Manganese Geochemistry in the Catchment, Waters and Sediments of Loch Bradan, S.W. Scotland

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Declaration

The work presented in this thesis is entirely my own work, except where reference is made to other sources. Some of the work has been published elsewhere, but the work has not been submitted in part or in whole for any other degree.

Edinburgh, 24.09.99

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Manganese Geochemistry in the Catchment, Waters and Sediments of Loch Bradan, S.W. Scotland

Loch Bradan, a drinking water reservoir in a mineralised area of the Galloway Hills, south-west Scotland, frequently exhibits dissolved Mn concentrations of greater than 50 $\mu g\ l^{-1}$, the EC maximum admissible concentration for Mn. As a result of this problem, West of Scotland Water employs expensive ozonation treatment to precipitate out MnO_2 before the water is distributed to customers.

The underlying reasons for the surprisingly high dissolved Mn concentrations, given the well-oxygenated status of the loch, were investigated by determining Mn concentrations, associations and behaviour in both Loch Bradan and its catchment. Peat cores and input stream water from the catchment along with sediment cores, pore water and loch water from Loch Bradan were collected. In sections of the peat and thinly sliced sediment cores, pseudo-total Mn, as well as easily reducible Mn, and humic-associated Mn were determined. Concentrations of dissolved Mn at different depths in the Loch Bradan water column, pore water and input streams were measured in filtered and subsequently fractionated (< 1 kDa and > 1 kDa) samples.

Near-surface enrichments (up to 7 % dry weight) of Mn were present in all sediment cores leading to the conclusion that redox cycling was the principal process controlling the vertical distribution of Mn in the upper regions of the sediments. The occurrence of redox cycling in sediments typically results in the retention of Mn within the solid phase and thus minimal release of Mn into water column. At greater depth within the sediment, the presence of insoluble inorganic species such as carbonates and Fe oxides also influenced the vertical distribution of Mn. Although redox cycling also influenced the distribution of Mn within the peat cores, it was concluded that, in contrast to the loch sediments, Mn was not necessarily retained within the peat since lateral water flow could result in transport of dissolved Mn from reducing zones of the peat into proximal stream waters. The peaty catchment, therefore, represented a source of Mn to the stream waters feeding into Loch Bradan.

Analysis of both stream and loch waters showed total dissolved Mn concentrations greatly in excess of the EC maximum admissible concentration. Humic substances clearly play an

important role in sustaining these high concentrations, with > 50 % and 33-67 % of the total dissolved Mn for the loch and stream water, respectively, occurring in the > 1 kDa size fraction. Nevertheless, kinetic factors inhibiting the oxidation of Mn(II) must also be important in maintaining the concentration of dissolved inorganic Mn.

Further investigation of the associations of Mn within the sediment and pore waters showed that Mn also interacted with humic substances in the sediment. In particular, association with humic substances inhibited, to some extent, the oxidation and precipitation of dissolved Mn in the pore water. Diffusion of Mn-humic complexes into the overlying waters provided an additional route by which Mn could enter the loch waters. The terrigenous nature of the sediment humic material meant, however, that release of Mn-humic complexes from the sediment could not be distinguished from transport of catchment Mn-humic complexes via stream waters.

1. Rationale for Study and Layout of Thesis

Loch Bradan, a drinking water reservoir situated in the Galloway Hills, south-west Scotland (Fig 1.1), exhibits dissolved Mn levels that exceed the EC maximum admissible concentration of 0.05 mg l^{-1}. As a consequence West of Scotland Water have installed an expensive ozonation treatment plant in order to reduce the dissolved Mn levels. This phenomenon is not restricted to Loch Bradan or, indeed, to Scotland, and is known to occur elsewhere in the world.

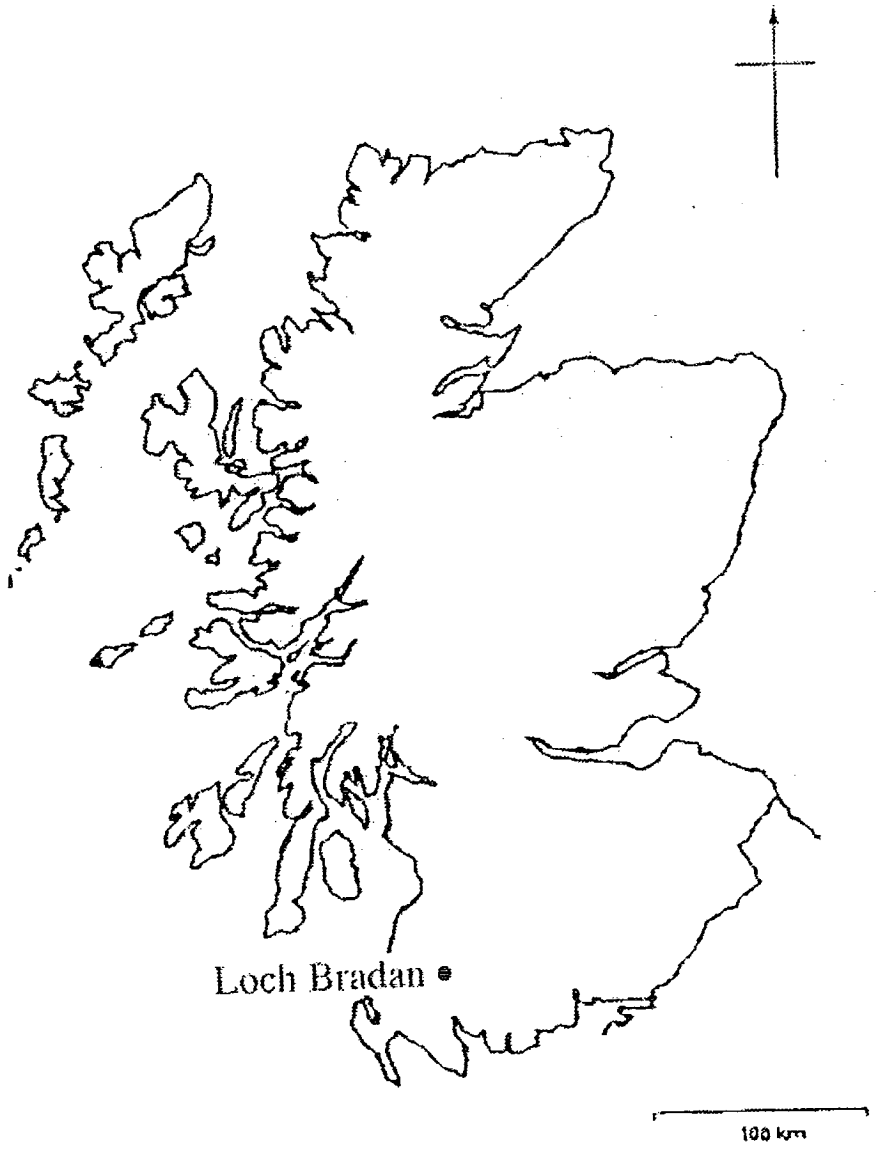

Fig. 1.1: Location of Loch Bradan

Dissolved Mn has been linked with neurological disorders (Kondakis *et al.*, 1989), but at levels much higher than those observed at Loch Bradan. The levels in Loch Bradan lead to aesthetic and distribution problems. If Mn precipitates out in the distribution pipes it can lead to restricted water flow, the presence of black particulates in tap water, and the staining of clothes in washing machines.

This study has investigated the factors that are controlling the concentration of dissolved Mn in Loch Bradan. In addition, comparisons have been made with the behaviour of other chemical entities in both Loch Bradan and the nearby Loch Riecawr.

The thesis has the following structure. Chapter 2 is a review of the behaviour of manganese and other entities within lake systems. Chapter 3 is an overview of the site locations and also the experimental methods used during this study. Chapters 4, 5 and 6 contain the results and discussion of the processes occurring in Loch Bradan. Chapter 4 focuses on the metal concentrations observed in the sediments of Loch Bradan with particular attention being paid to the role of redox cycling. Chapter 5 deals with the catchment of Loch Bradan, relating to both the effect of redox cycling on the observed results, and also the association of Mn, and Fe, with the organic component of the catchment and its effect on mobility. In Chapter 6 the associations of naturally occurring organics are further investigated in the sediments of both Loch Bradan and Loch Riecawr, and also in the water column of Loch Bradan. Concluding remarks and an overall summary can be found in Chapter 7, with the results of the previous three chapters being considered as a whole in order to identify and assess the possible causes of the high levels of dissolved Mn observed in Loch Bradan.

2. The Behaviour of Manganese and Other Redox Active Elements in Lake Systems

The behaviour of metals in lake systems is affected by a number of controlling factors, including pH, redox potential, and associations of the metals with organic and inorganic components of the system. All of these factors affect the concentration, form and mobility of metals within the lake water and sediment (including pore water) and, indeed, in the surrounding catchment area.

2.1 Sources of Manganese in Lake Systems

2.1.1 The Release of Manganese from Lake Catchments

Manganese is a member of the first transition series, which is present exclusively as ^{55}Mn which has an atomic number of 25. It has seven electrons in its valence shell, $3d^5$, $4s^2$, meaning that a maximum charge of 7+ can be seen for Mn.

Manganese enters lakes principally as a result of weathering of basement rocks, with direct anthropogenic atmospheric inputs being comparatively negligible (Eisenreich, 1980). The worldwide emission of Mn into the atmosphere in 1983 was 10.56×10^6 - 65.97×10^6 kg yr^{-1} (Nriagu and Pacyna, 1988). The majority of Mn present in rocks occurs as reduced Mn(II) because crystallisation of the rocks occurred under reducing conditions. Examples of Mn-containing minerals can be seen in Table 2.1 which includes oxides, hydroxides, sulphides, chlorides and carbonates. As well as the minerals shown in Table 2.1, Mn can also exist as silicates, arsenates, arsenites, phosphates, sulphates and borate minerals. The weathering of the basement rocks results in Mn being released directly into the lake and also into the surrounding catchment. The Mn released into the catchment can be transported into the lake essentially in three forms, soluble dissolved Mn(II), insoluble particulate Mn(IV) oxides and Mn present in mineral lattice structures (Davison, 1993).

Mineral Name	Chemical Formula
Maganosite	MnO
Hausmannite	Mn_3O_4
Partidgeite	α - Mn_2O_3
Pyrolusite	MnO_2
Groutite	α - MnOOH
Feitknechtite	β - MnOOH
Mangatite	γ - MnOOH
Alabandit	α - MnS
Scacchite	$MnCl_2$
Rhodochrosite	$MnCO_3$
Galaxite	$MnAl_2O_4$
Jacobsite	$MnFe_2O_4$
Rhodonite	$MnSiO_3$
Braunite	$3Mn_2O_3.MnSiO_3$

Table 2.1 : Mineral forms of Mn found in natural systems (Rankama and Sahama, 1950).

The input of dissolved Mn(II) in the run off from catchments is influenced by acidification (Neal *et al.*, 1986) and microbiological and hydrological processes (Giusti and Neal, 1993) (section 2.2.6).

2.1.2 Affect of Acidification on the Input of Manganese to Lakes via Catchment Run-Off

Over the past 150 years, freshwater lake catchments in poorly-buffered, granitic areas have become acidified, leading to an increase in the leaching of Mn and other metals from catchment soils (Walls *et al.*, 1986). This recent acidification is the result of two anthropogenic effects, namely the increased acidity of both wet and dry deposition, and the afforestation of catchment areas.

The increase in the acidity of rain as a result of anthropogenic emissions, especially of SO_2 from fossil fuel combustion, has led to acidification of catchments, especially those in areas that are poorly buffered (e.g. granitic) relative to those in well buffered areas (limestone) (Jones *et al.*, 1986; Walls *et al.*, 1986; Battarbee *et al.*, 1989).

In the forested areas of lake catchments, acidification can be enhanced by the presence of the trees (Best, 1994; Morrison, 1994). Acidification of soils due to afforestation occurs principally due to two effects. The first is when the needles drop off the coniferous trees present in most forested areas, and subsequently decay (Best, 1994). Secondly coniferous trees scavenge atmospheric pollutants that are concentrated in the tree needles which subsequently drop off and decay (Morrison, 1994).

The more acidic the catchment, via acid rain and afforestation, the greater the release of Mn from the soils through acid leaching (Neal *et al.*, 1986; Young and Harold, 1992), hence leading to enhanced inputs of Mn to lakes.

The pH of rainfall in the Galloway Hills is 4.4 - 4.6 (Battarbee *et al.*, 1989), considerably more acidic than the minimum (~ 5.6) of the natural pH range for rainwater (Wayne, 1991). This, coupled with the afforestation of the area, has led to acidification of many catchments in this area, especially since large parts of the Galloway Hills lie on granitic bedrock .

2.2 The Effects of Redox Conditions upon the Biogeochemical Behaviour of Manganese Within Lake Systems

2.2.1 Speciation of Manganese within Lake Systems

In the oxic and sub-oxic regions of a lake system, Mn behaviour is principally controlled by its oxidation state and solubility. In aquatic systems manganese is found mainly in two oxidation states, Mn(II) and Mn(IV). The reduced form, Mn(II), generally exists as a soluble free aquated cation, $[Mn(H_2O)_6]^{2+}$ (DeVitre *et al.*, 1988; Davison, 1993). The oxidised form, Mn(IV), exists as a number of insoluble oxides and oxyhydroxides, such as MnO_2 (Laxen and Chandler, 1983; Tipping *et al.*, 1984; Sunda and Huntsman, 1987; Santschi *et al.*, 1990), which will henceforth be called oxyhydroxides. The specific form of the Mn present depends on available surfaces, pH, and the concentration of Mn(II) and oxygen in the water column (Santschi *et al.*,

1990; Huckeriede and Meischner, 1996). A third oxidation state, Mn(III), may be present, but is unstable with respect to disproportionation, giving Mn(II) and Mn(IV). It may exist, however, in a mixed oxidation state complex, Mn_3O_4 (Davison, 1993).

The principal factor which affects the oxidation state of the Mn is the redox potential (Eh or pE) of the water column and sediment (Fig. 2.1)

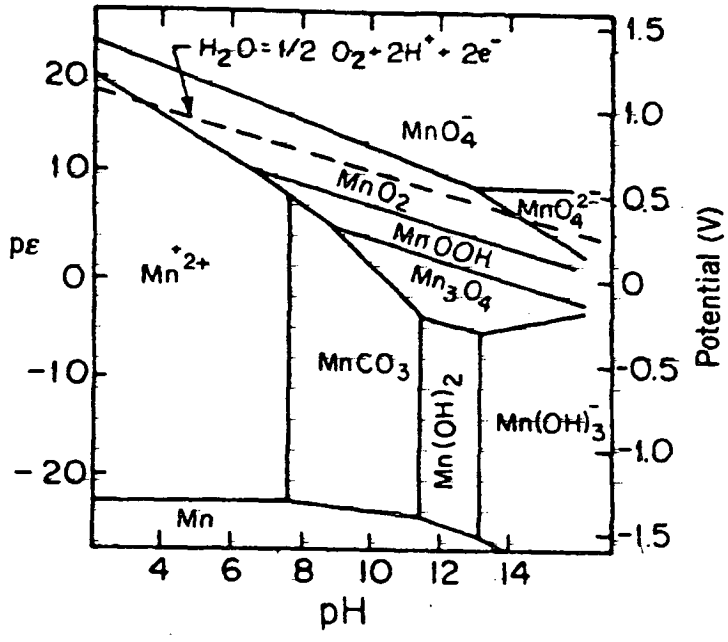

Figure 2.1: pE-pH diagram for manganese (Stumm and Morgan, 1996)

The pE may vary greatly within lake waters and sediment, especially in lakes with anoxic bottom waters, resulting in a change in the speciation of Mn.

2.2.2 Redox-Driven Cycling of Manganese

Within lake water and sediment there is a limited amount of dissolved O_2 present, which diffuses down from the water surface. This dissolved O_2 is consumed in the decomposition of organic material in the water and upper regions of the sediment, resulting in lower concentrations of O_2 and hence a lower pE. During summer months the supply of organic matter increases as a result of higher temperatures

leading to greater primary production. When O_2 is consumed and conditions become more reducing, other oxidising agents become involved in the oxidation of the organic material. One of the first oxidising agents to contribute to this reaction is Mn(IV), which is reduced to Mn(II) during the oxidation of organic material (Table 2.2) (Berner, 1980). In this reaction the organic molecule is rapidly adsorbed to the Mn(IV)-oxides, followed by a slower electron transfer at the oxide surface (Sunda and Kieber, 1994).

Reaction	ΔG° / kJ mol^{-1} of CH_2O
$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-475
$5\ CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$	-448
$CH_2O + 3\ CO_2 + H_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 4HCO_3^-$	-349
$CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O$	-114
$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$	-77
$2CH_2O \rightarrow CH_4 + CO_2$	-58

Table 2.2 : Free energy for oxidation of organic matter (taking CH_2O to represent organic material) (Berner, 1980).

The soluble Mn(II) formed just below the Mn redox boundary, the area where Mn(IV) is reduced to Mn(II), diffuses away from the point of its formation. Mn(II) which diffuses upwards crosses back over the redox boundary into more oxic conditions within the sediment or water column where it re-oxidises to Mn(IV) and precipitates. This redox cycling of Mn produces the characteristic maximum in solid phase Mn just above the redox boundary (Fig. 2.2). The maximum concentration of soluble Mn is generally observed below the redox boundary as a result of the insoluble Mn(IV) peak being buried and reduced, leading to a large point source of Mn(II) (Fig. 2.2).

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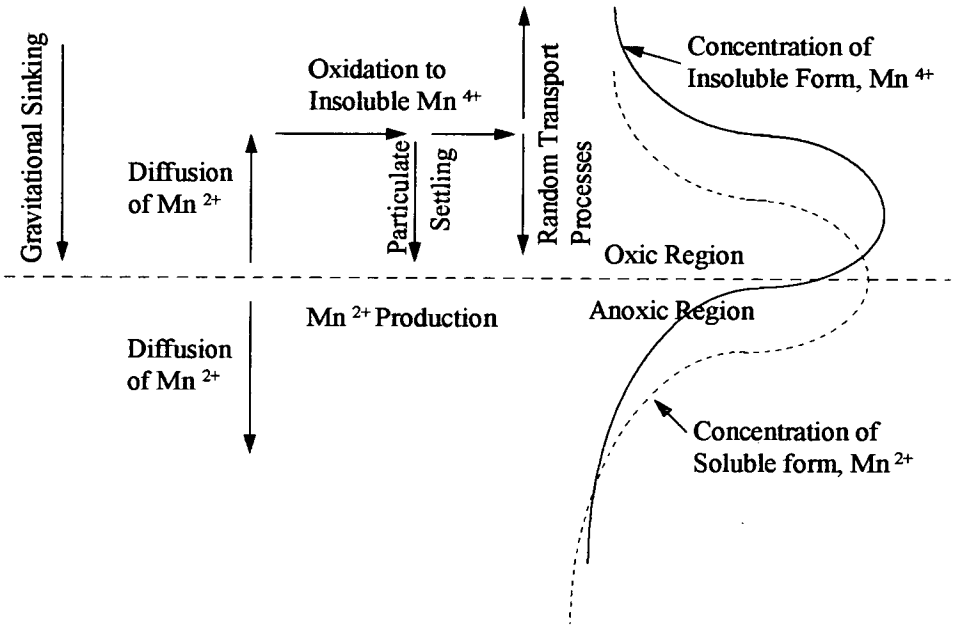

Figure 2.2: Schematic model for manganese cycling within a natural lake system (modified from Davison, 1993)

Within well oxygenated lakes, the redox boundary for Mn and the solid phase Mn maximum usually occur in the top few centimeters of sediment, due to O_2 being restricted to the uppermost layers. This leads to the Mn maxima being observed in the upper regions of the sediment profile (Bryant *et al.*, 1991, Wersin *et al.*, 1991; Bryant *et al.*, 1997).

If, however, the bottom water becomes fully anoxic, which can occur seasonally (or permanently) in some lakes, pore water Mn(II) can diffuse back into the water column. Once in the water column, its behaviour is controlled mainly by the comparatively rapid currents within water rather than the relatively slow competing oxidation and precipitation processes which occur at the same time (Davison *et al.*, 1982). Oxidation of the Mn(II) still occurs in the oxic region of the water column, however, resulting in the precipitation of Mn(IV) oxyhydroxides. On settling, these cross back over the redox boundary and are rapidly reduced, resulting in an absence

of any large Mn(IV) particles in the anoxic water (Laxen and Chandler, 1983; Davison *et. al.*, 1988).

2.2.3 Oxidation of Manganese Within Lake Sediment and Water

The rate of oxidation of Mn(II) to Mn(IV) is important with respect to the amount of soluble Mn(II) that is released into the water column, with faster oxidation resulting in lower dissolved Mn concentrations in oxic waters. Stumm and Giovanoli (1976) calculated the half life of Mn(II) in simulated lake water to be ~ 200 days at 20 °C and pH 8.06, and 100 x longer at pH 7. In acidic waters the formation of Mn oxyhydroxides is not observed (Tessier *et al.*, 1996), while in circumneutral lake water the residence time for soluble Mn(II) species is much shorter, of the order of a few days (Sung and Morgan, 1981; Emerson *et al.*, 1982; Tipping *et al.*, 1984). It is apparent, therefore, that other factors must be involved in the oxidation of Mn(II) in natural waters, increasing the oxidation rate. The rate of oxidation has been shown to increase by catalytic surface reactions on Mn oxide particles (Hsiung and Tisue, 1991) and FeOOH (Sung and Morgan, 1981), both of which have large surface areas. It has also been reported (Sung and Morgan, 1981; Tipping, 1984; Sunda and Huntsman, 1987; Johnson *et al.*, 1996) that bacteria can catalyse Mn(II) oxidation in natural waters. The actual rate of oxidation by bacteria depends on a number of factors, including temperature (Tipping, 1984; Sunda and Huntsman, 1987), O_2 concentration, pH (Johnson *et al.*, 1996) and also the type of organism present in the system (Tipping, 1984). The mechanism for the oxidation of the Mn(II) catalysed by bacteria is not fully understood, but may involve a two-step reaction: firstly, the Mn(II) is bound to the bacteria, and then it is oxidised (Emerson *et al.*, 1982). This oxidation is believed to proceed via a short-lived Mn(III) intermediate phase (Kostka *et al.*, 1995) prior to the formation of MnO_2 (Tipping *et al.*, 1984).

2.2.4 Reduction of Manganese Within Lake Sediment and Water

The reduction of Mn(IV) to Mn(II) occurs predominantly in anoxic regions of the sediment as a result of oxidation of organic matter (Davison, 1993). The reduction

Although reduction of Mn(IV) occurs predominantly in anoxic zones, it has been observed that certain micro-organisms are capable of this reduction under aerobic conditions (Hilton *et al.*, 1985; Johnson *et al.*, 1991). This biologically catalysed reduction is believed to occur via either an enzymatic mechanism or through its metabolic end products (Johnson *et al.*, 1991). As with the oxidation of Mn(II), it has been suggested that the aerobic reduction of Mn(IV) by bacteria occurs via a Mn(III) intermediate (Kostka *et al.*, 1995)

$$MnO_2 + 4H^+ + e^- \rightarrow Mn^{3+}\ \text{complex} + 2H_2O$$

$$Mn^{3+}\ \text{complex} + e^- \rightarrow Mn^{2+}$$

2.2.5 Redox Cycling of Manganese within Catchments

The redox cycling of Mn is observed in the lake catchments as well as in the water column and sediment, resulting in a maximum in the concentration of Mn in the upper regions of the soil, similar to those observed in the sediment (Damman, 1978). The position of the insoluble Mn(IV) maximum is generally above the level of the permanent water table (Damman, 1978), with Mn(II) being the main oxidation state below this. This results in the Mn being able to move laterally as well as vertically in anoxic regions, and hence to be transported to the lake through groundwater flow, especially important during times when stream water levels are low (Heal *et al.*, 1997).

2.2.6 Hydrological and Microbiological Effects Controlling Manganese Release from Catchment Areas

The release of Mn from catchments depends upon a number of factors, including acidification (Section 2.1.2) and also microbiological and hydrological processes. Hydrological factors play an important role all year, but are more significant in catchments with a high mineral soil content, especially during summer months when stream water levels are low and groundwater becomes a more important source of

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Upon entering the lake, the dissolved Mn(II) will be dispersed and, if the water is circumneutral and well oxygenated, may be oxidised to insoluble Mn(IV) oxhydroxides (Section 2.2.3), which will be deposited onto the sediment surface. Mn can also enter the lake associated with colloidal particles, e.g. as insoluble Mn(IV) oxyhydroxides, and as Mn present in insoluble mineral structures, also deposited onto the sediment.

Interactions of Mn with organic molecules are also important for the mobility and transport of Mn in catchments, especially those that are rich in naturally occurring organic matter. This will be discussed in greater detail in Section 2.7.3.

2.3 The Effect of Redox Conditions upon the Behaviour of Other Redox-Active Elements in Lake Systems

2.3.1 Redox Cycling of Fe Within Lake Systems

Fe, like Mn, is a metal that exists principally in two oxidation states in a natural lake system. Fe(II) is its reduced form which, like Mn(II), generally forms soluble compounds, while Fe(III) is the oxidised counterpart of Mn(IV). This leads to the redox cycling of Fe in similar fashion to that for Mn (Section 2.2.2) (Davison, 1993). Fe (Fe(II)/Fe(III)), however, has a lower redox potential and hence is more readily oxidised than Mn (Mn(II)/Mn(IV)), resulting in the formation of a peak in both solution- and solid-phase Fe below those of Mn (Davison *et al.*, 1982; Laxen and Chandler, 1983; Sigg *et al.*, 1991; Hamilton-Taylor *et al.*, 1996).

Due to its faster rate of oxidation Fe may be present in solid-phase particles in water where the Mn is present in a soluble form (Laxen and Chandler, 1983). Nevertheless, soluble Fe(II) may still be found in the bottom waters of lakes with anoxic bottom waters (Davison *et al.*, 1982; Achterberg *et al.*, 1997). The zone of production of the soluble Fe(II) may, however, differ from that of Mn(II) as a result of the variations in the redox potentials of these two metals. Hamilton-Taylor *et al.* (1996) found that in Esthwaite Water, which is a seasonally anoxic lake in North West England, the Fe was reduced in the sediment and released into the water column while the Mn was reduced in the water column and diffused into the sediment.

2.3.2 Redox Cycling of Fe in a Peaty Catchment

As with Mn, redox cycling of Fe can occur in the catchment of a lake as well as within the lake water or bottom sediment. This results in the maximum concentration of insoluble Fe(III) being found in the region of fluctuation of the water table (Damman, 1978). Below the water table, the Fe is present mainly as soluble Fe(II), capable of transportation to the lake via groundwater flow.

Solid phase concentration peaks of As are, however, often observed in the upper regions of sediment at similar depths to those observed for Fe (Farmer and Lovell, 1986; Belzile *et al.*, 1989). This occurs as a consequence of adsorption of As onto Fe(III) oxyhydroxide (Belzile *et al.*, 1989; Belzile and Tessier, 1990) and Mn(IV) oxide (Peterson and Carpenter 1986) surfaces. The As adsorbs to Fe(III) oxyhydroxides as As(V) (DeVitre *et al.*, 1991; Spittlehoff *et al.*, 1995) and as a consequence exhibits peak concentration at the same depth as the redox-driven peaks for Fe (Farmer and Lovell, 1986; Belzile *et al.*, 1989).

The associations of As with Mn(IV) are not as easily seen as a result of the As released during the reduction and dissolution of Mn(IV) being re-adsorbed rapidly onto Fe oxyhydroxides (Peterson and Carpenter, 1986), further promoting the association of As(V) with Fe(III).

2.4 Lake Structure and Seasonal Effects on Manganese, Iron and Arsenic Redox Cycling

The depth of the redox boundary for Mn, Fe and As in the sediment or water column changes according to season as a result of the varying temperature profile of lakes. These seasonal variations can have a significant effect on conditions within the sediment and water column, which will in turn affect Mn, Fe and As geochemistry.

The density of water varies as a function of temperature, the maximum density being observed at 4°C with densities decreasing in warmer and cooler waters. By late summer a temperature gradient can be formed, with the upper water (epilimnion), which receives greater amounts of sunlight, being warmer than the bottom water (hypolimnion). As a result a thermal gradient (thermocline) is formed, with the warmer, less dense water on top of the colder, more dense water (Fig. 2.3). This is a stable situation and mixing between the two levels is inhibited, hence leading to the hypolimnion being isolated from an oxygen supply. The isolation of the hypolimnion from an oxygen source along with the increased biological activity associated with the

warmer temperatures can lead to the formation of anoxic bottom waters (Section 2.2.2). This results in the raising of the redox boundary, raising the position of the maximum observed concentration of Mn, Fe and hence As. If the redox boundary is then in the water column it results in the release of soluble Mn(II), Fe(II) and As(III) into the water column (Laxen and Chandler, 1983; Davison *et al.*, 1988; Hsiung and Tisue, 1991; Skowronek *et al.*, 1994; Huchriede and Meishner 1996). The separation of the epilimnion and hypolimnion by the thermocline in the summer months is called summer stagnation, which can extend from April to November in the northern hemisphere (Pankow, 1991) and is only disturbed by autumn overturn. Autumn overturn is where the temperature of the epilimnion cools enough so that it reaches the same temperature as the hypolimnion (Fig. 2.3). With the same temperature profile throughout the water column, mixing between the hypolimnion and epilimnion occurs again and, with the assistance of the autumn winds, the hypolimnion becomes oxygenated as a result of O_2-rich water mixing with the anoxic bottom waters. This sudden input of oxygen enables the oxidation of the Mn(II) and Fe(II) present in the water column and as a result, maximum amounts of particulate Mn(IV) and Fe(III) in bottom waters are observed (Davison *et al.*, 1982), with the As(III) being oxidised to As(V), scavenged and coprecipitated (Peterson and Carpenter, 1986).

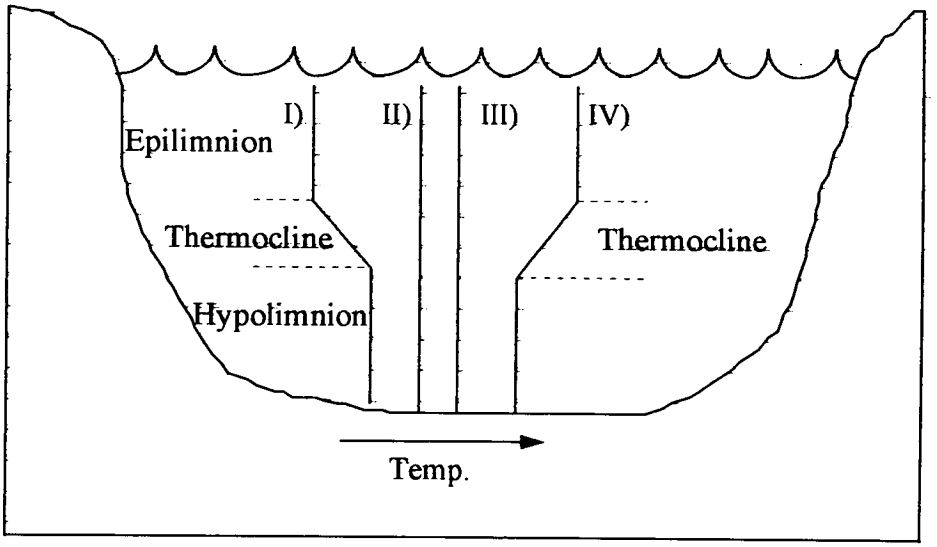


Fig. 2.3: Annual thermal structure of lakes showing the four extreme temperature profiles: i. winter stagnation ; ii. spring overturn ; iii autumn overturn and iv. summer stagnation.

A period of winter stagnation can also occur when the epilimnion becomes colder than the hypolimnion. If a covering of ice forms on top of the water, the water just below it is essentially at 0°C whereas the water in the hypolimnion is slightly warmer and hence more dense (Fig. 2.3). Due to the density differences and also the ice stopping disturbance of the water by wind mixing the water in the epilimnion and hypolimnion cannot mix. Winter stagnation continues until spring when the ice melts and a uniform temperature profile in the water column is achieved (Fig. 2.3). This allows spring overturn which, as with the autumn overturn, is assisted by wind mixing of the surface water. Winter stagnation usually does not result in the same degree of anoxia in the bottom water due to the lower biological activity associated with the colder temperatures. If anoxia was achieved a secondary maximum in particulate Mn in bottom waters would be observed just after the spring turnover. Davison *et al.* (1982) observed no such secondary maximum in Esthwaite Water, UK.

2.5 Solubility of Manganese, Iron and Arsenic in the Anoxic Pore Waters of Lake Sediments

2.5.1 Formation of Insoluble Manganese and Iron Species in Anoxic Pore Waters of Lake Systems

Manganese (II) and Fe(II) are the main oxidation states of dissolved Mn and Fe in anoxic pore waters of sediment and peat, but their solubility can be affected by the concentration of sulphide, phosphate and bicarbonate. If high concentrations of these three components are present within the sediment it can lead to the formation of insoluble compounds of Mn (Sigg *et al.*, 1991; Huckriede and Meischner, 1996; Hongve, 1997) and of Fe (Emerson, 1976; Wersin *et al.*, 1991; Friedl *et al.*, 1997).

Sulphides form insoluble Fe species (Carignan and Nriagu, 1985) and also MnS species have been identified at depth within marine sediment (Huckriede and Meischner, 1996). Sulphides are present in the sediment as a result of the reduction of SO_4^{2-} during the microbiological decomposition and oxidation of organic matter (Table 2.1), leading to a high S^{2-} concentration in the upper regions of the sediment. As a consequence the precipitation of comparatively Fe-rich sulphide species, such as Fe_3S_4 and amorphous FeS (Boulegue *et al.*, 1982), is preferred in the regions of the sediment where the S^{2-} concentration are highest, which, in the case of well oxygenated lakes, is below the diagenetic Fe enrichment in the sediment (Wersin *et al.*, 1991). Enrichments in the concentration of Fe and Mn have, however, been noted deeper within marine sediments due to formation of FeS_2 (Thomson *et al.*, 1998) and MnS (Huckriede and Meischner, 1996).

It is more common for Mn solubility at depth in freshwater lake sediments to be controlled by the formation of insoluble phosphate and carbonate species, such as $MnHPO_4$ and $MnCO_3$ (Hongve, 1997), again potentially leading to the presence of maxima in solid-phase Mn at depth within the sediment. Similarly Fe solubility can

also be affected by the formation of insoluble carbonate, $FeCO_3$, and phosphate, $Fe_3(PO_4)_2$ (Hongve, 1997).

2.5.2 Formation of Insoluble Arsenic Species in Anoxic Pore Waters

In anoxic pore waters, arsenite, As(III), is the principal form of dissolved As present, but, as with Mn and Fe, its solubility can be affected by high concentrations of other species. If high concentrations of S^{2-} are present within the sediment it can result in the formation of insoluble As, either as a result of coprecipitation with insoluble Fe sulphide compounds, such as FeS_2 (Thomson *et al.*, 1998), or due to the formation of insoluble As sulphide species such as As_2S_3 (Splietoff *et al.*, 1995).

2.6 Behaviour of Trace Metals in Lake Systems

2.6.1 Associations with Redox Active Elements

The behavior of many trace metals in the water column and sediments of lakes has been shown to be affected by the redox cycling of Mn and Fe. Mn oxyhydroxides have been shown to adsorb Cu (Sigg *et al.*, 1987; Achterberg *et al.*, 1997), Co (Balistrieri *et al.*, 1992), Pb (Canfield *et al.*, 1995), Po (Benoit and Hemond, 1990) and Zn (Sigg *et al.*, 1987; Davison *et al.*, 1997), while Fe oxyhydroxides have been shown to adsorb Cu (Hamilton-Taylor *et al.*, 1996; Achterberg *et al.*, 1997), Pb (Benoit and Hemond, 1990; Erel *et al.*, 1991; Balistrieri *et al.*, 1995; Canfield *et al.*, 1995) and Zn (Sigg *et al.*, 1987). The associations of trace metals with Mn and Fe oxyhydroxides occur as a result of their large surface area to which both cations and anions can adsorb. If, for example, dissolved Zn and Cu are present in the water column of a lake they may adsorb to particulate MnO_2, which will precipitate out. The MnO_2 will subsequently be reduced and solubilised, leading to the release of the Zn and Cu into the water column in a soluble form (Sigg *et al.*, 1987). Despite these associations of Mn and Fe with trace metals the depths of the maximum

concentrations may not correlate (Hamilton-Taylor *et al.*, 1996, Davison *et al.*, 1997), indicating that other factors may be affecting trace metal mobility and retention.

2.6.2 Other Factors Affecting Metal Profiles in Sediments

Cu and Zn, which are both micronutrients, can be scavenged by organisms in the water column, both by binding onto their surface and by physiological uptake (Sigg *et al.*, 1987). When the organism dies and sinks to the sediment bed it will decompose, releasing the Cu and Zn and hence resulting in enrichment of these metals near the sediment-water interface (Sigg *et al.*, 1987; Hamilton-Taylor *et al.*, 1996; Achterberg *et al.*, 1997). Once the metals are in the sediment in a soluble form their behaviour may be affected by a number of factors.

In sulphidic regions of the sediment Cu and Zn have been reported to coprecipitate with FeS (Hamilton-Taylor *et al.*, 1996), and also form insoluble metal sulphide, e.g. CuS (Elderfield 1981; Balistrieri *et al.*, 1992; Achterberg *et al.*, 1997), PbS (Benoit and Hemond, 1990; Balistrieri *et al.*, 1995; Canfield *et al.*, 1995) and ZnS (Balistrieri *et al.*, 1992; Achterberg *et al.*, 1997).

Another factor that can control the concentration profiles of metals in lake sediments is varying historical inputs resulting from changing anthropogenic inputs from combustion of fossil fuels and industrial processes. One such metal is Pb which despite the possibility of being mobile within sediments (Benoit and Hemond, 1990; Balistrieri *et al.*, 1995; Canfield *et al.*, 1995) has still been reported to retain a record of historical inputs (Farmer *et al.*, 1997).

The mobility and retention of metals may also be affected by interactions with organic molecules within the sediment.

2.7 Organic Matter and its Affect on Metals in Lake Systems

2.7.1 Organic Matter in Lake Systems

Organic matter in lakes originates from decaying plant and animal material from both autochthonous (originating at or close to the point of deposition) and allochthonous (external) sources. Autochthonous sources include aquatic plants and animals, such as algae and plankton, while allochthonous organic matter may originate from terrigenous sources such as higher plants.

The deposited organic matter can be separated into four main chemical groups, carbohydrates, proteins, lipids and lignin (originating from higher plants), which will be broken down to varying extents in the natural environment. Proteins are broken down fastest, followed by carbohydrates, resulting in the formation of amino acids and monosaccharides, respectively. These decomposition reactions are caused mainly by fungi in aerobic terrestrial environments and by bacteria in aerobic aquatic and anaerobic aquatic and terrestrial environments. Lipids degrade to a much lesser extent than carbohydrates and proteins, with alterations to lignin being even less extensive, both degradations occurring as a result of bacterial action (Killops and Killops, 1993).

2.7.2 Formation and Characteristics of Humic Substances

The organic matter present in soils and waters can be split into two groups, non-humic substances and humic substances. Non-humic substances are those that exhibit recognisable chemical characteristics of the parent molecule, e.g. proteins, carbohydrates. Humic substances, which comprise the bulk organic matter in soils and waters, exhibit a greater degree of alteration from the original precursors. In stream water, humic substances are found to comprise ~ 45 - 50 % of the dissolved organic matter, while in marine systems this can be as high as 90 % (Christman *et al.*, 1989). In sediments, humic substances have been reported as accounting for 40 - 70

% of organic matter (Nissenbaum and Swaine, 1976). The formation of humic substances is currently thought to occur mainly through the four mechanisms summarised in Fig. 2.4 (Stevenson, 1994).

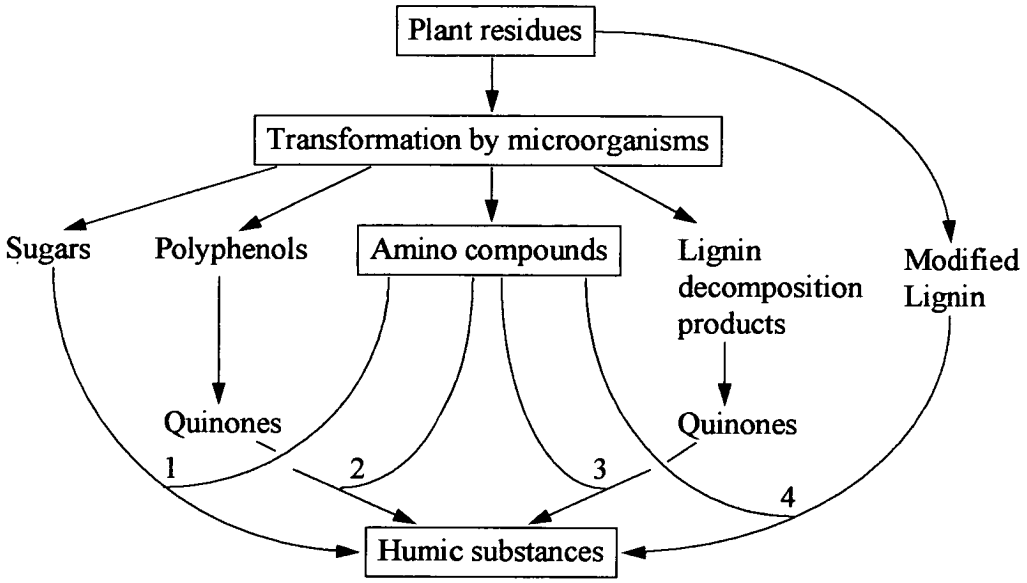


Fig. 2.4: Suggested mechanisms of formation of humic material from plant residues.

Pathway 1 involves the non-enzymatic polymerisation of reducing sugars and amino compounds formed as a by-product of microbial metabolism.

In pathway 2 polyphenols, such as phenolic aldehydes and acids, formed by microorganisms from non-lignin sources such as cellulose, are enzymatically oxidised to quinones. These quinones polymerise in the presence or absence of amino compounds, forming humic substances.

Pathway 3 is very similar to pathway 2 with the exception that the source of the polyphenols is lignin, which will then form quinones and finally humic substances.

Altered lignin is the main source of the humic material in pathway 4. This route assumes that lignin is incompletely utilised by microorganisms but is modified,

resulting in the loss of methoxyl groups, the generation of o-hydroxyphenols and the oxidation of aliphatic side chains to form COOH groups.

Although humic substances comprise a large portion of naturally occurring organic matter, their composition and metal-binding properties are not well defined. This is partially due to their complex nature and also to the difficulties associated with their extraction (see Section 2.7.4)

The humic substances formed consist of large heterogeneous mixtures of acidic molecules with a large molecular weight range of ~ 500 to > 250,000 a.m.u. (Hedges, 1988). Although humic substances are highly heterogeneous in nature they can still be partially characterised according to elemental composition and functionality. Humic substances are generally separated into three forms before characterisation, i.e. fulvic acid (alkali- and acid-soluble), humic acid (alkali-soluble and acid-insoluble), and humin (insoluble at all pHs).

The elemental composition of humic substances varies depending on the source and nature of the humic, e.g. humic acid differs from fulvic acid. The mean elemental composition and atomic ratios of humic and fulvic acids from four different environments can be seen in Table 2.3 (Rice and MacCarthy, 1991). Possibly the most useful way of looking at the elemental composition of humics is via atomic ratios. This shows that soil and peat humic acid have a lower H/C atomic ratio than freshwater and marine. The H/C atomic ratio gives an indication as to the amount of aromaticity within the humic, with a lower H/C indicating a more aromatic nature of the humic. The higher aromatic content of the soil and peat humic acid can be explained by the source of the humic which, in the case of terrigenous soils, has a major lignin input which is highly aromatic (Killops and Killops, 1993). Marine humic acid has the highest H/C atomic ratio which is explained by the marine organic material originating from the more aliphatic algal input (Nissenbaum and Kaplin, 1972). Typical H/C values for freshwater humic acid are intermediate, indicating that

there may be both algal and soil organic matter contributing to the humic substances (Rice and MacCarthy, 1991).

Sample	C	H	N	S	O	O/C	H/C
Soil HA	55.1 ± 3.8	4.8 ± 1.0	3.6 ± 1.3	0.8 ± 0.6	36.0 ± 3.7	0.50 ± 0.09	1.04 ± 0.25
Soil FA	45.3 ± 5.4	5.0 ± 1.0	2.6 ± 1.3	1.2 ± 0.9	46.2 ± 5.1	0.75 ± 0.14	1.35 ± 0.34
Freshwater HA	51.2 ± 3.0	4.7 ± 0.6	2.6 ± 0.6	2.6 ± 1.6	1.9 ± 1.4	0.60 ± 0.08	1.12 ± 0.17
Freshwater FA	46.7 ± 4.3	4.2 ± 0.7	2.3 ± 2.1	1.2 ± 0.9	45.9 ± 5.1	0.75 ± 0.14	1.10 ± 0.13
Marine HA	56.3 ± 6.6	5.8 ± 1.4	3.8 ± 1.5	3.1 ± 1.4	31.7 ± 7.8	0.45 ± 0.18	1.23 ± 0.23
Marine FA	45.0 ± 4.0	5.9 ± 0.9	4.1 ± 2.3	2.1	45.1 ± 6.0	0.77 ± 0.17	1.56 ± 0.13
Peat HA	57.1 ± 2.5	5.0 ± 0.8	2.8 ± 1.0	0.4 ± 0.2	35.2 ± 2.7	0.47 ± 0.06	1.04 ± 0.17
Peat FA	54.2 ± 4.3	5.3 ± 1.1	2.0 ± 0.5	0.8 ± 0.6	37.8 ± 3.7	0.53 ± 0.094	1.20 ± 0.33

Table 2.3: Elemental composition and atomic ratios for humic acids (HA) and fulvic acids (FA) extracted from different sources (adapted from Rice and MacCarthy, 1991)

Fulvic acids are reported as having a higher O content and a lower C content than the humic acids, resulting in a higher O/C ratio (Table 2.3) (Rice and MacCarthy, 1991). This variation in the O/C ratio is indicative of fulvic acid having a greater number of O- containing functional groups, especially COOH, OH, and C=O. Much of the behaviour of humic substances, including chelation of metals, is controlled by their many functional groups of which many have been reported, including COOH, phenolic OH, enolic OH, quinone, hydroxyquinone, lactone, ether, alcoholic OH and free amino groups (Stevenson, 1994).

2.7.3 Metal Binding by Humic Substances

Humic substances can be thought of as both hard and soft ligands, represented by O-containing functional groups and N, P and S donor groups, respectively. The affinity of the functional groups present in humics for metals varies depending on whether the metal ion can be considered as hard, borderline or soft. Hard ions are small and highly charged, e.g. Cr(III), Mn(III), Fe(III) and Co(III), while soft ions are more diffuse with a lower charge, e.g. Zn(II), Pb(II) and Cu(I). The extent of retention of metals by humic substances depends upon a number of factors, including pH, concentration of metal and concentration of humic substances. The sorption efficiency of humic substances has been shown to increase with an increase in the concentration of humic, a decrease in the concentration of metal and an increase in the pH of the system (Kerndorff and Schnitzer, 1980). The exact order of retention of metals also varies with pH, one example of which is shown below, with decreasing retention on going from left to right (Evans, 1989):

At pH 4.7: Hg = Fe = Pb = Al = Cr > Cd > Ni = Zn > Co > Mn

At pH 5.8: Hg = Fe = Pb = Al = Cr = Cu > Cd > Zn > Ni > Co > Mn.

The binding of metals to humics occurs principally through chelation (Schnitzer and Skinner, 1965; Kerndorff and Schnitzer, 1980), i.e. the metal is coordinated to the humic molecule at two or more places, although in certain cases, e.g. Mn and Cu, it has been suggested that single electrostatic bonding may occur between the metal and the humic (McBride, 1979). It is therefore apparent that there are different mechanisms of metal retention by humic substances, leading to different types of bonding and hence different degrees of selectivity for different humic substances. The type of bonding formed may also change within one system. For example Garnier *et al.* (1997) found that when Mn(II) came in contact with organic matter it formed an instantaneous complex with ligands which weakly bound the Mn. Over a period of time, 120 hours in this study, it was shown that the Mn transferred from the fast forming, but weaker binding, sites to slower forming, but stronger (but still comparatively weak), binding sites.

Although many previous studies have found that under all pH conditions Mn is only weakly bound to humic material (Rashid, 1974; Samanidou *et al.*, 1991; Smith *et al.*, 1992) and can be displaced by other metals, including Pb (Kerndorff and Schnitzer, 1980), Mn - humic interactions may still play an important role in the mobility and retention of Mn within lake systems.

In organic-rich, peaty lake catchments there are a large number of organic binding sites available to Mn (Bryant *et al.*, 1997), which can result in a greater Mn mobility, Mn - organic complexes being washed away in ground water (Damman, 1978). Laxen and Chandler (1983) indicated that dissolved Mn in oxic waters could be present as Mn^{2+} and / or Mn - organic complexes, with a high organic content present within the water column potentially leading to high concentrations of dissolved Mn (Hilton *et al.*, 1985).

2.7.4 Extraction of Humic Substances

Extraction of humic substances has traditionally been based on the solubility of the three fractions according to pH. Humic and fulvic acids are extracted using dilute alkali such as 0.1 M NaOH, which is then acidified to precipitate out the humic acid fraction. The main problem with using these extraction techniques is that it subjects the humic to extremes in pH which are not encountered in the natural environment, possibly leading to alteration of the humics through hydrolysis and autoxidation (Stevenson, 1994).

Humic substances have also been extracted from aqueous environments by the use of resins such as Amberlite XAD-8, but as with the classic extraction techniques this subjects the humics to extremes in pH not seen in nature (Aitken, 1985).

Techniques have been employed in an attempt to isolate humic substances from environmental samples without the use of harsh conditions. These include the use of milder reactants such as sodium pyrophosphate, salts of weak acids and organic

chelating agents, but due to the weaker nature of the extractant the processes remove a much lower amount of the humic. Centrifugal ultrafiltration has been used to separate soluble humic substances from aqueous samples based on the size of the humic molecules, with a range of ultrafilters used in an attempt to fractionate the humics (Yagi, 1988). As well as the size of the humics, their charge can also be utilised in order to extract them from a natural matrix. Humic molecules have an overall negative charge, making electrophoretic separation possible (Vinogradoff *et al.*, 1998).

2.8 Specific Objectives

Mn behaviour within lake systems is complex and even though it has been studied for over five decades (see Mortimer, 1941, 1942), it is still not fully understood. As well as the classical redox cycling of Mn, a number of other factors, including the pH and associations with inorganic and organic components of the system, appear capable of significantly influencing Mn behaviour. Mn geochemistry is also important in the behaviour of other metals within the system, including Cu, Co, Pb, Po and Zn, influencing their mobility and retention. This study has investigated the interactions of Mn in the Loch Bradan system in an attempt to identify the causes of the unusually high dissolved Mn observed in the water column of Loch Bradan by considering the following topics:

1. the concentration of total and easily reducible Mn (and Fe, As, Cu, Pb and Zn) in the sediment of Loch Bradan, and Loch Riecawr.
2. the concentration of readily oxidisable organic matter in the sediment of Loch Bradan and Loch Riecawr.
3. the concentration of total and easily reducible Mn (and Fe, As, Cu, Pb and Zn) in the catchment of Loch Bradan.
4. the concentration of readily oxidisable organic matter in the catchment of Loch Bradan.
5. the concentration of humic substances and the concentration of Mn (and Fe) associated with the humic substances in the catchment of Loch Bradan.

6. the total concentration of Mn (and Fe) and also humic associated Mn (and Fe) in the stream run-off from the catchment of Loch Bradan.
7. the concentration of humic and the concentration of Mn (and Fe) associated with the humic in the sediment of Loch Bradan and Loch Riecawr.
8. the total and humic-associated concentration of Mn (and Fe) in the water column of Loch Bradan.
9. the speciation of Mn within the water column of Loch Bradan.

3. Sampling and Analysis

3.1 Loch Bradan and Loch Riecawr Site Description

3.1.1 Loch Bradan Site Location

Loch Bradan, a drinking water reservoir serving South West Scotland, is situated in the Galloway Hills, (55° 14.8' N, 04° 28.7' W) at a height of ~ 320 m above sea level (Fig. 3.1) and has an average depth of ~ 10 m with a maximum of 16 m.

Fig. 3.1: Location of Loch Bradan and Loch Riecawr (Ordnance Survey, 1995). Reproduced by kind permission of Ordnance Survey © Crown Copyright NC-99-279.

Historically, Loch Bradan was two lochs, Loch Bradan and Loch Lure, which were joined by a short stretch of river (Fig. 3.2). In 1913 a dam was built on the north-eastern shore, thereby raising the water level to provide a larger supply of water (Fig. 3.3). Due to a further increase in demand for water from Loch Bradan a further two dams were built in 1972, raising the water to the present-day level (Fig. 3.4). The main dam is situated slightly north of the original dam, with the second, smaller dam located on the north-west bank of the loch. In the construction of the dams in 1972 the original 1913 dam was breached to allow easier flow of water through the loch.

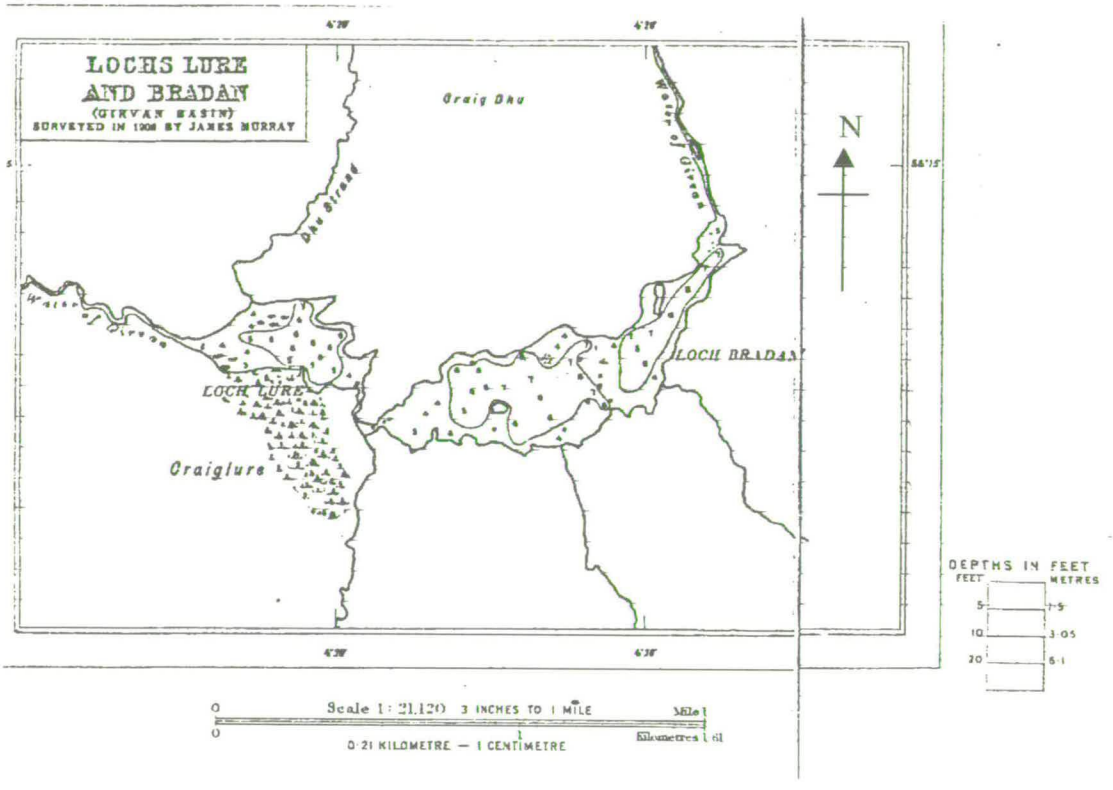


Fig. 3.2: Map of Loch Bradan (pre 1913) (Murray and Pullar, 1916)

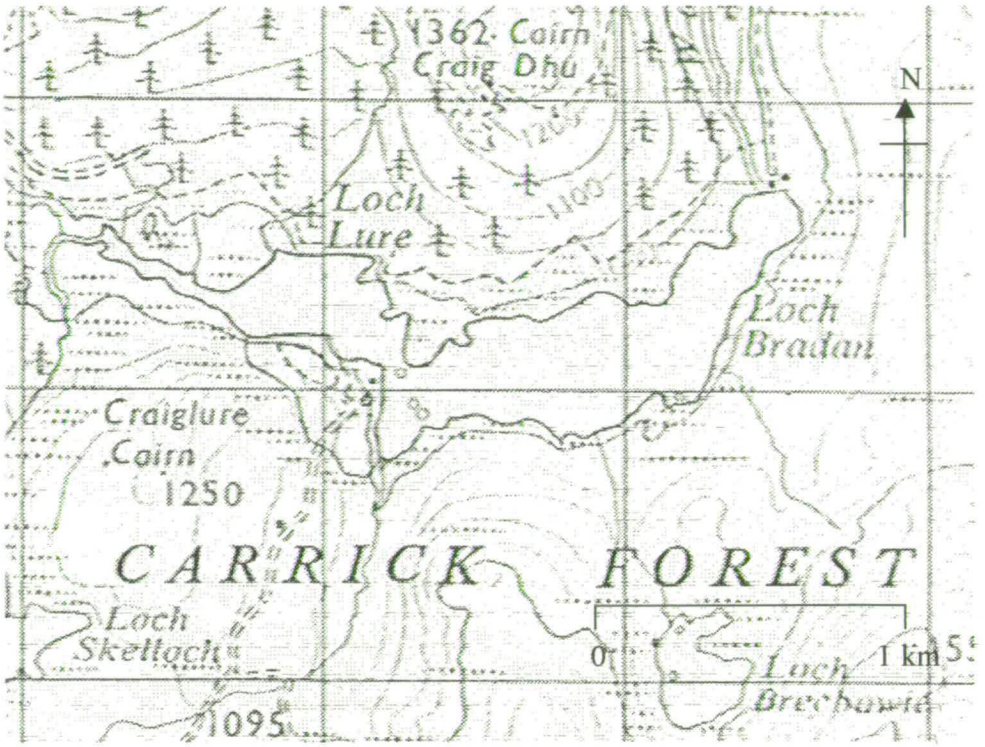


Fig. 3.3: Map of Loch Bradan (1913-1972) (Ordnance Survey, 1956) Reproduced by kind permission of Ordnance Survey © Crown Copyright NC-99-279.

Fig. 3.4: Map of Loch Bradan (post 1972) (Ordnance Survey, 1995) Reproduced by kind permission of Ordnance Survey © Crown Copyright NC-99-279.

The major inflow to Loch Bradan is the Water of Girvan, which enters the loch from the south-west after passing through three other lochs south of Bradan, Loch Skelloch, Cornish Loch and Loch Girvan Eye (Fig. 3.1). The major output is again called the Water of Girvan that exits the loch at the main dam on the east bank. Due to the location of the main input and output, the overall flow of water within the loch is from west to east. As well as the Water of Girvan there are five other main input streams, three entering the loch from the south, one from the north, and the other, which is manmade, at the smaller dam on the western bank of Bradan (Fig. 3.4).

3.1.2 Loch Bradan Geology and Pedology

Loch Bradan lies on a band of thin- to medium-bedded, and medium to thick-bedded greywacke and also sandstone and siltstone ~ 1 km north of the large Loch Doon granite intrusion (Fig. 3.5). The main input stream, the Water of Girvan, originates from Loch Girvan Eye, which lies within the granite region that renders many lochs in this area susceptible to acidification.

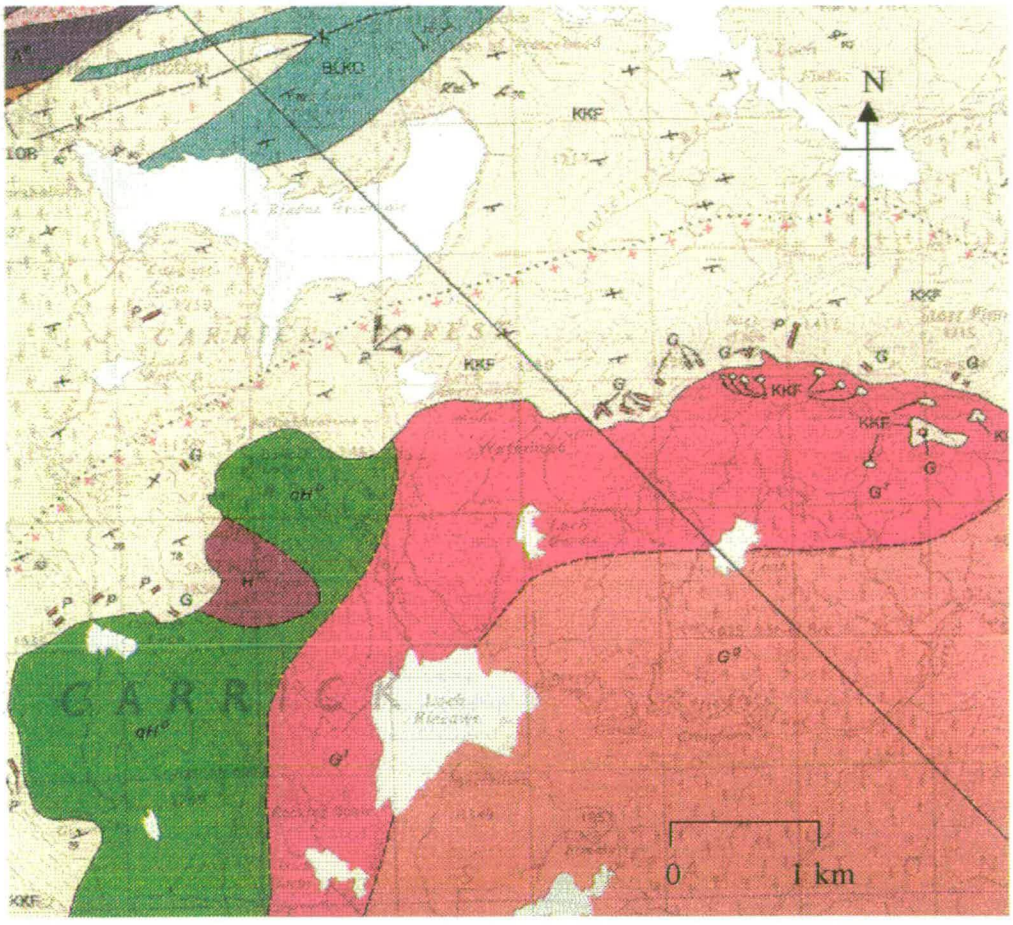


Fig. 3.5: Geological map of the area surrounding Loch Bradan (and Loch Riecawr) (British Geological Survey, 1994). Reproduced from Loch Doon, Scotland Sheet 8E, Solid Edition by permission of the Director, British Geological Survey © NERC. All rights reserved

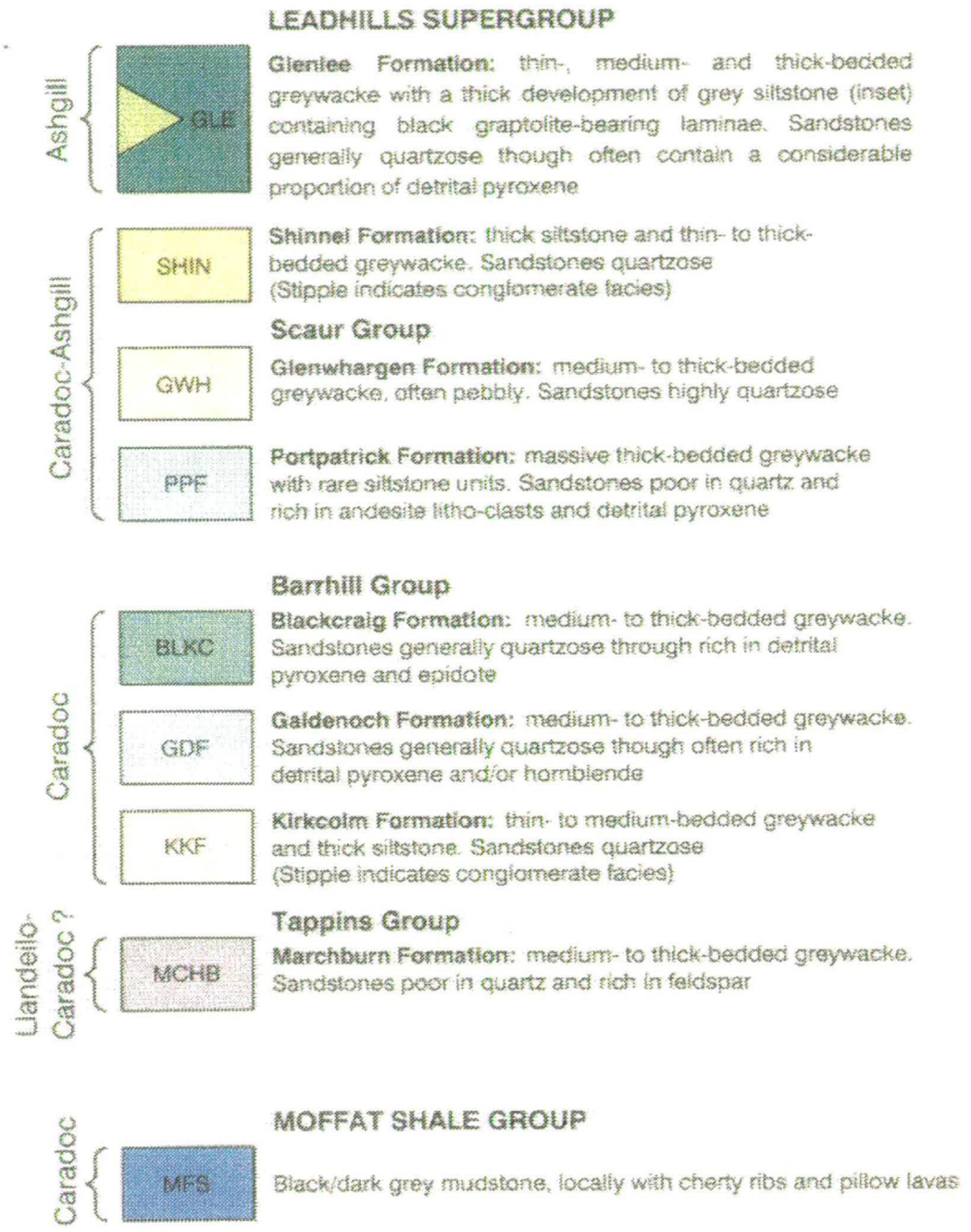


Fig. 3.5 (cont'd): Geological map of the area surrounding Loch Bradan (and Loch Riecawr) (British Geological Survey, 1994). Reproduced from Loch Doon, Scotland Sheet 8E, Solid Edition by permission of the Director, British Geological Survey © NERC. All rights reserved

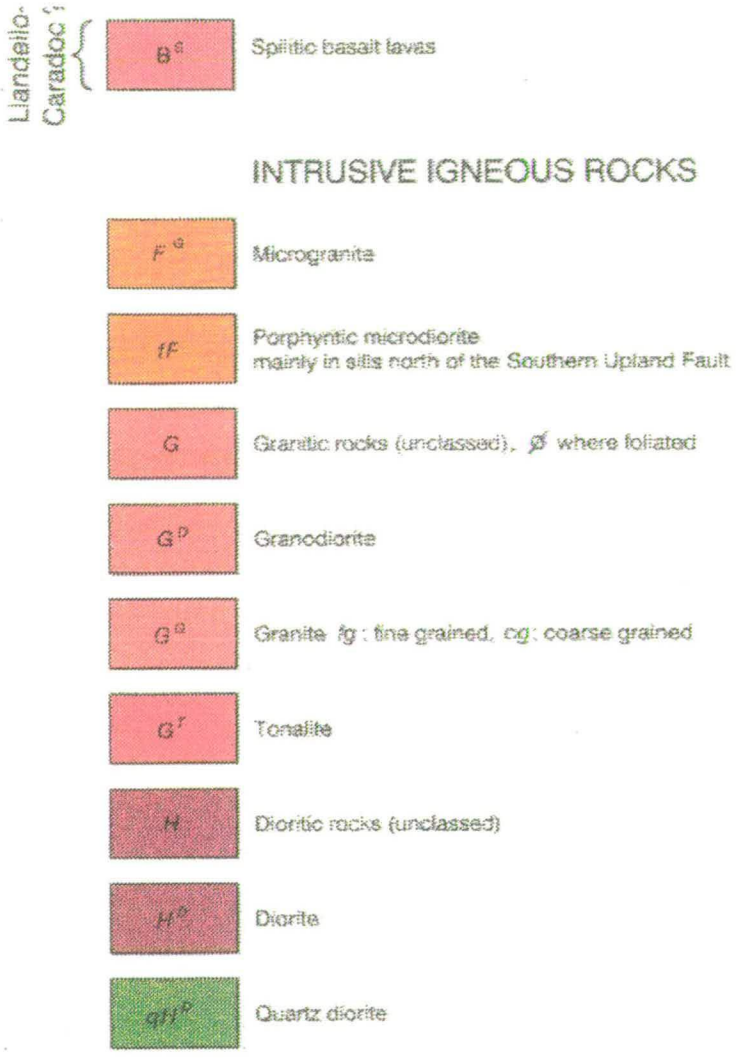


Fig. 3.5 (cont'd): Geological map of the area surrounding Loch Bradan (and Loch Riecawr) (British Geological Survey, 1994). Reproduced from Loch Doon, Scotland Sheet 8E, Solid Edition by permission of the Director, British Geological Survey © NERC. All rights reserved

The Loch Bradan catchment is peaty, and hence highly organic in nature (Fig. 3.6). The immediate surroundings are principally peaty gleys, peaty podzols and also some peat rankers.

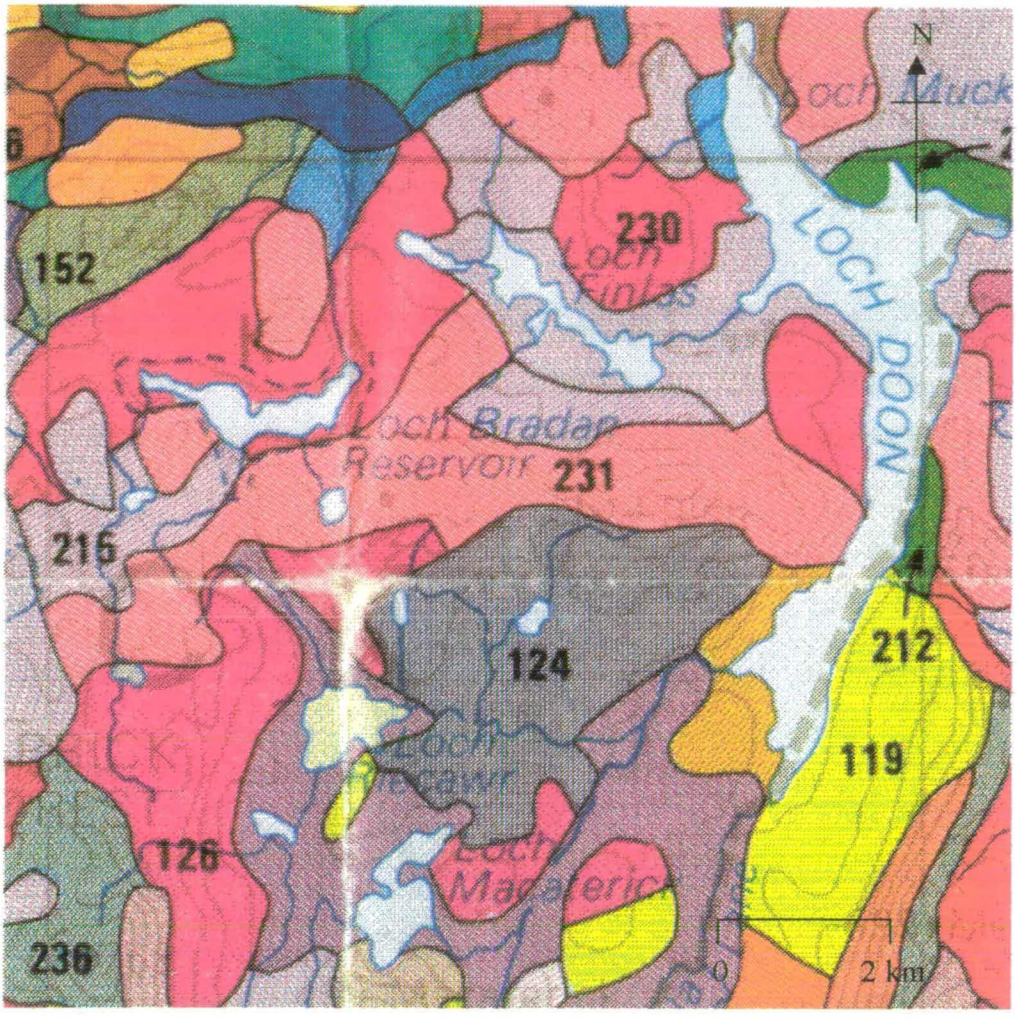


Fig 3.6: Soil map of the area surrounding Loch Bradan (and Loch Riecawr) (Soil Survey of Scotland, 1982) © MLURI.

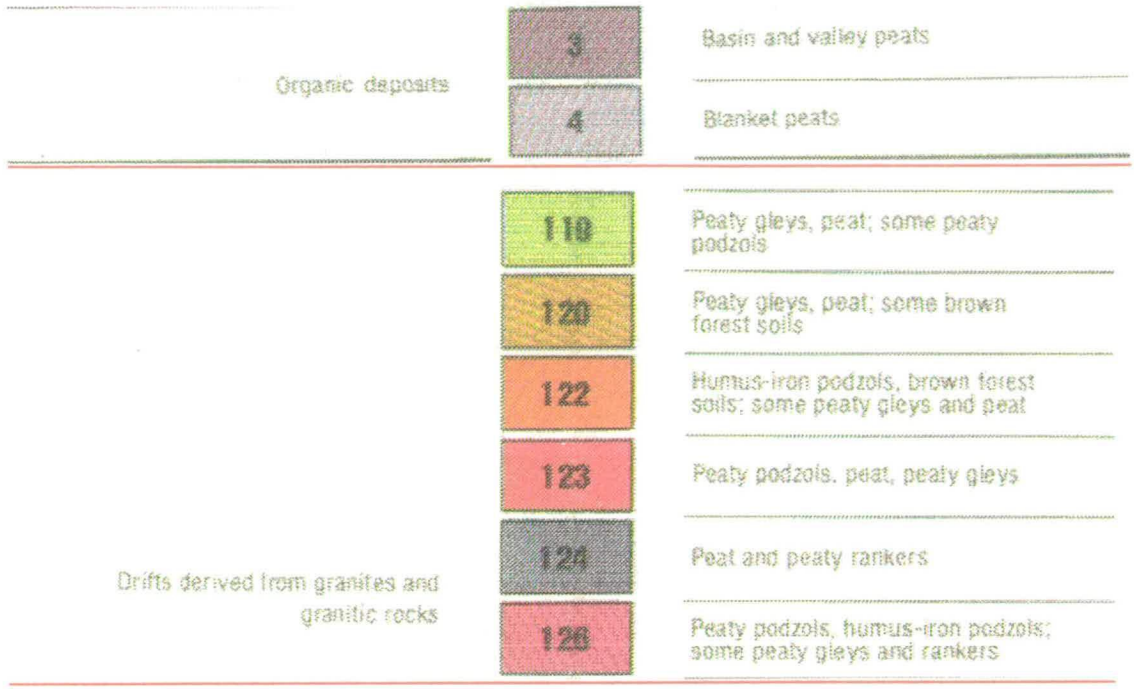


Fig 3.6 (continued): Soil map of the area surrounding Loch Bradan (and Loch Riecawr) (Soil Survey of Scotland, 1982) © MLURI.

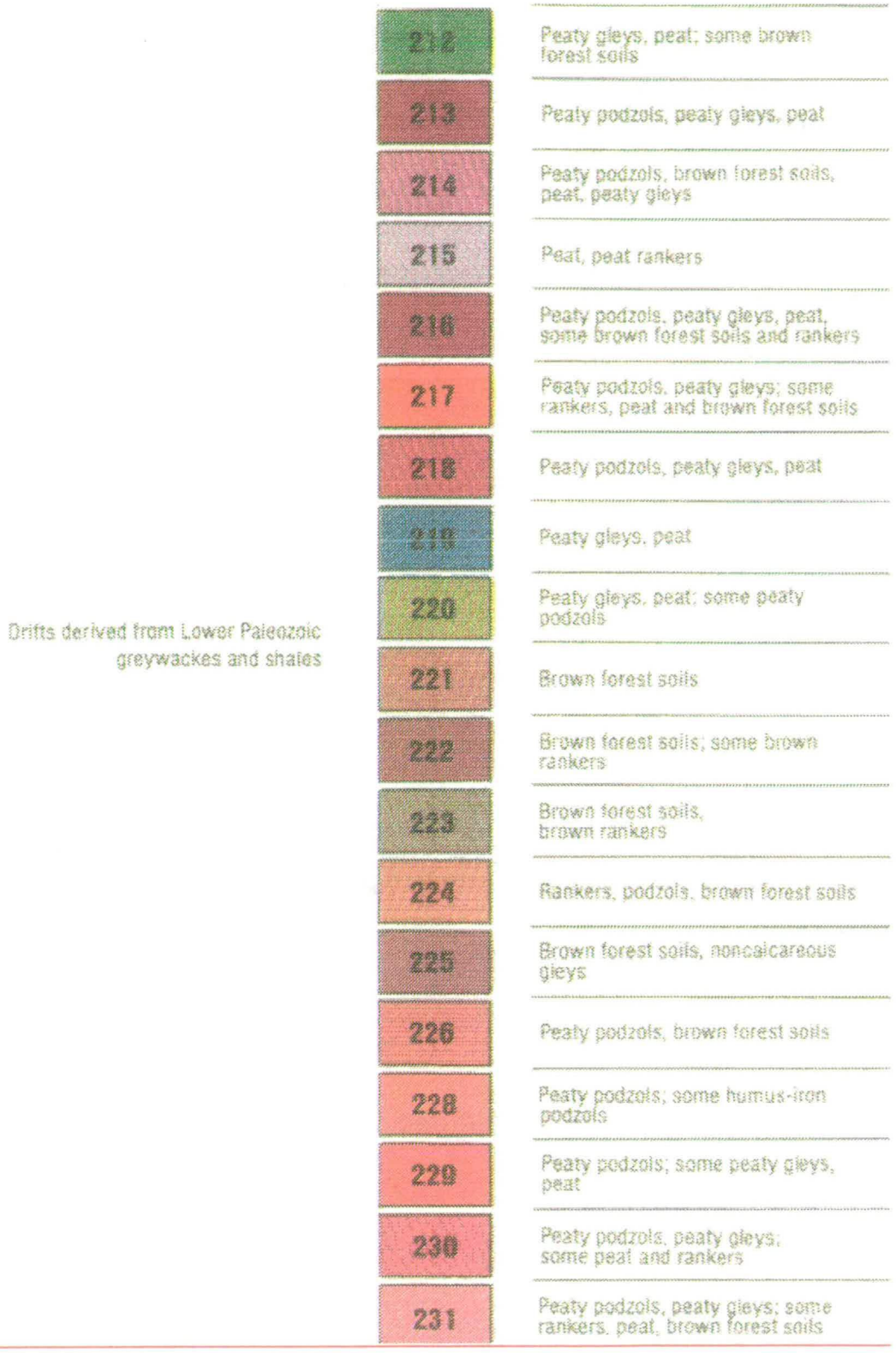


Fig 3.6 (continued): Soil map of the area surrounding Loch Bradan (and Loch Riecawr) (Soil Survey of Scotland, 1982) © MLURI.

3.1.3 Land Use of Area Surrounding Loch Bradan

The land around Loch Bradan can be considered as two separate components, approximately equal in area. The northern and western half has been used since the 1950's as a tree plantation, mainly for Sitka Spruce, which are hardy coniferous trees. Most of the southern and eastern side of the loch's catchment is un-forested and used in part for sheep grazing, with a covering of naturally occurring mosses, grasses and heathers.

3.1.4 Loch Riecawr Site Location

A second loch, Loch Riecawr, which is situated ~ 3 km south of Loch Bradan, was used for comparison purposes in this study. Loch Riecawr supplies extra water to the Loch Bradan treatment works at times when the Loch Bradan water level is very low.

As with Loch Bradan, the water level in Loch Riecawr was artificially raised by the construction of a dam in 1952 (Fig. 3.7). The dam was built on the northern bank of the loch, resulting in a maximum water depth of 8 m.

Fig. 3.7 : Map of Loch Riecawr post-1972 (Ordnance Survey, 1995). Reproduced by kind permission of Ordnance Survey © Crown Copyright NC-99-279.

3.1.5 Loch Riecawr Geology and Pedology

Loch Riecawr lies within the Loch Doon granite intrusion, approximately one half on tonalite, the other on granodiorite (Fig. 3.5).

Loch Riecawr, like Loch Bradan, has a catchment which is peaty (basin and valley) and hence highly organic in nature (Fig. 3.6).

3.2 Sampling Strategy

For this study it was decided that sediment, pore water and loch water should be collected from Loch Bradan, with peat and stream water being collected from the surrounding catchment area. For Loch Riecawr, only bottom sediment was collected.

3.2.1 Collection of Sediment Cores

Ten sediment cores (LBSC 1 to LBSC 10) were collected from Loch Bradan on dates between February 1996 and July 1996 (Fig. 3.8, Table 3.1). As the level of water in Loch Bradan has been raised on two occasions, after the construction of the dams in 1913 and 1972 (Section 3.1.1), much of the current loch bed has been accumulating sediment for less than three decades. With an accumulation rate of ~ 12 mg cm^{-2} yr^{-1} (Short, 1995), insufficient sediment was present at the time of sampling to obtain sediment cores from many areas outwith the original loch basins. As a result, all of the sediment cores collected lie within the original basins of Loch Bradan and Loch Lure.

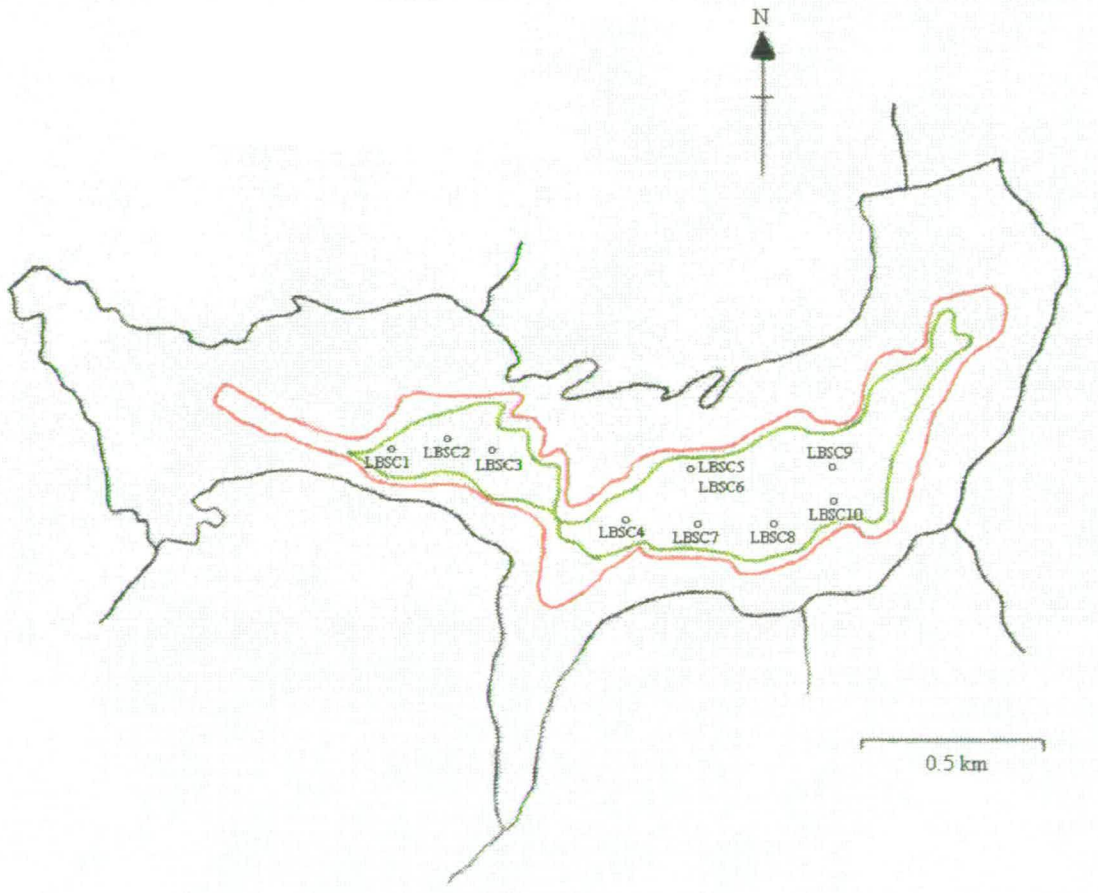


Fig. 3.8: Map of Loch Bradan sediment coring sites with the black line indicating the presented water level, the red line indicating the water level between 1913 and 1972, and the green line pre-1913.

Two sediment cores were collected from Loch Riecawr (LRSC 1 and LRSC 2) in July 1996, using the same method as used in Bradan (Fig. 3.9, Table 3.1).

Sediment Core	Date of Collection	Depth of overlying water / m	Length of cores collected / cm	Length of cores analysed / cm
LBSC 1	29 / 2 / 96	10.1	15	3
LBSC 2	29 / 2 / 96	8.0	7	3
LBSC 3	28 / 7 / 96	11.0	15.5	3
LBSC 4	29 / 2 / 96	13.1	28	3
LBSC 5	29 / 2 / 96	13.9	29	3
LBSC 6	29 / 2 / 96	10.1	46	45
LBSC 7	1 / 2 /96	9.9	10	3
LBSC 8	28 / 7 / 96	12.0	28	27
LBSC 9	29 / 2 / 96	13.9	16.5	3
LBSC 10	1 / 2 / 96	13.0	20	19
LRSC 1	27 / 7 / 96	7.0	24	23
LRSC 2	27 / 7 / 96	8.0	20	19

Table 3.1 : Table of depths of sediment cores and dates of collection in Loch Bradan and Loch Riecawr.

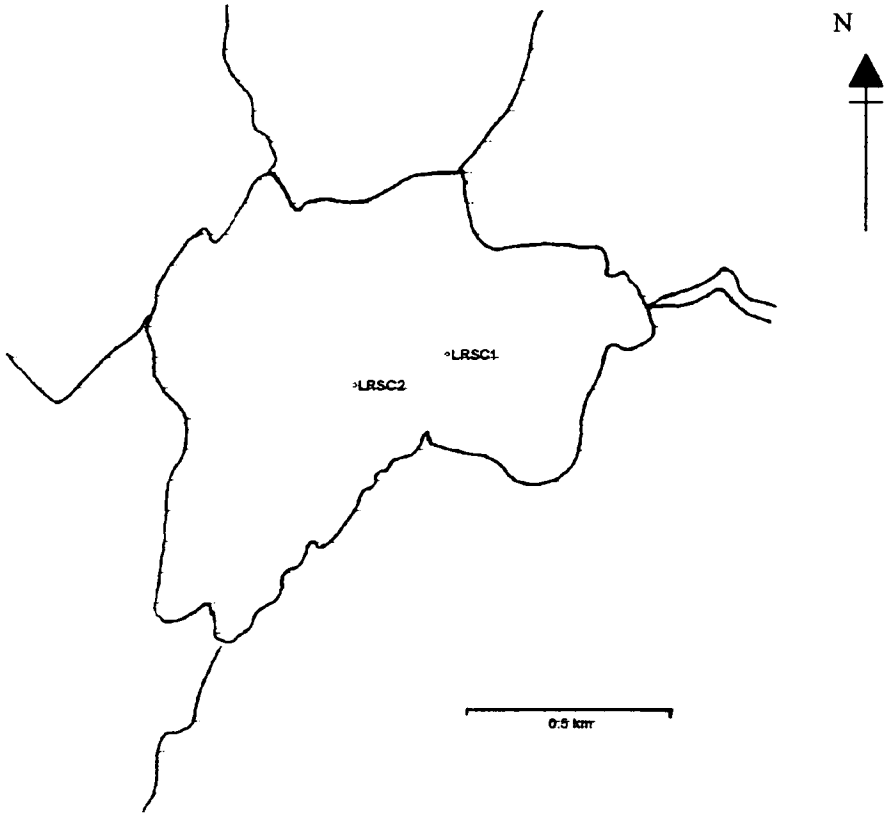


Fig. 3.9 : Map of Loch Riecawr sediment coring sites

Sediment cores were collected using a Jenkin sub-surface mud sampler (Fig. 3.10), a hand-operated gravity corer which permits the collection of relatively undisturbed sediment cores of the order of 20 cm in length in normal sediment.

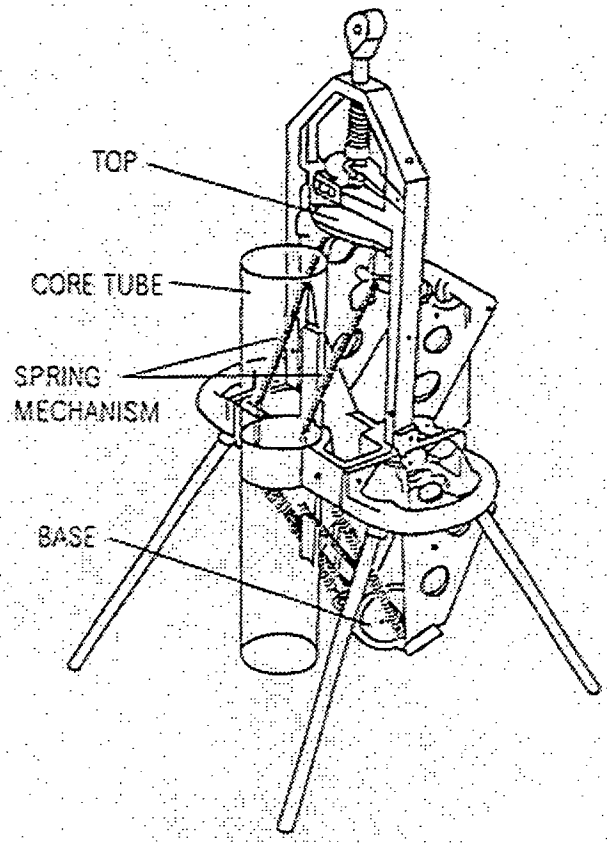


Fig. 3.10: Diagram of Jenkin corer

Before collection of a core, a flat area of the sediment bed had to be found in order to avoid sampling at an angle on a slope. This was achieved by taking depth readings using an echo sounder as the boat traversed the water surface.

The corer, attached to a rope, was lowered over the side of the boat and allowed to descend within the water column until it was ~ 1 m above the sediment surface. It was then held still for ~ 1 minute to stop any lateral movement before being carefully lowered onto the sediment. The corer and core tube would then sink into the sediment as far as the weight of the corer and tube would allow, resulting in the tension being taken off the rope. This triggered the firing mechanism which entraps the sediment within the core tube via caps on the top and bottom of the tube. The corer and sediment were then brought back to the surface and a plastic bung inserted

into the bottom of the core tube to prevent loss of sediment from the edges of the bottom cap. Cores were usually collected by attaching a single plastic core tube to the Jenkin corer, but for LBSC 6 two coring tubes were strapped together to enable a longer core of sediment to be obtained. In addition to the modification made by attaching two core tubes together, in all cases extra weights were also added to the Jenkin corer to enable it to sink deeper into the sediment and hence facilitate the collection of longer cores. The collected cores had no visible variation either within individual cores or from cores collected from different areas of Loch Bradan or Loch Riecawr.

Once taken, the cores were transported to the shore, where the overlying water was siphoned off. The top 3 cm of sediment was carefully sliced into 2-mm sections using simple hydraulic extrusion equipment and plastic sectioning gear, discarding any sediment below 3 cm. The sections were placed into small, pre-weighed, plastic, sealable pots and stored in a cool box for transport back to the laboratory. For sediment cores LBSC 2, LBSC 6, LBSC 10 and both cores from Loch Riecawr, which were longer, the top 3 cm were sectioned as above, and the remainder of the sediment below 3 cm sliced into 1-cm sections, again using simple hydraulic extrusion equipment. These sections were placed into plastic bags, tied and sealed before they were transported back to the laboratory, in cool boxes, along with the 2-mm sections.

In the laboratory the samples were weighed wet, in the case of the 2-mm sections in the plastic pots in which they had been collected, or, in the case of the 1-cm sections, after the sediment had been transferred to pre-weighed plastic pots. The samples were then allowed to dry for a week in an oven at 30-40 °C, re-weighed, and ground using a porcelain mortar and pestle, discarding any large pieces of vegetation which were occasionally present, before storage in labeled, re-sealable, plastic bags. The weighing of the sediment when wet and after it had been dried allowed the calculation of the water content (% by weight) of the samples (Appendix 19). All of the sediment cores from Loch Bradan and Loch Riecawr had a high water content (> 90 %) in the top 3 cm of sediment, with a general loss of water with depth (Fig. 3.11 A - J, Fig.

This loss of water with depth is seen below the top 3 cm of sediment in LRSC 1 and 2 (Fig. 3.12 A - B), and with slightly more variability in LBSC 6, 8 and 10 (Fig. 3.13 A - C).

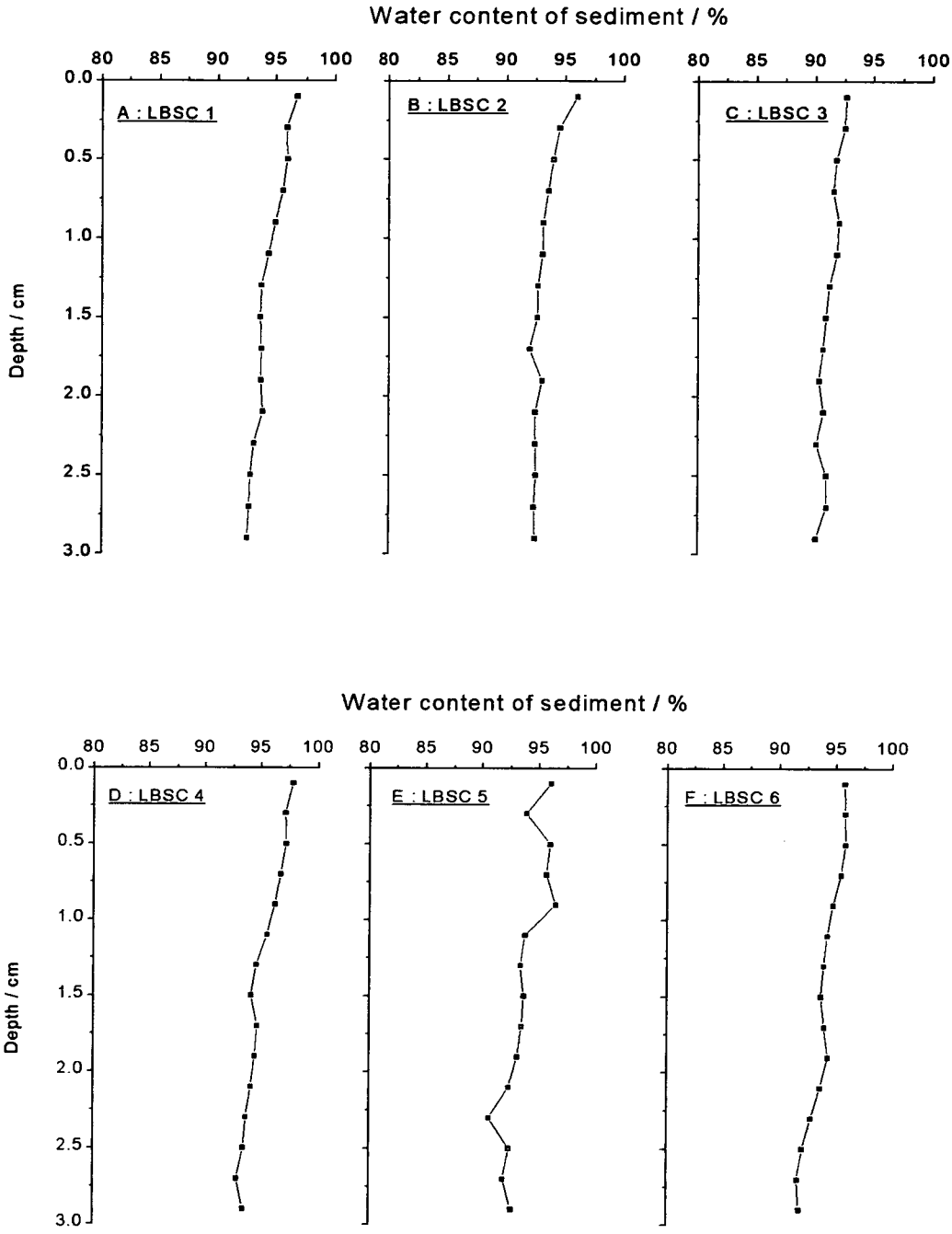


Fig 3.11 A - F: Water content of the top 3 cm of sediment cores LBSC 1 to 6.

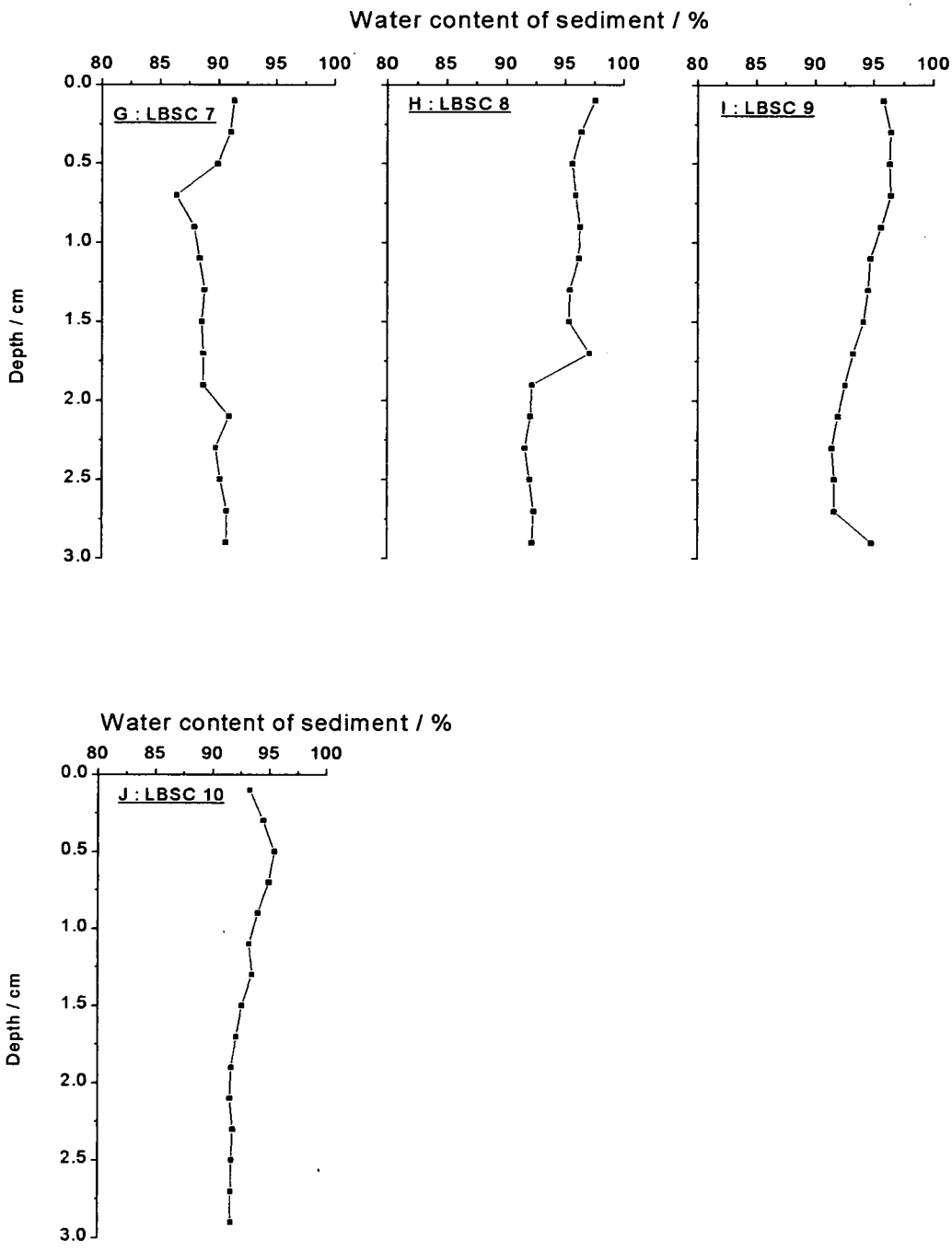


Fig 3.11 G - J: Water content in the top 3 cm of sediment cores LBSC 7 to 10.

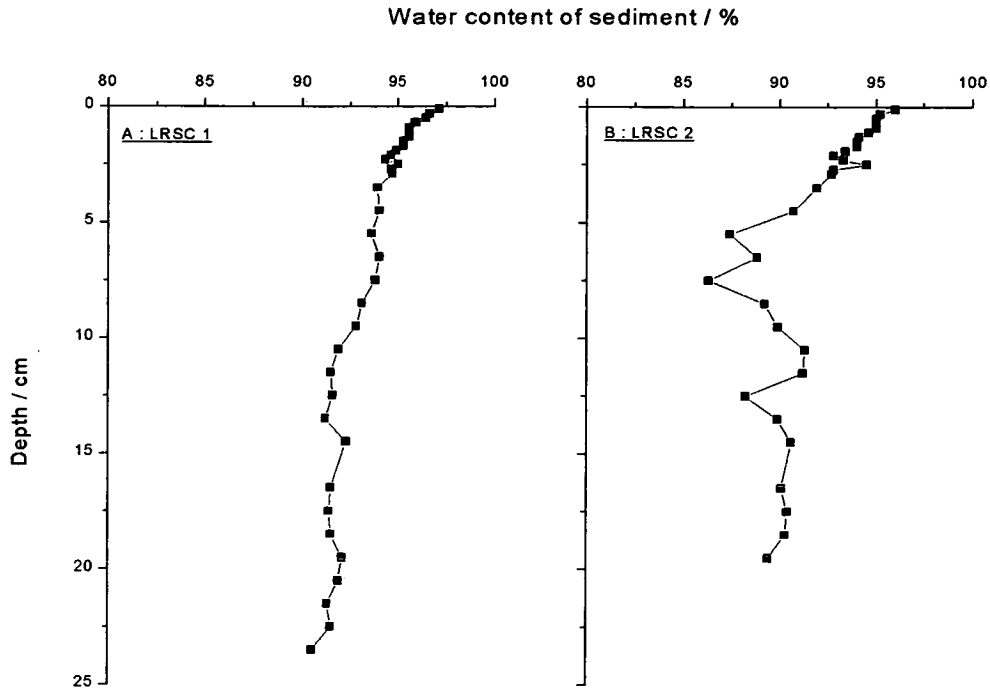


Fig. 3.12 A - B: Water content of the sediment from LRSC 1 - 2.

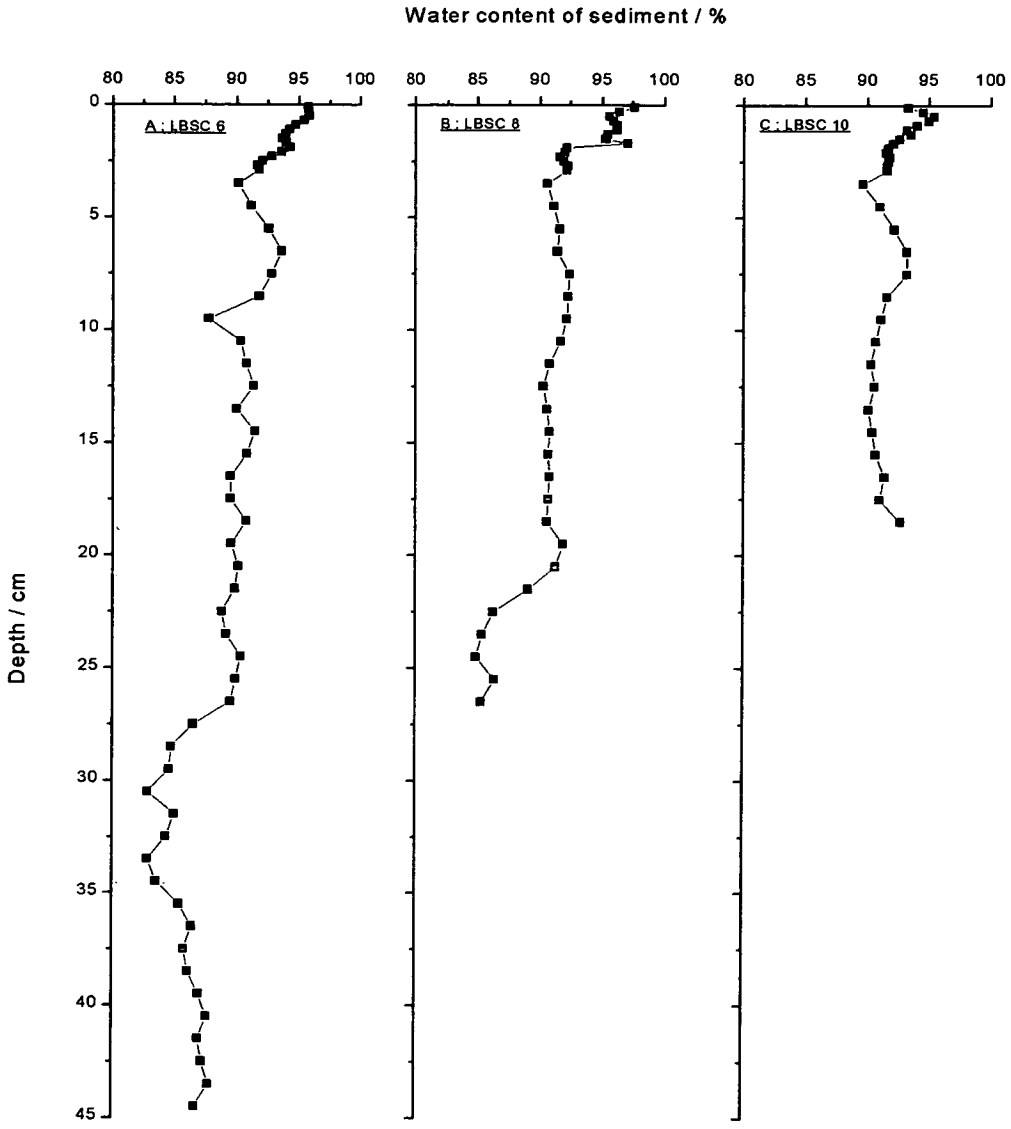


Fig. 3.13 A - C: Water content of sediment from LBSC 6, 8 and 10.

The general decrease in the water content of the sediment with depth at all sites arises from compaction of the sediment.

On the first sampling trip a bulk sample of sediment was collected which, once dried, ground and homogenised, was used as an in-house standard to monitor the reproducibility of the experimental methods. This standard was initially tested and

compared with a certified reference material, Lake Sediment SL-1 (International Atomic Energy Agency).

On each sampling trip the dissolved O_2, pH, conductivity and temperature were measured in surface water and in water from just above the sediment-water interface at one of the coring sites (Table 3.2). The measurements were taken using a Checkmate Probe for the surface water collected from over the edge of the boat and for bottom water overlying the collected sediment core. The readings of the bottom water were taken immediately after the core was brought back onto the boat to prevent any major alteration of the conditions. Unfortunately due to problems experienced with the probe, not all of the readings could be taken on some of the sampling trips. The results obtained from the surface water and the water from above the sediment-water interface were, in general, very similar, indicating that no thermal stratification was present in the loch at the time of sampling.

Site and depth of reading / m	Date of sampling	Temp. / °C	Dissolved O_2 / %	pH	Conductivity / mS
LBSC 3 - 0.0	28/7/96	16.5	-	6.5	53.2
- 11.0		14.8	-	6.4	55.0
LBSC 5 - 0.0	29/2/96	1.4	-	-	-
- 13.9		2.0	-	-	-
LBSC 10 - 0.0	1/8/97	0.3	-	-	-
- 13.0		0.7	-	-	-
LBWS 1 - 0.0	1/8/97	15.3	91	5.8	44.6
- 13.0		15.3	90	5.7	45.1
LBWS 4 - 0.0	25/5/98	11.6	89	5.6	51.1
- 15.5		11.4	89	4.8	53.2
LRSC 2 - 0.0	27/7/96	17.0	-	6.7	53.6
- 8.0		15.8	-	6.8	54.7

Table 3.2: Temperature, dissolved oxygen, pH and conductivity of water at the surface and at the sediment-water interface in Loch Bradan and Loch Riecawr.

3 .2.2 Collection of Pore Water

One sediment core was collected specifically for pore water extraction (LBPW 1), the only modification to the procedure being the use of a pre-drilled Jenkin core tube with holes spaced at 1-cm intervals in a spiral fashion and covered with water-resistant tape. The sediment and pore water were extracted using a stainless steel needle (attached to a 20-ml syringe) inserted through the holes in the coring tube. The sediment and pore water were then injected into an argon-flushed filter holder which held a GF-C (1.2 μm) filter (Whatman) on top of a 0.45 μm cellulose nitrate membrane filter (Whatman). While the sediment was being injected into the filter holder, a second syringe, on the opposite side of the filters, was used to suck and collect the pore water. The pore water was then injected into an argon-flushed sealed bottle through a rubber septum. This procedure was carried out at 1-cm intervals, starting at the top of the sediment core. The pore waters were then stored in the sealed bottles in a refrigerator at ~ 4 °C until analysis.

The sediment from this core was also collected by removing the deposit that had been retained by the GF-C filter paper. This sediment was dried at 30 - 40 °C, ground using a mortar and pestle, and stored in labeled, re-sealable plastic bags.

3.2.3 Collection of Loch Water Samples

Loch water was collected on the two sampling trips on 1/8/97 and 22/5/98. Four sites (LBWS 1 to LBWS 4) were sampled (Fig. 3.14, Table 3.3), with three samples being collected at each site, at the water surface, 5 m depth and just above the sediment-water interface, respectively. The surface water was collected in a 1-l acid-washed, screw-top, polyethylene bottle from over the side of the boat. The water at 5 m depth was collected using a mini-Friedinger water sampler after which it was transferred to an acid-washed 1-l screw-top plastic bottle. The water from above the sediment-water interface was collected by siphoning the water overlying the sediment from cores collected using the Jenkin sub-surface mud sampler. All of the sediment from

these collected cores was discarded with the exception of LBWS 4, which is the same sediment coring site (LBPW 1) from which the pore water was extracted. All samples of water were then taken back to the shore where they were filtered through a GF-C (1.2 μm) (Whatman) filter within two hours of collection. Half of the water was acidified using 16 M HNO_3 (Analar, 2 ml per 500 ml water), and the other half was stored in a cool box for return to the laboratory ~ 24 hours later, where they were frozen at ~ -10 °C.

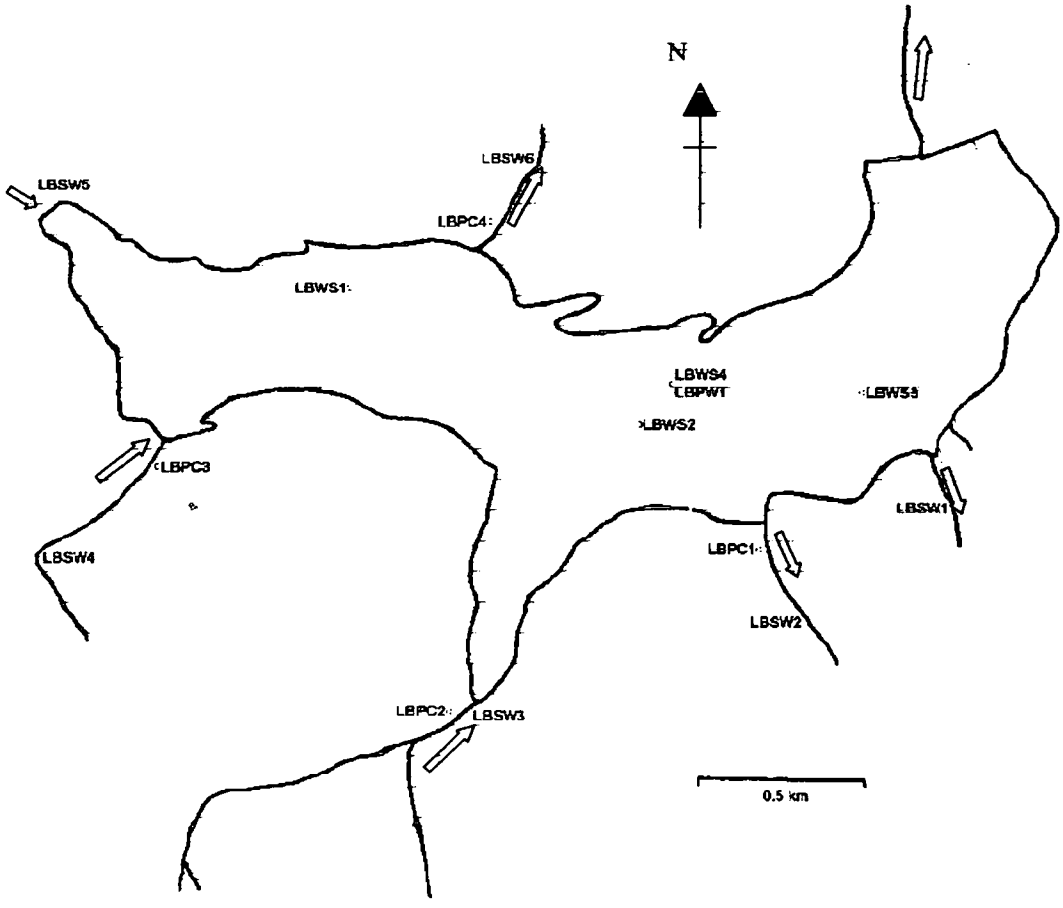


Fig. 3.14 : Map of peat core sites and loch water, pore water and stream water sample sites, with the arrows indicating the direction of the stream water flow.

Sample	Date of Collection	Depth of Bottom Water / m
LBWS 1	1 / 8 / 97	13.0
LBWS 2	1 / 8 / 97	14.5
LBWS 3	1 / 8 / 97	15.0
LBWS 4	25 / 5 / 98	15.5

Table 3.3: Table of depths of water samples and dates of collection.

3.2.4 Collection of Peat Cores

Four peat cores (LBPC 1 to LBPC 4) were collected from the catchment of Loch Bradan, as close as possible to the four main input streams, typically ~ 10 - 20 m away (Fig. 3.14). To collect these, holes (~ 1 m x 1 m across) were dug in the peat using a spade, with the hole being dug as deep as possible, generally until rock was hit or the water table was reached (Table 3.4). One face of the hole was made as vertically flush as possible, using a spade and a trowel, before sections of peat of ~ 15 x 15 cm and 2 - 3 cm thickness were cut using a trowel. The sections were stored in plastic bags and returned to the laboratory in cool boxes, where each peat sample was weighed wet in a clean pre-weighed plastic pot before being dried in an oven at 30-40 °C for a week. The dried peat was then re-weighed and ground using a mortar and pestle until it was able to pass through a 1-mm sieve, thus removing any large pieces of roots or vegetation, after which the samples were stored in labeled, clean, re-sealable plastic bags.

Sample	Date of Collection	Depth of Core / cm	Visual Features of Core
LBPC 1	24 / 5 / 97	70	Sandy material noted below ~ 35 cm of peat.
LBPC 2	24 / 5 / 97	56	Thin layer of more sandy material at ~ 30 cm.
LBPC 3	24 / 5 / 97	48	Hit rock at the base of the core
LBPC 4	24 / 5 / 97	46	Crumbly with a sandy texture.

Table 3.4: Depths of peat cores and features noted at the time of sampling

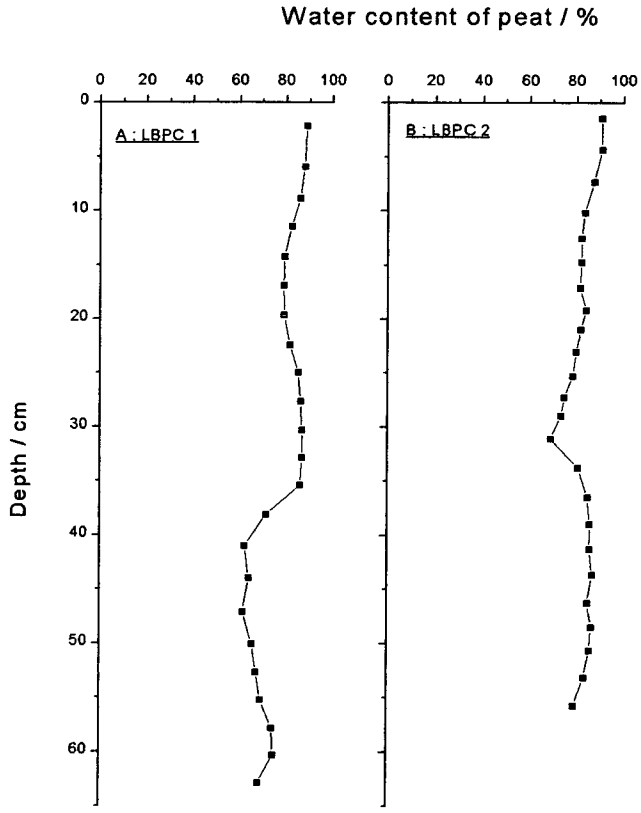


Fig. 3.15 A - B: Water content of peat cores LBPC 1 - 2.

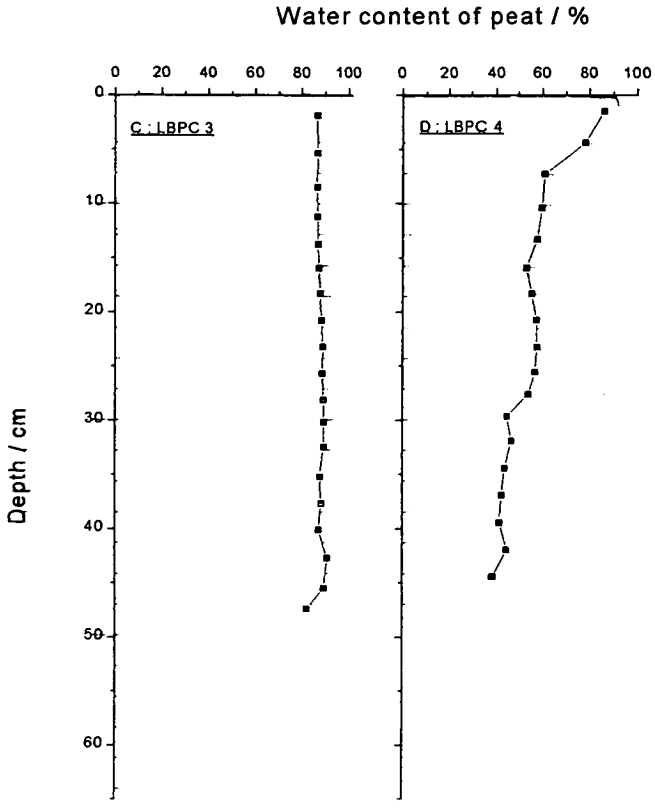


Fig. 3.15 C - D: Water content of peat cores LBPC 3 - 4.

The weighing of the peat before and after drying of the peat allowed calculation of the water content of the peat (Fig. 3.15, Appendix 19). In all peat cores the water content in the upper region was 80 - 90 %. In LBPC 1 the water content did not vary much over the top 36.7 cm of the core, with an average of 84.1 ± 3.4 %, but below 36.7 cm the water content decreased to a minimum of 61.4 % at 45.5 - 48.7 cm (Fig. 3.15 A). LBPC 2 showed a general decrease in water content from the surface, reaching a minimum at 29.7 - 32.4 cm, the same depth as the sandy deposit (Fig. 3.15 B, Table 3.4). LBPC 3 showed little variation in the water content until the base of the core where it decreased (Fig. 3.15 C). The water content of LBPC 4 showed a general decrease from the surface to the base of the core, and was much lower than at any of the other coring sites (Fig. 3.15 D).

3.2.5 Collection of Stream Water Samples

Stream water was collected from 6 streams (LBSW 1 - LBSW 6) (Fig. 3.14) in 1-l acid-washed, screw-top, polyethylene bottles, and treated in the same way as the loch water samples.

3.3 Experimental Procedures

3.3.1 Acid Washing of Glassware

Before sample treatment and analysis in the laboratory, all glassware had to be acid washed to ensure that no metal ions were present on the glass surface. The glassware was first washed in detergent and well rinsed in tap water. The detergent-cleaned glassware was rinsed with MilliQ water (~ 18 $M\Omega\ cm^{-1}$ resistivity) and then heated in 5M HNO_3 (Analar) for 4 hours before it was rinsed with MilliQ water and heated in a water bath (MilliQ) for a further 4 hours. The clean glassware was again rinsed with MilliQ water and dried in a drying cabinet, before being sealed with clingfilm for storage until use.

3.3.2 Pseudo-Total Metal Extraction

Pseudo-total metal extraction was carried out on all samples of sediment and peat, with duplicate analysis performed on selected samples to check reproducibility of methods and results.

0.05-0.1 g of each sediment or peat sample was accurately weighed out into a clean 100 ml beaker, to which 20 ml HNO_3 (8 M Analar) was added and heated for 2 hours at 90 °C on a hotplate, after covering each beaker with a watch glass. After this, 10 ml HCl (11.6 M Analar) was added and the samples, re-covered by the watch glasses, heated for a further hour, after which the hotplate was switched off. Once cool, the samples were filtered through Whatman No. 40 filter papers into clean 100 ml

beakers, washing the original beakers and the filter papers with HCl (1 M Analar) to yield ~ 25 ml in total. The samples were then reheated, uncovered, allowing the volume to decrease to ~ 5 - 10 ml, to which 5-10 ml portions of HCl (11.6 M Analar) were added until brown fumes of NO_2 were no longer produced. This removal of the HNO_3 normally took 3-4 hours and required the addition of ~ 50 ml HCl (11.6 M Analar). At this point the additions of HCl were stopped and the solutions allowed to evaporate to ~ 1 ml, after which they were transferred to 25 ml volumetric flasks, rinsing the original beakers with ~ 15 ml HCl (1M Analar), and making the solutions up to a final volume of 25 ml with HCl (1 M Analar). The resultant solutions were stored in 30 ml polypropylene tubes ready for analysis by flame atomic absorption spectrometry (FAAS) (Section 3.4.1).

This procedure was carried out for an average of ten samples of sediment or peat at one time, with each run including a pseudo-total metal extraction of the in house reference material and also a reagent blank. This was done to check for continuity between runs and also for any contamination of the samples.

This method of metal extraction removes virtually all of the metals present in the sediment and peat, although a small fraction of metal held within mineral lattices will not be extracted. To remove the remaining metal present in the sediment and peat stronger acids such as HF would have to be used. In view of the hazards associated with the use of HF, this method was not employed.

3.3.3 Extraction of the Easily Reducible Manganese Fraction

The easily reducible fraction of the Mn, along with associated metals, was extracted from all of the sediment and peat samples, again repeating the analyses on selected samples.

0.05-0.1g of each sediment or peat sample was weighed out accurately into a clean 250-ml screw top conical flask, to which 20 ml $NH_2OH.HCl$ (0.1 M Analar) made up

in HNO_3 (0.01 M Analar) was added and the flasks shaken for 30 minutes at room temperature on a wrist action shaker (Stuart Scientific Flask Shaker SF-1) (Chao, 1972). The resulting solutions were filtered through Whatman No. 40 filter paper into 30-ml polypropylene tubes ready for analysis. A maximum of 16 flasks could be shaken at any one time, consisting typically of 14 samples, an in-house reference standard and also a reagent blank. Analysis of the samples was carried out using FAAS (Section 3.4.1).

3.3.4 Extraction of Arsenic from Sediment and Peat

Arsenic was extracted from all peat and most of the sediment samples, as in some cases insufficient sediment from certain sections remained.

0.05-0.1 g of each sediment or peat sample was weighed out accurately into a clean 100-ml glass beaker. To this a few drops of diluted Decon 90 detergent were added before the addition of 2 ml of $Mg(NO_3)_2$ (25 % w/v Analar). The diluted Decon 90 detergent was added to break the surface tension and allow complete mixing of the sample and $Mg(NO_3)_2$. The beakers containing the samples were placed in a muffle furnace at 100 °C for a minimum of 4 hours before the temperature was increased to 450 °C, again heating for a minimum of 4 hours. The addition of $Mg(NO_3)_2$ and the ashing of the samples were employed to destroy the organic content of the sediment or peat and allow full extraction of the As. After ashing, the cooled beakers were removed from the furnace and 5 ml HCl (11.6 M Analar) added to each before the beakers were covered with parafilm and shaken overnight on a wrist action shaker (Stuart Scientific Flask Shaker SF-1). Once shaken, the solutions were filtered through Whatman No. 40 filter papers into 25-ml volumetric flasks, rinsing the beakers and the filter papers with MilliQ water, before making the final volume up to 25 ml. Arsenic concentrations of these samples were measured using hydride generation atomic absorption spectrometry (HGAAS) (Section 3.4.2).

3.3.5 Extraction of the Total Humic Component

The humic fraction of each peat and sediment sample (where sufficient sediment remained) was extracted using NaOH.

Approximately 0.1 g of sediment or peat was accurately weighed out into a clean 250-ml screw top conical flask to which 10 ml NaOH (0.1 M Analar) was added. The conical flasks were then shaken for 2 hours on a wrist action shaker (Stuart Scientific Flask Shaker SF-1), before the overlying liquid was decanted off into 50-ml polyethylene centrifuge tubes and centrifuged for 5 minutes at 6000 rpm (MSE Mistral 1000 centrifuge). After centrifugation, the overlying liquid was removed using Pasteur pipettes, being careful not to pick up any particulate material, and was then centrifuged in a clean polyethylene centrifuge tube for a further 5 minutes at 6000 rpm. The overlying water from the second centrifugation was removed, again using a Pasteur pipette, and stored in an acid-cleaned 100-ml beaker. The remaining solid at the bottom of each centrifuge tube was washed back into the 250-ml screw top conical flasks with approximately 20 ml NaOH (0.1 M Analar). This was then shaken for a further 2 hours before the same procedure was repeated again. This overall procedure was repeated (usually four times) until the overlying solution remained colourless after shaking for 2 hours. In the case of some of the more organic-rich peat samples, five or six repeats were required, and the final period of shaking extended to overnight to ensure complete extraction of the humic.

The NaOH extracts were dialysed using 12,000 - 14,000 molecular weight cut off (MWCO) dialysis tubing (Medicell) against MilliQ water. This allowed Na^+ and OH^- ions and molecules smaller than 12,000 - 14,000 Daltons to flow out of the dialysis tubing and be replaced by MilliQ water, but retained the larger molecules. The dialysis water was changed regularly until the pH of the MilliQ water remained unchanged overnight (~ pH 5.5), indicating that all of the NaOH had been removed. Each dialysed sample was transferred to a pre-weighed 30-ml polypropylene tube, in

which the extract was freeze-dried (Heto CT 60E) and the tube re-weighed to obtain the weight of humic extracted.

3.3.6 Extraction of Humic-Associated Metals

5-10 mg of each freeze-dried NaOH humic extract was accurately weighed out into an ultra-light tin cup (Sartorius ultra-micro balance). The weighed samples were transferred into clean 100-ml beakers that were then covered with Nescofilm. To obtain the accurate weight, the tin cups were then re-weighed empty and any increase in mass was taken into account when calculating the weight of humic analysed. After removing the Nescofilm covering, the samples and blank were ashed, at 100 °C for a minimum of 4 hours, followed by an increase in temperature to 450 °C, again for a minimum of 4 hours. The ashed humics were subjected to the pseudo-total metal extraction procedure as described in Section 2.3.2, except that all volumes in the extraction were halved and the samples were made up to a final volume of 10 ml. Determination of the metals was carried out using FAAS (section 3.4.1).

3.3.7 Size Fractionation of Loch Water

Total metal concentrations in the filtered, acidified loch water were determined directly by FAAS (Section 3.4.1).

The samples of loch water that were left unacidified and frozen soon after collection were thawed and separated into two size fractions, < 1 kDa and > 1 kDa, using 1 kDa cut off Macrosep™ centrifugal concentrators. This was done after the samples were first filtered through 0.2 μm cellulose nitrate filter (Whatman) to stop the blocking of the Macrosep™ membrane. 20 ml of the loch water was then pipetted into the centrifugal concentrators and centrifuged for 99 minutes (the maximum time of centrifugation permitted by the centrifuge) at 6000 rpm (MSE Mistral 1000 centrifuge). After 99 minutes, the < 1 kDa and > 1 kDa fractions were transferred into 30-ml polypropylene tubes and stored in the refrigerator at ~ 4 °C. This was

repeated using a fresh sample of loch water, collecting the two size fractions. The two aliquots of > 1 kDa size fraction were combined and centrifuged for a further 99 minutes at 6000 rpm, again collecting the two size fractions, and the final volumes of the > 1 kDa and the < 1 kDa fractions then measured.

The two size fractions collected were acidified to 1 % v/v HNO_3 (by the addition of 20 µl HNO_3 (16 M Analar) to 2 ml of sample) before analysis by FAAS (section 3.4.1).

3.3.7 Size Separation of Pore Water

Metal concentrations in pore water were determined for both acidified pore water and also pore water that had been size fractionated.

To acidify the pore water, a 1-ml sample was removed from the argon-flushed vial via the rubber septum using syringe and needles. Exactly 1 ml of each pore water sample was acidified by the addition of exactly 1 ml HCl (2 M Analar) and metal concentration determined by FAAS (Section 3.4.1).

The pore water was separated into two size fractions, < 1 kDa and > 1 kDa, by a similar method as used for the loch water (Section 2.3.6). Aliquots (3 ml) of pore water were pipetted into 1 kDa Millisep™ centrifugal concentrators and centrifuged for 99 minutes at 6000 rpm (MSE Mistral 1000 centrifuge). Unlike the procedure used for the loch water, the centrifuge step was carried out only once, after which the volume of both size fractions was measured using a 10 µl pipette. Both size fractions were acidified, the < 1 kDa fraction by adding 1 ml HCl (2 M Analar) to 1 ml of sample and the > 1 kDa size fraction by the addition of 10 µl HCl (11.6 M Analar), before analysis of the samples for metal content using FAAS (section 3.4.1). Mn and Fe were determined in all samples of pore water that was not separated according to size, but due to the small volumes obtained only Mn could be determined for the samples separated according to size.

3.4 Analytical Measurements

3.4.1 Flame Atomic Absorption Spectrometry

Determination of the metal content (Mn, Fe, Pb, Cu, Zn) of the solutions was carried out using flame atomic absorption spectrometry (FAAS), principally using a Solaar Unicam 929, but on occasions a Pye Unicam SP9 was also used.

At least three standard solutions were prepared for the determination of each of the metals. These were made up by diluting a 1000 mg l^{-1} stock solution (Fisher Scientific high purity reagents) with the same reagent matrix present in the sample solution, i.e. HCl (1 M Analar), for samples prepared by the pseudo-total metal extraction procedure (Section 2.3.2).

The instrumental set up of the FAAS varied according to metal concentration. More concentrated sample solutions required rotation of the burner head and / or selection of a less sensitive wavelength (Table 3.5). For samples with a low concentration of metal, close to the detection limit of the FAAS, the sensitivity was increased by using the slotted tube atom trap (STAT) tube. With samples which exhibited large differences in metal concentration, varying standard solution concentrations in the appropriate concentration range had to be made up.

Metal	Wavelength / nm	Bandpass / nm	Burner Rotation	Use of STAT Tube
Mn	279.5 403.1 (10 x)	0.2	0 - 30 ^{0}	None
Fe	248.3 372.0 (10 x)	0.2	0 - 30 ^{0}	None
Cu	324.8	0.2	0 ^{0}	On occasion
Pb	217.0	0.2	0 ^{0}	Frequently
Zn	213.9	0.2	0 ^{0}	On occasion

Table 3.5 : Operating parameters for FAAS. All readings were taken using an air / acetylene flame, using D_2 background correction for wavelengths less than 300 nm. Two wavelengths had to be used for Mn and Fe due to the high concentration range, the number in brackets being the reduction in the sensitivity achieved by changing the wavelength.

3.4.2 Hydride Generation Atomic Absorption Spectrometry (HGAAS)

Arsenic concentrations in sample solutions were determined by HGAAS using a Pye Unicam continuous flow vapour system attached to a Pye Unicam SP9 atomic absorption spectrometer.

Before analysis the arsenic in each of the samples had to be reduced to As(III) by adding 1 ml of a 25 % w/v KI / 2.5 % w/v ascorbic acid solution, 11.6 M HCl (4 ml Analar) and 18 ml MilliQ water to 2 ml of sample solution.

Standard As solutions were made up from a 1 mg l^{-1} stock solution, (made by diluting 1 ml of a 1000 mg l^{-1} stock solution to 100 ml), as shown in Table 3.6

	As Concentration / mg l^{-1}				
	0.02	0.04	0.06	0.08	0.10
Stock	0.5	1.0	1.5	2.0	2.5
conc. HCl	4.0	4.0	4.0	4.0	4.0
25 % KI	1.0	1.0	1.0	1.0	1.0
MilliQ water	19.5	19.0	18.5	18.0	17.5
Total vol. / ml	25	25	25	25	25

Table 3.6 : composition of standard As solutions, made up from a 1 mg l^{-1} stock solution of As, using a 25 % w / v KI / ascorbic acid solution (12.5 g KI and 1.25 g AA dissolved in 50 ml MilliQ water and used within a week of preparation)

3.4.3 Sulphur and Phosphorus Determination using Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES)

The sulphur and phosphorus content of LBSC 6 sections extracted using the pseudo-total metal extraction procedure were determined by ICP-OES (Thermo Jarrell Ash IRIS). The ICP-OES was set up as shown in Table 3.7, with standard solutions of 1, 10 and 100 mg l^{-1} S and P being used, taking emission readings at two wavelengths (Table 3.7).

Parameters	Settings
R.F. Power	1150 watts
Auxiliary flow	0.5 l min^{-1}
Nebuliser flow	30.06 psi
Sample introduction rate	1 ml min^{-1}
S Wavelength	180.731 nm, 182.034 nm
P Wavelength	177.499 nm, 178.287 nm

Table 3.7: ICP-OES operating parameters.

3.4.4 Determination of Oxidisable Organic Matter

Oxidisable organic matter, which includes humic material, was determined for all peat and most of the sediment samples, although in some cases insufficient sediment from certain sections was left to allow this analysis to be carried out.

0.05 g of dried, ground sediment or peat was accurately weighed out and placed in a 500-ml Erlenmeyer flask, into which exactly 10 ml of $K_2Cr_2O_7$ (1 N Analar) solution was pipetted followed by the addition of 20 ml H_2SO_4 (18 M Analar) containing Ag_2SO_4 (2.5g Ag_2SO_4 per litre of H_2SO_4). The resultant solution was gently rotated, to ensure complete mixing of the reagents with the sample, and left to stand for 30 minutes, whereupon the solution was diluted to 200 ml with MilliQ water, and 10 ml H_3PO_4 (85 % GPR), 0.2 g NaF and 15 drops of diphenylamine indicator added.

The resultant solution was then back titrated with $Fe(NH_4)_2(SO_4)_2$ (0.5 N GPR) with the end point occurring when the solution turned from blue to green on addition of a single drop of $Fe(NH_4)_2(SO_4)_2$ (0.5 N GPR).

For every new batch of samples a standardization blank was run, using the same procedure, but with no sediment or peat sample present. To check the solutions were of the correct concentration, glucose, which has a known oxidisable organic C concentration of 39.99 %, was used as a reference material.

The concentration of readily oxidisable organic matter was then calculated using equation 3.1:

Eqn 3.1: $$\text{Readily oxidisable organic matter / \%} = 10 \times \left(1 - \frac{T}{S}\right) \times F$$

S = standardisation blank titration, ml ferrous solution

T = sample titration, ml ferrous solution

F = factor derived as follows

$$= (1.0\,N) \times \frac{12}{4000} \times 1.72 \times \frac{100}{\text{sample weight}}$$

1.72 = factor for organic matter from carbon.

3.4.5 Elemental Analysis

Elemental analysis for C, H, N (%) was carried out on selected samples of freeze-dried humic extracted from sediment and peat using a Perkin Elmer 2400 CHN Elemental Analyser. Percentage O was estimated by difference assuming that C, H, N and O were the only components in the extracted humics material.

3.4.6 Infrared Spectrometry of Extracted humics

IR spectra of the humic extracted from the sediment of LBSC 7 were obtained using a Perkin Elmer Paragon 1000 FTIR spectrometer, after pressing the humic into a KBr disc (Specpure).

3.4.7 Electron Spin Resonance Spectrometry

The ESR spectra of all of the unacidified water samples were obtained using a Bruker ER 200 D-SRC spectrometer.

Unacidified water samples were pipetted into a quartz flat cell ESR tube with enough water to fill the flat cell completely. The ESR spectrum of each sample was obtained using the instrumental conditions shown in Table 3.8. In between sample runs the cell was rinsed thoroughly with MilliQ water and with the next water sample.

Parameter	Settings
Frequency	9.69 GHz
Center Field	3440 Gauss
Sweep Width	700 Gauss
Gain	5×10^5
Modulation	4 Gpp
Time Constant	100 ms
Sweep Time	100s
Attenuation	100 mW

Table 3.8: ESR operating parameters

3.4.8 Mineralogy of Manganese and Iron

To investigate sediment mineralogy, X-ray diffraction spectroscopy (XRD) was carried out on selected samples of sediment using a Siemens D5000 Diffractometer at the Macaulay Land Use Research Institute in Aberdeen. The XRD was performed using Co K-alpha radiation and a graphite crystal diffracted beam monochromator.

In addition scanning electron microscopy – energy dispersive x-ray spectroscopy (SEM-EDX) (Phillip XR30 CP with Oxford Instruments X-ray analyser) was carried out on one sample of peat from LBPC 1 to try to identify its mineral content.

3.5 Concluding Remarks

The results from the described results are presented and discussed in chapters 4 - 6 and also listed in appendices 1 to 18. Appendices 1-10 contain the results for LBSC 1 to 10, appendices 11 and 12 contain the results for LRSC 1 and 2, appendices 13 - 16

contain the results for LBPC 1 - 4, appendix 17 contains the results from LBSW 1 - 6 and appendix 18 contains the results for LBWS 1 - 4 and LBPW 1.

4. Sediment Core Metal Data and the Influence of Redox Cycling

4.1 Manganese, Iron, Arsenic and Organic Matter in the Sediments of Loch Bradan and Loch Riecawr

Since Mn, Fe and As are known to be redox-active, their concentration profiles within the sediment will be discussed together. The concentrations of organic matter will also be considered in this section in view of its involvement in redox cycling.

4.1.1 Manganese, Iron and Arsenic in the Top 3 cm of Sediment from Loch Bradan

All of the sediment concentration profiles for total Mn, Fe and As show similar trends, with an enrichment in concentration observed within the top 3 cm of sediment (Figs. 4.1 A - J, Appendices 1 - 10).

The Mn concentration profiles can be split into two categories based on the depth of the maximum enrichment:

Group I:	surface Mn peak	LBSC 2, 3, 7 (Fig. 4.1 B, C, G)
Group II :	near-surface Mn peak	LBSC 1, 4, 5, 6, 8, 9, 10 (Fig. 4.1 A, D, E, F, H , I , J)

Group I Mn concentration profiles show enrichment in the 0.0 - 0.2 cm section of the sediment (Table 4.1) .

Group II Mn profiles all exhibited their maximum enrichment within the top 1 cm of the sediment, with the exception of LBSC 8 (Fig. 4.1 H) where the maximum enrichment was at 1.0 - 1.2 cm depth (Table 4.1).

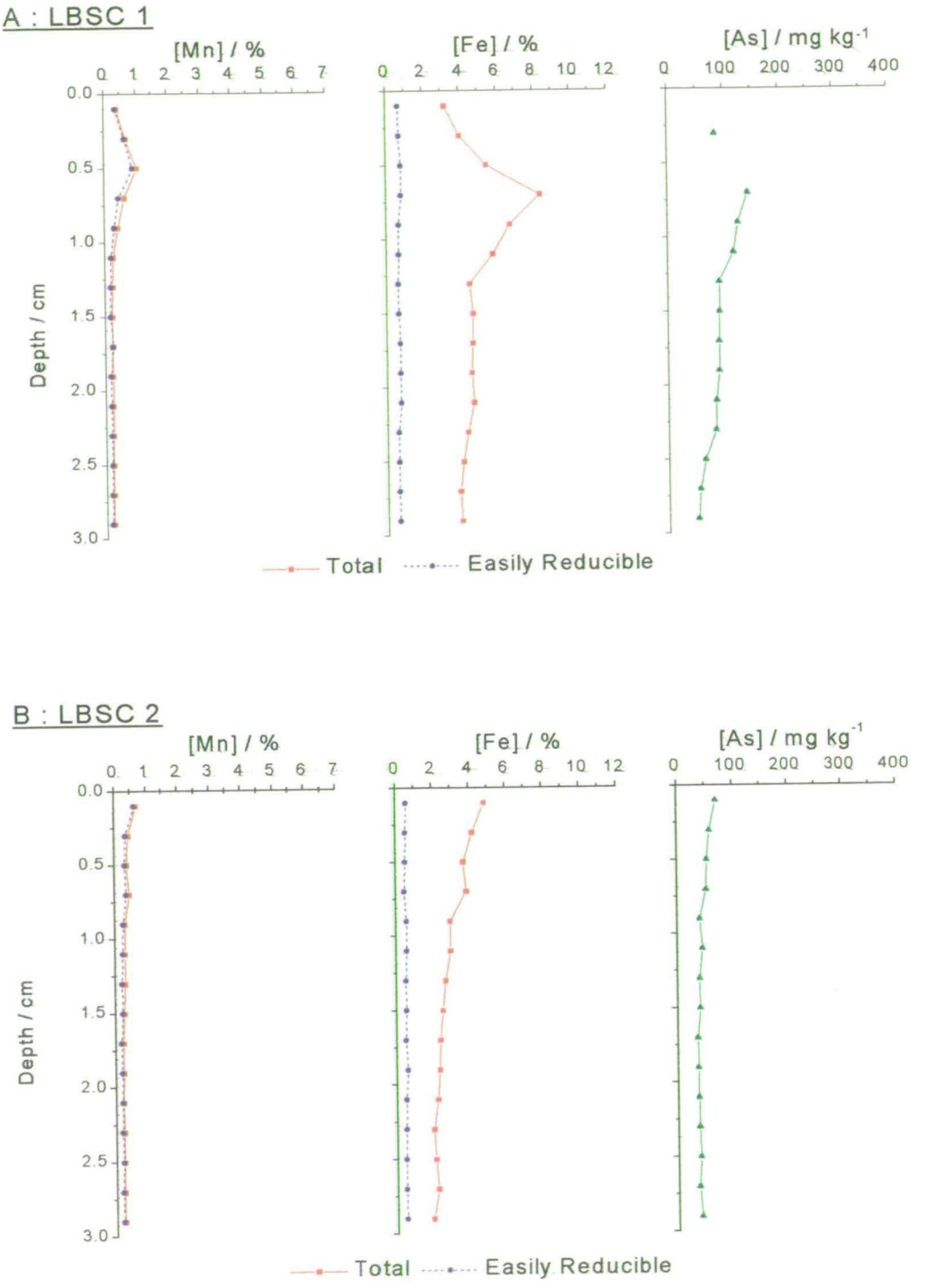
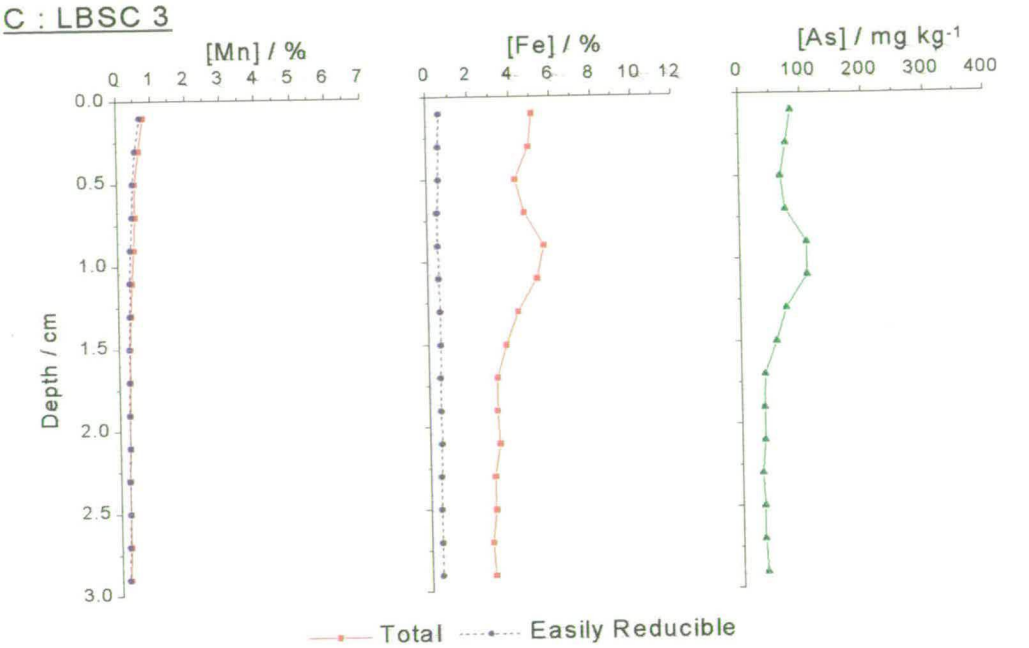


Fig. 4.1 A - B : Total and easily reducible Mn and Fe, and As concentrations in LBSC 1 and 2.



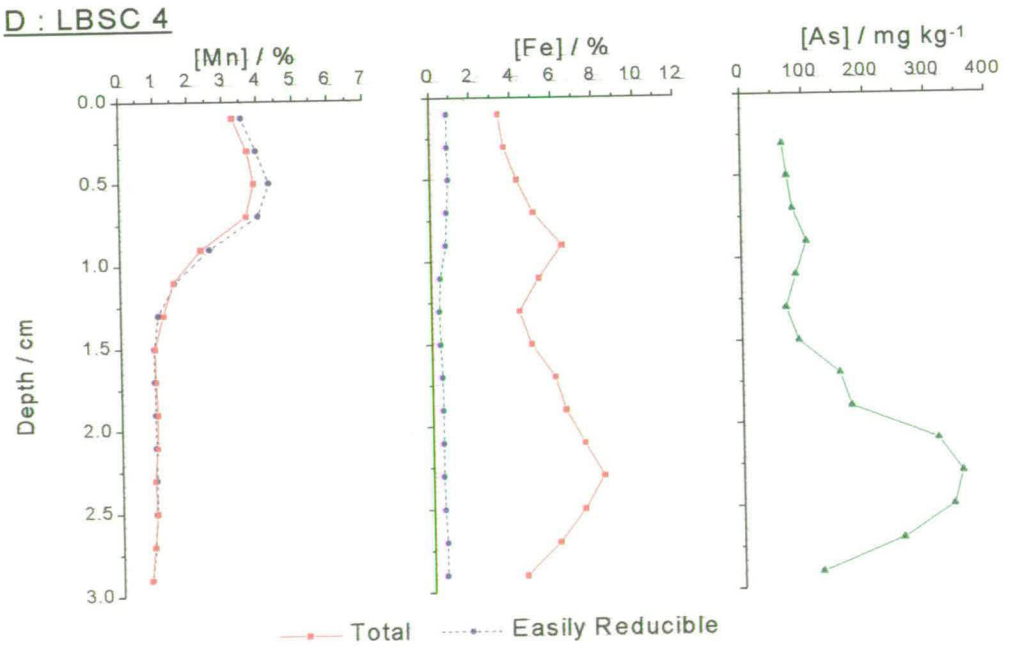
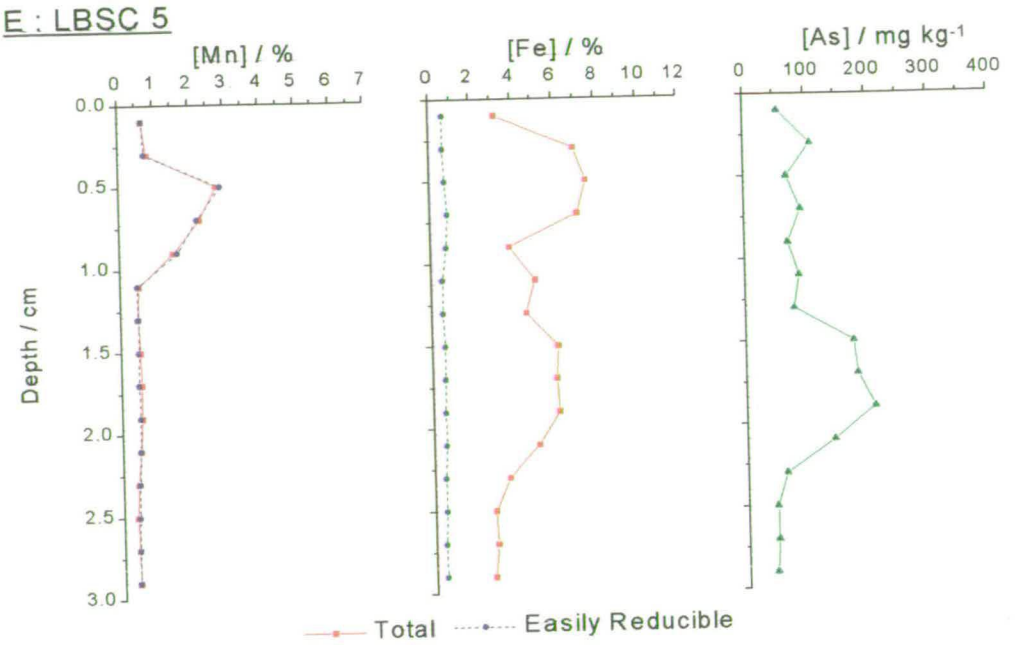


Fig 4.1 C - D : Total and easily reducible Mn and Fe, and As concentrations in LBSC 3 and 4.



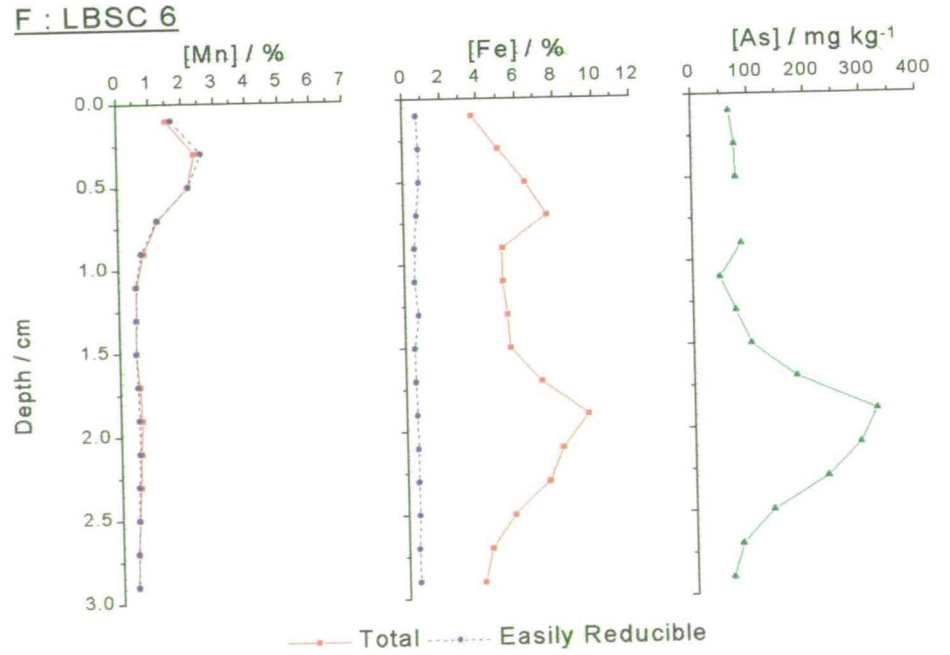
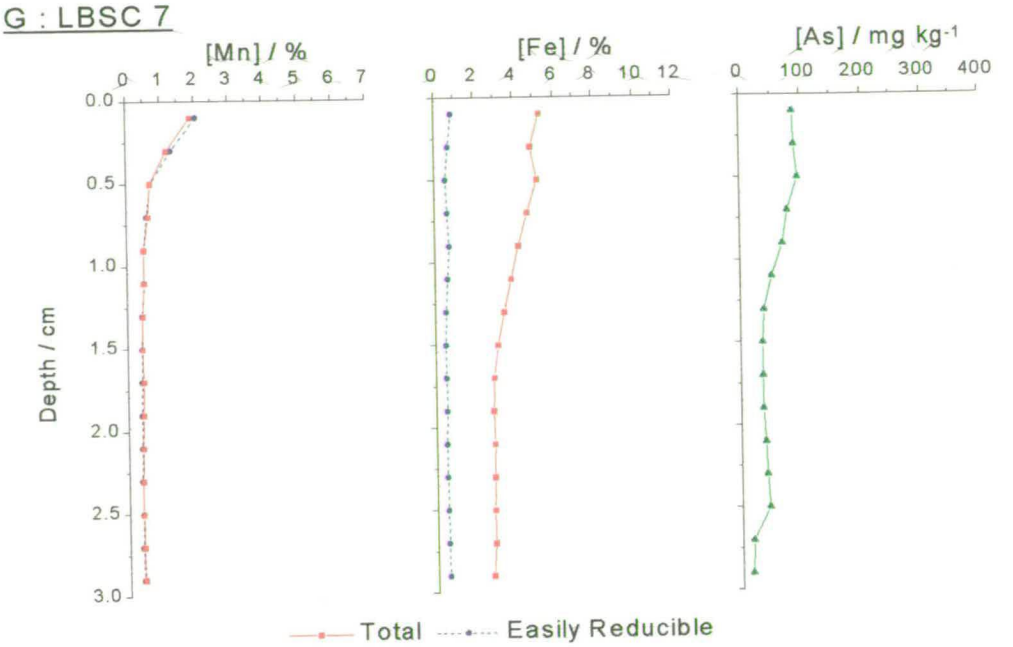


Fig 4.1 E - F : Total and easily reducible Mn and Fe, and As concentrations in LBSC 5 and 6.



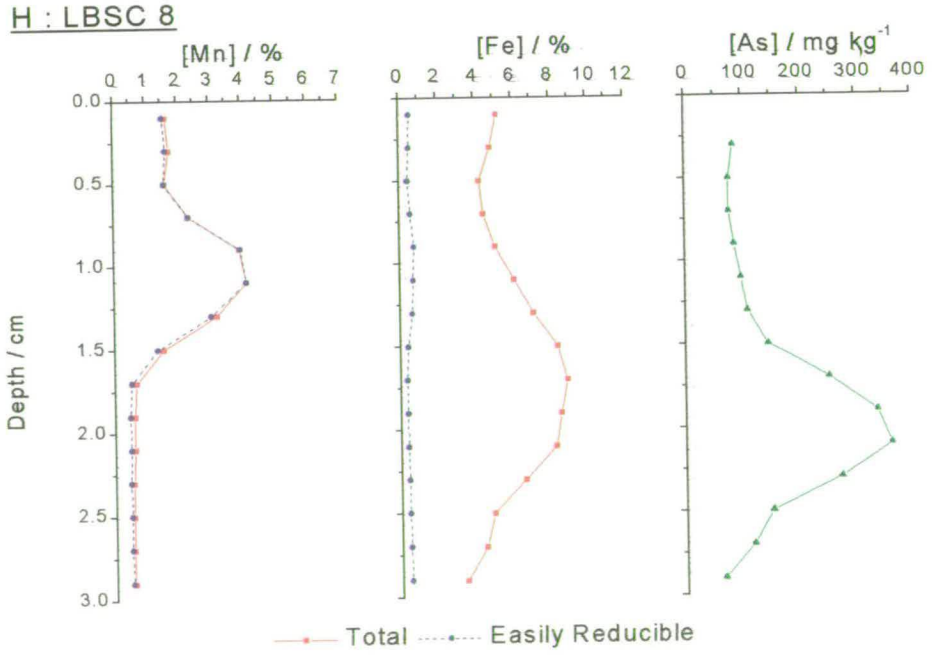
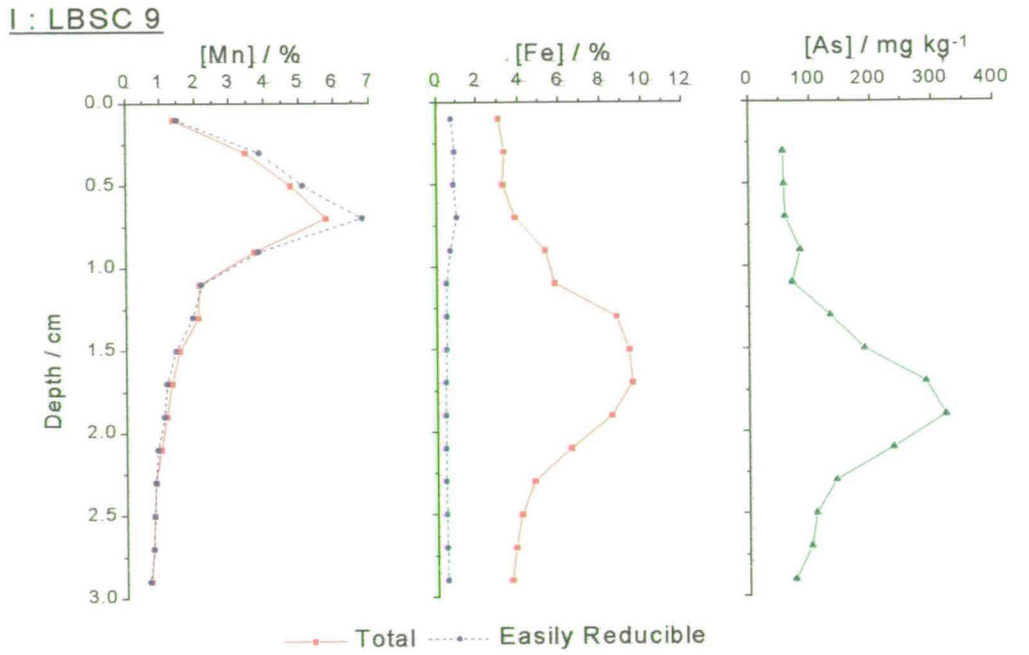


Fig. 4.1 G - H : Total and easily reducible Mn and Fe, and As concentrations in LBSC 7 and 8.



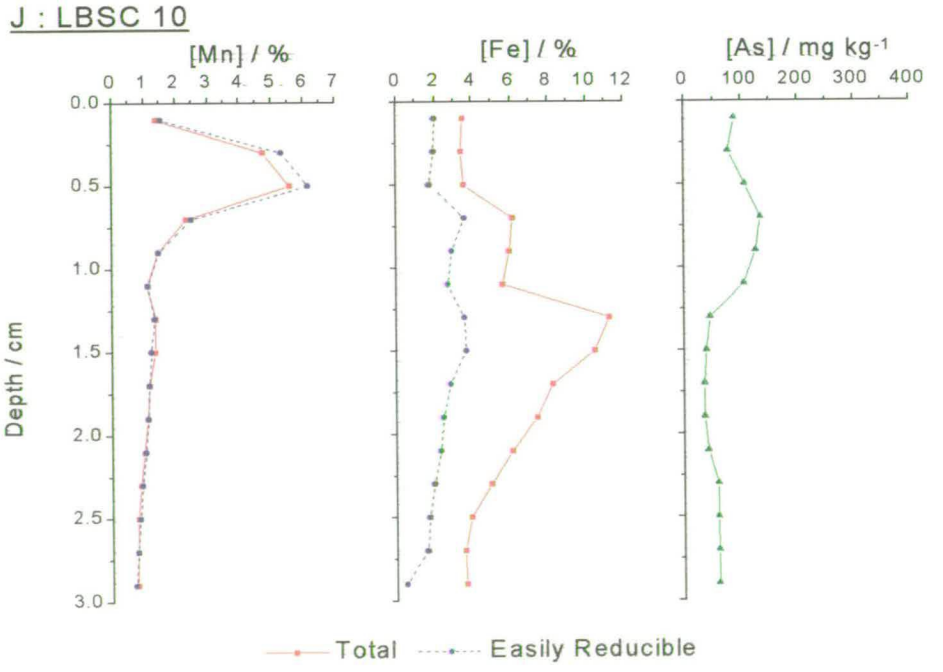


Fig. 4.1 I - J : Total and easily reducible Mn and Fe, and As concentrations in LBSC 9 and 10.

There is a considerable variation in the maximum concentrations observed for Mn in the top 3 cm, ranging from 0.66 % to 5.75 % (Table 4.1). The sediments with the lowest concentrations (0.66 - 0.99 %) of Mn were collected from the western basin of Loch Bradan (LBSC 1 - 3), while the highest concentrations (1.86 - 5.75 %) were found to be present in the eastern basin (LBSC 4 - 10) (Table 4.1, Figs. 4.1 A-J).

Sediment Core Site	Depth of Water / m	$[Mn]_{max}$ / %	$[Mn]_{baseline}$ / %	Depth of Maximum / mm	Percentage of Mn in an easily reducible form / %
LBSC 1	10.1	0.99	0.2	4 - 6	80.5 ± 12.0
LBSC 2	8.0	0.66	0.2	0 - 2	81.6 ± 7.2
LBSC 3	8.3	0.75	0.2	0 - 2	87.9 ± 6.3
LBSC 4	13.1	3.86	0.9	4 - 6	98.6 ± 12.5
LBSC 5	13.9	2.74	0.4	4 - 6	99.2 ± 7.4
LBSC 6	13.9	2.36	0.5	2 - 4	97.4 ± 6.6
LBSC 7	9.9	1.86	0.4	0 - 2	98.0 ± 6.0
LBSC 8	12.0	4.12	0.55	10 - 12	90.1 ± 9.0
LBSC 9	13.9	5.75	0.8	6 - 8	100.7 ± 7.9
LBSC 10	13.0	5.54	0.8	4 - 6	102.9 ± 6.3

Table 4.1 : Maximum and baseline Mn concentrations, and percentage of Mn present in an easily reducible form in the top 3 cm of sediment cores collected from Loch Bradan.

The percentage of the total Mn that is present in the sediment in an easily reducible form (i.e. extractable with $NH_2OH.HCl$ / HNO_3) can also be seen to vary from the western to eastern basins of Loch Bradan (Table 4.1). In the western basin 80.5 ± 12.0 % to 87.9 ± 6.3 % of the Mn was found to be present in an easily reducible form compared with 90.1 ± 9.0 % to 102.9 ± 6.3 % in the eastern basin. In all cases the relative proportion of the easily reducible Mn shows little variation with depth in the top 3 cm of the sediment cores.

The Fe concentration profiles can be split into three groups, again based on the depth of the observed enrichment:

Group I: surface Fe peak LBSC 2, 7 (Figs. 4.1 B, G)

Group II:	near-surface Fe peak	LBSC 1, 3, 4, 5, 6 (Figs. 4.1 A, C, D, E, F)
	(secondary Fe peak	LBSC 4, 5, 6 (Figs. 4.1 D, E, F))
Group III:	broad subsurface Fe peak	LBSC 8, 9, 10 (Figs. 4.1 H, I, J)

Group I Fe concentration profiles show the maximum enrichment of Fe to be in the 0.0 - 0.2 cm section of the sediment core, where the maximum enrichment of Mn was also found (Table 4.2).

Sediment Core Site	Depth of Water / m	$[Fe]_{max}$ / %	Depth of $[Fe]_{max}$ / mm	Percentage of Fe in an easily reducible form / %	$[As]_{max}$ / mg kg^{-1}	Depth of $[As]_{max}$ / mm
LBSC 1	10.1	8.35	6 - 8	13.4 ± 2.6	143	6 - 8
LBSC 2	8.0	4.80	0 - 2	19.0 ± 6.1	70	0 - 2
LBSC 3	8.3	5.60	8 - 10	11.0 ± 2.1	106	8 - 12
LBSC 4	13.1	8.35	22 - 24	11.4 ± 6.1	356	22 - 24
LBSC 5	13.9	7.51	4 - 6	11.8 ± 3.6	209	18 - 20
LBSC 6	13.9	9.51	18 - 20	10.2 ± 3.6	321	18 - 20
LBSC 7	9.9	5.27	0 - 2	15.7 ± 6.0	94	4 - 6
LBSC 8	12.0	8.84	16 - 18	8.1 ± 3.3	362	20 - 22
LBSC 9	13.9	9.50	16 - 18	12.4 ± 8.3	321	18 - 20
LBSC 10	13.0	11.21	12 - 14	41.1 ± 11.3	133	6 - 8

Table 4.2 : Maximum Fe and As concentrations and the percentage of Fe in an easily reducible form in the top 3 cm of sediment cores collected from Loch Bradan.

Group II Fe profiles all display near-surface enrichments in the top 1 cm of the sediment, 0.0 - 0.8 cm below those observed for Mn in the corresponding cores (Tables 4.1, 4.2). LBSC 4, 5 and 6 also contain a further Fe enrichment between 1 and 3 cm which, in the cases of LBSC 4 and 6, is greater than the enrichment observed in the top 1 cm (Figs. 4.1 D, F).

Group III Fe profiles all contain a broad subsurface Fe enrichment, with the maximum concentration at 1 - 2 cm depth within the sediment, 0.6 - 1.0 cm below the Mn maxima (Table 4.2).

The position of the maximum As enrichment within the sediment also varies between coring sites, but in all cases it is at the same depth as enrichments in the Fe concentration profile (Table 4.2, Figs. 4.1 A-J). With the exception of LBSC 5 and 10, (where the As maxima occur at the same depths as secondary, smaller enrichments in Fe (Figs. 4.1 E, J)) the As maxima coincide with the area of maximum Fe enrichment.

Fe and As show similar concentration trends to those observed for Mn, with lower concentrations in the western basin. In the western basin, maximum concentrations observed range from 4.80 to 8.35 % for Fe and 70 - 143 mg kg^{-1} for As, whereas in the eastern basin these concentrations are 5.27 - 11.21 % and 94 - 362 mg kg^{-1}, respectively (Table 4.2).

Unlike Mn, there is no major variability in the percentage of the Fe that is in an easily reducible form (i.e. extractable with $NH_2OH.HCl$ / HNO_3), with all cores, except LBSC 10, lying in the range of 8.1 ± 3.3 % to 19.0 ± 6.1 %. LBSC 10 has a higher percentage of easily reducible Fe, 41.1 ± 11.3 % (Table 4.2).

4.1.2 Mn, Fe and As in the Longer Sediment Cores from Loch Bradan

The longer sediment cores (LBSC 6, 8 and 10) exhibit interesting trends in their Mn, Fe and As concentration profiles at depths below 3 cm (Appendices 6, 8 and 10).

With the exception of a peak in Fe concentration between 6 and 9 cm depth, which is present in all three longer cores (Figs. 4.2 A-C), the cores show different concentration profiles and as a result will be presented individually in this section.

A : LBSC 6

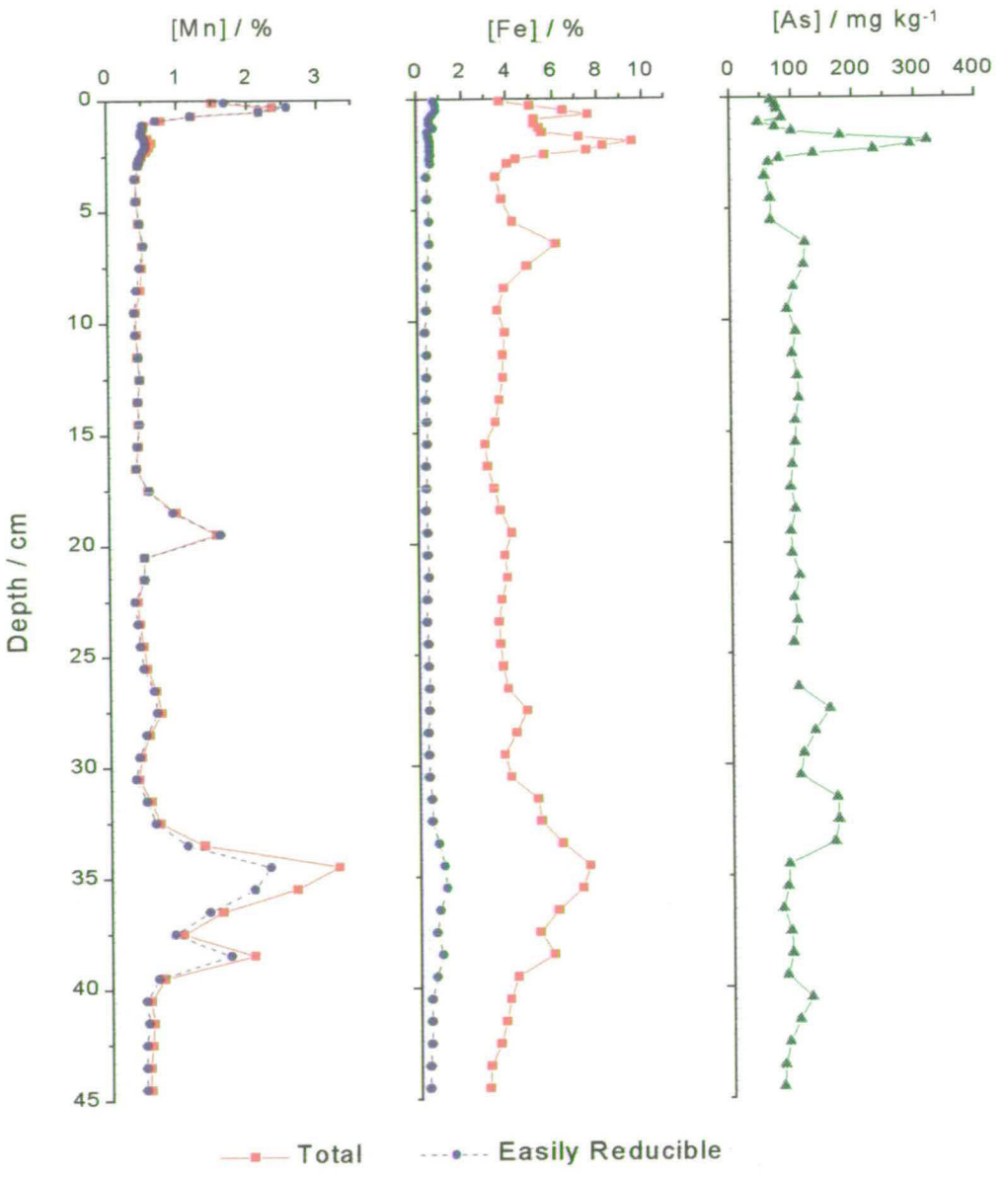


Fig. 4.2 A : Total and easily reducible Mn and Fe, and As concentrations in LBSC 6.

B : LBSC 8

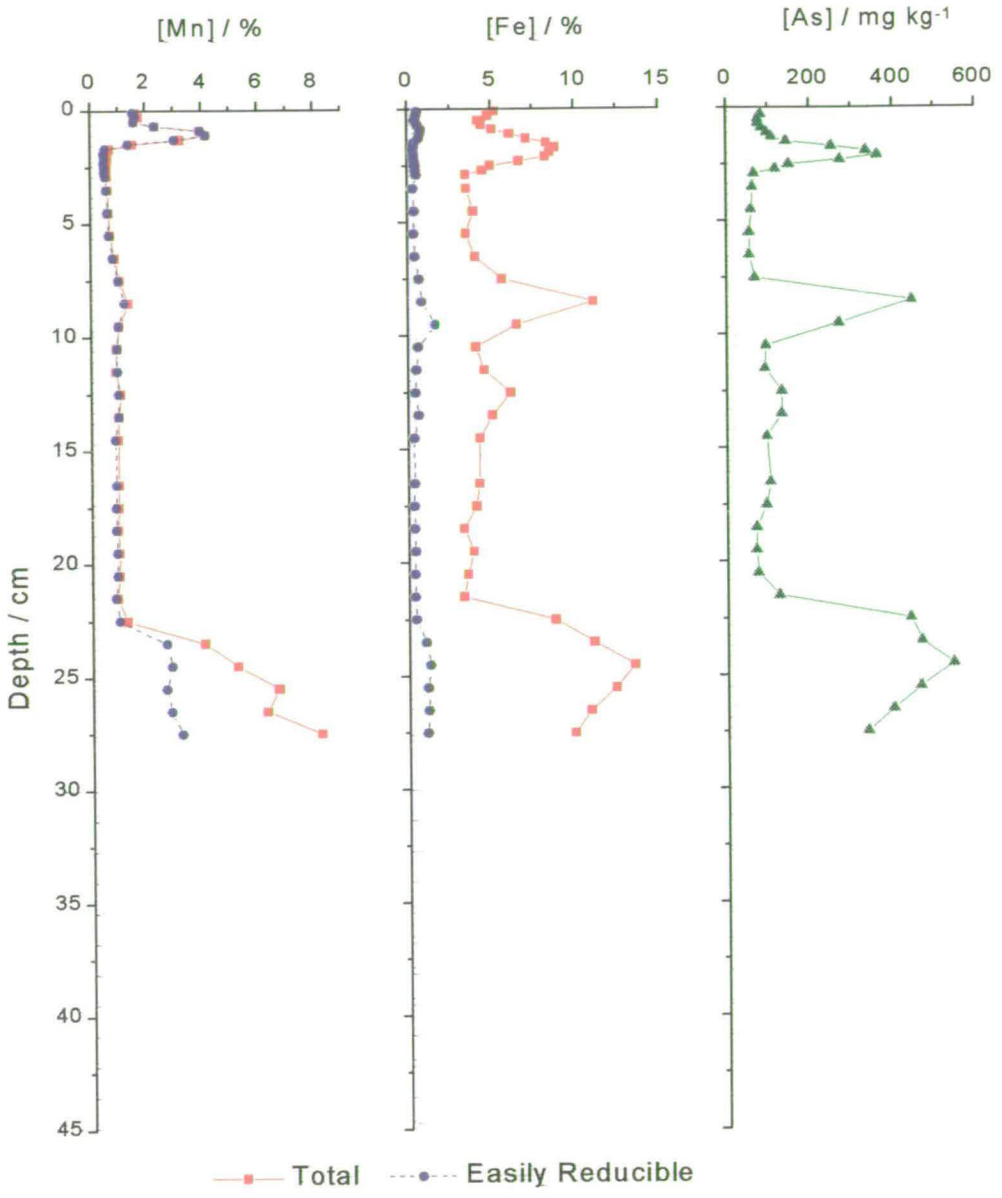


Fig. 4.2 B: Total and easily reducible Mn and Fe, and As concentrations in LBSC 8.

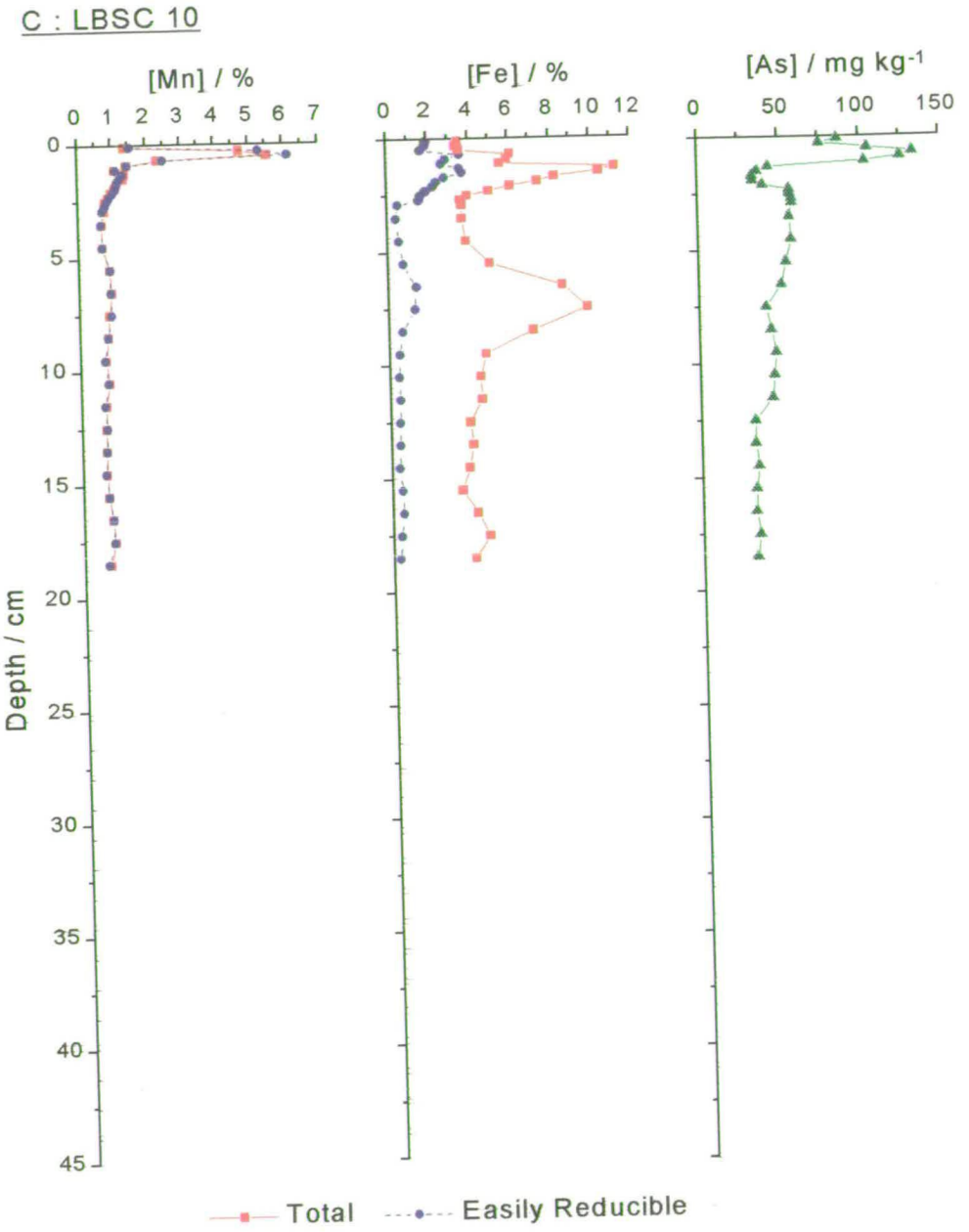


Fig 4.2 C: Total and easily reducible Mn and Fe, and As concentrations in LBSC 10.

4.1.2.1 LBSC 6

LBSC 6, the longest (45 cm) of the sediment cores taken, shows a further two areas enriched in Mn and Fe, at ~20 cm and between 30 and 40 cm depth, with the latter also exhibiting an As enrichment (Fig. 4.2 A). The areas of enrichment are very pronounced for Mn, rising from a baseline value of ~ 0.4 % to peaks of 1.52 % and 3.25 % at 19 - 20 cm and 34 - 35 cm, respectively. For Fe, however, the enrichments are not as pronounced, increasing from a baseline concentration of ~ 3.5 % to 4.09 % and 7.46 % at 19 - 20 cm and 34 - 35 cm, respectively. For As, there is no enrichment at ~ 20 cm, but increases in concentration from ~ 65 mg kg^{-1} to 121 mg kg^{-1} at 6 - 7 cm and ~ 100 mg kg^{-1} to 170 mg kg^{-1} at 32 - 33 cm, the latter 2 cm above the enrichments observed for Mn and Fe, are present.

The percentage of the total Mn present in an easily reducible form stays comparatively constant at 94.0 ± 7.5 % for LBSC 6. The only area where this shows any major deviation is at the peak at 30 - 40 cm, where the proportion drops to a minimum of 69.5 % at 34 - 35 cm, the depth of the maximum enrichment.

For Fe there is little variation in the proportion present in an easily reducible form, 9.5 ± 2.6 % being the average for the entire length of the core.

4.1.2.2 LBSC 8

LBSC 8, like LBSC 6, has enrichments in Mn, Fe and As below the top 3 cm of sediment, including peaks in Fe and As between 8 and 9 cm (Fig. 4.2 B). The peaks at 8 - 9 cm, especially for As, are, however, more pronounced in LBSC 8 than in LBSC 6. Further enrichments in all three elements are also observed below 22 cm, increasing from ~ 0.9 % to 8.21 %, ~ 3.5 % to 12.37 % and ~ 70 mg kg^{-1} to 543 mg kg^{-1} for Mn, Fe and As, respectively. The depths of the maximum observed concentrations are the same for Fe and As, 24 - 25 cm, while for Mn the maximum concentration is at 27 - 28 cm, the deepest section of sediment from LBSC 8.

The percentage of the total Mn in an easily reducible form in LBSC 8 stays comparatively constant, at 92.3 ± 6.7 %, to a depth of 22 cm. Below 22 cm, this percentage drops off dramatically, reaching a minimum of 38.9 % at 27 - 28 cm.

The percentage of Fe which is present in an easily reducible form again shows little variation with depth, 8.6 ± 3.7 % being the average over the entire core.

4.1.2.3 LBSC 10

LBSC 10, the shortest (18 cm) of the three longer cores does not show further areas of enrichment below the top 3 cm of the sediment (Fig. 4.2 C), with the exception of a peak in Fe concentration between 7 and 8 cm. Unlike LBSC 6 and 8, there is no enrichment of As at the same depth as the Fe enrichment.

The percentage of the total Mn present in an easily reducible form does not vary greatly in LBSC 10, with virtually all, 100.5 ± 5.6 %, being extracted by $NH_2OH.HCl$ / HNO_3.

For Fe there is a larger variation in the proportion present in an easily reducible form, 25.3 ± 17.3 %. The top 2.8 cm of the sediment has the highest proportion of the Fe in an easily reducible form, 43.1 ± 8.7 %, compared with 10.6 ± 2.5 % below 2.8 cm.

4.1.3 Manganese, Iron and Arsenic in the Sediments of Loch Riecawr

Both of the sediment coring sites from Loch Riecawr (LRSC 1 and 2) show very similar concentration profiles for Mn, Fe and As (Fig. 4.3 A, B, Appendices 11-12).

In both cores, Mn shows a maximum enrichment in the 0 - 2 mm section of the sediment, with maximum concentrations of 0.80 % and 0.70 % for LRSC 1 and 2, respectively. The concentrations below these maxima decrease to constant values at depth of 0.25 ± 0.03 % and 0.16 ± 0.03 %, respectively (Table 4.3, Figs. 4.3 A, B).

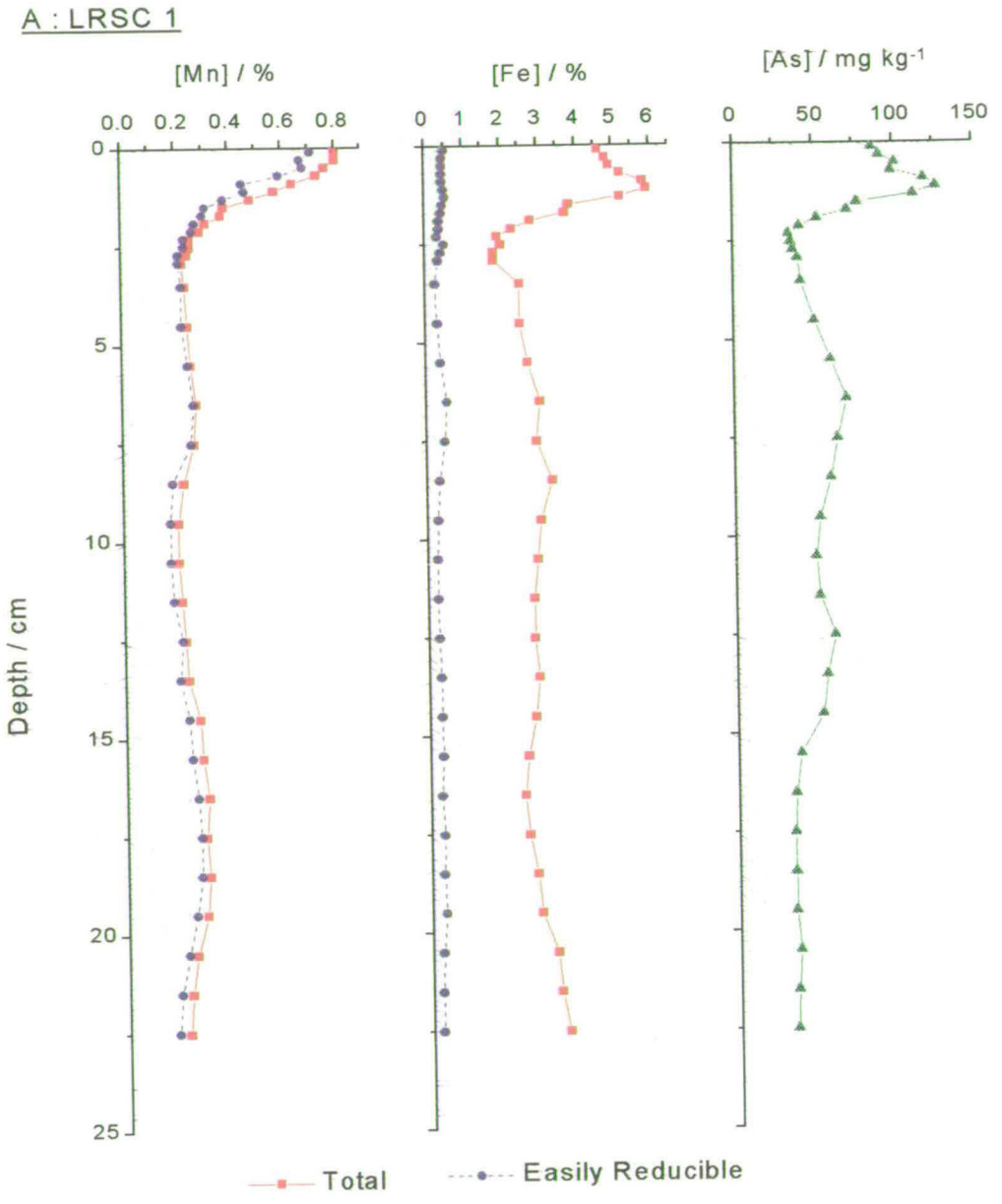


Fig 4.3 A : Total and easily reducible Mn and Fe, and As concentrations in LRSC 1.

B : LRSC 2

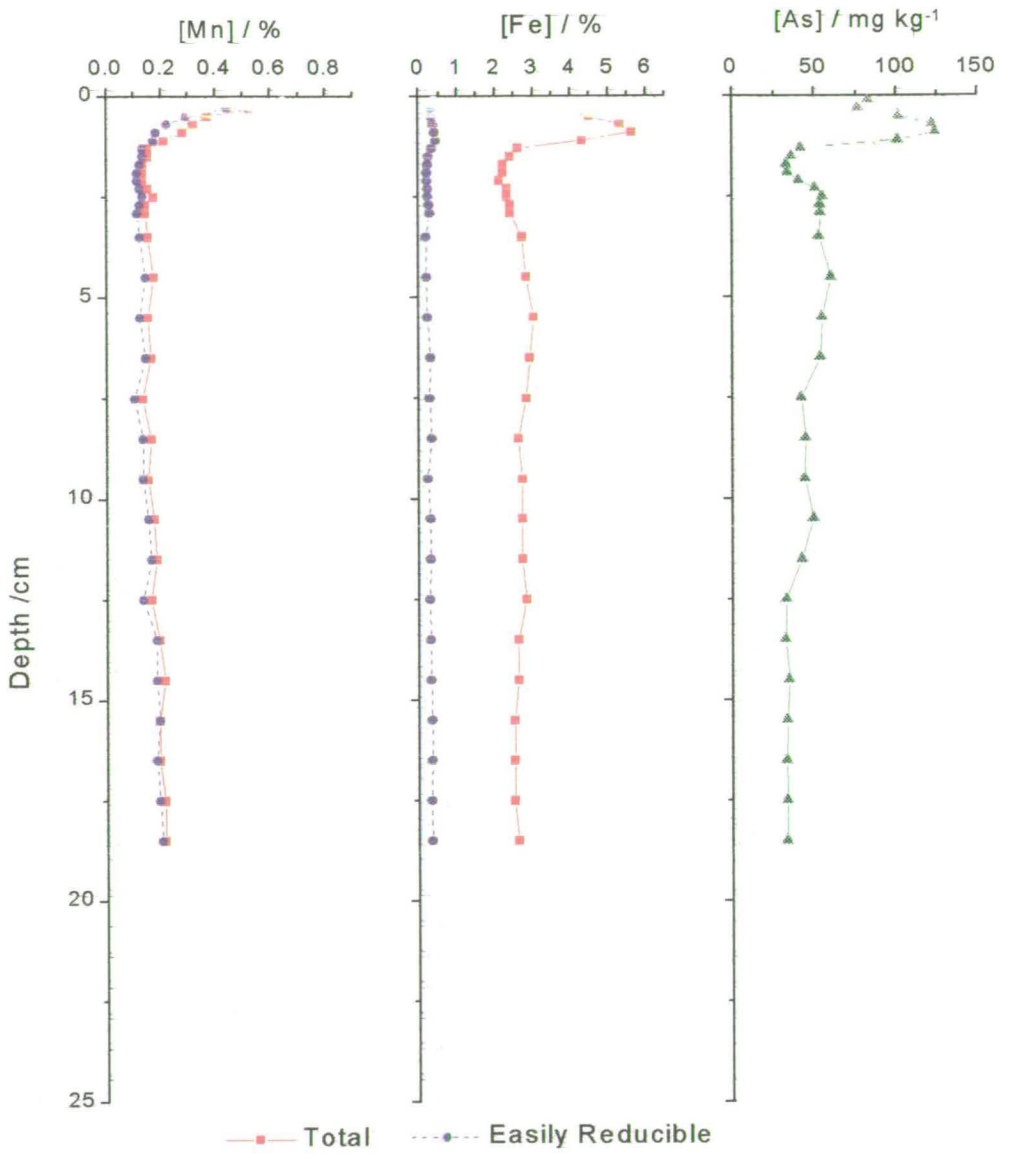


Fig 4.3 B : Total and easily reducible Mn and Fe, and As concentrations in LRSC 2.

The percentage of total Mn that is easily reducible is very similar for both cores at 85.3 ± 6.3 % and 81.7 ± 7.5 % over the top 3 cm of LRSC 1 and 2, respectively (Table 4.3).

Sediment Core Site	Depth of Water / m	$[Mn]_{max}$ / %	$[Mn]_{baseline}$ / %	Depth of Maximum / mm	Percentage of Mn in an easily reducible form / %
LRSC 1	7.0	0.80	0.2	0 - 2	85.3 ± 6.3
LRSC 2	8.0	0.70	0.2	0 - 2	81.7 ± 7.5

Table 4.3 : Maximum and baseline Mn concentrations and percentage of Mn present in an easily reducible form in the top 3 cm of sediment coring sites in Loch Riecawr.

The Fe concentration profiles show maxima of 5.89 % at 1.0 - 1.2 cm in LRSC 1 and 5.61 % at 0.8 - 1.0 cm in LRSC 2. Below the near-surface maxima the concentrations level off, reaching values of 2.79 ± 0.43 % and 2.69 ± 0.14 % below 3 cm in LRSC 1 and 2, respectively (Table 4.4, Figs 4.3 A, B).

The percentage of the total Fe that is extractable by $NH_2OH.HCl$ / HNO_3 in the top 3 cm of LRSC 1 and 2 is 12.4 ± 4.6 % and 9.1 ± 1.6 %, respectively (Table 4.4).

Sediment Core Site	Depth of Water / m	$[Fe]_{max}$ / %	Depth of $[Fe]_{max}$ / mm	Percentage of Fe in an easily reducible form / %	$[As]_{max}$ / mg kg^{-1}	Depth of $[As]_{max}$ / mm
LRSC 1	7.0	5.92	10 - 12	12.4 ± 4.6	127	10 - 12
LRSC 2	8.0	5.64	8 - 10	9.1 ± 1.6	124	8 - 10

Table 4.4 : Maximum Fe and As concentrations and the percentage of Fe in an easily reducible form in the top 3 cm of sediment cores from Loch Riecawr.

The As concentration profiles in LRSC 1 and 2 show sub-surface maxima of 127 mg kg^{-1} and 124 mg kg^{-1} at 1.0 - 1.2 cm and 0.8 - 1.0 cm, respectively, the same

depths as the Fe enrichments. Below 3 cm the concentration levels off to a fairly steady background of 47.9 ± 11.4 mg kg^{-1} and 41.8 ± 9.3 mg kg^{-1} (Figs 4.3 A, B).

4.1.4 Readily Oxidisable Organic Matter in the Top 3 cm of Loch Bradan Sediment

The readily oxidisable organic matter (referred to as organic matter from now on) varies in concentration from 27.7 - 41.3 % (Figs. 4.4 A-J, Table 4.5, Appendices 1 - 10). As with the concentrations of Mn, Fe and As, there are observable differences between the western and the eastern basins, with the organic matter concentrations being slightly higher in the western basin, ranging from 33.6 ± 1.2 % to 36.1 ± 2.5 %, compared with the eastern basin which ranges from 30.2 ± 2.0 % to 33.2 ± 1.8 % (Table 4.5). There are only minor variations in the organic matter concentrations with depth, as demonstrated by the small standard deviations of the average values (Table 4.5), but the profiles can again be subdivided into different Groups, as in Section 4.1.1.

For Group I profiles (LBSC 2, 7) the organic matter remains fairly constant over the top 2 cm of sediment, the same depth as a significant decrease in Fe, and then an increase over 2 to 3 cm, at the same depth as decreases in Fe concentration (Figs. 4.4 B, G).

For Group II profiles (LBSC 1, 3, 4, 5, 6) the organic matter shows no change or a slight decrease in concentration with depth in the top 3 cm of sediment with minima co-incident with Fe maxima. In the case LBSC 6, the position of the organic matter minimum is 0.2 cm above the Fe maximum (Figs 4.4 A, C, D, E, F).

Group III profiles (LBSC 8, 9, 10) show organic matter profiles that have a broad minimum at 1 - 2 cm, the same depths as the Fe enrichments, with the organic matter having similar concentrations near the surface and below the minima, at 2.5 - 3.0 cm (Fig. 4.4 H, I, J).

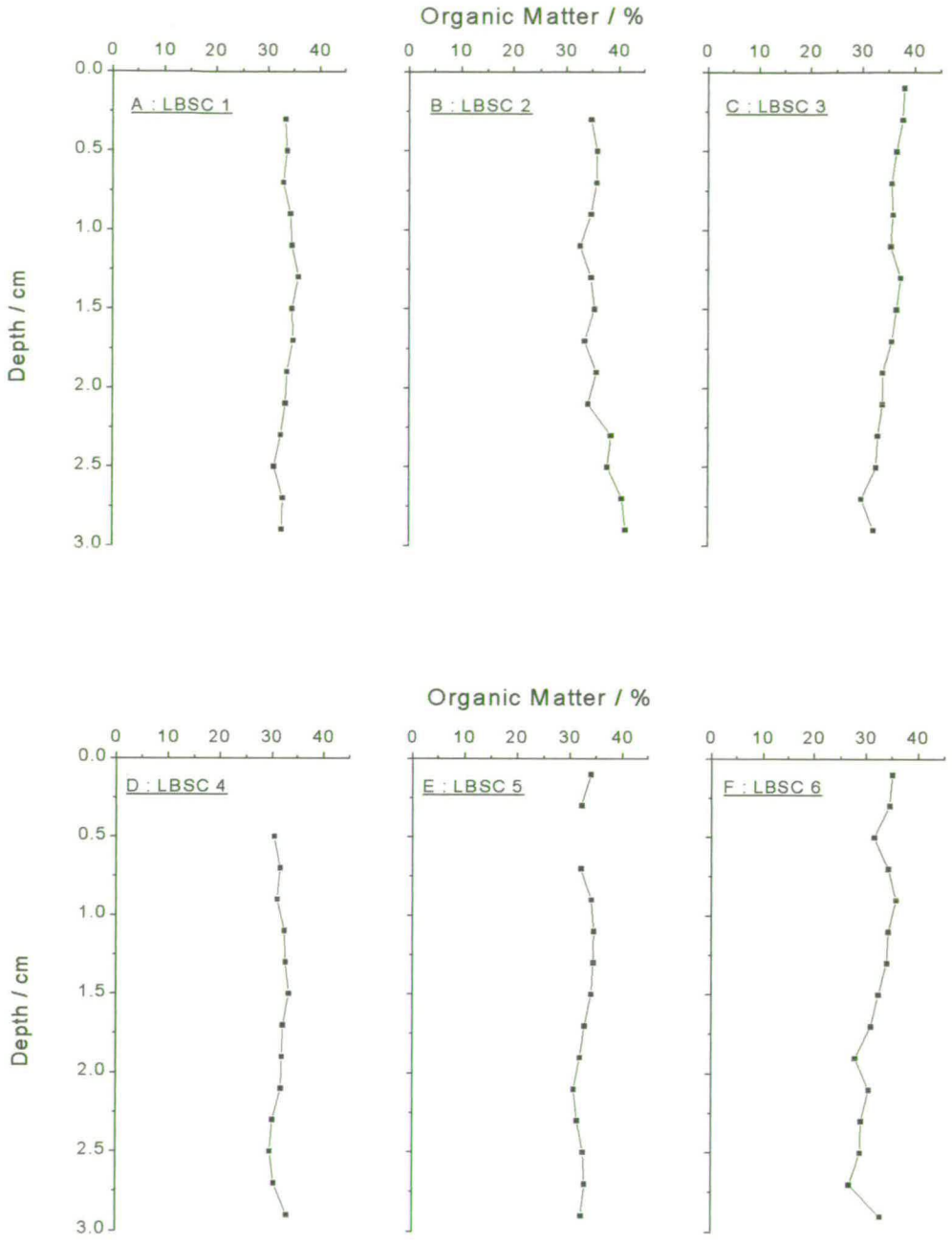


Fig 4.4 A - F : Readily oxidisable organic matter concentrations in the top 3 cm of LBSC 1 to 6.

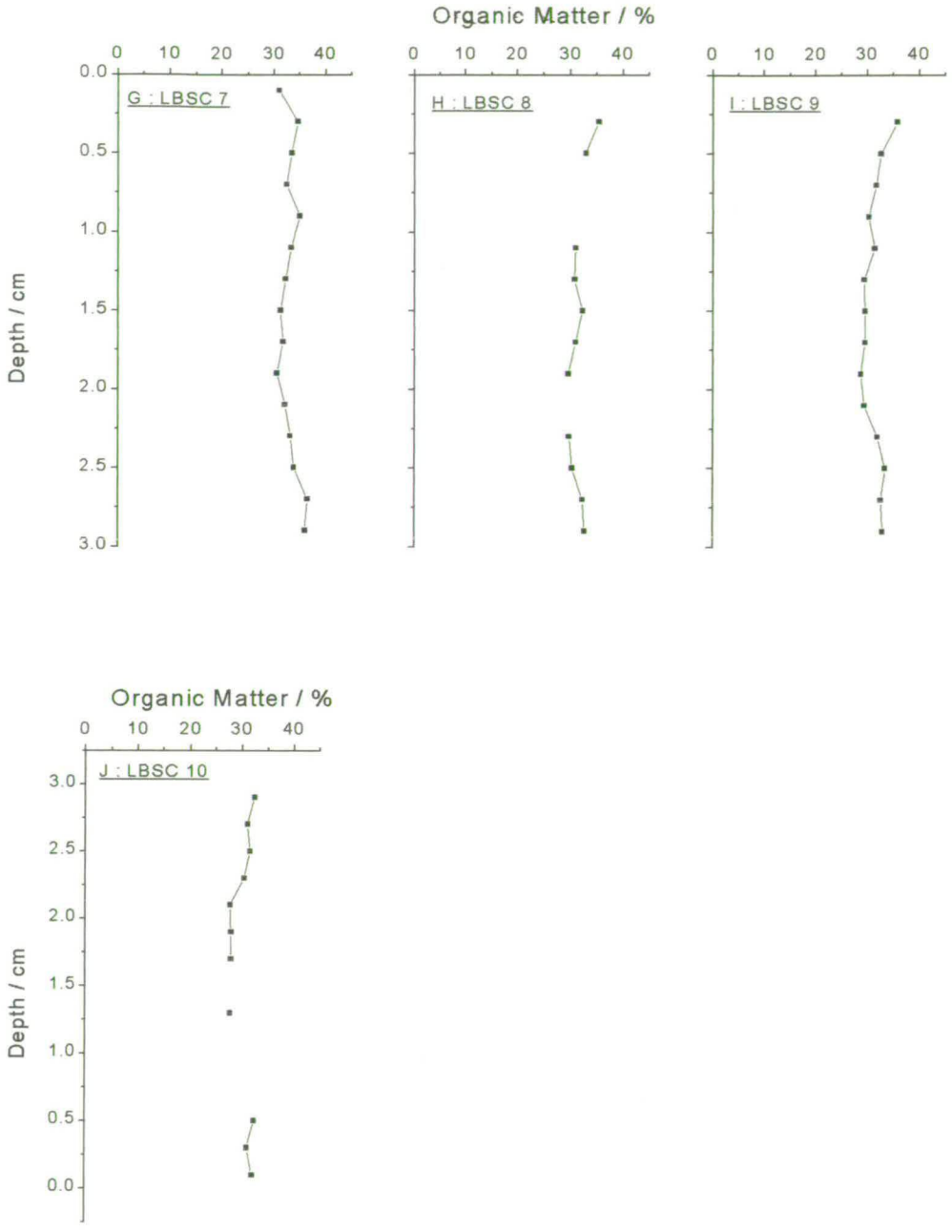


Fig. 4.4 G - J : Readily oxidisable organic matter concentrations in the top 3 cm of LBSC 7 to 10.

Sediment Core Site	Organic matter concentration range / %	Average organic matter concentration / %
LBSC 1	31.1 - 35.9	33.6 ± 1.2
LBSC 2	32.7 - 41.3	36.1 ± 2.5
LBSC 3	29.8 - 38.0	34.9 ± 2.3
LBSC 4	29.6 - 33.0	31.6 ± 1.2
LBSC 5	30.8 - 34.7	33.0 ± 1.2
LBSC 6	27.9 - 35.8	32.0 ± 2.8
LBSC 7	30.6 - 36.6	33.2 ± 1.8
LBSC 8	29.6 - 35.4	31.6 ± 1.7
LBSC 9	28.7 - 35.8	31.4 ± 2.0
LBSC 10	27.7 - 32.3	30.2 ± 2.0

Table 4.5 : Readily oxidisable organic matter concentration ranges and the average concentration in the top 3 cm of sediment from Loch Bradan

4.1.5 Readily Oxidisable Organic Matter in the Longer Sediment Cores from Loch Bradan

In LBSC 6 the organic matter concentration varies between 24 and 42 %, with minima observed at 2 - 3 cm, just above and below 20 cm, and also from 28 to 40 cm in depth (Fig. 4.5 A).

In LBSC 8, the organic matter concentration shows little change over the top 21 cm of sediment at 33.5 ± 2.3 %, followed by a sudden drop below 21 cm to a minimum of 6.0 % at 24 - 25 cm (Fig. 4.5 B), the same depth as a large enrichment in Fe (Fig. 4.2 B).

LBSC 10 does not show any major variation in the organic matter concentration, 30.8 ± 1.9 % being the average over the 18 cm length of the core. Slight minima are, however, present in the top 3 cm, at 6 - 8 cm and also below 17 cm (Fig. 4.5 C).

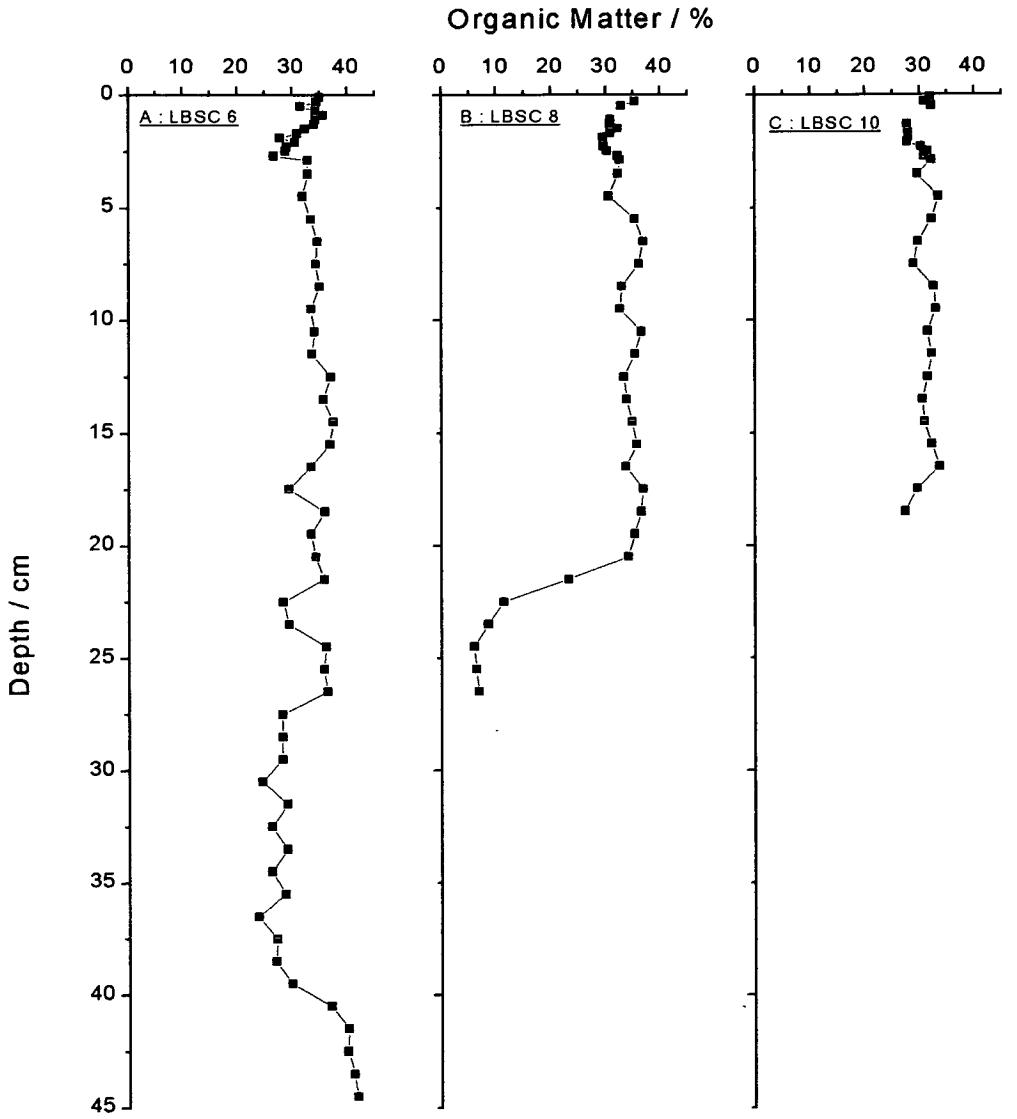


Fig 4.5 A - C : Readily oxidisable organic matter content in LBSC 6, 8 and 10.

4.1.6 Organic Matter in the Sediment of Loch Riecawr

In Loch Riecawr the organic matter concentration observed in the top 3 cm of sediment varies markedly, with LRSC 1 having the higher concentration range of 36.5 - 44.2 %, compared with 28.7 - 35.9 % in LRSC 2 (Table 4.6). Deeper in the sediment both LRSC 1 and 2 show similar organic matter concentration profile shapes, exhibiting minima between 5 and 15 cm (Figs 4.6 A, B). The minima are, in contrast with Group II and III Loch Bradan cores, unrelated to variations in Fe (Fig. 4.3 A, B). Although the profile shapes of LRSC 1 and 2 are similar the concentrations differ, with LRSC 1 ranging from ~ 27 to 45 % over the length of the core, whereas in LRSC 2 the concentrations range from 27 to 36 %.

Sediment Core Site	Organic matter concentration range / %	Average organic matter concentration / %
LRSC 1	36.5 - 44.2	40.9 ± 2.5
LRSC 2	28.7 - 35.9	34.4 ± 1.8

Table 4.6 : Organic matter concentration ranges and average concentrations in the top 3 cm of sediment from Loch Riecawr.

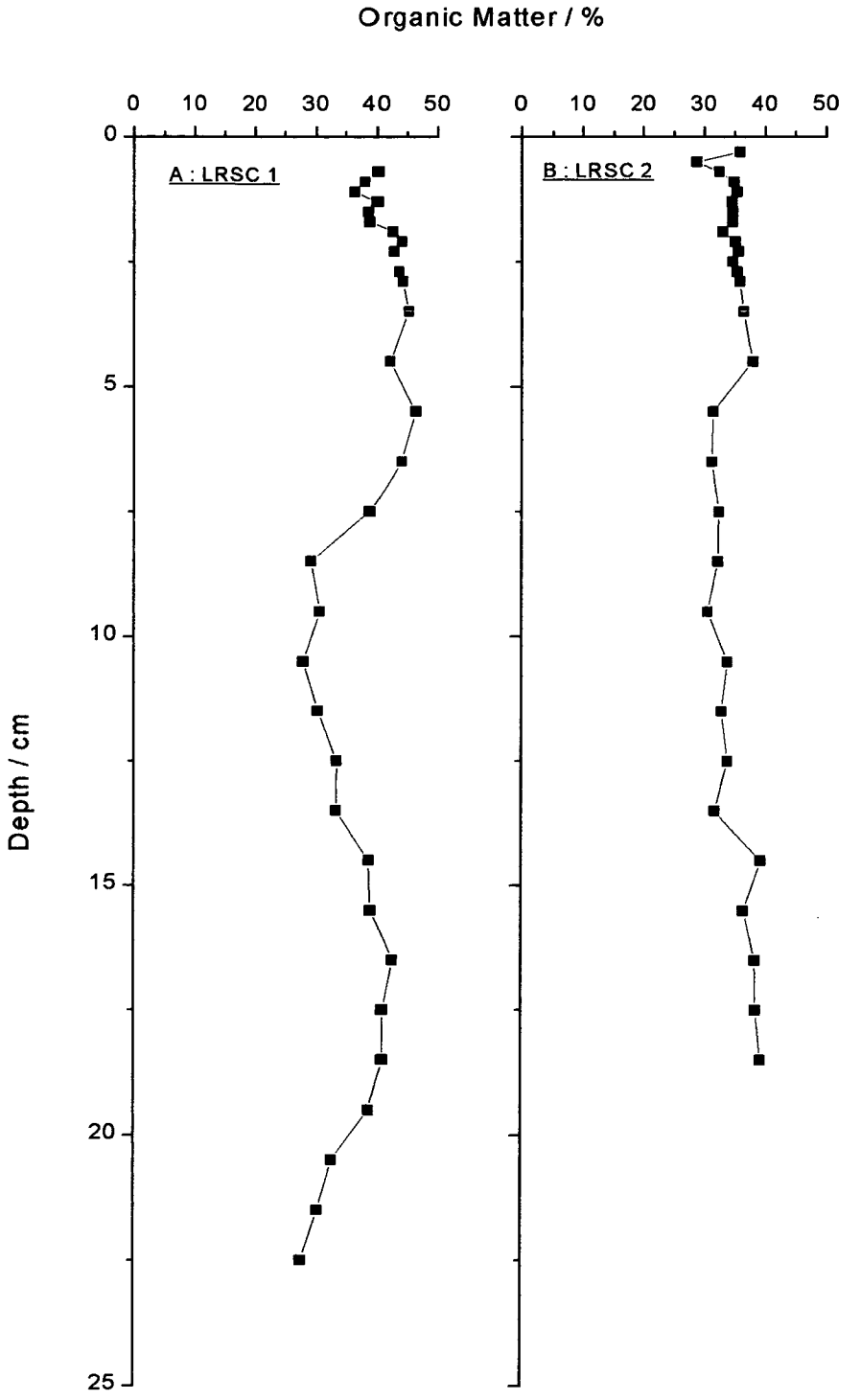


Fig 4.6 A - B: Readily oxidisable organic matter concentration in LRSC 1 and 2.

4.1.7 Sulphur and Phosphorus Concentrations in LBSC 6

In addition to Mn, Fe, As and organic matter concentrations, the S and P concentrations of LBSC 6 were also measured.

The S profile shows a minimum concentration of 0.30 % at the surface, increasing to 0.94 % at 6 - 7 cm, the same depth as a sub-surface Fe peak, dropping to a minimum of 0.55 % at 7 - 8 cm, and then increasing to 0.88 % at 11 - 12 cm before tailing off to ~ 0.27 % at depth (Fig 4.7).

The P concentration profile shows one outstanding feature, a peak concentration of 0.29 % at 6 - 7 cm, the same depth as a sub-surface Fe peak. The remainder of the profile ranges from 0.10 - 0.21 %, with no major variation with depth (Fig. 4.7).

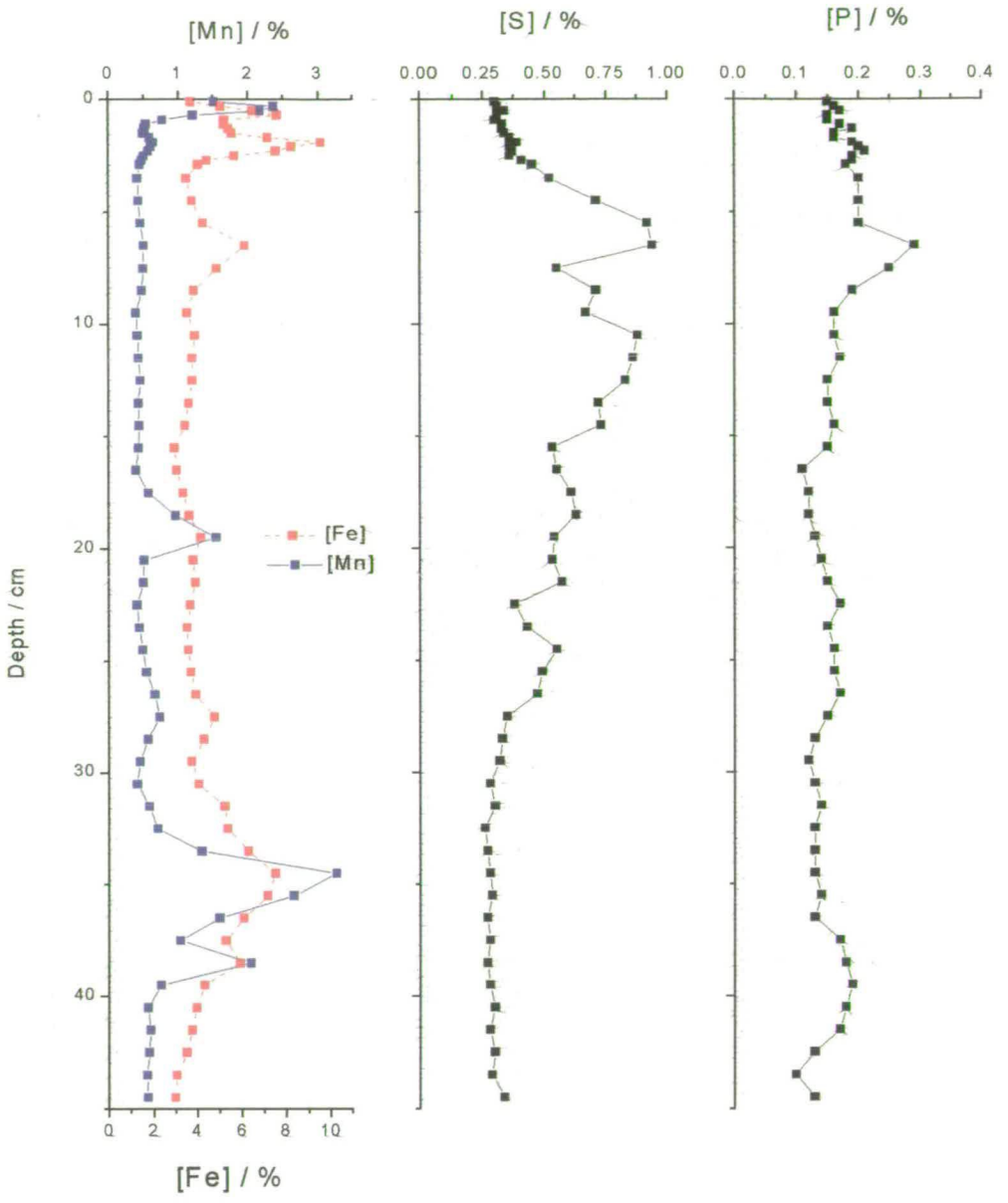


Fig 4.7 : Mn, Fe, S and P concentrations in the LBSC 6

4.2 Discussion of Factors Controlling Manganese, Iron, Arsenic and Organic Matter Profiles in the Sediment of Loch Bradan and Loch Riecawr

4.2.1 Manganese, Iron, Arsenic and Organic Matter in the Top 3 cm of Sediment in Loch Bradan

The observed distribution of Mn, Fe and As in the uppermost 3 cm of sediment is, in general, in good agreement with the predicted behaviour, based on classical redox-cycling theory, of these three elements in a relatively shallow, well-oxygenated lake such as Loch Bradan.

The enrichments of Mn, Fe and As in the top 3 cm of the sediment (Figs. 4.1 A-J) are explicable in terms of the redox cycling of these elements, known to result in enrichments in the upper regions of sediments (Bryant *et al.*, 1991; Davison, 1993; Bryant *et al.*, 1997). The redox-active nature of Mn, Fe and As results in the release of the soluble reduced forms of the elements, Mn(II), Fe(II) and As(III), in the anoxic regions of the sediment (see Section 2.2.2). These soluble species can diffuse vertically upwards and downwards from the respective points of maximum concentration within the sediment, with the upwards diffusing species (e.g. Mn^{2+}, Fe^{2+}, $H_2AsO_3^-$) entering into a region of sediment with a redox potential that permits oxidation. This region of sediment acts as a barrier to the vertical movement of these elements with the formation of solid-phase compounds of the oxidised forms, Mn(IV) and Fe(III) (upon which oxidised As(V) species such as $H_2AsO_4^-$ can be adsorbed), which accumulate, resulting in the observed concentration peaks (Davison, 1993). The general location of the maximum enrichments of Mn, Fe and As below the sediment-water interface and, with the exception of only one or two (Mn Group I) cores, below the uppermost section of sediment sampled, confirms that the bottom waters of Loch Bradan are indeed oxygenated. Sub-oxic conditions would therefore appear to occur within a centimeter or two of the surface as a result of oxidation of organic matter, leading to the observed redox boundary positions.

The relative depths of the Mn and Fe concentration peaks are also in good agreement with theoretical predictions, with the Mn peaks observed, in general, above the Fe peaks (Figs. 4.1 A-J). Fe(II) is more readily oxidised than Mn(II) and is thus oxidised at lower pE and hence deeper in the sediment column (Davison *et al.*, 1982; Laxen and Chandler, 1983; Sigg *et al.*, 1991; Hamilton-Taylor *et al.*, 1996), resulting in an Fe enrichment below that of Mn. The occurrence of the As maxima at the same depth as Fe enrichments is again in good agreement with literature data, notably for Loch Lomond (Farmer and Lovell, 1986). As(V) is know to adsorb to insoluble Fe(III) oxyhydroxides (Belzile *et al.*, 1991; De Vitre *et al.*, 1991; Splietoff *et al.*, 1995), resulting in As peaks at the same depths as Fe(III) enrichments.

None of the organic matter profiles in the top 3 cm of Loch Bradan sediment show any major variation with depth (Table 4.5). There are, however, small deviations which would seem, in general, to be related to the concentration of Fe in the sediment cores. For Group II (near-surface Fe peak) and Group III (broad subsurface Fe peak) Fe profiles, the organic matter concentrations show an approximate inverse relationship to Fe concentration, with organic matter minima at the position of Fe maxima. This relationship most likely occurs as a result of the diagenetic enrichment of Fe causing other components of the sediment, including organic matter, to appear relatively depleted. This effect is observed for Fe but not Mn in the top 3 cm of sediment because of the larger concentration of Fe observed in the sediment. For Group I (surface Fe peak) Fe profiles, the organic matter concentration does not seem to have the same inverse relationship with the Fe concentration.

There is a marked difference in the concentration of Mn, Fe, As and organic matter observed in the western and eastern basins of Loch Bradan. The western basin has a lower concentration of Mn, Fe and As and a higher organic matter concentration than the eastern basin. These observed variations in concentration could be explained by differing concentrations of the Mn and Fe entering the loch from the input streams. As will be discussed in Section 5.3, streams 3 (entering from the south) and 6 (entering from the north) (Fig. 3.14) consistently have a higher concentration of

dissolved Mn and Fe than any of the other streams. Considering that the overall flow of the loch is from west to east it is plausible that the western basin does not receive much, if any, water from these two streams and hence has a lower metal input, although the lack of flow data from the streams prevents confirmation of this hypothesis.

As well as the differences observed in the total concentration of Mn between the western and eastern basins, there are also variations in the percentage of Mn present in an easily reducible form. In the western basin a smaller proportion, 80.5 ± 12.0 % to 87.9 ± 6.3 %, of the Mn is in an easily reducible form compared with the eastern basin, 90.1 ± 8.0 % to 102.9 ± 6.3 %. This may well derive from the different stream inputs of Mn to the loch. In all areas of the loch, however, most of the Mn is in an easily reducible form and hence able to undergo oxidation / reduction reactions and thereby participate in redox cycling. As a consequence this Mn could be released from the sediment into the water column if bottom waters became anoxic (Hsiung and Tisue, 1991; Skowronek, 1994; Huchriede and Meishner, 1996). It is possible to calculate the amount of Mn that could be released from the sediment into the water column, or the inventory of excess Mn, using Equation 4.1.

Eqn 4.1 : $$\text{Inventory of Excess Mn } (g\ m^{-2}) = \frac{\Sigma\{(\text{conc.} - \text{baseline conc.}/\ \mu g\ g^{-1}) \times \text{mass of section} / g\} \times 100}{\text{Cross sectional area of coring tube} / cm^2}$$

Cross sectional area of Jenkin coring tube = 37.39 cm^2

As can be seen from the results in Table 4.7 the potential amount of Mn that could be released from the sediment ranges from 1.8 - 2.5 g m^{-2} in the western basin to 3.9 - 10.7 g m^{-2} in the eastern basin. This relates to concentrations of dissolved Mn in the water column of between ~ 0.18 mg l^{-1} and 0.83 mg l^{-1} (calculated by dividing the amount of Mn released from the sediment by the depth of the overlying water), which even at the lower concentration range still greatly exceed the EC maximum admissible concentration of 0.05 mg l^{-1}.

Sediment Core Site	Inventory of excess Mn / g m^{-2}	Potential concentration of Mn in overlying water column / μg l^{-1}
LBSC 1	1.8	178
LBSC 2	1.9	237
LBSC 3	2.5	227
LBSC 4	6.8	519
LBSC 5	5.3	381
LBSC 6	4.1	406
LBSC 7	3.9	394
LBSC 8	10.0	833
LBSC 9	10.7	770
LBSC 10	9.4	723

Table 4.7: Inventory of excess Mn in the top 3 cm of Loch Bradan sediment and the potential concentration of Mn in the overlying water resulting from its release

The percentage of the total Fe that is extracted by $NH_2OH.HCl$ / HNO_3 is much lower than that observed for Mn. This is an expected result as diagenetically formed Mn compounds are more readily reduced and solubilised than Fe compounds (Davison *et al.*, 1982; Laxen and Chandler, 1983; Sigg *et al.*, 1991; Hamilton-Taylor *et al.*, 1996), and harsher reagents are required to extract the proportion of the Fe that participates in redox cycling (Bryant *et al.*, 1991).

4.2.2 Manganese, Iron, Arsenic and Organic Matter in the Longer Sediment Cores

It might be anticipated that the peaks in Mn, Fe and As concentration observed below 3 cm, unlike the enrichments in the top 3 cm, are not directly related to the redox chemistry of oxides, hydroxides and oxyhydroxides of Mn and Fe. Previous workers have noted that the solubility of Mn(II) and Fe(II) in the sub-oxic and anoxic zones of sediment is controlled by the formation of insoluble sulphides, carbonates and phosphates (Emerson, 1976; Carignan and Nriagu, 1985; Sigg *et al.*, 1991; Thomson

et al., 1991; Huckriede and Meischner, 1996; Friedl *et al.*, 1997; Hongve, 1997), potentially leading to concentration peaks at depth. The concentration profiles of S and P in LBSC 6 were therefore obtained to try to identify if either of these two elements was involved in the enrichments in Mn, Fe and As concentrations at depth.

4.2.2.1 LBSC 6

There are enrichments in the concentration of S and P at 6 - 7 cm depth, the same depth as a maximum Fe concentration is observed in LBSC 6 (Fig. 4.7). It is therefore possible that the Fe is forming insoluble compounds with the S(II-) (e.g. Fe_3S_4, FeS_2 and FeS), as reported in the sediment of Greifensee, a small perialpine lake in Switzerland, below ~ 5 cm (Wersin *et al.*, 1991), and P. Thomson *et al.* (1998) found that at depth in an ocean sediment core there was an enrichment in Fe (and As) as the result of high S(II-) concentrations leading to precipitation of pyrite, FeS_2. The XRD results (Table 4.8), however, show that no observable FeS_2 is present in the sediment at 6 - 7 cm. Therefore if S is contributing to a peak in Fe concentration it would therefore appear that it is not FeS_2, but of some other insoluble compound, possibly FeS (Carignan and Nriagu, 1985; Wersin *et al.*, 1991). The stoichiometry of the Fe, S and P in the sediment at 6 - 7 cm indicates formulae of $FeS_{0.69}$ and $FeP_{0.09}$, calculated using the total concentration of Fe in the sediment. The As maximum at the same depth could result from co-precipitation with the insoluble FeS compound or be due to the formation of an insoluble compound such as As_2S_3 (Splietoff *et al.*, 1995). XRD does not give any information about Fe phosphates, but their formation could also be contributing to the enrichment of Fe at 6 - 7 cm in LBSC 6 (Emerson, 1976; Friedl *et al.*, 1997). The S and P data are only available for LBSC 6, but it is assumed that a similar process will account for the peaks in Fe and As at 6 - 9 cm in all of the longer sediment cores.

Sample	Minerals present
LBSC 5 : 0.6 - 1.2 cm	Quartz (SiO_2), Albite ($NaAlSi_3O_8$), Muscovite ($KAl_2Si_3AlO_{10}$).
LBSC 5 : 1.4 - 2.4 cm	Quartz (SiO_2), Albite ($NaAlSi_3O_8$), Muscovite ($KAl_2Si_3AlO_{10}$).
LBSC 6 : 6 - 8 cm	Quartz (SiO_2), Albite ($NaAlSi_3O_8$).
LBSC 6 : 8 - 9 cm	Quartz (SiO_2), Albite ($NaAlSi_3O_8$).
LBSC 6 : 13 - 14 cm	Quartz (SiO_2), Albite ($NaAlSi_3O_8$), Muscovite ($KAl_2Si_3AlO_{10}$).
LBSC 6 : 19 - 20 cm	Quartz (SiO_2), Albite ($NaAlSi_3O_8$), Muscovite ($KAl_2Si_3AlO_{10}$).
LBSC 6 : 34 - 35 cm	Quartz (SiO_2), Albite ($NaAlSi_3O_8$), Muscovite ($KAl_2Si_3AlO_{10}$).
LBSC 8 : 25 - 26 cm	Quartz (SiO_2), Albite ($NaAlSi_3O_8$), Muscovite ($KAl_2Si_3AlO_{10}$), Rhodochrosite ($MnCO_3$).

Table 4.8: Mineral forms identified by XRD in sediment samples from Loch Bradan.

The enrichments in Mn, Fe and As concentrations at ~ 20 cm and 30 - 40 cm in LBSC 6 are, however, unlikely to be the result of sulphide or phosphate compound formation since neither S nor P shows any enrichment at these depths (Fig. 4.7). Neither was $MnCO_3$ observed by XRD in the sediment at these depths, although it is possible that the concentration of Mn in LBSC 6 may be too low to be detected by XRD (compare with LBSC 8). If the enrichment of Mn is due to the presence of a $MnCO_3$ enrichment at ~ 20 cm it would also explain the findings that all of the Mn at this depth is extracted by acidified $NH_2OH.HCl$ as $MnCO_3$ is solubilised by this reagent (Fig. 4.2 A).

The peaks in Mn, Fe and As concentration at 30 - 40 cm in LBSC 6 are associated with a decrease in organic matter content and also a decrease in water content of the sediment (Fig. 3.13 A). These, along with the result showing that less of the Mn at

this depth is in an easily reducible form than at all other depths could indicate the presence of other forms of Mn, Fe and As. At this depth there is no increase in the concentration of S or P and also the XRD results shows no detectable Fe or Mn minerals present. The cause of these enrichments in Fe and As is therefore not known, although relict peaks of crystalline oxides could perhaps be at least partially responsible.

4.2.2.2 LBSC 8

In LBSC 8, a large enrichment in Mn, Fe and As, and depletion in organic matter, is observed below 22 cm, with the proportion of the Mn in an easily reducible form decreasing dramatically. The XRD results show that $MnCO_3$ is present at this depth (Table 4.8) which will be insoluble and may account, at least partially for the observed enrichment of Mn (M^{c}Bride, 1979; Carignan and Nriagu, 1985; Sigg *et al.*, 1991; Hongve, 1997). The reduction in the concentration of the Mn that is easily reducible will, however, not be explained exclusively by the presence of $MnCO_3$ as this species will be soluble in $NH_2OH.HCl$ / HNO_3, indicating the presence of other unidentified Mn species. Although the XRD gives no information on Fe carbonate species in the sediment at this depth, it is possible that the cause of the Fe enrichments will be due to insoluble $FeCO_3$ formation (Emerson, 1976; Carignan and Nriagu, 1985; Wersin *et al.*, 1991; Friedl *et al.*, 1997). As with the Mn it is also possible that other insoluble species of Fe may be present within the sediment at this depth contributing to the Fe enrichment. The enrichment in Fe, and Mn, as in other sediment cores, is thought to result in the decrease observed in the organic matter at the same depth within the sediment.

4.2.2.3 LBSC 10

LBSC 10 is the shortest (19 cm) of the three longer sediment cores, and displays no enrichment in Mn, Fe of As below the enrichment of Fe at 7 - 8 cm.

4.2.3 Discussion of Manganese, Iron, Arsenic and Organic Matter Results from Loch Riecawr Sediments

As with Loch Bradan, the Mn, Fe and As concentration profiles in the upper 3 cm can all be explained by the redox cycling of these elements (Davison, 1993). The surface peak of Mn, and the near-surface peaks of Fe and As, are due to the oxidation / precipitation of soluble reduced forms of the elements above the redox boundary in the sediment, resulting in enrichments.

The concentrations of Mn, Fe and As in the sediment of Loch Riecawr are very similar to those observed in the western basin of Loch Bradan. In addition, the proportion of the Mn which is easily reducible is consistent with the western basin of Loch Bradan.

As with the sediment of Loch Bradan, the Fe and As peaks coincide as a the result of associations of As(V) with Fe(III) oxyhydroxides. (Belzile *et al.*, 1991; DeVitre *et al.*, 1991; Splietoff *et al.*, 1995). Also, the maximum peak concentrations of Fe and As are observed below those for Mn, a consequence of the lower redox potential for Fe (Davison *et al.*, 1982; Laxen and Chandler, 1983; Sigg *et al.*, 1991; Hamilton-Taylor *et al.*, 1996), with the As being associated with the oxidised Fe.

Unlike the case with Loch Bradan, there are no major variations in concentration of redox-active elements below the top 3 cm of sediment, at least over the lengths of the two cores collected from Loch Riecawr. It would therefore appear that the formation of insoluble sulphides, phosphates or carbonates is not a major controlling factor of Mn(II) and Fe(II) solubility in anoxic pore waters of Loch Riecawr. The constant concentrations of Mn, Fe and As at depth indicate that below the point of production of the soluble reduced forms, they are vertically dispersed, reaching equilibrium concentrations at depth.

The organic matter concentrations in LRSC 1 and 2 are, in general, higher than those observed in the sediment cores collected from Loch Bradan. Also, unlike Group II and III sediment cores from Loch Bradan, major changes in the organic matter profiles do not show any inverse relationship with Fe profiles. In LRSC 1 and 2 the major decrease in organic matter content occurs between 5 and 15 cm, but at the same depth there are no variations in the Fe concentration, which is constant in both cores below 3 cm. It would appear, therefore, that as in LBSC 2 and 7 factors other than Fe concentration are controlling the variations in organic matter concentration in LRSC 1 and 2.

4.3 Copper, Lead and Zinc in the Sediments of Loch Bradan and Loch Riecawr

4.3.1 Copper, Lead and Zinc Profiles in the Sediment of Loch Bradan

The concentration of Cu, Pb and Zn in the short (3 cm) sediment cores of Loch Bradan can be found in appendices 1 to 10, with this section concentrating on the results from LBSC 6, LBSC 8 and LBSC 10, the three longer cores.

In LBSC 6 the concentration of Cu varies between 1 and 40 mg kg^{-1}, with the maximum concentration being observed at 16 - 17 cm depth, and the minimum at 44 - 45 cm (Fig. 4.8 A). Other features are a comparatively steady concentration of 27.4 $\pm$ 3.3 mg kg^{-1} in the top 16 cm; a second, smaller, enrichment of 33 mg kg^{-1} at 21 - 22 cm and a generally lower concentration of 10.7 $\pm$ 1.8 mg kg^{-1} between 28 and 40 cm. The concentration of Cu extracted by $NH_2OH.HCl$ / HNO_3 was below the detection limit of the FAAS (corresponding to < 0.04 mg kg^{-1}), which was found to be the case in all three cores.

In LBSC 8 the Cu concentration exhibits an increase from a near-surface concentration of 15 - 20 mg kg^{-1} to a maximum concentration of 30 mg kg^{-1} at 22 cm,

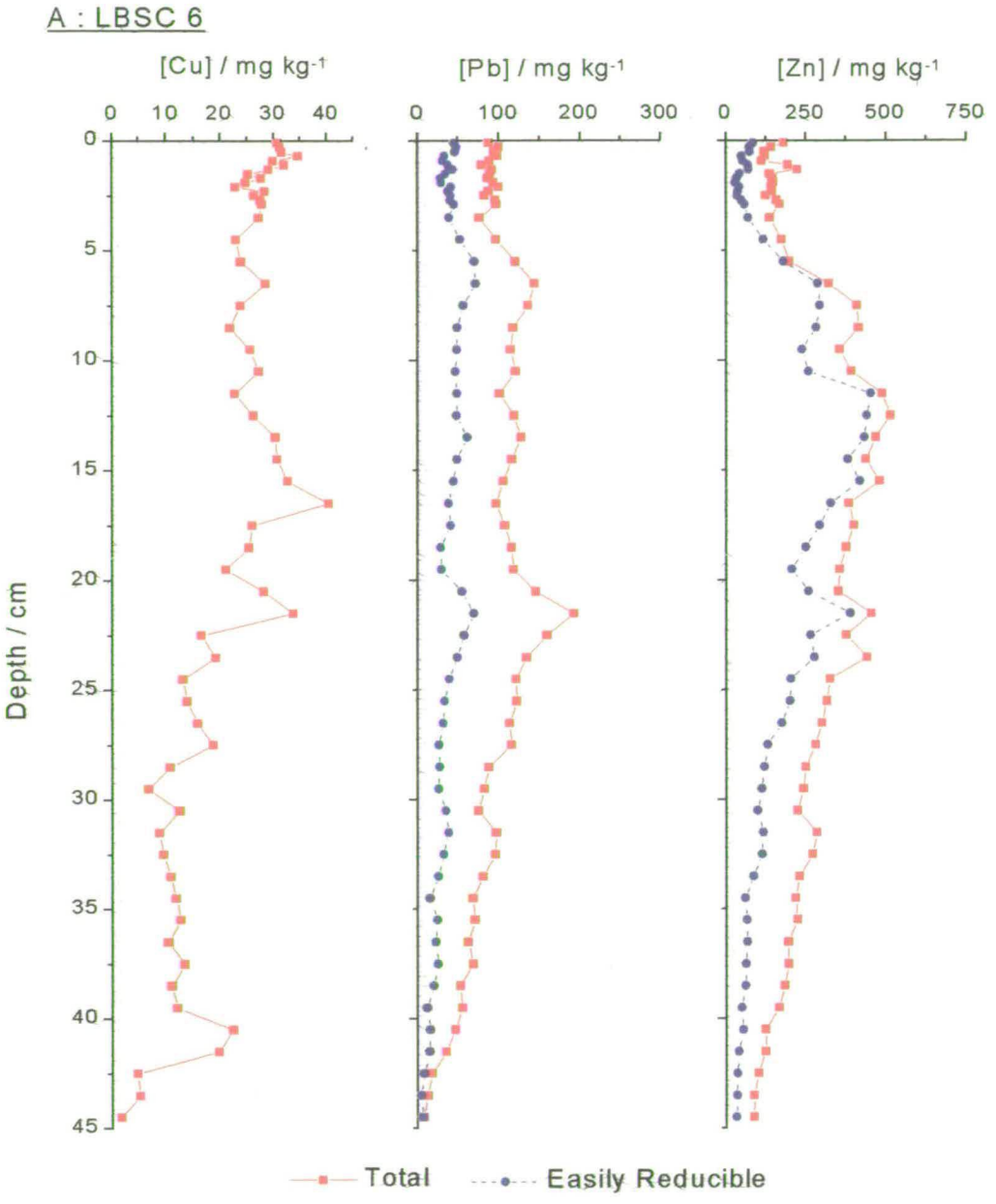


Fig. 4.8 A : Total and easily reducible Cu, Pb and Zn concentrations in LBSC 6.

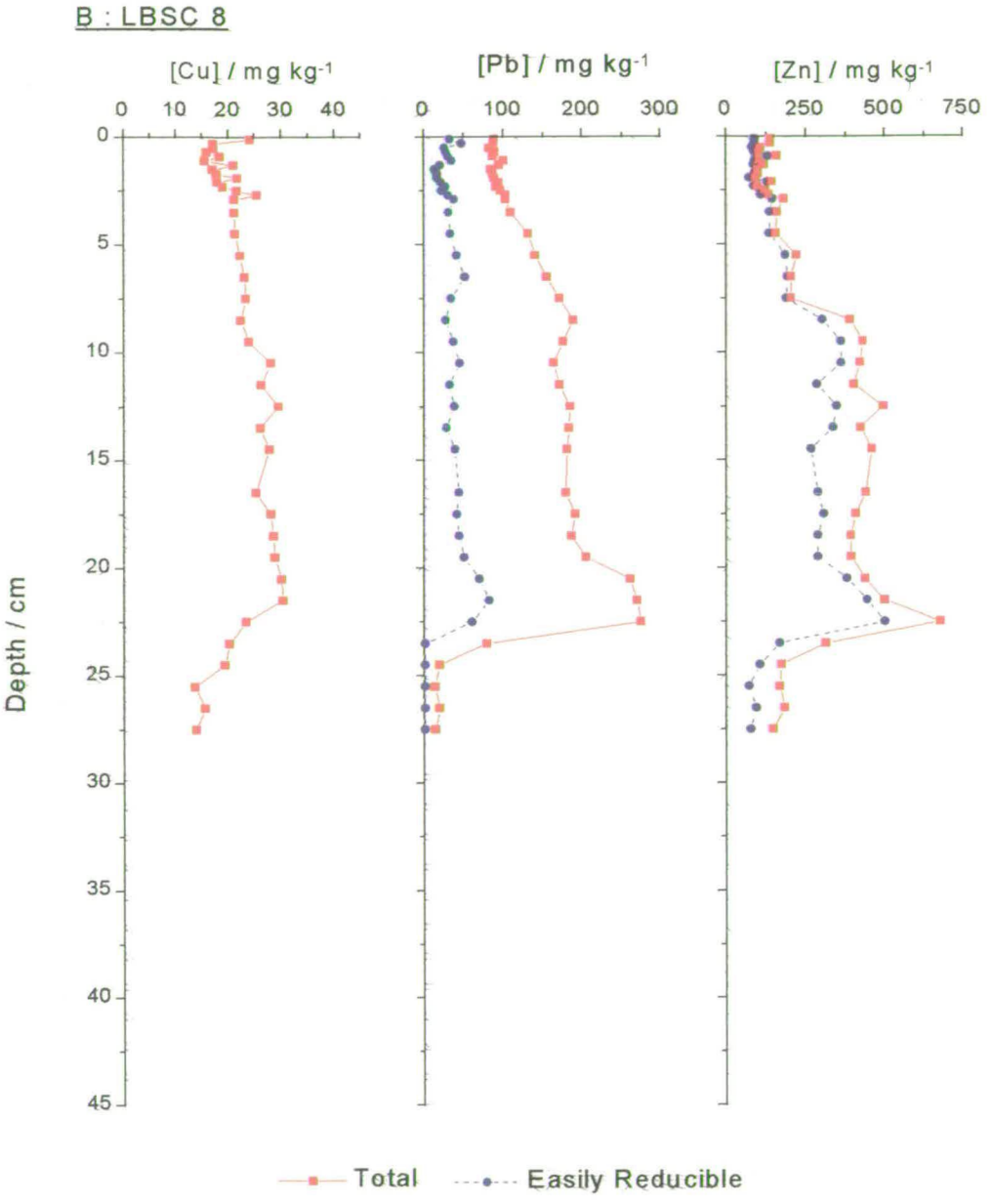


Fig 4.8 B : Total and easily reducible Cu, Pb and Zn concentrations in LBSC 8.

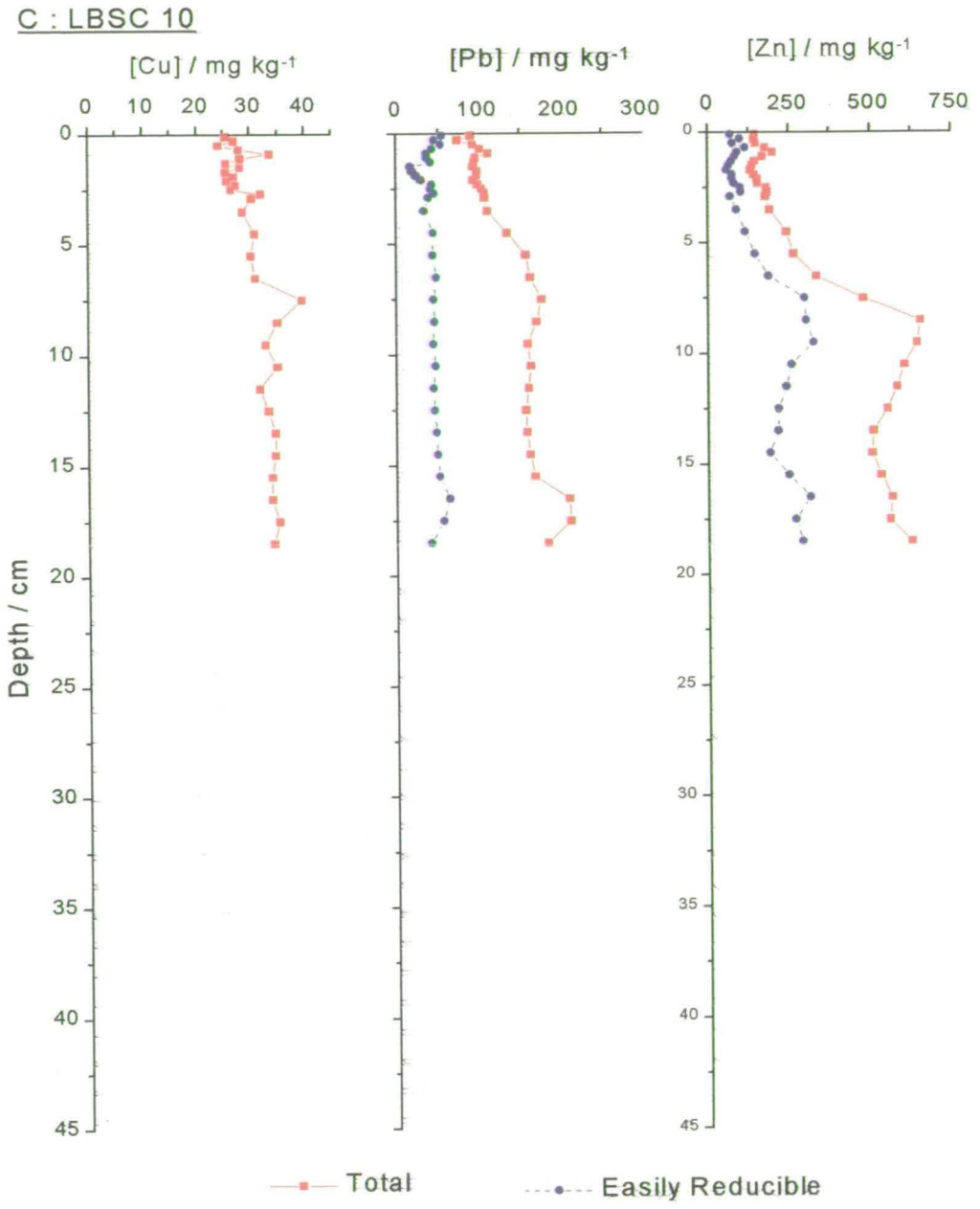


Fig. 4.8 C : Total and easily reducible Cu, Pb and Zn concentrations at LBSC 10.

below which the concentration decreases to a minimum of 14 mg kg^{-1} at 25 cm (Fig 4.8 B).

In LBSC 10 the concentration shows a slight increase in concentration from 25 mg kg^{-1} at the surface to a maximum of 39 mg kg^{-1} at 7 - 8 cm, below which the concentration remains comparatively constant at 33.9 ± 1.0 mg kg^{-1} (Fig. 4.8 C).

The Pb and Zn concentration profiles in the three cores are more closely related to each other than to those of Cu, with minima of 72 mg kg^{-1} to 90 mg kg^{-1} for Pb and 136 mg kg^{-1} to 180 mg kg^{-1} for Zn observed at the surface. These concentrations increase, reaching maxima of 191 mg kg^{-1} to 228 mg kg^{-1} Pb and 451 mg kg^{-1} to 674 mg kg^{-1} Zn between 15 and 25 cm depth. Below the maxima the concentrations in LBSC 6 and 8 decrease, with the decrease being much more marked for LBSC 8 than LBSC 6 and 10.

The concentration of the Pb and Zn which is extracted by $NH_2OH.HCl$ / HNO_3 shows trends similar to those observed for the total Pb and Zn. The percentage of the total Pb which is extractable by $NH_2OH.HCl$ / HNO_3 ranges from 15.1 to 71.8 %, < 1 % to 64.0 % and 17.3 to 59.9 % in LBSC 6, 8 and 10, respectively, while for Zn the ranges are 18.0 to 92.6 %, 42.3 to 94.1 % and 37.5 to 68.4 %. In general, in the top 3 cm of the sediment the proportions for both Pb and Zn released in the easily reducible fraction are highest in the same sections as the diagenetic enrichments of Mn, and lower in the region of Fe enrichment. Other major variations in the percentage of Pb and Zn which are released in the easily reducible fraction are observed in the regions where variations in the concentrations of Mn and Fe are present. With the exception of Zn in LBSC 10, low proportions are observed in the same region as the Fe enrichment at 6 - 8 cm. In LBSC 6 low proportions are also observed for both Pb and Zn at ~ 20 cm, the region of Mn enrichment, and low Zn and variable Pb values between 30 and 40 cm, a region of Mn and Fe enrichment. In LBSC 8 low values for Pb and Zn, < 1 % in the case of Pb, are observed below 22 cm, the region of Mn and Fe enrichment.

4.3.2 Copper, Lead and Zinc Profiles in the Sediment of Loch Riecawr

In the sediment cores of Loch Riecawr, LRSC 1 and 2, the profiles of Cu, Pb and Zn all show similar concentration profiles (Fig. 4.9 A-B). Concentration minima of 19 mg kg^{-1} and 14 mg kg^{-1} of Cu, 93 mg kg^{-1} and 111 mg kg^{-1} of Pb and 65 mg kg^{-1} and 122 mg kg^{-1} of Zn are observed at, or close, to the surface of the sediment for LRSC 1 and 2, respectively. The concentrations of all three metals increase below the minima, reaching maxima at 5 - 15 cm in LRSC 1 and at 2 - 3 cm in LRSC 2 of 25 mg kg^{-1} and 28 mg kg^{-1} of Cu, 234 mg kg^{-1} and 225 mg kg^{-1} of Pb and 643 mg kg^{-1} and 388 mg kg^{-1} Zn, respectively. Below the maxima the concentrations of Cu, Pb and Zn decrease, all reaching minima at the base of the cores. Another feature present in the profiles of Zn in LRSC 1 and Cu and Zn in LRSC 2 is an increase in concentration observed at the sediment-water interface.

The concentration of Cu extracted by $NH_2OH.HCl$ / HNO_3 was below detection (corresponding to < 0.04 mg kg^{-1}) in the sediment of Loch Riecawr. In contrast, the easily reducible concentration profile for both Pb and Zn was found to be similar to that of the total concentration. The proportion of Pb that was easily extractable ranged from < 0.05 % to 47.2 % in LRSC 1 and 13.6 to 45.2 % in LRSC 2, with corresponding figures for Zn of 47.5 to 91.0 % and 37.9 to 94.5 %, respectively. General trends seen in the proportions of Pb and Zn that are easily reducible are maxima at the surface, at the same depth as the redox-driven Mn maxima, minima at the same depth as the diagenetic enrichment of Fe, and also generally lower values below 10 cm depth.

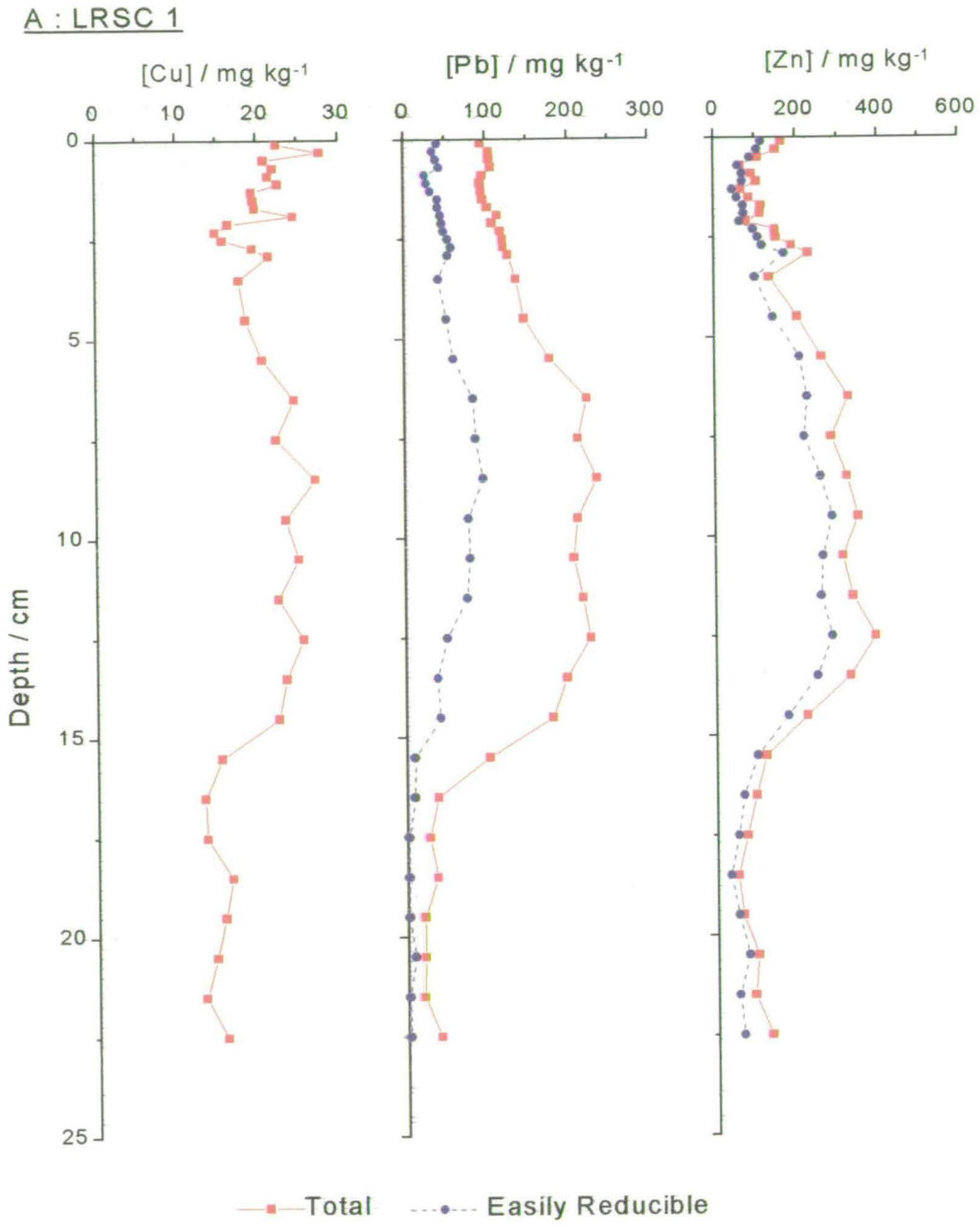


Fig. 4.9 A : Total and easily reducible Cu, Pb and Zn concentrations in LRSC 1.

B : LRSC 2

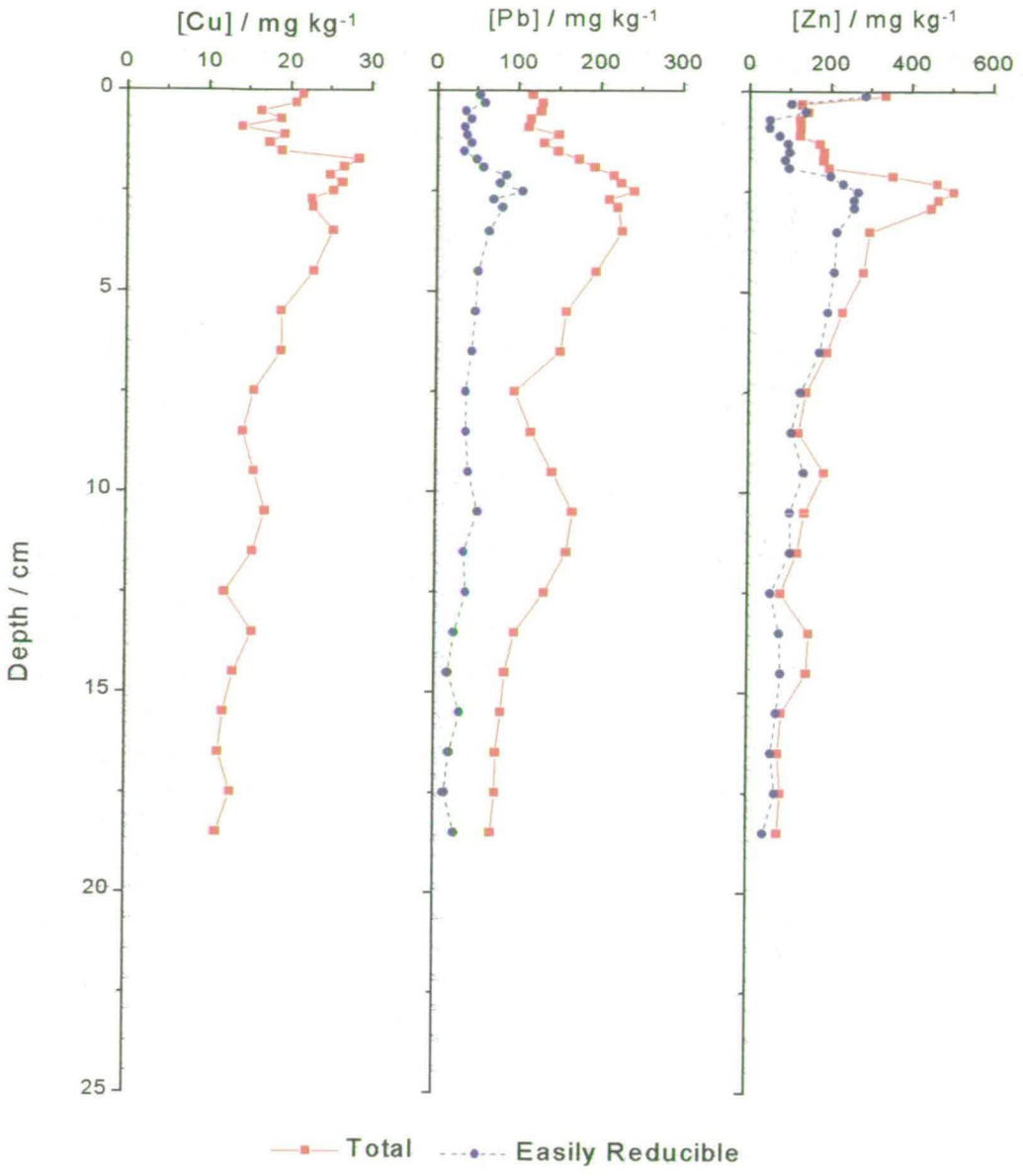


Fig. 4.9 B : Total and easily reducible Cu, Pb and Zn concentrations in LRSC 2.

4.4.1 Discussion of Copper, Lead and Zinc Profiles in the Sediment of Loch Bradan and Loch Riecawr and the Importance of Associations with Manganese and Iron

The concentration profiles of Cu, Pb and Zn can be affected by a number of factors including varying historical inputs, associations with Mn and Fe, formation of insoluble sulphides and associations with organic matter. This study will concentrate on the associations of the Cu, Pb and Zn with Mn and Fe.

The concentration profiles of Cu, Pb and Zn do not appear to be significantly affected by interactions with Mn or Fe since the total metal concentration profiles of Cu, Pb and Zn do not show any major correlation with either Mn or Fe concentrations, with the exception of below 22 cm in LBSC 8.

Copper does not appear to not be associated with Mn at any depth within the sediment of Loch Bradan or Loch Riecawr since no Cu was found to be extracted with the easily reducible Mn. A sizeable fraction of Pb and Zn was found to be extracted by $NH_2OH.HCl$ / HNO_3, up to ~ 70 % of the Pb and ~ 95 % of the Zn, indicating that these two metals may be associated with Mn species within the sediment of both Loch Bradan and Loch Riecawr.

In general it was observed that the proportion of Pb and Zn that was released in the easily reducible fraction was high at the same depth within the sediment as the redox-driven Mn enrichments. This suggests that Pb and Zn are associated with the Mn(IV) oxyhydroxides that are produced as a result of the Mn cycling, and hence will be associated with particulates in the oxic regions of the sediment and water column. Below the redox boundary for Mn, where Mn is reduced / solubilised, the proportion of the Pb and Zn in an easily reducible form generally exhibits a decrease, with minima occurring at the same depth as the diagenetic enrichment of Fe. This indicates that as well as associating with Mn, the Pb and Zn are also possibly adsorbing to the surface of Fe oxyhydroxides, accounting for the minima of Pb and Zn that are extracted by

by $NH_2OH.HCl$ / HNO_3. It is impossible to say if Cu is also adsorbing to Fe oxyhydroxides since the $NH_2OH.HCl$ / HNO_3 only extracts a small fraction of the Fe compounds and adsorbed metals.

Deeper within the sediment of LBSC 6 and 8 there are further regions of interest with respect to the association of Pb and Zn with Mn.

At ~ 20 cm in LBSC 6, the same region as a Mn enrichment, there is a reduction in the proportion of the Pb and Zn which is easily reducible. This may indicates that the speciation of the Mn is changing at this depth, possibly to $MnCO_3$ (compare with LBSC 8), resulting in a reduction in its ability to adsorb Pb and Zn, despite the fact that the Mn is still found to be in an easily reducible form.

Between 30 and 40 cm in LBSC 6, a region where Mn and Fe were found to be enriched, the proportion of the Pb that is easily reducible is variable while for Zn it is low. Again this could indicate that the speciation of the Mn is altered at this depth, changing its ability to adsorb metals.

In LBSC 8 there is a decrease in the concentration of Cu, Pb and Zn below 22 cm which is associated with enrichments in Mn and Fe, decrease in the organic matter content and a reduction in the proportion of the Pb and Zn that was found to be present in an easily reducible form. Unlike LBSC 6, the change in the concentration of the Mn at depth is associated with a change in the concentration of Pb and Zn as well as a reduction in the percentage of the total Pb and Zn extracted by $NH_2OH.HCl$ / HNO_3. It is apparent therefore that the $MnCO_3$, or other unidentified Mn species, have a lower capacity to bind Pb and Zn than the Mn that is present above this region of the sediment column. It is also apparent that an increase in the concentration of Mn at 22 cm in LBSC 8 is associated with a decrease in the concentration of Cu, Pb and Zn, possibly resulting from a change in the nature of the sediment.

4.5 Conclusions

Within the top 3 cm sediment of Loch Bradan and Loch Riecawr sediment the concentration profiles of Mn, Fe and As are principally controlled by redox cycling, resulting in surface or near-surface enrichments. Concentrations are higher in the eastern basin than in the western basin, possibly as a result of the differing concentrations in the input streams around the loch. The concentrations observed in Loch Riecawr closely resemble those seen in the western basin of Loch Bradan for all three redox-active elements. In Loch Bradan the organic matter concentrations, in general, show an inverse correlation with the Fe concentration, a trend which is not observed in the sediments of Loch Riecawr.

At depth within the sediment of Loch Bradan the concentrations of Mn, Fe and As appear to be controlled by a number of factors, including the formation of insoluble sulphides and phosphates, and possibly the trapping of historical peaks. These are not observed in Loch Riecawr.

In view of the high organic matter content in the sediments of Loch Bradan and in the surrounding catchment and the persistently elevated concentrations of dissolved Mn in the Loch Bradan water column, the role of organic matter and humic substances in the behaviour and cycling of Mn clearly warrants investigation, as reported in Chapters 5 and 6.

5. The Behaviour of Manganese and Other Metals in the Peaty Catchment of Loch Bradan

5.1 Vertical Distribution of Manganese, Iron, Arsenic and Organic Matter in Loch Bradan Peat Cores

5.1.1 Results

The results for the redox active elements and the organic matter in the peat cores collected from the Loch Bradan catchment, LBPC 1 to 4, are tabulated in Appendices 13 to 16.

5.1.1.1 Vertical Distribution of Manganese in Loch Bradan Peat Cores

The Mn concentration profiles for the four peat cores all show surface, or near-surface, enrichments (Fig. 5.1 A - D). The maximum concentrations of these enrichments vary greatly at the differing core sites, with LBPC 1 having the greatest enrichment at 18,000 mg kg^{-1}, and LBPC 2 the smallest at 36 mg kg^{-1} (Table 5.1, Figs. 5.1 A - D).

In addition to the enrichment in the uppermost layers of the peat, LBPC 2 and 4 exhibit further enrichments of Mn deeper within the core (Figs. 5.1 B, D). In LBPC 2, the concentration of Mn increases from < 0.027 mg kg^{-1} to 20 mg kg^{-1} below 49.4 cm, reaching the maximum at 54.4 -57.0 cm, the bottom section of the core. In LBPC 4 there is a broad Mn peak at depth between 26.6 and 45.6 cm, reaching a maximum concentration of 5780 mg kg^{-1} at 30.6 - 33.2 cm.

The percentage of the total Mn present in an easily reducible form varies greatly at the four different coring sites and also within individual cores. The average percentages vary from 24.9 ± 24.2 % at LBPC 2 to 102.0 ± 20.1 % at LBPC 3

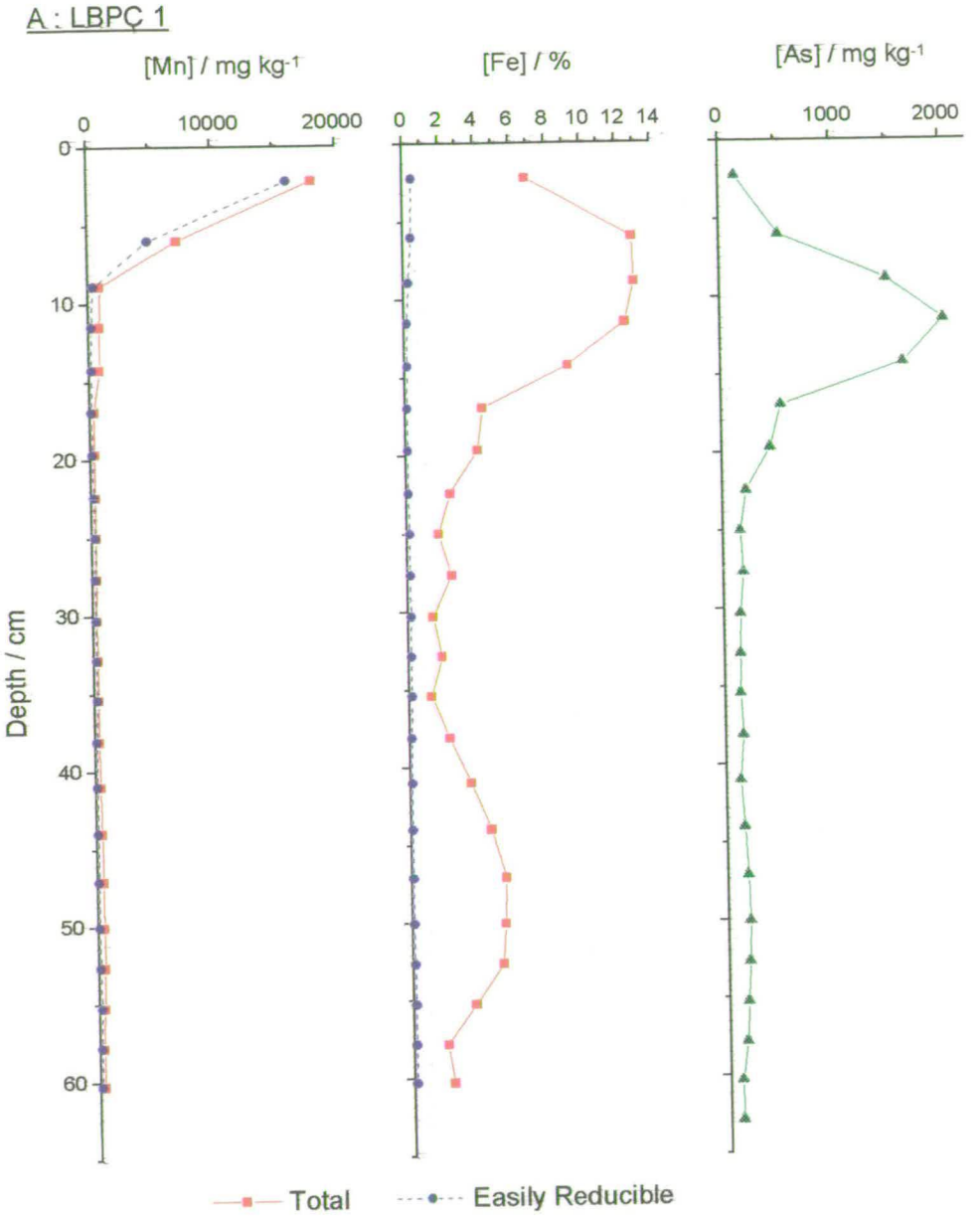


Fig. 5.1 A : Total and easily reducible Mn and Fe, and As concentrations in LBPC 1.

B : LBPC 2

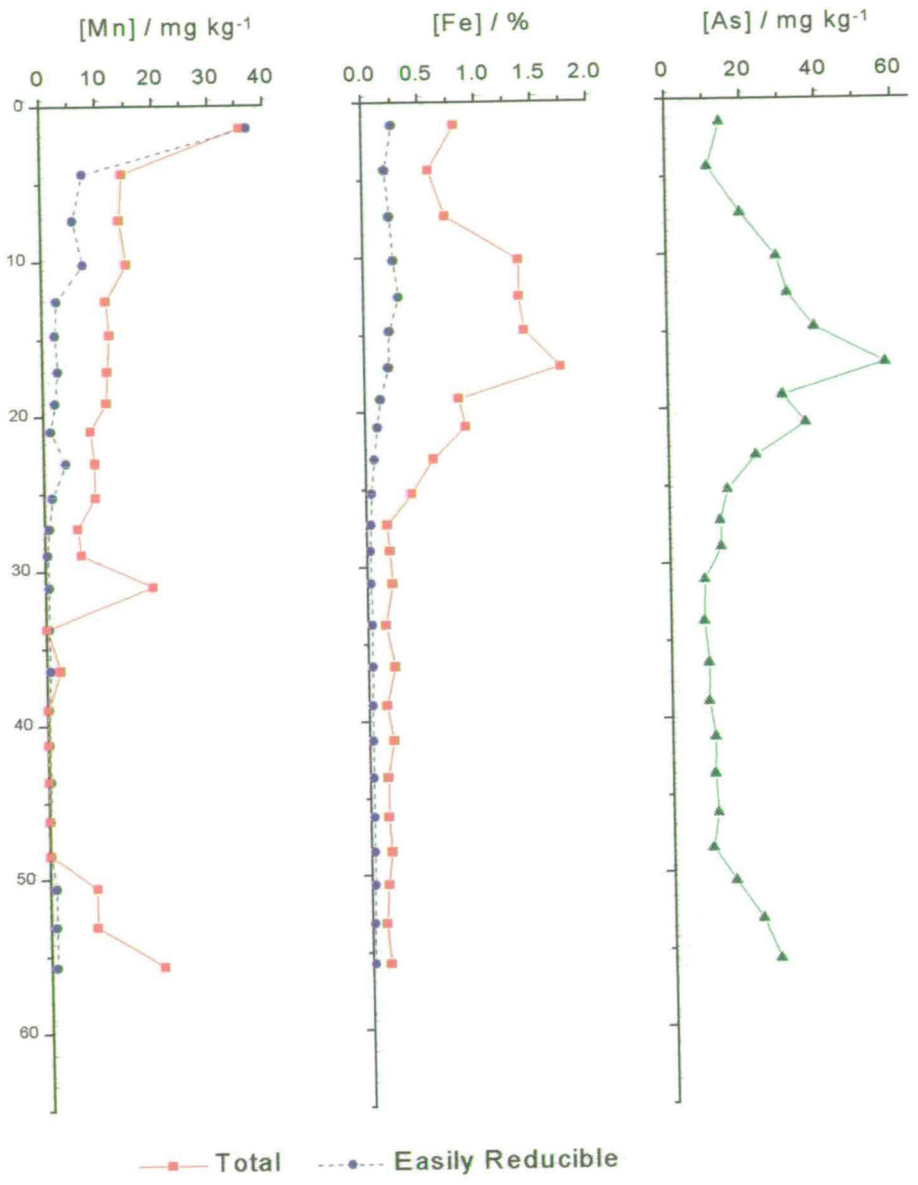


Fig. 5.1 B : Total and easily reducible Mn and Fe, and As concentrations in LBPC 2.

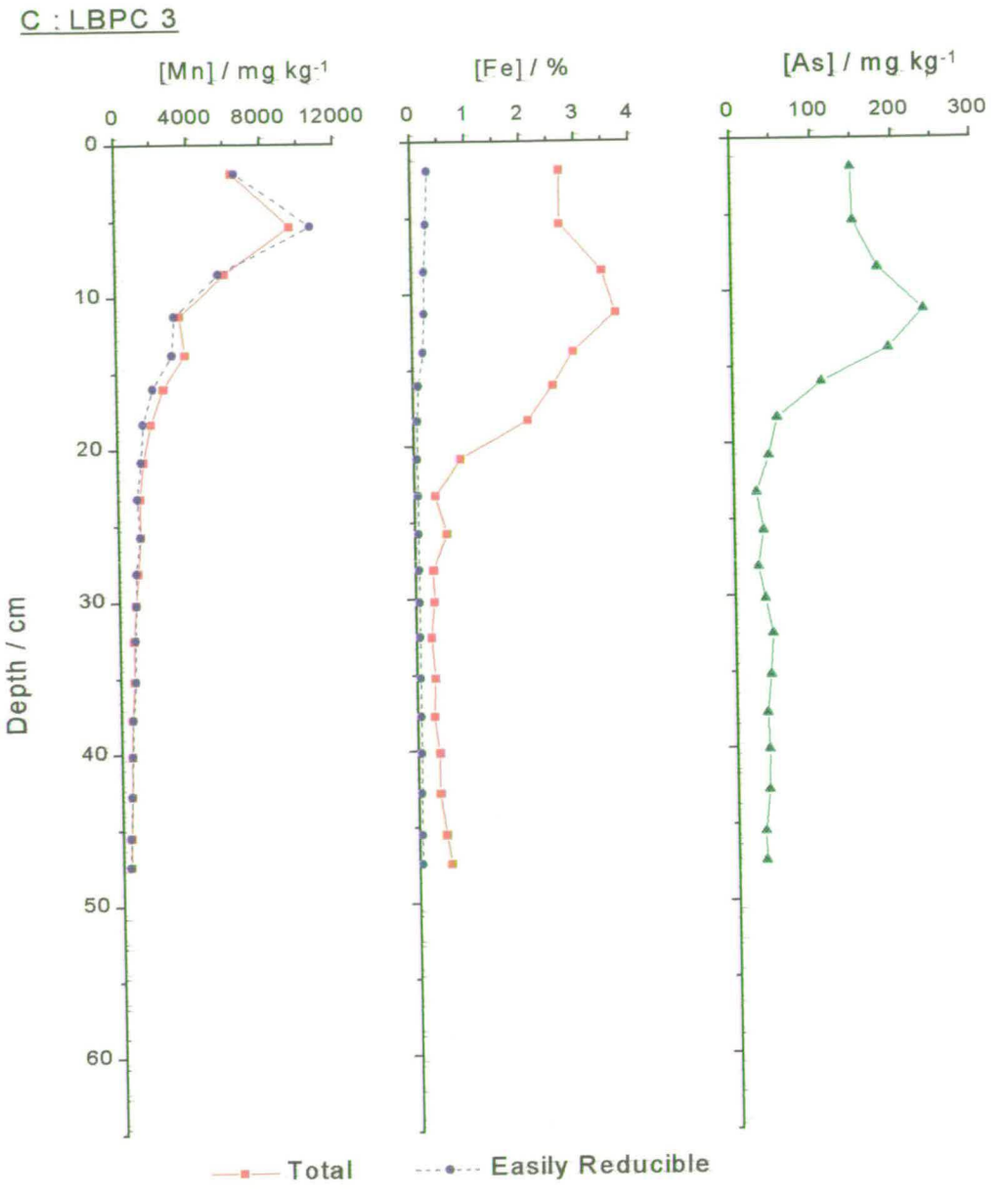


Fig. 5.1 C : Total and easily reducible Mn and Fe, and As concentrations in LBPC 3.

D : LBPC 4

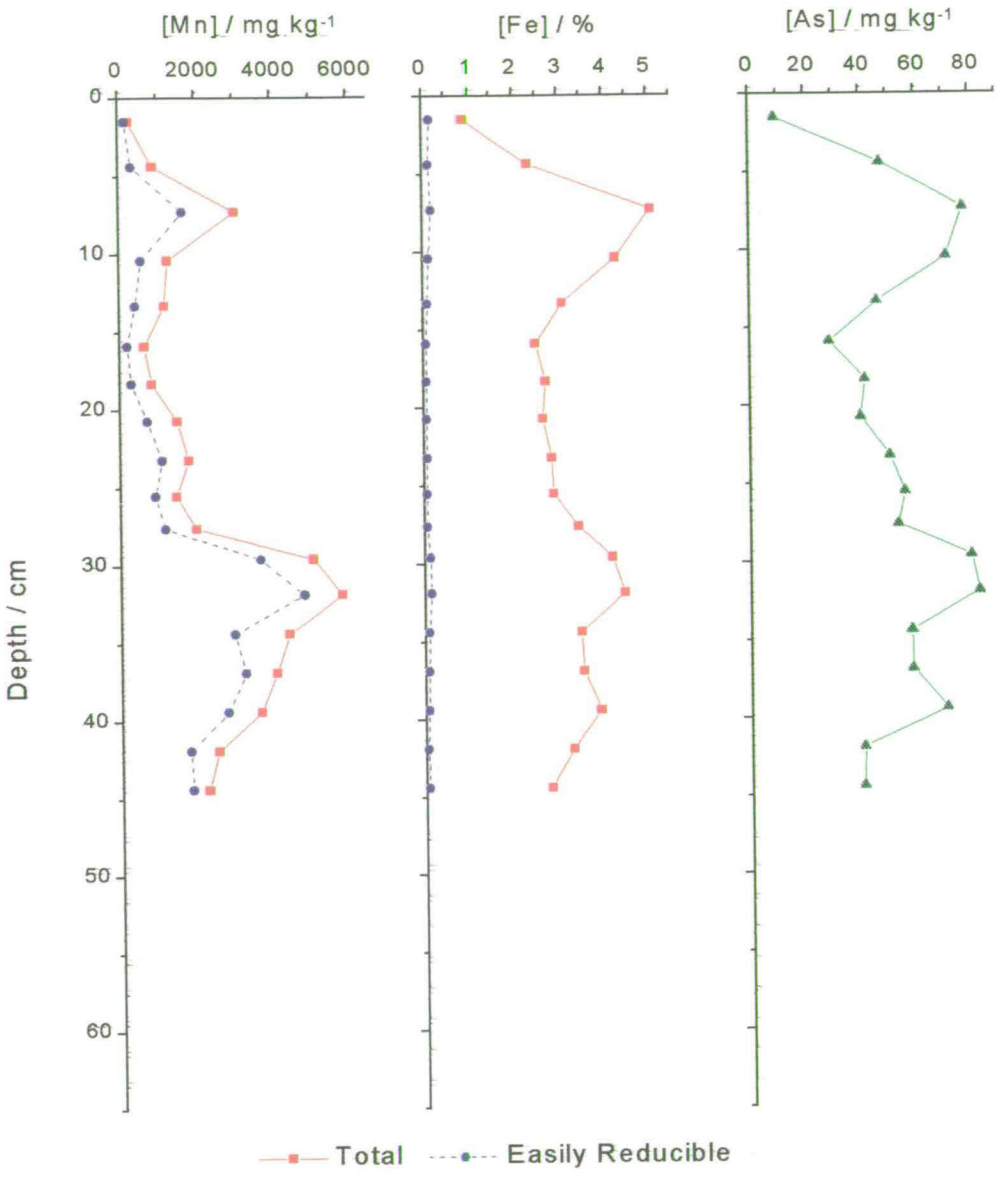


Fig. 5.1 D : Total and easily reducible Mn and Fe, and As concentrations in LBPC 4.

(Table 5.1), with the maximum percentages, up to ~ 100 %, generally being observed at, or near the peat surface, the same region as the enrichments of Mn.

Peat Core	$[Mn]_{max}$ / mg kg^{-1}	$[Mn]_{max}$ depth / cm	Percentage of Mn in an easily reducible form
LBPC 1	18000	2.2	39.0 ± 24.8
LBPC 2	36	1.45	24.9 ± 24.2
LBPC 3	9502	5.4	102.0 ± 20.1
LBPC 4	3008	7.3	58.4 ± 17.1

Table 5.1 : Maximum Mn concentration in the upper regions of the peat, the depth of the maximum, and the mean percentage (± 1 std. dev.) of the Mn in an easily reducible form over the length of the core.

5.1.1.2 Vertical distribution of Iron and Arsenic in Peat Cores from the Loch Bradan Catchment

In each case, there is an enrichment of Fe and As within the top 20 cm of the peat with the depths of enrichments of the two elements coinciding (Figs 5.1 A - D). For both Fe and As, the concentrations of the maximum enrichments vary like those for Mn, with LBPC 2 exhibiting the lowest concentrations, 1.73 % and 58 mg kg^{-1} for Fe and As, respectively, and LBPC 1 the highest, 12.94 % and 2022 mg kg^{-1} for Fe and As, respectively (Table 5.2).

Further enrichments of Fe are observed deeper within the peat in LBPC 1 and 4 (Figs. 5.1 A, D). The enrichment in LBPC 1 is observed between 45.5 and 64.6 cm, with the maximum concentration of 5.25 % observed at 45.5 - 48.7 cm, but with no corresponding enrichment for As. In LBPC 4 the enrichment of Fe is between 26.6 and 45.6 cm, with the maximum concentration of 4.42 % being observed at 30.6 - 33.2 cm. The enrichment of Fe in LBPC 4 between 26.6 and 45.6 cm is at the same depth as an enrichment of As which, like Fe, exhibits its maximum concentration, of 83 mg kg^{-1}, at 30.6 - 33.2 cm. In LBPC 2 there is a small enrichment of As below 49.4 cm which is at the same depth as an enrichment of Mn, but not Fe (Fig. 5.1 B).

LBPC 2 there is a small enrichment of As below 49.4 cm which is at the same depth as an enrichment of Mn, but not Fe (Fig. 5.1 B).

The average proportion of Fe which is an easily reducible form within the peat cores ranges from 3.1 ± 2.6 % in LBPC 1 to 15.5 ± 6.9 % in LBPC 2, with no vertical trends within individual cores (Table 5.2).

Peat Core	$[Fe]_{max}$ / %	$[Fe]_{max}$ depth / cm	Percentage Fe in easily reducible form	$[As]_{max}$ / mg kg^{-1}	$[As]_{max}$ depth / cm
LBPC 1	12.94	8.9	3.1 ± 2.6	2022	11.5
LBPC 2	1.41	14.75	15.5 ± 6.9	58	17.1
LBPC 3	3.71	11.25	10.1 ± 4.6	238	11.25
LBPC 4	5.05	7.3	3.2 ± 3.6	78	7.3

Table 5.2 : Maximum Fe and As concentration in the upper regions of the peat, the depth of the maximum, and the percentage of the total Fe in an easily reducible form over the length of the core.

5.1.1.3 Organic Matter in Peat Cores from the Loch Bradan Catchment

LBPC 1 has an organic matter content that varies between ~ 10 and 60 % over the length of the core (Fig. 5.2 A). The maximum concentration of 58.5 % is observed in the 0 - 4.4 cm section of the core, below which there are two main regions where the organic matter is depleted, at 4.4 to 18.2 cm and 36.7 to 53.9 cm. The minimum organic matter concentrations in these two regions are 30.3 % at 10.2 - 12.8 cm and 11.5 % at 42.5 - 45.5 cm.

In LBPC 2 (Fig. 5.2 B), the organic matter content of the peat remains comparatively constant at 69.9 ± 2.3 % in the top 50 cm of the core, apart from one section at 29.7 - 32.4 cm where the organic matter content drops to 44.4 %. Below 50 cm, the organic matter content decreases to a minimum of 51.9 % at the base of the core.

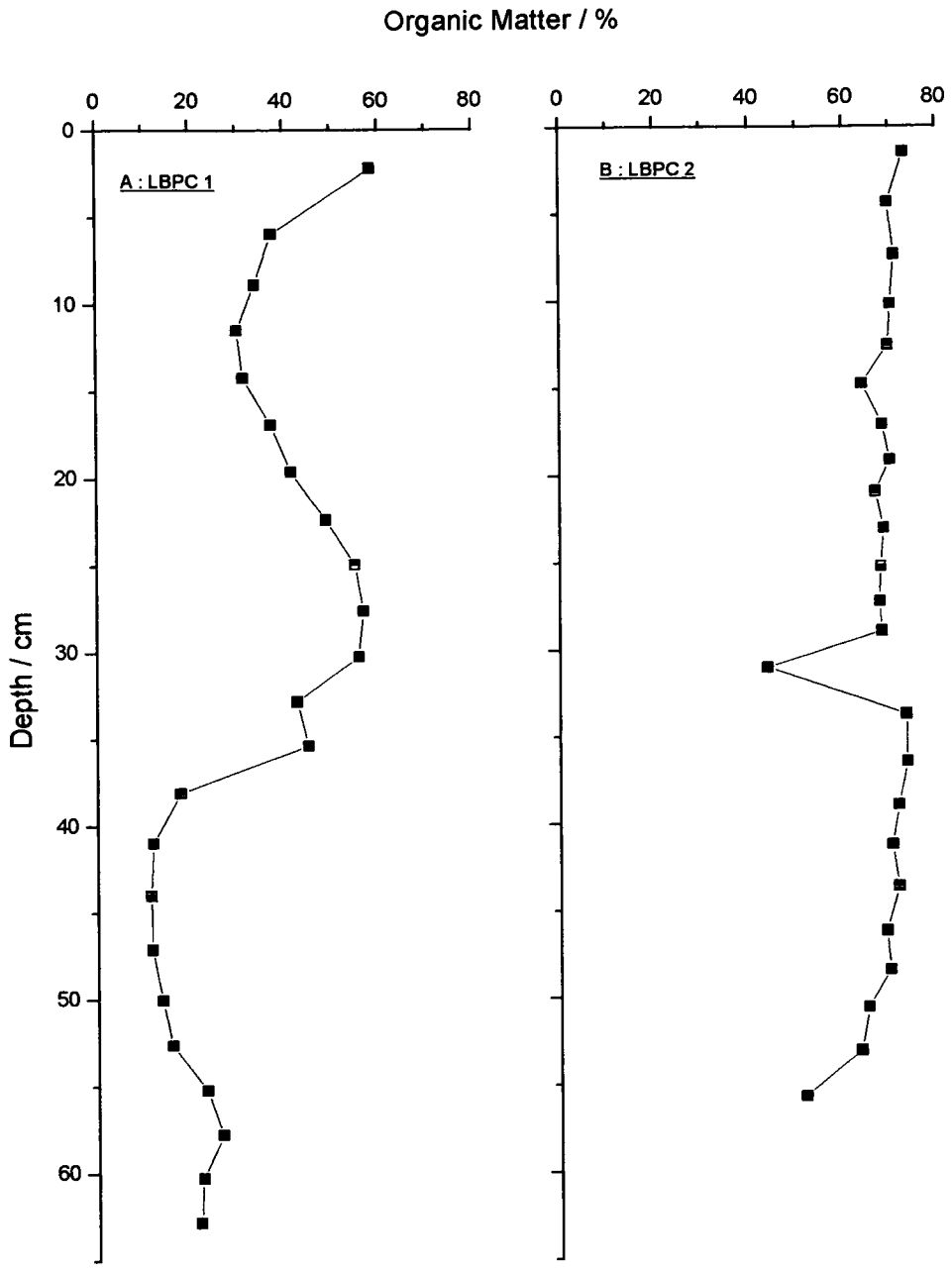


Fig. 5.2 A - B : Organic matter concentrations in LBPC 1 and 2.

In LBPC 3 (Fig. 5.2 C) the organic matter content varies between ~ 50 and 77 % with the lower concentrations being observed at the surface and at the base of the peat core, and the maximum concentration between ~ 20 and 40 cm.

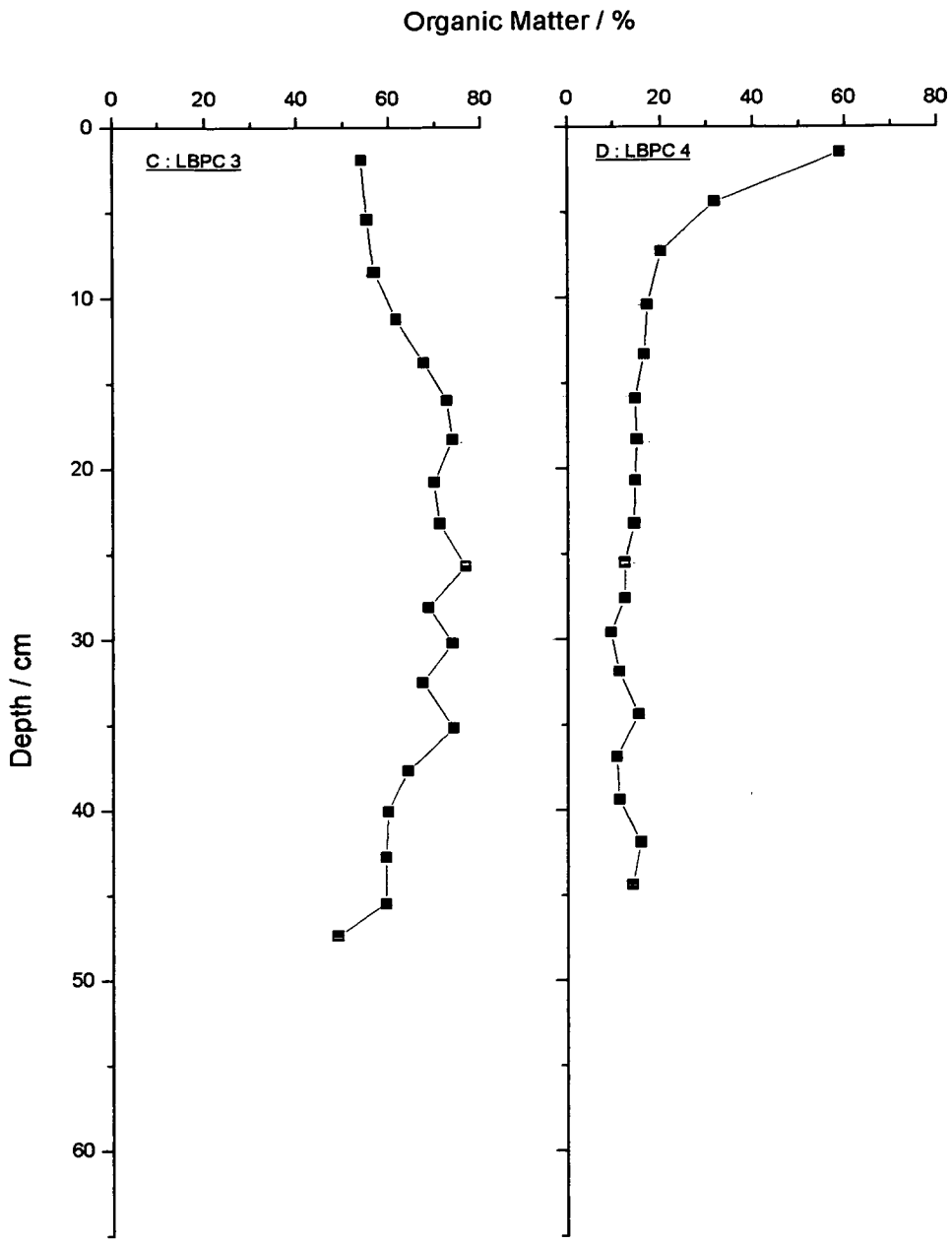


Fig. 5.2 C - D : Organic matter concentrations in LBPC 3 and 4.

In LBPC 4 (Fig. 5.2 D) the organic content for most of the core is much lower than that observed at the other three peat coring sites. The organic matter concentration shows a surface maximum of 59.0 %, falling to a level of 14.1 ± 2.7 % below 5.8 cm.

5.1.2 Discussion of Vertical Distribution of Manganese, Iron and Arsenic and Organic Matter in Peat Cores from the Loch Bradan Catchment

5.1.2.1 Manganese, Iron and Arsenic in the Upper Regions of the Peat

The surface or near-surface enrichment of Mn usually occurs 5 - 15 cm above that of Fe and As. The one exception to this is LBPC 4 where the depths of the maximum Mn, Fe and As enrichments are the same, although the peaks for Fe and As are broader. These enrichments are the result of the redox cycling of these three elements within the peat.

Redox cycling within the peat occurs in an analogous fashion to that described in Section 4.1 for Loch Bradan sediments. Reduction and solubilisation of Mn (IV) and Fe(III) (hydr)oxides in suboxic zones results in increased Mn(II) and Fe(II) concentrations in the solution phase. The relative importance of vertical (upwards and downwards) diffusion and lateral groundwater flow will determine the fate of these soluble species. Only if the reduced forms diffuse upwards will they be subject to re-oxidation followed by precipitation leading to characteristic near-surface enrichments of Mn(IV) and Fe(III). The importance of downwards diffusion and of lateral flow will be considered separately in the following sections. The lower reduction potential of the Fe(II)/Fe(III) couple means that Fe(II) will be oxidised at a lower pE than Mn(II) and so the enrichment in solid phase Fe(III) occurs below that of Mn(IV) (Damman, 1978).

The presence of ~ 100 % (LBPC 2) and > 60 % (LBPC 4) of total Mn in an easily reducible form supports redox cycling as the process controlling Mn distribution within the upper zone of the peat.

The maximum concentrations of As are, as in the sediment of Loch Bradan, at the same depth as the peaks in Fe. This is a consequence of the strong association of As, especially As(V), with Fe(III) oxyhydroxides (DeVitre *et al.*, 1991). In the suboxic

zones of the peat, reduction of As(V) occurs, and the fate of the soluble As(III) species is determined by the same transport processes outlined for Mn and Fe. Upwards diffusion into the oxic zone will result in re-oxidation to As(V), possibly with Fe(III) or Mn(IV) as the oxidant (Oscarson *et al.*, 1981), and the sorption/coprecipitation with Fe(III) (hydr)oxides. As a consequence of the latter sorption process, the depths of the As and Fe enrichments coincide.

The depths of the maximum enrichments of Mn and Fe give an indication as to the level of the water table at the peat coring sites. Damman (1978) reported that the maximum enrichment for Mn was typically above the water table, while that for Fe was in the zone of water table fluctuation. This suggests that the water table level in LBPC 1 and 4 is in the top 10 cm of the peat, while in LBPC 2 and 3 the water table is between 10 and 20 cm in the peat.

5.1.2.2 Manganese, Iron and Arsenic Below the Near-Surface Redox-Driven Maxima Within the Peat

Section 5.1.2.1 has highlighted the importance of formation of insoluble (hydr)oxides in the near-surface zone of the peat for the retention of Mn, Fe and As within the peat. Other processes can lead to the retention of these elements at greater depth, e.g. the formation of more stable oxides, of sulphides under extremely reducing conditions, and of phosphates and carbonates. The fate of downwards diffusing Mn(II), Fe(II) and As(III) species may be determined by the relative stability and solubility of the solid phase oxides, sulphides, phosphates and carbonates of these elements. Associations of Mn and Fe with organic matter can also lead to the formation of both soluble and insoluble species within natural systems, but this will be discussed in Section 5.3.

Data obtained by SEM-EDX for LBPC 1 (45.5-48.7 cm) shows that there are mineral phases present (~ 200 μm diameter particles) (Fig. 5.3 A) which have high concentrations of Fe and O, but an absence of S and P (Fig. 5.3 B). This indicates

that the enrichment of Fe at depth is probably due to the presence of more stable, crystalline oxides. Retention of Mn and As by sorption to these specific Fe phases does not occur, however, to any significant extent, as suggested by the absence of Mn and As enrichment at this depth.

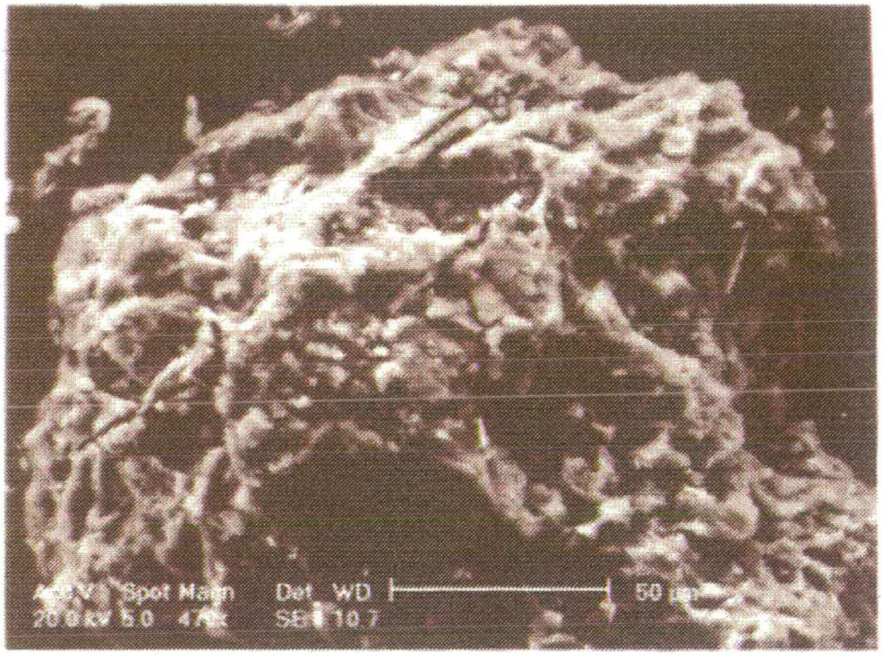


Fig 5.3 A: SEM of peat sample from LBPC 1 (45.5 - 48.7 cm)

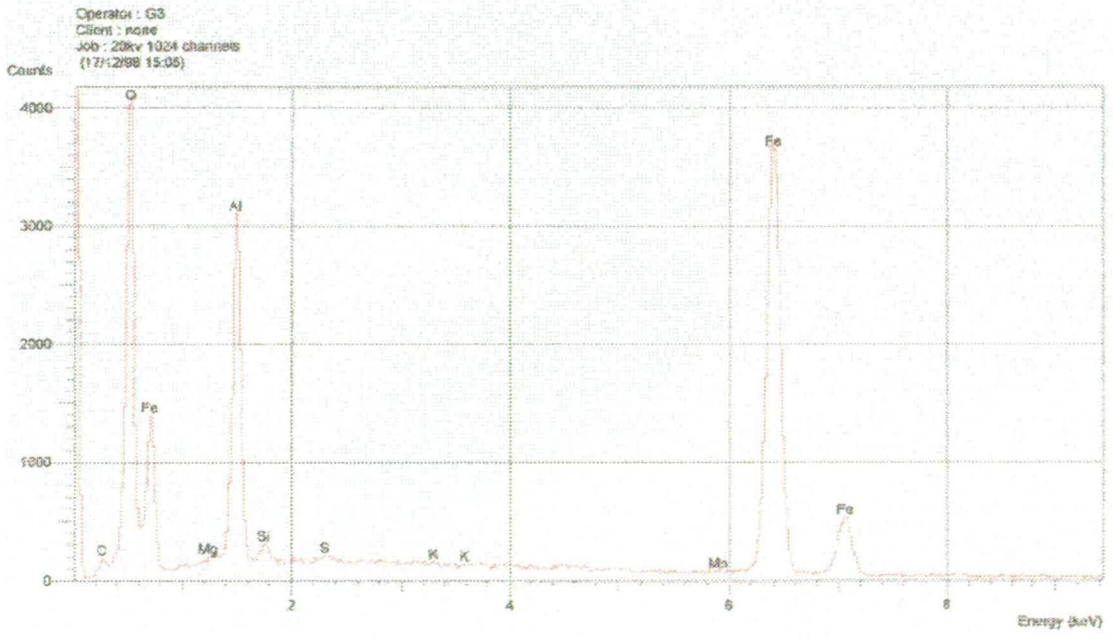


Fig 5.3 B: XRF of peat sample from LBPC 1 (45.5 - 48.7 cm)

There is a more consistent change in concentration of Mn, Fe and As at depth (>30 cm) in LBPC 4. An explanation for the Mn, Fe and As profiles could arise from the observation that this core has horizons analogous to a forest soil, i.e. an organic-rich surface horizon (0-10 cm) overlying a more mineral-rich A (10-30 cm) and B (> 30 cm) horizons. Weathering of the A horizon results in the alteration of primary and secondary minerals and soluble species are lost by downwards leaching (Nortcliff, 1988). The downwards displacement of Fe observed during podzolisation of soils can be explained by considering the effect of pH and complex formation on the solubility of Fe. For example, species of Fe soluble under quite strongly acidic conditions are transported from the A horizon but often retained in the B horizon via precipitation of insoluble (hydr)oxides (Nortcliff, 1988). Mn(II) and As(III) may become enriched in the B horizon as a result of sorption on/coprecipitation with Fe oxides. Soluble organic matter may also be transported downwards from upper horizons and accumulate in the B horizon as a result of sorption onto Fe oxide surfaces.

Alternatively, the material below 30 cm contains a higher proportion of partially weathered Mn-rich bedrock and hence may perhaps be the source of Mn to overlying soils as a result of chemical weathering processes. The decrease in the concentration at the bottom of the core favours the former explanation.

In the preceding paragraphs, mechanisms for retention of species within the peat have been considered. With respect to characterisation of the source of Mn in the waters and sediments of Loch Bradan, the key requirement was to identify the potential mechanisms by which Mn could be lost from the catchment. It has been clearly demonstrated that Mn undergoes redox cycling within the peat and thus that under certain conditions (sub-oxic and anoxic), a proportion of the Mn enters the solution phase as Mn(II) species. Whilst solubilised, there is a potential for loss of Mn from the peat via lateral groundwater flow from the peat into receiving waters (directly into the loch water or indirectly via the feeder streams). The balance between retention by the formation of various solid phases and loss via physical transport will depend on the geochemical and hydrological conditions at each location.

5.1.2.3 Organic Matter Profiles in Peat Cores from the Loch Bradan Catchment

The organic matter profiles in LBPC 1 and 3 both show a broad minimum in the top 20 cm of the peat, at the same depth as the diagenetic enrichments of Fe. It would therefore appear that, as in the sediment of Loch Bradan (Section 4.2.1), the organic matter content of the peat is reduced as a consequence of the diagenetic enrichment of Fe. This is not seen in LBPC 2, however, probably due to the lower Fe concentrations present, or in LBPC 4, perhaps due to the lower organic content at that site.

LBPC 1 also shows a marked decrease in organic matter concentration below 40 cm that is at the same depth as an increase in Fe concentration. The Fe enrichment is, however, an order of magnitude smaller than the decrease in organic matter, indicating that the variation in the latter is not just solely an inverse relationship with Fe, but possibly relates to a change in the nature of the peat.

The large decrease in organic matter at 29.7 - 32.4 cm in LBPC 2 may be related to the observed mineral nature of the soil at that depth, supported also by the reduction in the water content (Fig. 3.15 B).

The organic matter content of LBPC 4 is markedly different from that of the other peat cores. At the time of sampling it was noted that the peat appeared more sandy in texture. This is reflected in the overall lower concentration of organic matter present within the core, especially below 5.8 cm. The greater contribution of organic matter at the top of the core is probably the result of the input of organic matter from the overlying vegetation, while at depth a more mineral soil is apparent.

The role of organic matter in complexing Mn and Fe cannot be established from organic matter concentration profiles, but requires quantification and characterisation which is discussed in Section 5.3.

5.2 Vertical Distribution of Copper, Lead and Zinc in the Catchment of Loch Bradan

5.2.1 Results

The concentrations of Cu, Pb and Zn are tabulated in appendices 13 to 16.

5.2.1.1 Vertical Distribution of Copper in Loch Bradan Peat Cores

The concentration of Cu in the peat cores is, in general, below 40 mg kg^{-1} (Fig. 5.4 A - D), with a general decrease in concentration from the surface of the peat to the bottom of the core. LBPC 4 shows a slight increase in Cu concentration over the top 25 cm of the core, followed by a sudden drop from 37 mg kg^{-1} to a baseline value of 3.9 ± 2.5 mg kg^{-1} below this point (Fig 5.4 D).

The concentration of Cu that was extractable using $NH_2OH.HCl$ / HNO_3 was below the detection limit of the FAAS, < 0.04 mg kg^{-1}.

A : LBPC 1

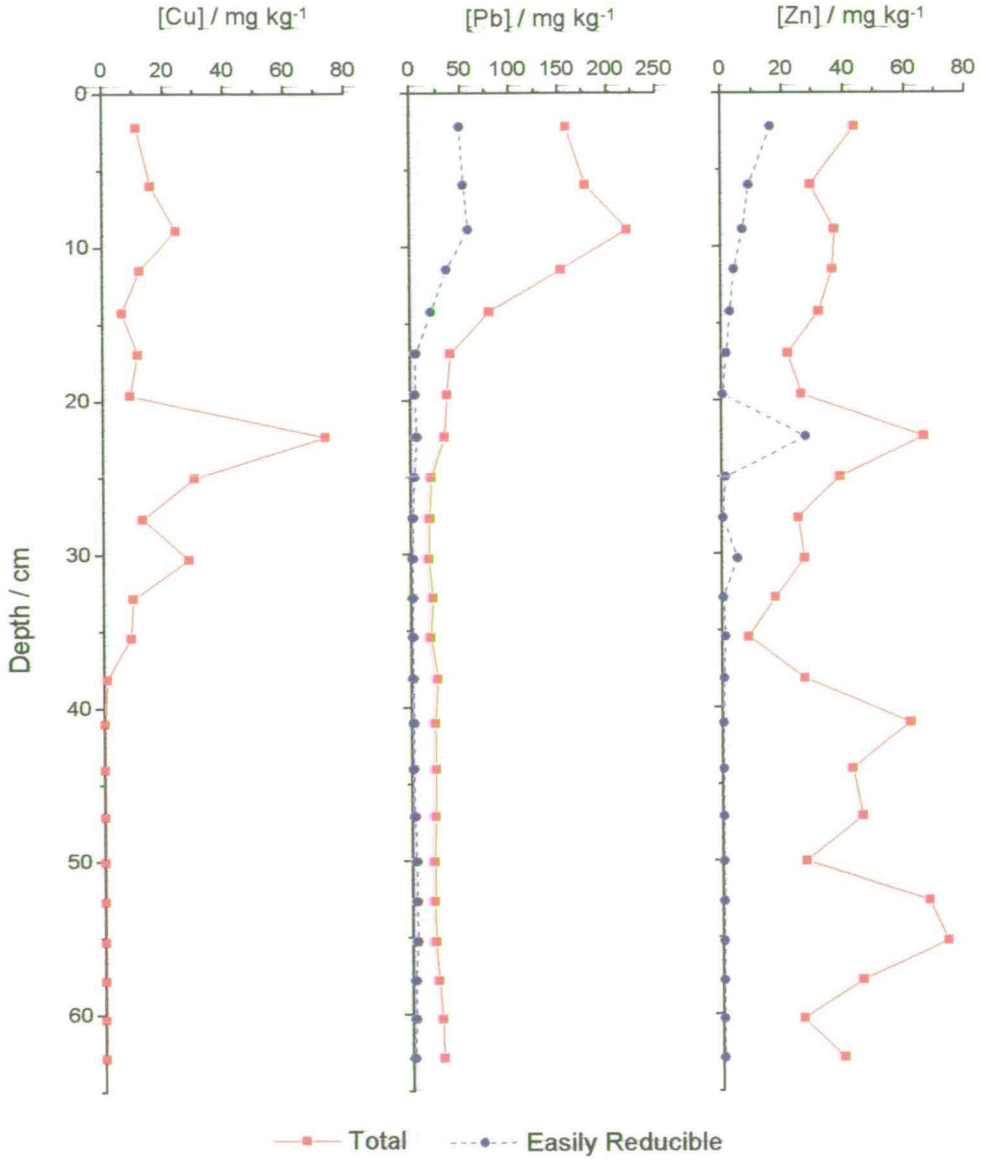


Fig. 5.4 A : Total and easily reducible Cu, Pb and Zn concentrations in LBPC 1.

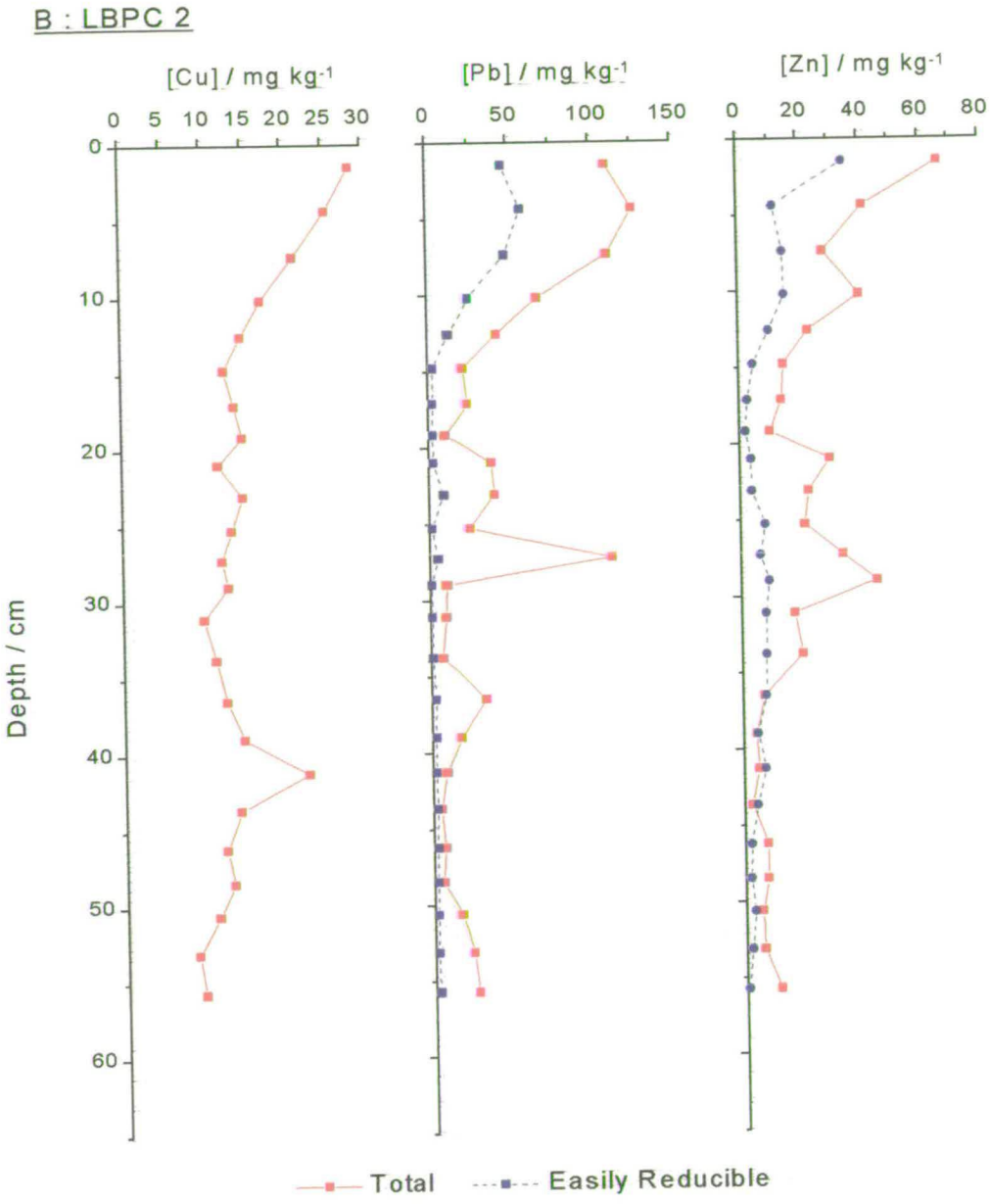


Fig. 5.4 B : Total and easily reducible Cu, Pb and Zn concentrations in LBPC 2.

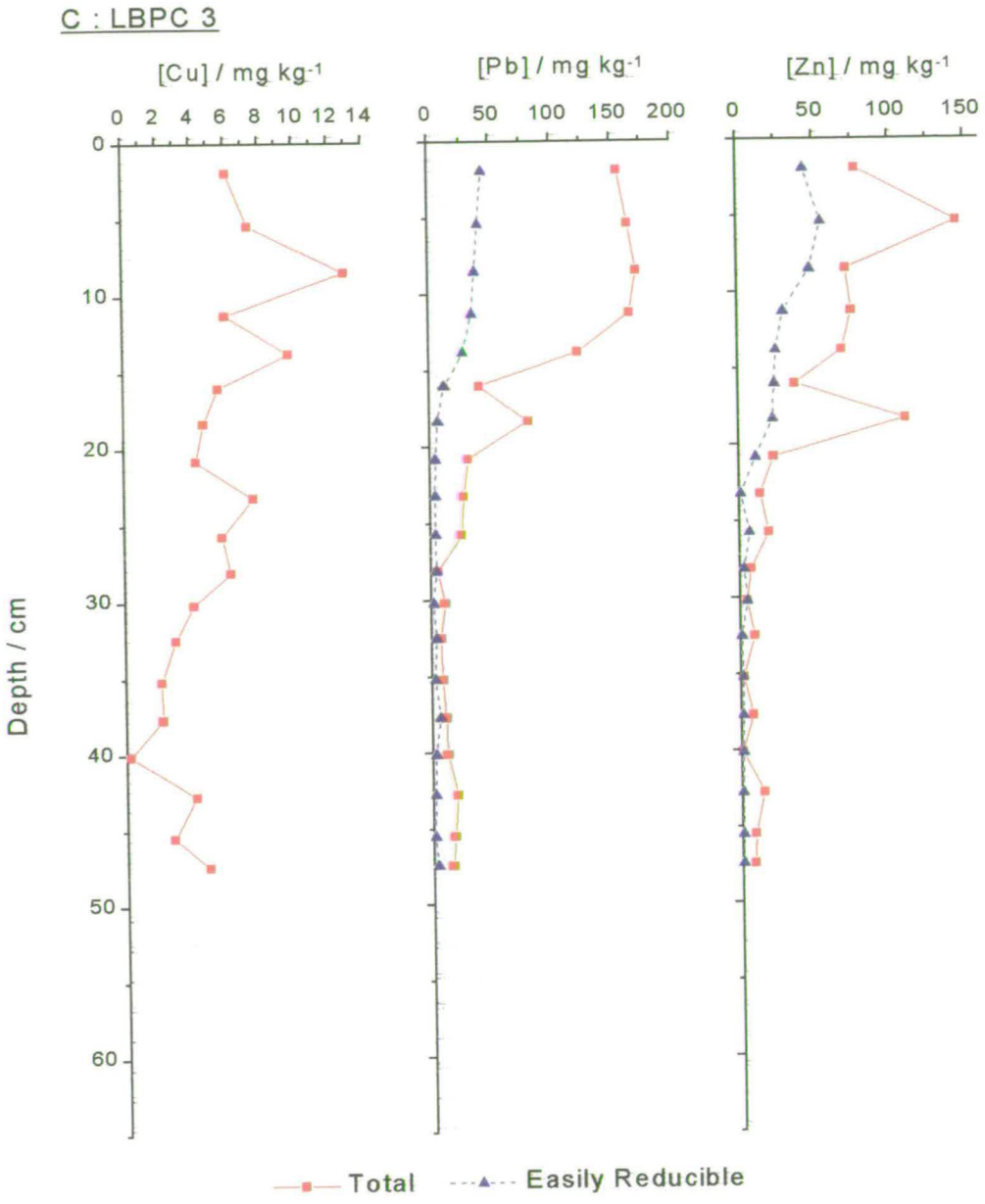


Fig. 5.4 C : Total and easily reducible Cu, Pb and Zn concentrations in LBPC 3.

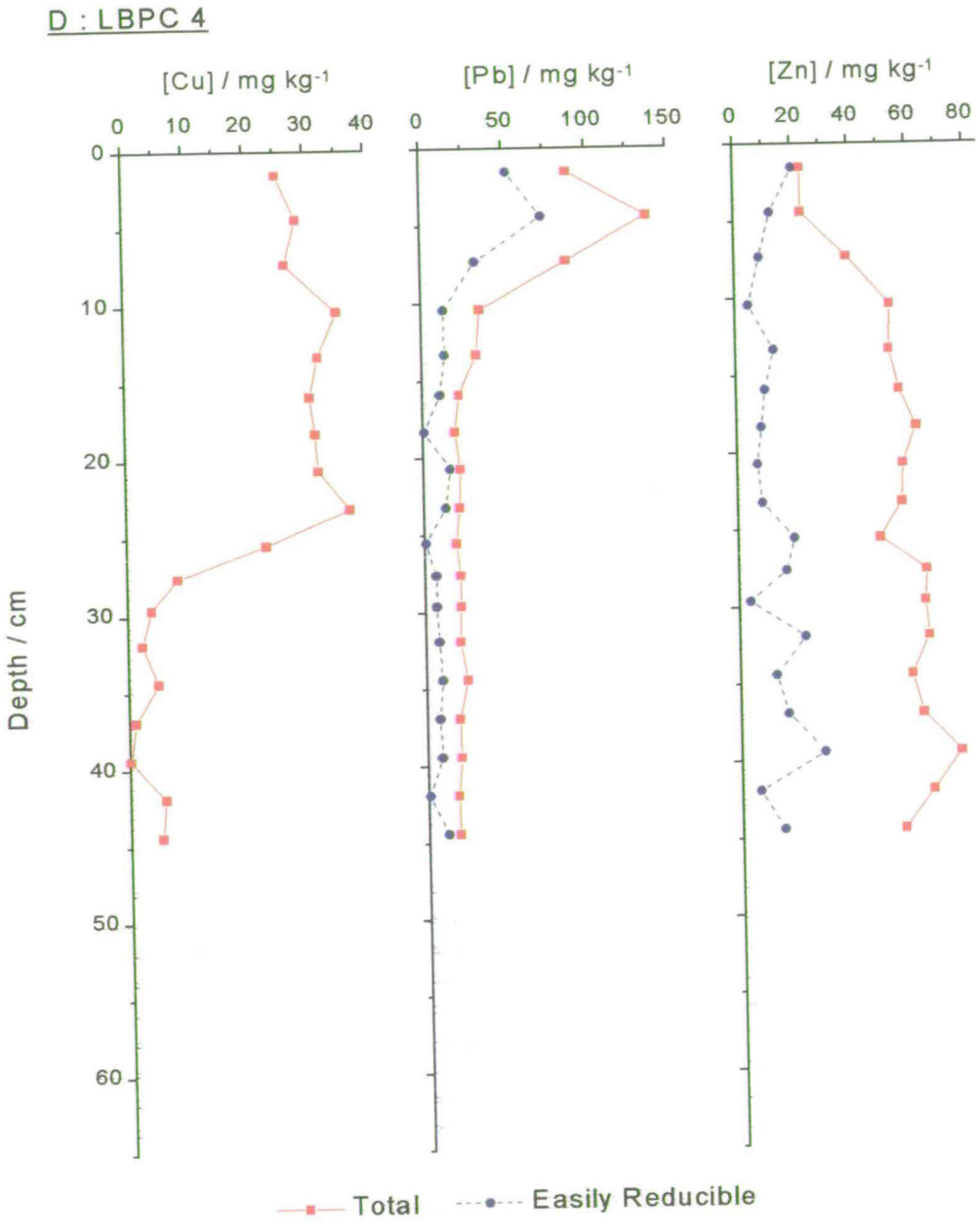


Fig. 5.4 D : Total and easily reducible Cu, Pb and Zn concentrations in LBPC 4.

5.2.1.2 Vertical Distribution of Lead in Loch Bradan Peat Cores

The Pb concentration profiles in the peat cores from the Loch Bradan catchment are similar (Fig. 5.4 A - D). From a minimum of ~14 - 25 mg kg^{-1} at the base of each core, the Pb concentration increases between 10 and 20 cm, reaching maxima of 125 - 220 mg kg^{-1} in the top 10 cm of the core. Above these maxima, the concentrations decrease, resulting in minima located in the top section of the peat.

The proportion of the total Pb which was present in the easily reducible fraction varied greatly between the coring sites and also within each individual core, e.g. 9.8 ± 9.9 % was the lowest average percentage, observed in LBPC 1, and 35.7 ± 19.6 % the highest, seen in LBPC 4. In general, the highest percentage of Pb in the easily reducible fraction was found to be in the upper sections of the peat.

5.2.1.3 Vertical Distribution of Zinc in Loch Bradan Peat Cores

The concentration profiles of Zn in the peat cores are more varied than those of Cu and Pb. In general the observed Zn concentrations are less than 80 mg kg^{-1}, with either a variable concentration with depth (LBPC 1), a general decrease with depth (LBPC 2 and 3), or a general increase with depth (LBPC 4).

Unlike the total concentration, the concentrations of Zn in the easily reducible fraction in the four peat cores are, similar, with near surface maxima of 20 mg kg^{-1} to 50 mg kg^{-1} being observed. With the exception of LBPC 4 the near-surface maxima of Zn extractable by $NH_2OH.HCl$ / HNO_3 coincide with the redox-driven Mn maxima. The percentage of the total Zn that was found in the easily reducible fraction varied from 8.4 ± 13.1 % in LBPC 1 to 46.9 ± 44.3 % in LBPC 2, with no observable trend within individual cores.

5.2.2 Discussion of Copper, Lead and Zinc Results in the Loch Bradan Catchment

As with the sediments of Loch Bradan and Loch Riecawr there are a number of factors that may influence the concentration profiles of Cu, Pb and Zn in the catchment of Loch Bradan. This section will, however, deal mainly with interaction of Cu, Pb and Zn with Mn and Fe.

5.2.2.1 Copper

None of the Cu present in the catchment of Loch Bradan was found to be extracted by $NH_2OH.HCl$ / HNO_3, indicating that Cu is not associated with the redox active Mn. With the data available it is impossible to determine the extent of association of Cu with Fe, but in any case it is more likely to be associated with the generally high organic nature of the catchment (Bryant *et* al., 1991; Achterberg *et al.*, 1997).

5.2.2.2 Lead

That part of the Pb which is in the easily reducible fraction shows, in general, a maximum in the upper sections of the peat core, indicating that the Pb could be associated with the diagenetically enriched Mn. Lead has previously been shown to associate with Mn (Canfield, 1995), but more commonly Fe (Swallow *et al.*, 1980; Balistrieri *et al.*, 1995; Achterberg *et al.*, 1997). In this case it would appear that any associations have only a minor effect on the Pb profile since in LBPC 2 and 4 the depths of the Pb and Mn / Fe maxima do not coincide. A more likely explanation for the general profile shapes is historical change in the atmospheric deposition of anthropogenic Pb.

5.2.2.3 Zinc

The maximum concentration of Zn in the easily reducible fraction is found, in general, at the same depth as the redox-driven Mn maxima indicating that, as with Pb, interactions with Mn may have an effect on the mobility and retention of Zn in the peat cores from the Loch Bradan catchment. The variable proportion of Zn that was found in the easily reducible fraction within individual cores and also between different coring sites indicates that the interactions of Zn with Mn may be affected by factors other than Mn redox chemistry such as involvement in biological processes (Sigg *et al.*, 1987; Achterberg *et al.*, 1997).

5.3.1 Concentration and Composition of Humic Substances and the Concentration of Humic-Associated Manganese and Iron in Peat Cores LBPC 1-4

5.3.1.1 Concentration of Humic Substances in Peat Cores LBPC 1-4

The concentrations of humic material in the peat are expressed as percentage dry weight of the peat and are shown in Appendices 13 to 16.

The proportion of humic material extracted from LBPC 1 did not vary significantly over the entire length of the core and had an average value of 24.6 ± 3.1 % dry weight (Fig. 5.5 A). In the top 36.7 cm, humic substances generally comprised more than 50 % of the total organic matter. Below this depth, 0.1 M NaOH extracted a mass of humic material equivalent to almost twice the organic matter concentration (see Section 5.3.3.1 for explanation).

The amount of humic material extracted from LBPC 2 showed a general increase from ~ 20 % dry weight at the surface to nearly 70 % at 50 cm (Fig 5.5 B). Below this, the proportion of humic substances decreased with depth to less than 40 % at the bottom of the core. The fraction of organic matter which comprised humic

substances also showed a general increase with depth from ~ 30 % at the surface to ~ 100 % at 50 cm. LBPC 2 was, in general, more organic-rich than LBPC 1 and, with the exception of the near-surface sections (0-10 cm), had a greater amount of extractable humic material.

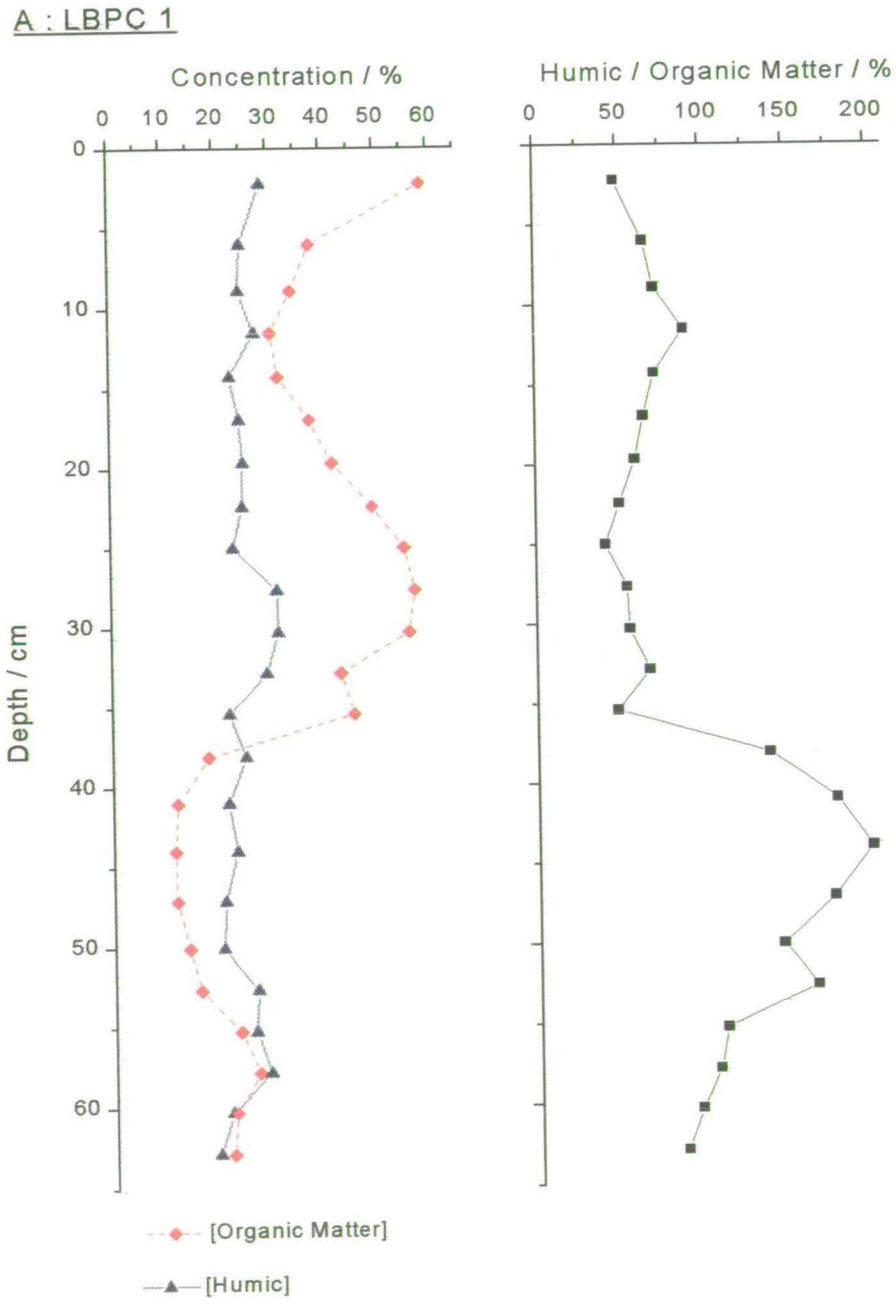


Fig 5.5 A : Humic and organic matter concentration profiles in LBPC 1 and the proportion of the organic matter that is humic in nature.

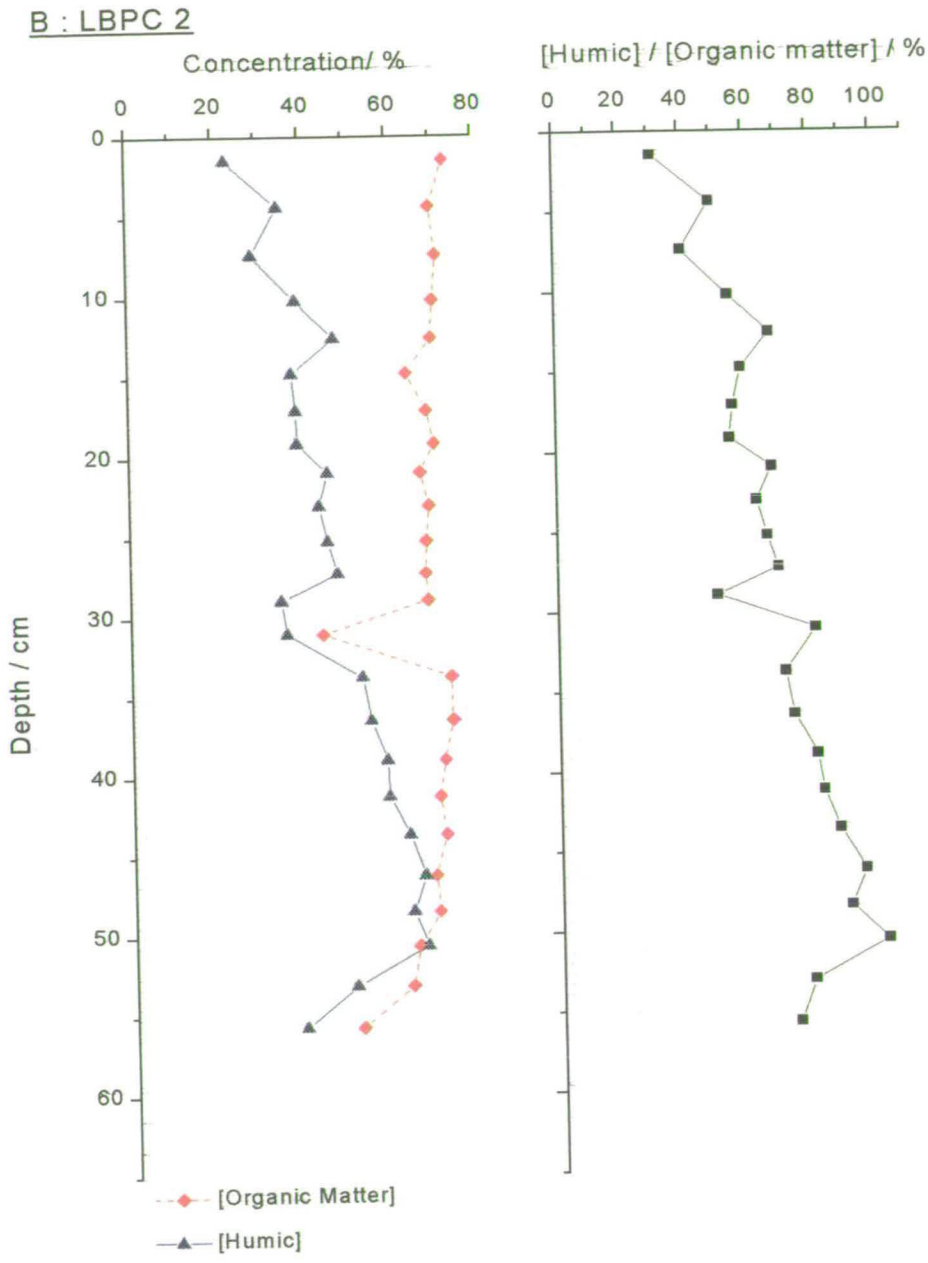


Fig 5.5 B : Humic and organic matter concentration profiles in LBPC 2 and the proportion of the organic matter that is humic in nature.

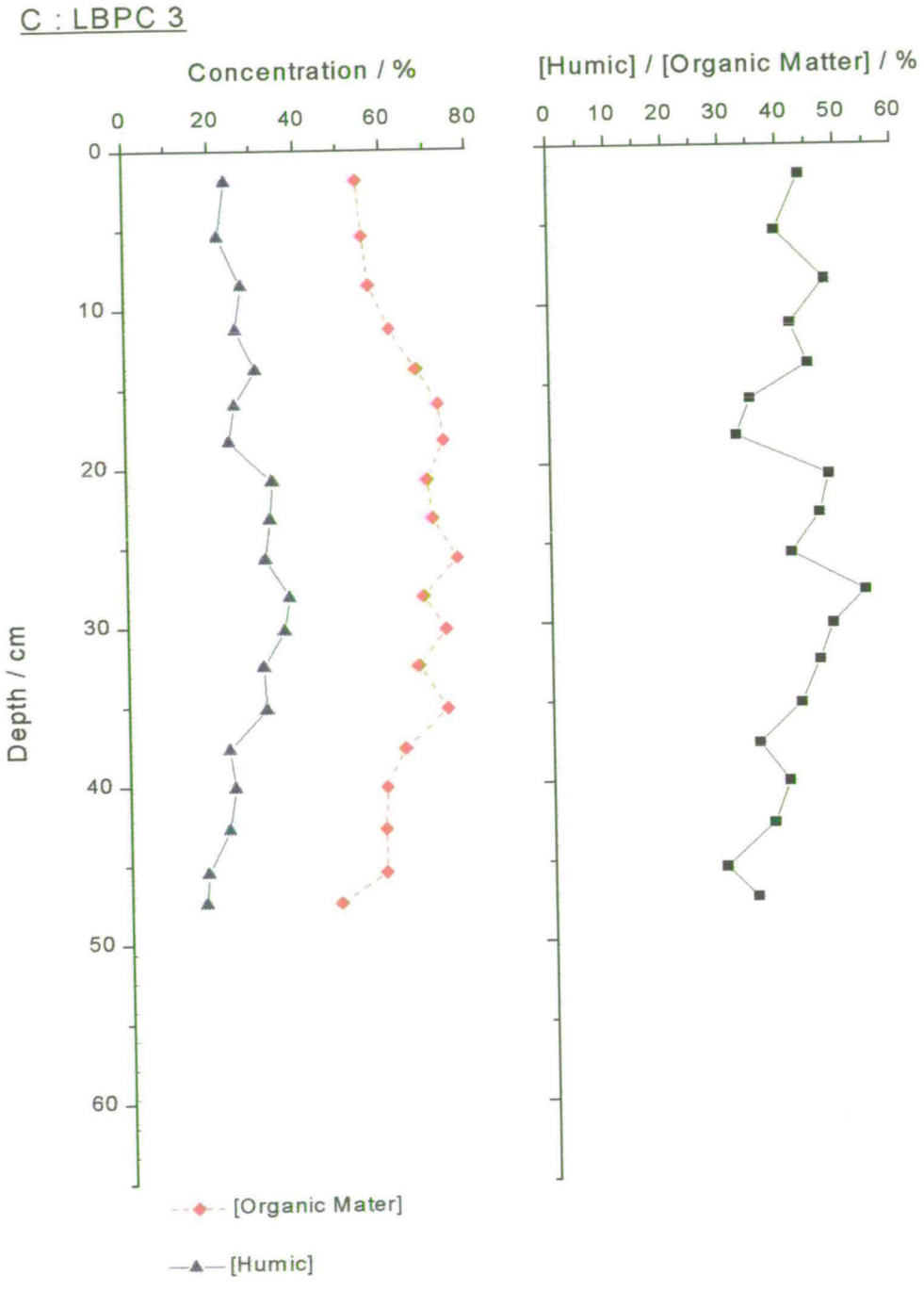


Fig 5.5 C : Humic and organic matter concentration profiles in LBPC 3 and the proportion of the organic matter that is humic in nature.

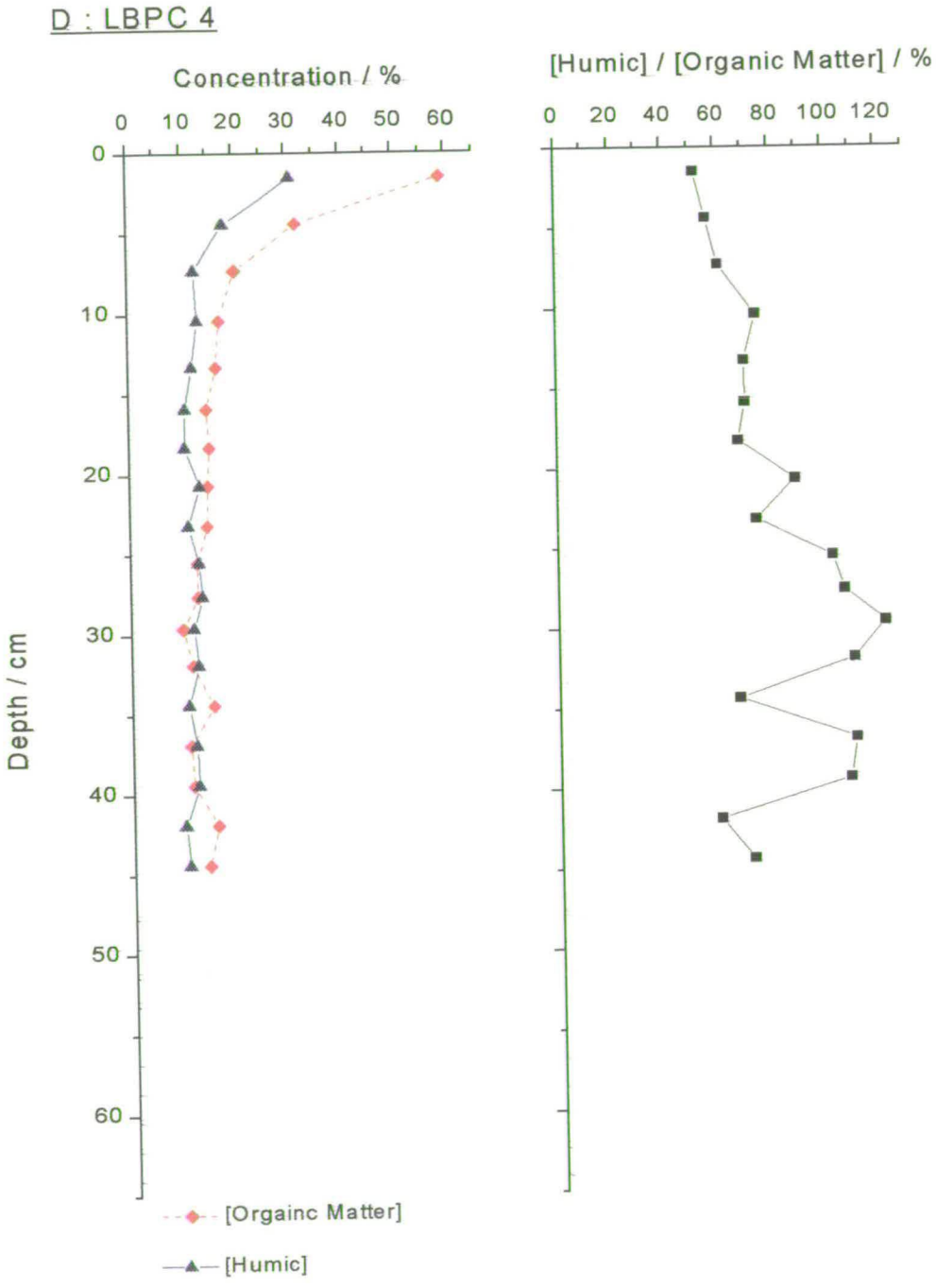


Fig 5.5 D : Humic and organic matter concentration profiles in LBPC 4 and the proportion of the organic matter that is humic in nature.

As for LBPC 1, there was little variation with depth in the amount of humic material extracted (per dry weight of peat) from LBPC 3 (Fig. 5.5 C). The average concentration of humic material, ~27 ± 6 %, was also similar to that of LBPC 1. In contrast to both LBPC 1 and 2, there was some correlation between the amount of extracted humic material and the total organic matter, which was reflected in the relatively constant ratio of humic/organic matter ratio (42.0 ± 6.2 %). Lower concentrations of both humic and organic material obtained for near-surface sections, the region of maximum total Fe concentration (Fig. 5.1 C).

In strong contrast with LBPC 1-3, the humic and organic matter content of LBPC 4 was greater than 10 % only in the top 5 cm of peat (Fig. 5.5 D). Below this depth, the humic and organic matter content were approximately constant at ~ 10 % dry weight. Clearly only the 0-5 cm section can be described as peaty soil. In this part of the core, humic substances comprised between 50 and 60 % of the total organic matter, slightly greater than obtained for LBPC 3.

5.3.1.2 Elemental Composition of Humic Substances Extracted from LBPC 1-4

Elemental analysis (CHN) was performed on selected humic extracts from each core. The elemental composition and atomic ratios (H/C, N/C and O/C) are shown in Table 5.3. Values of percentage C, H and N range from ~ 29-47 %, 3.5-5.5 % and 1.6-3.9 %, respectively. Average H/C, O/C and N/C were 1.43 ± 0.09, 0.96 ± 0.29 and 0.06 ± 0.01, respectively. Within each core, the H/C ratio did not vary significantly with depth, e.g. a value of 1.4 was obtained for both the surface section and the 51.4-53.9 cm section of LBPC 1. There might be a slight change in elemental composition with depth in LBPC 2 and 3 as indicated by a small decrease in the H/C ratio with increasing depth. Further evidence of changing composition with depth was provided by the N/C ratio that decreased consistently with depth in all four cores. For example, values of 0.05 at depths of ~ 50 cm compared with 0.07 - 0.08 for surface sections of both LBPC 1 and 3.

Sample and depth / cm	C / %	H / %	N / %	O / %	H / C	O / C	N / C
LBPC 1 0.0 - 4.4	41.16	4.93	3.45	50.46	1.43	0.92	0.07
LBPC 1 10.2 - 12.8	29.94	3.81	2.08	64.17	1.52	1.61	0.06
LBPC 1 29.0 - 31.6	47.16	5.48	3.77	43.59	1.39	0.69	0.07
LBPC 1 51.4 - 53.9	28.86	3.51	1.62	66.01	1.45	1.72	0.05
LBPC 2 0.0 - 2.9	44.35	5.52	3.45	46.68	1.48	0.79	0.07
LBPC 2 8.9 - 11.5	46.15	4.84	3.07	45.94	1.25	0.75	0.06
LBPC 3 3.8 - 7.0	43.64	5.52	3.93	46.61	1.51	0.81	0.08
LBPC 3 21.9 - 24.5	46.16	5.34	2.96	45.54	1.38	0.74	0.06
LBPC 3 38.9 - 41.3	46.16	5.13	2.83	45.88	1.32	0.75	0.05
LBPC 4 5.8 - 8.8	37.81	4.83	3.24	54.12	1.52	1.08	0.07
LBPC 4 14.6 - 17.2	39.73	4.62	2.82	52.83	1.39	1.00	0.06
LBPC 4 30.6 - 33.2	32.62	4.17	2.16	61.05	1.52	1.41	0.06

Table 5.3: Elemental composition and atomic ratios of humic substances extracted from peat, without correcting for the concentration of co-extracted FeOOH.

In the first instance, percentage O was calculated by difference, but further calculations were undertaken to assess the influence of co-extracted Fe on the elemental ratios (Table 5.4). Conversion of the mass of co-extracted Fe to the mass of various Fe compounds (Fe_2O_3, FeOOH and $Fe(OH)_3$) was also undertaken to take account of humic coated Fe (hydr)oxide mineral phases which may have been mobilised by the NaOH. The influence of the presence of each of the phases on the value of the O/C ratio is shown in columns 3, 4 and 5, respectively, of Table 5.4. Clearly, the greatest effect on the ratio value was obtained by assuming that all Fe was in the form of $Fe(OH)_3$. Although the mineral composition of the peat cores has not

been fully characterised, it is clear that, for the cores with high Fe concentrations, and at the positions of subsurface Fe peaks, some degree of correction of the O/C ratio for co-extracted Fe phases is required. Further characterisation would be required to determine the exact contributions of different Fe phases at each depth in the peat profiles.

Sample and depth / cm	O / C {Fe}	O / C {Fe_2O_3}	O / C {FeOOH}	O / C {$Fe(OH)_3$}
LBPC 1 0.0 - 4.4	0.87	0.85	0.85	0.83
LBPC 1 10.2 - 12.8	1.20	1.02	0.95	0.82
LBPC 1 29.0 - 31.6	0.67	0.66	0.66	0.65
LBPC 1 51.4 - 53.9	1.26	1.07	1.00	0.85
LBPC 2 0.0 - 2.9	0.77	0.77	0.76	0.76
LBPC 2 8.9 - 11.5	0.72	0.71	0.71	0.70
LBPC 3 3.8 - 7.0	0.79	0.78	0.78	0.77
LBPC 3 21.9 - 24.5	0.73	0.73	0.73	0.72
LBPC 3 38.9 - 41.3	0.75	0.75	0.75	0.75
LBPC 4 5.8 - 8.8	1.00	0.97	0.95	0.93
LBPC 4 14.6 - 17.2	0.97	0.95	0.95	0.93
LBPC 4 30.6 - 33.2	1.11	0.98	0.94	0.84

Table 5.4: O/C atomic ratios of humic substances extracted from Loch Bradan peat cores, calculated after correcting the O concentration of the humic substances for various Fe species, shown in brackets.

5.3.1.3 Relationships Between the Concentration of Humic-Associated Manganese and Total Manganese in LBPC 1-4

The maximum concentration of humic-associated Mn in LBPC 1 was ~ 500 mg kg^{-1} peat but, in general, concentrations were less than 300 mg kg^{-1} (Fig. 5.6A). The maximum in humic-associated Mn concentration (peak 1) occurred in the top section and co-coincided with the maximum in total Mn concentration. There was, however, a second sharp peak (peak 2) in humic-associated Mn below the total Mn peak at ~ 10 cm. A further feature which is not seen to the same extent in the total Mn concentration profile was a broad peak (peak 3) in humic-associated Mn at ~ 40 - 50 cm. Consideration of humic-associated Mn as a percentage of total Mn provided further information for these three main areas of the core. At peak 1, humic-associated Mn represented only a very small fraction of the total Mn whereas peak 2 represented ~ 50 % of the total Mn. An even greater portion (60 - 80 %) of the total Mn was humic-associated in peak 3. The nature of these associations is discussed further in Section 5.3.3.2.

LBPC 2 differs from the other cores in several significant ways. In addition to having higher and almost constant organic matter content over the entire length of the core (Section 5.1.2.3), the concentration of total Mn was several orders of magnitude lower than for all other cores. Despite the high concentration of humic material, the amount of humic-associated Mn was extremely small with a maximum value of 1 mg kg^{-1} dry weight of peat and was, in fact, detected in only two sections of the entire core (Fig. 5.6 B). As for LBPC 1, the first peak co-coincides with the maximum in total Mn concentration and the second occurs below the total Mn peak. The second peak, however, represents < 10 % of total Mn.

A : LBPC 1

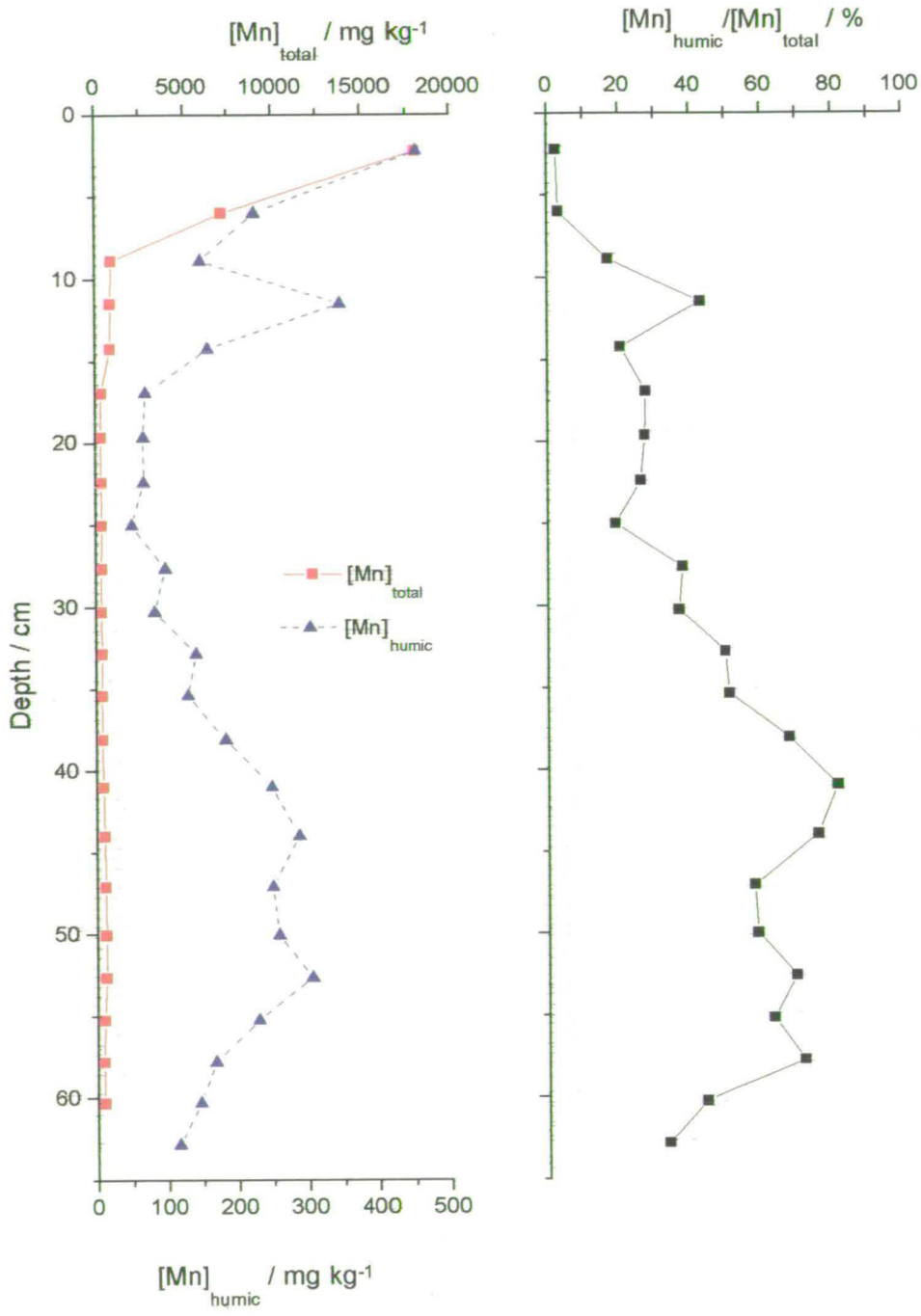


Fig. 5.6 A : Total and humic-associated Mn, and proportion of total Mn associated with humics in LBPC 1.

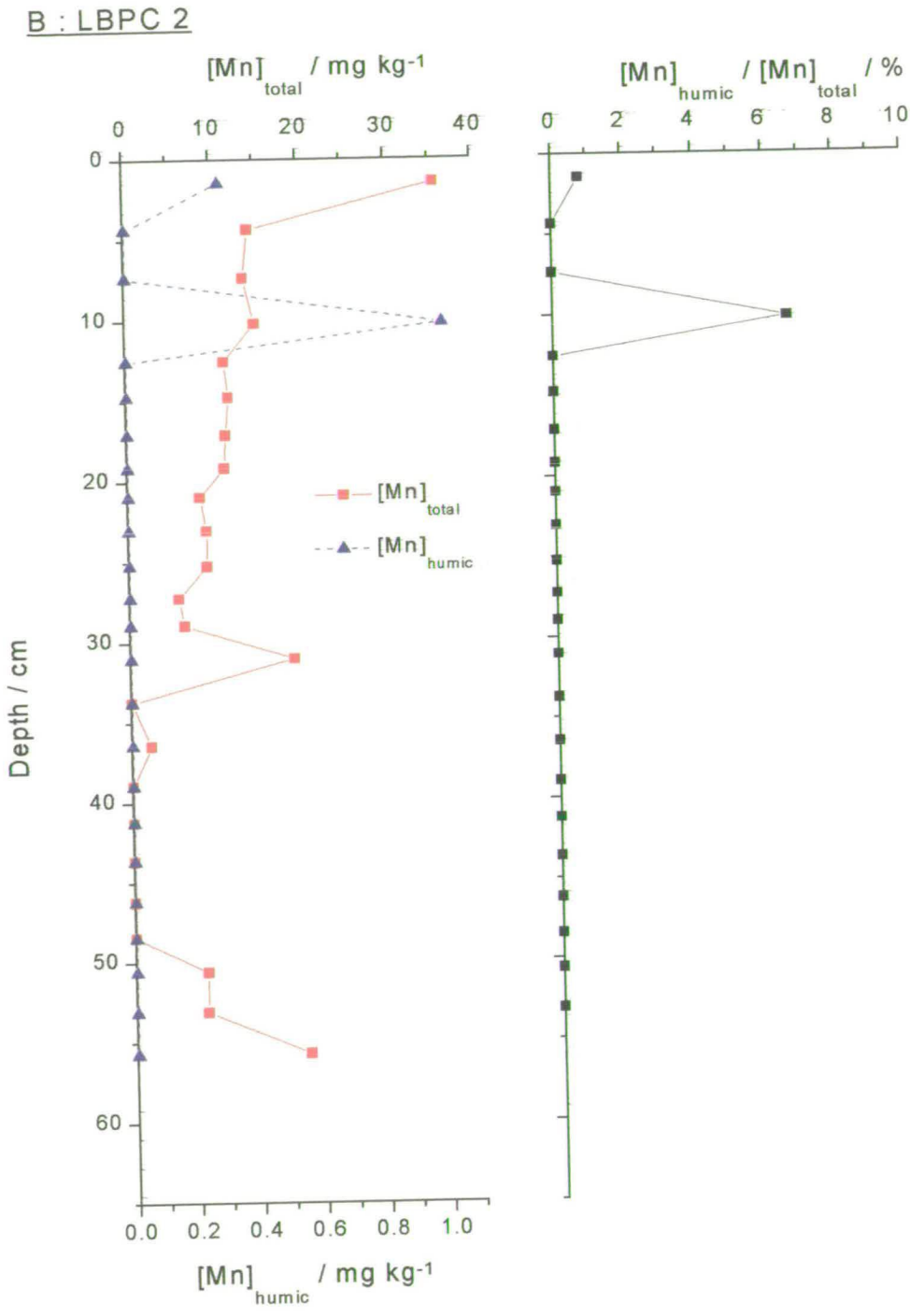


Fig. 5.6 B : Total and humic-associated Mn, and proportion of total Mn associated with humics in LBPC 2.

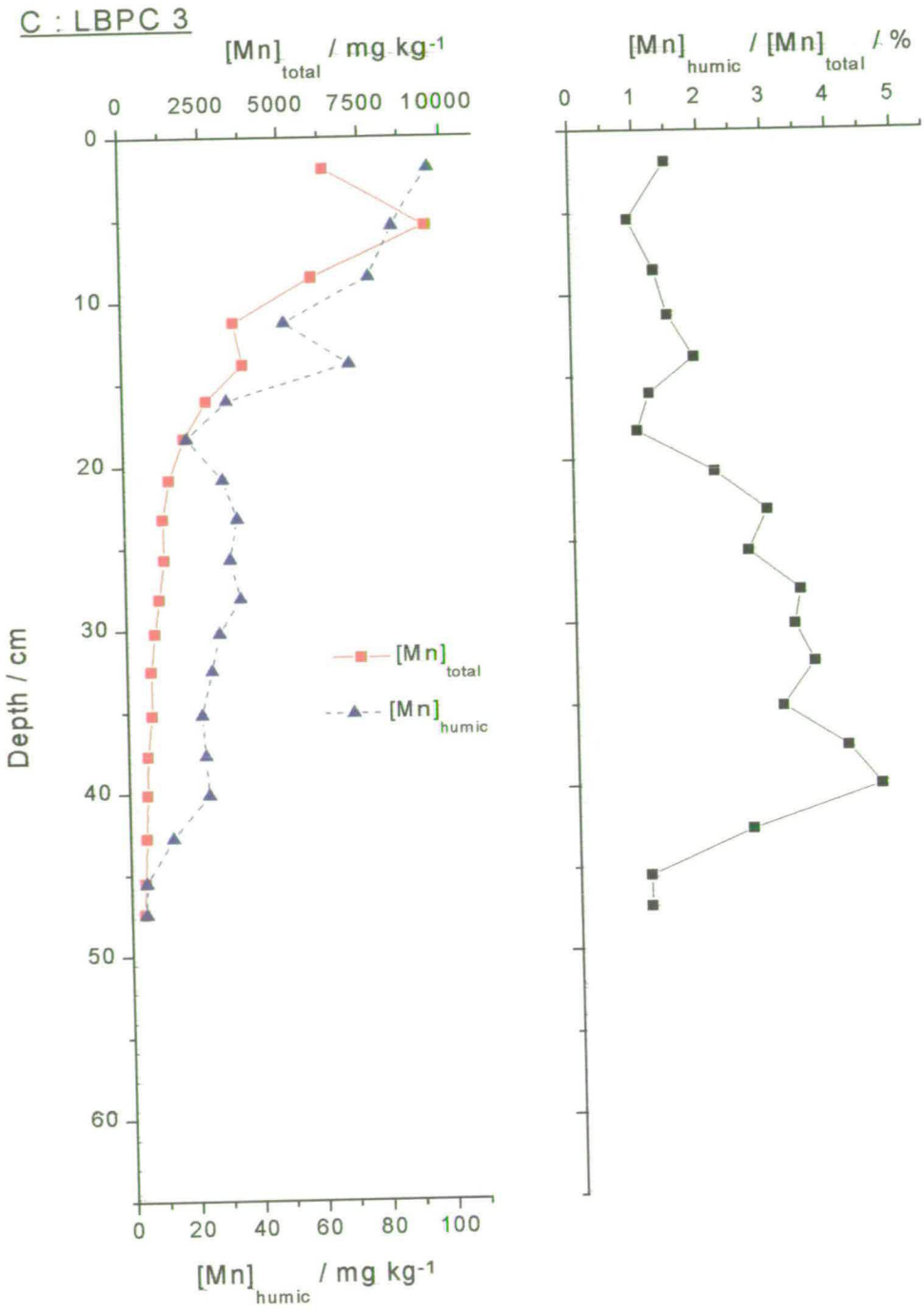


Fig. 5.6 C : Total and humic-associated Mn, and proportion of total Mn associated with humics in LBPC 3.

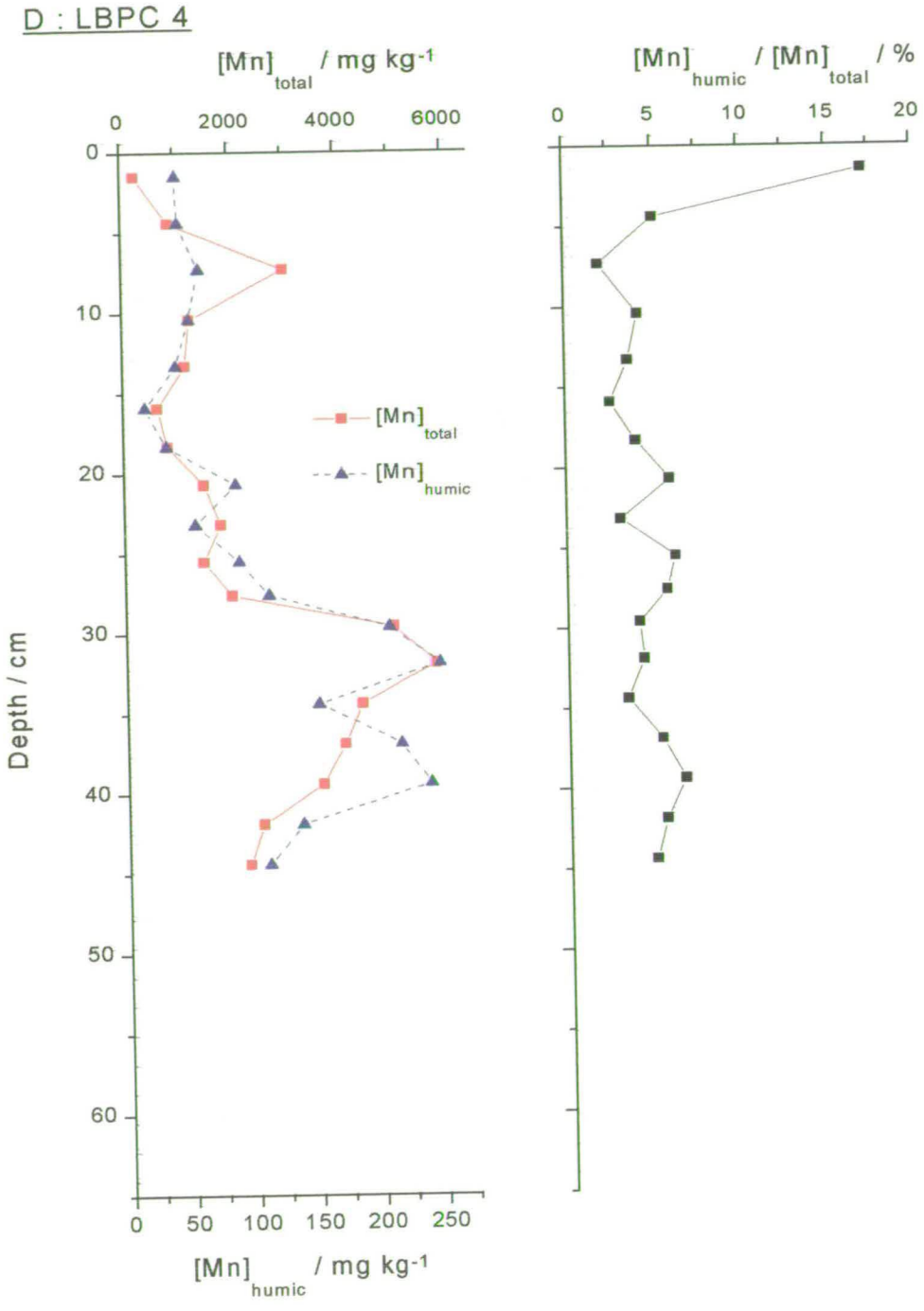


Fig. 5.6 D : Total and humic-associated Mn, and proportion of total Mn associated with humics in LBPC 4.

LBPC 3 is characterised by relatively large humic-associated Mn concentrations (~ 60 - 100 mg kg^{-1} dry weight peat) to a depth of almost 20 cm, below which the concentration decreases to ~ 30 mg kg^{-1} dry weight of peat (Fig. 5.6 C). Maximum concentrations of humic-associated Mn again occur in the vicinity of the total Mn peak and, although less marked than for LBPC 1 and 2, there is a small, sharp peak in humic-associated Mn just below the total Mn peak. A similar pattern to LBPC 1 emerges when humic-associated Mn is considered as a fraction of total Mn. In the top section of the core (0 - 20 cm) this fraction is significantly smaller than that at greater depth. All values are notably small and at most 5 % of the total Mn was humic-associated.

The correlation between humic-associated Mn and total Mn was greatest for LBPC 4. This is particularly evident from the approximately constant fraction of the total Mn that was humic-associated in the mineral-rich 10 - 45 cm section of the core (Fig 5.6 D). In the relatively organic-rich 0 - 3 cm section, > 15 % of the total Mn was humic-associated compared with a value of ~ 5 % in the mineral rich section. As for LBPC 1 - 3, the fraction of humic-associated Mn was low at the position of the near-surface peak in total Mn concentration.

5.3.1.4 Relationships Between the Concentration of Humic-Associated Iron and Total Iron in LBPC 1 - 4

In LBPC 1, the maximum concentration of humic-associated Fe was ~ 5 % dry weight peat (Fig 5.7 A). Although the near-surface peak in total Fe concentration was broad, there was a much sharper near-surface peak in humic-associated Fe, co-incident with the second humic-associated Mn peak, at the lower edge of the total Fe peak. At much greater depth (~ 40 - 50 cm), there was a second broader peak in humic-associated Fe as has been described for Mn (Section 5.3.1.3). Again as for Mn, the core can be divided into three sections on the basis of ratio of humic-bound to total Fe. The top section, comprising the 0 - 10 cm samples, was characterised by very low values with only ~ 10 % of Fe being humic-bound. In the middle section, from the

peak in humic-associated Fe at ~ 11 cm to 35 cm, ~ 40 % of Fe was humic-associated whilst in the > 40 cm section, almost all the Fe was humic-bound.

As was noted for Mn, the concentrations of total Fe in LBPC 2 were lower than for all other cores (Fig. 5.7 B). Whereas the Mn concentration was several orders of magnitude lower, the total Fe concentration was at most one order of magnitude lower than the other cores. In contrast with Mn associations, a much greater proportion of the total Fe was bound to humic substances (36.1 ± 14.6 %). The general similarity between humic-associated and total Fe depth profiles is reflected in relatively little change with depth in the fraction of total Fe bound to humic substances, although there is a slight decrease with depth. The apparently large variations at > 30 cm are attributed to artifacts from the low concentrations of both total and humic-associated Fe.

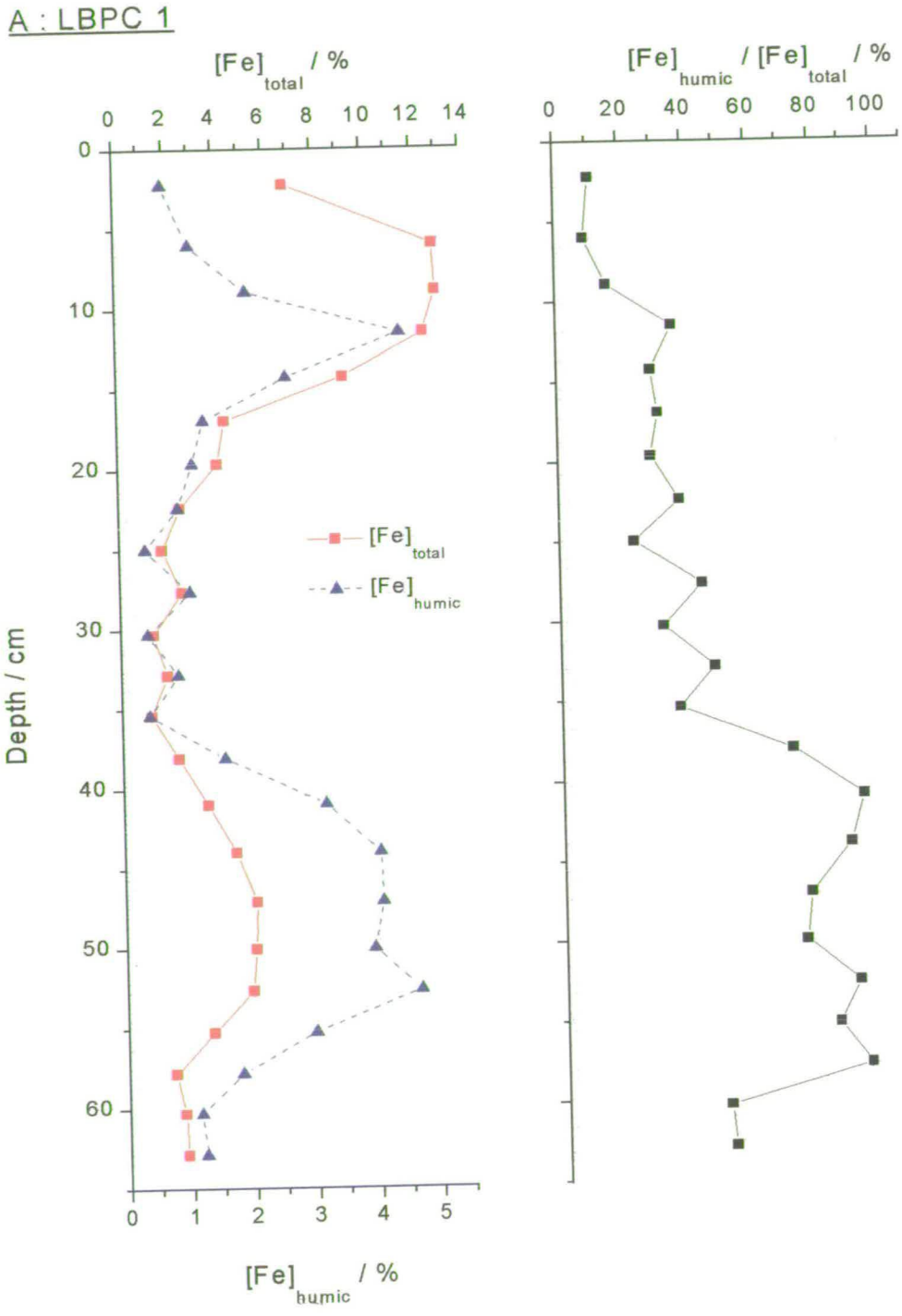


Fig. 5.7 A : Concentration of total and humic-associated Fe, and percentage of total Fe associated with humic in LBPC 1.

B : LBPC 2

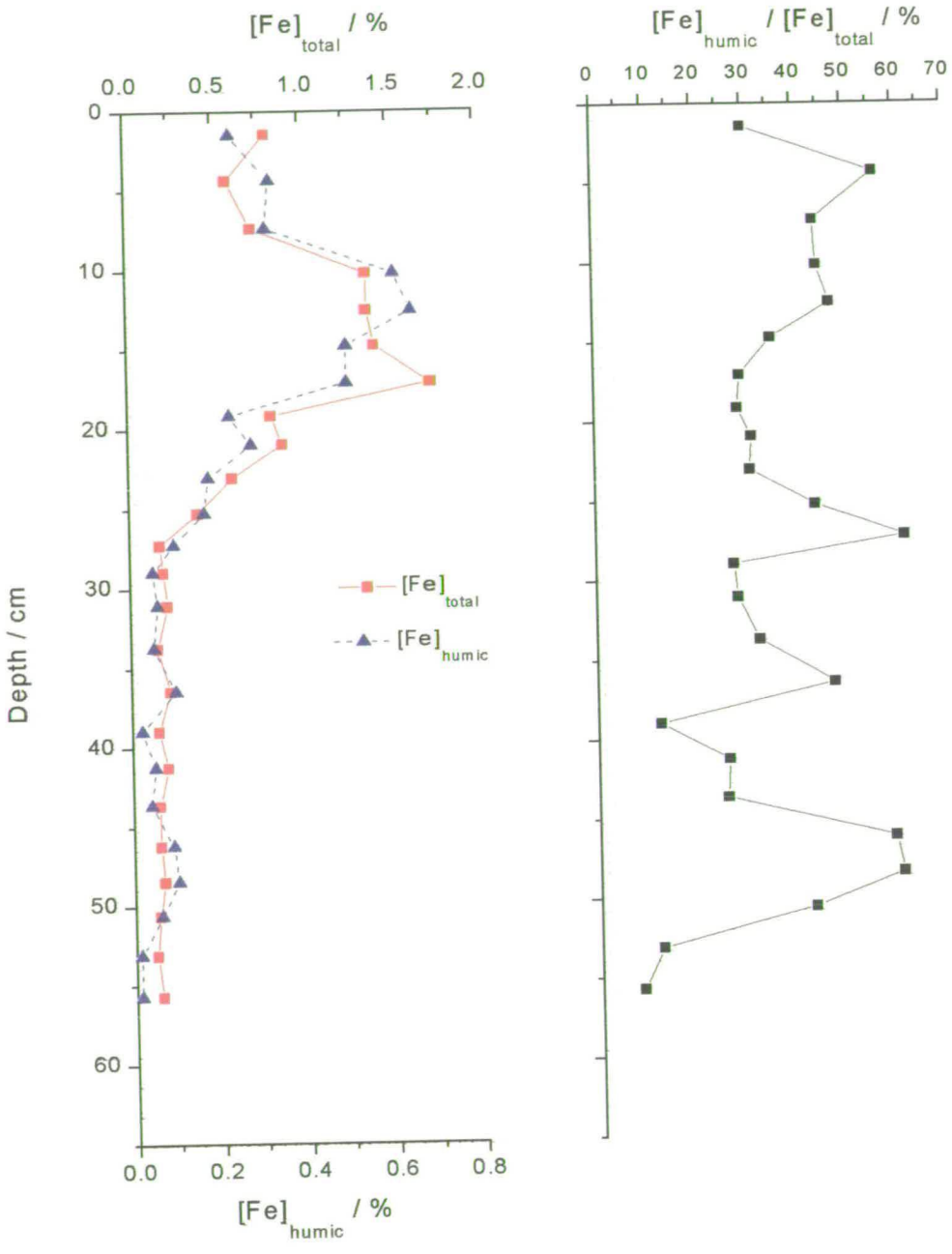


Fig. 5.7 B : Concentration of total and humic-associated Fe, and percentage of total Fe associated with humic in LBPC 2.

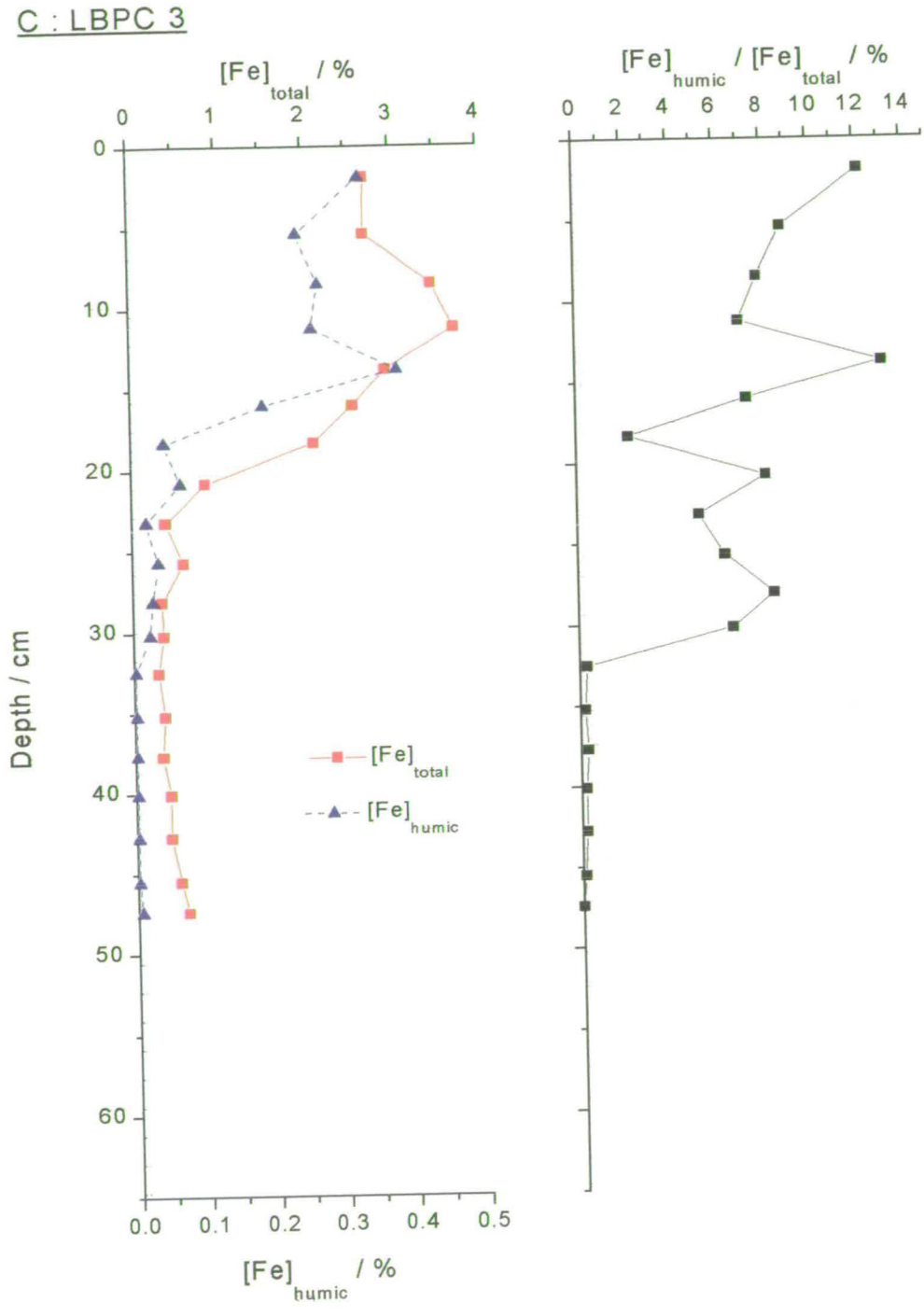


Fig. 5.7 C : Concentration of total and humic-associated Fe, and percentage of total Fe associated with humic in LBPC 3.

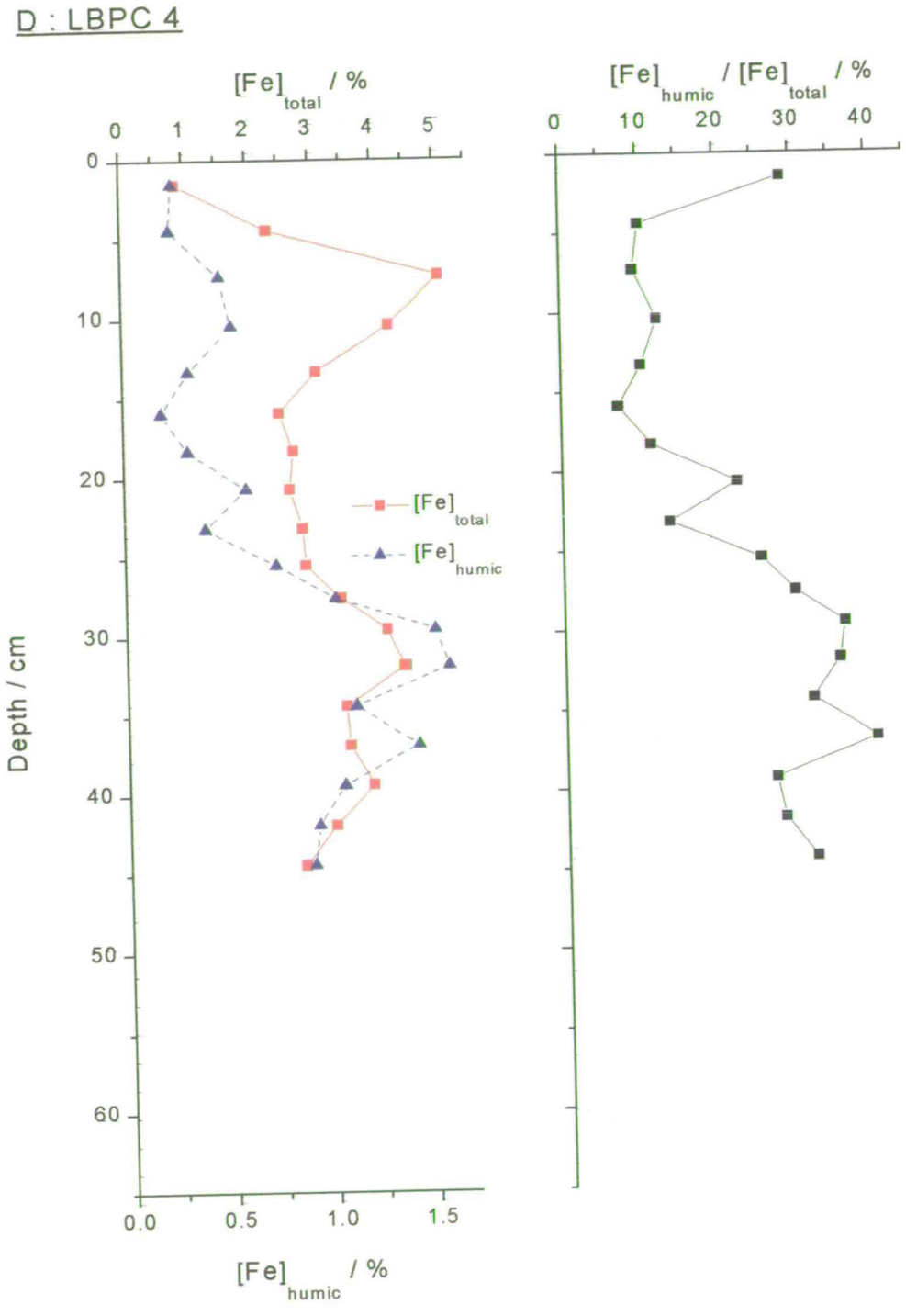


Fig. 5.7 D : Concentration of total and humic-associated Fe, and percentage of total Fe associated with humic in LBPC 4.

In LBPC 3, the maximum concentration of humic-associated Fe was ~ 0.4 %, notably less than in LBPC 2 (and also LBPC 1), which had generally lower total Fe concentrations (Fig. 5.7 C). Maxima in humic-associated Fe concentrations above and at the lower end of the peak in total Fe were the main feature of this core. The maximum at ~ 15 cm coincided with a peak in humic-associated Mn (Section 5.3.1.3). Below 20 cm, the concentrations of both humic-associated and total Fe were almost constant and low (~ 0 and 0.5 % respectively). Again as in LBPC 1, a smaller fraction of total Fe was humic-associated in the upper part of the total Fe peak compared with that at the sub-surface humic-associated Fe peak, although at the surface there is an increase in $[Fe]_{humic}/[Fe]_{total}$.

Concentrations of humic-associated Fe range from ~ 0.1 to 1.5 % dry weight peat in LBPC 4 and, in contrast to LBPC 1 - 3, are greatest at depth (~ 30 - 45 cm) (Fig. 5.7 D). Approximately 30 % of total Fe is humic-bound in the organic-rich surface section, but this value drops to ~ 10 % in the 5 - 15 cm section. In contrast to Mn, the fraction of humic-associated Fe increases to ~ 40 % in the relatively organic-poor 15 - 45 cm section.

5.3.2 Manganese and Iron Concentrations in Unfractionated and Fractionated (< 1 kDa and > 1 kDa) Stream Waters Entering Loch Bradan

The concentrations of dissolved Mn and Fe in the six feeder streams of Loch Bradan (Fig. 3.14) are shown in Tables 5.5 and 5.6. The concentrations of Mn and Fe in streams 3 and 6 are generally higher than those observed in any of the other feeder streams with maximum observed concentrations of 0.11 - 0.99 mg l^{-1} and 0.17 - 0.59 mg l^{-1} Mn and 0.20 - 0.83 mg l^{-1} and 0.25 - 1.12 mg l^{-1} Fe, respectively (Table 5.5). The size-fractionated stream water data show that between 33 and 67 % of the total dissolved Mn was in the > 1 kDa size fraction (Table 5.7). Similarly, between 45 and 57 % of the total dissolved Fe was in the > 1 kDa size fraction (Table 5.8)

	$[Mn]_{Dissolved}$ mg l^{-1}					
Stream	25/ 5/95	6/ 6/95	6/10/95	12/10/95	26/9/96	22/5/98
LBSW 1	-	0.05	-	0.04	-	0.11
LBSW 2	0.06	0.01	-	0.05	-	0.04
LBSW 3	0.15	0.13	0.12	0.11	0.99	0.24
LBSW 4	0.01	0.02	0.08	0.04	0.02	0.06
LBSW 5	0.02	0.01	0.10	0.04	0.01	0.06
LBSW 6	0.59	0.17	-	-	0.36	0.47

Table 5.5 : Dissolved Mn concentrations observed in the Loch Bradan feeder streams (- indicates that the concentrations are not available).

	$[Fe]_{Dissolved}$ mg l^{-1}					
Stream	25/ 5/95	6/ 6/95	6/10/95	12/10/95	26/9/96	22/5/98
LBSW 1	-	-	-	0.43	-	0.24
LBSW 2	-	-	-	0.14	-	0.13
LBSW 3	-	-	0.20	0.49	0.65	0.83
LBSW 4	-	-	0.19	0.17	0.02	0.46
LBSW 5	-	-	0.39	0.09	0.44	0.63
LBSW 6	-	-	-	-	0.25	1.12

Table 5.6 : Dissolved Fe concentrations observed in the Loch Bradan feeder streams (- indicates that the concentrations are not available).

Stream	$[Mn]_{total}$ / mg l^{-1}	$[Mn]_{<1\ kDa}$ / mg l^{-1}	$[Mn]_{>1\ kDa}$ / mg l^{-1}
LBSW 1	0.11	0.06	0.04
LBSW 2	0.04	0.01	0.02
LBSW 3	0.24	0.11	0.10
LBSW 4	0.06	0.04	0.04
LBSW 5	0.06	0.04	0.03
LBSW 6	0.47	0.28	0.14

Table 5.7 : Total and size-fractionated Mn concentrations found in the Loch Bradan feeder streams on 22 / 5 / 98.

Stream	$[Fe]_{total}$ / mg l^{-1}	$[Fe]_{<1k\ Da}$ / mg l^{-1}	$[Fe]_{>1k\ Da}$ / mg l^{-1}
LBSW 1	0.24	0.13	0.16
LBSW 2	0.13	0.13	0.11
LBSW 3	0.83	0.31	0.41
LBSW 4	0.46	0.26	0.31
LBSW 5	0.63	0.33	0.34
LBSW 6	1.12	0.44	0.51

Table 5.8 : Total and size-fractionated Fe concentrations found in the Loch Bradan feeder streams on 22 / 5 / 98.

Peat cores LBPC 1, 2, 3 and 4 were taken close to streams 2, 3, 4 and 6, respectively (Fig. 3.14), with run off from the peat contributing to the metal content, such as Mn and Fe, of the stream water.

5.3.3 The Role of Humic Substances in the Geochemical Behaviour of Manganese and Iron in the Catchment of Loch Bradan

5.3.3.1 Variability of the Composition of Catchment Soils

The results for organic and humic matter content of the four cores, LBPC 1 - 4, described in sections 5.1.2.3 and 5.3.1.1, respectively, clearly illustrate the variability in composition of the catchment soils. The differences between the cores are now discussed in the context of potential for Mn and Fe complexation, mobilisation and removal from the catchment via waters entering Loch Bradan.

LBPC 1

More than 50 % of the total organic matter was extracted by 0.1 M NaOH from all samples in the 0 - 35 cm zone. Below this depth, the value increased to apparently ~ 200 % of the total organic matter. Although the total organic matter profile is inversely related to the total Fe concentration, there is no direct or inverse relationship between extracted humic substances and total Fe concentration. The NaOH extract

is, however, not entirely organic in nature, with high concentrations of Fe being co-extracted, making the concentration of humic substances extracted appear artificially high. Subtraction of the amount of co-extracted Fe from extracted humic substances, however, reveals an inverse relationship between the amount of "true" humic substances and the total Fe concentration and a direct relationship between "true" humic substances and total organic matter (Fig. 5.8 A). Of particular importance is the change occurring at ~ 40 cm. Above this depth, the ratio of humic to organic material is approximately constant at ~ 50 % whereas below this depth, the ratio increases to ~ 100 %, i.e. all of the organic matter is in the form of humic substances. Although this clearly represents a major change in the composition of the peat, it has to be noted that below 40 cm the organic matter only contributes 10 to 15 % of the peat.

The elemental composition of the humic from LBPC 1 (corrected for the presence of various Fe oxyhydroxides) shows that with depth there is an overall loss of oxygen-containing functional groups (reduction in O/C and N/C atomic ratio). This is characteristic of diagenetic alteration of the humic material with depth (Steelink, 1985). Below 50 cm the O/C atomic ratio increases again, indicating that there may be an increase in the number of functional groups on the humic substances at this depth.

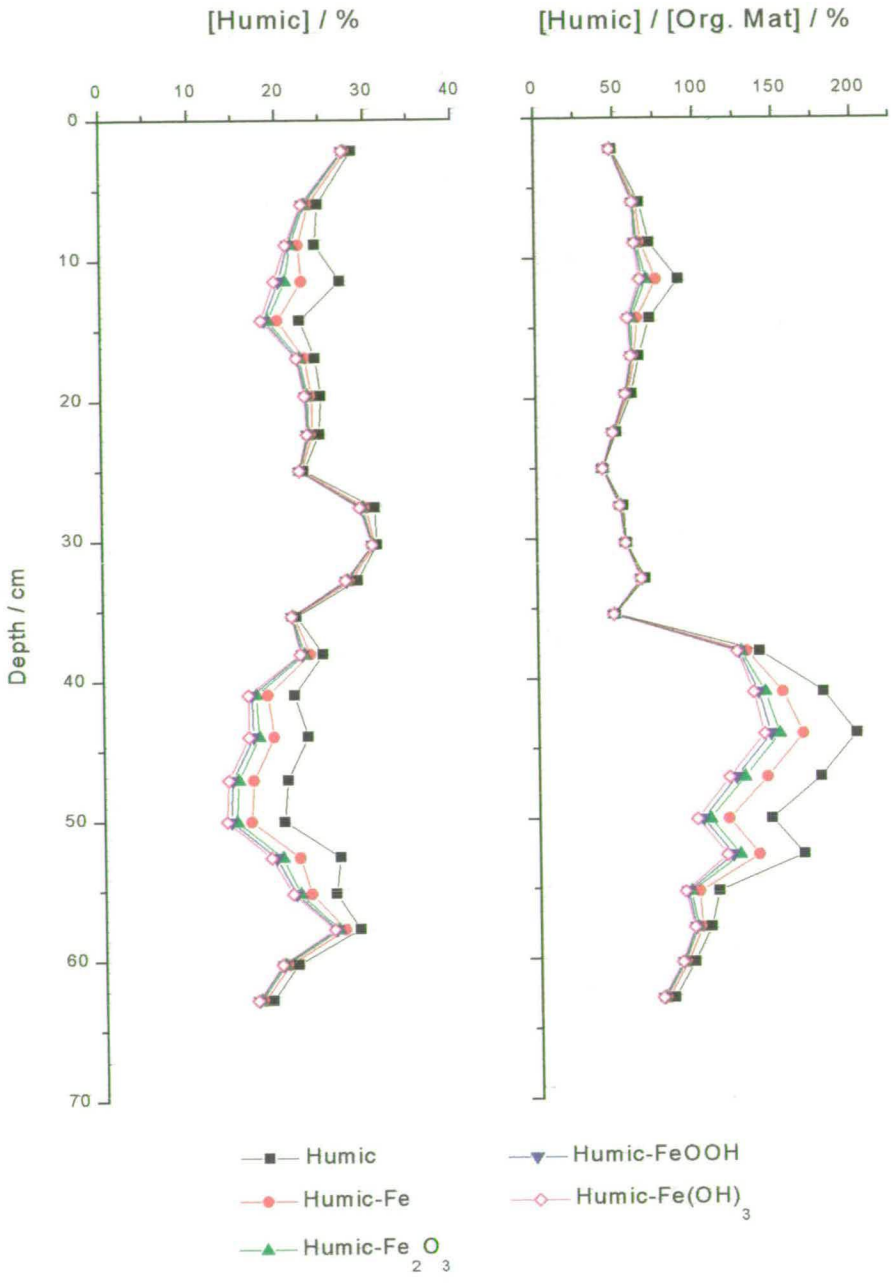


Fig 5.8 A : Concentration of humic substances corrected for co-extracted Fe compounds in LBPC 1 and the corrected proportion of organic matter that is humic in nature.

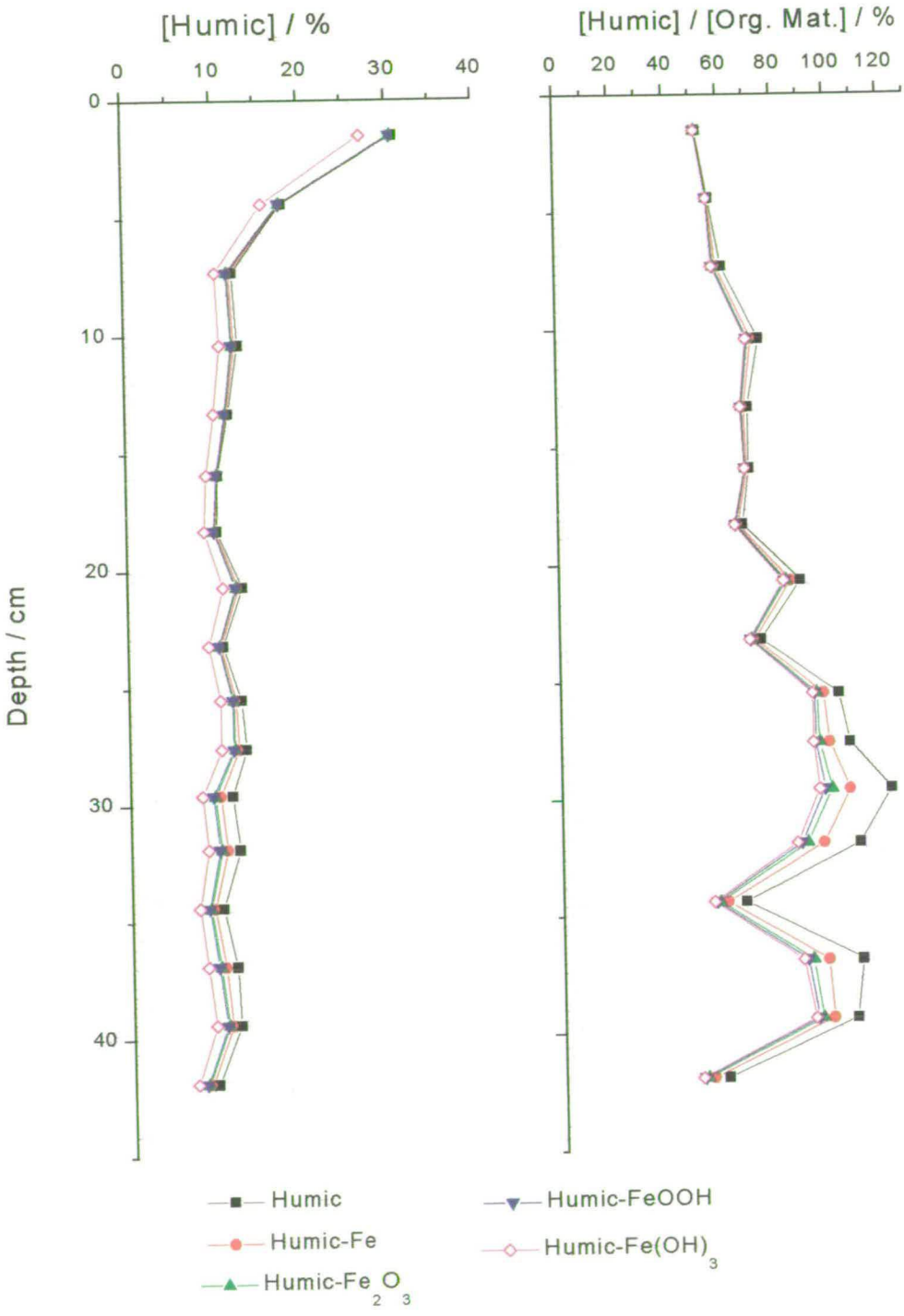


Fig 5.8 B : Concentration of humic substances corrected for co-extracted Fe compounds in LBPC 4 and the corrected proportion of organic matter that is humic in nature.

LBPC 2

The depth profile for the ratio of humic substances to total organic matter represents a more typical pattern of diagenetic alteration of organic matter, with a ratio of ~ 30 % at the surface increasing to almost 100 % at the bottom of the core. This is consistent with an increasing degree of humification with increasing depth. The elemental data tentatively supports the occurrence of humification, with the loss of oxygen and nitrogen functional groups (decrease in O/C and N/C atomic ratios) and a decrease in aliphatic character (decrease in H/C atomic ratio) with depth. Further samples, especially from deeper in the core, would need to be analysed for elemental composition before this could be confirmed.

The diagenetic alteration of the organic fraction and, in particular, humic substances generally has implications for metal binding behaviour, as the loss of functional groups (O, N) will reduce the overall complexation capacity of the humic material. The influence of alteration on complexation of all species may not be affected to similar extents as this depends on the specific nature of interactions with humic material.

A more mineral-rich layer at ~ 30 cm, observed as a relatively minor feature in the humic and organic matter profiles does not mark a change in the processes affecting organic matter, as the organic matter content is unchanged below this and the humic content continues to increase.

LBPC 3

There is very little change with depth in the fraction of organic matter comprising humic substances, ~ 40 % at all depths. There is, however, evidence for the diagenetic alteration of the humic substances with depth as seen in its elemental composition (Tables 5.3 and 5.4). As seen in LBPC 1 and 2, with depth there is a loss of N functionality and also an increase in the aromaticity of the extracted humics from LBPC 3.

LBPC 4

As for LBPC 2, there is a general increase in the proportion of organic matter comprising humic substances from ~ 50 % at the surface to ~ 100 % at depth, with the concentration of extracted humic appearing artificially high as the result of co-extracted Fe compounds (Fig. 5.8 B), as in LBPC 1.

Unlike any of the other peat cores, only the near-surface sections (0 - 5 cm) of this core are significantly organic in character and in this part of the core the concentration of humic material is similar to that present in the surface sections of LBPC 1, as is the concentration of total organic matter (Figs. 5.5 A, D). Below this depth, LBPC 4 should be considered as a relatively mineral-rich soil, but with nearly 100 % of the organic matter being in the form of humic substances.

The elemental composition of the extracted humic suggests that with depth there is a loss of functional groups (O and N) and a variable amount of aromaticity.

5.3.3.2 The Importance of Manganese Interactions with Humic Substances in Peat Cores LBPC 1 - 4 : Near-Surface Zone

The minimum percentage of total Mn associated with humic substances occurs in the region of the near-surface redox-driven enrichment of Mn for LBPC 1-4. It is well known that interactions between Mn and humic substances are weak and thus the Mn from such complexes may be readily released, i.e.

$$Mn^{2+}\text{-humic} \leftrightarrows Mn^{2+}_{(aq)} + \text{humic}$$

In the oxic zone, Mn(II) is oxidised, resulting in the precipitation of Mn(IV), and so the equilibrium will be forced further to the right, i.e. more Mn(II) released from humic complexes.

Below the redox enrichment, in LBPC 1 - 3, humic complexation of Mn increases and there is a second, sharp, peak in humic-associated Mn just below the redox enrichment. It is postulated that humic substances, by providing surface functional groups, form weak complexes with Mn that has been reduced and solubilised. Humic substances will be present in both solid and aqueous phases, but the sharp nature of this peak might suggest that Mn has been immobilised by complexation with solid phase humic material, i.e. not broadened by diffusion.

LBPC 4, with its organic-rich surface horizon overlying a more mineral-rich soil, differs from the other three cores with respect to its humic-associated Mn profile. The peak percentage of total Mn associated with humics occurs above the near-surface enrichment observed for total Mn. The former coincides with the maximum concentration of both humic and organic matter. It would, therefore, appear that the amount of organic, and specifically humic, material is important in influencing the percentage of total Mn that is organically associated.

5.3.3.3 The Importance of Fe interactions with Humic Substances in Peat Cores LBPC 1 - 4 : Near-Surface Zone

As with the humic-associated Mn, the minimum percentage total Fe that is humic associated occurs in the same region as the redox-driven maximum of total Fe, although this is less marked than for Mn. This indicates that, as with Mn, the Fe-organic complexes are, to an extent, insufficiently strong to prevent the Fe(II) being oxidised.

In LBPC 1 and 3 there are sharp peaks in the concentration of humic-associated Fe slightly below the redox-driven Fe maxima, also coincident with the maximum humic-associated Mn concentrations. Again the data suggests that humic substances are particularly effective at complexing soluble metal ions at this depth. Perhaps the sharp nature of this peak indicates a very specific interaction between metal ions and humic molecules. Alternatively, it may be a more complicated interaction involving Mn, Fe

and humic substances. It is certainly not, however, related to change in the concentration of humic substances.

The observation of these peaks in humic-associated Fe and Mn may be indicative of the role played by humic substances in the redox cycling of both Fe and Mn. Investigations of the mechanisms involved in Fe cycling suggest that organic ligands may be important, e.g. in the ligand-promoted dissolution of Fe(III) (hydr)oxides (Stumm and Sulzberger, 1992)

$$\equiv Fe(III)\text{-}OH + humic_{(aq)} \leftrightarrows \equiv Fe(III)\text{-}humic_{(s)}$$

$$\equiv Fe(III)\text{-}humic_{(s)} \leftrightarrows \equiv Fe(II)\text{-}ox.humic_{(s)}$$

$$\equiv Fe(II)\text{-}ox.humic_{(s)} \leftrightarrows \equiv Fe(II)_{aq} + ox.humic_{(aq)}$$

ox.humic – oxidised humic substances

It is, therefore, postulated that:

1. the increase in humic-associated Fe occurs at the lower edge of the redox enrichment because this is the zone where reductive processes are actively occurring,
2. the humic material is present as organic matter coatings on the oxide and the coated particles are mobilised by NaOH, whereas the overlying uncoated material is not extracted,
3. the humic material at the point of Fe enrichments is more oxidised than at other parts of the core because of the extensive cycling of Fe.

The coincidence of the humic-associated Mn peak would also suggest that Mn may also be intimately involved in these processes, but it is beyond the scope of the current study to consider more complicated mechanistic details of these redox cycles.

In LBPC 2, the position of the maximum concentration of total Fe and of humic-associated Fe are essentially the same. In fact the correlation between total Fe and humic-associated Fe over the entire length of the core suggests that the extent of

complexation is influenced by the concentration of total Fe at any depth. Assuming that the major variations in the percentage of Fe that is humic-associated are artifacts due to the low concentration of both, it would appear that there is a slight decrease in the ratio value with increasing depth, which can be related to the increasing degree of humification, i.e. loss of functionality.

There is a maximum in in the percentage of total Fe that is humic-associated, like that observed for Mn, occurring in the top section of LBPC 4 and this is again thought to be a consequence of the high humic substance concentration in the uppermost section of this core.

5.3.3.4 The Importance of Manganese and Iron Interactions with Humic Substances in Peat Cores LBPC 1 - 4 : Lower Zone

In LBPC 1 and 4 enrichments in the concentration of humic-associated Mn and Fe can be observed in the lower zone of the peat cores. At the same depth in both cores it was observed that the concentration of humic extracted by 0.1 M NaOH exceeded the concentration of organic matter. The discrepancies in the concentration of humic compared with organic can be explained by co-extracted Fe species. Calculating the concentration of extracted humic in the peat, taking into account the presence of high concentrations of various Fe (hydr)oxides, shows that at depth in LBPC 1 and 4, ~ 100 % of the organic matter is humic in nature (Fig. 5.8 A, B).

Characterisation of the peat in the zone of the sub-surface peak in LBPC 1 by SEM-XRF revealed that particles, most probably of Fe oxide, were present (Fig. 5.3 B). Given that 0.1 M NaOH extracted almost 100 % of total Fe at this depth, it is clear that iron oxides, with associated Mn, must be mobilised during the extraction procedure. The evidence to support the mobilisation of these phases as a result of the presence of alkali soluble humic coatings on particle surfaces comes from the observations that there was no precipitation of Fe oxides during dialysis (particularly low solubility of Fe oxides at near neutral pH), i.e. humic coatings stabilise the oxides.

This is further supported by the observation of amorphous material on the particle surfaces prior to extraction with NaOH (Fig. 5.3 A).

In LBPC 4, the most probable explanation of the enrichment of both Fe and Mn in the deeper zones of the core assumes the existence of a B horizon, in which organic matter is again present as surface coatings on precipitated Fe and Mn (hydr)oxides (Nortcliff, 1988).

In the upper region of the peat cores, where redox-driven maxima of Fe oxides are present, the co-extraction of Fe-oxides with humic substances is not observed to the same extent as seen at depth in LBPC 1 and 4. This indicates that the interactions of humic material with Fe at depth in LBPC 1 and 4 must differ from the upper zone of the peat.

At depth in LBPC 1 and 4 it is apparent, therefore, that due to the presence of oxide species of Fe and Mn that the Mn and Fe are essentially immobile, and hence retained, within the peat, with the surface coatings of humic substances also being immobilised.

In LBPC 2, where the concentration of Mn and, to a lesser extent, of Fe are much lower than at other peat coring sites, there is evidence of diagenetic alteration and loss of functionality (Section 5.3.3.1) of humic substances at depth. This along with the high water content (~80 - 90 %) of the peat at depth leads to the potential for loss of Fe and Mn at depth in LBPC 2 being significantly greater than in LBPC 1 and 4. It may, therefore, be hydrological conditions that are most important at this location and, although it cannot be demonstrated, solution phase organic material may be important for the removal of Mn and to a lesser extent Fe.

As in LBPC 2, LBPC 3 has a high water content (~90 %) and also the extracted humic substances exhibit a loss of functionality with depth, although just N groups (Section 5.3.3.1). Also, as with LBPC 2, there is a low concentration of Mn and Fe

at depth within the core, indicating that there is, again, a potential for loss of Mn and Fe at depth at this site, again with humic associations potentially being important.

The mobility and potential loss of Mn and Fe from the catchment of Loch Bradan is seen in the consistently high concentrations in the feeder streams, especially in streams LBSW 3 and 6. A large proportion of the dissolved Mn and Fe in the feeder streams is found to be associated with humics (in the > 1 kDa size fraction (Yagi, 1988)), 33 - 67 % and 45 - 57 %, respectively. This suggests that Mn and Fe which are associated with humics are being washed out of the peat into the streams and ultimately into Loch Bradan.

The locations of the sampled peat cores with respect to input streams possibly indicate a link with Mn and Fe mobility in the catchment and dissolved concentration in the streams. Stream 2, which has a consistently lower dissolved Mn and Fe concentration, is located next to LBPC 1 where the Mn and Fe was found to be retained at depth within the peat. Also, stream 3, which has consistently high dissolved Mn and Fe concentrations, is located next to LBPC 2 where the Mn and Fe was found to be depleted, especially at depth. In LBPC 3 and 4 the correlation is not as apparent, but due to the highly heterogeneous nature of the catchment discrepancies would be expected.

5.4 Conclusions

Within the peat cores of Loch Bradan the behaviour of Mn, Fe and As are controlled by redox cycling in the upper regions of the peat, and at depth in certain cores by the presence of insoluble compounds identified as being Fe oxides and associated species.

Clearly humic substances do play a role in Mn and/or Fe geochemical behaviour at all four catchment locations. All cores show that humic substances are involved in the redox cycling of Mn and Fe in the near surface zones of the peat cores, with the humic-associations being, in general, too weak to prevent oxidation of the reduced

species. At depth, humic interactions are also important with respect to the geochemical behaviour of Mn and/or Fe. In LBPC 1 and 4 it was found that Mn and humic substances existed as coatings on insoluble Fe oxide species, resulting in retention of these species at depth. In LBPC 2 and 3, however, it has been shown that the interactions between Mn and/or Fe and humic substances do not result in the retention of these species to any extent at depth. It is apparent, therefore, that within the catchment of Loch Bradan a number of different interactions can occur between Mn, Fe and humic substances. Of particular importance, however, is the finding of > 33 % of dissolved Mn and Fe in association with humic substances in the feeder streams of Loch Bradan, indicating that humic Mn/Fe complexes formed in the catchment play a significant role in Mn and Fe mobility and hence input into Loch Bradan.

The role of humic substances in the mobility of Mn and Fe in Loch Bradan feeder streams, as well as sediment, pore water and loch water, will be further discussed in Chapter 6.

6. The Role of Humic Substances in Manganese Geochemistry In Loch Bradan and Loch Riecawr

6.1 Quantification and Characterisation of Humic Substances in the Sediment of Loch Bradan (LBSC 1-10) and Loch Riecawr (LRSC 1-2)

6.1.1 Concentration of Humic Substances in the 0-3 cm Loch Bradan Sediment

Humic substances comprised ~ 11 - 33 % of the top 3 cm of sediments from Loch Bradan (LBSC 1-10) (Table 6.1, Appendices 1-10). The average concentration of humic substances for individual cores ranged from 15.9 ± 2.8 % to 29.3 ± 2.3 % (Table 6.1, Fig 6.1). The consistent trend of increasing organic matter from eastern to western parts of the loch was not, however, reflected in a similar consistent change in the average concentration of humic substances. Nevertheless, the highest average humic concentration was observed in the western basin (LBSC 2), but the lowest values were observed for centrally located cores (LBSC 4 and 6) (Fig. 6.1).

Core	[Humic] range / %	[Humic] ave. / %	[Humic] / [Org. Mat.] range	[Humic] / [Org. Mat.] ave.
LBSC 1	19.0 - 25.8	22.3 ± 1.7	0.57 - 0.75	0.66 ± 0.04
LBSC 2	24.4 - 33.3	29.3 ± 2.3	0.65 - 1.02	0.88 ± 0.09
LBSC 3	14.3 - 30.2	21.3 ± 5.8	0.40 - 1.01	0.61 ± 0.20
LBSC 4	11.3 - 19.6	15.9 ± 2.8	0.35 - 0.62	0.50 ± 0.09
LBSC 5	20.4 - 29.5	22.7 ± 2.2	0.62 - 0.87	0.69 ± 0.06
LBSC 6	11.1 - 24.2	15.9 ± 3.8	0.32 - 0.90	0.51 ± 0.16
LBSC 7	16.7 - 25.0	20.2 ± 2.1	0.52 - 0.78	0.61 ± 0.06
LBSC 8	14.2 - 25.7	21.8 - 4.2	0.46 - 0.87	0.69 ± 0.13
LBSC 9	12.1 - 25.5	20.2 ± 4.4	0.36 - 0.87	0.65 ± 0.16
LBSC 10	14.5 - 29.3	21.8 ± 5.8	0.46 - 1.05	0.74 ± 0.21

Table 6.1 : Range and average concentration of humic substances and the range and average humic/organic matter ratio for 0 - 3 cm Loch Bradan sediments.

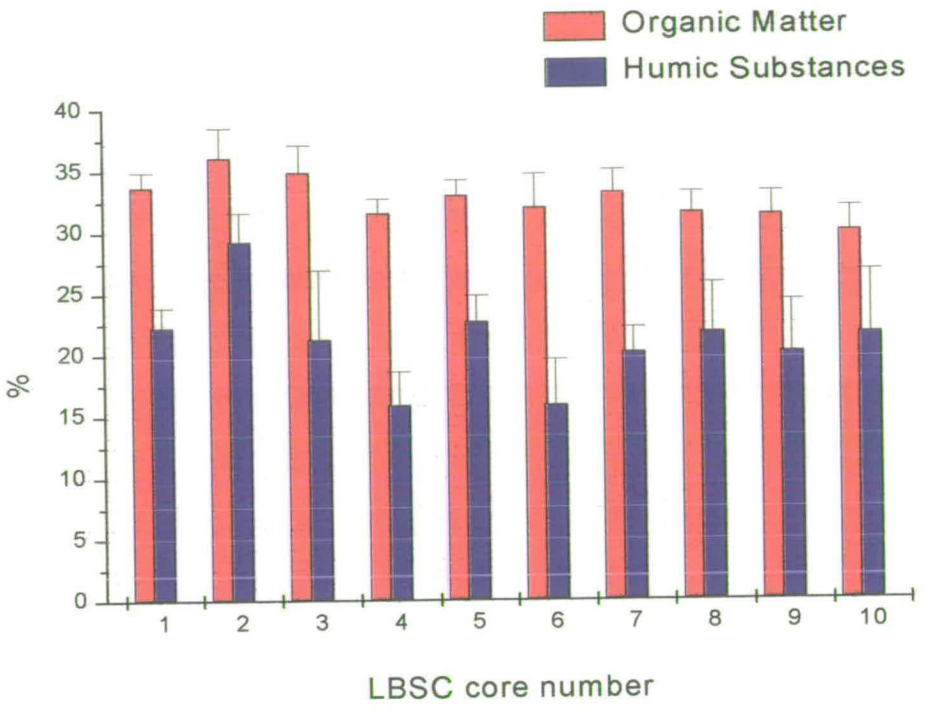


Fig. 6.1 : Bar chart showing average total organic matter (± 1 std. dev.) and average humic substances (± 1 std. dev.) for 0 - 3 cm LBSC 1 - 10 sediments.

There was considerable variability (30 - 100 %) in the fraction of total organic matter which comprised humic substances (Table 6.1), but the average value of ~ 64 % is typical for many soils/sediments (Nissenbaum and Swaine, 1976). In addition, the variability in humic concentration within each core was much greater than for total organic matter, with standard deviations of ± 1.7 to ± 5.8 % compared with ± 1.2 to ± 2.8 % (Fig 6.1).

For further discussion of these cores, it is useful to separate them into four groups on the basis of the organic matter and humic substances profiles. The main features of each group are summarised below.

Group I (LBSC 1, 2 and 5) (Fig. 6.2) depth profiles are characterised by:

1. little variation in total organic matter (33.7 ± 1.2 %, 36.1 ± 2.5 %, 33.0 ± 1.2 %, respectively)..
2. little variation in humic concentration (22.3 ± 1.6 %, 29.3 ± 2.4 %, 22.7 ± 2.1 %, respectively).
3. almost constant humic/organic matter ratio (0.66 ± 0.04, 0.81 ± 0.09, 0.69 ± 0.06, respectively).
4. only small perturbations at the position of Fe maxima (Fig. 4.1 A, B and E).

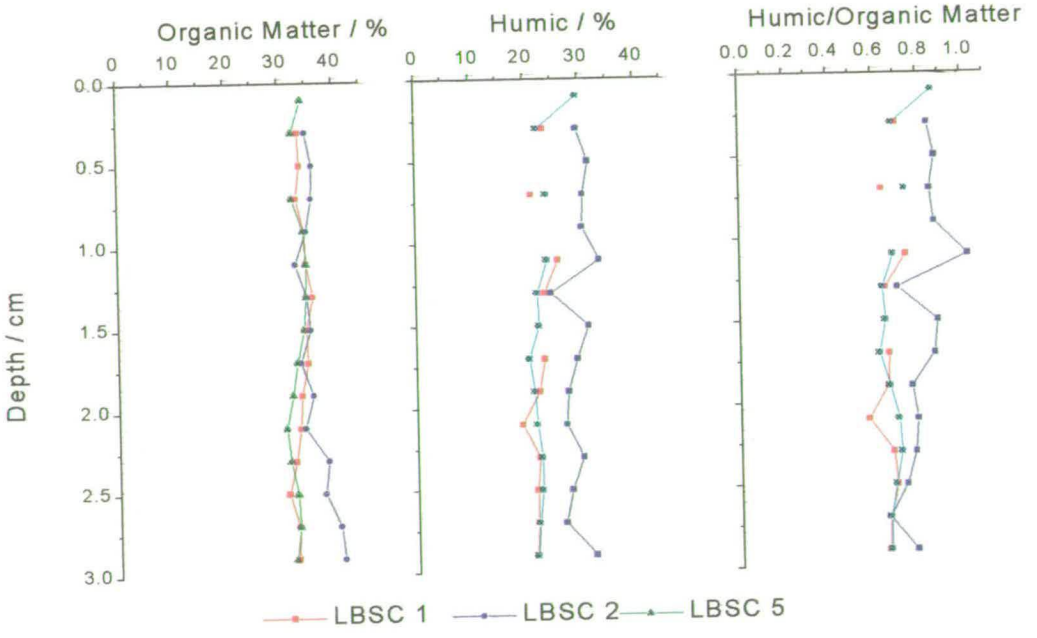


Fig. 6.2: LBSC 1, 2 and 5 total organic matter, humic substances and humic/organic matter ratio

Group II (LBSC 3, 4 and 6) (Fig. 6.3) depth profiles exhibit the same characteristics as group I depth profiles in the 0 - 1.7 cm zone, but below this depth:

1. there is a sharp increase in the amount of humic material (from ~ 15, 10, 10 % to 30, 20, 20 % respectively).
2. there is a sharp increase in the humic/organic matter ratio (>0.6).

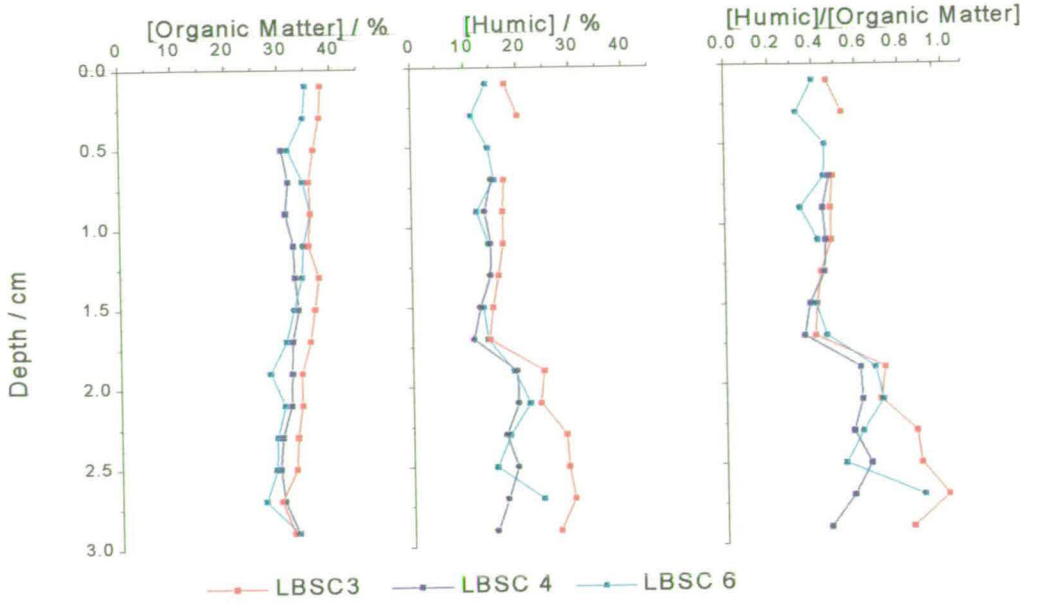


Fig. 6.3: LBSC 3, 4 and 6 total organic matter, humic substances and humic/organic matter ratio.

Group III consists only of LBSC 7 (Fig. 6.4) and is characterised by:

1. little variation in total organic matter.
2. a distinct peak in the concentration of humic substances at ~ 1.3 cm (increased from 20 to 25 %)
3. almost constant humic/organic matter ratio, except at ~ 1.3 cm (increased from 0.6 to 0.8)

Group IV (LBSC 8, 9 and 10) profiles (Fig. 6.5), despite the limited available data, although similar to Group I in the 0 - 2 cm zone, exhibit a different trend below 2 cm:

1. a decrease in the concentration of humic substances.
2. a decrease in the proportion of organic matter comprising humic substances.

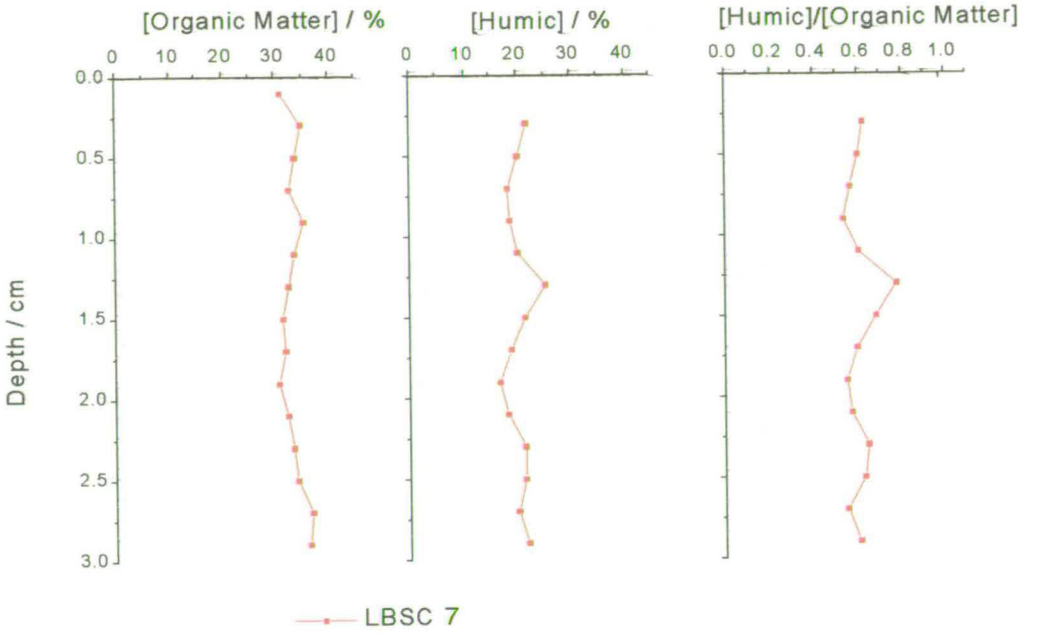


Fig. 6.4 : LBSC 7 total organic matter, humic substances and humic/organic matter ratio.

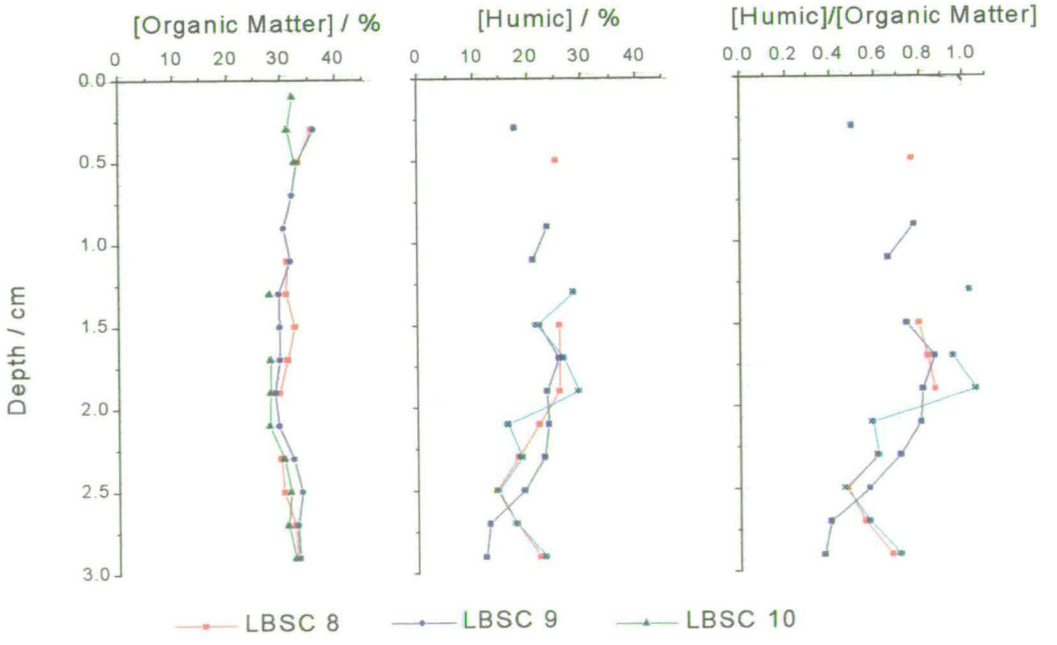


Fig. 6.5 : LBSC 8, 9 and 10 total organic matter, humic substances and humic/organic matter ratio.

6.1.2 Concentration of Humic Substances in One of the Long Loch Bradan Sediment Cores, LBSC 6

As described in Section 6.1.1, the humic substances in LBSC 6 comprised ~ 10 % of the sediment in the 0 - 1.7 cm section and increased to ~ 20 % in the 1.7 - 3 cm section. This increase continued below 3 cm to ~ 40 % dry weight of the sediment by 5 cm (Fig. 6.6). After the initial increase, the concentration of humic substances remained approximately constant to ~ 15 cm, below which there was a sharp decrease to a minimum concentration of ~ 10 % at 18 – 22 cm, which was coincident with a Mn peak but not an Fe peak (Fig. 4.2 A). Below the Mn peak, concentrations of humic substances of ~ 20 % persisted down to ~ 32 cm, the start of a second minimum which coincided with peak Mn and Fe concentrations. Below this minimum of ~ 12 %, the concentration of humic in the sediment returned to ~ 20 %.

The concentration profile of humic substances is in strong contrast with the total organic matter concentration profile which remains approximately constant, ~ 35 %, below 3 cm, apart from the region between 30 - 40 cm where a minimum is observed (Fig. 6.6). As with the humic substances, this concentration increases again below the minimum to ~ 40 % below 40 cm.

The humic/organic matter ratio changes mainly at the same points as changes identified in the humic substance profile, i.e. ~ 0.3 in 0 - 1.7 cm, ~ 1 in 5 - 15, ~ 0.3 in 18 - 22 cm, 0.6 in 22 - 45 cm sediments (Fig. 6.6.).

Excluding the 0 - 5 cm zone, there are two main regions of the core separated by the Mn peak at ~ 20 cm (Fig. 4.2 A). The data suggests a major change in organic matter composition in these two zones, e.g. an overlying well-humified layer separated from a less humified, but nevertheless organic-rich, sediment, and may correspond to some major change in the nature of the sediment.

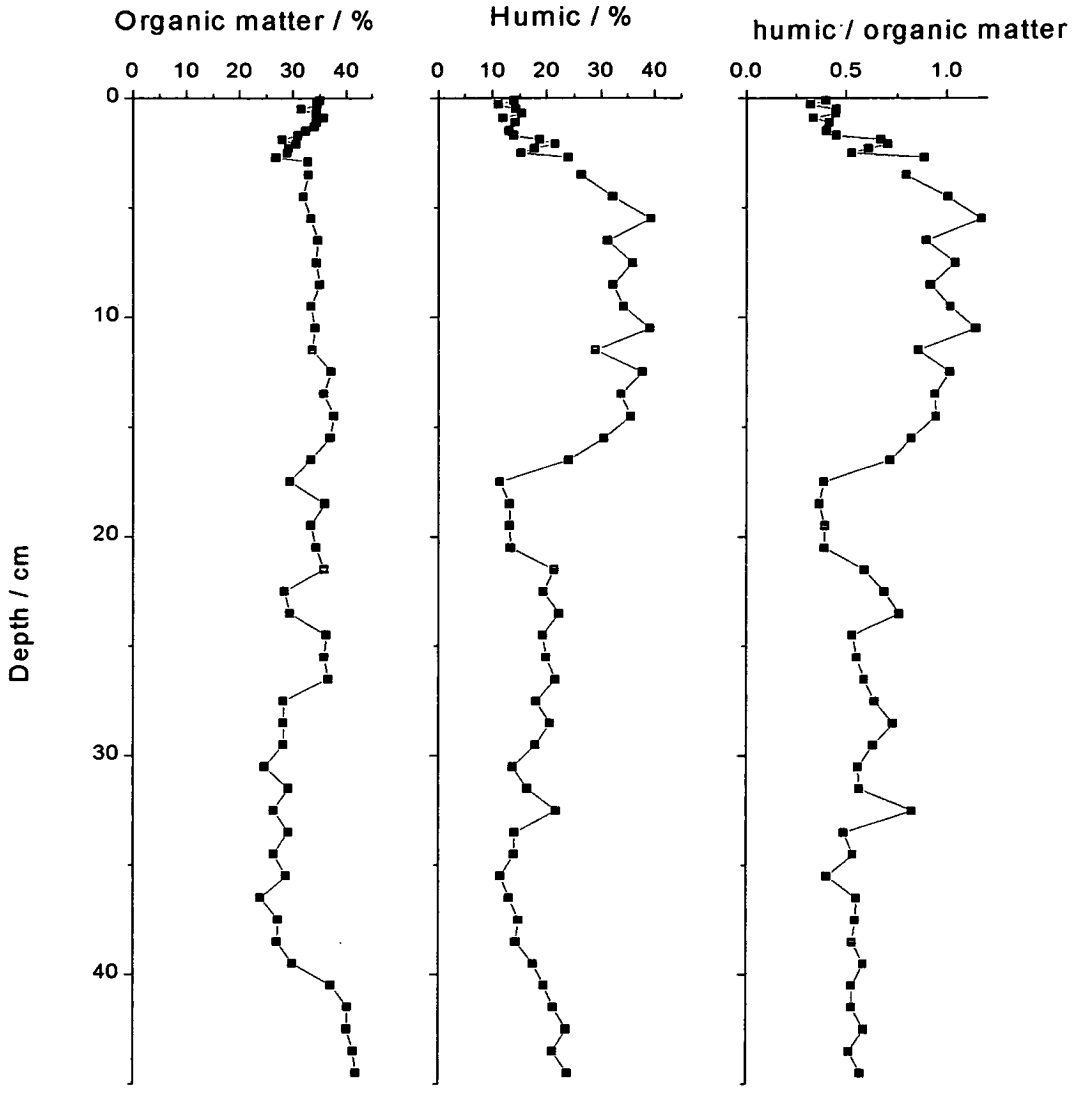


Fig. 6.6: LBSC 6 showing total organic matter, humic substances (corrected for co-extracted $Fe(OH)_3$) and humic/organic matter ratio for 0 - 45 cm sediment.

6.1.3 Concentration of Humic Substances in the 0 - 3 cm Loch Riecawr Sediment (LRSC 1 - 2)

The average concentration of humic substances for LRSC 1 and 2 (26.2 ± 5.6 % and 18.2 ± 2.2 %, respectively) (Table 6.2) lie within the range observed for the Loch Bradan sediments. The humic/organic matter ratios for these cores (0.63 ± 0.14 and 0.59 ± 0.12, respectively) (Table 6.2) are also similar to those obtained for Loch Bradan cores.

LRSC 1 perhaps falls into Group I (especially in the 1 - 2.7 cm section), with an approximately constant humic/organic matter ratio, 0.6 ± 0.1 (Fig. 6.7). Variations in the organic matter concentration (which affect the humic/organic matter ratio) over the 0 - 3 cm section are, in the main, attributable to the presence of a redox enrichment of Fe at ~ 1 cm.

Sample	[Humic] range / %	[Humic] average / %	[Humic] / [Org. Mat.] range	[Humic] / [Org. Mat.] ave.
LRSC 1	16.5 - 38.6	26.4 ± 5.6	0.37 - 0.82	0.63 ± 0.14
LRSC 2	15.4 - 21.6	18.2 ± 2.2	0.43 - 0.66	0.59 ± 0.12

Table 6.2 : Range and average concentration of humic substances and the range and average humic/organic matter ratio for 0 - 3 cm Loch Riecawr sediments.

LBSC 2 is most similar to Group II, although there is a more consistent increase in the humic/organic matter ratio with increasing depth (Fig. 6.7).

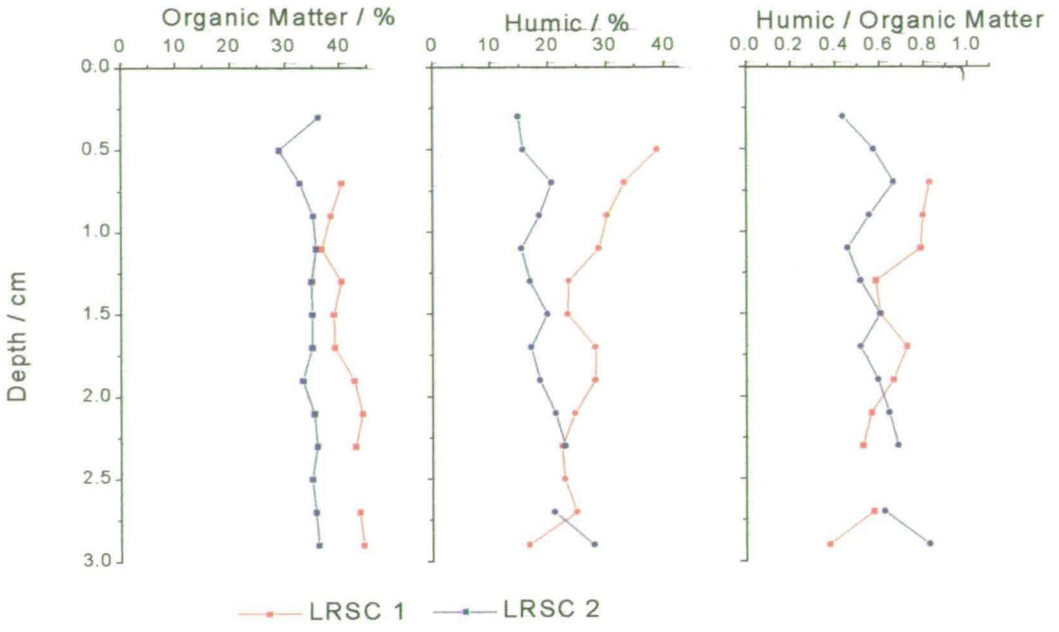


Fig. 6.7: LRSC 1 and 2 showing total organic matter, humic substances and humic/organic matter ratio for 0 - 3 cm sediments.

6.1.4 Elemental (C, H, N, O) Composition of Humic Substances Extracted from Loch Bradan Sediments (LBSC 2, 5, 7, 9)

The elemental composition and atomic ratios (H/C, N/C and O/C) for selected samples of sediment are shown in Table 6.3. The atomic oxygen data have been calculated (i) by difference and (ii) by difference and correcting for co-extracted Fe (in the form of Fe (hydr)oxides)

The average elemental composition of humic substances extracted from 0 - 3 cm sediments was C 37.7 ± 2.0 %, H 4.8 ± 0.2 %, N 3.0 ± 0.4 %, and O 54.6 ± 2.0 % (corrected O 52.7 ± 1.9 %). Calculation of the average relative atomic composition gave C 3.1 ± 0.2, H 4.8 ± 0.2, N 0.2 ± 0.003, and O 3.4 ± 0.1 (corrected 3.3 ± 0.1). Average atomic ratios were thus H/C 1.5 ± 0.1, N/C 0.07 ± 0.01, O/C 1.1 ± 0.1 (corrected O/C 1.1 ± 0.1). Although there were some minor variations between

Sample	C	H	N	O	O – $Fe(OH)_3$	H/C	N/C	O/C	Corrected O/C
LBSC 2 0.2 - 0.4 cm	40.28	4.85	2.97	51.90	49.57	1.435	0.06	1.0	0.9
LBSC 2 1.8 - 2.0 cm	40.78	4.90	3.12	51.20	49.84	1.432	0.07	0.9	0.9
Average						1.44 ± 0.02	0.064 ± 0.002	0.95 ± 0.02	0.92 ± 0.004
LBSC 5 0.0 - 0.2 cm	40.91	4.74	3.06	51.29	49.80	1.381	0.06	0.9	0.9
LBSC 5 1.0 - 1.2 cm	37.04	4.39	2.85	55.72	53.08	1.412	0.07	1.1	1.1
LBSC 5 1.2 - 1.4 cm	38.64	4.73	2.73	53.90	51.26	1.459	0.06	1.0	1.0
LBSC 5 2.2 - 2.4 cm	36.74	4.68	2.60	55.98	53.08	1.518	0.06	1.1	1.1
Average						1.45 ± 0.06	0.063 ± 0.003	1.06 ± 0.09	1.02 ± 0.08
LBSC 7 0.2 - 0.4 cm	38.37	4.79	3.35	53.49	52.25	1.488	0.08	1.1	1.0
LBSC 7 0.4 - 0.6 cm	38.43	4.86	3.01	53.70	52.25	1.507	0.07	1.1	1.0
LBSC 7 0.6 - 0.8 cm	35.80	4.76	2.69	56.75	55.13	1.584	0.06	1.2	1.2
LBSC 7 0.8 - 1.0 cm	35.34	5.01	2.85	56.80	55.02	1.689	0.07	1.2	1.2
LBSC 7 1.0 - 1.2 cm	36.06	4.66	2.51	56.77	55.11	1.540	0.06	1.2	1.2
LBSC 7 1.2 - 1.4 cm	36.21	5.02	2.62	56.15	54.24	1.652	0.06	1.2	1.1
LBSC 7 1.4 - 1.6 cm	34.44	4.69	4.03	56.84	55.46	1.623	0.10	1.1	1.1
LBSC 7 1.6 - 1.8 cm	37.88	4.79	2.95	54.38	52.58	1.507	0.07	1.2	1.0
LBSC 7 1.8 - 2.0	36.21	5.02	3.28	55.49	53.69	1.652	0.08	1.2	1.1
Average						1.59 ± 0.08	0.071 ± 0.012	1.14 ± 0.07	1.11 ± 0.07
LBSC 9 0.8 - 1.0 cm	39.76	4.75	3.25	52.24	51.04	1.424	0.07	1.0	1.0
LBSC 9 2.2 - 2.4 cm	37.19	4.43	2.46	55.92	53.09	1.419	0.06	0.057	1.1
Average						1.43 ± 0.003	0.063 ± 0.009	1.06 ± 0.10	1.02 ± 0.08

Table 6.3 : Elemental composition and atomic ratios for humic substances extracted from 0 - 3 cm Loch Bradan sediments (LBSC 2, 5, 7, and 9), with O-(HFO) and corrected O/C referring to percentage O calculated after subtracting the concentration of co-extracted $Fe(OH)_3$.

cores and also with increasing depth, it is clear that the elemental composition of humic substances from these sediments is fairly uniform. This can be illustrated further on plots of H/C vs O/C and N/C vs O/C which both show closely grouped data points, with the exception of LBSC 7 which has some slight variations (Fig. 6.8).

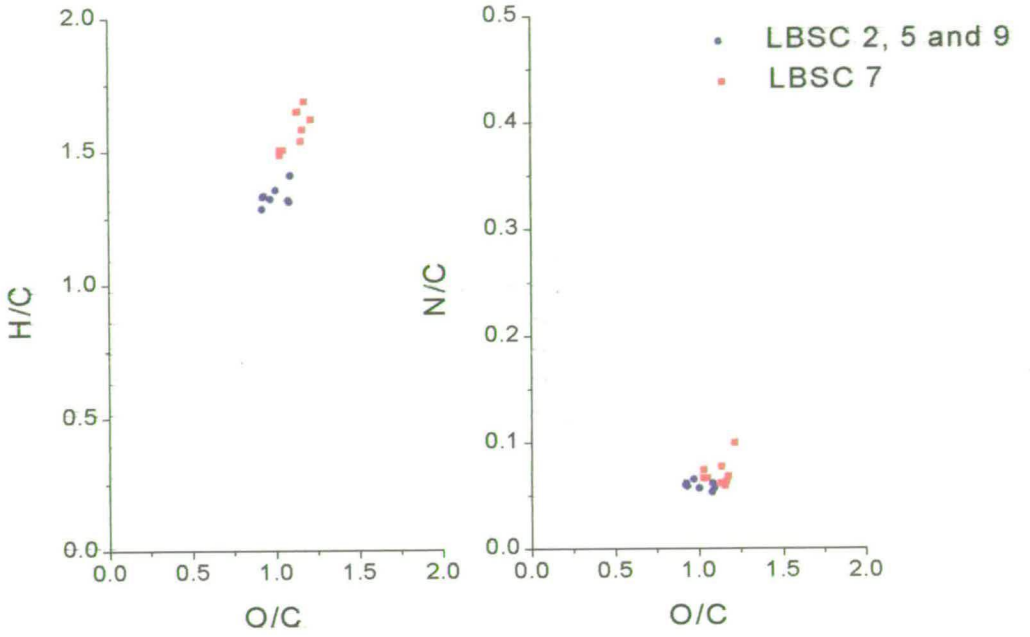


Fig. 6.8 : (a) H/C vs O/C and (b) N/C vs O/C values for humic substances extracted from 0 - 3 cm Loch Bradan sediments.

Atomic ratios were obtained for humic materials extracted from nearly all sections between 0 and 2 cm in LBSC 7 and a depth profile of the atomic ratios (H/C, N/C and O/C) are shown in Fig. 6.9. There is a slight increase in the O/C and H/C ratio in the 0.7 - 1.5 cm zone and a small peak at 1.5 cm in the O/C and N/C ratios.

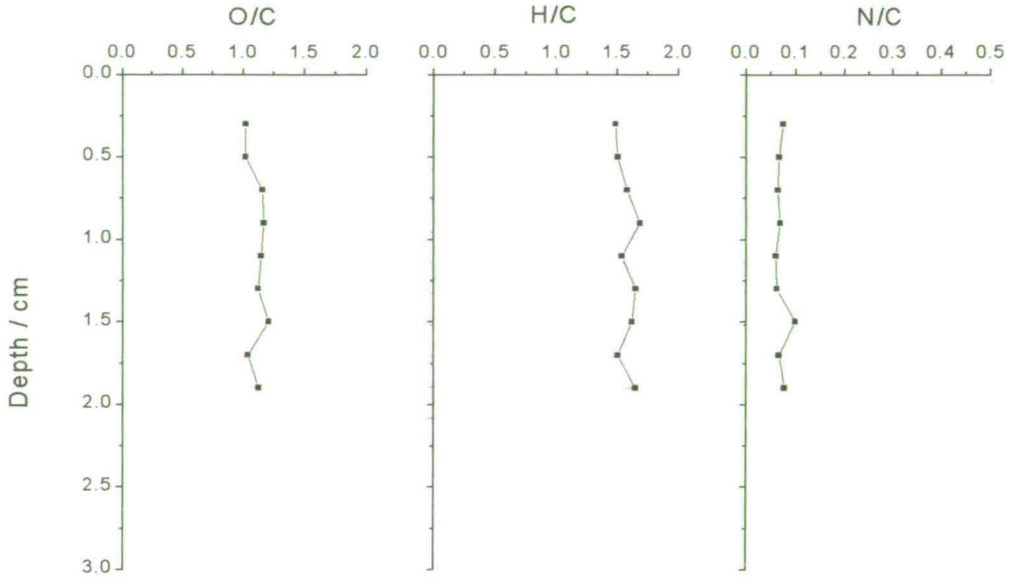


Fig. 6.9: Variations in H/C, N/C and O/C atomic ratios for humic substances extracted from 0 - 2 cm sections of LBSC 7.

Further comparison will be made with humic substances from the peaty catchment and from deeper loch sediments in section 6.2.3.

6.1.5 FTIR Spectroscopic Investigation of the Functionality of Humic Substances Extracted from 0 - 3 cm Loch Bradan Sediments (LBSC 7)

- These spectra are typical of those obtained for humic materials in that the peaks are generally broad. The positions of the main peaks do not change significantly with increasing depth (Table 6.4). The overall IR absorbances were greatest for humic substances extracted from the top sections (0 - 0.5 cm), below which absorbances did not decrease significantly with increasing depth. There were, however, some minor changes in the relative intensity of certain peaks. In particular there was some change in the nature of functional groups with increasing depth - increase in COO^- in 1 - 2 cm sections and 2.6 - 3 cm sections (Table 6.5).

Depth / cm	O-H (cm^{-1})	C-H (cm^{-1})	C-H (cm^{-1})	C=O (cm^{-1})	COO^- (cm^{-1})	COOH (cm^{-1})	COOH (cm^{-1})	COO^- (cm^{-1})
0.2-0.4	3405	2920	2850	1630	1550	1450	1260	1045
0.4-0.6	3435	2930	2850	1635	1550	1450	1260	1045
0.6-0.8	3430	2935	2850	1625	1550	1450	1270	1050
0.8-1.0	3435	2925	2855	1655	1550	1450	1260	1050
1.0-1.2	3425	2925	2855	1625	1550	1450	1270	1040
1.2-1.4	3435	2925	2855	1625	1550	1450	1270	1045
1.4-1.6	3450	2935	2855	1655	1550	1450	1270	1050
1.6-1.8	3430	2925	2855	1635	1550	1450	1270	1045
1.8-2.0	3450	2925	2855	1635	1550	1450	1270	1045
2.0-2.2	3420	2925	2855	1635	1550	1450	1270	1055
2.2-2.4	3450	2925	2855	1635	1550	1450	1270	1045
2.4-2.6	3440	2920	2855	1635	1550	1450	1270	1045
2.6-2.8	3420	2930	2855	1635	1550	1450	1270	1050
2.8-3.0	3430	2930	2855	1635	1550	1450	1270	1060

Table 6.4 : Positions of the major peaks in FTIR spectra of humic substances extracted from 0 - 3 cm LBSC 7 sediments.

The main features of the FTIR spectra are:

O-H ~ 3400 - 3450 cm^{-1}

CH_2, CH_3 ~ 2859 - 2920 cm^{-1}

C=O ~ 1650 cm^{-1}

COOH ~ 1450 and 1260 cm^{-1}

COO^- ~ 1550 and 1050 cm^{-1}

Depth / cm	O-H 3400 cm^{-1}	C-H 2920 cm^{-1}	C-H 2850 cm^{-1}	C=O 1650 cm^{-1}	COO^- 1550 cm^{-1}	COOH 1450 cm^{-1}	COOH 1260 cm^{-1}	COO^- 1050cm^{-1}
0.2-0.4	S	S	W	S	M	W	S	S
0.4-0.6	S	W	W	M	W	W	W	W
0.6-0.8	S	M	W	S	W	W	M	M
0.8-1.0	S	S	S	S	S	M	W	S
1.0-1.2	S	S	W	S	M	M	W	S
1.2-1.4	S	M	W	M	W	M	W	M
1.4-1.6	S	W	W	W	S	M	W	M
1.6-1.8	S	M	W	M	M	M	W	S
1.8-2.0	S	W	W	W	W	W	W	W
2.0-2.2	S	M	W	M	W	W	W	W
2.2-2.4	S	W	W	W	W	M	W	W
2.4-2.6	S	M	W	W	W	W	W	M
2.6-2.8	S	S	M	S	M	M	M	S
2.8-3.0	S	S	S	M	M	M	W	M

Table 6.5 : Relative strength of the major peaks in FTIR spectra of humic substances extracted from 0 - 3 cm LBSC 7 sediments (S = strong, M = medium, W = weak; shading M = red and S = blue indicating the presence of carboxylate peaks)

6.2 Discussion of the Quantification and Characterisation of Humic Substances Extracted from the Sediments of Loch Bradan (LBSC 1 - 10) and Loch Riecawr (LRSC 1 - 2)

6.2.1 Concentration and Characterisation of Humic Substances Extracted from the 0 - 3 cm sediments of Loch Bradan

As described in Section 6.1.1, the cores have been divided into four groups. Each of these will be discussed in turn.

Group I

The near constant relationship between the concentration of humic substances and organic matter indicates that there are no major processes leading to alteration of organic matter operating over the 0 - 3 cm zones of these cores. Typically humic

substances comprised ~ 65 - 80 % of the organic matter, suggesting a significant degree of humification (particularly in LBSC 2). The elemental composition of humic substances from LBSC 2 and 5 is very similar (Table 6.3), indicating that the source of organic matter is the same (predominantly terrigenous) and that there is little change over the top 0 - 3 cm.

Group II

The near constant relationship between humic substance and organic matter concentrations, as identified for Group I cores, was again evident for 0 - 1.7 cm sediment sections, although the values of the humic/organic matter ratio were much lower (typically 0.4 - 0.5). Below 1.7 cm, a sharp increase in the humic/organic matter ratio to ~ 0.6 - 0.8 characterised this group of cores. These cores are closest to stream 3 (Figs. 3.8, 3.14), one of the major inputs of water from the catchment to the loch, but it is difficult to explain the profile shape on the basis of the proximity of the cores to this potential input source, and no elemental data for the 0 - 3 cm sections of these cores are available. The lack of change in total organic matter profile over the top 0 - 3 cm supports the proposal that there is no major change in the sediment type at ~ 1.7 cm. A possible explanation for the sharp increase in the humic/organic matter ratio could be a change in geochemical conditions, e.g. redox processes involving Fe/Mn and organic matter. It should be noted that the increase in the ratio for LBSC 6 continues below 3 cm to a value of ~ 1, suggesting a major process is occurring, leading to the formation of humic substances from ~ 1.7 cm downwards.

Group III

LBSC 7 has some features that distinguish it from all other cores.

The humic substance profile, although similar to LBSC 1 and 5 with respect to the concentration of humic material, has a peak at 1.3 cm which is absent from the total

organic matter profile. There is no obvious explanation for this in terms of geochemical processes, and it may simply be an example of the heterogeneous nature of the sediments.

The wet/dry ratio for LBSC 7 (Fig. 3.11 G) is lower than that for all other cores, particularly in the 1 - 2 cm section, which may be due to differences in the inorganic composition of the sediment (as no significant decrease in the average total organic matter or average humic substances was observed for this sediment), with a coarse grained sediment leading to a lower wet/dry ratio. It should be noted that this is a relatively minor point as the magnitude of difference between LBSC 7 and other cores is comparatively small and does not indicate a major change in sediment composition.

The humic substances extracted from LBSC 7 have more N, H and O relative to C than all other cores analysed. This suggests that the source of organic matter may be slightly more influenced by autochthonous aquatic material that is relatively rich in N (proteinaceous material) and more aliphatic (lack of lignified material). In addition, organic material that is altered in situ (i.e. in the loch sediment) generally gives rise to humic substances with a greater proportion of O (as observed here) (Rice and MacCarthy, 1991). This core, therefore, provides an example of the compositional differences between humic substances formed in situ in the loch sediment and those formed in the catchment.

Comparison of the humic substances profile with the atomic ratio profiles revealed that the peak at 1.3 cm in the former does not correlate exactly with the change in elemental composition (peak N/C ratio at 1.5 cm). Incorporation of N into the structure of humic substances has been implicated as an important final step in the formation of humic substances (Killops and Killops, 1993), generally thought to confer greater stability to humic molecules compared with other components of the organic fraction. It would be expected that the N/C ratio would then be maintained at this value in underlying sediments (only slow loss of N). Thus these minor features

are simply indicative of small scale heterogeneity rather than major processes occurring with changing geochemical conditions.

Group IV

Group IV cores are located furthest east of all the sampled sites on the loch, and have the lowest organic matter content of all the cores. In the 0 - 2 cm sections the humic/organic matter ratio is, however, very similar to that of Group I cores (~0.8). Below this there is a general sharp decrease to ~ 0.4 - 0.5 (Fig. 3.11 H). Although there is a sharp change in the wet/dry ratio for LBSC 8 at ~ 2 cm, there is insufficient evidence to support a major change in the sediment composition for all three cores.

The elemental composition of the humic substances from LBSC 9 suggests that the source of organic matter is essentially the same as that at LBSC 2 and 5 and so there is no major change in source occurring across the loch (i.e. from western to eastern basin).

6.2.2 Concentration and Characterisation of Humic Substances Extracted from One of the Long Loch Bradan Sediment Cores, LBSC 6

It would appear that diagenetic processes leading to the formation of humic substances are of great significance over the top 0 - 5 cm of the sediment (Fig. 6.6). From 5 - 15 cm humic substances make up almost all of the sediment organic matter, indicating a very high degree of humification. The distinct minimum in concentration of humic substances and in the humic/organic matter ratio at ~ 20 cm (co-incident with a Mn peak) may be indicative of a past redox enrichment prior to some major change, such as the extension of the dam in 1972. There is no change in the wet/dry ratio at this depth. It is proposed, therefore, that the Mn enrichment at ~ 20 cm marks a past near-surface redox enrichment which has been preserved in the sediment, possibly in the form of $MnCO_3$ (see Section 4.2.2.1). Below this, also preserved in the sediment, there is evidence of diagenetic alteration of humic substances. These

alteration processes result in decreasing O/C, H/C and N/C ratios with increasing depth in the sediment (Fig. 6.10).

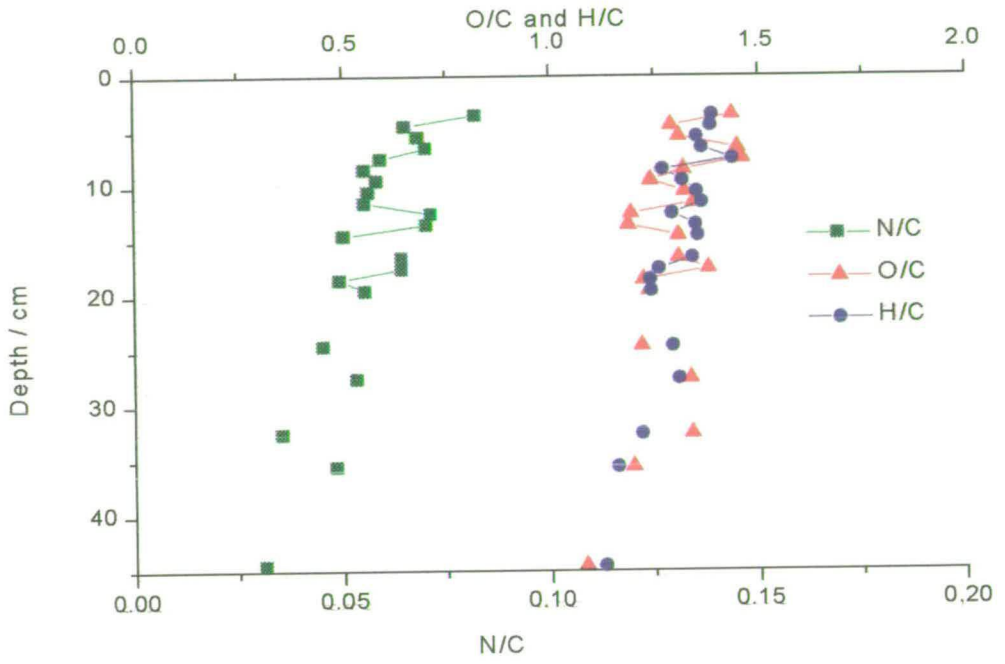


Fig. 6.10: H/C, N/C and O/C ratios for humic substances extracted from the long core, LBSC 6.

6.2.3 Characterisation of Humic Substances Extracted from the Sediments and Surrounding Catchment of Loch Bradan

As can be seen from Tables 6.6 and 6.7, there is a strong terrigenous influence on the organic matter present in the loch sediment, on the basis of the similar H/C, N/C and O/C atomic ratios and C/H and C/N ratios for peaty catchment and loch sediment humic materials (Fig 6.11). There is, however, some influence of the geochemical environment on the composition of the humic substances present in the surface sediment as shown by the slightly higher O, N and H values in the surface sediments compared with the peat (Fig. 6.11). There is clearly no evidence to support a major planktonic autochthonous source to the sediment, but LBSC 7 surface sediment

humic substances have slightly more H, N and O relative to C than peaty humic materials than all other loch sediment cores, as discussed in Section 6.2.1.

Sample Type	Average H/C	Average N/C	Average O/C	Corrected Average O/C
Surface Loch Sediment	1.52 ± 0.10	0.068 ± 0.01	1.09 ± 0.10	1.06 ± 0.09
Deeper Loch Sediment	1.33 ± 0.05	0.065 ± 0.01	1.03 ± 0.08	0.97 ± 0.07
Peaty Catchment	1.44 ± 0.09	0.062 ± 0.01	1.02 ± 0.36	0.97 ± 0.29

Table 6.6 : H/C, N/C and O/C atomic ratios for humic substances extracted from surface (0 - 3 cm LBSC 2, 5, 7 and 9) and deeper (3 - 45 cm LBSC 6) loch sediments and from peaty catchment (LBPC 1 - 4) (corrected oxygen value by subtracting co-extracted $Fe(OH)_3$).

Sample Type	Average C/H	Average C/N	Average C/O	Corrected Average C/O
Surface Loch Sediment	7.9	12.6	0.69	0.72
Deeper Loch Sediment	9.1	13.5	0.73	0.77
Peaty Catchment	8.4	13.6	0.78	0.81

Table 6.7: Average C/H, C/N and C/O ratios for humic substances extracted from surface (0 - 3 cm LBSC 2, 5, 7 and 9) and deeper (3 - 45 cm LBSC 6) loch sediments and from peaty catchment (LBPC 1 - 4) (corrected oxygen value by subtracting co-extracted $Fe(OH)_3$).

There is evidence to support a small degree of diagenetic alteration of loch sediment humic material with increasing depth (comparing 0-3 cm sediment with 3 - 45 cm sediment), with a decrease in the H/C, O/C and N/C atomic ratios (Fig. 6.11), which is characteristic of diagenetic alteration (Steelink, 1986).

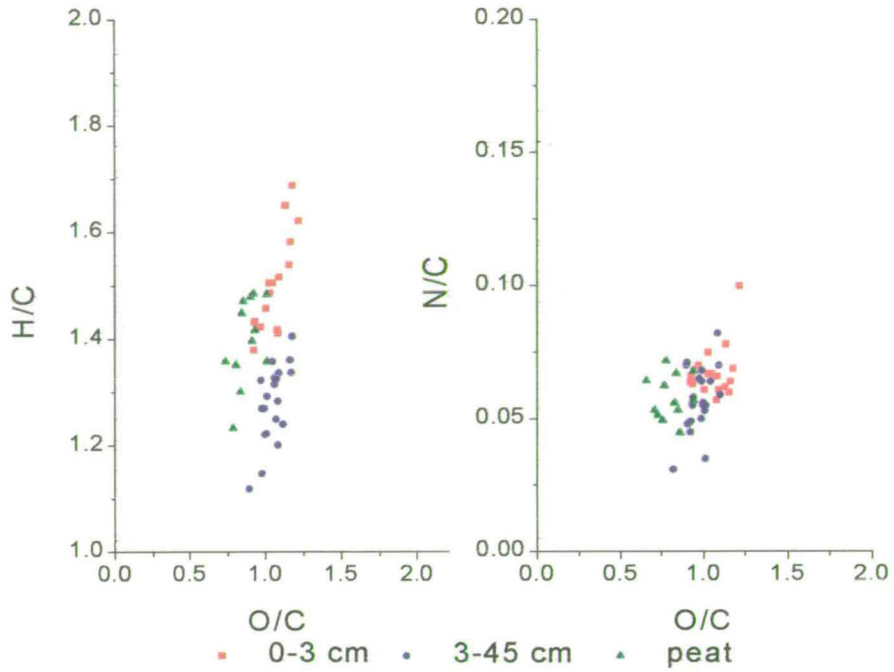


Fig. 6.11: a) H/C vs O/C and b) N/C vs O/C for humic substances extracted from surface (0 - 3 cm) and deeper (3 - 45 cm) loch sediments and from the peaty catchment of Loch Bradan.

6.2.4 Concentration of Humic Substances Extracted From Loch Riecawr Sediments (LRSC 1 - 2)

The humic substance concentration profile for LRSC 1 shows, in similar fashion to Group I humic substance profiles from the sediment of Loch Bradan, a comparatively constant relationship with organic matter (Fig. 6.7). The relationship, however, is not as strong as that seen in Loch Bradan and the percentage of organic matter that is humic in nature is generally lower than that of Loch Bradan, ~ 50 - 70 % compared with 70 - 80 %. Nevertheless, the results show that there are no major alteration processes occurring in the top 0 - 3 cm of LRSC 1.

The humic concentration profile for LRSC 2 is most similar to Group II humic profiles from Loch Bradan, although the increase in the humic/organic matter ratio is

seen throughout the top 0 -3 cm of the core and not just below ~ 1.7 cm. As with Group II humic profiles there is no significant variation in the concentration of organic matter over the top 0 - 3 cm of the sediment, indicating no major change in the sediment type over the length of the core but instead a process that is resulting in the formation of humic substances.

6.2.5 Summary

- The sediment of Loch Bradan is highly organic in nature, with a high proportion of the organic matter being humic in nature.
- There are variations in the humic concentration relative to the organic mater profiles at the different coring sites.
- In general there are processes occurring in the sediment of Loch Bradan that are leading to increasing humification of organic matter with increasing depth.
- The humic material in the sediment of Loch Bradan originates principally from the surrounding peaty catchment.

6.3 Humic-Associated Manganese and Iron in the Sediment of Loch Bradan (LBSC 1 - 10) and Loch Riecawr (LRSC 1 - 2)

6.3.1 Humic-Associated Manganese in 0 - 3 cm Loch Bradan Sediment (LBSC 1 - 10)

Similar to Section 6.1.1, it is useful to separate the cores into the same groups to describe the results, with all the results being shown in appendices 1-10.

Group I (LBSC 1, 2 and 5) humic-associated Mn concentration profiles all show low values (~ 300 mg kg^{-1} dry weight of sediment) in the 0 - 1 cm section of the sediment (Fig. 6.12). LBSC 1 and 5 show an increase in humic-associated Mn at ~ 1.1 cm, to values of ~ 2000 mg kg^{-1}. There is, however, a sharp decrease in concentration at 2 - 3 cm in LBSC 1 that is not seen in either of the other cores. LBSC 2 stands out as

being very different to the other two cores of Group I type with almost no humic-associated Mn concentration change with depth.

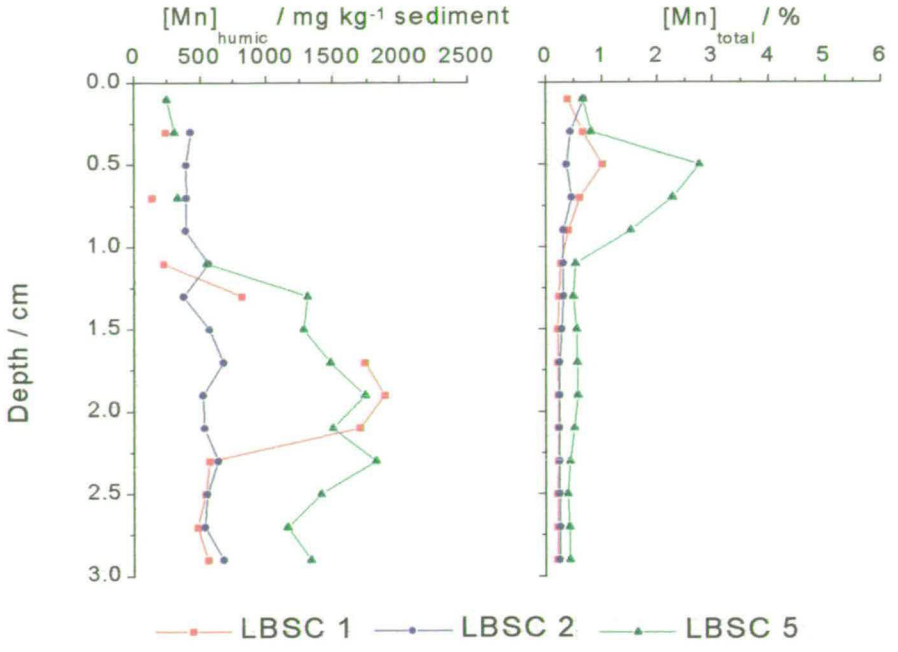


Fig. 6.12 : Humic-associated and total Mn in Group I cores from Loch Bradan (LBSC 1, 2 and 5)

Group II (LBSC 3, 4 and 6) humic-associated Mn profiles, as with Group I, show a low concentration in the top 0 - 1 cm of the sediment which increases at about 1.3 - 1.7 cm, again to values of ~ 2000 mg kg^{-1} (Fig 6.13).

As with the humic substance concentration profile itself (Section 6.1.1), Group III (LBSC 7) is different from all other cores, with a much steeper increase over the 0 - 1 cm zone of the sediment (Fig. 6.14). Below 0.9 cm (i.e. outwith the region of redox 'influence') there is some correlation with the amount of humic material, with the peak in humic substances at 1.3 cm reflected in the peak in humic-bound Mn at this depth (Fig. 6.14). Below 1.3 cm the concentration of humic substances does not change significantly and this is reflected in the almost constant concentration of humic-bound Mn (Fig. 6.14).

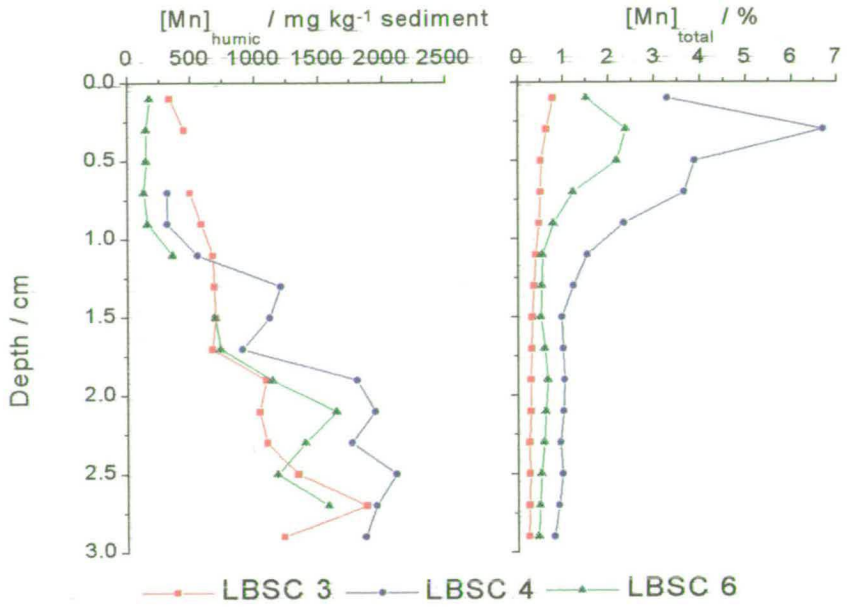


Fig. 6.13 : Humic-associated and total Mn in Group II cores from Loch Bradan (LBSC 3, 4 and 6)

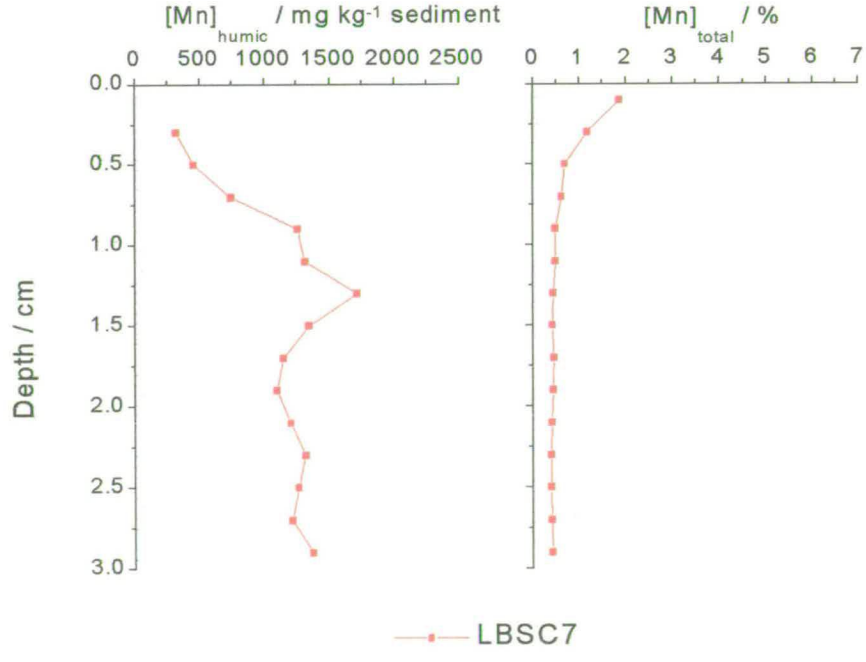


Fig. 6.14 : Humic-associated and total Mn in Group III cores from Loch Bradan (LBSC 7).

In Group IV (LBSC 8, 9 and 10) profiles there is again a low concentration of humic-associated Mn in the 0 - 1 cm zone of the sediment (where data are available) (Fig. 6.15). The increase in concentration, however, starts at ~ 1.5 - 1.7 cm, much deeper than in other cores. It is noticeable that the decrease in the humic/organic matter ratio is partially reflected in the Mn-humic profile (Figs. 6.5, 6.15), so at the detailed level there is perhaps a correlation between % humic substances and % Mn-humic complexation.

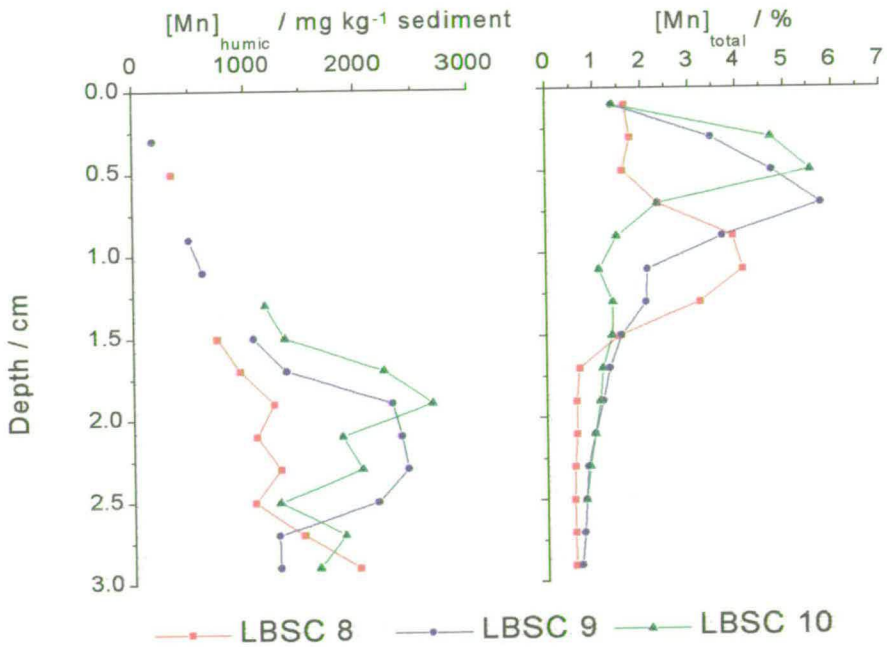


Fig. 6.15 : Humic-associated and total Mn in Group IV cores from Loch Bradan (LBSC 8, 9 and 10)

In all cases (apart from LBSC 2) the maximum concentration of humic-associated Mn is ~ 2000 - 3000 mg kg^{-1} dry weight of sediment, and the maximum concentration always occurs outwith the 0 - 1 cm zone. For some cores the maximum is in the 1 - 2 cm zone, e.g. LBSC 1 and 7, for others the 2 - 3 cm zone, e.g. LBSC 8 and 9. The position of the minimum concentration of humic-associated Mn generally occurs in the 0 - 1 cm zone, the region of diagenetic enrichment of total Mn.

6.3.2 Humic-Associated Iron in 0 - 3 cm Loch Bradan Sediment (LBSC 1 - 10)

Concentrations of humic-associated Fe are generally about one order of magnitude higher than those for Mn, i.e. ~ 1% compared with 0.1 - 0.2 % dry weight. As with Mn it is useful to split the humic-associated Fe results into the same groupings.

Group I humic-associated Fe profiles are different from those of Mn, and the three cores also show some differences from each other. LBSC 1 shows very little change in the concentration of humic-associated Fe with depth, LBSC 2 shows a slight decrease with depth, and LBSC 5 shows an increase below 1 cm, but a decrease below 2 cm (Fig. 6.16).

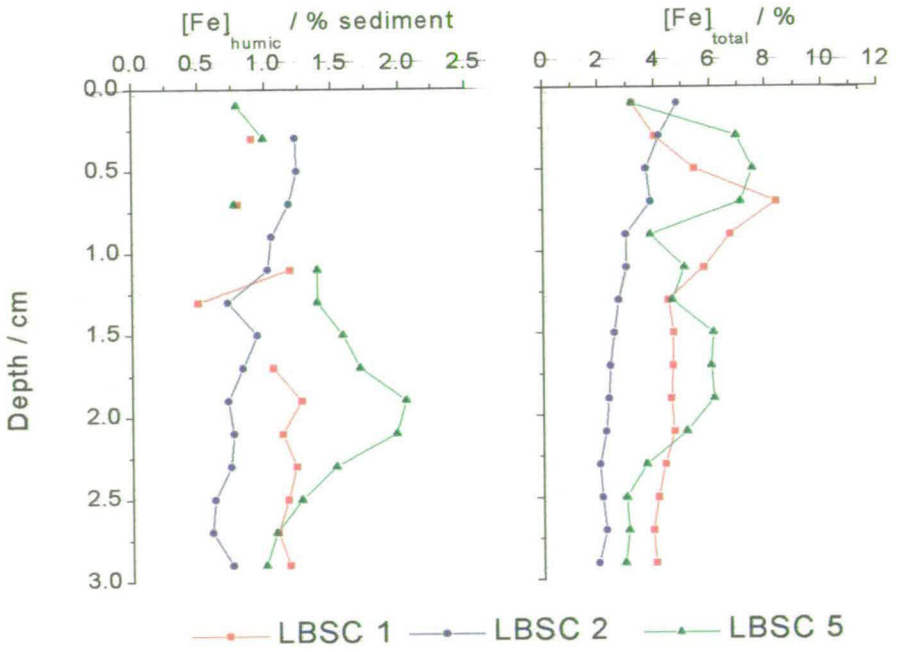


Fig. 6.16: Humic-associated and total Fe in Group I cores from Loch Bradan (LBSC 1, 2 and 5)

Group II (LBSC 3, 4 and 6) humic-associated Fe profiles are more akin to those of Mn than is observed in Group I (Fig. 6.17). Also, unlike Group I cores, there is a

degree of similarity between total Fe profiles within Group II. All profiles show a minimum of ~ 0.5 % at the surface, with an increase occurring below 1.7 cm, which is coincident with an increase in the concentration of humic substances and also the percentage of organic matter that it humic in nature (Fig. 6.3), reaching maximum concentrations of ~ 1.75 %. This increase generally occurs lower down than the increase in humic-associated Mn in the same cores.

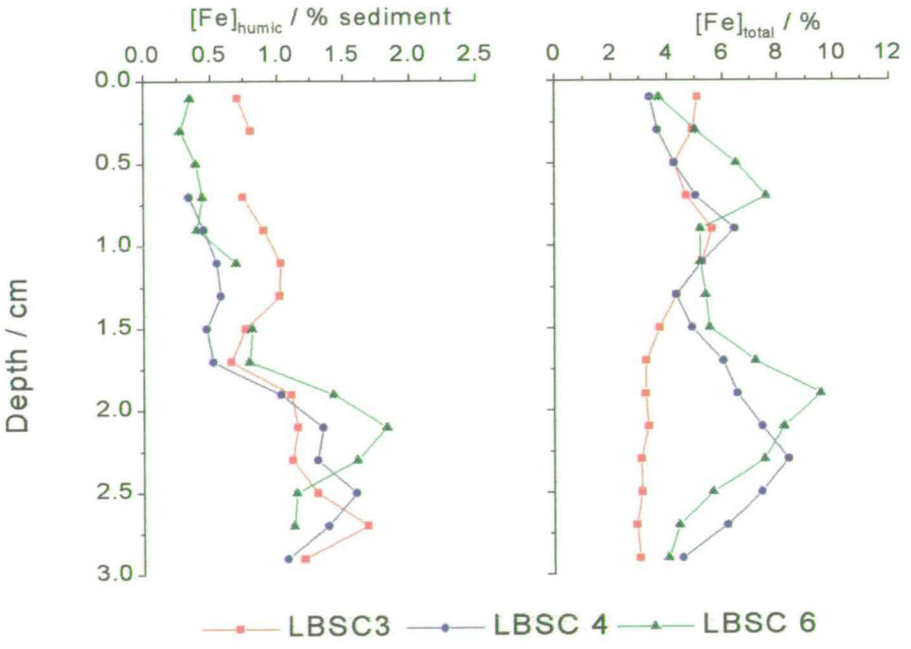


Fig. 6.17: Humic-associated and total Fe in Group II cores from Loch Bradan (LBSC 3, 4 and 6)

The Group III (LBSC 7) humic-associated Fe profile, in contrast to the corresponding Mn profile, changes very little with depth over the entire 0 - 3 cm zone, exhibiting a concentration of ~ 0.75 % at all depths (Fig. 6.18).

Group IV (LBSC 8, 9 and 10) humic-associated Fe profiles show a very consistent pattern, even more so than for Mn profiles, with low near-surface values of ~ 0.5 % increasing below 1.7 cm to ~ 1.75 - 2.0 % (Fig. 6.19). As for Mn, the pattern reflects to some extent the concentration of humic substances (Fig. 6.5).

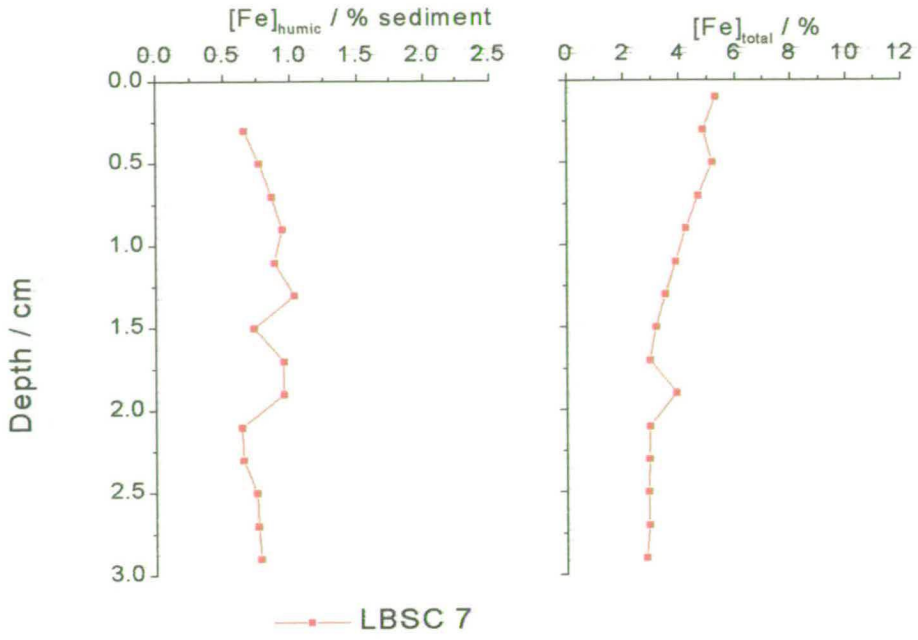


Fig. 6.18: Humic-associated and total Fe in Group III cores from Loch Bradan (LBSC 7)

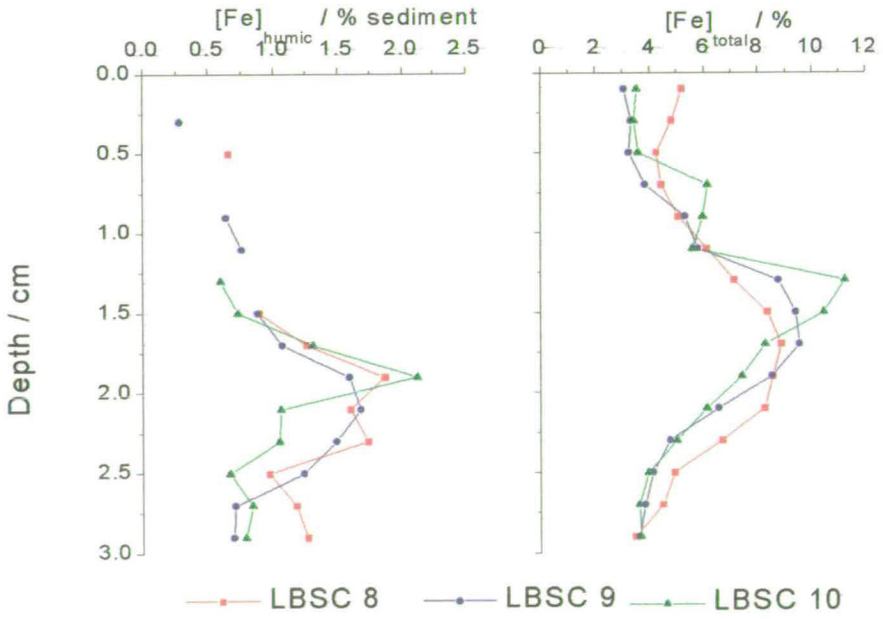


Fig. 6.19: Humic-associated and total Fe in Group IV cores from Loch Bradan (LBSC 8, 9 and 10).

6.3.3 Association of Manganese and Iron with Humic Substances as a Percentage of Total Manganese and Iron, Respectively, in 0 - 3 cm Loch Bradan Sediments (LBSC 1 - 10)

This section will examine the associations of Mn and Fe with humic substances in a way that will first require some explanation.

1. Mn-humic (mg kg^{-1} sediment) as a percentage of total Mn (mg kg^{-1} sediment) ($[Mn]_{humic}$ / $[Mn]_{total}$ / %) shows the relative importance of humic complexation of Mn relative to total Mn in the sediment.

2. Mn-humic (mg kg^{-1} humic material) / total Mn (mg kg^{-1} sediment), called normalised Mn-humic (unitless). This value adjusts the apparent Mn binding capacity of humic substances to remove the effect of total Mn concentration, i.e. peak concentration of Mn-humic (mg kg^{-1} humic substances) at peak concentration of total Mn (mg kg^{-1} sediment) vs peak concentration of Mn-humic (mg kg^{-1} humic substances) at minimum concentration of total Mn (mg kg^{-1} sediment) would indicate differing affinities of humic material for Mn. The normalised Mn-humic is > 1 if the concentration of humic-Mn is greater than the total Mn concentration in the sediment, giving an indication of the importance of humic substances. The use of this value allows greater comparison of the relative affinities of humic substances for Mn and Fe.

6.3.3.1 Manganese

Group I

Group I cores show an increase in the percentage of Mn that is humic-associated below 1.1 cm. This increase is slight for LBSC 2 and 5 from ~ 10 - 20 % to ~ 30 - 40 %, but is much sharper for LBSC 1, increasing to almost 100 % (Fig. 6.20 a).

The normalised values show a low value of ~ 0.2 to a depth of ~ 1.1 cm, below which it exhibits an increase, large in LBSC 1, and to a lesser extent LBSC 5, and very small in LBSC 2 (Fig. 6.20 b).

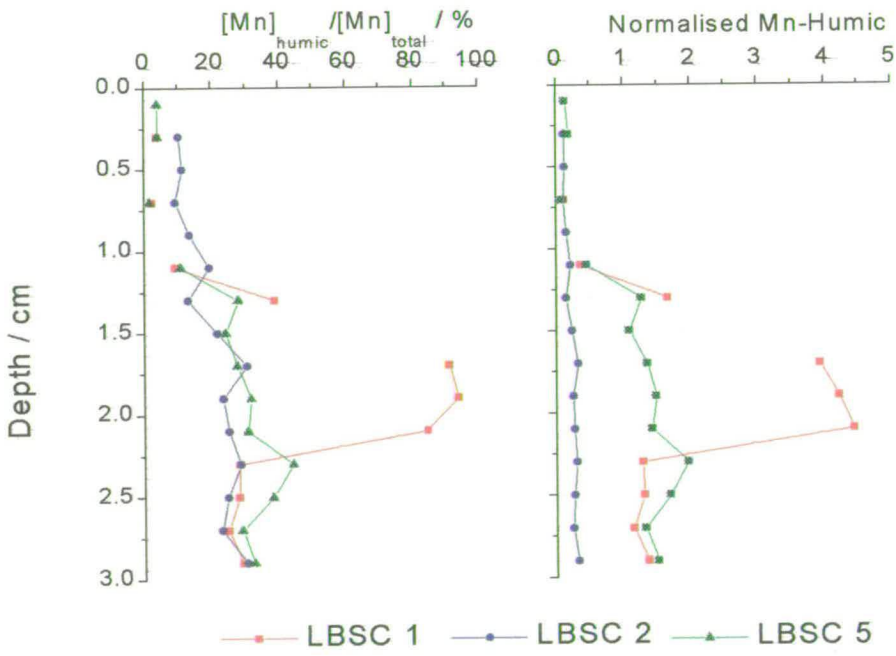


Fig. 6.20: a) humic-associated Mn as a percentage of total Mn and b) Mn-humic (mg kg^{-1} humic material normalised to total Mn in the sediment) in the 0 - 3 cm Group I cores (LBSC 1, 2 and 5).

Group II

As for Group I cores, Group II cores show an increase in percentage of the total Mn that is humic-associated with depth, but at ~ 1.3 - 1.7 cm, with LBSC 4 and 6 increasing to ~ 20 % and LBSC 3 to ~ 80 % (Fig. 6.21 a).

The normalised data show in all cases an increase with depth, in the case of LBSC 3 starting at the surface, and in the cases of LBSC 4 and 6 at ~ 0.7 cm with a plateau being reached at ~ 1.5 cm in all cases (Fig. 6.21 b).

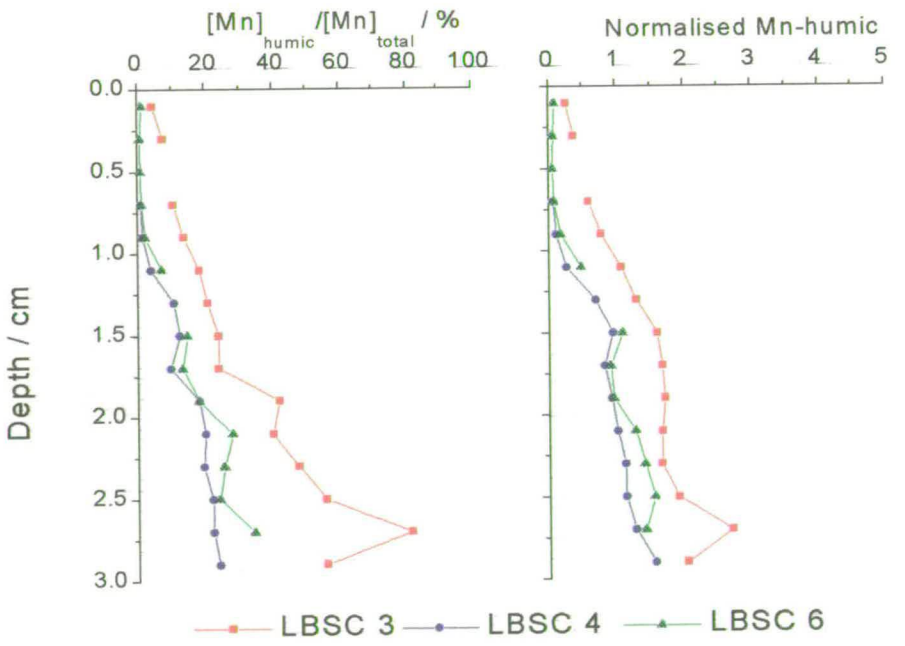


Fig. 6.21: a) humic-associated Mn as a percentage of total Mn and b) Mn-humic (mg kg^{-1} humic material normalised to total Mn in the sediment) in the 0 - 3 cm Group II cores (LBSC 3, 4 and 6)

Group III

LBSC 7 shows an increase in the percentage of the Mn that is humic-associated over the 0 -1.3 cm sections, to a value of ~ 40 %, with very little change observed below 1.5 cm (Fig. 6.22 a).

The normalised values for LBSC 7 show an increase over the 0 - 1 cm section, with little variation below 1 cm (Fig. 6.22 b).

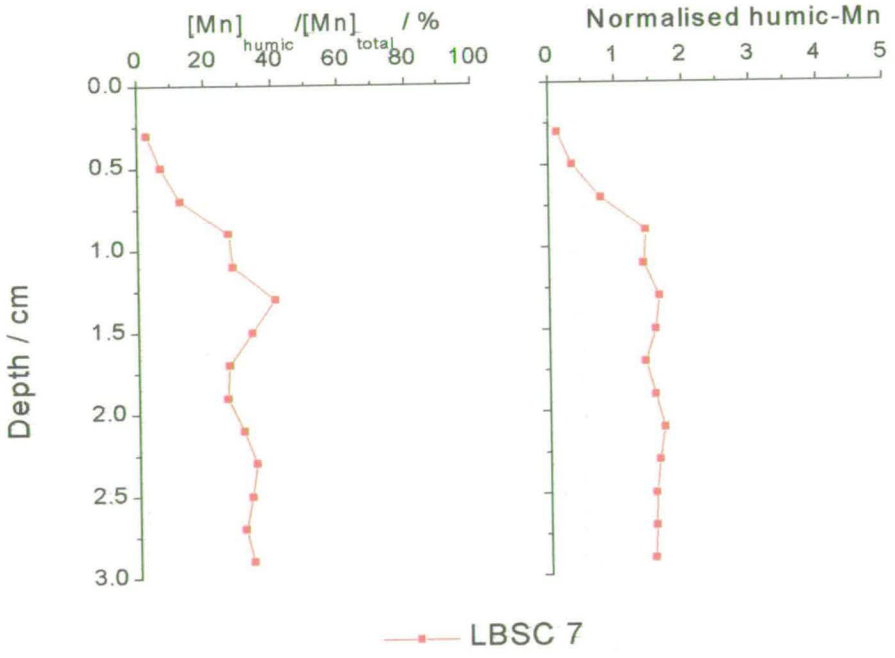


Fig. 6.22: a) humic-associated Mn as a percentage of total Mn and b) Mn-humic (mg kg^{-1} humic material normalised to total Mn in the sediment) in the 0 - 3 cm Group III cores (LBSC 7).

Group IV

Again there is a strong similarity between LBSC 8, 9 and 10, all showing an increase in the percentage of the Mn that is humic-associated at ~ 1.7 cm to ~ 30 - 40 % (Fig. 6.23 a).

The normalised values for Group IV cores are low from 0 to 1.5 cm but increase below 1.5 cm (Fig. 6.23 b)

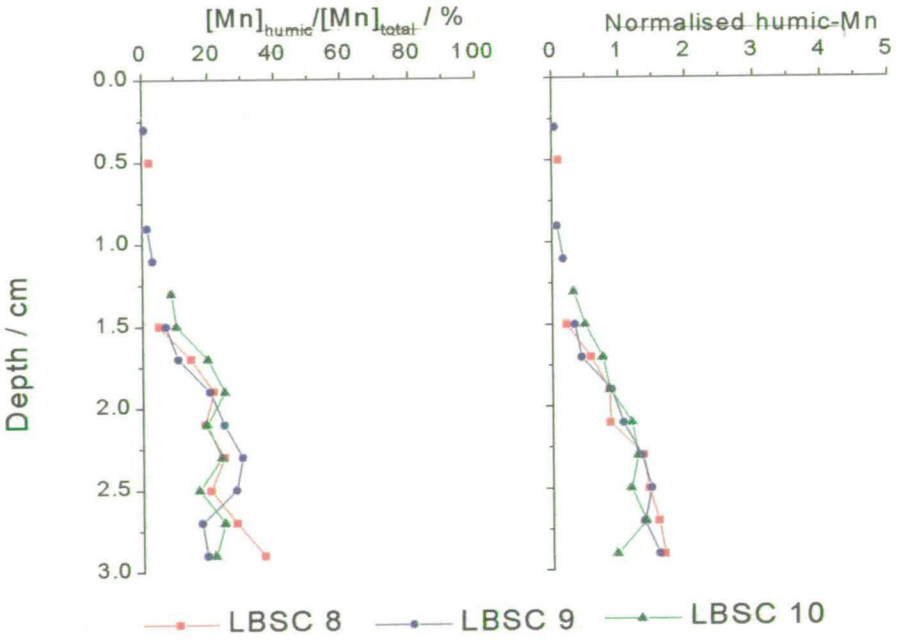


Fig. 6.23: a) humic-associated Mn as a percentage of total Mn and b) Mn-humic (mg kg^{-1} humic material normalised to total Mn in the sediment) in the 0 - 3 cm Group IV cores (LBSC 8, 9 and 10)

6.3.3.2 Iron

Group I

There is less change in the percentage of the total Fe that is humic-associated than for Mn, particularly in LBSC 2, with maximum values of ~ 40 % being reached (Fig. 6.24 a).

With the exception of LBSC 2 the normalised Fe data shows a minimum in the top 0 - 1.5 cm of the sediment that increases below this depth. Similar to the normailsed Mn values, the normalised Fe value for LBSC 2 shows little variation over the 0 - 3 cm section of the sediment (Fig. 6.24 b).

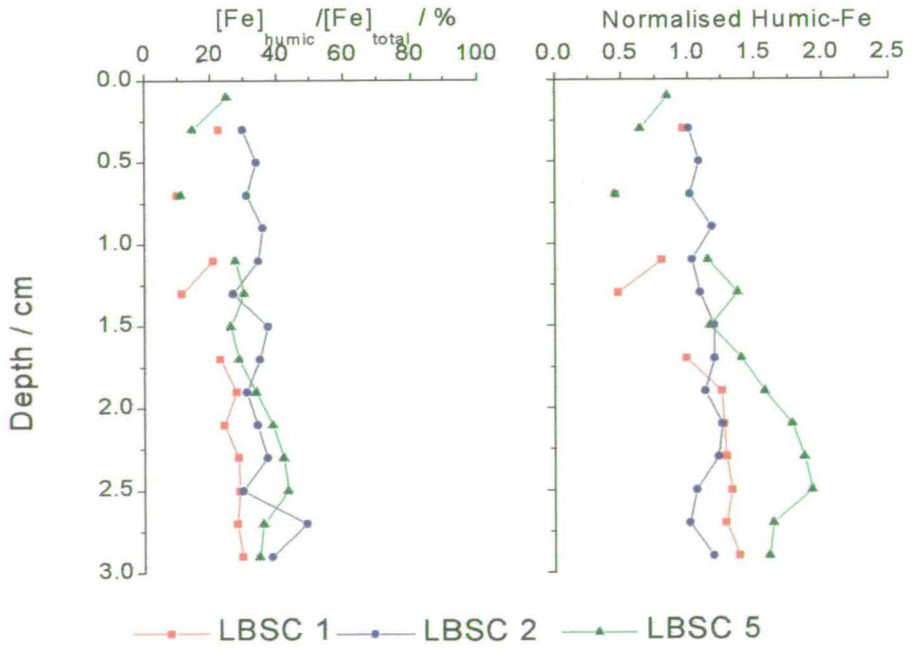


Fig. 6.24 : a) humic-associated Fe as a percentage of total Fe and b) Fe-humic (mg kg^{-1} humic material normalised to total Fe in the sediment) in the 0 - 3 cm Group I cores (LBSC 1, 2 and 5)

Group II

There is considerable similarity between the percentages of Fe and Mn that are humic-associated in Group II profiles, with an increase observed below ~ 1.7 cm (Fig. 6.25 a).

The normalised values for Fe also show marked similarities with Mn, low values at, or near, the surface, increasing to a plateau at ~ 1.3 cm (Fig. 6.25 b).

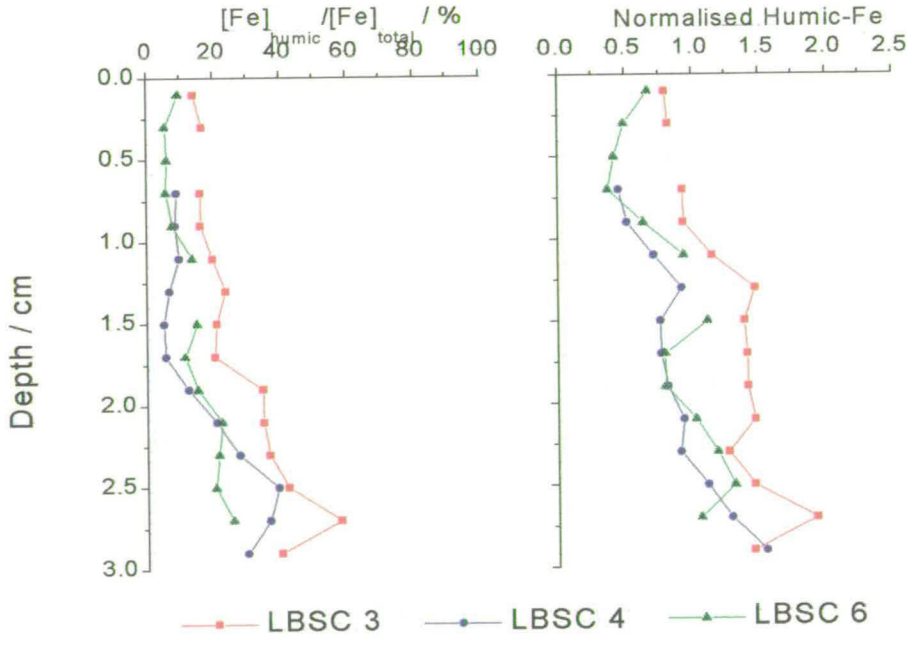


Fig. 6.25: a) humic-associated Fe as a percentage of total Fe and b) Fe-humic (mg kg^{-1} humic material normalised to total Fe in the sediment) in the 0 - 3 cm Group II cores (LBSC 3, 4 and 6)

Group III

LBSC 7 shows very little change with depth in the percentage of the total Fe that is humic-associated, although there is a slight maximum at ~ 1.3 - 1.7 cm, the same depth as for the Mn-humic peak (Fig. 6.26 a).

The normalised Fe profile in LBSC 7 shows a minimum at the surface, increasing to a plateau at ~ 0.9 cm, thereafter interrupted only at ~ 1.7 cm, where a maximum is observed (Fig. 6.26b).

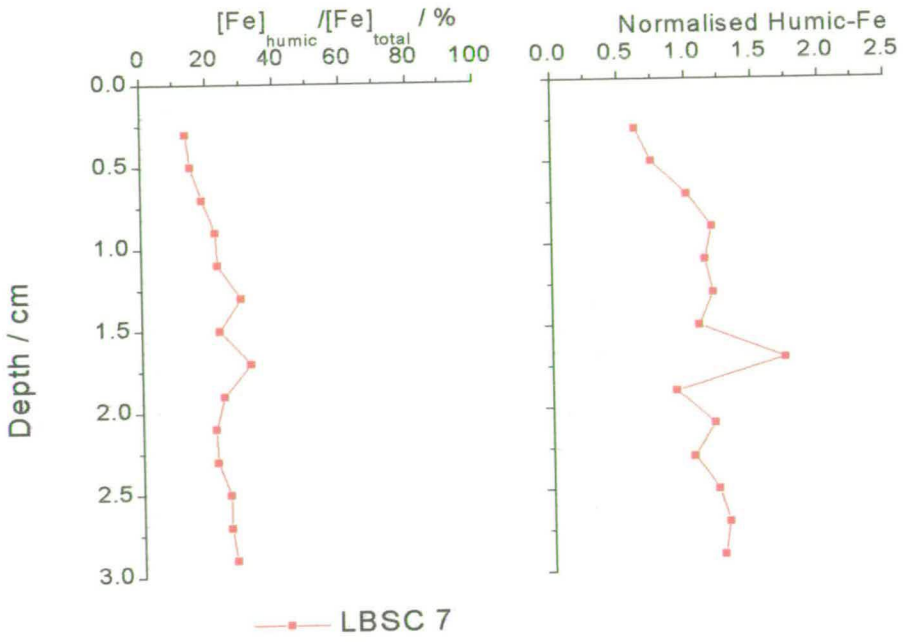


Fig. 6.26 : a) humic-associated Fe as a percentage of total Fe and b) Fe-humic (mg kg^{-1} humic material normalised to total Fe in the sediment) in the 0 - 3 cm Group III cores (LBSC 7)

Group IV

Again, as for Mn, there are strong similarities between LBSC 8, 9 and 10, with an increase in the percentage of the Fe that is humic-associated from 10 - 20 % to 30 - 40 % occurring at 1.5 cm (Fig. 6.27 a).

Similar to the percentage of Fe that is humic-associated, the normalised Fe values for LBSC 8, 9 and 10, increasing below ~ 1.3 - 1.7 cm (Fig. 6.27 b).

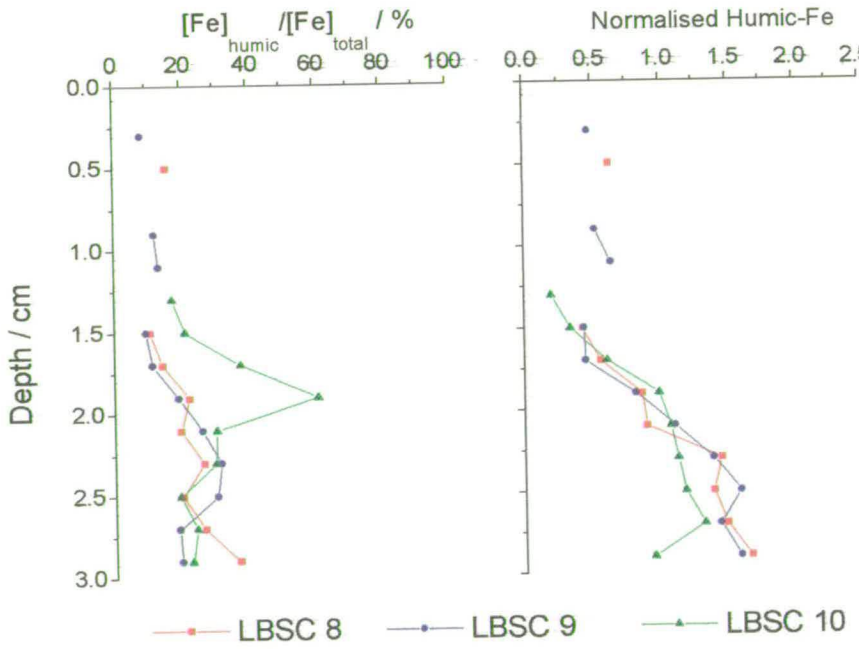


Fig. 6.27: a) humic-associated Fe as a percentage of total Fe and b) Fe-humic (mg kg^{-1} humic material normalised to total Fe in the sediment) in the 0 - 3 cm Group IV cores (LBSC 8, 9 and 10)

6.3.3.3 Manganese and Iron

A common feature of all cores is the lower percentage association of Mn with humic substances in the 0 - 1 cm sections compared with the 1 - 3 cm sections. With the exception of LBSC 2, 3 and 7, this value is < 5 % of the total Mn. Values for the 1 -

3 cm sediments range from 15 - 50 % of the total Mn. The Mn / Fe ratio for humic materials extracted from 0 - 1 cm sediments is also significantly lower than that for the 1 - 3 cm sediments (Table 6.8). It should be noted that the 0 - 1 cm sediments contain the redox enrichment of Mn, i.e. Mn is present predominantly in the solid phase as $Mn(IV)O_2$.

		LBSC 1	LBSC 2	LBSC 3	LBSC 4	LBSC 5	LBSC 6	LBSC 7	LBSC 8	LBSC 9	LBSC 10
Mn-humic (% tot Mn)	0-1 cm	2.9 ± 1.0	10.9 ± 2.0	8.7 ± 3.8	1.1 ± 03	3.0 ± 1.3	1.1 ± 0.6	12.1 ± 10.5	2.1	0.9 ± 0.6	-
	1-3 cm	47.4 ± 32.7	23.8 ± 5.3	40.9 ± 20.2	16.0 ± 6.8	29.5 ± 8.8	20.4 ± 9.0	31.8 ± 4.4	23.4 ± 10.9	17.7 ± 9.2	18.7 ± 5.9
	0-3 cm	39.3 ± 34.4	20.1 ± 7.6	31.7 ± 22.6	13.5 ± 8.5	23.4 ± 13.9	13.0 ± 12.0	26.2 ± 11.1	21.0 ± 12.4	14.6 ± 10.7	18.7 ± 5.9
Fe-humic (% tot Fe)	0-1 cm	15.9 ± 9.2	32.3 ± 2.7	15.5 ± 1.1	6.7 ± 0.2	26.6 ± 7.3	6.8 ± 1.6	17.2 ± 3.9	15.4	10.1 ± 2.6	-
	1-3 cm	29.3 ± 15.5	35.1 ± 6.1	33.0 ± 12.4	15.9 ± 5.5	33.9 ± 6.0	17.9 ± 5.1	25.6 ± 3.5	21.8 ± 8.1	19.7 ± 8.0	17.4 ± 7.5
	0-3 cm	26.9 ± 15.1	34.3 ± 5.4	28.0 ± 13.2	14.4 ± 6.1	29.9 ± 9.7	13.6 ± 6.9	23.2 ± 5.2	21.1 ± 7.8	17.9 ± 8.2	17.4 ± 7.5
Mn-humic / Fe-humic	0-1 cm	0.02 ± 0.01	0.03 ± 0.01	0.06 ± 0.01	0.08 ± 0.02	0.04 ± 0.01	0.04 ± 0.01	0.08 ± 0.03	0.05	0.07 ± 0.01	-
	1-3 cm	0.09 ± 0.06	0.07 ± 0.02	0.09 ±0.02	0.16 ± 0.04	0.09 ± 0.03	0.09 ± 0.03	0.17 ± 0.03	0.10 ± 0.03	0.15 ± 0.04	0.19 ± 0.03
	0-3 cm	0.08 ± 0.06	0.06 ± 0.02	0.08 ± 0.02	0.15 ± 0.02	0.08 ± 0.04	0.07 ± 0.03	0.14 ± 0.05	0.09 ± 0.04	0.13 ± 0.05	0.19 ± 0.03

Table 6.8: Average percentage association of Mn and Fe with humic substances and Mn/Fe ratio for humic substances extracted from 0 - 1 cm, 1 - 3 cm and 0 - 3 cm Loch Bradan sediment.

There is some correlation between the concentration of humic substances and the amount of humic-bound Mn. This is evident from 0 - 3 cm data, but closer examination of the data again provides contrast between 0 - 1 cm and 1 - 3 cm sections, with particularly strong correlation for 1 - 3 cm sediments (Fig. 6.28).

There is also a clear difference between western and eastern basins, with the stronger correlation between Mn-humic complexation and total humic substance concentrations being observed for the eastern basin cores, particularly LBSC 8 - 10 (Fig. 6.28).

Although the percentage association of Fe with humic substances is lower in the 0 - 1 cm sediment (5 - 15 %) compared with the 1 - 3 cm sediments (15 - 35 %) (Fig. 6.29), this trend is not as marked as that observed for Mn. The lower Mn/Fe ratio in humic substances from 0 -1 cm sediments compared with that from 1 - 3 cm sediments (Table 6.8) also suggests that relatively more Fe is bound to humic substances in the 0 - 1 cm sediments.

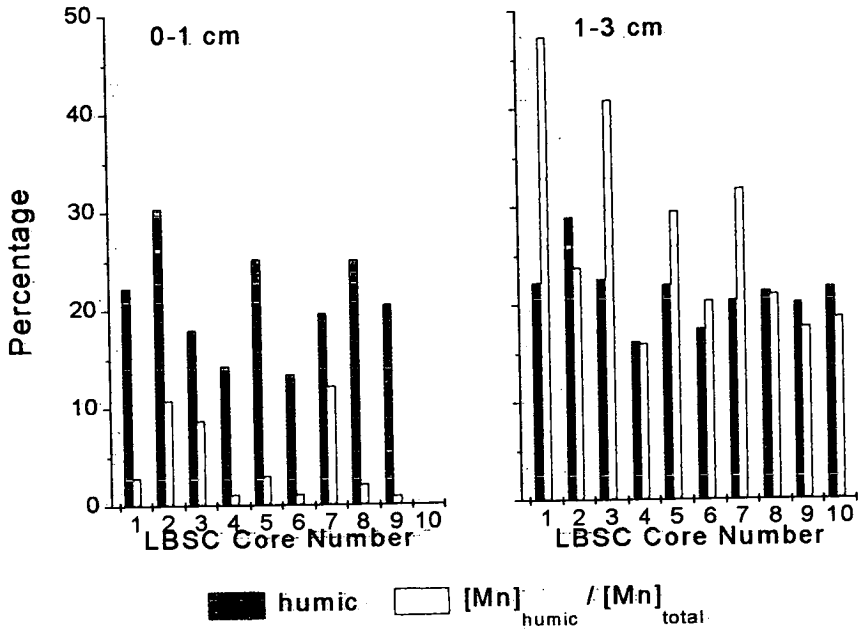


Fig. 6.28 : Bar chart showing average percentage association of Mn with humic substances and the average percentage of humic substances a) in the 0 - 1 cm sediments and b) in the 1 - 3 cm sediments.

As for Mn, there appears to be some relationship between Fe-humic complexation and total humic substances, especially for 1 - 3 cm sediments and for the eastern basin, particularly LBSC 8 - 10 (Fig. 6.29).

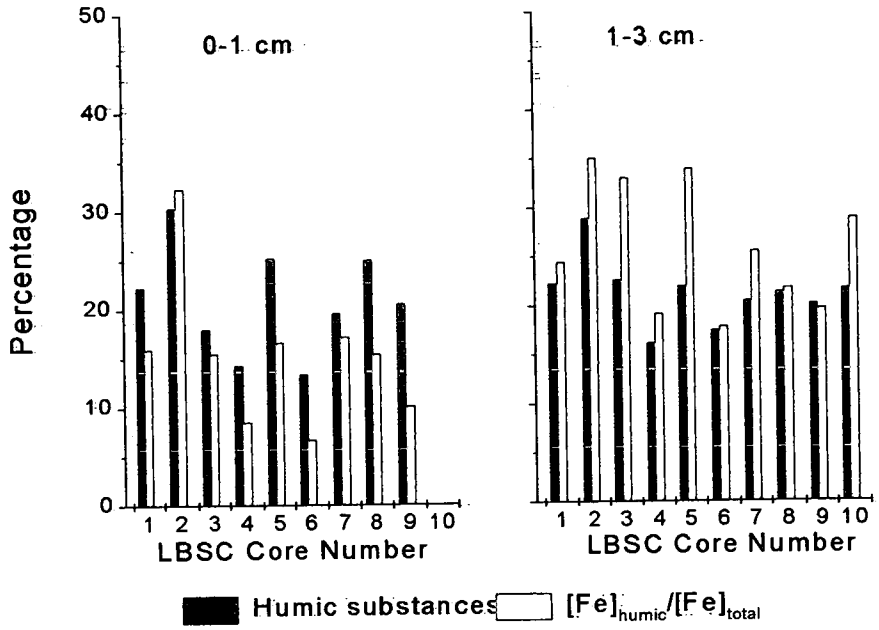


Fig. 6.29: Bar chart showing average percentage association of Fe with humic substances and the average percentage of humic substances a) in the 0 - 1 cm sediments and b) in the 1 - 3 cm sediments.

6.3.4 Concentration of Humic-Associated Manganese and Iron in the Loch Bradan Long Core, LBSC 6

As described for 0 - 3 cm LBSC 6 sediment, minimum concentrations of humic-associated Mn and Fe are observed in the 0 - 1 cm sediment, increasing below 1.7 cm to ~ 1800 mg kg^{-1} and ~ 2 % dry weight of sediment, respectively, at ~ 2 cm (Fig. 6.30). The humic Mn/Fe ratio in the 0 - 1 cm sediment is very different from that of the total sediment, whereas in the 2 - 3 cm section the ratio of humic-associated Mn/Fe is very similar to that of the total sediment (Table 6.9, Fig. 6.31). The increase in concentration of humic-associated Mn and Fe continues below 3 cm to ~ 2200 mg kg^{-1} and ~ 3 % dry weight sediment, respectively, at ~ 5 cm (Fig. 6.30). There is little change in these concentrations in the 5 - 15 cm zone of the sediment.

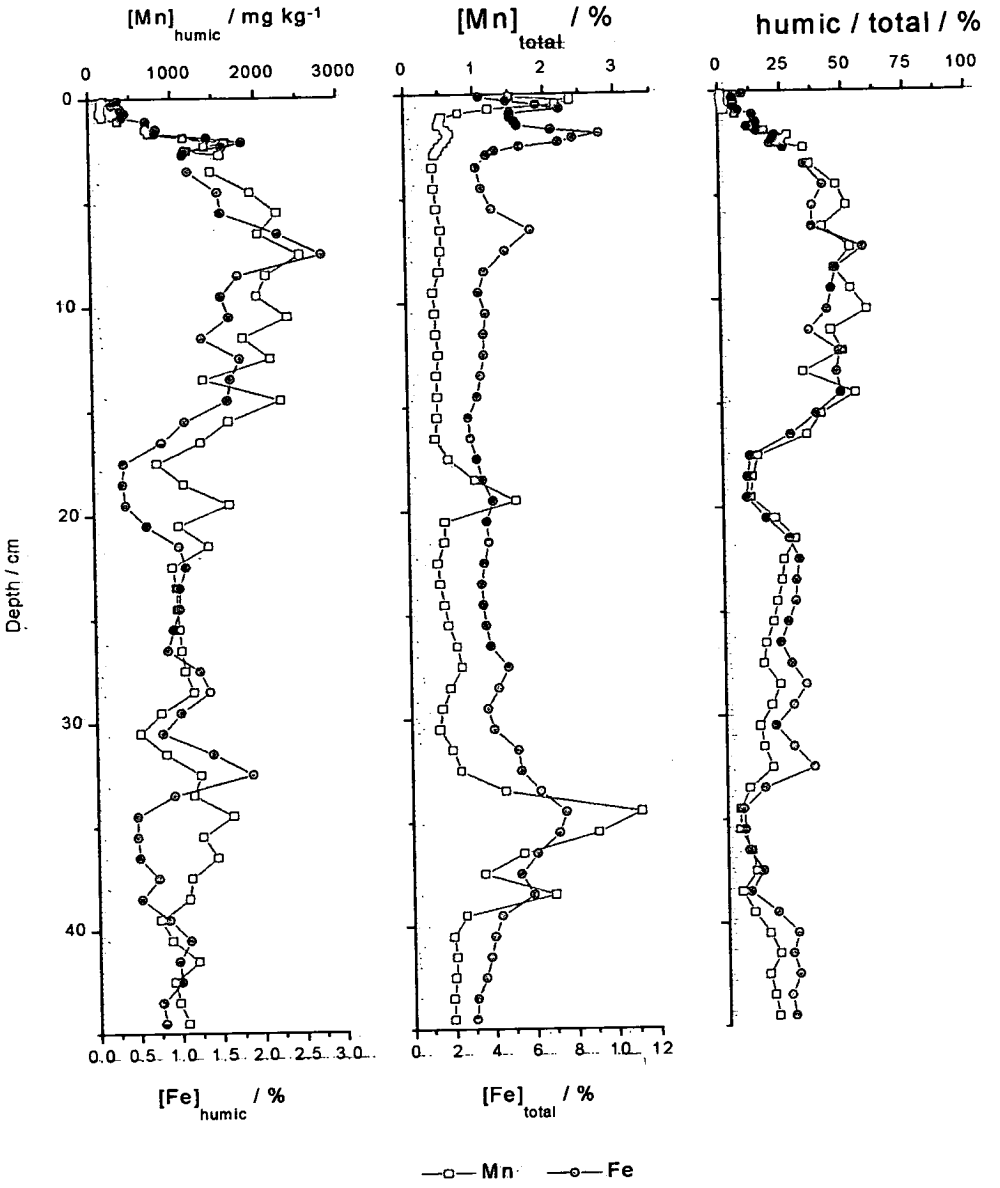


Fig. 6.30: Humic-associated and total Mn and Fe, and the percentage of total Mn and Fe that is humic associated in LBSC 6.

Depth / cm	Mn Peak	Fe Peak	Mn/Fe (humic substances relative to sediment values
0-3	✓	✓	<<
5-15			=/>
18-20	✓	✗	>
22-30			<
32-39	✓	✓	</=
41-45			<

Table 6.9: Variation in Mn/Fe ratio for humic substances extracted from long core LBSC 6 and proximity of changes in the ratio to major Mn and Fe peaks in the sediment.

There is a major change in the proportion of total Mn that is humic-associated at the position of the Mn sediment peak at ~ 20 cm (Fig. 6.30), which coincides with the position of a minimum in the percentage humic substances (Fig. 6.6). In addition there is a decrease in the percentage of total Fe that is humic-associated despite the absence of a peak in total Fe at this depth (Fig. 6.30). These variations are accompanied by a large increase in the Mn/Fe ratio for the extracted humic substances, similar to that observed for total Mn/Fe (Fig. 6.31).

In the 20 - 30 cm zone, the humic-associated Mn/Fe is lower than the total Mn/Fe ratio, more so with increasing depth (Fig. 6.31), i.e. relatively less Mn than Fe is associated with humic substances in this zone than was observed in the nearer surface zones.

A final major feature is the reduction in the proportion of total Mn and Fe associated with humic substances at the position of the deep sub-surface Mn and Fe peaks (Fig. 6.30). Mn/Fe ratio for extracted humic substances is again markedly increased at this depth, but this increase is slightly lower than for the total Mn/Fe ratio (Fig. 6.31).

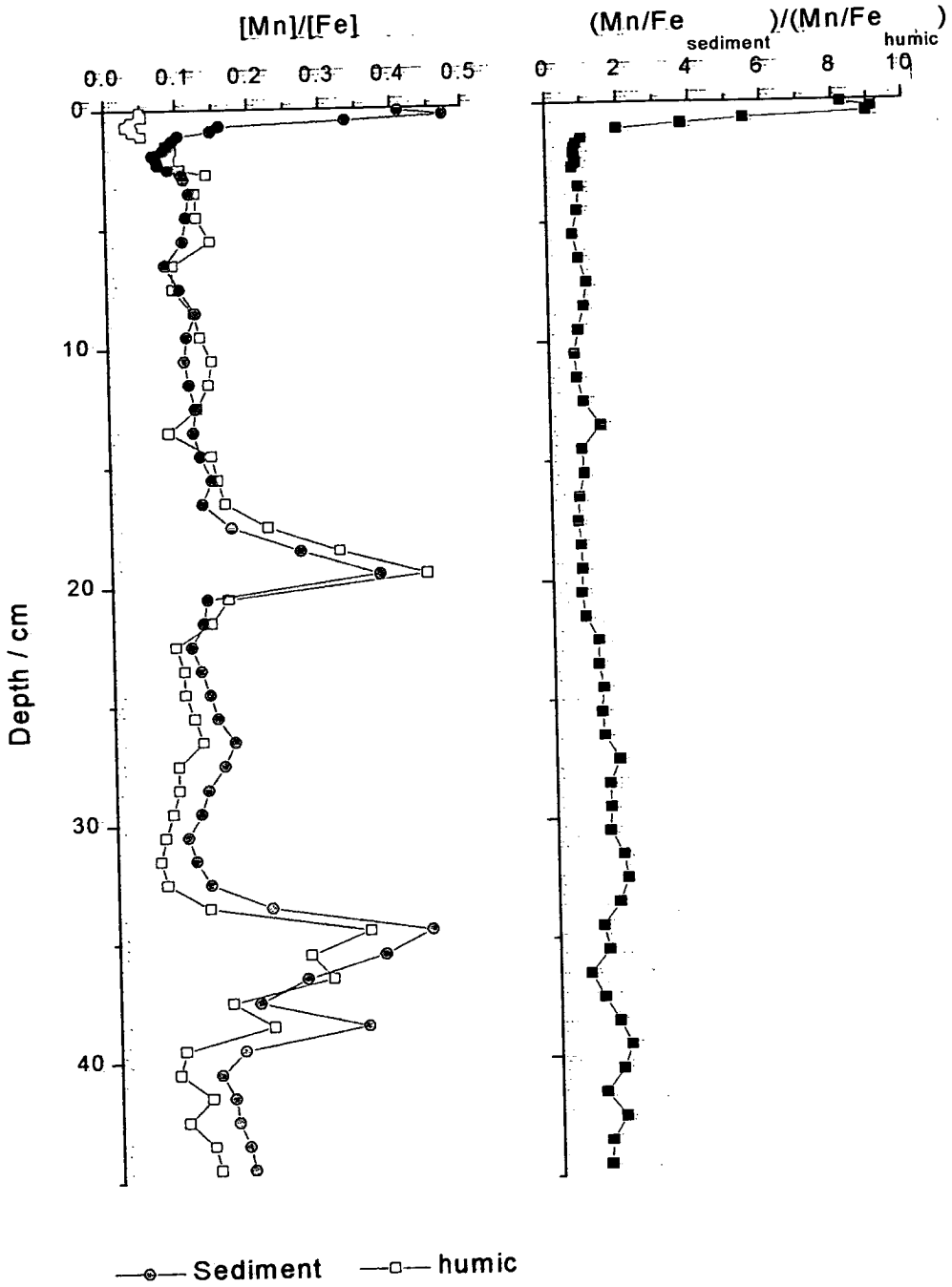


Fig. 6.31 : Mn/Fe ratio in the sediment relative to Mn/Fe for humic substances extracted from LBSC.

6.3.4.1 Association of Manganese and Iron With Humic Substances as a Percentage of Total Manganese and Iron, Respectively, in LBSC 6

The percentage of the total Mn that is associated with humic substances increases from a minimum of < 5 % in the top 1 cm of the sediment to a maximum of ~ 50 % at 5 cm (Fig 6.32a). This percentage stays approximately constant to a depth of ~ 15 cm, below which it decreases to a minimum of ~ 10 % at 17 - 20 cm (Fig. 6.32 a), the same region as the Mn enrichment (Fig. 4.2a). Below 20 cm the percentage increases to 20 - 30 %, with another minimum occurring at 30 - 40 cm (Fig. 6.32), the depth of the total Mn and Fe enrichments (Fig. 4.2a).

The normalised value shows a minimum at the surface of the sediment which increases to a depth of ~ 3 cm (Fig. 6.32b). Between 3 cm and 20 cm the only regions where the value deviates greatly are at ~ 13 cm and 20 cm where minima are exhibited. Below 20 cm the normalised value shows a general decrease, with marked minima between 30 and 40 cm.

The percentage of total Fe that is associated with humics shows a very similar pattern as that of Mn, with minima at the surface, at ~ 20 cm and between 30 - 40 cm (Fig 6.33a).

As with the percentage of total Fe that is humic-associated, the normalised humic-Fe value shows minima positioned at the surface, at ~ 20 cm and between 30 - 40 cm (Fig 6.33b).

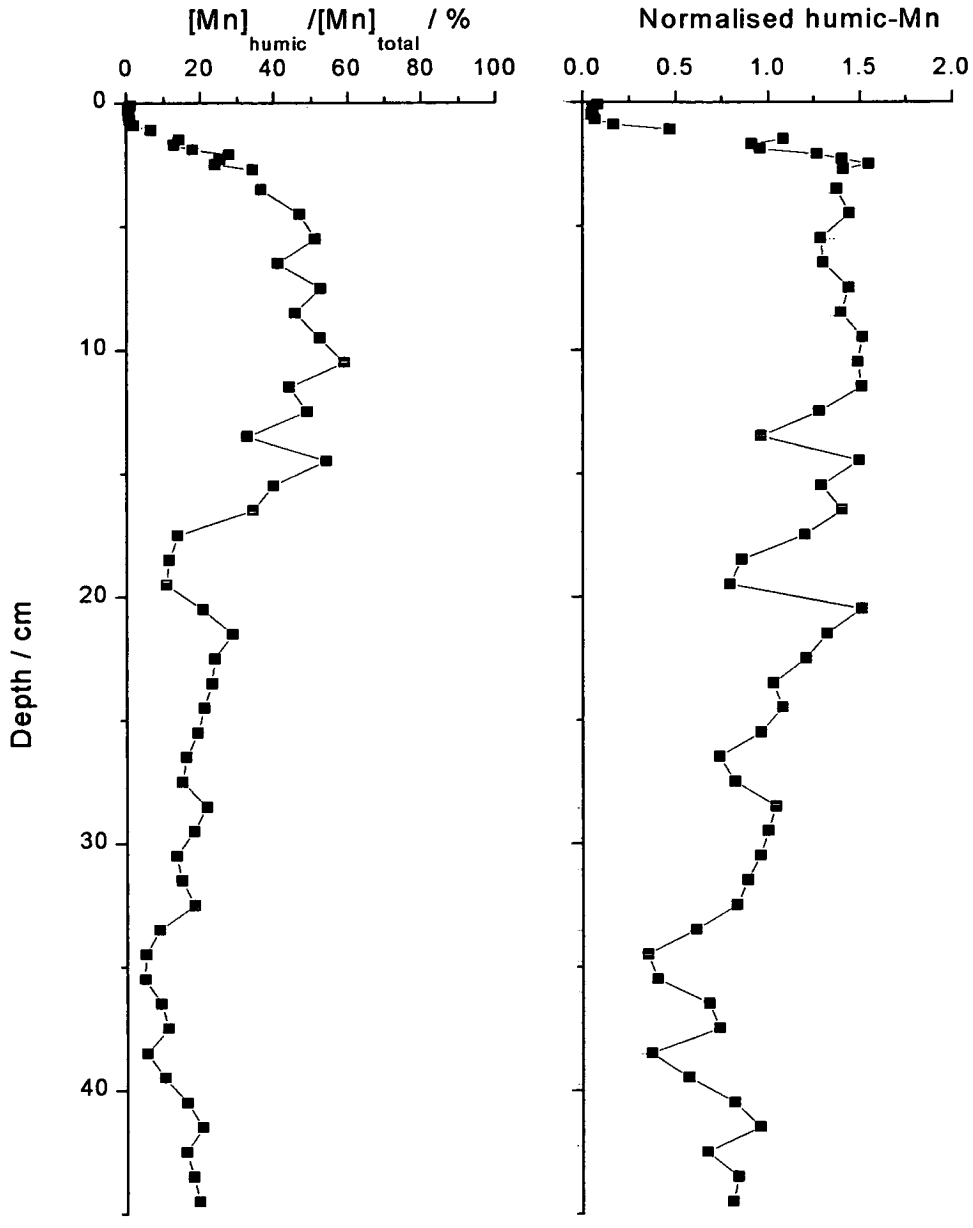


Fig. 6.32: a) Humic associated Mn as a percentage of total Mn and b) Mn-humic (mg kg^{-1} humic material normalised to total Mn in the sediment) in 0 - 45 cm sediments of LBSC 6

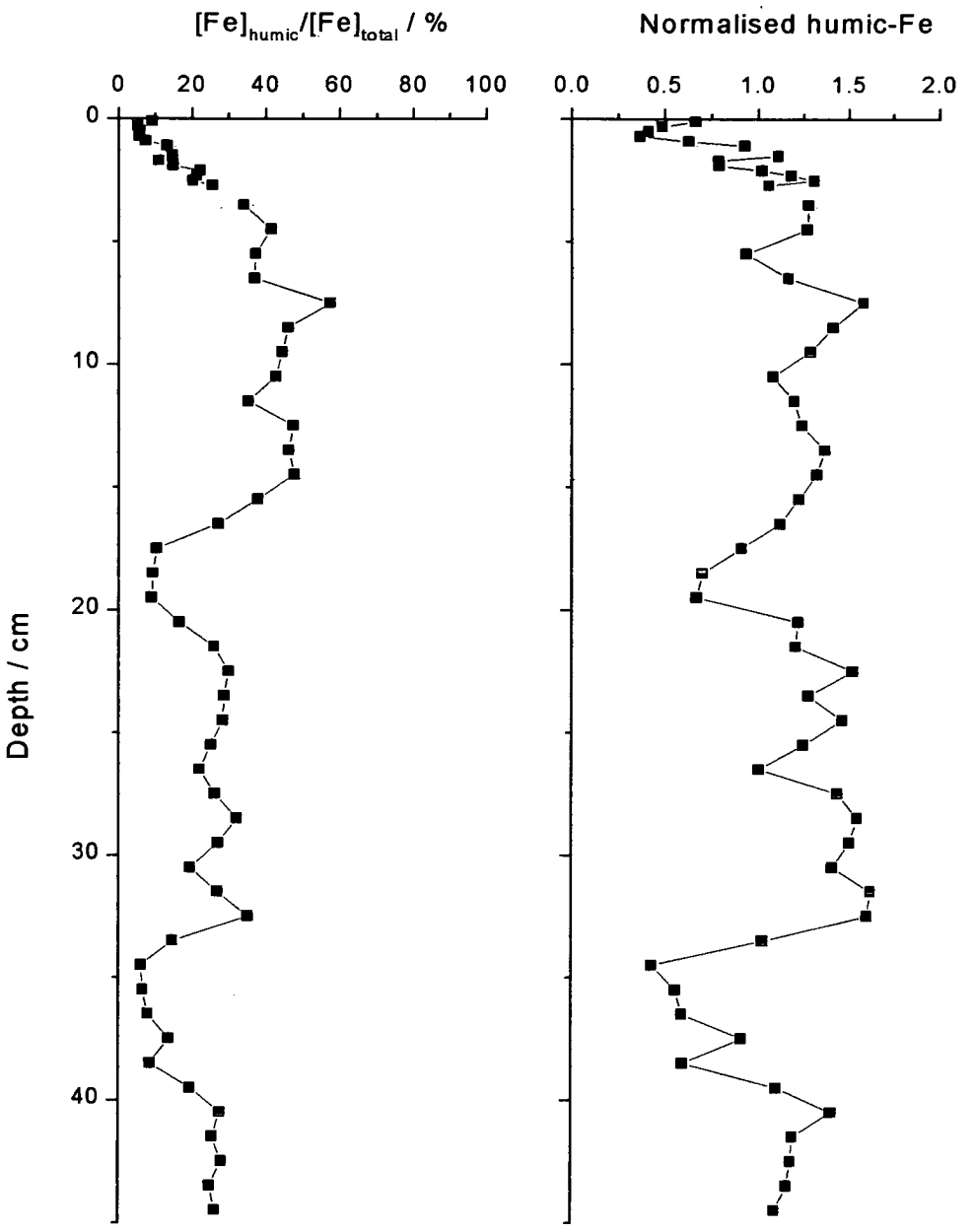


Fig. 6.33: a) Humic associated Fe as a percentage of total Fe and b) Fe-humic (mg kg^{-1} humic material normalised to total Fe in the sediment) in 0 - 45 cm sediments of LBSC 6

6.3.5 Concentration of Humic-Associated Manganese and Iron in 0 - 3 cm Loch Riecawr Sediment (LRSC 1 - 2)

In contrast with all of the Loch Bradan sediment cores, the concentration of humic-associated Mn in LRSC 1 clearly decreases with depth, and indeed the shape of the depth profile is very similar to that of the total Mn (Fig 6.34). The maximum concentration, ~ 500 mg kg^{-1}, occurs in the 0 - 1 cm zone and is up to four times lower than maximum Loch Bradan concentrations.

There is also a decrease with depth for humic-associated Fe, although there is a small increase in the concentration below the sediment redox enrichment, with the maximum concentrations a factor of two to four lower than those in Loch Bradan (Fig 6.35).

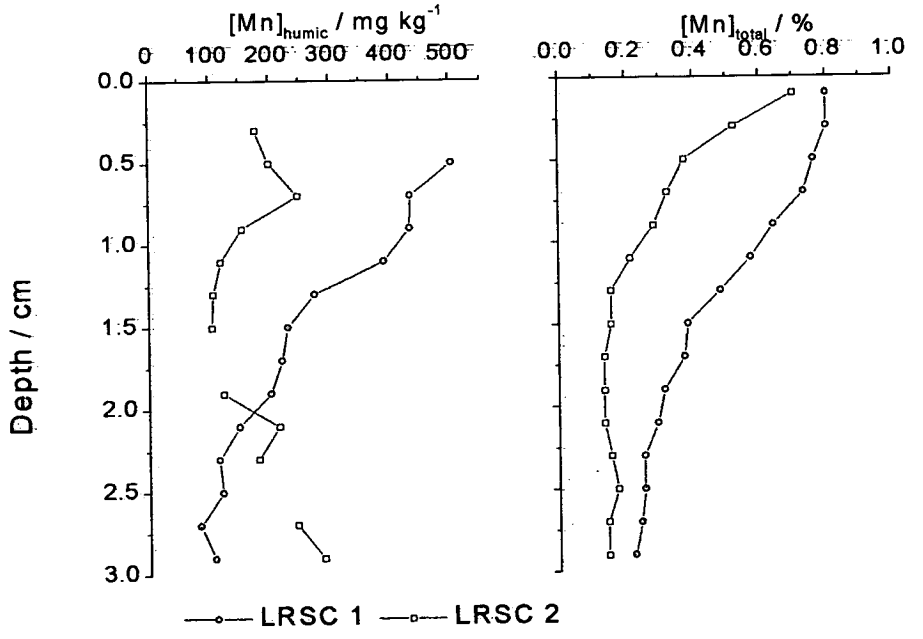


Fig. 6.34 : Humic-associated and total Mn LRSC 1 and 2.

LRSC 2 is again different from the Loch Bradan sediment cores in that the maxima in humic-associated Mn and Fe occur at the position of the sediment redox enrichment of Fe (Figs. 6.34, 6.35). Below the maxima, LRSC 2 is more like the Loch Bradan

profiles than LRSC 1, with low values in the 1 - 2 cm zone and maxima in the 2 - 3 cm zone of ~ 300 mg kg^{-1} and ~ 0.8 % dry weight of sediment for Mn and Fe, respectively.

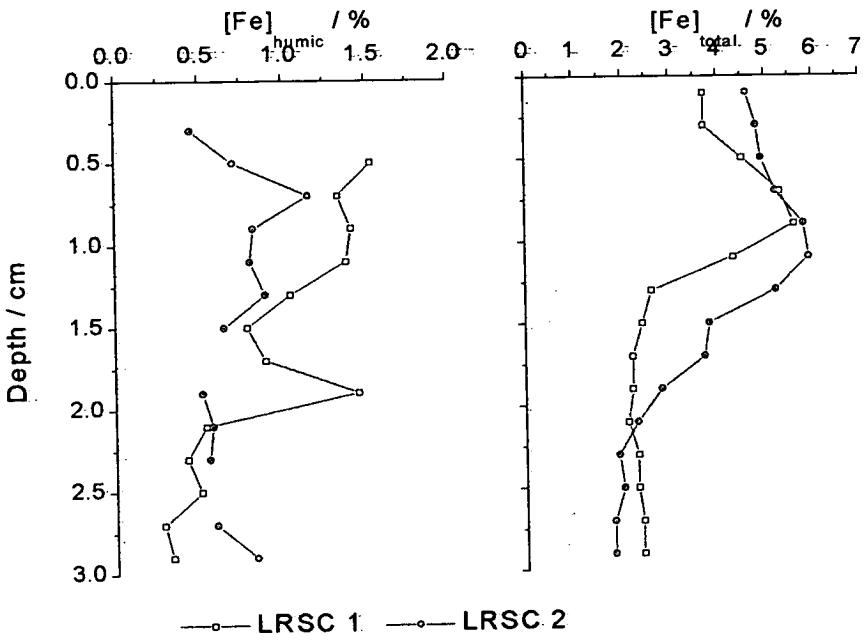


Fig. 6.35 : Humic-associated and total Fe in LRSC 1 and 2.

6.3.5.1 Association of Manganese and Iron With Humic Substances as a Percentage of Total Manganese and Iron, Respectively, in the Sediments of Loch Riecawr

The percentage of Mn that is humic-associated in the top 3 cm of sediment from LRSC 1 is unlike the results for Loch Bradan, with a low, and approximately constant value of ~ 5 % (Fig. 6.36a). LRSC 2 is more like Loch Bradan in that a low percentage, ~ 5 %, is observed in the top 0 - 1.5 cm of sediment, increasing to > 20 % below (Fig 6.36a)

The normalised humic-Mn value for LRSC 1 is also unlike the results obtained in Loch Bradan in that the value is approximately constant over the 0 - 3 cm section of the sediment (Fig. 6.36b). LRSC 2 is again similar to Loch Bradan with respect to

the normalised humic-Mn value, low values at the surface increasing below 1.5 cm (Fig. 6.36b).

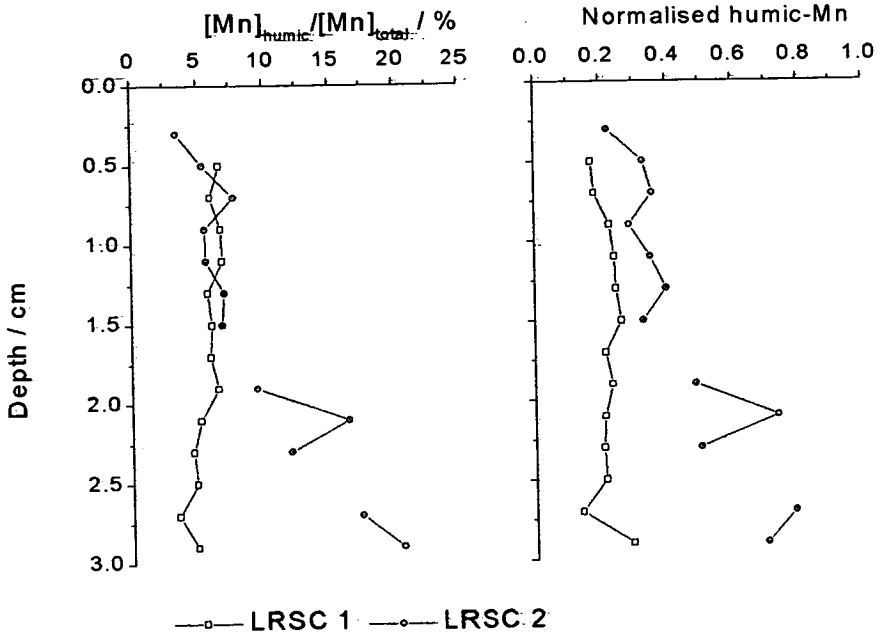


Fig. 6.36 : a) Humic associated Mn as a percentage of total Mn and b) Mn-humic (mg kg^{-1} humic material normalised to total Mn in the sediment) in 0 - 3 cm sediments of LRSC 1 and 2.

The percentage of the total Fe that is humic-associated in LRSC 1 shows a maximum at the surface, below which it decreases, with the exception of a peak at ~ 2 cm (Fig. 6.37a). LRSC 2 shows a minimum percentage of total Fe associated with humics in the top 0 - 1 cm of the sediment, with an increase below 1 cm (Fig. 6.37a).

The normalised humic-Fe profiles for both LRSC 1 and 2 show little variation with depth, with the exception of sharp peaks at ~ 2 cm in LRSC 1 and ~ 1.2 cm in LRSC 2 (Fig. 6.37b).

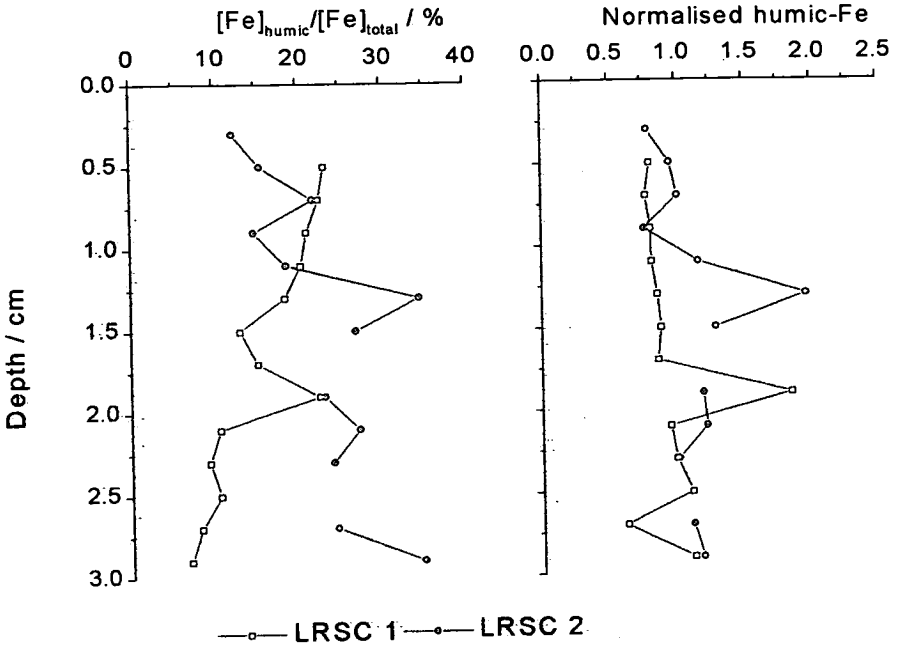


Fig. 6.37 : a) Humic associated Fe as a percentage of total Fe and b) Fe-humic (mg kg^{-1} humic material normalised to total Fe in the sediment) in 0 - 3 cm sediments of LRSC 1 and 2.

6.4 Discussion of Humic-Associated Manganese and Iron in Loch Bradan (LBSC 1 - 10) and Loch Riecawr (LRSC 1 - 2) Sediment

6.4.1 Humic-Associated Manganese in 0 - 3 cm Loch Bradan Sediment (LBSC 1 - 10)

In the 0 - 1 cm section of Loch Bradan sediment it is clear that redox conditions control the behaviour of Mn, with the key process being the oxidation of dissolved Mn(II) to Mn(IV) and the precipitation of $Mn(IV)O_2$. The association of Mn with humic substances is weak and so Mn(II) is readily released from the humic substances present to solution, i.e. Mn(II) species. Removal of Mn(II) from solution by oxidation will result in the release of more humic-bound Mn to re-establish

equilibrium, i.e. the net effect is enrichment of $Mn(IV)O_2$ in the solid phase of the sediment.

Cores LBSC 2, 3 and 7 appear to have greater Mn-humic association in 0 - 1 cm section (5 - 15 % compared with 0 - 5 % at the other sites) and also have a surface (0.0 - 0.2 cm) enrichment of total Mn. These factors may be important for the release of Mn-humic complexes to the water column, particularly if the maximum enrichment does actually move into the water column, because some of the humic complexes may be present in solution phase.

For all other cores, a major process is the retention of significant proportions of Mn within the sediment as a result of redox cycling of Mn, leading to solid phase enrichments of Mn.

Within the top 3 cm there is generally a good correlation between the base of the enriched zone of Mn and the onset of the increase in importance of Mn-humic complexation, e.g. LBSC 6 at 1.1 cm, LBSC 9 at 1.5 cm, suggesting that this is the limit of influence of the redox front, i.e. for the removal of Mn from solution.

6.4.2 Humic-associated Fe in 0 - 3 cm Loch Bradan Sediment (LBSC 1 - 10)

The changes observed with depth over the 0 - 3 cm sections of these cores are in general less than for Mn, as more Fe than Mn is humic-bound in the 0 - 1 cm sections. The positions of the peaks in humic-associated Fe, where present, do not correlate directly with the positions of the sediment total Fe peaks, the increase generally overlapping with the bottom of the diagenetic Fe enrichment. There are some examples of increased humic-Fe occurring at a similar, although not identical, depth as secondary Fe peaks, e.g. LBSC 4 and 6.

The lower Mn-humic/Fe-humic ratio in the 0 - 1 cm section of the sediment indicates that the release of Mn(II) from humic complexes and subsequent oxidation occurs to a greater extent than for Fe.

6.4.3 Humic-Associated Manganese and Iron in the Loch Bradan Long Core, LBSC 6

The behaviour of both humic-associated Mn and Fe in the 0 - 3 cm sediment is the same as described in previous sections (Section 6.4.1 and 6.4.2)

The percentage of humic-bound Mn and Fe increased to 50 - 60 % by 5 cm, and thereafter was unchanged to ~ 20 cm. This is expected on the basis of the high degree of humification of this part of the core (where organic matter is ~ 100 % humic substances).

The peak in total Mn at ~ 20 cm is at the same depth as a minimum in the concentration of humic substances and the humic/organic matter ratio, indicating that the Mn peak at this depth is clearly not humic-associated. There is also a minimum in the percentage association of both Mn and Fe with humic substances. In explanation this would seem to relate to the decrease in the amount of humic material and also possibly due to a change in the speciation of Mn and Fe.

Below ~ 20 cm, however, there is a change in the nature of the organic material, which is much less humified (i.e. smaller proportion of humic substances), explaining the decrease in the percentage association of both Mn and Fe with humic substances. The dependence of this association on the amount of humic material appears to be greater for Mn than for Fe, as seen by the increase in $\{(Mn_{sediment}/Fe_{sediment})\}/\{(Mn_{humic})/(Fe_{humic})\}$ at this depth (Fig. 6.31).

The large sub-surface peaks in sediment Mn and Fe at 33 - 40 cm are likely to be crystalline oxides, on the basis of lack of S at this depth and also past sequential

extraction work (Section 4.2.2). It is notable that in LBSC 6 between 33 and 40 cm the major enrichments are not reflected in peaks in humic-associated Mn and Fe, indicating that the reagent used to extract humic substances does not mobilise the Mn/Fe (hydr)oxides in the sediment at this depth.

6.4.4 Humic-Associated Manganese and Iron in 0 - 3 cm Loch Riecawr Sediment (LRSC 1 - 2)

In LRSC 1 the complexation of Mn by humic substances plays only a minor role in the 0 - 3 cm sediment as shown by the low percentage (< 7%) of the total Mn that is humic-associated at all depths. It is, however, possible that some of the humic-bound Mn in these near-surface sediments may be able to enter the porewaters and subsequently diffuse into the loch water, thereby releasing Mn from the sediment (as described for LBSC 2, 3 and 7).

The significant peak in humic-associated Fe at 1.9 cm in LRSC 1, at the lower edge of the sediment redox enrichment of Fe, indicates the importance of humic substances as complexing agents in the region where Fe is reduced and solubilised. In this particular core, however, the role is transient and is observed in only one 2-mm thick section.

The associations of Mn and Fe with humic substances in LRSC 2 are, unlike LRSC 1, similar to those observed in Loch Bradan, with the associations becoming more important below the redox boundaries for the respective metals. It would therefore appear that the same factors as previously discussed in the sediments of Loch Bradan apply to LRSC 2.

6.4.5 Summary of Manganese and Iron Interactions With Humic Substances in the Sediments of Loch Bradan

- The associations of Mn and Fe with humic substances are weak and are reversible.
- The interactions are most prominent below the redox peaks for Mn and Fe, with only a relatively small proportion of the total Mn and Fe being associated with humic substances in the 0-1 cm section of the sediment.

6.5 Manganese and Iron in the Sediment Porewater, Water Column and Feeder Stream Waters of Loch Bradan

6.5.1 Manganese and Iron Concentrations and Associations in Porewaters and Sediments from a Loch Bradan Sediment Core, LBPW 1 (Near LBSC 4)

As for all other cores, there is a redox enrichment of Mn in the 0 - 1 cm sediment in LBPW 1 (Fig. 6.38 a). Also similar to a number of other cores there is a slight redox enrichment of Fe in the 0 - 1 cm sediment (Fig. 6.38 b, Appendix 18).

The porewater profiles are typical for relatively shallow well-oxygenated lakes, with a maximum concentration of Mn and Fe at depth which decreases towards the surface, with the Fe decrease being more rapid than the Mn (Fig. 6.38). There is clearly a very low concentration of both Mn and Fe in the 0 - 1 cm porewater, the position of the redox enrichments, which is consistent with the oxidation of Mn and Fe and removal from the aqueous phase.

Comparison of the Mn/Fe ratio in the porewater and sediment of LBPW 1 shows that the values are consistently higher, approximately three times, in the porewater compared with the sediment. The one exception to this is the 0 - 1 cm sediment where the Mn/Fe ratio was found to be an order of magnitude greater in the porewater compared with the sediment (Fig. 6.39).

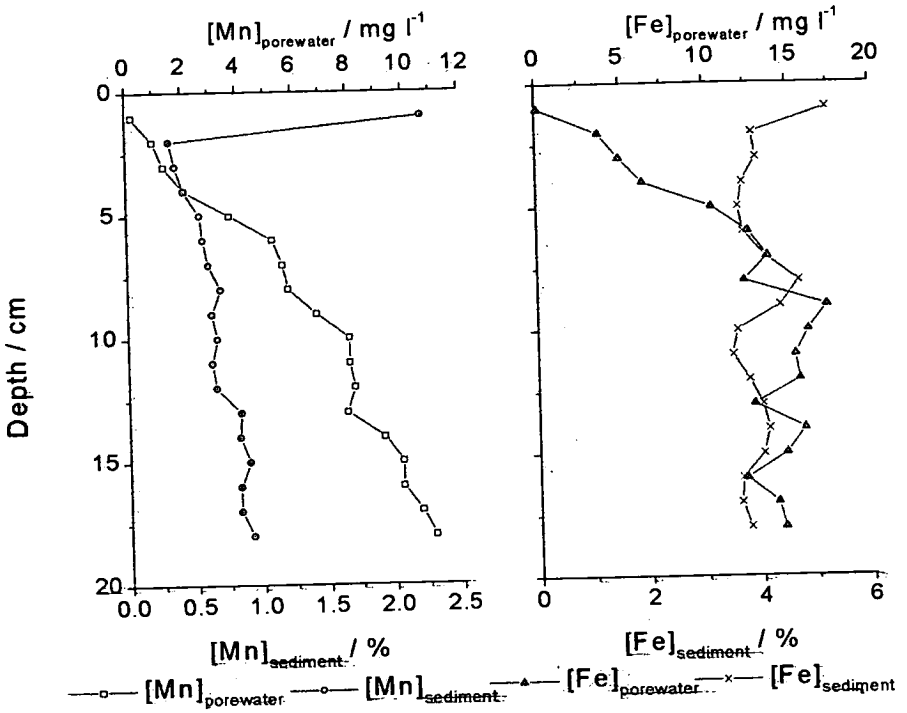


Fig. 6.38 : Sediment and Porewater profiles for a) Mn and b) Fe in LBPW 1 (N.B. 1-cm sections).

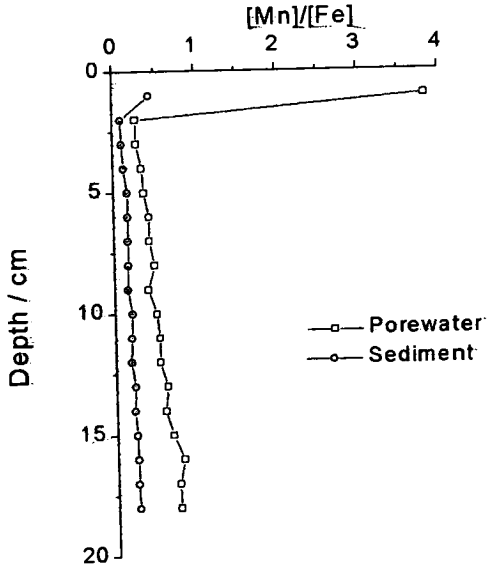


Fig. 6.39 : Sediment and porewater Mn/Fe ratios for LBPW 1 (N.B. 1-cm sections)

Partitioning of the Mn into < 1 kDa (truly dissolved) and > 1 kDa (humic-complexed) size fractions shows that:

1. ~ 35 % Mn was humic-complexed in the 0 - 1 cm zone which is in strong contrast to typical values of < 5 % in the 0 - 1 cm sediment,
2. in the 1 - 3 cm sediment, ~ 16 - 17 % of the Mn was humic-complexed, a factor of two lower than the 0 - 1 cm value,
3. in the 3 - 12 cm section, the humic-complexed portion comprised ~ 20 - 25 % before decreasing again to 16 - 20 % in the remaining samples (Fig. 6.40).

The association of Mn with humic substances described in 2 and 3 is similar to that observed in the total sediment (not as extreme as LBSC 6, but nevertheless an increase to a near constant value in the 5 - 13 cm zone, then a decrease below this).

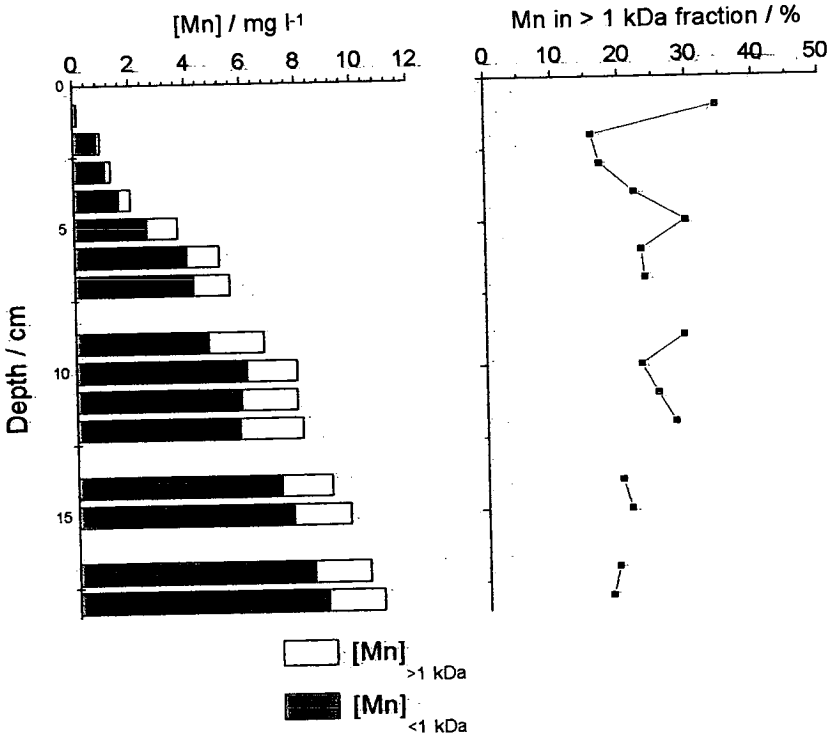


Fig. 6.40 : Porewater Mn in < 1 kDa and > 1 kDa size fractions for LBPW and the percentage in the > 1 kDa size fraction (N.B. 1-cm sections).

6.5.2 Concentration and Associations of Manganese And Iron in the Loch Bradan Water Column

The average total dissolved Mn concentration in surface waters over the sampling period was 0.12 ± 0.02 mg l^{-1} (Appendix 18, Table 6.10), which is in excess of the EC MAC of 0.05 mg l^{-1}. This is a frequent occurrence, with the concentration of dissolved Mn in the water extracted from Loch Bradan by West of Scotland Water frequently exceeding the EC MAC.

Depth	Ave. Total Dissolved Mn / mg l^{-1}	Ave. Total Dissolved Fe / mg l^{-1}	Ave. Mn/Fe (total dissolved fraction)	Ave. particulate Mn / mg l^{-1}	Ave. particulate Fe / mg l^{-1}	Ave. Mn/Fe (particulate fraction)
Surface	0.12 ± 0.02	0.21 ± 0.04	0.62 ± 0.13	0.18 ± 0.20	3.8 ± 1.4	0.04 ± 0.03
Middle	0.13 ± 0.02	0.25 ± 0.05	0.54 ± 0.16	0.22 ± 0.08	7.1 ± 2.5	0.03 ± 0.01
Bottom	0.17 ± 0.08	0.36 ± 0.12	0.61 ± 0.02	0.99 ± 0.98	12.5 ± 2.7	0.08 ± 0.07

Table 6.10: Average total dissolved and particulate Mn and Fe concentrations and average Mn/Fe ratios for total dissolved and particulate fractions of Loch Bradan water samples.

The average total dissolved Mn concentration in the water immediately overlying the sediment (~ 13 - 15 m below the surface of the loch) is higher than at the two other depths, although there is significant variation (Table 6.10). The average total dissolved Fe concentration is also greater in the bottom waters (0.36 ± 0.12 mg l^{-1}) compared with the surface water (0.21 ± 0.04 mg l^{-1}) (Table 6.10). The Mn/Fe ratio in the water taken from the three different depths was, however, found to be constant.

The concentrations of particulate Mn and Fe are also found to be greater in the bottom waters than in the surface waters. This may be accompanied by a slight increase in the Mn/Fe ratio for particulate matter, but the data available are not conclusive. The Mn/Fe ratio for the particulate matter is, however, significantly lower than the dissolved Mn/Fe ratio at all depths.

Depth	Ave. Mn / mg l^{-1} <1 kDa size fraction	Ave. Fe / mg l^{-1} <1 kDa size fraction	Mn/Fe < 1 kDa size fraction	Ave. Mn / mg l^{-1} >1 kDa size fraction	Ave. Fe / mg l^{-1} >1 kDa size fraction	Mn/Fe > 1 kDa size fraction
Surface	0.06 ± 0.00	0.20	0.30	0.068 ± 0.019	0.21	0.19
Middle	0.058 ± 0.01	0.15	0.33	0.073 ± 0.017	0.18	0.28
Bottom	0.11 ± 0.04	0.29	0.41	0.128 ± 0.04	0.25	0.6

Table 6.12 : Average Mn and Fe concentrations and Average Mn/Fe ratios in < 1 kDa and > 1 kDa size fractions for Loch Bradan water samples.

The partitioning of Mn between truly dissolved ($Mn^{2+}_{(aq)}$, i.e. < 1 kDa) and humic-complexed (Mn^{2+}-humic, i.e. >1 kDa) is such that ~ 50 - 60 % of the Mn is associated with humic substances (Appendix 18, Table 6.11). The ESR spectra confirm this result with the spectra all showing six peaks which are associated with Mn(II). Inorganic Mn(II) would have six fairly symmetrical peaks (Carpenter, 1983) (Fig. 6.41) , unlike those observed in Loch Bradan water. Adbul-Halim *et al.* (1981) found that when Mn(II) interacted with humic molecules the resultant spectra showed a similar form to those observed in this study, caused by relatively low distortion of the symmetry of the electric field about the Mn(II) by the humic molecules (Carpenter, 1983) (Fig. 6.41). Humic substances have been shown to form outer sphere complexes with $Mn(H_2O)_6^{2+}$ (Alberts *et al.*, 1976; Gamble *et al.*, 1977; Lu *et al.*, 1997), resulting in spectra that have the same characteristics as those obtained in this study (Gamble *et al.*, 1977). The ESR does, however, not show any evidence of change in the dissolved humic-Mn associations with depth.

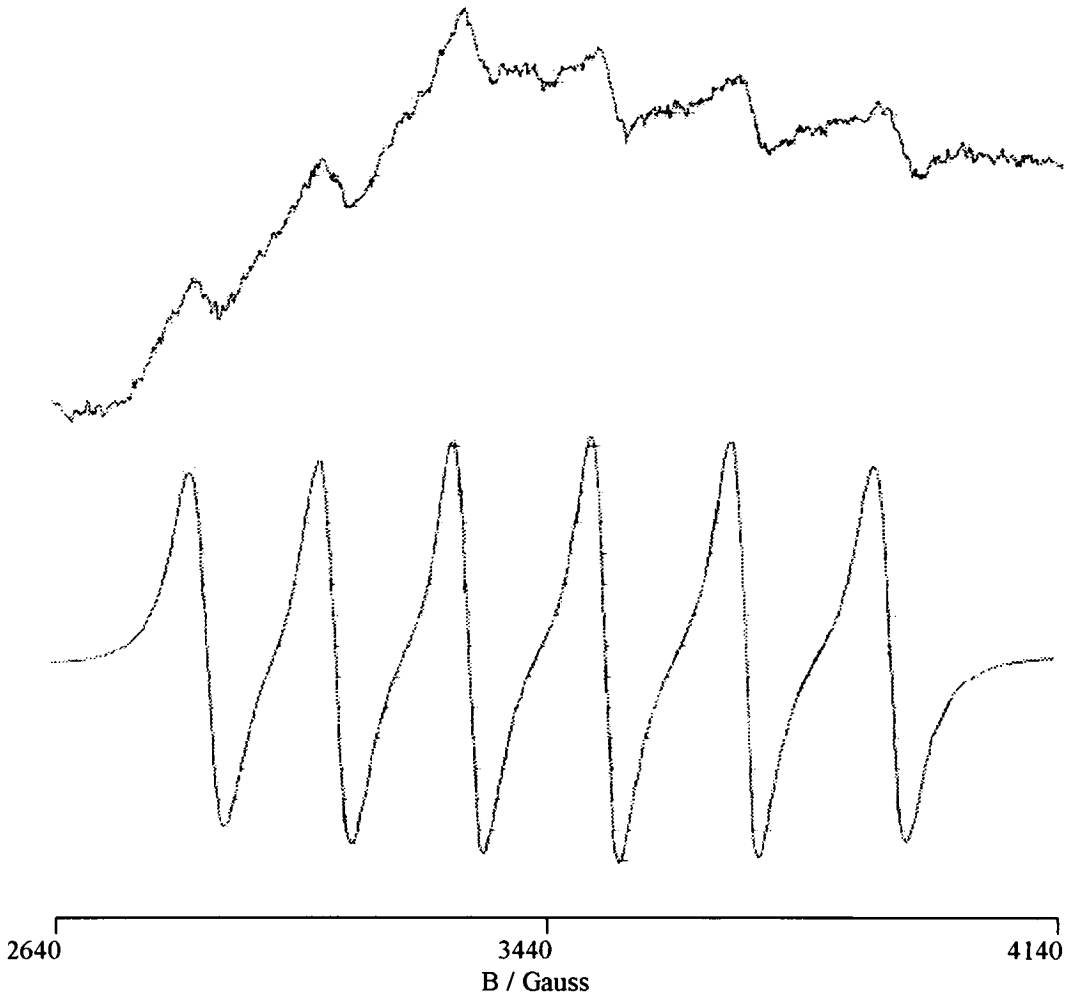


Fig 6.41: ESR spectra of outer-sphere Mn-humic complexes in loch water (upper) and of Mn(II) standard solution (lower), both spectra having the same scale for magnetic field.

A similar result as observed for Mn is seen for Fe, with ~ 45 - 55 % of the dissolved Fe found to be associated with humic substances.

One further piece of information can be obtained from Mn/Fe ratio for the truly dissolved and humic-complexed fractions. From the small amount of data available it appears that the Mn/Fe ratio increases with depth, more significantly in the humic-complexed fraction compared with the truly dissolved fraction (0.2 vs 0.3 in the surface water compared with 0.6 vs 0.4 in bottom waters (Table 6.11)).

6.5.3 Concentrations and Associations of Manganese and Iron in the Feeder Stream Water of Loch Bradan (LBSW 1 - 6)

As previously discussed in Section 5.3.2, the average total dissolved Mn concentration in stream water entering Loch Bradan is 0.095 ± 0.11 mg l^{-1}, showing that there is considerable variability between streams (Appendix 17, Table 6.12). The highest concentrations are typically found in LBSW 3 and 6, both of which have average concentrations higher than the average total dissolved Mn concentrations in the loch water, with the remainder of the streams having average concentrations close to or less than the EC MAC.

Stream	Ave. total dissolved Mn / mg l^{-1}	Ave. total dissolved Fe / mg l^{-1}	Ave. Mn/Fe (total dissolved)	Ave. total particulate Mn / mg l^{-1}	Ave. total particulate Fe / mg l^{-1}	Ave Mn/Fe (particulate)
LBSW 1	0.06 ± 0.04	0.13 ± 0.07	0.45 ± 0.26	0.016 ± 0.013	0.065 ± 0.042	0.22 ± 0.07
LBSW 2	0.03 ± 0.02	0.07 ± 0.04	0.41 ± 0.25	0.007 ± 0.008	0.050 ± 0.050	0.11 ± 0.07
LBSW 3	0.18 ± 0.06	0.66 ± 0.18	0.31 ± 0.16	0.028 ± 0.021	0.81 ± 0.87	0.05 ± 0.03
LBSW 4	0.03 ± 0.02	0.32 ± 0.16	0.11 ± 0.05	0.004 ± 0.001	0.11 ± 0.06	0.04 ± 0.03
LBSW 5	0.03 ± 0.02	0.47 ± 0.14	0.05 ± 0.04	0.004 ± 0.003	0.14 ± 0.001	0.03 ± 0.02
LBSW 6	0.26 ± 0.16	0.58 ± 0.38	0.46 ± 0.10	0.015 ± 0.007	0.23 ± 0.04	0.07 ± 0.04
Average	0.095 ± 0.11	0.36 ± 0.28	0.29 ± 0.23	0.012 ± 0.012	0.23 ± 0.38	0.09 ± 0.08

Table 6.12: Average total dissolved and particulate Mn and Fe concentrations and average Mn/Fe ratios for total dissolved and particulate fractions of stream waters entering Loch Bradan.

The average total dissolved Fe concentration in stream water LBSC 1 - 6 is 0.36 ± 0.28 mg l^{-1}, again showing that there is a high degree of variability between streams (Table 6.12). As with the Mn, the highest concentrations are again typically found in LBSC 3 and 6 (LBSW 5 is also high), both having average concentrations higher than the average total dissolved Fe concentrations observed in the loch water at all depths. This is partially true for most of the remaining streams (compared with the surface water dissolved Fe concentrations), the only stream with lower average values being LBSW 2.

The average dissolved Mn/Fe ratio in the stream waters is lower than in the loch water. As observed for the loch water, however, the Mn/Fe ratio for stream water particulates is much lower than that for the total dissolved fraction.

Stream	Dissolved Mn / mg l^{-1}	Dissolved Fe / mg l^{-1}	Mn/Fe (dissolved)	humic-Mn / mg l^{-1}	humic-Fe / mg l^{-1}	humic Mn/Fe
LBSW 1	0.06	0.13	0.46	0.04	0.16	0.25
LBSW 2	0.01	0.13	0.08	0.02	0.11	0.18
LBSW 3	0.11	0.31	0.35	0.10	0.41	0.24
LBSW 4	0.04	0.26	0.15	0.04	0.31	0.13
LBSW 5	0.04	0.33	0.12	0.03	0.34	0.09
LBSW 6	0.28	0.44	0.64	0.14	0.51	0.27
Average	0.09 ± 0.10	0.27 ± 0.12	0.3 ± 0.2	0.06 ± 0.05	0.31 ± 0.15	0.2 ± 0.07

Table 6.13: Average Mn and Fe concentrations and average Mn/Fe ratios in < 1 kDa and > 1 kDa size fractions from stream waters entering Loch Bradan.

The average truly dissolved Mn concentration of 0.09 ± 0.1 mg l^{-1} (Table 6.13) is slightly lower than the average concentration in the surface and middle depth loch water (Table 6.10). The average humic-complexed Mn concentration of 0.06 ± 0.05 mg l^{-1} is very similar to those of the surface and middle depth loch water. The average truly dissolved and humic-complexed Fe concentrations are slightly greater than those for the loch water. About 45 - 55 % of the total dissolved Mn and Fe were found to be present in the > 1 kDa size fraction, again similar to the figures for the loch water (Table 6.11).

6.6 Discussion of Manganese and Iron in the Sediment Porewaters, Water Column and Feeder Stream Waters of Loch Bradan.

6.6.1 Porewater

Although the total sediment and porewater profiles are typical for those expected for redox-controlled retention of Mn within the sediment, the disproportionately smaller removal of humic-Mn compared with non-humic-associated Mn(II) from the 0 - 1 cm

porewaters suggests that Mn-humic complexation inhibits, to a small extent, the oxidation of Mn(II). This prevents a small proportion of Mn being retained within the sediment, i.e. less than 100 % of the Mn is trapped within the sediment as a consequence of redox cycling. The proximity of the enrichment zone to the interface with the loch water means that diffusion is a likely means of escape for humic-bound Mn from the sediment to the water column (further discussed in Section 6.6.2).

The same mechanism for release from the sediment may also be observed for Fe, but due to the small sample size it was impossible to complete the fractionation study for both Mn and Fe (Mn being the key element of interest).

6.6.2 Loch Water

It is clear that there is an increase in the concentration of total dissolved Mn, total dissolved Fe, particulate Mn and particulate Fe in the water immediately overlying the sediment compared with the surface waters.

The increase in particulates could be due to gravitational settling of particulate matter, or to turbation of the near-surface sediments. The latter is, however, unlikely due to the extremely sharp nature of the redox enrichments, even for those very close to the sediment-water interface.

The increase in the concentration of the total dissolved fraction immediately overlying the sediment could be the result of seepage from the sediment and diffusion away from the sediment-water interface. Also, some 50 - 60 % of the Mn and Fe is humic-complexed, and the bottom water is distinctly darker in colour than the loch-surface water. It is proposed, therefore, that the 0 - 1 cm sediment porewater is a source of Mn (and Fe) to the overlying water, and that it is humic-complexed Mn (and perhaps Fe) in particular that is able to escape from the sediment. Although the proportion of the sediment Mn that is potentially released in this way is low, the concentrations in

the 0 - 1 cm pore water are similar to those in the bottom waters and are sufficient to ensure the loch water exceeds the EC MAC.

The Mn/Fe ratio in the total dissolved fraction, and < 1 kDa and > 1 kDa size fractions, is much greater than that in the particulate fraction, which implies that, as expected, the oxidation of soluble Mn(II) species to insoluble Mn(IV) species is much slower than that observed for Fe.

6.6.3 Stream Water

Clearly release from the sediment is not the only route by which Mn (and Fe) enter the loch water, the stream waters also having elevated (>EC MAC) concentrations of Mn which are generally similar to those of the loch water. The greater concentration of Fe in stream water compared with loch water may indicate that a proportion of soluble Fe is readily removed from input waters.

As was discussed in Section 5.3.3, a significant proportion of the Mn and Fe is humic-complexed, and this provides evidence of the transport of allochthonous humic material from the catchment into the loch water. This study provides clear evidence for humic-complexation of Mn and Fe in the sediments, porewaters, peaty catchment, stream waters and loch waters. As the humic material is mainly terrigenous in nature, the relative contribution of the catchment and sediments cannot be readily distinguished.

As found in the loch water, there is relatively more Mn than Fe in the stream water than in particulates, again supporting the slow oxidation kinetics for Mn.

6.6.4 Summary

- Within the pore water and loch water of Loch Bradan, a sizeable fraction of the dissolved Mn is humic-associated.
- The association of dissolved Mn with humics becomes relatively more important in the oxic regions of the sediment and the overlying water.
- The input streams of Loch Bradan have a high Mn concentration, with a large proportion of this being humic-associated.
- Fe which is associated with humics is oxidised and precipitated at a faster rate than Mn associated with humics.

6.7 Conclusions

The concentration of Mn in the waters of Loch Bradan frequently exceeds the EC MAC of 0.05 mg l^{-1}, with the concentrations of Mn found to be highest, in general, in the bottom waters, i.e. those closest to the sediment. The reasons for the elevated Mn concentration in the water column are two-fold: firstly the slow oxidation kinetics of $Mn(II)_{(aq)}$ and secondly humic complexation, which to some extent inhibits oxidation of Mn. Humic substances are important in Mn complexation in the loch waters, with outersphere complexation (relatively weak associations) predominating.

This study has identified two main sources of Mn to the Loch Bradan water column:

1. the peaty catchment via stream inputs, with a large proportion of the Mn being humic-associated.
2. the sediments via porewater, again with a significant portion of the Mn diffusing out of the sediment being humic-associated.

7: Overall Summary

Loch Bradan, situated in the Galloway Hills, Southwest Scotland, is a major drinking water reservoir under the jurisdiction of West of Scotland Water. Routine monitoring of water quality at the Loch Bradan treatment works, however, has shown that the concentration of dissolved Mn frequently exceeds the EC maximum admissible concentration of 50 $\mu g\ l^{-1}$. Thus the water requires expensive ozonation treatment to precipitate out MnO_2 and thereby reduce dissolved Mn levels before it can be distributed to customers. Although the Mn-rich nature of the bedrock in this area is well known, the well-oxygenated nature of Loch Bradan should promote removal of dissolved Mn from these waters via oxidation and precipitation and so this study was initiated to determine the underlying reasons for the high dissolved Mn concentrations..

Both Loch Bradan and its catchment were investigated, with the Mn concentrations, associations and behaviour in the surrounding peaty catchment, input streams, loch water, bottom sediments and pore waters all being examined. In the thinly sliced sediment cores and peat cores, pseudo total (extracted by 8 M HNO_3 / 11.6 M HCl) as well as easily reducible (extracted by 0.1 M $NH_2OH.HCl/HNO_3$, pH 2) and humic associated (extracted by 0.1 M NaOH) Mn were determined. The total dissolved and size fractionated (< 1 kDa and > 1 kDa) Mn were determined in the stream waters, the loch waters and also in the pore water, with the proportion of Mn in the >1 kDa size fraction indicating the relative contribution of humic-associated Mn to total dissolved Mn. The overall aim of this project was, therefore, to:

1. characterise the potential sources of Mn and the processes controlling Mn behaviour within these environments.
2. determine the processes leading to release of Mn into the loch water.
3. investigate the role of humic substances in promoting and sustaining the observed high dissolved Mn concentrations.

Determination of pseudo-total and easily reducible Mn in the thinly sliced sediment cores showed that the maximum concentration of pseudo-total Mn occurred in the top 3 cm of the sediment and the majority of the Mn was in an easily reducible form. Clearly within the upper region of the sediment cores, redox cycling is the principal process controlling the vertical distribution of Mn. The concentration of the Mn enrichments observed in the sediments of Loch Bradan ranges from ~ 1 - 7 % (dry weight, with higher concentrations occurring in the eastern basin, possibly as a result of inputs of Mn from the streams around Loch Bradan. The oxidation/precipitation of the Mn(II) in the upper regions of the sediment column, which results in the Mn enrichments observed, is also reflected in a minimum concentration of total Mn in the pore water at the same depth. The observed behaviour of Mn, typical for lakes which have a water column which is well-oxygenated, is indicative of retention of Mn within the sediment and minimal release to overlying waters.

Deeper within the sediment of Loch Bradan a number of Mn enrichments occur which are attributed to formation of insoluble $MnCO_3$ and the preservation of previous redox-derived enrichments as crystalline oxides.

As with the top 3 cm of Loch Bradan sediment, there is a redox-driven maximum in the concentration of Mn in the top 10 cm of the peat in the loch's catchment. The concentrations of these maxima, however, vary greatly, from ~ 35 mg kg^{-1} to 2 %, indicating the highly heterogeneous nature of the catchment. In contrast with the sediment, the process of redox cycling does not necessarily lead to retention of Mn within the sloping peaty catchmment. Low concentrations of total Mn may result where lateral sub-surface flow of water transports dissolved Mn(II) from the peat into proximal stream waters. Thus the low concentrations of Mn are indicative of release of Mn from some parts of the peaty catchment, i.e. a source of Mn to the receiving loch waters.

In both the bottom sediment and peaty catchment of Loch Bradan, there are also diagenetic enrichments of Fe, generally occurring below those of Mn. The redox

cycling of Fe in the bottom sediments produces a typical pore water profile, with elevated dissolved Fe(II) concentrations in the reducing zone, overlain by lower concentration of dissolved Fe in the upper zone of the sediment. At depth within both the sediment and certain peat cores enrichments of Fe can be seen due to the presence of insoluble crystalline oxides and also sulphide and phosphate species.

Analysis of the well-oxygenated loch waters showed total dissolved Mn concentrations greatly in excess of the EC maximum admissible concentration, at up to 340 $\mu g\ l^{-1}$. Size fractionation revealed that >50 % of total dissolved Mn was associated with humic substances (>1 k Da) size fraction). Confirmation that Mn(II) in the > 1 kDa fraction was indeed associated with humic substances was provided by esr spectroscopy which showed outer sphere $Mn(H_2O)_6^{2+}$-humic complexes. Clearly, humic substances are important in sustaining the high dissolved Mn concentrations in the loch water. The source(s) of the Mn and of the humic substances, however, required further investigation.

The catchment was found to comprise up to ~ 80 % organic matter, up to 100 % of which was humic in nature. Given the proposed mechanism for release of Mn from this highly organic rich environment and an observed association of Mn with humic substances within the peat, it is probable that a proportion of Mn is released from the catchment in association with dissolved humic substances. Size fractionation of the stream waters showed that 33 - 67 % of total dissolved Mn was associated with humic substances, thus providing evidence of a terrigenous source of organic matter and also of catchment derived humic-associated Mn into the loch waters.

Organic matter comprised ~ 27 - 42 % of the top 3 cm of sediment, with generally higher organic content in the western basin. Some 35 - 100 % of the organic matter was found to be humic in nature and further characterisation (CHN analysis) showed that it originated principally from the highly organic catchment. Only at one location was there some evidence of an autochthonous source of organic matter and so the

source of humic associated Mn to the overlying loch water cannot be unambiguously determined by the characterisation of organic matter *per se*.

Vertical profiles showed an approximately inverse relationship between sediment organic content and total Fe concentration whilst the relationship between organic matter content and humic concentrations varied between cores and with depth. The 'with depth' variations, in conjunction with elemental ratio data, suggested progressive humification with increasing depth.

Within the sediment cores, associations of Mn with humic substances were found to be of greatest importance below the redox driven maxima, with ~ 20 - 100 % of the total Mn being humic-associated. In contrast, typically < 5 % was humic-associated in the zone of the solid phase redox enrichment. The change in association indicates the importance of humic substances in complexing Mn(II) or perhaps participation in the reductive dissolution of Mn(IV) oxides below the redox front. The potential role of humic substances in release of Mn from the sediment to overlying waters, however, is provided by the results of porewater size fractionation. Below the top 1 cm, ~ 16 - 25 % of the total dissolved Mn in the pore water was found to be humic associated, but in the 0 - 1 cm section, the zone of the solid phase Mn enrichment, this value increased to 35 %. This result, in conjunction with the observed minimum in total dissolved Mn(II) concentration, indicates that proportionally more 'inorganic' Mn(II) is removed from the pore water. Not only does the association with humic substances inhibit the oxidation and precipitation of Mn but the proximity to the sediment-loch water interface means that diffusion into the overlying waters represents a mechanism by which humic-associated Mn can be released into the loch waters. Indeed the maximum concentrations of dissolved Mn, similar to those in the 0 - 1 cm pore waters, were found in the bottom loch waters.

Overall, the source of Mn-humic complexes to the waters are two-fold:

1. Mn-humic complexes formed below the Mn redox boundary in the highly organic catchment, transported via streams, contributing significant quantities of both Mn and humic material to the water column.
2. soluble Mn-humic complexes formed below the Mn redox boundary in the sediment column, but from which Mn(II) is not subsequently released at the redox boundary, diffuse into the overlying water column.

It is clear that humic substances contribute significantly to the high dissolved Mn(II) concentrations in the waters of Loch Bradan. Even in the absence of humic substances, however, the concentration of dissolved Mn(II) may still exceed EC maximum admissible concentration, suggesting that kinetic factors inhibiting the oxidation of Mn(II) must also be important.

From the point of view of the water company, West of Scotland Water, the problem of high dissolved Mn concentrations in Loch Bradan is likely to remain, necessitating continued treatment to produce water which will comply with the current EC maximum admissible concentration.

Further Work

Several areas of further work could be undertaken to improve the current understanding of Mn geochemistry in Loch Bradan and its surrounding catchment. Some examples of these are:

1. characterisation of contrasting environments in the peaty catchment with particular reference to weathering of bedrock material, chemical form of Mn in near- and sub-surface solid phase enrichments, and water flow paths (streams vs runoff) into the loch. The purpose of this work would be to gain a better understanding of features of the geochemical environment which may promote retention vs release of Mn and, in the case of the latter, to quantify this source of Mn to the loch waters.

2. characterisation of humic substances (catchment pore waters, stream waters, loch waters, sediments and sediment pore waters) involving more detailed size, gel chromatographic and/or gel electophoretic fractionation. Analysis of such fractions (e.g. for Mn concentration, CHN, $\delta^{13}C$, ^{13}C NMR) would provide a more detailed understanding of the composition and source of humic substances, the nature of humic substances involved in complexing Mn(II) and perhaps those responsible for inhibiting Mn(II) oxidation in the 0 - 1 cm pore waters.

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Appendix 1: Results from LBSC 1

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 0.2	0.37	0.33	3.17	0.62	
0.2 - 0.4	0.64	0.61	3.97	0.66	83.8
0.4 - 0.6	0.99	0.86	5.41	0.75	
0.6 - 0.8	0.59	0.42	8.35	0.75	143.3
0.8 - 1.0	0.39	0.28	6.70	0.61	125
1.0 - 1.2	0.24	0.17	5.76	0.61	116.5
1.2 - 1.4	0.21	0.15	4.46	0.57	90.4
1.4 - 1.6	0.19	0.14	4.64	0.59	90.5
1.6 - 1.8	0.19	0.22	4.61	0.65	89.4
1.8 - 2.0	0.20	0.14	4.55	0.66	89.5
2.0 - 2.2	0.20	0.15	4.66	0.68	84.2
2.2 - 2.4	0.20	0.15	4.32	0.53	82.7
2.4 - 2.6	0.19	0.16	4.06	0.54	63.3
2.6 - 2.8	0.19	0.15	3.88	0.55	53.4
2.8 - 3.0	0.19	0.15	3.97	0.57	50

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBSC 1

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 0.2	38.7	97.8	66.2	157.4	94.7
0.2 - 0.4	31.3	91.3	40.8	133.0	45.8
0.4 - 0.6	35.8	101.5	32.8	144.3	61.1
0.6 - 0.8	32.1	92.1	26.1	139.6	32.3
0.8 - 1.0	29.6	93.5	25.5	135.2	49.6
1.0 - 1.2	27.8	92.3	26.8	139.9	48.3
1.2 - 1.4	30.5	87.4	27.3	149.9	63.2
1.4 - 1.6	31.4	92.7	33.5	153.8	70.5
1.6 - 1.8	32.8	90.8	33.7	157.1	68.6
1.8 - 2.0	30.8	81.6	29.2	145.2	51.7
2.0 - 2.2	30.1	87.6	35.7	131.3	47.3
2.2 - 2.4	29.6	87.8	32.0	128.9	53.1
2.4 - 2.6	28.6	87.0	33.6	142.7	41.1
2.6 - 2.8	29.6	83.2	30.1	144.2	44.7
2.8 - 3.0	34.0	83.1	34.9	156.7	34.2

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBSC 1

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 0.2	96.7				
0.2 - 0.4	95.9	33.4	23.4	232.9	0.89
0.4 - 0.6	95.9	33.7			
0.6 - 0.8	95.6	33.0	21.1	125.7	0.79
0.8 - 1.0	94.9	34.4			
1.0 - 1.2	94.4	34.7	25.8	215.4	1.18
1.2 - 1.4	93.8	35.9	23.3	809.0	0.49
1.4 - 1.6	93.7	34.7			
1.6 - 1.8	93.8	34.9	23.2	1728.4	1.05
1.8 - 2.0	93.7	33.7	22.2	1872.8	1.26
2.0 - 2.2	93.9	33.4	19.0	1691.6	1.12
2.2 - 2.4	93.1	32.5	22.1	561.4	1.22
2.4 - 2.6	92.8	31.1	21.6	530.7	1.16
2.6 - 2.8	92.7	32.9	21.7	470.2	1.08
2.8 - 3.0	92.5	32.7	21.4	550.2	1.17

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBSC 1.

Appendix 2: Results from LBSC 2

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 0.2	0.66	0.60	4.80	0.54	69.6
0.2 - 0.4	0.42	0.33	4.14	0.49	57.8
0.4 - 0.6	0.35	0.30	3.66	0.47	52.3
0.6 - 0.8	0.44	0.34	3.81	0.42	51.4
0.8 - 1.0	0.29	0.24	2.93	0.52	39.2
1.0 - 1.2	0.29	0.22	2.95	0.52	43.9
1.2 - 1.4	0.29	0.19	2.67	0.47	38.5
1.4 - 1.6	0.26	0.21	2.51	0.49	39.2
1.6 - 1.8	0.22	0.16	2.37	0.45	34.6
1.8 - 2.0	0.22	0.18	2.31	0.55	35.0
2.0 - 2.2	0.21	0.19	2.21	0.46	35.6
2.2 - 2.4	0.22	0.18	1.98	0.44	36.8
2.4 - 2.6	0.22	0.20	2.07	0.43	38.7
2.6 - 2.8	0.23	0.18	1.21	0.43	35.9
2.8 - 3.0	0.22	0.20	1.93	0.45	40.3

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBSC 2

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 0.2	33.5	96.5	40.2	161.3	50.0
0.2 - 0.4	30.0	93.0	41.5	163.6	48.1
0.4 - 0.6	36.2	90.1	32.0	128.0	45.8
0.6 - 0.8	30.9	91.0	30.9	125.7	50.6
0.8 - 1.0	33.2	95.9	33.5	129.2	46.1
1.0 - 1.2	32.4	98.8	43.4	133.4	46.3
1.2 - 1.4	29.6	99.4	38.3	139.8	41.3
1.4 - 1.6	30.3	100.1	36.9	149.7	61.3
1.6 - 1.8	31.0	100.6	39.0	153.7	69.1
1.8 - 2.0	32.0	107.7	46.6	163.4	85.0
2.0 - 2.2	32.7	109.6	51.2	172.8	73.8
2.2 - 2.4	31.4	105.0	49.3	180.3	81.8
2.4 - 2.6	29.1	103.2	49.3	172.2	80.5
2.6 - 2.8	33.3	106.9	51.4	185.3	87.3
2.8 - 3.0	33.2	129.3	49.8	206.1	93.6

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBSC 2

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 0.2	96.0				
0.2 - 0.4	94.5	34.7	29.3	421.3	1.22
0.4 - 0.6	94.0	35.9	31.5	386.6	1.23
0.6 - 0.8	93.6	35.8	30.4	389.5	1.17
0.8 - 1.0	93.1	34.7	30.2	383.3	1.04
1.0 - 1.2	93.1	32.7	33.3	552.8	1.01
1.2 - 1.4	92.7	34.7	24.4	368.7	0.71
1.4 - 1.6	92.6	35.4	31.3	559.7	0.93
1.6 - 1.8	92.0	33.5	29.1	663.6	0.82
1.8 - 2.0	93.0	35.8	27.4	510.6	0.71
2.0 - 2.2	92.5	34.2	27.0	522.7	0.75
2.2 - 2.4	92.5	38.5	30.0	622.9	0.73
2.4 - 2.6	92.5	37.8	27.9	541.5	0.61
2.6 - 2.8	92.3	40.6	26.7	525.3	0.59
2.8 - 3.0	92.4	41.3	32.2	665.4	0.74

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBSC 2.

Appendix 3: Results from LBSC 3

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 0.2	0.75	0.65	5.07	0.51	82.8
0.2 - 0.4	0.61	0.50	4.89	0.46	74.0
0.4 - 0.6	0.49	0.42	4.21	0.45	64.7
0.6 - 0.8	0.48	0.39	4.65	0.38	71.9
0.8 - 1.0	0.44	0.33	5.60	0.39	106.4
1.0 - 1.2	0.37	0.30	5.24	0.40	106.5
1.2 - 1.4	0.33	0.29	4.29	0.44	71.7
1.4 - 1.6	0.29	0.26	3.68	0.44	55.9
1.6 - 1.8	0.28	0.26	3.22	0.41	36.6
1.8 - 2.0	0.26	0.25	3.19	0.42	34.8
2.0 - 2.2	0.26	0.25	3.30	0.43	35.1
2.2 - 2.4	0.23	0.22	3.04	0.38	30.6
2.4 - 2.6	0.24	0.23	3.07	0.37	33.6
2.6 - 2.8	0.23	0.20	2.89	0.38	33.6
2.8 - 3.0	0.22	0.19	3.00	0.38	37.1

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBSC 3

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 0.2	18.2	81.2	13.2	129.4	58.1
0.2 - 0.4	19.9	78.6	25.9	96.9	66.4
0.4 - 0.6	19.4	66.7	36.8	135.2	68.5
0.6 - 0.8	20.9	81.5	21.1	107.8	61.3
0.8 - 1.0	18.8	73.6	9.6	67.2	39.0
1.0 - 1.2	24.1	66.6	18.5	90.9	49.1
1.2 - 1.4	21.7	78.8	20.8	117.0	65.8
1.4 - 1.6	23.7	86.7	22.6	131.8	76.8
1.6 - 1.8	34.0	77.0	18.1	135.6	92.6
1.8 - 2.0	24.9	75.3	48.2	101.4	87.6
2.0 - 2.2	27.3	70.7	29.8	137.9	89.2
2.2 - 2.4	26.7	63.3	17.6	139.0	121.2
2.4 - 2.6	26.3	82.9	44.6	119.0	89.5
2.6 - 2.8	25.0	83.5	42.7	160.6	85.4
2.8 - 3.0	44.0	99.4	42.7	168.2	102.2

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBSC 3

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 0.2	92.6	38.0	17.6	326.2	0.70
0.2 - 0.4	92.5	37.7	20.0	440.8	0.80
0.4 - 0.6	91.8	36.5			
0.6 - 0.8	91.5	35.6	17.3	489.2	0.74
0.8 - 1.0	92.0	35.8	17.0	580.0	0.89
1.0 - 1.2	91.8	35.4	17.0	671.1	1.02
1.2 - 1.4	91.2	37.3	16.1	681.0	1.01
1.4 - 1.6	90.9	36.5	15.0	691.3	0.76
1.6 - 1.8	90.6	35.6	14.3	666.1	0.65
1.8 - 2.0	90.3	33.9	24.5	1086.4	1.10
2.0 - 2.2	90.7	33.9	23.8	1034.3	1.15
2.2 - 2.4	90.1	33.0	28.7	1094.4	1.11
2.4 - 2.6	90.9	32.7	29.1	1337.8	1.30
2.6 - 2.8	90.9	29.8	30.2	1875.2	1.68
2.8 - 3.0	90.0	32.2	27.4	1230.8	1.20

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBSC 3.

Appendix 4: Results from LBSC 4

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 0.2	3.27	3.53	3.34	0.82	
0.2 - 0.4	6.68	3.93	3.61	0.82	65.6
0.4 - 0.6	3.86	4.29	4.21	0.86	72.6
0.6 - 0.8	3.63	3.97	5.00	0.76	81.3
0.8 - 1.0	2.31	2.56	6.39	0.69	103.9
1.0 - 1.2	1.51	1.54	5.24	0.38	85.7
1.2 - 1.4	1.20	1.05	4.28	0.32	69.3
1.4 - 1.6	0.94	0.92	4.86	0.36	89.4
1.6 - 1.8	0.97	0.93	5.98	0.44	155.6
1.8 - 2.0	1.00	0.94	6.48	0.46	174.2
2.0 - 2.2	0.98	0.95	7.40	0.47	316.2
2.2 - 2.4	0.91	0.96	8.35	0.46	356.0
2.4 - 2.6	0.96	0.94	7.39	0.51	341.5
2.6 - 2.8	0.88	0.89	6.13	0.60	257.8
2.8 - 3.0	0.78	0.80	4.51	0.58	125.0

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBSC 4

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 0.2	40.1	83.2	64.1	372.3	302.9
0.2 - 0.4	35.2	86.4	51.2	189.5	118.0
0.4 - 0.6	37.9	85.6	49.0	271.0	96.2
0.6 - 0.8	29.9	85.1	35.9	212.1	76.6
0.8 - 1.0	27.6	84.0	34.1	140.4	58.9
1.0 - 1.2	31.7	86.3	25.3	125.8	56.4
1.2 - 1.4	28.1	84.9	31.4	123.9	41.6
1.4 - 1.6	30.7	78.5	22.7	111.6	38.0
1.6 - 1.8	29.8	84.6	24.2	118.0	36.6
1.8 - 2.0	26.9	94.7	22.3	114.5	37.1
2.0 - 2.2	22.9	90.4	24.8	114.6	43.2
2.2 - 2.4	24.6	88.2	19.6	120.1	39.4
2.4 - 2.6	30.6	87.0	27.0	138.0	44.0
2.6 - 2.8	33.5	78.3	38.1	129.9	41.3
2.8 - 3.0	32.2	81.0	37.0	150.2	42.3

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBSC 4

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 0.2	97.8				
0.2 - 0.4	97.2				
0.4 - 0.6	97.2	30.4			
0.6 - 0.8	96.7	31.6	14.9	305.9	0.33
0.8 - 1.0	96.2	31.0	13.6	302.4	0.44
1.0 - 1.2	95.6	32.5	14.7	549.1	0.54
1.2 - 1.4	94.6	32.7	14.6	1202.3	0.57
1.4 - 1.6	94.1	33.4	12.6	1114.6	0.46
1.6 - 1.8	94.7	32.2	11.3	896.6	0.51
1.8 - 2.0	94.4	32.0	19.4	1797.9	1.02
2.0 - 2.2	94.1	31.8	19.6	1937.1	1.34
2.2 - 2.4	93.6	30.1	17.3	1757.9	1.30
2.4 - 2.6	93.4	29.6	19.4	2102.9	1.59
2.6 - 2.8	92.8	30.4	17.5	1949.0	1.38
2.8 - 3.0	93.3	33.0	15.4	1865.8	1.07

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBSC 4.

Appendix 5: Results from LBSC 5

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 0.2	0.65	0.66	3.15	0.57	55.6
0.2 - 0.4	0.79	0.72	6.92	0.56	107.9
0.4 - 0.6	2.74	2.86	7.51	0.64	68.5
0.6 - 0.8	2.26	2.18	7.07	0.76	91.0
0.8 - 1.0	1.50	1.61	3.80	0.68	69.4
1.0 - 1.2	0.51	0.47	5.05	0.45	87.0
1.2 - 1.4	0.47	0.48	4.60	0.45	78.1
1.4 - 1.6	0.53	0.48	6.07	0.54	175.6
1.6 - 1.8	0.54	0.47	5.99	0.52	181.8
1.8 - 2.0	0.55	0.5	6.09	0.51	208.7
2.0 - 2.2	0.49	0.48	5.12	0.52	142.2
2.2 - 2.4	0.41	0.44	3.64	0.45	62.5
2.4 - 2.6	0.37	0.42	2.92	0.48	46.4
2.6 - 2.8	0.40	0.42	3.00	0.43	47.8
2.8 - 3.0	0.41	0.41	2.87	0.46	44.7

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBSC 5

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 0.2	29.5	75.5	42.7	116.2	50.6
0.2 - 0.4	28.9	85.8	22.7	112.0	49.2
0.4 - 0.6	27.8	95.6	41.8	127.6	52.0
0.6 - 0.8	26.6	95.0	28.7	111.0	43.9
0.8 - 1.0	28.1	88.8	31.7	110.8	48.6
1.0 - 1.2	27.3	93.3	25.5	113.3	52.4
1.2 - 1.4	27.2	87.5	27.1	114.7	49.0
1.4 - 1.6	28.1	85.3	23.8	123.2	48.8
1.6 - 1.8	29.5	94.4	25.5	148.8	42.5
1.8 - 2.0	28.7	99.0	36.4	130.9	53.2
2.0 - 2.2	36.0	81.7	28.7	153.5	49.1
2.2 - 2.4	28.0	95.8	41.8	149.7	62.7
2.4 - 2.6	28.1	92.8	43.0	154.1	66.7
2.6 - 2.8	32.2	110.9	43.8	200.4	76.7
2.8 - 3.0	33.3	113.4	50.3	202.4	93.2

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBSC 5

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 0.2	96.1	34.1	29.5	241.5	0.78
0.2 - 0.4	93.9	32.3	22.2	300.2	0.98
0.4 - 0.6	96.0				
0.6 - 0.8	95.7	32.2	23.8	324.5	0.76
0.8 - 1.0	96.5	34.2			
1.0 - 1.2	93.8	34.7	23.8	540.7	1.38
1.2 - 1.4	93.4	34.6	22.0	1301.8	1.38
1.4 - 1.6	93.7	34.2	22.2	1271.2	1.57
1.6 - 1.8	93.5	32.9	20.4	1477.7	1.7
1.8 - 2.0	93.1	32.0	21.3	1729.3	2.04
2.0 - 2.2	92.3	30.8	21.7	1496.9	1.97
2.2 - 2.4	90.6	31.5	22.5	1809.7	1.52
2.4 - 2.6	92.4	32.7	22.5	1406.7	1.26
2.6 - 2.8	91.9	33.0	21.9	1147.6	1.07
2.8 - 3.0	92.6	32.3	21.5	1326.2	0.99

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBSC 5.

Appendix 6: Results from LBSC 6

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 0.2	1.50	1.66	3.67	0.68	65.1
0.2 - 0.4	2.36	2.56	5.00	0.78	73.3
0.4 - 0.6	2.16	2.16	6.45	0.79	75.5
0.6 - 0.8	1.20	1.19	7.57	0.63	
0.8 - 1.0	0.76	0.68	5.17	0.49	83.7
1.0 - 1.2	0.52	0.50	5.17	0.48	45.3
1.2 - 1.4	0.50	0.50	5.37	0.66	72.3
1.4 - 1.6	0.48	0.48	5.51	0.42	100.1
1.6 - 1.8	0.57	0.52	7.16	0.45	179.0
1.8 - 2.0	0.63	0.54	9.51	0.51	321.4
2.0 - 2.2	0.59	0.54	8.20	0.52	292.6
2.2 - 2.4	0.55	0.50	7.50	0.52	233.2
2.4 - 2.6	0.49	0.48	5.62	0.54	135.9
2.6 - 2.8	0.46	0.45	4.39	0.49	79.1
2.8 - 3.0	0.43	0.44	4.00	0.53	61.7
3.0 - 4.0	0.40	0.39	3.47	0.35	55.1
4.0 - 5.0	0.41	0.40	3.72	0.37	64.4
5.0 - 6.0	0.44	0.45	4.21	0.45	64.6
6.0 - 7.0	0.49	0.50	6.09	0.46	121.4
7.0 - 8.0	0.48	0.45	4.84	0.37	118.8
8.0 - 9.0	0.46	0.40	3.81	0.32	101.7
9.0 - 10.0	0.38	0.37	3.51	0.30	91.0
10.0 - 11.0	0.40	0.38	3.85	0.25	104.8
11.0 - 12.0	0.41	0.42	3.74	0.32	99.0
12.0 - 13.0	0.44	0.44	3.74	0.31	107.5
13.0 - 14.0	0.41	0.41	3.57	0.27	109.5
14.0 - 15.0	0.42	0.43	3.39	0.31	103.6
15.0 - 16.0	0.41	0.40	2.92	0.30	103.4
16.0 - 17.0	0.38	0.38	3.02	0.26	98.2
17.0 - 18.0	0.55	0.56	3.32	0.27	95.2
18.0 - 19.0	0.94	0.89	3.59	0.25	102.8
19.0 - 20.0	1.52	1.57	4.09	0.30	95.1
20.0 - 21.0	0.49	0.49	3.77	0.30	96.6
21.0 - 22.0	0.48	0.49	3.86	0.35	109.3
22.0 - 23.0	0.39	0.35	3.63	0.27	100.1
23.0 - 24.0	0.42	0.39	3.49	0.26	105.7
24.0 - 25.0	0.47	0.42	3.55	0.30	99.0
25.0 - 26.0	0.52	0.47	3.67	0.32	
26.0 - 27.0	0.64	0.61	3.88	0.35	106.5

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBSC 6

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
27.0 - 28.0	0.71	0.65	4.73	0.34	157.1
28.0 - 29.0	0.54	0.50	4.25	0.28	133.5
29.0 - 30.0	0.43	0.40	3.71	0.30	114.3
30.0 - 31.0	0.39	0.35	4.01	0.32	108.7
31.0 - 32.0	0.56	0.50	5.17	0.41	168.6
32.0 - 33.0	0.68	0.62	5.30	0.42	170.8
33.0 - 34.0	1.32	1.07	6.23	0.70	164.7
34.0 - 35.0	3.25	2.26	7.46	0.96	89.0
35.0 - 36.0	2.64	2.02	7.13	1.06	86.8
36.0 - 37.0	1.57	1.39	6.04	0.75	78.9
37.0 - 38.0	1.01	0.88	5.23	0.60	91.8
38.0 - 39.0	2.02	1.68	5.85	0.85	93.9
39.0 - 40.0	0.73	0.65	4.27	0.59	85.6
40.0 - 41.0	0.54	0.48	3.92	0.38	126.1
41.0 - 42.0	0.58	0.51	3.72	0.37	106.0
42.0 - 43.0	0.56	0.48	3.47	0.36	89.0
43.0 - 44.0	0.53	0.48	3.03	0.31	81.1
44.0 - 45.0	0.54	0.48	2.97	0.29	79.5

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBSC 6 (cont'd)

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 0.2	30.6	86.5	36.9	180.0	83.0
0.2 - 0.4	31.0	98.5	39.3	139.4	71.4
0.4 - 0.6	31.3	93.2	37.7	117.5	73.0
0.6 - 0.8	34.5	97.1	26.4	120.2	46.5
0.8 - 1.0	29.7	87.7	24.1	110.7	50.8
1.0 - 1.2	31.9	78.1	30.1	190.6	67.2
1.2 - 1.4	28.9	90.3	35.3	221.1	68.9
1.4 - 1.6	25.1	88.4	27.6	134.5	40.8
1.6 - 1.8	27.4	85.1	22.0	143.0	31.8
1.8 - 2.0	24.6	92.1	22.6	145.7	26.2
2.0 - 2.2	22.7	98.4	33.5	140.7	39.4
2.2 - 2.4	28.2	86.4	30.1	141.3	34.9
2.4 - 2.6	26.1	81.0	32.9	122.9	33.2
2.6 - 2.8	27.3	94.5	32.4	154.7	46.5
2.8 - 3.0	27.6	95.8	36.6	165.9	55.6
3.0 - 4.0	27.0	75.2	31.4	134.9	67.4
4.0 - 5.0	22.8	95.4	42.9	170.3	115.0
5.0 - 6.0	23.7	119.4	57.4	195.7	176.1
6.0 - 7.0	28.3	143.2	58.5	320.8	284.5
7.0 - 8.0	23.6	135.0	46.1	406.5	290.9
8.0 - 9.0	21.7	116.4	39.9	411.9	279.5
9.0 - 10.0	25.4	113.4	39.5	352.8	234.3
10.0 - 11.0	27.0	119.6	37.9	389.2	255.2
11.0 - 12.0	22.6	99.9	39.6	486.1	450.1
12.0 - 13.0	26.0	117.2	39.3	512.0	437.2
13.0 - 14.0	30.1	126.3	50.3	465.9	429.5
14.0 - 15.0	30.4	114.6	39.7	435.2	377.7
15.0 - 16.0	32.4	104.2	35.9	478.0	415.4
16.0 - 17.0	40.2	95.2	30.7	381.8	325.8
17.0 - 18.0	25.8	106.1	32.7	397.3	290.3
18.0 - 19.0	25.2	114.5	21.9	372.8	246.8
19.0 - 20.0	20.9	117.1	22.7	352.5	203.0
20.0 - 21.0	27.9	144.3	44.8	349.0	255.5
21.0 - 22.0	33.5	190.9	56.8	451.5	386.1
22.0 - 23.0	16.3	158.4	46.8	373.0	261.6
23.0 - 24.0	19.0	133.0	39.9	438.8	273.6
24.0 - 25.0	12.9	120.1	31.3	323.7	199.0
25.0 - 26.0	13.7	121.1	26.1	313.1	197.0
26.0 - 27.0	15.6	112.1	24.3	297.8	171.7

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBSC 6

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
27.0 - 28.0	18.5	114.4	19.8	277.3	127.6
28.0 - 29.0	10.6	86.6	20.9	246.9	117.7
29.0 - 30.0	6.7	80.9	19.7	239.5	109.9
30.0 - 31.0	12.3	74.0	27.4	221.1	96.8
31.0 - 32.0	8.7	95.8	30.4	282.7	114.0
32.0 - 33.0	9.4	94.6	25.1	268.6	110.5
33.0 - 34.0	10.7	79.7	19.3	227.6	83.7
34.0 - 35.0	11.6	67.4	10.7	215.4	58.0
35.0 - 36.0	12.5	69.8	18.3	220.3	63.4
36.0 - 37.0	10.3	61.8	16.8	192.5	64.2
37.0 - 38.0	13.2	67.7	19.0	192.7	60.0
38.0 - 39.0	10.9	51.5	14.6	181.6	58.7
39.0 - 40.0	11.9	54.3	8.2	162.5	46.6
40.0 - 41.0	22.3	45.6	10.9	122.8	51.4
41.0 - 42.0	19.6	33.5	10.5	121.2	37.5
42.0 - 43.0	4.6	15.8	5.4	99.4	32.9
43.0 - 44.0	5.1	10.4	2.6	87.0	32.3
44.0 - 45.0	1.6	6.1	4.4	86.0	29.8

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBSC 6 (cont'd)

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 0.2	95.7	35.1	14.0	168.3	0.34
0.2 - 0.4	95.8	34.6	11.1	140.0	0.27
0.4 - 0.6	95.8	31.6	14.3	141.3	0.38
0.6 - 0.8	95.4	34.4	15.4	122.4	0.43
0.8 - 1.0	94.7	35.8	12.0	151.2	0.39
1.0 - 1.2	94.2	34.4	14.3	347.4	0.69
1.2 - 1.4	93.9	34.1			
1.4 - 1.6	93.7	32.5	13.2	686.9	0.81
1.6 - 1.8	94.0	31.0	14.0	728.7	0.79
1.8 - 2.0	94.3	27.9	18.9	1136.9	1.42
2.0 - 2.2	93.6	30.6	21.8	1632.6	1.83
2.2 - 2.4	92.8	29.1	18.0	1390.7	1.60
2.4 - 2.6	92.1	28.9	15.5	1177.7	1.14
2.6 - 2.8	91.6	26.8	24.2	1570.8	1.12
2.8 - 3.0	91.8	32.9			
3.0 - 4.0	90.1	33.0	26.6	1462.0	1.18
4.0 - 5.0	91.2	32.0	32.6	1925.8	1.54
5.0 - 6.0	92.6	33.5	39.7	2249.1	1.57
6.0 - 7.0	93.6	34.7	31.6	2014.4	2.25
7.0 - 8.0	92.8	34.4	36.4	2515.5	2.78
8.0 - 9.0	91.8	35.1	32.7	2102.6	1.76
9.0 - 10.0	87.8	33.5	34.5	1987.8	1.56
10.0 - 11.0	90.3	34.2	39.6	2361.4	1.65
11.0 - 12.0	90.8	33.7	29.3	1814.2	1.32
12.0 - 13.0	91.4	37.2	38.2	2151.0	1.77
13.0 - 14.0	90.0	35.8	34.0	1338.5	1.66
14.0 - 15.0	91.5	37.7	36.1	2266.1	1.62
15.0 - 16.0	90.9	37.0	30.8	1629.9	1.10
16.0 - 17.0	89.5	33.5	24.3	1296.3	0.82
17.0 - 18.0	89.5	29.4	11.5	761.5	0.35
18.0 - 19.0	90.8	36.1	13.4	1077.6	0.34
19.0 - 20.0	89.6	33.5	13.5	1629.4	0.37
20.0 - 21.0	90.1	34.4	13.6	1008.3	0.63
21.0 - 22.0	89.9	35.9	21.6	1373.0	1.01
22.0 - 23.0	88.9	28.4	19.7	927.9	1.09
23.0 - 24.0	89.2	29.4	22.5	971.5	1.01
24.0 - 25.0	90.4	36.3	19.5	986.3	1.01
25.0 - 26.0	90.0	35.9	20.2	1006.1	0.93
26.0 - 27.0	89.6	36.6	21.9	1031.9	0.86
27.0 - 28.0	86.6	28.2	18.3	1067.9	1.25

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBSC 6

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
28.0 - 29.0	84.8	28.2	20.9	1174.4	1.37
29.0 - 30.0	84.6	28.2	18.1	776.7	1.01
30.0 - 31.0	82.9	24.6	13.9	518.8	0.79
31.0 - 32.0	85.1	29.1	16.7	829.1	1.40
32.0 - 33.0	84.4	26.3	22.0	1246.7	1.87
33.0 - 34.0	82.9	29.1	14.4	1158.5	0.92
34.0 - 35.0	83.6	26.3	14.4	1628.0	0.47
35.0 - 36.0	85.5	28.7	11.9	1264.7	0.47
36.0 - 37.0	86.5	23.9	13.5	1438.0	0.49
37.0 - 38.0	85.9	27.2	15.1	1122.0	0.72
38.0 - 39.0	86.2	27.0	14.6	1086.1	0.51
39.0 - 40.0	87.1	29.9	17.8	737.0	0.84
40.0 - 41.0	87.7	37.2	19.8	873.1	1.09
41.0 - 42.0	87.0	40.2	21.5	1191.9	0.95
42.0 - 43.0	87.3	40.1	23.9	893.9	0.98
43.0 - 44.0	87.9	41.3	21.4	953.6	0.75
44.0 - 45.0	86.7	41.8	24.1	1057.4	0.78

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBSC 6 (cont'd)

Appendix 7: Results from LBSC 7

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 0.2	1.86	2.03	5.27	0.84	86.1
0.2 - 0.4	1.16	1.29	4.83	0.67	88.1
0.4 - 0.6	0.67	0.68	5.14	0.52	93.7
0.6 - 0.8	0.60	0.57	4.65	0.60	76.2
0.8 - 1.0	0.47	0.47	4.20	0.69	67.6
1.0 - 1.2	0.47	0.47	3.83	0.59	49.4
1.2 - 1.4	0.42	0.41	3.45	0.50	36.5
1.4 - 1.6	0.40	0.40	3.11	0.48	34.1
1.6 - 1.8	0.43	0.39	2.90	0.49	34.5
1.8 - 2.0	0.42	0.37	3.85	0.50	34.3
2.0 - 2.2	0.39	0.37	2.90	0.48	37.7
2.2 - 2.4	0.38	0.36	2.89	0.49	39.9
2.4 - 2.6	0.38	0.38	2.86	0.52	43.3
2.6 - 2.8	0.39	0.36	2.88	0.54	16.6
2.8 - 3.0	0.41	0.39	2.79	0.57	15.5

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBSC 7

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 0.2	23.6	89.8	36.6	112.8	72.7
0.2 - 0.4	23.0	83.8	30.3	120.7	64.2
0.4 - 0.6	23.2	83.6	30.2	119.0	47.2
0.6 - 0.8	25.3	82.3	29.3	125.2	45.1
0.8 - 1.0	23.9	82.3	30.9	108.3	33.5
1.0 - 1.2	25.9	82.5	38.5	124.2	61.7
1.2 - 1.4	26.0	87.8	37.3	130.0	57.4
1.4 - 1.6	26.0	93.9	42.3	153.3	62.8
1.6 - 1.8	26.6	94.1	42.8	156.5	65.8
1.8 - 2.0	27.2	99.1	47.2	167.4	66.3
2.0 - 2.2	30.1	109.0	49.9	188.3	77.5
2.2 - 2.4	29.1	120.2	50.9	204.9	90.4
2.4 - 2.6	28.5	135.8	54.6	227.4	105.9
2.6 - 2.8	29.7	145.7	57.0	239.2	107.1
2.8 - 3.0	28.8	145.1	64.6	255.9	117.3

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBSC 7

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 0.2	91.3	31.0			
0.2 - 0.4	91.0	34.7	21.6	311.3	0.65
0.4 - 0.6	89.9	33.5	20.0	449	0.76
0.6 - 0.8	86.4	32.5	18.2	741.1	0.85
0.8 - 1.0	87.9	35.1	18.6	1253.8	0.93
1.0 - 1.2	88.3	33.4	20.0	1309	0.87
1.2 - 1.4	88.8	32.3	25.0	1706.3	1.02
1.4 - 1.6	88.5	31.3	21.3	1342.9	0.72
1.6 - 1.8	88.7	31.8	18.8	1144.9	0.94
1.8 - 2.0	88.6	30.6	16.7	1092.3	0.94
2.0 - 2.2	90.9	32.2	18.2	1201.7	0.63
2.2 - 2.4	89.7	33.2	21.3	1315.2	0.64
2.4 - 2.6	90.1	33.9	21.3	1262.5	0.74
2.6 - 2.8	90.7	36.6	20.0	1213.8	0.75
2.8 - 3.0	90.6	36.1	21.8	1374.9	0.77

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBSC 7.

Appendix 8: Results from LBSC 8

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 0.2	1.62	1.52	5.18	0.49	
0.2 - 0.4	1.73	1.61	4.79	0.45	82.8
0.4 - 0.6	1.57	1.56	4.21	0.37	74.6
0.6 - 0.8	2.32	2.31	4.39	0.51	75.0
0.8 - 1.0	3.91	3.93	5.03	0.70	83.9
1.0 - 1.2	4.12	4.12	6.06	0.64	96.0
1.2 - 1.4	3.19	3.01	7.07	0.57	107.6
1.4 - 1.6	1.51	1.33	8.32	0.34	143.2
1.6 - 1.8	0.65	0.50	8.84	0.28	251.2
1.8 - 2.0	0.59	0.45	8.52	0.29	334.8
2.0 - 2.2	0.59	0.47	8.23	0.32	361.7
2.2 - 2.4	0.54	0.45	6.63	0.35	272.5
2.4 - 2.6	0.53	0.47	4.89	0.37	149.8
2.6 - 2.8	0.54	0.47	4.45	0.40	116.8
2.8 - 3.0	0.55	0.50	3.44	0.44	64.3
3.0 - 4.0	0.58	0.54	3.49	0.26	60.0
4.0 - 5.0	0.61	0.58	3.90	0.32	56.8
5.0 - 6.0	0.66	0.63	3.43	0.29	52.9
6.0 - 7.0	0.82	0.76	3.98	0.35	52.3
7.0 - 8.0	0.99	0.95	5.58	0.56	65.6
8.0 - 9.0	1.32	1.17	11.08	0.70	442.6
9.0 - 10.0	0.97	3.07	6.45	1.49	268.3
10.0 - 11.0	0.89	0.89	4.02	0.50	91.5
11.0 - 12.0	0.84	0.90	4.50	0.40	89.3
12.0 - 13.0	1.02	0.94	6.07	0.35	130.6
13.0 - 14.0	0.95	0.94	4.98	0.52	130.1
14.0 - 15.0	0.93	0.81	4.25	0.27	93.3
15.0 - 16.0	0.94	0.85	4.19	0.28	102.1
16.0 - 17.0	0.93	0.83	4.01	0.27	92.1
17.0 - 18.0	0.90	0.83	3.26	0.29	67.7
18.0 - 19.0	0.95	0.87	3.84	0.32	67.3
19.0 - 20.0	0.94	0.87	3.49	0.28	71.4
20.0 - 21.0	0.86	0.80	3.22	0.28	123.5
21.0 - 22.0	1.23	0.94	8.72	0.34	436.9
22.0 - 23.0	4.01	2.65	11.05	0.87	465.4
23.0 - 24.0	5.20	2.83	13.50	1.11	543.5
24.0 - 25.0	6.65	2.64	12.37	0.98	462.1
25.0 - 26.0	6.23	2.81	10.86	1.01	396.2
26.0 - 27.0	8.21	3.19	9.88	0.95	335.8

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBSC 8

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 0.2	24.0	72.3	30.6	136.0	87.6
0.2 - 0.4	17.0	71.9	46.0	134.8	85.9
0.4 - 0.6	17.0	67.5	23.9	104.5	79.5
0.6 - 0.8	15.8	73.3	25.8	100.4	86.9
0.8 - 1.0	18.3	71.4	28.3	154.7	126.9
1.0 - 1.2	15.5	83.0	33.2	101.2	88.0
1.2 - 1.4	20.8	77.8	18.0	115.7	84.5
1.4 - 1.6	16.9	69.1	11.7	97.6	92.2
1.6 - 1.8	17.6	71.2	14.2	97.6	87.6
1.8 - 2.0	21.5	72.6	14.5	91.2	71.1
2.0 - 2.2	17.8	77.1	18.8	139.6	125.6
2.2 - 2.4	18.8	74.6	25.3	93.6	85.4
2.4 - 2.6	21.4	79.3	19.7	119.1	105.1
2.6 - 2.8	25.4	84.5	28.5	128.0	106.2
2.8 - 3.0	20.9	84.5	36.0	178.3	141.1
3.0 - 4.0	20.9	90.2	28.9	155.8	133.0
4.0 - 5.0	21.1	108.2	31.3	151.7	131.1
5.0 - 6.0	22.0	115.7	39.5	219.1	182.4
6.0 - 7.0	22.9	127.5	49.8	201.0	189.2
7.0 - 8.0	23.2	141.3	32.1	200.9	185.3
8.0 - 9.0	22.2	156.1	25.3	385.8	299.3
9.0 - 10.0	23.8	145.2	35.4	427.1	356.9
10.0 - 11.0	27.9	135.0	43.3	418.1	357.7
11.0 - 12.0	26.1	141.3	30.5	397.6	282.2
12.0 - 13.0	29.3	152.4	36.3	492.8	343.3
13.0 - 14.0	25.9	151.6	26.2	420.2	332.5
14.0 - 15.0	27.6	149.5	37.2	456.7	263.9
15.0 - 16.0	25.1	148.0	42.3	436.4	285.6
16.0 - 17.0	27.9	158.3	39.5	403.6	303.2
17.0 - 18.0	28.4	154.0	42.4	388.4	285.6
18.0 - 19.0	28.6	169.6	48.7	389.6	285.6
19.0 - 20.0	29.9	215.5	67.8	434.4	375.8
20.0 - 21.0	30.1	223.2	80.3	497.1	441.0
21.0 - 22.0	23.1	227.6	58.4	674.0	498.5
22.0 - 23.0	20.0	64.3	0.0	311.0	163.6
23.0 - 24.0	19.1	14.0	0.0	169.3	102.6
24.0 - 25.0	13.5	9.8	0.0	164.0	69.3
25.0 - 26.0	15.5	14.6	0.0	180.8	91.5
26.0 - 27.0	13.7	10.5	0.0	143.2	74.9

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBSC 8

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 0.2	97.6				
0.2 - 0.4	96.4	35.4			
0.4 - 0.6	95.6	32.9	25.0	332	0.65
0.6 - 0.8	95.9				
0.8 - 1.0	96.2				
1.0 - 1.2	96.2	31.0			
1.2 - 1.4	95.4	30.8			
1.4 - 1.6	95.3	32.3	25.6	740	0.88
1.6 - 1.8	97.1	31.0	25.7	937	1.25
1.8 - 2.0	92.2	29.6	25.6	1251	1.86
2.0 - 2.2	92.0		21.8	1089	1.59
2.2 - 2.4	91.6	29.8	18.1	1313	1.73
2.4 - 2.6	91.9	30.3	14.2	1070	0.96
2.6 - 2.8	92.3	32.3	17.8	1512	1.17
2.8 - 3.0	92.2	32.7	22.0	2013	1.26
3.0 - 4.0	90.6	32.3			
4.0 - 5.0	91.1	30.6			
5.0 - 6.0	91.6	35.4			
6.0 - 7.0	91.4	37.0			
7.0 - 8.0	92.4	36.1			
8.0 - 9.0	92.3	33.0			
9.0 - 10.0	92.2	32.7			
10.0 - 11.0	91.7	36.6			
11.0 - 12.0	90.8	35.4			
12.0 - 13.0	90.3	33.4			
13.0 - 14.0	90.6	33.9			
14.0 - 15.0	90.8	34.9			
15.0 - 16.0	90.7	35.8			
16.0 - 17.0	90.8	33.7			
17.0 - 18.0	90.7	37.0			
18.0 - 19.0	90.6	36.6			
19.0 - 20.0	91.9	35.4			
20.0 - 21.0	91.3	34.2			
21.0 - 22.0	89.1	23.2			
22.0 - 23.0	86.3	11.4			
23.0 - 24.0	85.4	8.6			
24.0 - 25.0	84.9	6.0			
25.0 - 26.0	86.4	6.4			
26.0 - 27.0	85.3	6.9			

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBSC 8.

Appendix 9: Results from LBSC 9

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 0.2	1.36	1.47	3.02	0.71	
0.2 - 0.4	3.44	3.84	3.28	0.88	54.7
0.4 - 0.6	4.72	5.08	3.20	0.81	56.1
0.6 - 0.8	5.75	6.76	3.78	0.98	58.0
0.8 - 1.0	3.68	3.81	5.28	0.64	82.5
1.0 - 1.2	2.09	2.15	5.73	0.43	69.1
1.2 - 1.4	2.06	1.90	8.72	0.44	131.5
1.4 - 1.6	1.53	1.42	9.35	0.42	188.0
1.6 - 1.8	1.29	1.16	9.50	0.38	287.9
1.8 - 2.0	1.15	1.08	8.49	0.38	320.9
2.0 - 2.2	0.98	0.89	6.49	0.36	234.6
2.2 - 2.4	0.82	0.82	4.72	0.36	140.9
2.4 - 2.6	0.78	0.79	4.07	0.39	107.9
2.6 - 2.8	0.74	0.76	3.78	0.41	99.6
2.8 - 3.0	0.68	0.65	3.59	0.45	73.2

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBSC 9

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 0.2	42.6	93.3	52.3	127.5	56.7
0.2 - 0.4	39.8	95.0	53.8	321.5	90.0
0.4 - 0.6	32.5	87.8	41.2	241.5	59.7
0.6 - 0.8	37.5	88.3	49.1	200.0	61.0
0.8 - 1.0	36.5	90.5	30.9	155.0	59.2
1.0 - 1.2	31.7	80.9	27.3	160.5	54.1
1.2 - 1.4	34.4	82.9	21.8	150.1	50.6
1.4 - 1.6	30.0	89.3	24.7	160.8	45.5
1.6 - 1.8	28.1	83.2	13.5	151.6	38.8
1.8 - 2.0	29.7	81.1	14.2	149.1	41.2
2.0 - 2.2	30.1	87.9	19.3	126.2	37.3
2.2 - 2.4	29.8	93.3	24.8	149.8	52.9
2.4 - 2.6	29.4	101.0	30.5	174.3	60.6
2.6 - 2.8	33.0	99.7	35.5	174.7	71.2
2.8 - 3.0	28.8	101.7	39.2	190.7	81.4

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBSC

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 0.2	95.8				
0.2 - 0.4	96.4	35.8	17.6	165.8	0.27
0.4 - 0.6	96.3	32.7			
0.6 - 0.8	96.4	31.8			
0.8 - 1.0	95.6	30.3	23.3	489.9	0.63
1.0 - 1.2	94.7	31.5	20.7	615.2	0.75
1.2 - 1.4	94.5	29.4			
1.4 - 1.6	94.1	29.6	21.8	1059.6	0.87
1.6 - 1.8	93.2	29.6	25.5	1368	1.06
1.8 - 2.0	92.5	28.7	23.2	2303.5	1.58
2.0 - 2.2	91.9	29.4	23.5	2386.2	1.67
2.2 - 2.4	91.4	32.0	22.7	2444.2	1.48
2.4 - 2.6	91.6	33.5	19.1	2177.1	1.23
2.6 - 2.8	91.6	32.7	12.9	1291.6	0.7
2.8 - 3.0	94.8	33.0	12.1	1300.1	0.69

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBSC 9.

Appendix 10: Results from LBSC 10

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 0.2	1.38	1.53	3.49	1.92	86.6
0.2 - 0.4	4.71	5.28	3.38	1.87	75.4
0.4 - 0.6	5.54	6.12	3.54	1.67	105.3
0.6 - 0.8	2.31	2.47	6.08	3.56	133.0
0.8 - 1.0	1.44	1.45	5.92	2.85	125.0
1.0 - 1.2	1.08	1.11	5.55	2.63	103.3
1.2 - 1.4	1.36	1.32	11.21	3.55	43.4
1.4 - 1.6	1.34	1.22	10.43	3.67	36.6
1.6 - 1.8	1.15	1.15	8.23	2.77	33.4
1.8 - 2.0	1.09	1.11	7.37	2.37	33.8
2.0 - 2.2	0.98	1.03	6.06	2.21	39.9
2.2 - 2.4	0.87	0.92	4.98	1.87	56.5
2.4 - 2.6	0.78	0.84	3.91	1.63	56.8
2.6 - 2.8	0.77	0.77	3.57	1.55	57.9
2.8 - 3.0	0.76	0.69	3.63	0.47	58.0
3.0 - 4.0	0.68	0.65	3.63	0.36	56.2
4.0 - 5.0	0.69	0.68	3.80	0.49	57.3
5.0 - 6.0	0.89	0.90	4.96	0.71	53.7
6.0 - 7.0	0.94	0.91	8.54	1.36	50.6
7.0 - 8.0	0.86	0.92	9.78	1.28	40.8
8.0 - 9.0	0.82	0.81	7.07	0.61	43.7
9.0 - 10.0	0.73	0.70	4.71	0.43	46.7
10.0 - 11.0	0.83	0.79	4.42	0.39	45.3
11.0 - 12.0	0.71	0.67	4.46	0.42	44.0
12.0 - 13.0	0.70	0.72	3.85	0.39	32.9
13.0 - 14.0	0.70	0.70	3.98	0.37	32.8
14.0 - 15.0	0.69	0.66	3.78	0.31	34.5
15.0 - 16.0	0.73	0.73	3.41	0.43	32.9
16.0 - 17.0	0.84	0.85	4.13	0.48	32.5
17.0 - 18.0	0.91	0.88	4.72	0.35	34.6
18.0 - 19.0	0.75	0.69	4.00	0.26	32.7

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBSC 10

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 0.2	25.3	89.8	53.8	144.0	65.9
0.2 - 0.4	26.8	73.7	43.9	141.2	96.6
0.4 - 0.6	23.9	92.7	52.6	146.0	73.3
0.6 - 0.8	27.8	100.9	41.1	175.0	113.5
0.8 - 1.0	33.5	111.0	34.2	198.8	87.7
1.0 - 1.2	28.1	95.4	34.4	166.9	80.4
1.2 - 1.4	25.4	94.2	39.4	143.1	71.2
1.4 - 1.6	28.0	92.7	16.0	133.9	62.0
1.6 - 1.8	25.3	98.0	17.7	129.3	54.4
1.8 - 2.0	26.8	97.3	22.3	141.0	71.7
2.0 - 2.2	25.5	92.5	27.6	150.7	72.1
2.2 - 2.4	27.2	98.5	40.7	151.1	78.3
2.4 - 2.6	26.3	103.2	39.3	178.6	98.5
2.6 - 2.8	31.9	106.5	44.0	182.4	99.8
2.8 - 3.0	30.2	107.0	36.3	176.3	66.2
3.0 - 4.0	28.5	110.4	30.9	189.7	85.6
4.0 - 5.0	30.7	133.6	42.4	240.2	113.5
5.0 - 6.0	30.0	156.7	41.6	262.0	143.1
6.0 - 7.0	30.8	161.9	46.2	332.9	185.8
7.0 - 8.0	39.4	175.8	42.4	476.3	295.2
8.0 - 9.0	34.8	169.8	43.5	651.5	300.2
9.0 - 10.0	32.7	159.0	42.1	642.1	324.1
10.0 - 11.0	34.8	162.7	44.9	602.4	254.3
11.0 - 12.0	31.6	159.9	42.5	580.0	238.5
12.0 - 13.0	33.2	156.5	43.7	549.2	215.4
13.0 - 14.0	34.4	157.8	46.3	505.3	213.4
14.0 - 15.0	34.4	161.5	47.6	501.8	189.4
15.0 - 16.0	33.8	167.5	50.2	529.4	245.9
16.0 - 17.0	33.8	208.7	62.8	563.8	312.5
17.0 - 18.0	35.1	210.6	55.0	556.4	265.7
18.0 - 19.0	34.1	183.4	39.0	624.4	287.5

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBSC 10

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 0.2	93.3	32.0			
0.2 - 0.4	94.5	31.0			
0.4 - 0.6	95.4	32.3			
0.6 - 0.8	95.0				
0.8 - 1.0	94.0				
1.0 - 1.2	93.2				
1.2 - 1.4	93.5	27.7	28.4	1171.6	0.59
1.4 - 1.6	92.6		21.4	1353.5	0.72
1.6 - 1.8	92.1	27.9	26.5	2230.1	1.3
1.8 - 2.0	91.7	27.9	29.3	2675.7	2.11
2.0 - 2.2	91.5	27.7	16.3	1862.3	1.05
2.2 - 2.4	91.8	30.4	18.7	2043.8	1.04
2.4 - 2.6	91.7	31.5	14.5	1303.3	0.66
2.6 - 2.8	91.6	31.0	17.7	1882.6	0.83
2.8 - 3.0	91.6	32.3	23.0	1645.3	0.78
3.0 - 4.0	89.6	29.6			
4.0 - 5.0	91.0	33.5			
5.0 - 6.0	92.2	32.3			
6.0 - 7.0	93.2	29.8			
7.0 - 8.0	93.2	28.9			
8.0 - 9.0	91.6	32.7			
9.0 - 10.0	91.1	33.0			
10.0 - 11.0	90.7	31.5			
11.0 - 12.0	90.3	32.3			
12.0 - 13.0	90.6	31.6			
13.0 - 14.0	90.1	30.6			
14.0 - 15.0	90.4	31.0			
15.0 - 16.0	90.7	32.3			
16.0 - 17.0	91.4	33.7			
17.0 - 18.0	91.0	29.6			
18.0 - 19.0	92.7	27.3			

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBSC 10.

Appendix 11: Results from LRSC 1

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 0.2	0.80	0.71	4.61	0.48	86.6
0.2 - 0.4	0.80	0.67	4.85	0.43	91.0
0.4 - 0.6	0.76	0.68	4.87	0.13	101.1
0.6 - 0.8	0.73	0.59	5.23	0.42	98.7
0.8 - 1.0	0.64	0.45	5.76	0.43	119.1
1.0 - 1.2	0.57	0.46	5.89	0.46	126.8
1.2 - 1.4	0.48	0.38	5.20	0.49	112.7
1.4 - 1.6	0.38	0.31	3.80	0.43	77.4
1.6 - 1.8	0.37	0.30	3.74	0.39	71.2
1.8 - 2.0	0.31	0.27	2.75	0.34	52.3
2.0 - 2.2	0.29	0.26	2.32	0.34	41.3
2.2 - 2.4	0.25	0.23	1.91	0.29	34.6
2.4 - 2.6	0.25	0.23	1.99	0.46	35.9
2.6 - 2.8	0.24	0.21	1.80	0.37	37.1
2.8 - 3.0	0.22	0.21	1.84	0.31	40.0
3.0 - 4.0	0.23	0.22	2.51	0.23	41.8
4.0 - 5.0	0.24	0.22	2.53	0.28	50.2
5.0 - 6.0	0.25	0.24	2.67	0.35	60.1
6.0 - 7.0	0.27	0.26	3.02	0.49	70.0
7.0 - 8.0	0.26	0.25	2.86	0.43	64.1
8.0 - 9.0	0.22	0.18	3.33	0.29	59.6
9.0 - 10.0	0.2	0.17	3.04	0.24	52.7
10.0 - 11.0	0.2	0.17	2.88	0.22	49.9
11.0 - 12.0	0.21	0.18	2.83	0.22	51.9
12.0 - 13.0	0.22	0.21	2.84	0.23	61.3
13.0 - 14.0	0.23	0.20	2.90	0.26	56.1
14.0 - 15.0	0.27	0.23	2.83	0.27	53.0
15.0 - 16.0	0.28	0.24	2.61	0.28	38.8
16.0 - 17.0	0.3	0.26	2.50	0.24	35.4
17.0 - 18.0	0.29	0.27	2.58	0.29	34.7
18.0 - 19.0	0.3	0.27	2.79	0.27	34.7
19.0 - 20.0	0.29	0.25	2.90	0.31	34.8
20.0 - 21.0	0.25	0.22	3.32	0.23	37.1
21.0 - 22.0	0.23	0.19	3.37	0.21	35.7
22.0 - 23.0	0.22	0.18	3.62	0.21	35.2

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LRSC 1

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 0.2	22.4	93.1	40.2	164.0	114.8
0.2 - 0.4	27.7	103.6	34.0	149.6	105.2
0.4 - 0.6	20.8	103.8	38.5	107.1	88.4
0.6 - 0.8	21.9	105.5	42.8	64.7	58.9
0.8 - 1.0	21.3	95.2	24.1	91.7	69.5
1.0 - 1.2	22.5	92.9	26.5	104.1	70.2
1.2 - 1.4	19.3	94.2	31.4	67.2	45.5
1.4 - 1.6	19.5	96.1	40.8	85.6	57.0
1.6 - 1.8	19.7	101.4	40.8	114.5	71.5
1.8 - 2.0	24.4	113.4	44.2	112.5	73.0
2.0 - 2.2	16.4	106.8	45.7	78.3	62.3
2.2 - 2.4	14.8	116.6	47.7	147.5	95.5
2.4 - 2.6	15.7	119.5	52.7	150.4	106.1
2.6 - 2.8	19.4	120.6	56.9	188.3	116.1
2.8 - 3.0	21.3	125.9	52.9	229.6	168.9
3.0 - 4.0	17.7	135.9	41.0	132.8	98.6
4.0 - 5.0	18.5	145.7	50.8	201.3	141.0
5.0 - 6.0	20.5	176.2	58.8	260.5	205.8
6.0 - 7.0	24.4	222.0	82.5	324.9	224.5
7.0 - 8.0	22.1	210.2	85.1	281.4	216.4
8.0 - 9.0	27.0	233.9	94.2	320.1	255.7
9.0 - 10.0	23.3	209.5	75.9	347.1	282.8
10.0 - 11.0	24.9	204.5	77.7	309.3	260.4
11.0 - 12.0	22.3	215.7	74.0	333.2	255.6
12.0 - 13.0	25.4	224.8	49.0	388.1	281.6
13.0 - 14.0	23.3	195.1	36.6	325.7	245.3
14.0 - 15.0	22.3	177.7	40.1	220.0	172.7
15.0 - 16.0	15.3	100.2	7.2	118.8	98.2
16.0 - 17.0	13.2	36.8	7.0	94.9	65.0
17.0 - 18.0	13.4	25.3	0.0	72.5	50.7
18.0 - 19.0	16.5	35.3	0.0	49.4	30.3
19.0 - 20.0	15.6	18.3	0.0	61.5	50.6
20.0 - 21.0	14.5	18.5	6.7	97.6	75.0
21.0 - 22.0	13.2	17.3	0.0	89.6	51.3
22.0 - 23.0	15.8	39.0	0.7	130.2	61.8

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LRSC 1

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 0.2	97.1				
0.2 - 0.4	96.6				
0.4 - 0.6	96.4		38.6	502.0	1.53
0.6 - 0.8	95.9	40.2	33.0	432.0	1.33
0.8 - 1.0	95.6	38.2	30.0	431.0	1.41
1.0 - 1.2	95.6	36.5	28.6	388.0	1.38
1.2 - 1.4	95.6	40.1	23.4	273.0	1.04
1.4 - 1.6	95.3	38.7	23.2	228.0	0.78
1.6 - 1.8	95.3	38.9	28.0	218.0	0.89
1.8 - 2.0	94.9	42.5	28.0	200.0	1.45
2.0 - 2.2	94.6	44.0	24.5	148.0	0.53
2.2 - 2.4	94.3	42.7	22.2	113.0	0.42
2.4 - 2.6	95.0		22.7	119.0	0.50
2.6 - 2.8	94.6	43.5	24.8	81.0	0.28
2.8 - 3.0	94.7	44.2	16.5	105.0	0.33
3.0 - 4.0	93.9	45.2			
4.0 - 5.0	94.0	42.0			
5.0 - 6.0	93.6	46.4			
6.0 - 7.0	94.0	44.0			
7.0 - 8.0	93.8	39.0			
8.0 - 9.0	93.1	29.2			
9.0 - 10.0	92.8	30.6			
10.0 - 11.0	91.9	28.0			
11.0 - 12.0	91.5	30.3			
12.0 - 13.0	91.6	33.5			
13.0 - 14.0	91.2	33.4			
14.0 - 15.0	92.3	38.9			
15.0 - 16.0	91.5	39.2			
16.0 - 17.0	91.4	42.5			
17.0 - 18.0	91.5	40.9			
18.0 - 19.0	92.1	40.9			
19.0 - 20.0	91.9	38.9			
20.0 - 21.0	91.3	32.7			
21.0 - 22.0	91.5	30.3			
22.0 - 23.0	90.5	27.7			

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LRSC 1.

Appendix 12: Results from LRSC 2

Depth / cm	$[Mn]_{total}$ / %	$[Mn]_{reducible}$ / %	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 0.2	0.7	0.65	3.70	0.4	82.7
0.2 - 0.4	0.52	0.44	3.67	0.29	76.1
0.4 - 0.6	0.37	0.29	4.52	0.29	101.6
0.6 - 0.8	0.32	0.22	5.34	0.34	121.9
0.8 - 1.0	0.28	0.18	5.58	0.38	123.6
1.0 - 1.2	0.21	0.17	4.30	0.41	100.6
1.2 - 1.4	0.15	0.13	2.58	0.31	41.6
1.4 - 1.6	0.15	0.13	2.44	0.23	35.7
1.6 - 1.8	0.13	0.12	2.21	0.21	32.5
1.8 - 2.0	0.13	0.11	2.20	0.19	33.2
2.0 - 2.2	0.13	0.11	2.14	0.2	40.3
2.2 - 2.4	0.15	0.12	2.35	0.21	50.2
2.4 - 2.6	0.17	0.13	2.33	0.21	54.6
2.6 - 2.8	0.14	0.12	2.44	0.24	53.2
2.8 - 3.0	0.14	0.11	2.40	0.26	53.3
3.0 - 4.0	0.15	0.12	2.66	0.17	52.5
4.0 - 5.0	0.17	0.14	2.78	0.18	59.7
5.0 - 6.0	0.15	0.12	3.00	0.2	54.3
6.0 - 7.0	0.16	0.14	2.93	0.27	53.4
7.0 - 8.0	0.13	0.10	2.84	0.24	41.8
8.0 - 9.0	0.16	0.13	2.60	0.29	44.3
9.0 - 10.0	0.15	0.13	2.69	0.2	43.7
10.0 - 11.0	0.17	0.15	2.66	0.26	49.0
11.0 - 12.0	0.18	0.16	2.70	0.26	42.0
12.0 - 13.0	0.16	0.13	2.83	0.24	32.1
13.0 - 14.0	0.19	0.18	2.62	0.26	31.5
14.0 - 15.0	0.21	0.18	2.64	0.27	33.8
15.0 - 16.0	0.19	0.19	2.48	0.29	32.7
16.0 - 17.0	0.19	0.18	2.51	0.29	32.2
17.0 - 18.0	0.21	0.19	2.50	0.28	32.7
18.0 - 19.0	0.21	0.20	2.63	0.29	32.7

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LRSC 2

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 0.2	21.4	115.8	51.6	331.9	282.7
0.2 - 0.4	20.5	128.3	58.0	126.2	100.3
0.4 - 0.6	16.3	126.2	34.0	141.8	135.3
0.6 - 0.8	18.7	114.0	41.2	122.4	47.5
0.8 - 1.0	13.9	111.4	32.4	123.1	46.7
1.0 - 1.2	19.1	147.9	35.6	121.8	71.7
1.2 - 1.4	17.3	129.8	41.2	170.5	92.3
1.4 - 1.6	18.8	147.0	31.5	181.5	96.0
1.6 - 1.8	28.3	172.2	47.9	179.6	85.6
1.8 - 2.0	26.5	190.7	56.3	193.1	95.2
2.0 - 2.2	24.8	214.2	83.8	350.1	196.8
2.2 - 2.4	26.3	223.6	76.2	459.5	228.2
2.4 - 2.6	25.2	239.6	103.9	500.0	265.1
2.6 - 2.8	22.5	208.7	68.6	462.6	255.1
2.8 - 3.0	22.7	219.0	79.5	444.5	255.7
3.0 - 4.0	25.2	224.7	63.3	293.6	212.9
4.0 - 5.0	22.8	193.1	50.3	279.6	206.8
5.0 - 6.0	18.8	157.8	46.7	228.4	190.8
6.0 - 7.0	18.8	150.7	42.4	189.2	170.8
7.0 - 8.0	15.5	95.0	34.3	138.9	124.5
8.0 - 9.0	14.1	115.3	34.9	121.3	103.7
9.0 - 10.0	15.5	141.5	38.2	183.6	133.5
10.0 - 11.0	16.9	166.3	50.7	136.8	101.1
11.0 - 12.0	15.4	158.8	32.4	118.8	102.1
12.0 - 13.0	11.9	132.3	35.5	79.1	54.0
13.0 - 14.0	15.4	96.3	20.4	148.8	76.5
14.0 - 15.0	13.0	84.8	13.1	142.6	80.2
15.0 - 16.0	11.8	80.6	27.7	83.0	69.9
16.0 - 17.0	11.2	74.5	15.5	74.6	56.9
17.0 - 18.0	12.7	74.0	10.1	81.2	67.3
18.0 - 19.0	11.0	68.7	21.7	74.0	39.2

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LRSC 2

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 0.2	96.0				
0.2 - 0.4	95.2	35.9	15.4	176.1	0.45
0.4 - 0.6	95.0	28.7	16.3	197.8	0.70
0.6 - 0.8	95.0	32.5	21.6	245.5	1.15
0.8 - 1.0	95.0	34.9	19.3	153.4	0.82
1.0 - 1.2	94.6	35.4	16.0	117.3	0.80
1.2 - 1.4	94.1	34.6	17.6	104.2	0.89
1.4 - 1.6	94.0	34.7	20.8	101.6	0.64
1.6 - 1.8	94.0	34.7	17.8		
1.8 - 2.0	93.4	33.0	19.4	121.5	0.51
2.0 - 2.2	92.8	35.1		212.9	0.57
2.2 - 2.4	93.3	35.6	18.2	179.4	0.55
2.4 - 2.6	94.5	34.7	1.9		
2.6 - 2.8	92.8	35.4		243.0	0.59
2.8 - 3.0	92.7	35.9		287.2	0.83
3.0 - 4.0	91.9	36.5			
4.0 - 5.0	90.7	38.0			
5.0 - 6.0	87.4	31.5			
6.0 - 7.0	88.8	31.3			
7.0 - 8.0	86.3	32.5			
8.0 - 9.0	89.2	32.3			
9.0 - 10.0	89.9	30.6			
10.0 - 11.0	91.3	33.9			
11.0 - 12.0	91.2	32.9			
12.0 - 13.0	88.2	33.9			
13.0 - 14.0	89.9	31.8			
14.0 - 15.0	90.6	39.4			
15.0 - 16.0	90.1	36.6			
16.0 - 17.0	90.4	38.4			
17.0 - 18.0	90.3	38.5			
18.0 - 19.0	89.4	39.4			

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LRSC 2.

Appendix 13: Results from LBPC 1

Depth / cm	$[Mn]_{total}$ / mg kg^{-1}	$[Mn]_{reducible}$ / mg kg^{-1}	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0 - 4.4	18000	16000	6.87	0.48	140.1
4.4 - 7.6	7122	4787	12.85	0.42	523.5
7.6 - 10.2	862	316	12.94	0.23	1500.7
10.2 - 12.8	797	133	12.41	0.12	2021.5
12.8 - 15.7	769	124	9.14	0.10	1644.5
15.7 - 18.2	249	65	4.30	0.06	529.2
18.2 - 21.1	241	86	3.99	0.05	429.3
21.1 - 23.7	253	158	2.43	0.07	206.5
23.7 - 26.3	260	186	1.70	0.11	151.1
26.3 - 29.0	252	166	2.45	0.11	173.9
29.0 - 31.6	219	166	1.30	0.12	141.1
31.6 - 34.1	277	167	1.81	0.10	136.8
34.1 - 36.7	248	168	1.17	0.11	134.4
36.7 - 39.5	267	66	2.21	0.05	153.5
39.5 - 42.5	302	51	3.37	0.04	123.4
42.5 - 45.5	374	46	4.46	0.03	151.8
45.5 - 48.7	425	47	5.25	0.02	178.3
48.7 - 51.4	434	47	5.19	0.03	192.7
51.4 - 53.9	433	80	5.03	0.04	182.7
53.9 - 56.6	357	132	3.45	0.07	166.3
56.6 - 59.0	290	100	1.86	0.06	151.2
59.0 - 61.6	323	70	2.21	0.05	102.6
61.6 - 64.1	335	65	2.30	0.05	106.9

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBPC 1

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0 - 4.4	11.2	157.6	48.5	40.6	15.8
4.4 - 7.6	15.7	177.3	51.8	27.4	8.7
7.6 - 10.2	24.0	219.7	56.9	34.6	6.7
10.2 - 12.8	11.9	151.7	34.8	34.0	3.9
12.8 - 15.7	6.2	78.3	18.3	29.8	2.5
15.7 - 18.2	11.3	38.6	3.7	20.1	1.3
18.2 - 21.1	8.8	35.0	2.7	24.4	0.0
21.1 - 23.7	73.2	32.6	4.4	61.7	27.3
23.7 - 26.3	29.9	18.2	1.6	35.9	0.9
26.3 - 29.0	12.7	16.4	0.4	23.2	0.0
29.0 - 31.6	27.9	15.3	0.0	25.2	4.6
31.6 - 34.1	9.5	19.5	0.0	16.0	0.0
34.1 - 36.7	8.8	17.1	0.0	7.7	0.8
36.7 - 39.5	0.8	24.7	0.0	25.0	0.2
39.5 - 42.5	0.0	21.5	0.5	57.3	0.0
42.5 - 45.5	0.0	22.3	0.0	39.5	0.0
45.5 - 48.7	0.0	21.5	0.9	42.5	0.0
48.7 - 51.4	0.0	20.2	2.2	25.5	0.0
51.4 - 53.9	0.0	20.6	2.7	63.1	0.0
53.9 - 56.6	0.0	21.3	2.8	68.9	0.0
56.6 - 59.0	0.0	24.6	1.0	42.5	0.0
59.0 - 61.6	0.0	28.4	1.3	24.6	0.0
61.6 - 64.1	0.0	29.5	0.0	36.7	0.0

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBPC 1

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0 - 4.4	88.7	58.5	28.7	451.3	0.74
4.4 - 7.6	87.8	37.7	24.8	222.7	1.16
7.6 - 10.2	85.9	34.1	24.5	146.9	2.05
10.2 - 12.8	82.2	30.3	27.3	343.7	4.49
12.8 - 15.7	79.1	31.6	22.7	157.6	2.68
15.7 - 18.2	78.8	37.5	24.4	69.0	1.35
18.2 - 21.1	79.0	41.6	25.0	66.1	1.16
21.1 - 23.7	81.5	49.0	24.8	66.3	0.92
23.7 - 26.3	85.1	54.9	23.0	49.5	0.40
26.3 - 29.0	86.1	56.8	31.0	95.7	1.09
29.0 - 31.6	86.8	55.7	31.2	81.1	0.42
31.6 - 34.1	86.9	42.8	29.0	139.1	0.88
34.1 - 36.7	85.9	45.2	22.0	127.2	0.43
36.7 - 39.5	71.5	17.9	25.0	181.4	1.60
39.5 - 42.5	62.2	12.0	21.7	246.1	3.19
42.5 - 45.5	63.9	11.5	23.2	284.8	4.04
45.5 - 48.7	61.4	11.7	20.9	247.4	4.07
48.7 - 51.4	65.3	13.9	20.5	256.1	3.93
51.4 - 53.9	67.2	16.0	26.7	302.7	4.66
53.9 - 56.6	69.2	23.4	26.3	226.4	2.97
56.6 - 59.0	74.2	26.8	28.9	209.4	1.79
59.0 - 61.6	74.8	22.5	21.8	143.8	1.13
61.6 - 64.1	68.2	20.6	19.8	113.8	1.20

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBPC 1.

Appendix 14: Results from LBPC 2

Depth / cm	$[Mn]_{total}$ / mg kg^{-1}	$[Mn]_{reducible}$ / mg kg^{-1}	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 2.9	35.6	36.9	0.81	0.25	14.3
2.9 - 5.8	14.3	7.4	0.58	0.19	10.9
5.8 - 8.9	13.7	5.5	0.72	0.22	19.5
8.9 - 11.5	14.9	7.3	1.37	0.25	28.9
11.5 - 13.6	11.3	2.4	1.37	0.29	31.7
13.6 - 15.9	11.8	2.0	1.41	0.21	38.9
15.9 - 18.3	11.4	2.5	1.73	0.20	57.6
18.3 - 20.0	11.2	1.9	0.82	0.13	30.1
20.0 - 21.9	8.3	1.1	0.88	0.10	36.3
21.9 - 24.2	9.0	3.7	0.59	0.07	22.9
24.2 - 26.3	9.0	1.2	0.39	0.04	15.2
26.3 - 28.2	5.7	0.6	0.17	0.03	13.1
28.2 - 29.7	6.3	0.2	0.19	0.02	13.3
29.7 - 32.4	18.9	0.4	0.21	0.02	8.8
32.4 - 35.1	0.0	0.0	0.15	0.03	8.5
35.1 - 37.8	2.2	4.3	0.22	0.03	9.6
37.8 - 40.1	0.0	1.5	0.15	0.02	9.5
40.1 - 42.4	0.0	1.6	0.20	0.02	11.1
42.4 - 44.9	0.0	1.7	0.15	0.02	10.8
44.9 - 47.5	0.0	1.5	0.15	0.02	11.6
47.5 - 49.4	0.0	1.8	0.17	0.02	10.1
49.4 - 51.8	8.3	0.9	0.14	0.02	16.1
51.8 - 54.4	8.2	0.8	0.12	0.01	23.2
54.4 - 57.0	20.0	0.8	0.15	0.01	27.7

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBPC 2

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 2.9	28.4	108.8	46.4	66.4	34.7
2.9 - 5.8	25.3	125.5	57.6	41.3	11.5
5.8 - 8.9	21.3	109.2	47.7	27.9	14.6
8.9 - 11.5	17.2	66.7	23.5	39.9	15.0
11.5 - 13.6	14.6	41.9	11.7	22.7	9.6
13.6 - 15.9	12.5	19.8	2.4	14.4	4.2
15.9 - 18.3	13.7	22.6	2.1	13.7	2.3
18.3 - 20.0	14.7	9.4	2.0	9.7	1.5
20.0 - 21.9	11.7	37.8	2.2	29.5	3.2
21.9 - 24.2	14.7	39.5	8.0	22.4	3.4
24.2 - 26.3	13.3	23.4	0.9	21.0	7.6
26.3 - 28.2	12.0	110.3	4.3	33.4	5.9
28.2 - 29.7	12.8	9.1	0.0	44.6	8.7
29.7 - 32.4	9.8	8.4	0.2	17.3	7.5
32.4 - 35.1	11.2	6.3	0.3	19.8	7.5
35.1 - 37.8	12.5	32.6	1.7	6.6	7.2
37.8 - 40.1	14.5	16.1	1.6	3.8	4.2
40.1 - 42.4	22.5	7.5	1.5	4.4	6.7
42.4 - 44.9	14.0	4.2	1.7	2.1	3.8
44.9 - 47.5	12.2	6.1	1.6	7.2	1.6
47.5 - 49.4	13.1	4.8	1.3	7.2	1.4
49.4 - 51.8	11.2	15.1	1.4	5.2	2.6
51.8 - 54.4	8.6	22.6	1.1	5.7	1.5
54.4 - 57.0	9.4	25.5	1.9	11.0	0.2

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBPC 2

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 2.9	90.5	73.3	23.0	0.7	0.24
2.9 - 5.8	90.7	69.8	34.9	0.0	0.33
5.8 - 8.9	87.3	71.2	28.8	0.0	0.32
8.9 - 11.5	83.4	70.3	38.7	6.8	0.61
11.5 - 13.6	82.2	69.8	47.4	0.0	0.65
13.6 - 15.9	82.1	64.0	37.6	0.0	0.50
15.9 - 18.3	81.5	68.5	38.5	0.0	0.50
18.3 - 20.0	84.1	70.2	38.7	0.0	0.23
20.0 - 21.9	81.9	66.9	45.6	0.0	0.28
21.9 - 24.2	79.9	68.8	43.5	0.0	0.18
24.2 - 26.3	78.4	68.1	45.4	0.0	0.17
26.3 - 28.2	74.9	67.9	47.6	0.0	0.10
28.2 - 29.7	73.5	68.3	34.6	0.0	0.05
29.7 - 32.4	68.8	44.0	35.8	0.0	0.06
32.4 - 35.1	80.8	73.6	52.9	0.0	0.05
35.1 - 37.8	84.8	73.8	54.8	0.0	0.10
37.8 - 40.1	85.8	71.9	58.4	0.0	0.02
40.1 - 42.4	85.7	70.5	58.7	0.0	0.05
42.4 - 44.9	86.8	71.9	63.4	0.0	0.04
44.9 - 47.5	84.8	69.3	66.7	0.0	0.09
47.5 - 49.4	86.5	70.0	64.0	0.0	0.10
49.4 - 51.8	85.7	65.2	67.1	0.0	0.06
51.8 - 54.4	83.4	63.6	50.6	0.0	0.01
54.4 - 57.0	79.1	51.9	38.9	0.0	0.01

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBPC 2.

Appendix 15: Results from LBPC 3

Depth / cm	$[Mn]_{total}$ / mg kg^{-1}	$[Mn]_{reducible}$ / mg kg^{-1}	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 3.8	6377	6558	2.71	0.30	148.8
3.8 - 7.0	9502	10640	2.70	0.26	150.6
7.0 - 10.0	5946	5596	3.46	0.22	180.4
10.0 - 12.5	3465	3190	3.71	0.21	237.5
12.5 - 15.1	3733	3059	2.92	0.18	192.9
15.1 - 16.9	2566	1965	2.55	0.08	108.9
16.9 - 19.7	1854	1390	2.08	0.06	54.1
19.7 - 21.9	1372	1240	0.83	0.04	43.1
21.9 - 24.5	1159	993	0.37	0.05	27.1
24.5 - 26.9	1175	1150	0.56	0.05	34.9
26.9 - 29.3	1006	884	0.32	0.05	28.1
29.3 - 31.1	850	862	0.33	0.05	36.5
31.1 - 33.9	712	783	0.27	0.05	45.1
33.9 - 36.5	712	765	0.33	0.05	42.3
36.5 - 38.9	561	594	0.30	0.05	37.3
38.9 - 41.3	522	525	0.38	0.05	39.1
41.3 - 44.2	471	473	0.38	0.04	38.6
44.2 - 46.8	416	383	0.48	0.04	32.9
46.8 - 48.0	369	348	0.56	0.04	33.7

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBPC 3

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 3.8	6.1	155.1	42.9	77.4	43.3
3.8 - 7.0	7.3	163.6	39.2	144.2	54.4
7.0 - 10.0	12.9	170.3	36.2	70.7	46.9
10.0 - 12.5	5.9	164.6	33.4	74.4	29.4
12.5 - 15.1	9.6	120.7	25.3	67.9	24.4
15.1 - 16.9	5.5	92.0	10.3	74.5	23.2
16.9 - 19.7	4.6	79.2	5.6	109.4	22.0
19.7 - 21.9	4.2	29.4	3.5	22.5	10.4
21.9 - 24.5	7.5	25.3	3.3	13.3	0.3
24.5 - 26.9	5.7	23.1	3.0	19.0	6.0
26.9 - 29.3	6.2	4.6	3.4	6.9	2.0
29.3 - 31.1	4.0	9.9	1.0	3.9	4.2
31.1 - 33.9	2.9	6.4	3.0	8.9	0.2
33.9 - 36.5	2.0	7.4	1.8	1.3	0.9
36.5 - 38.9	2.1	9.5	5.4	7.4	0.6
38.9 - 41.3	0.2	10.5	1.7	0.2	0.4
41.3 - 44.2	4.0	17.7	0.9	14.2	0.0
44.2 - 46.8	2.7	15.4	0.4	8.3	0.0
46.8 - 48.0	4.8	13.7	2.5	8.0	0.0

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBPC 3

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 3.8	86.6	54.2	23.8	95.9	0.33
3.8 - 7.0	86.7	55.4	21.9	84.7	0.24
7.0 - 10.0	86.6	56.8	27.4	77.2	0.27
10.0 - 12.5	86.7	61.7	26.0	50.6	0.26
12.5 - 15.1	86.8	67.6	30.5	70.9	0.38
15.1 - 16.9	87.2	72.6	25.5	32.0	0.19
16.9 - 19.7	87.7	73.8	24.1	19.4	0.05
19.7 - 21.9	88.2	69.8	33.9	30.4	0.07
21.9 - 24.5	89.0	71.0	33.3	34.7	0.02
24.5 - 26.9	88.7	76.7	32.1	32.3	0.04
26.9 - 29.3	89.2	68.6	37.5	35.3	0.03
29.3 - 31.1	89.4	73.8	36.2	28.6	0.02
31.1 - 33.9	89.3	67.3	31.4	26.0	0.00
33.9 - 36.5	87.7	74.0	32.0	22.6	0.00
36.5 - 38.9	88.3	64.2	23.2	23.6	0.00
38.9 - 41.3	87.2	59.7	24.5	24.4	0.00
41.3 - 44.2	90.9	59.3	22.9	12.9	0.00
44.2 - 46.8	89.4	59.3	17.8	4.4	0.00
46.8 - 48.0	82.2	48.8	17.3	3.6	0.00

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBPC 3.

Appendix 16: Results from LBPC 4

Depth / cm	$[Mn]_{total}$ / mg kg^{-1}	$[Mn]_{reducible}$ / mg kg^{-1}	$[Fe]_{total}$ / %	$[Fe]_{reducible}$ / %	[As] / mg kg^{-1}
0.0 - 3.0	249	158	0.87	0.15	9.0
3.0 - 5.8	869	308	2.31	0.12	47.3
5.8 - 8.8	3008	1641	5.05	0.18	77.6
8.8 - 12.0	1242	544	4.25	0.11	71.3
12.0 - 14.6	1150	392	3.07	0.08	45.9
14.6 - 17.2	631	181	2.46	0.04	28.3
17.2 - 19.4	817	280	2.68	0.04	41.3
19.4 - 22.0	1474	691	2.61	0.04	39.7
22.0 - 24.4	1776	1068	2.81	0.05	50.5
24.4 - 26.6	1449	892	2.85	0.04	55.7
26.6 - 28.6	1974	1145	3.40	0.04	53.4
28.6 - 30.6	5011	3639	4.15	0.11	80.2
30.6 - 33.2	5780	4780	4.42	0.13	83.1
33.2 - 35.6	4389	2939	3.46	0.08	58.0
35.6 - 38.2	4060	3224	3.51	0.07	58.2
38.2 - 40.6	3640	2758	3.88	0.06	71.0
40.6 - 43.2	2503	1770	3.27	0.03	40.6
43.2 - 45.6	2249	1831	2.77	0.05	40.5

Total Mn, Fe and As concentration and easily reducible Mn and Fe concentration in LBPC 4

Depth / cm	$[Cu]_{total}$ / mg kg^{-1}	$[Pb]_{total}$ / mg kg-1	$[Pb]_{reducible}$ / mg kg-1	$[Zn]_{total}$ / mg kg-1	$[Zn]_{reducible}$ / mg kg^{-1}
0.0 - 3.0	25.2	88.4	51.7	23.0	20.1
3.0 - 5.8	28.5	136.7	72.9	23.0	12.4
5.8 - 8.8	26.5	87.6	32.3	38.9	8.5
8.8 - 12.0	34.9	34.7	12.0	53.7	4.4
12.0 - 14.6	31.8	32.6	12.3	53.2	13.0
14.6 - 17.2	30.4	21.3	9.3	56.5	9.8
17.2 - 19.4	31.2	18.3	0.0	62.4	8.4
19.4 - 22.0	31.6	21.6	14.9	57.6	6.8
22.0 - 24.4	36.7	20.6	11.7	57.1	8.4
24.4 - 26.6	22.8	18.3	0.0	49.3	19.1
26.6 - 28.6	8.1	20.7	5.6	65.4	16.3
28.6 - 30.6	3.8	20.7	5.6	64.8	3.7
30.6 - 33.2	2.2	19.8	6.8	65.9	22.5
33.2 - 35.6	4.8	24.3	8.3	59.9	12.4
35.6 - 38.2	0.9	18.8	6.5	63.6	16.2
38.2 - 40.6	0.0	19.5	7.4	76.5	28.9
40.6 - 43.2	5.7	17.4	0.0	66.8	6.2
43.2 - 45.6	5.1	18.0	10.4	56.8	14.4

Total Cu, Pb and Zn concentration and easily reducible Pb and Zn concentration in LBPC 4

Depth / cm	$[H_2O]$ / %	Organic Matter / %	Humic / %	$[Mn]_{humic}$ / mg kg^{-1}	$[Fe]_{humic}$ / %
0.0 - 3.0	86.2	59.0	30.8	42.7	0.25
3.0 - 5.8	78.1	31.8	18.1	44.1	0.23
5.8 - 8.8	61.0	20.1	12.3	59.9	0.47
8.8 - 12.0	59.9	17.2	12.9	51.9	0.53
12.0 - 14.6	57.8	16.5	11.7	41.3	0.32
14.6 - 17.2	53.3	14.6	10.3	16.7	0.18
17.2 - 19.4	55.7	15.0	10.2	33.1	0.31
19.4 - 22.0	57.6	14.6	13.0	87.4	0.59
22.0 - 24.4	57.8	14.4	10.7	54.9	0.39
24.4 - 26.6	57.1	12.4	12.7	89.5	0.73
26.6 - 28.6	54.2	12.4	13.3	112.6	1.02
28.6 - 30.6	44.7	9.5	11.6	207.8	1.52
30.6 - 33.2	46.6	11.2	12.4	247.2	1.58
33.2 - 35.6	43.6	15.3	10.4	151.2	1.12
35.6 - 38.2	42.1	10.7	11.8	216.6	1.42
38.2 - 40.6	41.3	11.2	12.2	238.8	1.05
40.6 - 43.2	44.5	15.8	9.5	137.2	0.93
43.2 - 45.6	38.4	14.1	6.8	4.1	0.89

Water content of sediment, organic matter and humic content of dried sediment and Mn and Fe concentration of humic (expressed as mg kg^{-1} and % of extracted humic) in LBPC 4.

Appendix 17: Concentration of Total Dissolved and Size Fractionated Manganese and Iron in the Loch Bradan Feeder Streams

	$[Mn]_{Dissolved}$ mg l^{-1}					
Stream	25/ 5/95	6/ 6/95	6/10/95	12/10/95	26/9/96	22/5 98
LBSW 1		0.05		0.04		0.11
LBSW 2	0.06	0.01		0.05		0.04
LBSW 3	0.15	0.13	0.12	0.11	0.99	0.47
LBSW 4	0.01	0.02	0.08	0.04	0.02	0.06
LBSW 5	0.02	0.01	0.10	0.04	0.01	0.06
LBSW 6	0.59	0.17			0.36	0.47

Dissolved Mn concentrations observed in the Loch Bradan feeder streams on various dates.

	$[Fe]_{Dissolved}$ mg l^{-1}					
Stream	25/ 5/95	6/ 6/95	6/10/95	12/10/95	26/9/96	22/5 98
LBSW 1				0.43		0.24
LBSW 2				0.14		0.13
LBSW 3			0.20	0.49	0.65	0.83
LBSW 4			0.19	0.17	0.02	0.24
LBSW 5			0.39	0.09	0.44	0.63
LBSW 6					0.25	1.12

Dissolved Fe concentrations observed in the Loch Bradan feeder streams on various dates.

Stream	$[Mn]_{total}$ / mg l^{-1}	$[Mn]_{<1k\ Da}$ / mg l^{-1}	$[Mn]_{>1k\ Da}$ / mg l^{-1}
LBSW 1	0.11	0.06	0.04
LBSW 2	0.04	0.01	0.02
LBSW 3	0.24	0.11	0.10
LBSW 4	0.06	0.04	0.04
LBSW 5	0.06	0.04	0.03
LBSW 6	0.47	0.28	0.14

Concentration of total dissolved and size fractionated (< 1 kDa and > 1 kDa) Mn found in the Loch Bradan feeder streams on 23 / 5 / 98.

Stream	$[Fe]_{total}$ / mg l^{-1}	$[Fe]_{<1k\ Da}$ / mg l^{-1}	$[Fe]_{>1k\ Da}$ / mg l^{-1}
LBSW 1	0.24	0.13	0.16
LBSW 2	0.13	0.13	0.11
LBSW 3	0.83	0.31	0.41
LBSW 4	0.46	0.26	0.31
LBSW 5	0.63	0.33	0.34
LBSW 6	1.12	0.44	0.51

Concentration of total dissolved and size fractionated (< 1 kDa and > 1 kDa) Fe found in the Loch Bradan feeder streams on 23 / 5 / 98.

Appendix 18: Concentration of Total Dissolved and Size Fractionated Manganese and Iron in the Loch Bradan Water Column

Sample	$[Mn]_{total}$ / mg l^{-1}	$[Mn]_{< 1000\ Da}$ / mg l^{-1}	$[Mn]_{> 1000\ Da}$ / mg l^{-1}	$[Mn]_{particulate}$ / mg l^{-1}
LBWS 1 - 0 m	0.11	0.06	0.08	0.23
LBWS 1 - 5 m	0.12	0.05	0.08	0.24
LBWS 1 - 13 m	0.19	0.08	0.13	0.33
LBWS 2 - 0 m	0.11	0.06	0.07	0.25
LBWS 2 - 5 m	0.13	0.06	0.07	0.31
LBWS 2 - 14.5 m	0.34	0.16	0.16	2.93
LBWS 3 - 0 m	0.15	0.06	0.08	0.66
LBWS 3 - 5 m	0.14	0.07	0.09	0.32
LBWS 3 - 15 m	0.14	0.07	0.07	0.31
LBWS 4 - 0 m	0.09	0.06	0.04	
LBWS 4 - 5 m	0.09	0.05	0.05	
LBWS 4 - 15 m	0.24	0.12	0.15	

Dissolved and particulate Mn concentrations in water column of Loch Bradan, and the concentration of Mn measured in the < 1 kDa and > 1 kDa size fractions.

Sample	$[Fe]_{total}$ / mg l^{-1}	$[Fe]_{< 1000\ Da}$ / mg l^{-1}	$[Fe]_{> 1000\ Da}$ / mg l^{-1}	$[Fe]_{particulate}$ / mg l^{-1}
LBWS 1 - 0 m	0.32			5.63
LBWS 1 - 5 m	0.29			6.51
LBWS 1 - 13 m	0.60			12.01
LBWS 2 - 0 m	0.28			5.42
LBWS 2 - 5 m	0.29			7.73
LBWS 2 - 14.5 m	0.33			13.17
LBWS 3 - 0 m	0.28			6.03
LBWS 3 - 5 m	0.28			6.30
LBWS 3 - 15 m	0.28			7.80
LBWS 4 - 0 m	0.30	0.20	0.21	
LBWS 4 - 5 m	0.30	0.15	0.18	
LBWS 4 - 15 m	0.44	0.29	0.25	

Dissolved and particulate Mn concentrations in water column of Loch Bradan, and the concentration of Mn measured in the < 1 kDa and > 1 kDa size fractions.

Appendix 19: Wet and Dry Weights of Sediment Collected from Loch Bradan and Loch Riecawr, and Wet and Dry Weights of Peat Cores Collected from the Loch Bradan Catchment

Depth/ cm	LBSC 1		LBSC 2		LBSC 3	
	Wet / g	Dry / g	Wet / g	Dry / g	Wet / g	Dry / g
0.1	4.720	0.154	10.136	0.408	6.512	0.483
0.3	10.033	0.413	12.360	0.677	6.867	0.518
0.5	6.848	0.278	10.840	0.652	4.430	0.365
0.7	8.722	0.387	9.225	0.595	9.296	0.787
0.9	8.643	0.438	8.561	0.589	7.808	0.626
1.1	8.685	0.486	13.310	0.923	11.536	0.944
1.3	9.817	0.611	9.791	0.718	9.958	0.878
1.5	8.935	0.566	11.265	0.832	7.177	0.654
1.7	9.664	0.604	12.073	0.971	10.403	0.974
1.9	9.958	0.626	9.381	0.654	11.608	1.126
2.1	8.271	0.505	8.030	0.606	5.686	0.530
2.3	11.687	0.807	10.681	0.806	15.199	1.508
2.5	10.900	0.786	11.986	0.899	7.969	0.724
2.7	8.959	0.656	11.243	0.861	7.888	0.714
2.9	7.157	0.536	8.249	0.625	13.514	1.347

Wet and dry weights of sediment from coring sites LBSC 1 to 3.

Depth/ cm	LBSC 4		LBSC 5	
	Wet / g	Dry / g	Wet / g	Dry / g
0.1	5.705	0.126	7.781	0.307
0.3	5.163	0.147	7.720	0.474
0.5	5.399	0.151	7.014	0.282
0.7	8.646	0.281	9.451	0.410
0.9	8.261	0.31	8.972	0.316
1.1	8.164	0.362	10.094	0.629
1.3	7.589	0.411	11.517	0.765
1.5	8.67	0.513	12.137	0.769
1.7	7.22	0.386	11.175	0.728
1.9	9.08	0.505	9.150	0.631
2.1	10.381	0.616	8.014	0.614
2.3	8.008	0.511	14.275	1.134
2.5	6.07	0.401	10.926	0.834
2.7	6.95	0.5	14.431	1.172
2.9	7.574	0.504	16.005	1.188

Wet and dry weights of sediment from coring sites LBSC 4 and 5.

Depth/ cm	LBSC 6	
	Wet / g	Dry / g
0.1	7.573	0.323
0.3	6.579	0.276
0.5	6.894	0.288
0.7	7.394	0.338
0.9	8.761	0.462
1.1	6.922	0.399
1.3	5.038	0.306
1.5	7.630	0.482
1.7	10.042	0.606
1.9	9.112	0.519
2.1	9.699	0.618
2.3	8.643	0.620
2.5	6.741	0.534
2.7	10.907	0.913
2.9	9.023	0.741
3.5	27.390	2.703
4.5	31.260	2.757
5.5	34.380	2.552
6.5	33.048	2.109
7.5	32.745	2.356
8.5	34.904	2.852
9.5	25.158	3.075
10.5	34.136	3.298
11.5	33.151	3.055
12.5	33.638	2.895
13.5	28.207	2.819
14.5	35.440	3.025
15.5	34.959	3.199
16.5	36.865	3.857

Depth	LBSC 6	
	Wet / g	Dry / g
17.5	35.660	3.730
18.5	35.317	3.257
19.5	35.755	3.725
20.5	36.728	3.623
21.5	38.250	3.386
22.5	34.734	3.869
23.5	37.459	4.045
24.5	34.210	3.298
25.5	37.546	3.772
26.5	36.160	3.778
27.5	34.881	4.689
28.5	41.010	6.235
29.5	34.404	5.284
30.5	37.979	6.492
31.5	36.871	5.511
32.5	36.123	5.643
33.5	37.522	6.424
34.5	37.668	6.165
35.5	39.165	5.700
36.5	40.489	5.484
37.5	38.374	5.426
38.5	38.946	5.386
39.5	30.067	3.893
40.5	37.282	4.585
41.5	33.429	4.337
42.5	36.114	4.574
43.5	38.301	4.648
44.5	42.366	5.617

Wet and dry weights of sediment from coring site LBSC 6.

Depth/ cm	LBSC 7		LBSC 8		LBSC 9		LBSC 10	
	Wet / g	Dry / g	Wet / g	Dry / g	Wet / g	Dry / g	Wet / g	Dry / g
0.1	4.407	0.382	5.360	0.131	3.913	0.166	4.289	0.288
0.3	5.244	0.471	8.624	0.314	7.352	0.265	6.013	0.334
0.5	8.165	0.824	11.172	0.490	7.865	0.291	8.609	0.395
0.7	12.254	1.673	7.348	0.303	7.199	0.258	6.057	0.306
0.9	13.676	1.655	6.104	0.229	10.994	0.489	5.856	0.352
1.1	9.834	1.148	7.538	0.290	7.956	0.425	5.214	0.353
1.3	6.850	0.769	7.042	0.325	7.674	0.421	9.556	0.621
1.5	8.794	1.009	8.110	0.380	8.700	0.513	6.080	0.452
1.7	10.569	1.200	10.030	0.295	9.670	0.655	9.269	0.735
1.9	10.981	1.248	9.673	0.759	10.279	0.769	9.109	0.761
2.1	7.907	0.721	8.180	0.652	9.289	0.753	8.774	0.743
2.3	10.754	1.107	12.222	1.030	10.173	0.875	8.375	0.689
2.5	10.398	1.028	10.347	0.833	10.642	0.899	8.004	0.668
2.7	7.827	0.729	6.526	0.501	8.104	0.678	11.090	0.933
2.9	11.416	1.069	8.736	0.683	20.129	1.053	7.671	0.645
3.5			34.011	3.187			35.705	3.713
4.5			33.640	3.000			34.197	3.093
5.5			33.692	2.823			34.287	2.671
6.5			33.160	2.861			31.106	2.131
7.5			34.067	2.579			34.327	2.351
8.5			34.100	2.628			37.148	3.134
9.5			32.743	2.562			33.132	2.941
10.5			33.700	2.781			34.382	3.195
11.5			35.833	3.297			35.618	3.452
12.5			35.949	3.492			34.521	3.26
13.5			35.666	3.361			36.430	3.62
14.5			34.226	3.147			40.040	3.836
15.5			35.104	3.263			35.934	3.337
16.5			37.388	3.449			36.127	3.108
17.5			34.671	3.223			38.183	3.444
18.5			34.949	3.288			37.831	2.754
19.5			36.533	2.945				
20.5			38.546	3.350				
21.5			37.854	4.133				
22.5			38.037	5.221				
23.5			38.511	5.627				
24.5			39.330	5.944				
25.5			41.146	5.603				
26.5			23.530	3.452				

Wet and dry weights of sediment from coring sites LBSC 7 to 10.

Depth/ cm	LRSC 1		LRSC 2	
	Wet / g	Dry / g	Wet / g	Dry / g
0.1	5.642	0.161	6.306	0.253
0.3	7.431	0.254	9.765	0.468
0.5	6.876	0.250	8.422	0.424
0.7	8.405	0.342	9.075	0.456
0.9	9.726	0.428	8.274	0.416
1.1	8.797	0.383	6.571	0.357
1.3	6.536	0.290	6.700	0.396
1.5	7.612	0.357	5.813	0.351
1.7	6.531	0.309	6.182	0.368
1.9	9.037	0.460	6.593	0.438
2.1	6.464	0.346	11.382	0.823
2.3	11.264	0.641	7.624	0.510
2.5	4.817	0.242	3.863	0.214
2.7	8.846	0.476	7.642	0.547
2.9	6.330	0.333	8.706	0.639
3.5	35.675	2.169	36.620	2.961
4.5	37.979	2.296	36.862	3.420
5.5	37.390	2.408	37.773	4.778
6.5	33.434	2.022	39.492	4.432
7.5	35.755	2.233	38.986	5.326
8.5	37.357	2.594	34.873	3.778
9.5	35.140	2.516	38.415	3.889
10.5	34.143	2.749	38.288	3.332
11.5	36.386	3.110	37.787	3.338
12.5	34.781	2.932	39.874	4.708
13.5	38.937	3.433	38.174	3.845
14.5	36.642	2.811	37.342	3.522
15.5	40.108	3.406	37.950	3.754
16.5	38.020	3.255	38.320	3.669
17.5	39.842	3.404	36.801	3.584
18.5	37.749	2.986	34.091	3.603
19.5	38.138	3.073		
20.5	35.915	3.134		
21.5	38.639	3.282		
22.5	27.270	2.587		

Wet and dry weights of sediment from coring sites LRSC 1 and 2.

Depth / cm	LBPC 1	
	Wet / g	Dry / g
2.2	331.247	37.310
6	273.919	33.400
8.9	182.941	25.780
11.5	247.672	44.124
14.25	374.435	78.307
16.95	204.495	43.369
19.65	369.641	77.767
22.4	314.925	58.246
25	315.732	46.976
27.65	334.972	46.452
30.3	293.531	38.651
32.85	234.566	30.621
35.4	388.614	54.679
38.1	301.269	85.924
41	435.062	164.525
44	481.033	173.779
47.1	510.040	196.756
50.05	388.119	134.788
52.65	282.660	92.601
55.25	359.455	110.873
57.8	231.611	59.852
60.3	268.296	67.496
62.85	246.452	78.452

Depth / cm	LBPC 2	
	Wet / g	Dry / g
1.45	232.977	22.131
4.35	298.221	27.749
7.35	412.622	52.430
10.2	300.761	49.978
12.55	234.513	41.817
14.75	264.853	47.288
17.1	235.067	43.483
19.15	187.925	29.960
20.95	259.780	47.102
23.05	228.614	45.870
25.25	235.792	51.031
27.25	196.529	49.312
28.95	186.456	49.438
31.05	242.427	75.571
33.75	193.231	37.146
36.45	204.767	31.146
38.95	187.990	26.614
41.25	157.277	22.541
43.65	155.138	20.497
46.2	124.668	18.931
48.45	99.789	13.469
50.6	138.139	19.819
53.1	179.889	29.845
55.7	190.272	39.785

Wet and dry weights of peat from coring sites LBPC 1 and 2.

Depth / cm	LBPC 3	
	Wet / g	Dry / g
1.9	369.19	49.411
5.4	457.671	61.069
8.5	345.935	46.287
11.25	332.999	44.209
13.8	322.935	42.723
16	192.211	24.568
18.3	270.847	33.44
20.8	237.906	28.15
23.2	229.182	25.139
25.7	235.121	26.64
28.1	204.575	22.169
30.2	142.57	15.064
32.5	231.78	24.69
35.2	185.809	22.876
37.7	188.097	21.931
40.1	214.792	27.495
42.75	233.946	21.296
45.5	194.361	20.611
47.4	102.125	18.15

Depth / cm	LBPC 4	
	Wet / g	Dry / g
1.5	244.011	33.564
4.4	332.931	73.04
7.3	380.704	148.573
10.4	397.951	159.606
13.3	349.235	147.35
15.9	289.424	135.262
18.3	351.177	155.435
20.7	243.852	103.309
23.2	277.009	116.875
25.5	221.991	95.228
27.6	233.531	106.977
29.6	197.562	109.257
31.9	281.008	149.933
34.4	372.441	209.987
36.9	234.883	135.962
39.4	258.659	151.833
41.9	267.956	148.716
44.4	229.384	141.301

Wet and dry weights of peat from coring sites LBPC 3 and 4.