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Impact of low ionic strength on DGT sampling with standard APA gels: effect of pH and analyte

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Abstract

Only a limited and scattered knowledge is currently available on the conditions leading to the occurrence of sampling alteration at low ionic strength ($< 10^{-3}$ mol L⁻¹) with DGT (diffusive gradients in thin films technique). In this study, the role of the pH and the charge of the analyte were comprehensively evaluated with DGT equipped with APA (polyacrylamide with agarose-derivative crosslinker) diffusive gels and ZrO or Chelex binding phases. The sampling of four cations (Cd^{II}, Cu^{II}, Ni^{II} and Pb^{II}) and two anions (As^V and Cr^{VI}) was compared for pH 4, 6 and 8 at common (10^{-2} mol L⁻¹) and low (10^{-4} mol L⁻¹) ionic strengths. Results showed that the sampling was modified at low ionic strength only in the most acidic condition (pH 4) for both anions and cations with an opposite incidence: cations' sampling was halved whereas anions' sampling was increased. Furthermore, cations sampling alteration was similarly reproduced using diffusion cell experiments, which requires only the APA gel, indicating that the binding layer does not participate in the low ionic strength effect. The intensity of DGT sampling modification was consistent with a prediction based on Donnan partitioning of analytes at gel/solution interface for several valences (from -I to +III). All these results strongly suggest that the APA diffusive gels carry positive charges that create a Donnan effect at low ionic strength. Since no ionic strength effect could be evidenced at pH 6 and 8, it can be reasonably assumed that this effect occurs only marginally for DGT deployments in most natural waters.

Keywords

diffusive gradients in thin films technique; passive sampling; metals; metalloids; Donnan effect

Introduction

The diffusive gradients in thin films technique (DGT) is widely used for passive sampling of labile trace metals and metalloids in water systems. Its advantages and complementarity over spot sampling make it a very suitable tool for monitoring trace elements [1]–[3]. Although the DGT is a robust tool in most conditions [4], altered samplings were reported in low ionic strengths medium ($< 10^{-3}$ mol L⁻¹) during the early stage of DGT development [5]–[7]. Using standard polyacrylamide gels with agarose-derivative crosslinker (APA), Alfaro de la Torre *et al.* [7] reported that the concentrations of some cationic metals were overestimated whereas Peters *et al.* [5] found an erratic behaviour (both over and under estimations). Torre *et al.* [7] suggested that the diffusion of the counter-ion (e.g. Na⁺) of the binding resin out of the DGT device induces an enhanced diffusion of cationic analytes within the diffusive gel to fulfil the electroneutrality. However, such phenomenon was not able to explain the results from Peters *et al.* [5], which may be rather explained by an alteration of elements sampling due to interactions with local charges of the diffusive gel. Warnken *et al.* [8] finally demonstrated that an insufficient washing of the gels was responsible for Cu²⁺ and Cd²⁺ overestimations due to the presence of residual anionic reagents. Nevertheless, when gels are sufficiently washed, a ~2-fold underestimated concentration of different metallic cations was still reported [9], [10].

Several works for other diffusive gels, *i.e.* pure agarose gels [11] or polyacrylamide gels crosslinked with N,N'-Methylenebisacrylamide [12], have highlighted that part of these misestimations results from a Donnan equilibrium at the solution/diffusive gel interface. Briefly, the presence of non-mobile ionic charges in the gel

induces a conflict between the homogenization of the concentrations of ions at both sides of the gel/solution interface and the respect of the electroneutrality. For example, if the gel carries immobile negative charges (Figure 1a), then a homogenization of concentrations would result in an imbalanced electroneutrality (Figure 1b). This would then imply a migration of ions until the electroneutrality is reached, inducing a heterogeneous repartition of concentrations at the gel/solution interface (Figure 1c). As a result, anions and cations will tend to diffuse forward and backward to reach an equilibrium between the concentration gradient and the electrical gradient, corresponding to the Donnan equilibrium. In this example, the phenomenon would lead to an enrichment of cationic analytes in the gel at the diffusive gel/solution interface [12]. This would correspond to an increased concentration of the analyte at this side of the diffusive gel and thus to a stronger concentration gradient along the gel. As a consequence, the flux of this analyte will be increased, resulting in an overaccumulation and so, in an overestimation of its concentration by DGT. The same issue would occur with anions if the gel carries positive charges. The Donnan potential varies according to the concentration of charges in the gel and to the concentration of ions in solution. Concerning the concentration of ions in solution, the absolute value of the Donnan potential exponentially increases when the ionic strength decreases. When gels are deployed in solutions with a typical ionic strength ($\geq 10^{-3} \text{ mol L}^{-1}$), the immobile charges of the gel are mainly shielded by the major ions from solution, preventing a significant change of the targeted analyte's concentration at gel/solution interface. Several studies, based on gels of agarose or polyacrylamide reticulated with N,N'-Methylenebisacrylamide, showed that the Donnan potential, or its impacts, were almost null at $10^{-2} \text{ mol L}^{-1}$ ionic strength but significant at $10^{-4} \text{ mol L}^{-1}$ ionic strength [11]–[13]. Detailed examples of the consequences of the Donnan effect on DGT measurements can be found in the literature [13], [14].

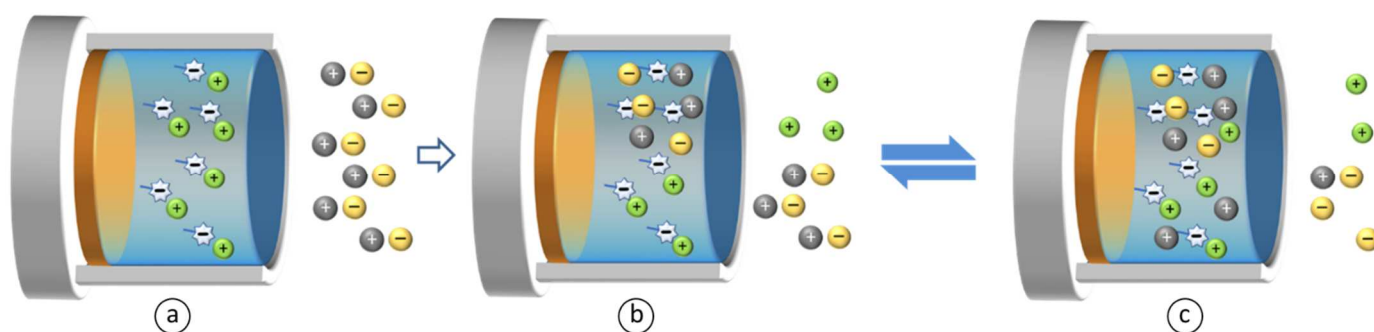


Figure 1 : Distribution of anions and cations at the diffusive gel/solution interface: (a) at initial state, (b) if the diffusion allows an even repartition of concentrations and (c) if the ions migrate to respect the electroneutrality (the green cations are the initial counter-ions of the negatives charges of the diffusive gel, e.g. Na^+ , the grey cations and yellow anions correspond to the analytes of the solution)

When DGT equipped with standard APA gels are used at low ionic strength ($10^{-4} \text{ mol L}^{-1}$), about 2-fold underestimated concentrations were reported for different cations [12]. The existence of a Donnan potential is usually mentioned to explain these results. The underestimation for cations would be explained by the Donnan potential if the APA gel presents positive charges. However, only negative charges were reported in the literature for polyacrylamide gels [15]. More specifically, the hydrolysis of acrylamide during the gel preparation creates negatively charged acrylate functions ($\text{pK}_a = 4.25$). Moreover, it can be reasonably hypothesized that anions would behave oppositely to cations [12], resulting in an overestimation of anions concentration by DGT. Surprisingly, the anions behaviour in the literature does not fit with such hypothesis : Ding *et al.* [16] found that anions sampling at low ionic strength ($< 10^{-3} \text{ mol L}^{-1}$) was not altered whereas Luo *et al.* [17] observed a very low reproducibility and Bennett *et al.* [18] reported a slight ($\leq 20\%$) underestimation of concentrations.

Although alterations of DGT sampling at low ionic strength have been reported for a while, only a limited and scattered knowledge is currently available in the literature for standard APA gels. The role of the Donnan effect on the sampling alteration with these gels, although presented as the most probable explanation, has not been strictly established. Indeed, when anions are considered, their behaviour appears inconsistent from one study to another. Therefore, a more comprehensive evaluation of DGT sampling robustness at low ionic strength is needed to allow relevant interpretations of DGT deployments in poorly mineralized systems. For this purpose, this study presents a direct comparison of both cationic and anionic trace elements sampling over a large pH range (4-8) at two different

ionic strengths : one considered as a reference (10^{-2} mol L⁻¹, commonly used for DGT development and validation) and another sufficiently low (10^{-4} mol L⁻¹) to observe sampling alteration according to the literature.

Material and methods

1. General procedures

All solutions were prepared using ultrapure water (UPW; MilliQ, Sartorius, resistivity >18.2 M Ω) and analytical grade reagents. Stock solutions were prepared from Ni(NO₃)₂ · 6H₂O, Cd(NO₃)₂ · 4H₂O, Pb(NO₃)₂, Cu(NO₃)₂ · 3H₂O, Al(NO₃)₃ · 9H₂O, Cr(NO₃)₃ · 9H₂O, Na₂HAsO₄ · 7H₂O or K₂CrO₄ salts and stored at 4 °C. Working solutions were prepared the day before the experiments in order to allow their equilibration. The pH adjustments were made using 1 mol L⁻¹ HNO₃ or NaOH. All experiments were performed at (20 ± 1)°C.

2. Diffusive gels and DGT devices

0.77 mm thick APA gels (15% acrylamide, 0.3% agarose-derivative crosslinker) and binding layers (Chelex or Zirconium oxide) were purchased at DGT research. Before running the experiments, APA diffusive gels were left for equilibration one night at room temperature in a solution with the same pH and ionic strength than the targeted conditions but without the analytes. Complete DGT devices were constituted by enclosing a Chelex (for cations) or a Zirconium oxide (for anions) binding layer and an APA gel inside a moulding. Unless stated otherwise, no filter membrane was used in DGT assembly or during diffusive cell experiments.

3. Elements flux across the diffusive gel investigation

Six different elements were studied, including four cations (Cd^{II}, Cu^{II}, Ni^{II}, Pb^{II}) and two anions (As^V, Cr^{VI}). Experiments were performed at pH 4, 6 or 8 (adjusted with 1 mol L⁻¹ HNO₃ or NaOH) for all elements with the following exceptions: Pb^{II} was not studied at pH 6 and 8 as well as Cu^{II} at pH 8 since they were prone to precipitate at the tested concentration (1 μ mol L⁻¹).

The element flux across APA was investigated at two distinct ionic strengths. The first one, 10^{-2} mol L⁻¹, is a reference ionic strength where no alteration occurs according to the literature [9]. The second one, 10^{-4} mol L⁻¹, is a low ionic strength where flux alteration has already been demonstrated [8], [9]. The ionic strength of each solution was adjusted by addition of an appropriate amount of sodium nitrate (NaNO₃) to reach the targeted value, taking into account the initial ionic strength set by the solution composition (elements and pH adjustment).

a. DGT method

Triplicate Chelex-DGT and Zirconium oxide-DGT devices were deployed in a solution containing 1 μ mol L⁻¹ of each studied element. After 8 h of exposure, the DGT were disassembled and the binding gels were eluted at room temperature prior to metal quantification. The Chelex binding gels were eluted with 1 mL of 1 mol L⁻¹ HNO₃ during 24 h [19]. The zirconium oxide binding gels were eluted during 4 h with a mix of 0.2 mol L⁻¹ NaOH and 0.5 mol L⁻¹ H₂O₂ [16].

The solution concentration was also determined through a direct measurement. To do so, each solution was sampled every hour for cations and every 4 h for anions and immediately filtered (0.45 μ m nylon syringe filters) and acidified with 2% (V/V) HNO₃.

b. Diffusion cell method

To exclude the possibility of an alteration of the element flux induced by the binding layer, the diffusion cell method was also applied to investigate the ionic strength effect on the element flux in APA gels.

The method used was the diaphragm cell method described by Davison and Zhang [20]. It consists of two Teflon compartments connected by a 1.5 cm diameter cylindrical window where a standard 0.8 mm APA gel was placed [21]. The source compartment was filled (70 mL) with a solution of analytes (1 μ mol L⁻¹ for cations and 30 μ mol L⁻¹ for anions) set at the targeted pH and ionic strength, whereas the receptor compartment was filled with a NaNO₃ solution set at the same pH and ionic strength than the source compartment. Each compartment was stirred during the whole experiment and the pH was measured at the beginning and at the end of experiment. 1 mL

of solution was sampled in the receptor and in the source compartment every hour and immediately acidified with 1% (V/V) HNO₃.

c. Complementary experiment

To further discuss the mechanisms involved at low ionic strength, a complementary experiment was run with two trivalent elements (Al^{III} and Cr^{III}). The sampling of these two elements was evaluated with the DGT method at low ionic strength (10⁻⁴ mol L⁻¹) and pH 4. Experimental conditions were identical as the ones describe above except for the presence of a polycarbonate filter in DGT devices.

4. Element analysis and quality control

The concentrations in solution were determined with an Agilent 7700X ICP-MS using the following internal standards: ¹¹⁵In for As, Cd, Cu, Cr, Ni and ²⁰⁹Pb for Pb. The measured elemental concentrations were in the range 5 to 70 µg L⁻¹. The stability of the ICP-MS measurements was checked with a control solution (10 µg L⁻¹) every 10 samples. Accuracy was verified using a river water reference material (SLRC-5 from the National Research Council, Canada). For anions (ZrO DGT), eluates were diluted 20-fold to reduce Na⁺ concentration (< 5 mmol L⁻¹) and avoid the signal suppression due to its presence [22]. All solutions were acidified prior analysis to reach a 2% (V/V) HNO₃ concentration.

5. Calculations and statistical analysis

After analysing the eluates by ICP-MS, the mass of a given element accumulated in the binding gel (m) was determined by Eq. 1:

$$m = \frac{C V_e}{f_e} \quad (1)$$

where C is the element concentration in the eluate, V_e is the eluent volume and f_e is the elution efficiency. For the cations, an average value of 0.8 was chosen for f_e [19] whereas values of 0.8 and 0.96 were applied for As and Cr respectively [16, p. 201].

When the DGT method was used, the solution concentration estimated by DGT was then calculated for a given element using Eq. 2:

$$C_{DGT} = \frac{m \Delta g}{D t A} \quad (2)$$

where Δg is the thickness of the diffusive gel, D is the diffusion coefficient of the element (taken from [16], [21] and [23]; Table S1), t is the deployment time and A is the area of exposure (3.14 cm²).

For the diffusion cell method, the mass (m) of each element was determined in the acceptor compartment for a given time (t). By plotting m = f(t), the effective diffusive coefficient across the gel (D_{eff}) could be estimated from the slope (k) of the linear regression according to Eq. 3:

$$D_{eff} = \frac{k \Delta g}{C_{source} A_{cell}} \quad (3)$$

where C_{source} represents the average element concentration of the source solution and A_{cell} represents the area of exposure (1.77 cm²).

For all experiments, D and D_{eff} were corrected for the solution temperature (T) using the Stokes-Einstein relationship (Eq. 4), where η is the water viscosity (taken from NIST chemistry WebBook, <http://webbook.nist.gov>):

$$\frac{D_1 T_1}{\eta_1} = \frac{D_2 T_2}{\eta_2} \quad (4)$$

Statistical analyses were performed to determine if there was a significant difference between the two ionic strength for the determined values of C_{DGT} or D_{eff}. First, a Fisher test was used to verify the equality of the variances then, if so, a Student t-test was performed to verify the equality of the means. All tests were conducted with a statistical significance level of p ≤ 0.05.

Results and discussion

1. Cationic species

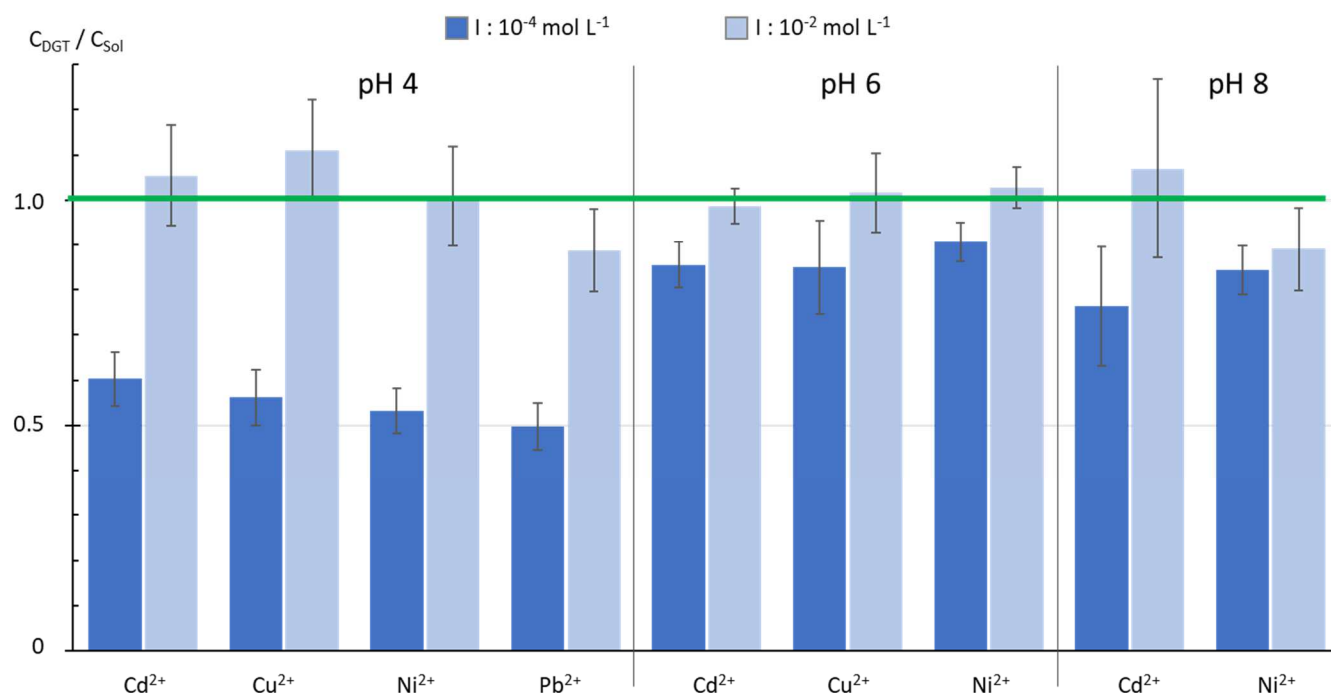


Figure 2 : C_{DGT}/C_{Sol} ratios for cations at pH 4, 6 and 8 for 10^{-4} and $10^{-2} \text{ mol L}^{-1}$ ionic strengths

The estimation of solutions concentrations using DGT (C_{DGT}) is compared to the direct measurements (C_{Sol}) using the C_{DGT}/C_{Sol} ratio (Figure 2). For the standard $10^{-2} \text{ mol L}^{-1}$ ionic strength, C_{DGT} differed from C_{Sol} by less than 15% for all cations, regardless of the pH. This behaviour confirms the adequacy of the parameters used in Eq. 2 to determine C_{DGT} , in particular the diffusion coefficients taken from the literature. When a low ionic strength ($10^{-4} \text{ mol L}^{-1}$) is considered, the solution concentration is systematically underestimated by DGT. However, different behaviours were observed depending on the pH. At pH 4, an underestimation of 40 to 50% was observed for all tested cations. These results are in accordance with the studies of Warnken *et al.* [8] and Scally *et al.* [9] that reported ~50% underestimation for Cd and/or Cu. For higher pH (6 and 8), marginal underestimations were observed ($\leq 16\%$), except for Cd at pH 8 where it reached 24%. However, the C_{DGT}/C_{Sol} ratios were found to be statistically different between 10^{-4} and $10^{-2} \text{ mol L}^{-1}$ ($p < 0.05$) only for Ni and Cd at pH 6 and for Cd at pH 8. It is therefore unclear whether the slight underestimations observed at pH 6 and 8 were linked to an ionic strength effect. Anyway, if an ionic strength effect was to occur at pH 6 and 8, it would be strongly reduced compared to the one evidenced at pH 4. Concerning the consequences for environmental applications, it can thus be assumed that a low ionic strength would marginally impact the cations sampling in natural waters, except for the most acidic waters.

2. Anionic species

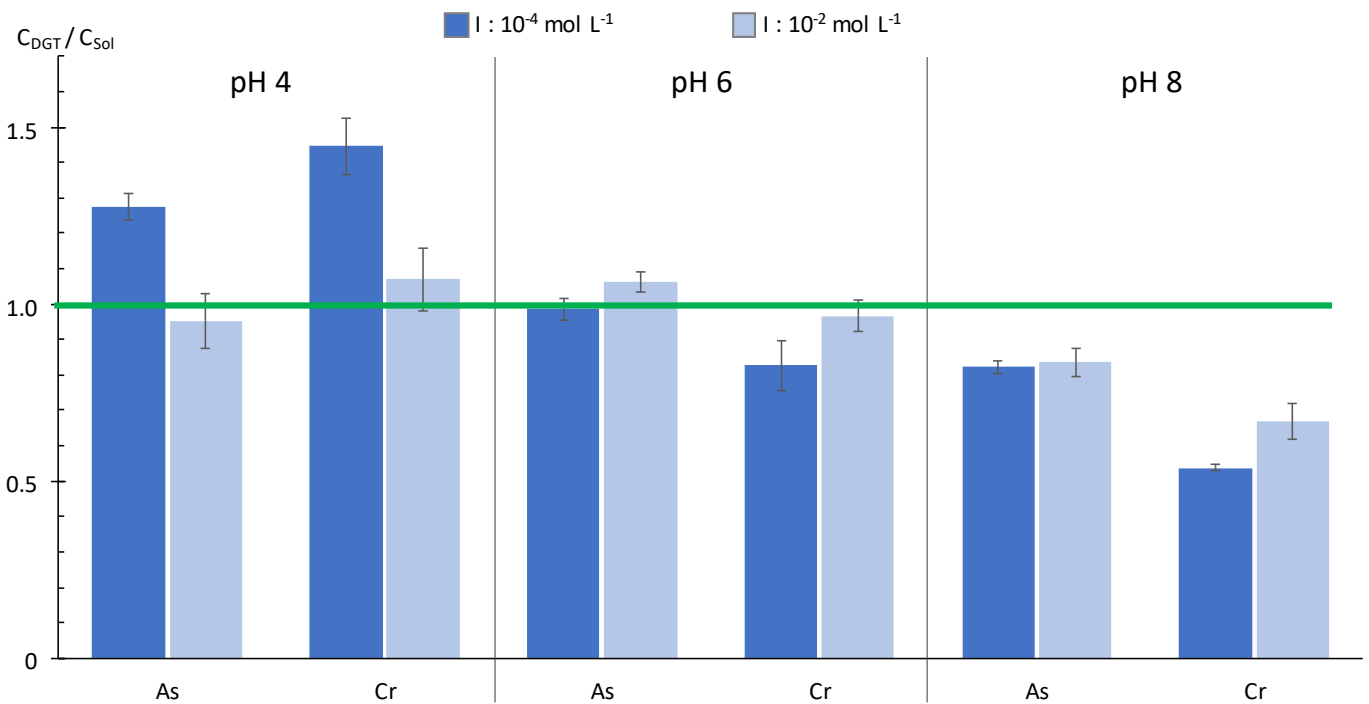


Figure 3 : C_{DGT}/C_{sol} ratios for anions at pH 4, 6 and 8 for 10^{-4} and 10^{-2} mol L $^{-1}$ ionic strengths

For the standard ionic strength (10^{-2} mol L $^{-1}$), the estimations of As^V and Cr^{VI} using DGT were within 7% of the direct measurement at pH 4 and 6 (Figure 3), which confirms the adequacy of the parameters used for both elements in Eq. 2 at these pH. However, at pH 8, an underestimation of 17% or 33% was observed for As^V and Cr^{VI} respectively. For As^V, it may indicate a slight inadequacy of some parameters, but quantification is still acceptable. For Cr^{VI} this limited accuracy is in accordance with Devillers *et al.* [21] who observed an altered sampling of Cr^{VI} above pH 6.

Like for the cations, pH-dependant behaviours were observed for the anions at a 10^{-4} mol L $^{-1}$ ionic strength. At pH 4, the solution concentrations were overestimated by DGT for both As^V and Cr^{VI} with C_{DGT}/C_{sol} ratios significantly higher, by 27% and 45% respectively, than the ones at 10^{-2} mol L $^{-1}$ ionic strength ($p < 0.05$). At pH 6, As^V was accurately quantified whereas Cr^{VI} was slightly underestimated (17%) but no significant difference was observed between the two ionic strengths ($p < 0.05$). Therefore, Cr underestimation could not be attributed to an ionic strength effect. At pH 8, both As^V and Cr^{VI} were underestimated (18% and 46%, respectively) but once again, no significant difference ($p < 0.05$) was found between both ionic strengths. Consequently, no ionic strength effect was evidenced at pH 8. As stated for the 10^{-2} mol L $^{-1}$ ionic strength, the significant underestimation for Cr^{VI} has already been observed by Devillers *et al.* [21]. However, a slight ionic strength effect cannot be definitely excluded at this stage. Indeed, Bennett *et al.* [18] reported a slightly decreased sampling ($\leq 22\%$) of anions (As^V and Se^{IV}) at pH 6.7.

To sum up, a significantly enhanced anion flux is observed at low ionic strength for pH 4 but not for higher pH. At pH 6 and 8, no ionic strength effect could be evidenced, but a slight anion flux decrease is not to be excluded. To our knowledge, this is the first time that an enhanced element flux is reported at low ionic strength for anions. Ding *et al.* [16] reported unaltered anions sampling at low ionic strength (10^{-4} mol L $^{-1}$). Unfortunately, no information is given about the pH of solutions used during their experiments. However, under the hypothesis of no acidification of their solutions, pH should have been above 5 and therefore their results might be in accordance with our study.

3. DGT sampling alteration mechanism

DGT sampling alterations at low ionic strength, at least for cations, have been reported for a long time [5]–[7]. Two main mechanisms have been proposed to explain the low ionic strength effect: an altered diffusion of the analytes due to the diffusion of counter-ions from the binding phase [7] or an altered concentration gradient due to charges in the diffusive gel (*i.e.* Donnan effect) [5]. To discriminate between these two options, the effect of the low

ionic strength was also evaluated at pH 4 and 6 using the diffusion cell method. Because this method does not require the use of any binding layer, it removes the hypothetical intervention of the diffusion of counter-ions from the binding phase as well as the hypothesis of an alteration of the binding properties.

The effective diffusion coefficients determined from the experimental results for cations are presented in Figure 4 (results for anions are not discussed since they were poorly reproducible). At pH 4 and low ionic strength, the effective diffusion coefficients were reduced to ~60% compared to the standard ionic strength, whereas they were not significantly altered at pH 6. This behaviour is in agreement with the results observed using a whole DGT assembly (Figure 2). It can therefore be reasonably assumed that the binding layer does not participate to the flux alterations observed in this study and thus that the ionic strength effect is induced by a phenomenon occurring within the diffusive gel only. In light of these results, the option of a Donnan effect would fit to explain our data.

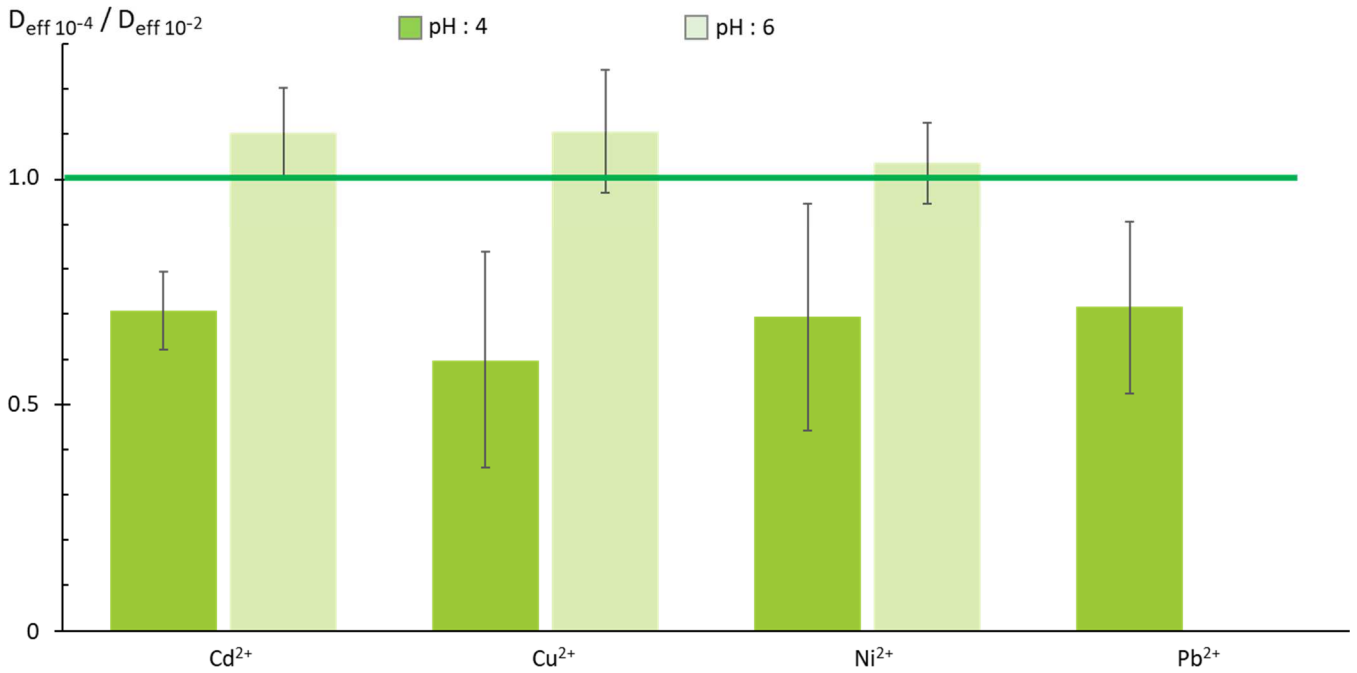


Figure 4: Ratios of the effective diffusion coefficients of cations (D_{eff}) obtained at 10^{-4} and 10^{-2} mol L⁻¹ ionic strengths

Although the Donnan effect has been frequently highlighted to explain DGT sampling alterations at low ionic strength with the standard APA gel [8], [9] no experimental demonstration has been made for this specific gel. Eq. 5 ([11], [24]) describes the Donnan partitioning of the concentrations of a charged species M at the diffusive gel/solution interface (Π_M):

$$\Pi_M = \frac{C_M^{gel}}{C_M^{sol}} = \exp\left(-\frac{z_M F \Psi}{RT}\right) \quad (5)$$

where C_M^{gel} and C_M^{sol} are the concentration of M at the gel and solution side, respectively; z_M is the charge of M; F is the Faraday constant, Ψ is the average difference in potential (Donnan potential); R is the ideal gas constant and T is the absolute temperature.

C_{DGT} corresponding to the virtual concentration that would occur at the diffusive gel/solution interface, it could thus be assimilated to C_M^{gel} . Consequently, Π_M can be estimated by using the C_{DGT}/C_{sol} ratio. From Figure 2, at 10^{-4} mol L⁻¹ ionic strength and pH 4, the average Π_M value for the four studied divalent cations is found to be 0.55 ± 0.05 . According to Eq. 5, this partitioning would correspond to a Donnan potential of 7.6 mV between the diffusive gel and the solution. For such a Donnan potential, Eq. 5 predicts a Π_M value of 1.35 for As^V and Cr^{VI} ($z_M = -1$ at pH 4, Table S2). This value is in agreement with the values estimated from Figure 3 for As^V (1.27 ± 0.04) and Cr^{VI} (1.45 ± 0.08) at 10^{-4} mol L⁻¹ ionic strength and pH 4. The predictability of the C_{DGT}/C_{sol} ratio from Eq. 5 was verified for other charges using Al^{III} and Cr^{III}, with z_M values of, respectively, +2.91 and +2.28 (Table S2) at pH 4 and 10^{-4} mol L⁻¹

ionic strength. The predicted Π_M from Eq. 5 are 0.42 and 0.51, for Al^{III} and Cr^{III} respectively, which is once again in agreement with the measured C_{DGT}/C_{sol} ratio : 0.43 ± 0.04 and 0.51 ± 0.03 . These results highlight that the DGT sampling alteration at low ionic strength could thus be predicted when considering occurrence of a Donnan effect. To our knowledge, this is the first experimental demonstration for APA gels.

Under the Donnan effect hypothesis, only the presence of positive charges would explain the simultaneous observation of a reduced cations sampling and an increased anions sampling at pH 4. A charge density (ρ) of $6.1 \cdot 10^{-5}$ mol kg^{-1} can be estimated from Eq. 6 [24]:

$$\rho = 2I \sinh\left(\frac{yF}{RT}\right) \quad (6)$$

The absence of effect at pH 6 and 8 indicates that these positive charges would disappear or be counterbalanced, strongly suggesting the presence of ionic sites with acid/base properties in the gel. The absence of positive charges at higher pH could result from acidic BH^+/B type sites with a pK_a value around 4. In this hypothesis, the complete deprotonation at pH 6 or above would result in the absence of positive charges in the gel. Another possibility would be the simultaneous presence of positive and negative charges in the gel. In this scenario, the positive charges are supposed permanent (not pH-dependent). Polyacrylamide gels are known to bear negative charges due to acrylates groups (AH/A^- , $pK_a = 4.25$) resulting from amides hydrolysis [15]. When pH raises above 4, acrylates groups are mainly negatively charged and can counter the permanent positive charges, explaining the pH dependency.

Negative charges have been reported in polyacrylamide gels crosslinked with N,N'-Methylenebisacrylamide [12] but, to date, no positive charge has been reported or identified. The only difference between these gels and the APA gels studied here being the crosslinker, it could be hypothesized that the positive charges responsible for the ionic strength effect in the APA gels are carried by the agarose-derivative crosslinker. Only few information is available on this patented crosslinker, however the approximative structure given in Davison *et al.* [25] does not show any obvious source of positive charges. The exact origin of the Donnan effect in APA gels is thus still unclear.

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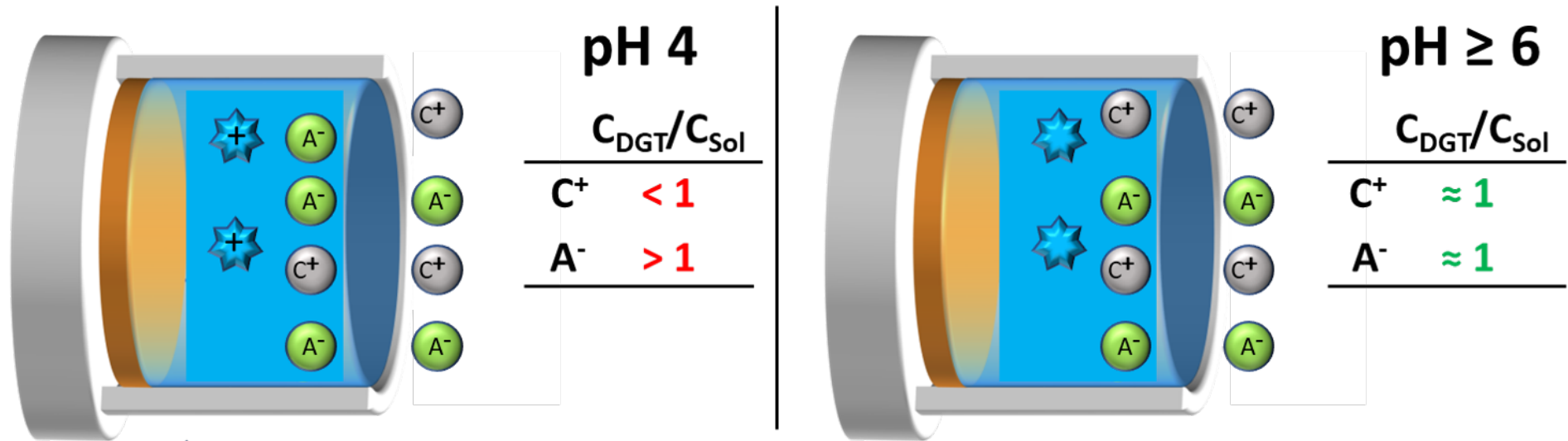
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Effect of low ionic strength ($< 10^{-3} \text{ mol L}^{-1}$)



 Hypothesized pH-dependent positive charges of the APA gel