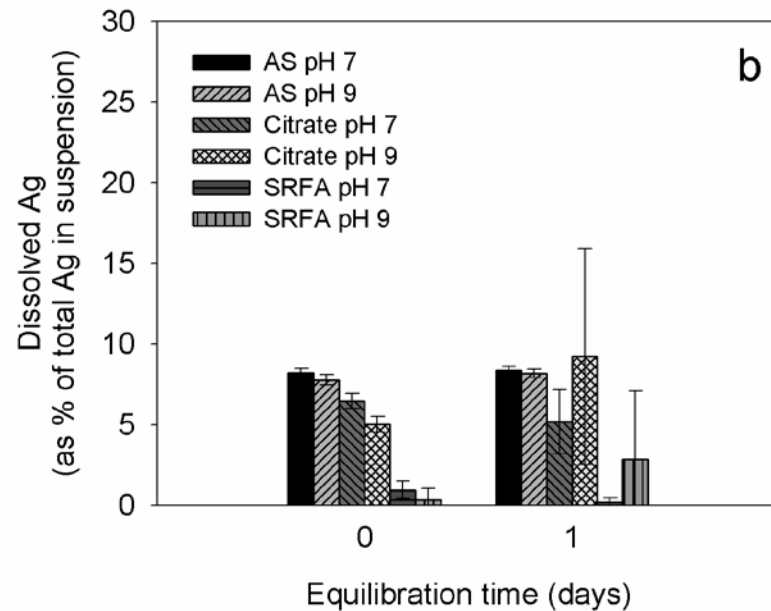
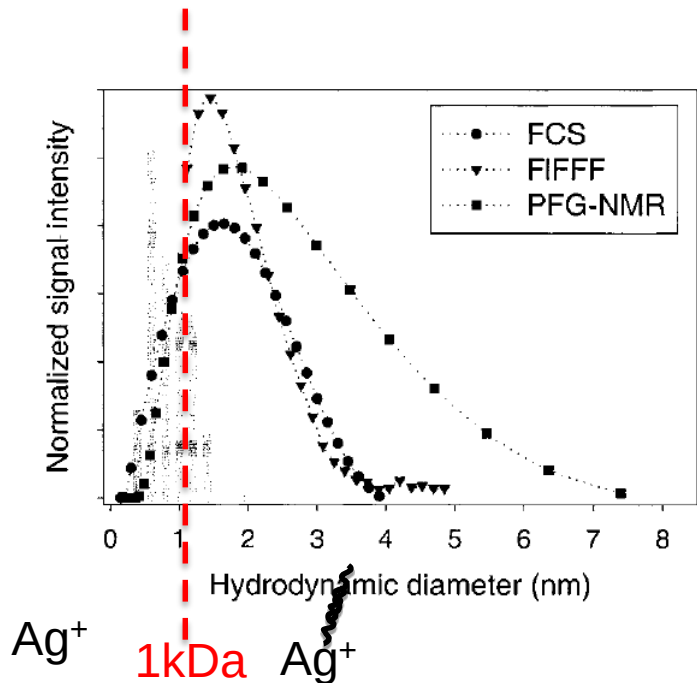
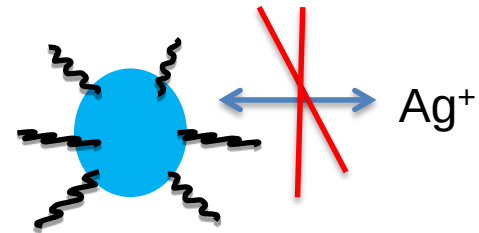
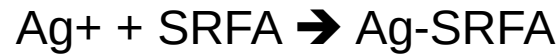
- Size cut-off expressed in "Daltons": Molecular weight cut-off (MWCO)
 - ➔ Molecular weight of a PEG molecule that is retained for at least 90 %
 - ➔ Always a distribution of sizes that is filtered



Separation of ENP: filtration

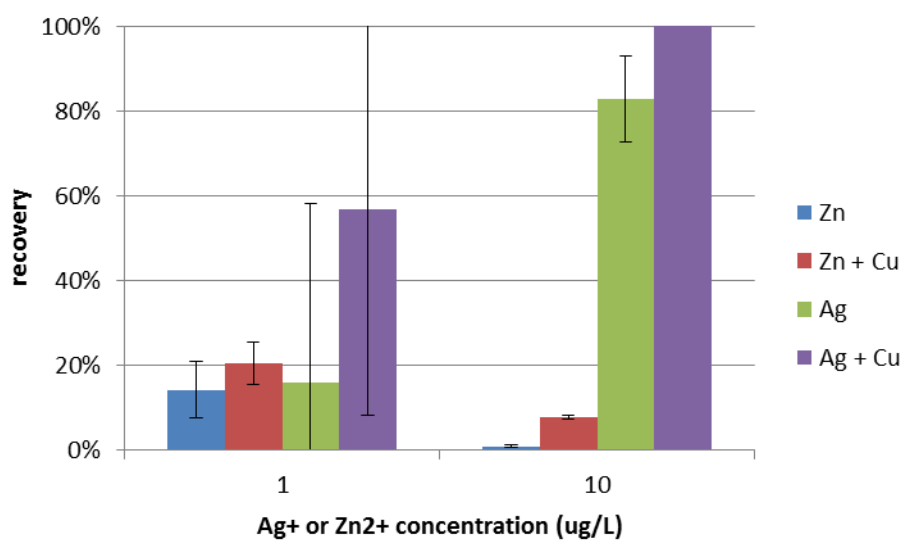


Dissolution of Ag NP

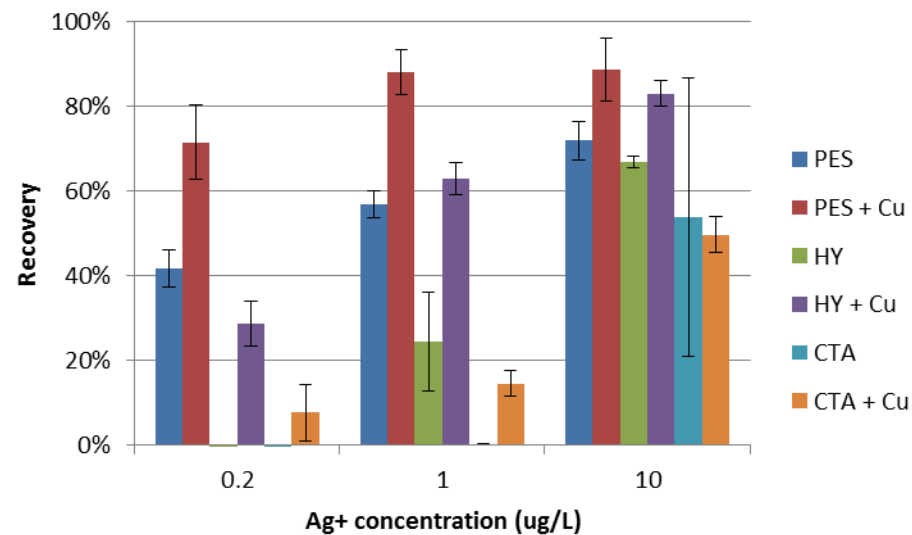


Separation of ENP: filtration

0.45 um filtration



Ultrafiltration





Centrifugation

Down:

- centrifugal force

Up:

- Drag (viscous)
- Buoyant force

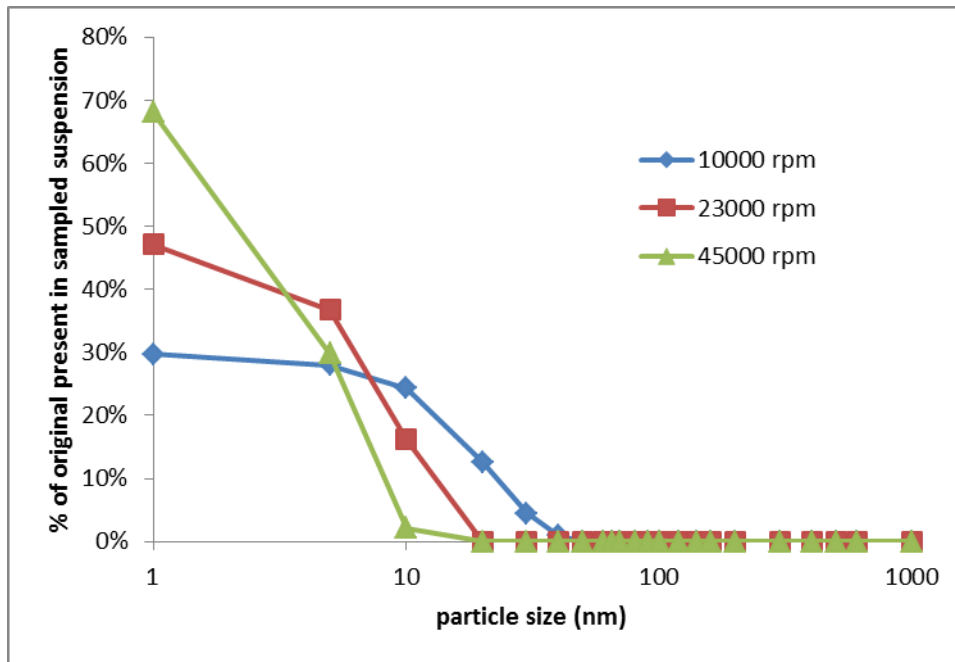
→ Terminal velocity
$$V = \frac{2(\rho_p - \rho_f)}{9\mu} g R^2$$

Both ways:

- Diffusion (Lamn equation)

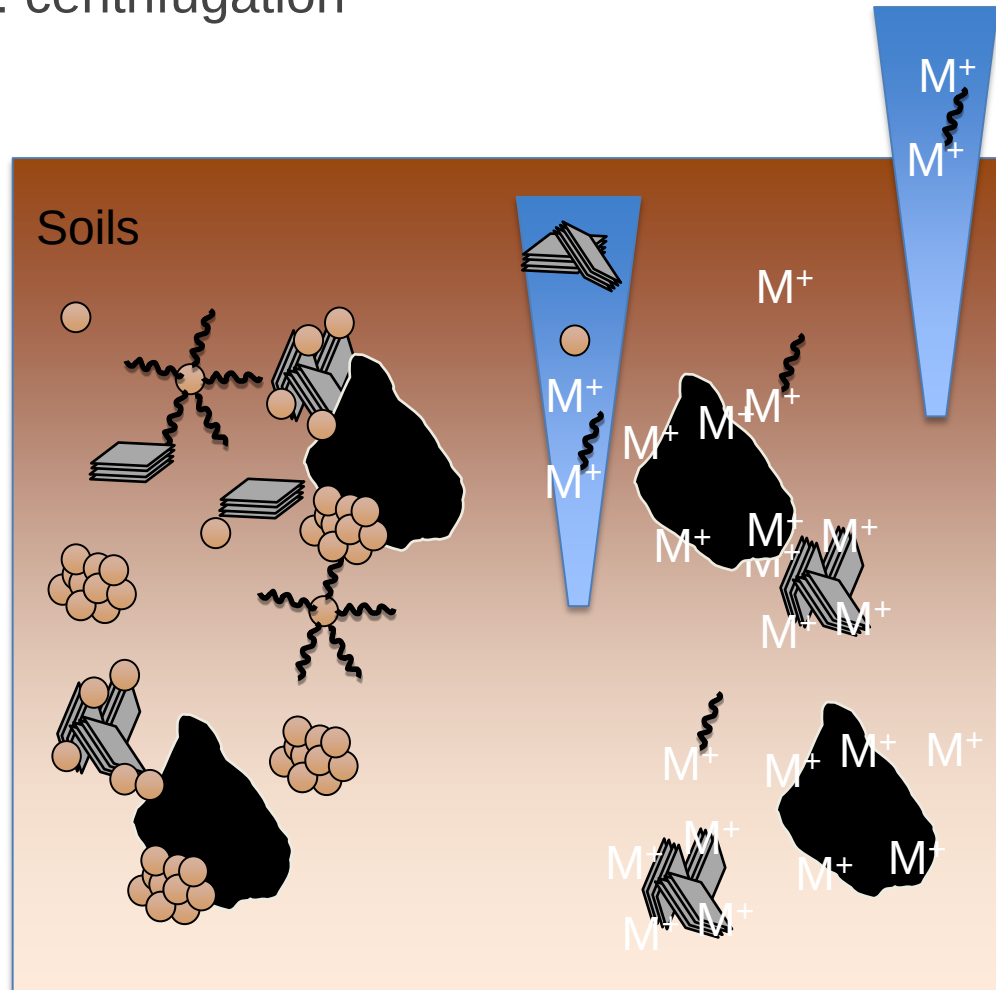
$$\frac{\partial c}{\partial t} = D \left[\left(\frac{\partial^2 c}{\partial r^2} \right) + \frac{1}{r} \left(\frac{\partial c}{\partial r} \right) \right] - s\omega^2 \left[r \left(\frac{\partial c}{\partial r} \right) + 2c \right]$$

Centrifugation

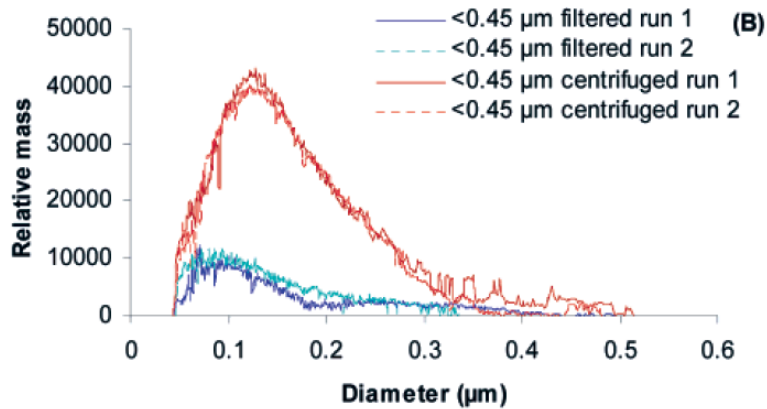


- Silver nanoparticles evenly distributed from 1 to 1000 nm in a 12 cm vial.
- Sampling at 4 cm depth
- Different spinning speeds
- ➔ No sharp cut-off
- ➔ High speeds required for NP/dissolved separation

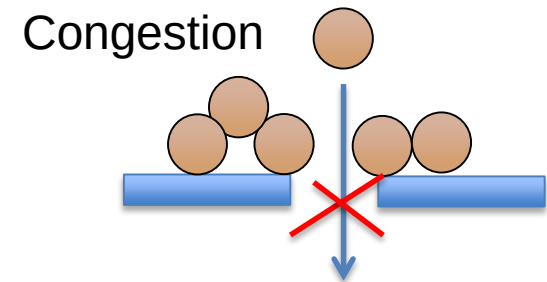
Separation of ENP: centrifugation



Separation of ENP Centrifugation vs. filtration



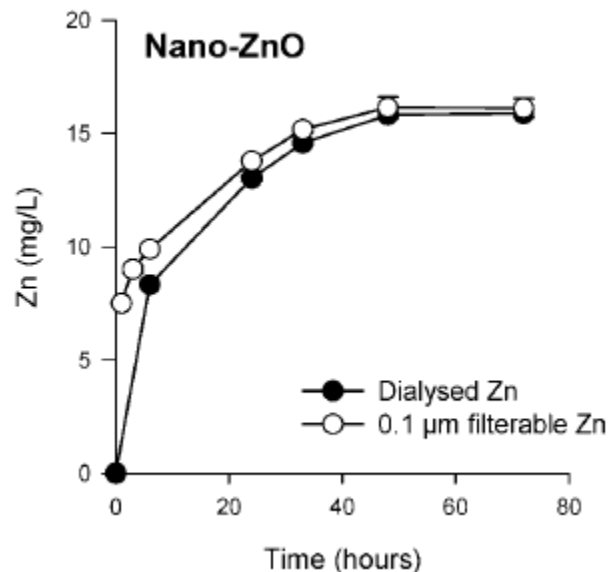
Natural particles in filtrates vs. centrifuged supernatants analysed with cFFF (Gimbert et al., 2006):



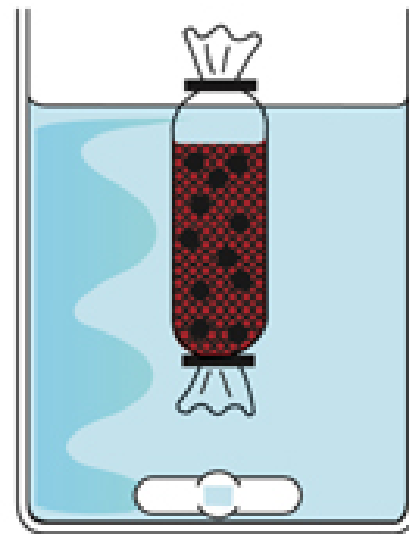
Better recovery with centrifugation
but filtration is more convenient and
does not require prior knowledge of
density

Filtration vs. dialysis

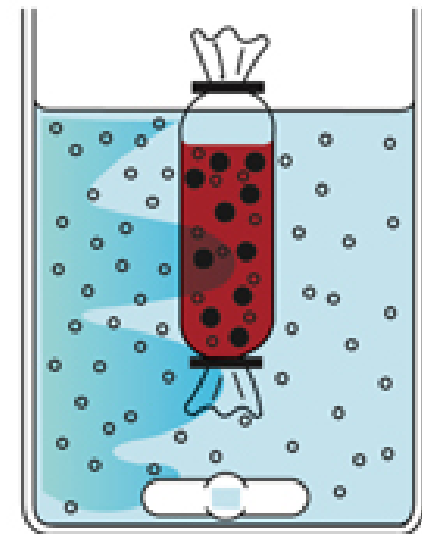
Delay in measurement because of equilibration



Franklin et al. 2007. ES&T



Start Dialysis
(high concentration gradient)

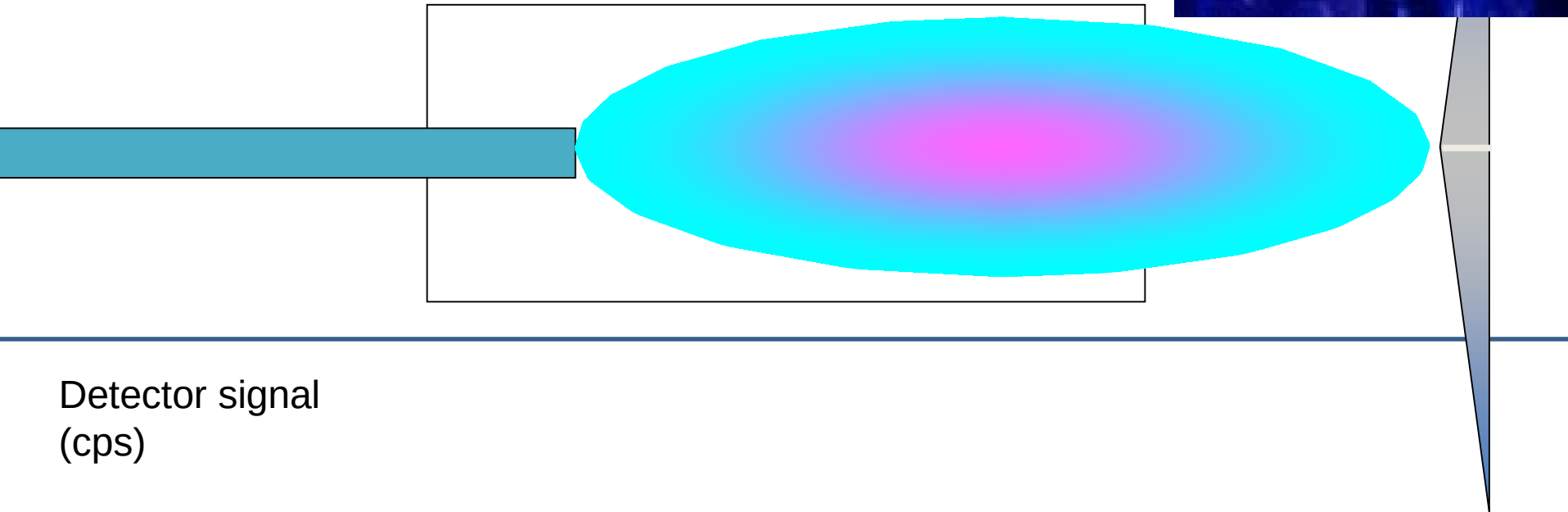


End Dialysis
(equilibrium)



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Conventional mode ICP-MS

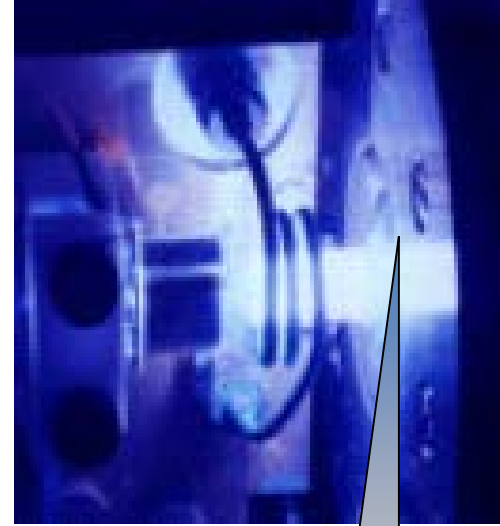
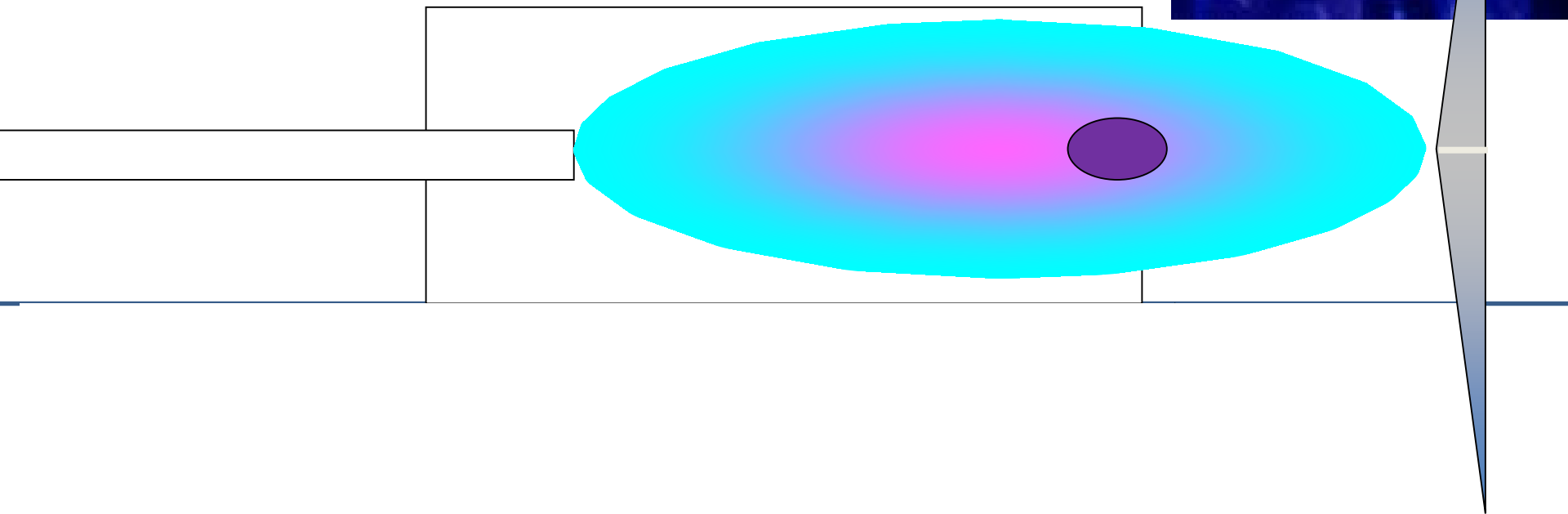


Aquisition time (ms)



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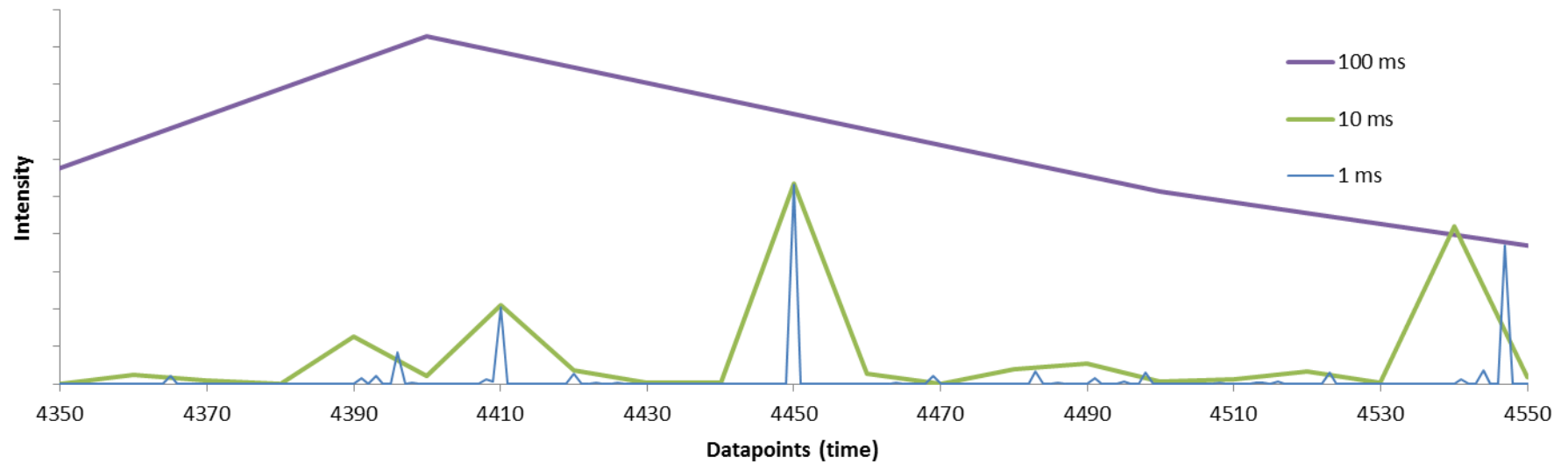
Single particle ICP-MS



Aquisition time (ms)

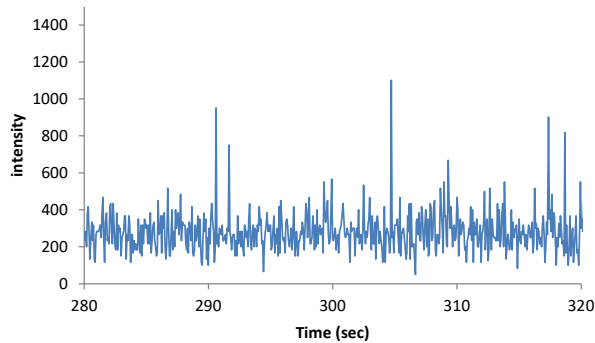
www.gu.se

spICP-MS vs. Conventional ICP-MS: effect of dwell time

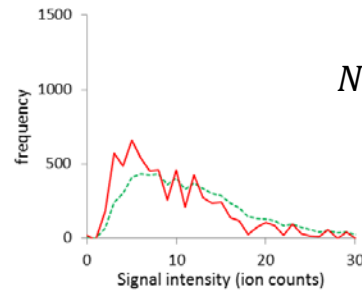


Single particle ICP-MS

Particle signal

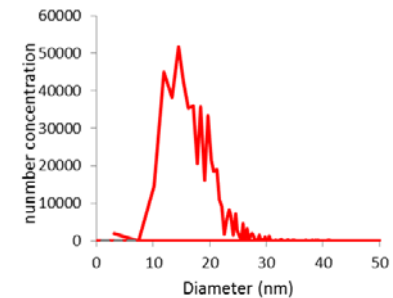


Particle signal histogram



$$N_i = \frac{f(P_i)}{\eta_e q D t_d}$$

Particle size distribution calculation

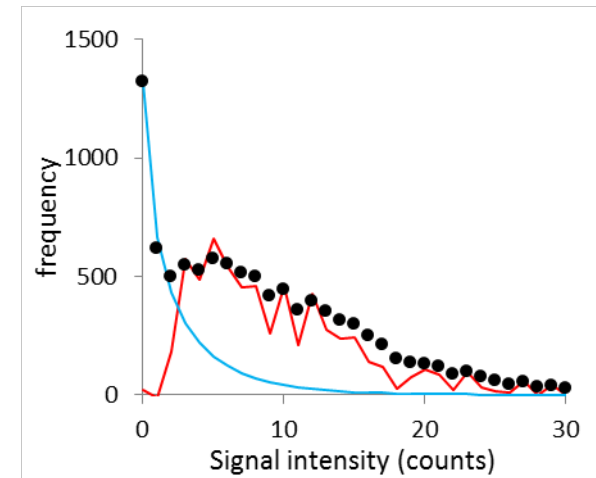
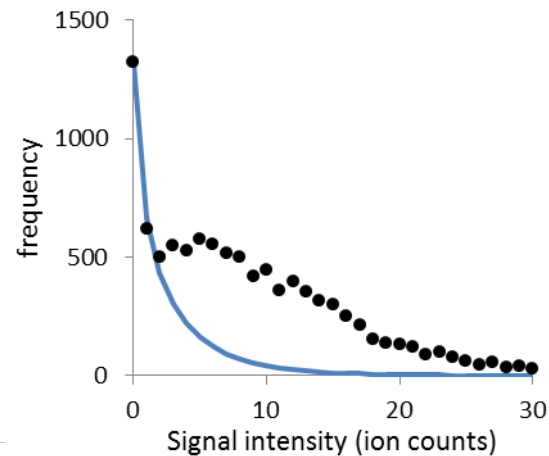
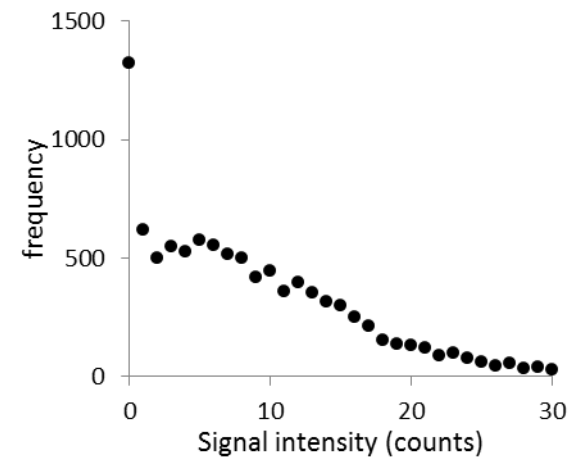


$$d = \sqrt[3]{\frac{(I - I_d - I_{bkg}) 6 q \eta_e M_w}{\pi m t_d \rho}}$$

To be determined:

- q (using a flow meter)
- η_e
- **Dissolved** calibration curve

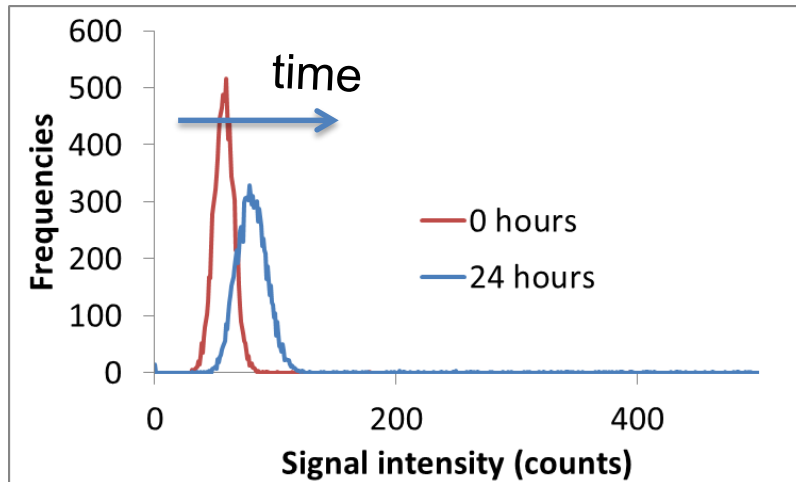
spICP-MS: Signal discrimination



Dissolved and nanoparticle signal can be distinguished.

Monitor dissolution using spICP-MS

Above detection limit



10⁶ dilution of AgNP (40 nm) in an ecotoxicological medium

Below detection limit

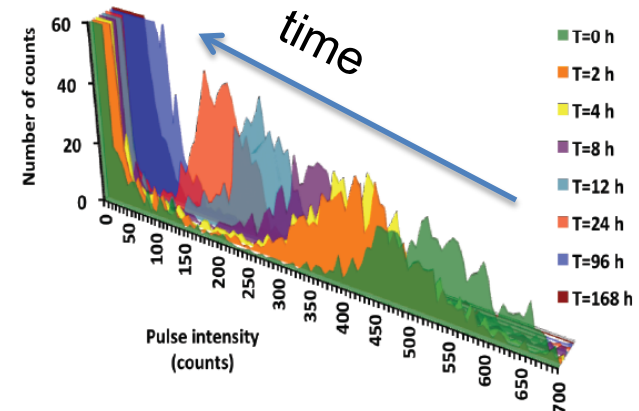
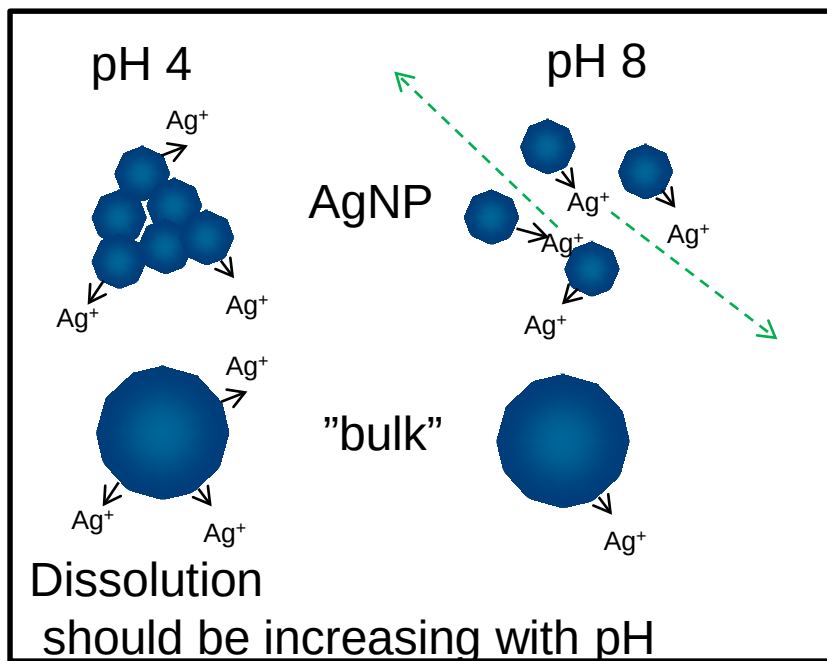


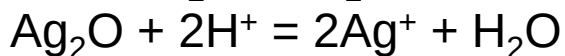
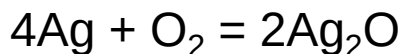
Figure 1. Dissolution of 100nm TA capped Ag ENP at 50 ng/L over time, as evidenced by the decrease pulse intensity over time. Raw pulse intensity is proportional to particle mass (x-axis) and so smaller pulses indicate less Ag associated with each particle. The number of particles observed (y-axis) is similar for each analysis.

Mitrano et al. (2014) Environ. Sci. Nano.

Effect of pH

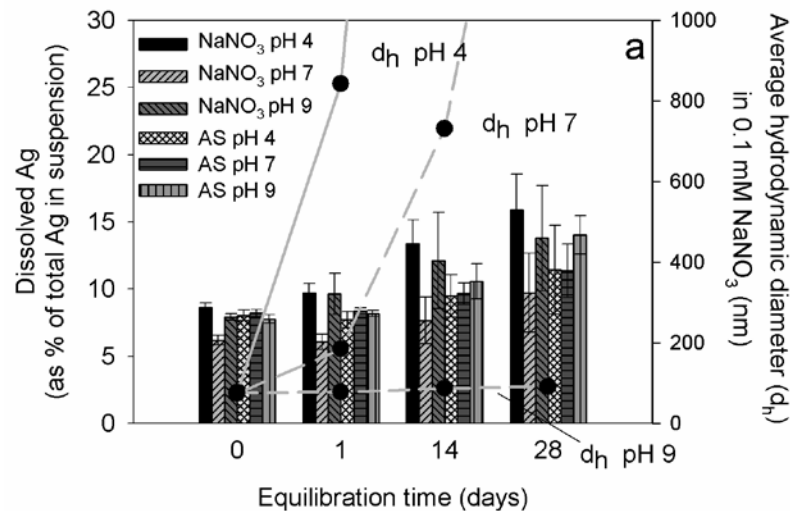


versus

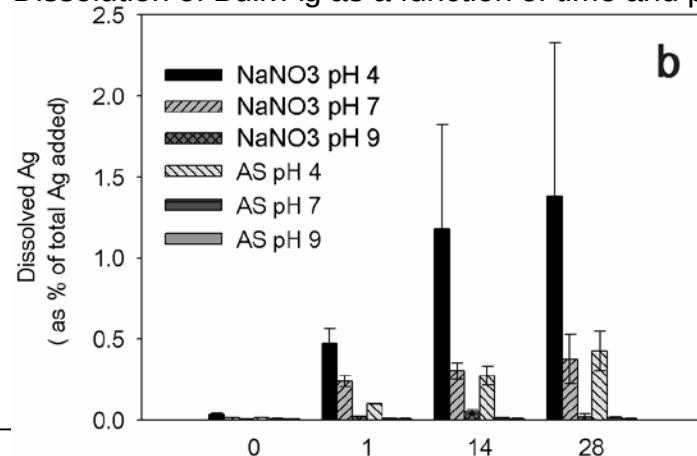


→ Dissolution should be decreasing with pH

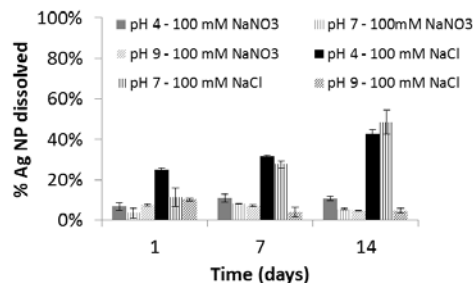
Dissolution of AgNP as a function of time and pH



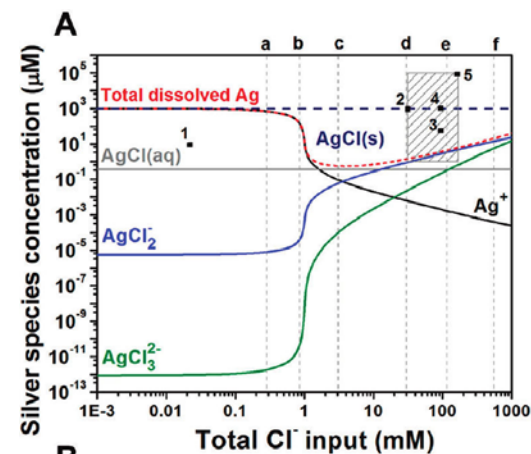
Dissolution of Bulk Ag as a function of time and pH



Dissolution: silver NP

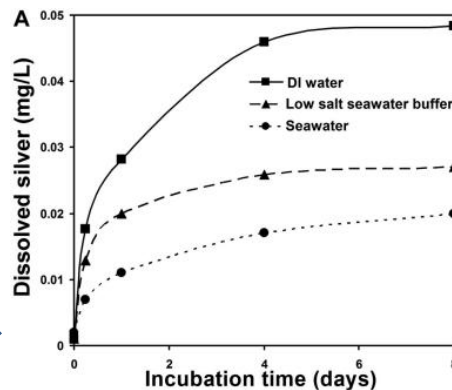


Cornelis et al., 2010, *unpublished*

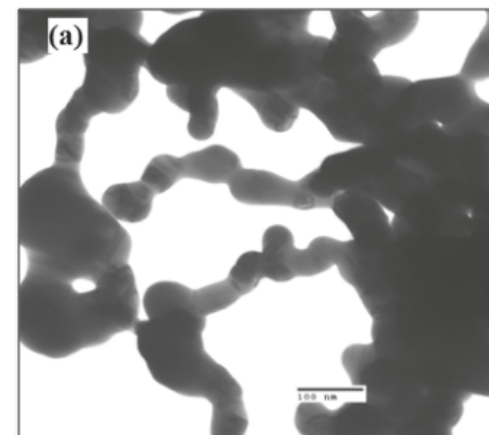


Liu et al., 2010.

ACS Nano 4: 6903-6913.

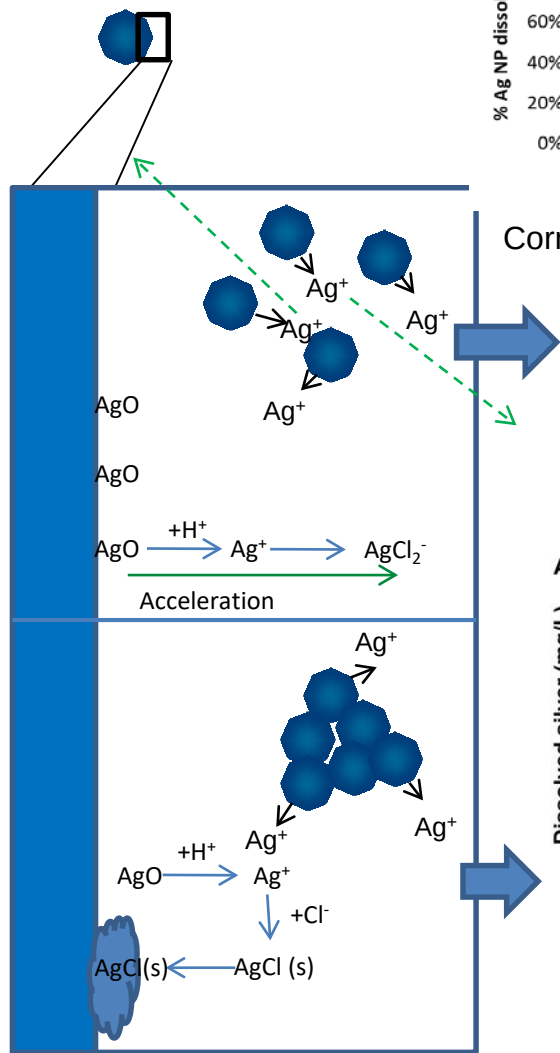


Liu and Hurt 2011, *ES&T*.
44, 2169–2175



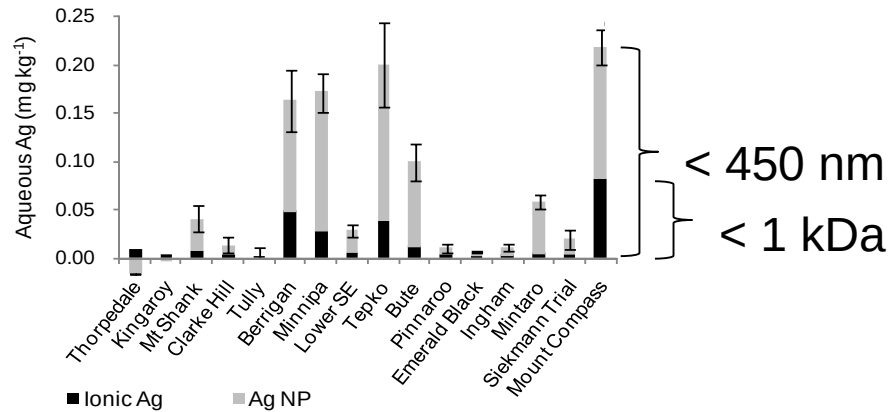
Li et al., 2010, *Langmuir* 26, 16690-16698.

High [Cl⁻]
and low [AgNP]



High [Cl⁻] and
High [AgNP]

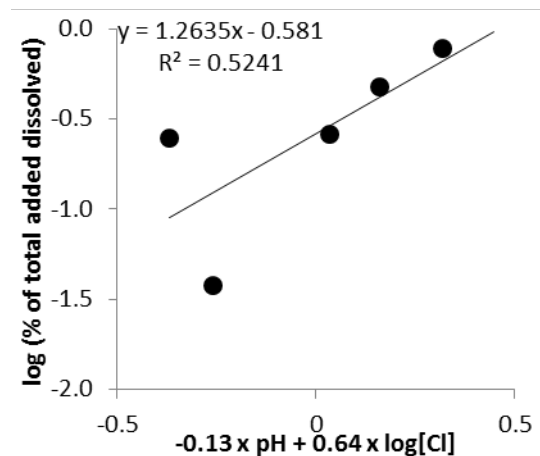
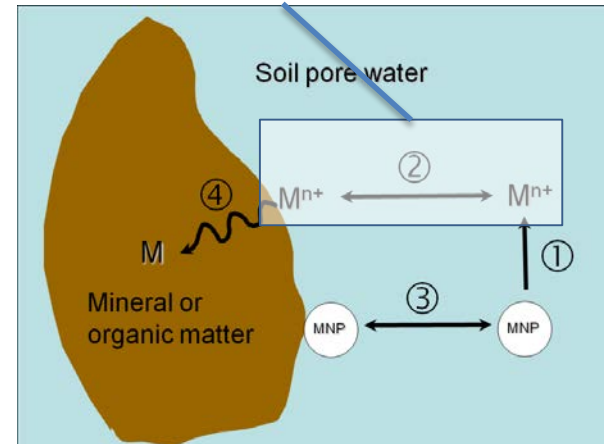
Dissolution in soils



- $AgNP_{dissolved} = [Ag]_{UF} - [Ag]_{UF} + [Ag]_{adsorbed}$
- $K_d = [Ag]_{adsorbed} / [Ag]_{1kDa} \times L/S$

$$\left(\frac{K_d S}{L} + 1 \right) ([Ag]_{UF} - [Ag]_{geogenic}) = AgNP_{dissolved}$$

Total dissolved [M]





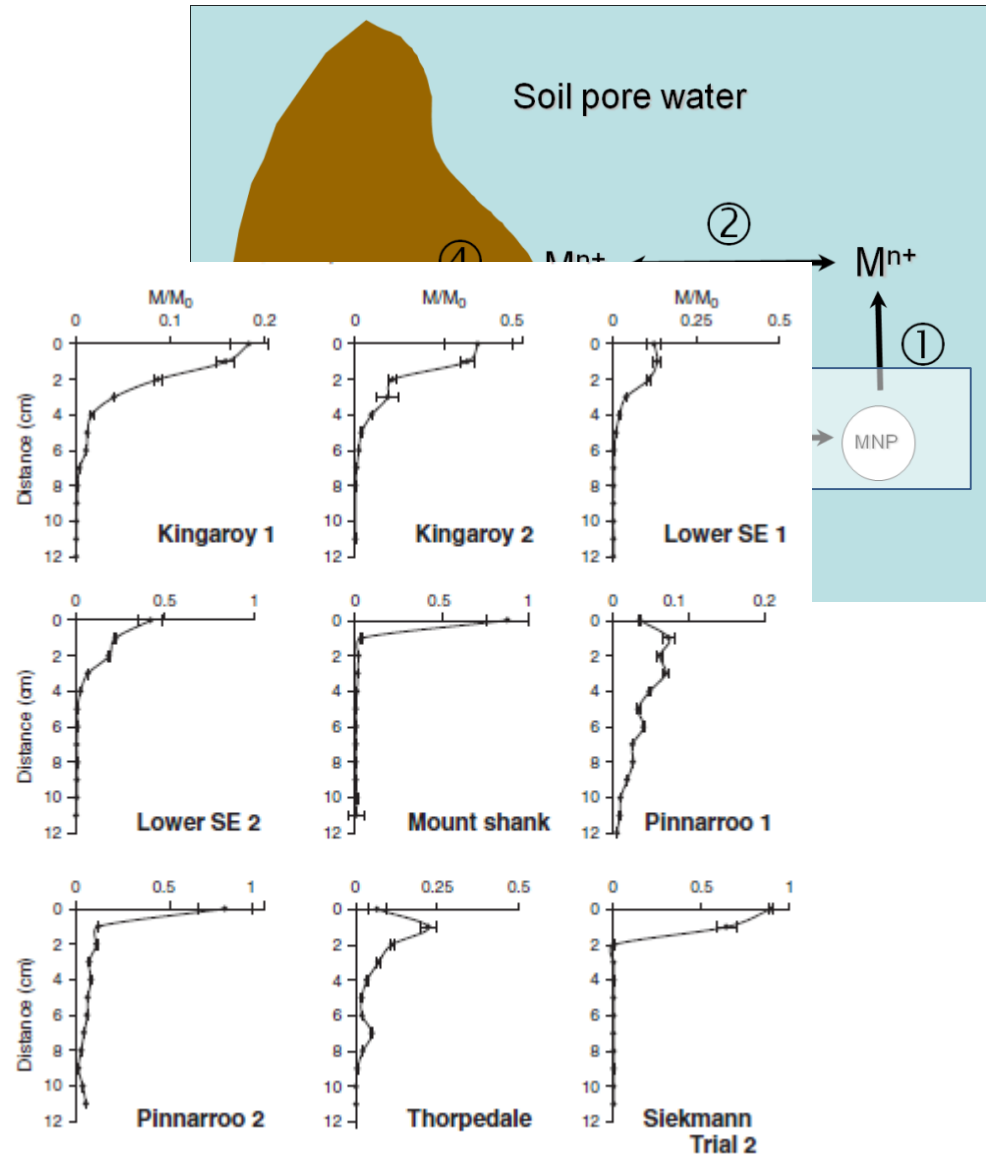
Retention

- Intro
- Descriptors for retention
 - K_d
 - α
 - K_r
- How to predict bio-availability

Retention

The interaction of NP with surfaces affecting their

- Release
- Attachment
- Transport
- Bio-availability



Descriptors for retention

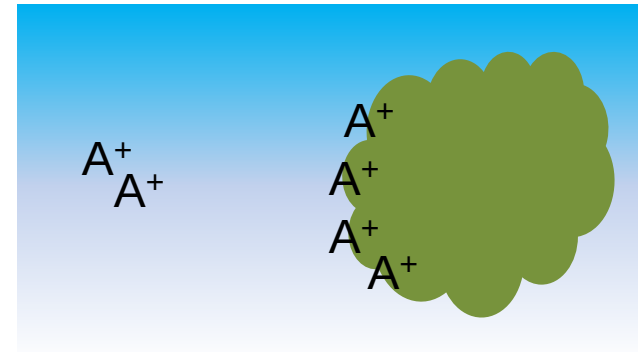
 K_d K_r α

Discussion in ESNano

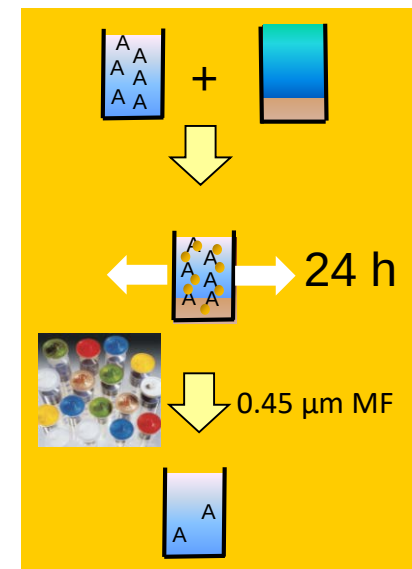
- Praetorius et al. 2014. "The road to nowhere: Equilibrium partition coefficients for nanoparticles" *ESNano* 1, 317-322.
- Cornelis et al. 2015: "Fate descriptors for engineered nanoparticles: the good, the bad, the ugly" *ESNano* 2, 19-26.
- Dale et al. 2015. "Much ado about alpha: reframing the debate over appropriate fate descriptors in nanoparticle environmental risk modeling" *ESNano* 2, 27-32.

K_d values

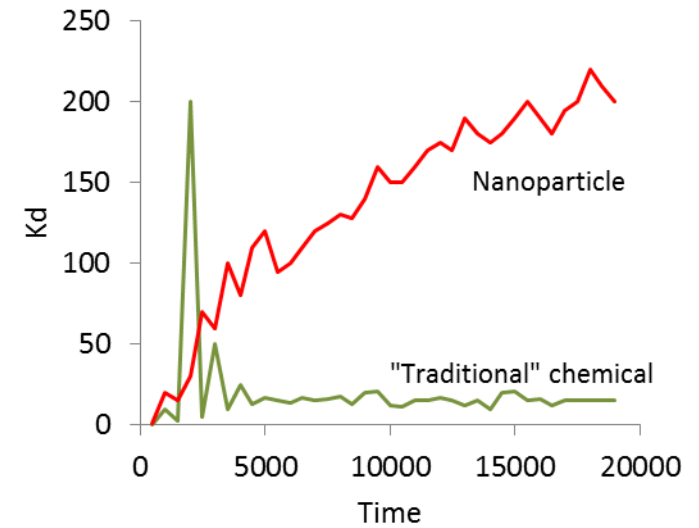
- OECD guideline 121
- Operationally defined
- Assume equilibrium
- Use:
 - Model bioavailability (e.g. in combination with speciation modelling, decomposition rates).
 - Transport modelling



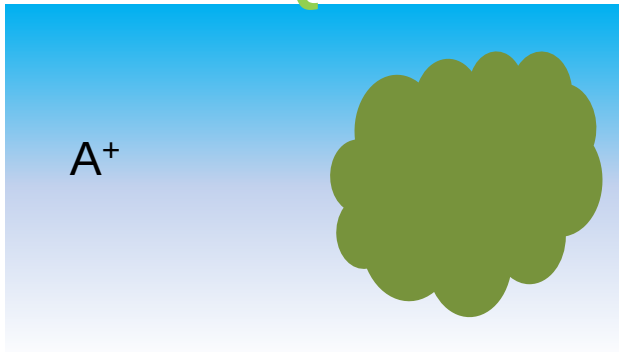
$$K_d = [A]_{\text{solid}}/[A]_{\text{aqueous}}$$



K_d values for nanoparticles?



OFTEN EQUILIBRIUM



$$K_d = [A]_{\text{solid}}/[A]_{\text{aqueous}}$$



$$K_d = [NP]_{\text{solid}}/[NP]_{\text{aqueous}}$$

K_d values for nanoparticles?

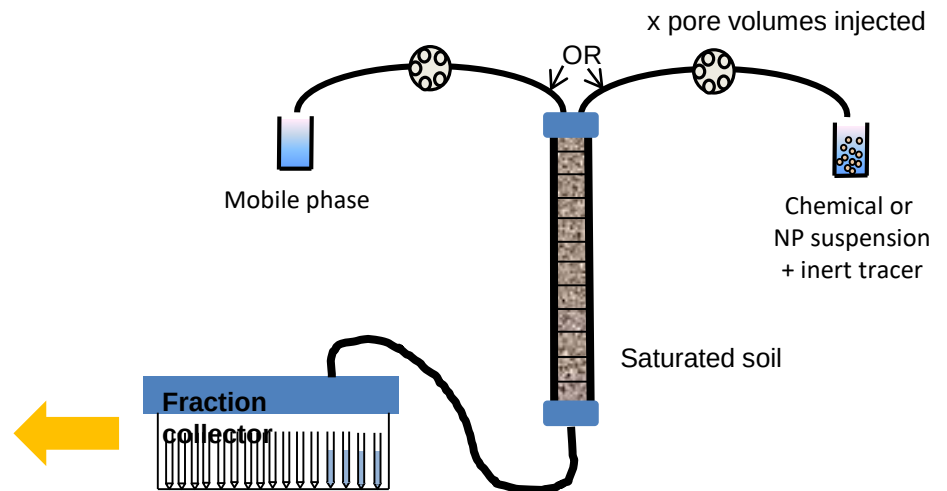
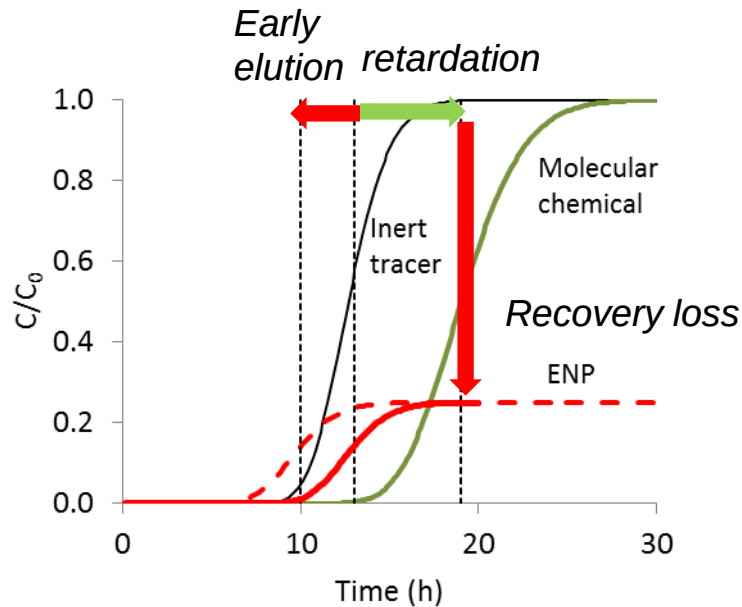
Soil column transport studies (~ OECD 312):

Traditional chemicals: **retardation**

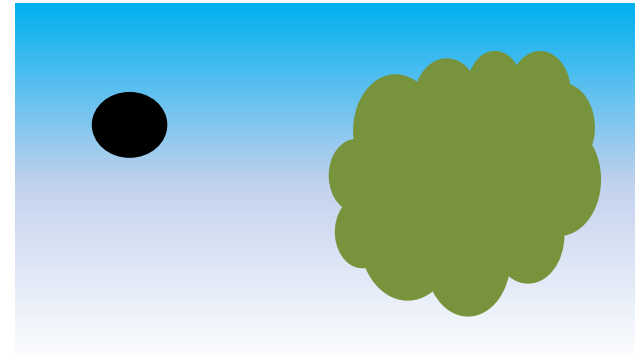
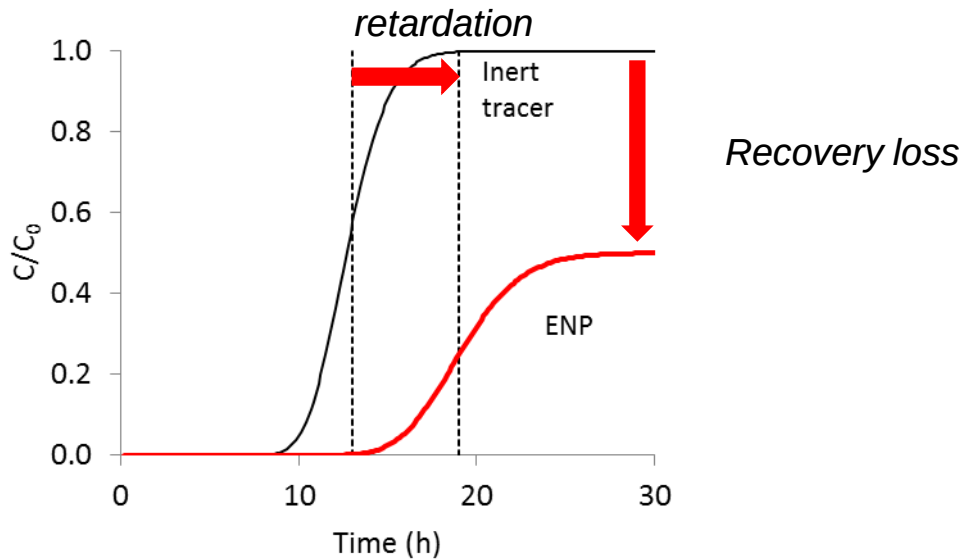
$$R = 1 + (r_b/q_e)K_d$$



Nanoparticles: **loss in recovery**



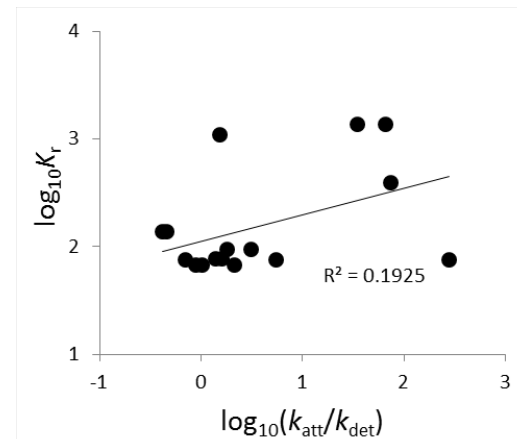
K_d values for nanoparticles?



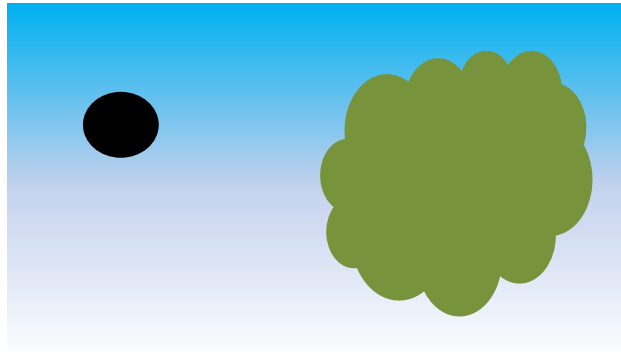
$$V_{attach} = k_{attach} * [NP]_{aqueous}$$

$$V_{detach} = k_{detach} * [NP]_{solid}$$

$$K_d \sim k_{attach} / k_{detach} ?$$



α values

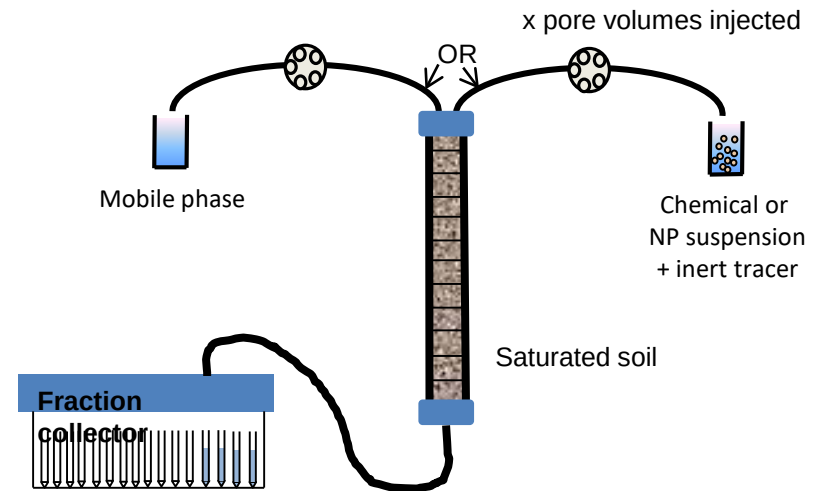


$$V_{max} = k_{max} * [NP]_{aqueous}$$

$$V_{attach} = k_{attach} * [NP]_{solid}$$

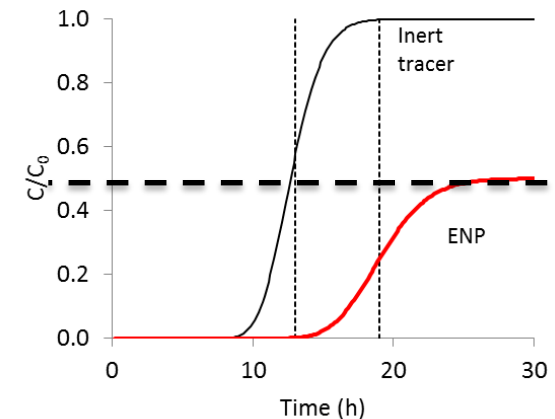
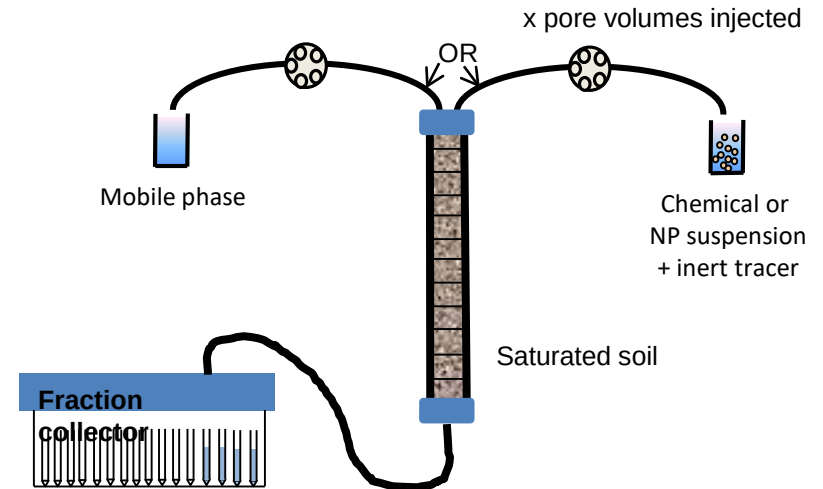
$$\alpha = k_{attach} / k_{max}$$

- Ratio of attachment rate at real vs. Ideal conditions
- The probability that a particle will "stick" to other particles or surfaces



α values

- Can be predicted based on DLVO theory (requires hamaker constant and surface potential)
- Sometimes obtained from QCMD experiments
- Most often fitted to breakthrough curves from columns
Assumes clean bed filtration, i.e. only irreversible attachment



$$\alpha_{att} = \frac{2d_{50}}{3(1-\theta)\eta_0 L} \ln(C/C_0)$$

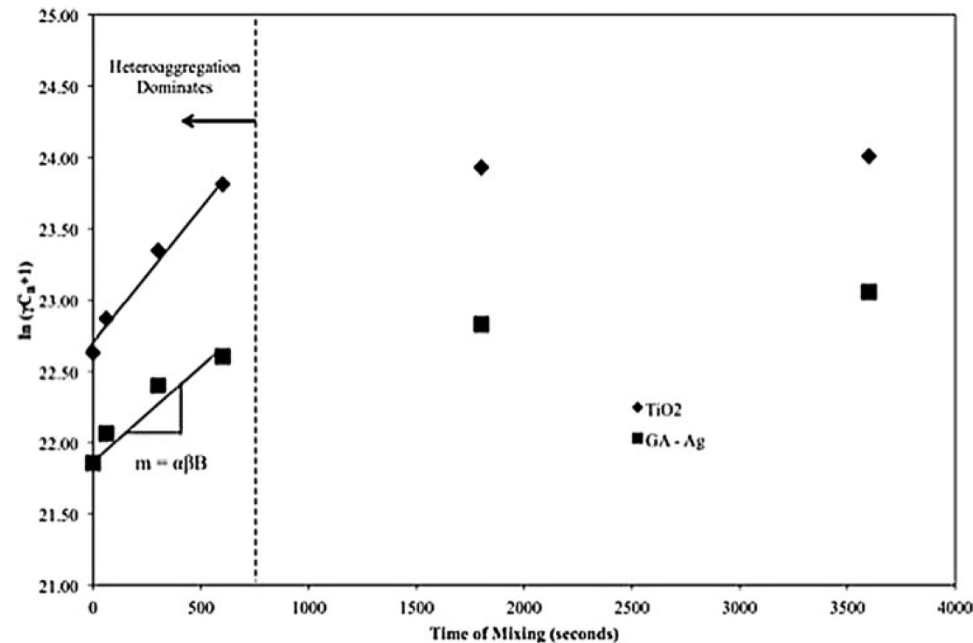
Determining attachment rates via batch tests

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

- $\gamma(t)$ time-dependent distribution coefficient

$$\gamma(t) = \frac{\frac{n_0 - n(t)}{C_B}}{n}$$

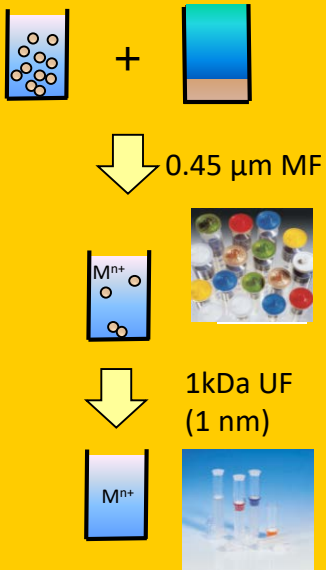
- α : attachment efficiency
- $\beta(n, B)$: second-order attachment rates
- B : number concentration of background particles



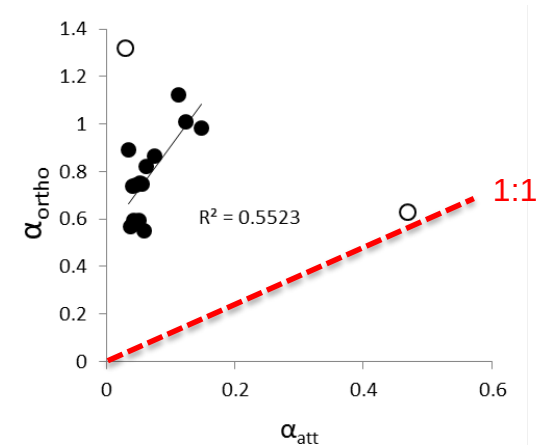
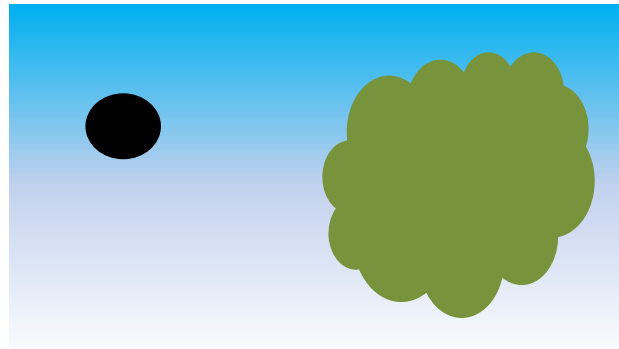
Barton et al. 2014, Environ. Eng. Sci. 31 421-427.

K_r values

Batch method:



$$K_r = \frac{n_{ENP,t=0}}{n_{ENP,t=T}} \times L/S = \exp\left(\frac{G\alpha_{ortho}}{\pi L/S \rho} T\right) \times L/S$$

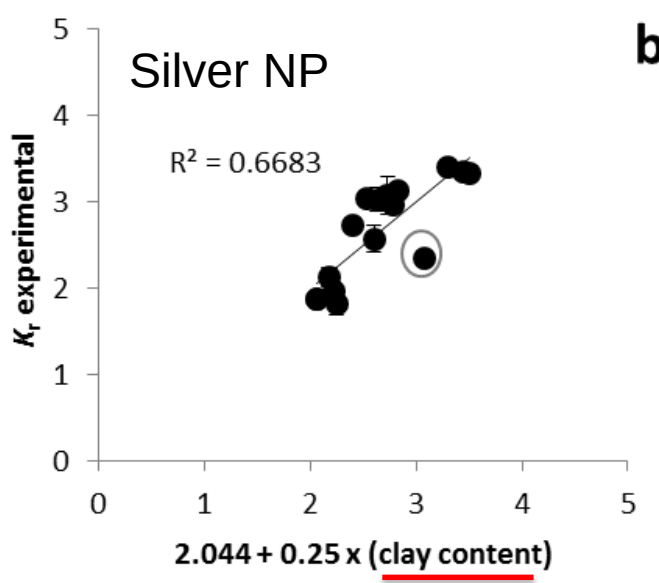


Intense shear conditions during shaking $\Leftrightarrow$ column experiment

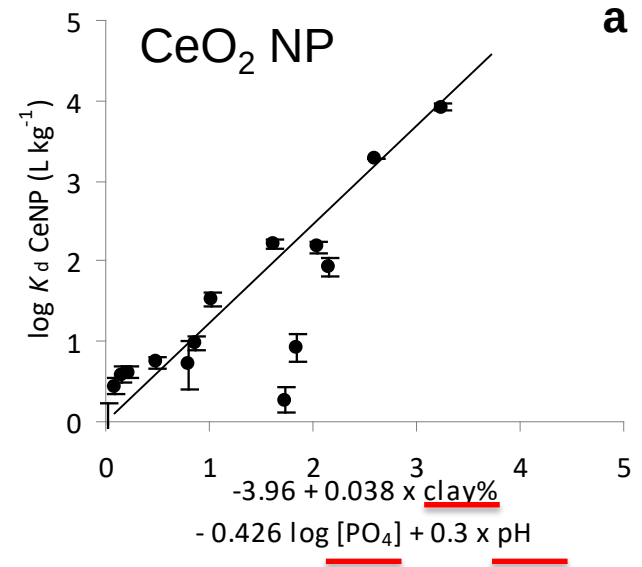
➔ Different parameter (α_{ortho}) than in a column experiment (α_{att}), but possibly related

α_{ortho} calculated from K_r values vs. α_{att}
(Cornelis, ES Nano)

K_r values

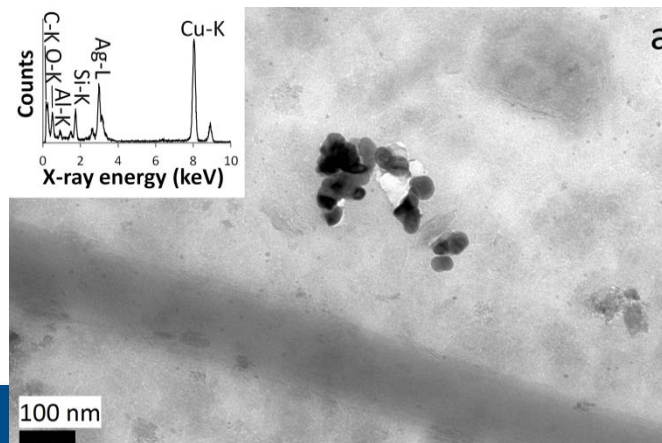


Cornelis et al, SSSAJ
2012, 76, 891-902.

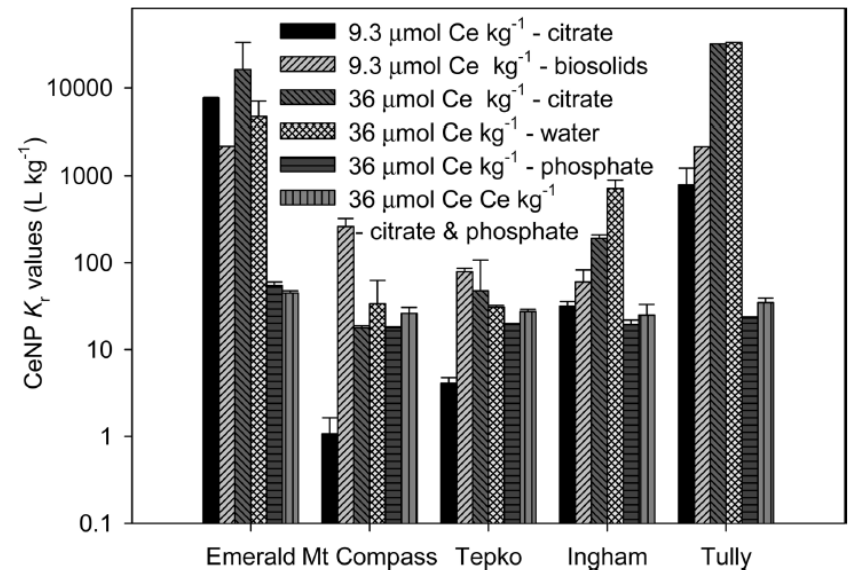
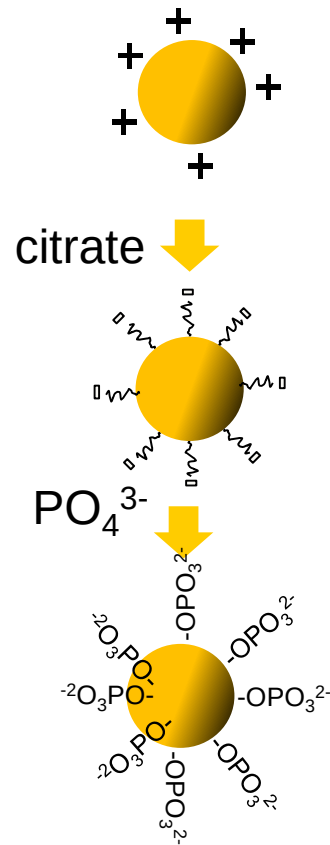


Cornelis, G. et. al. ES&T.
2011, 45 (7), 2777-2782.

AgNP in 0.45 μm
filtrate

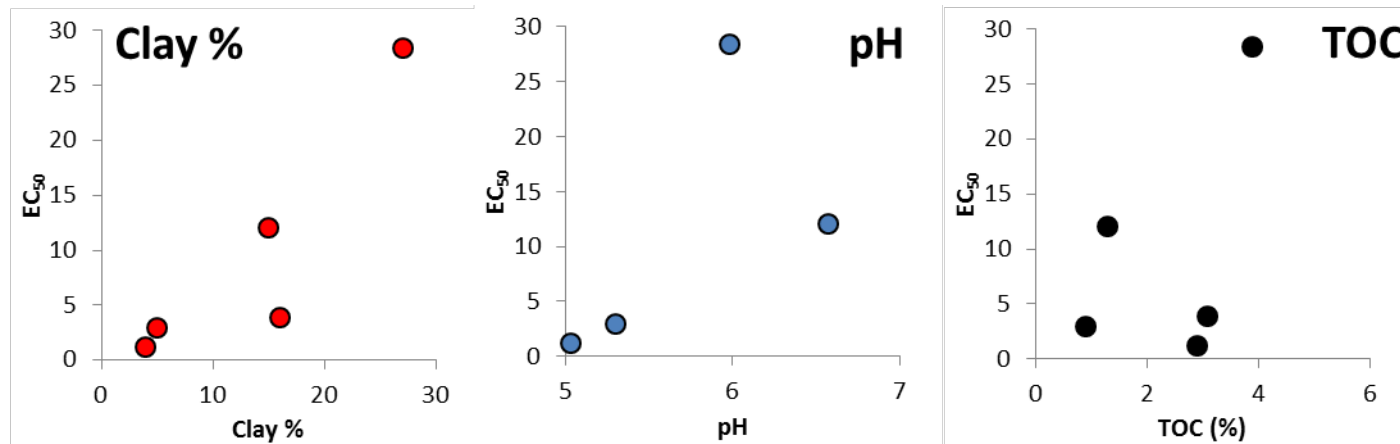


K_r values: screening tool, comparison



Cornelis, G. et. al. *ES&T*.
2011, 45 (7), 2777-2782.

Relation with bioavailability

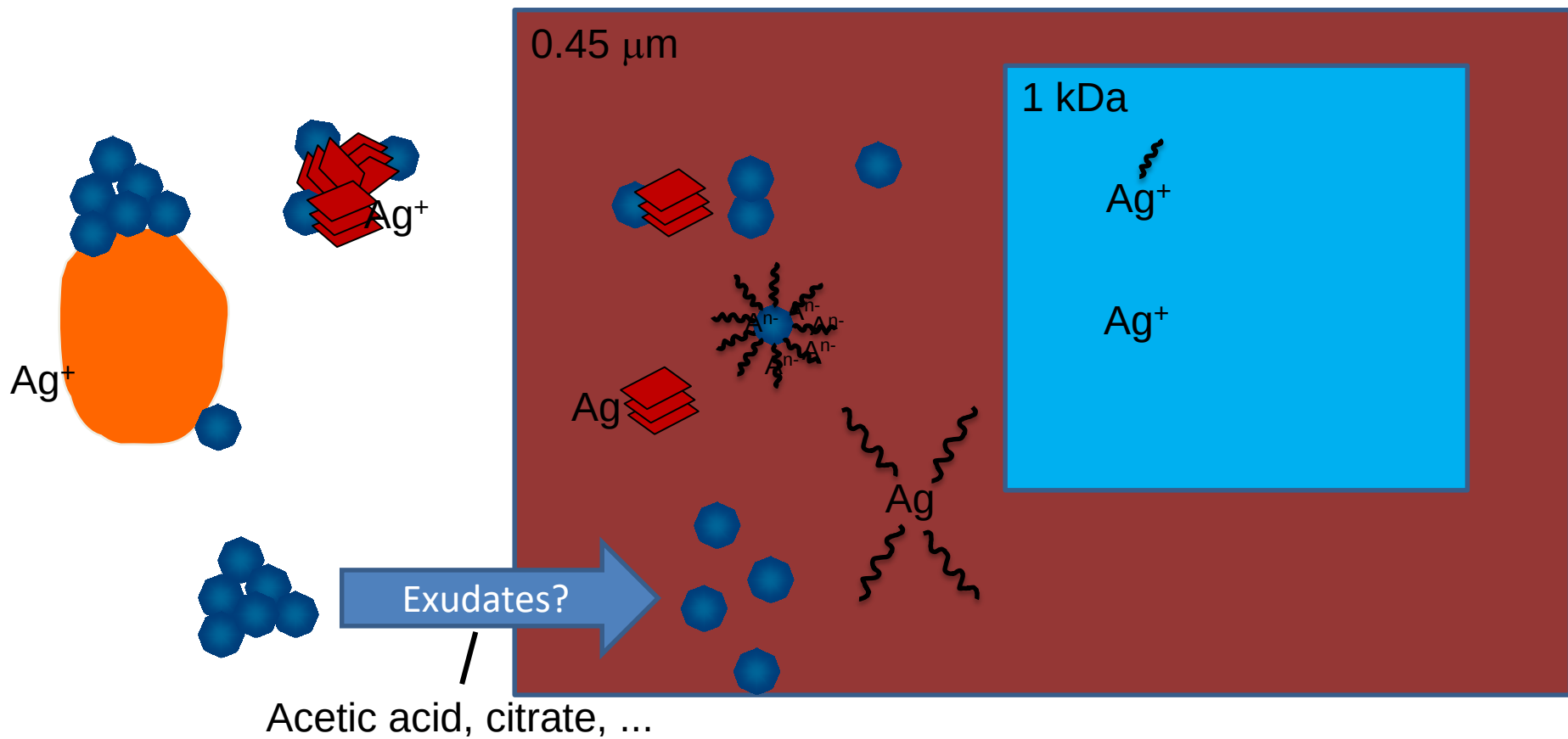


EC₅₀ of AgNP (NM300K) in different soils

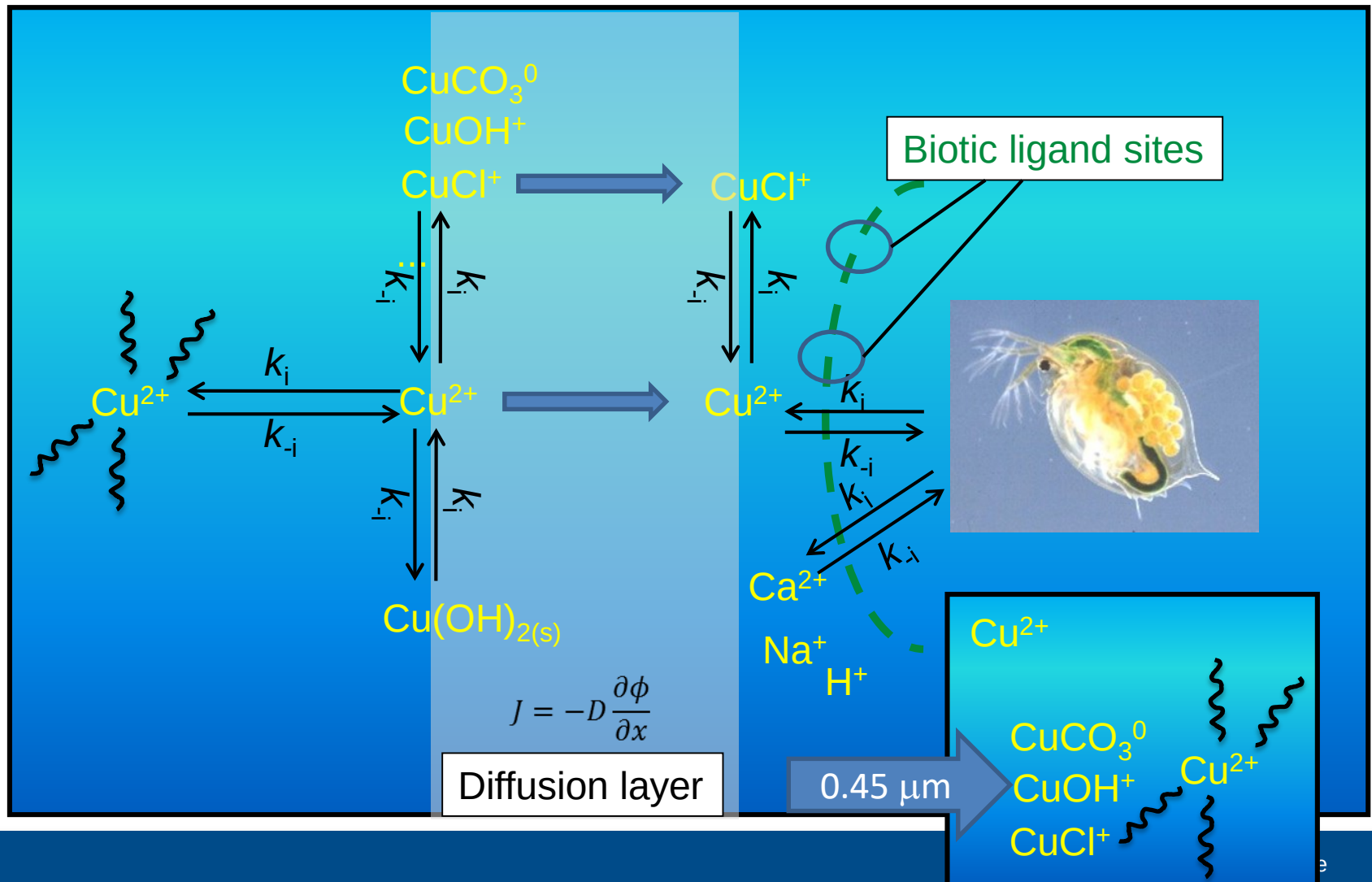
(Schlich et al., 2015 *Env. Poll.* 195, 321-330.)

Bioavailability

Effective dose ?



Biotic Ligand model





Complete physico-chemical analysis of medium or natural water

Table 3. Physicochemical data for the Chilean natural waters used in the chronic toxicity study with *Daphnia magna*, and the corresponding measured copper 21-d EC50 and 21-d LC50

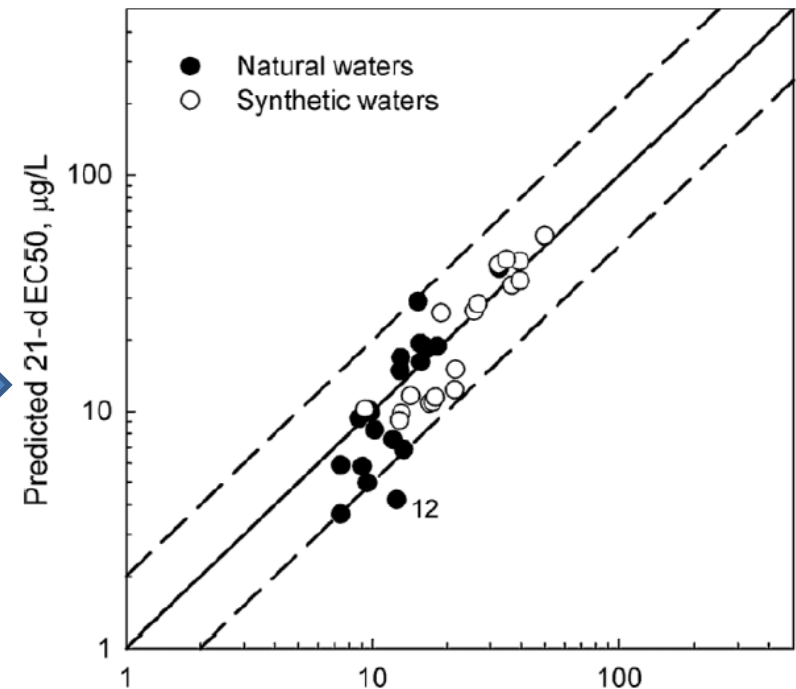
Water body	Key	pH	Cu (µg/L)	DOC (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Alkalinity mg/L as CaCO ₃	Hardness mg/L as CaCO ₃	Cu, 21-d EC50 (µg/L)	Cu, 21-d LC50 (µg/L)
Hurtado River	1	8.32	2.8	1.0	31.6	7.7	7.2	1.5	68.2	4.2	63	128	16.3	15.6
Choapa River	2	8.36	1.0	0.8	34.0	9.0	13.1	1.1	59.5	10.2	98	141	15.6	16.6
Petorca River	3	8.59	0.6	0.7	45.1	21.2	20.6	0.9	81.0	27.9	235	222	32.6	35.2
Pocuro River	4	8.26	4.4	1.0	34.2	5.8	9.9	1.4	64.5	9.6	84	145	18.3	18.2
Putuendo Brook	5	8.51	3.8	0.8	21.2	4.2	6.9	0.5	34.3	2.5	59	87	13.0	13.9
Yeso River	6	8.53	1.3	0.6	81.4	14.1	25.7	1.9	313.0	43.6	83	262	8.1	26.7
Maipo River	7	8.58	2.6	0.4	142.2	20.4	109.2	3.0	248.5	275.2	89	440	15.3	19.7
Teno River	8	7.89	0.0	0.3	26.5	2.3	10.2	1.2	48.1	12.5	29	92	7.4	8.2
Mataquito River	9	8.02	0.0	1.3	22.7	9.0	11.8	2.1	45.0	11.9	43	88	15.7	14.9
Maule River	10	8.00	0.2	1.0	9.0	2.2	6.6	0.8	13.0	5.3	26	34	9.8	9.6
Putagan River	11	7.76	0.1	0.8	4.5	0.7	1.6	0.2	4.4	0.2	17	16	9.5	7.7
Longavi River	12	7.99	0.5	0.5	5.4	1.2	2.9	0.4	7.6	1.3	20	21	12.5	11.2
Nuble River	13	7.90	0.7	1.1	2.7	0.9	2.4	0.6	1.2	1.3	15	11	10.2	9.3
Chillan River	14	7.99	0.8	1.1	2.8	1.2	2.4	0.8	3.1	1.2	19	12	8.8	8.8
Itata River	15	7.97	1.3	1.8	3.5	1.0	2.8	1.1	2.2	1.1	25	20	12.9	13.6
Laja River	16	7.99	1.0	1.2	3.9	1.0	2.0	0.5	2.5	0.7	18	14	9.6	9.3
Bio-Bio River	17	8.00	0.5	0.6	7.0	2.0	4.5	0.7	6.0	5.0	28	29	9.1	9.3
Mallico River	18	7.97	0.2	0.7	3.2	1.0	2.2	0.4	1.5	1.1	21	12	7.4	7.1
Indio River	19	8.35	0.0	0.2	15.2	7.8	40.0	1.9	20.1	56.0	68	70	12.1	12.1
Cautin River	20	8.18	0.1	0.5	8.2	3.0	6.7	1.4	5.3	2.1	45	33	13.4	13.5

Cu, 21-d EC50 = Copper 21-d half-maximal effective concentration values of chronic reproduction test with *D. magna*; Cu, 21-d LC50 = Copper 21-d half-maximal lethal concentration values of chronic test with *D. magna*; DOC = dissolved organic carbon.

Table 6. Summary of the parameter values for the Hydroqual (Hq) biotic ligand model (BLM), version 2.2.3, and De Schampelaere et al. (2004) c-CuBLM-3 (DSch) [15,28]

Parameter/condition	Value Hq	Value DSch
Log <i>K</i> of gill-Cu ²⁺	7.4	8.02
Log <i>K</i> of gill-CuOH ⁺	6.2 (−1.3) ^a	8.02 (0.52) ^a
Log <i>K</i> of gill-CuCO ₃	—	7.44
Log <i>K</i> of gill-Ca ²⁺	3.6	—
Log <i>K</i> of gill-Mg ²⁺	3.6	—
Log <i>K</i> of gill-H ⁺	5.4	6.67
Log <i>K</i> of gill-Na ⁺	3.0	2.91
% Humic acids	0.01	4.17 ^b 24.1 ^c 11.7 ^d
Log <i>K</i> of CuOH ⁺	6.48	6.48
Log <i>K</i> of Cu(OH) ₂	11.78	11.81
Log <i>K</i> of CuHCO ₃ ⁺	14.62	12.13
Log <i>K</i> of CuCO ₃	6.75	6.77
Log <i>K</i> of Cu(CO ₃) ₂ ^{2−}	9.92	10.2
Log <i>K</i> of CuCl ⁺	0.4	0.2
Log <i>K</i> of CuSO ₄	2.36	2.36

Better prediction of toxicity

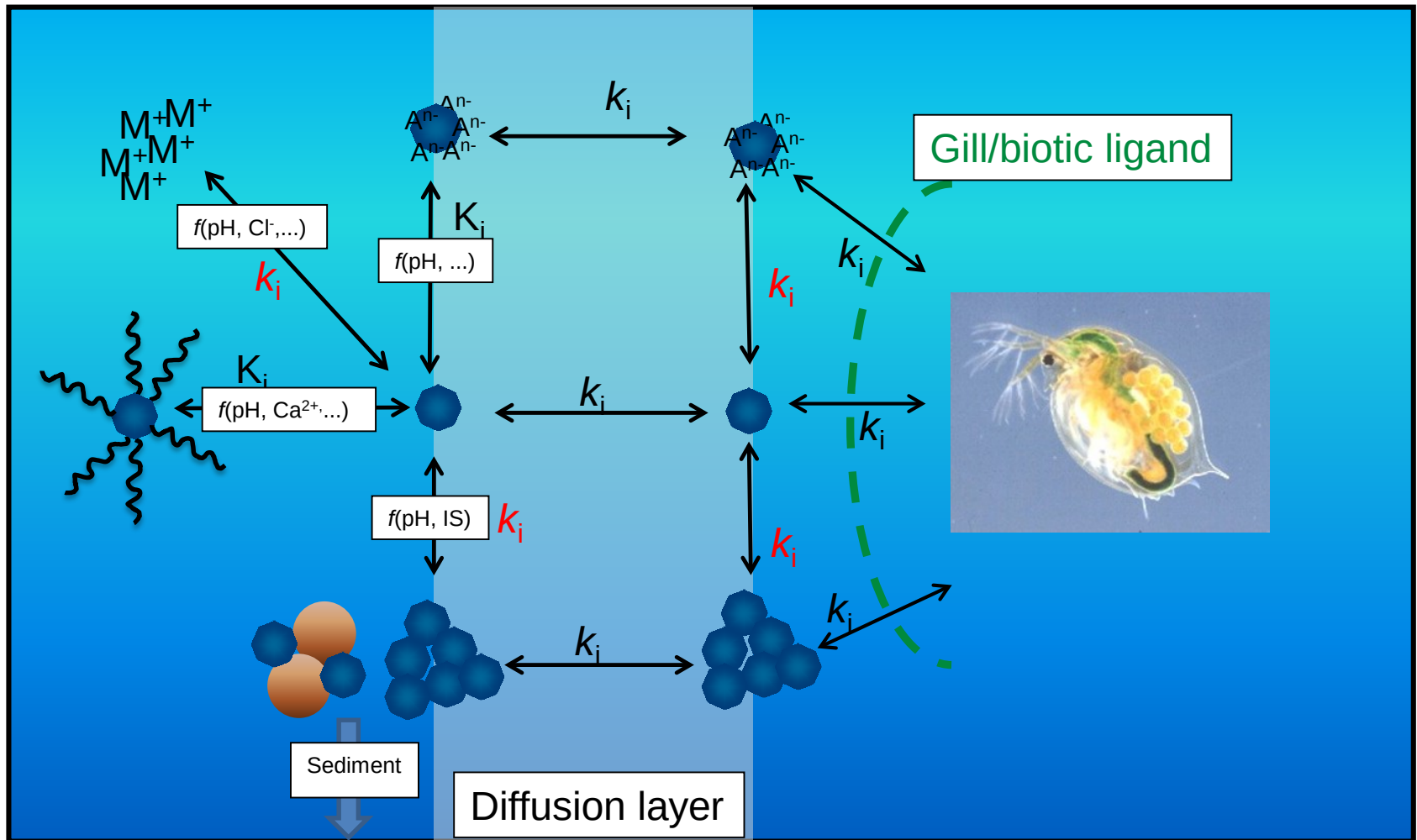


Observed 21-d EC50, µg/L of Copper

Villavicencio et al., 2011.

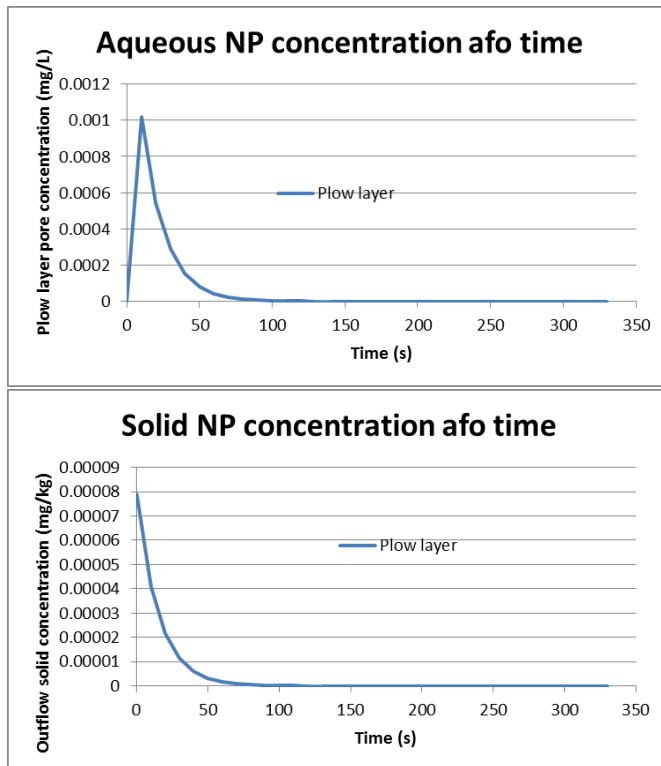
ET&C 30, 2319-2325.

a nano Biotic Ligand model?

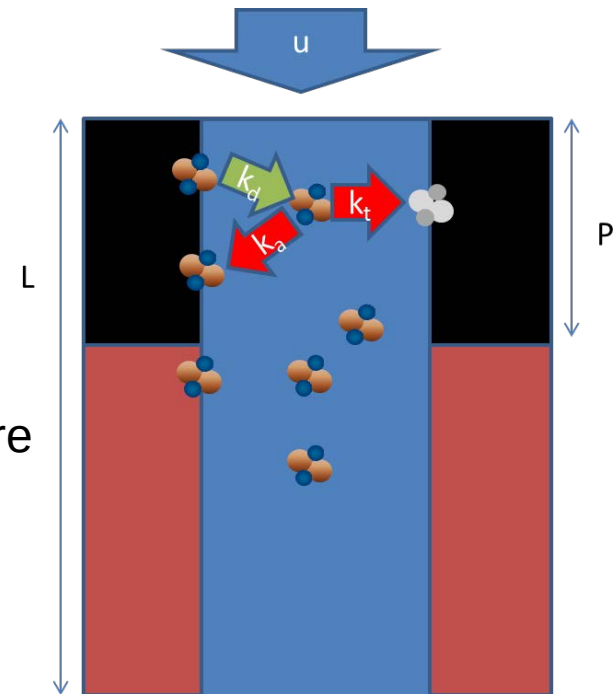


Modelled bioavailability

Modelled AgNP concentration afo time in a plow layer



How to compare
to single effect
levels ?



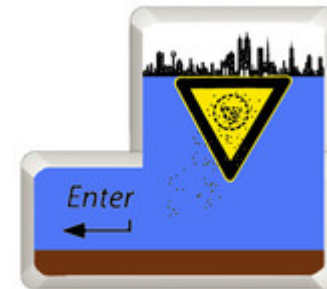


Conclusions

- Dissolution
 - Is operationally defined
 - Beware of artefacts: check recovery!
 - Recalculation for dissolution in soils
- Retention
 - Different descriptors available: take your pick!
 - Kinetic ones are conceptually more accurate
 - Relation with bio-availability is not yet established



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Forskningsrådet Formas

Formas främjar framstående forskning för hållbar utveckling



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