Two dimensional images of dissolved sulphide and metals in anoxic sediments by a novel DGTprobe and optical scanning techniques

Gao, Yue; Van De Velde, Sebastiaan; Williams, P.; Baeyens, Willy; Zhang, Hao

Published in:
TrAC. Trends in Analytical Chemistry

DOI:
10.1016/j.trac.2014.11.012

Publication date:
2015

Document Version:
Submitted manuscript

Two dimensional images of dissolved sulphide and metals in anoxic sediments by a novel DGT probe and optical scanning techniques

Yue Gao [1,#]
Sebastiaan van de Velde [1]
Paul N. Williams [2,3]
Willy Baeyens [1]
Hao Zhang [2]

[1] Analytical, Environmental and Geo-Chemistry (AMGC), Faculty of Science, Vrije Universiteit Brussel, Pleinlaan 2, Brussels, Belgium
[2] Lancaster Environmental Centre, Lancaster University, Lancaster LA1 4YQ, UK
[3] Insititute for Global Food Security, Queen's University Belfast, Belfast BT9 5HN, UK
[#] Corresponding author: yuegao@vub.ac.be (Tel. +32 2 629 32 61)

Submitted to: Trends in Analytical Chemistry
Keywords: DGT, 2D image, trace metal, dissolved sulphide, remobilisation, LA-ICP-MS
Version: final

ABSTRACT

A novel Diffusive Gradients in Thin Film (DGT) probe is developed consisting of a diffusive AgI gel layer and a back-up microchelex resin gel layer. 2D high resolution images of sulphide and trace metals were determined respectively on the AgI gel by densitometric analysis and on the microchelex resin layer with Laser Ablation (LA)-ICPMS.

The validity of the analytical procedures used for the determination of sulphide and trace metals has been investigated: low RSDs on replicate measurements, linear trace metal calibration curves between the LA-ICP-MS signal and the true trace metal concentration in the resin gel and a good agreement of the sulphide results obtained with the AgI resin gel and with other analytical methods were found.

The method was applied on anoxic sediment pore waters in an estuarine and a marine system. Simultaneous remobilisation of sulphide and trace metals was observed in the marine sediment.

1. INTRODUCTION

Diagenetic processes control the geochemical behaviour of trace metals in contaminated lacustrine and marine sediments. They are the result of the oxidation of organic matter by a suite of oxidants whereby O2 will be first consumed and then successively NO3-, Mn4+, Fe3+ and SO42- and induce changes in redox potential and pH as well as in the levels of sulphide, carbonate and organic matter. These changes affect the trace metal speciation for example their immobilisation by dissolved sulphide but also their re-dissolution by a decrease of the pH or an increase of the redox potential and their release back to the water column thereby threatening the ecosystem.

To understand these complex processes, geochemists need information about the spatial distribution of the trace metals and of the most important parameters influencing that distribution. In anoxic sediments, dissolved sulphide is without any doubt the most important parameter that controls the trace metal distribution [1, 2]. Therefore in this paper we will focus on the analytical tools available to determine the spatial distributions of trace metals and sulphide in anoxic sediment pore waters. Redox potential and pH distributions are also very important but they are determined by different, electrochemical methods [3, 4].

Initially, undisturbed sediment cores were sampled and then sliced and centrifuged in a flow hood under nitrogen to assess vertical profiles of trace metal and sulphide concentrations [5, 6]. There are at least three major constraints with this procedure: (1) the analyses of the very low concentrations of the trace metals and the sulphide require relatively large pore water volumes; (2) but even with more sensitive techniques, the slicing of the sediment cores is nevertheless limited to about 0.5 cm and (3) the slightest introduction of air during the treatment of the sediment in the flow hood jeopardizes the results. A much better solution is to use the passive sampler technique of Diffusive Gradients in Thin Films (DGT), a kinetic regime passive sampler, because it allows a much higher spatial resolution and it is an in situ technique, eliminating the risk of contamination during sample treatment [7, 8].

The rectangular DGT probe used in sediments is 180 mm x 40 mm, with a window of 150 x18 mm open to sediments and consisting of two hydrogel layers: mostly a polyacrylamide gel covered with a membrane (0.45 μm) is used as the diffusive layer, and is backed up by a second thin gel layer containing an AgI resin gel for dissolved sulphide and a Chelex cation-exchange resin (100 μm bead size) selective for metals. With this technique, only the labile metal and sulphide fractions, small enough to diffuse through the diffusive gel and capable of binding to the resin layer are assessed. After deployment, the Chelex resin gel is sliced into 5

mm strips and the metals are eluted with 1M HNO3 solution, then the elute is analysed with ICPMS. The sulphide concentration in the AgI resin gel is directly analysed by computer-imaging densitometry (CID). Using Fick's law, metal and sulphide concentrations in the sediment pore waters are calculated and vertical profiles with a resolution of 5 mm for trace metals [9, 10], but smaller for sulphide (here the resolution depends on the software that is used) was obtained [11]. In addition, from those 1-D vertical solute profiles the exchange fluxes at the water-sediment interface were estimated [3].

Most studies in anoxic sediments, involving trace metals and sulphide determinations by the DGT technique, were limited to 1-D vertical profiles and a spatial resolution of 5 mm, with the trace metals limiting this resolution [7, 8, 10, 11]. Recently, it became clear that neither a spatial resolution of 5 mm, nor the limitation to 1-D profiles allow the detection of microniches which are important features in anoxic sediments [12, 13]. In fact, in anoxic sediments, burrow formation, irrigation, feeding and associated processes create distributions of localized geochemical features, facilitating translocation of surface deposited material [13]. These localized small scale microniches are formed when discrete particles of reactive organic matter are introduced at depth in the sediment. Their diameter can in principle vary from a few microns up to the centimetre scale. Microniches give us information about the geochemical processes occurring between the trace metals and sulphide, but with a low resolution of a few mm many of the microniches remain invisible. Moreover, due to the heterogeneity of the sediment, a 1-D profile cannot resolve their complete scale.

As yet mentioned above, increasing the spatial resolution and the extension from 1-D profiling to 2D imaging for sulphide is only a question of improving the densitometry software. For the trace metals, however, a new analysis technique is required. Indeed, the classic resin-gel slicing technique has practical limitations for 2D imaging and for achieving high resolution: a spatial resolution of smaller than a mm is a practical limit and even the scale of mm is often not sufficient for understanding the sediment microstructure. Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS) can overcome both limitations by offering a spatial resolution of about 100 µm in horizontal and vertical dimensions, thus producing high resolution 2D images of the trace metal distribution in anoxic sediments. Unfortunately, the Chelex-100 resin beads are too large for these experiments, ~100 µm, and must be replaced by much smaller suspended particulate reagent-iminodiacetate (SPR-IDA) resin beads (0.2 µm) [14].

The final challenge now is to combine the results of the trace metal profiles or images with those of sulphide. In the past, 1-D profiles of metals with a relatively low resolution of 5 mm

were matched with high resolution 1-D profiles [15] or 2D images of sulphide suggesting simultaneous remobilisation of both constituents [12]. However, these results were neither derived from high resolution (sub mm scale) profiles, nor from superimposed 2D images, implying that the uncertainty about the exact location of the increase in metal and sulphide concentration is quite large. 2D imaging with a much higher spatial resolution (µm scale) and the use of a single DGT probe for both trace metal and sulphide imaging is necessary to gain a better understanding of local, small-scale remobilisation/precipitation zones.

We present here the first results of metal and sulphide mobilization in two dimensions in highly polluted and organic rich sediments, using a new, combined DGT sampling probe (the diffusive gel layer is formed by the AgI gel while the back-up layer is formed by the SPR-IDA resin gel) and high resolution Laser Ablation ICP-MS (LA-ICP-MS) analysis, providing superimposed 2D images of metals and sulphide at a resolution of about 100 µm.

2. EXPERIMENTAL

2.1 Preparation of the SPR-IDA resin gel layer

To prepare SPR-IDA resin gel, 1.25 mL gel solution (15% acrylamide, 0.3% DGT cross-linker) was mixed with 1.25 mL of SPR-IDA resin (0.2 µm bead size). Sequentially, 17.5 µL of 10% ammonium persulphate (APS, Merck) and 5.0 µL tetramethylethylenediamine (TEMED, >99%, Merck) were added and mixed well. Following mixing, the mixture was immediately cast between glass plates separated by a 0.25 µm plastic spacer, resulting in a 0.4 mm-thick resin gel after hydration. The resin gels were kept in 0.03 M NaCl (suprapur, Merck) solution before their application.

2.2 Preparation of the diffusive AgI gel layer

In order to prepare AgI gel, 0.153 g of AgNO3 (AnalaR, Merck) was dissolved in 0.45 mL MilliQ water in a pre-cleaned polypropylene (PP) tube and 8.55 mL of gel solution (15% acrylamide, 0.3% DGT cross-linker) was added and mixed well. Three mL of the mixture was transferred to another PP tube and 10 µL of 5% (w/w) APS (APS, >98%, Merck) was added and mixed well. The gels were cast immediately between glass plates spaced by a 0.25 µm plastic spacer, resulting in a 0.4 mm-thick gel after hydration. Following polymerization (45 minutes in the dark at room temperature), the glass plates were opened. The gel remained on one plate, which was then immersed in a 0.2 M potassium iodide solution in a dark condition. The gel became pale yellow within a few minutes and was peeled off from the glass plate. Gels were kept in the KI solution overnight to allow full formation of the AgI gel.

Subsequently the AgI gels were washed several times in MilliQ water to remove the ions that were adsorbed on the gel. The pH of the gel was also monitored and reached a value around 6 after rinsing. Then AgI gels were kept in 0.03 M NaCl (suprapur, Merck) solution before their application.

2.3 Preparation and application of the combined DGT probe

To prepare the combined DGT probes in this study, the SPR-IDA resin gel was placed behind an AgI gel, which was used as the diffusive gel. Motelica-Heino et al [12] compared the diffusion rates of free metals in polyacrylamide (PA) and AgI gels deployed in metal standard solutions and they found the same diffusion coefficients for both diffusive gels [12].

Since the resin is binding only free metals in solution, the contribution of metal-complexes (ML) to the amount sequestered by the resin is a function of the ML dissociation kinetics in the diffusive gel layer and at the resin interface. While the behaviour of most metal-complexes will be the same in the classic polyacrylamide-chelex DGT as in the AgI-chelex DGT, there could be a difference for metal-sulfide complexes. Silver reacts with free sulphide and as a consequence it will compete and eventually dissociate metal-sulfide compounds that are less stable than Ag2S. This is not the case in the polyacrylamide diffusive gel layer. Conditional stability constants corrected for side-reactions of the metal in seawater reported in the literature [16] suggest that for example Fe(II), Mn(II) and Zn(II) sulphide complexes can dissociate in the AgI gel layer while this is not the case for Cu(I) and Cu(II). Hence, for some metals the AgI-chelex DGT result can be slightly higher than in the case of the classic DGT involving a polyacrylamide gel layer, due to metal-sulfides that eventually dissociate in the AgI gel layer. Further research must clarify the difference that may occur between polyacrylamide and AgI gels with respect to metal-sulfide dissociation.

The AgI and SPR-IDA gels were overlain by a Millipore Durapore 0.45 µm filter membrane (thickness 0.13 mm). All probes were deoxygenated prior to deployment by purging N2 for 24 h in 0.03 M NaCl (suprapur, Merck) solution. Sediment cores were collected from the field allowing 5-10 cm overlying water to remain above the sediment. The combined DGT probes were inserted into the sediment for several hours at field temperature and in a dark room.

2.4 Calibration procedure for trace metals and dissolved sulphide

Combined DGT pistons were deployed in well-stirred 0.03 M NaCl solutions containing five different concentration levels of Fe, Mn, Co, Cu and Ni, which were added as acidified stock and metal salt standards (1000 mg L-1), to give a final solution pH of 5. These experimental conditions were necessary to avoid losses from the deployment solutions due to adsorption to the container walls and from the formation of colloidal species. Every hour sub-samples (1 ml) were taken from the bulk solution, acidified and analysed by ICPMS. Four DGT pistons were removed from each of the deployment solutions after 5h. One of the resin gel standards was immediately transferred onto new acid-washed 0.45-µm cellulose nitrate filters, similar to those that were used in the deployment, and dried using a commercial gel dryer (BioRad, Germany) at 60 °C for 24 h according to the procedure presented by Warnken et al. [14]. Once dried, these gel standards were cut into a suitable size and then mounted on a glass plate, using double sided tape, for Laser Ablation ICPMS analysis (Thermo Elemental X-SeriesII ICPMS connected to an ESI 193FX laser ablation system). Three of the above resin gel standards were eluted with 1 mL of 1 mol L-1 HNO3 and analysed with ICPMS against certified solution standards to quantify the mass of metal present on the resin gel. The laser ablation data was plotted as the normalized metal count rate (metal count rate divided by the internal standard 13C-count rate) versus the amount of metal determined per unit area of resin gel (nmol cm-2).

A sulphide stock solution of 1,000 mg L-1, was prepared from Na2S.9H2O (>98%, Sigma Aldrich, USA) in a deoxygenated borate buffer (pH = 8.2) and stored in a refrigerator. The sulphide standard solutions of 5 to 100 µmol L-1 were prepared in brown glass bottles by diluting the sulphide stock solution in 500 mL of deoxygenated borate buffer solution (pH = 8.2). Three combined DGT pistons were deployed in the standard solution for 4 hours under oxygen free condition. The AgI gels were peeled off from the piston after the deployment and the colour change from pale yellow to black, due to the formation of silver sulphide at various concentrations, was scanned by a flat-bed scanner (HP 3100). ImageJ software allows measurement of average optical density for a chosen area. The optical density for AgI gel deployed in sulphide standard solutions was plotted as greyscale density versus the amount of sulphide determined per unit area of AgI gel (nmol cm-2).

To make sure the sulphide concentrations remained stable during the deployment, sub-samples of the sulphide solutions were taken before and after the experiment. These solutions were checked with methylene blue method [17]. The first mixed diamine reagent was

prepared by dissolving 2.0 g of N,N-dimethyl-p-phenylenediamine oxalate (ICN Biochemicals, USA) and 3.0 g of FeCl3 (P.A. >99%, Merck, Germany) in 500 mL of 30 % HCl acid (Suprapur 30%, Merck, Germany). The second mixed diamine reagent was prepared by dissolving 8.0 g of the oxalate and 12.0 g of the FeCl3 in 500 mL of 30 % HCl acid. The first one was used for the 5, 10 and 20 µmol L-1 solution (1:1 ratio) and the second one for the 50 and 100 µmol L-1 solution (also 1:1 ratio). The absorbance (A) of the sulphide solutions was measured at a wavelength of 670 nm with a UV-vis spectrometer (Spectronic Genesys 5, Thermo Electron, USA).

2.5 Retrieval and Analysis of the AgI and SPR-IDA gels

After the deployment of the combined DGTs in sediment cores, the SPR-IDA and AgI gels were peeled from the combined DGT probes and the SPR-IDA gels were dried onto a Durapore filter at 60°C for 24 hours using the gel drier. Analysis of trace metals at 100 µm spatial resolution was performed by LA-ICP-MS using a line scan mode procedure [15]. Briefly a 100 µm diameter beam was scanned across the gels in a series of lines (100 µm apart) at 50 µm s-1. C13 was used as an internal standard. The laser data obtained for trace metals in gel samples were transformed into concentration based on the calibration curves. For sulphide analysis, the AgI gels were scanned by a flat-bed scanner to provide a grey-scale image of sulphide. Image processing software ImageJ and SigmaPlot were used to convert the scanned images into 2D images of sulphide concentration with a resolution of 85 µm based on the sulphide calibration curve.

3. RESULTS AND DISCUSSION

3.1 Calibration and validation

Trace metal calibration curves were established with 5 different trace metal standards: the LA-ICP-MS signal (number of counts) was plotted against the mass of trace metal on the resin (nmol cm-2). Each of the 5 standards is the average of the results obtained on 3 replicate resin gels deployed in the same metal concentration solution. These replicates show in general a RSD (relative standard deviation) around 5%. The fourth resin gel deployed in the same metal concentration solution is analysed by LA-ICP-MS using a line scan mode procedure [18]. Mandel's fitting test was used to check the regression of these calibration curves. Linear regression was preferred over quadratic for trace metals. The regression coefficient for Fe, Mn, Co, Cu and Ni was 0.994, 0.987, 0.992, 0.974 and 0.997, respectively.

Detection limits (LOD's) of Fe, Mn, Co, Cu and Ni concentrations in the SPR-IDA resin were respectively 0.23, 0.33, 0.0039, 0.060 and 0.10 nmol.cm-2. The method was sensitive enough because all our field results were above these LODs. Repeatability for these metals was below the Horwitz threshold [19] of 14.7%, whilst reproducibility was below the threshold of 22%.

Sulphide calibration curve, where the optical density (OD) was plotted as greyscale density versus the amount of sulphide determined per unit area of AgI gel (nmol.cm-2), were established with 5 different sulphide standard concentrations (Fig 1). The sulphide standard concentrations (5, 10, 20, 50 and 100 µmol L-1) were checked before and after use with the methylene blue method [17]. To calibrate the pixel density as function of the sulphide concentration (nmol cm-2), a non-linear regression was used. A hyperbolic function gave the best fit, with p-values for all coefficients lower than 0.05 for the 95% confidence interval, which means that our coefficients are very likely. The LOD of the sulphide analysis method was 6.5 nmol cm-2. The method is sensitive enough to determine sulphide in the pore waters of our estuarine and marine sediments. The calibration equation was as follows:

$$y = y0 + (a * x) / (b + x)$$

where y0 = (46.2 + 4.0), a = (173.0 + 9.0) and b = (870 +150) nmol.cm-2.

Different studies compared the sulphide results obtained by the AgI-DGT method with other analytical methods. A procedure for measuring in situ sulphide concentrations by coupling diffusive gradients in thin films (DGT) to solid state ion-selective electrodes (ISE) was compared to computer imaging densitometry (CID) and methylene blue method [20]. Regressions of the sulphide mass accumulation versus the independent variables of time and inverse diffusive thickness proved to be linear. All performance tests of the DGT-ISE method compared favourably with previous results that were generated by DGT probes coupled to methylene blue and densitometric measurements. Also Lesven [21] measured sulphide pore water profiles in sediments of the Espierre River, northern France, with different analytical methods. The results obtained with AgI-DGT, voltammetry and methylene blue method compared well [21].

3.2 Sediment pore water fluxes and concentrations

When a sustained ion flux from pore water to the DGT resin exists, it is possible to calculate the ion concentration in the pore water by using Fick's diffusion law and the mass of ion determined in the resin gel.

$$Cdgt = (M * \Delta g) / (D * t * A)$$

where Cdgt is DGT measured concentration; M is mass of metals, which is obtained by LA-ICP-MS analysis; Δg is thickness of diffusive gel; D is the diffusive coefficient of solute in diffusive gel; A is the surface of the gel exposed to the bulk solution and t is deployment time. In case of sustained supply we can express the results in concentrations instead of fluxes, which is the case in our sediments [22].

3.3 Estuarine sediments

The Zenne River in Belgium receives high loads of organic material, pollutants like trace metals and micro-organic pollutants that partly accumulate in the sediments. DGT Fe concentration increased steadily from the sediment water interface (SWI) and reached a maximum concentration around -0.5 cm (Fig. 2). In this narrow zone the concentration ranges from 5 µM to 25 µM, but below this zone and down to 6 cm, a constant Fe concentration level of around 10 µM prevailed. The sulphide concentration started to increase immediately below the SWI, achieving a maximum value of 7 µM at -0.1 cm of depth, a few mm above the Fe production zone (Fig 3). The reduction of sulphate happens very close to the reduction zone of Fe3+, but dominates it, leading to FeS precipitation.

Lower in the sediments, a sulphide hotspot was found with a maximum concentration of 6 µM at around -4.1 to -4.6 cm (Fig 3). This hotspot was superimposed on a relatively constant background of 2 to 3 µM. None of the metals investigated showed elevated concentrations at the same location as the sulphide hotspot, indicating that they were not simultaneously released with the sulphide.

3.4 Marine sediments

Sulfide hotspot formation

The Belgian coastal zone (BCZ) is strongly influenced by eutrophic rivers such as Scheldt, Rhine and Meuse resulting in phytoplankton blooms. Spring blooms begin in March when nutrient, light and temperature conditions become sufficient for phytoplankton growth and terminate in April-May with the onset of nutrient limitation, after which large amounts of organic material sediment out [23, 24]. As a consequence, the degradation of increasing amounts of freshly deposited organic matter changes the physicochemical conditions in the sediment interface potentially releasing trace metals from the sediments into the water column [7, 25].

The dissolved sulphide profiles showed 2 zones of elevated levels: zone 1 (SWI to - 1 cm of depth) and zone 2 (- 5 cm of depth to the bottom of the DGT probe). At the SWI the sulphide concentration was around 2 µM and then dropped gradually to 1 µM. In the

intermediate zone (between - 1 and - 5 cm of depth) the sulphide concentration remained at 1 µM (Fig. 4a). Metals showed a different pattern from that of dissolved sulphide. The concentrations of Fe, Mn and Co increased as soon as the sulphide concentration decreased to a value of 1 µM (Fig 4b, 4c, 4d). This trend of decreasing sulphide concomitantly with increasing trace metals reflects the classic relationship between them.

Dissolved sulphide concentrations in zone 2 (-5 cm to the bottom of the DGT probe) are again high with concentrations ranging from 2 µM to 14 µM, indicating that the sediments were completely anoxic with sulphate reduction occurring. The consequence of this sulphide production was metal precipitation, so that the metal concentrations were low (Fig 5).

Simultaneous remobilisation of sulphide and metals:

In marine sediments, the sulphide concentrations are much higher than estuarine sediment which means that if there is a hotspot it will be superimposed on a high sulphide background, making it harder to detect. The AgI gel showed a rather broad zone of aggregated hotpots at a depth of -10 to -12 cm in the deeper sediment layer (Fig 6). At a depth of -11.10 to -11.80 cm, Fe, Mn, Co and Ni were released at the same location inside a much larger sulphide hotspot area (Fig 7). The dissolved sulphide concentration increased from -10.8 cm and reached a maximum concentration of around 55 µM at -11.17 cm. This generally high level of sulphide extended to a depth of -11.40 cm. Inside the sulphide elevation zone (7 mm of length), Co and Ni had single sharp maxima at a depth of -11.17 cm with concentrations of 0.12 µM and 0.42 µM, respectively (Fig 7). Fe and Mn also reached their highest concentration values of 33 µM and 2.6 µM at this depth, but they also had several smaller maxima at slightly greater depths. The shape of the sulphide hotspots was like a “butterfly” with the remobilisation of metals appearing on the left wing area, but with no release of metals corresponding to the right wing area, even though the sulphide concentration there was higher (Fig 6). The remobilisation of metals probably only happened in a few small niches of the agglomerated overall hotspot. Visual Minteq software was used to calculate the saturation index of FeS, MnS, CoS and NiS minerals at -11.17 cm of depth. The calculation showed that there was super-saturation for FeS, CoS and NiS at that location, but not for MnS.

4. CONCLUSION

To investigate the prevalence of simultaneous remobilisation of sulphide and trace metals in aquatic sediments a novel method, combining a DGT probe consisting of a SPR-IDA micro-chelex resin with an AgI diffusive gel and a LA-ICP-MS measuring technique, was used. Very low concentrations of sulphide and trace metals can be determined in the pore

waters because the passive DGT sampler can be deployed for long term meanwhile accumulating these ions. In addition, since the gel layers for sulphide and trace metals are superimposed, an elevated concentration of a trace metal can be exactly positioned versus a sulphide hotspot.

The low RSDs on replicate measurements, the linearity of the trace metal calibration curves and the good agreement of the sulphide results obtained with different analytical methods are indicators of the validity of the analytical procedures. Since the scale of sulphide and trace metal remobilisation in anoxic sediments is very small (down to sub-mm level), high resolution imaging is necessary. With the LA-ICP-MS and densitometric scanning procedures, a resolution of the order of 100 µm is routinely achievable. The application of the novel method allowed observing, for the first time, 2D-images of simultaneous metals and sulphide remobilisation in marine sediments. In Zenne sediments, no simultaneous remobilisation of sulphide and metals was detected.

As the background concentration of sulphide is much higher in marine than in estuarine sediments (about a factor of 10), it is commonly more difficult to distinguish in the marine environment hotspots of sulphide release. However, in the pore waters of the marine sediments we observed two distinctive geochemical phenomena; the progressive release of low concentrations of sulphide in the sub-surface layer coupled with isolated hotspots in the deeper layers. The former observation is consistent with the activity of Desulfoculbaceae bacteria, which are known to be prevalent in the Belgian Coastal Zone [26]. Consuming dissolved sulphide these strictly anaerobic, filamentous bacteria act as electrical cells passing electrons generated by sulphide oxidation to the upper sediment layer where they are consumed by oxygen reduction [27]. Preliminary results from laboratory experiments indicate that the activity of these bacteria induces strong pH gradients.

Coincident remobilisation of sulphide and metals in microniches zones of heightened sulphide release, as evidenced in the marine sediments below -11 cm can be explained by the supersaturation of metal sulphide; a process driven by electron dispensing, highly reactive organic parcels [12].

This study shows the first measurements of simultaneous trace metals and sulphide release in marine sediments and contrasts directly with the conventional view of sediments that dissolved metal concentrations are very low in the presence of elevated sulphide. The importance of this overlooked mechanism of metal release requires further study, in particular future work should target environments where either filament bacteria or reactive organic

parcels are present. The method we presented in this paper constitutes an essential element for the performance of such studies.

5. ACKNOWLEDGEMENTS

Yue Gao thanks FWO for a postdoc fellowship. The authors are also grateful to André Cattrijsse and the crew of RV Simon Stevin.

References

1. D. M. Di Toro, J. D. Mahony, D. J. Hansen, K. J. Scott, M. B. Hicks, S. M. Mayr, M. S. Redmond, Toxicity of cadmium in sediments: the role of acid volatile sulfide. Environ. Toxicol. Chem. 9 (1990) 1487.

2. G. T. Ankley, G. L. Phipps, E. N. Leonard, D. A. Benoit, V. R. Mattson, P. A. Kosian, A. M. Cotter, J. R. Dierkes, D. J. Hansen, J. D. Mahony, Acid volatile sulphide as a factor mediating cadium and nickel bioavailability in contaminated sediments. Environ. Toxicol. Chem. 10 (1991) 1299.

3. Y. Gao, L. Lesven, D. Gillan, K. Sabbe, G. Billon, S. De Galan, M. Elskens, Baeyens, W. Leermakers, M, Geochemical behavior of trace elements in sub-tidal marine sediments of the Belgian coast, Mar. Chem. 117 (2009) 88–96.

4. Y. Gao, M. Leermakers, A. Pede, A. Magnier, K. Sabbe, B. Lourino Cabana, G. Billon, W. Baeyens, D. C. Gillan, Response of DET and DGT trace metal profiles in sediments to phytodetritus mineralization, Environ. Chem. 9 (2012) 41-47.

5. S. Panutrakul, W. Baeyens, Behavior of heavy-metals in mud flat of the Scheldt estuary, Belgium. Mar. Pollut. Bull. 22 (1991), 128-134.

6. G. Billon, B. Ouddane, P. Recourt, A. Boughriet, Depth variability and some geochemical characteristics of Fe, Mn, Ca, Mg, Sr, S, P Cd and Zn in anoxic sediments from Authie Bay (Northern France), Estuar. Coast. Shelf Sci. 55 (2002), 167-181.

7. Y. Gao, M. Leermakers, C. Gabelle, M. Wartel, G. Billon, B. Ouddane, J. C. Fischer, W. Baeyens, High Resolution Profiles of Trace Metals in the Pore Waters of Riverine Sediment Assessed by DET and DGT, Sci. Total Environ. 362 (2006) 266-277.

8. Y. Gao, M. Leermakers, M. Elskens, G. Billon, B. Ouddane, J. C. Fischer, W. Baeyens, High Resolution Profiles of Thallium, Manganese and Iron Assessed by DET and DGT Techniques in Riverine Sediment Pore Waters, Sci. Total Environ. 373 (2007) 526-533.

9. W. Davison, H. Zhang, In situ speciation measurements of trace components in natural waters using thin-film gels, Nature. 367 (1994) 546–548.

10. H. Zhang, W. Davison, R. J.G. Mortimer, M. D. Krom, P. J. Hayes, I. M. Davies, Localised remobilization of metals in a marine sediment, Sci. Total Environ. 296 (2002) 175–187.

11. P. R. Teasdale, S. Hayward, W. Davison, In situ, High-Resolution Measurement of Dissolved Sulphide Using Diffusive Gradients in Thin Films with Computer-Imaging Densitometry, Anal. Chem. 71 (1999) 2186-2191.

12. M. Motelica-Heino, C. Naylor, H. Zhang, W. Davison, Simultaneous Release of Metals and Sulphide in Lacustrine Sediment, Environ. Sci. Technol. 37 (2003) 4374-4381.

13. A. Stockdale, W. Davison, H. Zhang, Micro-scale biogeochemical heterogeneity in sediments: A review of available technology and observed evidence, Earth Sci. Res. J. (2009) 81–97.

14. K. W. Warnken, H. Zhang, W. Davison, Performance characteristics of suspended particulate reagent-iminodiacetate as a binding agent for diffusive gradients in thin films, Anal. Chim. Acta. 508 (2004a) 41–51.

15. C. Naylor, W. Davison, M. Motelica-Heino, G. A. Van Den Berg, M. L. Van Der Heijdt, Simultaneous release of sulphide with Fe, Mn, Ni and Zn in marine harbour sediment measured using a combined metal/sulphide DGT probe, Sci. Total Environ. 328 (2004) 275–286.

16. R. Al-Farawati, C. M. G. van den Berg, Metal-sulfide complexation in seawater, Mar. Chem. (1999) 331-352.

17. J. D. Cline, Spectrophotometric determination of hydrogen sulphide in natural waters, Limnol. Oceanogr. 14 (1969) 454-58.

18. Y. Gao, N. Letho, A simple laser ablation ICPMS method for the determination of trace metals in a resin gel, Talanta. 92 (2012) 78– 83.

19. M. Thompson, Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relating to fitness for purpose criteria in proficiency testing, Analyst. 125 (2000) 385-386.

20. S. Rearick, C. C. Gilmour, A. Heyes, R. P. MASON, Measuring sulphide accumulation in diffusive gradients in thin films by means of purge and trap followed by ion-selective electrode, Environ. Toxicol. Chem. 24 (2005) 3043-3047.

21. L. Lesven, Fate of trace metals in sediment, a key compartment of the aquatic environment (translated from the French title), PhD thesis. Defended on 02112/2008.

22. B. Lourino-Cabana, G. Billon, L. Lesven, K. Sabbe, D. C. Gillan, Y. Gao, M. Leermakers, W. Baeyens, Monthly variation of trace metals in North Sea sediments. From experimental data to modeling calculations, Mar. Pollut. Bull., in press (2014).

23. V. Rousseau, S. Bequevort, J. Y. Parent, S. Gasparini, M. H. Daro, M. Tackx, C. Lancelot, Trophic efficiency of the planktonic food web in a coastal ecosystem dominated by Phaeocystis colonies, J. Sea Res. 43 (2004) 357–372.

24. K. Muylaert, R. Gonzales, M. Franck, M. Lionard, C. Van der Zee, A. Cattrijsse, K. Sabbe, L. Chou, W. Vyverman, Spatial variation in phytoplankton dynamics in the Belgian coastal zone of the North Sea studied by microscopy, HPLC-CHEMTAX and underway fluorescence recordings, J. Sea Res. 55 (2006) 253–265.

25. S.T. Pakhomova, P.O.J. Hall, M.Y. Kononets, A.G. Rozanov, A. Tengberg, A.V. Vershinin, Fluxes of iron and manganese across the sediment–water interface under various redox conditions, Mar. Chem. 107 (2007) 319–331.

26. S. Y. Malkin, A. M. F. Rao, D. Seitaj, D. Vasquez-Cardenas, E. M. Zetsche, H. T. S. Boschker, F. J. R. Meysman, Natural occurrence of microbial sulphur oxidation by long-range electron transport in the seafloor, ISME J. in press (2014).

27. C. Pfeffer, S. Larsen, J. Song, M. D. Dong, F. Besenbacher, R. L. Meyer, K. U. Kjeldsen, L. Schreiber, Y. A. Gorby, M. Y. El-Naggar, K. M. Leung, A. Schramm, N. Risgaard-Petersen, L. P. Nielsen, Filamentous bacteria transport electrons over centimetre distances, Nature. 49 (2012) 219-221.

Figure legend and figures

Figure 1 Plot of greyscale density (0-255) versus sulphide per cm^2 for 5 sulphide standards and the black line is the fitted calibration curve.

Figure 2 2D image of Fe at the Sediment Water Interface (SWI) of an estuarine sediment

Figure 3 (a) Greyscale image of AgI gel deployed in an estuarine sediment; (b) 1D vertical profile of sulphide concentration; (c) 2D image of sulphide at the SWI of an estuarine sediment; (d) 2D image of a sulphide hotspot

Figure 4 2D images of sulphide, Fe, Mn and Co at the SWI of a marine sediment

Figure 5 2D images of sulphide and Fe (zone 2, below 4.5 cm of depth) in a marine sediment

Figure 6 (a) Greyscale image of AgI gel deployed in a marine sediment; (b) 2D contour figure drawing of sulphide hotspots in a marine sediment; (c) the corresponding 2D contour figure drawing of Fe hotspots

Figure 7 1D vertical profiles of Fe, Mn, Co and Ni concentrations a marine sediment

Figure 1:

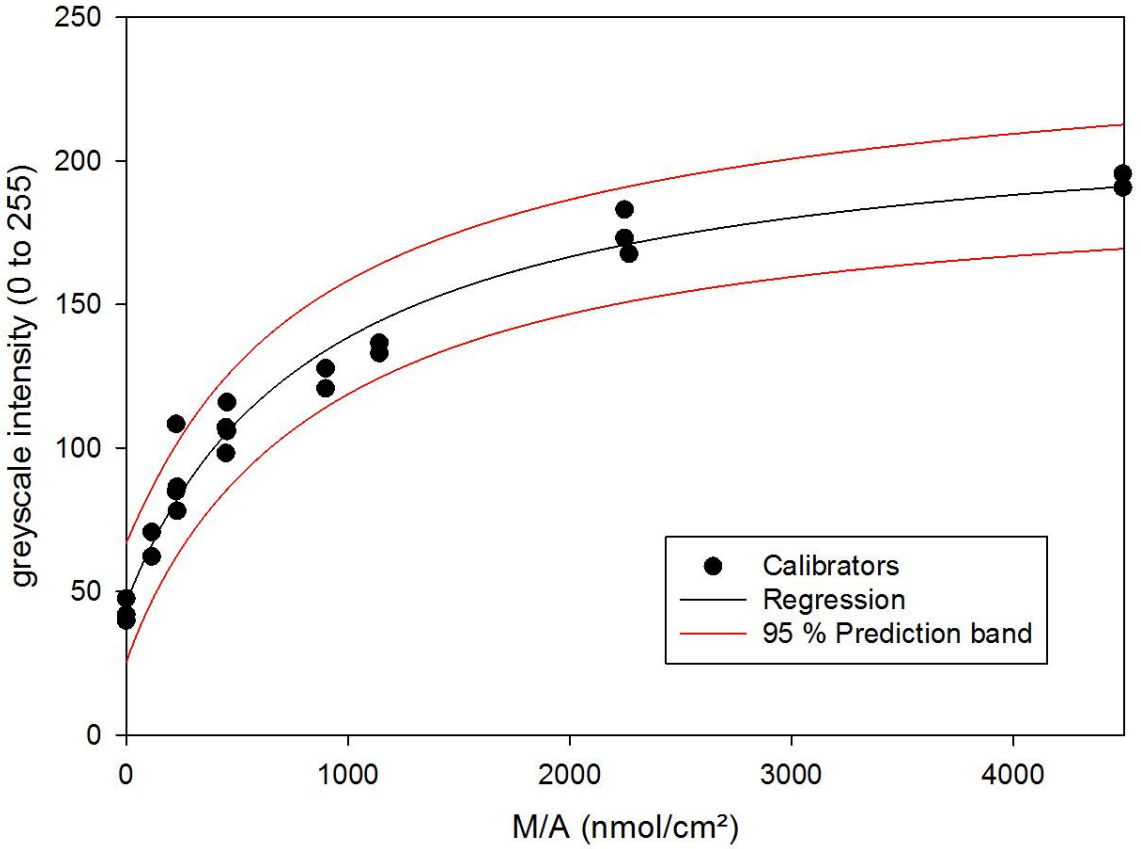

250
200
150
100
50
0
greyscale intensity (0 to 255)
0
1000
2000
3000
4000
M/A (nmol/cm²)
Calibrators
Regression
95 % Prediction band

Figure 2:

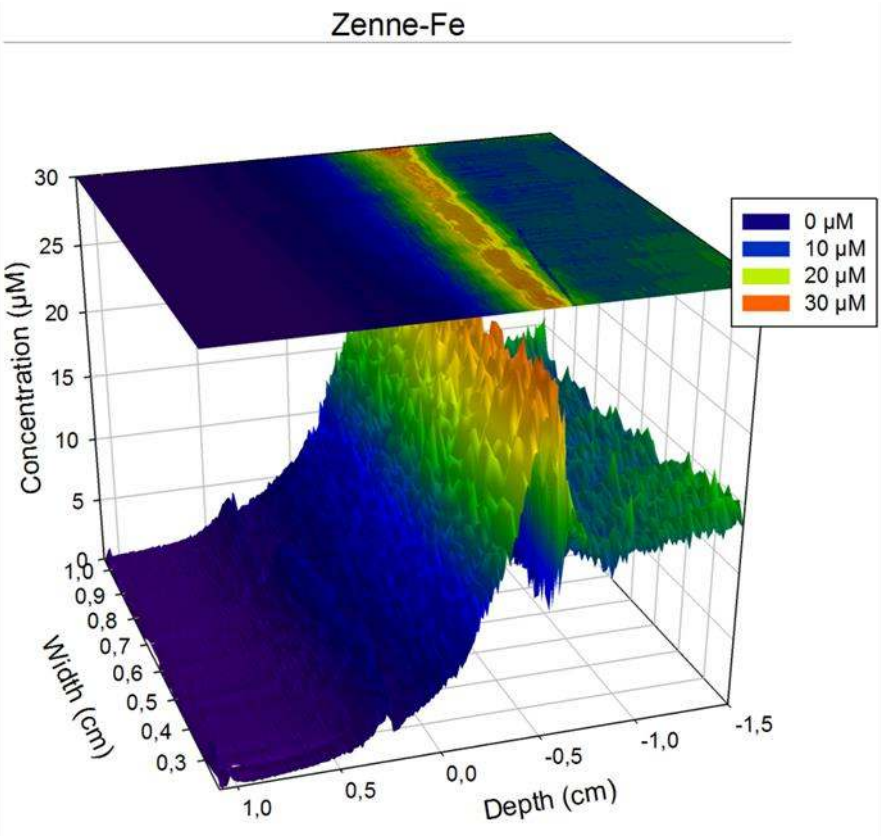

Zenne-Fe
Concentration (µM)
30
25
20
15
10
5
0
0 µM
10 µM
20 µM
30 µM
Width (cm)
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
Depth (cm)
1,0
0,5
0,0
-0,5
-1,0
-1,5

Figure 3:

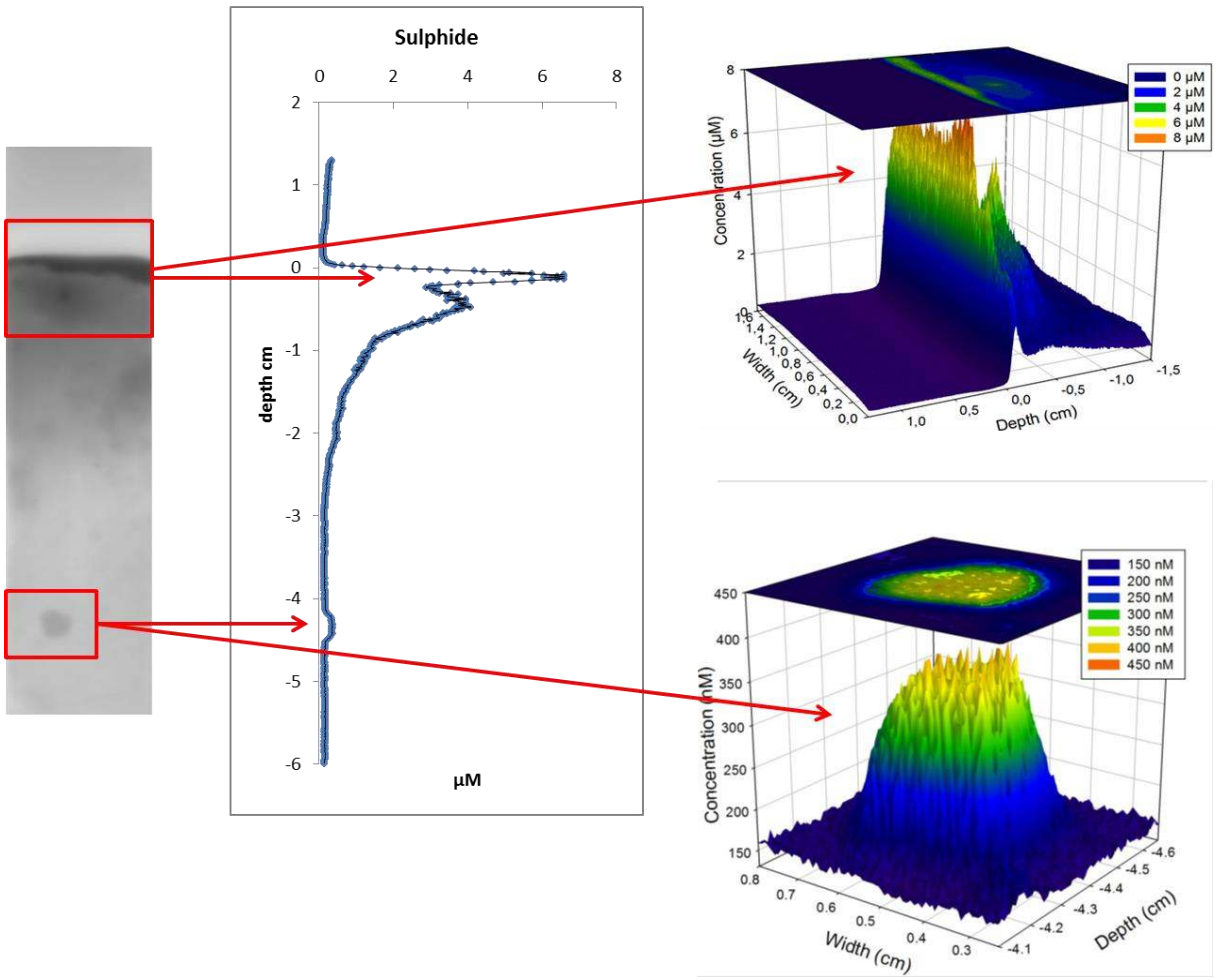

Sulphide
depth cm
µM
Concentration (µM)
Width (cm)
Depth (cm)
0 µM
2 µM
4 µM
6 µM
8 µM
Concentration (nM)
Width (cm)
Depth (cm)
150 nM
200 nM
250 nM
300 nM
350 nM
400 nM
450 nM

Figure 4:

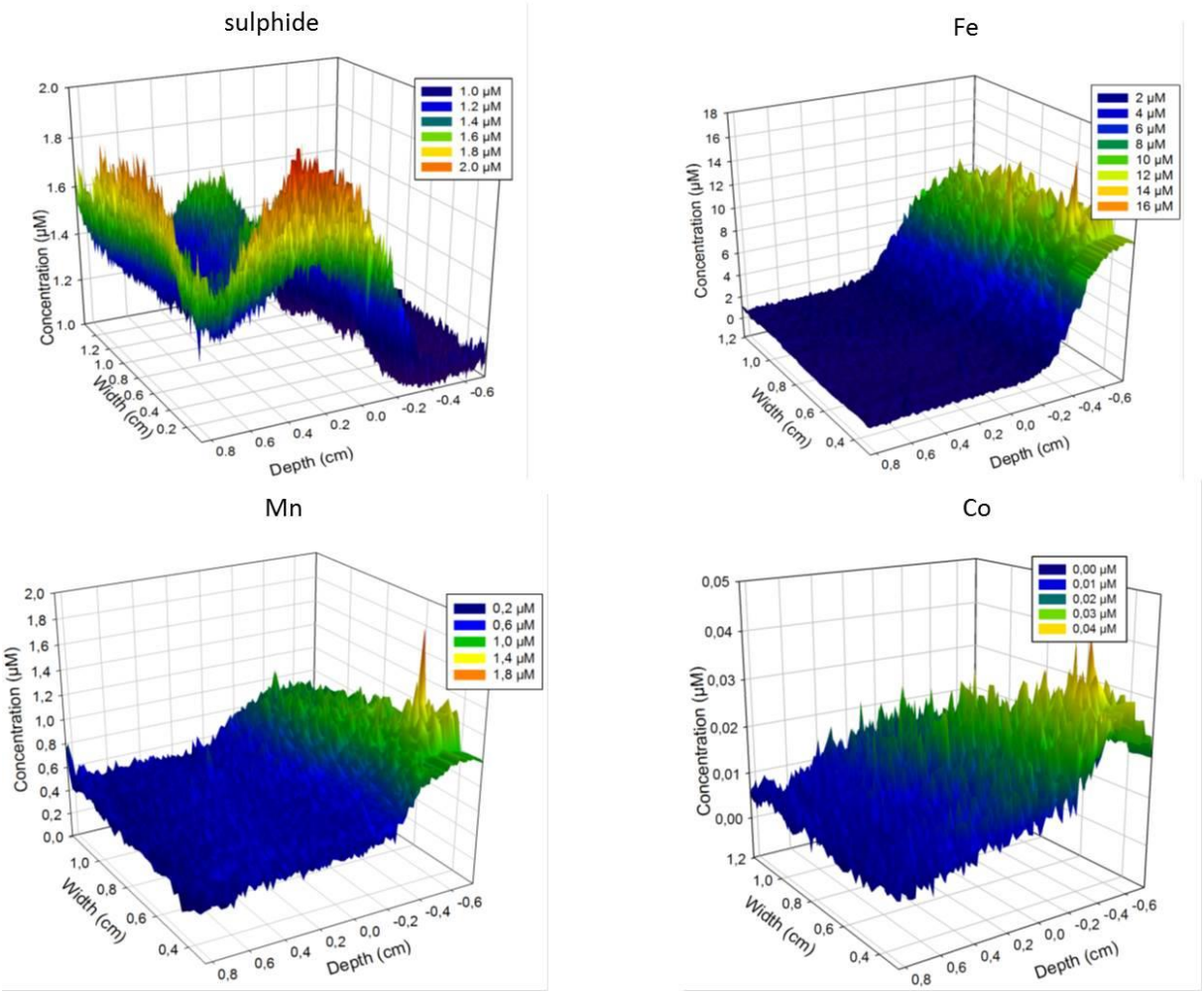
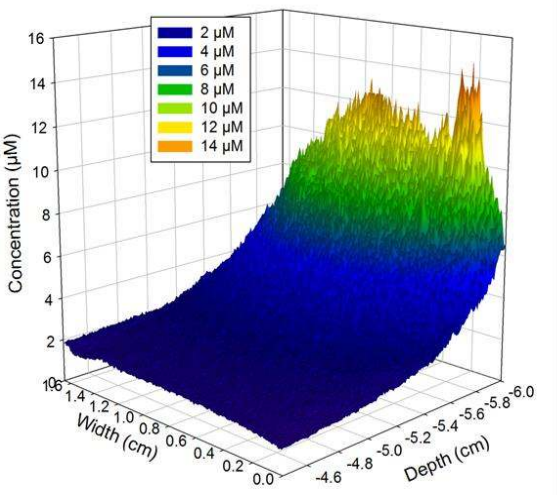

sulphide
1.0 µM
1.2 µM
1.4 µM
1.6 µM
1.8 µM
2.0 µM
Concentration (µM)
Width (cm)
Depth (cm)
Fe
2 µM
4 µM
6 µM
8 µM
10 µM
12 µM
14 µM
16 µM
Concentration (µM)
Width (cm)
Depth (cm)
Mn
0,2 µM
0,6 µM
1,0 µM
1,4 µM
1,8 µM
Concentration (µM)
Width (cm)
Depth (cm)
Co
0,00 µM
0,01 µM
0,02 µM
0,03 µM
0,04 µM
Concentration (µM)
Width (cm)
Depth (cm)

Figure 5:


2 µM
4 µM
6 µM
8 µM
10 µM
12 µM
14 µM
Concentration (µM)
Width (cm)
Depth (cm)

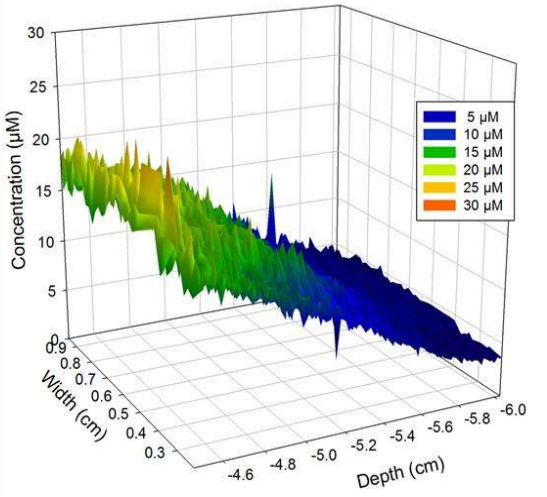

5 µM
10 µM
15 µM
20 µM
25 µM
30 µM
Concentration (µM)
Width (cm)
Depth (cm)

Figure 6:

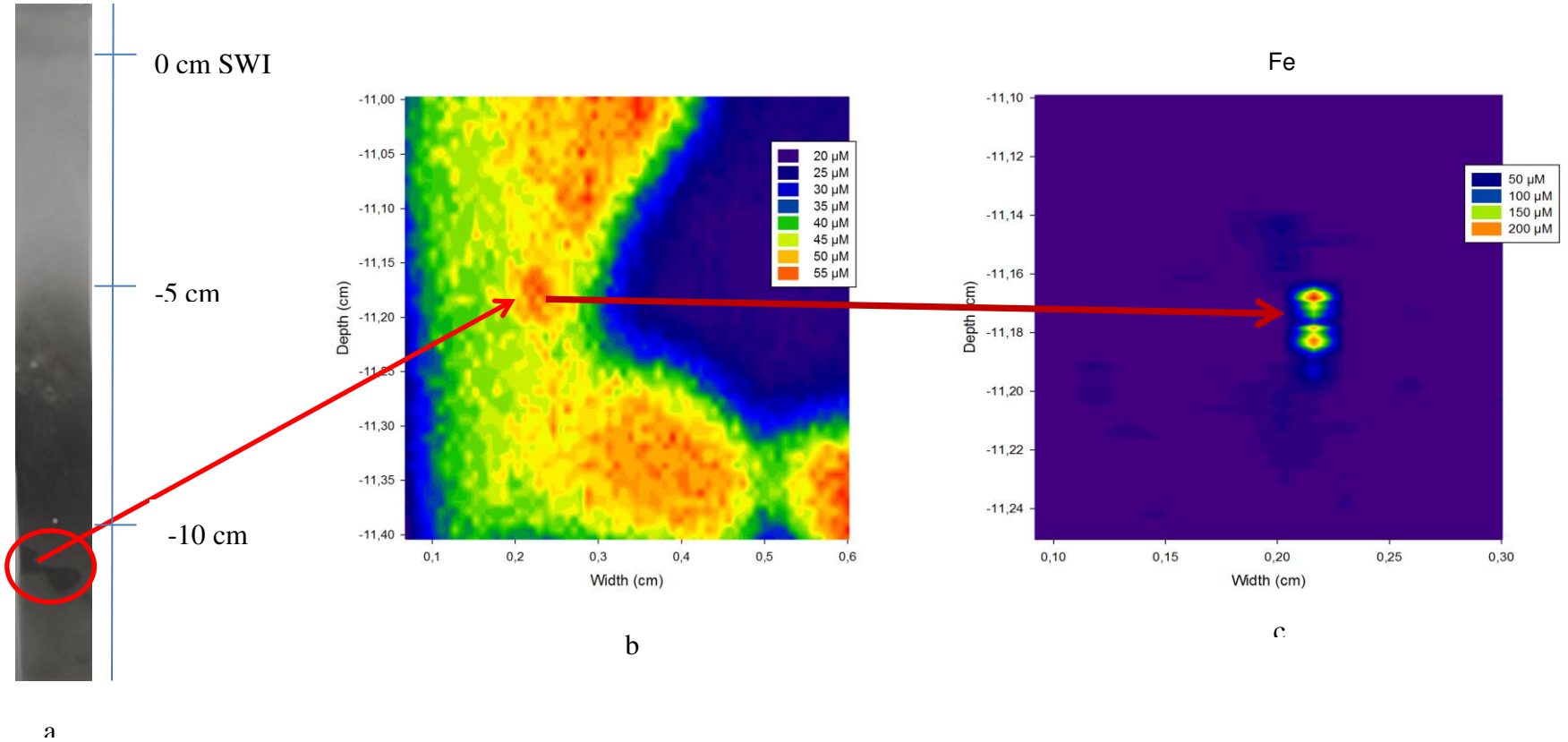
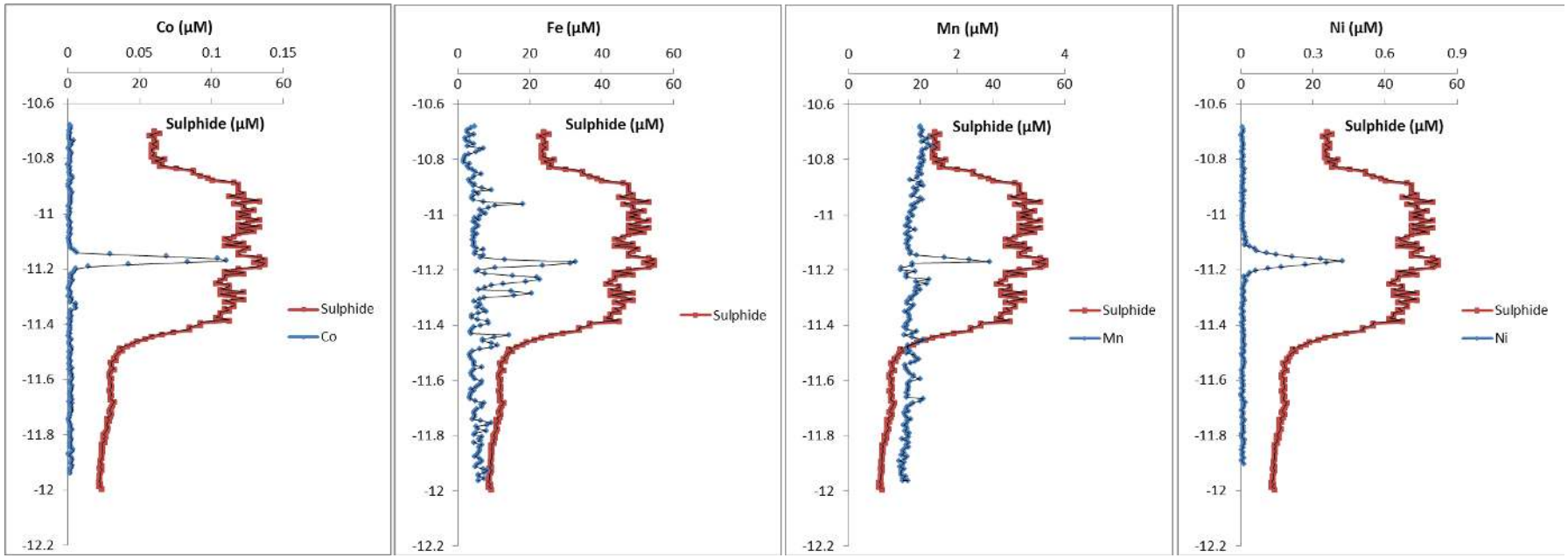

0 cm SWI
-5 cm
-10 cm
Fe
20 µM
25 µM
30 µM
35 µM
40 µM
45 µM
50 µM
55 µM
Depth (cm)
Width (cm)
50 µM
100 µM
150 µM
200 µM
a
b
c

Figure 7:


Co (µM)
0
0.05
0.1
0.15
Sulphide (µM)
0
20
40
60
-10.6
-10.8
-11
-11.2
-11.4
-11.6
-11.8
-12
-12.2
Sulphide
Co
Fe (µM)
Sulphide
Mn (µM)
0
2
4
Sulphide
Mn
Ni (µM)
0
0.3
0.6
0.9
Sulphide
Ni