# New insights into biogeochemical processes from DET gel probes

R. J. G. Mortimer
M. D. Krom

School of Earth Sciences, University of Leeds, Leeds LS2 9JT, UK

Our understanding of inorganic and microbial reactions below the sediment-water interface is limited by the resolution of sampling. Over the last 30 years, low resolution (cm-scale) pore-water measurements on cores have allowed us to describe these processes in some environments using a sequential scheme of biogeochemical zones. However, we still have a poor understanding of some of the precise roles of microbes, particularly at the boundaries between these zones. Furthermore, certain environments such as peat wetlands and coarse littoral sands have remained largely inaccessible to sampling, even at low resolution.

This abstract describes the development of the high resolution (mm-scale) pore-water sampling technique using DET (diffusive equilibrium in thin films) gel probes to gain new insights into the biogeochemical zones in marine and estuarine sediments and to make the first high resolution measurements in previously inaccessible environments.

## DET probes

High resolution pore-water sampling using DET gel probes was initially developed to measure Fe and nutrients in freshwater environments (Davison *et al.*, 1991; Krom *et al.*, 1994). We have modified the technique for use in estuarine and marine environments (Mortimer *et al.*, 1998a), as well as pioneering its use in wetlands and for measuring advective processes. The technique involves inserting a perspex probe containing a mm-thick polyacrylamide gel protected by a filter membrane into the sediment. The gel, being 96% water, equilibrates with the pore-water within 6–24 hours, depending on the solute to be determined. It is then removed from the sediment and the ions back extracted into MilliQ water. The resulting solutions are analysed using flow injection ($NH_4^+$ and $\Sigma CO_2$) or ion chromatography ($F^-$, $Br^-$, $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$). Iron and manganese can also be measured using a slightly modified procedure in which the gel is fixed with NaOH immediately upon retrieval from the sediment and the Fe/Mn then extracted using $HNO_3$ and analysed by flow injection (Fe) or atomic adsorption spectroscopy (Mn). Laboratory experiments have shown the gel to recover $100 \pm 1\%$ of the solutes measured, although a minor correction may be required for sulphate in marine environments due to incomplete recovery (93–97%).

The DET gel probes have several advantages over conventional pore-water sampling techniques such as coring and centrifugation: they provide high resolution (mm-scale) profiles enabling delineation of steep gradients and narrow peaks; they avoid the need for a nitrogen glovebox when measuring redox sensitive species such as iron and manganese; they can be

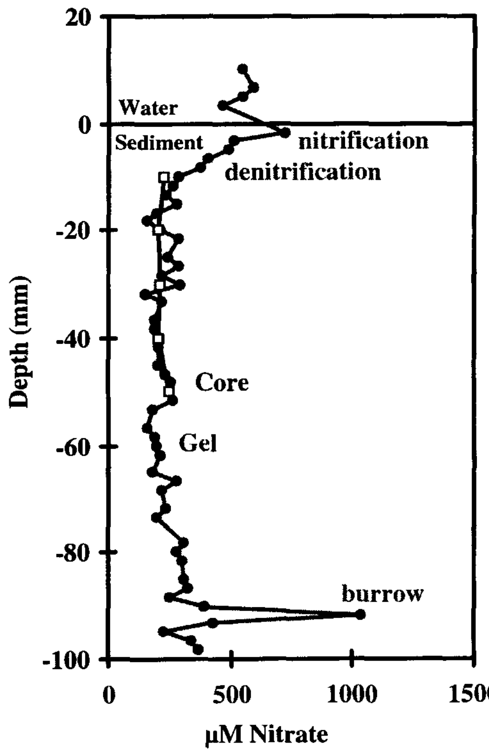


FIG. 1. Nitrate profiles, Skeffling mudflat, Humber Estuary, UK (circles = gel profile; squares = core profile).

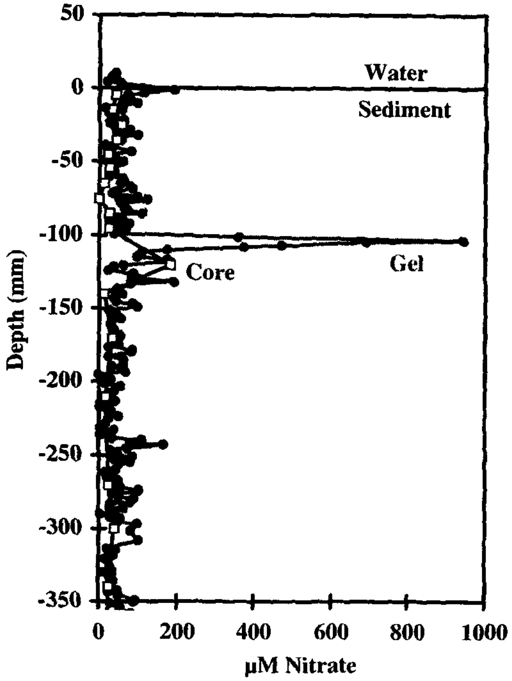


FIG. 2. Nitrate profiles, Loch Duich, Scotland, UK.

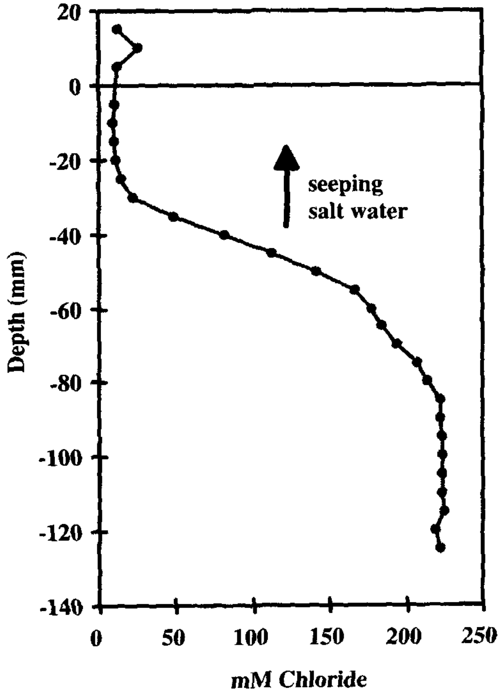


FIG. 3. Chloride profile, offshore Tiberias, Sea of Galilee, Israel.

deployed in areas which cannot be cored e.g. peat wetlands and coarse littoral sands; they can be used in laboratory mesocosms, cores, or *in situ* with deployment by hand (intertidal areas), divers (lakes and shallow seas) or benthic lander (deep ocean).

## New insights

Deployment in intertidal muds along the Humber Estuary, UK (Mortimer *et al.*, 1998b) showed that the higher resolution afforded by DET allowed much more accurate delineation of steep subsurface gradients, particularly associated with nitrification and denitrification (Fig. 1). It also enabled pinpointing of burrows at depth and allowed sampling of sites with highly compacted muds which were not amenable to coring/centrifugation or more invasive *in situ* samplers such as multilevel sippers. Finally, although calculated Fickian fluxes from the DET pore-water profiles underestimated the measured fluxes (due to enhancement by bioirrigation and resuspension), they were much closer approximations than those calculated from low resolution profiles obtained by coring.

Deployment of DET probes in a Scottish sea loch, Loch Duich, defined a large (1mM) nitrate peak exactly at the boundary between the iron and sulphate reduction zones (Fig. 2). We are currently investigating this peak further to define the precise chemical reactions occurring.

Finally, we have used the gel probes to measure saline water seeping up through clean coarse sandy sediments below the Sea of Galilee in Israel (Fig. 3). This has lead to the development of a tracer probe which allows us to measure advective processes.

## References

Davison, W., Grime, G.W., Morgan, J.A.W. and Clark, K. (1991) *Nature*, **352**, 323–24.

Krom, M.D., Davison, P., Zhang, H. and Davison, W. (1994) *Limnol. Oceanogr.*, **39**, 1967–72.

Mortimer, R.J.G., Krom, M.D., Hall, P.O.J., Hulth, S. and Stahl, H. (1998a) *Mar. Chem.* (in press).

Mortimer, R.J.G., Krom, M.D., Watson, P.G., Frickers, P.E., Davey, J.T. and Clifton, R.J. (1998b) *Mar. Poll. Bull.* (submitted).