

Developing and applying new techniques for measuring steep chemical gradients of trace metals and inorganic ions at the sediment–water interface

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Introduction

In natural waters, gradients in physical, chemical and biological properties are greatest at the sediment–water interface. To study reaction rates, to measure chemical fluxes, to investigate mechanisms and to separate the role of mass transport, it is necessary to measure chemical concentrations with sufficient resolution to define adequately these gradients. Measurements made using micro-electrodes, sensitive for example to O_2 , NO_3^- , SO_4^{2-} , NH_3 and pH, have shown that the chemical gradients established at the sediment–water interface are usually very sharp, typically extending over 1–2mm. In order to define these gradients and hence the fluxes, it is necessary to make measurements at finer spatial intervals. Given adequate spatial resolution for the chemical measurements it should be possible to detect heterogeneity within sediment systems as already demonstrated for the consumption of oxygen. It has been long recognised that most established procedures for measuring pore water generally provide inadequate spatial resolution (typically 1cm, at best 1mm).

The current research is developing procedures based on polyacrylamide gels, for measuring a range of elements including trace metals at mm and sub-mm intervals.

Results and discussion

Diffusional equilibration in thin film (DET) has recently been developed and shown to be capable of measuring iron, manganese, nitrate and sulphate in interstitial waters at sub-mm intervals (Davison *et al.*, 1991; Davison *et al.*, in press; Krom *et al.*, in press). The technique uses a thin gel layer made of polyacrylamide and relies on establishing diffusional equilibration between the thin film of gel (approximately 96% water) and the pore waters. The gels are held in a probe assembly and are inserted into the sediment and allowed to equilibrate with the pore waters. After

removal from the sediment, the gel is either rapidly sliced or chemically fixed. The chemical components of interest are then extracted from the gel and measured by widely available analytical techniques such as AAS and ion exchange chromatography. Alternatively, the elemental composition of the fixed solid phase is measured using proton induced X-ray emission spectroscopy (PIXE). So far, this technique has been used to measure Fe, Mn, NO_3^- and SO_4^{2-} in pore waters of fresh water and marine systems, with a spatial resolution on a scale of mm or better.

By backing the gel layer with a layer of ion exchange resin, it is possible to accumulate continuously labile metal and quantitatively define the extent of the lability. This new speciation technique depends on the gel thick-

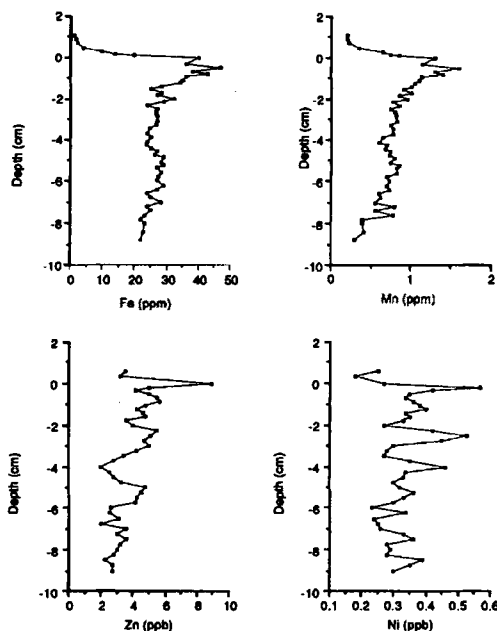


FIG. 1.

ness. It is a kinetic measurement which relies on the establishment of a diffusional gradient in thin-film (DGT). Measurement of the accumulated species can then be made using techniques such as AAS or PIXE. The attainable resolution on this technique largely depends upon the size of the resin beads and the analytical technique applied. Small ($1\mu\text{m}$) resin particles have recently become available and using a technique such as PIXE, it

should be possible to attain spatial resolution to $100\mu\text{m}$. This technique has been successfully deployed in the measurement of trace metals in sea water (Davison and Zhang, 1994) and preliminary work is under way to test its applicability to sediments. So far, concentrations of Fe, Mn, Zn, Ni and Cu in sediments have been determined using acid-extraction, providing resolution on a mm scale (Fig. 1).