



Iron and copper isotope fractionation during filtration and ultrafiltration of boreal organic-rich waters

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Typical feature of all boreal surface waters is high concentration of dissolved ($< 0.22 \mu\text{m}$) organic matter (DOM) and iron, notably in the form of Fe(III)-OM complexes. Organic and organo-mineral colloids are the most likely carriers of trace metals such as Cu in rivers of the boreal zone. This work addresses colloidal speciation of Cu and Fe using conventional size separation technique, on-site frontal ultrafiltration. Specifically, we aimed to test the possibility of the presence of different pools of metal having specific isotopic signatures in different colloidal fractions using stable isotope measurements. We have chosen Cu for its high affinity to colloidal DOM and Fe for its tendency to form stable organo-mineral colloids of various size.

Samples of natural waters were collected from small rivers, lakes, bogs, groundwater and soil environments in the Northern Karelia (NW Russia) during summer baseflow period. Large volumes (20-40 L) of water were filtered in the field through progressively decreasing pore size filters: 20, 10, 5, 0.8, 0.45, 0.22, 0.1 μm and 100, 10 and 1 kDa (1 kDa $\sim 1 \text{ nm}$) using nylon and regenerated cellulose membranes and frontal ultrafiltration (Millipore, Amicon) devises. The homogeneity of the sample was verified by tracing radiogenic Sr isotopes in each fraction. In all filtrates and ultrafiltrates (permeates), and in selected retentates, stable isotopic composition of Cu and Fe was measured using double focusing high resolution MC-ICP MS (Neptune). We observe rather constant Cu isotopic ratio in all filtrate series and a systematic enrichment of heavy isotope of Fe with decreasing poresize. These preliminary results can be explained by strong complexation of Cu with small-size organic ligands of fulvic nature and its partial association with organo-mineral colloids. Both Fe(III) – OM complexation and Fe(III) oxyhydroxides precipitation can be invoked to explain Fe isotope fractionation.

This work allows, for the first, time, multi-isotopic approach to trace the origin of colloids in surficial waters and it provides new constrains on chemical speciation (and, thus, bioavailability) of metals in colloids of various size. The work is executed at a Russian Federal Property Fund and CNRS support (№№ 08-05-00312_a, 07-05-92212-CNRS_a).