Environmental fate modelling and measurement of nanomaterials

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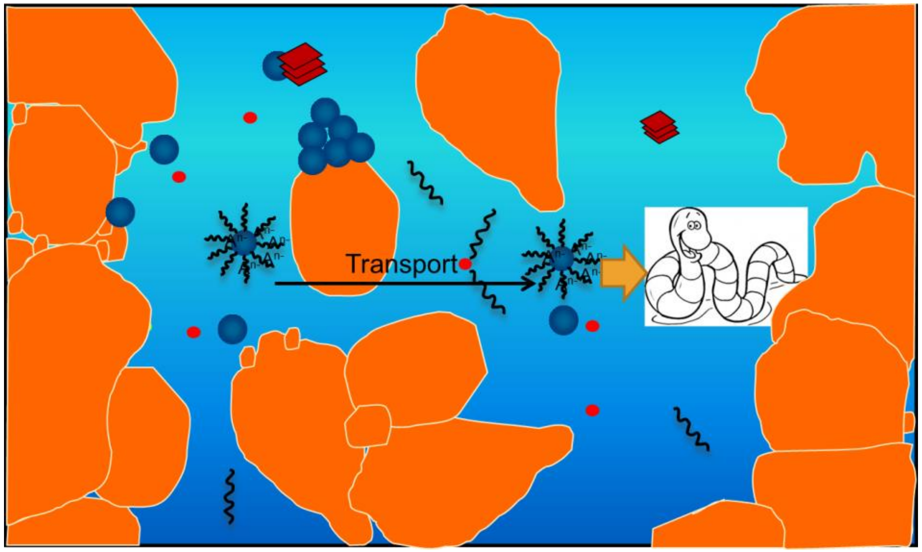
MANAGING RISKS OF NANOMATERIALS

Messages

- Why do we need models?
- Types of models for NM environmental fate
- How do models work in practice?
- What are the dominant reactions that should be modelled?
- How do we capture these on a routine basis, e.g. for regulation?
- How can the models be validated?

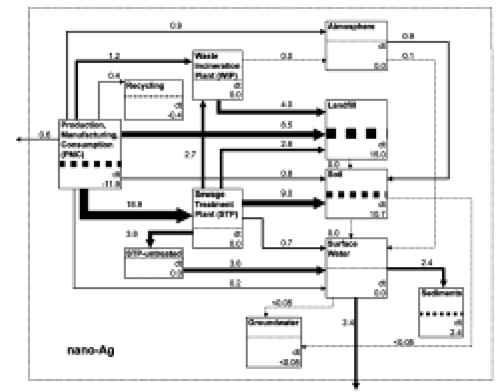
Risk = exposure x hazard

1. ”What NM **form** is the organism really exposed to”: **speciation**
2. ”What NM **concentration** is the organism really exposed to”: **transport**

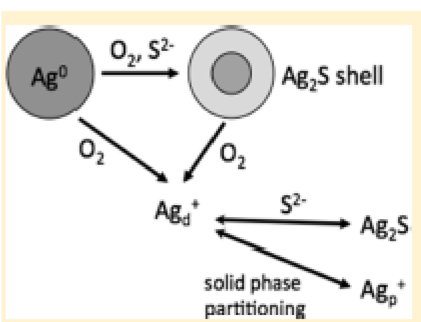


NM Models

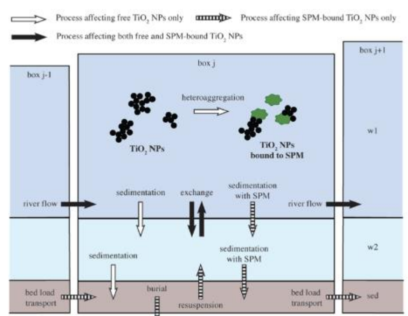
- Large-scale mass flow models (e.g. Gottschalk et al.)
  - ❑ Input/Output = mass
  - ❑ Accurate Industrial production volumes needed
- Local, mechanistic models:
  - – Speciation models
  - – Transport in rivers
  - – Soil transport models
    - ❑ Many parameters needed
    - ❑ Often site - specific



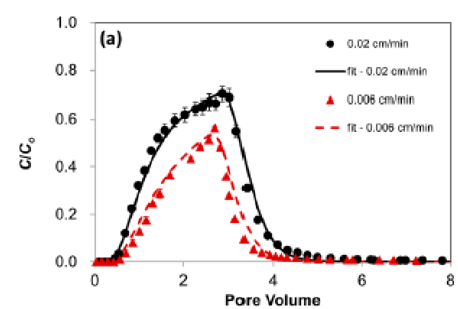
Gottschalk et al. 2010. ES&T 25, 320-332.



Dale et al., 2013. ES&T 47, 12920−12928



Praetorius, et al.. 2012. ES&T 46, 6705-6713

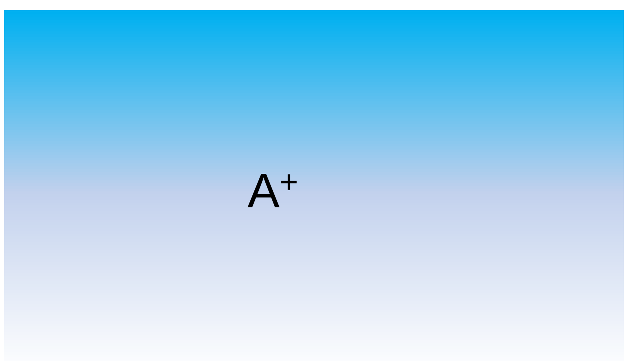


Liang et al. 2014 ES&T 2013, 47, 12229-12237.

Fate descriptors

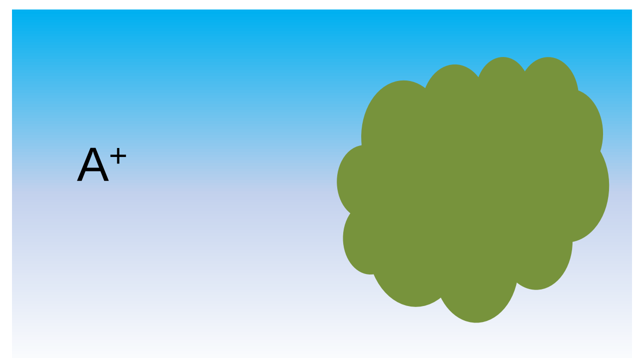
” A set of parameters describing the fate of **a chemical** in the environment”

Concentration in pure water



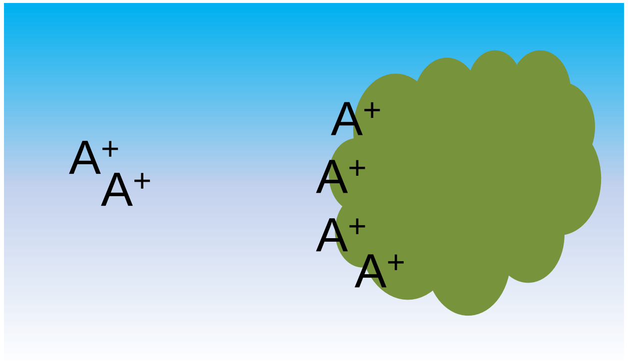
$[A]_{aqueous}$

Concentration in the environment



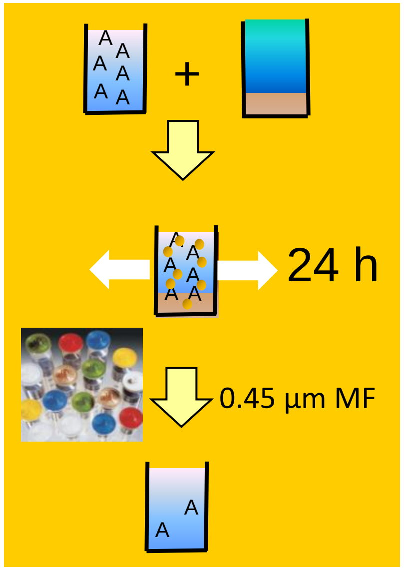
$K_d = [A]_{solid}/[A]_{aqueous}$

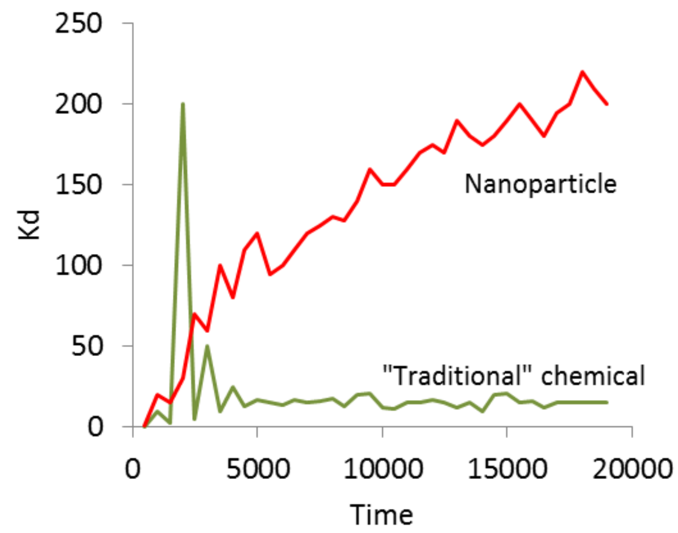
K_d values



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

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

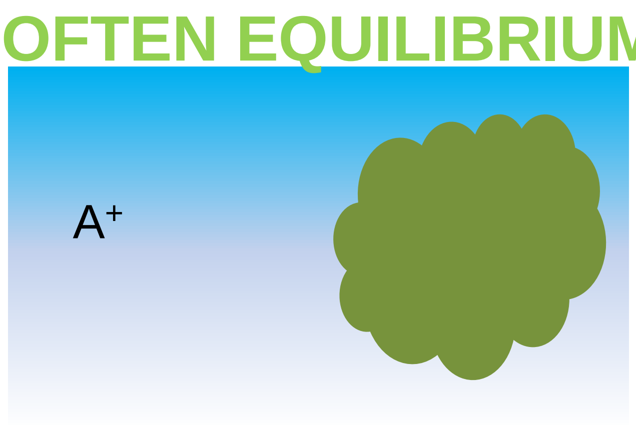




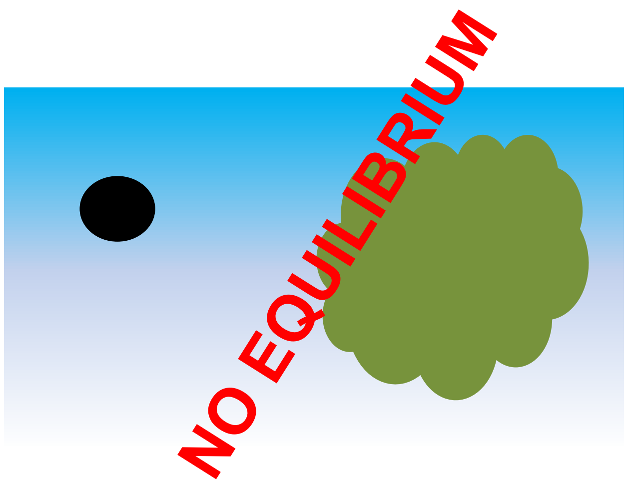
K_d values for nanoparticles?

ESNano (*In press*)

- Praetorius et al. " The road to nowhere: Equilibrium partition coefficients for nanoparticles"
- Cornelis et al. "Fate descriptors for engineered nanoparticles: the good, the bad, the ugly"



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



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

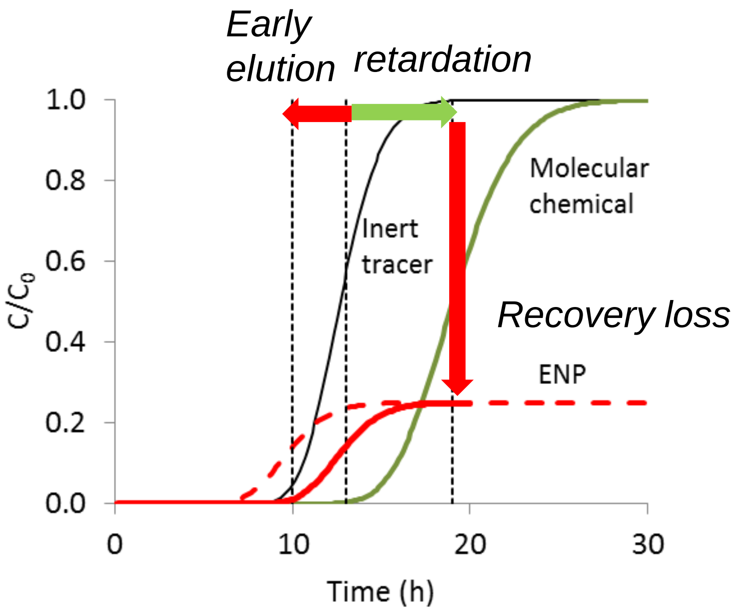
K_d values for nanoparticles?

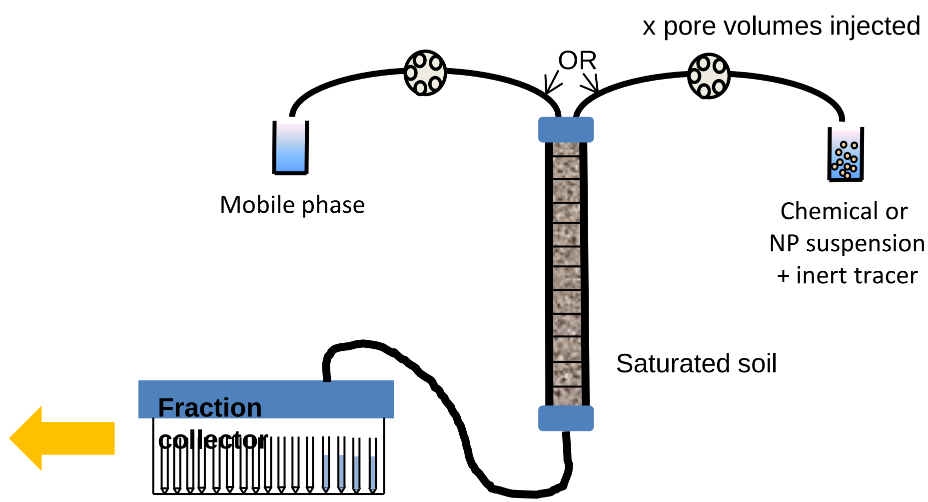
Soil column transport studies (~ OECD 312):

Traditional chemicals: **retardation**

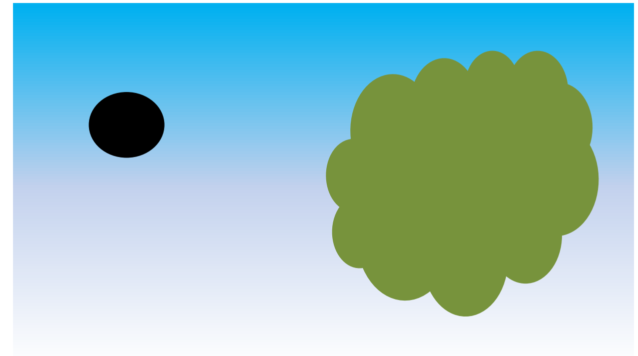
$R = 1 + (r_b/q_e)K_d.$

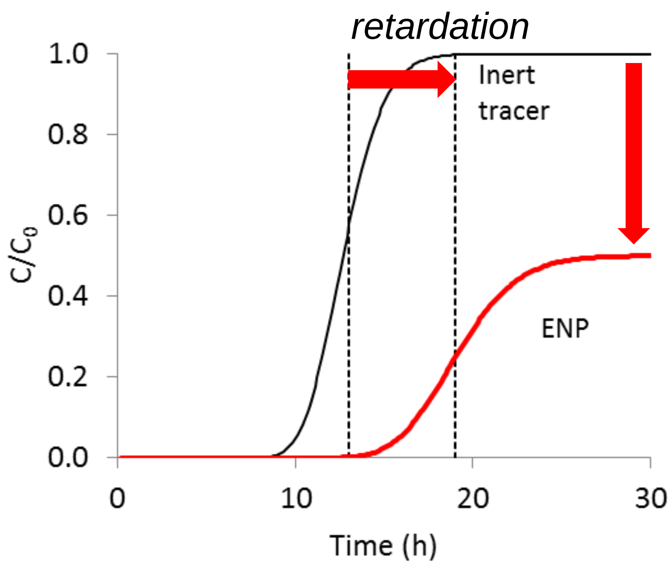
Nanoparticles: **loss in recovery**





K_d values for nanoparticles?



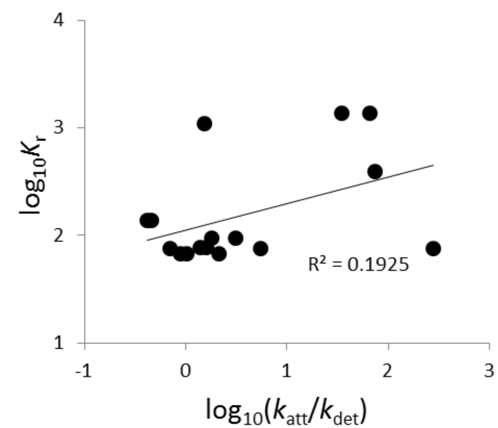


Recovery loss

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

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

$$K_d \sim k_{\text{attach}} / \text{k}_{\text{detach}}\ ?$$



α values

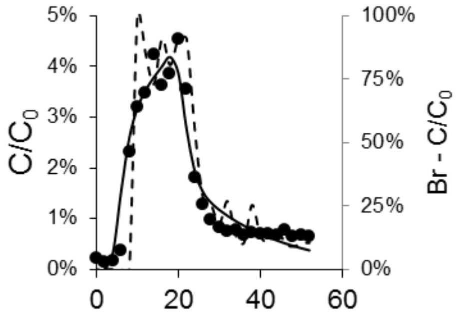
$V_{max} = k_{max}*[NP]_{aqueous}$

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

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

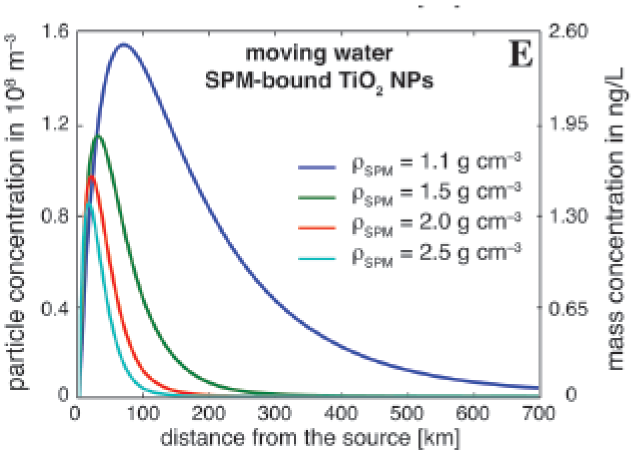
- Ratio of attachment rate at real vs. Ideal conditions
- The probability that a particle will ”stick” to other particles or surfaces

Soil



Experimental and fitted Ag mass concentration as a function of time in an outflow of a sandy soil, also showing the experimental breakthrough of the inert tracer (Br) (Cornelis, et al. 2013. Sci. Tot. Environ. 463-464. 120-130.)

Freshwater

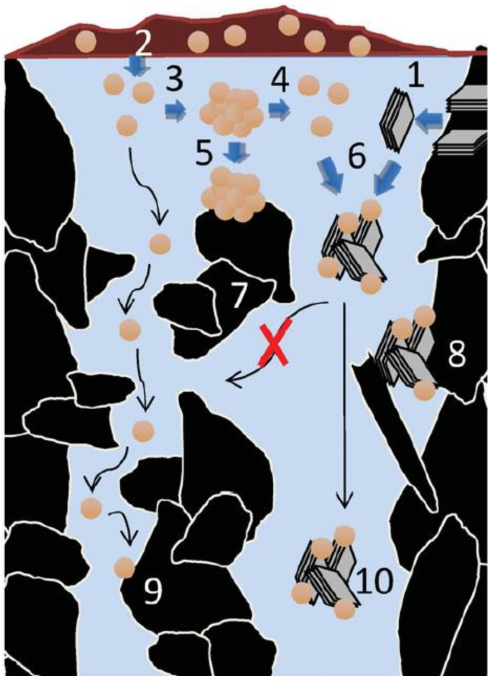


Modeled TiO2 number concentration afo distance from emmission in the Rhine river. (Praetorius, et al.. 2012. ES&T 46, 6705-6713.)

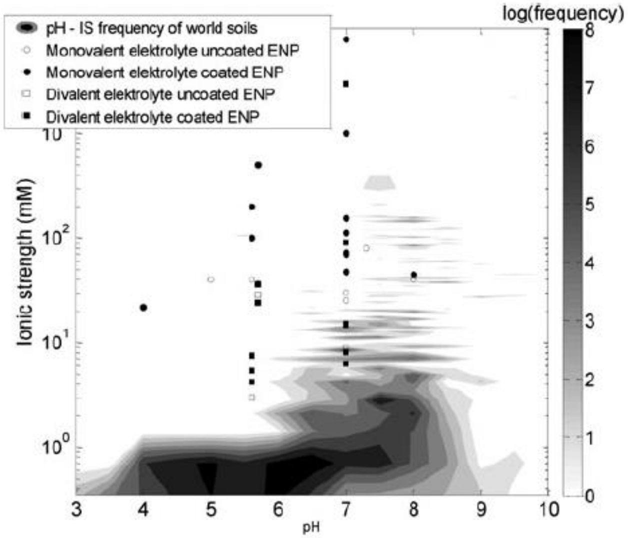
Fate of NM in soils

Main soil parameters determining NM fate

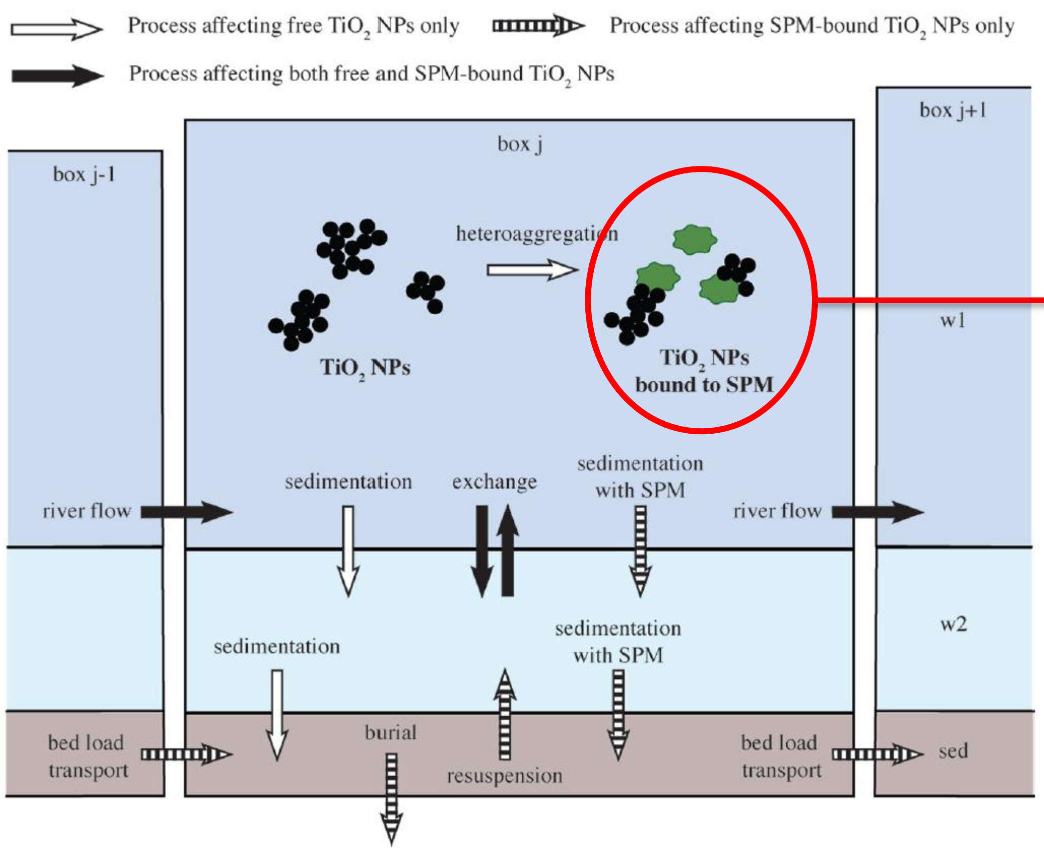
1. **(granulometric) Clay content** ➔ **Heteroaggregation α**
2. Dissolved organic matter
3. Degree of saturation
4. Ionic strength



Fate reactions of NM in soils. (Cornelis, et al.. 2014. Crit. Rev. Environ. Sci. Technol. 44: 2720–2764.)



Aquatic systems



Most important reaction:

Heteroaggregation

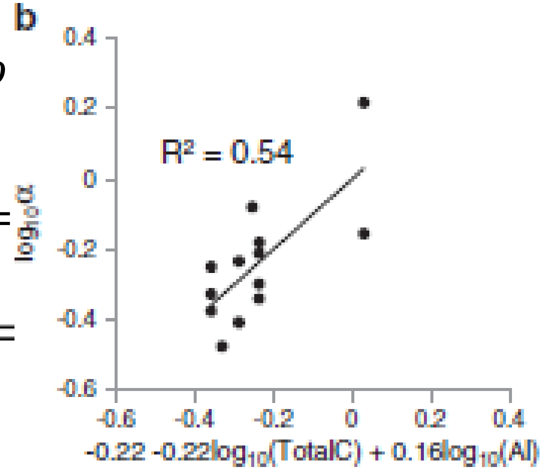
α

Praetorius, et al. Environ. Sci. Tech 46 (12), 6705-6713.

$$\theta \frac{\partial c}{\partial t} + \rho$$

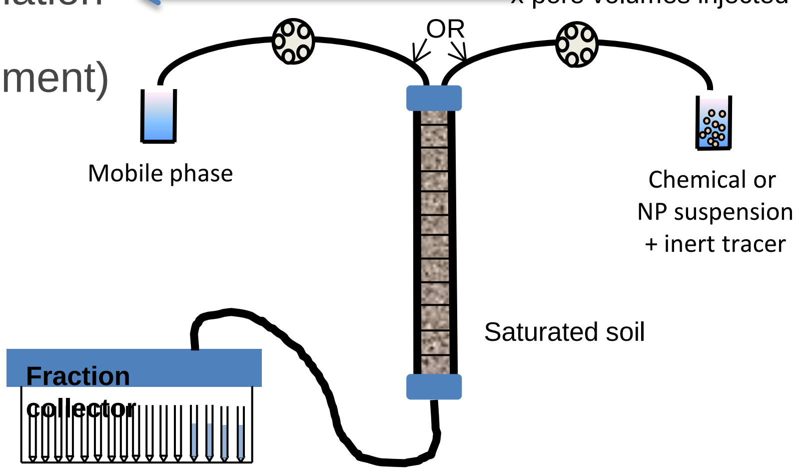
$$\rho \frac{\partial S_i}{\partial t} =$$

$$k_{att} =$$



α values: determination

- Operationally defined (though less so than K_d values)
- Are always fitted to data, requiring additional parameters
- Are specific to a particular soil – NP combination
- Many other mechanisms (other than attachment) are relevant
- Labour and cost-intensive



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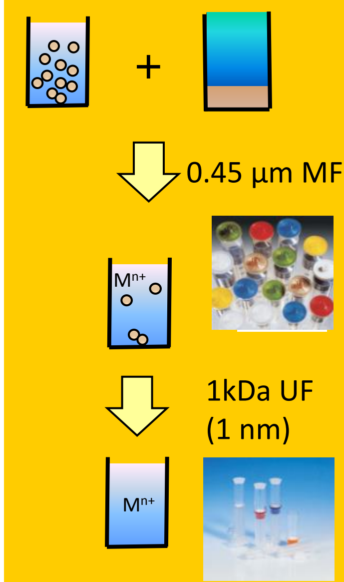
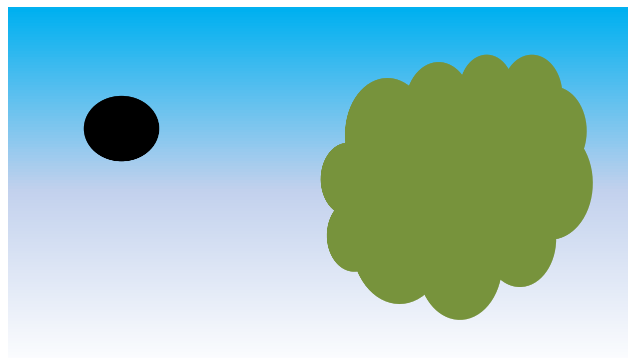
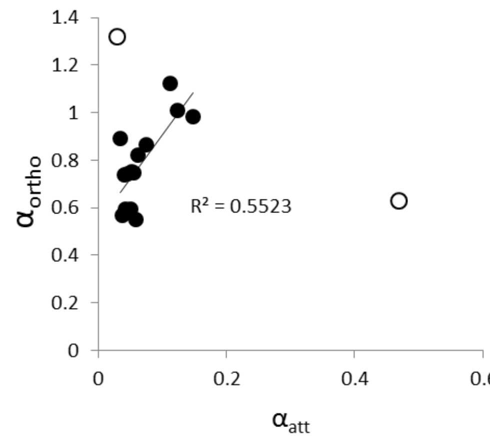
Alternative methods: K_r values

Batch method:



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





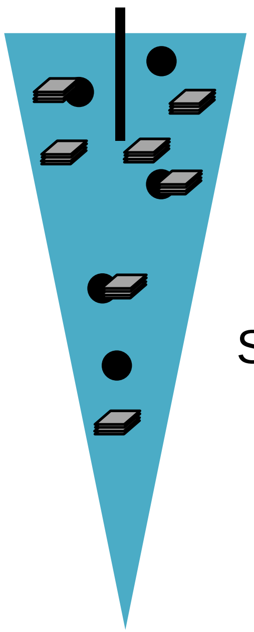
α_{ortho} calculated from K_r values vs. α_{att} (Cornelis , ES Nano)

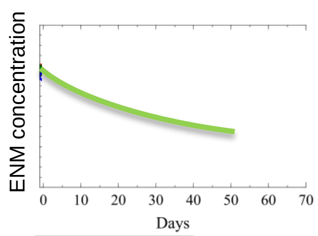
Intense shear conditions during shaking ⇔ column experiment

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

Alternative methods

Aquatic: Sedimentation cones

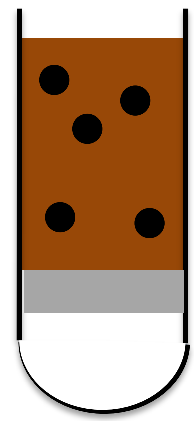




Sedimentation rate

α value

Terrestrial: pore water extraction



”K_r-type” value

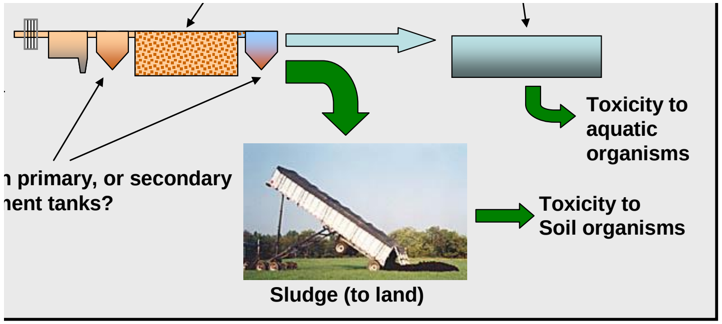
α value

How to use?

- ”Trigger values?”: Very few studies consider both fate and hazard, at least not in realistic media

➔relation between fate descriptors and bioavailability is unknown.

- ”Priority environmental compartment”:
  - Fate descriptors are context-dependent, i.e. an a value means something different in water, soil, wastewater.
  - Wastewater fate determines where ENM will go
  - Sedimentation in WWTP as standard test?

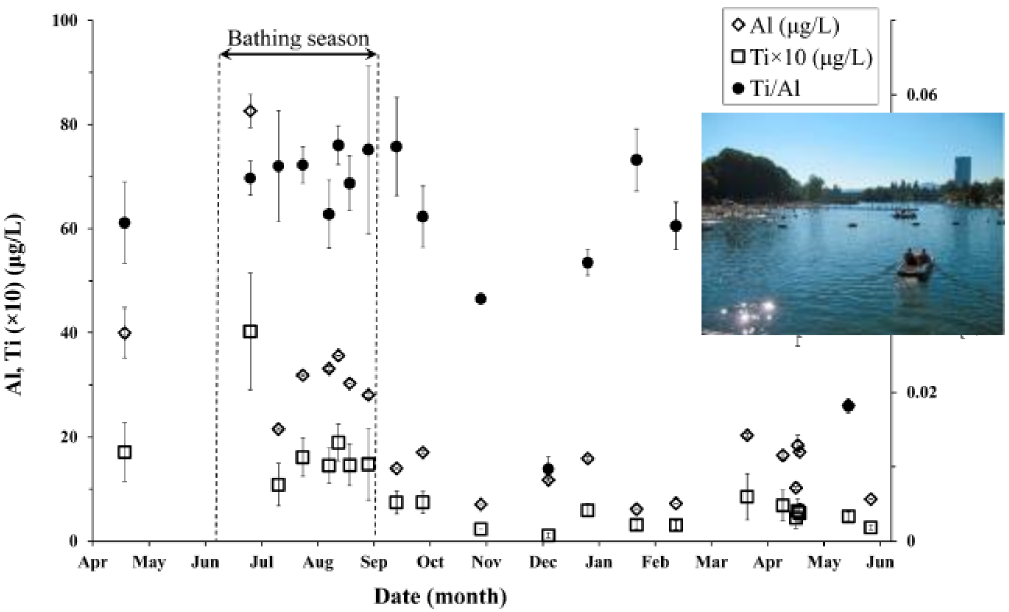


Model validation and environmental NM monitoring

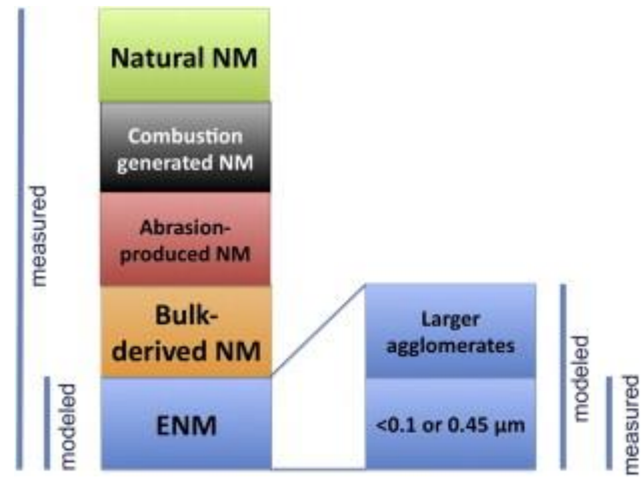
	Inorganic NM	Organic NM
Aquatic systems	• TEM-SEM • DLS • **spICP-MS** • FFF-spICP-MS	• TEM - SEM • FTIR (CNT) • HPLC (C60)
Terrestrial systems	• Extraction, filtration • Backscatter SEM	• HPLC (C_{60})

Heavy focus on size. Detecting **speciation** at early stages (e.g. SEM-Raman)

Model validation and environmental NM monitoring



Al and Ti measurements as a function of time in waters of the old Danube. (Gondikas et al. 2013 ES&T 48, 5415−5422).

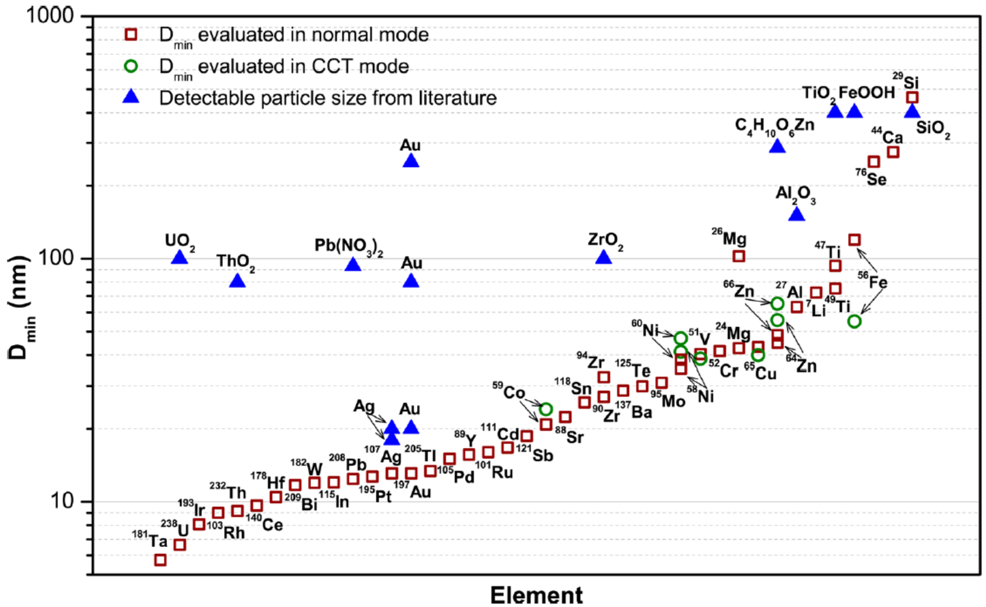


The NM model valdiation contradiction (Gottschalk et al. 2013 Environ. Poll. 181: 287-300.)

Models, especially mass-based ones predict something that we cannot always measure

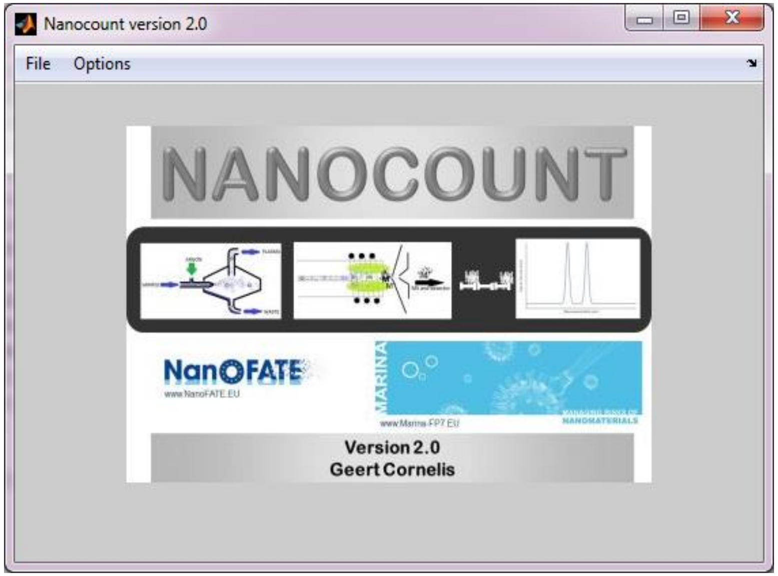
Example: spICP-MS

Size detection limits of spICP-MS



Lee et al. (2014) ES&T 48, 10291-10300

spICP-MS analysis software



Critical data gaps

- Finding fate descriptors that are the best possible compromise between technical accuracy and operational simplicity.
- Development of models that predict dose metrics that can realistically be validated and monitored
- Development of techniques that can measure low concentrations of NMs specifically
- Development of techniques that can probe NM speciation

Acknowledgments

Nanomaterial NANOSPHERE Risk Research

formas

Forskningsrådet Formas

Formas främjar framstående forskning för hållbar utveckling

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