2D simultaneous measurement of the oxyanions of P, V, As, Mo, Sb, W and U.

Anthony Stockdale,*[a, b] William Davison[a] and Hao Zhang[a]

[a]Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, UK.

[b]Current address: Centre for Ecology and Hydrology, Lancaster Environment Centre, Lancaster, LA1 4AP, UK.

The published version is available from http://dx.doi.org/10.1039/b925627j

*Corresponding Author

E-mail: tony @ biogeochemistry.org.uk

Fax: +44 1524-61536 Tel: +44 1524-595800

Environmental impact statement: This paper presents advances in a sampling technique that allows the co-analysis of anions of P, V, As, Mo, Sb, W, U and sulphide in sediment. Co-analysis of sediment solutes is particularly valuable as it allows interpretation of geochemical processes based on the behaviour of multiple analytes at the same precise time and locations. This technique has the ability to provide information on sub-mm scale processes within sediment, including in two-dimensions, and also profiling across the sediment-water interface. It has potential applications in the monitoring or assessment of the mobility of pollution from mine wastes (e.g. As and Sb). The technique can also be adapted for looking at the geochemistry of the target elements at the soil-plant root interface.

Summary

Previous work used the sampling technique diffusive gradients in thin-films analysed by laser ablation mass spectrometry to measure sulphide, P, V and As at a microniche of reactive

organic carbon in a freshwater sediment. Here we present new developments of this technique. The number of analytes has been extended and we demonstrate the technique for depth profiling of analytes in both one and two dimensions. The physical dimensions of the cell in the laser ablation unit restrict the maximum length of gel that can be analysed. We address this problem by proposing a method for obtaining better data continuity when analysing multiple segments of gel from the same probe. ^{13}C is used as the internal standard for each gel segment. For the cross standardisation of different gel segments ^{58}Fe signals are obtained from ablation of a small piece of standard ferrihydrite gel analysed during the same run as the sample gel. As the ferrihydrite gel is a subsection of a much larger gel (i.e. the Fe concentration is consistent for all subsection), then any difference in signal can be attributed to changes in detector sensitivity and gels across different runs and performed on different days can be standardised.

Introduction

With recent developments of new sensors there is increasing interest in studying chemical processes in sediment at high-resolution. Such measurements allow processes occurring on a localised scale to be observed and the effect of these processes on diagenesis of the whole system can be reported. Furthermore, co-analysis of multiple sediment solutes is particularly valuable as it allows interpretation of geochemical processes based on the behaviour of multiple analytes at the same precise time and locations. Two-dimensional probes are currently available for trace metals, nutrients, dissolved gases and pH.[1] Planar optodes have been used to investigate, in two-dimensions and at sub-mm resolution, profiles of single components across the sediment water interface (SWI).[2] Two components have been analysed simultaneously across the SWI using a combination of the sampling techniques diffusive gradients in thin-films (DGT) and diffusive equilibration in thin-films (DET).[3] DGT when deployed in sediment gives a measurement that reflects the porewater concentration and the amount of solute that can be re-supplied to the sediment-probe interface via diffusion and desorption from the solid phase (C_{DGT}). We have previously

reported the use of a combined silver iodide – ferrihydrite binding phase for the DGT technique for the 2D analysis of the anions of P, V, As, and S within sediment.[4] Here we present new developments of this technique. The number of analytes has been extended to additionally include ^{94}Mo, ^{121}Sb, ^{182}W and ^{238}U, and we demonstrate the technique for depth profiling of these analytes across the SWI. The physical dimension of the cell in the laser ablation unit restrict the maximum length of gel that can be analysed. To overcome this problem we propose a method for obtaining better data continuity when analysing multiple segments of gel from the same probe.

Experimental

Sample collection and gel preparation, deployment, drying and analysis procedures followed those previously used.[4, 5] The DGT binding phase used was a combined silver iodide – ferrihydrite binding layer capable of binding sulphide and a range of anions.[4] To reduce blank levels we used ultra-pure reagents to prepare the gels: silver nitrate (Alfa Aesar, Premion grade, 99.9995%), sodium hydrogen carbonate (Alfa Aesar, Puratronic grade, 99.998%), iron nitrate nonahydrate (Sigma-Aldrich, 99.999+%) and potassium iodide (Merck, Suprapur grade, 99.995%). For this work three probes were deployed in individual intact sediment cores with temperature controlled flowing overlying water. Cores were collected from Esthwaite Water, a freshwater lake in the English Lake District. Post deployment preparation of gels for analysis followed previously reported procedures.[4] Briefly, gels dried onto a backing filter (maximum dimensions ~1.8 × 15 cm) were cut into ~1.5 × 4 cm pieces and mounted onto glass slides with double sided tape. Analysis was performed on the upper segment of gel (across the SWI) for all three probes, with one probe being selected for the analysis of a larger depth range across three slices. The ablation is performed in lines of spots vertically down the gel, with a distance between spots of 500 µm, There are typically 22-28 ablation lines on each gel.

Detector counts from laser ablation coupled with inductively coupled mass spectrometry (LA-ICP-MS) tend to be relatively stable over the time of ablating one gel. However, detector peak or background counts do not tend to be equal over a period of days or weeks. In laboratories where the ICP-MS is used for aqueous as well as LA samples, the switching of dedicated consumables (e.g. torch, cones) and the requirement to re-tune, mean that peak detector counts at a given analyte concentration will give large variations between LA runs.

^{58}Fe has several properties that make it an ideal candidate for use as an internal standard on gels. Namely, a very low detector background, high peak signals and a mass within the range of the other analytes. However, ^{58}Fe cannot be used to standardise signals across a deployed gel, as iron oxides precipitate within the gel at the oxic sub-oxic interface. We use a procedure that uses two different analytes for standardisation. ^{13}C (a major component of the gel matrix[6]) is used for internal standardisation of single gel segments. Each ablation spot is standardised to ^{13}C based on the average for all ablation spots on the gel segment. Due to a relatively low peak to background ratio and high background counts, ^{13}C is not ideal for standardisation of data generated on different days and across gel segments. To improve continuity when analysing multiple gels, including segments from the same probe, we used a procedure that fixes a piece of a standard ferrihydrite gel (~0.5 cm^2; a subsection of a much larger piece of gel ~1.5 × 15 cm) on the same slide as each segment of deployed gel. As the ferrihydrite gel is a subsection of a much larger gel (i.e. the Fe concentration is consistent for all subsections), then any difference in signal can be attributed to changes in detector sensitivity. An average value from multiple ablation spots on this gel yield data for standardising variations in detector signals on different days.

Results and discussion

The results of the high-resolution two-dimensional profiling are shown in Figure 1 with quantitative data for P, V and As, and qualitative data for ^{94}Mo, ^{121}Sb, ^{182}W and ^{238}U. Previous work[4] has reported the detection limits for the quantitative analysis so this

discussion is not repeated here. Colorimetric sulphide data were obtained for deployed probes, however, results of this type have previously been reported in several studies[3, 5, 7] so are not included here. The data in Figure 1 shown the potential of the technique for profiling in 2D and at sub-mm intervals across the SWI, adding to the toolbox of existing techniques.[1,3] Quantitative data was obtained for P, V, and As by analysis of standard gels prepared for previously reported work[4] and using the cross calibration techniques described above. Future work should focus on the improvement of calibration procedures to include the other analytes.

Many of the porewater solutes included in this study are generally measured using slicing of sediment cores and centrifugation to isolate the solutes. The technique presented here allows trends in these analytes to be studied at high-resolution, not only in 2D, but also in 1D. This technique is particularly valuable in demonstrating heterogeneity in sediment systems. However, we also sought to demonstrate how representative, averaged profiles could be obtained when data from multiple probes are averaged. This may allow the co-analysis of vertical profiles of these elements obtained in situ, and at higher resolution than other measurement techniques. Data for specific depths on multiple probes can be averaged to give 1D vertical profiles of analytes with error bars based on the standard deviations of the means (Figure 2). Here we show 1D averaged data, based on three individual deployed probes. Multiple probes were deployed to reduce the effects of heterogeneity across individual probes.

Figure 3 presents the results of the cross standardisation testing. Data for P and As are presented as they represent analytes with contrasting peak to background count ratios. P data show a high level of continuity between the gel segments. The effectiveness of the technique can be illustrated by comparing the percent change in the detector counts to the calculated concentration across the two gel transitions. From the upper to the central gel, the peak area (based on the detector signal) is increased by 39% whereas the corrected

concentration only varies by -6%. For the centre to lower section the changes are -8% and 3% respectively. This highlights the effectiveness of the procedure. Results for As show lower level of continuity, however, data at the transition between the segments are within one standard deviation of the mean values. A small amount of instrument drift in the As signal may cause this small deviation.

Our data were obtained from an unpolluted lake in the English Lake District. Several of the analytes studied here may be present in mine spoil or smelter wastes.[8] This technique could be applied to the assessment or monitoring of sites affected by such activities. There has also been an increase in interest in the environmental impact of Sb[9] and this gel has the potential to be used in monitoring of this element. Recently DGT with this binding phase has been used for the measurement of phosphate at plant roots.[10] The expansion of the number of analytes, as presented here, may aid interpretation of biogeochemical processes occurring in both soils and sediments. Measurement of additional analytes has no additional requirements on the ICP-MS (provided interferences are considered). Therefore, additional data can be obtained relatively easily, potentially allowing wider interpretation of the results.

Acknowledgements

We thank Debbie Hurst for assistance with sample collection. A Stockdale was supported by the UK Natural Environment Research Council during the practical elements of this work (NER/S/A/2005/13679).

References

1 A. Stockdale, W. Davison, H. Zhang, *Earth-Sci. Rev*., 2009, **92**, 81–97.
2 Q.Z. Zhu, R.C. Aller, Y.Z. Fan, *Geochim. Cosmochim. Acta*, 2006, **70**, 4933–49.
3 D. Robertson, D.T. Welsh, P.R. Teasdale, *Environ. Chem*., 2009, **6**, 60-9.
4 A. Stockdale, W. Davison, H. Zhang, *Environ. Chem*., 2008, **5**, 143-9.
5 A. Widerlund, W. Davison, *Environ. Sci. Technol*., 2007, **41**, 8044-9.
6 K.W. Warnken, H. Zhang, W. Davison, *Anal. Chem*., 2004, **76**, 6077-84.
7 C.R. Devries, F. Wang, *Environ. Sci. Technol*., 2003, **37**, 792-7.
8 S.N. Luoma, P.S. Rainbow, *Metal Contamination in Aquatic Environments*, Cambridge University Press, New York, 2008.

9 W.A. Maher, *Environ. Chem*., 2009, **6**, 93-94.
10 J. Santner. Presented at the 2009 Conference on DGT and the Environment, Santa Margherita di Pula, Sardinia, October 2009.

Figures

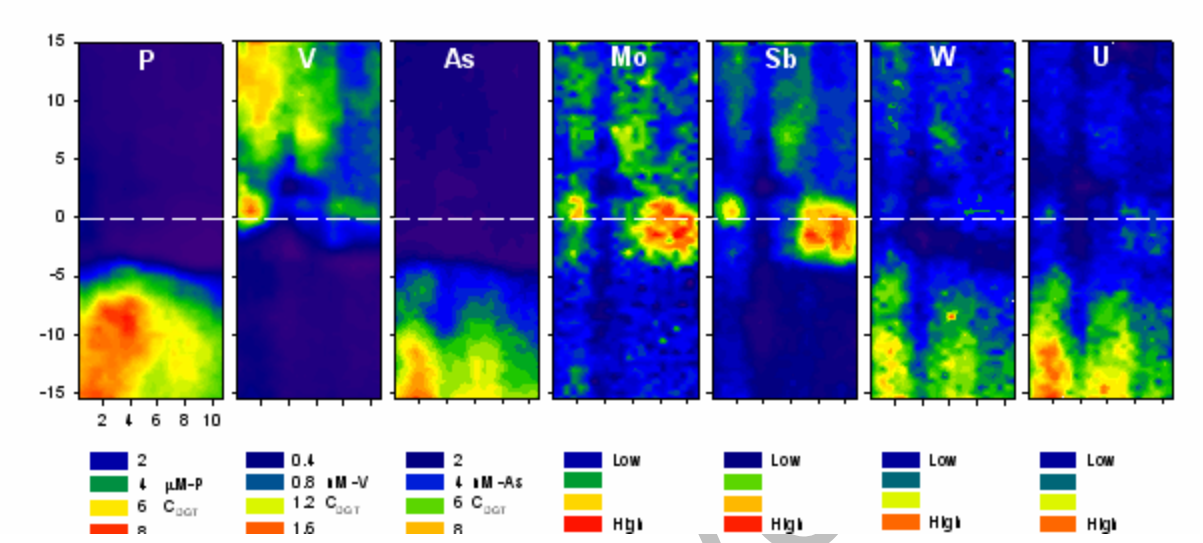

Figure 1. Two dimensional profiles of the anionic species of P, V, As, ^{94}Mo, ^{121}Sb, ^{182}W and ^{238}U across the sediment water interface (SWI) of a freshwater sediment. The dashed line represents the SWI. The data for P, V, and As are presented as C_{DGT} concentrations. Other analytes are presented as ICP-MS counts. Ratios between the high and low counts are not equal for all analytes. For example the W and U have significantly lower ratios than the other analytes.

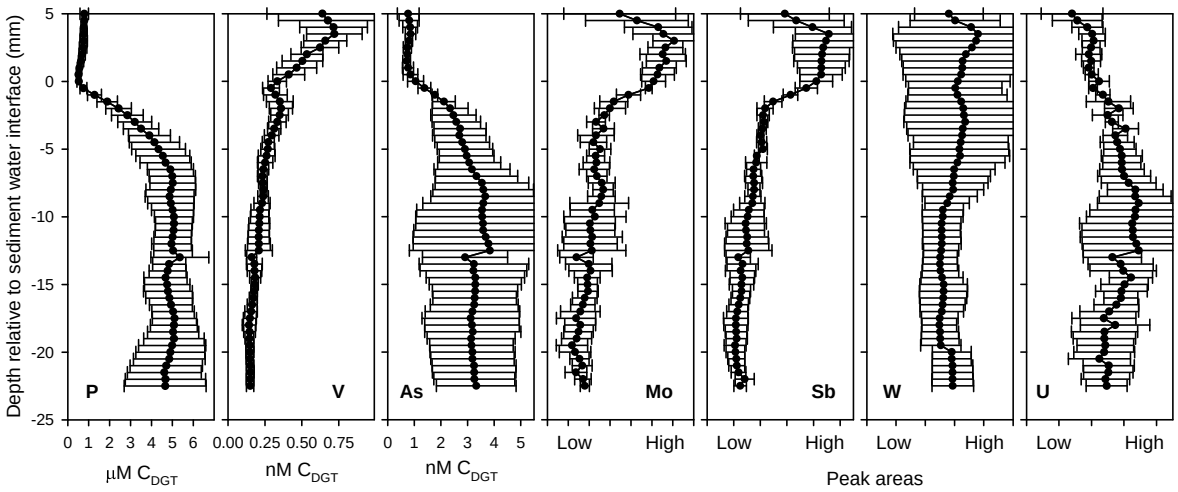

Figure 2. One-dimensional profiles of analytes averaged for 3 ablated gels. For each probe the mean counts for each depth were calculated. The average of this value for each of the three probes was then determined. The standard deviation, represented by the error bars, reflects this variation between the three probes. The P, V, and As data are C_{DGT} concentrations; other analytes are based on ICP-MS counts.

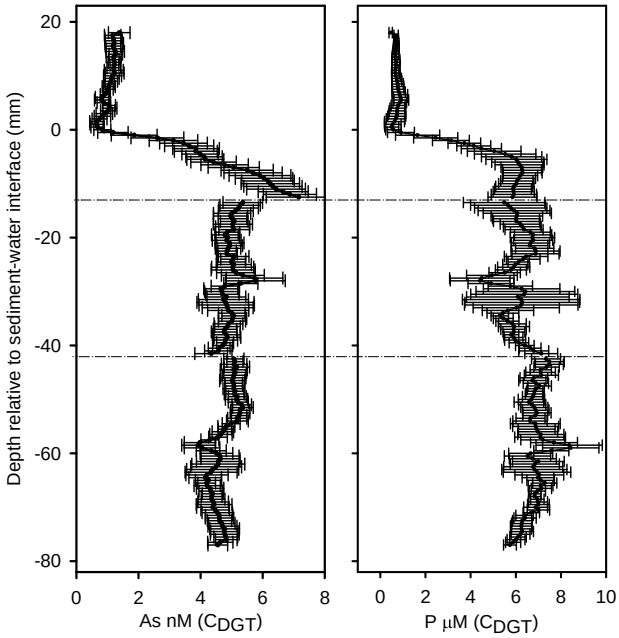

Figure 3. One-dimensional profiles of As and P for a full depth profile of a single DGT probe. The profiles are based on three pieces of gel as the maximum length for the cell in the laser ablation unit is 4 cm. The dashed line indicates the transitions between gels. Error bars represent one standard deviation from the mean of each averaged depth value (n=22, 23, and 13, for sections upper, middle and lower respectively; fewer data were obtained for the lower section due to an data recording error on the ICP-MS half way through the analysis).