Supporting Information

Uncertainty evaluation of the diffusive gradients in thin films technique

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CALCULATION OF COMBINED UNCERTAINTY.

In a bottom-up uncertainty evaluation, all individual contributors to uncertainty are determined and a mathematical model is used for the propagation of all errors in the full analytical process. The measurement uncertainty can be determined rigorously using a function based on partial derivatives but for most applications this is impractical due to its complexity. Therefore a spreadsheet approach for the approximation of uncertainty can be used which also covers the full analytical process (Eq. S1) to calculate the combined standard uncertainty \( u_c \), characterizing the dispersion of the measurand during the experiment. In Eq. S1 \( u_c \) is the combined uncertainty of the measurand \( y \) depending on its input quantities \( x_1, x_2, \ldots, x_n \) which is calculated by taking the square root of the sum of squares of the contributor uncertainties \( u(x_1), u(x_2), \ldots, u(x_n) \). The Kragten spreadsheet approximation can handle simple, linear model equations, the parameters used have to be mutually independent and compensating errors have to be avoided. If dependent variables occur other equations have to be used for the estimation of uncertainty.\(^1\)

\[
\begin{align*}
\text{Eq. S1:} \quad u_c(\mathbf{y}_{x_1, x_2, \ldots}) &= \sqrt{u_{x_1}^2 + u_{x_2}^2 + \ldots} \\
\end{align*}
\]

The variability of the observed values for the sources of uncertainty are transformed into normally distributed standard uncertainties \( (u_{x_1}, u_{x_2}, \ldots) \) by assigning probability distributions. If the input quantity is estimated from independent repeated observations the arithmetic mean and standard deviation are used as the input estimate (Type A distribution). However, if an estimate of an input quantity has not been obtained from repeated observations, the associated estimated variance or the standard uncertainty is evaluated by scientific judgment based on all available information on the possible variability (Type B distribution). If a stated value and standard deviation are available from, e.g., a manufacturer’s handbook, the quantity value and standard deviation are directly used. If a value is equally probable to lie anywhere within a range of \( \pm a(x_i) \) (a uniform or rectangular distribution of possible values) an equivalent of the standard deviation is estimated by \( u^2(x_i) = (a(x_i))^2/6 \). In a case where it is more realistic to expect that values near the bounds are less likely than those near the midpoint (a triangular distribution of possible values) an equivalent of the standard deviation is estimated by \( u^2(x_i) = (a(x_i))^2/6 \). The resulting combined uncertainty is normally distributed and multiplied with a coverage factor to give the expanded uncertainty \( U \) which is equivalent to a confidence interval of 68 % (coverage factor of \( k = 1 \)), \( k = 2 \) is equivalent to a 95 % and \( k = 3 \) to a 99 % confidence interval.

S-2
CAUSE AND EFFECT DIAGRAM OF THE UNCERTAINTY SOURCES.

A Cause-and-effect diagram is used to identify all relevant contributors to uncertainty. This step aims at a comprehensive identification of uncertainty sources, but also to avoid including uncertainty contributors more than once. Figure S1 shows cause-and-effect diagrams with all contributors for bulk and DGT LA-ICP-MS measurements which are defined in Table 1. The main branches represent the parameters of the DGT equations (Eq. 1-3). The uncertainty contributors to each parameter are added as sub-branches, until the contribution becomes negligible.3

Figure S1. Cause-and-effect diagram of uncertainty components (according to Table 1). Top: Bulk DGT measurement according to Eq. 1, and, if the DBL is included Eq. 3 (DBL influence is shown in dotted lines). Bottom. DGT LA-ICP-MS measurement according to Eq. 2B.

DETERMINATION OF UNCERTAINTIES OF THE CONTRIBUTING VARIABLES

Effective Sampler Window Size. The diameter of the sampling window was found to be $19.86 \pm 0.03$ mm. The investigated sampler caps were taken from two separate production batches with about one year between the deliveries. The variability within each batch was $19.86 \pm 0.04$ mm and $19.86 \pm 0.03$ for 2012 and 2013, respectively.

Deployment Time. In a common experiment including many samplers, retrieval of DGT samplers and removal of the resin gel can be performed with an uncertainty of $\pm 5$ minutes, resulting in an uncertainty of 0.35 % for a 24 h deployment. This uncertainty was converted to a standard deviation equivalent using a rectangular distribution.
**Diffusive Layer Thickness.** The measurement of the thickness of 8 diffusive gels provided by DGT Research Ltd. (Lancaster, UK) gave a value of 0.78 ± 0.01 mm (RSD = 1.6 %). The same measurement with a diffusive gel produced in a laboratory of the University of Natural Resources and Life Sciences Vienna (Austria) gave a similar result of 0.79 ± 0.01 mm (RSD = 1.8 %).

**Eluate Dilution Factor and Eluate Volume.** An uncertainty of 1 % was used to account for the uncertainty of pipetting. This uncertainty value was assigned to the eluate volume ($V_s$) as well as of the eluate dilution factor ($f_d$) and was considered to be triangularly distributed.

**CRITICAL ASPECTS OF GEL ELUTION AND REPORTED ELUTION PROCEDURES.**

**Elution of As from Ferricydrate-Containing Resin Gels.** The elution efficiencies for oxyanions from ferricydrate gels were investigated based on the elution procedure of a commonly used colorimetric determination method for P (10 mL of 0.25 mol L$^{-1}$ H$_2$SO$_4$) and elution in nitric acid for subsequent ICP-MS analysis (10 mL of 1 mol L$^{-1}$ HNO$_3$). Ferricydrate dissolves in acids, therefore 100 % analyte recovery is usually assumed. The P elution efficiencies of 97 ± 2.5 % (1 mol L$^{-1}$ HNO$_3$) and 100 ± 2.2 % (0.25 mol L$^{-1}$ H$_2$SO$_4$) determined in this study, and literature reports of 100.9 ± 5.4 %$^4$ and 101.4 ± 2.1 %$^5$, are in line with this assumption. However, the elution efficiencies for As were considerably lower with 81 ± 4.4 % (1 mol L$^{-1}$ HNO$_3$) and 89 ± 1.9 % (0.25 mol L$^{-1}$ H$_2$SO$_4$). The As elution efficiency from ferricydrate gels, 78 ± 4.8 % (1 mL of 1 mol L$^{-1}$ HNO$_3$) and 78 ± 7.7 % (1 mL of 0.3 mol L$^{-1}$ H$_2$SO$_4$), reported by Luo et al.$^6$, also deviated considerably from full recovery. Given the dissolution of the sorbing phase this incomplete recovery is surprising. These experimental data suggest that phosphate is completely in solution while a fraction of undissolved iron arsenate remains in the resin gel at least in dilute acids. Only for elution with concentrated acids complete recovery of As was reported (conc. HCl: 100 ± 5 %$^7$; conc. HNO$_3$: 99 %$^8$).

**Gel Swelling during Elution.** The calculation of elution factors usually assumes that the resin gel disc volume (196 µL; 2.5 cm diameter, 0.4 mm thickness) consists largely of water and therefore dilutes the eluent volume in which it is placed. However, an increased resin gel weight of 332 ± 15 µg (n = 12) was observed after placing Chelex 100 gels in the eluent (1 mol L$^{-1}$ HNO$_3$, $\rho = 1.027$ g ml$^{-1}$). Presumably, the known effect of gel-swelling in acid$^9$ leads to the removal of more volume from the solution causing a systematic overestimation of the eluate volume. If this is left unaccounted, e.g. by assuming a constant eluate volume which is directly used for the further sample preparation, this systematic error is introduced into the analysis. In case of large elution volumes, the bias is small (for 10 mL: ~1 %) but if the elution is performed in 1 mL of eluent and the loss of volume is not accounted for, this can cause a bias of ~ 10 %. As a systematic error, this can easily be corrected for by using defined eluate aliquots for sample preparation or by considering gel swelling during the elution process. Also, the use of larger eluate
volumes (10 mL instead of 1 mL) minimizes systematic as well as random errors introduced by the elution procedure.

**Measured and Reported Values for the Elution Factor.** The elution factors for different elution procedures were investigated. A summary of the reported and measured values is shown in Table S1.

**Table S1.** Overview on measured and reported elution efficiencies for As, Cd, Cu and P for different eluents and resin gel types.

| $f_e$ Cd [%] | $f_e$ Cu [%] | Eluent | Resin Type and Source |
|-------------|-------------|--------|-----------------------|
| 92 ± 1.9    | 82 ± 1.2    | 10 mL 1 mol L$^{-1}$ HNO$_3$ (8 h) | Chelex 100; this study |
| 86 ± 3.1    | 83 ± 3.0    | 1 mL 1 mol L$^{-1}$ HNO$_3$ (8 h) | Chelex 100; this study |
| 81          | 84          | 1 mL 1 mol L$^{-1}$ HNO$_3$ (12 h) | SPR-IDA$^{10}$ |
| 78 ± 4      | 83 ± 4      | 1 mL 1 mol L$^{-1}$ HNO$_3$ (12 h) | Chelex 100$^{11}$ |
| 85 ± 2.3    | 83 ± 4      | 1 mL 1 mol L$^{-1}$ HNO$_3$ (24 h) | Chelex 100$^{12}$ |
| 83.9 ± 2.7  | 79.3 ± 6.4  | 1 mL 2 mol L$^{-1}$ HNO$_3$ (overnight or shaken for a few hours) | Chelex 100$^{13}$ |
| 98.8 ± 0.9  | 97.7 ± 1    | 1 mL conc. HNO$_3$ (24 h) | Chelex 100$^{14}$ |
| > 95        |             | 2 mL 2 mol L$^{-1}$ HNO$_3$ (30 min) | Chelex 100$^{15}$ |
| 71 ± 1      | 79 ± 1      | 1.2 mL 3 mol L$^{-1}$ HNO$_3$ | MBL (Chelex and ferrihydrite)$^{16}$ |

| $f_e$ As [%] | $f_e$ P [%] | Eluent | Resin Type and Source |
|-------------|-------------|--------|-----------------------|
| 81 ± 4.4    | 97 ± 2.5    | 10 mL 1 mol L$^{-1}$ HNO$_3$ (8 h) | Ferrihydrite Gel; this study |
| 89 ± 1.9    | 100 ± 2.2   | 10 mL 0.25 mol L$^{-1}$ H$_2$SO$_4$ (8 h) | Ferrihydrite Gel; this study |
| 100.9 ± 5.4 | 100.9 ± 5.4 | 10 mL 0.25 mol L$^{-1}$ H$_2$SO$_4$ (72 h) | Ferrihydrite Gel$^4$ |
| 101.4 ± 2.1 | 0.25 mol L$^{-1}$ H$_2$SO$_4$ | Ferrihydrite Gel$^5$ |
| 78 ± 4.8    |             | 1 mL of 1 mol L$^{-1}$ HNO$_3$ | Ferrihydrite Gel$^6$ |
| 78 ± 7.7    |             | 1 mL of 0.3 mol L$^{-1}$ H$_2$SO$_4$ | Ferrihydrite Gel$^6$ |
**DIFFUSION COEFFICIENTS.**

**Diffusion Coefficients Reported in Literature.** The reported values for the diffusion coefficient are summarized in Table S2.

### Table S2. Overview on reported diffusion coefficients for As(V), Cd, Cu and P at 25°C

| Literature Values (DGT Device) | As       | Cd       | Cu       | P        |
|--------------------------------|----------|----------|----------|----------|
| Average Literature Value       | 5.84E-06 | -        | -        | 6.01E-06 |
| Range of Literature Values (relative to Mean) | 34%      | -        | -        | -        |
| Literature Sources             | 7,6,17,18| -        | -        | 18       |

| Literature Values (Diffusion Cell) | As       | Cd       | Cu       | P        |
|------------------------------------|----------|----------|----------|----------|
| Average Literature Value           | 5.68E-06 | 6.22E-06 | 6.31E-06 | 6.07E-06 |
| Range of Literature Values (relative to Mean) | 19.9%    | 4.2%     | 2.5%     | 0.7%     |
| Literature Sources                 | 19,8,6,7,18 | 20*,21  | 20*,21  | 18,21   |

* Three values for Cd and Cu at ionic strengths from 0.1 – 0.001 mol L⁻¹ were reported. Here the average of these three values was used.

**Measurement of Diffusion Coefficients and Calculation of Combined Uncertainty.** A diffusion cell comprises two compartments which have a circular, 1.5 cm diameter window. A 2.5 cm diameter gel disc is placed between these openings and the assembly is clamped together. One compartment contains a solution containing the target analyte (source solution) and the other compartment an analyte-free solution (receptor solution).²⁰ The solutions in both compartments (each compartment contained 100 mL solution) are well stirred with magnetic stirrers and solution temperature was monitored. Subsamples were taken every 20 minutes during at least 3 h from both compartments. The pH value was very similar in both compartments (pH ± 0.2) and ionic strength was controlled (I = 10 mmol L⁻¹) by adding NaNO₃ (Sigma Aldrich, Reagent Plus).

The diffusion coefficient was calculated using Eq. S2 according to Scally et al.²⁰

\[ D = \frac{a \times \Delta g}{A \times C \times 60} \]  
Eq. S2

Where \( A \) (cm²) is the exposure area, \( \Delta g \) is the diffusive layer thickness (cm) between the two compartments, \( C \) is the initial concentration of the analyte containing solution (ng cm⁻³), and \( a \) is the slope of the plotted mass flow versus time in ng min⁻¹. The factor ‘60’ is correcting the value from minutes to seconds.
The uncertainty of the diffusion coefficients was calculated using the Kragten approach as described in the main paper based on Eq. S2. The parameters, their description, type, distribution and unit are shown in Table S2.

**Table S4. Input quantities considered in the calculation of diffusion coefficient uncertainty.**

| Parameter | Quantity | Type | Distribution | Unit  |
|-----------|----------|------|--------------|-------|
| $a$       | Slope of the plotted mass flow versus time | A    | normal       | ng min$^{-1}$ |
| $\Delta g$ | Diffusive layer thickness | A | normal       | cm |
| $A$       | Exposure area | B    | rectangular  | cm$^2$ |
| $C$       | Initial concentration of the analyte receiving solution | A    | normal       | ng mL$^{-1}$ |

**Temperature Correction of Diffusion Coefficients.** The measured values for the diffusion coefficient as well as the literature values were all converted to 25 °C using a modification of the Einstein-Stokes-Equation (see Zhang et al.$^{13}$ for details) to allow for comparability of the values.$^{13, 20}$

$$
\log D_t = \frac{1.37023(t - 25) + 8.36 \times 10^{-4}(t - 25)^2}{109 + t} + \log \frac{D_{25}(273 + t)}{298}
$$

**Eq. S3**

**INSTRUMENTAL MEASUREMENT CHARACTERISTICS AND SOLUTION PREPARATION.**

**Preparation of Deployment Solutions.** Single-element stock solutions were prepared by dissolving appropriate amounts of analytical grade KH$_2$PO$_4$ (Merck, pro analysi), Na$_2$HAsO$_4$ (Alfa Aesar, 98−102%), Cd(NO$_3$)$_2 \times 5$H$_2$O (Fluka, purum) and Cu(NO$_3$)$_2 \times 3$H$_2$O (Fluka, puriss), to give stock solution mass concentrations of 100 mg L$^{-1}$. Single- or multi-element solutions for DGT deployment were prepared from these stocks as required.

**Analytical Performance for the Investigated Analytes.** Estimations of the LOD (Limit of Detection) and LOQ (limit of quantification) of the instrumental performance as well as estimations of the MDL (method detection limit) and PQL (practical quantification limit) considering the DGT deployment were made. The PQL is the lowest concentration that can be reliably measured during routine laboratory operating conditions. This was done by the measurement of blank solutions (i.e. of DGT eluate samples of blank DGT gels) carried out on a ELEMENT XR (Thermo Fisher Scientific, Bremen, Germany) ICPMS instrument. LOD and LOQ were calculated as 3 times and 10 times the standard deviation of calibration blanks; MDL and PQL were calculated as 3 times and 10 times the standard deviation of DGT gel blank eluates.
**Table S3.** Analytical performance for the investigated analytes.

|          | As   | Cd   | Cu   | P    |
|----------|------|------|------|------|
| LOD [µg L⁻¹] | 0.04 | 0.03 | 0.03 | 0.09 |
| LOQ [µg L⁻¹] | 0.12 | 0.10 | 0.09 | 0.29 |
| MDL [µg L⁻¹] | 0.22 | 0.05 | 0.25 | 0.29 |
| PQL [µg L⁻¹] | 0.73 | 0.18 | 0.83 | 0.97 |

**EXAMPLE OF UNCERTAINTY CONTRIBUTORS IN DGT LA-ICP-MS.**

The contributors to the uncertainty of a DGT based LA-ICP-MS measurement were investigated (see Table 2). The relative distributions of uncertainty contributors of a representative measurement are visualized in Fig. S2.

**Figure S2.** Relative distributions of uncertainty contributors ($k = 2$) for $F_{DGT}$ (Cu) based on an exemplary measurement of a DGT gel homogeneously loaded with Cu. Note that the other contributors to the uncertainty are not represented in this graph because of their minor contribution (in total 0.05 %).
FITS FOR DGT – LA-ICP-MS CALIBRATIONS.

Four calibrations for As, Cd, Cu and P were computed using the widely used ordinary least squares regression (OLS) and the bivariate weighted fitting (BWF).\textsuperscript{22, 23} The resulting data is shown in Table S5.

**Table S5.** Calibration data for OLS and BWF fits for As, Cd, Cu and P in the form of $y = ax + b$ with the corresponding uncertainties, for which the standard errors of the line parameter estimates (slope, intercept) were adopted.

|       | OLS | BWF |
|-------|-----|-----|
| $a$   | 4.93 | 4.83 |
| $b$   | -0.01 | 0.00 |
| $U_a$ | 0.20 | 0.35 |
| $U_b$ | 0.07 | 0.01 |

|       | As | Cd | Cu | P |
|-------|----|----|----|---|
| $a$   | 4.93 | 0.31 | 7.05 | 2.47 |
| $b$   | -0.01 | -0.01 | -0.15 | -0.01 |
| $U_a$ | 0.20 | 0.01 | 0.40 | 0.09 |
| $U_b$ | 0.07 | 0.011 | 0.12 | 0.09 |

|       | As | Cd | Cu | P |
|-------|----|----|----|---|
| $a$   | 4.83 | 0.31 | 5.90 | 2.35 |
| $b$   | 0.00 | -0.01 | 0.01 | 0.07 |
| $U_a$ | 0.35 | 0.021 | 0.42 | 0.16 |
| $U_b$ | 0.01 | 0.01 | 0.04 | 0.07 |
### Exemplary spreadsheet for the calculation of uncertainties using a standard DGT sampler

| Parameter | Values | Parameter Uncertainty | Unit* | Type | Distribution | Standard Uncertainty |
|-----------|--------|-----------------------|-------|------|--------------|---------------------|
| $y$       | 293.9  | 4.395                 | cps/cps | A   | normal      | 4.395               |
| $y_0$     | 0.029  | 0.031                 | cps/cps | A   | normal      | 0.031               |
| $b_{cal}$ | 1.391  | 2.025                 | cps/cps | A   | normal      | 2.025               |
| $a_{cal}$ | 3.22   | 0.025                 | 1/µL    | A   | normal      | 0.025               |
| $f_{0,s}$ | 1.00   | 0.01                  | 1      | B   | triangular  | 0.204               |
| $V_s$     | 10.00  | 0.100                 | mL     | B   | triangular  | 10.00               |
| $V_{gel}$ | 2.500  | 0.025                 | cm     | A   | normal      | 0.025               |
| $f_{gel}$ | 0.093  | 0.002                 | cm     | A   | normal      | 0.002               |
| $f_s$     | 0.920  | 0.019                 | A      | A   | normal      | 0.019               |
| $d_{sw}$  | 2.000  | 0.003                 | cm$^2$ | A   | normal      | 0.003               |
| $t$       | 43200  | 300.0                 | s      | B   | rectangular | 173.2               |
| $D_{gel}$ | 5,97E-06 | 1,19E-07               | cm$^2$/s | A   | normal      | 1,19E-07               |

| Coeff | Model Eq. 1 | Model Eq. 2 | Model Eq. 3 | Model Eq. 4 |
|-------|--------------|--------------|--------------|--------------|
| 98 µg/L | 99           | 98           | 97           |

| 4 | Difference | 1.5 | Model Eq. 1 - Model Eq. 2 | Model Eq. 1 - Model Eq. 3 | Model Eq. 1 - Model Eq. 4 |
|---|------------|-----|---------------------------|---------------------------|---------------------------|
| 5 | Squared Difference | 2.2 | Difference$^2$ | Difference$^2$ | Difference$^2$ |
| 6 | Sum of the Squares | 14.6 | |
| 7 | Squareroot of the Sum of the Squares | 3.8 | |

**Suggested Procedure for the Calculation of Uncertainty**

1. Adapt the Parameter Spreadsheet according to the previously developed influence diagram and model equation.
2. Create a Perturbation Matrix with (a) values of the parameters in the white fields, and (b) value + standard uncertainty in the yellow fields.
3. Solve the model equation for the values in the (a) Parameter Spreadsheet and (b) the Perturbation Matrix.
4. Calculate the difference of of the model equation (3a) and the results of the model equation based on the perturbation matrix (3b).
5. Calculate the squares of the differences and take the square-root of the sum of squares.
6. The resulting value is the combined uncertainty with a coverage factor of 1.
7. Expand the uncertainty based on the required confidence: $k = 2$ for 95%; $k = 3$ for 99%

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**Model equation in this exemplary calculation:**

$$ e_{DGT} = \frac{y - y_0 - b_{cal} \times f_{gel} \times f_e (V_s + \frac{d_{sw}}{4} \pi) \Delta g_{gel} \Delta g_{gel}}{a_{cal} D_{gel} \frac{d_{sw}}{4} t} $$

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**Note:** The blue fields show exemplary data providing indicative values. These values should serve as an exemplary calculation but are not generally applicable for DGT experiments.
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