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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.

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; Szyrkiewicz 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 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) (Desaulty 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 (~50 °C) concentrated HNO₃, 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” (1mL of diluted HNO₃) 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 MΩ.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 μm 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 (Figure 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) (Figure 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 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 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 equation (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 cm²), 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 (Figure 1).

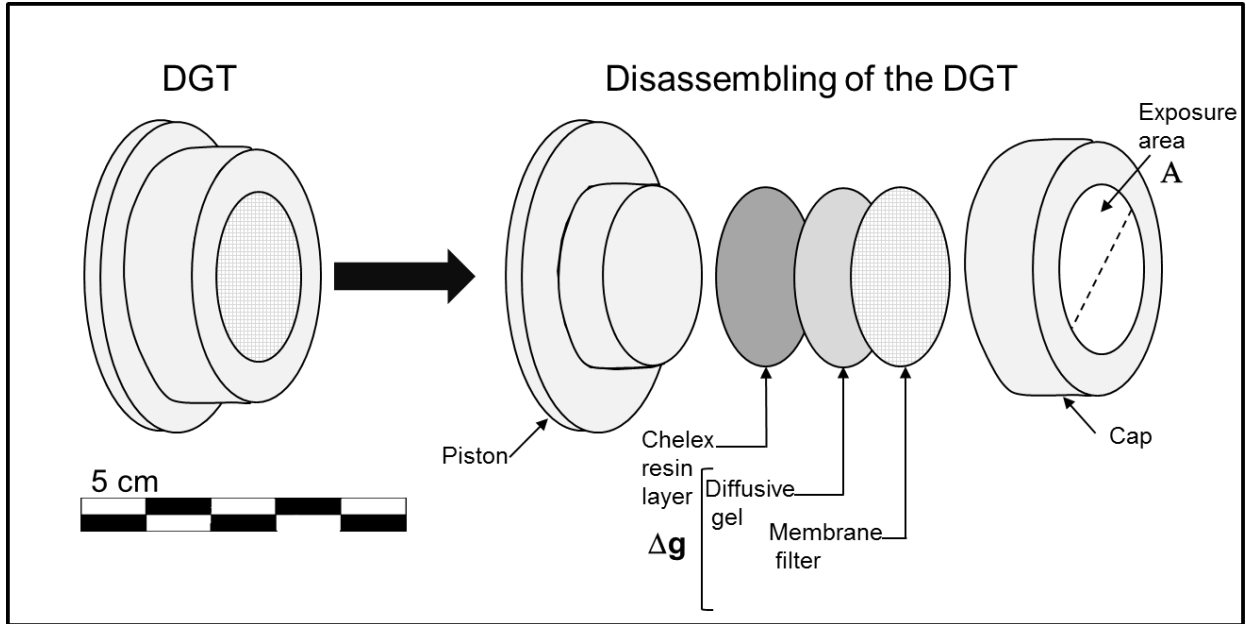


Figure 1: Schematic representation of DGT unit assembled and disassembled, A is the exposure surface area of the membrane, Δg is the thickness of the diffusion layer (diffusive gel + filter membrane).

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 monoelementary 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 by “Suez Environnement” (Figure 2). DGT were immersed in 3 vertical clear PVC columns (height= 3.50 meters, internal diameter=0.4 meters) supplied continuously by water coming from Pecq-Croissy groundwater level, located within the Seine river basin to the west and downstream of Paris (France). Before its introduction into the columns the raw groundwater was filtered (< 5 μ m) and disinfected by UV lamp to avoid the

development of biofilm. The columns were also covered by black plastic sheet to prevent photodegradation. Water was pumped upwards through each column with 3 different rates of water flow 1, 2 and 4 meters/day (corresponding to 87, 174 and 349 mL/min) for respectively column 3, 2 and 1. These values are close to flow rates in alluvial groundwater and 70×10^6 times lower compared to river discharges (Grosbois et al., 2000). DGT holders were fixed on plastic chains and were located in the middle of the column, where the flow rate was more stable. Our experiments and those of Berho et al. (2015) took place together, but we used our own DGT devices. The experiments for Zn and Pb were carried out simultaneously. In this pilot, Zn was derived only from groundwater ($\approx 5 \mu\text{g/L}$), Pb was a mixture of groundwater and an added spike (Merck solution) to have a total Pb content of about $0.7 \mu\text{g/L}$. This concentration in Pb of the immersion solution ($0.7 \mu\text{g/L}$) was allowing to have an adequate mass of Pb fixed in the DGT device to determine its isotopic signature, after just few days of deployment.

This addition was done by injection of spike solution, diluted with groundwater at $25 \mu\text{g/L}$. Sampling points, located on the middle of the columns close to DGT holders allowed collect water and to measure its elemental composition by Quadrupole-ICPMS, several times per week. Sensors installed at the columns input allow controlling several parameters like T ($^{\circ}\text{C}$), flow rate and pH. The thickness of the DBL for each flow rate has been experimentally determined during the study previously conducted by Berho et al. (2015). Immersion solutions supplying each column were analyzed by MC-ICP-MS at the beginning (day=0) for Zn and Pb, and at the end of the experiment (day=21) for Pb. Concerning Pb isotopic analyses, DGT with 3 thicknesses of hydrogel 0.78, 1.18, and 1.96 mm placed in the same DGT holder were immersed during 6, 13 and 21 days in each column and extracted by “classical” protocol (see §2.3). For Zn, only DGT with a 0.76 mm polyacrylamide gel were immersed in other DGT holders during 21 days in the columns 1, 2 and 3. Metals fixed on these DGT were eluted using two different protocols of extraction (see §2.3), and Pb isotopic signatures were also determined. This experiment, simulating a water flow environment with well-controlled parameters (flow rate, elemental and isotopic composition, thickness of the DBL...), allowed testing the feasibility of the DGT/MC-ICP-MS coupling under conditions that are close to real field conditions. The low water flow rate, especially for column 3 (1 m/day), enabled us to verify the impact of the DBL on the isotopic composition of metals immobilized in each DGT.

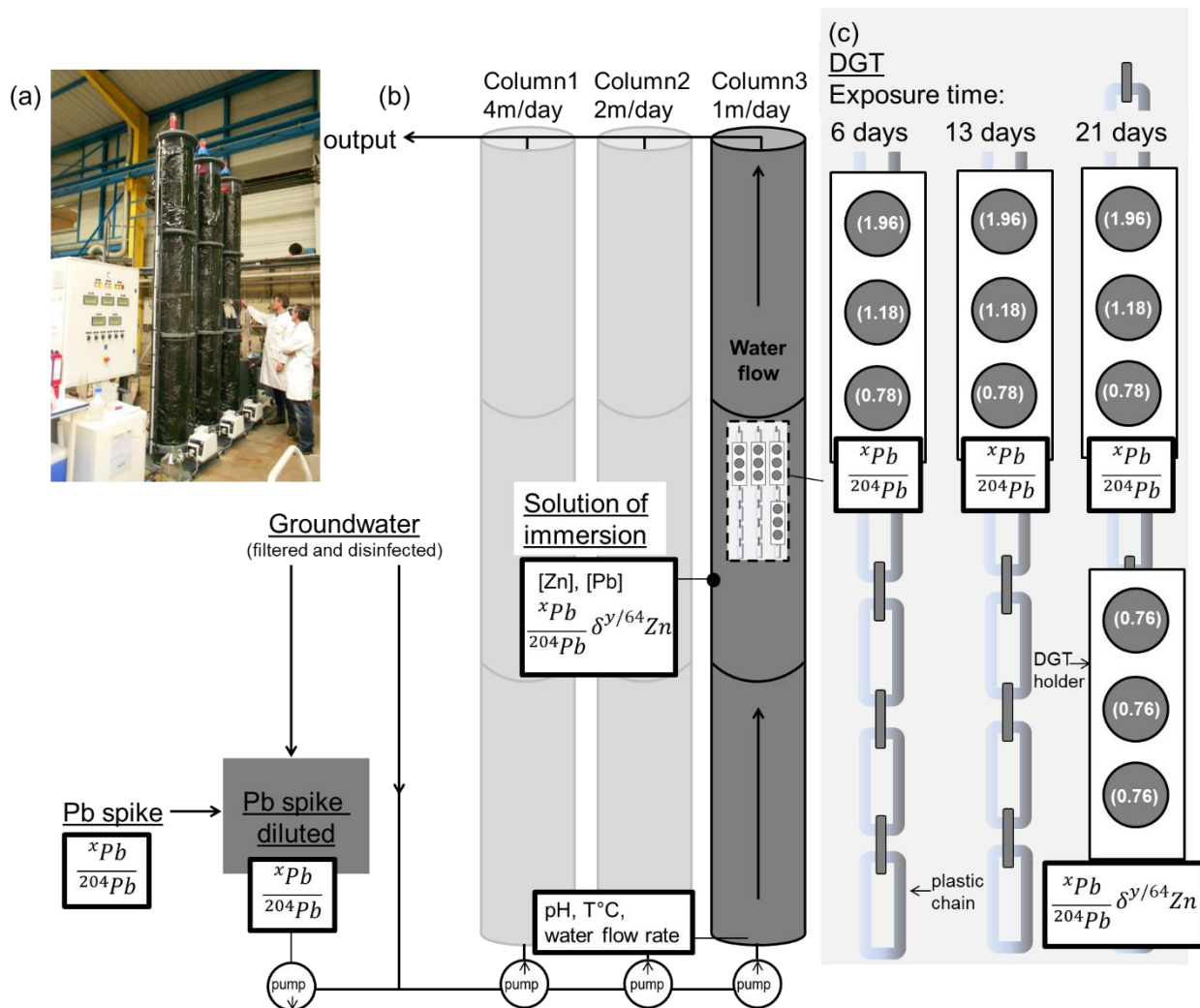


Figure 2: (a) Picture of the experimental pilot simulating a water flow designed and built by “Suez Environnement” (Berho et al., 2015). (b) Schematic representation of the experimental pilot. (c) Zoom on the DGT immersed in column 3. The thickness of DGT diffusive gel is indicated in brackets. Parameters measured are represented in black boxes (with $x = 206, 207, 208$ and $y = 66, 67, 68$).

2.3 Elution of Zn and Pb from chelex resin

After the immersion, the DGT units were disassembled (Figure 1) and the resin gels were transferred into polypropylene tubes in the cleanroom. Several protocols were used by previous studies to extract metals from chelex resin. The “classical” protocol of elution described by Davison and Zhang (1994) consists of addition of 1mL of diluted HNO_3 to the resin, followed by the shaking overnight of the acid-Chelex mixture. For this protocol, in the first studies, 1mL of 2N HNO_3 was added (Zhang and Davison, 1995; Zhang et al., 1995), but now 1mL of 1N HNO_3 is routinely used (Davison et al., 2007; Dragun et al., 2008; Warnken et al., 2006). For this “classical” protocol, regardless of the acid normality (1 or 2 N HNO_3), the recovery is about 80 % for Zn with a standard deviation of 2–6 % (Alfaro-De laTorre et al., 2000; Zhang et al., 1995). Garmo et al. (2003)

demonstrated that the use of concentrated HNO₃ followed by a step of “Milli-Q” water rinse increased the elution efficiency to 97–99 % for most metals including Zn. From these results, Malinovsky et al. (2005) developed a new extraction protocol with concentrated HNO₃ and a yield close to 100 %. Consequently this second protocol is processed in three successive steps: first 5 ml of 3 N HNO₃ are added to the resin and equilibrated overnight, then the resin is rinsed with 5 ml of “Milli-Q” water. Finally, 5 ml of concentrated HNO₃ (~15 N) are added and the tubes containing this extractant are placed in a water bath on a hot plate (~50 °C) and equilibrated with the resin for 3 hours. In this study, we followed two different protocols: 1/ the “classical” protocol with 1 N HNO₃ and 2/ the one developed by Malinovsky et al. (2005) . For Zn, the recovery yields for each protocol were determined from tests in cleanroom. Extractions without sample were also performed to verify the metal contaminations (“blanks”) introduced by the two protocols.

2.4 Elemental and isotopic analyses

The metals contents in various immersion solutions, in procedural “blanks” and in different fractions issued from recovery yield tests were determined. Elemental analyses were performed by X series II ICP-MS (Quadrupole - Inductively Coupled Plasma -Mass Spectrometry) (Thermo Fisher Scientific) at the BRGM laboratory.

Prior to isotopic analyses, an anion-exchange purification was necessary to separate Zn from coexisting matrix elements, that include mostly Na, K, Ca and traces of Ba, Cu, Ni and Ti. The protocol used was adapted from Borrok et al. (2007). After evaporation to dryness, the sample was taken up in a mixture of 10 M HCl and 0.001% H₂O₂ and passed through an anion-exchange column loaded with macroporous resin AG MP-1. The unwanted matrix elements were eluted successively in 10 M HCl + 0.001% H₂O₂, 5 M HCl +0.001% H₂O₂ and 1 M HCl. Zn was eluted next in 0.5 M HNO₃. For DGT, one passing on column was sufficient to purify Zn, while for immersion solution a two-step chemical separation procedure was needed to eliminate completely the other elements. For this chemical purification, the procedural “blank” was <5ng. Recovery of Zn from this protocol was checked by analyzing one aliquot before and after the chemical separation by Q-ICPMS. For all samples, the recoveries were close to 100%. For Pb, the method is less time-consuming and costly, indeed the isotopic ratios of Pb were analyzed without protocol of purification as described by Cocherie and Robert (2007). The Zn and Pb isotopic compositions were measured by using a Neptune MC-ICP-MS (Thermo Fisher Scientific) at the BRGM laboratory. The Zn data were externally normalized to Cu using an exponential mass-fractionation law, instrumental drift was corrected by standard bracketing using JMC 3-0749 L solution called “JMC Lyon” (Maréchal et al., 1999). The Zn isotopic compositions were measured at a Zn concentration of 1 mg/L and a Zn/Cu elemental ratio of 2.0 (to give close ion beam intensities for ⁶³Cu and ⁶⁴Zn). The Zn isotopic composition of each sample is expressed in δ-notation (parts per 1,000) relative to the mean value of the bracketing Zn standard (JMC Lyon):

$$\delta^{x/64}\text{Zn} = \left[\frac{({}^x\text{Zn}/{}^{64}\text{Zn})_{\text{sample}}}{({}^x\text{Zn}/{}^{64}\text{Zn})_{\text{JMC Lyon}}} - 1 \right] \times 1000 \quad \text{with } x = 66, 67 \text{ and } 68$$

The external reproducibility (2σ) reported in the various figures and tables was calculated by measuring the same sample multiple times over many analytical sessions, the precision (external reproducibility) on the Zn isotopic composition is typically ±0.03 ‰. The samples analyzed in this study are represented in three-isotope plot (Supplementary Figure 1), data points lie upon the expected mass fractionation line, attesting the quality of the MC-ICP-MS measurement and the absence of isobaric interferences during analysis.

The Pb isotopic compositions were measured by MC-ICP-MS, the instrument drift was corrected by standard bracketing using NIST SRM981. Two methods were used according to the Pb quantity in the sample: 1/ with secondary electron multiplier (SEM) in dynamic mode at a Pb concentration of 0.1 µg/L, and 2/ with Faraday Cups and Tl-doping correction method at a Pb contents between 10-50 µg/L (Cocherie and Robert, 2007). The precision on isotopic ratios is typically ±0.1 for the first method and between ±0.005 and ±0.02 according to the Pb contents for the second method.

3. Results and discussion

3.1 Metal contaminations introduced by the use of the DGT device

For the “classical” elution protocol used to extract Zn and Pb from Chelex, procedural “blanks” were determined for DGT rinsed and non-rinsed by “Milli-Q” water. The analyses of these “blanks” showed that the pre-rinse significantly decreases metal contaminations (Figure 3, Figure 4). For protocol 2, we obtained procedural “blanks” for Zn between 16 and 76 ng close to those analyzed by Malinovsky et al. (2005) which are between 20 to 80 ng and more elevated compared to Garmo et al. (2003) which used “cold” concentrated HNO₃ (6.3 ± 2.2ng). For both elements, contaminations introduced by protocol 2 are 2 to 3 times higher compared to protocol 1. This is probably related to the step with “hot” and concentrated HNO₃ that could alter hazardously the resin gel and/or tube involving release of metals. Garmo et al. (2003) showed that the complete acid digestion of the resin gel induced a considerably higher “blank” level compared to the elution with only “cold” nitric acid. As shown by previous studies, compared to Pb, Zn “blanks” were very variable and higher (Berho et al., 2015; Uher et al., 2013). For example, Zn procedural “blanks” represented between 1-18 % of the total amount accumulated by one DGT ($\Delta g=0.14+0.78\text{mm}$, $A=3.14\text{ cm}^2$) immersed for 10 days in river water with typical concentrations of Zn and Pb (3 µg/l and 0.3 µg/l respectively), while Pb “blanks” represented only 0.1 % to 1 % of the mass fixed on this DGT. After the DGT pre-rinse in “Milli-Q” water, the total “blanks” for Zn ($\approx 25\text{ ng}$) and Pb ($\approx 0.3\text{ ng}$) were negligible as compared to the amounts of Zn and Pb used in this study. However for future studies, especially to analyze water with very low levels of metals, it will be necessary to develop a new protocol of DGT cleaning, limiting the amount of Zn provided by the extraction protocol. Concerning the Zn chemical purification, that is necessary prior to MC-ICP-MS analyzes, the total “blank” is negligible relative to the amounts of Zn used in this study and the masses fixed in environmental conditions (Figure 3).

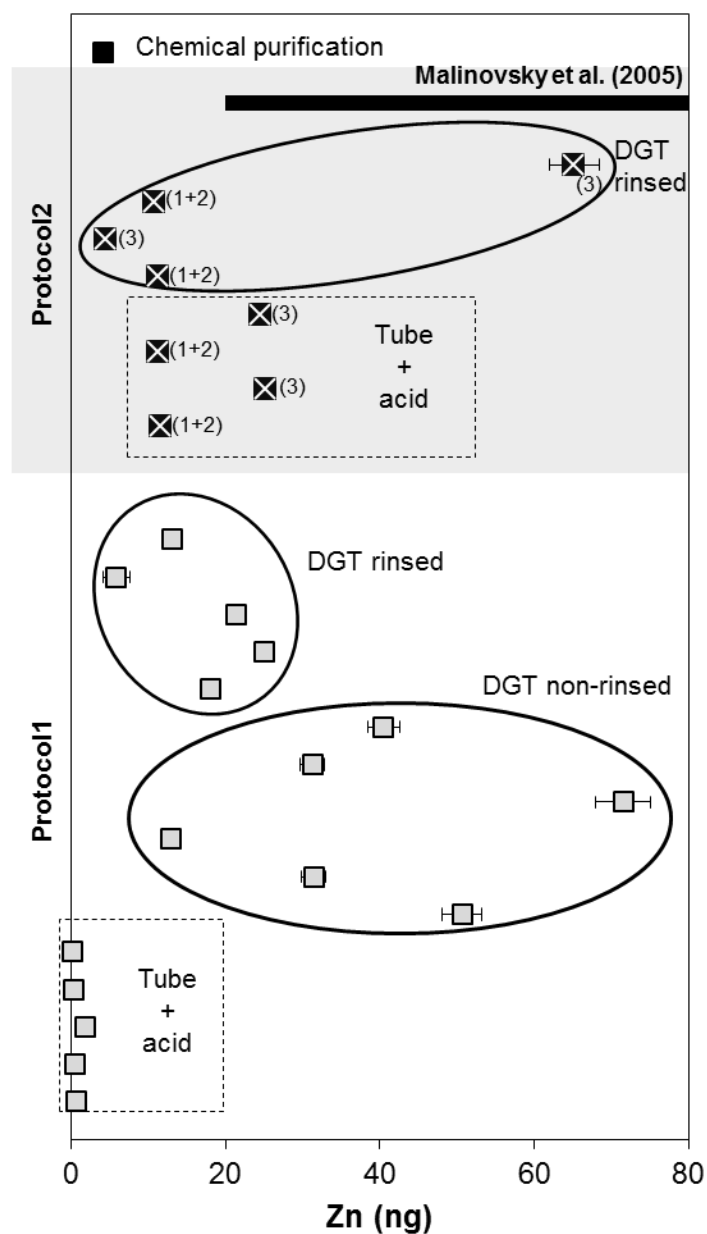


Figure 3: Zn contaminations introduced by the use of DGT device: elution from chelex resin (“classical” protocol 1 and “new” protocol 2 developed by Malinovsky et al. (2005)) and chemical purification on column with anion exchange resin (black square). For protocol 1 (grey square) and protocol 2 (crossed square) in addition to total procedural “blanks”, the Zn contaminations coming from acid and tube are determined. For protocol 1, “blanks” for non-rinsed DGT are also measured. For protocol 2 the steps of elution are indicated in brackets. The range of total “blank” obtained by Malinovsky et al. (2005) for protocol 2 is also shown (black line).

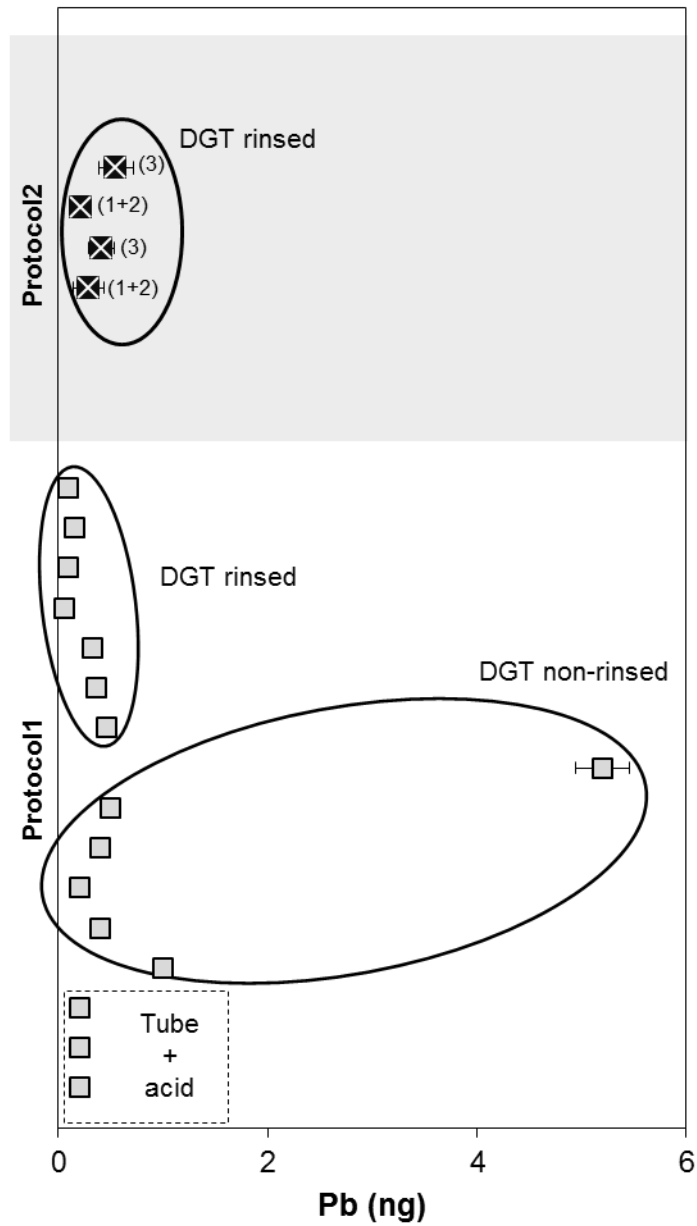


Figure 4: Pb contaminations introduced by elution from chelex resin (“classical” protocol 1 and “new” protocol 2 developed by Malinovsky et al. (2005)). For protocol 1 (grey square) in addition to total procedural “blanks”, the Pb contaminations coming from acid and tube are determined, “blanks” for non-rinsed DGT are also measured. For protocol 2 (crossed square) the steps of elution are indicated in brackets.

3.2 DGT and Zn isotopes

To test the feasibility of utilizing DGT samplers to determine the isotopic abundance of soluble Zn, a first step was to conduct tests under laboratory conditions. DGT with a 0.76 mm diffusive gel were immersed in mineral water (Volvic) spiked with a mono-elementary solution of Zn for 1 day. For these experiments, the value of the Zn content in the immersion solution calculated from the mass of metal ions fixed in the chelex resin using equation (1) is accurate. Thus, as shown by previous studies, for solution stirring with speed of 400 rpm the DBL is negligibly small compared to diffusive gel (Uher et al., 2013).

Quantitative elution of Zn from the chelex resin gel is a prerequisite for its meaningful isotopic analysis as an incomplete recovery may result in isotopic fractionation. So, the recoveries for the two extraction protocols were tested (Figure 5). For protocol 1, the yield was about 80%. This value is consistent with the results given by previous studies (Alfaro-De laTorre et al., 2000; Zhang et al., 1995). For the second protocol, the elution with 3N HNO₃ was able to extract about 95% of total Zn, in agreement with the results obtained by Malinovsky et al. (2005). However the use of “hot” concentrated HNO₃ did not increase significantly the elution efficiency (0.2%). This is the second step of rinse by “Milli-Q” water that ensured a Zn recovery from the resin approaching 100%. As shown previously, the binding of metals on chelex resin is strongly pH-dependent. According to Pai et al. (1988), at pH=1.5 the distribution coefficient D (metal mass on the wet resin divided by that in solution, multiplied by 100) is close to zero, and Zn is not retained by the resin. In the chemical protocols used to separate Zn from natural water prior to isotopic analyses, the eluent used to extract metal from chelex resin is 0.12-2.5 N HNO₃ (pH≈0) (Bermin et al., 2006; Chen et al., 2009). The use of concentrated HNO₃ is not recommended, especially because it can damage the resin gel and introduce metal contamination. So for protocol 2 (test2), the Zn recovery yield higher than 100% is probably due to contamination. However one may wonder why the yield is better for the protocol described in Malinovsky et al. (2005) compared to the “classical” protocol. According to ion exchange chromatography theory, the necessary volume ($V_{\text{necessary}}$) for which the maximum mass of the element is eluted is given by: $V_{\text{necessary}} = V_0 \times (D+1)$, where V_0 is the interstitial volume (about 35% of the resin volume), and D is the distribution coefficient (Marechal, 1998). For DGT, from pH=1.5, $V_{\text{necessary}}$ is close to V_0 , i.e. in theory 53μl (35% of chelex resin volume, 0.15 ml), the volume of 1mL classically used is thus normally sufficient. However experiments undergone by Chen et al. (2009) have shown that, due to the extreme pH sensitivity of Chelex resin and the probable influence of ionic strength on the distribution coefficient or tailing buffering effect, more important volume of elution was necessary compared to the theoretical value to elute Zn from the chelex resin. The comparison between the quantities of Zn extracted by the first “classical” protocol (1 mL of 2N HNO₃) and the first step of the Malinovsky et al. (2005) protocol (5 mL of 3N HNO₃) shows that for close pH solutions a most important volume of elution allows to increase the Zn recovery yield (80% vs. 95%). For the step of rinse in “Milli-Q” water, few residual drops of 3N HNO₃ are sufficient to lower the pH < 1.5 and continue the metal extraction (5% of the total mass of metal fixed in the resin). Consequently a largest elution volume at pH < 1.5 would allow a better recovery yield. Given these results, for the “classical” protocol a last step, consisting into loading three times 2ml of “Milli-Q” water on the resin, has been added. This “classical” protocol upgraded with this last step may be employed for extracting efficiently metals from DGT. For these same tests in the laboratory, the Zn isotopic compositions for mono-elementary solution added to mineral water, immersion solution at day=0 and day=1 and DGT extracted by protocol 1 and protocol 2 are shown in Figure 6. There is no difference in isotopic signature between the two extraction protocols. However, Zn extracted from DGT was

systematically depleted in heavy isotopes compared to the spike and the immersion solution (about -0.06 ‰ for $\delta^{66}\text{Zn}/^{64}\text{Zn}$).

This very weak fractionation was not observed by Malinovsky et al. (2005) probably due to the fact that in this previous study the reported uncertainty of MC-ICP-MS measurements was more important (2SD= 0.09‰) compared to the fractionation induced by the DGT (0.06‰). Even if this fractionation is very low, given the small isotope variations observed in the environment (Chen et al., 2008; Desaulty et al., 2014), it has to be corrected. This difference between DGT and solution cannot be attributed to an incomplete recovery from the chelex resin or a contamination linked to the DGT use because: 1) a yield of 100% was obtained specifically for protocol 2 and 2) the mean “blank” level that could be attributed to the use of DGT represented less than 0.05% compared to the Zn mass fixed on DGT in these experiments (60µg). As shown previously by Rodushkin et al. (2004), diffusion of metals through a diffusion cell can induce changes in isotopic compositions. This isotopic fractionation is due to the fact that two isotopes of the same element will not diffuse with the same rate. According to Bourg and Sposito (2007) and Richter et al. (2006), the ratio of self-diffusion coefficients of solute isotopes (D_1/D_2) is an inverse power-law function of their molar masses ratio, m_1 and m_2 .

$$\frac{D_1}{D_2} = \left(\frac{m_2}{m_1}\right)^\beta \quad (2)$$

where β is a dimensionless exponent, independent of diffusion coefficients and thickness of the diffusion layer.

From equation (1) and (2), we further obtain the isotopic ratio $\left\{\frac{M_1}{M_2}\right\}_{DGT}$ of two isotopes M_1 and M_2 of molar masses m_1 and m_2 diffusing through the polyacrylamide gel and fixed in DGT as:

$$\left\{\frac{M_1}{M_2}\right\}_{DGT} = \left(\frac{m_2}{m_1}\right)^\beta \left\{\frac{M_1}{M_2}\right\}_{Solution} \quad (3)$$

Equation (3) shows that the isotopic ratio of an element fixed on the DGT after diffusion will be independent of the time of exposure and of the thickness of the diffusive gel. From equation (3), it is possible to determine a simple relation between the isotopic composition of solution and DGT which gives for Zn:

$$\delta^{x/64}\text{Zn}_{DGT} - \delta^{x/64}\text{Zn}_{solution} = -1000 \ln \left[\frac{m(^x\text{Zn})}{m(^{64}\text{Zn})} \right] \times \beta \quad (4)$$

with $x = 66, 67$ and 68

Where m is the mass molar for different isotopes. The value of β has been estimated at 0.0019 for Zn by Rodushkin et al. (2004), for a 10 g/L $\text{Zn}(\text{NO}_3)_2 + 0.84 \text{ M HNO}_3$ solution at 20°C. Question arises in which extent this value may be used in our case, and in all the possible natural environments. In our experiments, the temperature is similar, but Zn diffuses in much more diluted solutions and within a diffusive gel. Temperature, however, is not expected to have a significant effect on β , as discussed for Li^+ between 25 and 75°C by Richter et al. (2006) (based on experiments), or by Bourg and Sposito (2007) (based on molecular dynamics modeling). Based on molecular dynamics modeling, Hofmann et al. (2012) further showed the independence of β with temperature for Li^+ , K^+ , Rb^+ , Ca^{2+} , Sr^{2+} , and Ba^{2+} . Regarding the effect of the medium, it has been demonstrated that β was different in gas, silicate melts and solutions. However, in an aqueous solution, so far, no experimental study assessed the potential effect on β of complexation, ionic pairing, or the difference between a diffusive gel and a solution. Molecular dynamics studies by Bourg and Sposito (2007) or Hofmann et al. (2012) conclude that β are independent of ionic

pairing, and should depend primarily on the nature of the first solvation layer of the cations. In our solution and gel, as well as in Rodushkin et al. (2004), Zn^{2+} is majorly under the hexa-hydrated form (free Zn^{2+}), and the same β should apply. In the environment, however, Zn^{2+} can be complexed, in particular by carbonate ions or organic matter. These metal complexes dissociate in the diffusion layer, and only the free metal ion and not the metal complex, reacts with the binding resin of the DGT device (Scally et al., 2003). Prediction of any effect of complexation on β cannot be done on a firm basis so far. However, the DGT device samples only free Zn^{2+} , so as a first approximation, it seems reasonable to consider the β of hexa-hydrated Zn^{2+} . Consequently, the Zn isotopic compositions obtained for DGT were corrected using equation (4) with $\beta=0.0019$ (Figure 6, **Erreur ! Source du renvoi introuvable.**).

The corrected values for DGT extracted by the two protocols are identical with the isotopic composition of the immersion solutions. Thus, even if the use of DGT device involves an isotopic fractionation due to the metal diffusion through the gel layer, this one can be easily corrected by equation (4). Moreover the “classical” protocol of elution with a final rinse step did not induce isotopic fractionation. These tests under laboratory conditions showed the potential of coupling DGT passive samplers and MC-ICP-MS to determine the Zn isotopic compositions in diluted solutions. However to validate this method, more tests under conditions close to those of field sampling are necessary. For that purpose, DGT were deployed in an experimental pilot simulating a water flow designed and built by “Suez Environnement” (Figure 2). The parameters ($T^{\circ}C$, pH, flow rate) measured in the immersion solution at the columns input were constant during the experiment. The temperature stability for each column ensured a diffusion of elements with a constant rate through the DGT device. With a value of 7.3, pH was in the range of values of the optimal use of DGT device. The flow rates were in conformity with the values expected: 4, 2 and 1 meters/day for column 1, 2 and 3. The thicknesses of DBL for each column 1, 2 and 3 were estimated by previous study (Berho et al., 2015) and were respectively 0.18, 0.22 and 0.24 cm. The DBL thicknesses measured in this experiment (0.18-0.24 cm) are large compared to those calculated in surface waters, for example 0.062 to 0.082 cm in river with a flow rate of 0.1m/s (Turner et al., 2014), but are in agreement with those estimated in unstirred solutions: 0.15 ± 0.01 cm (Warnken et al., 2006). For DGT immersed in this pilot, the diffusion zone, defined by the thickness of diffusive gel (+filter membrane) plus the thickness of the DBL, is thus important (up to 0.45 cm). This will allow testing the efficiency of correction (equation (4)) for a large diffusion layer.

The three columns being supplied by the same groundwater (Pecq-Croissy groundwater level), Zn contents were similar for all the columns ($\approx 5 \mu g/L$) and $\delta^{66/64}Zn$ for groundwater sampled in each column at day=0 are also similar ($0.37 \pm 0.05 \text{ ‰}$) (Figure 7, **Erreur ! Source du renvoi introuvable.**). The Zn isotopic composition of Pecq-Croissy groundwater is in the range of values of Seine river waters sampled close to Paris (0.12 - 0.42‰)(Chen et al., 2008). In Figure 7, $\delta^{66/64}Zn$ for DGT immersed for 21 days and extracted by the two protocols and the data for DGT corrected by equation (4) are also shown. The results are the same for the two extraction protocols except for the column 3 where $\delta^{66/64}Zn$ ratios are lower for protocol 2. This is probably related to the fact that this protocol with a “hot” concentrated HNO_3 step can provide a hazardous and high amount of Zn contamination, that can change the initial isotopic composition (cf. §3.1). Apart from these samples, the values of Zn isotopic composition for DGT corrected are similar to the isotopic composition of groundwater.

As shown previously in the cleanroom experiments, the diffusion process correction (equation (4)) applied to the isotopic composition depend neither on the time of immersion nor on the thickness

of the diffusion layer. Thus, in this experiment even with a long time of immersion (21 days) and a large thickness of diffusion layer (until 0.45cm), equation (4) allows correcting the data accurately for DGT. These results open the way for using DGT in environment to determine the Zn isotopic composition of natural waters.

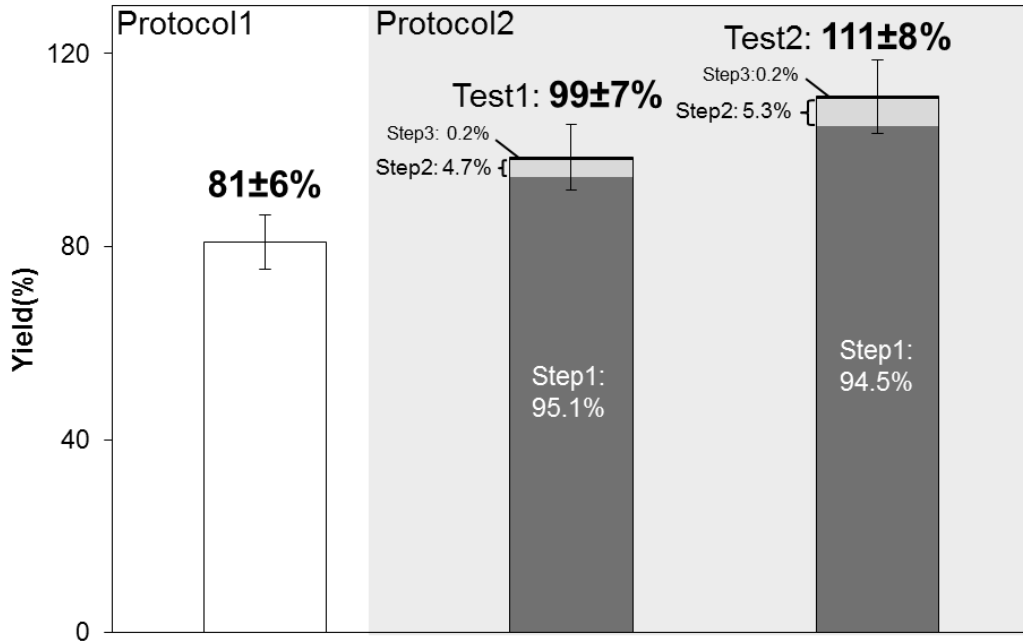


Figure 5: Zn recovery yields for extraction from chelex resin for protocol 1 (white bar) and protocol 2 (grey bars).

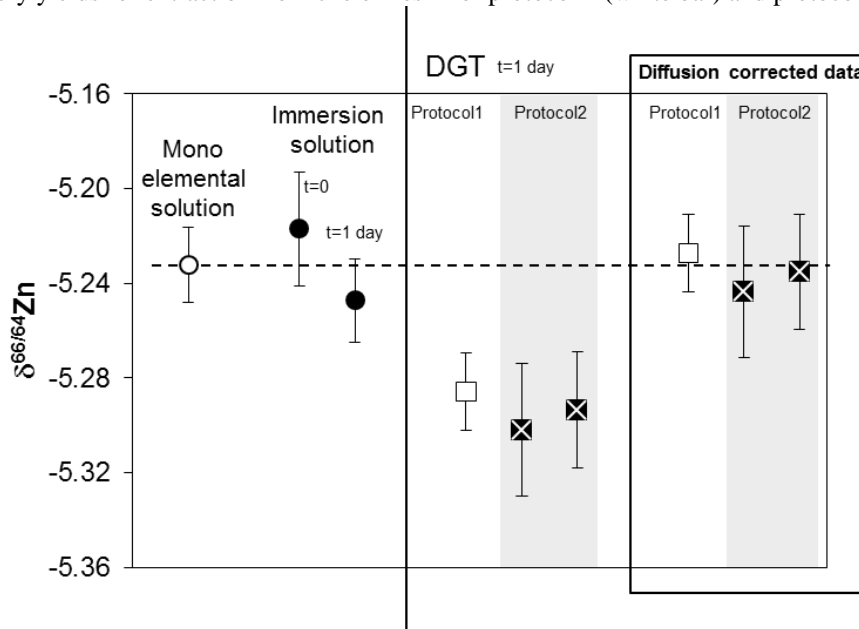


Figure 6: Zn isotopic compositions for samples issued from tests performed in cleanroom. Data are represented for solutions: mono-elemental solution spex (white dot) used to spike mineral water in which are immersed DGT (black dot) sampled at time=0 and time=1 day, and for DGT extracted with protocol 1 (white square) and protocol 2 (crossed square). Data for DGT corrected by equation (4) are represented in black box. . The mean value for immersion solutions are represented by the dotted line.

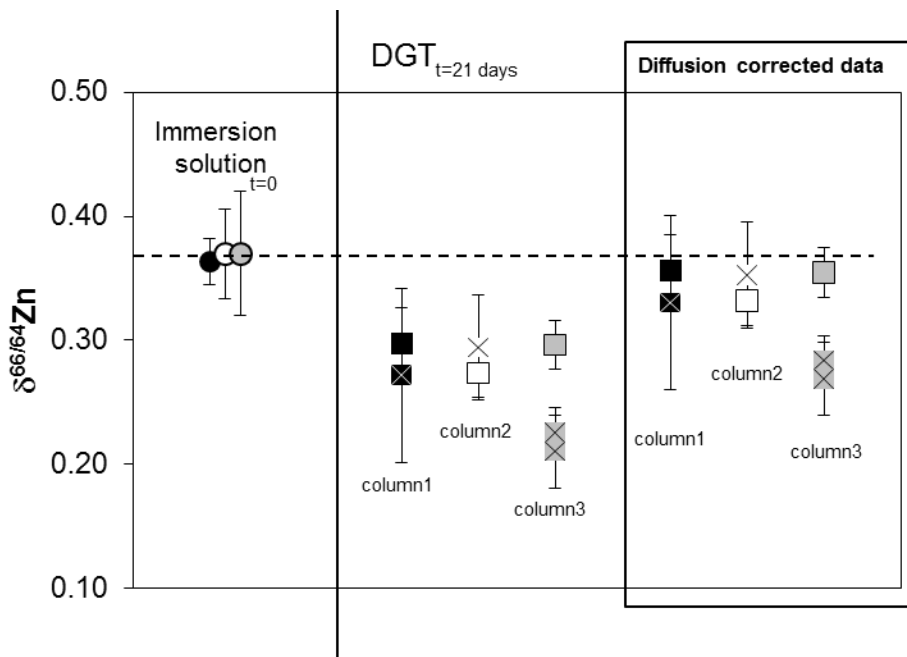


Figure 7: Zn isotopic compositions for samples issued from tests performed in pilot simulating the groundwater flow. Data are represented for immersion solutions at time=0 in column 1 (black dot), column 2 (white dot) and column 3 (grey dot) and for DGT immersed during 21 days in column 1, 2, 3 (respectively black, white and grey squares) extracted with protocol 1 (filled square) and protocol 2 (crossed square). Data for DGT corrected by equation (4) are represented in black box. The mean value for immersion solutions are represented by the dotted line.

Table 1: Summary of Zn isotopic data and description of the samples issued from tests performed in cleanroom.

Name	Thickness of diffusive gel (mm)	Time of exposure (days)	Protocol of extraction	$\delta^{66/64}\text{Zn} \pm 2\sigma$	$\delta^{67/64}\text{Zn} \pm 2\sigma$	$\delta^{68/64}\text{Zn} \pm 2\sigma$	Method (number of measurements)
Solutions							
spex				-5.23 ± 0.02	-7.79 ± 0.05	-10.34 ± 0.02	0.5ppm Cu and 1ppm Zn (6)
isoinitial		0		-5.22 ± 0.02	-7.79 ± 0.05	-10.32 ± 0.04	0.5ppm Cu and 1ppm Zn (6)
isoend		1		-5.25 ± 0.02	-7.83 ± 0.03	-10.37 ± 0.02	0.5ppm Cu and 1ppm Zn (6)
DGT							
Ch1	0.76	1	1	-5.29 ± 0.02	-7.89 ± 0.02	-10.45 ± 0.03	0.5ppm Cu and 1ppm Zn (6)
Ch2-1	0.76	1	2	-5.30 ± 0.03	-7.93 ± 0.05	-10.48 ± 0.05	0.5ppm Cu and 1ppm Zn (6)
Ch2-2	0.76	1	2	-5.29 ± 0.02	-7.92 ± 0.08	-10.47 ± 0.02	0.5ppm Cu and 1ppm Zn (6)
DGT (corrected data)							
Ch1	0.76	1	1	-5.23 ± 0.02	-7.81 ± 0.02	-10.34 ± 0.03	0.5ppm Cu and 1ppm Zn (6)
Ch2-1	0.76	1	2	-5.24 ± 0.03	-7.84 ± 0.05	-10.37 ± 0.05	0.5ppm Cu and 1ppm Zn (6)
Ch2-2	0.76	1	2	-5.24 ± 0.02	-7.84 ± 0.08	-10.35 ± 0.02	0.5ppm Cu and 1ppm Zn (6)

Table 2: Summary of Zn isotopic data and description of the samples issued from tests performed in pilot simulating the groundwater flow.

Name	Thickness of diffusive gel (mm)	Time of exposure (days)	column	Protocol of extraction	$\delta^{66/64}\text{Zn} \pm 2\sigma$	$\delta^{67/64}\text{Zn} \pm 2\sigma$	$\delta^{68/64}\text{Zn} \pm 2\sigma$	Method (number of measurements)
Solutions								
C1		0	1		0.36 ± 0.02	0.53 ± 0.10	0.74 ± 0.08	0.5ppm Cu and 1ppm Zn (4)
C2		0	2		0.37 ± 0.04	0.52 ± 0.14	0.72 ± 0.04	0.5ppm Cu and 1ppm Zn (4)
C3		0	3		0.37 ± 0.05	0.55 ± 0.14	0.75 ± 0.07	0.5ppm Cu and 1ppm Zn (4)
DGT								
Ch1-C1	0.76	21	1	1	0.30 ± 0.03	0.39 ± 0.12	0.60 ± 0.06	0.5ppm Cu and 1ppm Zn (3)
ZnCh2C1-2	0.76	21	1	2	0.27 ± 0.07	0.45 ± 0.14	0.57 ± 0.11	0.5ppm Cu and 1ppm Zn (2)
Ch1-C2	0.76	21	2	1	0.27 ± 0.02	0.42 ± 0.05	0.59 ± 0.03	0.5ppm Cu and 1ppm Zn (3)
Ch2-C2	0.76	21	2	2	0.29 ± 0.04	0.40 ± 0.06	0.58 ± 0.03	0.5ppm Cu and 1ppm Zn (3)
Ch1-C3	0.76	21	3	1	0.30 ± 0.02	0.46 ± 0.12	0.63 ± 0.04	0.5ppm Cu and 1ppm Zn (3)
PbCh2C3	0.76	21	3	2	0.23 ± 0.02	0.48 ± 0.08	0.56 ± 0.06	0.5ppm Cu and 1ppm Zn (2)
ZnCh2C3-2	0.76	21	3	2	0.21 ± 0.03	0.43 ± 0.06	0.57 ± 0.02	0.5ppm Cu and 1ppm Zn (2)
DGT (corrected data)								
Ch1-C1	0.76	21	1	1	0.36 ± 0.03	0.48 ± 0.12	0.72 ± 0.06	0.5ppm Cu and 1ppm Zn (3)
ZnCh2C1-2	0.76	21	1	2	0.33 ± 0.07	0.54 ± 0.14	0.68 ± 0.11	0.5ppm Cu and 1ppm Zn (2)
Ch1-C2	0.76	21	2	1	0.33 ± 0.02	0.50 ± 0.05	0.71 ± 0.03	0.5ppm Cu and 1ppm Zn (3)
Ch2-C2	0.76	21	2	2	0.35 ± 0.04	0.49 ± 0.06	0.69 ± 0.03	0.5ppm Cu and 1ppm Zn (3)
Ch1-C3	0.76	21	3	1	0.35 ± 0.02	0.54 ± 0.12	0.74 ± 0.04	0.5ppm Cu and 1ppm Zn (3)
PbCh2C3	0.76	21	3	2	0.28 ± 0.02	0.57 ± 0.08	0.67 ± 0.06	0.5ppm Cu and 1ppm Zn (2)
ZnCh2C3-2	0.76	21	3	2	0.27 ± 0.03	0.52 ± 0.06	0.68 ± 0.02	0.5ppm Cu and 1ppm Zn (2)

3.3 DGT and Pb isotopes

To evaluate the feasibility of coupling DGT samplers and isotopic analyses, experiments were performed first in the cleanroom. For these tests, the Pb isotopic ratios for DGT with a 0.76 mm diffusive gel immersed for different times of exposure (1, 5 and 7 days) and extracted by protocol 1 and protocol 2 were similar to the bulk isotopic composition of the immersion solution (Figure 8, **Erreur ! Source du renvoi introuvable.**). No measurable fractionation could be observed within the reported precision of MC-ICP-MS measurements. As seen previously, more the difference of mass is important more the isotopic signature will be affected by the diffusion process (see equation (4)). When we represent the data in δ -notation (parts per 1,000), which allows to highlight small variations in isotopic composition, for the ratio with the largest mass difference ($\delta^{208/204}\text{Pb}$), a slight shift toward heavy isotope depletion can be seen (Figure 9). As for Zn, the diffusion process could be responsible for such isotopic fractionation, however the shift observed is within the analytical error.

For the experiment taking place in the pilot simulating a water flow, the Pb contents measured from the middle of each column were variable over time. From the 6th day, the Pb concentrations in the immersion solution increased (

Figure 10), this rise was due to the increase of the spike injection volume to reach the expected value of 0.7 $\mu\text{g/l}$ (Berho et al., 2015). Due to its low Pb content ($<0.10\mu\text{g/l}$), it has not been possible to determine the isotopic composition of Pecq-Croissy groundwater located in the Seine river basin. Figure 11 shows $^{206}\text{Pb}/^{204}\text{Pb}$ versus $1/\text{Pb}$ for spike, diluted spike, immersion solutions and water from the Seine river flowed in Paris (Roy, 1996). This figure shows that the water in the column was a mixture between two end members: spike solution and natural water with low Pb contents, this pole corresponding to Pecq-Croissy groundwater. Compared to the beginning of experiment, at day=21 the immersion solution contained a greater proportion of spike solution (Figure 11), this result is in agreement with the augmentation of the spike injection volume from the 6th day.

In this study, for a given time of immersion (6, 13, 21 days), the Pb isotopic compositions for all DGT were similar whatever the thickness of diffusive gel (1.96, 1.18, 0.78 mm) and the column flow rate (1, 2, 4 m/day) (

Figure 10, **Erreur ! Source du renvoi introuvable.**). This result suggests that there is no apparent impact of the thickness of diffusive layer (diffusive gel + filter membrane + DBL) on the isotopic compositions of the Pb fixed in DGT. For DGT with a thickness of diffusive gel of 0.76mm, Pb isotopic ratios for protocol 2 are more variable and slightly different as compared to protocol 1. This result is probably related to a hazardous Pb contamination occurring during protocol 2 (cf §3.1). As the immersion time increases, the Pb isotopic signature for DGT tends toward the Pb isotopic ratio of the spike solution. This result is consistent with the increased proportion of the spike solution relative to the immersion solution over time. Finally after 21 days of immersion, $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for DGT in the 3 columns are close to the isotopic ratio of the immersion solutions sampled the 21st day, with a slight enrichment in heavy isotopes compared to this immersion solution. This enrichment reflects the fact that DGT isotopic composition represents a 21 days integrated signature and not a single isotopic composition at day=21. The fingerprint of the more radiogenic Pb signature of the immersion solution at the beginning of the experiment is still identified.

These experiments show that the DGT device does not introduce significant isotopic fractionation even for a long time of exposure and for a large diffusion layer. This sampler is then suitable to determine the Pb isotopic compositions in natural waters.

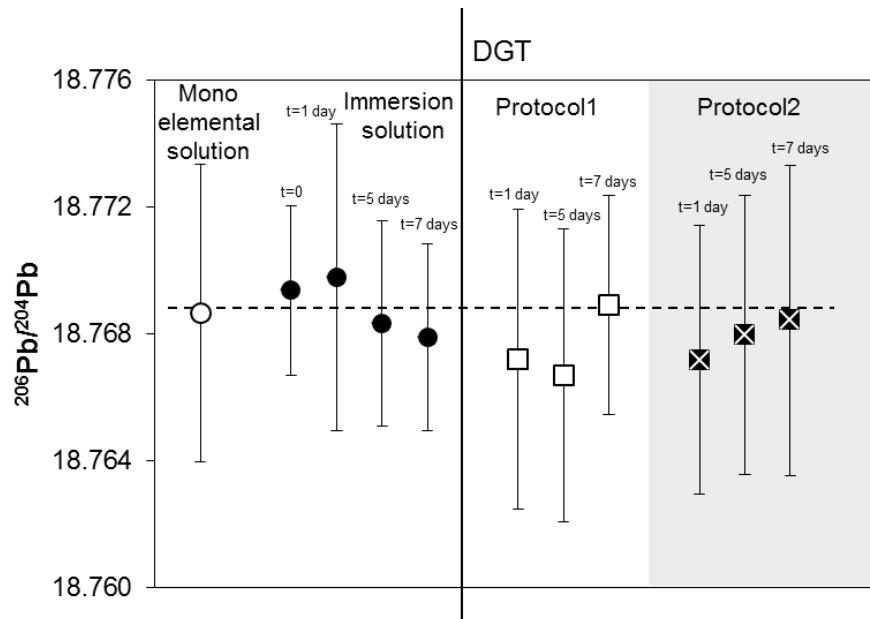


Figure 8: Pb isotopic compositions for samples issued from tests performed in cleanroom. Data are represented for solutions: mono-elemental solution spex (white dot) used to spike mineral water in which are immersed DGT (black dot) sampled at time=0, 1, 5 and 7 days , and for DGT immersed during 1, 5 and 7 days and extracted with protocol 1 (white square) and protocol 2 (crossed square). The mean value for immersion solutions are represented by the dotted line.

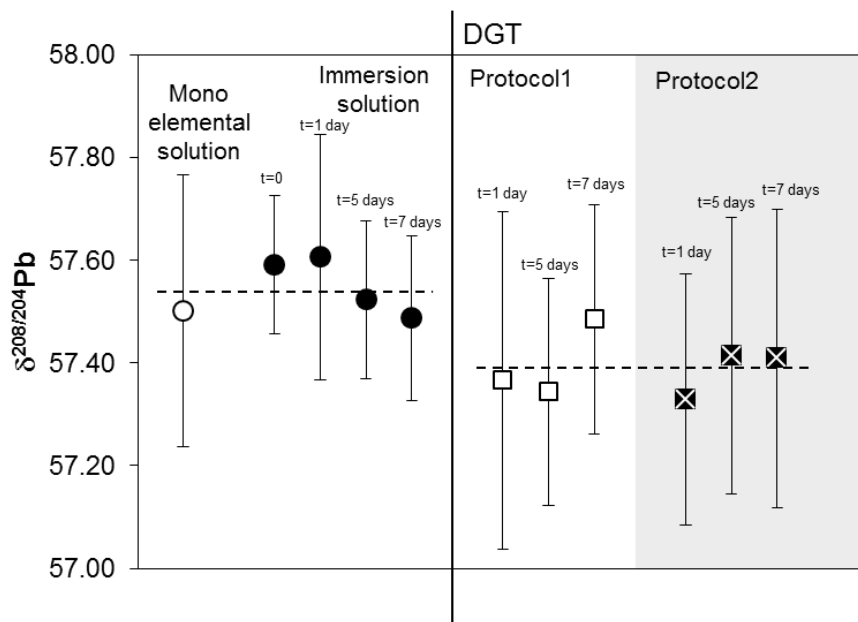


Figure 9: $\delta^{208/204}\text{Pb}$ for samples issued from tests performed in cleanroom. Same caption as in Figure 8. The mean value for immersion solutions and DGT are represented by the dotted line. The Pb isotopic composition of the samples is expressed in δ -notation (parts per 1,000) relative to the mean value of the bracketing Pb standard (NIST SRM981): $\delta^{208/204}\text{Pb} = [(^{208}\text{Pb}/^{204}\text{Pb})_{\text{sample}} / (^{208}\text{Pb}/^{204}\text{Pb})_{\text{standard}} - 1] \cdot 10^3$

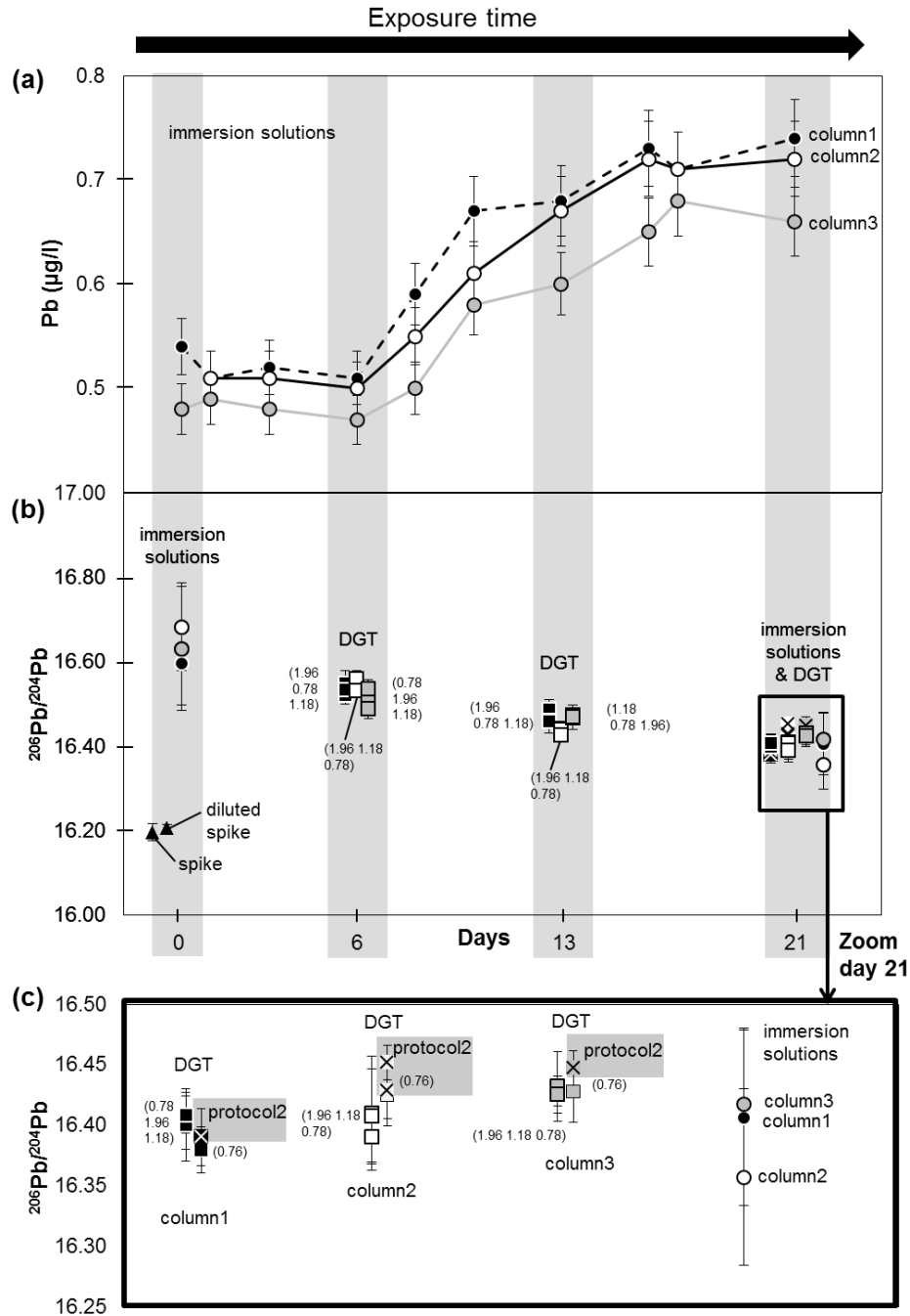


Figure 10: Results for samples issued from tests performed in pilot simulating the groundwater flow. (a): Pb content for the immersion solutions in column 1 (black dot), column 2 (white dot) and column 3 (grey dot). (b): $^{206}\text{Pb}/^{208}\text{Pb}$ ratios for spike and diluted spike (black triangles) added to have a content of about $0.7\mu\text{g/L}$ in pilot, immersion solution at day=0 and day=21 in column 1, 2, 3 (respectively black, white, and grey dots), DGT immersed during 6 days, 13 days and 21 days in column 1, 2 and 3 (respectively black, white and grey squares). (c): Zoom of figure (b) $^{206}\text{Pb}/^{208}\text{Pb}$ ratios for DGT with different gel diffusive thickness (indicated in brackets) immersed during 21 days in column 1, 2, 3 and extracted by protocol 1 (filled square) and protocol 2 (crossed square). DGT which were placed in the same DGT holder (see Figure 2) are in the same vertical line in this figure.

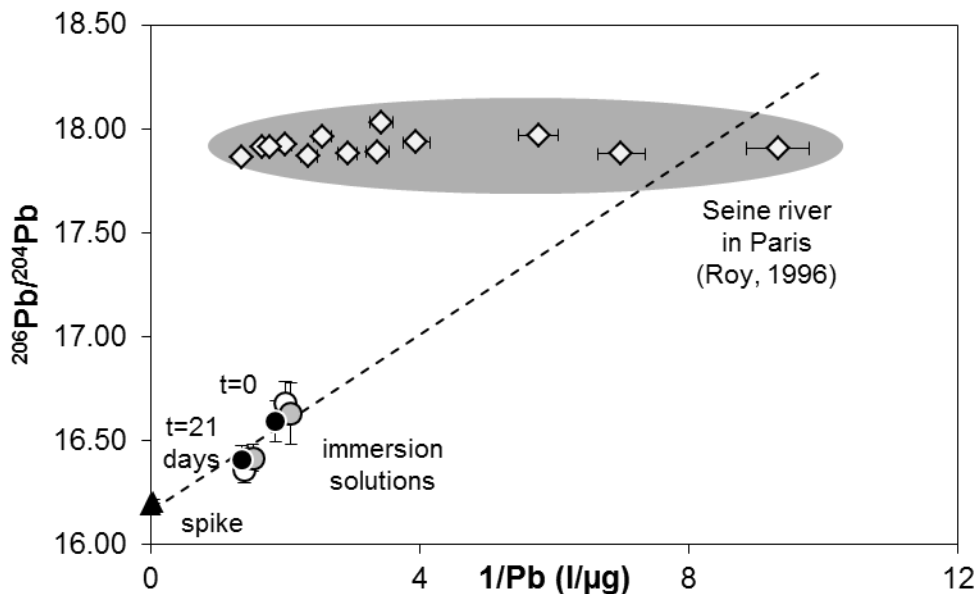


Figure 11: $^{206}\text{Pb}/^{204}\text{Pb}$ versus $1/\text{Pb}$ ($\text{l}/\mu\text{g}$) for immersion solutions at time=0 and time=21 days in column 1 (black dot), column 2 (white dot) and column 3 (grey dot), spike and diluted spike (black triangles) and data obtained by Roy (1996) for Seine River in Paris (white diamonds), the $1/\text{Pb}$ variations are linked to the seasonal flow rate differences. The dotted line represents the correlation slope for the data of this study ($y = 0.2117x + 16.166$, $R^2 = 0.8755$).

Table 3: Summary of Pb isotopic data and description of the samples issued from tests performed in cleanroom.

Name	Thickness of diffusive gel (mm)	Time of exposure (days)	Protocol of extraction	$^{206}\text{Pb}/^{204}\text{Pb} \pm 2\sigma$	$^{207}\text{Pb}/^{204}\text{Pb} \pm 2\sigma$	$^{208}\text{Pb}/^{204}\text{Pb} \pm 2\sigma$	Method (number of measurements)
Solution							
SPEX				18.769 ± 0.005	15.654 ± 0.004	38.838 ± 0.010	Faraday cups 50ppb (27)
ini		0		18.769 ± 0.003	15.655 ± 0.002	38.841 ± 0.005	Faraday cups 50ppb (5)
sampl-1		1		18.770 ± 0.005	15.656 ± 0.004	38.842 ± 0.009	Faraday cups 50ppb (5)
sampl-2		5		18.768 ± 0.003	15.654 ± 0.003	38.839 ± 0.006	Faraday cups 50ppb (5)
sampl-3		7		18.768 ± 0.003	15.654 ± 0.002	38.837 ± 0.006	Faraday cups 50ppb (5)
DGT							
Chem1-1	0.76	1	1	18.767 ± 0.005	15.653 ± 0.005	38.833 ± 0.012	Faraday cups 50ppb(5)
Chem1-2	0.76	5	1	18.767 ± 0.005	15.652 ± 0.004	38.832 ± 0.008	Faraday cups 50ppb(6)
Chem1-3	0.76	7	1	18.769 ± 0.003	15.654 ± 0.003	38.837 ± 0.008	Faraday cups 50ppb (6)
iso-1	0.76	1	2	18.767 ± 0.004	15.652 ± 0.004	38.832 ± 0.009	Faraday cups 50ppb (5)
iso-2	0.76	5	2	18.768 ± 0.004	15.653 ± 0.003	38.835 ± 0.010	Faraday cups 50ppb (10)
Iso-3	0.76	7	2	18.768 ± 0.005	15.654 ± 0.005	38.835 ± 0.011	Faraday cups 50ppb (5)

Table 4: Summary of Pb isotopic data and description of the samples issued from tests performed in pilot simulating the groundwater flow.

Name	Thickness of diffusive gel (mm)	Time of exposure (days)	column	Protocol of extraction	$^{206}\text{Pb}/^{204}\text{Pb} \pm 2\sigma$	$^{207}\text{Pb}/^{204}\text{Pb} \pm 2\sigma$	$^{208}\text{Pb}/^{204}\text{Pb} \pm 2\sigma$	Method (number of measurements)
Solution								
C1initial		0	1		16.60 ± 0.10	15.56 ± 0.20	36.35 ± 0.15	SEM (2)
C1end		21	1		16.41 ± 0.07	15.48 ± 0.15	36.17 ± 0.07	SEM (3)
C2initial		0	2		16.68 ± 0.10	15.58 ± 0.08	36.51 ± 0.19	SEM (2)
C2end		21	2		16.36 ± 0.06	15.45 ± 0.24	35.94 ± 0.46	SEM (9)
C3initial		0	3		16.63 ± 0.15	15.53 ± 0.20	36.45 ± 0.04	SEM (2)
C3end		21	3		16.42 ± 0.06	15.47 ± 0.06	36.19 ± 0.22	SEM (3)
spike					16.20 ± 0.02	15.47 ± 0.02	35.93 ± 0.05	Faraday cups 10ppb (16)
pilotdilu2		0			16.21 ± 0.01	15.47 ± 0.01	35.94 ± 0.02	Faraday cups 10ppb (10)
DGT								
J6_C1_h_P_1.96	1.96	6	1	1	16.55 ± 0.03	15.52 ± 0.03	36.34 ± 0.07	Faraday cups 10ppb (1)
J6_C1_h_P_1.18	1.18	6	1	1	16.52 ± 0.02	15.51 ± 0.02	36.30 ± 0.05	Faraday cups 10ppb (1)
J6_C1_h_P_0.78	0.78	6	1	1	16.53 ± 0.02	15.50 ± 0.02	36.30 ± 0.05	Faraday cups 10ppb (1)
J13_C1_h_&_1.96	1.96	13	1	1	16.49 ± 0.02	15.50 ± 0.02	36.26 ± 0.05	Faraday cups 10ppb (2)
J13_C1_h_&_1.18	1.18	13	1	1	16.46 ± 0.01	15.50 ± 0.02	36.22 ± 0.03	Faraday cups 10ppb (2)
J13_C1_h_&_0.78	0.78	13	1	1	16.46 ± 0.03	15.50 ± 0.03	36.22 ± 0.06	Faraday cups 10ppb (2)
J21_C1_h_X_1.96	1.96	21	1	1	16.40 ± 0.02	15.49 ± 0.02	36.15 ± 0.05	Faraday cups 10ppb (4)
J21_C1_h_X_1.18	1.18	21	1	1	16.40 ± 0.03	15.48 ± 0.03	36.14 ± 0.07	Faraday cups 10ppb (4)
J21_C1_h_X_0.78	0.78	21	1	1	16.41 ± 0.02	15.49 ± 0.01	36.16 ± 0.04	Faraday cups 10ppb (4)
ch1-C1	0.76	21	1	1	16.38 ± 0.02	15.49 ± 0.02	36.13 ± 0.04	Faraday cups 10ppb (5)
ZnCh2C1	0.76	21	1	2	16.39 ± 0.02	15.49 ± 0.02	36.14 ± 0.05	Faraday cups 10ppb (4)
J6_C2_b_U_1.96	1.96	6	2	1	16.56 ± 0.02	15.50 ± 0.02	36.32 ± 0.05	Faraday cups 10ppb (1)
J6_C2_b_U_1.18	1.18	6	2	1	16.56 ± 0.02	15.50 ± 0.01	36.33 ± 0.03	Faraday cups 10ppb (1)
J6_C2_b_U_0.78	0.78	6	2	1	16.53 ± 0.02	15.50 ± 0.02	36.31 ± 0.04	Faraday cups 10ppb (1)
J13_C2_b_11_1.96	1.96	13	2	1	16.44 ± 0.01	15.50 ± 0.01	36.21 ± 0.03	Faraday cups 10ppb (2)
J13_C2_b_11_1.18	1.18	13	2	1	16.44 ± 0.02	15.48 ± 0.01	36.19 ± 0.03	Faraday cups 10ppb (2)
J13_C2_b_11_0.78	0.78	13	2	1	16.43 ± 0.01	15.48 ± 0.01	36.17 ± 0.02	Faraday cups 10ppb (2)
J21_C2_b_J_1.96	1.96	21	2	1	16.41 ± 0.05	15.48 ± 0.04	36.15 ± 0.10	Faraday cups 10ppb (3)
J21_C2_b_J_1.18	1.18	21	2	1	16.41 ± 0.04	15.49 ± 0.04	36.17 ± 0.09	Faraday cups 10ppb (4)
J21_C2_b_J_0.78	0.78	21	2	1	16.39 ± 0.02	15.48 ± 0.02	36.13 ± 0.05	Faraday cups 10ppb (5)
ch1-C2	0.76	21	2	1	16.42 ± 0.03	15.48 ± 0.02	36.17 ± 0.06	Faraday cups 10ppb (5)
ch2-C2	0.76	21	2	2	16.45 ± 0.01	15.50 ± 0.02	36.22 ± 0.04	Faraday cups 10ppb (5)
PbCh2C2	0.76	21	2	2	16.43 ± 0.02	15.49 ± 0.02	36.19 ± 0.05	Faraday cups 10ppb (6)
J6_C3_h_15_1.96	0.78	6	3	1	16.52 ± 0.02	15.51 ± 0.02	36.30 ± 0.04	Faraday cups 10ppb (1)
J6_C3_h_15_1.18	1.96	6	3	1	16.49 ± 0.02	15.49 ± 0.02	36.25 ± 0.06	Faraday cups 10ppb (1)
J6_C3_h_15_0.78	1.18	6	3	1	16.54 ± 0.02	15.50 ± 0.02	36.31 ± 0.04	Faraday cups 10ppb (1)
J13_C3_h_8_1.96	0.78	13	3	1	16.47 ± 0.03	15.49 ± 0.02	36.22 ± 0.05	Faraday cups 10ppb (2)
J13_C3_h_8_1.18	1.96	13	3	1	16.48 ± 0.02	15.50 ± 0.02	36.24 ± 0.05	Faraday cups 10ppb (2)
J13_C3_h_8_0.78	1.18	13	3	1	16.47 ± 0.01	15.50 ± 0.01	36.23 ± 0.02	Faraday cups 10ppb (2)
J21_C3_h_4_1.96	0.78	21	3	1	16.43 ± 0.01	15.48 ± 0.01	36.17 ± 0.03	Faraday cups 10ppb (3)
J21_C3_h_4_1.18	1.96	21	3	1	16.43 ± 0.03	15.49 ± 0.03	36.19 ± 0.06	Faraday cups 10ppb (4)
J21_C3_h_4_0.78	1.18	21	3	1	16.43 ± 0.02	15.48 ± 0.01	36.17 ± 0.03	Faraday cups 10ppb (4)
ch1-C3-1	0.76	21	3	1	16.43 ± 0.03	15.49 ± 0.03	36.17 ± 0.06	Faraday cups 10ppb (5)
PbCh2C3	0.76	21	3	2	16.45 ± 0.02	15.49 ± 0.02	36.20 ± 0.05	Faraday cups 10ppb (5)

4. Conclusions

We have developed a new tool to measure Pb and Zn isotopic composition in dilute aqueous solutions by coupling DGT passive samplers and multi-collector ICP-MS. This coupling offers a large number of advantages: DGT device allows achieving an isotopic composition of natural water integrated over time and to pre-concentrate metals in situ. This new development will greatly facilitate the field collection of samples and their preparations in cleanroom prior to their isotopic analyses, minimizing matrix effect and reducing analysis costs. Moreover compared to discrete techniques, like conventional “grab” samples, providing a measurement of the isotopic composition only at the time of measurement, DGT passive samplers allow a continuous monitoring of water bodies which have fluctuating levels of metal contaminants. The tests performed to validate this coupling have shown that the “classical” protocol of extraction upgraded with a last step of rinse in “Milli-Q” water can be used successfully to extract metal from DGT resin. For Pb, there is no fractionation of its isotopes due to the use of DGT within the reported precision of MC-ICP-MS measurements. For Zn, the diffusion process, inherent to the use of DGT devices, 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 tests made in this study were carried out with well-controlled parameters (T°C, water flow rate, ionic strength ...), this will not be the case when DGT will be deployed in the field. Previous studies show that these parameters principally modify the value of diffusion coefficient (D) of metal in the gel (Sangi et al., 2002; Zhang and Davison, 1995). So, if these factors have an important role for the determination of the metal concentrations in water by modifying the kinetic of the fixation on the resin, it should not have an effect on the isotopic signature fixed on the DGT. However, for a long deployment, the formation of a biofilm (bacteria, algae, fungi...) overlaying the DGT device and interacting with metals in solution by various processes (biosorption, complexation, precipitation...) could fractionate the isotopic composition fixed on DGT relative to the bulk solution (Uher et al., 2012). The biofouling is a particularly impacting factor to measure the Zn isotopic signature, strongly dependent of the biotic processes (Cloquet et al., 2008). For a long deployment in the field, chemical or physical method (biocide, smoother membranes) should be used to prevent the biofilm formation.

The DGT deployment in the field to monitor rivers and groundwaters offers new perspectives concerning the support to public policy development by facilitating the isotopic monitoring of natural water, allowing to better combat the metal pollutions in environment.

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References

- Alfaro-De laTorre, M.C., Beaulieu, P.Y., Tessier, A., 2000. In situ measurement of trace metals in lakewater using the dialysis and DGT techniques. *Anal. Chim. Acta* 418, 53–68. doi:10.1016/S0003-2670(00)00946-6
- Berho, C., Robert, S., Ghestem, J.-P., Laurieux, T., Bruchet, A., 2015. Calibration en pilote d' échantillonneurs passifs de type DGT pour le suivi des métaux dans les eaux souterraines. Orléans. doi:Rapport BRGM, RP-64944-FR
- Bermin, J., Vance, D., Archer, C., Statham, P.J., 2006. The determination of the isotopic composition of Cu and Zn in seawater. *Chem. Geol.* 226, 280–297. doi:10.1016/j.chemgeo.2005.09.025
- Bio-Rad Laboratories, 2000. Chelex® 100 and Chelex 20 Chelating Ion Exchange Resin Instruction Manual. Bio-Rad Lab. 1–24.
- Borrok, D.M., Wanty, R.B., Ridley, W.I., Wolf, R., Lamothe, P.J., Adams, M., 2007. Separation of copper, iron, and zinc from complex aqueous solutions for isotopic measurement. *Chem. Geol.* 242, 400–414. doi:10.1016/j.chemgeo.2007.04.004
- Bourg, I.C., Sposito, G., 2007. Molecular dynamics simulations of kinetic isotope fractionation during the diffusion of ionic species in liquid water. *Geochim. Cosmochim. Acta* 71, 5583–5589. doi:10.1016/j.gca.2007.01.021
- Chen, J., Gaillardet, J., Louvat, P., 2008. Zinc isotopes in the Seine River waters, France: A probe of anthropogenic contamination. *Environ. Sci. Technol.* 42, 6494–6501. doi:10.1021/es800725z
- Chen, J. Bin, Louvat, P., Gaillardet, J., Birck, J.L., 2009. Direct separation of Zn from dilute aqueous solutions for isotope composition determination using multi-collector ICP-MS. *Chem. Geol.* 259, 120–130. doi:10.1016/j.chemgeo.2008.10.040
- Cloquet, C., Carignan, J., Lehmann, M.F., Vanhaecke, F., 2008. Variation in the isotopic composition of zinc in the natural environment and the use of zinc isotopes in biogeosciences: A review. *Anal. Bioanal. Chem.* doi:10.1007/s00216-007-1635-y
- Cocherie, A., Robert, M., 2007. Direct measurement of lead isotope ratios in low concentration environmental samples by MC-ICP-MS and multi-ion counting. *Chem. Geol.* 243, 90–104. doi:10.1016/j.chemgeo.2007.05.011
- Dahlqvist, R., Andersson, P.S., Ingri, J., 2005. The concentration and isotopic composition of diffusible Nd in fresh and marine waters. *Earth Planet. Sci. Lett.* 233, 9–16. doi:10.1016/j.epsl.2005.02.021
- Davison, W., Zhang, H., 1994. In-situ speciation measurements of trace components in natural waters using thin-film gels. *Nature* 237, 546–548. doi:10.1038/367546a0
- Davison, W., Zhang, H., Warnken, K.W., 2007. Theory and applications of DGT measurements in soils and sediments, in: R.Greenwood; Vrana, G., Mills; B. (Eds.), *Comprehensive Analytical Chemistry: Passive Sampling Techniques in Environmental Monitoring*. pp. 353–378.
- Denney, S., Sherwood, J., Leyden, J., 1999. In situ measurements of labile Cu, Cd and Mn in river waters using DGT. *Sci. Total Environ.* 239, 71–80. doi:10.1016/S0048-9697(99)00304-6
- Desaulty, A.-M., Millot, R., Widory, D., Guerrot, C., Bourrain, X., 2014. Multi-isotopic monitoring of industrial metal emissions (Cu-Zn-Pb) within the Loire River Basin, France, in: Goldschmidt. Sacramento, p. 542.

- Dragun, Z., Raspor, B., Roje, V., 2008. The labile metal concentrations in Sava River water assessed by diffusive gradients in thin films. *Chem. Speciat. Bioavailab.* 20, 33–46. doi:10.3184/095422908X299164
- Garmo, Ø.A., Naqvi, K.R., Røyset, O., Steinnes, E., 2006. Estimation of diffusive boundary layer thickness in studies involving diffusive gradients in thin films (DGT). *Anal. Bioanal. Chem.* 386, 2233–2237. doi:10.1007/s00216-006-0885-4
- Garmo, Ø.A., Røyset, O., Steinnes, E., Flaten, T.P., 2003. Performance study of diffusive gradients in thin films for 55 elements. *Anal. Chem.* 75, 3573–3580. doi:10.1021/ac026374n
- Grosbois, C., Négrel, P., Fouillac, C., Grimaud, D., 2000. Dissolved load of the Loire River: Chemical and isotopic characterization. *Chem. Geol.* 170, 179–201. doi:10.1016/S0009-2541(99)00247-8
- Hanousek, O., Santner, J., Mason, S., Berger, T.W., Wenzel, W.W., Prohaska, T., 2016. Diffusive gradients in thin films measurement of sulfur stable isotope variations in labile soil sulfate. *Anal. Bioanal. Chem.* doi:10.1007/s00216-016-9949-2
- Hofmann, A.E., Bourg, I.C., DePaolo, D.J., 2012. Ion desolvation as a mechanism for kinetic isotope fractionation in aqueous systems. *Proc. Natl. Acad. Sci. U. S. A.* 109, 18689–94. doi:10.1073/pnas.1208184109
- Kingston, H.M., Barnes, I.L., Brady, T.J., Rains, T.C., Champ, M. a., 1978. Separation of eight transition elements from alkali and alkaline earth elements in estuarine and seawater with chelating resin and their determination by graphite furnace atomic absorption spectrometry. *Anal. Chem.* 50, 2064–2070. doi:10.1021/ac50036a031
- Malinovsky, D., Dahlgvist, R., Baxter, D.C., Ingri, J., Rodushkin, I., 2005. Performance of diffusive gradients in thin films for measurement of the isotopic composition of soluble Zn. *Anal. Chim. Acta* 537, 401–405. doi:10.1016/j.aca.2005.01.047
- Marechal, C., 1998. Géochimie des isotopes du cuivre et du zinc: méthode, variabilité naturelle et application océanographique. PhD dissertation. Université Joseph Fourier Grenoble I, France.
- Maréchal, C.N., Télouk, P., Albarède, F., 1999. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chem. Geol.* 156, 251–273. doi:10.1016/S0009-2541(98)00191-0
- Monna, F., Lancelot, J., Croudace, I.W., Cundy, A.B., Lewis, J.T., 1997. Pb isotopic composition of airborne particulate material from France and the Southern United Kingdom: Implications for Pb pollution sources in urban areas. *Environ. Sci. Technol.* 31, 2277–2286. doi:10.1021/es960870+
- Pai, S.C., Whung, P.Y., Lai, R.L., 1988. Pre-concentration efficiency of chelex-100 resin for heavy metals in seawater. Part 1. Effects of pH and Salts on the Distribution Ratios of Heavy Metals. *Anal. Chim. Acta* 211, 257–270. doi:10.1016/S0003-2670(00)83685-5
- Richter, F.M., Mendybaev, R.A., Christensen, J.N., Hutcheon, I.D., Williams, R.W., Sturchio, N.C., Beloso, A.D., 2006. Kinetic isotopic fractionation during diffusion of ionic species in water. *Geochim. Cosmochim. Acta* 70, 277–289. doi:10.1016/j.gca.2005.09.016
- Rodushkin, I., Stenberg, A., Andren, H., Malinovsky, D., Baxter, D.C., 2004. Isotopic Fractionation during Diffusion of Transition Metal Ions in Solution. *Anal. Chem.* 76, 2148–2151.
- Roy, S., 1996. Utilisation des isotopes du Pb et du Sr comme traceurs des apports anthropiques et naturels dans les précipitations et les rivières du bassin de Paris, PhD dissertation. Université Denis Diderot

Paris VII, France.

- Roy, S., Négrel, P., 2001. A Pb isotope and trace element study of rainwater from the Massif Central (France). *Sci. Total Environ.* 277, 225–239. doi:10.1016/S0048-9697(00)00883-4
- Sangi, M.R., Halstead, M.J., Hunter, K.A., 2002. Use of the diffusion gradient thin film method to measure trace metals in fresh waters at low ionic strength. *Anal. Chim. Acta* 456, 241–251. doi:10.1016/S0003-2670(02)00012-0
- Scally, S., Davison, W., Zhang, H., 2003. In situ measurements of dissociation kinetics and labilities of metal complexes in solution using DGT. *Environ. Sci. Technol.* 37, 1379–1384. doi:10.1021/es0202006
- Szynkiewicz, A., Borrok, D.M., 2016. Isotope variations of dissolved Zn in the Rio Grande watershed, USA: The role of adsorption on Zn isotope composition. *Earth Planet. Sci. Lett.* 433, 293–302. doi:10.1016/j.epsl.2015.10.050
- Turner, G.S.C., Mills, G.A., Bowes, M.J., Burnett, J.L., Amos, S., Fones, G.R., 2014. Evaluation of DGT as a long-term water quality monitoring tool in natural waters; uranium as a case study. *Environ. Sci. Process. Impacts* 16, 393–403. doi:10.1039/c3em00574g
- Uher, E., Tusseau-Vuillemin, M.-H., Gourlay-France, C., 2013. DGT measurement in low flow conditions: diffusive boundary layer and lability considerations. *Environ. Sci. Process. Impacts* 15, 1351. doi:10.1039/c3em00151b
- Uher, E., Zhang, H., Santos, S., Tusseau-Vuillemin, M.H., Gourlay-Francé, C., 2012. Impact of biofouling on diffusive gradient in thin film measurements in water. *Anal. Chem.* 84, 3111–3118. doi:10.1021/ac2028535
- Warnken, K.W., Zhang, H., Davison, W., 2006. Accuracy of the diffusive gradients in thin-films technique: Diffusive boundary layer and effective sampling area considerations. *Anal. Chem.* 78, 3780–3787. doi:10.1021/ac060139d
- Zhang, H., Davison, W., 1995. Performance Characteristics of Diffusion Gradients in Thin Films for the in Situ Measurement of Trace Metals in Aqueous Solution. *Anal. Chem.* 67, 3391–3400. doi:10.1021/ac00115a005
- Zhang, H., Davison, W., Miller, S., Tych, W., 1995. In situ high resolution measurements of fluxes of Ni, Cu, Fe, and Mn and concentrations of Zn and Cd in porewaters by DGT. *Geochim. Cosmochim. Acta* 59, 4181–4192. doi:10.1016/0016-7037(95)00293-9