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Ferrihydrite Containing Gel for Chemical Imaging of Labile Phosphate Species in Sediments and Soils Using Diffusive Gradients in Thin Films

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Abstract

We report on a novel binding gel for phosphate, based on ferrihydrite, and its use in diffusive gradients in thin films (DGT) for measuring labile phosphate species in waters, sediments, and soils. An existing method of binding layer preparation was modified to overcome potential problems with deterioration of ferrihydrite due to conversion to goethite. The gel was characterized regarding its suitability for conventional DGT measurements as well as for measuring two-dimensional distributions of P with high spatial resolution using laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS). The effects of pH, ionic strength and storage time of gels on phosphate binding were investigated and the kinetics of binding and the maximum binding capacity were determined. The gel is shown to have a considerably higher P capacity than the conventional ferrihydrite DGT binding layers. LA-ICPMS analysis of DGT standards with P concentrations ranging from 0.088 ± 0.005 to $4.47 \pm 0.16 \mu\text{g cm}^{-2}$ resulted in reproducible calibration curves which could be described using a simple power function. We demonstrate that the new gel is well suited for analyzing small-scale changes of P concentrations in soils. Moreover, the gel can be used as an alternative to conventional DGT gels that incorporate powdered ferrihydrite, with improved characteristics for the determination of labile phosphate.

Diffusive gradients in thin films (DGT) is a passive sampling technique that was originally developed as a tool to measure trace metal speciation in natural waters.¹ It measures the amount of solute that diffuses across a concentration gradient, which is established in a layer of hydrogel and an overlying protective filter membrane. The solutes are immediately bound by a binding agent that is contained in a second layer of hydrogel after passing the diffusive layer of the DGT assembly. Constant removal of solutes at the rear surface of the diffusive

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gel maintains the concentration gradient throughout the deployment. The well-defined geometry of DGT allows the calculation of time-averaged fluxes, F , into the sampler and time averaged concentrations, C_{DGT} , at the sampler–solution interface:

$$F = \frac{M}{At} \quad 1$$

$$C_{DGT} = \frac{M\Delta g}{DA t} \quad 2$$

Calculation of these parameters requires knowledge of the deployment time, t , the exposed gel surface, A , the diffusion coefficient of the analyte in the diffusive gel, D , the diffusive layer thickness, Δg , and the mass of analyte, M , that was taken up. M is usually determined after acid elution of the resin gel, while D can be measured using two-compartment diffusion cells.² Values of D as a function of temperature are provided by DGT Research Ltd. (Quernmore, Lancaster, U.K., www.dgtresearch.com) for a range of analytes. Most commonly, Chelex 100 (Bio-Rad, Hercules, CA), which is highly selective for polyvalent metal cations, has been used as a binding agent in DGT assemblies. It was shown that out of 55 elements studied, reliable DGT measurements with Chelex 100 gels can be made for 24 elements.³ This study also showed that DGT measurements using Chelex 100 for anionic elements, monovalent cations, and group I and II cations are not possible. Alternative binding layers have thus been developed for environmentally relevant analytes that have little or no affinity to Chelex 100, including mercury⁴ and cesium.⁵ Gels containing ferrihydrite have been used for phosphate measurements.⁶

DGT is able to discriminate between labile solute species which can diffuse through the gel layer and bind to the resin and nonlabile species such as strong complexes and solutes bound to colloidal surfaces. This capability was exploited in the first in situ trace metal speciation measurements using DGT.¹ Extensive subsequent studies have included discrimination between inorganic and organically bound metal species⁷ and investigations of the dissociation kinetics of metal complexes.⁸

Similarities in solute uptake by DGT samplers and living organisms⁹ led to the repeated use of DGT to estimate the bioavailability of solutes in waters and soils. DGT measured solute concentrations correlated well with solute uptake by aquatic¹⁰ and terrestrial organisms.¹¹

Another field of application of DGT is the measurement of solute distributions at high spatial resolution. A spatial resolution of ~1 mm can be achieved by slicing DGT gels after exposure to sediments.¹² Higher spatial resolutions can be obtained by drying gels and analyzing them using microprobe techniques like proton induced X-ray emission (PIXE)¹³ or laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS).¹⁴ The application of such techniques allows a resolution of ~100 μm . Resin gels with relatively coarse resin beads like Chelex 100 or gels cast using ferrihydrite powder are unsuitable for analysis by highly spatially resolving techniques as inhomogeneities in the distribution of the binding agents affect the results. Therefore the SPR-IDA (Cetac Technologies, Omaha, NE) resin with a bead size of <0.2 μm was used to analyze the distribution of metal cations in sediments,^{14c} while Stockdale et al.^{14b} used a binding layer in which ferrihydrite is precipitated inside a conventional diffusive gel for measurement of anionic species. Detailed performance characteristics are available for the SPR-IDA resin gel but not for recent formulations of ferrihydrite gels. In the present work, we describe an adapted method for ferrihydrite precipitation in DGT gels and report on important properties of this novel DGT

binding layer for PO_4^{3-} analysis that will be relevant to its future use in DGT measurements at high spatial resolution.

EXPERIMENTAL SECTION

Gel Preparation

The presented method of preparing ferrihydrite impregnated gels is a modification of the procedure described by Stockdale et al.^{14b} Sodium hydrogen carbonate, which is used to promote hydrolysis of Fe, was replaced with MES (2-(*N*-morpholino)ethanesulfonic acid) as a pH buffer to reduce the risk of transformation of ferrihydrite to goethite. As the rate of conversion of ferrihydrite to goethite increases with pH,¹⁵ traces of NaHCO_3 that remain in the gel might change the form of the oxide and thus the binding properties of the gel, which could affect DGT performance. In the present work, ferrihydrite was precipitated from a solution of FeCl_3 instead of $\text{Fe}(\text{NO}_3)_3$. A low nitrogen content of the gels is preferable for subsequent LA-ICPMS measurements of P to reduce the occurrence of possible isobaric interferences of $^{14}\text{N}^{16}\text{O}^{1}\text{H}$ and $^{15}\text{N}^{16}\text{O}$ on ^{31}P .^{6b}

Diffusive gels with a thickness of 0.6 mm were prepared according to standard methods.¹⁶ To prepare the ferrihydrite gel, 2.70 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Analar grade reagent, VWR BDH Prolabo, Poole, U.K.) were dissolved in about 40 mL of reagent grade water type 1 (18.2 MΩ cm water provided by a Milli-Q water purification system, Millipore, Watford, U.K.). Up to three gels were put into this solution which was then filled up to 100 mL with reagent grade water. The resulting FeCl_3 concentration was 0.1 mol L^{-1} . The gels remained at least 2 h in this solution to allow uniform distribution of the Fe concentration inside and outside of the gel. Subsequently, each gel was rinsed with reagent grade water for a few seconds to remove surface Fe and was then placed in a MES solution ($c = 0.05 \text{ mol L}^{-1}$; Analar grade reagent, VWR BDH Prolabo) which had been adjusted to pH 6.7 using a 1 mol L^{-1} NaOH solution (Analar grade reagent, VWR BDH Prolabo). Ferrihydrite precipitation started immediately. The gels were removed from the buffer after 30 min, rinsed, and placed in reagent grade water to wash off excess reagents. Washing periods were at least 2 h, after which the water was replaced at least 2 times. After washing, gels were transferred to a 0.03 mol L^{-1} NaCl solution (Analar grade reagent, VWR BDH Prolabo) for gel conditioning for at least 24 h. Gels were stored for up to 33 days at the same NaCl concentration in a refrigerator.

Gel Characterization Experiments

Effects of pH and ionic strength on DGT performance and the capacity of the novel ferrihydrite gels were determined by immersing loaded DGT units in experimental solutions. Binding kinetics, elution efficiency, and the effect of aging on the binding of P was investigated by immersing ferrihydrite gel discs. All solutions used were prepared from KH_2PO_4 (Analytical reagent, Fisher Scientific, Loughborough, U.K.) and were adjusted to an ionic strength of $I = 0.01 \text{ mol L}^{-1}$ using NaCl unless stated differently. This work hence studied the binding of orthophosphate on the ferrihydrite gel. In the used pH range 3–8, phosphate is mainly present as H_2PO_4^- and HPO_4^{2-} ions. The solutions for DGT experiments were prepared at least 1 h before DGT immersion. Three DGT units were exposed to 4 L of experimental solution for each experiment. This setup ensured that no considerable depletion of P occurred in the immersion solution, which would complicate the DGT results. The solutions were well stirred throughout the experiment. All experiments were carried out in triplicate. Standard DGT moldings supplied by DGT Research Ltd. were used for assembling DGT devices. Ferrihydrite gels were overlaid by 0.8 mm thick diffusive gels which were then covered by 0.14 mm thick polyethersulfone membranes (Supor, Pall

Corporation, Port Washington). After the experiment, the DGT units were rinsed with reagent grade water, carefully opened, and the gel(s) retrieved using tweezers.

Phosphate was eluted from ferrihydrite gel discs by placing the discs in 10 mL of 0.25 mol L⁻¹ H₂SO₄ (Analytical grade reagent, Fisher Scientific) for at least 12 h. The P concentration in the eluates was determined colorimetrically (Jenway 6300 Spectrophotometer, Jenway, Dunmow, U.K.) using molybdenum blue.^{6a} The mass of eluted P was calculated by multiplying the P concentration in the eluates with the total eluate volume. This total volume is the sum of the volume of the eluant and the volume of the gel(s) that get eluted. In cases where the diffusive gel was eluted together with the ferrihydrite gel, both volumes were added to the eluant volume. C_{DGT} values were calculated using eq 2.

pH and Ionic Strength

Possible effects of solution pH on DGT measurements were investigated by exposing loaded DGT assemblies to solutions with a P concentration of 200 $\mu\text{g L}^{-1}$ for 4 h. The pH of the solution was adjusted to pH values of about 3, 4, 5, 6, 7, and 8 using either HCl or NaOH.

To determine the impact of electrolyte concentration, DGT measurements were performed in solutions that were adjusted to $I = 0.001, 0.01, 0.1,$ and 0.5 mol L^{-1} with NaCl. The solutions had a P concentration of 200 $\mu\text{g L}^{-1}$ and DGT deployment times of 4 h were used.

Capacity

To determine the P binding capacity of the precipitated ferrihydrite gels, DGT assemblies were immersed for 4 h in solutions with a range of concentration of P (0.2, 1, 3, 7, 14, 24, and 37 mg L⁻¹).

Kinetics of Uptake and Efficiency of Elution

Kinetics of phosphate binding to the ferrihydrite gel was investigated by placing gel discs in 10 mL of a solution with a P concentration of 200 $\mu\text{g L}^{-1}$. After shaking the gel and solution containing vials for 1, 3, 6, 10, 30, 60, 120, 300, or 1440 min on a horizontal shaker at 200 rpm, the gels were removed and eluted. Amounts of P in the solutions were determined before and after exposure to the ferrihydrite discs and in the gel disk eluates. In addition to binding kinetics, mass balance calculations were performed to compute elution efficiencies of phosphate from the ferrihydrite gels.

Aging

Shelf life of the ferrihydrite gels was evaluated by immersing gel discs in 10 mL of a solution with a P concentration of 200 $\mu\text{g L}^{-1}$ 1, 2, 3, 6, 15, and 33 days after production of the gels. The vials containing the immersed discs were shaken overnight using a horizontal shaker at 200 rpm.

Laser Ablation ICPMS

P loaded standard gel discs were prepared by immersing 3.3 cm diameter gel discs into 10 mL of solutions containing different amounts of P. After shaking the gel and solution containing vials on a horizontal shaker (200 rpm) overnight, the discs were retrieved and cut into halves. One half was eluted and P was quantified colorimetrically. The other half, which was used for LA-ICPMS analysis, was placed on a polyethersulfone membrane and dried using a gel drier (Gibco GD40/50, Life Technologies, Carlsbad, CA). The membrane and the gel were inseparable from each other after drying. This assembly was mounted on microscope slides prior to analysis by LA-ICPMS. Surface concentrations of P, which were

calculated using the mass of P measured in the eluates, were correlated with signal intensities measured in LA-ICPMS for obtaining calibration curves.

In LA-ICPMS analysis of the standard gel discs, only one side of a gel disk gets ablated. However, in colorimetry measurements the P bound on all surfaces (top, bottom, and circumferential surfaces) of a gel disk is quantified as the whole amount of P is eluted prior to analysis. For accurate quantification it was thus necessary to cut smaller discs (2.5 cm in diameter) out of the P loaded 3.3 cm discs before cutting the discs in halves. Thereby an error that could be introduced by the P sorbed onto the circumferential surface of the 3.3 cm discs (which amounts to 3.5% of the total area of a 3.3 cm diameter, 0.08 cm thick disk) was avoided. As a result, only the P bound on the top and bottom surfaces of the gel discs was eluted and measured. The so determined mass of P was divided by two in order to only account for the P bound on one side of the gel disk.

Laser ablation was accomplished with a UP-193 (New Wave Research, Fremont, CA) laser ablation system coupled to an ELAN DRCE (Perkin-Elmer, Waltham, MA) ICPMS to record ^{14}N , ^{31}P , and ^{57}Fe signals. Fe is homogeneously distributed in the gel matrix after ferrihydrite precipitation, and thus ^{57}Fe was used as an internal normalization standard as suggested by Stockdale et al.^{14b} Line scans of the gels were performed at a scanning speed of $200\text{ }\mu\text{m s}^{-1}$, a beam diameter of $120\text{ }\mu\text{m}$, and a repetition rate of 10 Hz. The laser energy level was set to 45%. The readout time for a single reading was 0.384 s. Because polyacrylamide contains about 20 mass % N, $^{14}\text{N}^{16}\text{O}^1\text{H}$, and $^{15}\text{N}^{16}\text{O}$ interferences could be substantial. To evaluate the contribution of NO containing interferences to the ^{31}P signal, measurements of P as $^{31}\text{P}^{16}\text{O}$ using the dynamic reaction cell with O_2 as the reaction gas were compared to measurements without the reaction cell. Moreover, measurements using a Nu Plasma HR (Nu Instruments, Wrexham, U.K.) ICPMS were performed in high resolution ($m/\Delta m = 4000$) to monitor possible interfering species.

In order to obtain an accurate estimate of measurement uncertainty for the LA-ICPMS gel standard series, the total combined standard uncertainties (SU) or relative standard uncertainties (RSU) were calculated according to EURACHEM/ISO¹⁷ by propagating the uncertainties of the input parameters to the final result. For the SU of the P surface concentrations of gel standards as well as of the LA-ICPMS analysis of the dry gel standards, the uncertainties of calibration, of the measured signal of the sample, and of the blank correction were considered.

Chemical Mapping of the Distribution of DGT Labile P in a Soil

We conducted a laboratory experiment to demonstrate the suitability of the novel ferrihydrite DGT gel for chemical imaging of the distribution of dissolved P in a soil. A box with removable lids was filled with a low P Cambisol which was compacted to a bulk density of 1.4 g cm^{-3} . This soil had a total P concentration of $2270 \pm 70\text{ mg kg}^{-1}$.¹⁸ The soluble P concentration, measured as molybdate-reactive P in soil saturation extracts,¹⁸ was $93.7 \pm 7.8\text{ }\mu\text{g L}^{-1}$. After the soil was moistened to 30% maximum water holding capacity, the soil was incubated at room temperature for several days. The lid on one side of the box was then opened, allowing direct access to a plane soil surface. Subsequently, the soil was moistened to 100% water saturation. Total water saturation ensures homogeneous diffusive properties for P throughout the sampled soil area. A piece of 0.014 cm thick polyethersulfone membrane was placed on the soil to serve as a diffusion layer and to prevent contamination of the ferrihydrite gel. A small piece of ferrihydrite gel was placed on the membrane. This assembly was covered by a perspex plate to prevent dehydration of the soil as well as the gel. After 24 h of deployment, the gel was dried, mounted on a glass plate, and analyzed by LA-ICPMS. Measured concentrations of P on the gel were transformed to C_{DGT} concentrations using eq 2.

RESULTS AND DISCUSSION

The procedure of direct ferrihydrite precipitation in diffusive gels results in gels densely impregnated with ferrihydrite. These gels are compact and do not tear easily in contrast to ferrihydrite gels prepared according to Zhang et al.^{6a} The gel surface is sticky. In DGT experiments, we observed adhesion of the ferrihydrite gels to diffusive gels. Gel conditioning in 0.03 mol L⁻¹ NaCl was found to alleviate such adhesion, but it could not be avoided entirely. DGT devices as provided by DGT Research Ltd. are designed to host a 0.4 mm thick resin (Chelex) gel, a 0.8 mm thick diffusive gel, and a 0.14 mm thick covering membrane. Compaction of the DGT gels in the DGT device due the use of our thicker ferrihydrite gel (0.6 mm) was one reason for gel adhesion. If compaction was minimized by not pushing the piston and the molding entirely together, adhesion was reduced. In cases where ferrihydrite and diffusive gel were inseparable from each other, both gels were eluted together and the additional volume introduced by the diffusive gel was taken into account during data processing. The P introduced by additionally eluting the diffusive gel is <1% of the P bound on the resin gel for a 4 h DGT deployment at 20 °C in a solution containing 200 µg L⁻¹ P using a 0.08 cm thick diffusive gel. This small amount of additional P was considered insignificant and thus neglected.

pH and Ionic Strength

The DGT measured concentrations (C_{DGT}) were in good agreement with the directly measured concentrations in the immersion solutions (C_{Soln} ; Figure 2a) in a pH range of 3.2–6.9. A decreased C_{DGT}/C_{Soln} ratio of $83.8\% \pm 7.8\%$ at pH 7.9 indicates an effect of pH on the binding of P by the ferrihydrite gel. P binding to ferrihydrite gels was not reduced at this slightly alkaline pH for other gels containing ferrihydrite powder.⁶ The reliable working pH range for precipitated ferrihydrite gels is thus somewhat smaller than for gels using ferrihydrite powder.

The DGT measurement of phosphate at ionic strengths between 0.001 and 0.5 mol L⁻¹ agreed well with the respective C_{Soln} concentrations (Figure 2b), which is in line with previous results.^{6b,19} At lower ionic strengths, erroneous DGT measurements were reported and are attributed to local charges in the diffusive gel.² These charges may bind ions in the diffusive gel or lead to Donnan partitioning effects²⁰ and thereby influence diffusion of ions through the gel. By extensive gel washing, Warnken et al.²¹ obtained accurate measurements at ionic strengths even lower than 0.001 mol L⁻¹. As the ionic strength of natural waters and soil solutions are typically >0.001 mol L⁻¹,^{6b,22} standard gel washing procedures should be sufficient to ensure accurate DGT measurements.

Capacity

Phosphorus bound to the ferrihydrite gel used in DGT measurements increased linearly with the concentration of P in solution, as predicted by eq 2 up to a P loading of 6.94 µg cm⁻² (Figure 3). This is about 5 times higher than the capacity of conventional gels using ferrihydrite powder.

Kinetics of Uptake and Efficiency of Elution

The mass of P bound onto the ferrihydrite gel discs increased linearly with time until 10 min, after which the binding rate decreased (Figure 1). Maximum P loading was reached after 60 min of exposure to the P solution. The uptake of P on our ferrihydrite gel was considerably faster than values reported by Mason et al.^{6b} for Mn, Cu, Zn, and Cd binding to Chelex gels and to gels containing both powdered ferrihydrite and Chelex. This observed fast binding of P demonstrates that our gel is able to act as an infinite sink in a DGT sampler, which is a prerequisite for reliable DGT measurements. The average elution

efficiency, calculated as the ratio of P eluted from the gel to the P sorbed, was $100.9 \pm 5.4\%$, which is very close to the elution efficiency of the ferrihydrite containing gel described by Zhang et al.^{6a}

Aging

For the storage periods tested, P recovery after elution of precipitated ferrihydrite discs that were exposed to P containing solutions was close the 100% (Figure 2c). Therefore, precipitated ferrihydrite gels can be stored for up to 1 month after production.

LA-ICPMS Measurements

In previous LA-ICPMS analyses of DGT gels, both spot^{14b,c} and continuous ablation (line scans)^{14a} of samples were performed. Spot analysis requires a washout delay time between each spot which leads to a significant increase of the total measurement time. Line scan analysis only requires a washout delay after each line. Therefore we optimized the line scan analysis regarding analysis time and lateral resolution. Spatial resolution along the lines is a result of scan speed and measurement time of the ICPMS for a single reading. Using continuous line scans, we were able to analyze a 2 cm wide and 4 cm long sample in 4 h, giving 31 200 readings when using a interline distance of 333 μm and a 10 s delay between each line (data not shown). The horizontal resolution was 77 μm , while the vertical resolution, identical with the interline distance, was 333 μm . In this ablation mode, a single ICPMS reading took 0.42 s (reading time plus a fraction of the line delay), while in the previously described spot mode, one reading took 29^{14c} and 14 s.^{14b} This distinct advantage in data collection time outweighs the disadvantage of different horizontal and vertical spatial resolution.

The occurrence of possible N containing interferences was studied in order to avoid analytical artifacts at low levels of P concentration. First, ¹⁴N was monitored along with the laser ablation signal. No significant increase could be observed during laser ablation of the polyacrylamide gel compared to the gas blank levels. Count rates did not change from gas blank levels when laser ablation was started. The Elan DRCe was operated both in standard and DRC mode with O₂ as the reaction gas in order to exclude possible interferences on mass 31. The results showed no significant influence of possible interferences. Significant formation of interfering species from N liberated from the polyacrylamide gel matrix can thus be excluded, which was finally proven by measuring the standards using the Nu Plasma HR sectorfield instrument in high-resolution mode. The interferences observed at the high mass side correspond to a background equivalent concentration (BEC) of $2.82 \pm 1.51 \text{ ng cm}^{-2}$ and showed constant signal heights. Interference signal heights were not significantly different for gas blanks as well as for DGT standard aerosols. As a consequence, this small contribution can be accurately corrected for by blank subtraction. Analysis of these gels can therefore be performed using quadrupole instruments in standard mode.

Surface concentrations of P in the standard gels measured colorimetrically were 0.088 ± 0.005 , 0.130 ± 0.005 , 0.197 ± 0.007 , 0.397 ± 0.012 , 0.742 ± 0.029 , 1.32 ± 0.05 , 1.96 ± 0.07 , 3.03 ± 0.12 , and $4.47 \pm 0.16 \mu\text{g cm}^{-2}$. The errors given for these values represent total combined standard uncertainties (SU, coverage factor $k = 1$). No P could be detected colorimetrically on blank gels. The correlation between LA-ICPMS signals and known standard concentrations was not linear (Figure 4). Correlation coefficients of 0.99 were obtained for fits of the calibration data to a simple power function of the form

$$y = ax^b \quad 3$$

Parameters a and b are curve fit parameters which depend on the response curves of the ICPMS and thus of the actual optimization parameters. The high correlation coefficients were obtained for quadrupole ICPMS in standard mode and DRC mode as well as for sectorfield ICPMS in high-resolution mode.

Signal intensities were always below 8×10^4 (Elan) and 2.25×10^6 (Nu Plasma HR) cps. No deviations from linearity were reported in previous studies involving laser ablation analysis of DGT gels.^{14b,c} This is probably due to the low concentrations of standards and possibly also due to small concentration ranges used in those studies. However, the experiment on mapping P in a soil presented in this paper (Figure 5), as well as our unpublished data, showed the need for a wide calibration range up to the concentrations used in the present study.

A possible explanation for the observed nonlinear behavior at higher concentrations could be interactions of Fe oxide containing particles and P in the aerosol produced by the laser. Increased P contents of the gels and thus of the aerosol could lead to decreasing signal intensities if interactions of P and Fe particles lead to increased depositions and agglomeration of particles at the ablation line rim or during transport to the ICP. Moreover, decreasing particle vaporization efficiencies in the plasma caused by such interactions could result in the observed calibration curves as exposure time of particles in the plasma is only about 5 ms.²³ Similar fractionation effects have been observed repeatedly in laser ablation studies.²⁴ We did not further investigate this interesting observation because the high correlation coefficients obtained for curve fits enabled accurate calibration which was fit for purpose.

Figures of Merit

The limit of detection (LOD, $3 \times \text{SD}$ of the blank) was 0.94 ng cm^{-2} for the quadrupole LA-ICPMS measurements in standard mode, which corresponds to a P concentration in porewater of $\sim 3 \text{ ng L}^{-1}$ for a DGT deployment time of 24 h at 20°C . This LOD is considerably lower than the 15 ng cm^{-2} (equivalent with $\sim 47 \text{ ng L}^{-1}$) reported by Stockdale et al.^{14b}

The relative standard uncertainties (RSU) of the LA-ICPMS P signals (measured as $^{31}\text{P}/^{57}\text{Fe}$ ratios) of the dry gel standards were $<20\%$ over the whole calibration range. A major contributor to the SU was the SD of the P signals (contribution of 50–98%). The RSDs of the signals observed in this work were in the range of 2.7% to 8.1%.

Chemical Mapping of the Distribution of DGT Labile P in a Soil

P C_{DGT} concentrations obtained for the majority of the soil area that was subjected to chemical imaging using the ferrihydrite DGT gel ranged from ~ 10 to $16 \mu\text{g L}^{-1}$ (Figure 5). A distinct, circular area with elevated C_{DGT} concentrations of up to $41 \mu\text{g L}^{-1}$ was observed as well. The circular shape and the diameter of about 2 mm of this localized elevation of P resembles the shape of hotspots of microbial activity observed in aquatic sediments.^{14a,b,25} This zone of increased P concentration could therefore be the result of a local hotspot of microbial activity in soil. Decomposition of organic matter by microbes with associated release of P or release of P due to lysis of microbial cells could lead to locally elevated P concentrations in soil. The large variations in DGT labile P concentration in this soil show that the ferrihydrite gel is well suited for measuring small-scale changes in P concentration in soils.

CONCLUSIONS

The new precipitated ferrihydrite gel has improved performance characteristics compared to existing gels used for P measurements, especially for the P binding capacity. The applicable pH range is somewhat smaller than for gels incorporating powdered ferrihydrite. However, precipitation of the ferrihydrite phase is convenient and the gels are more robust and homogeneous compared to gels made from powdered ferrihydrite. These properties render this novel DGT gel a practical alternative for the measurement of P, not only when high-resolution information is needed but also for conventional deployments of DGT samplers in waters, soils, and sediments.

The new binding gel is also well suited for the accurate analysis of the P distribution by LA-ICPMS with low LOD. Preliminary results of 2D imaging of P in a soil clearly underpin the potential to image P variations. This novel precipitated ferrihydrite DGT gel is therefore highly suitable for the investigation of P dynamics at submillimeter scales in sediments and soils. High-resolution measurements of localized changes of the P concentration in soils are of great interest, especially when considering P depletion and mobilization processes in the rhizosphere of plant roots.

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Figure 1. Kinetics of P binding onto the precipitated ferrihydrite gel. Error bars represent the standard deviation ($n = 3$).

Figure 2.

(a) Effect of immersion solution pH on P measured by the precipitated ferrihydrite gel given as the percent ratio of C_{DGT} to the immersion solution concentration (C_{Soln}). (b) Effect of ionic strength on the percent C_{DGT}/C_{Soln} ratio. (c) Recovery of P using ferrihydrite gels which were stored in a refrigerator for up to 33 days. Error bars represent the standard deviation ($n = 3$).

Figure 3. DGT measured mass of P at increasing solution P concentrations. The solid line gives the theoretical mass of P taken up by the DGT device according to eq 2. Error bars represent the standard deviation ($n = 3$).

Figure 4. Calibration curve measured with an ELAN DRCE instrument. The line was fitted to the measured data points using eq 3. Error bars represent the standard deviation of the mean of the ICPMS readings recorded for each standard gel.

Figure 5.
Chemical image of the DGT labile P measured on a plane surface of a Cambisol using the precipitated ferrihydrite gel.