Heteroaggregation of manufactured nanoparticles with suspended particulate matter analogues as compared to a natural river system

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The fate of manufactured nanoparticles in natural aqueous environments is influenced by dispersion and transport processes as well as aggregation and deposition. These processes depend on both environmental factors and properties intrinsic to the nanoparticles themselves. For example, at environmentally relevant concentrations (μg/L), titanium dioxide nanoparticles (TiO$_2$ NPs) likely have a higher probability of interacting with suspended particulate matter (SPM) present at mg/L or greater concentrations in natural surface waters, rather than with themselves, favoring a heteroaggregation scenario. With both high specific surface area and reactivity, the SPM may act as a TiO$_2$ NP carrier in the water column, strongly affecting their fate and transport via the heteroaggregation process. Herein, mechanistic evaluation of TiO$_2$ NP fate in surface waters was assessed by measuring their heteroaggregation with different types of mineral SPM previously identified in the Rhône River (e.g., quartz, calcite, chlorite, feldspar, montmorillonite). The TiO$_2$ NPs (μg/L) were spiked into synthetic riverine waters containing one of the main SPM analogues, their mixture, or the natural Rhone water SPM. The TiO$_2$ NPs demonstrated a significant affinity for montmorillonite clay colloids as well as the natural SPM, leading to rapid heteroaggregation measured by time-resolved laser diffraction. In addition to determining the NP/SPM heteroaggregation kinetics and attachment efficiencies for the natural and analogue SPM, the influence of natural organic matter (NOM) on TiO$_2$ NP fate and behavior was also assessed. Four common families of NOM analogues (i.e., proteins, polyhydroxy aromatics, polysaccharides, and amino sugars) were added to the SPM-containing synthetic waters to evaluate the role of NOM on the TiO$_2$ NP compartmentalization. Together, these mechanistic data, coupled to a river-scale fate model, will aid in ranking potential TiO$_2$ NP fate scenarios and assessing their risk within natural aqueous environments.