

EGU24-8778, updated on 20 May 2024

<https://doi.org/10.5194/egusphere-egu24-8778>

EGU General Assembly 2024

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Nanoparticle Heteroagglomeration with Natural and Synthetic Suspended Particulate Matter

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The assessment of nanoparticle NP transformation in the aquatic environment is essential for comprehending the fate of nanoparticles and conducting accurate risk assessments. Nanoparticles encompass a variety of materials, including manufactured nanomaterials, nanoplastics, and natural colloids. Environmental transformation comprises four main routes: dissolution/leaching, abiotic transformation/degradation, biotic transformation/degradation and (hetero-)agglomeration.

The kinetics of heteroagglomeration play a pivotal role in nanoparticle (NP) transport mechanisms in rivers. The parametrization of heteroagglomeration processes between NPs and suspended particulate matter (SPM) was hampered by the variability of SPM floc composition and conformation/size on spatial and temporal scales. Available analytical methods were either unsuitable or required unrealistic high NP concentrations. The SPM used in heteroagglomeration studies was either unrealistically simple (silica particles, clays) or exceptionally unique (specific natural SPM sample).

After a thorough analysis of mechanisms of floc formation and the relevant building blocks of natural, riverine SPM and the successful and reproducible laboratory synthesis of model SPM flocs, we designed a method to determine the heteroagglomeration attachment efficiency α_{hetero} under environmentally relevant conditions. This allows well controlled laboratory experiments as well as standardization for risk assessment purposes. The heteroagglomeration attachment efficiency (α_{hetero}) constitutes the most suitable parametrization of particle-particle interactions. The presented test matrix combines synthetic model SPM flocs with the model freshwater composition suggested in OECD TG 318, both designed to represent agglomeration-relevant characteristics of natural systems. The test matrix was employed in a newly developed stirred-batch method addressing the shortcomings of existing strategies to determine α_{hetero} . Time-resolved inductively coupled plasma mass spectrometry allowed to work at realistic concentrations of NP (5 ppb) and SPM flocs (20 and 40 ppm).

The approach was evaluated by testing the heteroagglomeration of CeO₂ nanoparticles in four different combinations of SPM and water chemistry.

- Natural flocs in natural water
- Natural flocs in synthetic (TG318) water
- Synthetic flocs in natural water
- Synthetic flocs in synthetic water

The results show the applicability and precision of the invented test system and the synthetic SPM but also reveal some differences between results from natural and synthetic water chemistry which can be explained by the type and quality of the NOM. Calculated transport distances for 50% unassociated NPs reached up to 370 km, what is unexpectedly high.