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In situ, High-Resolution Measurement of Dissolved Sulfide Using Diffusive Gradients in Thin Films with Computer-Imaging Densitometry

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The technique of diffusive gradients in thin films (DGT) has been developed for the measurement of dissolved sulfide. Sulfide species from the sampled waters diffuse through a polyacrylamide hydrogel and then react with pale yellow $AgI_{(s)}$, incorporated at the surface of a second gel, to form black $Ag_2S_{(s)}$. The accumulated sulfide can be measured with a conventional purge-and-trap method followed by colorimetry (methylene blue). This enables the dissolved-sulfide concentration to be calculated under suitable conditions. Alternatively, the color change in the accumulating gel can be used to measure sulfide. A conventional flat-bed scanner, allied to imaging software, provided a densitometric measurement that was quantitatively related to the amount of sulfide accumulated. DGT measurements on synthetic solutions accurately determined the sulfide concentration (95% recovery), thereby confirming the unobstructed diffusion of HS^- through the gel. The accumulated mass was inversely proportional to the diffusion-layer thickness as theoretically predicted. With the selected geometry, the limit of detection of the densitometric procedure for a 24-h deployment was 0.13 μmol L^{-1}, and the maximum concentration measurable was 60 μmol L^{-1}. When used in anoxic lacustrine waters, DGT provided sensible concentrations. It was also used to measure depth profiles at submillimeter resolution in estuarine surface sediments.

Variation in the concentration of sulfide with sediment depth in the pore water provides important biogeochemical information[1] and is one of the major controls of the dissolved concentration and toxicity of trace metals.[2−4] Consequently, several methods have been developed for measuring dissolved sulfide concentrations, both in situ and in extracted pore waters[1]. Spectrophotometric (usually with methylene blue) or chromatographic methods provide ex situ measurements of total dissolved sulfide (S^{2-} + HS^- + H_2S). Total sulfide concentrations have also been measured directly in sediment cores by voltammetry with 100-μm diameter electrodes.[5] In situ measurements of the free sulfide ion, S^{2-}, have been made with potentiometric microelectrodes[6] and of dissolved H_2S with amperometric microsensors.[7] These electrochemical techniques allow concentrations to be measured at high spatial resolution in biofilms or across sediment−water interfaces (SWI), but can have problems with poor sensitivity, surface fouling, or interferences[1].

In this paper we describe the development of a method for measuring total dissolved sulfide with the diffusive gradients in thin films (DGT) technique.[8] DGT has been used to measure trace metals,[9−13] major ions,[14] and nutrients.[15,16] During the in situ deployment, analyte species from the sampled waters diffuse through a layer of polyacrylamide gel of known thickness and are then trapped by an immobilized binding agent incorporated within a second gel layer. Ideally the reaction with the binding agent will cause the analyte to be rapidly and irreversibly removed from solution under the sampling conditions. This effectively causes a diffusion gradient for the analyte to be maintained across the diffusion gel layer, as long as the binding capacity within the second gel is not exceeded and the analyte concentration is constant in the sampled water. The mass of analyte accumulated in the binding gel is measured on retrieval, and Fick's first law of diffusion is used to calculate the in situ analyte concentration in the sampled water. The analyte is fixed in a stable form, thereby allowing it to be eluted under controlled conditions and then measured using sensitive lab-based techniques. The built-in

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accumulation results in the method having low overall detection limits. Alternatively, elution can be avoided by using surface analytical techniques which allow measurements to be performed at high spatial resolution (submillimeter).[11]

The objectives of this study were to develop a DGT method for measuring total dissolved sulfide in waters and sediments. A key requirement was the provision of a suitable immobilized binding agent that allows for irreversible and stable binding of sulfide under sampling conditions, but from which it can be readily released under lab conditions. Gel impregnated with $AgI_{(s)}$ fits the criteria well. $Ag_2S_{(s)}$ is formed in situ on exposure to dissolved sulfide.

A laboratory method for elution and measurement of the accumulated sulfide was developed on the basis of the purge-and-trap approach with the methylene blue colorimetric technique that is used for acid volatile sulfide measurements.[17] An alternative measurement procedure based on densitometry, which makes use of a change in the color or intensity (optical density) of a surface, was also used. This was possible because of the $AgI_{(s)}$ being pale yellow and the $Ag_2S_{(s)}$ being black. While densitometry can be performed using readily available software and inexpensive hardware, it has the same advantages as other surface analytical techniques: high potential sensitivity and high spatial resolution in two dimensions.

This approach is superficially similar to a sulfide "dipstick" sampler,[18] which used a gel formed in lead acetate solution. A visible pattern of dark PbS was observed after sampling sulfide-containing waters. However, as the "dipstick" method did not use a diffusional gel layer, it was less quantitative than DGT. Furthermore, as the lead acetate was not immobilized, it could presumably diffuse out of the gel.

The assumptions, limitations, and other quantitative applications of the DGT method have been described elsewhere.[10,19,20] In sediment pore waters and other poorly mixed waters, the concentration external to the DGT assembly can become depleted, and the assembly then measures a flux of analyte from the external water rather than a concentration. Precise interpretation of the sulfide measurement obtained with the DGT assembly described here, in various environments, will be dealt with in a subsequent study. This paper is concerned with the development and verification of the technique, and both concentration and flux values are given where appropriate.

EXPERIMENTAL SECTION

Preparation of Diffusive Gels, Binding Gels, and DGT Assemblies. The diffusive gel was prepared according to previously described procedures.[10,18,21] A stock solution comprising 25 mL of 30% acrylamide (Boehringer Manheim), 7.5 mL of 2% agarose-derivatized acrylamide cross-linker (DGT Research), and 17.5 mL of deionized water was mixed well. Any foam that formed was allowed to collapse before the solution was used. Diffusion gels were prepared by adding 70 μL of freshly prepared 10% (w/w) ammonium persulfate (BDH) solution and 25 μL of 99% *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (TEMED, Sigma) to 10 mL of the stock solution. This polymerization solution was inverted several times, in a way that produced a minimal amount of foam, and immediately pipetted into suitable moulds. The moulds comprised two slightly offset, clean glass plates, an inert plastic spacer of known thickness, which can be routinely varied between 0.1 and 1.5 mm, and clips to hold the mould firmly together. The mould was then placed in an oven set at 42 °C for 45−60 min. The set gels were then hydrated (during which process they swell by a factor of about 1.4) and rinsed in deionized water for 24 h before being stored in 0.01 M $NaNO_3$.[18]

AgI was chosen as the binding agent because it is very insoluble ($K_{sp} = 8.51 \times 10^{-17}$) in water, it readily forms Ag_2S which is even more insoluble ($K_{sp} = 6.69 \times 10^{-50}$), and its rapid reaction with sulfide is accompanied by a color change from pale yellow to black. Two procedures were investigated for the preparation of a binding gel incorporating AgI. In the first procedure, 0.6 g of AgI (Aldrich) was finely ground in a mortar and pestle (so that each particle was <10 μm in diameter) and then added to 6 mL of acrylamide/cross-linker stock solution, which was stirred vigorously for about 10 min, to form a stable, well-dispersed suspension. Then 42 μL of 10% ammonium persulfate solution and 15 μL of TEMED were added, and the procedure described above was followed. A 0.25-mm spacer was used in the mould which must be laid down flat during the setting so that the AgI settles toward one face. This produced a AgI layer of about 50-μm thickness at one surface of the gel (which could readily be identified by looking at the edge of the gel when in water). The resulting gel contained about 6 μmol cm^{-2} of AgI and had a maximum sulfide capacity of about 3 μmol cm^{-2}. The side of the gel containing AgI was placed against the diffusive gel. On deployment, an immobile layer of Ag_2S was formed at this surface of the gel.

The second method involved the successive immersion of normal diffusion gel in solutions of $AgNO_3$ and KI, which caused $AgI_{(s)}$ to form in the gel in situ. Although this produced a very even and finely dispersed binding gel, sulfide measurements were irreproducible; Ag_2S was formed preferentially at the exterior surface of the gel and was consequently prone to becoming detached with handling. The first method of preparing the binding gel was therefore adopted.

The AgI in the binding gel was prone to darkening upon prolonged exposure to light, because of the photoreduction of silver halides to silver metal. This was mainly a problem during setting of the gel, which took place at elevated temperatures. When the gel was minimally exposed to light, during and after this step, and stored in a dark container, it was stable.

Two different DGT assemblies were used. For deployment in solution the previously described piston design which used 25-mm diameter disks of gel was used.[10] A flat probe design was used for deployment in sediments.[11] In each case, the binding gel (AgI surface up) was overlaid with the diffusive gel and a cellulose nitrate membrane filter (0.45 μm, Whatman). They were held together within the plastic assembly with the filter exposed through a window. The assemblies were deoxygenated by submerging them in 0.01 M $NaNO_3$ bubbled with high-purity nitrogen.

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Sulfide Measurement and Elution from the Binding Gel. Sulfide stock solution of 5−20 mmol L^{-1} was prepared by washing a single crystal of $Na_2S{\cdot}9H_2O$ (Aldrich) with deionized water, blotting it dry on tissue paper, accurately weighing it, and dissolving it in 500 mL of deoxygenated deionized water. This solution was stored in a refrigerator and was stable for several weeks if exposure to air was minimized. It was standardized each week using an iodometric method.[22]

After preliminary trials, the following version of the methylene blue colorimetric method was adopted. Reagent solutions were: (a) 2 g of *N*,*N*-dimethyl-*p*-phenylenediamine sulfate (Sigma) dissolved in 1:1 sulfuric acid (BDH, AnalR) and diluted to 200 mL in deionized water and (b) 18 g of ammonium iron (III) sulfate (BDH) dissolved in 200 mL of deionized water. One milliliter of each reagent (a + b) was added, in that order, to 20 mL of sulfide solution and thoroughly shaken. After 20 min, the absorbance was measured at 670 nm. An absorbance of 1 corresponded to 24.3 μmol L^{-1} of sulfide, and the linear range was 0−30 μmol L^{-1}. Deoxygenated 0.25 M NaOH was used to prepare the sulfide standards or to trap the sulfide (see below).

The purge-and-trap method of measuring acid-volatile sulfide in sediment developed by Allen *et al.*[19] was modified for this work. Preliminary studies of elution of sulfide from the binding gel indicated that concentrated HCl was required to produce $H_2S_{(g)}$ from the $Ag_2S_{(s)}$. Thus, a sulfide-containing sample (solution or gel) was placed in a 250-mL round-bottom flask through a sidearm. Then about 5 mL of 12 M HCl (BDH, AnalR) was added and the flask stoppered and placed in a hot water bath (∼60 °C). High-purity nitrogen was passed through a gas-flow controller at 150 mL min^{-1} and then bubbled through the flasks contents and finally through a series of gas traps. Any H_2S gas that had been evolved through the acidification is carried to the gas traps. The first one contained deionized water and was placed in a beaker of cool (∼4 °C) water. This cooled the gas flow and seemed to neutralize some of the acidity. The second and third traps contained 20 mL of 0.25 M NaOH which neutralized and trapped the H_2S gas as S^{2-}. Sulfide was observed infrequently in the third trap after the optimal collection time of 20 min. A 90% recovery efficiency was achieved for standard sulfide solutions passed through the apparatus over the entire concentration range of the calibration curve.

Preparation and Performance of the Computer-Imaging Densitometry. After exposure to sulfide, the accumulating gels were removed from the DGT assembly and spread out on blotting paper (Bio-Rad), with the binding side face-up, and a thin acetate sheet was placed over the gel to protect the surface. The layered assembly was then placed in a commercial gel dryer (Bio-Rad, Model 543) for at least 2 h operating at 60 °C under vacuum. This treatment dries the gel by shrinking it only in the thickness dimension; during this process no discernible change in color occurs. The Ag_2S does not readily oxidize in air. It is stable during drying and can be stored for over 12 months without visible change.

The dried gel was then placed in a flat-bed scanner (Hewlett-Packard ScanJet IIc) and the image recorded by the software (Hewlett-Packard Deskscan II), giving a final image quality of 4.2 pixels per millimeter (offering a potential spatial resolution of 238 μm). The brightness of the scanned images was manually optimized so that the lightest gel (an unreacted portion of the gel or a blank) was just discernible from the white background of the blotting paper when using the image-analysis software. The same brightness setting was used for subsequent image scans and was found to give consistent image densities. All images were recorded as 8-bit gray scale tagged image file format (TIFF) files. The 8-bit images produce 256 shades of gray from white (0) to black (255). This procedure enabled the largest gel-density range to be recorded before black saturation of the gray scale occurred.

NIH Image (US National Institutes of Health) is a public domain image processing and analysis software package for Macintosh systems (available on the Internet at http://rsb.info.nih.gov/nih-image/). A PC version is available from Scion Corporation (at http://www.scioncorp.com/). It allows selection and measurement of particular areas of the image, measurement of average optical density for a chosen area, or measurement of changes in optical density with distance to be used. It is therefore suitable for both uniform exposures to solution and for assessing spatial changes in optical density associated with pore water concentration gradients. Calibration was performed by exposing AgI gels to a range of sulfide concentrations. As the sulfide present in the scanned samples is not affected, it could also be subsequently eluted and measured by wet-chemical methods, as described above, to obtain a direct comparison of the two procedures.

Laboratory and Field Deployments. AgI gels or DGT assemblies were exposed to known concentrations of sulfide in a temperature-controlled, well-mixed solution in laboratory experiments. Sulfide losses were minimized by purging all solutions with N_2 gas before addition of the sulfide and by minimizing the volume of the headspace in the container to reduce volatilization.

Field deployments were carried out in northwest England. Assemblies were transported to the sites in a container filled with deoxygenated 0.01 M $NaNO_3$. Concentration profiles across the sediment−water interface were obtained for the estuary of the Conder River, south of Lancaster, by deploying and retrieving by hand (<0.25 m depth at low tide). On retrieval, the diffusion layer was removed from the sampler immediately, while it was made sure that exposure of the binding gel to sunlight was minimized. DGT assemblies were deployed in Esthwaite Water (15-m-deep) about 1 m above the sediment−water interface, using a benthic lander.

RESULTS AND DISCUSSION

Testing sulfide uptake and elution with the binding gel. The uptake process was investigated by exposing binding gels directly to known amounts of sulfide (0.098−3.92 μmol S^{2-} in 5 mL) for 24 h. Without a diffusion layer, full uptake of the available sulfide occurred within this time. The amount of sulfide taken up was measured using the distillation procedure, corrected for its 90% efficiency. For three different concentrations of the exposure solution (>1 μmol S^{2-}) the recoveries were greater than 90% (Table 1). It was not possible to work reliably at lower sulfide concentrations with these 24-h uptake experiments because of loss of sulfide, either by oxidation, volatilization, or adsorption.

Preparing a Calibration Curve for the Densitometric Detection of Sulfide. Twenty DGT solution assemblies with 0.08-cm-thick diffusion gels were exposed to sulfide solutions ranging

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Table 1. Mass Balance and Efficiency of Sulfide Uptake and Elution

amt of sulfide exposed to AgI gel (μmol)	amt of sulfide measured after elution (μmol)	% recovery
1.47	1.34	90.8
2.45	2.43	99.3
3.92	3.76	96.0
mean		95.4 ± 4.3

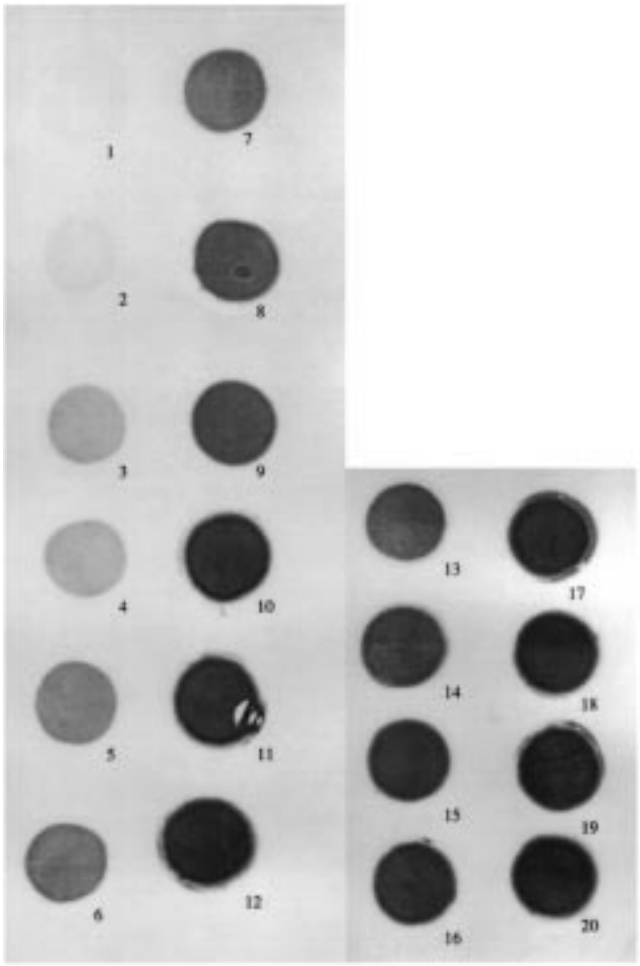

Figure 1. Scanned images of 20 AgI binding gels exposed to various concentrations of sulfide for the calibration process: (1) 0.0; (2) 3.0; (3) 6.4; (4) 10.7; (5) 17.0; (6) 21.3; (7) 27.7; (8) 42.5; (9) 63.6; (10) 95.2; (11) 147; (12) 209; (13) 42.5; (14) 74.2; (15) 84.7; (16) 127; (17) 168; (18) 189; (19) 230; (20) 270 μmol L^{-1}.

from 0 to 270 μmol L^{-1} for 15 h. The exposed binding gels were dried and scanned (Figure 1). After the gray-scale intensity for each gel was measured using the imaging software, the gels were cut out of the sheet, and the sulfide accumulated was measured using the purge-and-trap technique with analysis by methylene blue. The resulting concentrations, corrected for the distillation efficiency, were used to calculate the density of sulfide on the binding gel (μmol cm^{-2}). There was a systematic, but nonlinear, relationship between sulfide (μmol cm^{-2}) and gray-scale intensity (Figure 2). The data were well-fitted ($R^2 = 0.98$) by

$$y = a \ln(b x) \quad (1)$$

where a and b are fitting constants; $a = 40.1$ and $b = 568.2$. The

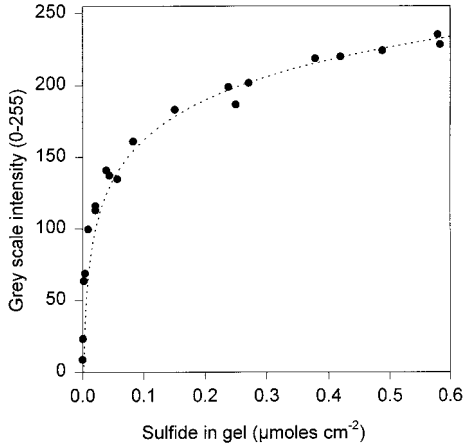

Figure 2. Plot of greyscale density (0−255) versus sulfide μmol per cm^2 for the 20 prepared standards (Figure 1). The line is the fitted calibration curve (eq 1).

consequences of this relationship are that the densitometric measurement is very sensitive at low sulfide concentrations and less sensitive at high sulfide concentrations.

The nonlinearity can be rationalized. At higher concentrations the surface AgI sites available to react with unreacted sulfide decrease considerably in number. Consequently, sulfide may either pass into the solid AgI to react with fresh material or, more likely, it may diffuse to and react with the back of an AgI particle or even a particle further away from the interface with the diffusion gel (introducing a maximum possible flux error of 2.5%). In either case, the additional Ag_2S will not contribute in a proportional manner to the densitometric measurement, but will do for the chemical elution and measurement.

The standard deviation (SD) of the sulfide density of a series of blank binding gels was determined (0.00141 μmol cm^{-2}). A limit of detection (LOD = 3 × SD) of 0.00423 μmol cm^{-2} was thus estimated. For a typical 24-h deployment, with a 0.08-cm diffusion-layer thickness, a LOD of about 0.26 μmol L^{-1} is expected in natural waters. By using longer deployments and thinner diffusion layers this value can be reduced by over an order of magnitude[10] (0.033 μmol L^{-1} for a 0.03-cm diffusion-layer thickness and a 3-day deployment), making it comparable with many of the most sensitive sulfide techniques currently in use and superior to most in situ techniques[1]. The reproducibility of the AgI binding gel was also tested by conducting DGT uptake experiments in standard sulfide solutions for a given time and was found to be satisfactory (5.3% rsd, $n = 10$, at 0.389 μmol cm^{-2}).

At the other end of the concentration range, the densitometric technique saturates at sulfide concentrations of 62.6 μmol L^{-1}. This is less than the dynamic range for other in situ techniques[1]. It is equivalent to about 1 μmol cm^{-2} of sulfide, which is less than the estimated capacity of the binding gel. The sulfide concentration can still be measured using the purge-and-trap/colorimetric technique, however, when the densitometry has reached its upper limit. Alternatively, shorter deployment times or thicker diffusion gels can be used to extend the upper limit. This can also be extended by varying the imaging-software settings, but at the cost of overall sensitivity.

Testing Sulfide Measurement by DGT. The performance of DGT can be assessed by checking the validity of the standard DGT equation for calculating the measured mass

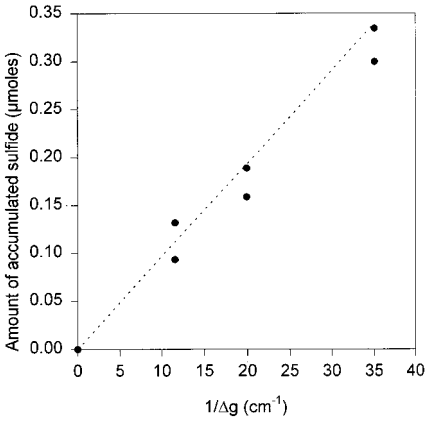

Figure 3. Dependence of the measured amount of sulfide accumulated by DGT on the reciprocal of diffusion-layer thickness (Δg). The line is the theoretical response calculated from the known concentration in solution and eq 2.

of the analyte, M:

$$M = CDtA/\Delta g \qquad (2)$$

C (g or mol mL^{-1}) is the concentration of the analyte in the sampled solution. D (cm^2 s^{-1}) is the diffusion coefficient of the analyte, corrected for temperature. t (s) is the deployment time. A (cm^2) is the surface area of the diffusional interface. Lastly, Δg (cm) is the thickness of the diffusion layer (includes the diffusion gel and any membrane covering).

DGT units with constant values of A, but different diffusion layer thicknesses, were exposed to a measured concentration of dissolved sulfide for a predetermined time. The experiment was performed in an anaerobic cabinet (Forma Scientific) to minimize interference from oxidation. A 10-L plastic container was filled with 0.01 M $NaNO_3$, which was deoxygenated for 3 days. NaOH was added to keep the pH about 8. DGT assemblies with diffusion-layer thicknesses of 0.087, 0.050, and 0.029 cm were prepared in triplicate, with one of each diffusion-layer thickness used as a blank and the other two used in the experiment. These were deoxygenated for 2 days. Sulfide stock solution was added to the $NaNO_3$ to make a final concentration of about 25 μmol L^{-1}, which was then stirred for about 5 min before the DGT assemblies were placed within the container. About half of the sulfide was lost to adsorption/volatilization during this time. A lid was then placed on the container to eliminate headspace volume, and the container was wrapped in a black plastic bag to obstruct light. The solution was stirred, and the experiment carried out for 4.5 h. The DGT assemblies were then removed and rinsed thoroughly and the mass of accumulated sulfide measured using the densitometric procedure and the calibration curve of Figure 2.

The plot of accumulated sulfide versus the reciprocal of diffusion-layer thickness (Δg^{-1}) was linear, with an R^2 value of 0.98 (Figure 3). The mean sulfide concentration during deployment of 12.8 $\pm$ 1.05 μmol L^{-1} was used to calculate the theoretical response using eq 2. The points lie very close to the theoretical line (95 $\pm$ 13% recovery), showing that eq 2 is valid and also that diffusion of sulfide through the gel and filter is unrestricted. This result indicates that the calibration curve need not be prepared on each occasion, provided that the settings and equipment are not changed for the imaging procedures. Consequently, the binding gel can be used with DGT samplers to measure sulfide concentrations, using either the purge-and-trap and colorimetric or the densitometric technique. The average rsd, larger than that described above, on these measurements, of 12.1%, is mainly due to the smaller sample size ($n = 2$).

The value of D used in these calculations was that for HS^- in water (14.8×10^{-6} cm^2 s^{-1} at 18 °C[23]). Above pH 7, the main form of sulfide in solution is $HS^-_{(aq)}$, although equilibrium with H_2S and S^{2-} is rapid. The reaction to form $Ag_2S_{(s)}$ can be written as:

$$2AgI_{(s)} + HS^-_{(aq)} \rightarrow Ag_2S_{(s)} + H^+_{(aq)} + 2I^-_{(aq)} \qquad (3)$$

In many natural-water systems, colloidal forms of sulfide will often be present, some of which may react with the DGT assembly (e.g., FeS). These forms will have much smaller diffusion coefficients through the gel than $HS^-_{(aq)}$ and are unlikely to contribute a significant fraction to the overall measurement.

Field Deployments. Flat-probe DGT assemblies were deployed in situ in sediment in the estuary of the Conder River during summer. Two of the profiles obtained are shown in Figure 4 along with the scanned images of the exposed binding gels. The images clearly show the outline of the sampler and the approximate position of the SWI. They provide, directly, a visual impression of the spatial variation in sulfide concentration. The intensity of image (a) has exceeded the upper limit for the densitometric technique and thus the concentration profile appears to saturate (24-h deployment). The purge-and-trap technique could still be used on this sample to measure the actual concentration over this depth range, although at a lower resolution. The DGT assembly producing image (b) was deployed for a shorter period (11 h) at the same location but several weeks later. Zones of sulfide production and depletion are readily apparent in each profile. It is also clear that sulfide production was much greater during the first deployment (a).

The concentration profile was obtained by selecting a 1-pixel-wide vertical section of the scanned image and obtaining a vertical profile of gray-scale intensity. This was then converted to sulfide mass (μmol) through the calibration relationship (eq 1) and then to a pore-water concentration through the DGT Equation (eq 2). Fluxes (J, μmol cm^{-2} s^{-1}) are calculated from the following relationship:

$$J = M/At \qquad (4)$$

The profile did not change significantly when alternative vertical sections were selected. The resolution of the imaging process is about 0.24 mm. However, the actual resolution of the technique is also limited by the thickness of the diffusion-gel layer, as relaxation of sharp features occurs as a result of partial vertical diffusion of the analyte as it passes through the gel.[24] If the diffusion-layer thickness is greater than 0.24 mm (which it usually is), measurements made at the diffusion-layer thickness are of high fidelity. Measurements made at smaller intervals may reflect some diffusional averaging of sharp features.

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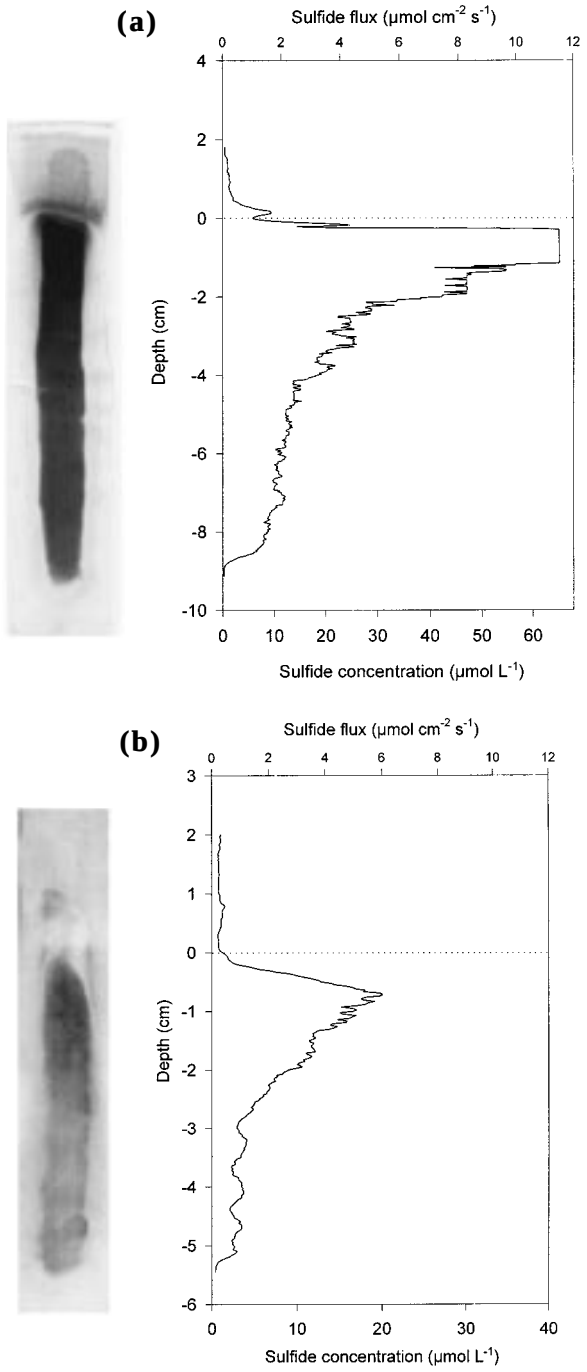

Figure 4. Scanned images of two AgI gels and the calculated-sulfide-concentration profile from DGT assemblies deployed in sediment in the Conder River estuary, near Lancaster: (a) $\Delta g = 0.84$ mm, $t = 24$ h, LOD $= 0.28$ μmol L^{-1}; (b) $\Delta g = 0.49$ mm, $t = 11$ h, LOD $= 0.35$ μmol L^{-1}.

Close examination of the scanned images reveals two features that can interfere with the quantitative determination of sulfide. There is a brown band between the intense black deposit and the SWI. This is due to natural diagenetic formation of iron oxyhydroxides and results in a more elevated image intensity in this region. This band extends beyond the limits of the gel window because iron (II) is not immobilized by the binding gel but by oxidation. By contrast sulfide is fixed immediately upon contact with AgI, and therefore, its image is more well-defined.

Above the SWI there is some darkening of the whole of the AgI gel, both that exposed through the window and that under the Perspex sheet. The membrane covering the diffusion gel extends beyond the window and filters out much more light than the Perspex does. This is consistent with discoloration by exposure to light, which would have occurred at low-tide levels. Although this will lead to overestimation of the sulfide concentration in the overlying water, it was still less than about 2 μmol L^{-1}.

Clearly, caution must be exercised when using this procedure close to an oxic−anoxic boundary or in the presence of light. Except in quite productive systems, sulfide is present at sufficient depth within sediments that these two potential problems will not exist. Furthermore, as both of these phenomena leave traces beyond the gel window, it may be possible to take a vertical section through the image outside of the gel window (the Perspex being transparent to visible light, which is responsible for the darkening) as a control measurement and subtract this from the vertical section obtained within the window.

A sulfide DGT assembly for use in sediments ($\Delta g = 0.084$ cm, $t = 25$ h, 10 °C) was also deployed in the sulfidic bottom waters of Esthwaite Water during the late summer of 1997 about 1 m above the SWI. The intensity was uniform throughout the 10 × 1 cm of exposed gel. The single interpreted sulfide concentration of 40.5 μmol L^{-1} was similar (within 25%) to measurements made, in previous years, with the colorimetric method at this site in late summer.

CONCLUSIONS AND FUTURE WORK

We have demonstrated that sulfide can be measured in a quantitative manner with AgI-DGT and that the response is virtually that predicted by theory. Either a conventional purge-and-trap and colorimetric method or the densitometry using computer imaging, developed during this study, can be used. The latter provides sulfide measurement at high-resolution (submillimeter). Both procedures have been successfully used for in situ measurements in the field.

This newly developed DGT technique is complementary to the in situ electrochemical methods that are available. Microelectrodes can make measurements at higher spatial resolution and provide time-series information. DGT, however, uses very simple, readily available equipment and, by deploying rectangular sheets, can be used to obtain two-dimensional images of concentration. Whereas most in situ microsensor systems have greater dynamic ranges, DGT has a potentially lower limit of detection. The technique is also much less expensive than the microsensor techniques.

DGT measures, directly, the mean flux to the device. Interpretation as concentration assumes that there is a rapid resupply of sulfide from the solid phase to solution. Use of DGT alongside more conventional measurements will enable this assumption to be tested and possibly allow direct determination of in situ desorption fluxes of sulfide.

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