## High resolution sampling of pore waters using a gel probe from Esthwaite Water, Lake District

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## Introduction

The chemistry of interstitial waters have been used to study biogeochemical processes in recent sediments and gradients at the sediment water interface have been used to calculate fluxes into or out of the sediment. In this study pore waters were sampled using a gel sampling procedure. The gel sampling method is described in detail together with laboratory experiments to test its viability in Krom *et al.*, (in press). Here a set of results are shown from Esthwaite Water, a small productive lake in N.W.England, to illustrate the power of this method. Sampling and methods: Jenkin cores of the sediment/water interface were taken from the deepest part of Esthwaite water. The cores were taken on May 20th and on July 8th 1993. The gels, which are made of polyacrylamide, are cast on a plastic probe, hydrated with DDW, and purged with N<sub>2</sub> gas prior to arrival at the sampling site. The cores were transported to a boathouse where gels were inserted into the mud within 1 h of collection. The cores were incubated for 6 hours. The results for interstitial water iron, manganese and sulphate obtained by the gel sampler were similar to those measured by conventional (syringe) sampling (Fig 1).

## **Results and discussion**

In May, the overlying water of the lake was oxic (>25% saturation). Nitrate and sulphate in the



FIG. 1. Concentrations of nitrate (▲), sulphate (•), manganese (■) and iron (△) in the pore waters of sediment sampled by high resolution gel sampler from Esthwaite Water in a) May 1993 and b) July 1993.

pore waters decreased linearly to a depth of 20mm and then continued to decrease though less sharply to 80 mm (Fig 1). In July, after further input of labile organic matter, after the hypolimnion became anoxic, pore water nitrate was low ( $\sim 1.5$ µM) with a few individual analyses giving values up to 9 µM. Sulphate values showed a marked decrease from 54  $\mu$ M in the overlying waters to  $\sim 10 \mu M$  in the sediment. The July profiles were similar to those obtained in mid-summer in Blelham Tarn, a similar productive lake in the English Lake District (Jones and Simon, 1981). These authors found high rates of sulphate reduction in the upper centimeter of Blelham Tarn (25  $\mu$ moles g<sup>-1</sup> d<sup>-1</sup>) which decreased sharply below 5 cms. The pore water profiles from this study suggest a similar pattern in Esthwaite.

Davison et al., (1991) sampled the same station in Esthwaite Water in December 1990 and found a similar subsurface maximum for iron at 8mm depth (Fig 1). The concentration of this winter peak was much lower, 3.2 ppm compared to the 30-50 ppm observed here. By July, a bimodal distribution is no longer evident (Fig 1). Oxyhydroxides appear to be reduced at the sediment-water interface where there is a very steep concentration gradient. This gradient provides a means for rapidly removing Fe(II) to the overlying water. The level of manganese in the pore waters in summer (Fig 1) was similar to that observed previously in Esthwaite Water (Hamilton-Taylor and Morris, 1985). The much greater resolution afforded by the gel shows a well defined maximum in dissolved manganese at about 1cm depth in May (Fig 1). Mn (II) is evidently diffusing upwards and downwards away from this peak. The absence of the near-surface maximum in July may be due to exhaustion of readily reducible Mn oxyhydroxides in this zone. Depletion of the Mn reservoir has been observed before in these sediments (Davison, 1993).

The transport of anions through the sedimentwater interface by diffusional processes can be determined using Fick's first law of diffusion. The calculated flux of nitrate into the sediment due to molecular diffusion in May 1993 was 78-90

 $\mu$ moles.m<sup>-2</sup>.d<sup>-1</sup>. and for sulphate was 220  $\mu$ moles.m<sup>-2</sup>.d<sup>-1</sup>. These fluxes are likely to be minimum values since they do not take into account bioturbation which may be important in this system during May when the overlying water was oxic. In July the flux of sulphate into the sediment was 240  $\mu$ moles.m<sup>-2</sup>.d<sup>-1</sup>. By comparison Jones and Simon (1981) determined the sulphide accumulation rate of Blelham Tarn in midsummer, in the hypolimnion. This quantity, which is likely to correspond to the sulphate reduction rate, was  $400-550 \text{ }\mu\text{moles.m}^{-2}.\text{d}^{-1}$ . Davison (1993) estimated the iron flux to the water to be in the range  $0.2-3.9 \times 10^{-12}$  mol  $cm^{-2} s^{-1}$ . Hamilton-Taylor and Morris (1985) suggested that the pore water maximum which gave rise to these fluxes had to occur over the upper millimeters in the sediment which they were unable to resolve adequately using conventional sampling. Using high resolution gel sampling a gradient from the sediment into the overlying water is always discernable (Fig 1). Davison et al. (1991) calculated the flux for a single winter value as  $1.5 \times 10^{-12}$  mol cm<sup>-2</sup> s<sup>-1</sup>. In this study the iron flux was  $1.5 \times 10^{-12}$  mol cm<sup>-2</sup> s<sup>-1</sup> (May) and 2.9  $\times 10^{-12}$  mol cm<sup>-2</sup> s<sup>-1</sup> (July). We estimated the manganese flux to be  $0.22 \times 10^{-12}$  mol cm<sup>-2</sup> s<sup>-1</sup> (May) and  $0.04 \times 10^{-12}$  mol cm<sup>-2</sup> s<sup>-1</sup> (July) within the ranges estimated for manganese fluxes into lakes of 0.04 to 2  $\times$  10<sup>-12</sup> mol cm<sup>-2</sup> s<sup>-1</sup> (Davison, 1993).

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