

## Riding down the river sitting on natural suspended matter? Assessing the fate of nanoparticles

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The increasing use of engineered nanoparticles (ENPs) inevitably entails emissions to surface waters, which raises concerns about their fate. The water column is an inherently heterogeneous system: a range of components from truly dissolved, via macromolecular to particulate matter, the separation of which is only operationally defined. Within this continuum of matter particulate contaminants like engineered nanoparticles (ENPs) can undergo various processes such as stabilisation by natural organic matter (NOM), attachment to each other, or to natural suspended particulate matter (SPM), termed homo- and heteroaggregation respectively. These processes are decisive for advective transport or sedimentation of ENPs and likely impact on their bioavailability.

In natural waters interaction between SPM and ENPs (heteroaggregation) is much more likely than homoaggregation. Still, we are lacking simple experimental protocols capturing the complexity of the aqueous system, when assessing the fate of contaminants in the water column. Designing an experimental protocol that addresses heteroaggregation requires an informed selection of system components reflecting relevant characteristics of natural water systems, such as encountered pH ranges, electrolyte composition & concentrations, and composition and concentration of both NOM and SPM. With regards to the hydrochemistry, this has been effected in course of the development of the recently adopted OECD test guideline No. 318 on ENP dispersion stability, which covers homoaggregation and NOM stabilisation.

In order to also tackle heteroaggregation as the most environmentally relevant process, the challenge of selecting adequate SPM analogues has to be faced. Therefore, we did a thorough literature review on riverine SPM composition. Typically we find complex flock-like structures consisting of mineral and organic fractions colonised by microbes. The dominant minerals were found to be phyllosilicates (clays, chlorite and micas), but also feldspars, quartz, carbonates and oxides (mainly iron); with Illite, kaolinite and smectite being the most abundant clays. The organic carbon fraction in SPM is typically <10 %wt and includes a range of substances from refractory (humic/fulvic-like) to rather labile organic polymers, associated with microbial exopolymeric substances (EPS).

Aiming at covering a diverse spectrum of surface chemistries, we selected illite, quartz and hematite as model mineral SPM components and conducted screening tests to optimise their mixing ratios. Furthermore, screening tests involved various "labile" EPS-like molecules (carbohydrates and protein-like substances) up to 6 %wt organic carbon. Selected mixtures were then investigated regarding their flock formation behaviour in different hydrochemistries, as well as their heteroaggregation behaviour and removal of ENPs from the water column after gravity separation.

Flock formation as well as heteroaggregation behaviour involving ENPs differed depending on the level of complexity of the SPM mix. Positive surface charges introduced by iron oxides, as well as bridging-flocculation effects by EPS-like molecules seem to be crucial for SPM flock formation. Furthermore, complex SPM flocks deviated from simple SPM analogues with regards to their heteroaggregation behaviour and ENP removal, indicating that complexity of SPM cannot be ignored when studying the fate of ENPs in surface water systems.