# Analysis and modelling of arsenic dynamics in coastal sediments

DUC HUY DANG[1*], ERWAN TESSIER[1], VÉRONIQUE LENOBLE[1], GAËL DURRIEU[1], CHRISTOPHE LE POUPON[1], JEAN-ULRICH MULLOT[2], STÉPHANE MOUNIER[1] AND CÉDRIC GARNIER[1]

[1]Laboratoire PROTEE, Université du Sud Toulon Var, BP20132, 83957 La Garde, France, duc-huy.dang@univ-tln.fr

[2]LASEM-Toulon, Base Navale de Toulon, BP 61, 83800 Toulon, France

Sediments of the Toulon bay (SE, France) are significantly polluted by trace metals, metalloids and organic contaminants, due to historical events (2nd World War...). Contaminants behavior in sediments and transfer to the water column should be investigated to evaluate the risks linked to such pollution. This work focused on As dynamics in the Toulon Bay by studying two major processes: effect of early diagenesis and subsequent diffusive flux.

Interface sediment cores were sampled at contrasted locations and seasons, followed by porewater analysis of physico-chemical parameters (pH, Eh, DOC), diagenesis tracers (Fe, Mn, S, Ca, DIC, …) and As species. The obtained sediment depth profiles showed a significant variation of Eh, $SO_4^{2-}$, DOC and arsenic in porewaters between the campaigns. Such observation could result from different diagenesis activities, linked to inputs of labile organic matter (e.g. plankton bloom). Additionally, in the deepest layer (> 15 cm), As appeared to be significantly correlated ($R^2$ 0.89) to the DOC content, indicating a possible association between As and organic matter.

Based on the measured phyco-chemical parameters and the dissolved species concentration (majors, diagenesis tracers, arsenic,...), PHREEQC was used to calculate As chemical speciation [1]. Then, PROFILE fitting of diagenesis tracers and As depth profiles allowed the evaluation of their diffusive fluxes at the sediment/water column interface [2]. Finally, As depth profiles were successively simulated by PHREEQC, taking account of solid As concentration, dissolved organic matter, carrier solid phases (clays, calcite, iron oxy(hydroxide), iron (mono)sulfide), and the affinity of these components for each As species.

The As dynamics in Toulon coastal sediment appears to be mainly controled by its chemical speciation in porewater, immobilization on carrier phase, and interaction with dissolved organic matter (as AsV but also as AsIII). Association of analysis and modelling tools (thermodynamic calculation, reactive transport fitting and sorption simulation) is suitable to better understand trace elements behavior at the sediment/water interface.

[1] Couture et al. (2010) *Geochim. Cosmochim. Acta* **74**, 1238-1255.
[2] Berg et al. (1998) *Limnol. Oceanogr.* **43**, 1500-1510.

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# Colloidal stability of $TiO_2$ nanoparticles in the presence of phenolic carboxylic compounds

KARIN DANIELSSON*, JENNY PEREZ HOLMBERG, JULIÁN GALLEGO-URREA, ELISABET AHLBERG, ZAREEN ABBAS, MARTIN HASSELLÖV, AND CAROLINE M. JONSSON

University of Gothenburg, Department of Chemistry and Molecular Biology, Gothenburg, Sweden
karin.danielsson@chem.gu.se (* presenting author),
perezj@chem.gu.se, julian.gallego@chem.gu.se,
ela@chem.gu.se, zareen@chem.gu.se,
martin.hassellov@chem.gu.se, caroline.jonsson@chem.gu.se

Nanotechnology is a rapidly growing industry, which leads to an increased amount of synthetic nanoparticles released into the environment. Nanoparticles generally have higher reactivity than larger particles of the same material. As the particle size is decreased to the nanometer size range (1-100nm), the surface chemistry changes and this might influence the surface charging and aggregation behavior. Further, nanoparticles can interact with natural organic material (NOM), such as humic and fulvic acids, which is present in most natural waters. Adsorption of NOM affects the surface speciation and net charge of the nanoparticles and is therefore of great importance for their colloidal stability. This might alter the mobility of nanoparticles in surface waters and in soils, thus determing their bioavailability and toxicity.

The focus of the present study was to investigate the aggregation behavior of nanoparticles in aqueous solution as a function of pH, ionic strength, and in the presence of NOM. Well-characterized $TiO_2$ nanoparticles obtained from hydrolytic synthesis were used as test nanoparticles, and selected phenolic carboxylic compounds were used as model substances to mimic the interactions of nanoparticles with NOM. The selection of organic compounds was based on the possibility of determining the influence of various types, numbers, and positions of functional groups on the surface charging and colloidal stability of the $TiO_2$ nanoparticles. The aggregation and surface charging of the particles were studied by simultaneously monitoring the changes in particle size and zeta potential during the reactions.