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Relevance

In the risk assessment of manufactured nanomaterials, heteroaggregation of engineered nanoparticles (ENPs) with naturally occurring suspended particulate matter (SPM) is a key factor for designing realistic environmental fate models. A parameterization of this pivotal process can be achieved by determining the heteroaggregation attachment efficiency ( $\alpha_{hetero}$ ). Studies that have engaged in experimentally determining  $\alpha_{hetero}$  are rare, almost all using simple model SPM (e.g. SiO<sub>2</sub> or clay minerals). Two-component systems hardly represent reality, where SPM is much more complex. Real SPM comprises mineral as well as organic components with heterogeneous and varying physicochemical properties. Here we evaluate existing experimental approaches regarding their abilities to reliably determine  $\alpha_{hetero}$  and their applicability to more complex systems. We then explore ways to increase SPM analogue complexity and achieve higher environmental relevance of heteroaggregation studies.

Key messages

Existing methods to determine  $\alpha_{hetero}$  are missing out on either of the following:

- complex SPM analogues representative of natural SPM
- extracting primary  $\alpha_{hetero}$  from the sum of aggregation processes
- resolving a broad range of  $\alpha_{hetero}$  values (from slow to fast aggregation)
- a sound underlying theoretical or mathematical concept

Complex SPM analogues can be built from model substances.

Pre-tests with kaolinite, quartz, hematite, alginate and tryptophan teach us the following:

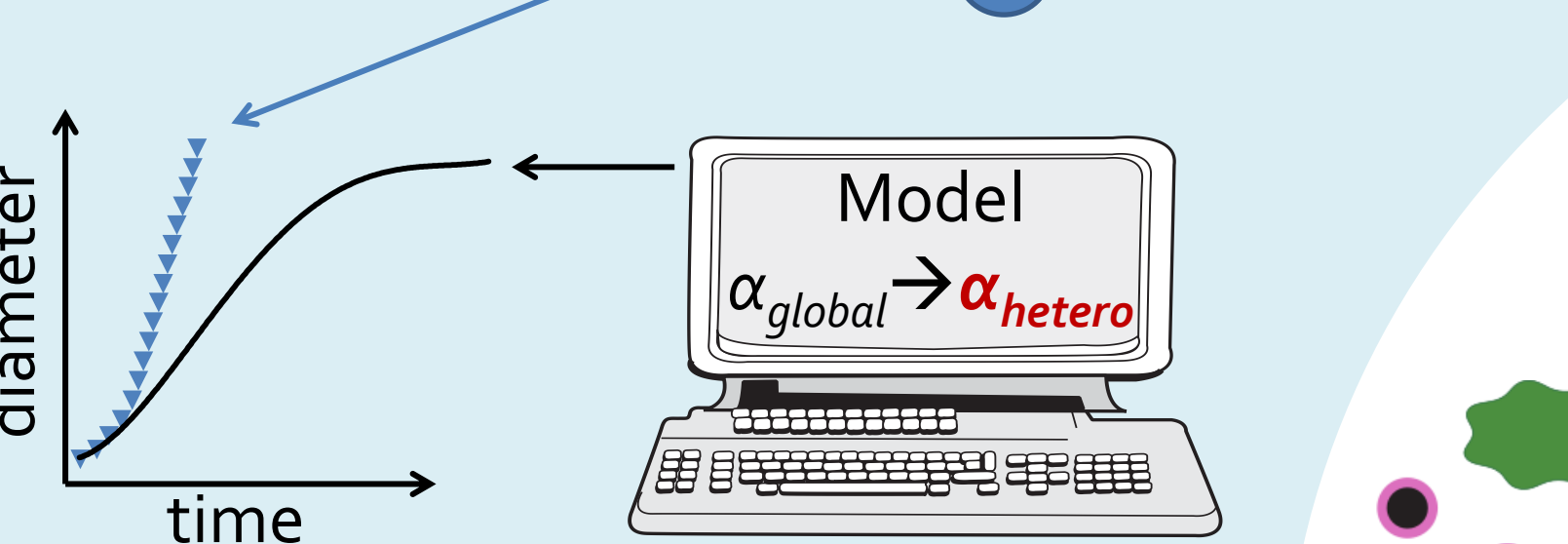
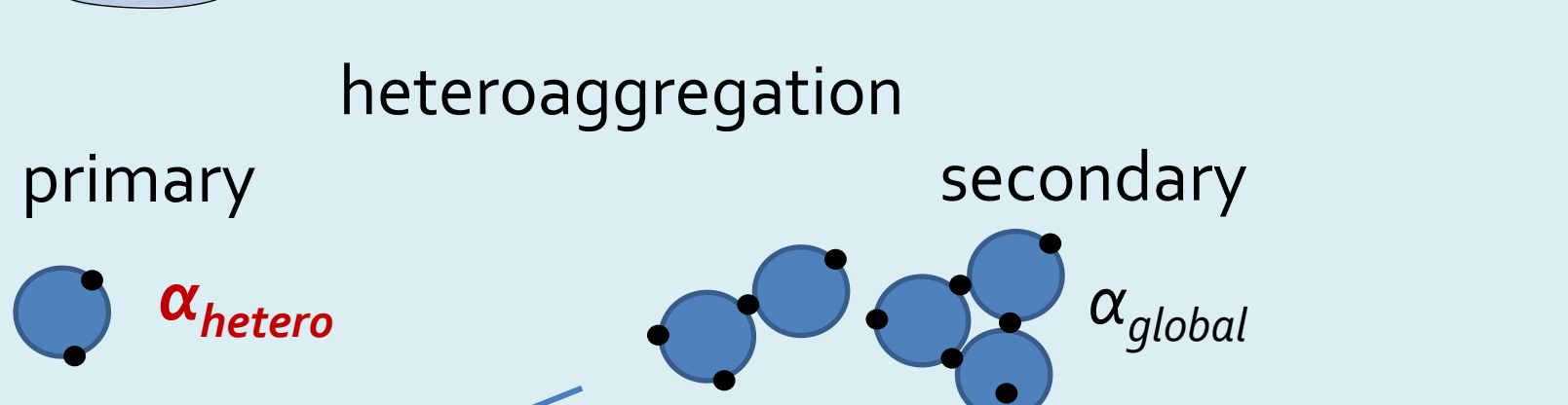
- alginate stabilizes particle suspensions in all cases (no aggregate formation)
- hematite or divalent cations (positive charge) required for the formation of complex SPM

**Future challenges:** systematic selection of SPM analogues stable in various aquatic chemistries and applying them with refined experimental methods to determine  $\alpha_{hetero}$ .



Heteroaggregation experiments

Time-resolved laser diffraction [1]



$\alpha_{global} (\alpha_{homo\ ENP}, \alpha_{homo\ SPM}, \alpha_{hetero}, f_{ENP})$   
 $f_{ENP}$ : SPM surface fraction covered by ENPs

- + model separates  $\alpha_{hetero}$  from  $\alpha_{global}$
- + concentration independent  $\alpha_{hetero}$
- secondary aggregation necessary
- slow aggregation (low  $\alpha_{hetero}$ ) not resolved
- no complex SPM (model limits, light scattering issues)
- model assumptions ( $f_{ENP}$ )

Heteroaggregation [4]

$$\frac{dn_{ENP}}{dt} = -k_{hetero} n_{ENP} n_{SPM}$$

$$k_{hetero} = \alpha_{hetero} k_{coll}$$

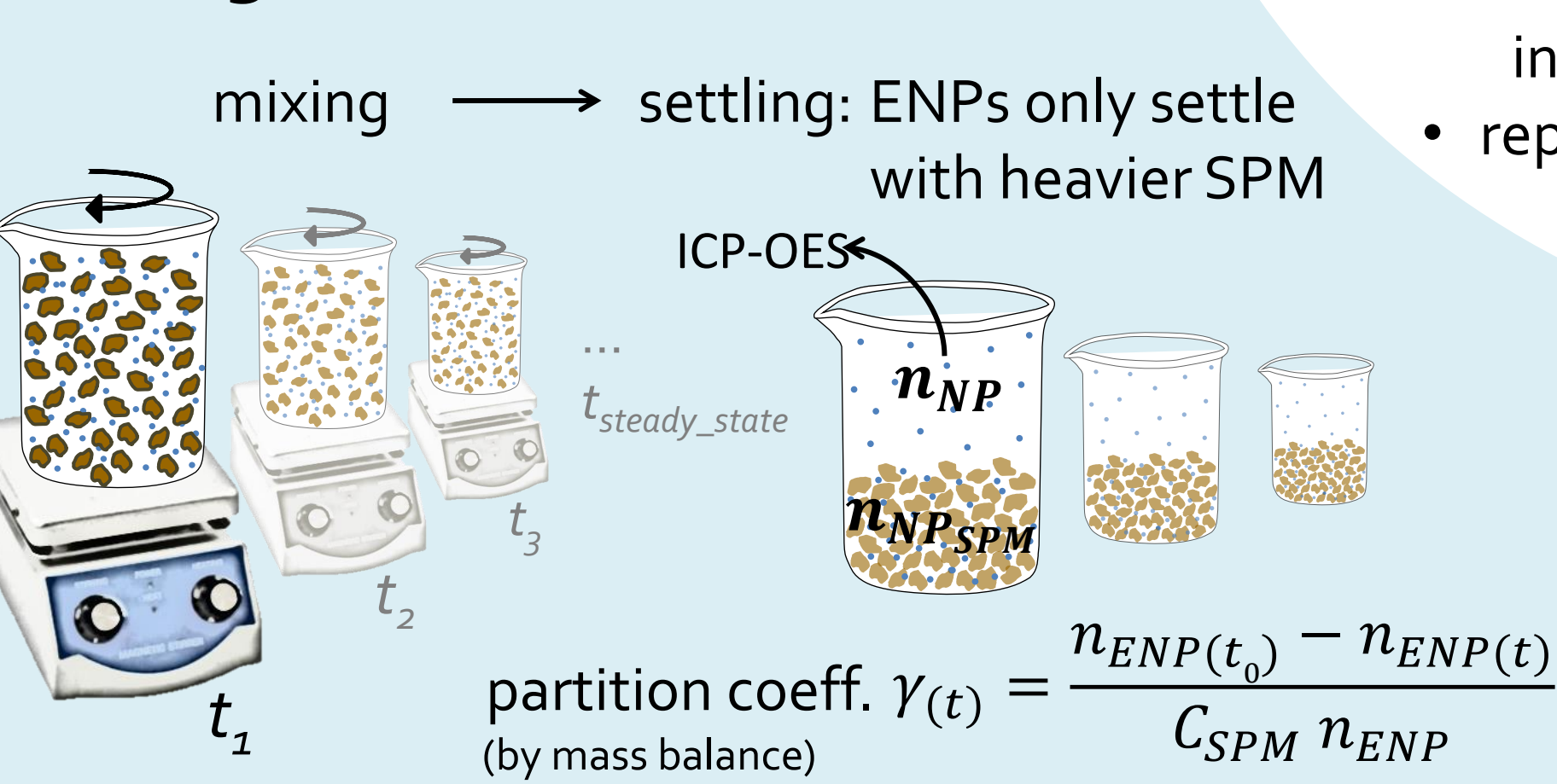
$k_{hetero}$ : heteroaggregation rate constant  
 $k_{coll}$ : collision rate constant

$\alpha_{hetero}$ : attachment efficiency

probability for attachment upon ENP ↔ SPM collision

- input-parameter for fate models that
- represents interaction forces ENP ↔ SPM
- is concentration independent

Settling Batch Method [2]



$$\text{partition coeff. } \gamma(t) = \frac{n_{NP}(t_0) - n_{NP}(t)}{C_{SPM} n_{NP}}$$

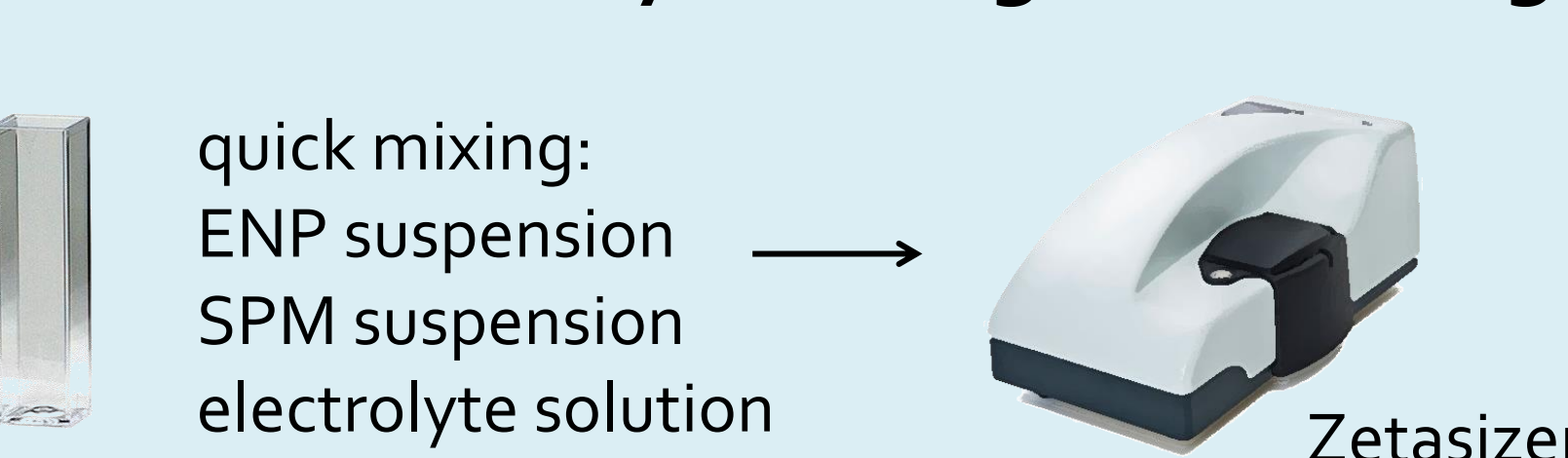
aggregation      breakup

$$\frac{dn_{ENP}}{dt} = -\alpha_{hetero} k_{coll} n_{ENP} n_{SPM} + k_{breakup}(n_{NP}(t_0) - n_{NP}(t))$$

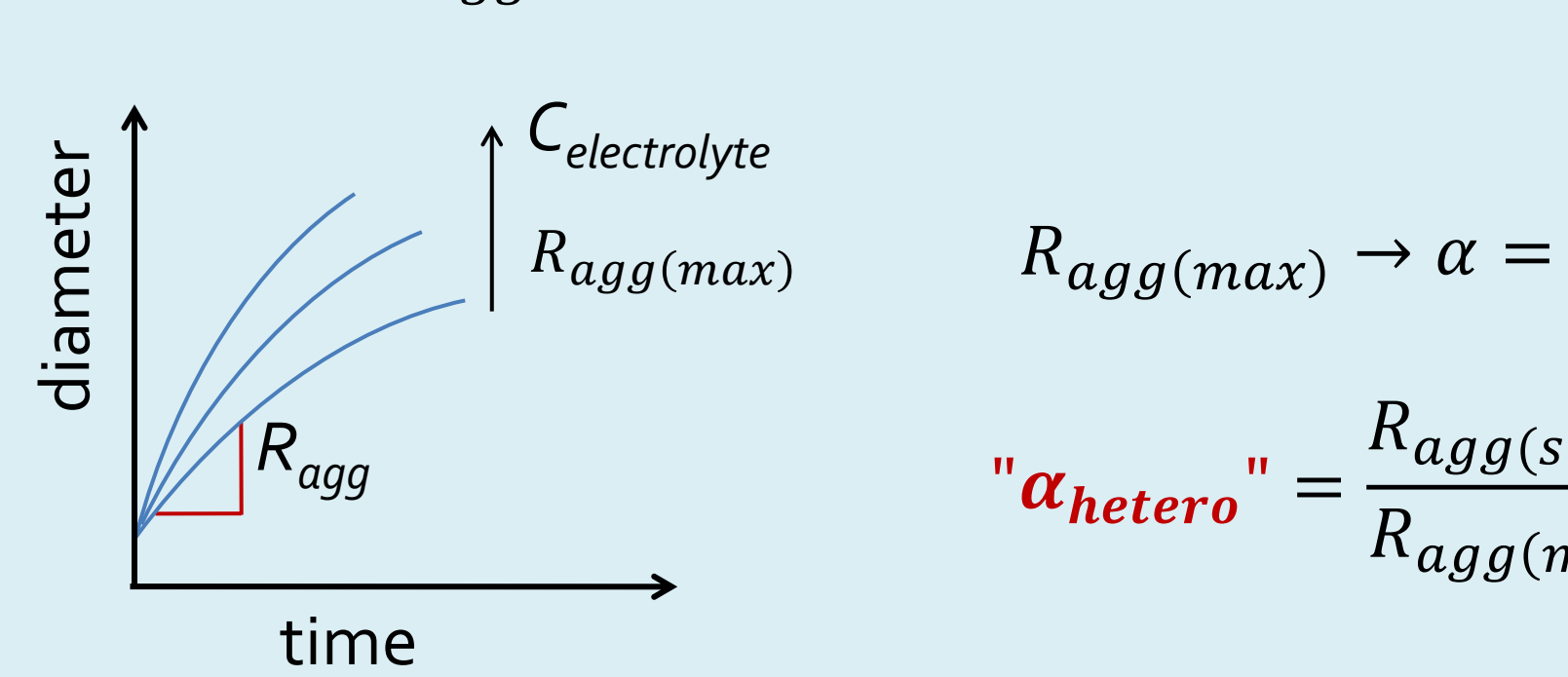
steady state: aggregation = breakup  
early aggregation: breakup = 0

$$\ln[\gamma(t)C_{SPM}] = \alpha_{hetero} k_{coll} n_{ENP} t$$

Time-resolved dynamic light scattering (DLS) [3]



$$R_{agg} = \alpha_{hetero} k_{coll} n_{ENP} n_{SPM}$$



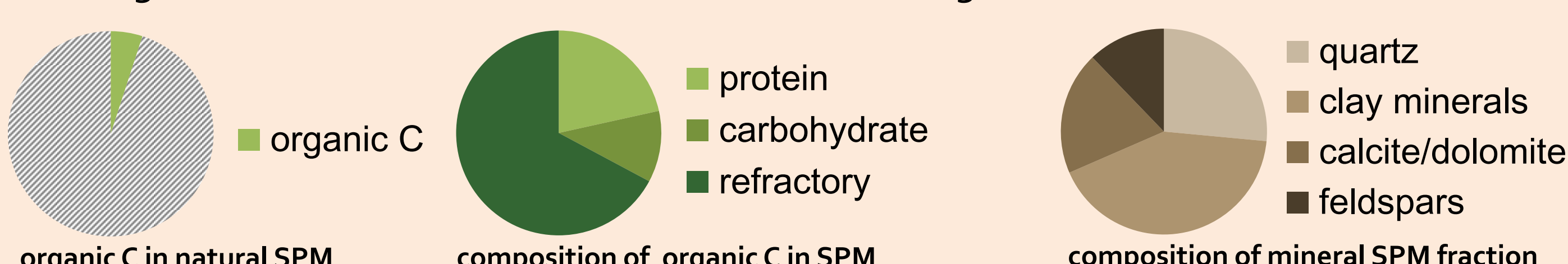
- + low ENP concentrations
- + applicable with complex SPM (sludge was used)
- equilibrium aggregation ↔ breakup? (or rather stabilised ENP fractions?)
- small/light SPM fractions may stay suspended
- continued aggregation while settling
- differential settling: ENP scavenging by SPM
- fast aggregation (high  $\alpha_{hetero}$ ) not resolved (limited by sampling times)

- + low ENP concentrations
- no distinction btw. homo- & heteroaggregation
- not suitable for complex SPM (polydispersity, various refractive indices) → light scattering issues
- SPM/aggregates too large for upper size limit (~1 μm)
- diffusion based sizing biased by aggregate settling
- concentration independence not yet shown
- time-lag between mixing and first size measurement

Complex SPM analogues

Composition of natural SPM

Natural SPM is very complex, comprising inorganic and organic components. The organic carbon fraction amounts to 1.6-8.4% and comprises slowly degrading refractory (50-81%) and easily degradable labile fractions: carbohydrates (5-17%) and proteins (7-35%). Both total organic and labile fraction increase with decreasing total SPM load.[5]



Major mineral components identified in natural SPM comprise clay minerals (23-58%) quartz (22-34%), calcite & dolomite (8-37%) and feldspars (~12%). Iron oxides are also claimed to be important, due to their mostly positive surface charge.[6-7]

Systematic testing of SPM analogues

minerals	organics
<ul style="list-style-type: none"><li>• illite, kaolinite,...</li><li>• quartz</li><li>• hematite</li></ul>	<ul style="list-style-type: none"><li>• CH: alginate,...</li><li>• prot.: tryptophan,...</li><li>• algal EPS</li></ul>
water chemistry	mixing conditions
<ul style="list-style-type: none"><li>• pH 5-8.5</li><li>• CaCl<sub>2</sub>/MgSO<sub>4</sub> (4:1) 0.1-10 mM</li><li>• SR-NOM 0.1-10 ppm</li></ul>	<ul style="list-style-type: none"><li>• mixing ratios</li><li>• mixing sequences</li><li>• stirring speed</li><li>• stirring conditions</li></ul>

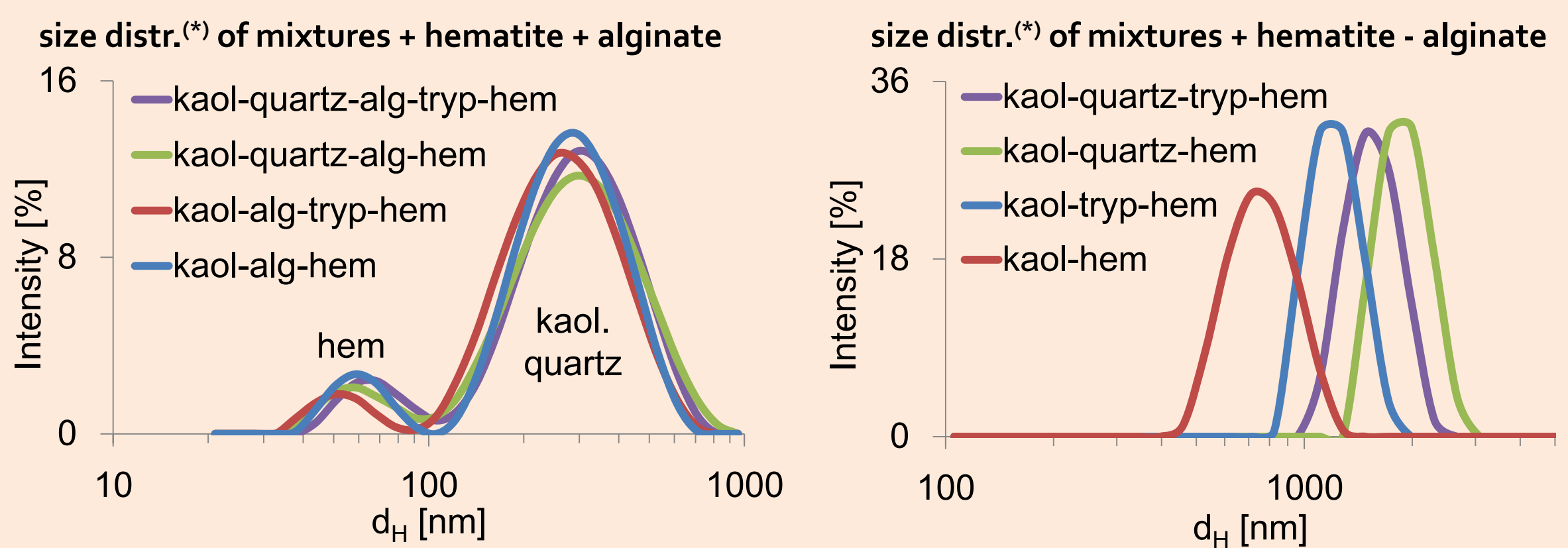
Preliminary test results

natural river SPM [8]	15 mixtures (kaolinite + 1/2/3/4 other components) → final total concentration 100 mg/L (à 100 mL) mass-based mixing ratios: kaolinite quartz hematite alginate(Δ) tryptophan(Δ) 51.7 38.8 6.5 1.1 1.9 (Δ) based on organic C mass
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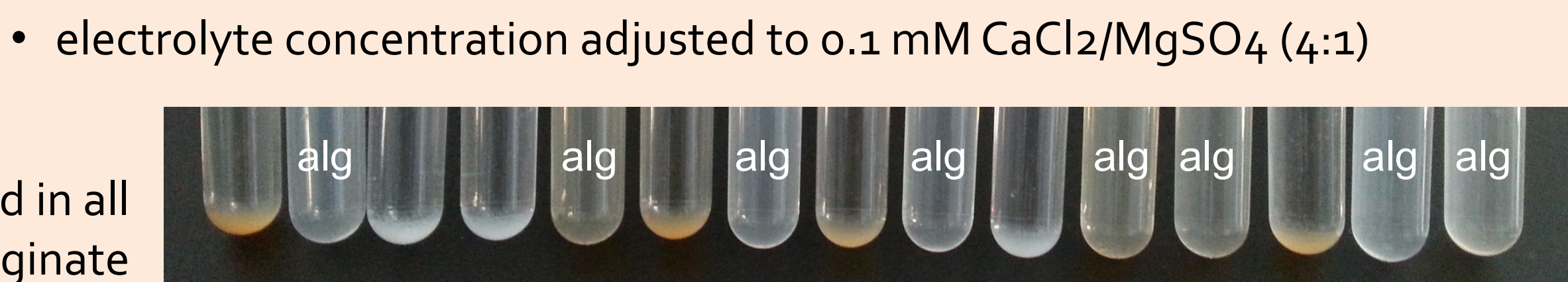
characteristics of single components (by DLS, 100 ppm, pH 7):

	kaolinite	quartz	hematite	alginate	tryptophan
d <sub>H</sub> [nm]	260.7	539.2	66.7	597.7	361.0
ZP [mV]	-40.0	-56.6	+28.9	-76.5	-52.8

- mixing sequence: kaolinite – quartz – alginate – tryptophan – hematite
- magnetic stirring at 400 rpm, pH 6.9-7.2 (unadjusted)
- à 10 mL settled in cuvettes for 24 h
- aggregate settling observed in 4 mixtures containing hematite, no alginate
- DLS\*: average d<sub>H</sub> > 1 μm (vs. mixtures with alginate d<sub>H</sub> < 370 nm)



(\*) after 10 min resuspension in ultrasonic bath & >6 h magnetic stirring at 400 rpm



References

[1] Praetorius et al., *Env. Sci. Technol.* 48, 10690–10698 (2014). [5] Ittekkot & Laane, *Biogeochem. Major World Rivers*, 233–243 (1993).  
[2] Barton et al., *Env. Eng. Sci.* 31, 421–427 (2014). [6] Slomberg et al., *Environ. Chem.* 13, 804–815 (2016).  
[3] Zhou et al., *Env. Sci. Technol.* 46, 7520–7526 (2012). [7] Mao et al., *Clays Clay Miner.* 58, 691–706 (2010).  
[4] Praetorius et al., *Env. Sci. Technol.* 46, 6705–6713 (2012). [8] Henning et al., CD-ROM "Interakt. Schwebstoffatlas" - Elbe, Saale, Havel (2000).

Acknowledgements

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