Aluminum sampling by Chelex, titanium dioxide and zirconium oxide DGT: Influence of pH on accumulation behaviors

Juliette Rougerie, Rémy Buzier, Stéphane Simon, Gilles Guibaud

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Authors: Rougerie Juliette, Buzier Rémy*, Simon Stéphane, Guibaud Gilles.

Université de Limoges, PEIRENE-Equipe DIQeau - URA IRSTEA, 123 Avenue Albert Thomas, Limoges Cedex, 87060, France

*Corresponding author: remy.buzier@unilim.fr

Abstract

Diffusive gradient in thin film (DGT) is used for aluminum monitoring in waters, where content can reach more than 1 mg L^{-1}, but no information is available concerning its limit of linear accumulation, leading to a risk of an underestimation of the water concentration. Furthermore, this limit can be strongly affected by the pH due to changes of the aluminum speciation and global charge of the binding phase. The linear accumulation capacities of three types of DGT, based on Chelex-100® (DGT-Ch), titanium dioxide (DGT-Ti) and zirconium oxide (DGT-Zr), were determined as a function of pH by time-series accumulation over 30 days. For DGT-Ch, it decreased with increasing pH: around 16 µg at pH 4.1, 5 µg at pH 5.3 and null at pH 8.6. The DGT-Ti and DGT-Zr had similar performances and could accumulate aluminum over the whole tested pH range, but with a significantly higher limit of linear accumulation at pH 8.6 (≈15 µg) compared to pH 4.1 (≈1 µg). The evolution of the accumulated mass over time agreed with the predicted values except for DGT-Zr at pH 4.1 and 5.3, where a *ca.* 30% higher accumulation was observed. Application in natural freshwaters containing various aluminum species and potential competitors confirmed the linear limits for the three types of DGT and also the DGT-Zr tendency to over-estimate aluminum (up to 200% in some freshwater samples compared to DGT-Ch and DGT-Ti). This phenomenon observed for DGT-Zr cannot be explained yet. Currently, DGT-Zr is not recommended for aluminum monitoring.

Keywords: Aluminum speciation, Passive sampling, Binding capacity, Natural waters, Metals.

I. INTRODUCTION

The presence of aluminum (Al) in freshwaters, varying from a few µg L^{-1} to several mg L^{-1} (Habs et al., 1997), is a major concern regarding its potential toxicity. Many studies have shown that it can have detrimental effects on aquatic organisms (Chassard-Bouchaud et al., 1992; Roy and Campbell, 1997). If freshwaters are used as drinking water resources without removal treatment, this element can also impact human health as it is considered as a risk factor for degenerative diseases (Exley, 2013). The environmental effects of Al are governed by its speciation rather than its total concentration. The speciation of Al mostly depends on pH (Harris et al., 1996). Acidic conditions lead to the presence of cationic species such as Al^{3+}, $AlOH^{2+}$ and $Al(OH)_2^+$ which, along with weak complexes (mainly inorganic), are generally recognized as the most reactive, and therefore the most bioavailable forms (Gensemer and Playle, 1999). In the pH range 6.0-7.5, Al is commonly precipitated as $Al(OH)_{3(s)}$ (Sposito, 1995). The anionic $Al(OH)_4^-$ form found in alkaline freshwaters is considered less toxic than cationic species but its toxicity mechanism is not clearly known (Wilson, 2011). It should be noted that the presence of ligands, such as dissolved organic matter, decreases the toxicity of Al (Roy and Campbell, 1997) by limiting its bioavailability. Therefore, the toxicity of Al in freshwaters varies with both pH and the presence of ligands such as organic matter (Sposito, 1995). A quantitative determination of the most reactive forms of Al is thus required for a relevant toxicity risk assessment.

The passive sampling by diffusive gradients in thin films (DGT), developed by Davison and Zhang (1994), is a suitable tool for speciation studies (Menegário et al., 2017; Zhang and Davison, 2015). The DGT samples only the labile fraction (*i.e.,* free element and fast-dissociating complexes) (Davison and Zhang, 2012), which is considered to be the most bioavailable, thus allowing a better assessment of the impacts on organisms (Røyset et al., 2005; Eismann et al., 2020). In addition, as an *in situ*

sampling technique, the DGT eliminates the issues associated to the sample storage by reducing the risk of speciation change or contamination. Furthermore, this technique allows the determination of time-weighted average concentrations and is thus more representative of organism's exposure than concentrations determined from grab sampling (Allan et al., 2006), especially in dynamic systems where the concentration and the speciation can vary over several hours.

When considering the different DGT configurations already available, various behaviors can be expected for Al sampling. Several studies have shown that a conventional DGT device based on a Chelex binding phase is able to sample Al, but only under acidic conditions (Panther et al., 2012; Shiva et al., 2017). Another DGT, based on a titanium dioxide binding phase has also been used for Al and allows its sampling under both acidic and alkaline conditions (Panther et al., 2012). It should be noted that no information is yet available concerning the linear accumulation capacity of these two binding phases for Al. However, this parameter is essential to ensure that there is no saturation, even partial, of the binding phase which would induce an underestimation of the contamination. Such a situation is particularly of concern in the case of waters with high labile Al content. It has been shown that a DGT device based on a zirconium oxide binding phase has better binding capacities for several oxyanions (Ding et al., 2016), but it has not been evaluated yet for Al sampling.

Furthermore, pH may strongly affect both the speciation of Al and the ionization state of binding phase functions, consequently modifying the binding capacity. Indeed, according to pH, Al can be positively charged (varying from +1 to +3), neutral or negatively charged (-1) ***(Figure S1)***. Concerning the binding phase, depending on the pH and its pH of zero-point charge (pH_{ZPC}), it can have a negative, neutral or positive global charge ***(Figure S1)***. These changes can lead to different binding capacities: the amount of binding sites and / or the interactions between the Al species and the binding phase can vary. The linear accumulation capacity of a binding phase shall thus be determined considering the effect of pH.

In this paper, we propose an in-depth study of the accumulation capacities of DGT for Al to take full advantage of its time integrative capacities in natural waters. The objectives of this work are to

77 determine the limits of linear accumulation of three binding phases (Chelex, titanium dioxide or
78 zirconium oxide) considering the effect of pH and to evaluate the DGT based on a zirconium oxide
79 binding phase as an alternative for Al sampling in freshwaters.

80 # II. MATERIALS AND METHODS

81 ## II.1. MATERIALS, REAGENTS AND SOLUTIONS

82 All reagents were analytical grade or higher. Ultrapure water (Milli-Q system, water
83 resistivity > 18.2 MΩ.cm) was used to prepare all the solutions. All the reusable materials, including
84 the DGT devices, were cleaned by immersion in a 10% (V/V) HNO_3 bath for 24 h then rinsed with
85 ultrapure water prior to use. A 1000 mg L^{-1} Al stock solution was prepared from $Al(NO_3)_3.9H_2O$
86 (Honeywell Fluka, ACS quality).

87 ## II.2. DGT PROCEDURES

88 ### II.2.1. DGT SAMPLERS

89 Three DGT binding gels were studied: Chelex-100® (iminodiacetic functions), Metsorb®
90 (titanium dioxide) and zirconium oxide. The Chelex and titanium dioxide binding gels were purchased
91 from DGT Research Ltd. The zirconium oxide binding gels were prepared according to the protocol
92 used by Devillers et al. (2017). The DGT devices were assembled using plastic holders (DGT Research
93 Ltd.) enclosing a binding gel, a polyacrylamide diffusive gel (0.78 mm thick, DGT Research Ltd.) and a
94 polycarbonate filter membrane (0.4 µm pore diameter, 0.01 mm thick, Whatman). The
95 corresponding DGT devices were labelled DGT-Ch, DGT-Ti and DGT-Zr.

96 ### II.2.2. ELUTION

97 After exposition, the DGT were dismantled and the binding gels were eluted during 24 h at
98 21 ± 1 °C in a temperature controlled room. The elution step was performed using 1 mL of 1 mol L^{-1}
99 HNO_3 for the Chelex binding gels (Warnken et al., 2007), 1 mL of 0.1 mol. L^{-1} NaOH for the titanium

dioxide binding gels and 2 mL of 0.2 mol L^{-1} NaOH for the zirconium oxide binding gels. The protocol for the titanium dioxide binding gels was adapted from Bennett et al. (2010) by decreasing the NaOH concentration by ten times to avoid matrix effect caused by sodium during Al analysis by atomic absorption spectrometry. The protocol for the zirconium oxide binding gels was adapted from Ding et al. (2016) by removing H_2O_2 to avoid apparition of zirconium oxide precipitates in the eluate over time, as highlighted in their publication.

An elution yield of 0.84 was used for the Chelex binding gels according to Panther et al. (2012) and Devillers et al. (2017). The elution yield for the titanium and zirconium oxide binding gels were determined since the protocols were adapted from Bennett et al. (2010) and Ding et al. (2016), respectively. For this purpose, binding gels were directly immersed in 9 mL of 10^{-2} mol L^{-1} $NaNO_3$ solution containing 50 µg L^{-1} of Al at pH 4.0 or 8.5 (triplicates for titanium dioxide and six replicates for zirconium oxide). The pH was adjusted using 1 mol L^{-1} HNO_3 and NaOH, with addition of 5.10^{-3} mol L^{-1} Na_2CO_3 for pH 8.5. After 24 h, the gels were recovered and eluted prior analysis. Samples of each exposure solution were taken before and after gel immersion to determine the accumulated mass of Al in each binding gel. The elution yield was calculated as the ratio between the eluted mass and the accumulated mass.

II.2.3. DGT BLANKS

As Al is a ubiquitous element, the device contamination level was measured for each type of DGT. For this purpose, triplicates of unexposed DGT devices were assembled, dismantled, and eluted with the same procedure than applied to the exposed DGT.

II.3. pH INFLUENCE ON TIME-SERIES ACCUMULATION

To study the influence of pH only on the linear accumulation capacities, time-series accumulation were performed in $NaNO_3$ solutions in absence of competitors. pH values close to the neutrality (pH 6.0 to 7.5) could not be studied in laboratory because of the precipitation of Al,

impeding having a quantifiable and stable concentration. The time-series accumulation of Al by DGT were consequently studied at pH 4.1, 5.3 and 8.6. These three pH allowed covering the main range of dissolved inorganic Al species present in aquatic systems ***(Figure S1)***. To guarantee the Al concentrations in the exposure solutions, they were set to the highest possible value preventing the formation of insoluble $Al(OH)_{3(s)}$, for each studied pH. The corresponding concentrations were 45, 17 and 85 µg L^{-1} for pH 4.1, 5.3 and 8.6, respectively. The ionic strength of these solutions was imposed using 10^{-2} mol L^{-1} $NaNO_3$ and the pH was adjusted using 1 mol L^{-1} HNO_3 and NaOH, with addition of 5.10^{-3} mol L^{-1} Na_2CO_3 for pH 8.6. Before starting the experiments, the solutions were left to equilibrate for at least 72 h.

For each pH, DGT-Ch, DGT-Ti and DGT-Zr were deployed in a well-stirred solution at 20 ± 1 °C using 20 L polyethylene containers (up to 24 DGT per container). The accumulation of Al was evaluated over eight deployment times between 4 h and 30 days, with triplicates for each duration. The pH was monitored daily and the solutions were sampled at each DGT deployment and removal (or daily if no device was added/retrieved) to monitor Al concentration.

II.4. DGT DEPLOYMENT IN NATURAL WATERS

DGT deployments were performed in natural waters to confirm both the linear accumulation capacity and the accumulation behavior of the three studied binding phases obtained in $NaNO_3$ solutions. For this purpose, three natural waters were selected for their significant dissolved Al concentrations (between 100 and 300 µg L^{-1}) and their pH (between 5 and 7) covering a large part of the environmental range ***(Table 1)***. They correspond to a subsurface runoff used for drinking water purpose (water C) and two rivers from headwaters located in the North-West of the Massif Central in France (water M and R). More details about their physicochemical composition can be found in ***Table S1***.

Table 1 : Main characteristics of the natural waters studied. (Mean ± SD, n ≥ 3, DOC: Dissolved Organic Carbon)

	pH	Conductivity (µS cm^{-1})	Dissolved Al (µg L^{-1})	DOC (mg L^{-1})
Water C	5.0 ± 0.2	26 ± 2	290 ± 40	1.0 ± 0.7
Water M	6.0 ± 0.1	27 ± 2	97 ± 5	8 ± 1
Water R	7.1 ± 0.1	163 ± 3	260 ± 50	9 ± 4

Preliminary experiments showed that only DGT deployments in water C would allow to get close to the limits of linear accumulation of the studied DGT in an acceptable deployment time (*i.e.* < 2 weeks to avoid major changes in water composition). Only this natural water was therefore used to verify that the linear accumulation capacities determined in synthetic solutions are still valid in natural waters. DGT-Ch, DGT-Ti and DGT-Zr were thus deployed in triplicates in water C for two durations (4 h and 40 h) to guarantee the absence of saturation by comparing the results of short and long deployments. The longer deployment time was estimated according to ***Equation 1*** from the dissolved Al concentration to get close to the limit of linear accumulation obtained in the $NaNO_3$ solution at pH 5.3.

In addition to the water C, the natural waters M and R were used to compare the behavior of each type of DGT in a non-saturating condition. The duration of deployment, set to stay far below the beginning of saturation of the binding gels, was chosen based on the results obtained in $NaNO_3$ solutions and according to the DGT-available Al content of each water (estimated during preliminary experiments). DGT were thus deployed during 3 days in water M and 7 days in water R.

To control as much as possible the conditions during DGT deployment, the experiments were performed in the lab directly after sampling the natural waters. DGT-Ch, DGT-Ti and DGT-Zr were deployed in 5 L (for water C and M) or 20 L (for water R) of well-stirred solution in polyethylene containers. The exposition temperature was set to 6 ± 1 °C (controlled by Tinytag temperature loggers) to remain close to the field conditions (waters were sampled in winter 2021). During DGT

exposure, the pH and Al concentration were monitored daily. The dissolved Al concentration was determined after filtration at 0.2 µm (cellulose acetate, Sartorius). In addition, ultrafiltration with a low cutoff membrane (3 kDa, Vivaspin) was performed to separate large complexes from "free" Al and/or small complexes. The ultrafiltration was carried out by centrifugation of 5 mL of natural waters at 6000 *g* for 10 min at 6 ± 1 °C. Filters and ultrafilters were systematically pre-conditioned with 5 mL of the solution to be filtered to avoid Al sorption or release.

II.5. ALUMINUM MEASUREMENTS

II.5.1. ANALYSIS

The eluates and exposure solutions were analyzed by atomic absorption spectrometry with electrothermic atomization (ET-AAS, Agilent 240 Z) using a platform graphite tube. A modifier consisting in 0.64 mg L^{-1} (final concentration) of NH_4NO_3 and $Ca(NO_3)_2$ was used. All samples and standards were acidified at 1% (V/V) with HNO_3. The standard addition method was applied to eluates of DGT exposed in natural waters to detect any potential matrix effects. For quality assurance, blanks (HNO_3 1% V/V) and a control solution (20 µg L^{-1}, prepared daily) were analyzed every ten samples. In addition, a 20 µg L^{-1} laboratory certified solution was analyzed at the beginning and the end of each sequence (recovery > 95%). The limit of quantification of the method (according to IUPAC) was estimated at 5 µg L^{-1}.

II.5.2. C_{DGT} DETERMINATION

The concentration estimated by DGT, C_{DGT} (µg L^{-1}), was calculated using ***Equation 1*** (Davison and Zhang, 1994):

$$C_{DGT} = \frac{m\Delta_g}{DAt} \qquad \textbf{Equation 1}$$

where m (ng) is the mass of Al accumulated in the binding phase, Δg is the thickness of the diffusive layer (0.079 cm), t (s) is the exposure duration, A is the exposure area to solution (3.14 cm^2) and D (cm^2 s^{-1}) is the diffusion coefficient of Al. The values of D were taken from the literature (Panther et

al., 2012; Shiva et al., 2017) according to the pH of the solution and corrected according to the average temperature during the deployment using the Stokes-Einstein relationship (values are listed in ***Table S2***).

II.5.3. SPECIATION CALCULATION AND STATISTICS

Visual MINTEQ 3.1 software was used with the default database constants to determine the speciation of Al according to pH, considering $Al(OH)_{3(s)}$ as the dominant solid phase (log K = 10.8) and equilibrium with atmospheric CO_2. The Stockholm Humic Model (SHM) was used to simulate Al interactions with organic matter in natural waters.

For experiments in natural waters, statistical analyses were performed to compare the results obtained by each type of DGT. ANOVA tests were used to verify the equality of the means and completed, if necessary, by a Student LSD (least significant difference) test to identify the different means. All tests were conducted with a statistical significance level of p = 0.05. In addition, for experiments in water C, the uncertainty of the ratios between the C_{DGT} obtained for 40 h and 4 h deployment was calculated by propagation of uncertainty.

III. RESULTS AND DISCUSSION

III.1. ELUTION

III.1.1. BLANK CONTAMINATION

The eluates of unexposed DGT revealed a rather low and constant contamination (0.024 ± 0.004 µg, 0.032 ± 0.001 µg and 0.040 ± 0.004 µg per binding gel for DGT-Ch, DGT-Ti and DGT-Zr, respectively). The mean DGT blank value was consequently systematically subtracted to the results of each exposed DGT.

III.1.2. Elution yields

There was no difference between the elution yields determined at pH 4.0 and 8.6. Values of 0.66 ± 0.03 (n = 12) and 0.65 ± 0.02 (n = 6) were obtained for the zirconium oxide and titanium dioxide binding gels respectively. For the titanium dioxide binding gels, the elution yield obtained with 0.1 mol L^{-1} NaOH was 17% lower than with 1 mol L^{-1} NaOH (Panther et al., 2012). However, this adapted elution protocol allows analyzing undiluted eluates without suffering any matrix effect from NaOH. In the end, it allows decreasing the quantification limit to around an accumulated mass of 10 ng, by avoiding the systematic ten times dilution of the original procedure.

III.2. DGT linear accumulation capacities

III.2.1. Time-series accumulation in $NaNO_3$ solutions

To determine the linear accumulation capacities of each type of DGT according to pH only, the accumulation of Al species by DGT-Ch, DGT-Ti and DGT-Zr was investigated in controlled $NaNO_3$ solutions at pH 4.1 ± 0.1, 5.3 ± 0.1 and 8.6 ± 0.1. Note that to avoid Al precipitation and thus control the concentration of "DGT available Al", the pH range 6.0 to 7.5 was not considered. The Al speciation as a function of pH, determined using Visual MINTEQ, is given in ***Table 2***. The studied range of pH allowed investigating the accumulation of both cationic and anionic species.

The Al concentration remained stable throughout the DGT deployment, with variations lower than 5%. Consequently, the DGT exposure concentration (C) used for the calculation was the mean concentration of samples taken over time. The accumulated mass m (µg) was plotted as a function of the deployment duration, t (day) ***(*Figure 1*)***. According to ***Equation 1***, the plot of m *versus* t should be linear, with CDA/Δg as slope, up to the beginning of the saturation of the binding phase. Therefore, for each type of DGT, the linear accumulation capacity can be determined as the m value associated to the linearity disruption. Given the uncertainty between the DGT triplicates (RSD

generally lower than 10%), the accumulation linearity was considered lost when a difference higher than 10% was observed between the measured and the extrapolated linear value. In addition, the predicted accumulation was determined using ***Equation 1*** (diffusion coefficients were taken from literature according to the pH, ***Table S2***) to assess the compliance of the linear accumulation with the DGT theory.

Table 2: Aluminum speciation according to pH in $NaNO_3$ solutions, determined by Visual MINTEQ.

		% of Al species				
pH	**[Al] (µg L^{-1})**	**Al^{3+}**	**$AlOH^{2+}$**	**$Al(OH)_2^+$**	**$Al(OH)_{3(aq)}$**	**$Al(OH)_4^-$**
4.1 ± 0.1	45	94.7	5.2	0.1	-	-
5.3 ± 0.1	17	44.0	38.1	16.9	0.9	0.1
8.6 ± 0.1	85	-	-	-	0.5	99.5

At pH 4.1 ***(*Figure 1*, a)***, a linear and theoretically predictable accumulation was obtained with DGT-Ch up to 30 days. The mean accumulated mass of 15.9 µg obtained is 10% lower than the predicted one, suggesting a beginning of saturation, but staying in the limit of the accepted deviation. The limit of linear accumulation of the DGT-Ch is thus probably around 16 µg. With DGT-Ti and DGT-Zr, a linear accumulation was observed for 2 days only, up to a mass of 1.11 ± 0.07 µg and 1.3 ± 0.1 µg respectively. The experimental accumulation on DGT-Ti followed the predicted trend, but a surprisingly higher accumulated mass was observed with the DGT-Zr (33% slope offset compared to prediction).

At pH 5.3 ***(*Figure 1*, b)***, the DGT-Ch and DGT-Ti had the same behavior, with a linear and theoretically predictable accumulation up to 20 days (accumulated mass of 4.0 ± 0.2 µg and 4.6 ± 0.3 µg respectively). The mean accumulated mass for 30 days of exposition was 10% lower than the linear part, suggesting a potential beginning of saturation of both binding phases. The linear accumulation capacity of DGT-Ch and DGT-Ti can thus be estimated around 5 µg. DGT-Zr showed a slightly different behavior. Its accumulation was also linear, but the saturation did not seem to be

reached over the 30 days of exposition (linear accumulation up to 8.1 ± 0.8 µg). However, it should be noted that the accumulation was slightly higher than the prediction (23% deviation between experimental and predicted slope).

At pH 8.6 ***(*Figure 1*, c)***, the DGT-Ch showed a very low accumulation. These results are in agreement with Panther et al. (2012) who have already observed an under-accumulation above pH 7.5 with this setup. The DGT-Ti and DGT-Zr presented the same behavior with a linear accumulation, consistent with the theory, up to 10 days, corresponding to an accumulated mass of 11.6 µg. The mass of 17 µg obtained after 17 days of exposition being 15% lower than the linear part, the limit of linear accumulation of DGT-Ti and DGT-Zr is thus between 11 and 17 µg. At this pH, no higher accumulation compared to the prediction was observed for DGT-Zr.

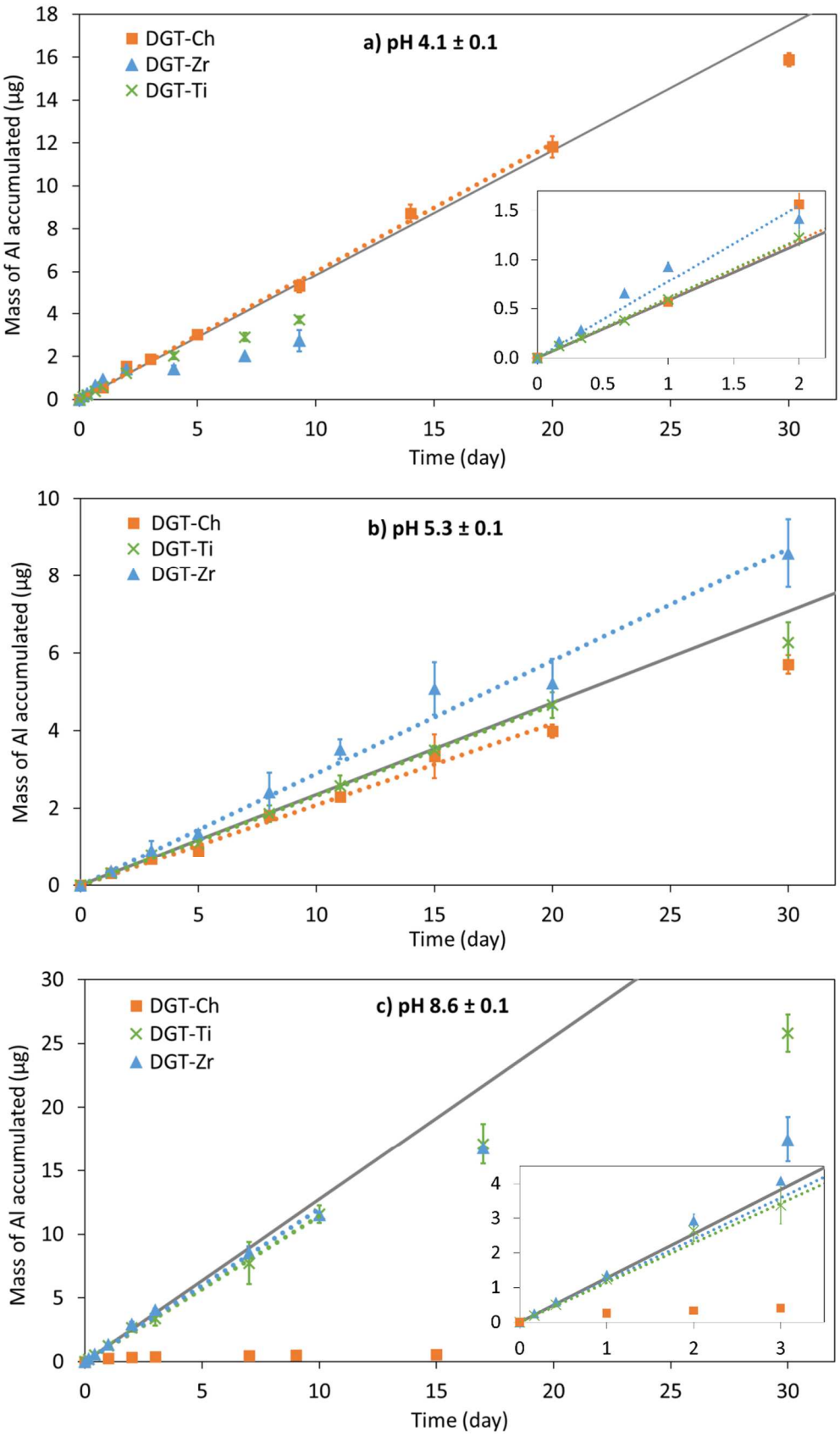

Figure 1: Accumulated mass of Al as a function of time at pH 4.1 ± 0.1 (a); 5.3 ± 0.1 (b) and 8.6 ± 0.1 (c) (mean ± SD, n = 3, grey line: predicted accumulation using Equation 1, dotted lines: linear accumulation).

270

These results show that the DGT-Ch cannot be used at pH 8.6 but offers the highest linear accumulation capacity at pH 4.1. The DGT-Ti and DGT-Zr can accumulate Al over the whole tested pH range, with a higher linear accumulation capacity at pH 8.6. The effect of pH on both Al speciation and binding phase's charge could explain the differences in accumulation capacities ***(Figure S1)***. Indeed, Al species and the binding phase having charges of the same sign would generate electrostatic repulsions, potentially resulting in a decreased accumulation capacity. In the case of the Chelex binding gel, the speciation of the chelating iminodiacetic functions leads to an overall negative charge above pH 6. At pH 4.1, Al is almost totally under the most positively charged species: Al^{3+} ***(Table 2)***. It has already been demonstrated that Chelex-100 is the binding phase of choice for accumulating trivalent cations (Warnken et al., 2009; Zhang and Davison, 1995). However, at pH 8.6, the dissolved Al is almost totally present as the anionic form $Al(OH)_4^-$ ***(Table 2)*** and the DGT-Ch is negatively charged. Thus, Al is hardly accumulated probably due to electrostatic repulsions.

The charge of the titanium dioxide and zirconium oxide binding gel can be determined from their pH_{ZPC} ***(Figure S1)***. With a pH_{zpc} of 5.9 (Kosmulski, 2002a), the titanium dioxide is overall positively charged below pH 5.9 and negatively charged above. In the literature, the pH_{ZPC} of zirconium (hydr)oxide is given from 4 to 8.6, with an average and median values at 6.5 (Kosmulski, 2002b). Due to the different structures of the zirconium oxides, the concept of one recommended pH_{ZPC} does not work particularly well (Kosmulski, 2002b). Thus, to estimate the charge of the zirconium oxide phase used in our study, measurements of the zeta potential as a function of pH have been performed and a pH_{ZPC} of 5.5 was determined (the procedure and values are detailed in ***Figure S2***). This value is in a close range of the median value proposed by Kosmulski (2002b). According to our results, at pH 4.1, the DGT-Ti and DGT-Zr have a linear accumulation capacity at least eight times lower than the DGT-Ch. At this pH, these two sorbents are positively charged, like Al. Thus, the lowered capacity could be due to electrostatic repulsions. At pH 5.3, it clearly appears that DGT-Ti and DGT-Zr have a higher linear accumulation capacity (at least 4 times higher) compared to pH 4.1. At this pH, the dissolved Al species are still mostly positively charged ***(Table 2)*** but the two

297 sorbents are nearly neutral, therefore strongly reducing the electrostatic repulsions and thus
298 resulting in an increased accumulation capacity. However, at pH 8.6, whereas DGT-Ti, DGT-Zr and Al
299 are negatively charged, significantly higher linear accumulation capacities were determined. This
300 observation is consistent with reports of oxyanions sorption by these phases in the literature (Ding et
301 al., 2016), meaning that the potential electrostatic repulsions do not seem to significantly reduce the
302 accumulation capacity compared to pH 5.3. It should be noted that DGT-Zr was shown to accumulate
303 a higher mass of Al compared to the prediction at pH 4.1 and 5.3 but at this stage, there is no clear
304 explanation.

305 ### III.2.1. EXPERIMENTS IN A NATURAL WATER

306 DGT deployments were performed in the natural water C to check that the limits of linear
307 accumulation determined in $NaNO_3$ solutions are also valid in environmental conditions. Indeed,
308 compared to the $NaNO_3$ solutions used, a freshwater represents a complex matrix, with a more
309 complex speciation of Al and the presence of competitors (*e.g.* Fe, Mn, Ca, see ***Table S1***) for sites
310 onto DGT binding phase. The selected freshwater has a high DGT available Al concentration that
311 allows reaching a potential saturation of the binding phases in a short duration. Two deployment
312 durations (4 h and 40 h) were compared to verify the absence of saturation.

313 For the short deployment time (4 h), the accumulated masses were lower than 1 µg, ensuring no
314 risk of saturation. After 40 h exposition, as expected, the accumulated masses (3.2 ± 0.8, 4.5 ± 0.3
315 and 4.1 ± 0.8 µg for DGT-Ch, DGT-Ti and DGT-Zr respectively) were close to the linear accumulation
316 capacity previously determined in $NaNO_3$ at a similar pH (≈5 µg at pH 5.3). The corresponding C_{DGT}
317 value were then calculated for each deployment duration according to ***Equation 1***. In case of
318 saturation, even partial, the C_{DGT} values obtained from the 40 h exposed DGT should be significantly
319 lower than the one obtained for 4 h. The ratios between C_{DGT} obtained with 40 h deployment and 4 h
320 deployment were 1.19 ± 0.24, 1.02 ± 0.08 and 0.95 ± 0.20 for DGT-Ch, DGT-Ti and DGT-Zr,
321 respectively. These ratios are not statistically different from 1, which means that no significant

difference can be found between the short and long deployment duration. It can thus be concluded that none of the three binding phases was saturated when accumulating ~4 µg of Al. Consequently, the linear accumulation capacities determined in the $NaNO_3$ solution appear to remain valid in this type of natural water, with a more complex Al speciation and potential competitors.

This application in water C also highlights the importance of knowing the limit of linear accumulation of DGT to properly set the deployment duration. Indeed, in this case of highly contaminated water by Al, it can be nearly reached within two days of deployment, considerably reducing the duration of the monitoring and the DGT time integrative capacity (which is typically 1 or 2 weeks).

III.3. COMPARISON OF BINDING PHASES BEHAVIORS IN NATURAL WATERS

To confirm the accumulation behaviors observed in $NaNO_3$ solutions, additional experiments were performed using natural waters (waters C, M and R) with high dissolved Al concentrations, and presence of organic matter ***(Table 1)***. To correctly compare the accumulation by each type of DGT, these experiments needed to be performed in non-saturating conditions. This condition has already been confirmed for experiments in the water C. For the waters M and R, the accumulated Al masses were all lower than 1.2 µg ***(Table S3)*** and thus far below the estimated linear accumulation capacities as expected. These accumulated masses were used to calculate C_{DGT} according to ***Equation 1*** and using diffusion coefficients selected from literature ***(Table S2)***. The corresponding results are presented in ***Figure 2*** with the Al concentrations determined in the natural waters after filtration ("dissolved" Al) and ultrafiltration ("truly dissolved" Al).

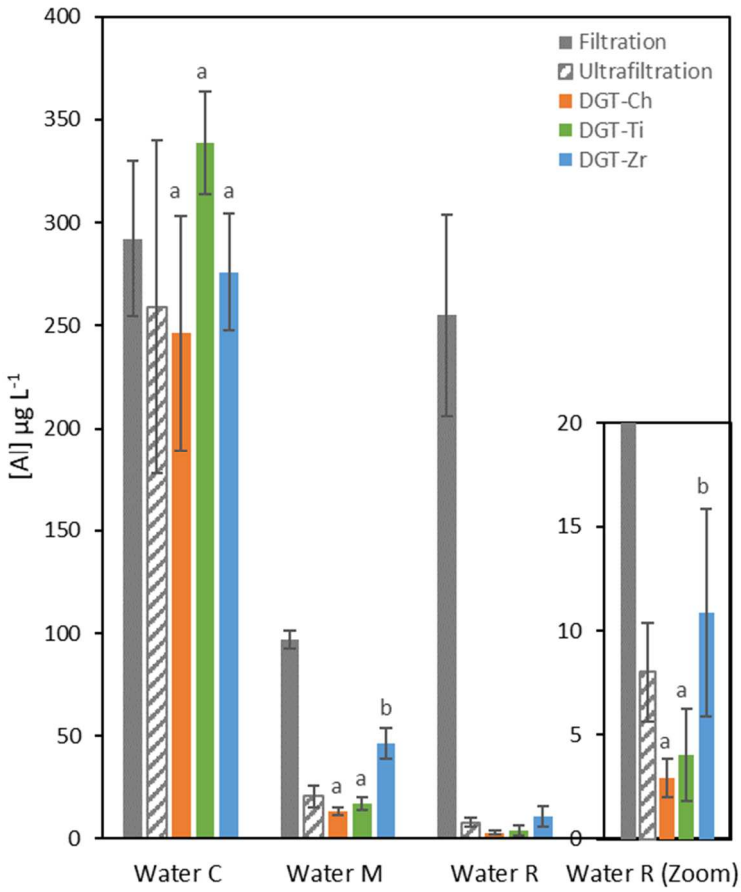

Figure 2: Concentration of Al obtained by filtration, ultrafiltration and DGT in natural waters (mean ± SD, n ≥ 2)**.** For each water, the means obtained by DGT with the same letter are statistically not different.

In each water, the C_{DGT} obtained with DGT-Ch and DGT-Ti were in agreement, as previously observed in $NaNO_3$ solutions at pH 4.1 and 5.3. This seems to confirm their similar accumulation behavior of Al species between pH 4.1 and 7.1, even in the presence of organic matter. The DGT-Zr had the same accumulation behavior than DGT-Ch and DGT-Ti in the water C but led to significantly higher (about two times) accumulations in the waters M and R. After exposure in these two waters, a systematic orange coloration of the zirconium oxide binding gels was observed ***(Figure S3)***, indicating a potential accumulation of other compounds. The hypothesis that these compounds may induce matrix effects during the analysis was tested and discarded by performing standard addition quantifications. The significant presence of iron in waters M and R compared to water C ***(Table S1)***, where this phenomenon was not observed, was also suspected to induce the coloration. The

zirconium oxide binding gels could have accumulated iron oxyhydroxides, known to be brown-orange. After elution, the gels became colorless ***(Figure S3)***, suggesting the potential transfer of iron into the eluate. However, analysis of the eluates did not reveal any significant presence of iron. This hypothesis was thus discarded. Another hypothesis could be the accumulation of other Al species by the zirconium oxide binding gel (*e.g.* complexes with organic matter). For the waters M and R, the ultra-filtered concentration was considerably lower than the filtered concentration ***(Figure 2)***, indicating that most part of the dissolved Al was probably present as large-size complexes. This observation can be consistent with the presence of significant organic matter in these waters ***(Table 1)***. In the water C with a low content of organic matter ***(Table 1)***, there was no significant difference between the filtered and ultrafiltered concentrations ***(Figure 2)***, suggesting that all the aluminum was "truly dissolved". Thus, the Al complexes with organic matter are probably more present in the waters M and R than in the water C. These observations are consistent with the Al speciation predicted by Visual MINTEQ which shows that more than 90% of Al would be bound to organic matter in waters M and R against only 25% in water C. The Al complexes with organic matter could perhaps be partly accumulated by the DGT-Zr, resulting in a higher accumulation compared to DGT-Ch and DGT-Ti in waters M and R.

III.4. GENERAL EVALUATION OF DGT-ZR

This work evaluates for the first time the DGT-Zr as an alternative for the sampling of Al. The experiments revealed that the DGT-Zr could sample both cationic and anionic Al species from pH 4.1 to 8.6. However, in contrast to the higher capacities reported in the literature for other oxyanions (Ding et al., 2016), no higher linear accumulation capacity has been observed for Al in the tested conditions. In addition, compared to DGT-Ch and DGT-Ti, the use of DGT-Zr induces an over-estimation of Al concentration in both $NaNO_3$ solutions and natural waters. Indeed, a ~30% higher accumulation compared to the predicted value was observed in $NaNO_3$ solutions at pH 4.1 and 5.3. DGT-Zr had a similarly behavior to DGT-Ch and DGT-Ti in one of the studied natural water but it

accumulated up to 200% more Al in the others. The potential accumulation of some organic Al species by only the DGT-Zr could be assumed in the natural waters but would not explain the higher accumulation observed in $NaNO_3$ solutions. This phenomenon observed in both synthetic and natural waters for DGT-Zr cannot be explained yet. Consequently, this setup is not recommended for Al monitoring without further investigations.

IV. CONCLUSION

By impacting both the Al speciation and the global charge of the binding phase, the pH strongly affects the binding capacities of DGT. The linear accumulation capacities of DGT-Ch, DGT-Ti and DGT-Zr vary up to a factor ten (from ≈1 µg to ≈15 µg) between pH 4.1 and 8.6. These capacities can easily be reached within few tens of hours field deployment in freshwaters with high Al concentrations. This parameter must therefore be cautiously considered to avoid DGT saturation. In contrast to what could be expected, DGT-Zr did not offer higher capacity compared to DGT-Ti and, surprisingly, induces an over-estimation of Al concentration in water. Consequently, the DGT-Zr is not currently recommended for Al sampling.

Based on our results, it appears that DGT-Ti should be used for pH > 7 since DGT-Ch shows poor accumulation. DGT-Ch and DGT-Ti can both be used for Al sampling at pH ≤ 7 as they present relative similar accumulation behaviors in this pH range. However, the DGT-Ch should be preferred for pH ≤ 5.3 and the DGT-Ti seems more suitable for pH > 5.3 because of their respective higher linear accumulation capacity. The higher capacity will allow longer deployments and consequently a better temporal integration of the Al contamination without the risk of DGT saturation.

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Al sampling by DGT