

## Analytical Strategy to characterize Lake Geneva Colloidal Matter and associated Trace Metals

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This ongoing project is motivated by two important phenomena observed in summer 2022: significant blooms of cyanobacteria on Lake Geneva and Rhône River, downstream, and very high intensity with low frequency precipitations. These two phenomena, related to a severe heat wave, were expected to alter the natural cycle of organic matter (OM), and thus must affect the remanence of trace metals (TMs) whatever their forms (OM-complex; natural nanoparticles (NNPs)) in the surface of lakes.<sup>[1]</sup> It is thus important to set-up methodologies enabling the quantitative measurements of TMs preferential association to either OM or NNPs, both acting as TMs nano-carriers from sources to water reservoirs. In this study we present the first step towards the development of a methodology able to determine size-distribution of TMs, in low OM and NNPs containing waters: Lake Geneva, sampled at 2 different depths, 2 different seasons (summer, winter), impacted or not by precipitation events. A centrifugal-ultrafiltration method was first applied to concentrate the colloidal matter. Its impact on the losses of OM components, TMs, and effect on NNPs size distribution was addressed. Asymmetrical-flow fractionation linked to multi-detectors including ICP-MS (AF4-MD-ICP-MS) analysis enable the in-depth size-elemental fingerprint of natural nanocomponents and associated TMs.<sup>[2]</sup> The methodology presented here allowed to gain in sensitivity for TMs size-speciation measurements compared to our previous study performed on Lake Geneva.<sup>[3]</sup> Our results also show that despite discrete changes in OM composition (based on fluorophores types and abundances), the elemental size-profiles of NNPs clearly varied according to depths and seasons but was not impacted by storm scenario, at the location chosen for the sampling. To date, the effects of external conditions, such as changes in OM composition, on toxic TMs behaviour under relevant environmental scenario (other than in polluted systems) is unclear and hinders our understanding of the key risks and issues associated to TMs detection according to their physico-chemical forms. The development and optimization of procedures which allow to maintain size-based speciation of TMs at ultra-low concentrations, open new opportunities to make a link between environmental toxic metals exposure doses, their bioavailability to aquatic organisms and their potential ecotoxicological impacts.

[1] L. E. Anderson, B. F. Trueman, D. W. Dunnington, G. A. Gagnon, *npj Clean Water* **2021**, *4*, 26, DOI: 10.1038/s41545-021-00115-4.

[2] I. A. M. Worms, V. I. Slaveykova, *CHIMIA* **2022**, *76*, 34, DOI: 10.2533/chimia.2022.34.

[3] I. A. M. Worms, Z. A. G. Szigeti, S. Dubascoux, G. Lespes, J. Traber, L. Sigg, V. I. Slaveykova, *Water Research* **2010**, *44*, 340, DOI: 10.1016/j.watres.2009.09.037.