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High-resolution metal gradients measured by in situ DGT/DET deployment in Black Sea sediments using an autonomous benthic lander

Abstract—DET (Diffusive equilibration in thin films) and DGT (diffusive gradients in thin films) have been deployed in situ using an autonomous benthic lander to measure concentrations and induced fluxes of Fe and Mn (DET/DGT) and trace metals (DGT) in pore waters at millimeter spatial resolutions. The newly developed deployment system is described, and based on these first results, its strengths and weaknesses are discussed. Deployments were made in the Western Black Sea in shelf sediments overlain by well-oxygenated water at a water depth of 77 m. Maxima of the redox-sensitive metals at 4 and 8 cm deep within the sediment indicated that two zones of reduction dominated the geochemistry. Sharp, but systematic, features were superimposed on this general picture and were well replicated in the profiles of Mn, Co, and Cd, but the sharp features in the Fe profile were offset from those of the others elements by several millimeters. Detection of this functional discrimination between Fe and Mn as regulators of trace metals would not have been possible using more conventional sampling procedures.

The sediment–water interface is chemically and microbially the most active site in natural waters, with steep gradients in physical, chemical, and biological properties (Santschi et al. 1990). Over the last 20 yr, the spatial resolution of measurements of solute concentrations in pore waters has been improved to a submillimeter scale for a limited range of determinands (e.g. O_2 , NO_3^- , pH, pCO_2) through the development of microelectrodes and optrodes (Larsen et al. 1997; Glud et al. 1999). These techniques have demonstrated the existence of concentration gradients across the sediment–water interface over millimeter and submillimeter depth scales (Cai and Reimers 1993). Although the resolution of conventional (Carrigan et al. 1985) slicing/squeezing and dialysis procedures has been improved (Shaw et al. 1990; Aller et al. 1998) and voltametric electrodes have been used for Mn and Fe and other solutes (e.g., I^- and $S(-II)$) (Bren-

del and Luther 1995; Luther et al. 1998), only the emerging techniques of DET (diffusive equilibration in thin films) and DGT (diffusive gradients in thin films) have provided high-resolution data for a wide range of components that include trace metals other than Fe and Mn (Davison et al. 2000).

DET is directly comparable to more traditional “peeper” systems, except that diffusive equilibrium is attained between solutes in the pore waters and in a thin film of gel. The thinness (<1 mm) of the film results in much faster diffusive equilibration than with traditional peepers. DET has been used to measure Ca^{2+} , Mg^{2+} , Na^+ , K^+ , $Fe^{2/3+}$, Mn^{2+} , Cl^- , SO_4^{2-} , NO_3^- , alkalinity, and ΣCO_2 in pore waters at a resolution of 1–2 mm (Davison et al. 1994; Brunnegard 1997; Mortimer et al. 1998; Zhang et al. 1999) and Fe at a resolution of 400 μm (Fones et al. 1998) and in two dimensions (Shuttleworth et al. 1999).

DGT (Davison et al. 2000) uses an extra backing layer of gel impregnated with chelating resin. Metal continuously diffuses across the outer layer of gel (95% water) and accumulates on the chelating resin. After deployment, the resin gel layer is sliced and eluted with acid, and metals are determined by atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectrometry (ICP-MS). Deployment for a given time at a known temperature allows calculation of the mean flux to the resin gel during deployment. If pore waters are effectively buffered by rapid resupply from a local source, such as a desorbing solid phase, the measured flux can be quantitatively interpreted as a concentration (Zhang et al. 1995; Harper et al. 1998).

DET/DGT assemblies were initially deployed in situ in shallow waters by SCUBA divers (Davison et al. 1994; Zhang et al. 1995; Brunnegard 1997) or placed by hand (Davison et al. 1997). For deeper waters, they were usually deployed in retrieved sediment cores. A lander was developed for the deployment of cylindrical DET assemblies in

the deep sea up to a depth of 4,850 m. Its use for measuring Ca^{2+} and alkalinity was reported in an undergraduate report (Brunnegard 1997) and for Ca^{2+} in an EU project report (ALIPOR 1999). This paper reports the first results obtained from the deployment of both DET and DGT assemblies using an autonomous benthic lander.

DET/DGT gel probes—The Perspex probes containing the gels were $250 \times 36 \times 5$ mm with a window 190×10 mm. Gel preparation has been previously described in detail (Zhang et al. 1995; Davison et al. 2000). For DET, the hydrated gel is cut to size, placed in the probe, and overlain by a membrane filter. The window plate, which is placed on top, is fixed in place by plastic screws. The DGT probes used a layer of gel impregnated with a Chelex 100 binding agent underneath the diffusional layer. All handling was undertaken in a laminar flow cabinet before storage in clean plastic bags.

Benthic lander—The autonomous benthic lander used in this study was designed and built at the Max Plank Institute (MPI), Bremen, Germany. A new gel deployment system (GDS) for deployment and retrieval of four DET/DGT assemblies simultaneously was designed to bolt directly onto the lander. It comprised four Perspex cylinders with central drive rods to which the probes were connected (Fig. 1). The bottom of the cylinder was covered by Teflon film. A drive rod was sealed with a watertight O-ring and passed through the top of the cylinder. The four rods were connected to a main drive shaft that was raised and lowered by a worm gear driven by a pressure-compensated, oil-filled marine motor. The motor was fully computer controlled and could be programmed from a PC before deployment. The gel probes were placed in the cylinders along with deionized water and were deoxygenated using N_2 for more than 24 h prior to deployment. For the DET probes, a syringe containing ~ 10 cm³ NaOH (1 M) was attached to the head of the cylinder. When the probes were retrieved, they came higher into the cylinder than before deployment, forcing the injection of NaOH into the seawater, giving a solution concentration in the cylinder of ~ 10 mM. This fixes the position of the Fe and Mn in the gel by oxidation and hydrolysis, converting them to a solid phase (Davison et al. 1994).

Although this fixing system relies on the NaOH being mixed throughout the cylinder, it does not have to be distributed homogeneously. The movement of the probe assembly and the injection of the NaOH from the syringe should ensure some mixing. Fe is oxidized in a matter of minutes at pH 8 and in seconds at higher pH. Any concentration of NaOH above 1 mM is adequate to ensure its oxidation prior to diffusion from the gel (Davison et al. 1994). Analysis of Fe and Mn transects at micron scale resolution through a section of gel have clearly shown how the metals are trapped in a zone within the gel by reaction with inwardly diffusing hydroxide ions (Davison et al. 1994). With DGT, the metals are fixed immediately in situ as they bind to the resin. The good locational agreement (see later) between observed features for DET and DGT measurements of Fe and Mn suggests that the in situ fixing for DET is satisfactory in recording spatial variations.

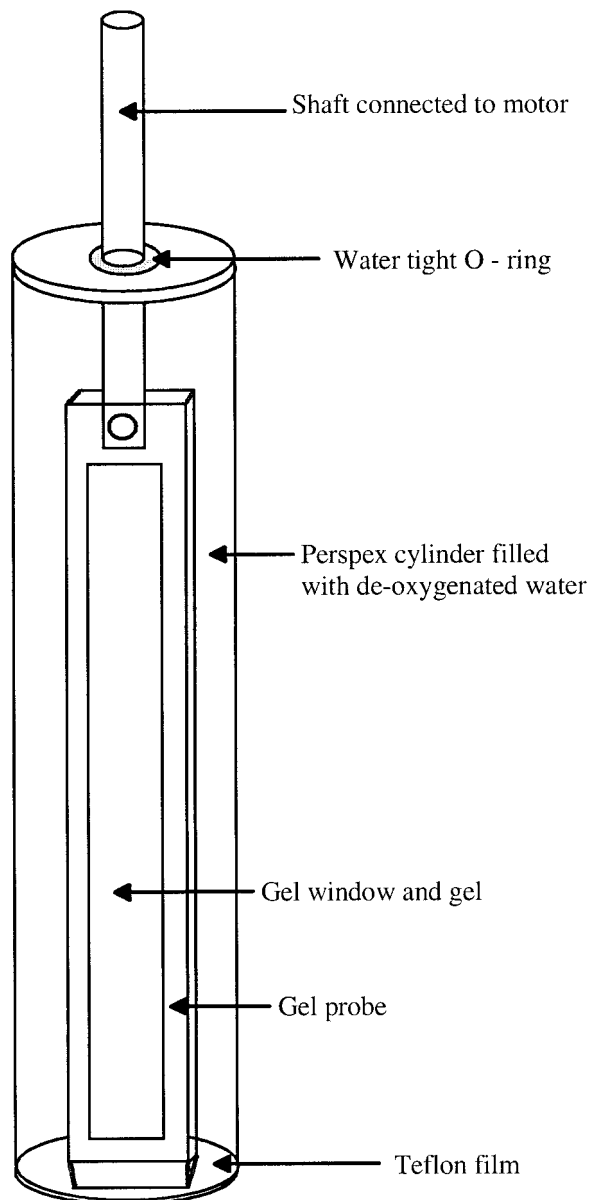


Fig. 1. Gel deployment system: Perspex cylinder containing gel probe.

Field site—The Black Sea is a land-locked deep basin and contains the largest permanently anoxic water body in the world with a volume of 423,000 km³ (Deuser 1974). DGT and DET in situ deployments were made at Sta. 2, position 43°53'84N, 29°58'57E, on 8 September 1997 as part of a MPI cruise aboard the research vessel *Petr Kottsov*. Sta. 2 is located in the western region of the Black Sea at a depth of 77 m. It is still in the oxic zone, and there is an absence of sulfide in the water column. The bottom water characteristics for this site were a temperature of 6.9°C, oxygen concentration of 213 μm , and salinity of 18.6. The sediment was a light grey, occasionally greenish, soft mud with a superficial fluffy layer or yellow-brownish fluffy aggregates. The water content was 62%, and there was 1.5% (dry wt.) organic carbon. Incubation experiments undertaken by MPI

(Weber et al. 2001) showed that sulfate reduction was the only significant carbon oxidizing process below a depth of 1 cm in the sediments. Weber et al. (2001) reported that total (TOU) and diffusive (DOU) oxygen uptake and dissolved inorganic carbon (DIC) flux were 11.1, 5.8, and 10.4 mmol m⁻² d⁻¹, respectively, and the sulfate reduction rate was 0.82 mmol m⁻² d⁻¹.

Sta. 2 sediments were completely covered by living mussels and empty shells, dominated by *Modiolus phaseolinus*. There was a diverse community on a group level with a significant share of foraminifera and small ophiuroids. Most of the animals were found in the upper 2 cm. Bioturbation of deeper sediment layers did not play an important role because tube-dwelling or burrowing macrofauna were not present (Riess et al. 2001). The meiofauna consisted mainly of nematodes and were found to be concentrated in the upper 2 cm of the sediment, filling the interstitial area between mussel shells. The 2- to 3-cm-thick layer of living bivalves appears to control remineralization, allowing for a small portion of microbial degradation in the underlying sediment (Riess et al. 2001).

In situ measurements—The self-contained Perspex cylinders were deoxygenated before being secured onto the GDS, and the rods were connected to the drive shaft. It took less than 30 min to place the lander in the water and for it to travel 77 m through the water column. Although a sharp spike, such as the gel probe, easily ruptured the Teflon film seals at the base of the cylinders, they were robust enough to withstand normal pressure, such as being lowered into the sea.

Once the lander had reached the seabed, there was a rest period of 30 min to allow any sediment disturbance to subside. The gel probes were then driven through the Teflon film into the sediment to a predetermined depth that left a portion of the gel window above the sediment–water interface. The probes were then left for 10 h before being withdrawn from the sediment back into the canisters. The ballast was then released and the lander recovered at the surface. Time from retrieval from the sediment to handling on the ship deck was estimated to be less than 30 min.

Sample processing and analysis—Upon return to the deck, the perspex tubes, complete with probes, were removed from the GDS. The sediment–water interface for both the DGT and DET probes was estimated to within ± 2 mm where a sediment mark was visible on the filter covering the gel window. Because the same procedure was used for DET and DGT probes, their relative positions should be within this tolerance. Just how well this position represents the true interface is questionable.

The DGT probes were thoroughly rinsed with Milli-Q water to remove any remaining sediment and to prevent any further accumulation of trace metals. Excess sediment was wiped from the DET probes using a clean tissue, and they were then plunged into 10 mM NaOH for a further 2 h to ensure that all Fe and Mn was fixed. The probes were placed into clean plastic bags and returned to Lancaster University, where they were removed from the bags and disassembled in a clean laboratory. The DGT resin layer and DET gel

were sliced at 2-mm intervals using a micromanipulator guillotine with a replaceable Teflon-coated razor blade (Shuttleworth et al. 1999). Each slice was eluted with 2 M HNO₃ for 24 h and analyzed. Mn, Co, and Cd from DGT resin gels were analyzed using a Varian Ultramass ICP-MS. Fe and Mn from DET gels and Fe from DGT resin gels were analyzed using Zeeman furnace atomic absorption spectroscopy (ZFAAS, Perkin-Elmer Zeeman 4100 ZL).

Conventional pore-water analysis for Fe and Mn was also undertaken during the MPI cruise. Sediment cores collected on 8 September 1997 were obtained by a multicorer in 60-cm-long, 9.6-cm (i.d.) PC liners (~ 75 cm³ cm⁻¹). The recovered sediment cores had a brownish mussel layer on the surface (shells ~ 1 cm, some living) and brown sediment to ~ 2 cm and was greyish below, grading toward dark grey/brown. From ~ 12 cm deep, there were many coarse shells, and from ~ 20 cm, shells were so abundant that it was impossible to section. The water phase was completely clear. Immediately after retrieval, the core was taken to a cold container at bottom water temperature, where all subsequent handling took place. A sample of the overlying water was taken, and the core was sliced in a N₂-filled glove bag into the following sections: 0–0.5, 0.5–1, 1–1.5, 1.5–2, 2–3, 3–4, 4–5, 5–6, 6–8, 8–10, . . . 18–20 cm.

The sediment was loaded into 30-ml PP centrifuge tubes that were closed with screw caps leaving no headspace. The tubes were centrifuged at 4,500 rpm for 15 min. This yielded an estimated 12 ml of pore water near the surface, decreasing with increasing compaction to about half as much below 10 cm. Pore water was withdrawn with a syringe in the glove bag, and filtered through N₂-flushed 0.45- μ m cellulose acetate filters. About 2 ml of sample was preserved with 20 μ l 6 N HCl for Mn and Fe²⁺ analysis and stored cold. Fe²⁺ was colorimetrically analyzed with Ferrozine on board the ship (1 g l⁻¹ Ferrozine in 50 mM HEPES at pH 7, 100 μ l sample + 1,000 μ l Ferrozine, absorption at 562 nm). Mn was analyzed in the laboratory by flame AAS (Perkin-Elmer) using standard methods.

Interpretation of pore-water profiles—Plots against depth of DGT-measured fluxes obtained from a single probe show strikingly sharp features (Fig. 2). For Mn, Co, and Cd, there is a sharp peak at -4 cm, subsidiary peaks at -3.2 and -4.8 cm, and another large flux spike at -7.4 to -7.6 cm. Many smaller maxima are also well replicated. The two sharp peaks in the Fe profiles, however, occur at -4.4 and -7.0 cm at troughs in the other three profiles. The precise coincidence of Co and Cd with Mn and not Fe strongly suggests that Mn rather than Fe is mechanistically linked to the remobilization of Co and Cd. Strong linkages between Co and Mn have been reported previously in the literature for water column measurements (Lienemann et al. 1997) in the vicinity of oxic/anoxic boundaries (Oztruk 1995) and during particle remobilization (Hamilton-Taylor et al. 1999). Their oxidation has been attributed to a similar microbially moderated mechanism (Moffett and Ho 1996). Reductive remobilization of redox-sensitive Co may require very similar conditions to Mn and consequently occur simultaneously. Alternatively, Co(II) may be incorporated in manganese oxyhydroxides, because it has been shown to form an interlayer

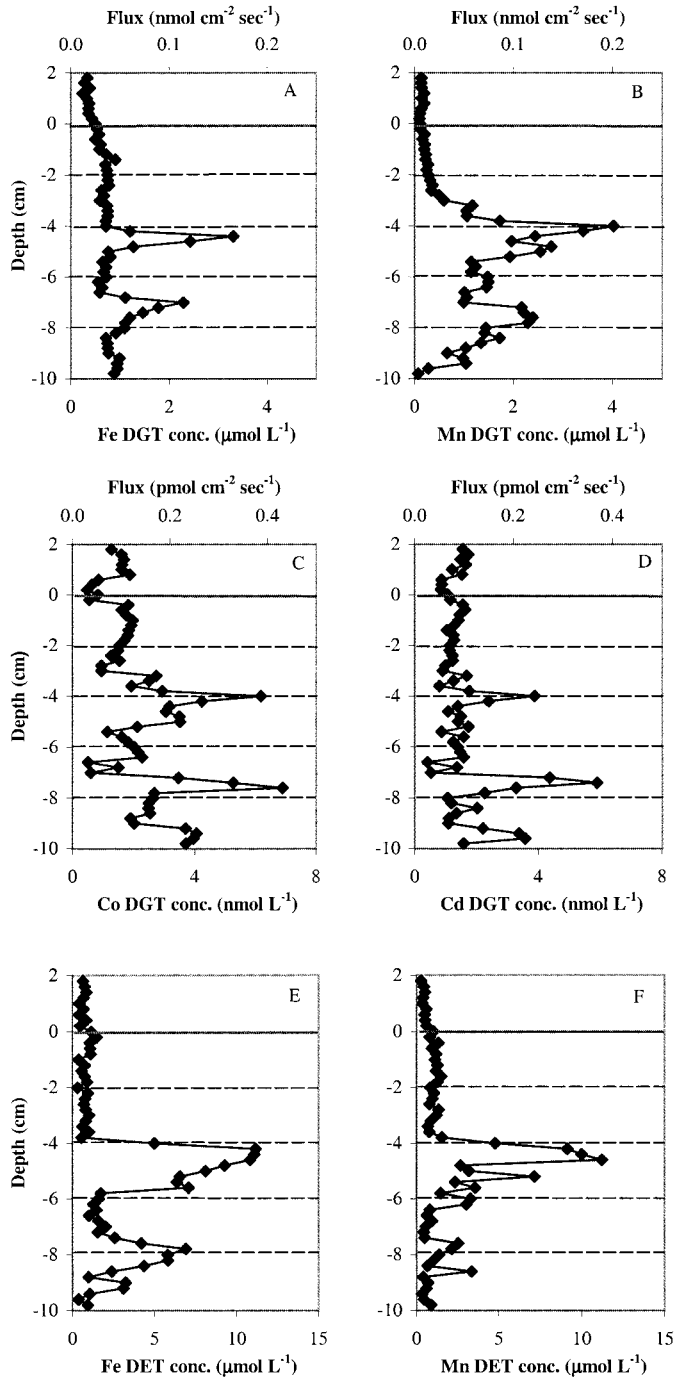


Fig. 2. Plots (A, B, C, D) against depth of DGT fluxes of Fe, Mn, Co, and Cd measured by a single probe and plots (E and F) against depth of DET-measured concentrations of Fe and Mn from a separate probe. Dashed horizontal lines are intended to guide the eye in aligning features. The solid horizontal line is the sediment-water interface. The concentration axis for the DGT profiles represents the interfacial concentration of the probe. These are calculated from the induced fluxes, which can be interpreted only as pore-water concentrations if the assumption of rapid resupply holds.

structure (Manceau et al. 1992), and then be released concomitantly with Mn(II). The latter mechanism of prior incorporation into the reducible solid phase may be responsible for the coincidence of Cd and Mn features, but Cd is much less likely to be incorporated into a lattice structure than Co. However, as the electrons required for Mn reduction are most probably supplied locally from the decomposition of organic matter, release of Cd from the associated organic material cannot be ruled out.

In benthic chamber experiments, Cd release has been found to be associated with oxidation of a thin zone of surface sediment (Westerlund et al. 1986), whereas Co was released as this zone became reducing (Sundby et al. 1986). This suggests that the Cd link to manganese (as reported here) is indirect, through the concomitantly oxidized organic material, rather than by Cd incorporation at an earlier stage in the oxide.

The DET probe was deployed at a distance of ~ 20 cm from the DGT probe. Therefore, precise alignment of sharp features is not expected between the different probes. Considering this spatial separation, the main features of two main zones of remobilization at about -4 and -8 cm deep are, however, well reproduced. The sediments appear, then, to have a degree of horizontal uniformity, at least on a local scale, suggesting that these zones of remobilization may reflect systematic recent changes in recruitment of organic material. Although the overall features of the measured profiles reflect this vertical zoning, it is likely that the very sharp local maxima spanning less than 1 cm, such as those close to depths of -4 and -8 cm, may be due to more local remobilization from microniche sources. Recent 3D modeling of solute distributions in pore waters (Harper et al. 1999a) has shown that very sharp features are generated if solutes are transported in three dimensions away from a point source. The DGT measurements are for 2×10 -mm slices of gel. Because they respond to a 1-mm layer of adjacent sediment, the effective volume sampled is only $20 \mu\text{l}$. They may, therefore, detect solutes generated within microniches. By contrast, the conventional procedure reported here extracts pore water from 0.5- to 2-cm slices of a 9.6-cm-diameter core of sediment. Because $\sim 75 \text{ cm}^3$ sediment cm^{-1} core is sampled, all such microniche activity can be expected to be averaged out. Shaw et al. (1990) have produced profiles at 2–2.5 mm resolution on recovered cores, but these were again averaged over a larger volume of sediment than DET/DGT samples, so they miss any small-scale features. These sharp features cannot be due to artifacts associated with sampling, handling, or recovery or they would not have been observed by both DGT and DET probes and in other freshwater (Zhang et al. 1995; Davison et al. 1997) and marine (Zhang et al. 2001) systems. Blank concentrations measured in undeployed gels are much lower than those values reported here. The DET blank concentrations for Fe and Mn were 0.06 ± 0.03 and $0.04 \pm 0.02 \mu\text{mol L}^{-1}$, respectively, compared to the range of concentrations measured, which were 0.31–11.2 (Fe) and 0.28–11.2 (Mn) $\mu\text{mol L}^{-1}$. The DGT blank values measured for Fe and Mn were 0.05 ± 0.02 and $0.03 \pm 0.01 \mu\text{mol L}^{-1}$, respectively, compared to measured concentration ranges of 0.24–3.31 (Fe) and 0.07–4.02 (Mn) $\mu\text{mol L}^{-1}$. Measured trace metal blank

values were $0.08 \pm 0.04 \text{ nmol L}^{-1}$ for Co and $0.12 \pm 0.05 \text{ nmol L}^{-1}$ for Cd, compared to the measured concentration ranges for Co and Cd of $0.49\text{--}6.89 \text{ nmol L}^{-1}$ and $0.41\text{--}5.91 \text{ nmol L}^{-1}$, respectively. Analysis of probes sliced at millimeter intervals after deployment in stirred solutions of metals does not show any vertical structure.

The Fe and Mn data are geochemically consistent with known redox behavior (Shaw et al. 1990), in that elevated Mn concentrations generally occur a few millimeters higher in the sediment than Fe. This separation, which is particularly apparent for the DGT measurements, would not have been revealed using conventional pore-water procedures. The minimum in Fe and Mn fluxes and concentrations at depths of 5–7 cm indicates that an active removal process is occurring for both metals. Without further data, the mechanistic basis for these removal processes is purely speculative. Fe and Mn fluxes from the sediment measured by a benthic lander at a site (142 m) close to this work were ~ 0.014 and $0.001 \text{ nmol cm}^{-2} \text{ s}^{-1}$ (Friedl et al. 1998). The Fe value agrees well with the induced flux at the sediment surface of this work of $0.027 \text{ nmol cm}^{-2} \text{ s}^{-1}$. The lower Mn value is consistent with the very low oxygen concentration observed at this site. This would have led to long-term depletion of Mn by reductive remobilization with consequently a poor reservoir available for release from an isolated sediment.

Comparison with other data—A DGT flux measurement can be directly interpreted as the mean concentration during deployment time at the surface of the filter in contact with the pore water (Zhang et al. 2001). If as metal is removed to the resin it is rapidly supplied from the solid phase, this interfacial concentration will be the same as the bulk pore-water concentration. If there is no resupply, the interfacial concentration will be about one-tenth of the bulk pore-water concentration.

The interpreted concentrations of Fe and Mn maxima from DGT-measured fluxes in the Black Sea sediment are about three times less than those measured by DET. The discrepancy may be partly due to genuine horizontal variations in concentration. It is more likely, however, that the assumption of rapid resupply from the solid phase does not hold. There must be some resupply to account for the observed structure (Harper et al. 1999b), but it may be insufficient to sustain fully the concentration at the surface of the DGT device.

Conventional pore-water sampling (slicing, centrifugation, and filtering) was also undertaken on Sta. 2 sediments. This produced profiles with a Mn maximum at 1.5 cm and an Fe maximum at 3 cm (Fig. 3). The location of these maxima, at less depth in the sediment than those observed for DET and DGT, questions whether the sediment adhering to the filter surface is a sufficiently reliable indicator of the sediment–water interface. Precise agreement between the DET, DGT, and conventional measurements should not be expected. DET and DGT probes were deployed simultaneously from the same lander at only 20-cm distance from one another. Although conventional cores were collected from the same site, they were probably many meters away from the lander. Although the same general features may be expected for the adjacent DET and DGT probes, as observed, hori-

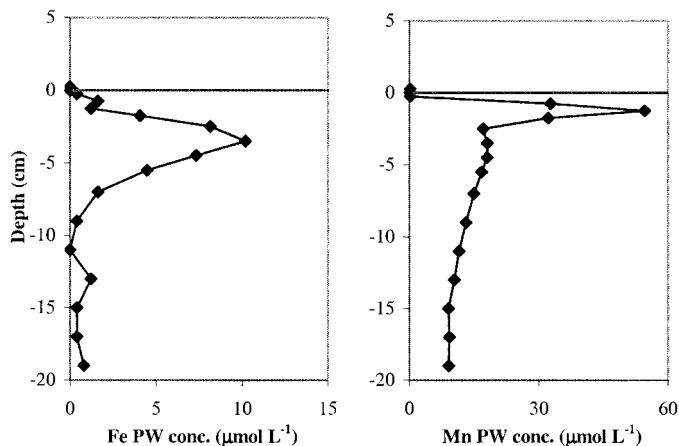


Fig. 3. Fe and Mn pore-water profiles measured by conventional techniques (slicing and centrifugation).

zonal heterogeneity at the centimeter scale could not be anticipated to extend over many meters. The DET and DGT measurements were made on effectively 20- μl of sediment, whereas the conventional measurements averaged between 35 and 70 ml of sediment. Therefore, it is entirely consistent that the profiles from conventional measurements are much smoother than those from DET and DGT. There should, however, be reasonable agreement between overlying water concentrations measured at different locations. This was found to be the case. For Mn, the values were DGT = $0.2 \mu\text{M}$, DET = $0.46 \mu\text{M}$, and conventional = $0.2 \mu\text{M}$, whereas for Fe, the values were DGT = $0.4 \mu\text{M}$, DET = $0.76 \mu\text{M}$, and conventional was undetectable at a detection limit $0.5 \mu\text{M}$.

Comparison of pore-water concentrations measured by conventional sampling and DET were in good agreement for Fe, with a maximum of $10.2 \mu\text{M}$ for conventional and $11.2 \mu\text{M}$ for DET sampling. The background levels in the pore waters (regions without peaks) also agreed at $\sim 1 \mu\text{M}$. However for Mn, the background and the maxima were higher for the conventional than for DET sampling. For DET, the background level was $2 \mu\text{M}$ and the maxima was $11.2 \mu\text{M}$, but for the conventional technique, the background level was $10 \mu\text{M}$, and the maxima was $54 \mu\text{M}$. This difference may be due to a number of reasons. There may be a genuine difference because of a difference in location on a meter scale. Poor fixing of Mn by NaOH could explain the lower values if the Mn data were considered alone. However, the Fe:Mn ratios and structure for DET and DGT probes are very similar, suggesting very strongly that this is not the case. There may be substantial colloidal Mn that is sampled by the conventional method but not by DET. However if this were the case, the DET and conventional Fe concentrations would be expected to differ as well. The diminished Mn concentrations for DET sampling may be partly due to the deployment time. The probes were only equilibrated for 9 h 15 min, whereas 15 to 27 h is required to achieve full equilibration for a diffusion-only resupply mechanism (Harper et al. 1997).

Concentrations of Co in the overlying water ($0.6\text{--}1.6 \text{ nM}$) interpreted from DGT-measured fluxes are in good agree-

ment with those measured in the water column of the Black Sea (Lewis and Landing 1992) of 0.36–3.5 nM. For Cd, the DGT-estimated values of 0.9–2 nM are slightly higher than the previously reported water column values of 0.3 nM, indicating either some baseline contamination or higher levels in the vicinity of the sediment–water interface. Guieu et al. (1998) found much higher concentrations of some trace metals in the bottom waters of the Western Black Sea compared to the surface waters, probably indicating benthic inputs.

Potential problems of the gel deployment system—This simple deployment system has several potential problems. Although oxygen removal in individual Perspex cylinders should be assured at the degassing stage, there will be some ingress by diffusion through the plastic walls during their attachment to the lander and deployment through a well-oxygenated water column. More importantly, once the Teflon seal is broken, the probes will contact oxygenated water during the 2 min they are lowered into position. As this short exposure time has been shown to have little effect on DET measurements (Davison et al. 1994), it is unlikely to affect appreciably DGT results where metal ions are accumulated. In the 2 min during retraction from the sediment before NaOH is released, the Fe and Mn profile shape will relax slightly because of diffusion of solutes, but this effect will be negligible at the 2-mm vertical resolution chosen for measurements (Harper et al. 1997). The retrieved DGT probe is open to seawater after retraction while the lander is in the water. In this total time of 30 min from retraction to recovery onto the boat, trace metals will continue to accumulate. The uptake will be uniform throughout the assembly so it will represent a general increase in the background mass and should not contribute to any observed solute structures. Because the deployment time in the sediment was 10 h, this background contribution should be negligible (<5%) if metal concentrations in the water column are the same or less than in the pore waters. If Mn was not fixed in the DET probes by NaOH, it would diffuse out during this 30-min recovery period. The reasonable agreement between DGT- and DET-measured Mn shows that this was not a problem.

However, one major advantage of the deployment system and the gel probes in general is their robustness during deployment. Because of the large amount of mussel shells in the sediment and at the interface, the microelectrodes deployed were all broken, whereas the Perspex gel probes were unaffected and were deployed with no problems or breakage. The smooth filter that overlies the gel layers helps to minimize smearing of the sediment. Because this filter is removed prior to analysis, it does not affect the results directly. However, if a particle is carried down from the surface layer to greater depth, it could affect the in situ accumulation process. Again, the agreement between DET and DGT argues against this determining the observed profiles.

This work has demonstrated the feasibility of making high-resolution measurements of solutes in marine pore waters by deploying DET and DGT in situ using an autonomous lander. These preliminary results reveal sharp features in solute distributions similar to those observed in freshwater systems. The mechanistic information that is available from measurements on this scale, including discrimination be-

tween Fe and Mn as controlling phases for trace metal release, would have been obscured by the averaging of lower resolution procedures. Further refinements in the deployment system are still required, including the incorporation of a system to define the sediment–water interface and a system of sealing the DGT/DET units on the seafloor prior to retrieval of the lander.

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