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Using DGT passive samplers and MC-ICPMS to determine Pb and Zn isotopic signature of natural water

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Abstract

Increasing numbers of studies use zinc (Zn) and lead (Pb) isotopic compositions to track anthropogenic pollutions in surface water and groundwater. However, given the low content in Pb and Zn in natural waters, we are often restricted for analysis by MC-ICPMS. One solution is to use passive Diffusive Gradients in Thin films (DGT) samplers for in-situ pre-concentration of these metals. The technique of DGT is a useful tool for in situ measurements of metals concentration in surface waters. In these devices, labile fractions of metals are fixed in a layer of chelex resin after diffusion through a polyacrylamide gel. The goal of this study is to validate the use of DGT samplers to determine the isotopic signature of dissolved metals. We focused our work on Zn and Pb isotopic systems. First, this development was tested under laboratory conditions using mineral water (Volvic) spiked in Zn and Pb. The second experiment was performed in 3 PVC columns simulating piezometer systems with 3 different water flow rates (1, 2 and 4 meters/day). Two protocols were used to extract metals from chelex resin: the “classical” protocol in one step and a more recent protocol in three steeps. For Zn isotopes, a fractionation of 0.06‰ between dissolved and adsorbed metal is measured , likely related to diffusion processes. However, in agreement with systematics of diffusion-driven fractionation in solution, this Zn fractionation is systematic, and can therefore be corrected. Despite a recovery yield of 80% the extraction protocol 1, commonly used, does not induce isotopic fractionation. Moreover, this protocol provides a weak amount of metal pollution compared to protocol 2.
In the case of Pb, no measurable fractionation could be observed within the reported precision of MC-ICPMS measurements. The tests performed in an experimental system simulating a piezometer suggest that DGT samplers are suitable for studies of the Zn and Pb isotopic composition in water with a low water flow rate.

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Keywords: DGT; lead isotopes; zinc isotopes; MC-ICPMS; surface water; groundwater

1. Introduction and objective of this study

Several studies have shown the interest of Zinc (Zn) and lead (Pb) isotopic compositions to track anthropogenic pollutions in surface water and groundwater[1,2]. However, given the low content in Pb and Zn in natural waters, several litres are needed to perform a single isotopic analysis by MC-ICPMS. One solution is to use DGT (Diffusive Gradients in Thin films) passive samplers for in-situ pre-concentration of these metals. In

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these devices, 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 allows the estimation of the mean labile soluble concentration in the environment where the DGT are immerged. Thus, DGT passive samplers are already commonly used to determine the concentration of metals in natural waters[3]. In contrast, few studies using DGT passive samplers to determine isotopic signature of natural water exists, this is related to the fact that many effects can alter the isotopic composition obtained by the DGT compared to the natural composition. First isotopic fractionation of natural composition can occur during the fixation on the resin, the Diffusive Boundary Layer (DBL) effects, more important for poorly or unstirred environments should particularly be controlled[4]. Secondly, a quantitative elution, especially for Zinc, from the resin gel is a prerequisite for its meaningful isotopic analysis as an incomplete recovery may result in isotopic fractionation. Moreover various contaminations can also impact the isotopic metal signature fixed on DGT. The aim of this study was to investigate these effects to use DGT passive samplers for the determination of Pb and Zn isotopic signature in natural waters.

2. Methodology

All plastic equipment involved in the experiments was acid-cleaned before use. All acids used were purified by sub-boiling distillation. DGT were thoroughly rinsed by MQ water.

Two types of experiment were conducted:

(1) DGT samplers, with a 0.76 mm polyacrylamide gel, were immerged under laboratory conditions in 4.5L of mineral water (Volvic) spiked with Zn and Pb monoelementary solution at 1g/L. The solution was continuously stirred during the experiment using a shaking device. For Zn, DGT were immerged during 1 day and for Pb the exposure times were 1, 5 and 7 days.

(2) The second experiment was performed in experimental hall of “Suez Environnement”. DGT were immerged in 3 PVC columns (height= 3.60 meters, internal diameter=0.4 meters) simulating piezometer systems with 3 different rates of water flow (1, 2 and 4 meters/day). The system was supplied by groundwater, Zn was coming only from groundwater ($\approx$5µg/L), Pb was a mixing between groundwater and added spike with a content of about 0.7µg/L. This experiment allowed to simulate a low water flow rate environment and to verify the impact of the DLB on the isotopic composition of metals immobilized in DGT. For Zn, only DGT with a 0.76 mm polyacrylamide gel were used and immerged during 21 days. For Pb, DGT with 3 thicknesses of the hydrogel 0.78, 1.18, and 1.96 mm were immerged and the times of exposure were 6, 13 and 21 days.

After the immersion, the DGT units were disassembled and the resin gels were transferred into tubes in cleanroom. Two protocols were used to extract metals from chelex resin: (1) The "classical" protocol of elution described by Zhang et al.[3] is the addition of 1mL of 1N HNO_3 to the resine overnight. For this protocol, the recovery is about 80%[5]. As an incomplete recovery may result in isotopic fractionation, Malinovsky et al.[5] developed a new extraction protocol with a yield close to 100%. (2) This second protocol is processed in three successive steps: first 5ml of 3N HNO_3 are added to the resin and equilibrated overnight, then the resin is rinsed with 5ml of Milli-Q water. Finally, 5ml of concentrated HNO_3 ($\sim$15N) are added and the tubes containing this extractant are placed in a water bath on a hot plate ($\sim$50 °C) and equilibrated with the resin for 3 hours. For the two protocols, blanks were proceeded to verify the metal contaminations introduced by the extraction protocols. The various fractions were evaporated in teflon beakers to dryness in cleanroom and analyzed by Q-ICPMS to measure the recovery yields and the blanks of extraction.

Prior to isotopic analyses, an anion-exchange purification was necessary to separate Zn from concomitant matrix elements, that include mostly Na, K, Ca and traces of Ni and Ti. The protocol used was adapted from Shiel[6]. Recovery of Zn from this protocol was checked by analyzing one aliquot before and after the chemical separation by Q-ICPMS. For all tests, the recoveries were close to 100%.

Zn and Pb isotopic compositions were measured using a Neptune MC-ICPMS (Thermo Fisher Scientific) at the BRGM. According to the contents, Pb isotopes were measured using two methods either with SEM-electron multiplier and standard-sample bracketing method vs. NIST SRM981, or with Faraday Cups with standard-sample bracketing and Tl-doping correction method. Zn isotopes were measured after addition of Cu for external normalization and with standard-sample bracketing method vs. JMC Lyon.

3. Results and discussion

3.1 Metal contaminations introduced by the extraction protocol

The analyses of blanks showed that the DGT rinsing by MQ water before use allowed decreasing significantly metal contaminations. The blanks were higher for protocol 2 compared to protocol 1. This is related to the step with “hot” and concentrated HNO_3, which probably can alter the resin and/or tube with the release of metals. Compared to Pb, Zn blanks were very variable and higher. For example, Zn blanks (protocol 1) represented between 0.5-2% of amount accumulated by DGT immerged during 10 days in river, while Pb blanks represented only 0.05%. The blanks for Zn and Pb were negligible compared to the amounts of Zn and Pb used in this study. However for future studies, especially in order to analyze water with very low levels of metals, it will be necessary to develop a new protocol of DGT washing, limiting the amount of Zn provided by extraction protocol.

3.2 DGT and Zn isotopes

The recoveries for the two extraction protocols were tested in cleanroom. For protocol 1, the yield was about 80%. This value is consistent with the results given by previous studies[5]. For the second, the use of “hot” concentrated HNO_3 did not increase significantly the elution efficiency (0.2%). This is the step of rinse by Milli-Q water that allowed ensuring recovery of Zn from the resin approaching 100%. For this protocol 2, we also measured yields higher than 100% (for example 111% for test 2). These high values for yields were probably related to metal contamination that occurs during the protocol of extraction.

For tests performed in cleanroom and in system simulating piezometers, there was no difference in isotopic signature between the two extraction protocols. Thus despite a recovery of 80%, the extraction protocol 1 commonly used, did not induce isotopic fractionation. However for two experiments, Zn extracted from DGT was depleted in heavy isotopes compared to the immersion solution (-0.06 ‰ for $\delta^{66}Zn/^{64}Zn$). This difference can be explained by the diffusion process, heavy isotopes diffuse more slowly compared to lighter isotopes through the hydrogel. A simple relation between the isotopic fractionation due to diffusion process and mass ratio is established by Richter[7]. With this relation it is possible to correct the isotopic ratios for DGT. As shown by Fig. 1., the corrected values for DGT are similar to the isotopic composition of the immersion solution.

$$\delta^{\frac{m1}{m2}}Zn_{DGT} - \delta^{\frac{m1}{m2}}Zn_{sol} = -10^3 \, ln\left[\frac{m1}{m2}\right] \times \beta \qquad (1)$$

For the tests performed in system simulating piezometer, the Zn isotopic compositions were the same in the three columns with different flows and the values corrected by (1) were similar to the isotopic composition of groundwater supplying the system. The results suggest that DGT samplers are suitable for studies of the Zn isotopic composition in water even with a low water flow rate (1 meter/day).

3.3 DGT and Pb isotopes

For tests performed in cleanroom, the isotopic ratios for DGT with different times of exposure 1, 5 and 7 days were similar to the bulk isotopic composition of the solution. No measurable fractionation could be observed within the reported precision of MC-ICPMS measurements (Fig. 1.).

For each system simulating piezometer, $^{206}Pb/^{204}Pb$ ratios were similar at day= 6, 13 and 21 for the 3 thicknesses of the DGT hydrogel. After 21 days of immersion, $^{206}Pb/^{204}Pb$ ratios for all DGT were similar to the isotopic ratio of the immersion solution, even for the lowest water flow column (1 meter/day). These results suggest that there is no influence of the "diffusive boundary Layer” effect on the Pb isotopic compositions fixed in DGT.

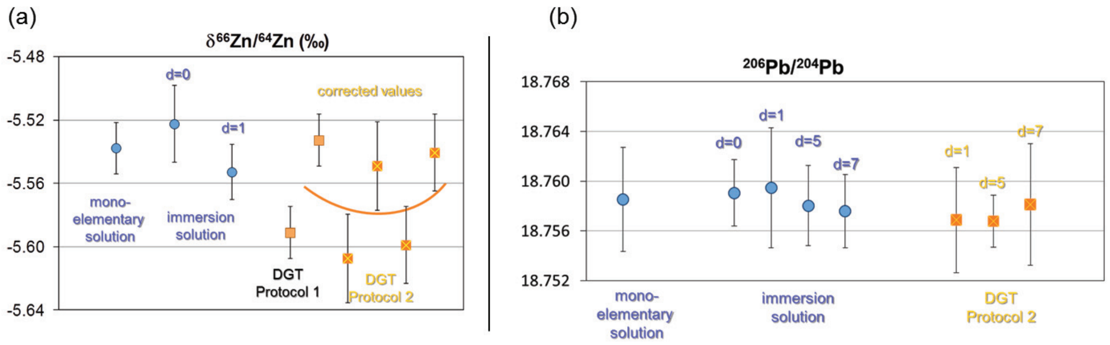

Fig. 1. Results for tests performed in cleanroom, DGT were immerged in 4.5L of mineral water (Volvic) spiked with Zn and Pb monoelementary solution: (a) $\delta^{66}Zn/^{64}Zn$ for immersion solution at day=0 and 1 and Zn monoelementary solution (blue dots), DGT immerged during 1 day extracted with protocol 1 and 2 (orange squares). The corrected values are calculated with the equation (1); (b) $^{206}Pb/^{204}Pb$ ratios for immersion solution at day=0, 1, 5 and 7, and Pb monoelementary solution (blue dots), DGT immerged during 1, 5 and 7 days and extracted with protocol 2 (orange squares).

4. Conclusion

Zinc fixed in DGT resin has an isotopic composition fractionated compared to the immersion media, however this fractionation can be easily corrected by using the relation (1). Despite a recovery of 80% the extraction protocol 1, commonly used, does not induce isotopic fractionation. Moreover, this protocol provides a weak amount of metal pollution compared to protocol 2. For Lead, there is no significant isotopic fractionation between dissolved and adsorbed metal, the 2 extraction protocols can be used with a preference for protocol 1 less polluting. The tests performed in an experimental system simulating a piezometer system suggest that DGT samplers are suitable for studies on the Zn and Pb isotopic composition in groundwater with a low flow rate.

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