## Geochemistry of engineered nanoparticles (CdSe/ZnS quantum dots) in surface waters

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The difficulties when studying the behavior of engineered nanoparticles (ENPs) and the subsequent metal speciation in aquatic ecosystems at relevant environmental concentrations (ppt level) are often related to the high geochemical background in aquatic media (i.e. the occurrence of ENPs constitutive elements at higher concentrations). In this study, the behavior of CdSe/ZnS quantum dots (QDs) in surface waters at concentration relevant of these media was investigated.

The above issues were overcome with the use of spiked QDs (isotopic labelling), separation by centrifugal ultrafiltration (CU) and measurements by HR-ICP-MS, combined with the detection of free and labile metal ions by Scanned Stripping ChronoPotentiometry (SSCP). They firmly provided a thorough comprehension regarding the transformation of QDs in surface waters. The physicochemical conditions of the medium including the presence of an organic matter analogue and a mineral (i.e. fulvic acid, goethite), the manufactured coating of the QDs (here thioglycolic acid, TGA), and the occurence of added Zn in the medium, were considered in the study.

The overall results show that, in the absence of mineral/organic matter, the TGA ligands in solution detached from the QDs surface after dissolution, control the metal ions speciation, especially for Cd. Conversely, in a more representative aquatic ecosystem conditions (i.e. with Zn in the background media together with fulvic acid and goethite, almost no Zn nor Cd dissolution from the QDs is detected. SSCP measurements reveal that the Zn complexes formed with the organic/mineral material in the system are inert, whereas the speciation model calculations indicated that  $Cd^{2+}$  is bound to TGA ligands in solution and organic/inorganic matter – therefore suggesting that, under studied conditions, aquatic organisms will be exposed to a very low concentration of free and labile metal ions coming from the QDs.