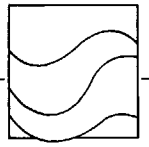

A biogeochemical comparison of sea loch sediments. Manganese and iron contents, sulphate reduction and oxygen uptake rates

Sediment profiles
Benthic remineralization rates
Manganese cycling
Authigenic sulphide

Profils dans le sédiment
Reminéralisation benthique
Cycle du manganèse
Sulfite authigénique

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ABSTRACT

The sediments of the upper basins of Lochs Goil, Fyne and Etive were high in both solid phase extractable manganese (up to 3.7% w/w), and high in pore water manganese (up to 600 µM), while Loch Linnhe sediments were low in manganese. Solid phase manganese from the surface sediments at the deepest stations was highest in those lochs where the mean residence time of the bottom water is longest, indicating the importance of manganese cycling through the water column.

Porewater iron concentrations in the top 2 cm of sediment were highest near the heads of the lochs, *i.e.* near the main freshwater inputs.

Within sediments of Lochs Goil, Fyne and Etive high rates of total sulphate reduction were associated with high relative rates of formation of acid volatile sulphide, but this correlation did not occur in Loch Linnhe; here the formation of pyrite was more important. Loch Linnhe sulphate reduction rates were higher than those in Lochs Goil and Etive, but fixed sulphur concentrations in the sediments were lower, indicating a greater proportion of the products of sulphate reduction were being reoxidised. The sulphide burial rate was high in Loch Etive and low in Loch Linnhe.

Oxygen uptake rates by sediments showed an increase near the heads of the lochs, implying the presence of a component of the terrestrial organic input which was readily degradable by marine sediment bacteria.

RÉSUMÉ

Comparaison biogéochimique des sédiments de lochs marins : teneurs en manganèse et en fer, réduction des sulfates, consommation de l'oxygène.

Les sédiments des bassins supérieurs des lochs Goil, Fyne et Etive sont riches en manganèse, en phase solide (jusqu'à 3,7 % en poids) et en phase dissoute dans l'eau interstitielle (jusqu'à 600 µM), alors que les sédiments du loch Linnhe sont pauvres en manganèse. Aux stations les plus profondes, la phase solide du manganèse des sédiments superficiels est la plus importante dans les lochs où le temps de résidence moyen de l'eau de fond est le plus long, ce qui traduit l'importance du cycle du manganèse dans la colonne d'eau.

Les concentrations du fer dans l'eau interstitielle des deux premiers centimètres du sédiment sont les plus élevées à l'amont des lochs, c'est-à-dire à l'arrivée de l'eau douce.

Dans les sédiments des lochs Goil, Fyne et Etive, aux valeurs élevées de la réduction des sulfates sont associées des valeurs élevées de formation d'acide sulfureux, mais cette corrélation n'est pas observée dans le loch Linnhe où la formation de pyrite est plus importante. La réduction des sulfates dans le loch Linnhe est plus élevée que dans les lochs Goil et Etive, mais les concentrations en sulfure fixé dans les sédiments y sont inférieures, ce qui indique qu'une plus grande proportion des produits de réduction des sulfates est réoxydée. La vitesse de disparition du sulfite est élevée dans le loch Etive et basse dans le loch Linnhe.
La consommation de l'oxygène augmente à l'amont des lochs, correspondant à l'arrivée d'un constituant organique d'origine terrestre qui est dégradable par les bactéries marines du sédiment.

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INTRODUCTION

Sea lochs are fjordic bodies of water which appear as invaginations of the sea. The morphology of these lochs is glacial in origin and they have basins separated from the sea by one or more sills. The water below the sill depth is retained for varying periods by a density gradient; the normal tidal exchange often involves only the surface waters which have been made less dense by mixing with freshwater run-off. This tidal exchange induces turbulent diffusion between the surface water and the underlying water, reducing the salinity of the latter. The process continues until (at a high spring tide) the density of the incoming water at sill depth is just higher than that of the bottom water in the basin. At this point the incoming water flows to the bottom of the basin by gravity and complete or partial renewal of the bottom water occurs. (For a general discussion of fjord dynamics and deep water renewal *see* Gade and Edwards, 1980). The discontinuity between the surface water of low salinity and the bottom water of high salinity can serve as a boundary for the formation of internal waves. These can be induced by tidal flows and manifest themselves as internal seiches giving rise to bottom currents flowing in the opposite direction to the surface tidal flows. These may be of such magnitude as to cause resuspension (*see* Overnell and Young, 1995).

Sea loch sediments are recent, invariably muddy, and are accumulating relatively fast (*ca.* 0.7 $cm.y^{-1}$ in Loch Linnhe (Overnell and Young, 1995). Differences in physical parameters such as dimensions and sill depth, catchment area and bathymetry produce a large spectrum of dependent biogeochemical characteristics in both the water and sediments. Thus lochs may have reduced oxygen tension in the bottom waters, or the whole water column may be well mixed throughout the year. Isolated bottom waters show an increase in nutrients and decrease in oxygen as a result of fluxes across the sediment/water interface (Edwards and Grantham, 1986; Edwards *et al.*, 1986). In addition, the freshwater input and the amount and composition of the sedimenting material may vary greatly. All these dependent characteristics can give rise to large differences in sediment processes and compositions. The physical parameters of Scottish sea lochs have been well summarized (Edwards and Sharples, 1985), but now need to be correlated with the biogeochemical characteristics of the sediments.

It has long been known that manganese oxides can be concentrated at the sediment surface and that manganese and iron oxides become reduced at depth after burial, and the resulting manganese profiles have been modeled (*e.g.* Burdige and Gieskes, 1983). The potential for manganese and iron oxides to act as terminal electron acceptors to provide energy for bacterial growth has been acknowledged (Froelich *et al.*, 1979). That this potential can be realized by bacterial strains isolated from aquatic sediments has been demonstrated recently (Lovley, 1991; Coleman *et al.*, 1993; Roden and Lovley, 1993), and manganese cycling has been shown to be quantitatively important in organic matter degradation in nearshore sediments (Canfield *et al.*, 1993*a*, *b*) and in hemipelagic sediments (Aller, 1990). Muddy near shore sediments usually have porewater pH 7.5 which varies little with depth down to 1.2 m (Boudreau and Canfield, 1988), however a reduction from seawater values down to a minimum of 7.3 is often observed in the top 1cm (*e.g.* Jørgensen and Revsbech, 1989).

We wished to measure the extent of variability within a range of lochs which appeared suitable for benthic remineralization measurements in ecosystem studies. The four lochs studied have relatively deep upper basins retained behind shallow sills, in which the validity of measuring sediment/water fluxes in laboratory incubations could be assessed by comparison with rates deduced by changes in the nutrient concentrations of the retained bottom water.

This paper reports the concentrations of manganese, iron and authigenic sulphides in the sediments at different stations in the upper basins of these lochs and the rates of oxygen consumption and sulphate reduction at the same stations. The factors which might determine the differences found between the lochs are assessed.

STUDY SITES, MATERIALS AND METHODS

Sampling Sites

The location of the four lochs, together with the sampling stations are illustrated in Figure 1. Except for station E5 in

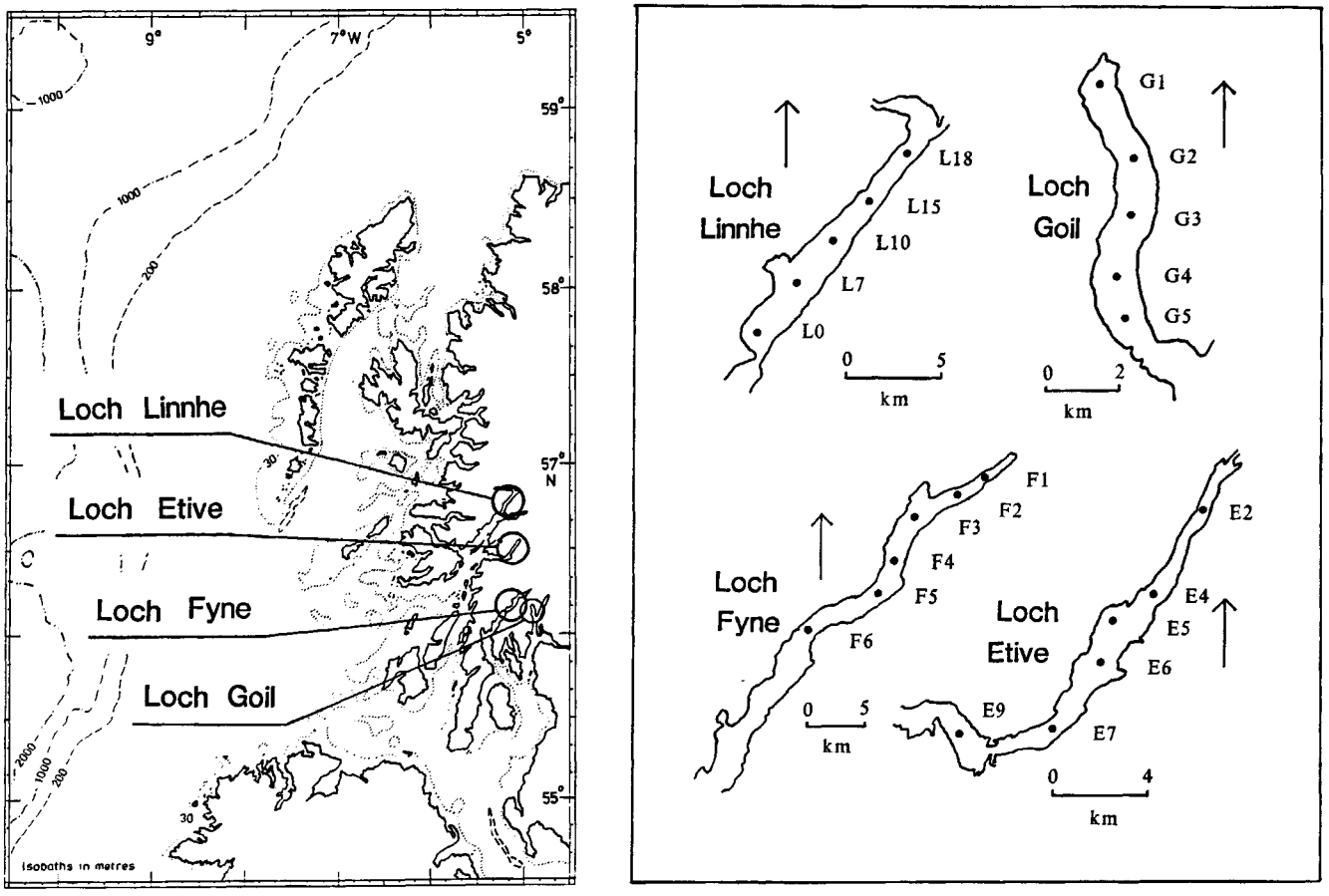

Figure 1

Location of sampling sites.

Etive, the stations are all along the line of deepest water in the lochs.

The existing knowledge of deep water renewal in the upper basins of the chosen lochs is variable. In the case of Goil the bottom water is renewed annually between January and March (Mackay and Halcrow, 1976; Edwards *et al.*, 1986). Before renewal oxygen levels fall asymptotically to 0.9-1.5 mg.l^{-1} (from 8 mg.l^{-1}). The waters do not become anoxic; presumably an equilibrium is reached between turbulent diffusion of oxygen downwards and uptake of oxygen by the sediment.

The hydrography of Fyne has been less well studied. However the oxygen concentration of the bottom water of the upper basin fell to 2.5 and 3.2 mg.l^{-1} in January 1981 and January 1982 and there was also evidence of increased nitrate at this time (Tett *et al.*, 1986). The bottom water of the upper basin is probably renewed annually (K.J. Jones and A. Edwards, Dunstaffnage Marine Laboratory (DML), pers. comm.).

Etive has a large freshwater input and many shallow sills between the upper basin and the sea, thus tidal exchange is poor. Oxygen concentrations in the bottom water fall to 2.8 mg.l^{-1} between deep water renewal events (Edwards and Grantham, 1986). The upper basin bottom water is renewed aperiodically, depending on freshwater input, with a mean repetition time of 16 months (Edwards and Edelsten, 1977).

In Linnhe thermistor chain measurements suggest that the deep water of the upper basin is partially renewed at most spring tides (D. Meldrum, DML, pers. comm.), and considerable bottom currents have been inferred from measurement of internal wave amplitudes (A. Edwards, DML, pers. comm.). Bottom water currents of up to 40 cm.sec^{-1} have been measured (G. Allen and J. Simpson, UCNW, pers. comm., discussed in Overnell and Young, 1995) and isolation of the bottom water has been shown during the period of spring freshwater run-off (K.J. Jones and B.E. Grantham, DML, pers. comm.).

Collection and handling of sediment samples

Cores with an undisturbed sediment/water interface were collected using a damped corer (Craib, 1965). Loch Goil sediments were sampled on 12 Jan, 2 Mar, 29 Mar and 8 Nov 1989; Loch Fyne sediments on 10 Jan, 28 Feb, 3 Apr and 9 Oct 1989; Loch Etive on 2 May 1989 and Loch Linnhe on 31 Jan 1991. Cores were sealed complete with overlying water and transported back to the laboratory in an insulated box containing ice (approx. 4 h).

The storage and handling of the cores depended on their subsequent use. Cores for oxygen uptake and sulphate reduction measurements were unstoppered, transferred to a tank of circulating, aerated, seawater taken from 10 m above the bottom at the deepest station of the loch, and maintained at *in situ* temperature, in the dark, overnight.

Cores for chemical analysis were stored overnight in a refrigerator (4°C) in the dark.

Cores for sulphate reduction rate measurements were sectioned into 5 cm intervals down to 15 cm by extrusion into a 5 cm collar under a stream of nitrogen. Each 5 cm section was subcored using 5 ml plastic disposable syringes, with the Luer end removed to form an open tube. Two subsamples were taken for sulphate reduction measurements and sealed with butyl rubber "Suba Seals" and one subsample each for porosity and pore water sulphate analysis. The samples for sulphate reduction analysis were stored in an anaerobic jar at *in situ* temperature before further handling.

Cores for analysis of solid phase manganese and iron, extractable with hydroxylamine/acetic acid, and porewater manganese and iron were taken (1) at the deepest part of the upper basins of the four lochs and sectioned at 2 cm intervals down to 12 cm (2) at all stations from the head of the loch down to the sill, the top 2 cm only being taken.

Porewater metals

Subsampling for porewater analysis was carried out in an anaerobic cabinet (Forma Scientific, Ohio, U.S.A.). Sections of sediment, 2 cm, were extruded and transferred to centrifuge tubes which were securely capped. Centrifugation was done outside the cabinet at room temperature (gav. = 1,200) for 15 min. The tubes were then returned to the cabinet and the porewater decanted and filtered through Whatman GF/F filter papers in Millipore Swinnex filter holders. Porewater was acidified with 6N HCl to give 55 mM HCl in the samples.

Porewater iron was measured by a modification of the ferrozine method of Stookey (1970) to include a reducing agent (Aller, 1980). 50 µl ferrozine reagent, (ferrozine, 50 mg; hydroxylamine HCl, 1.0 g; acetic acid, glacial, 3.5, ml; water, to 10 ml) was added to 1 ml of the sample. After 1 h at room temperature, 50 µl assay buffer (ammonium acetate, 4 g; ammonia, 18M, 3.5 ml; water, to 10 ml) was added and the absorbance read at 562 nm.

Porewater was analysed for manganese, after suitable dilution with 55 mM nitric acid, by graphite furnace atomic absorption spectrophotometry (Pye Unicam model SP9).

Manganese fluxes

Samples of water overlying the cores after oxygen uptake measurements (*see* below) were filtered (Whatman GF/F), diluted 10 fold with 55 mM nitric acid and the manganese concentration determined as for porewater (above).

Standards were prepared by dilution of standard manganese solution (BDH) with 55 mM nitric acid. There was no matrix effect due to material dissolved in the porewater even at the lowest dilution used.

Extractable iron and manganese

The sediment pellets formed by centrifugation after extraction of porewater (above) were lyophilized, and the dried samples extracted with 1 M hydroxylamine HCl, 25% acetic acid at room temperature for 4 h (Chester and Hughes, 1967). After centrifugation, iron and manganese concentrations in the supernatant were measured by flame atomic absorption of samples diluted with 0.1 N nitric acid, against standards (BDH) also in 0.1 N nitric acid. There was no matrix effect due to the hydroxylamine/ acetic acid even in the most concentrated solutions.

Sulphate reduction rates

Subcores (5 ml) were injected along their length with 2 µCi of carrier free $^{35}SO_4^{2-}$ and incubated for 24 h at *in situ* temperatures (between 9-11°C depending on site), in an anaerobic jar. Incubation was terminated by freezing (–20°C). The ^{35}S-sulphide produced as free hydrosuphide (HS^-) and as iron monosulphide (FeS) was released as H_2S into a stream of deoxygenated nitrogen by the addition of 1.6 ml of 6N degassed HCl to the frozed 5 ml subcore + 5 ml of degassed water. The flask was maintained at 80°C for 40 min and the hydrogen sulphide trapped in 15 ml of 10% Zn acetate. The ^{35}S produced as pyrite (FeS_2) and elemental sulphur was released as H_2S by reduction with $CrCl_2$. The washed and dried residue from the previous stage was heated under reflux with 25 ml of 1M $CrCl_2$ and 10 ml of 6 N HCl, while oxygen-free nitrogen was passed through. The H_2S produced was trapped in 15 ml of Zn Acetate as previously. Aliquots of the suspension of the trap contents were counted for ^{35}S (Howarth and Jørgensen, 1984; Parkes and Buckingham, 1986). Sulphate reduction rates were calculated from the radioactivity of the trapped sulphide, the radioactivity of the residual sulphate, the pore water sulphate concentration, the sediment porosity and the incubation time (with a small correction applied for the isotope effect) (Jørgensen, 1978). Porosity was calculated from wet volume and weight loss on freeze drying. Sulphate concentrations of porewater were measured, after suitable dilution with distilled water, by ion chromatography (Dionex, Sunnyvale, CA, U.S.A.) with conductivity detection (Cragg *et al.*, 1992).

Iron monosulphide and pyrite

Iron monosulphide + soluble sulphide in the sediment was estimated by measurement of the total sulphide trapped from the AVS distillation during the sulphate reduction rate measurements, and pyrite iron + elemental sulphur was estimated from the PVS sulphide. The sulphide in the traps was measured using the method of Cline (1969).

Oxygen uptake

Oxygen uptake rates were determined from the decrease in dissolved oxygen in the overlying water of intact incubated sediment cores, as described by Parkes and Buckingham (1986). At time zero the core tubes were fitted with submersible stirrers enclosing a seawater space of about 12 cm height above the sediment. The stirring speed was adjusted so that fine material at the sediment surface was just not

resuspended. The effect of stirring speed on the fluxes below this critical speed was not investigated in this work, although using the same apparatus Parkes and Buckingham (1986) found only relatively small changes in oxygen uptake with speed. Samples (11 ml) were taken at 3 and 6 h in glass syringes for measurement of oxygen by Winkler titration using potentiometric detection of endpoint. Sediment-water oxygen fluxes have been shown to be zero order with respect to oxygen down to an oxygen concentration of 100 μM (Anderson *et al.*, 1986; Hall *et al.*, 1989). Over the first six hours of measurement the oxygen concentration decreased typically from 310 to 260 μM; therefore incubations were assumed to be not oxygen limited.

Organic matter content

1 g aliquots of freeze dried sediment from each depth horizon were ashed in a muffle furnace at 500°C for 24 h. The organic matter content was calculated from the loss in weight.

RESULTS AND DISCUSSION

Manganese and iron

Distribution of solid phase extractable manganese and iron

• Variation within the lochs

Solid phase extractable manganese is mainly in the form of amorphous coatings of Mn^{IV} and/or Mn^{III} oxide and extractable iron mainly in the form of amorphous coatings of hydrated Fe^{III} oxide (oxyhydroxide), on sediment particles. However it should be bourne in mind that other authigenic forms would be expected to be extracted by the reagent used here (hydroxylamine + acetic acid). These include manganese carbonate (rhodochrosite, often found at depth and in manganese nodules), iron monosulphide and an operationally defined solid phase $iron^{II}$ component (Thamdrup *et al.*, 1994). The metal fractions measured here are probably the same operational fractions as studied by Lovley and Phillips (1987) and are of particular interest because they represent largely reactive manganese and iron which is potentially available to bacteria as an oxidant for organic matter degradation. The extractable manganese and iron concentrations in the top 2 cm of sediment were measured along the mid points of the lochs from the heads of the upper basins to the sills (Fig. 2). Goil and Fyne had the highest manganese and Linnhe the lowest. Within a loch the highest concentrations were found at the deepest stations. The greatest variation within a loch occurred in Etive with 0.01% Mn at the head and a maximum of 3.67% at station E6 with a water depth of 104 m. The deepest station (E7) was still significantly enriched in Mn compared with other stations. The Mn enrichments at the deep stations are consistent with X-ray fluorescence analysis data obtained from 0-2 cm sediment samples taken in a transect across the same part of the loch (Williams *et al.*, 1987). Even in Linnhe where manganese concentrations are very much lower, there was a strong tendency for the highest manganese concentrations to occur at the deepest stations.

The extractable iron concentrations in the surface sediments of the four lochs (Fig. 2) did not show such pronounced variation within each loch. However, again there was a tendency for the highest concentrations to be found in the deeper stations, especially in Fyne and Linnhe.

• Depth profile

The depth profiles of extractable manganese concentration at the deepest stations in the four lochs are presented in Figure 3. In Goil, Fyne and Linnhe there was considerable enrichment at the surface, with most of the enrichment in the top 4 cm. In Etive, although there was no pronounced gradient with depth, the concentrations at both deep stations (E6 and E7) nevertheless represent enrichment since these concentrations are much higher than those of surface sediments at shallower stations (Fig. 2). Manganese in surface sediments is often enriched with respect to sediment at lower depths. This is due to reduction of the oxide at depth with concomitant release of the uncomplexed Mn^{2+} ion (Eckert *et al.*, 1989), which diffuses to the surface where it is re-oxidised to solid phase (Sørensen and Jørgensen, 1987). Whether re-oxidation of the manganese ion takes place mainly within the sediment or within the water column, the effect is to maintain higher surface levels. Recent work by Thamdrup *et al.*, (1994*b*) has shown that much re-oxidation takes place within the top 2.5 mm of the sediment column in Aarhus Bay.

Although the geology of the catchment area must play a part in determining the extractable manganese concentrations of the sediment surface, this is probably not the most

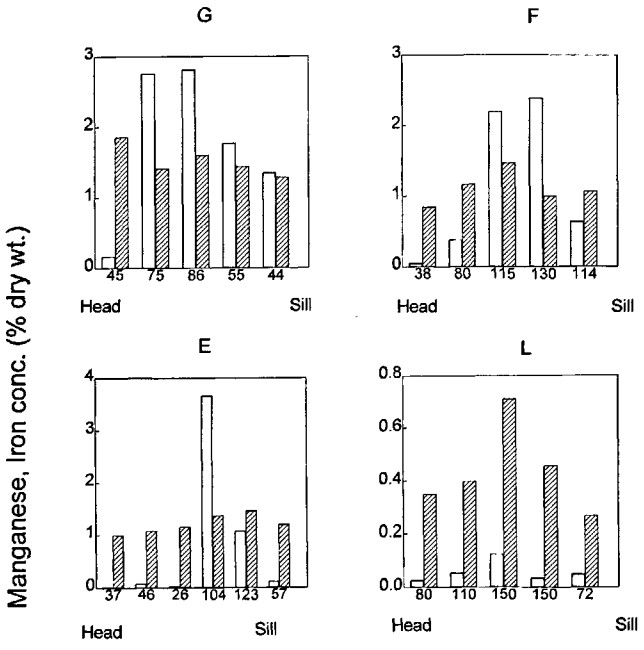

Figure 2

Concentrations of solid phase manganese (unfilled bars) and iron (diagonal shading) extractable with hydroxylamine/acetic acid from sediments at different stations; G, Loch Goil; F, Loch Fyne; E, Loch Etive and L, Loch Linnhe; 0-2 cm depth interval. The stations are in order from the head of the loch and are identified by their respective water depths. Values are for determinations on single cores.

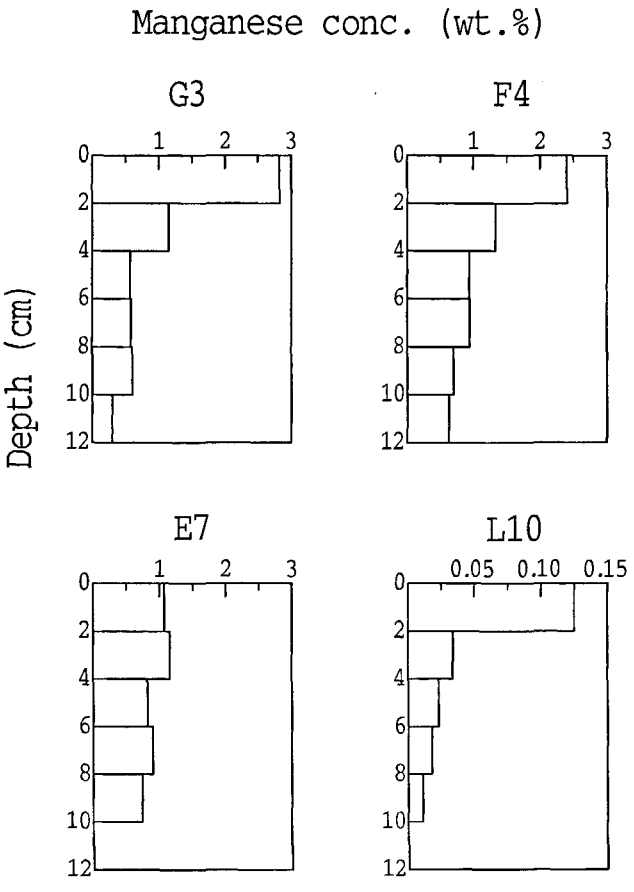

Figure 3

Concentrations of solid phase manganese extractable with hydroxylamine/acetic acid from sediments; G3, Loch Goil station G3; F4, Loch Fyne; E7, Loch Etive and L10, Loch Linnhe, as a function of depth in sediment. Values are means from two cores. Note: the difference between concentration scales for Loch Linnhe and the other lochs.

important factor. Thus, the manganese concentration in the surface sediments at the head of Etive was lower than any station in the other lochs, at the deep station the Mn concentration was higher than at any other station. As the extractable Mn concentrations were highest in the deeper stations in all the lochs it is unlikely that the Mn distributions are primarily controlled by detrital Mn inputs and hence the surrounding geology, as this would result in enrichment at the head of the lochs. Therefore, the controlling factor may be the efficiency of the Mn recycling mechanism within the waters of the loch, although additionally "sediment focusing" (Granéli, 1992) may transport the fine manganese-rich particles to the deeper water. An alternative mechanism could be the efficiency of recycling within the sediment. This would imply that where oxygen penetrated to the greatest, depth retention of dissolved Mn^{2+} would be greatest. It would be expected that oxygen penetration would be greatest near the sills of the lochs (oxygen depth profiles were measured only in Loch Linnhe station 14 (Overnell and Young, 1995)). Since the highest solid phase manganese concentrations occur at or near the deepest stations rather than the sills we chose the first explanation.

The maximum concentrations of extractable manganese in the top 2 cm of sediment surface for each loch are positively correlated to their bottom water renewal times (Fig. 4). (Renewal times are based on the following: Linnhe, spring tide repetition time, Goil and Fyne, annual turnover, Etive 1.3 year turnover time (*see* site description.)) This relationship implies that the mechanism of Mn enrichment involves a considerable flux of Mn^{2+} into the overlying water (*e.g.* Sundby and Silverberg, 1985), coupled with its oxidation and precipitation onto the sediment before it is advected out of the loch. In addition to loss of Mn due to partial or complete renewal of bottom water, loss may be due to vertical mixing of the bottom and surface waters during tidal exchange. These processes are related however, because the erosion of high salinity bottom water by vertical mixing with less dense surface water leads to bottom water renewal (Gade and Edwards, 1980). Using rate constants published by Yeats and Strain (1990) and unpublished manganese and oxygen concentration data (Yeats, pers. comm.) for Goil bottom water, a turnover time for Mn oxidation of 20 days can be calculated. Although water column Mn concentration data is not available for the other lochs, similar manganese turnover times may obtain. Lochs with renewal times significantly greater than 20 days, therefore should have similar Mn enrichment if bottom water renewal was the primary control mechanism. This is apparently not the case for Goil and Etive for which much longer turnover times have been published (*see* Fig. 4 and Sampling sites above). In addition, deep water renewal could lead to advective loss of dissolved manganese. Efficient recycling of buried manganese mediated by manganese oxidation within the trapped lower water, made possible by vertical diffusion of Mn^{2+} upwards from the sediment and oxygen down from the surface mixed layer, may be the process underlying the relationship in Figure 4.

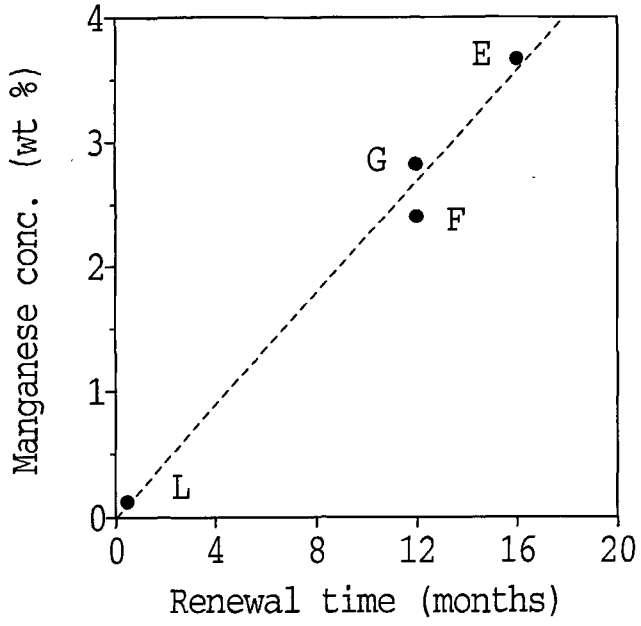

Figure 4

Relationship of maximum hydroxylamine/acetic acid extractable manganese in top 2 cm of sediment and mean interval between renewals of bottom water; G, Loch Goil; F, Loch Fyne; E, Loch Etive; L, Loch Linnhe.

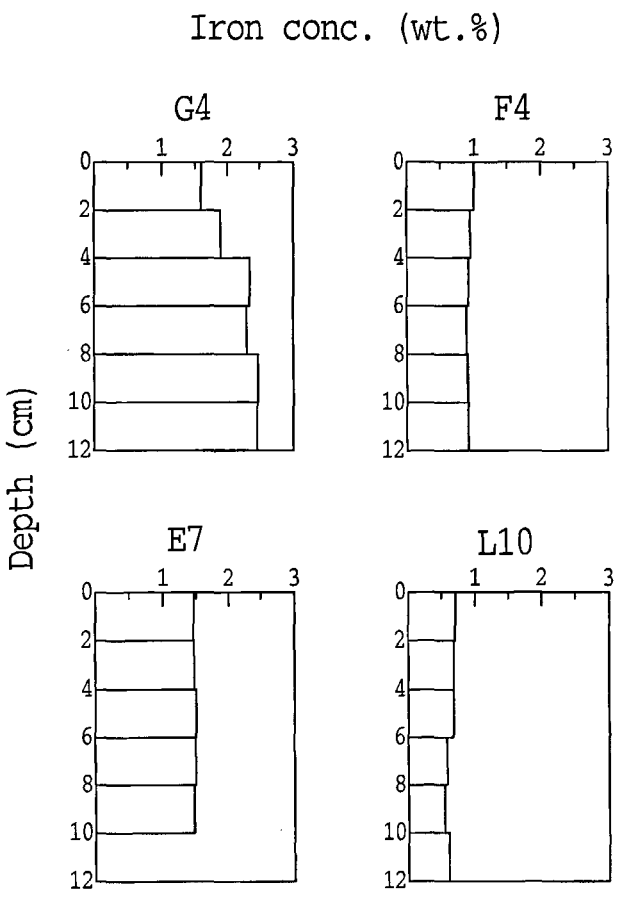

Figure 5

Concentrations of solid phase iron extractable with hydroxylamine/acetic acid from sediments; G3, Loch Goil station G3; F4, Loch Fyne; E7, Loch Etive; and L10, Loch Linnhe, as a function of depth in sediment. Values given are means of values obtained from two cores.

Depth profiles of extractable iron (Fig. 5), in contrast to manganese, showed no clear gradients with depth. In addition, the concentration differences between Linnhe and the other lochs were much less pronounced. Ferrous iron is very labile towards autoxidation and would be expected to be oxidised to ferric hydroxide at the redoxocline. The depth for 50% penetration of oxygen into the sediment was measured in Linnhe (Overnell *et al.*, 1995) and found to be approx. 2 mm. Oxygen would be expected to penetrate less in Goil because of the quieter water, but the redoxocline is probably still within the sediment since the bottom waters do not go anoxic (Mackay and Halcrow, 1976; Edwards *et al.*, 1986). Using the rate equation and rate constant for the autoxidation of Fe^{II} (Stumm and Morgan, 1970) at pH 8.0, 10°C and an oxygen partial pressure of 0.02 (0.2 for air-saturated water), the Fe^{II} oxidation turnover time is 2.5 min. Therefore, an enrichment process similar to that of Mn should operate for iron and hence insoluble iron should be similarly enriched near the surface. It was therefore surprising that there was no evidence for an elevated concentration of extractable iron at the surface. Although a small enrichment in the top few mm of the sediment would have been missed because of the 2 cm sampling intervals, other workers using 1 cm intervals (Sørensen and Jørgensen, 1987) or 1 mm intervals (Thamdrup *et al.*, 1994*a*) also found no surface enrichment of total extractable iron.

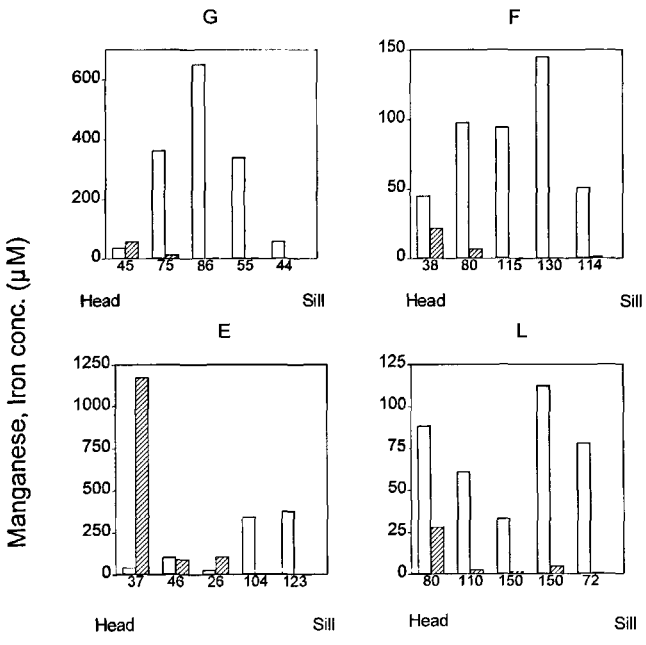

Figure 6

Concentrations of porewater manganese (unfilled bars) and iron (diagonal shading) from sediments from different stations; G, Loch Goil; F, Loch Fyne; E, Loch Etive and L, Loch Linnhe; 0-2 cm depth interval. Numbers on abscissae are station depths in metres. Note differences in ordinate values.

However the latter authors did find significant surface enrichment of solid phase oxalate-extractable $iron^{III}$, but this was nearly matched by a surface depletion of oxalate-extractable non-sulphide $iron^{II}$.

Distribution of porewater manganese and iron

The maximum concentrations of porewater manganese for Goil and Fyne, (600 µM); Etive, (400 µM) (Fig. 6 and 8) are higher than most reported values for marine sediments (5-400 µM) (Aller, 1980, 1990; Christensen, 1989; Sugai, 1987; Sundby and Silverberg, 1985). The maximum concentrations for Linnhe are considerably lower (100 µM) than for the other lochs. The concentration of porewater manganese will probably be controlled by the solubility product of rhodochrosite ($Mn(II)CO_3$) and the concentration of the carbonate ion (CO_3^{2-}). The carbonate ion is in turn controlled by pH and total CO_2 and hence by mineralization of organic matter.

In contrast to porewater Mn, porewater Fe concentrations in the top 2 cm were highest at the heads of the lochs (Fig. 6). This was most pronounced in Etive which had values of 1174 µM Fe^{2+} at the head and 4µM Fe^{2+} in the deep water. These porewater iron distributions are contrary to those of extractable iron (Fig. 2). The reason for this is unclear but one factor may be due to different reactivities of iron species (Canfield *et al.*, 1992) at the head compared to other sites in the loch.

Another factor may be that since manganese oxides probably act as efficient oxidants for Fe^{2+} (Canfield, 1993*b*; Thamdrup *et al.*, 1994*a*), low manganese in the sediment (Fig. 2) may allow the iron to break through to the oxic surface.

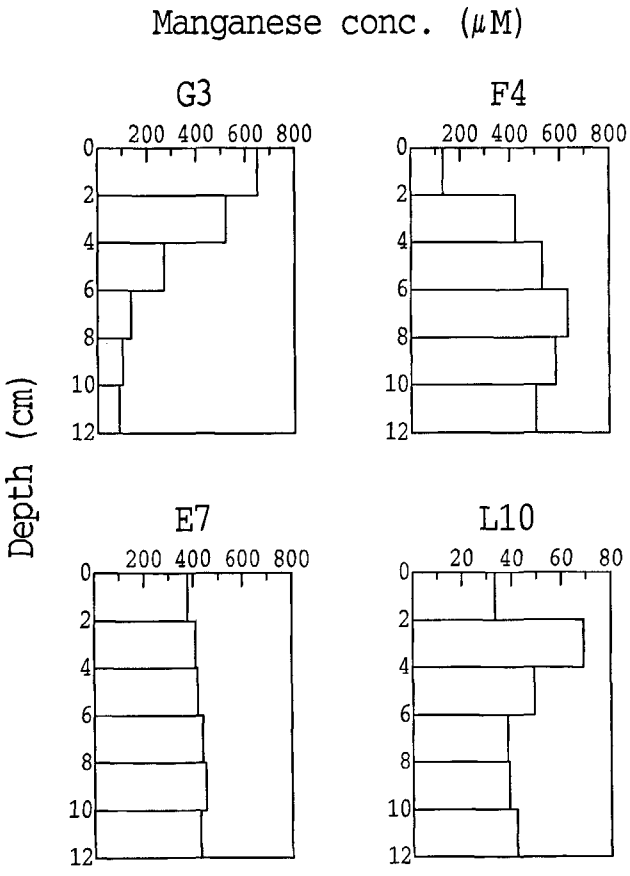

Figure 7

Concentrations of soluble manganese in porewater; G3, Loch Goil station G3; F4, Loch Fyne; E7, Loch Etive and L10, Loch Linnhe; as a function of depth in sediment. Values given are means obtained from two cores from four different sampling times for Goil and Fyne and one for Etive and Linnhe. Note: the difference between concentration scales for Loch Linnhe and the other lochs.

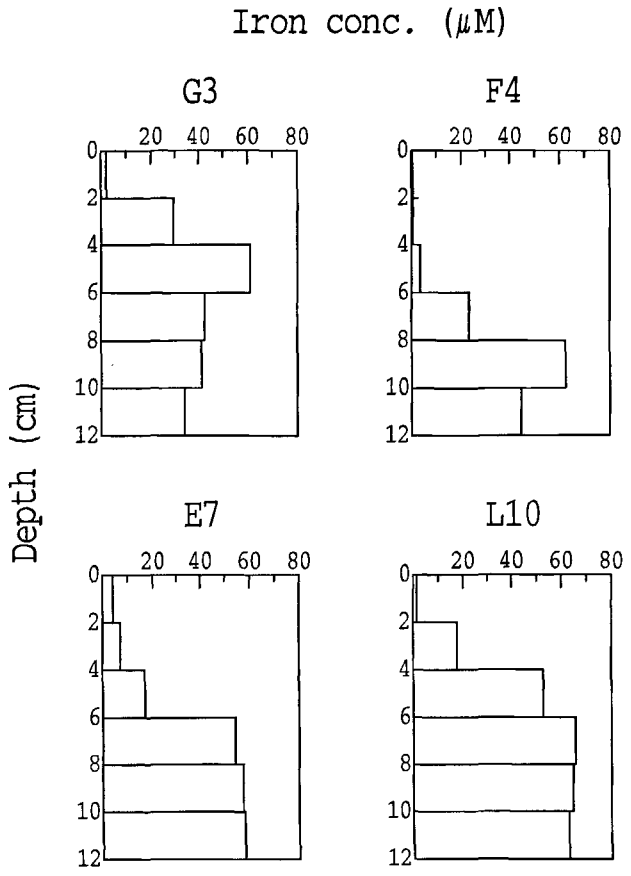

Figure 8

Concentrations of soluble iron in porewater; G3, Lochs Goil station G3; F4, Loch Fyne; E7, Loch Etive and L10, Loch Linnhe; as a function of depth in sediment. Values are means obtained from two cores obtained from four different sampling times for Goil and Fyne and one for Etive and Linnhe.

• Depth profiles

In Fyne and Linnhe the surface (0-2 cm) sediments are low in pore water manganese, but there are subsurface maxima (Fig. 7). These are deeper than those for solid phase manganese and are consistent with solution at depth followed by diffusion of the dissolved manganese upwards to be precipitated and deposited on or below the sediment surface. In contrast to these two lochs, Etive showed little variation in the pore water manganese concentrations with depth, whilst Goil showed high concentrations of both solid and dissolved Mn near the sediment surface (0-2 cm). Finer depth scale resolution for Goil might reveal a spatial separation of the different Mn phases similar to that for Fyne and Linnhe.

In Goil, Fyne and Linnhe, the maximum dissolved iron concentration occurs lower in the sediment than the peak of manganese concentration, presumably under more reducing conditions (Fig. 8). This situation may reflect the different reactivities of Mn and Fe oxides to either direct bacterial reduction (Froelich *et al.*, 1979) or to indirect reduction *via* bacterially produced sulphide (Canfield *et al.*, 1992) or other reduced compounds, or may reflect the lower $E^{o'}$ value for the reduction of FeOOH compared with that for MnO_2. In effect the low surface values generally found for Fe^{2+} profiles could represent the redox equilibrium between manganese and iron. There is, however, growing evidence that manganese and iron oxides are directly reduced in microbiological organic matter oxidation within sediments (Sørensen, 1982; Sørensen and Jørgensen, 1987; Lovley, 1991; Nealson, 1992 and references therein; Coleman *et al.*, 1993; Roden and Lovley, 1993; Lovley *et al.*, 1993). In sediment with similarly high metal oxide concentrations to this study, Mn and Fe reduction has been estimated to be the dominant pathway of organic matter degradation (50-90%, Canfield *et al.* 1993*a*, *b*), which would imply that this is probably also the case in Goil, Fyne and Etive.

Manganese^{2+} flux

Assuming steady state conditions, the efflux of manganese^{2+} should give an estimate of the amount of (solid phase) manganese^{IV} settling to the sediment surface following aerobic oxidation in the water column above. Directly measured manganese fluxes showed wide variation (Tab. 3) and were therefore not considered reliable, the values were however generally small compared with the oxygen uptake. For estimating fluxes from the porewater gradient at the surface a finer resolution profile near the surface is required than that measured here because porewater manganese can shows a steep gradient near the sur-

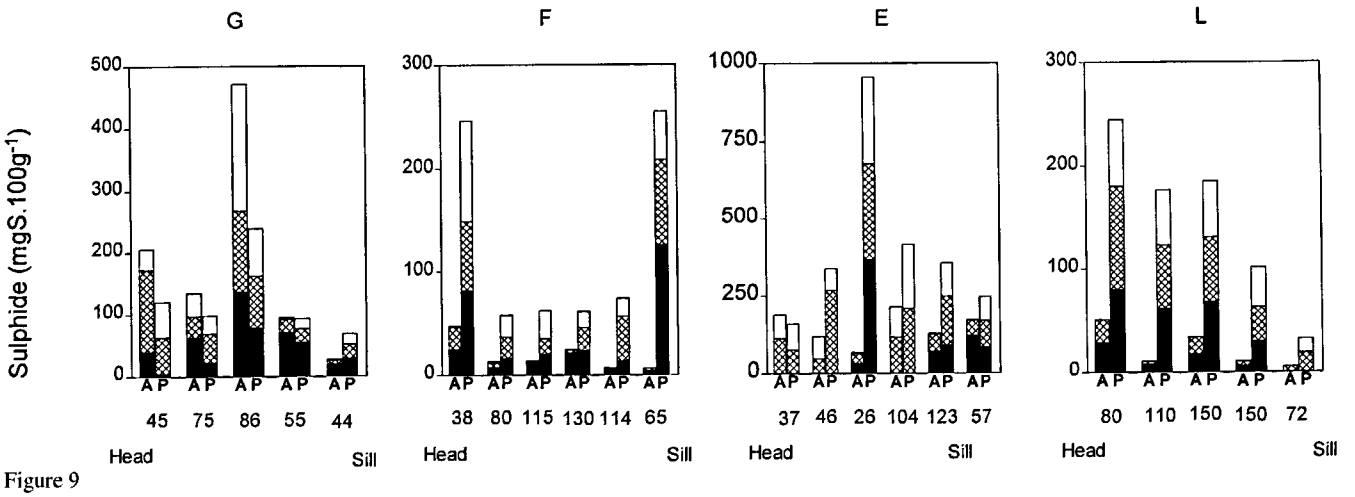

Figure 9

Concentrations of sulphide in sediment as AVS and as PVS, unfilled bar, 0-5 cm, hatched bar, 5-10 cm, filled bar 10-15 cm. A, AVS; P, PVS. Values for Lochs Goil and Fyne are averages of duplicate determinations on single cores from four dates and for Lochs Etive and Linnhe, averages of duplicate determinations on single cores. Note: for two stations in Etive and one in Linnhe 10-15 cm values are not available.

face (*e.g.* Lian and Hunter, 1986; Thamdrup *et al.*, 1994*b*). In addition, the calculated diffusive effluxes from sediments in Aarhus Bay were 3-16 times greater than those directly measured in a flux chamber, which must have been due to oxidation of the manganese^{2+} by oxygen at the sediment surface (Thamdrup *et al.*, 1994*b*). Although higher fluxes were observed from cores found to have larger animals (Thamdrup *et al.*, 1994*b*), in the absence of surficial oxidation of Mn^{2+} the effect of bioirrigation should have been to increase the observed fluxes to values higher than those calculated from the porewater gradients (*e.g.* Rutgers van der Loeff *et al.*, 1984). Therefore no estimates of manganese fluxes have been made based on the porewater profiles measured in this work.

Concentration of reduced sulphur in the sediment and rates of sulphate reduction

While sulphate is present methanogenesis is not important. Methanogenesis becomes important only at sulphate concentrations below approx. 2.5 mM (Devol *et al.*, 1984; Iversen and Jørgensen, 1985). In this work there was little depletion of sulphate with depth and the lowest porewater sulphate concentration was 25 mM.

There are considerable differences in the amounts of total sedimentary sulphide (TSS) as AVS and PVS at different depths in the sediment and at different stations in the four lochs (Fig. 9). This is particularly evident between Goil and Fyne – two lochs which are similar to each other in terms of near surface Mn and Fe distribution (Fig. 2 and 6). Thus not only are the concentrations of AVS higher than PVS in Goil compared with Fyne (*see* below), but also in Goil TSS is higher and is at a maximum at the deepest station, whereas in Fyne the maximum TSS is near the head and sill. The highest sulphide concentrations in Etive were at station E5 (26 m).

In the top depth interval (0-5 cm) the proportion of TSS as PVS is greater or much greater than that as AVS (Fig. 10), except for stations G2 (75 m), G3 (86 m) and E4 (46 m). Lower in the sediments the proportion of sulphide fixed as

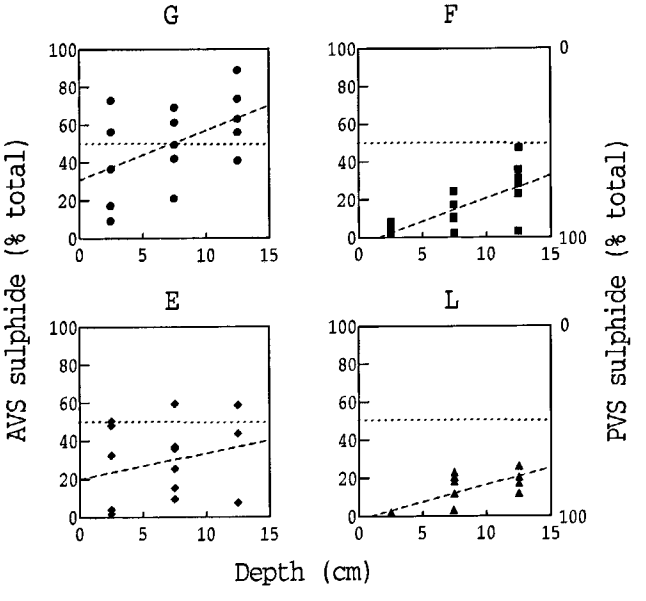

Figure 10

Distribution of sediment AVS sulphide as a percentage of total sulphide (AVS+PVS) with depth. G, Loch Goil; F, Loch Fyne; E, Loch Etive; L, Loch Linnhe. Data from all stations and all depths.

PVS decreases with depth, but with the exception of Goil, PVS is still the dominant form of reduced sulphur. Clear differences between the lochs are evident with Goil having the highest proportions of AVS and Fyne and Linnhe the lowest (Tab. 1). In terms of AVS and PVS concentrations (Tab. 1) Fyne and Linnhe are similar with lower total sulphide compared with Goil and Etive.

In addition to fixed sulphides, the rates of sulphate reduction were also measured (Fig. 11). Clear differences in the total rates are evident, with the highest rates in Linnhe and the lowest in Fyne. Within a loch, the highest total sulphate reduction rate occurs at the deepest station in Goil and at the head in Fyne. In the other two lochs higher values prevail at both the head and sill rather than at the deep stations.

Table 1

Concentrations of sulphur as iron monosulphide and as iron pyrite in sediment. Values are mean concentrations for all depths and stations within a loch. Relative sulphide retention is mean for all stations of total sulphide concentration divided by total sulphate reduction rate, normalised to 100 for Loch Etive.

Loch	AVS	PVS	Total	AVS (% of total)	Relative S^{2-} retention
	(mg S.100g sed^{-1})				
Goil	62	41	104	60	23
Fyne	6	42	49	13	22
Etive	62	168	230	27	100
Linnhe	8	53	61	12	6

The relative rates of sulphate reduction to AVS and to PVS at each station also shows considerable variation. There is an apparent association between the rate of sulphate reduction to AVS (expressed as a percentage of the total rate) and the total rate (AVS + PVS) for Goil, Fyne and Etive (Fig. 12), although only in Fyne and Etive is the association significant ($p < 0.05$, two tailed test). Thus in these lochs the higher the total rate of sulphate reduction the greater is the proportion of reduced sulphur in the form of AVS. This is in agreement with a number of previous studies (for example Parkes and Buckingham, 1986; Thode-Andersen and Jørgensen, 1989; Fossing, 1990). However, in the case of Linnhe there is no apparent association between the two. Here total rates are generally much higher than the other lochs and the proportion as AVS much lower. The explanation of these differences between lochs requires an understanding of the mechanism for the both the immediate formation of reduced sulphur products (*i.e.* as determined after the one day incubation period used in the sulphate reduction assays) and any longer term transformations. Mechanisms of the interaction of hydrosulphide with sedimentary minerals are poorly understood although they are the subject of much recent research (*e.g.* Elsgaard and Jørgensen, 1992; Canfield *et al.*, 1992). In Linnhe resuspension events, known to occur at most spring tides (Overnell and Young, 1995), may be responsible for both the higher total sulphate reduction rates, due to rapid burial of organic matter (Berner and Westrich, 1985) and the greater importance of PVS, due to frequent exposure of the sediment to oxygenated water and other oxidised compounds (*e.g.* iron oxides).

Temporal variation

Any influence of season, and in particular the input of phytoplankton organic carbon, on the rates and concentrations would be expected to be greatest at the topmost horizons of the sediment. Fyne and Goil were visited on four occasions on which oxygen and manganese fluxes, sulphate reduction rates and porewater manganese concentrations were measured. The results for these at the deepest stations are given in Table 3. (Sulphate reduction rates to AVS only is given because at this depth formation of PVS was small).

The annual spring phytoplankton bloom would have been expected around the end of March/beginning of April. Thus it is possible that the high oxygen uptake by the sediment in Fyne on the 3 April could reflect the impact of the spring bloom. This increase in oxygen uptake is similar to that expected on the basis of the phytoplankton carbon flux in Linnhe (Overnell *et al.*, 1995). This date also showed the highest porewater manganese in the 0-2 cm depth interval, consistent with more reducing conditions in the sediment. The oxygen uptake data for Goil imply that the expected phytoplankton bloom had not settled by the 29 March. The data presented in the figures are means of all these values. No data are available on the temporal variation in Etive, but in Linnhe there was no change in

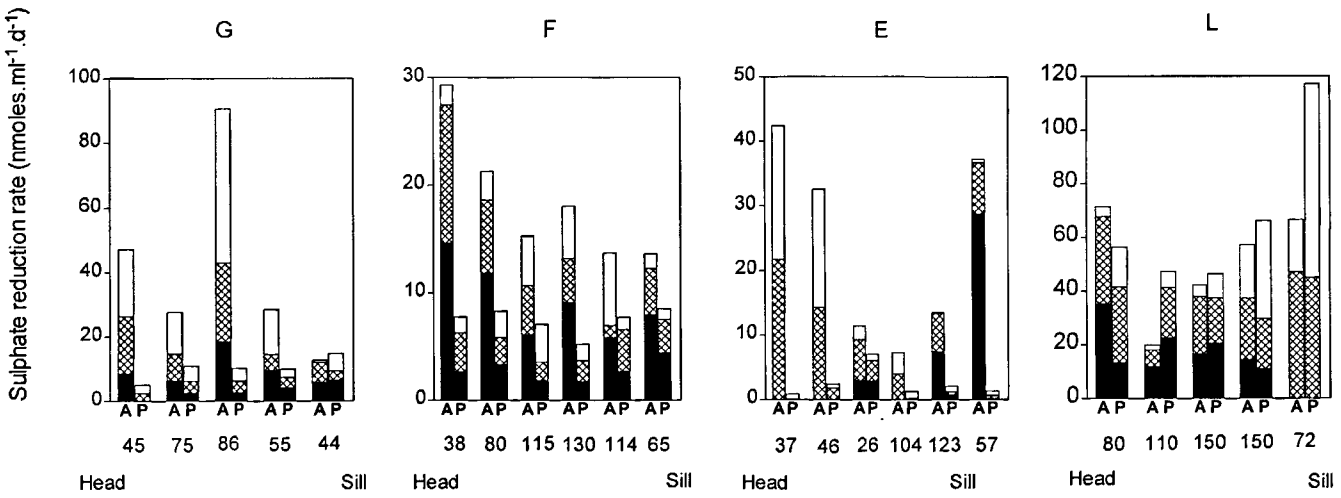

Figure 11

Sulphate reduction rates to AVS and to PVS. Unfilled bar, 0-5 cm, hatched bar, 5-10 cm, filled bar 10-15 cm. A, AVS; P, PVS. G, Loch Goil; F, Loch Fyne; E, Loch Etive; L, Loch Linnhe. Values for Lochs Goil and Fyne are averages of duplicate determinations on single cores from four dates and for Lochs Etive and Linnhe, averages of duplicate determinations on single cores. Note: differences in ordinate scales, and for two stations in Etive and one in Linnhe 10-15 cm values are not available.

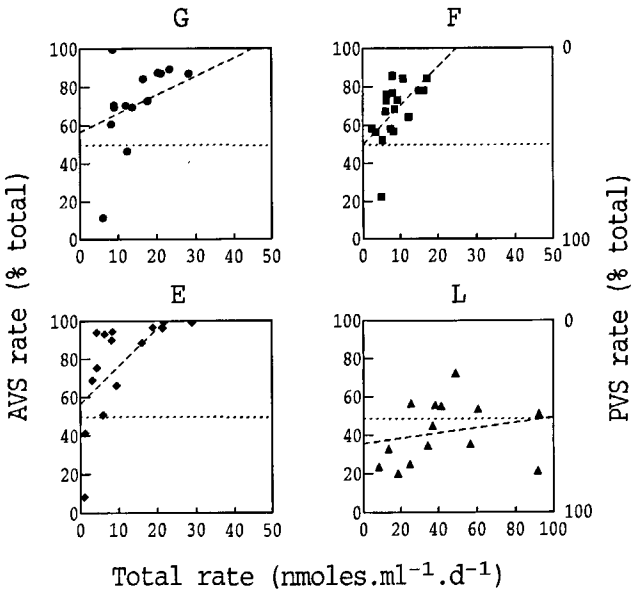

Figure 12

Relationship between the rate of sulphate reduction to AVS, expressed as a percentage of total rate (AVS+PVS), and the total rate of sulphate reduction; G, Loch Goil; F, Loch Fyne; E, Loch Etive; L, Loch Linnhe. Data included for all depths in the sediment and for all stations.

sulphate reduction rate following the impact of the bloom, although there was an increase in oxygen uptake of 8 mmoles.m^{-2}.d^{-1} (Overnell *et al.*, 1995).

The contribution of rates of oxygen uptake, manganese reduction and depth-integrated sulphate reduction to organic matter degradation

The oxygen uptake rates for these loch sediments ranged from 8-24 mmoles.m^{-2}.d^{-1} (Tab. 2) at ambient temperature (approx. 9-11°C). The oxygen uptake rates found here are similar to the values of 13.6- 24.6 mmoles.m^{-2}.d^{-1} found in Etive and Eil by Parkes and Buckingham (1986) at a similar temperature. Much higher rates, (38-106 mmoles.m^{-2}.d^{-1}) were found by Hopkinson (1985) for sediments of the Georgia Bight at 10-27°C and 40-120 mmoles.m^{-2}.d^{-1} for Cape Lookout Bight, North Carolina (Chanton *et al.*, 1987), also at 10-27°C - in both these cases the high values were correlated with the high temperatures. For sediments from Fanafjorden, Norway, (Wassmann, 1984) oxygen uptake rates of 16-30 mmoles.m^{-2}.d^{-1} were found at temperatures of 6-10°C.

Manganese cycling in Goil, Fyne and Etive is clearly important because of the high levels found. Whether the oxidised manganese represents a terminal electron acceptor available to bacteria involved in the mineralization of organic carbon can not be answered from these studies. To answer this question laboratory incubations need to be made as well as measurements of carbon inputs and of within-sediment manganese cycling, including biological mixing of solid manganese (*cf.* Aller, 1990). Oxygen uptake represents a measure of the amount of organic material directly oxidised by oxygen plus the amount oxidised via manganese (and iron) plus a fraction of the amount oxidised via sulphate reduction due to reoxidation of sulphide species produced from sulphate. Oxygen uptake and sulphate reduction are largely coupled provided that sulphide burial is small.

Table 2

Total sulphate reduction rates (AVS + PVS) calculated on an area basis down to 15 cm and oxygen uptake rates also calculated on an area basis. Lochs Goil and Fyne, averages of measurements on single cores on four dates, Lochs Etive and Linnhe, averages of determinations on single cores. Duplicate determinations for sulphate reduction, single for oxygen uptake. The last column (Relative sulphate reduction rate) is the ratio of the sulphate reduction rate (down to 15 cm) to the oxygen uptake rate, on a per unit area basis, expressed as a percentage (assuming that SO_4^{2-} has twice the oxidative capacity of O_2).

Station	Sulphate reduction	Oxygen uptake	Relative sulphate reduction	Station	Sulphate reduction	Oxygen uptake	Relative sulphate reduction
	(mmoles.m^{-2}.d^{-1})		%		(mmoles.m^{-2}.d^{-1})		%
Head				Head			
G1	2.62	23.6	22	F1	1.87	17.3	22
G2	1.94	21.5	18	F2	1.48	11.4	26
G3	5.13	18.8	55	F3	1.12	13.3	17
G4	1.93	15.1	26	F4	1.28	20.4	13
G5	1.38	17.9	15	F5	1.07	12.8	17
Sill				F6	1.11	10.7	21
				Sill			
Mean	2.60	19.4	27	Mean	1.32	14.3	19
Head				Head			
E2	2.17*	22.9	19	L18	6.40	19.0	67
E4	1.76*	8.0	44	L15	3.38	10.8	63
E5	0.93	16.9	11	L10	4.45	14.8	60
E6	0.43*	11.0	8	L7	6.18	11.8	105
E7	0.78	19.2	8	L0	9.40*	7.2	-
Sill				Sill			
E9	1.94	52.3	7				
Mean[a]	1.34	15.6	18	Mean[b]	5.10	14.1	74

* Integrated down to 10 cm only.
[a], [b] Mean values do not include E9 or L0 values.

Sulphate reduction rates calculated per unit area (Tab. 2, 0.43-6.2 mmoles.$m^{-2}.d^{-1}$, are similar to those for other coastal environments (0.65-7.75 mmoles.$m^{-2}.d^{-1}$ in the Gulf of Maine, Christensen, 1989; and 0.95-7.29 mmoles.$m^{-2}.d^{-1}$ for the Baltic-North Sea transition, Jørgensen *et al.*, 1990).

Measurements of the percentage of sulphide reoxidation have ranged from 96% at a low sedimentation site to 68% at a high sedimentation site (Jørgensen *et al.*, 1990). A value of 15% of precipitated sulphide permanently buried was estimated for Aarhus Bay (Thamdrup *et al.*, 1994). Sedimentation data is available for site L14, 12.7 g.$m^{-2}.d^{-1}$ (Overnell and Young, 1994). Assuming a similar burial rate at the adjacent L15 site gives a burial rate for sulphide of 0.27 mmoles.$m^{-2}.d^{-1}$, or only 2.5% of the 0-14 cm depth integrated sulphate reduction rate. Using the sedimentation rate for E7 of 0.86 cm.y^{-1} (Ridgway and Price, 1987) a figure of approx. 61% is obtained for the fraction of 0-15 cm depth integrated reduction rate which is buried. Thus the two processes were tightly coupled in Linnhe, possibly assisted by the frequent resuspension events suggested by other chemical differences between this and the other lochs, but only loosely coupled in Etive where the deep station is quiet.

The coring techniques used did not allow sulphate reduction rates to be made to sufficient depth to enable the total depth integrated rate to be estimated. Therefore the integrated rates down to 15 cm (or in some cases 10 cm) will represent an underestimate of the total sulphate reduction rate (*e.g.* Parkes and Buckingham, 1986 –43% sulphate reduction in the top 15 cm). Nevertheless, for Goil, Fyne and Etive aerobic oxidation (including that mediatied by manganese cycling) appears to be the dominant organic carbon degradation process with sulphate reduction only accounting for 27, 19 and 18% respectively of the oxygen uptake rate (Tab. 2). In Linnhe sulphate reduction is the dominant degradation process in the sediment with a mean of 74% (Tab. 2).

These calculations do not consider different amounts of sulphide potentially buried in each loch. In the absence of sedimentation rate data at all the stations, a first order approximation of the amount of sulphide available for burial, and hence the degree of coupling of sulphate reduction and oxygen uptake, can be obtained by comparing the ratios of the mean total sulphide and the mean total sulphate reduction rates in the same sediments. For clarity these values have been normalized to 100 for Etive (Tab. 1), as Relative Sulphide Retention (RSR), thus high RSR values correspond to a low degree of coupling and low RSR values to a high degree of coupling. On this basis the degree of coupling is greatest in Linnhe with a (normalised) value of 7 and least in Etive with a value of 100. This is consistent with Linnhe having one of the lowest sediment sulphide concentrations, and Etive the highest.

Oxygen uptake rates and organic matter content

All lochs show a small elevation in oxygen uptake rates at the sites nearest the head of the loch, and except in the case of Fyne, these values are the highest found in the loch (Tab. 2). These elevated values presumably reflect the degradation of riverine particulate organic carbon (POC) input, most of which may be expected to have settled near of the heads of the lochs. This would be consistent with studies in other river systems. For example C^{13} measurements in the Gironde estuary suggest that about half of the riverine POC is decomposed at the fresh/saltwater interface (Eisma, 1985).

The highest organic matter concentrations in the top 2 cm (as measured by loss on ignition) tend to occur at the deepest sites, with concentrations in Goil, Fyne and Etive being similar (Fig. 13). Significantly lower (two-tailed t test) organic matter concentrations occur in Linnhe compared with each of the other lochs, the mean concentration in Linnhe being about half that of the other lochs. Organic matter concentrations showed some elevation at the heads of Fyne and Etive, possibly reflecting the input of more recalcitrant organic matter fractions of terrestrial origin. The organic matter content at the deepest water stations varied little with depth in the sediment (data not shown) indicating that the organic material was largely recalcitrant with respect to anaerobic degradation. In Linnhe the lower levels of organic matter probably reflect the greater importance of aerobic degradation due to resuspension events (Overnell and Young, 1995). Aerobic degradation is more complete for terrestrially derived organic matter since anaerobic processes do not degrade cellulose. An alternative explanation for the lower organic carbon might be that bioturbation was greater in Linnhe than in the other lochs, however a ^{210}Pb profile in Linnhe showed no evidence for biological mixing below 9 cm (Overnell and Young, 1995).

As sedimentary organic matter largely consists of material which is resistant to decomposition, there is

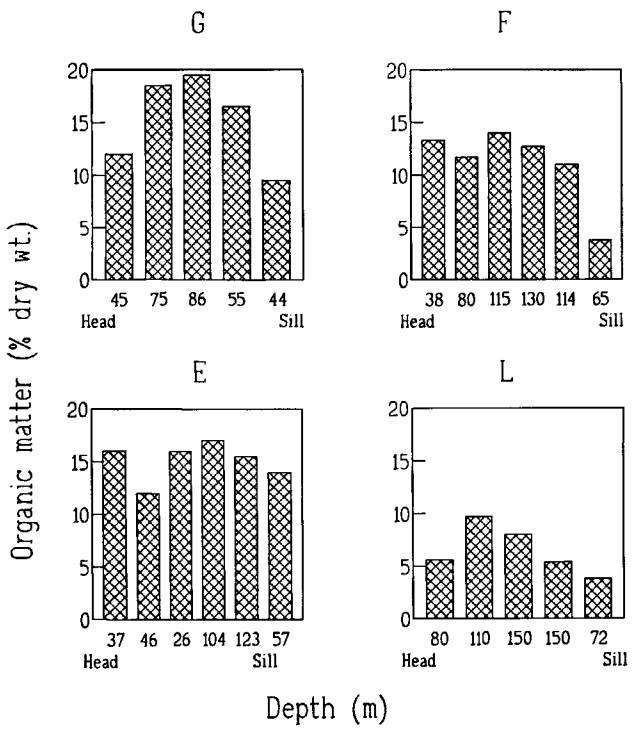

Figure 13

Concentrations of organic matter (loss on ignition) in top 2 cm of sediments from different stations; G, Loch Goil; F, Loch Fyne; E, Loch Etive and L, Loch Linnhe.

Table 3

Oxygen flux, manganese flux, sulphate reduction rate to AVS only and porewater manganese in 0-2 cm depth interval, at various dates at the deepest stations of Lochs Goil and Fyne.

Loch Goil Station G3

	12 Jan	2 Mar	29 Mar	8 Nov	
O_2 Flux	20.6	18.2	18.0	18.5	mmoles.m^{-2}.d^{-1}
Mn Flux	18.2	0.4	nm	0.18	mmoles.m^{-2}.d^{-1}
AVS 0-5cm	35	33	16	107	nmoles.ml^{-1}.d^{-1}
Porewater					
Mn 0-2cm	649	651	734	568	μM

Loch Fyne Station F4

	10 Jan	28 Feb	3 Apr	9 Oct	
O_2 Flux	10.3	16.6	41.3	13.1	mmoles.m^{-2}.d^{-1}
Mn Flux	0.13	1.3	nm	0.77	mmoles.m^{-2}.d^{-1}
AVS 0-5cm	13.2	1.6	1.9	2.6	nmoles.ml^{-1}.d^{-1}
Porewater					
Mn 0-2cm	101	21	155	135	μM

only a poor correlation between this material and degradative activity rates (oxygen consumption and sulphate reduction).

CONCLUSIONS

This study has revealed large differences in the sediment characteristics and organic matter degradation rates in four sea lochs. These appear outwardly similar in that they all have deep basins behind shallow sills which limit the tidal exchange with the basins to varying degrees. At the deepest stations in the lochs the surface concentrations of extractable manganese are positively correlated to the turnover times of the deep water, being highest in Etive and lowest in Linnhe. The mean ratio of buried sulphide to sulphate reduction rate (Relative Sulphide Retention) is also highest in Etive and lowest in Linnhe. Thus stagnant water allows the efficient return of reduced manganese to the sediments in the case of Etive and active tidal exchange, probably involving resuspension, gives rise to both increased sulphate reduction and chemical reoxidation of the authigenic sulphide in Linnhe. It is suggested that many of the biogeochemical differences between the lochs may be explained on the basis of the extent and vigour of the exchange of the bottom waters of the basins with the open sea.

These lochs appear to have many characteristics which would make them ideal as natural laboratories for studying the biogeochemistry of a range of marine environments and the biogeochemistry of the freshwater/marine transition. Goil, Fyne and Etive have seasonally stagnant deep water in which changes in nutrient concentrations could give estimates of sediment/water fluxes for comparison with flux chamber measurements. In addition the different manganese concentrations in the surface of the sediments of these lochs offer the opportunity to study the role of manganese in organic matter oxidation. Linnhe sediments are probably regularly resuspended and involvement of manganese is unlikely. This loch offers the opportunity to study the effects of regular resuspension on organic matter degradation (for example, Overnell *et al.*, 1995).

APPENDIX

Coordinates of station positions

Loch Goil

Station no.	Lat.	Long.	Depth (m)
Head			
G1	569.9'N	454.3'W	45
G2	8.9'	53.5'	75
G3	8.1'	53.5'	86
G4	7.3'	53.8'	55
G5	6.6'	53.6'	44
Sill			

Loch Fyne

Station no.	Lat.	Long.	Depth (m)
Head			
F1	56 14.9'N	4 57.9'W	38
F2	14.2'	5 0.3'	80
F3	13.2'	3,7'	115
F4	10.8'	5.6'	130
F5	9.7'	7.1'	114
F6	7.8'	12.6'	65
Sill			

Loch Etive

Station no.	Lat.	Long.	Depth (m)
Head			
E2	56 32.5'	5 05.1'	37
E4	30.5'	07.1'	46
E5*	29.9'	08.7'	26
E6	28.8'	09.2'	104
E7	27.4'	11.0'	123
Sill			
E9	27.3'	15.2'	57

Loch Linnhe

Station no.	Lat.	Long.	Depth (m)
Head			
L18	56 48.9'N	5 07.6'W	80
L15	47.5'	09.3'	110
L10	46.3'	11.2'	150
L7	45.4'	12.3'	150
L0	43.9'	14.3'	72
Sill			

*Note this station off the centre line of the loch.

Sill depths and currents

When more than one sill is present the lowest identifying number is closest to the open sea and the highest closest to the upper basin. Currents are the mean speeds over a spring tidal cycle. Data from Edwards and Sharples (1985).

Loch	Goil	Fyne		Etive						Linnhe
Sill no.		1	2	1	2	3	4	5	6	
Max. depth (m)	16	36	42	9	7	8	12	54	13	18
Mean depth (m)	13	20	16	7	4	5	8	12	8	9
Mean current ($cm.s^{-1}$)	14	37	13	61	172	76	26	17	66	164

Acknowledgement

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