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Coupling DGT passive samplers and multi-collector ICP-MS: A new tool to measure Pb and Zn isotopes composition in dilute aqueous solutions

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ABSTRACT

Using zinc (Zn) and lead (Pb) isotopes is a powerful tool to track metal pollution in environment. In this study we have developed the coupling between DGT passive samplers and multi-collector ICP-MS to measure Pb and Zn isotopic ratios in dilute aqueous solutions. The benefits of this coupling are multiple: the use of DGT device allows achieving an isotopic composition of natural water integrated over time and to pre-concentrate metals in situ. This development will greatly facilitate the field collection of samples and their preparations in cleanroom prior to their isotopic analyses. To test the capability of DGT samplers a series of experiments was achieved in cleanroom and in experimental pilot simulating a water flow. These tests have shown that there is no fractionation of Pb isotopes due to the use of DGT within the reported precision of MC-ICPMS measurements. For Zn, the diffusion process through a membrane, inherent to the use of DGT device, induces a fractionation between the isotopic composition obtained by the DGT and the natural composition. However, this bias can be easily corrected by using a simple relation independent of the time of exposure and the thickness of diffusion layer. The coupling DGT passive samplers and multi-collector ICP-MS is suitable to determine the Pb and Zn isotopic compositions in natural waters and offers new perspectives to track the anthropic pollutions in the hydrosphere.

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1. Introduction

Metal pollution in natural water is a major environmental, public health and economic issue. The anthropogenic sources of metals present in surface and ground water are multiple. For example, many industries release liquid effluents enriched in metals directly to rivers and, more indirectly, the weathering of cultivated lands and urban areas are also metals providers. Deciphering the origin and fate of these metals within the hydrosphere is an important challenge, as concentrations, although increasing, can be rather low. Recently the improvements in Multiple Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS) instrumentation allowed measurement of small isotope variations for non-traditional elements and isotopic compositions for elements present at low concentration in environmental samples. The isotopic signature of zinc (Zn) largely widespread in different anthropogenic effluents and environmental reservoirs (water, sediment, atmosphere...), and lead (Pb) toxic even at low levels to humans, are commonly used to track anthropogenic pollution in the environment (Aranda et al., 2012; Chen et al., 2008; Elbaz-Poulichet et al., 1986; Monna et al., 1995; Roy and Négrel, 2001; Szykiewicz and Borrok, 2016). Given the very low content in Pb and Zn in natural waters (<10 µg/l), a large volume of

liquid (up to several liters) must be sampled to perform a single isotopic analysis by MC-ICP-MS. The field collection and purification in cleanroom of these samples require difficult and time consuming protocols that could be a possible source of sample contamination. Moreover, in these studies, water collection is a “grab” sampling allowing to capture only an isotopic composition of the water at a specific time, not taking into account fluctuations related to punctual releases caused by anthropogenic activities (industry, waste water plant treatment...). In environmental studies, to achieve a trace elements composition of the natural water integrated over time, passive samplers DGT (Diffusive Gradients in Thin films) are commonly used (Davison and Zhang, 1994; Denney et al., 1999; Dragun et al., 2008). In this device, labile fractions of metals are fixed in a layer of chelex resin after diffusion through a polyacrylamide gel, the mass of metal ions accumulated in the DGT resin allowing to estimate the mean labile soluble concentration in the environment where the DGT was immersed.

The aim of this study is to test the coupling between DGT passive samplers and MC-ICP-MS, in order to 1/ in-situ pre-concentrate and integrate soluble Zn and Pb in water, 2/ measure their isotopic fingerprints allowing to determine their origins. A similar approach has already been used successfully to measure Nd isotopes in fresh and marine water by Thermal Ionization Mass-Spectrometer (TIMS) and S isotopes in labile soil sulfate by MC-ICP-MS (Dahlqvist et al., 2005; Hanousek et al., 2016). To validate the feasibility of this coupling, it

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must be verified that the use of DGT technique does not introduce artificial fractionation that would alter the isotopic composition obtained by the DGT compared to the natural composition. This work appears critical, especially for Zn for which only very small isotopic variations are observed in the environment, for example 0.15‰ in $\delta^{66/64}\text{Zn}$ between upstream/downstream of Loire river waters (France) (Desauty et al., 2014). For Pb, due to the huge isotopic variations existing between the various anthropogenic sources (Monna et al., 1997; Roy, 1996; Roy and Négrel, 2001), compared to Zn, the fractionations linked to the use of the DGT device are less critical. Thus, even if this study concerned the two isotopic systems Pb and Zn, we did more focus particularly on Zn isotopes. The determination of isotopic abundances of soluble Zn by DGT is eased by the fact that Zn having a single oxidation state under most environmental conditions (+2), it is not affected by redox processes. Therefore the isotopic abundances of Zn species in solution will not show dependent on the presence of oxidants. However other possible sources of fractionation that could occur when using DGT devices must be investigated. 1/ First, isotopic fractionation of natural composition may happen on site during the uptake of metals on the DGT unit, particularly during the diffusion of metals through the polyacrylamide gel. Rodushkin et al. (2004) demonstrated by experiments with diffusion cells that this process of diffusion can cause detectable changes in $^{66}\text{Zn}/^{64}\text{Zn}$ isotope ratios in excess of -0.3% , while Malinovsky et al. (2005) showed with tests on DGT in laboratory, that whatever the thickness of the diffusive layer no fractionation of Zn isotopes is detectable within the reported precision of MC-ICP-MS measurements ($2\text{sd} = 0.09\%$). In addition to the diffusive gel of the DGT unit, the thickness of the diffusion zone can be considerably increased due to the presence at the interface between the membrane surface and the bulk water of a water layer, called diffusive boundary layer (DBL), where mass transport is dominated by diffusion and not convection. Previous studies showed that the thickness of the DBL is ~ 0.20 mm in moderate to well-stirred solutions, but substantially thicker in poorly or unstirred solutions (Garmo et al., 2006; Warnken et al., 2006). The isotopic fractionations due to diffusion of metals through the polyacrylamide gel and the DBL were investigated in this study. The absorbent of the DGT unit is a layer of chelex resin known for its high selectivity for divalent ions (Bio-Rad Laboratories, 2000; Figura and McDuffie, 1980; Kingston et al., 1978; Pai et al., 1988; Sturgeon et al., 1980). The oxidation state of Zn being commonly +2, the use of this resin is optimal and should not induce a fractionation. 2/ Secondly, in the laboratory a quantitative elution, especially for Zn, from the chelex resin gel is a prerequisite for an accurate isotopic analysis, an incomplete recovery may result in significant isotopic fractionation (Chen et al., 2009). Malinovsky et al. (2005) demonstrated that a three step elution protocol, using hot ($\sim 50^\circ\text{C}$) concentrated HNO_3 , ensured a recovery of Zn from the resin approaching 100%. We compared, in terms of recovery and isotopic fractionation, this new protocol to the “classical protocol” (1 mL of diluted HNO_3) usually used for DGT extraction (Davison and Zhang, 1994). 3/ Lastly, various contaminations can also impact the metal isotopic signature fixed on the DGT. In this study the cleanliness of a commercial DGT was particularly investigated. In this study, our main goal was to test these different effects (diffusion, pollution...), which can fractionate Zn and Pb isotopic composition fixed on the DGT devices relative to the bulk solution in which they are immersed. For that, a series of experiments was designed and achieved first in the laboratory and then in an experimental pilot to best simulate field sampling and in situ conditions

2. Materials and methods

2.1. Reagents and materials

Anion exchange resin AG MP-1 (100–200 mesh, chloride form, Bio-Rad®) is used for Zn purification. All plastic and Teflon equipment involved in the experiments were acid-cleaned before use. All acids were purified by sub-boiling distillation before use. The water is

distilled “Milli-Q” water with resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$ (Millipore®). For experiments, immersion solutions were prepared by diluting SPEX CertiPrep (10,000 mg/L) Pb and Zn mono-elemental solutions in a cleanroom, and a Merck Millipore (1000 mg/L) Pb solution in the experimental pilot laboratory.

DGT devices were purchased from DGT® Research. Detailed descriptions of the sampler are found at DGT Research’s homepage (<http://www.dgtresearch.com/>). The DGT unit is formed by different layers, from outside to inside: 1/ a membrane filter (cellulose nitrate or polyethersulfone) with pore size of $0.45 \mu\text{m}$ to protect the diffusive gel, 2/ a diffusive gel with different thicknesses available (Δg), and 3/ a layer of chelating resin (chelex-100, 100–200 mesh, Bio-rad®) with a volume typically of 0.15 ml (Fig. 1) (<http://www.dgtresearch.com/>). These different layers are assembled with a plastic holder composed of two parts pressed together: a base part with a piston and a cap with an area window (A) (Fig. 1). Chelex-100 resin has been commonly used, in batch or in column, for about thirty years to concentrate metals from dilute aqueous solutions (Figura and McDuffie, 1980; Kingston et al., 1978; Pai et al., 1988; Sturgeon et al., 1980), and more recently to separate Zn from fresh or marine water prior to isotopic analysis (Bermin et al., 2006; Chen et al., 2009). This resin has a strongly pH-dependent behavior, acting as an anion exchanger at a $\text{pH} < 2$, and as a cation and chelate exchanger at higher pH levels (Bio-Rad Laboratories, 2000). According to the chelex behaviour, DGT can be used in natural water for a pH range of 5–8.3 (Zhang and Davison, 1995). At lower pH, the competition between metals and hydrogen ions for the binding agent prevents an optimal fixation of elements on chelex resin (Pai et al., 1988). Most metals can be measured accurately up to $\text{pH} = 11$, above which there are gel stability problems, however for pH values between 8 and 11, metals do not stay in solution because of adsorption and solubility considerations (Zhang and Davison, 1995) (<http://www.dgtresearch.com/>).

The flux of metal ions through the diffusion gel to the resin is controlled by Fick’s first law of diffusion. The mass (M) of metal ions fixed in the chelex resin of a DGT device immersed in a solution of concentration C during the time t is given by Eq. (1) (Davison and Zhang, 1994).

$$M = \frac{CDAt}{\Delta g} \quad (1)$$

Where D is the temperature-dependent diffusion coefficient of metal in the gel, A is the exposure surface area of the membrane (either 3.14 or 2.54 cm^2), Δg is the thickness of diffusion layer which represents for a sufficiently stirred solution the thickness of the diffusive gel (0.78, 1.18 or 1.96 mm) plus the thickness of the filter membrane (0.14 mm), the diffusive boundary layer being in this case negligibly small (Fig. 1).

2.2. Experiments

For this study two types of experiment were conducted 1/ in BRGM laboratories under cleanroom conditions and 2/ in experimental hall in CIRSEE, laboratory of “Suez Environnement” (Le Pecq, France).

For the first experiment DGT samplers, with a 0.76 mm diffusive gel, were immersed under laboratory conditions in a plastic beaker (5 L) filled with a total volume of 4.5 L mineral water (Volvic) spiked with Zn and Pb mono-elemental solution at 10,000 g/L (SPEX solution) to have a final concentration of 4mg/L. The laboratory temperature was controlled, and remained constant during the experiment (19°C). The solution was continuously stirred during the experiment using a shaking device with speed = 400 rpm. The experiments for Zn and Pb were conducted separately. For Zn, DGT were immersed for 1 day and for Pb the exposure times were 1, 5 and 7 days. Two protocols of metal extraction were used on these DGT (see §2.3).

The second experiment, precisely described in Berho et al. (2015), was conducted in a pilot simulating a water flow designed and built

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