

# Uncertainty Evaluation of the Diffusive Gradients in Thin Films Technique

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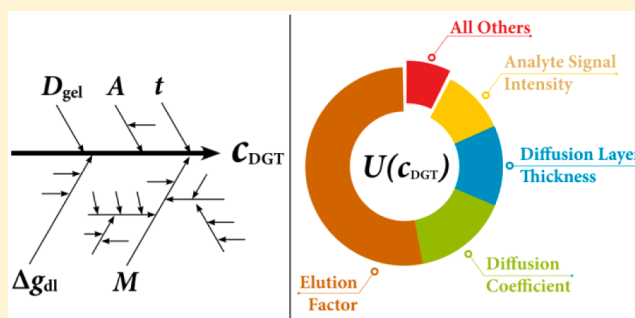
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## S Supporting Information

**ABSTRACT:** Although the analytical performance of the diffusive gradients in thin films (DGT) technique is well investigated, there is no systematic analysis of the DGT measurement uncertainty and its sources. In this study we determine the uncertainties of bulk DGT measurements (not considering labile complexes) and of DGT-based chemical imaging using laser ablation - inductively coupled plasma mass spectrometry. We show that under well-controlled experimental conditions the relative combined uncertainties of bulk DGT measurements are  $\sim 10\%$  at a confidence interval of 95%. While several factors considerably contribute to the uncertainty of bulk DGT, the uncertainty of DGT LA-ICP-MS mainly depends on the signal variability of the ablation analysis. The combined uncertainties determined in this study support the use of DGT as a monitoring instrument. It is expected that the analytical requirements of legal frameworks, for example, the EU Drinking Water Directive, are met by DGT sampling.



## INTRODUCTION

Diffusive gradients in thin films (DGT) was developed as an *in situ* passive sampling technique for trace metal measurements<sup>1,2</sup> and has been applied for the analysis of inorganic solutes in water, sediment and soil,<sup>2–8</sup> for organic pollutants<sup>9</sup> and for chemical imaging of solutes in plant rhizospheres.<sup>10–12</sup> Passive sampling of metals using DGT has been assessed and used as a monitoring instrument for labile metals in aquatic environments such as seawater,<sup>13</sup> rivers<sup>14–17</sup> and lakes.<sup>18</sup> The ability of the DGT technique to preconcentrate analytes on a resin with the resulting low limit of detection (LOD), its suitability for the use in various climatic conditions and simple field handling render it ideal for monitoring nutrients and pollutants in the environment. The need for quality assurance and method validation in environmental monitoring was already realized several decades ago.<sup>19</sup> For these purposes, the estimation of the measurement uncertainty has been established in analytical chemistry in recent years, which serves as a tool to ensure data quality and provide comparability of measurements.<sup>20,21</sup> Although the limit of detection (LOD), the limit of quantification (LOQ), the method detection limit (MDL), blank levels and relative standard deviation (RSD) of three replicate measurements are commonly reported for the various resin gel types, a systematic and consistent approach for the reporting of the uncertainty of DGT measurements is not established.

This study presents a first systematic and detailed assessment of the contributors to the uncertainty of DGT measurements based on measured data. This study uses a similar approach for estimating uncertainty as Knutsson et al.,<sup>22</sup> but provides a more comprehensive characterization of the uncertainties of all relevant parameters. Moreover, a set of measured data, providing a basis for the reduction and consistent reporting of uncertainty in future DGT-based studies, is presented. The calculation of uncertainty budgets for DGT sampling according to the bottom-up approach using the Kragten method<sup>23</sup> is demonstrated. Furthermore, this approach is extended to chemical imaging based on DGT and laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS).

## THEORY

**Diffusive Gradients in Thin Films.** DGT samplers are geometrically well-defined plastic sampling devices containing a diffusive layer, commonly a polyacrylamide gel, and a resin gel with incorporated resin material. This setup allows for the calculation of time averaged mass concentrations of labile solutes

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in the sampling medium,  $c_{\text{DGT}}$ , and time-averaged fluxes of labile solutes,  $F_{\text{DGT}}$ , into the sampler.

$$c_{\text{DGT}} = \frac{M \Delta g_{\text{dl}}}{D_{\text{gel}} A t} \quad (1)$$

$$F_{\text{DGT}} = \frac{M}{A t} \quad (2A)$$

$$F_{\text{DGT}} = \frac{c_{\text{surface}}}{t} \quad (2B)$$

$M$  is the mass of analyte taken up by the resin gel during the experiment,  $\Delta g_{\text{dl}}$  is the thickness of the diffusive layer,  $D_{\text{gel}}$  is the diffusion coefficient of the labile form of the analyte in the diffusive layer,  $A$  is the sampling window area, and  $t$  is the sampling time. If the surface concentration of a DGT resin gel is measured using LA-ICP-MS eq 2B gives the flux where  $c_{\text{surface}}$  is given as mass per area.

$$c_{\text{DGT}} = \frac{M}{A_{\text{eff}} t} \left( \frac{\Delta g_{\text{gel}}}{D_{\text{gel}}} + \frac{\Delta_f}{D_f} + \frac{\delta}{D_w} \right) \quad (3)$$

If the thickness of the diffusion boundary layer outside the DGT sampler cannot be neglected, the expanded DGT equation is used.<sup>2,3,24,25</sup>  $\Delta g_{\text{gel}}$  is the thickness of the diffusive gel,  $\Delta_f$  is the thickness of the protective membrane,  $A_{\text{eff}}$  is the effective sampling area,  $D_f$  is the diffusion coefficient in the prefilter,  $\delta$  is the thickness of the DBL and  $D_w$  is the diffusion coefficient in water. It has been shown by Scally et al.<sup>26</sup> that in a common DGT sampling device with a standard diffusive gel (APA2<sup>27</sup>)  $D_{\text{gel}} \approx D_f$  and therefore  $\Delta_f$  and  $\Delta g_{\text{gel}}$  can be added up to  $\Delta g_{\text{dl}}$  (diffusive layer).

Note that  $c_{\text{DGT}}$  is the time-averaged, labile solute concentration in the sampled medium. The standard DGT equation (eq 1) implicitly corrects for the flux decrease induced by the diffusive boundary layer (DBL) and the flux increase due to lateral diffusion inside the DGT sampler as these effects tend to cancel each other under defined conditions.<sup>24</sup> If these effects do not compensate each other the expanded DGT equation (eq 3), which explicitly corrects for the DBL and lateral diffusion by using the effective sampling area ( $A_{\text{eff}}$ ), has to be used. Both equations yield  $c_{\text{DGT}} \approx c_{\text{B}}$  (solute concentration of the bulk solution) for the DGT-labile analyte fraction in noncomplexing media if applied correctly. It is well established that  $c_{\text{DGT}}$  measures the free ion as well as solute that dissociates from labile complexes.<sup>28</sup> If different labile species contribute to  $c_{\text{DGT}}$  it might be necessary to account for different diffusion coefficients and complex dissociation. However, in this paper complexes are not considered, as this would exceed the scope of this work. If found necessary, complex dissociation could be implemented into the uncertainty scheme presented here in future work.

**Measurement Uncertainty.** According to the Guide to the Expression of Uncertainty in Measurement (GUM)<sup>21</sup> and International Vocabulary of Metrology (VIM)<sup>29</sup> a measurement results in a value of a well-defined physical quantity - the measurand - and a corresponding uncertainty which characterizes the dispersion of the values attributed to the measurand.<sup>21,30</sup> It is widely recognized that any measurement result has an uncertainty range within which the true value may be found with a certain probability.<sup>30</sup> While the measurement and reporting of the measurand is well established for DGT measurements, coherent determination and reporting of its uncertainty is lacking. Measurement uncertainty comprises of random

measurement errors but does neither account for systematic errors (bias) which can be corrected nor for principle measurement and sampling failures.

Measurement uncertainty can be determined using a top-down approach, which focuses on the determination of measurement uncertainty from measurement reproducibility.<sup>30</sup> Alternatively, in the bottom-up approach the measurement uncertainty is determined by identifying, assessing and combining all sources of uncertainty associated with the quantity value (Supporting Information (SI) eq S1).<sup>29,30</sup> A common and feasible bottom up method for uncertainty approximation is the Kragten approach (see SI),<sup>23</sup> which applies error propagation to calculate the combined standard uncertainty ( $u_c$ ). This parameter is a normally distributed uncertainty estimate, which is multiplied with a coverage factor ( $k$ ) to determine the expanded uncertainty ( $U$ ) at a desired confidence level (68% for  $k = 1$ , 95% for  $k = 2$ , 99% for  $k = 3$ ).<sup>21,30</sup>

**Uncertainties in DGT Measurements.** Systematic errors in DGT measurements like changes in the temperature of the sampled medium during the deployment, the diffusive gel thickness in different production batches or the resin gel blank can be accounted for by monitoring and appropriate correction of these parameters during each measurement. In contrast, the specific application condition for different resin gel types (e.g., applicable pH range, ionic strength, capacity) and for the sampling process (e.g., avoidance of analyte binding to hydrogels) have to be met in order to obtain valid DGT measurements, as failure to meet these criteria result in invalid measurements and have to be regarded critical measurement errors.

Potential sources of random errors of a DGT measurement include uncertainties in (1) the thickness of the diffusive gels ( $\Delta g_{\text{dl}}$ ), (2) the resin-gel blank, (3) the elution procedure, (4) the diffusion coefficients ( $D_{\text{gel}}$ ,  $D_w$ ), (5) lateral diffusion in the diffusive layer, (6) the DBL thickness, (7) the deployment time, and (8) the measurement of the resin gel eluate.<sup>24,25,28</sup> Based on these potential contributors, a uncertainty calculation scheme is developed in this work.

Many of the random error sources are well-known and clearly defined. However, considerable variation in the reported elution factors exist in literature and various elution procedures have been applied (differences in acid concentration, elution time and eluate volume) with some procedures being preferably used (SI Table S1).<sup>2,24,31</sup> The same is true for diffusion coefficients, for which a range of values have been reported, for example, for As(V),<sup>32–36</sup> but also for other analytes of interest.<sup>26,37</sup>

For DGT measurements in quiescent and slowly moving waters the analyte flux into the sampler is significantly lowered by the diffusive boundary layer (DBL) (eq 3).<sup>2,24,25,38</sup> Warnken et al.<sup>24</sup> investigated the effects of the DBL (analyte flux decrease) and of lateral diffusion inside the DGT sampler (analyte flux increase) and showed that in standard samplers ( $A = 3.14 \text{ cm}^2$ ,  $\Delta g_{\text{dl}} = 0.094 \text{ cm}$ ) these effects are almost exactly balanced. It was concluded that these parameters can be ignored under well-controlled conditions, while a thorough evaluation of the DBL thickness ( $\delta$ ) and the use of an effective sampling window area ( $A_{\text{eff}}$ ) is necessary otherwise.<sup>24</sup> In a recent modeling study we found that the effect of lateral diffusion inside the sampler is not constant, but depends on the sampler geometry. In this study we use an effective sampling area of  $3.37 \text{ cm}^2$  (i.e., effective sampling diameter,  $d_{\text{sw(eff)}} = 2.07 \text{ cm}$ ), based on our modeling results for a DGT sampler with  $\Delta g_{\text{dl}} = 0.093 \text{ cm}$  and a nominal physical sampling window area of  $3.14 \text{ cm}^2$ . Note that even if the effects of

**Table 1. Input Quantities Considered in the Model Equations (Eqs 4A, 4B, and 5) and the Values Used for the Exemplary Uncertainty Calculations**

parameter	quantity	unit (bulk DGT)	unit (DGT LA-ICP-MS)	As	Cd	Cu	P
$y$	analyte signal intensity <sup>b,d</sup>	cps cps <sup>-1</sup> <sup>a</sup>	cps				
$y_0$	measurement blank intensity <sup>b,d</sup>	cps cps <sup>-1</sup> <sup>a</sup>	cps				
$y_{\text{GasBl}}$	gas blank intensity <sup>b,d</sup>		cps				
$y_{\text{IS}}$	internal standard intensity <sup>b,d</sup>		cps				
$y_{0,\text{IS}}$	measurement blank internal standard intensity <sup>b,d</sup>		cps				
					measurement specific parameters		
$b_{\text{cal}}$	calibration line intercept <sup>b,d</sup>	cps cps <sup>-1</sup> <sup>a</sup>	cps cps <sup>-1</sup>				
$a_{\text{cal}}$	calibration line slope <sup>b,d</sup>	cps cps <sup>-1</sup> L $\mu\text{g}^{-1}$ <sup>a</sup>	cps cps <sup>-1</sup> cm <sup>2</sup> $\mu\text{g}^{-1}$				
$f_e$	elution factor <sup>b,d</sup>	1		0.81 ± 0.04	0.92 ± 0.02	0.82 ± 0.01	97 ± 0.03
$V_s$	eluate volume <sup>c,e</sup>	mL			10 ± 0.1		
$f_{\text{dil}}$	eluate dilution factor <sup>c,e</sup>	1		1 ± 0.01 (low conc.)	5 ± 0.1 (high conc.)		
$d_{\text{disc}}$	resin gel disc diameter <sup>b,d</sup>	cm			2.50 ± 0.025		
$\Delta g_{\text{rg}}$	resin gel thickness <sup>b,d</sup>	cm			0.04 ± 0.0006		
$\Delta g_{\text{dl}}$	diffusive layer thickness (diffusive gel + filter membrane) <sup>b,d</sup>	cm			0.093 ± 0.0017		
$\delta$	diffusive boundary layer (DBL) thickness <sup>c,d</sup>	cm			0.0107 ± 0.00107		
$D_{\text{gel}}$	analyte diffusion coefficient in the diffusive layer <sup>b,d</sup>	10 <sup>-6</sup> cm <sup>2</sup> s <sup>-1</sup>		5.93 ± 0.155	5.97 ± 0.119	6.08 ± 0.130	6.01 ± 0.147
$D_w$	analyte diffusion coefficient in water <sup>b,d</sup>	10 <sup>-6</sup> cm <sup>2</sup> s <sup>-1</sup>		8.34 ± 0.500	6.75 ± 0.500	6.75 ± 0.500	7.79 ± 0.500
$d_{\text{sw}}(\text{eff})$	effective sampling window diameter <sup>b,d</sup>	cm			2.07 ± 0.0035		
$t$	deployment time <sup>c,f</sup>	s	s				sampling specific ± 300

<sup>a</sup>Unit based on relative intensities. <sup>b</sup>Type A uncertainty. <sup>c</sup>Type B uncertainty. <sup>d</sup>Parameter normally distributed. <sup>e</sup>Parameter triangularly distributed. <sup>f</sup>Parameter rectangularly distributed; see SI for the cause and effect diagrams (Figure S1) and details on uncertainty types and parameter distributions.

the DBL and lateral diffusion cancel each other, their contributions to the measurement uncertainty do not. One aim of this study is therefore to compare the uncertainty associated with the expanded DGT equation (eq 3), where the contribution of the DBL and  $A_{\text{eff}}$  are explicitly considered, with that of the standard DGT equation (eq 1), where this is not the case.

**DGT and Chemical Imaging.** Apart from bulk analysis, DGT approaches are used to generate chemical images of labile solutes in soils or sediments, some of which work at a high spatial resolution (submm range). Different imaging methods have been developed which have in common that the calibration of the quantitative images is a challenging analytical step.<sup>4,6,39–41</sup> An established approach for preparing matrix matched standards for DGT - laser ablation - inductively coupled plasma mass spectrometry (DGT LA-ICP-MS) analysis is to load DGT gels with known amounts of analyte.<sup>11,39</sup> However, the resulting calibration curve (signal intensity vs gel loading), usually has considerable uncertainties on both axes. Because ordinary least-squares regression (OLS) requires that one parameter (usually  $x$ ) is known with negligible uncertainty, a line estimation method that accounts for uncertainties on both axes has to be used for this type of calibration.<sup>39,40</sup> Hyk et al.<sup>42</sup> recently used the bivariate weighted line fitting method (BWF) of York et al.,<sup>43</sup> that accounts for uncertainties on the  $x$ - and  $y$ -axis by using them as weights. In this study this method was used for the calculation of the calibration parameters for the LA-ICP-MS data.

While the basic sampling procedure for DGT chemical imaging is similar to bulk DGT sampling, there are important differences in the setup and accordingly also the uncertainty contributors. There is no DBL as in solution based sampling, lateral diffusion is negligible as the diffusion layers are very thin

and no elution is required prior to measurement. This reduces the number of potential uncertainty sources as shown in eq 5 and SI Figure S1.

**Identifying and Analyzing Uncertainty Sources of the DGT Equation.** We identified all non-negligible uncertainty contributors of a DGT measurement using cause-and-effect diagrams (see SI Figure S1) and an input table for all parameters that are considered (Table 1).<sup>44,45</sup>

All relevant parameters of the sampling and analysis steps (based on SI Figure S1 and Table 1) were included in the model equations for calculating the combined standard uncertainty. The resulting model equation for bulk DGT analysis without considering the DBL and lateral diffusion, eq 4A, is a modification of eq 1 using the instrument output (intensity or relative intensity) as well as the calibration parameters (slope and intercept) of an OLS curve fit. The model equation for bulk DGT analysis including the DBL and lateral diffusion (eq 4B) is a modification of eq 3.

$$c_{\text{DGT}} = \frac{y - y_0 - b_{\text{cal}}}{a_{\text{cal}}} \times \frac{f_{\text{dil}} \times f_e \left( V_s + \frac{d^2 \pi}{4} \Delta g_{\text{rg}} \right) \Delta g_{\text{dl}}}{\frac{d_{\text{sw}}^2 \pi}{4} t \times D_{\text{gel}}} \quad (4A)$$

$$c_{\text{DGT}} = \frac{y - y_0 - b_{\text{cal}}}{a_{\text{cal}}} \times \frac{f_{\text{dil}} \times f_e \left( V_s + \frac{d^2 \pi}{4} \Delta g_{\text{rg}} \right) \left( \frac{\Delta g_{\text{dl}}}{D_{\text{gel}}} + \frac{\delta}{D_w} \right)}{\frac{d_{\text{sw}}^2 \pi}{4} t} \quad (4B)$$



The model equation for DGT LA-ICP-MS analysis (eq 5) is a modified version of eq 2B and also uses the instrument output as input data. The calibration parameters are calculated using bivariate weighted line fitting (BWF).<sup>43</sup>

$$F_{\text{DGT}} = \frac{\frac{y - y_{\text{GasBl}}}{y_{\text{IS}}} - \frac{y_0}{y_{0,\text{IS}}} - b_{\text{cal}}}{a_{\text{cal}} \times t} \quad (5)$$

## ■ EXPERIMENTAL SECTION

**Experimental Design.** Two model anions, As and P (predominantly present as  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ ) and two model cations Cd and Cu (predominantly present as  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$ ) were chosen for the exemplary calculation of combined uncertainties of DGT measurements. The determination of elemental concentrations in liquid samples was performed on a Thermo Fisher ELEMENT XR (Thermo Fisher Scientific, Bremen, Germany) ICP-MS. The determined practical quantification limit (PQL) was  $0.73 \mu\text{g L}^{-1}$  for As,  $0.18 \mu\text{g L}^{-1}$  for Cd,  $0.83 \mu\text{g L}^{-1}$  for Cu and  $0.97 \mu\text{g L}^{-1}$  for P (see SI).

**DGT Gel Preparation.** Diffusive gels were prepared according to standard methods.<sup>1</sup> Chelex 100 resin gels and standard DGT samplers were provided by DGT Research Ltd. (Lancaster, UK). Ferrihydrite resin gels were prepared according to Santner et al.<sup>6</sup> The high resolution mixed binding gel (HR-MBG) was produced according to Kreuzeder et al.<sup>11</sup>

**Evaluation of the Uncertainties of the Contributing Variables.** *Effective Sampler Window Size.* The diameter of the sampling window of the DGT sampler caps provided by DGT Research Ltd. (Lancaster, UK) was measured with a sliding caliper ( $\pm 0.01 \text{ mm}$ ) on 20 caps from two different orders in 2012 and 2013.

*Diffusive Layer Thickness.* The thickness of diffusive gels (nominally 0.78–0.80 mm) was measured using a traveling microscope ( $\pm 0.02 \text{ mm}$ ; Vickers Instruments) on gels produced at the laboratory of the Institute of Soil Research (University of Natural Resources and Life Sciences Vienna, Austria) and gels provided by DGT Research Ltd. (Lancaster, UK).

*Eluate Volume and Eluate Dilution Factor.* The uncertainty of the eluate volume and the eluate dilution factor is determined by the uncertainty of the pipet used to transfer the eluent. Pipette uncertainty (Eppendorf Research, 0.2, 1, 5, and 10 mL adjustable) was specified by the manufacturer as  $\pm 0.6\%$  systematic error and  $\pm 0.15$ – $0.20\%$  random error. The pipettes were checked for systematic errors at least once a month gravimetrically.

*Elution Factor.* The elution factors for Cd and Cu from Chelex 100 gels were determined using a common elution procedure.<sup>24,46</sup> Using a modified elution procedure (i.e., increase of the elution volume from 1 to 10 mL) a possible reduction of uncertainty was investigated. It was assumed, that the use of a small elution volume leads to a larger error due to sample preparation and handling and that this error can be reduced by the use of larger elution volumes. However, this is only suitable if the analyte concentrations in the eluate remain high enough so that detrimental effects due to the dilution are avoided. Similarly, As and P elution factors were determined for eluting ferrihydrite gels in sulfuric acid solution (as commonly used in photometric measurements of P) and in nitric acid solution (as commonly used for ICP-MS analyses).<sup>3,6</sup>

For analyte loading the resin gel discs were put into 10 mL solutions containing cations ( $542 \mu\text{g L}^{-1}$  Cu and  $431 \mu\text{g L}^{-1}$  Cd) or anions ( $205 \mu\text{g L}^{-1}$  As and  $197 \mu\text{g L}^{-1}$  P) and were shaken for

4 h. After retrieval, the Chelex 100 resin gels were eluted for 8 h on a horizontal shaker in  $1 \text{ mol L}^{-1} \text{ HNO}_3$  in two batches (six gels per batch) using 1 and 10 mL of eluent, respectively. Two batches of ferrihydrite containing resin gels (10 gels per batch) were eluted in 10 mL of  $1 \text{ mol L}^{-1} \text{ HNO}_3$  and 10 mL of  $0.25 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ , respectively. The uncertainty was calculated as the standard deviation of the elution factors.

*Analyte Diffusion Coefficient in the Diffusive Layer.* A diffusion cell as described by Scally et al.<sup>26</sup> was used to determine the diffusion coefficients of As(V), Cd, Cu and P in common, commercially available APA2<sup>26,27</sup> diffusive gel. The solution pH was 5.4, at which the predominant species are  $\text{H}_2\text{PAO}_4^-$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{H}_2\text{PO}_4^-$ . Diffusion coefficients were calculated using SI eq S2, the combined uncertainty for the determined values was calculated using the Kragten method (see SI for details).<sup>23</sup>

*Repeatability of Bulk DGT Analysis.* The repeatability of a bulk DGT measurement was determined by measuring replicate bulk DGT samplers (7 replicates using Chelex 100 resin gels; eight replicates using ferrihydrite containing resin gels) after deployment for 12 h in analyte-containing solutions ( $200 \mu\text{g L}^{-1}$  Cd and Cu or  $200 \mu\text{g L}^{-1}$  As and P). After retrieval, the resin gels were eluted in 10 mL of  $1 \text{ mol L}^{-1} \text{ HNO}_3$  for 8 h and  $c_{\text{DGT}}$  was determined. The repeatability was expressed as the relative standard deviation of the  $c_{\text{DGT}}$  value.

*Uncertainty of Bulk DGT Analysis.* The combined uncertainty of  $c_{\text{DGT}}$  values for As, Cd, Cu and P was calculated for bulk DGT analysis. The calibration curve for bulk DGT measurements was based on aqueous standards and calculated using OLS regression. The standard errors of the regression line estimators were adopted as the uncertainties on the slope,  $u(a_{\text{cal}})$ , and the intercept,  $u(b_{\text{cal}})$ .

To investigate the influence of the deployment solution concentration as well as the eluate concentration on the uncertainty of the measurement, uncertainty budgets for increasing concentrations in the immersion solutions ( $1$ – $242 \mu\text{g L}^{-1}$  P for 12 h deployments) were calculated. In this experiment, where P was used as a model analyte, all contributors to the uncertainty were constant except for the eluate concentration and its associated standard deviation.

To investigate the effect of the elution procedure on the uncertainty, the uncertainty for the elution in 1 mL of  $1 \text{ mol L}^{-1} \text{ HNO}_3$  for 8 h and in 10 mL of  $1 \text{ mol L}^{-1} \text{ HNO}_3$  for 8 h were calculated.

*Uncertainty in DGT LA-ICP-MS Analysis.* Uncertainty budgets for LA-ICP-MS imaging using a UP 193-FX (ESI, NWR Division, Fremont, CA) laser ablation system coupled to a NexION 300D (PerkinElmer, Waltham, MA) ICP-MS instrument was calculated. Where applicable, the same uncertainties as in the bulk DGT analysis were used. An exemplary calibration for high spatial resolution measurements (submm scale) for As, Cd, Cu, and P on DGT gels using LA-ICP-MS was measured using a published procedure.<sup>11</sup> The uncertainty budgets were calculated for line ablations of DGT gels. The laser ablation settings were identical to those reported in Kreuzeder et al.<sup>11</sup>

## ■ RESULTS AND DISCUSSION

The values and uncertainties of the contributing variables are summarized in Table 1. The analyte specific variables with considerable variability in literature, specifically the elution factor and analyte diffusion coefficient, as well as the consideration of the effective sampling area are discussed in the following.

**Elution Factor.** The efficiency of the elution step was investigated by several authors. As shown in SI Table S1, the

values measured in this study are comparable to reported values if similar elution procedures were used. However, for As the elution efficiencies deviate up to 10%.<sup>46</sup>

Using Chelex 100 gels and elution in 10 mL HNO<sub>3</sub> ( $c = 1 \text{ mol L}^{-1}$ ) the elution efficiencies were  $92 \pm 1.9\%$  for Cd and  $82 \pm 1.2\%$  for Cu. The elution in 1 mL HNO<sub>3</sub> ( $c = 1 \text{ mol L}^{-1}$ ) yielded elution efficiencies of  $86 \pm 3.1\%$  (Cd) and  $83 \pm 3.0\%$  (Cu).

The elution efficiencies of oxyanions from ferrihydrite gels were  $97 \pm 2.5\%$  ( $1 \text{ mol L}^{-1} \text{ HNO}_3$ ) and  $100 \pm 2.2\%$  ( $0.25 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ) for P and  $81 \pm 4.4\%$  ( $1 \text{ mol L}^{-1} \text{ HNO}_3$ ) and  $89 \pm 1.9\%$  ( $0.25 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ) for As. Ferrihydrite dissolves in acids which makes the incomplete recovery of As surprising (see SI).

**Analyte Diffusion Coefficient in the Diffusive Layer.** Measurements of the diffusion coefficients for As(V), Cd, Cu and P were performed and the combined uncertainty was calculated using the Kragten approach (see SI). The determined diffusion coefficients as well as the values provided in literature were temperature-corrected to 25 °C for comparability<sup>2</sup> (SI eq S3). The measured diffusion coefficients and combined uncertainties ( $k = 1$ ; all values  $\times 10^{-6}$ ) are  $5.93 \pm 0.155 \text{ cm}^2 \text{ s}^{-1}$  for As(V),  $5.97 \pm 0.119 \text{ cm}^2 \text{ s}^{-1}$  for Cd,  $6.08 \pm 0.130 \text{ cm}^2 \text{ s}^{-1}$  for Cu and  $6.01 \pm 0.147 \text{ cm}^2 \text{ s}^{-1}$  for P, which is in good agreement with literature. The related relative combined uncertainties ( $k = 1$ ) were 2.0% (Cd), 2.1% (Cu), 2.5% (P) and 2.6% (As), which is small compared to the variability in published studies (see SI).

Diffusion coefficients of As(V), Cd, Cu, and P in APA2 gels<sup>26</sup> were investigated by several authors and are summarized in SI Table S2. Whereas for Cd, Cu, and P only a few studies reporting diffusion coefficients based on diffusion cell experiments are available,<sup>26,36,37</sup> there is a substantial number of literature data based on diffusion cell experiments for As(V). However, uncertainties of diffusion coefficients are only rarely reported.

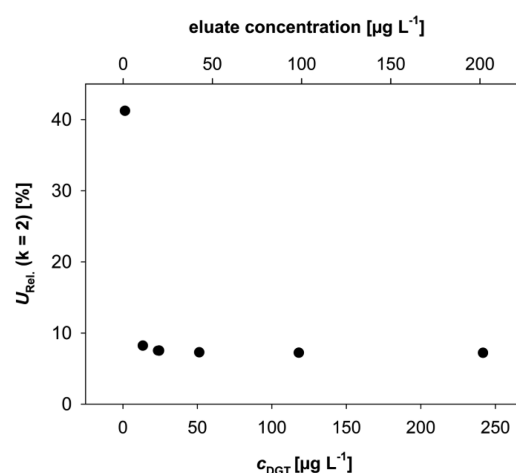
**Effective Sampling Area.** For the adopted  $d_{\text{sw(eff)}}$  value of 2.07 cm 3.37 cm<sup>2</sup> we estimated an uncertainty of 0.0017 cm, corresponding to the uncertainty obtained for the measurement of the physical sampling window size. As the effect of lateral diffusion and that of the DBL outside the sampler were shown to balance each other,<sup>24</sup> a corresponding value for the DBL thickness of 0.107 mm (Santner et al., in preparation) with an uncertainty of 10% was used. This relatively large uncertainty estimate was chosen as the variation in the DBL thickness might be considerable.<sup>24</sup>

**Repeatability of Bulk DGT Analysis.** The repeatability of bulk DGT sampling was determined to be 4.9% for As, 4.7% for Cd, 5.6% for Cu and 5.6% for P.

**Systematic Errors.** We identified two potential sources for systematic errors during DGT analysis. For the calculation of DGT uncertainty we adopted the measured values, as uncertainty only covers random error sources.

- (1) The diffusive gel thickness was found to be 1.1% - 2.2% smaller than the nominal value of 0.80 mm (see SI).
- (2) The sampling area was found to be systematically underestimated by 1.4% due to a smaller diameter of the caps ( $19.86 \pm 0.03 \text{ mm}$ ) than the nominal 20 mm.

**Low Analyte Concentrations in the Eluate as a Major Uncertainty Contributor.** Figure 1 shows that the eluate concentration strongly influences the uncertainty of a DGT measurement. The relative uncertainty for a  $c_{\text{DGT}}$  value of  $1.3 \mu\text{g L}^{-1}$  P is 41.2% ( $k = 2$ ) while this uncertainty sharply decreases to 8.2% at a  $c_{\text{DGT}}$  value of  $13.3 \mu\text{g L}^{-1}$  P and further slowly decreases to 7.2% at a  $c_{\text{DGT}}$ -concentration of  $242 \mu\text{g L}^{-1}$  of P. An extreme example is a  $c_{\text{DGT}}$ -value of  $1.7 \mu\text{g L}^{-1}$  Cd resulting in a relative



**Figure 1.** Relative uncertainty ( $k = 2$ ) plotted against increasing  $c_{\text{DGT}}$  values for P (lower axis) and eluate concentration (top axis) in a 12 h deployment in a  $c_{\text{DGT}}$ -range from  $1.3 \mu\text{g L}^{-1}$  to  $242 \mu\text{g L}^{-1}$  ( $\Delta g_{\text{dl}} = 0.093 \text{ cm}$ ,  $D (\text{P}) = 6.01 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ).

uncertainty of 80.2% while at a  $c_{\text{DGT}}$ -concentration of  $470 \mu\text{g L}^{-1}$  Cd the uncertainty is 7.9% ( $k = 2$ , Table 2). In this case the uncertainty of the intercept of the calibration curve contributes excessively to the combined uncertainty. When measurements are performed at low eluate concentrations, the major contributors to the uncertainty are predominantly the calibration parameters, especially the uncertainty of the intercept ( $b_{\text{cal}}$ ). At elevated concentrations the major contributors are  $f_{\text{c}}$  and  $D_{\text{gel}}$ , resulting in relative uncertainties of 7.0–12.9% ( $k = 2$ , Table 2). This clearly illustrates, that measurements of eluate concentrations close to the PQL lead to increased uncertainties. In such cases the uncertainty could be considerably reduced by increasing the eluate concentration, for example, by using longer DGT deployment times, by the use of a thinner diffusion layer or by using smaller eluate volumes. Furthermore, a change in analytical instrumentation, e.g., P measurement on an ICP-MS instrument instead of a photometer, can lead to better sensitivities and lower LODs.

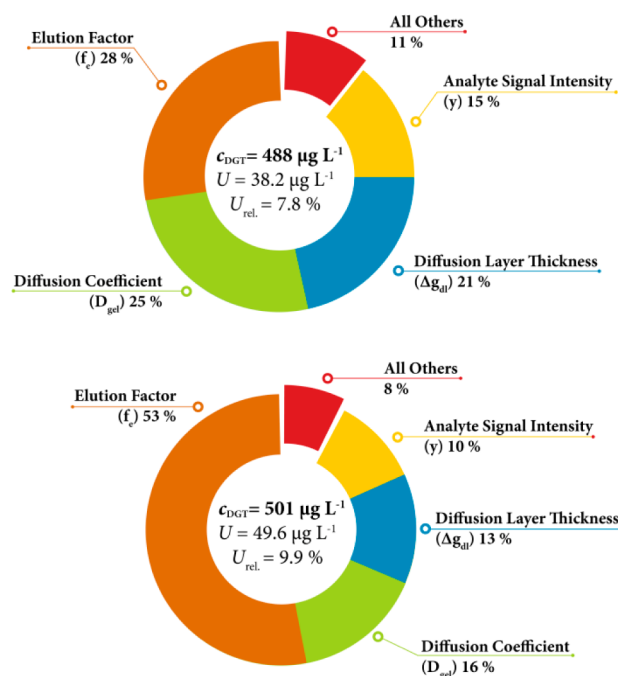
The elution factor and the corresponding elution strategy can strongly influence the resulting uncertainty as shown in Figure 2. The uncertainty of the elution step was considerably smaller when 10 mL of eluent were used (1.9% for Cd) compared to 1 mL of eluent (3.1% for Cd; see SI Table S1 for other analytes). The increase in the uncertainty of this single contributor leads to an increase of the relative expanded uncertainty from 7.8% ( $488 \pm 38.2 \mu\text{g L}^{-1}$ ;  $U$ ;  $k = 2$ ) to 9.9% ( $501 \pm 49.6 \mu\text{g L}^{-1}$ ;  $U$ ;  $k = 2$ ).

**Combined Standard Uncertainty of bulk DGT-Analysis.** The measurement uncertainty of bulk DGT measurements and the corresponding major uncertainty contributors are reported in Table 2. We found that at well-controlled experimental conditions the combined uncertainty of bulk DGT measurements is  $\sim 10\%$  based on a 95% confidence interval ( $k = 2$ ). Grouping the uncertainties to the DGT sampling, the sample preparation and the analytical step shows, that the uncertainty contributions from DGT sampling are low for the cases presented here, with values between 0.3% and 3.3% at low analyte concentrations ( $c_{\text{DGT}} 1.7\text{--}13.6 \mu\text{g L}^{-1}$ ) and between 2.9% to 6.0% at high analyte concentrations ( $c_{\text{DGT}} 251\text{--}470 \mu\text{g L}^{-1}$ ). At low analyte concentrations the contributions from the analytical steps (measurement and calibration) dominate while at higher analyte concentrations this contribution becomes increasingly smaller. It might be possible to achieve even lower

Table 2. Uncertainties of Exemplary DGT Measurements ( $\Delta g_{dl} = 0.093$  cm,  $t = 12$  h,  $V_s = 10$  mL,  $f_e$  and  $D_{gel}$ ; cf. Table 1)<sup>a</sup>

		unit	As	Cd	Cu	P
bulk DGT (low concentration)	$c_{DGT}$ (standard DGT eq 1) <sup>b</sup>	$\mu\text{g L}^{-1}$	4.9	1.7	2.4	13.4
	$c_{DGT}$ (expanded DGT eq 3) <sup>b</sup>	$\mu\text{g L}^{-1}$	5.0	1.7	2.5	13.6
	RSD (measurement)	%	0.18	1.33	0.38	1.9
	$U$ ( $k = 1$ ); $U_{Rel.}$ ( $k = 1$ )	$\mu\text{g L}^{-1}$ ; %	0.6; 11.7	0.7; 40.1	0.4; 16.6	0.6; 4.5
	grouped uncertainty contribution (analytical steps; sample preparation; sampling)	%	8.3; 0.0; 3.3	39.8; 0.0; 0.3	16.0; 0.0; 0.7	1.6; 0.1; 2.8
	$U_{Rel.}$ ( $k = 2$ )	%	23.3	80.2	33.3	9.0
	largest contributor (relative contribution to the uncertainty in %)		$b_{cal}$ (71)	$b_{cal}$ (99)	$b_{cal}$ (96)	$D_{gel}$ (24)
bulk DGT (high concentration)	$c_{DGT}$ (standard DGT eq 1) <sup>b</sup>	$\mu\text{g L}^{-1}$	249	456	440	348
	$c_{DGT}$ (expanded DGT eq 3) <sup>b</sup>	$\mu\text{g L}^{-1}$	251	470	453	353
	RSD (measurement)	%	0.95	1.60	0.53	0.38
	$U$ ( $k = 1$ ); $U_{Rel.}$ ( $k = 1$ )	$\mu\text{g L}^{-1}$ ; %	16.2; 6.4	18.6; 4.0	15.9; 3.5	12.8; 3.6
	grouped uncertainty contribution (analytical steps; sample preparation; sampling)	%	0.3; 0.1; 6.0	1.0; 0.1; 2.9	0.2; 0.1; 3.2	0.1; 0.1; 3.4
	$U_{Rel.}$ ( $k = 2$ )	%	12.9	7.9	7.0	7.2
	largest contributor (relative contribution to the uncertainty in %)		$f_e$ (71)	$f_e$ (27)	$D_{gel}$ (29)	$D_{gel}$ (37)
DGT LA-ICP-MS	$F_{DGT}$ (eq 2B)	$\text{pg cm}^{-2} \text{ s}^{-1}$	1.93	4.83	0.57	3.88
	RSD (signal)	%	11.2	16.0	14.3	10.5
	$U$ ( $k = 1$ ); $U_{Rel.}$ ( $k = 1$ )	$\text{pg cm}^{-2} \text{ s}^{-1}$ ; %	0.87; 45.2	1.47; 30.5	0.12; 21.2	0.67; 17.2
	$U_{Rel.}$ ( $k = 2$ )	%	90.5	61	42.4	34.4
	largest contributor (relative contribution to the uncertainty in %)		$b_{cal}$ (93)	$y$ (68)	$y$ (47)	$y$ (55)

<sup>a</sup>RSD: relative standard deviation.  $k$ : coverage factor (confidence interval 68% for  $k = 1$ , 95% for  $k = 2$ ).  $U_{Rel.}$ : relative combined uncertainty. Grouped Uncertainty Contributors: Analytical Steps ( $y, y_0, b_{cal}, a_{cal}$ ), Sample Preparation ( $f_{dil}, V_s$ ) and Sampling ( $d_{disc}, \Delta g_{reg}, \Delta g_{dl}, f_e, d_{sw} (eff), t, D_{gel}, \delta, D_w$ ). <sup>b</sup> $c_{DGT}$  calculated using the standard DGT equation (eq 1) is given to demonstrate the small deviation from  $c_{DGT}$  calculated using the expanded equation (eq 3). All other results ( $U, U_{Rel.}$ , uncertainty contributions) in this table are based on  $c_{DGT}$  (eq 3).



**Figure 2.** Relative distributions of uncertainty contributors ( $k = 2$ ) for  $c_{DGT}$  (Cd) based on two measurements with varying elution procedures using 10 mL (top) and 1 mL (bottom) eluent, respectively. Note that along with the variation in the resulting  $c_{DGT}$  also the uncertainty contributions of the elution factor ( $f_e$ ) and the signal ( $y$ ) vary due to the change in the eluate concentration.

uncertainties with careful optimization of DGT measurements, but also considerably higher uncertainties are possible if the experimental conditions are not optimized. The design of the

uncertainty calculation and the quantification of corresponding uncertainty contributors are critical. A study by Knutsson et al.<sup>22</sup> found very different results compared to this investigation due to the differential attribution of uncertainty values and the used model equation. While the estimate of the combined uncertainty is similar ( $c_{DGT} 1.32 \mu\text{g L}^{-1}$ ;  $U_{rel.} = 15.2\%$ ,  $k = 2$ ) to the results of this study, the uncertainties of individual contributors like  $A_{eff}$  time and the DBL thickness ( $\delta$ ) are very high while other important contributors (e.g., calibration) remained unconsidered.

The  $c_{DGT}$  values obtained from the standard (eq 1) and expanded (eq 3) DGT equations reveal that they do not yield identical results, but deviate by  $\sim 2\%$ . Deviations in the order of a few percent can hardly be avoided due to lateral diffusion inside the sampler and the DBL layer (Santner et al., in preparation). However, in many applications of environmental analytical chemistry deviations of this size are considered acceptable. The difference in the uncertainties, with and without considering the DBL and lateral diffusion inside the sampler, is in a similar range. This shows that the use of the standard DGT Equation (eq 1) does not underestimate the uncertainty of a DGT measurement.

The relative standard deviations of the eluate concentration measurement (0.18–1.90%, instrument precision) were considerably lower than the determined uncertainties of the DGT measurements, indicating the instrument measurement precision is not a suitable estimator of the analytical performance of DGT measurements. Moreover, the determined repeatability for the bulk DGT sampling and measurement (top-down uncertainty) is lower than the uncertainty determined using the Kragten method (bottom-up uncertainty) indicating that no major source of uncertainty during deployment and measurement of a DGT sample was omitted in the Kragten-based uncertainty assessment. However, if the repeatability is expected to cover



important uncertainty contributors that cannot be included in the Kragten method, it might be included in the bottom-up uncertainty estimation using SI eq S1 as additional parameter.

**Uncertainty of DGT LA-ICP-MS Analysis.** The data for chemical imaging analysis using DGT LA-ICP-MS are shown as  $F_{\text{DGT}}$  in Table 2 and an exemplary distribution of the contributors to the uncertainty is shown in SI Figure S2. The measured signal stability (here 10.5–16.0% standard deviation) is lower and the calibration procedure for LA-ICP-MS analysis of DGT gels involves more preparation and analytical steps than liquid analysis. This generates sources of additional uncertainty leading to relative uncertainties of the reported values for  $F_{\text{DGT}}$  of up to 10 times the values of bulk DGT analysis (34.4% for As, 90.5% for P;  $k = 2$ ). Our investigation of the uncertainty of chemical imaging using DGT LA-ICP-MS for multielement analysis show that the largest contributor to the uncertainty is the relatively low signal stability in laser ablation analysis which is also reported for other materials.<sup>47</sup> The uncertainty of DGT ablation analysis is higher by a factor of  $\sim 2$  when compared to geological samples or the uncertainty of NIST glass-standards (relative combined uncertainty of 6.4–42.9%;  $k = 2$ ).<sup>48</sup> This is most likely due to the complex polymer matrix and inhomogeneities in the distribution of the embedded resin.

**Implications for DGT Measurements.** Bulk DGT measurements and chemical imaging measurements based on the DGT method are associated with a significant and quantifiable uncertainty, which can be estimated and reported on a routine basis. This uncertainty determined in the “bottom-up” approach using the Kragten method is considerably higher than the measurement precision and higher than the standard deviation obtained in a “top-down” analysis (in-series repeatability) which is a good indication that no major source of uncertainty was omitted in this analysis. The common use of the standard deviation of a small number (often  $n = 3$ ) of replicate DGT measurements is an unreliable quality indicator. Correction for the small sample size using statistical methods (e.g., Student- $t$  factor) should be considered if this approach is used to determine sampling and measurement precision. Nevertheless, providing the standard deviation of three replicates is a suitable way to indicate the spread of results.

The results of continuous testing and development of the DGT method in the past two decades provide robust evidence for its suitability as a monitoring tool for labile solutes. Given the analytical requirements of the EU Drinking Water Directive (Annex III),<sup>49</sup> which requires a precision and a trueness of at least 10% for most dissolved ionic species, it can be expected that these can be fulfilled by DGT measurements. Although precision is not directly comparable with uncertainty, our results clearly show the potential of the DGT method for accurate monitoring applications. Conclusions on the required trueness cannot be drawn here because interlaboratory testing is not yet established for DGT-based passive sampling.

The calibration of chemical images based on DGT LA-ICP-MS allows for the assignment of a quantitative value for each data point and for the spatial differentiation of these values. However, when comparisons of absolute analyte concentrations in the chemical images are made, the uncertainty must be taken into consideration. Additionally to the aspects of the quantification strategy and associated uncertainties, the interpretation of DGT based LA-ICP-MS chemical images is usually based on differences in data point clusters, which may have characteristic shapes, and not the interpretation of single data points. The measured differences of the investigated features in previous

studies were large, that is, between a phosphorus depletion zone adjacent to a root and bulk soil a 10-fold difference of analyte signals was observed.<sup>10,11</sup> Even if the measured signal difference between bulk soil and distinct root features is low (approximately 2-fold), the obtained images allow for a sound interpretation.<sup>4</sup> Furthermore, the correct interpretation of spatially resolved images of labile species requires thorough consideration of the experimental setup. Alongside with the variability of the signal and the proper calibration strategy, imperfect contact of the sampler with the medium and series-to-series variability during laser ablation analysis can significantly alter the obtained results. These aspects, which are not included in uncertainty analysis but central to the proper application of chemical imaging techniques, have been addressed in previous work by Warnken et al.<sup>39</sup> and Stockdale et al.<sup>4,50</sup>

**Reporting of DGT-Uncertainties.** In DGT resin gel testing, a  $\pm 10\%$  deviation of  $c_{\text{DGT}}$  from the bulk solution concentration was adopted as a quality control threshold.<sup>24</sup> While this simple estimation is realistic in many cases, it can lead to an overestimation of uncertainty in well controlled experiments. At very low concentrations, when the contributions from the analytical contributors dominate, the uncertainty can be several times higher. Therefore, the uncertainty should not be assumed to be constant for different deployments. Ideally the use of an individually calculated uncertainty for each DGT application is desirable. Considering the practical limitations, adopting reported uncertainties for some less influential contributors, for example,  $A$ ,  $A_{\text{eff}}$ ,  $\Delta g_{\text{dl}}$  is a viable approach, whereas the contribution of critical parameters like  $f_{\text{e}}$ ,  $D_{\text{gel}}$  and calibration parameters should be assessed individually if possible. Consistent reporting of the uncertainty would increase the comparability of DGT measurements, which is highly desirable, especially if DGT is to be used in large scale monitoring programs, as a decision-support tool in environmental impact assessment, and in agronomic nutrient testing.

## ■ ASSOCIATED CONTENT

### ⑤ Supporting Information

Calculation of Combined Uncertainty, Cause and Effect Diagram of the uncertainty sources, Determination of uncertainties of the Contributing Variables, Critical Aspects of Gel Elution and Reported Elution Procedures, Diffusion Coefficients, Instrumental Measurement Characteristics and Solution Preparation, Example of Uncertainty Contributors in DGT LA-ICP-MS, Fits for DGT-LA-ICP-MS Calibrations, Kragten Spreadsheet of an exemplary Uncertainty Calculation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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