Evaluation of titanium dioxide nanoparticle heteroaggregation with suspended particulate and natural organic matter

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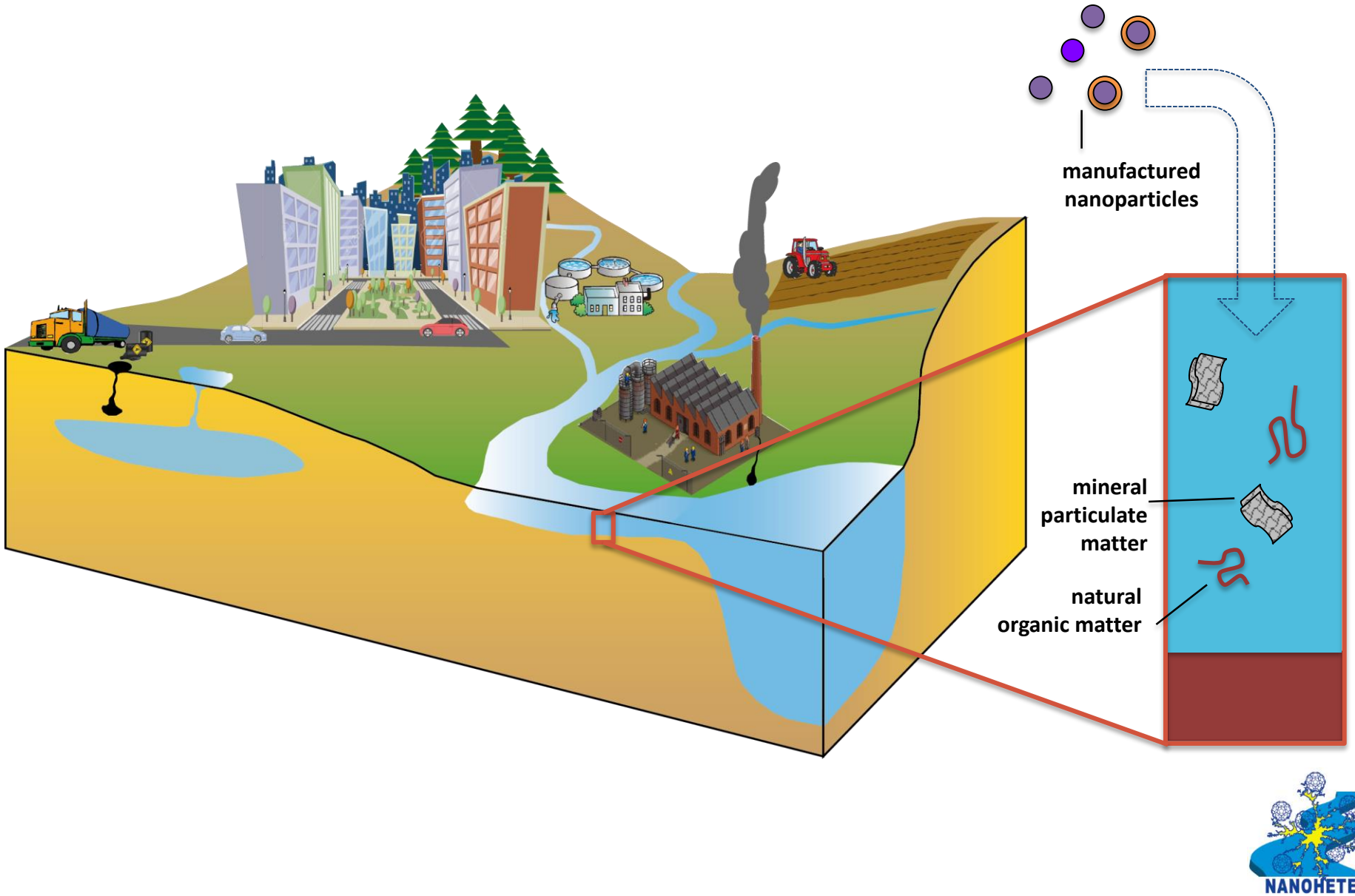
Fate of manufactured nanoparticles in the water column



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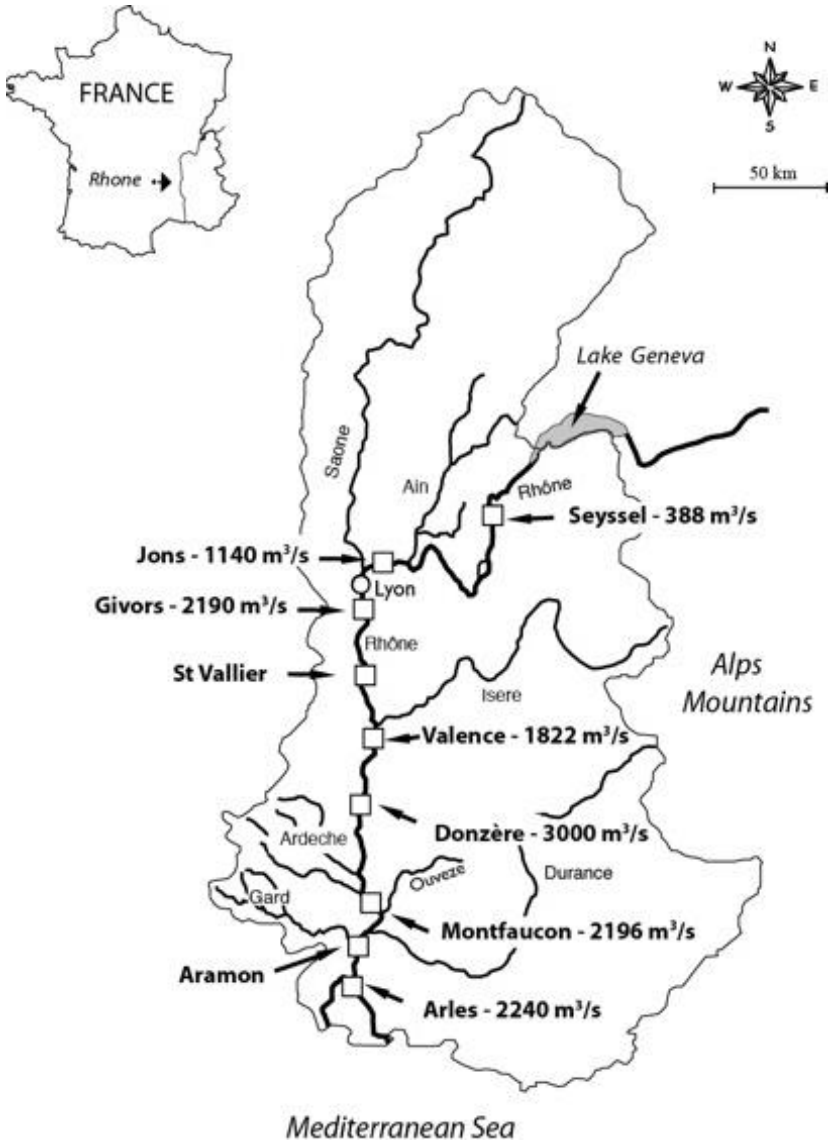
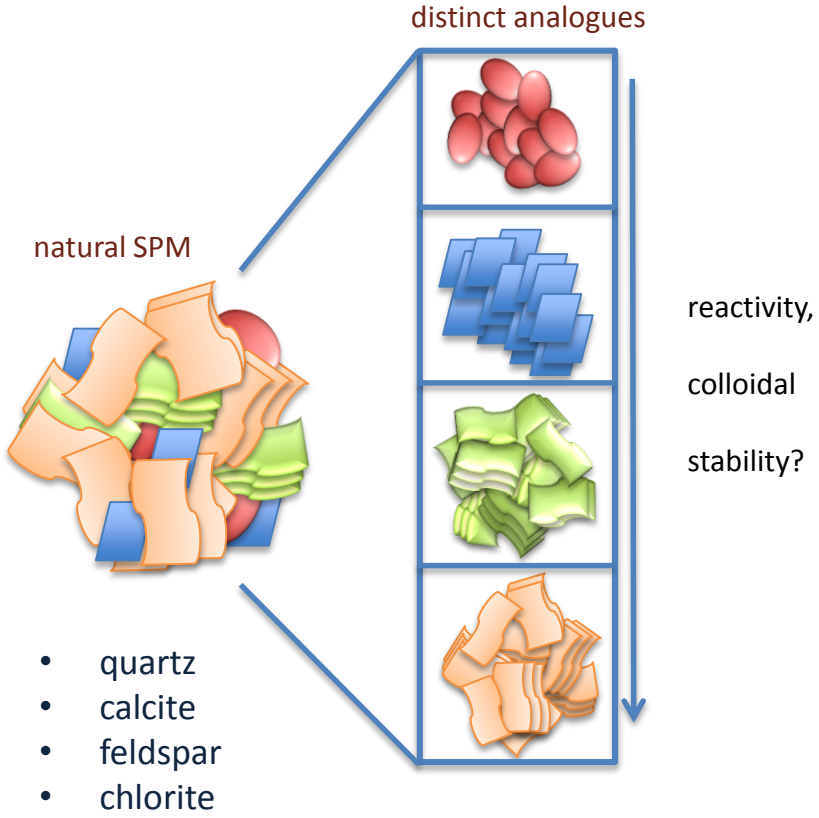
Selecting inorganic colloid analogues

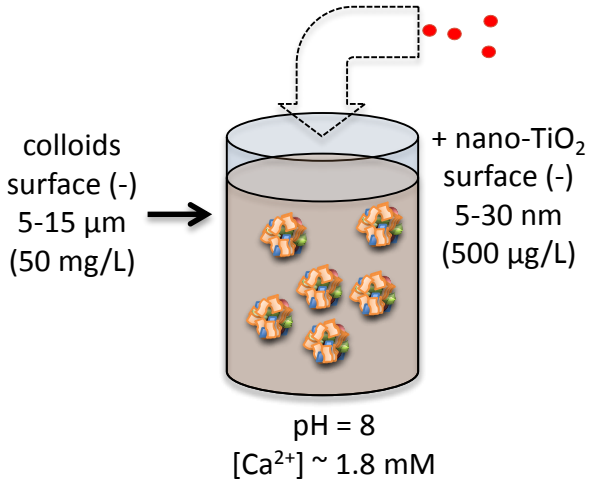
Rhone sampling campaign

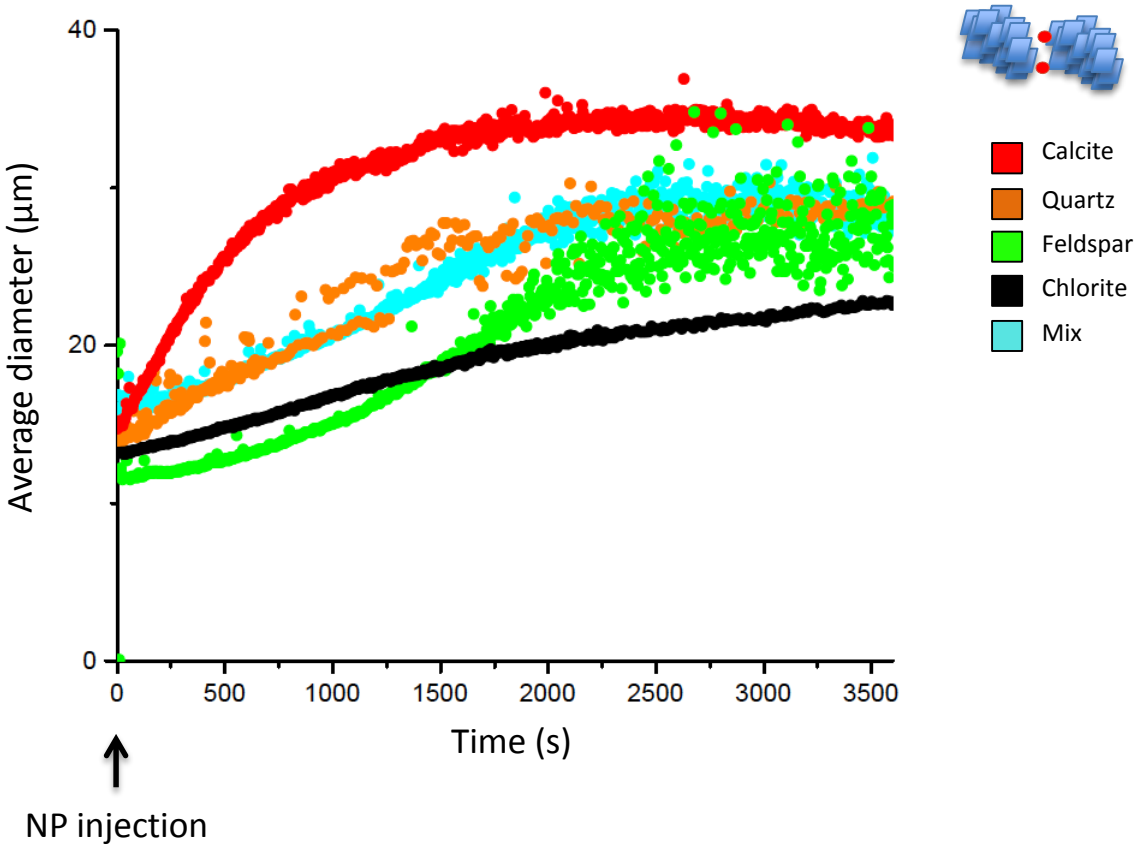




Slomberg et al. *Environ. Chem.*, **2016a**, *in press*, http://dx.doi.org/10.1071/EN15065.

Nanoparticle heteroaggregation with inorganic colloid analogues





Praetorius et al. *ES&T,* **2014**, *48*, 10690-10698.
Labille et al., *ES&T*, **2015**, *49*, 6608-6616.

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Determining heteroaggregate sticking efficiency

Von Smoluchowski 1917

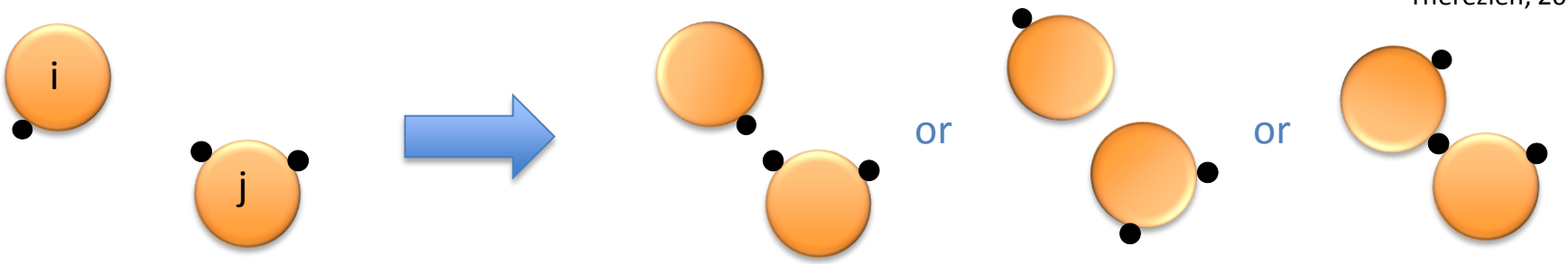
$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k} \alpha_{ij}\beta_{ij}n_i n_j - n_k \sum_{i=1}^{\infty} \alpha_{ik}\beta_{ik}n_i$$

sticking efficiency

collision frequency

2 materials = 3 possible types of collision

Therezien, 2014



f = NP / C surface coverage due to agitation, $f_i = f_j$

global sticking efficiency:

$$\alpha_{\text{global}}(f_i, f_j) = f_i f_j \alpha_{\text{NP-NP}} + (1-f_i)(1-f_j)\alpha_{\text{C-C}} + ((1-f_i)f_j + (1-f_j)f_i)\alpha_{\text{NP-C}}$$

This is measurable.

$$\alpha_{\text{NP-C}} = \frac{\alpha_{\text{global}} - f^2\alpha_{\text{NP-NP}} - (1-f)^2\alpha_{\text{C-C}}}{2(1-f)f}$$

We want this.

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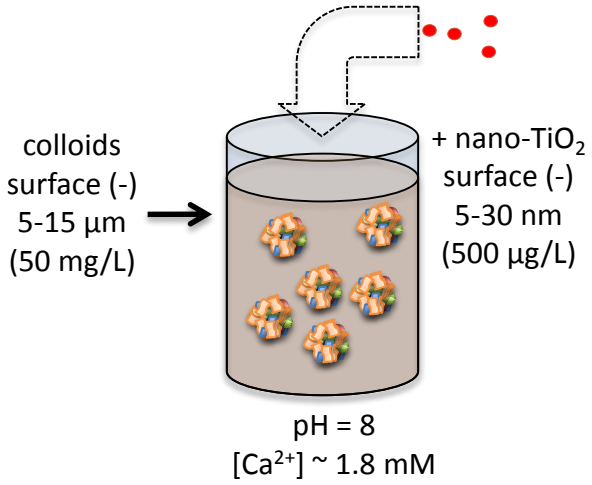
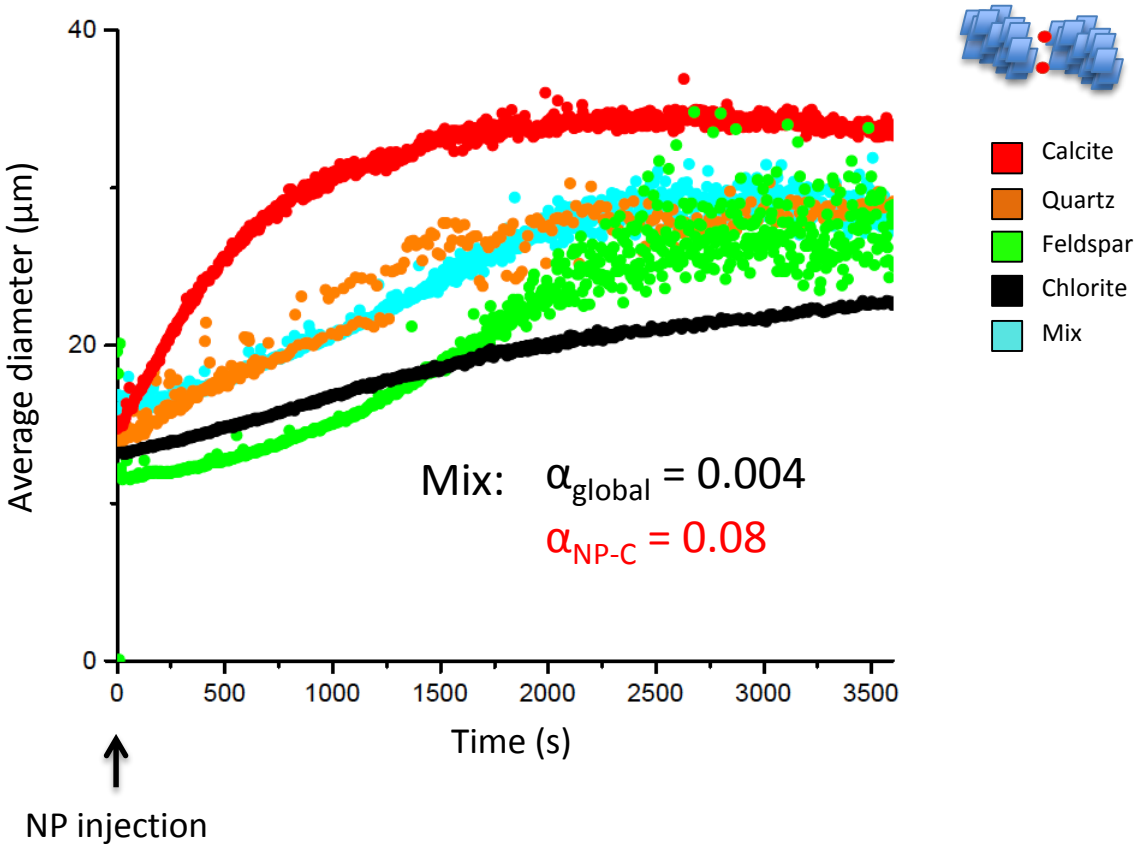
Nanoparticle heteroaggregation with inorganic colloid analogues





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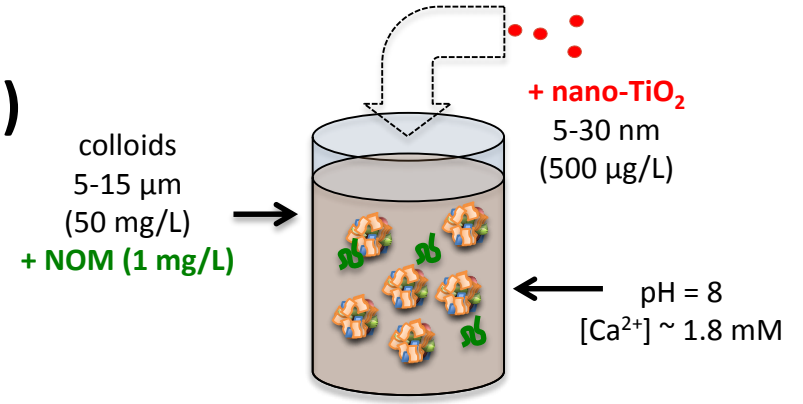
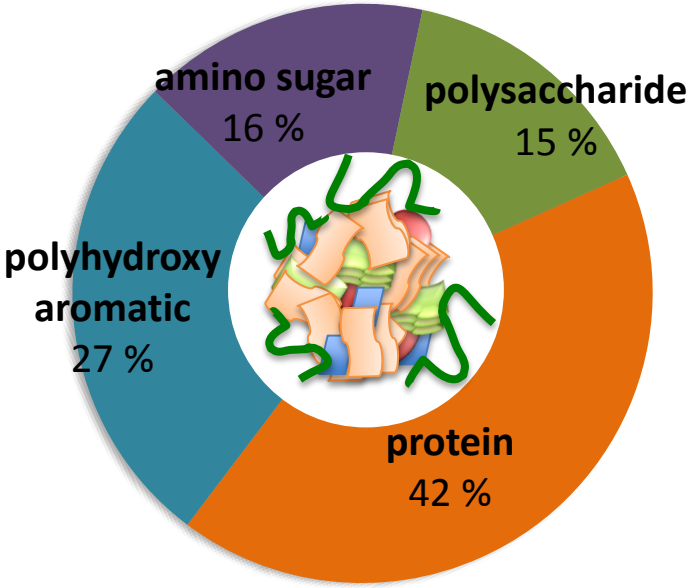
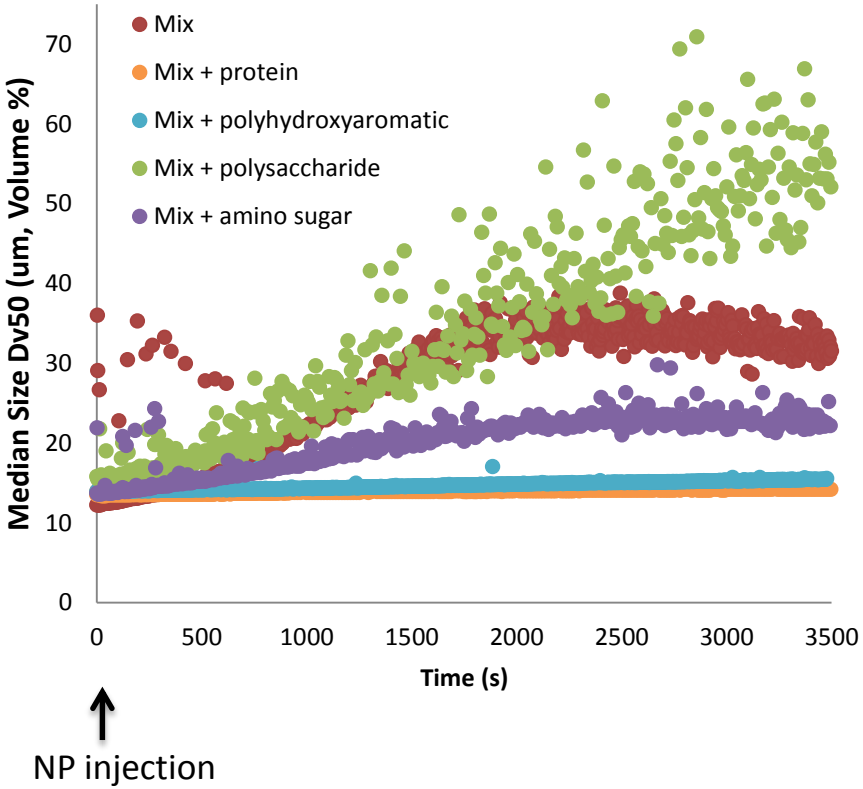
Nanoparticle heteroaggregation in the presence of natural organic matter (NOM)

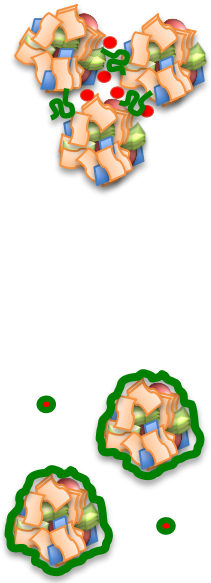


Rhone NOM characterization by pyrolysis GC-MS



Total organic carbon = 4 mg/L





- Opposite NOM effects as a function of NOM type
- Polysaccharide enhances aggregation
- Protein and PHA prevent aggregation

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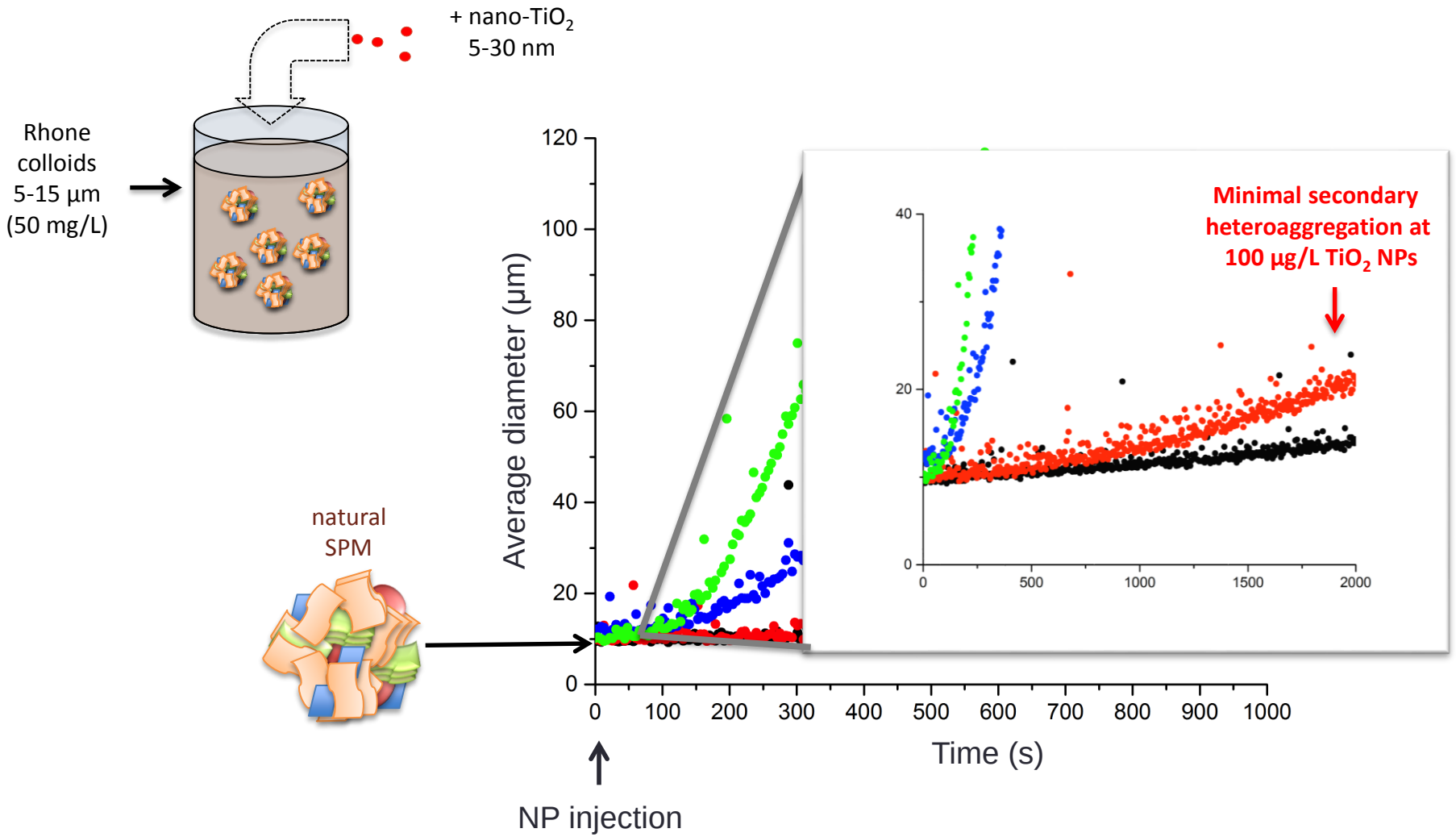
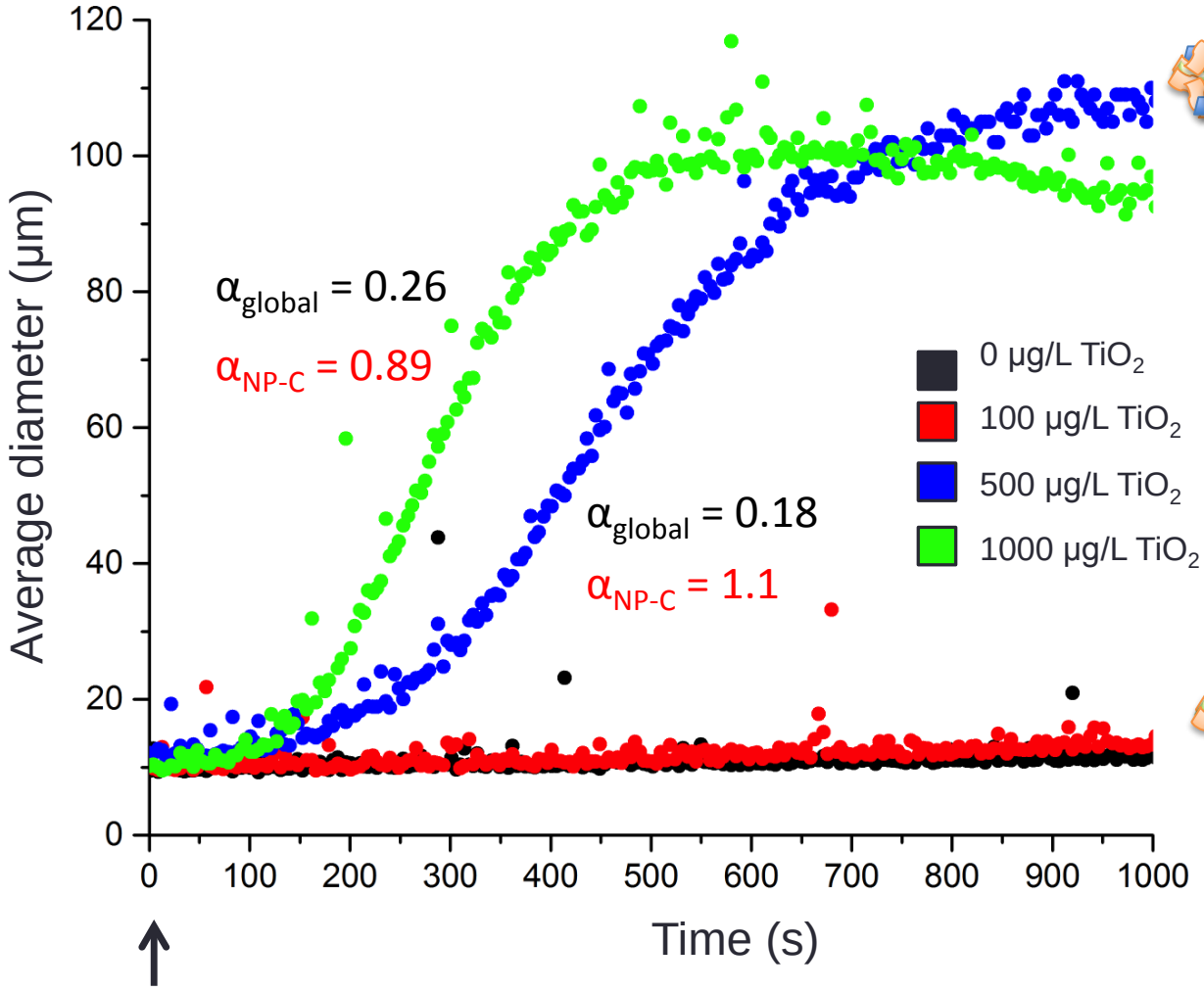
Slomberg et al. *Environ. Chem.*, **2016b**, *in press*, http://dx.doi.org/10.1071/EN16038.

Heteroaggregation of titanium dioxide NPs with Rhone river SPM



Heteroaggregation of titanium dioxide NPs with Rhone river SPM



- α_{NP-C} ~ 1
- α_{NP-C} not concentration dependent
- Can use this α_{NP-C} in fate model to determine NP fate at more relevant concentrations (ng/L)

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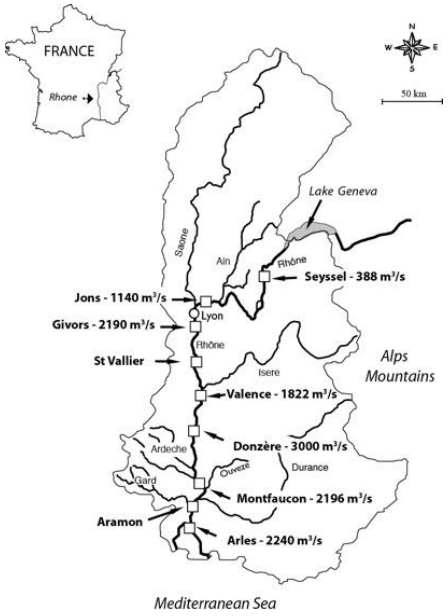
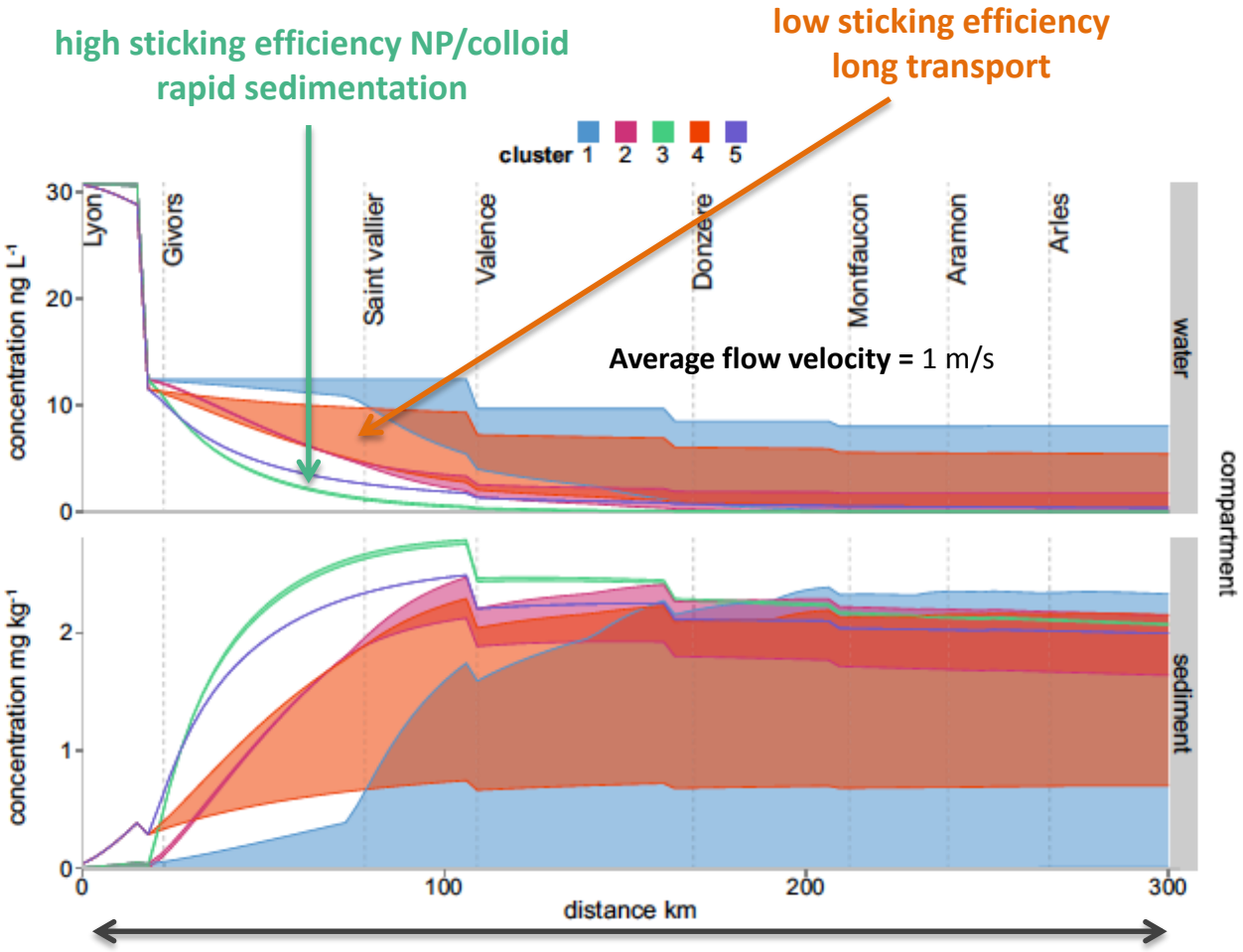
Predicting NP residence time in the water column: river fate model



Sun et al. 2014:
Predicted nano-TiO_2 emission after WWTP = 16 µg/L
Estimated nano-TiO_2 emission from Lyon = 1.5 kg per day

Concentration profile of NP:
water column vs. sediment,
simulated for a pollution source at Lyon
(d=0 km, C = 30 ng/L)



- For $\alpha_{NP\text{-}C}$ = 1, complete sedimentation of TiO_2 NPs within 100 km of emission
- Residence time of TiO_2 NPs ~ 1 day
- NP fate determined by water composition at or near source
- Early and substantial accumulation of TiO_2 NPs in sediment layer

Sun et al. *Environ. Pollut,* **2014**, *185*, 69-76.
Sani-Kast et al. *Sci. Total. Environ.,* **2015**, *535*, 150-159.

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Conclusions: Mechanistic approach

- Heteroaggregation drives NP fate, not homoaggregation
- Heteroaggregation of TiO_2 NPs with colloids easily assessed with laser diffraction
- Calcium-induced heteroaggregation between (-) NPs and (-) colloids
- Mineral and organic suspended matter composition influences heteroaggregation

Conclusions: Rhone case study

- Sticking efficiency can be determined as input parameter for fate models
- $\alpha_{NP\text{-}C}$ ~1
- Emission at Lyon of 30 ng/L TiO_2 NPs:
  - Distance of transport: 100 km
  - Residence time: ~1 day
  - Max [TiO_2 NPs] in sediment: ~ 3 mg/kg

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http://nanoheter.cerege.fr

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