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A systematic determination of diffusion coefficients of trace elements in open and restricted diffusive layers used by the diffusive gradients in a thin film technique

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Abstract

A systematic comparison of the diffusion coefficients of cations (Al, Cd, Co, Cu, Mn, Ni, Pb, Zn) and oxyanions (Al, As, Mo, Sb, V, W) in open (ODL) and restricted (RDL) diffusive layers used by the DGT technique was undertaken. Diffusion coefficients were measured using both the diffusion cell (D_{cell}) method at pH 4.00 and the DGT time-series (D_{DGT}) method at pH 4.01 and 7.04 (pH 8.30 was used instead of 7.04 for Al) using the Chelex-Metsorb mixed binding layer. The performance of Chelex-Metsorb as a new DGT binding layer for Al uptake was also evaluated for the first time. Reasonable agreement was observed between D_{cell} and D_{DGT} measurements for both ODL and RDL, except for V and W. The ratios of D_{cell}/D_{DGT} for V of 0.44 and 0.39, and for W of 0.66 and 0.63 with ODL and RDL respectively, were much lower due to the formation of a high proportion of polyoxometalate species at the higher concentrations required with the D_{cell} measurements. This is the first time that D values have been reported for several oxyanions using RDL. Except for Al at pH 8.30 with ODL, all D_{DGT} measurements were retarded relative to diffusion coefficients in water (D_w) for both diffusive hydrogels. Diffusion in RDL was further retarded compared with ODL, for all elements (0.66-0.78) with both methods. However, the degree of retardation observed changed for cations and anions at each pH. At pH 7.04 cations had a slightly higher D_{DGT} and oxyanions had a slightly lower D_{DGT} than at pH 4.01 for both ODL and RDL. It is proposed that this is due to partial formation of acrylic acid functional groups ($pK_a \approx 4.5$), which would be fully deprotonated at pH 7.04 (negative) and mostly protonated at pH 4.01 (neutral). As Al changes from being cationic at pH 4.01 to anionic at pH 8.30 the results were more complex.

Keywords: metal diffusion coefficients; passive sampler measurements; diffusion cell measurements; open diffusive gel; restricted diffusive gel; retarded diffusion

1. Introduction

In the last two decades the diffusive gradients in a thin film (DGT) technique has demonstrated its capability as an effective kinetic passive sampler for selective measurement of many elements in water [1-5]. An adsorbent material embedded in a polyacrylamide hydrogel (binding layer) accumulates reactive analyte species after they diffuse through another layer of known thickness. This diffusive layer (Δg , cm) usually consists of a protective membrane and a polyacrylamide hydrogel [2]. The concentration (C, ng mL⁻¹) of analytes in the measured solution can be calculated using Equation 1 [2], where D (cm² s⁻¹) is the diffusion coefficient of the element species in the hydrogel; t (s) is the deployment time; A (cm²) is the area of the gel exposed to the solution; and, M (ng) is the mass of accumulated analytes on the binding gel, determined by eluting the analytes from the binding layer [6-9] corrected for the elution efficiency.

$$C = M\Delta g / DtA \quad (\text{Eq. 1})$$

For elements with complex speciation and multiple labile forms, such as many cationic metals, the DGT concentration provides an operational measure of the free metal ions required to produce the accumulated mass [10]. For elements with one or two reactive species only, such as some oxyanions, the estimated concentration can be interpreted directly [7]. The diffusive boundary layer (DBL), a layer of quiescent water at all surfaces through which mass transport occurs only by diffusion, also needs to be determined for accurate DGT measurements as it can vary considerably (0.023-0.065 cm) [11-13].

The selectivity of DGT measurements can be regulated by using different binding layer materials [4, 6, 14] or by using a hydrogel with a different pore size as the diffusive layer [15]. For the latter approach, the diffusion coefficients of free metals change with differing pore sizes but this can also effectively exclude larger species such as complexes with natural

organic matter and colloids [15, 16]. Although various diffusive gels have been used previously, most applications have employed a type of polyacrylamide hydrogel with pore sizes >5 nm (open diffusive layer, ODL) [2, 13, 17], which uses a proprietary agarose-based cross-linker [4]. Some investigators, however, have used polyacrylamide gel with a bis-acrylamide cross-linker, which results in smaller pore sizes <1 nm (restricted diffusive layer, RDL) [10, 18, 19]. The RDL is thought to allow measurement of only free ions and small inorganic complexes, while the ODL also allows diffusion of many organic complexes [10, 20].

For determination of metal concentrations in solution by the DGT technique, with either ODL or RDL, it is essential to have an accurate estimation of analyte diffusion coefficients (D) in each diffusive layer. This then allows DGT measurements to be made without further calibration or validation. These D values for metals and oxyanions in the ODL have been determined using diffusion cell [15] or DGT time-series [17] methods. Few studies have measured the diffusion coefficient of analytes in the RDL [21, 22]; these have only used the diffusion cell method and the results seem to be highly variable. Consequently, this study has systematically determined and compared the diffusion coefficients, using both the diffusion cell and time-series DGT methods, for a wide range of cations (Al, Cd, Co, Cu, Mn, Ni, Pb, Zn) and oxyanions (Al, As, Mo, Sb, V, W) with both ODL and RDL. The recent mixed binding layer (MBL, containing both Chelex and Metsorb) described by Panther *et al.* [23] was used for the DGT time-series measurement of diffusion coefficients at both acidic and neutral pH to determine the effect of speciation changes on the diffusion coefficients. The performance of this DGT-MBL was also evaluated for Al uptake, based on the findings of Panther *et al.* [9] that DGT-Chelex measures Al in weakly acid waters and that DGT-Metsorb measures Al in seawater and other slightly basic waters. These data will support many

subsequent studies in which these metals are measured and fill a critical gap in the DGT research literature.

2. Experimental

2.1. General procedures

All plastic equipment was soaked in 10% nitric acid (AR grade, Merck) for at least 24 hours prior to rinsing with deionised water (Milli-Q Element, Millipore, >18.2 M^Ω cm⁻¹). All experiments were done in an ISO Class 6 (ISO 14644-1) clean room, wearing powder free latex gloves (Microtouch Dermaclean, Ansell) and hydrogel casting was conducted in a fume hood. Stock solutions (1000 mg L⁻¹) were prepared freshly for each element by dissolving the relevant salt (all AR grade) in deionised water. To minimize the risk of metal precipitation at such high concentrations, none of the stock solutions were mixed. Aluminium nitrate [Al(NO₃)₃.9H₂O], manganese chloride [MnCl₂.4H₂O], cobalt nitrate [Co(NO₃)₂.6H₂O], nickel chloride [NiCl₂], copper chloride [CuCl₂.2H₂O], zinc chloride [ZnCl₂], cadmium nitrate [Cd(NO₃)₂.4H₂O], lead nitrate [Pb(NO₃)₂], ammonium metavanadate [NH₄VO₃], sodium arsenate [Na₂HAsO₄.7H₂O], sodium molybdate [Na₂MoO₄.2H₂O], potassium antimonate [KSb(OH)₆] and sodium tungstate [Na₂WO₄.2H₂O] were used to prepare the required stock solutions.

2.2. Preparation of hydrogels

2.2.1. Diffusive layers

ODL and RDL hydrogels, with a final thickness of 0.08 cm, were prepared according to Scally *et al.* [21] with minor modifications. For ODL hydrogels, a gel stock solution was made by mixing 23.75 ml of Milli-Q water, 18.75 ml of 40% acrylamide solution (Bio-Rad) and 7.5 ml of proprietary agarose-based cross-linker (DGT Research Ltd., UK). For each 10 ml of gel stock solution, 70 µl of fresh ammonium persulphate solution (10%, Chem-Supply) and 25 µl of N,N,N,N-tetramethylethylenediamine solution (TEMED, Bio-Rad) were added, while being stirred vigorously. The solution was immediately cast between two acid washed glass plates (separated by a 0.05 cm thick plastic spacer) and placed in the oven at 45°C for 45-60 minutes. Following polymerisation, the gels were rinsed in deionised water for 24 hours (water changed at least three times) to allow unreacted reagents to diffuse out of the gels. The hydrated diffusive gels (~0.08 cm) were stored in NaNO₃ solution (0.01 mol L⁻¹, Chem-Supply) at room temperature.

For RDL hydrogels, a gel solution was prepared by mixing 40% acrylamide/bisacrylamide solution (Sigma-Aldrich) in a 1:1.66 ratio with chilled Milli-Q water. Then 70 µl of 10% ammonium persulphate solution and 20 µl of TEMED solution were added for every 10 ml of gel solution whilst stirring vigorously. Gel solution was cast between two acid washed glass plates separated by a 0.075 cm thick spacer and allowed to polymerise at room temperature for 20-30 minutes. After rinsing in deionised water for 24 h (water changed at least three times), the gels were stored in 0.01 mol L⁻¹ NaNO₃ solution at room temperature.

Three hydrated ODL and RDL were selected randomly, a filter membrane placed on one face (as in the DGT application), and the overall thickness of Δg was measured using digital vernier calipers [15].

2.2.2. Mixed binding layer

A new binding layer described by Panther and co-workers [23] was used in this study for simultaneous measurement of cations and oxyanions. The binding gel consists of a mixture of Chelex and Metsorb resins. Metsorb was cleaned with HNO_3 and NaOH prior to mixing with Chelex [9]. 2 g of dry Chelex-100 (sodium form, 200-400 mesh, Bio-Rad) and 1 g of cleaned Metsorb (Graver Technologies, USA) were used per 10 ml of acrylamide gel stock. 60 μl of ammonium persulphate (10%) and 20 μl of TEMED solutions were added while being stirred vigorously. The solution was then immediately cast between acid-washed glass plates (separated by a 0.025 cm thick plastic spacer) and polymerised for 1 h at 45°C. The gels were rinsed in deionised water for 24 h (three times water change) and hydrated binding gels (0.04 cm thick) were stored in deionised water at <4°C.

2.3. Diffusion coefficient measurements

2.3.1. Time-series DGT deployments

DGT samplers (purchased from DGT Research Ltd., Lancaster, UK) were assembled as described previously [2]. The DGT samplers were deployed in test solutions containing 20 $\mu\text{g L}^{-1}$ of each analyte. Large polyethylene containers (7 litres) were used as exposure chambers to minimize changes in concentration caused by DGT uptake. The experiments were carried out separately at pH 4.01 and pH 7.04 [0.01 mol L^{-1} NaNO_3 /0.004 mol L^{-1} $\text{Mg}(\text{NO}_3)_2$] using mixed metal solutions. Magnesium nitrate was added to the mixed solution in order to minimize metal surface adsorption [24]. Aluminium was not included in the pH 7.04 solution and a separate experiment was performed at pH 8.30 [0.01 mol L^{-1} NaNO_3 /0.0005 mol L^{-1} NaHCO_3 as buffer] to avoid formation of insoluble aluminium hydroxide at pH 6-7. To

provide a well-mixed solution and ensure a constant fluid velocity during the experiment, the solutions were stirred continuously. Before deploying the DGT samplers, the solutions were left for 72 h to stabilize and the pH was adjusted to the desired values by adding diluted HNO₃ or NaOH. pH was measured using a Mettler-Toledo pH meter (FiveGo, FG2). Four sets of triplicate DGT-MBL with ODL or RDL were deployed in the solutions and retrieved every 8 hours up to 32 h. The DGT samplers were then rinsed with deionised water and stored at <4°C until analysis (Section 2.4).

A linear regression and equation is obtained between the diffused mass and time. The slope of this line was used to calculate the effective diffusion coefficient for each metal and oxyanion in the ODL and RDL (Equation 2) [6]:

$$D = \text{slope} (\Delta g) / CA \quad (\text{Eq. 2})$$

where C represents the average metal concentration over time in the test solution. The thickness of DBL was not factored in diffusion path, assuming the solutions were well stirred. Measured diffusion coefficients were corrected for temperature using the Stokes-Einstein equation [2]. Upon deployment and removal of each set of DGT samplers, 0.45 µm filtered and unfiltered grab samples of the test solution were collected, acidified to 2% (v/v) HNO₃ (Baseline, High Purity Standards) and stored at <4°C to check for possible analyte precipitation. pH and temperature of the test solutions were measured with each grab sample being collected (24±1°C for pH 4.01 and 26±1°C for pH 7.04 and 8.30).

2.3.2. Diffusion cell

The procedure for the measurement of diffusion coefficients of free metal ions through polyacrylamide hydrogels using a diffusion cell apparatus has been described previously [8, 15]. Two 70 ml Perspex diffusion cell compartments with a 1.60 cm diameter window were

clamped together with a diffusive gel (0.08 cm thickness) and a filter membrane (0.01 cm thickness) in the window. The compartment to which the membrane faced became the source compartment. To prevent excessive compression of the gel, a plastic spacer of thickness 0.05 cm was also placed between the compartments but not overlapping with the gel. Both compartments were filled with 70 ml of 0.01 mol L⁻¹ NaNO₃ solution (pH 4.00). The source compartment had a final concentration of 5 mg L⁻¹ of either cations (Al, Cd, Co, Cu, Mn, Ni, Pb, Zn) or oxyanions (As, Mo, Sb, V, W). To minimize the risk of precipitation at these necessarily high concentrations, cation and oxyanion solutions were measured separately for each diffusive gel type. Therefore, four separate diffusion cell measurements were done to determine diffusion coefficients for each element in the ODL and RDL. The solutions in both compartments were stirred continuously by a magnetic stirrer. After allowing 20 min for diffusion to reach a steady state, 0.5 ml samples were taken from both sides at intervals of 10 minutes over a period of 2 h. These samples were preserved by adding HNO₃ to a final concentration of 2% and stored at <4°C. Following analysis, the diffusion coefficient of each analyte in the ODL and RDL was calculated from the slope of the accumulated mass versus time using Equation 2, assuming the thickness of DBL on each side of the gel is negligible. During the experiments, pH was checked regularly and temperature was maintained at 22±1°C for cations and 21±1°C for oxyanions.

2.4. Sample analysis and method detection limits

After removal from the DGT samplers, the elements in the MBL were eluted in 1 ml of 1 mol L⁻¹ HNO₃ and then, after rinsing in deionised water, 1 ml of 1 mol L⁻¹ NaOH, each for 24 h [23]. To elute Sb, the gels were then immersed in 1 ml of 1 mol L⁻¹ NaOH / 1 mol L⁻¹ H₂O₂ for another 24 h [8]. All the eluents were combined, diluted 10-fold and acidified to 2%

HNO_3 prior to analysis by ICP-MS. Solution grab samples were analysed directly without a dilution step.

The accumulated mass of analytes (M) on the Chelex-Metsorb mixed binding gel was calculated from analyte concentration in the eluent (C_e) using Equation 3 [2].

$$M = C_e (V_e + V_g) / f_e \quad (\text{Eq. 3})$$

Where V_e is the volume of the eluent, V_g is the volume of the gel (0.2 ml) and f_e is the elution factor for each element. The elution factors used in this study (except for Al) were those reported for the MBL by Panther *et al.* [23]. In terms of Al, an elution factor of 0.845 (using an average of Chelex and Metsorb gels) was utilized [9].

Elemental analyses were performed using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500a). All analytical standards for ICP-MS analysis were prepared with a multi-element standard (High Purity Standards) in 2% (v/v) HNO_3 , which was the same matrix as the DGT samples. Every 15-20 samples, a quality control blank was measured followed by a $10 \mu\text{g L}^{-1}$ quality control standard (High Purity Standards). No significant change in ICP-MS sensitivity or carry-over was observed. Sc, Y and In were added to each sample as internal standards ($100 \mu\text{g L}^{-1}$, High Purity Standards) to account for instrument drift. The recoveries of internal standard were within 88-99% of the measurements in the calibration standards and the quality control standards.

To monitor any contamination during synthesis and handling, DGT blanks were prepared in the same way as deployed DGT samplers and subjected to all procedures except for the deployment. Blanks were conducted in triplicate for each type of diffusive gel (total = 6) and mass measurements were calculated using Equation 3. The calculated blank masses were

subtracted from the accumulated mass of each analyte on the deployed DGT samplers to obtain the corrected mass values (ng).

Method detection limits (MDL, ng) were determined for all analytes (Table 1) as three times the standard deviation of the blanks [8, 25, 26]. The detection limits were also converted to concentration (ng mL^{-1}) using the diffusion thickness (Δg , 0.09 cm including diffusive gel and filter membrane), deployment time (t , 32 h at 25°C), gel area (A , 3.14 cm^2) and diffusion coefficients, obtained from the current study (Table 2), with either open (D_{ODL}) or restricted (D_{RDL}) diffusive layers.

2.5. Speciation modelling

The speciation program Visual MINTEQ (ver 3) [27] was used to determine the major cation and oxyanion species present in all solutions (in diffusion cell and DGT time-series experiments) to assist with interpretation of the results.

3. Results and discussion

3.1. Speciation of solutions for diffusion coefficient measurements

The dominant species in each solution for the time-series DGT and diffusion cell measurements of diffusion coefficients are given respectively in Table S1 and Table S2 in the Supporting Information (SI). These data indicate that each element was effectively 100% in solution for each measurement of D. This was supported by the ratios of filtered vs. unfiltered samples (0.94-1.04) measured for the DGT deployment solutions (Table S1). The cations and oxyanions were measured separately for the diffusion cell method, as higher concentrations

were required. Al was measured separately at pH 8.30, instead of at pH 7.04, for the DGT method to ensure Al was in a soluble form (Al(OH)_4^-).

3.2. DGT blanks and method detection limits

Table 1 shows the average DGT gel blanks and method detection limits (MDL) calculated for each element using DGT-MBL with both ODL and RDL. To lower the blank values, Metsorb was cleaned with 1 mol L⁻¹ HNO₃ and 1 mol L⁻¹ NaOH prior to mixing with Chelex [9] as high detection limits have been reported for Mn, Ni, Cu, Zn and V when using unwashed Metsorb [23]. All method detection limits in our study (except for Al and Zn) were below 0.7 ng mL⁻¹ and in most cases <0.2 ng mL⁻¹, indicating low-level contamination of MBL. These estimated detection limits are in line with the previously reported MDL values for DGT-MBL [23], DGT-Metsorb [8, 26] and DGT-ferrihydrite [28]. The higher DGT blanks for Al and Zn are due to their presence in Metsorb, even with the acid-washing step, and are responsible for the higher MDL for these elements. Nonetheless, these MDL are still low for these elements compared to their likely concentrations in many waters. The MDLs were quite similar for ODL and RDL. The MDL for Al was higher for ODL and Zn for RDL; this is likely to be due to random variation in the blanks.

3.3. Diffusion coefficient measurements using time-series DGT deployments

The effective diffusion coefficients determined by the time-series DGT deployments (D_{DGT}) of all elements measured in either ODL or RDL at different pH are shown in Table 2. The previously published diffusion coefficients with ODL using this method are given for comparison. This is the first time that D_{DGT} values have been reported for RDL. The effect of

the filter membrane is included in the effective diffusion coefficients as the 0.45 μm pore size of the membrane is likely to have minimal effect on the diffusion coefficient of the measured species.

The results of accumulated mass versus time for each element in either ODL or RDL at each pH are shown in Figure 1 and Figure S1 for pH 7.04/8.30 and pH 4.01, respectively. The capability of the Chelex-Metsorb mixed binding layer for appropriate uptake of a wide range of cations and oxyanions has been confirmed previously [23]. However, aluminium uptake by DGT-MBL has not been investigated previously and this is the first validation of this measurement. Good linearity ($R^2 = 0.9991$ for ODL and $R^2 = 0.9973$ for RDL at pH 8.30; $R^2 = 0.9938$ for ODL and $R^2 = 0.9974$ for RDL at pH 4.01) was observed for Al over the 32 h experiment, indicating the suitability of this binding layer for DGT measurements of Al. Excellent linearity ($R^2 \geq 0.9901$ for ODL and $R^2 \geq 0.9918$ for RDL at pH 7.04; $R^2 \geq 0.9931$ for ODL and $R^2 \geq 0.9926$ for RDL at pH 4.01) up to 32 h deployment was also observed for other analytes. This means that Equation 2 can be applied to determine D_{DGT} for each element. The slopes of the regression lines from Figure 1 and Figure S1 (equations not shown) were used to calculate the diffusion coefficients (Table 2). These calculations were based on average concentrations in the solution, which at pH 7.04 and pH 4.01 ranged between 13.75-21.79 (ng mL^{-1}) and 20.30-24.94 (ng mL^{-1}), respectively. Aluminium had an average solution concentration of 21.57 (ng mL^{-1}) at pH 8.30. For all analytes, the average concentration at the end of the experiment was within 10% of the initial concentration.

ODL diffusion coefficient results for cations are generally within 2%-17% of literature D values (Table 2). The D_{DGT} values for Al at pH 8.30 and pH 4.01 are within 8% and 2%, respectively, of the values reported by Panther *et al.* [9] at pH 8.35 and pH 5.05 using Metsorb-DGT. Garmo and co-workers [17] calculated the Al diffusion coefficient at pH 5.25 to be $5.10 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ using DGT-Chelex, which is comparable with our results at pH 4.01.

For Zn and Pb, although our values are very close to those of Panther *et al.* [23], they are 31% higher and 23% lower, respectively, than the values obtained by Garmo and co-workers [17]. It is promising that our diffusion coefficients (D_{DGT}) for oxyanions in the ODL are in good agreement with previously reported values. A study carried out by Osterlund and co-workers [28] has reported relatively similar diffusion coefficients (within 15%) for As (V), Mo (VI), Sb (V) and W (VI) at pH 4-8. However, some investigators have published diffusion coefficients 20-30% lower for V [26, 28, 29]. The possible sources of this range of results include measurement uncertainties, differences in solution pH and concentrations resulting in differences in element speciation, diffusive boundary layer (DBL) effects, the thicknesses of the diffusive gel and differences in gel casting methods between laboratories.

The ratios of the diffusion coefficient of each element in RDL compared to that in ODL were similar for cations and oxyanions at each pH (<6% difference). The ratios of the RDL to ODL lie between 0.69 and 0.78 for cations and 0.66-0.77 for oxyanions, which are similar to the previously reported data by Scally *et al.* [21] (ratios between 0.62 and 0.72). These results confirm that diffusion of free ions through RDL is retarded relative to ODL. Since both positive and negatively charged species are experiencing a similar slowing of their diffusion, the retardation of RDL relative to ODL is likely to be related to the smaller pore size of the RDL (\approx 1 nm), as suggested by Scally *et al.* [21]. However, since the radius of analyte ions are smaller (<0.300 nm) than the RDL pore size, the mechanism of retardation is likely due to the greater diffusional path length (tortuosity) within RDL compared with ODL (\approx 5 nm pore size).

The calculated diffusion coefficients (D_{DGT}) in either ODL or RDL are compared with the diffusion coefficient of free metal ions in water (D_w) where such data exist [30]. These ratios lie between 0.73 and 0.90 in ODL and 0.57-0.70 in RDL for cations, which are in good agreement with previous observations [21]. Oxyanions had ratios of D_{DGT} to D_w between

0.62 and 0.82 in ODL (not including Al) and 0.43-0.60 in RDL, which are consistent with results of Price *et al.* [26] and Luo *et al.* [29] for ODL and Uher *et al.* [22] for RDL. The average ratio (D_{DGT}/D_w) using diffusion coefficients in ODL for cationic metals was 0.82 ± 0.05 ($n=15$) and for oxyanions was 0.70 ± 0.06 ($n=8$), not including the results for Al at pH 8.30 (which were much higher perhaps due to the small radius of Al ions) and V (for which we could not find a published D_w). The average ratios (D_{DGT}/D_w) using diffusion coefficients in RDL was 0.62 ± 0.05 ($n=15$) for cations and 0.49 ± 0.06 ($n=8$) for oxyanions. These findings suggest that diffusion of oxyanion species overall is retarded more than for cations.

This retardation of oxyanions relative to cations is interesting and consistent with the presence of a negative charge on the polyacrylamide hydrogels. Such an effect was used deliberately by Panther *et al.* [31] who impeded diffusion of arsenate anions with a negatively charged Nafion membrane, relative to neutral As(III) species. Acrylamide functional groups are known to undergo partial hydrolysis to acrylic acid groups which are negatively charged when deprotonated [32]. This reaction occurs quickly at basic pH but could still happen to some extent in neutral solutions with storage and may mean that storage time of the polyacrylamide hydrogels becomes an important factor. In this study all diffusive gels were used within 1 month of being prepared. On the other hand cationic free ions would undergo enhanced diffusion in the presence of negative charges. We should note that this is not due to the Donnan effect, which has been investigated for DGT previously [33, 34], as the ionic strength of the solution used for these measurements is too high [3]. A detailed discussion of the state of knowledge concerning the effect of charges in diffusive gels, including how to minimize them, and on DGT measurements has been provided by Davison and Zhang [3].

Further evidence in support of this proposed effect was observed with the D_{DGT} measurements for each element at the two pH values. All cations had a lower D_{DGT} at pH

4.01 ($4.28\text{-}7.70 \times 10^{-6}$ vs $5.43\text{-}8.13 \times 10^{-6}$ at pH 7.04) and all oxyanions had a higher D at pH 4.01 ($5.96\text{-}8.92 \times 10^{-6}$ vs $5.59\text{-}8.24 \times 10^{-6}$ at pH 7.04); the ratios of D_{DGT} at pH 4.01 and pH 7.04 (8.30 for Al) are given for each element in Table 3 including measurement uncertainties. The effect was very small but consistent, which makes it unlikely to be due to random errors in the measurement. Acrylic acid functional groups have a pK_a of about 4.5 [32] and would therefore be fully deprotonated at pH 7.04 and above, with the strongest negative charge. These functional groups would be largely protonated at pH 4.01 and thereby have a very slight negative charge only. Therefore, oxyanion species would be retarded more at neutral pH than at pH 4.01, which is consistent with the results (Table 2). Conversely, cations are observed to have higher effective diffusion coefficients at neutral pH (Table 2) consistent with an enhanced diffusion effect due to the partial negative charge. The ODL and RDL are both affected to a similar extent within the measurement uncertainty (Table 3), which makes sense as they are both polyacrylamide hydrogels that differ only in the cross-linker used.

Al experiences a major change in speciation, with Al^{3+} predominant at pH 4.01 (94%) and Al(OH)_4^- predominant at pH 8.30 (99%), the biggest change in speciation for all the elements studied (Table S1). Assuming the negatively charged Al(OH)_4^- species are less hydrated than Al^{3+} species, the size of the diffusing Al species at pH 8.30 is expected to be smaller than pH 4.01 [9]. Consequently, the D values measured for Al change substantially between pH 4.01 and 8.30 (a ratio of 0.73 with ODL and 0.77 with RDL), while the effect is less than 13% for all elements. A consequence of this observation is that D values may vary somewhat from pH 4.5 to 5.5 from those reported here, but should vary little from 5.5 to neutral pH, assuming there is no major change in element speciation. Nevertheless, using the different D values reported here will increase the accuracy of DGT measurements. It should be noted that this effect may become more pronounced if the hydrogels are stored for longer times.

3.4. Diffusion coefficient measurements using diffusion cell

The diffusion coefficients obtained from the diffusion cell experiment (D_{cell}) are presented in Table 4. These are the first D_{cell} measurements made for several oxyanions. Separate plots of mass over time were obtained for each analyte in ODL ($R^2 \geq 0.9919$) and RDL ($R^2 \geq 0.9942$) and the slopes were used to determine the diffusion coefficients using Equation 2 (see Figure S2 and Figure S3).

There is reasonable agreement (<17% difference) between our D_{cell} values and earlier measurements with ODL for all elements (except for V and W). The D_{cell} results for V and W were clearly different to literature values - up to 46% and 38% lower, respectively. These discrepancies, however, may be due to the different pH or analyte concentrations at which the experiments were carried out; for instance, our D_{cell} experiment was conducted at pH 4.00 while other investigators have used pH 6 or 7 for their experiments. These differences may affect the speciation of elements. Table S2 indicates that both V and W had major fractions of polyoxometalate species (V was 23% $H_3V_{10}O_{28}^{3-}$ and W was 72% $HW_7O_{24}^{5-}$). Panther *et al.* [23] obtained a diffusion coefficient of $3.75 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for V at pH 4.01 using the same diffusion cell, which is very similar to the value obtained in this study ($3.88 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). At lower pH the fraction of polyoxometalate species may increase.

The D_{cell} values obtained in RDL for metals are within 18% of the values reported from other studies [21, 22, 35]. The variations in our D_{cell} and literature values might arise from discrepancies in solution pH and composition, measurement of the diffusion area between two compartments of the diffusion cell and the dialysis cell construction, which may lead to differing DBL thickness. The ratio of the RDL values to the ODL values ranged from 0.68 to 0.75 (Table 4), which are generally consistent with ratios of D values obtained by the DGT time-series method (Table 2) and are similar to the previously reported data [15, 21]. The

average ratio of diffusion coefficients (RDL/ODL), regardless of method or pH, for all cationic metals was 0.74 ± 0.03 ($n=23$) and for all oxyanionic elements was 0.71 ± 0.03 ($n=16$), with Al as a cation at pH 4.01 and an anion at pH 8.30. These results confirm that the retardation effect of increased tortuosity in the RDL is very consistent and could perhaps be used to estimate a diffusion coefficient for the RDL from the known ODL diffusion coefficient.

Table 4 provides a comparison between the two methods used for diffusion coefficient measurements (D_{cell} and D_{DGT}) at $pH \approx 4$. It is immediately apparent that all the ratios of D_{cell}/D_{DGT} are less than 1 (0.77-0.99, excluding V and W), which strongly suggests that values of D determined by diffusion cell method tend to be lower than those determined from DGT time-series results. This may be explained by the presence of a DBL on each side of the cell membrane, due to the cell design [6, 8]. Even though both solutions have a fast stirring rate, the construction of such cells often results in a zone at each side of the membrane that may produce DBLs. Moreover, the effect of lateral diffusion within DGT samplers, which results in a higher accumulated mass of analyte, could also contribute to higher D_{DGT} values and has been reported by other investigators [8, 11]. However, this effect is likely to be very small (<5%).

For the ODL, D_{cell}/D_{DGT} ratios are within 5% for several of the cationic metals (Al, Cd, Cu, and Mn) and several more have ratios of approximately 0.9 (Co, Ni, Pb and Zn). As is also at 0.9, Mo and Sb are approximately 0.8 and V (0.44) and W (0.66) have very low ratios. It is likely the higher concentration solutions required for the diffusion cell measurements of D (5 mg L^{-1} compared with $20\text{ }\mu\text{g L}^{-1}$ for the DGT measurement), resulting in higher proportion of polyoxometalate species for V and W (Table S2), are responsible for this observation [23]. A change in the speciation may also be responsible for the Mo result, although the speciation

was determined to be the same for Sb, which had similar ratios. The ratio of D values obtain between the two methods for RDL was quite similar (within 10%) for all analytes.

4. Conclusions

This is the first study to systematically determine diffusion coefficients for a wide range of cationic and oxyanionic elements for the ‘open’ and ‘restricted’ hydrogels used as diffusive layers by the DGT technique, using both the DGT time-series (at pH 4.01 and 7.04; 8.30 for Al) and the diffusion cell method (at pH 4.00). In several instances this is the first effective diffusion coefficient data reported for RDL (D_{DGT} for any elements and D_{cell} for several oxyanions). The effect of using the RDL with its smaller pore size and therefore greater tortuosity was quite consistent. The average ratios of diffusion coefficients (RDL/ODL) are consistent enough to perhaps be used to estimate a diffusion coefficient for the RDL, in the absence of actual data, from the known ODL diffusion coefficient. This study also confirmed the suitability of Chelex-Metsorb as a new DGT binding layer for Al, especially for deployment in waters in which Al^{3+} is not predominant.

The two methods for determining diffusion coefficients at pH 4 gave reasonable agreement using ODL for all cations and for As (ratios of 0.86-0.99 for D_{cell}/D_{DGT}). The D_{cell} results seem to be marginally lower than the D_{DGT} results, which is most likely due to the formation of a DBL on each side of the hydrogel membrane. The ratios for these elements with RDL were similar but tended to be somewhat lower in comparison, most likely due to the much higher concentrations used with the D_{cell} method resulting in a slight change of speciation. The ratios for Mo and Sb were about 0.8, likely for the same reason. The ratios for V (0.39-0.44) and W (0.63-0.66) were much lower with both ODL and RDL due to the formation of a high proportion of polyoxometalate species with the D_{cell} measurements at higher solution

concentrations. Overall, we recommend use of the DGT measurements for major experiments to determine diffusion coefficients at concentrations typical of natural waters and use of the diffusion cell for relatively quick quality control measurements, for instance, to compare batches of diffusive hydrogels.

The determination of D_{DGT} values at two different pH gave a useful insight into trends of diffusion coefficients for cationic and oxyanionic elements. Effective diffusion coefficients in ODL and RDL are retarded relative to diffusion coefficients in water at all pH. Moreover, in both diffusive hydrogels the D_{DGT} values for oxyanions were retarded more relative to D_w than for cations. We propose that this is due to the formation of acrylic acid functional groups by hydrolysis of a small proportion of amide groups, which would give both diffusive hydrogels sites of negative charge, and enhancing diffusion of cations relative to oxyanions. Furthermore, a close inspection of variation in D_{DGT} values between pH 4.01 and 7.04/8.30 revealed that pH was further modifying this trend slightly; at pH 7.04 cations had a slightly higher D_{DGT} and anions had a slightly lower D_{DGT} than at pH 4.01 with both ODL and RDL. This could be explained by the change in dissociation of any acrylic acid groups, because at pH 7.04/8.30 the acrylic acid functional groups ($pK_a \approx 4.5$) will be fully deprotonated and at pH 4.01 they will only be very slightly deprotonated. This hypothesis is consistent with all observations in this study, there were no exceptions to these trends in the data and the effect was observed for both ODL and RDL. This factor may be responsible for some of the variation in literature diffusion coefficients, especially for oxyanions, and may have important implications for the preparation and storage of polyacrylamide diffusive layers. This finding strongly demonstrates the importance of comprehensive data on diffusion coefficients being available to improve the accuracy of DGT measurements in waters.

Supporting Information

Additional information, as noted in the text, can be found in the online version of this article.

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	Mean MBL blanks	MDL for open gel	MDL for restricted gel
Al	97.9 ± 11.9	3.0	1.6
Cd	0.11 ± 0.15	0.03	0.01
Co	0.61 ± 0.07	0.01	0.01
Cu	23.6 ± 6.7	0.68	0.62
Mn	2.68 ± 0.88	0.13	0.18
Ni	6.81 ± 0.46	0.09	0.02
Pb	6.35 ± 3.10	0.23	0.41
Zn	85.6 ± 18.0	2.2	3.4
As	0.85 ± 0.23	0.01	0.04
Mo	1.34 ± 0.43	0.05	0.07
Sb	0.45 ± 0.16	0.02	0.04
V	1.39 ± 0.48	0.04	0.07
W	2.01 ± 0.66	0.06	0.16

Table 1. Mean blanks (ng) and calculated method detection limits (MDL, ng mL⁻¹) for DGT-MBL using diffusion coefficients obtained from current study. Conditions: Δg= 0.09 cm; t= 32 h; A= 3.14 cm².

Element	Diffusion coefficient (D_{DGT}) ^a								(D_{DGT} / D_W)	Literature	
	ODL		RDL		(RDL / ODL) ^b		ODL		RDL	ODL	
	pH 7.04	pH 4.01	pH 7.04	pH 4.01	pH 7.04	pH 4.01	pH 7.04	pH 4.01	pH 7.04	pH 4.01	
Al ^c	5.83 ± 0.26	4.28 ± 0.19	4.01 ± 0.20	3.10 ± 0.11	0.69± 0.07	0.72± 0.06	1.04	0.77	0.72	0.55	5.38 [9] 4.36 [9] 5.10 [17]
Cd	6.30 ± 0.28	5.56 ± 0.21	4.69 ± 0.21	4.07 ± 0.18	0.74± 0.06	0.73± 0.06	0.88	0.78	0.65	0.57	5.56 [23] 5.36 [17]
Co	6.24 ± 0.31	5.88 ± 0.20	4.89 ± 0.25	4.48 ± 0.17	0.78± 0.07	0.76± 0.05	0.89	0.84	0.70	0.64	5.29 [23] 5.99 [17]
Cu	6.04 ± 0.34	5.34 ± 0.19	4.70 ± 0.27	4.19 ± 0.13	0.78± 0.08	0.78± 0.05	0.82	0.73	0.64	0.57	5.61 [23] 6.25 [17]
Mn	5.43 ± 0.22	5.11 ± 0.22	4.07 ± 0.18	4.01 ± 0.16	0.75± 0.06	0.78± 0.06	0.79	0.74	0.59	0.58	4.68 [23] 5.82 [17]
Ni	6.08 ± 0.26	5.65 ± 0.22	4.69 ± 0.23	4.05 ± 0.20	0.77± 0.07	0.72± 0.06	0.90	0.83	0.69	0.60	5.13 [23] 6.29 [17]
Pb	8.13 ± 0.68	7.70 ± 0.29	5.89 ± 0.48	5.56 ± 0.10	0.72± 0.12	0.72± 0.04	0.86	0.81	0.62	0.59	8.03 [23] 9.91 [17]
Zn	6.23 ± 0.54	5.78 ± 0.24	4.71 ± 0.33	4.30 ± 0.15	0.76± 0.11	0.74± 0.05	0.87	0.81	0.66	0.60	6.22 [23] 4.38 [17]
As	5.59 ± 0.21	5.96 ± 0.20	3.88 ± 0.19	4.24 ± 0.23	0.69± 0.06	0.71± 0.06	0.62	0.66	0.43	0.47	6.02 [23] 6.05 [26] 6.83 [6] 6.78 [8] 5.26 [28] 5.25 [29]
Mo	6.67 ± 0.37	7.24 ± 0.19	4.40 ± 0.19	4.94 ± 0.16	0.66± 0.07	0.68± 0.04	0.67	0.73	0.44	0.50	6.33 [23] 6.81 [8] 5.42 [28]
Sb	6.25 ± 0.28	6.74 ± 0.24	4.48 ± 0.26	4.93 ± 0.22	0.72± 0.07	0.73± 0.06	0.76	0.82	0.54	0.60	6.22 [23] 6.86 [8] 5.38 [28] 5.46 [29]
V	8.24 ± 0.50	8.92 ± 0.27	6.19 ± 0.30	6.84 ± 0.34	0.75± 0.08	0.77± 0.06	-	-	-	-	7.98 [23] 8.02 [8] 6.73 [26] 6.66 [28] 6.26 [29]
W	6.05 ± 0.31	6.50 ± 0.34	4.21 ± 0.23	4.72 ± 0.27	0.70± 0.07	0.73± 0.08	0.66	0.70	0.46	0.51	6.88 [23] 6.26 [8] 5.56 [28]

Table 2. Diffusion coefficients (D_{DGT}) ($\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) of cations and oxyanions calculated from time-series deployments of DGT-MBL with open diffusive layer (ODL) and restricted diffusive layer (RDL) at pH 7.04 and 4.01, adjusted to 25°C [refer to section 2.3.1 for conditions of the experiment]. D_W is the diffusion coefficient of metal ions in water. ^aStandard deviations for the D values are derived from uncertainties associated with the slopes and the analyte concentration using the square root of the sum of the individual errors squared. ^bStandard deviations for the ratios are derived from uncertainties associated with the diffusion coefficient values using the square root of the sum of the individual errors squared. ^cAl was determined at pH 8.30 instead of 7.04.

D_{DGT}(pH 4.01) / D_{DGT}(pH 7.04)^a

	ODL	RDL
Al^b	0.73 ± 0.06	0.77 ± 0.06
Cd	0.88 ± 0.06	0.87 ± 0.06
Co	0.94 ± 0.06	0.92 ± 0.06
Cu	0.88 ± 0.07	0.89 ± 0.06
Mn	0.94 ± 0.06	0.99 ± 0.06
Ni	0.93 ± 0.06	0.87 ± 0.07
Pb	0.95 ± 0.09	0.94 ± 0.08
Zn	0.93 ± 0.10	0.91 ± 0.08
As	1.07 ± 0.05	1.09 ± 0.07
Mo	1.09 ± 0.06	1.12 ± 0.05
Sb	1.08 ± 0.06	1.10 ± 0.07
V	1.08 ± 0.07	1.11 ± 0.07
W	1.07 ± 0.07	1.12 ± 0.08

Table 3. The ratio of the calculated diffusion coefficients at pH 4.01 to the diffusion coefficients at pH 7.04 using DGT-MBL. ^aStandard deviations are derived from uncertainties associated with the diffusion coefficient values using the square root of the sum of the individual errors squared. ^bAl was determined at pH 8.30 instead of 7.04.

Element	Diffusion coefficient (D_{cell}) ^a			$(D_{cell} / D_{DGT})^{b, c}$		Literature	
	ODL	RDL	RDL / ODL	ODL	RDL	ODL	RDL
Al	4.14 ± 0.13	2.82 ± 0.38	0.68 ± 0.14	0.97± 0.05	0.91± 0.14	4.75 [36] 3.82 [35]	2.90 [35]
Cd	5.36 ± 0.18	3.87 ± 0.16	0.72 ± 0.05	0.96± 0.05	0.95± 0.06	5.52 [23] 6.45 [21] 6.09 [36]	3.58 [22] 4.02 [21]
Co	5.03 ± 0.17	3.59 ± 0.15	0.71 ± 0.05	0.86± 0.05	0.80± 0.06	5.17 [23] 5.94 [36]	3.64 [22]
Cu	5.27 ± 0.19	3.82 ± 0.17	0.72 ± 0.06	0.99± 0.05	0.91± 0.05	5.75 [23] 6.30 [21] 6.23 [36]	3.72 [22] 4.40 [21]
Mn	4.95 ± 0.18	3.52 ± 0.15	0.71 ± 0.06	0.97± 0.06	0.88± 0.06	4.88 [23] 5.85 [36]	3.64 [22]
Ni	5.13 ± 0.18	3.68 ± 0.15	0.72 ± 0.05	0.91± 0.05	0.91± 0.06	5.21 [23] 5.77 [36] 6.18 [21]	3.75 [22] 4.28 [21]
Pb	6.80 ± 0.24	4.99 ± 0.21	0.73 ± 0.05	0.88± 0.05	0.90± 0.05	7.75 [23] 8.03 [36]	5.28 [22] 6.14 [21]
Zn	5.39 ± 0.23	3.84 ± 0.18	0.71 ± 0.06	0.93± 0.06	0.89± 0.06	5.47 [23] 6.08 [36]	4.59 [22]
As	5.36 ± 0.22	3.83 ± 0.08	0.71 ± 0.05	0.90± 0.05	0.90± 0.06	5.26 [23] 5.21 [28] 5.54 [8] 5.57 [6] 6.10 [26] 5.18 [29]	-
Mo	5.58 ± 0.24	3.96 ± 0.09	0.71 ± 0.05	0.77± 0.05	0.80± 0.04	5.18 [23] 5.96 [28] 6.28 [8]	-
Sb	5.50 ± 0.22	4.14 ± 0.07	0.75 ± 0.04	0.82± 0.05	0.84± 0.05	4.90 [23] 5.55 [28] 5.40 [29] 6.04 [8]	-
V	3.88 ± 0.14	2.67 ± 0.06	0.69 ± 0.04	0.44± 0.05	0.39± 0.06	3.75 [23] 6.72 [28] 7.14 [8] 6.70 [26] 6.48 [29]	3.45 [22]
W	4.28 ± 0.22	2.98 ± 0.06	0.70 ± 0.05	0.66± 0.07	0.63± 0.06	6.22 [23] 6.89 [8] 5.45 [28]	-

Table 4. Diffusion coefficients ($\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) of cations and oxyanions in open diffusive layer (ODL) and restricted diffusive layer (RDL) determined using diffusion cells, adjusted to 25°C. ^aStandard deviations for the D values are derived from uncertainties associated with the slopes and the analyte concentration using the square root of the sum of the individual errors squared. ^bStandard deviations for the ratios are derived from uncertainties associated with the diffusion coefficient values. ^cConditions: D_{cell} values at pH 4.00 and D_{DGT} values at pH 4.01.

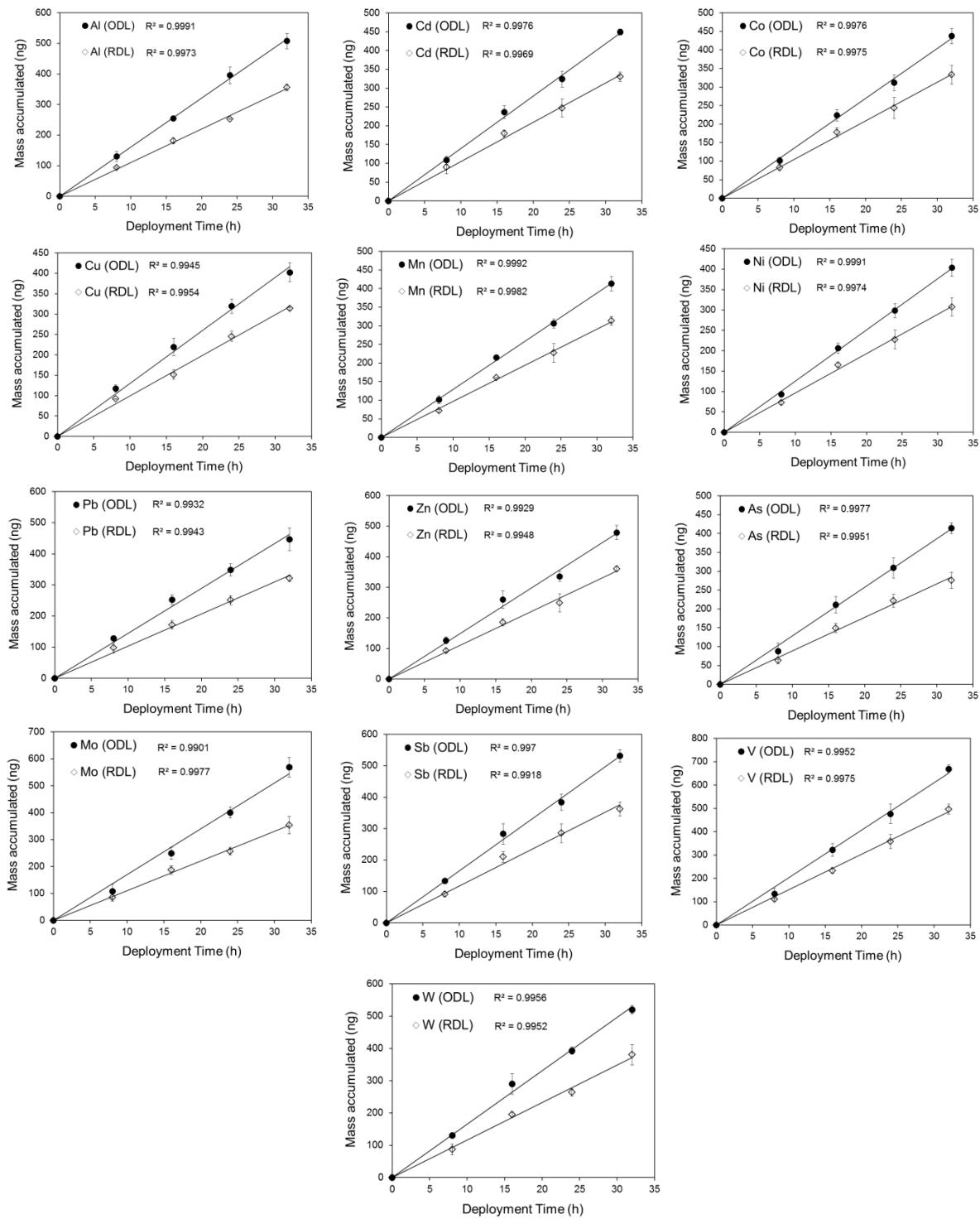


Figure 1. Time-series accumulation of cations and oxyanions by DGT samplers equipped with DGT-MBL using two different diffusive gels: open gel (ODL) and restricted gel (RDL). Conditions: pH 7.04 and 0.01 mol L⁻¹ NaNO₃/0.004 mol L⁻¹ Mg(NO₃)₂ [pH 8.30 and 0.01 mol L⁻¹ NaNO₃/0.0005 mol L⁻¹ NaHCO₃ for Al]. Average analyte concentration (ng mL⁻¹): 21.57 Al; 17.27 Cd; 16.57 Co; 16.64 Cu; 18.52 Mn; 16.09 Ni; 13.75 Pb; 18.39 Zn; 18.46 As; 20.19 Mo; 21.10 Sb; 18.97 V; 21.79 W.