

L'uranium en milieu marin, spéciation et bioaccumulation

M. R. Beccia [1], C. Berthomieux [2], C. Den Auwer [1], M. Maloubier [3], D. K. Shuh [4], M. Monfort [5], C. Moulin [5], J. Aupiais [5], B. Reeves [1,5], P. L. Solari [6], R. Stefanelli [1,5]

[1] Université Côte d'Azur, CNRS, ICN, 06108 Nice, France

[2] Commissariat à l'Energie Atomique, DRF, CNRS, BIAM, Cadarache 13108, St Paul lez Durance, France

[3] Université Paris Saclay, IJCLab, 91405 Orsay, France

[4] Lawrence Berkeley National Laboratory, Chemical Sciences Division, Berkeley, CA94720, USA

[5] Commissariat à l'Energie Atomique, DAM/DIF/DASE, 91297 Arpajon, France

[6] Synchrotron SOLEIL, MARS beam line, 91047 Gif sur Yvette, France

christophe.denauwer@univ-cotedazur.fr

The mechanisms of dissemination of radionuclides resulting from an accidental release in the environment, in particular in sea water, is a scientific but above all political and social issue. Hence, the need for managing the risk, for controlling the environmental fate and transport of radionuclides, and for preventing human exposure through direct contact and indirectly through the food chain is essential. Among the different environmental matrices, seawater represents the largest proportion of the hydrosphere, it covers by itself about 71% of the earth's surface and it is the final repository of pollution. It is therefore crucial to understand the transfer and accumulation mechanisms of radionuclides in marine environment and to attempt to perform direct speciation analysis in seawater. But speciation is poorly described in seawater systems but also more generally in the environment because of its complexity and large dilution factors that preclude direct determination. Therefore, it is required to shift from a purely descriptive radioecology approach to a mechanistic approach and this can be performed with the use of speciation tools in model (eco)systems.

Our group has been investigating the biochemical processes of uptake of several actinides among which uranium by marine species (sponge, sea urchin, mussels) in well-controlled marine systems. We have explored the speciation of soluble and insoluble species in seawater leading to potentially bioavailable and bio-transferred species [1]. We have addressed this question in semi natural systems by doping natural seawater with uranium in order to be able to perform direct spectroscopic investigation and thus to decipher the molecular speciation [2]. We have also monitored the uptake mechanisms in vivo [3]. For instance, the sea urchins *Paracentrotus Lividus* or mussle *Mytilus Galloprovincialis* are known as possible sentinel species for heavy metal accumulation and have been selected. After a specific contamination procedure, contaminated gonads of *P. lividus* were analyzed by X ray Absorption Spectroscopy (XAS) and Scanning Transmission X-ray Microscopy (STXM), a technique that couples XAS and microscopy in order to localize the element of interest in a 2-D space and define its speciation at the same time. Such a technique is suitable for element-selective imaging studies with a spatial resolution down to a few tens of nm. EXAFS data analysis at the U LII edge of contaminated gonads further suggested that the metal is coordinated to carboxylate residues of a biomolecule. The toposome protein, the main protein in *P. lividus* was identified as a possible target for U complexation because of its ability to store Ca²⁺ ions with carboxylate chemical functions

In conclusion, obtaining speciation data calls for a methodological compromise. Nevertheless, the input data so gathered is essential and can impact calculation codes developed on a larger scale.

- [1] M. Maloubier, P. L. Solari, P. Moisy, M. Monfort, C. Den Auwer, C. Moulin, Dalton Trans., 2015, 44, 5417-5427
- [2] M. Maloubier, D. K. Shuh, S. G. Minasian, J. I. Pacold, P.-L. Solari, H. Michel, F. R. Oberhaensli, Y. Bottein, M. Monfort, C. Moulin, C. Den Auwer, Env. Sci. Technol. 2016, 50, 10730-10738
- [3] B. Reeves, M. R. Beccia, P. L. Solari, D. E. Smiles, D. K. Shuh, L. Mangialajo, S. Pagnotta, M. Monfort, C. Moulin, C. Den Auwer, Environ Sci. Technol. 2019, 16, 7974-7983