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Study of exchangeable metal on colloidal humic acids and particulate matter by coupling ultrafiltration and isotopic tracers: Application to natural waters

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Abstract

A new method is proposed to characterize the complexation properties of colloids and metal–colloid interactions in natural waters. Based on the association of ultrafiltration with isotopic tracing, this method could quantify the pool of elements in an exchangeable position and also address the kinetic aspects of these exchanges. Basically, it consists of the comparison of isotopic compositions between the bulk sample and a succession of filtrates through time. Exchanges between colloidal humic acids (HA) and metals were first characterized, before applying such manipulations on natural waters. A few elements, representative of a wide range of complexation properties, were chosen: Cu, Zn, Cd, Pb, Sr, Nd, Ni, Th and U. In the case of humic acids, very small (less than 10% of isotopes), but significant isotopic shifts were observed compared to the isotopic equilibrium. It means that more than 90% of the isotopes were exchanged just after addition of isotopic tracers. Experiments on natural organic-rich waters (Mengong and Nyong streams) indicate isotopic composition variations close to those of humic acids. On the contrary, ultrafiltration performed on the total Sanaga River water (including suspended matter "SM") shows an important isotopic shift between the filtered and unfiltered solutions. It means that in the case of the Sanaga River, a significant part of the chemical elements did not exchange.

Keywords: Exchangeable elements; Colloids; Humic acids; Ultrafiltration; Isotopic tracers

1. Introduction

Understanding metal behaviour in aquatic environment, especially in terms of mobility and metal toxicity, implies to identify the speciation of elements. It is indeed essential to quantify their distribution in the different phases of the solution (i.e., dissolved phase, colloids, and particles).

Complexation properties of colloids and metal–colloid interactions in natural waters are currently determined by various techniques, among others, potentiometric and conductimetric titrations (Ephraim et al., 1995; Riggle and Von Wandruszka, 2002). Site density may be determined with ion-exchange resins (Köhler, 1992), whereas the acidic functional groups of colloids are characterised by acid–base titrations and by complexation reactions (Lubal et al., 1998; Fukushima et al., 1995, 1996). HPLC-ICPMS coupling, or more recently, the association of X-ray micro-fluorescence (µSXRF), micro-diffraction (µSXRD) and micro-extended absorption (µEXAFS) techniques were used to determine the structural form of elements in a heterogeneous medium at the micrometer scale (Manceau et al., 2002). Ultrafiltration techniques, which consist of

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passing a solution through very small pore size membranes, are the most convenient techniques to separate colloids. The comparison between metal contents in unfiltered and filtered solutions determines the amounts of metals associated to particles and indirectly gives some indications on element speciation and stability constants between colloids and metals (Viers et al., 1997; Dupré et al., 1999).

However, neither the pool of elements in an exchangeable position nor the kinetics of exchange can be quantified by any of these methods. The purpose of the present work is to associate both ultrafiltration and isotopic tracing techniques, in order to bring new information on the complexation properties of colloids and also suspended matter.

2. Analytical methods

Preliminary specific studies were carried out to check if there is a real isotopic exchange in a simple experimental case with few unknown parameters. The exchanges between colloidal humic acids (HA) and a few metals with a rather wide range of complexation properties (Cu, Zn, Cd, Pb, Sr, Nd, Ni, Th and U) were first examined before application of this technique to the natural waters. The kinetic aspect of these exchanges was also tested with successive ultrafiltrations through time.

The humic acids used in this study, from the "Acros Organics" company, are dehydrated sodium salts. Prior to experiments, the humic acids are cleaned, on one hand, to separate them from the others organic compounds (humins, fulvic acids) and minerals (mainly clays), and on the other hand, to purify them by removing unwanted chemical elements. Separation and purification procedures are from Chorover et al. (1999) and Anđelković et al. (2002), respectively. This method is essentially based on the solubility differences of humic compounds as a function of pH. The various fractions are separated by centrifugation.

After purification, a solution containing metals with a natural isotopic composition is added to the dissolved humic acids, to reach a metal content (Cd, Cu, Zn, Pb, Nd, Ni, Th, U and Sr) of about 10 μg l^{-1}. The mixture is put aside for 10 days until equilibration; then a solution of isotopic tracers or "spikes" is added to the initial solution. This mixture is then ultrafiltered through 5-kDa and 100-kDa pore size membranes at different time steps (≈1 h, 1 day and 1 week) (Fig. 1).

Element contents and isotopic ratios are measured by ICP-MS (Elan 6000) in the non-filtered solution and in each filtrate. Concentrations in major elements are determined by HPLC and by atomic absorption. The pH is measured, and also the dissolved organic carbon (DOC) on a Shimadzu ^{TOC}5000.

The ultrafiltration and isotopic tracing method was applied to a few natural waters from Cameroon: the Mengong stream and the Nyong River, particularly enriched in DOC, and the Sanaga River, mostly rich in carbonates. The analytical procedure was the same as for the humic acids. According to the measured normal isotopic composition and metal concentrations in these natural waters, known amounts of isotopic tracers were added. Ultrafiltrations were performed with a membrane pore size of 1 kDa.

3. Results

The evolution of the isotopic ratios with time (Fig. 2) indicates three important results:

- The isotopic composition in the first filtrate differs, whatever the metal, from that in the non-filtered solution (which represents the isotopic equilibrium)

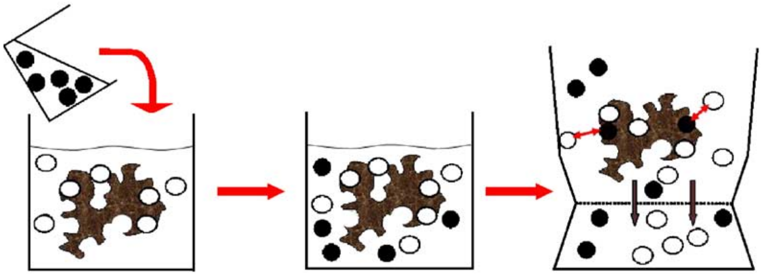

Fig. 1. The isotopic tracing consists of adding to a natural solution a known amount of dissolved elements characterized by isotopic abundances very different from the natural abundances. The natural element (white circles) could be present in an exchangeable (e.g., free ion) form or in a non-exchangeable form (e.g., in the crystal lattice of a mineral). The element added in the solution (black circles) with an abnormal isotopic composition ("spike") is present only in an exchangeable form. Isotopic ratios (black/white) are different before (black/white = 5/7) and after (red/blue = 3/4) the ultrafiltration, showing the isotopic exchange. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)