SUPPORTING INFORMATION

Two-Dimensional Visualization and Quantification of Labile, Inorganic Plant Nutrients and Contaminants in Soil

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S1. Laboratory procedures for trace element analysis

S1.1. Use laboratory water type 1 with a conductivity of ≤0.055 µS cm^{-1} at 25 °C (**Table of Materials**) for all experimental procedures and solutions.

S1.2. Use chemical reagents of analytical grade or higher for all experiments.

S1.3. Acid-clean all glassware and plastics used for DGT gel preparation and application by soaking for 24 h in 10 % (*w*/*w*) HNO_3 (**Table of Materials**) followed by rinsing at least three times with H_2O. Acid-cleaned glassware and plastics must only get in contact with metal-free materials to avoid contamination.

S1.4. Perform all DGT gel coating and handling in a laminar flow bench (**Table of Materials**) or any other dust- and metal-free environment.

S2. Fabrication of DGT gels

S2.1. Polyurethane-based mixed anion and cation binding gel (HR-MBG)[1]

S2.1.1. Pre-clean HydroMed D4 (**Table of Materials**) by washing in H_2O (1:15, *w*/*v*) for ≥120 h using an overhead shaker (**Table of Materials**) at ~5 rpm. Change the H_2O ≥4 times during this period. Dry the pre-cleaned HydroMed D4 at ~80 °C in an oven.

S2.1.2. Cut 8 g of pre-cleaned and dried HydroMed D4 to ~5 mm pieces and transfer into a 100 mL vial. Add an ethanol (**Table of Materials**)-water solution (10:1, *v*/*v*) to give a total volume of 80 mL, including the HydroMed D4 pieces. Place the vial on an overhead shaker at ~5 rpm overnight to get the polyurethane gel stock solution.

S2.1.3. Dissolve 5 g of $ZrOCl_2 \times 8H_2O$ (**Table of Materials**) in 180 mL of H_2O in a 500 mL beaker. Place the beaker on a magnetic stirrer (**Table of Materials**) at ~300 rpm and immerse a calibrated pH probe (**Table of Materials**) connected to a pH meter (**Table of Materials**) into the solution.

S2.1.4. Titrate with 0.1 mol L^{-1} NaOH (**Table of Materials**) under vigorous stirring until the pH stabilizes at 7.0.

S2.1.5. Filter the $Zr(OH)_4$ precipitate using a vacuum flask connected to a vacuum pump and equipped with a Buechner funnel (**Table of Materials**) with quantitative filter paper (**Table of Materials**). Rinse with ~3 L of H_2O and filter until excess H_2O is removed and a hydrous $Zr(OH)_4$ slurry is obtained (**Figure S1A**).

NOTE: Do not filter until the slurry falls completely dry and forms cracks.

S2.1.6. Transfer 15 g (wet weight) $Zr(OH)_4$ precipitate slurry into a 120 mL vial and add the polyurethane gel stock solution (prepared in S2.1.2) to give a total volume of 100 mL $Zr(OH)_4$ precipitate-polyurethane suspension.

S2.1.7. Mix and homogenize the $Zr(OH)_4$ precipitate-polyurethane suspension using a dispersion device (**Table of Materials**) for 5-10 min at 20,000 rpm (**Figure S1B**).

NOTE: Take apart and clean the dispersion device using ethanol immediately after deployment, as rapid setting of the $Zr(OH)_4$ precipitate-polyurethane suspension can result in damage of the components.

S2.1.8. Mix 9 mL of the homogenized $Zr(OH)_4$ precipitate-polyurethane suspension with 1 mL of suspended particulate reagent iminodiacetic acid (SPR-IDA) (**Table of Materials**).

S2.1.9. Homogenize the viscous gel suspension via vigorous shaking by hand followed by slow agitation in an overhead shaker at ~5 rpm for ≥2 h to remove air bubbles and get the final gel suspension (**Figure S1C**).

S2.1.10. Fix 0.25 mm-thin PTFE spacer strips (**Table of materials**) left and right on a glass plate (25 cm x 18 cm) using adhesive tape. Place a knife-coating device (**Table of Materials**) on the top end of the glass plate onto the spacer strips.

S2.1.11. Pipette 3-4 mL of bubble-free gel suspension as a homogeneous 1-2 cm-wide wet film on the top end of the glass plate between the spacer strips (**Figure S1D**). Immediately, coat the wet film in a continuous motion from top to bottom of the glass plate using the knife-coating device (**Figure S1E**).

S2.1.12. Place the glass plate into an oven at 65 °C until the solvent is evaporated (~10 min). Afterwards, remove the glass plate from the oven and allow to cool to room temperature.

S2.1.13. Repeat S2.1.11 - S2.1.12 two more times to obtain a triple-layer gel coating on the glass plate.

S2.1.14. Remove the spacer strips and carefully remove areas with inhomogeneous distribution of the $Zr(OH)_4$ and SPR-IDA binding phases at the outer (~2 cm) edges of the gel coating using PTFE-coated razor blades (**Figure S1F**).

S2.1.15. Immerse the glass plate in ≥1 L H_2O in a plastic container until the gel detaches by hydration. Subsequently, remove the glass plate from the H_2O container.

NOTE: If the gel does not detach from the glass plate by itself after ~3 h of hydration, the gel needs to be carefully detached manually using plastic tweezers.

S2.1.16. Hydrate the gel in the H_2O bath for 24 h at room temperature. Exchange the H_2O at least three times within 24 h to remove excess reagents from the gels.

S2.1.17. Store the hydrated 0.1 mm-thin HR-MBG in H_2O at 6 °C. The shelf life of the HR-MBG is 47 days.

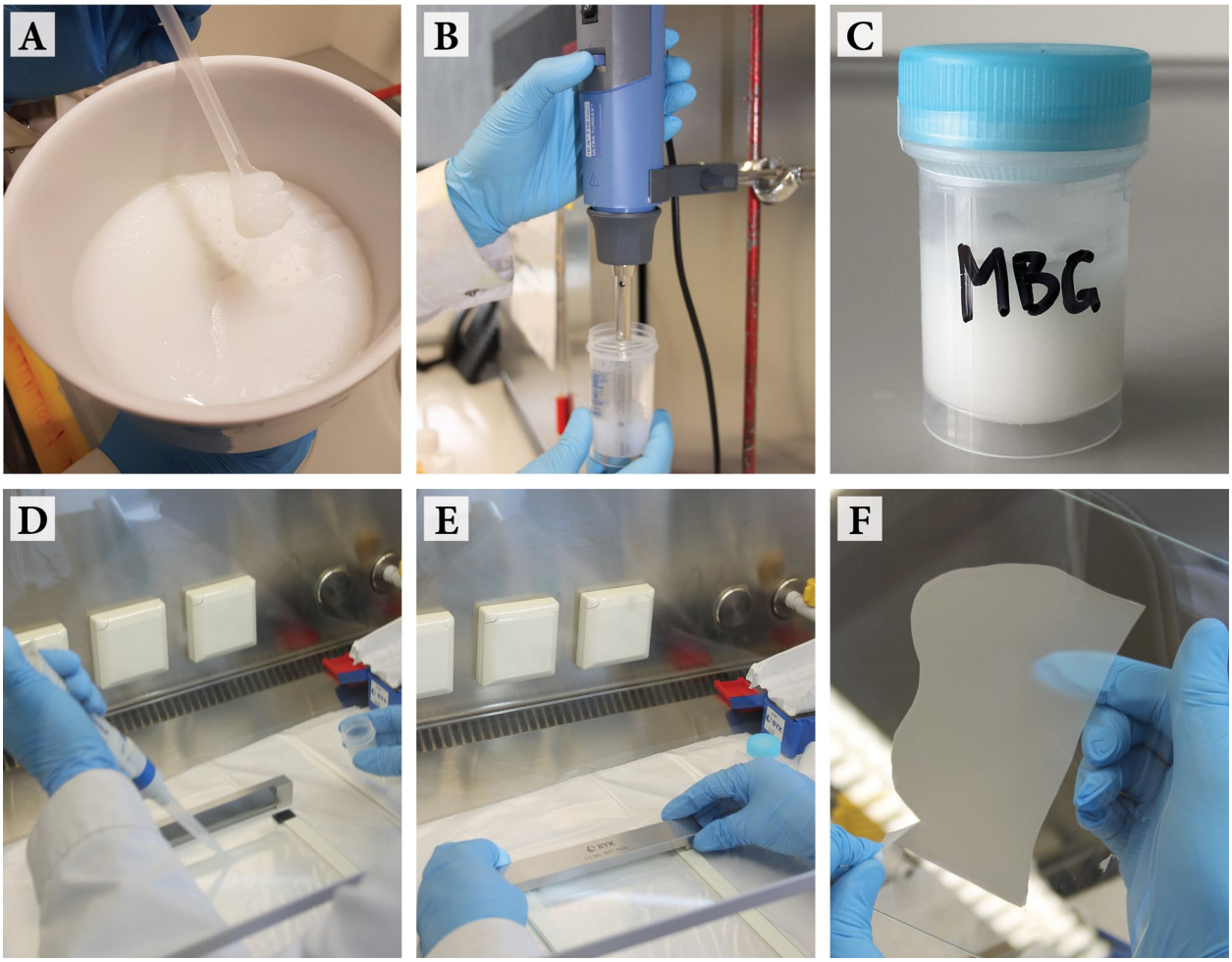

Figure S1: Fabrication of a HR-MBG for simultaneous sampling of anionic and cationic solutes. **(A)** $Zr(OH)_4$ slurry after filtration of the $Zr(OH)_4$ precipitate in a Buechner funnel. (**B**) Homogenization of the $Zr(OH)_4$ precipitate-polyurethane suspension using a dispersion device. (**C**) HR-MBG gel suspension in storage vial. (**D**) PTFE spacer strips are fixed left and right on a glass plate, the knife-coating device is placed on the top end of the glass plate, and the prepared gel suspension is pipetted as a thin film in front of the knife-coating device. (**E**) The knife-coating device is moved downwards to spread the gel suspension as a thin film on the glass plate. (**F**) Removal of gel areas with inhomogeneous material distribution before gel hydration.

S2.2. Polyacrylamide-zirconia anion binding gel (HR-ABG)[2]

S2.2.1. Prepare four 0.4 mm-thin APA gels as stated in S2.4.

S2.2.2. Dissolve 3.22 g of $ZrOCl_2 \times 8H_2O$ (**Table of Materials**) in 40 mL of H_2O in a 500 mL beaker.

S2.2.3. Immerse the four 0.4 mm-thin APA gels prepared in S2.2.1. into this solution and top up to a total volume of 100 mL (including the gels).

S2.2.4. Let the gels equilibrate for ≥2 h in the solution.

S2.2.5. Transfer each gel into 100 mL 0.05 mol L^{-1} 2-(N-morpholino)-ethanesulfonic acid (MES) (**Table of Materials**) buffer at pH 6.7. Immediately, stir the gel and solution using plastic tweezers during the first 60 s of immersion to ensure homogeneous precipitation of $Zr(OH)_4$ phases in the gel.

S2.2.6. Gently shake the vial containing the gel for a total of ~40 min to allow complete precipitation of $Zr(OH)_4$ in the gel.

S2.2.7. Remove the gel from the buffer and wash in ≥1 L H_2O for 24 h. Change the H_2O 5-6 times during this period to remove Cl^- ions and excess reagents.

S2.2.8. Store the hydrated 0.4 mm-thin HR-ABG in H_2O at 6 °C. The shelf life of the HR-ABG is ~13 months.

S2.3. Polyacrylamide-iminodiacetate cation binding gel (HR-CBG)[3]

S2.3.1. Mix 5.00 mL acrylamide (40 %; **Table of Materials**) and 1.25 mL DGT cross-linker (2 %; **Table of Materials**) to get the acrylamide gel stock solution.

CAUTION: Concentrated acrylamide solution is a classified toxin and suspected human carcinogen[4]. Do not inhale vapors, handle with gloves and follow general toxin reporting and safety requirements.

S2.3.2. Mix 1 mL of the acrylamide gel stock solution with 1 mL of suspended particulate reagent - iminodiacetate (SPR-IDA) resin suspension in a 20 mL vial to obtain a 5 % (*w*/*v*) resin-solution gel suspension.

NOTE: Vortex-mix the SPR-IDA resin suspension prior to pipetting.

S2.3.3. Homogenize the viscous gel suspension via vigorous shaking by hand followed by slow agitation in an overhead shaker at ~5 rpm for ≥2 h to remove air bubbles.

S2.3.4. Prepare a two-layer glass plate assembly separated by a U-shaped 0.25 mm-thin PTFE spacer for subsequent gel casting.

S2.3.5. Dissolve 0.1 g $(NH_4)_2S_2O_8$ (**Table of Materials**) in 1 mL of H_2O to get a 10 % (*w*/*v*) ammonium persulfate (APS) solution required for subsequent gel polymerization.

NOTE: The APS solution must be prepared immediately prior gel fabrication.

S2.3.6. Add 14 µL APS and 4 µL of N,N,N',N'-tetramethylethylenediamine (TEMED; **Table of Materials**) to the air-bubble-free gel suspension and mix well using the pipette.

NOTE: Immediately proceed with S2.3.7, as gel polymerization is initiated rapidly following APS and TEMED addition.

S2.3.7. Pipette 2 mL of this gel suspension into the middle of the glass plate assembly using a 1 mL pipette tip. Hold the glass plate assembly almost vertical during pipetting to enable degassing of air-bubbles.

NOTE: Do not knock on the glass plate to remove air-bubbles, as this will result in inhomogeneous distribution of the iminodiacetate phases in the gel.

S2.3.8. Place the glass plate assembly containing the gel solution into an oven for 45 min at 45 °C until the gel is completely polymerized.

S2.3.9. Take the glass plate assembly apart. Therefore, remove the plastic clips and carefully lever up the top glass plate using e.g. a razor blade. The gel stays on the bottom glass plate.

NOTE: The application of H_2O between the two glass plates using a spray bottle will help to lever up the top glass plate without damaging the gel.

S2.3.10. Remove the U-shaped PTFE spacer and rinse the gel from the bottom glass plate into a suitable container filled with ≥1 L of H_2O using an H_2O spray bottle.

S2.3.11. Hydrate the gel in the H_2O bath for 24 h at room temperature. Exchange the H_2O at least three times during this period to remove excess reagents from the gel.

S2.3.12. Store the hydrated 0.4 mm-thin HR-CBG in H_2O at 6 °C. The shelf life of the HR-CBG is ~3 months.

S2.4. Agarose cross-linked polyacrylamide gel (APA)[5]

S2.4.1. Mix 5.00 mL acrylamide (40 %; **Table of Materials**), 2.00 mL DGT cross-linker (2 %; **Table of Materials**) and 6.33 mL H_2O to get the acrylamide gel stock solution.

S2.4.2. Prepare a two-layer glass plate assembly separated by a U-shaped PTFE spacer for subsequent gel casting. Use a PTFE spacer thickness of 0.25 mm or 0.50 mm for preparing a 0.4 mm-thin or 0.8 mm-thin APA, respectively.

S2.4.3. Prepare an APS solution as described in S2.3.5.

NOTE: The APS solution must be prepared immediately prior gel fabrication.

S2.4.4. For 0.4 mm-thin APA, pipette 2 mL of the acrylamide gel stock solution into a 20 mL vial and add 14 µL APS and 5 µL TEMED (**Table of Materials**) and mix well using the pipette. For 0.8 mm-thin APA, use twice the amount of the reagents.

NOTE: Immediately proceed with S2.4.5, as gel polymerization is initiated rapidly following APS and TEMED addition.

S2.4.5. Pipette 2 mL for 0.4 mm-thin APA or 4 mL for 0.8 mm-thin APA of this acrylamide gel solution into the glass plate assembly.

NOTE: If air bubbles appear, they can be removed by knocking on the glass plate using e.g. a pen.

S2.4.6. Proceed as detailed in S2.3.8 - S2.3.11 for gel polymerization and hydration.

S2.4.7. Store the hydrated APA (0.4 mm- or 0.8 mm-thin) in 0.01 mol L^{-1} $NaNO_3$ at 6°C. The shelf life of the APA is ~12 months.

S3. Plant cultivation

S3.1. Rhizotron design

S3.1.1. Manufacture rhizotron frames (**Figure 1A)** made from clear acrylic with inner dimensions of 40 cm × 10 cm × 1.5 cm (H × W × D). Use a thickness of 0.5 cm and 1.0 cm for the side and back walls, respectively.

S3.1.1.1. For the front (root viewing window), manufacture a 41 cm × 11 cm acrylic plate with 0.5 cm thickness which is attached to the rhizotron by 2 acrylic rails fixed by 4 nylon screws each alongside the side walls (**Figure 1A**).

S3.1.1.2. In the back, drill 14 holes with a diameter of ~5 mm to enable watering of the soil inside the rhizotron (**Figure 1A**). The watering holes can be closed using adhesive tape when not in use.

S3.1.2. Manufacture a tool for compacting the soil inside the rhizotron (**Figure 2B**). The compaction tool is made from an acrylic block with dimensions of 13 cm × 5 cm × 1.5 cm (H × W × D).

S3.1.3. Manufacture eight small 5 cm × 11 cm acrylic plates with 0.5 cm thickness. The plates are required for filling soil into rhizotrons (**Figure 2C**).

S3.2. Soil preparation before filling into the rhizotron

S3.2.1. Spread a thin (~3-5 cm) layer of air-dried and ≤2 mm-sieved soil into a plastic box.

S3.2.2. Moisten the soil surface with a H_2O spray bottle. The soil should be moist, but not saturated. Spread more soil layers on top and moisten them by spraying. Mix the soil by hand avoiding the formation of clumps. Repeat the procedure until the soil can be compacted in the fist and does not fall apart by itself.

S3.2.3. Sieve the soil one more time to ≤2 mm to remove larger aggregates. Dry a subsample (~50 g) at 105 °C for 24 h to determine the gravimetric water content, w_{soil} (g g^{-1}), according to Eq. S1. Typical w_{soil} values for rhizotron filling are between 0.05-0.15 g g^{-1} depending on the soil (particularly its clay content).

(Eq. S1) $w_{\mathrm{soil}} = \frac{m_{\mathrm{w,soil}}}{m_{\mathrm{s,soil}}}$

Here, $m_{\mathrm{w,soil}}$ (g) is the mass of water in the soil sample and $m_{\mathrm{s,soil}}$ (g) is the mass of solids in the soil sample.

NOTE: It is recommended to equilibrate the pre-moistened soil for ~1 week at room temperature before filling into the rhizotron. Filling with (air-)dry soil is not recommended as this can result in the formation of cracks in the soil column following irrigation.

S4. Preparation of DGT LA-ICP-MS calibration standards

S4.1. Estimation of the analyte calibration range

S4.1.1. Conduct a preliminary DGT bulk soil experiment at the same conditions (i.e. temperature, soil water content, deployment time, material diffusion layer) as planned for the imaging experiment using conventional DGT bulk soil sampling procedures as described elsewhere[6,7].

NOTE: For DGT bulk soil sampling, assemble DGT samplers as detailed in S4.3, but replace the APA gel and polyethersulfone membrane (**Table of Materials**) with a polycarbonate membrane (**Table of Materials),** which is the sole material diffusion layer in DGT solute imaging experiments. Use a PTFE spacer (**Table of Materials**) at the bottom of the stack to compensate for the missing two layers.

S4.1.2. After bulk soil DGT sampling, retrieve the binding gel disc from the DGT sampler, rinse the gel thoroughly with water and recover the bound analytes from the gel via microwave assisted acid digestion or elution, depending on the binding gel used (see S4.4 for detailed procedures).

S4.1.3. Quantify the analyte concentration in the gel digest or eluate by a suitable analytical technique (e.g. ICP-MS, colorimetry) and calculate the bound mass of analyte per gel area, Γ_{DGT} (gel analyte loading; µg cm^{-2}), according to Eq. S2.

(Eq. S2) $\Gamma_{\mathrm{DGT}} = \frac{m_{\mathrm{a}}}{A_{\mathrm{p}}} = \frac{c_{\mathrm{e}} \times (V_{\mathrm{e}} + V_{\mathrm{bg}})}{A_{\mathrm{p}} \times f_{\mathrm{e}}}$

Here, m_{a} (µg) is the mass of analyte accumulated on the binding gel, A_{p} (cm^2) is the area of the DGT sampler exposure window, c_{e} (µg L^{-1}) is the analyte concentration in the gel digest or eluate, V_{e} (L) is the volume of the digest or eluate solution, V_{bg} (L) is the volume of the binding gel, and f_{e} is the analyte- and binding gel-specific elution factor.

NOTE: Binding gel- and analyte-specific elution factors for HR-ABG and HR-CBG can be found in the original gel characterization publications[2,3].

S4.1.4. Define the highest calibration standard Γ_{DGT} for each analyte based on the determined and/or expected Γ_{DGT}.

S4.1.5. Verify that the total gel analyte loading (i.e. $\sum \Gamma_{\mathrm{DGT}}$) of the highest calibration standard is well below the total analyte binding gel capacity (≤80 %).

NOTE: Gel- and analyte-specific binding capacities for the presented DGT binding gel types can be found in the original gel characterization publications[1-3].

S4.1.6. Divide the Γ_{DGT} of the highest calibration standard by the target number of calibration standards for each analyte. This will give the lowest calibration standard Γ_{DGT} and the distance between each standard to obtain an equidistant calibration series.

S4.1.7. If required, adjust the number of calibration points and/or the gel analyte loading of individual standards to encompass the expected gel analyte loading range.

S4.2. Preparation of the standard immersion solution

S4.2.1. Calculate the standard immersion solution analyte concentration corresponding to the target standard gel analyte loading derived from the calibration range estimated in section S4.1. In well-stirred solutions, a simple relationship between the actual analyte concentration in solution, c_{soln} (µg L^{-1}), and the analyte concentration measured by DGT samplers, c_{DGT} (µg L^{-1}), can be established[8]:

(Eq. S3) $c_{\mathrm{soln}} = c_{\mathrm{DGT}} = \Gamma_{\mathrm{DGT}} \times \frac{\Delta g}{t \times D}$

Here, Δg (cm) is the total thickness of the material diffusion layer (i.e. APA gel and polyethersulfone membrane), t (s) is the deployment time of the DGT sampler, and D ($cm^2\ s^{-1}$) is the diffusion coefficient of the analyte in the APA at a specific temperature[9].

NOTE: Eq. S3 defines a linear relationship between the deployment time t and the gel analyte loading Γ_{DGT}. Thus, increasing Γ_{DGT} can be obtained by increasing t at a constant c_{soln}. For the preparation of multi-point gel calibration standards, it is therefore recommended to use different sampler deployment times t in the same immersion solution rather than preparing individual immersion solutions with different c_{soln} for each gel standard.

S4.2.2. Prepare single-element standard stock solutions of the analytes by dissolving appropriate amounts of analytical grade analyte salts (**Table of Materials**) to obtain adequate stock solution concentrations (typically between 100-500 mg L^{-1}).

CAUTION: Pay attention to safety regulations as most metal compounds are potentially toxic.

S4.2.3. Dissolve 297.5 mg $NaNO_3$ in 2.5 L H_2O in a 4 L plastic container to obtain a final ionic background of 0.001 mol L^{-1} $NaNO_3$, considering a total volume of the final immersion solution of 3.5 L. Place the container on a magnetic stirrer (**Table of Materials**) at ~300 rpm and immerse a calibrated pH probe (**Table of Materials**) connected to a pH meter (**Table of Materials**).

S4.2.4. Add an appropriate volume of each single-element standard stock solution to the well-stirred immersion solution to give the target analyte concentration in solution, c_{soln} (Eq. S3).

NOTE: Pay attention to analyte-specific precipitation and complexation reactions, formation of colloidal species, and sorption to the container walls to make sure that analyte concentrations in solution remain constant over the experimental deployment period. If multi-analyte solutions are used, it is recommended to calculate the solubility equilibria using chemical equilibrium modelling software (**Table of Materials**).

S4.2.5. Adjust the pH of the immersion solution to ~5.6 using 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HNO_3.

S4.2.6. Top up the immersion solution volume to 3.5 L with H_2O and let the immersion solution equilibrate for ≥12 h under constant stirring. Close the container to avoid contamination and evaporation.

S4.2.7. Verify that the pH remained constant at ~5.6 upon equilibration.

S4.2.8. Sample and acidify an aliquot (5-10 mL) from the immersion solution to determine the initial analyte concentration in solution by e.g. ICP-MS.

S4.3. Standard gel loading

S4.3.1. Cut the DGT binding gels to individual discs with 2.5 cm diameter using a circular cutter made from either stainless-steel (**Table of Materials**) for HR-MBG and HR-ABG, or plastic (**Table of Materials**) for HR-CBG.

S4.3.2. Assemble standardized DGT piston samplers (**Table of Materials**) by stacking a binding gel disc, a 0.8 mm-thin APA diffusive gel (see S2.4 for fabrication details), and a 0.14 mm-thin polyethersulfone membrane (0.45 µm pore size; **Table of Materials**) on top of each other on the DGT base (**Figure S2**) using plastic tweezers. Apply water to facilitate positioning of the individual layers and ensure that no air bubbles are trapped between the layers and that each layer is centered on the DGT base.

NOTE: If HR-MBG is used, add a 0.4 mm-thin PTFE support at the DGT base to compensate for the lower gel thickness of the HR-MBG as compared to HR-ABG and HR-CBG.

S4.3.3. Close the DGT piston sampler with the DGT cap. Press the cap until the DGT sampler is tightly sealed and verify that the polyethersulfone membrane is flat and not damaged.

S4.3.4. Assemble four DGT piston sampler replicates per gel standard or blank. The samplers can be stored for a few days in a zip bag containing a few mL of water at 6 °C in the fridge until deployment in the immersion solution.

NOTE: For the standard gel blank, skip S4.3.5 - S4.3.10 and directly proceed with S4.3.11.

S4.3.5. Fix each DGT piston sampler (four per gel standard) in a custom-built support frame and deploy the samplers in the well-stirred immersion solution (**Figure S2**).

S4.3.6. Record the exact starting time of the sampler deployment.

S4.3.7. Deploy the DGT piston samplers in the immersion solution until the end of the deployment time *t*.

S4.3.8. Retrieve the DGT samplers from the immersion solution and the support frame and rinse thoroughly with water.

S4.3.9. Record the exact end time of the DGT piston sampler deployment.

S4.3.10. Sample an aliquot from the immersion solution as specified in S4.2.8 to assess the final analyte concentration in solution.

S4.3.11. Retrieve the binding gel discs from the DGT samplers and rinse the gels thoroughly with water.

S4.3.12. Dry one of the four gel replicates per gel standard or blank as detailed in the main document section 3.3. This gel will serve as standard for LA-ICP-MS analysis (**Figure S2**).

S4.3.13. Transfer the remaining three gel replicates per gel standard or blank into a 20 mL storage vial pending gel digestion or elution for analyte quantification (**Figure S2**).

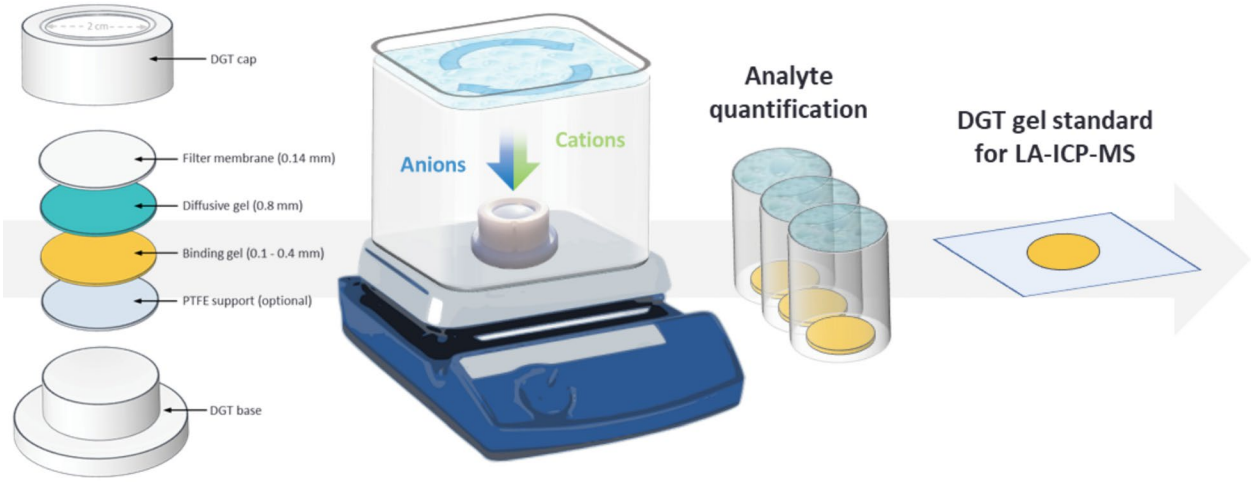

Figure S2: Laboratory workflow for the preparation of DGT LA-ICP-MS calibration standards.

S4.4. Standard gel digestion or elution

NOTE: Different procedures are applied to recover the bound analytes from the presented DGT binding gel discs. While the HR-MBG gel requires digestion for complete analyte recovery, HR-ABG and HR-CBG only need to be eluted.

S4.4.1. HR-MBG[1]

S4.4.1.1. Transfer the HR-MBG discs from the 20 mL storage vial into the vessels of a high-pressure microwave system (**Table of Materials**).

S4.4.1.2. Add 5 mL of 65 % (*w*/*w*) HNO_3 (**Table of Materials**) and 1 mL of 30 % (*w*/*w*) H_2O_2 (**Table of Materials**) to the gel discs and run the following settings on the microwave: Phase 1: power 1400 W, ramp 10 min, hold 60 min, fan 1; Phase 2: power 0 W, ramp 0 min, hold 5 min, fan 3.

S4.4.1.3. Dilute the digests to 2 % (*w*/*w*) HNO_3. If analyte concentrations are expected to be below <1 µg L^{-1}, matrix evaporation at 90 °C in perfluoroalkoxy alkane (PFA) vials (**Table of Materials**) may help to preconcentrate the analytes to reach ICP-MS detection limits.

S4.4.2. HR-ABG[2]

S4.4.2.1. Add 5-10 mL 0.5 mol L^{-1} NaOH directly to the HR-ABG discs in the 20 mL storage vial.

S4.4.2.2. Elute for 24 h under constant shaking on a horizontal shaker (**Table of Materials**).

S4.4.2.3. Retrieve the HR-ABG discs from the eluate and measure the analytes by ICP-MS or colorimetry.

S4.4.3. HR-CBG[3]

S4.4.3.1. Add 1-10 mL 1 mol L^{-1} HNO_3 directly to the HR-CBG discs in the 20 mL storage vial.

S4.4.3.2. Elute for 24 h under constant shaking on a horizontal shaker.

S4.4.3.3. Retrieve the HR-CBG discs from the eluate, dilute the eluates to 2 % (*w*/*w*) HNO_3 and measure the analytes by ICP-MS.

S5. Coupling the LA system to the ICP-MS

NOTE: The experimental system uses specific LA-ICP-MS instrumentation (**Figure 5**; **Table of Materials**). If systems from other manufacturers are used, modifications to the protocol may be required.

CAUTION: The LA system uses a class 4 laser which can cause severe injuries to skin and eyes and therefore requires proper safety management[10]. Conduct technical training before operation of the LA-ICP-MS instrumentation.

S5.1. Start the LA system and the ICP-MS instrument and perform a performance check on both systems according to the manufacturer's specifications.

NOTE: Stop the plasma on the ICP-MS after the performance check, i.e. before you connect the LA system.

S5.2. Connect N_2 as purge gas to 'N2 PRG GAS IN' and He as carrier gas to 'MFC 1 GAS IN' at the gas panel of the LA system. Verify that the gas properties (i.e. pressure and purity) are in line with the specifications of the LA system.

NOTE: The present protocol uses He as the aerosol carrier gas. Alternatively, Ar can be used as carrier gas. See Günther and Heinrich[11] for a detailed discussion of the effects of using either He or Ar as carrier gas.

S5.3. Connect the 'ONLINE GAS OUT' He carrier gas flow of the LA system and the 'NEB' Ar nebulizer gas flow of the ICP-MS to the ICP interface via a PTFE-coated Tygon tubing (**Table of Materials**) equipped with a two-way Y connector and a torch adapter fitting to the ICP injector (**Figure 5C**).

S5.4. Verify that all gas fittings are finger-tight, and that the tubing connection is sound and leak-free.

S5.5. Connect the 'SYNC OUT' port of the LA system to the 'I/O' port of the ICP-MS via a transistor-transistor logic (TTL) cable (**Table of Materials**) to trigger the ICP-MS data acquisition with the LA. In the LA software, set the 'Sync Out Mode' to 'Active when Laser Active' and 'Sync Out Polarity' to 'Active Closed'. Set the ICP-MS 'Sampling Device' to 'External' and the 'External Read Trigger' to 'Close' in the ICP-MS software.

S5.6. Click 'N_2 Purge' in the LA software to purge the laser optics with N_2. Click 'Mass Flow' to open the 'Mass Flow Control' window, tick 'Enable flow controller' and set the carrier gas flow rate to 900 mL min^{-1}. Switch from 'Bypass' to 'Online' to purge the LA cell with the carrier gas for ≥30 min.

S5.7. Reduce the carrier gas flow to 0 mL min^{-1} and start the plasma in the ICP-MS software. Subsequently, slowly ramp up the carrier gas flow to the desired 900 mL min^{-1} at a ramp up rate of 10-20 mL min^{-1} s^{-1}.

NOTE: Closely monitor the plasma stability during the carrier gas ramp up to ensure that the plasma is not extinguished by the increase in gas flow and that the torch is not overheating.

S5.8. Once the plasma is stabilized (after ~30 min), monitor the gas blank in the ICP-MS in real-time until the analyzed isotopes reach a constant level prior to the start of the measurement.

NOTE: If high and/or strongly scattering gas blank levels are present, this may indicate leaks or contamination in the LA-ICP-MS tubing connection or the ablation cell, which then needs to be considered in detail.

S5.9. Proceed with LA-ICP-MS analysis as specified in the main document section 4.2.

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