Transformation of Ag-NP in urban waste- and surface waters

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Metallic silver nanoparticles (Ag-NP) are used as antimicrobial agents due to the well-known antimicrobial properties of Ag⁺. To assess potential effects of Ag-NP on the biology of wastewater treatment plants (WWTP) and on downstream surface water ecology, the transformations of Ag-NP along their transport in the sewer system, in the WWTP and in urban surface waters have to be addressed. Important transformation reactions in urban wastewater systems include the sulfidation of Ag-NP which dramatically reduces the toxic response due to the limited solubility of the Ag₂S. However, it has been demonstrated that partially sulfidized Ag-NP can still have adverse effects on ecosystems. Therefore, the kinetics of Ag-NP sulfidation should be considered.

We performed lab-scale, pilot-scale and experiments in sewer systems and WWTP with Ag-NP and AgCl-NP with different sizes (10 nm, 100 nm) and different coatings (citrate, PVP). In laboratory experiments, Ag-NP were reacted with CuS and ZnS representing the most relevant metal sulfides present in urban waste- and surface waters, to simulate conditions in oxic aqueous environments where free sulfides are quickly oxidized. Solution and solid-phase samples were analyzed by a combination of bulk elemental, particlespecific and element-specific methods, including electron microscopy and X-ray absorption spectroscopy. Results indicate partial sulfidation of the Ag-NP and complete sulfidation of AgCl-NP during transport in sewer systems. The sulfidation continues in WWTP, primarily during anaerobic stages. Due to the formation of heteroaggregates with the sludge biomass, transformed Ag-NP are efficiently removed from the wastewater stream and concentrated in the sewage sludge. Kinetic sulfidation experiments show that the sulfidation of Ag-NP is possible under oxic conditions in the presence of metal sulfides. The transformation rates increase with decreasing Ag-NP size and increasing metal sulfide concentrations. Based on these experiments it is concluded that Ag-NP will completely transform into Ag₂S within a period of a few hours – days also in the absence of free sulfide.