The effect of soil hydrology, pedology and land use on manganese mobilisation in upland catchments

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Abstract

The trace metal manganese (Mn) occurs naturally in soils, principally from the weathering of parent material, and can exist in both soluble and insoluble forms. In its soluble forms, Mn can be mobilised from soils and transported to surface waters. Where these waters are subsequently used to supply drinking water, Mn concentrations in excess of the 0.05 mg l^{-1} EC standard can cause structural and aesthetic problems, while there is also evidence linking continued human exposure to elevated Mn concentrations in drinking water with the onset of neurological problems. Therefore, water authorities are actively seeking an understanding of processes controlling Mn mobilisation in order to provide better catchment management strategies for reservoirs and to reduce water treatment costs. Since the mobilisation of Mn from soils is a particular problem in many upland catchments where UK drinking water supplies originate, the principal objective of this research is to investigate the factors influencing Mn mobilisation from soils within a typical temperate upland catchment.

Instrumentation to monitor soil water chemistry and soil hydrology was installed within a sub-catchment of Loch Bradan water supply reservoir in SW Scotland. Following the dry summer of 1995, raw water samples from this reservoir contained Mn concentrations far greater than the EC standard. This increase in reservoir water Mn concentration is believed to have resulted from processes associated with the rewetting of exceptionally dry catchment soils. For this study, six field sites were chosen to allow comparison of the effect that major soil types (peat, peaty gley, peaty podzol) and land uses (Sitka spruce plantation, moorland) within the catchment had on Mn mobilisation upon rewetting following a dry period. Soil water and stream water samples were collected over an 18-month period from April 1999 to October 2000. Additional data were also collected concerning Mn concentrations in soil, stream sediment, precipitation and vegetation samples in order to characterise potential Mn sources within the catchment. Results from the field monitoring programme indicate that land use did not influence soil water Mn concentrations and that there was no seasonal peak in soil water Mn concentration from any of the instrumented soil horizons. However, the absence of extended drying conditions during the monitoring period may explain this lack of anticipated seasonal Mn mobilisation, as it is possible that soils did not dry out to the extent where Mn mobilisation would occur.

Laboratory experiments were undertaken to examine the potential of catchment soils to release Mn following prolonged drying conditions not encountered during the field monitoring programme. Soil cores were collected from the same major soil horizons and land uses that were instrumented during the field monitoring programme and allowed to dry under controlled conditions before rewetting. Soil water chemistry data from these experiments indicates that Mn mobilisation occurred within specific horizons, containing both mineral and organic matter, rather than from all soil horizons.

A process-based soil water simulation model (WAVE) was calibrated from the laboratory experiment data and successfully validated against field soil moisture data, before being used to determine the extent to which catchment soils had dried during 1995. The simulation results indicate a greater degree of drying during 1995 than in the instrumented soils during the field monitoring programme or in the soil cores during the laboratory experiment. This suggests that conditions within catchment soils during summer 1995 were sufficiently dry to promote Mn mobilisation similar to that observed during the soil core laboratory experiments, thereby inferring that reservoir Mn concentrations increased in the autumn of 1995 as a result of changes in soil water regime.

Based on the findings of this research, implications for the prediction of Mn mobilisation from catchment soils into reservoir water are discussed. While Mn mobilisation did not appear to be influenced by land use, changes in soil water regime and the range of soils present within a catchment may have a considerable effect on reservoir Mn concentration, as mobilisation was found to occur from within specific soil horizons approximately two weeks after the rewetting of dried soils.

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Chapter 1: Introduction

The purpose of this research was to investigate the effect changes in soil water regime, land use and soil type had on the concentration of manganese (Mn) in soil water from a typical upland water supply catchment in the UK. In addition to outlining the thesis structure, this chapter presents the rationale behind the project. After detailing the background and uses of Mn, consideration is given to its toxicity and the problems caused by high concentrations of Mn in water supplies. Following this, the chapter concludes by briefly outlining the structure and content of the subsequent chapters.

1.1 General background – what is Mn?

Although the transition metal Mn was first described during Roman times, it was not until 1774 that it was finally isolated and identified as a distinct chemical element by the Swedish chemist Johan Gottlieb Gahn. The origins of the name 'manganese' are not entirely clear and several different possibilities have been put forward. It has been suggested that the name comes from the Latin *magnes*, meaning 'magnet', and relates to the metal ore's early confusion with magnetic iron ore (Royal Society of Chemistry, 1980). Alternative sources propose that the Greek for 'magic' is in fact the root (Keen *et al.*, 2000), whereas others state that the Greek verb 'to purify' gave rise to the name (Graham and Quirk, 1988).

In common with other transition metals, Mn can exist in a number of different ionic forms covering a range of oxidation states. However, Mn is generally considered to exist in the soluble form when reduced (Mn^{2+}) and the insoluble form when oxidised (Mn^{4+}). The redox behaviour of Mn ions is of particular importance in environmental studies, as it governs solubility in water and is therefore largely responsible for determining Mn mobility in soils and water. Sections 1.3 & 1.4 provide a more complete analysis concerning the implications of elevated Mn concentrations for water supply, while the factors influencing Mn speciation in soils and water are discussed in sections 2.3 and 2.6 respectively.

1.1.1 Uses of Mn

Industrially, Mn is principally used in the form of ferromanganese alloys with iron, where it gives the alloy a hard, yet pliant, quality. The demand for Mn saw its production, from mining and smelting operations, increase by a factor of 30 during the 20th century. In terms of global production, Mn is currently the 4th most important metal used by man

(Jones, 1996). Mn compounds have a varied range of applications, and examples of their usage include components of dry cell batteries (MnO_2), industrial dyes ($MnSO_4$) and disinfectants ($KMnO_4$). Everyday use of Mn-containing products includes the organometallic compound methylcyclopentadienyl manganese tricarbonyl (MMT), which was introduced in North America as an anti-knock additive to petrol in place of lead. Agriculture too has made extensive use of Mn, with its incorporation into a range of agrochemicals, including several widely used fungicides.

1.1.2 Biological requirement for Mn

In addition to industrial and manufacturing applications, Mn is an essential trace element that plays a vital role within the tissues of living organisms. Plants require Mn for healthy growth. In addition to activating many enzymes, Mn is an integral part of the chloroplast membrane structure and is also involved in the photosynthetic reactions that split water within the chloroplast (Salisbury & Ross, 1992). Plant deficiency in Mn often results in spots of dead tissue scattered over leaf surfaces. Examples of recognised plant disease resulting from Mn deficiency include “gray-speck disease” in oats and “marsh spot” in peas (Leeper, 1947). Such diseases can lead to plant death or, at the very least, a reduction in crop yield.

In animals, significant biological functions of Mn include its roles as a constituent of metalloenzymes and as an enzyme activator. One example of a vital enzyme, relying upon the presence of Mn to function properly, is manganese-superoxide dismutase, which is an essential component in the free radical defence system (Keen *et al.*, 2000). The development of healthy bone structure requires incorporation of Mn into growing tissue. In humans this can account for approximately 25 % of the 8-12 mg of Mn found in the average body. Adult daily intake of Mn in food is between 2-9 mg, which easily satisfies the estimated daily nutritional requirement of 30-50 $\mu g\ kg^{-1}$ of body weight (World Health Organisation, 1993). Individuals suffering from Mn deficiency may exhibit significantly reduced growth rates along with an increased risk of sustaining broken bones. Induced Mn deficiency in experimental animals has also been shown to impair reproductive performance as well as producing defects in metabolism. In humans, the organs found to contain the highest concentrations of Mn include the liver, pancreas and pituitary gland (Barceloux, 1999) as well as regions of the central nervous system (Yase, 1972).

1.2 Toxic effects of excess Mn

In common with many other substances required for normal growth, Mn can cause problems when organisms are exposed to excessive levels. These problems can range in severity from reduction of growth rate to fatality, depending on the concentration of Mn the organism is exposed to and period of exposure.

1.2.1 Mn toxicity in plants

The toxic effects of Mn in plants do not produce any one clearly identifiable disorder. Rather, the symptoms and concentration of Mn required to cause them vary widely between species and also between varieties within the same species (El-Jaoual & Cox, 1998). This is thought to result from different plant genotypes having different biochemical pathways that are affected by the phytotoxic mechanisms of Mn poisoning. Examples of recognised conditions resulting from Mn toxicity to plants include “papery bark” in pear trees and “bark measles” in apple trees, both of which feature internal bark necrosis and die-back of shoots and branches (Grasmanis & Leeper, 1966).

1.2.2 Mn toxicity in animals

Little physiological evidence exists concerning the toxic effects of Mn in lower animals. Work with invertebrate communities living in areas containing high levels of naturally occurring Mn indicates that metal content can differ widely between species (Davidson *et al.*, 1999). The metal content can also vary depending on the developmental stage of a species, and in addition to losses during pupation, some form of active metal excretion may be employed by certain species. However, it remains unclear whether excess Mn can cause problems in these organisms.

There is considerably more data available on Mn toxicity in higher animals, particularly those species used in laboratory experiments designed to shed light on the mechanisms of human Mn toxicity. Experiments involving rats and primates have shown that exposure to high levels of Mn can result in developmental defects and damage to the central nervous system (World Health Organisation, 1981). Such effects are broadly analogous to those noted in human populations with similar exposure levels, and discussed in more detail below. In the natural environment, chronic Mn poisoning can occur when discharges from mining and smelting activities enter aquatic systems. When this happens, aquatic vertebrates, in particular fish, can often suffer as a result (Nyberg *et al.*, 1995). Deformities thought to be caused by elevated Mn levels in water following acidification have been reported in white sucker fish (*Catostomus commersoni*) (Fraser & Harvey, 1982), while Stubblefield *et al.* (1997) observed increases in mortality rates of developing brown trout (*Salmo trutta*), exposed to aquatic Mn concentrations exceeding 4 mg l^{-1}. In the case of trout mortality, the concentrations of calcium and magnesium present were found to alter the concentration of Mn required to produce a given mortality rate, thus illustrating the difficulties involved in calculating environmental thresholds for Mn toxicity.

1.2.3 Mn toxicity in humans

The severity of human responses to Mn poisoning depends largely upon the concentrations involved and length of exposure. Human exposure to exceptionally high concentrations of Mn, even for a short period, can cause chronic Mn poisoning with potentially fatal consequences. However, such cases are rare and long-term exposure to high levels of Mn, either through work-related activities or from background environmental levels, appears to be the most common threat. Long-term exposure of this nature, often over several decades, is thought to cause manganism, a neurotoxological disease with similar symptoms to Parkinsonism. Human intake of Mn can occur via three main pathways. Inhalation of airborne particles may be the primary route for the majority of anthropogenic sources, while ingestion of Mn in food or drinking water is often the result of Mn availability within environmental sources.

The link between anthropogenic Mn pollution and deleterious effects to human health is generally accepted. The first recognised cases were reported as long ago as 1837, in two pyrolusite mill workers who inhaled Mn oxides while grinding them (Couper, 1837). Further similar cases of Mn poisoning (often referred to as 'manganese madness') have been documented worldwide throughout the 20th century (Barceloux, 1999; Iwami *et al.*, 1994). However, other studies were unable to document any significant disturbance of neurological performance in workers exposed to low levels of Mn over a long time period (Deschamps *et al.*, 2001). Therefore, the thresholds at which Mn exposure over time becomes harmful remain unclear and are still the subject of much research.

Communities living in close proximity to, or individuals working in, Mn ore mining operations are believed to be most at risk from ingestion of airborne Mn particles (Mergler & Baldwin, 1997). Others at risk from occupational Mn exposure include workers at foundries where Mn alloys are made. Lander *et al.* (1999), Lucchini *et al.* (1999) and Mergler *et al.* (1994) have all reported elevated Mn concentrations in the bodies of employees working at such foundries. Once an individual has been exposed for long enough, simply removing them from a Mn-rich environment may have little or no effect on their condition. Studies involving foundry workers with symptoms of manganism have discovered that the disease can continue to develop long after exposure has ceased (Huang *et al.*, 1993).

A further potential source of anthropogenic airborne Mn exists in North America, where the Mn-containing compound MMT is added to petrol. Inhalation of particulate Mn produced by vehicle emissions is considered by some to pose a risk to human health. However, this is not fully accepted, and recent evidence suggests that personal Mn exposure in a major Canadian city largely originates from sources other than MMT (Crump, 2000).

In addition to the ingestion of airborne Mn, dietary intake of Mn can also produce elevated levels within the body. Bioaccumulation within the food web is only thought to be significant for plants and invertebrates, as higher animals have the ability to excrete large amounts of Mn in bile. However, dietary habits may influence human Mn exposure in the long term, as greater Mn concentrations have been found in the tissues of individuals following a vegetarian diet or consuming large quantities of tea (Barceloux, 1999; World Health Organisation, 1981).

1.2.4 Health risks from Mn in drinking water

Intake from food aside, contamination of drinking water supplies by Mn is thought by some to be the principal source of environmental exposure (Mergler and Baldwin, 1997). The findings of several studies investigating the toxicological effects of Mn in drinking water are summarised in Table 1.1, showing the range of concentrations measured and deleterious effects noted in the population.

In the 1930s, Mn leaking from dry cell batteries buried near a well in Japan produced excessively high concentrations of up to 30 mg l^{-1} in drinking water. This contamination caused sixteen cases of poisoning, two of which proved fatal, while a third person became mentally unbalanced and subsequently committed suicide (Kawamura *et al.*, 1941). Work in Greece has shown symptoms of the disease in communities drawing water from an aquifer located in an area of unmined Mn ore (Kondakis *et al.*, 1989). Within this study, the highest concentrations of Mn measured in drinking water were between 1.8 and 2.3 mg l^{-1}, approximately ten times less than those responsible for deaths in Japan. Further evidence for the possible link between environmental Mn levels and damage to human health comes from

Study	Location	Mn concentration in drinking water ($\mu g\ l^{-1}$)	Elevated levels found in	Effects noted in population
Kawamura *et al*. (1941)	Japan	20,000 – 30,000	Blood; liver	Poisoning; death
Kondakis *et al*. (1989)	Greece	1800 - 2300	Hair	Neurological signs of poisoning
Vieregge *et al*. (1995)	Germany	300 - 2160	None [1]	None
Hudnell (1999)*	China	241 - 346	Blood; hair	Learning deficits in children
Kilburn (1987)	Australia	n.r.	Blood; hair	Neurological disorders; congenital abnormalities
Yase (1972)	Japan & Guam	1 -100	Spinal cord tissue	Degenerative central nervous system diseases
Iwami et al. (1994)	Japan	2.3 [2]	n.r.	Motor neuron disease
Santos-Burgoa *et al*. (2001)	Mexico	0 – 242	Blood	Deficient cognitive performance

Table 1.1: Summary of studies reporting the effects of Mn in drinking water on human health

n.r. = not reported
* = data summarised from two Chinese papers
[1] = elevated levels measured in blood, but not found to be statistically significant
[2] = mean value; excess Mn intake attributed to food

Australia, where endemic neurological disorders, congenital malformations and psychiatric disorders were observed in an Aboriginal population living in an area of rich Mn deposits (Kilburn, 1987). This study not only linked high environmental Mn concentrations to the onset of neurological problems in later life, but also found that foetal and infant exposure could pose a serious hazard, producing different effects to those seen in adults. More recently, work in Mexico has also linked environmental Mn concentrations, including those in drinking water, to neurological problems (Santos-Burgoa *et al.*, 2001). However, the fact that deleterious effects can arise from long-term exposure to Mn in drinking water is not accepted to the same degree as the threat from ingestion of particulate Mn. For example, a study of German well water (Vieregge *et al.*, 1995) contradicts the findings of the studies in Greece, Australia and Mexico. The results of the German research indicate that communities drinking water from wells containing high concentrations of Mn show no increased occurrence of manganism relative to the general population. It is, however, possible that the symptoms of manganism had not yet become apparent in the younger German subjects, and so the debate over the risks of Mn in water supplies continues. An example of the uncertainty surrounding the effects of Mn on human health is provided by Iwami *et al.* (1994), who suggest that the actual risk may not be dependent on Mn concentrations in drinking water, but rather a high dietary intake of Mn coupled with low magnesium intake in drinking water.

In summary, the level of exposure to Mn at which deleterious effects begin to appear in humans remains unknown, and the risks to human health from Mn in drinking water may be complicated by factors such as age, gender, health and genetic susceptibility, as well as the presence of other metals in the diet (Hudnell, 1999; Kilburn, 1987; Mergler, 1999; Mergler *et al.*, 1999). It is apparent that, while a potential risk to human health exists, drinking water supplies should contain as little Mn as possible and should undergo treatment to ensure this.

1.3 Problems caused by Mn in drinking water

Aside from the potential risk to human health, further problems resulting from high Mn concentrations in drinking water supplies can be divided into structural and aesthetic categories. Structural problems result when the oxidation of soluble Mn within supply pipes produces a build up of insoluble Mn. These Mn oxides accumulate on supply pipe walls thus decreasing their effective diameter and reducing flows within the pipe or even stopping them completely (Gounot, 1994; World Health Organisation, 1996). In addition to this, the oxides accumulated on supply pipe walls may become dislodged and emerge from household taps as a black discharge (Gounot, 1994). This process can even occur when Mn concentrations in water are as low as 0.02 mg l^{-1} (Bean, 1974), a concentration that is below the current UK standards for water supply. Aesthetic problems of unpleasant taste and colour can also be produced by bacterial oxidation of Mn within supply pipes (Viessman & Hammer, 1993), with some bacteria known to concentrate total Mn in water supplies by oxidation of soluble Mn and formation of Mn-rich biofilms, thus producing taste, odour and turbidity problems (Griffin, 1960; Wolfe, 1960). A threshold concentration has been identified for water supplies, around 0.1 mg l^{-1}, above which Mn ions are recognised as imparting an undesirable taste to water and staining plumbing fixtures (Griffin, 1960). Finally, further aesthetic problems arise when Mn rich water is used in washing machines. In this instance, the elevated pH and strongly oxidising conditions present during the washing process lead to precipitation of the Mn as a dark stain on clothing.

1.3.1 Drinking water standards for Mn

As a result of the range of problems caused by high Mn concentrations, legislation exists to limit the levels supplied in drinking water. The World Health Organisation (1996) recommends that a provisional guideline of 0.5 mg l^{-1} Mn in drinking water supplies is adequate to protect public health. Standards are, however, often set much lower than this, owing to consumer objections arising from aesthetic Mn-related problems. Within the UK, the maximum admissible concentration (MAC) of Mn in drinking water is defined by the EC standard of 0.05 mg l^{-1} (EC, 1980 & 1998). For the purposes of UK legislation, this figure is referred to as the prescribed concentration or value (PCV). The majority of drinking water supply failures for Mn in the UK occur where the water originates in upland catchments. This is thought to be due to a combination of the underlying geology and the acidic, reducing conditions prevalent in the covering soils. In such cases, Mn released by weathering from the rocks and soil will tend to be present in the soluble reduced form and so be available for transport in water. Other cases of drinking water contamination by Mn often involve reports of dirty or discoloured water, caused by detachment of accumulated Mn deposits in supply pipes. In some cases, such events can result from a change in chlorination regime at treatment works. However, the primary cause of this type of contamination is a sudden change in the direction or speed of water flow within the pipes, often brought about by damage and repair of water mains or the rapid movement of water to meet large demands (Drinking Water Inspectorate, 2001a).

1.3.2 Drinking water failures for Mn content

In Scotland, many of the reservoirs supplying water for public consumption are located in upland areas and are therefore potentially at risk from episodic Mn contamination. Official figures show that in 1991 almost 9 % of water supply zones exceeded the 0.05 mg l^{-1} standard (Scottish Office, 1993). Five years later, 1.03 % of drinking water samples analysed were still found to exceed this standard (Scottish Office, 1997). Although this small percentage may not seem a major concern, when considered in terms of population, approximately 40,000-50,000 individuals could have been exposed to high levels of Mn in their drinking water. The region supplied by West of Scotland Water (WoSW) contains several water supply reservoirs that have proved particularly vulnerable to Mn contamination. Recent figures indicate that, during 1999, 2.54 % of drinking water samples analysed in the region contravened the PCV for Mn (WoSW, 2000).

Other regions in the UK, where water supplies originate in upland catchments, have also suffered from problems with elevated concentrations of Mn in drinking water. During 1995, 6 % of customers supplied by Yorkshire Water experienced drinking water failures related to excessive Mn content (Heal, 1996). The latest figures from England and Wales identify Mn failures as accounting for 3.1 % of all breaches of drinking water regulatory standards reported during 2000 (Drinking Water Inspectorate, 2001b). In total, 0.28 % of drinking water samples, collected from 97 English and Welsh water supply zones, contravened the PCV for Mn. Further analysis of the figures shows that 77 % of the Mn failures arose in just four regions (North West, Yorkshire, Northumbrian and Dyr Cymru), all of which contain substantial upland areas.

Within the European Union, water companies continually supplying water containing Mn concentrations in excess of the EC standards (EC, 1980 & 1998) are liable to incur heavy fines. Therefore, it is understandable that there is considerable concern within the water industry regarding the occurrence of high Mn levels in water from supply catchments.

1.4 Methods of Mn removal from water

Once in the soluble form, Mn is readily transported in soil water and may enter streams feeding water supply reservoirs. As a consequence of the structural, aesthetic and health-related effects resulting from high Mn concentrations in drinking water, there has been considerable effort to develop methods for reducing the soluble Mn content of water. These can be broadly divided into direct treatment methods (removing Mn already in potable water) and management procedures for catchments and reservoirs (preventing Mn entering water supplies in the first place).

1.4.1 Treatment of water supplies

The most basic treatment for removing dissolved metals from drinking water is to create conditions where formation of insoluble metal oxides is favoured, either by aerating the water and elevating its pH, or by direct addition of oxidising agents. Once insoluble oxides have started to form, coagulants are added to increase the particle size to a point where settling and filtration can remove the insoluble oxides. However, the chemical properties of Mn mean that it is considerably more difficult to remove from water supplies than other commonly occurring metals, such as iron (Viessman & Hammer, 1993). In particular, the degree of alkalinity or oxidation required to precipitate Mn oxides is far greater than for iron (Collins & Buol, 1970a).

Strong oxidising agents, such as chlorine or ozone, are required to oxidise dissolved Mn to insoluble forms of Mn^{4+}. Formation of carcinogenic trihalomethane compounds from the interaction between chlorine and dissolved organic carbon mean that its use is restricted to waters with a low organic content. Since many of the reservoirs in Scotland are situated in upland catchments with highly organic soils, their waters often contain large amounts of organic carbon. Therefore, the use of chlorine as an oxidising agent is unsuitable and ozone is preferred. The treatment works serving the reservoir in whose catchment this research is based, Loch Bradan in southwest Scotland, was used in a study to determine the effectiveness of ozone in Mn removal (Little & McFadzean, 1991). Following the success of this ozone trial, the treatment works were completely upgraded to remove Mn by ozonation and became fully operational in 1995 (A.Britton - WoSW, pers. comm.). However, problems of volatility mean that ozone must be produced on site by equipment that is costly to both install and operate. Therefore, the economic costs entailed by treatment methods mean that water authorities, tasked with supplying water to meet certain standards, are actively seeking less expensive ‘management’ strategies to achieve compliance.

Other methods of water treatment employed to remove Mn include several forms of biological Mn oxidation (Gounot, 1994). Colonies of Mn-oxidising bacteria utilised by the process are usually incorporated into filter units, through which the water passes. Providing conditions suitable for the growth of these bacteria are maintained, biological removal of Mn is thought to offer a cheaper, safer alternative to methods involving hazardous chemicals.

The use of treatment plants employing biological Mn removal is commonplace throughout mainland Europe (Mouchet, 1992).

A further option for Mn removal exists where water supplies are abstracted directly from groundwater. The Vyredox process involves injecting highly aerated water into the aquifer, thus oxidising Mn and other metal ions present in solution. The oxidised ions precipitate out and remain in the aquifer when water is abstracted. Despite doubts concerning the plugging of aquifer pores by metal oxide precipitates, Vyredox plants operate in many European countries (Jaudon *et al.*, 1989).

1.4.2 Reservoir management

Reservoir management accepts the fact that Mn is already in the water supply system and attempts to reduce the concentration reaching the treatment works.

Selective abstraction of water is an option where the reservoir becomes thermally stratified. Under these conditions, the well-aerated surface waters (epilimnion) will contain less Mn than the poorly aerated waters below them (hypolimnion). Therefore, intakes to water pipes from the reservoir which draw water from the epilimnion only will provide the treatment works with water containing less Mn than the average reservoir concentration. However, not all reservoirs experience stratification, and in those that do, stratification may only occur for a short period during the summer.

Artificial aeration of reservoir waters is another way of decreasing soluble Mn levels by promoting the formation of insoluble Mn oxides. The technique, however, does not appear to be universally successful (Chiswell & Zaw, 1991; Loos, 1987), and care must be taken to ensure that the aeration does not disturb anoxic bottom sediments thereby releasing more soluble Mn than the process removes (A.Britton - WoSW, pers. comm.).

1.4.3 Catchment management

The simplest form of catchment management in areas with a surplus of available water is to avoid abstracting water from reservoirs during periods when Mn concentrations in the reservoir are greatest. This method requires not only predictions of public water consumption, to ensure that alternative water supplies are available, but also an accurate estimate of the timing and likely duration of excessive Mn concentrations in the affected reservoir. At present, there are insufficient data available regarding Mn behaviour in water supply catchments to provide such an estimate.

A more complicated system of direct management of catchment water involves the use of intake regulation structures, which can be manipulated to prevent those streams with elevated Mn concentrations from entering the water supply system. Heal (1996) describes one example of this type of management practice, operating within a catchment in the Yorkshire Dales. Again, the ability to predict the timing and duration of excessive Mn concentrations is a requirement for the system to function with maximum efficiency.

Land use and management practices within a catchment may also provide an opportunity to influence reservoir Mn levels. Commercial conifer forestry plantations, common in many UK upland catchments, are known to increase soil acidity (UKAWRG, 1989). Production of acidic litter is an obvious way in which conifers increase soil acidity, but they can also exacerbate the effects of atmospheric deposition by scavenging acidifying anions from the air. The resultant increase in soil acidity, promoting abiotic reduction of Mn oxides, is one possible mechanism whereby conifer plantations can cause increased soluble Mn levels in soil water. Heal (2001) identifies percentage conifer cover as having a significant positive correlation with surface water Mn concentration in UK upland catchments. Neal *et al.* (1992) report Mn concentrations in waters draining from catchments with 50 % or greater Sitka spruce cover as being greater than those draining from nearby grassland catchments (Table 1.2).

Catchment	Sitka spruce cover (%)	Mean stream Mn (μg l^{-1})	Range (μg l^{-1})
Upper Hafren	0	19.0	9-23
Hafren	50	40.8	5-128
Upper Hore	0	21.9	6-51
Hore	77	34.9	8-84

Table 1.2: Total Mn concentrations in stream water from forested and unforested catchments in Plynlimon, central Wales
(After Neal *et al.*, 1992)

In addition to the effects of acidification, throughfall and stemflow in conifer plantations are known to be enriched in Mn with respect to rainfall (Neal *et al.*, 1992; Shanley, 1986).

Evidence suggests that the type of forest cover may influence metal concentrations in throughfall and stemflow. The Mn enrichment seen under conifer trees is greater than that reported in broadleaf woodland, and is often attributed to greater atmospheric deposition of Mn on the larger surface area presented by conifer needles.

One aspect of forestry known to have an impact on metal concentrations in runoff is the practice of clear-felling. Several studies indicate that there is a large-scale release of nutrients and metal ions following commercial harvesting of forestry plantations (Adamson & Hornung, 1990; Adamson *et al.*, 1987; Titus & Malcolm, 1991). The implications of this are considered in more detail in section 2.4.2.

Where catchments are predominantly covered by open moorland, management practices are more limited. One form of land management carried out in certain upland areas of Scotland and England is the periodic burning of heather moorland to improve the habitat for red grouse (*Lagopus lagopus scoticus*). The effect on Mn release is unclear, but Heal (2001) suggests that clearing moorland vegetation produces an increase of Mn in soil solution resulting from an increase in soil microbial activity. Other land management practices commonly employed in upland areas include ditching and fertilisation to improve the suitability of land for grazing animals. Digging drainage ditches may increase Mn concentrations in runoff as the increased soil drying and warming in summer create conditions more favourable to soil microbial activity (Heal, 2001). The addition of fertiliser to develop upland pastures is also reported to increase Mn concentrations in runoff (Kay & Stoner, 1988). Heal (2001) concludes that the net effect of land improvement practices in upland catchments is probably to increase the mobilisation of Mn into runoff during autumn storm events, by encouraging soil microbial activity and production of readily-soluble Mn stores in summer.

The methods of management described above can be employed singly or in combination with each other. Depending upon their net effect on reservoir water Mn concentrations, the adoption or discontinuation of such practices may offer a means of reducing, if not eliminating, Mn concentrations reaching treatment works. However, the safest management practice in the future would be to identify catchment areas at risk from high Mn concentrations and avoid constructing any new reservoirs in them.

1.5 Research aims

The behaviour of Mn in upland catchments has been the subject of recent scientific research, primarily because of implications concerning the cost of Mn removal from water supplies. Within the UK, other research projects in upland catchments have focused on Mn concentrations in runoff (Heal, 1996) and the behaviour of Mn in reservoir waters and sediments (Gavin, 1999). However, the principal aim of this research is to examine the environmental factors affecting Mn concentrations in soil water, as these will ultimately influence Mn concentrations in runoff and reservoirs. Accordingly, the following factors are investigated:

1. The effect that changes in soil water regime, specifically rewetting following an extended drying period, have on soil water Mn concentrations;
2. The effect that different upland soil types and land uses have on Mn mobilisation.

The range of soils and land uses studied allows the application of results from this research to upland catchments in general, and may therefore be used to identify reservoirs potentially at risk from Mn mobilisation. In addition to this, the results will aid in predicting when Mn mobilisation events are likely to occur in upland catchments, thereby warning water authorities of periods when costly treatment of water supplies may be required.

1.6 Thesis structure

Chapter 2 expands on the general introduction to Mn contained within this chapter by considering in more detail the effect that factors such as redox conditions, pH, soil water regime, soil type and land use have on Mn status. Knowledge of how Mn behaviour in soils and water is influenced by a wide range of environmental variables is vital in understanding the processes by which Mn can be mobilised (i.e. transformed from relatively immobile, insoluble forms into soluble forms). In particular, conditions favouring the mobilisation of Mn are discussed, as these can potentially cause the large-scale release of Mn from soils in upland catchments. A brief review of other studies investigating Mn behaviour in upland catchments is presented in order to relate the scope of this project to existing research on the subject. Further background information is contained in Chapter 3, covering the location and rationale behind the choice of field site. A full description of the field monitoring programme and the sites instrumented is presented, as well as a review of the equipment installed.

Data from the field monitoring programme are presented in Chapter 4, along with the results of statistical analysis carried out on them. Initial conclusions drawn from the data are presented and the rationale for implementing a series of laboratory experiments is introduced. The soil core laboratory experiments are detailed in Chapter 5, starting with discussion of the equipment used and experimental procedure. The data obtained from the soil core experiments are then presented, before statistical analysis and discussion of the results.

Simulation of the soil water regime, using a process-based computer model, provided a means of relating field and laboratory soil conditions encountered during the research, to those experienced by field soils during 1995 when a major increase in reservoir water Mn concentrations was recorded. Chapter 6 describes how the model was parameterised using data derived from the soil core laboratory experiments and validated against data from the field monitoring programme, before being used to 'hindcast' 1995 soil water deficits.

Finally, Chapter 7 combines the results from Chapters 4 - 6 and discusses issues arising from the research. Results from the field monitoring programme and soil core laboratory experiments are integrated with the simulated soil water regime data to infer possible changes of Mn status in field soils during 1995. Conclusions drawn from the research are outlined, in particular the identification of soil types and conditions most likely to give rise to excessive Mn concentrations in soil water. The implications of the results for water supply management are discussed and specific areas for further research are suggested.

Chapter 2: Manganese in the environment

This chapter introduces the forms of Mn commonly found in the natural environment and details the processes that influence the occurrence of those forms. An understanding of these processes is vital in explaining the behaviour of Mn in soils and the pathways by which it can enter soil water and thence water supply reservoirs. Following this, the geochemistry of manganese, and in particular its speciation in soils and water, is discussed. Finally, catchment-based studies where Mn concentrations in soil and runoff were measured are reviewed.

2.1 Occurrence of Mn

In its pure elemental form, Mn exists as a silvery white, brittle metal. However, this form does not occur naturally on the earth and the metal is instead found in over 100 different minerals (Graedel, 1978), the most common of which is pyrolusite or manganese dioxide (MnO_2) (Table 2.1). In terms of abundance Mn is extremely common, being the 12th most abundant element in the earth's crust (Manahan, 1994) and the 5th most common crustal metal (Gounot, 1994). This amounts to between 0.085 and 0.1 % of the earth's crust (Cotton & Wilkinson, 1968; Graedel, 1978).

High concentrations of Mn are found in base-rich igneous rocks, and in some sedimentary and metamorphic rocks (Table 2.2). When rocks containing high levels of Mn are found near the earth's surface, the processes of pedogenesis can incorporate Mn-rich stones and rock fragments into covering soils. Such fragments serve as a pool of Mn, which can be released into the soil by chemical and physical weathering. Indeed, this is thought to be the main source of Mn mobilised into surface waters in upland Scottish catchments (Heal, 2001).

According to Mortvedt (2000), concentrations of total Mn in soils range from 20 to 6000 mg kg^{-1}, with a mean concentration of 600 mg kg^{-1}. However, the levels in any particular soil are not correlated with the composition of the underlying bedrock, indicating the great mobility of Mn within the environment.

Common name	Chemical formula
Nsutite	$Mn^{4+}Mn^{3+}(O,OH)_2$
Pyrolusite	MnO_2
Hollandite	$Ba(Mn^{4+}Mn^{3+})_8O_{16}$
Vernadite	$MnO_2.nH_2O$
Groutite	α-MnOOH
Feitknechite	β-MnOOH
Manganite	γ-MnOOH
Birnessite	$(Na,Ca,Mn^{2+})Mn_7O_4.2.8H_2O$
Bixbyite	$(Fe,Mn)_2O_3$
Buserite	$Na_4Mn_{14}O_{27}.21H_2O$
Hausmannite	Mn_3O_4
Lithioporite	$LiAl_2Mn_2^{4+}Mn^{3+}O_6(OH)_6$
Manganosite	$Mn^{2+}O$
Rhodochrosite	$MnCO_3$

Table 2.1: Common Mn-containing minerals and their chemical formulae (After Stuki, 2000)

Rock type	Average Mn concentration ($\mu g\ g^{-1}$)
Igneous	
Diorite	1400
Basalt	1300
Andesite	1200
Peridotite	1200
Gabbro	1200
Rhyolite	600
Granite	400
Metamorphic	
Amphibolites	1500
Granulite	800
Gneiss	600
Sedimentary	
Deep sea clays	6000
Greywacke	700
Shale	600
Limestone	550
Sandstone	170

Table 2.2: Mn concentrations found in common rock types (After Heal, 1996)

2.2 Chemical speciation of Mn

The speciation of a chemical element refers to its existence in different chemical forms in the gaseous, solid or aqueous solution phases (Ritchie & Sposito, 1995). Knowledge of the processes governing Mn speciation is of vital importance, as this allows an understanding of the environmental conditions liable to enhance the mobility of Mn in upland soils.

Although able to form compounds in which its oxidation state can range from –3 to +7 (Cotton & Wilkinson, 1968), Mn ions are regarded by many as being present in soils and water as one of two main forms. These are the soluble, reduced form (Mn^{2+}) and the insoluble, oxidised form (Mn^{4+}) (Manahan, 1994; Sparrow & Uren, 1987). With the exception of the Mn^{3+} state, which can form insoluble oxides that rapidly break down into Mn^{2+} and Mn^{4+}, the other oxidation states rarely occur in the natural environment, although the permanganate ion (MnO_4^-) containing Mn in the +7 oxidation state is commonly used as an industrial and laboratory oxidant (Cotton & Wilkinson, 1968). The relative abundance of Mn^{2+} and Mn^{4+} has often been used to determine the extent to which Mn is present in solution, or held as an insoluble form in the soil. This assumption may not, however, be strictly true. Although Mn^{2+} is the only form of Mn stable as a soluble cation, it can also form its own insoluble compounds (e.g., $MnCO_3$) and bind to a variety of different solids, including Mn oxides. The assumption that all of the insoluble Mn present in soils exists in the +4 oxidation state is also flawed. Complex minerals containing multiple valence states of Mn are common (Table 2.1) and interactions between Mn oxides can produce insoluble complexes containing both Mn^{2+} and Mn^{4+} ions (Fujimoto & Sherman, 1948).

In aqueous systems at standard temperature and pressure, these non-stoichiometric compounds of mixed valence are the most common products of redox processes involving Mn (Ponnamperuma *et al.*, 1969). The particular Mn oxide formed depends upon the ratio of the different Mn valences incorporated into the oxides as well as the overall ratio of Mn to oxygen. These ratios themselves depend upon the temperature, pH and oxygen partial pressure at the time of formation, therefore providing many possible alternative forms of Mn oxides.

Approximately 150 oxides of Mn, ranging in their stoichiometry from $MnO_{1.2}$ to MnO_2 have been discovered, 36 of which are known to occur in near-surface environments (Jenne, 1967; Ponnamperuma *et al.*, 1969). The most common forms of Mn found in soils are the complex oxides birnessite, hollandite, and lithiophorite, which contain many other elements in addition to Mn (Rowell, 1981; Taylor *et al.*, 1964). Formation of these non-stoichiometric oxides in which Mn may be present in mixed valence states with other metals presents a major problem in attempting to accurately understand the nature of Mn present in soils. It appears that the majority of Mn oxides in soils that undergo reversible oxidation and reduction are complex oxides of Mn and Fe, whose composition and solid state vary with the environment in which they are found (Ponnamperuma *et al.*, 1969).

The reduced and oxidised forms of Mn have been further classified by some researchers, based upon steps in a sequential extraction, to produce a list of four types of Mn known to exist in soils (Gotoh & Patrick, 1972; Leeper, 1947) (Table 2.3).

Reduced form - Mn^{2+}		**Oxidised form – Mn^{3+} and Mn^{4+}**	
Water soluble	*Exchangeable*	*Reducible*	*Residual*
Free hydrated ion	Cation attached to negatively-charged colloids (inorganic/organic)	Higher oxides of Mn	Minor constituent of soil minerals
$Mn^{2+}_{(aq)}$	Mostly Mn^{2+}	MnO_2; Mn_2O_3; Mn_3O_4; MnOOH	

Table 2.3: Simple extractant-defined classification of soil Mn
(After Gotoh & Patrick, 1972; Leeper, 1947)

2.3 Mn behaviour in soils

Much of the early work on the behaviour of Mn in soils was linked to its role as a plant micronutrient. These studies sought to describe the soil Mn cycle and establish the factors giving rise to Mn deficiency in plants (Mann & Quastel, 1946). Although in complete contrast to this research, which is concerned with excess Mn rather than Mn deficiency, these earlier studies provide an understanding of Mn behaviour in soils that is vital to the work reported here.

2.3.1 Controls on soil Mn speciation

It is essential to understand the controls on Mn speciation, and hence availability, in soils in order to accurately predict its concentration in runoff from soil. The principal Mn systems found in soils are thought to involve MnO_2, Mn_2O_3, Mn_3O_4, $MnCO_3$ and $Mn(OH)_2$ in equilibrium with Mn^{2+} ions (Equations 2.1 – 2.5; after Gotoh & Patrick, 1972).

$MnO_2 + 4H^+ + 2e^- \leftrightarrows Mn^{2+} + 2H_2O$ **Equation 2.1**

$Mn_2O_3 + 6H^+ + 2e^- \leftrightarrows 2Mn^{2+} + 3H_2O$ **Equation 2.2**

$Mn_3O_4 + 8H^+ + 2e^- \leftrightarrows 3Mn^{2+} + 4H_2O$ **Equation 2.3**

$MnCO_3 + H^+ \leftrightarrows Mn^{2+} + HCO_3^-$ **Equation 2.4**

$Mn(OH)_2 \leftrightarrows Mn^{2+} + 2OH^-$ **Equation 2.5**

The position of the idealised reversible reaction between soluble and insoluble forms of Mn (shown in Figure 2.1) is largely controlled by soil water regime, pH and redox conditions (Jarvis, 1984). The theoretical effect of these three environmental variables on Mn speciation in soils is summarised in Figure 2.2. Other factors, such as soil organic matter content, microbial activity, soil temperature and Mn species concentrations further complicate matters. The end result is a sensitive chemical equilibrium with a complex set of controlling variables, which are further discussed during the remainder of section 2.3.

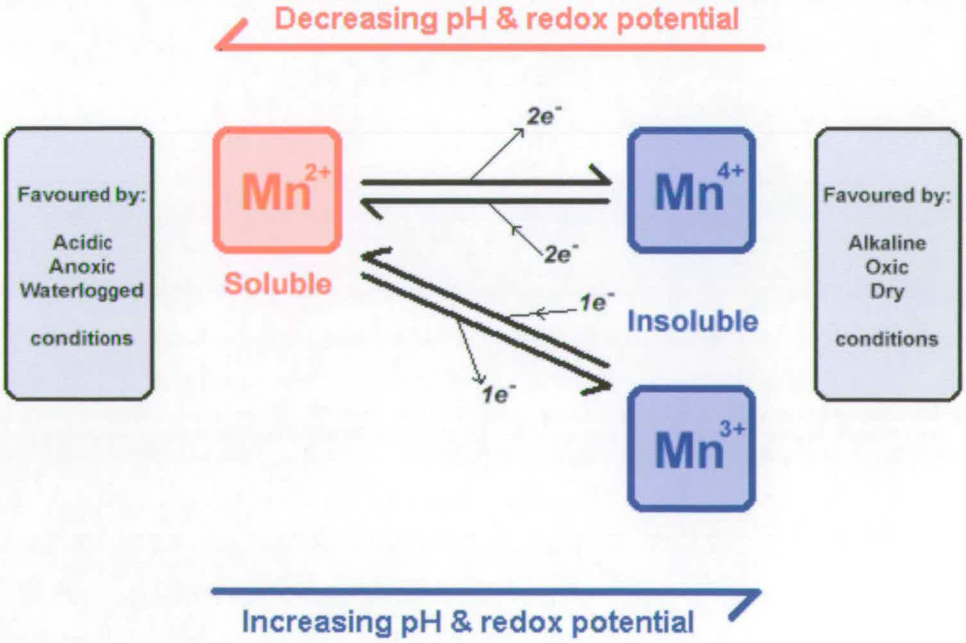


Figure 2.1: Idealised abiotic speciation of Mn in soil

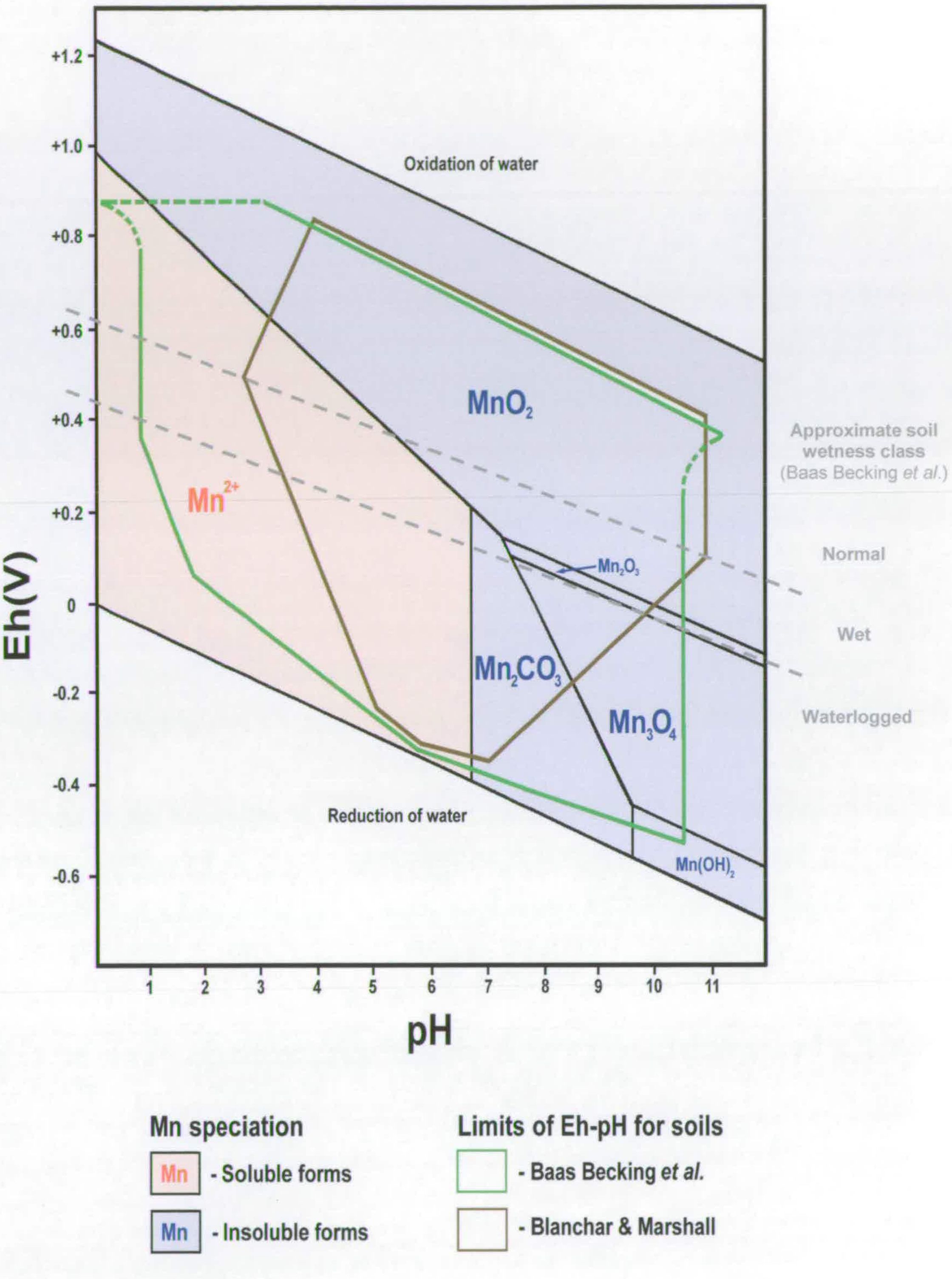


Figure 2.2: Theoretical Eh-pH diagram showing expected Mn speciation in soils of varying water regime

(Adapted from Baas Becking *et al.*, 1960; Blanchar & Marshall, 1981; Evangelou, 1998)

2.3.2 Effect of soil water regime on Mn speciation

Of the three major abiotic factors affecting Mn availability, soil water regime is perhaps the most important, as it not only induces changes in Mn speciation itself, but also directly influences the other two factors (pH and redox conditions). In fact, waterlogging of soil has the potential to release greater amounts of Mn than changes in other soil properties (Grasmanis & Leeper, 1966). Depending upon the soil water regime experienced, Mn can either be fixed as the oxidised forms, or released as the reduced forms. The effects different aspects of soil water regime (saturated / unsaturated conditions) have on soil Mn status are discussed in the following sections (2.3.2.1 & 2.3.2.2).

2.3.2.1 Mn speciation under sustained saturated conditions

Atmospheric gases normally diffuse into soils from the surface by way of air-filled pore spaces, enabling oxygen to reach areas where respiration has depleted soil atmosphere and soil water oxygen levels. The same process of diffusion also removes to the surface the excess carbon dioxide produced by respiration in the soil. However, when soils become waterlogged, the pore spaces fill with water and the rate of gas diffusion is slowed by a factor of 10,000 (Wild, 1981). The rate of oxygen diffusion into the soil is unable to keep pace with the rate of oxygen usage by actively respiring soil organisms, apart from an approximately 1 cm thick layer at the soil surface. The resultant poor aeration in the rest of the soil produces a series of chemical and biochemical reduction reactions that alter the soil pH and redox conditions (Rowell, 1981).

The effect of waterlogging on soil pH has long been recognised, and depends upon the initial pH value of the soil (Baver, 1927). In general, the pH of acidic soils will increase following waterlogging, while that of alkaline soils will decrease (Ponnamperuma, 1972; Takkar, 1969). Ponnamperuma *et al.* (1966) discovered that waterlogging for 4-6 weeks induced pH changes in acidic and alkaline soils resulting in the pH of both soils approaching neutral. After 16 weeks of flooding, all the soils tested had attained a fairly stable pH in the range 6.7 to 7.2. In alkaline soils, the concentration of carbon dioxide produced by anaerobic microbial respiration builds up, as it is unable to diffuse quickly to the atmosphere via air-filled pore spaces. This shifts the equilibrium in equation 2.6 to favour the production of H_2CO_3, thereby lowering the pH. Although this also occurs in acidic soils, the formation under reducing conditions of NH_4^+ and H_2S, as well as hydroxides of Fe and Mn, contributes toward an increase in pH (Equations 2.7 – 2.9).

Alkaline soil:

$CaCO_3 \leftrightharpoons Ca(HCO_3)_2 \leftrightharpoons H_2CO_3$ **Equation 2.6**

Acidic soil:

$Fe_2O_3 + Mn_2O_3 + 6H_2O \leftrightharpoons 2Fe(OH)_3 + 2Mn(OH)_3$ **Equation 2.7**

$Fe(OH)_3 + Mn(OH)_3 + 2e^- \leftrightharpoons Fe(OH)_2 + Mn(OH)_2 + 2OH^-$ **Equation 2.8**

$FeS + 2H^+ \leftrightharpoons Fe^{2+} + H_2S$ **Equation 2.9**

While the increase in pH observed in waterlogged acidic soils would appear to promote the formation of insoluble forms of Mn, the increased microbial activity resulting from less acidic conditions actually produces a net increase in soluble Mn forms. In alkaline soils, the resultant decrease in pH with waterlogging will shift the equilibrium between Mn^{2+} and Mn^{4+} towards the formation of the soluble ions. Thus, increased concentrations of Mn^{2+} may even occur in neutral or alkaline soils, thought to favour insoluble Mn fractions, under waterlogged conditions (Weil *et al.* 1997). The amount of Mn released by waterlogging of soils can vary widely, depending upon the total amount present in the soil and also the horizon involved. Weil and Holah (1989) reported increases in water-soluble Mn concentrations of up to 560 % following 21 days of saturated conditions in some surface horizons. Waterlogging of soils may not result in an immediate release of Mn however, and there can be a period of several weeks following flooding when Mn^{2+} concentrations remain unchanged. During this time, the demand for electron acceptors induced by the waterlogged conditions may be satisfied by preferential nitrate reduction (Iu *et al.*, 1981). Once the supply of nitrates within the soil is exhausted, the oxidised forms of Mn present become electron acceptors and are reduced to Mn^{2+}. In soils deficient in nitrates, such as many upland soils, this delay in Mn release will not occur. Therefore, the possibility exists for rapid Mn mobilisation soon after waterlogging, depending upon soil type. This could have considerable implications for Mn release during fluctuations in soil water regime brought about by short term flooding events.

2.3.2.2 Mn speciation under unsaturated conditions

Wetting of soil to a lesser degree than waterlogging is reported to favour Mn speciation in the insoluble forms, rather than mobilise it (Fujimoto & Sherman, 1946). The explanation put forward for this is that the water added forms part of a complex insoluble hydrated Mn oxide, which is stable when moisture is present and temperatures are low.

Upon drying, levels of exchangeable Mn in the soil have been shown to increase (Shuman, 1980), apparently in contradiction to the forms of Mn predicted by simple redox chemistry. One theory is that this release of Mn from the oxidised state may result from a decrease in the activity of oxidative soil bacteria, therefore shifting the equilibrium of the Mn cycle to favour Mn^{2+} (Jarvis, 1984). An abiotic explanation was proposed by Fujimoto and Sherman (1946; 1948), who postulated that a percentage of soil Mn was found as a complex, hydrated oxide with the general formula $(MnO)_x(MnO_2)_y(H_2O)_z$. When the water of hydration is split off on drying, the molecule becomes unstable and splits into its constituent Mn oxides (Equation 2.10).

$$(MnO)_x(MnO_2)_y(H_2O)_z \leftrightarrows xMnO + yMnO_2 + zH_2O \qquad \textbf{Equation 2.10}$$

The manganous oxide (MnO) may then undergo reduction allowing Mn ions to enter solution upon rewetting, leading to an increase of available Mn^{2+} ions in the soil water.

2.3.3 Effect of pH on soil Mn speciation

The term pH is used to describe the acidity of a solution, and is defined as the negative logarithm of the hydrogen-ion activity (Glasstone, 1956) (Equation 2.11).

$$pH = -\log_{10} a_{H^+} \qquad \textbf{Equation 2.11}$$

Acidic solutions contain large amounts of free H^+ ions and therefore have low pH values. In such conditions the equilibrium of the redox reaction governing Mn speciation will shift towards production of Mn^{2+}. Therefore, acidic conditions will favour the production of the soluble/reduced forms of Mn while alkaline conditions will favour the formation of the insoluble/oxidised forms of Mn (Sherman & Harmer, 1943). Although, thermodynamically, the oxidation of Mn^{2+} is favoured at pH 7 and atmospheric oxygen levels, the activation energy is high and therefore the process is normally very slow.

The ratio of the different soluble forms of Mn present in soil is also affected by pH. As pH decreases, more of the Mn is present as the water-soluble ion and less as the exchangeable fraction. This is because, under acidic conditions, the large number of H^+ ions and Al^{3+} ions produced preferentially replace Mn^{2+} ions on the surface of the cation exchange complex, displacing them into solution. Excess H^+ ions can also displace Mn^{2+} from higher oxides of Mn in a similar manner (Collins & Buol, 1970a). Because some of these oxides are a combination of Mn^{4+} and Mn^{2+}, the H^+ ions are able to compete for cation exchange sites on the solid oxide surface and therefore release Mn^{2+} into solution. The disproportionation reactions involved are shown in equations 2.12 – 2.14, with equation 2.14 thought to be of particular importance in acid and neutral soils (Sato, 1960; Wadsley & Walkley, 1951).

$Mn_3O_4 + 2H^+ \leftrightarrows Mn_2O_3 + Mn^{2+} + H_2O$ **Equation 2.12**

$Mn_2O_3 + 2H^+ \leftrightarrows MnO_2 + Mn^{2+} + H_2O$ **Equation 2.13**

$2MnOOH + 2H^+ \leftrightarrows MnO_2 + Mn^{2+} + H_2O$ **Equation 2.14**

Early scientific work dealing with soils low in concentrations of available Mn^{2+} (i.e. the form required for plant uptake) found that they had relatively high pH values of 6.5 and greater (Leeper, 1947). This was because almost all Mn present in these soils was in the form of normally insoluble higher oxides and therefore unavailable to plants. In general, increasing pH was identified as "fixing" Mn, (i.e. producing Mn^{4+}) while decreasing pH was linked to "releasing" Mn (i.e. producing Mn^{2+}) (Fujimoto & Sherman, 1948). More recently, a threshold of pH 5.6 has been identified, above which oxidation begins to increase, leading to greater Mn^{4+} production (Weil *et al.*, 1997). Further evidence concerning the effect of pH on soil Mn status was presented by Blake *et al.* (1999) in an investigation into the effect of long-term soil acidification, resulting from acid deposition, on soil chemistry at forested and grassland sites in England. Increasing soil acidity was found to increase weathering of clay minerals, thereby decreasing the cation exchange sites available in the soil and mobilising Mn into soil solution.

2.3.4 Effect of redox conditions on soil Mn speciation

The redox potential (Eh) of a solution, such as soil water, is defined as its ability to donate electrons to a reducible substance or accept electrons from an oxidisable substance (Hillel, 1998). It is quantified as the voltage required by an electrical cell to produce oxidation at the anode and reduction at the cathode while in this solution. As a solution becomes more reducing, its Eh falls and larger numbers of electrons are available to take part in reduction reactions. Therefore, low Eh favours the production of Mn^{2+}, while higher values result in the production of the oxidised Mn^{4+} (see Figure 2.2). At neutral pH, the greatest change in soil Mn speciation occurs over the range 0.3-0.4 V. Above 0.4 V, reducible forms of Mn dominate, while below 0.3 V exchangeable Mn is prevalent (Patrick & Turner, 1968).

The effect of redox potential on Mn mobilisation can also depend upon the presence of other ions in the soil. Laboratory experiments have shown that the preferential reduction of a sequence of different ions may result in alterations to the redox potentials expected to provide Mn mobilisation. Additional complications can arise from co-precipitation of Mn with other metal ions. Hydrous iron complexes have been found to remove some Mn^{2+} from soil solution at Eh (and pH) values not normally high enough to cause Mn to precipitate on its own (Collins & Buol, 1970a). Further investigation of this phenomenon found that the iron oxides involved had a negative charge at pH values greater than 5.1 and so adsorbed Mn^{2+} ions on their surface (Collins & Buol, 1970b). Another explanation is that the amount of Mn^{2+} removed by co-precipitation is too large for simple adsorption alone and that some Mn^{2+} may be incorporated into the ferric hydroxide crystal lattice (Hem, 1964).

Changes in redox conditions have been shown to be of secondary importance to pH, in terms of influencing Mn speciation, in soils where the pH is below 5.0. Once the pH decreases below 5.0, the effect of acidity becomes so marked that changes in Eh have little effect on Mn solubility (Gotoh & Patrick, 1972).

2.3.5 Effect of organic matter on soil Mn speciation

Experimental work has shown that addition of organic matter to soil produces an increase in the concentrations of soluble forms of Mn present in the soil (Shuman, 1988). Possible reasons for this include an increase in microbial reductive activity, a release of complexing agents, or a decrease in soil oxidative processes. In particular, the addition of organic matter containing a high carbon-nitrogen ratio (i.e. decaying vegetation) has been found to release large amounts of Mn from soils (Fujimoto & Sherman, 1948). This is because biological oxidation of the starches and sugars contained in the organic matter occurs at such a rate that it outstrips the available oxygen supply. In the resulting anaerobic conditions, soil bacteria reduce the higher oxides of Mn, thus releasing Mn^{2+}.

Abiotic reduction of Mn can also take place when organic matter decays and is oxidised at MnO_2 surfaces. The rapid disappearance of polyhydroxy-phenolic acids (organic matter breakdown products) and appearance of Mn^{2+} alongside coloured humic substances in experimental work undertaken by Pohlman and McColl (1989) has been taken as evidence of this.

Simple organic compounds with the ability to chelate metal ions such as aluminium, iron and Mn are known to occur widely in soils and are derived from decomposing plant residues (Dickinson & Pugh, 1974). By forming a soluble complex with the metal ions, such compounds can help mobilise metals from previously insoluble soil constituents. However, chelating agents may not have as great an effect on Mn mobilisation as for other metals, such as aluminium or iron. Khan (1969) reported that the chelates formed by Mn and common organic ligands are less stable than those formed with other metals. Other evidence suggests that the dissolution of Mn^{2+} by chelation is not an influential process in comparison to abiotic oxidation of organic matter coupled to Mn^{4+} reduction (Pohlman & McColl, 1989). This is supported by Patrick & Turner (1968), who reported that chelated Mn accounted for less than 5 % of measured soil Mn content and was unaffected by soil water regime. It is probable that the extent of Mn chelation depends on the soil physical properties and type of vegetation present.

Organic matter decomposition can slow the oxidative processes that normally take place in soils. This is because electrons are produced, which lower the redox potential, thus promoting the reduction of Mn (Lindsay, 1979). In acidic soils, increased organic matter decomposition has been correlated with increased Mn reduction. However, when organic matter was added to aerated soils with an alkaline pH, the amount of Mn^{2+} present actually decreased (Takkar, 1969). It is thought that the acids produced by the microbial breakdown of cellulose under these conditions formed Mn salts, which were readily oxidised by atmospheric oxygen.

All organic matter does not behave in the same manner, with respect to Mn, and there is evidence to suggest that freshly added organic matter differs from existing soil organic matter in its ability to alter Mn speciation (Takkar, 1969). This has obvious implications for Mn speciation in connection with any large, seasonal inputs of organic matter to soils. Such large-scale organic matter inputs may occur as the result of human activities, usually involving unwanted plant remains discarded after the harvesting of crops. One example common in Scotland is the ‘brash’ (branches, twigs and needles), which is left behind following clear-felling of commercial forestry plantations. Another, completely natural, source of organic matter input to soils is the litter produced by vegetation. The effect of vegetation on Mn cycling in soils will be discussed later in section 2.4.

2.3.6 Effect of microbial activity on soil Mn speciation

In the natural environment, the action of soil bacteria plays a major role in the biogeochemistry of Mn as well as influencing a variety of other soil properties. Species of bacteria exist which are able to either, directly or indirectly, reduce or oxidise the forms of Mn present. Some species are even able to accomplish both reduction and oxidation of Mn, depending on the environmental conditions. Therefore, the fate and mobility of Mn in the environment is strongly linked to the bacterial community present.

2.3.6.1 Microbial reduction

The fact that micro-organisms can reduce Mn has been recognised for over 100 years (Gounot, 1994; Lovley, 1995). Leeper (1947) suspected that anaerobic bacteria utilised Mn oxides as a source of oxygen at any pH value if the oxygen tension was low enough. Initially, Mn-reducing bacteria were not thought to come from any specific physiological groups and Mn reduction was not considered to be necessary for their development. However, distinct species have now been identified (e.g., *Shewanella* sp.) which directly reduce Mn as part of their normal metabolism. To date, a wide variety of Mn-reducing organisms has been described, ranging from highly aerobic species to strict anaerobes (Gounot, 1994).

Bacterial reduction of Mn can be either direct (linked to the organism's metabolism) or indirect (caused by excretory substances or changes in pH and Eh brought about by bacterial activity) (Table 2.4). In addition to direct and indirect metabolic reduction, some species of bacteria may use Mn reduction as a detoxification mechanism.

Direct	**Indirect**	
Enzyme activity	*Production of reductants*	*Modification of Eh & pH*
1. Mn reductase	1. Hydrogen peroxide	1. Production of acidic substances
2. Other non-specific reductases	2. Sulphide	2. Supply of electrons from organic matter oxidation
	3. Ferrous iron	
	4. Organic compounds	
	5. Quinones, phenols	

Table 2.4 : Methods of bacterial Mn reduction
(After Nealson *et al.*, 1989)

Direct Mn reducers use enzymes to catalyse the reduction of manganese oxides. Some direct reducers of Mn have been identified that are capable of using Mn^{4+} as a terminal electron acceptor in their metabolism (e.g., *Shewanella putrefaciens* – a facultative anaerobe). Research by Myers & Myers (2000; 2001) indicates that this form of direct Mn reduction is centred on the outer membrane cytochromes of the bacteria. However, other bacteria capable of metabolic Mn reduction (e.g., *Geobacter metallireducens* – a strict anaerobe) are thought to generate energy for growth by coupling the oxidation of organic compounds or hydrogen to enzymatic metal reduction (Equations 2.15 – 2.18) (Lovley *et al.*, 1996).

$H_2 + Mn^{4+} = 2H^+ + Mn^{2+}$ **Equation 2.15**

$\text{Formate}^- + Mn^{4+} + H_2O = HCO_3^- + Mn^{2+} + 2H^+$ **Equation 2.16**

$\text{Lactate}^- + 2Mn^{4+} + 2H_2O = \text{Acetate}^- + HCO_3^- + 2Mn^{2+} + 5H^+$ **Equation 2.17**

$\text{Pyruvate}^- + Mn^{4+} + 2H_2O = \text{Acetate}^- + HCO_3^- + Mn^{2+} + 3H^+$ **Equation 2.18**

Oxidation of organic matter coupled to metal reduction is regarded as one of the most important biogeochemical reactions in aquatic sediments, soils and groundwater (Lovley, 1991). For soil Mn in particular, these reactions will be most significant in anoxic conditions such as those encountered during waterlogging. This is because oxygen availability in aerobic conditions inhibits strict anaerobes, while the facultative anaerobes will preferentially divert their electron flow to the available oxygen.

Evidence suggests that microbial oxidation of some organic compounds, such as acetate, can indirectly cause Mn reduction (Lovley *et al.*, 1996). In this case, although the metal reduction is not directly associated with bacterial metabolism, it is brought about by the oxidation of humic substances that were initially reduced by bacteria (Figure 2.3).

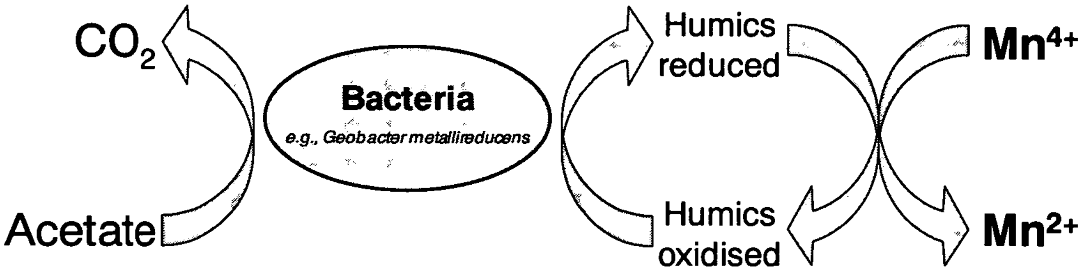


Figure 2.3: Indirect Mn reduction by bacterial reduction of humic acids (After Lovley *et al.*, 1996)

Further indirect bacterial reduction of Mn oxides can arise from interactions with excreted metabolites such as hydrogen peroxide, nitrites, sulphides, ferrous iron (especially under anaerobic conditions) and organic acids (Myers & Nealson, 1988; Nealson *et al.*, 1989; Lovley, 1991). Hydrogen sulphide (H_2S) is a powerful reductant of Mn^{4+} and is thought to represent the major mechanism for Mn reduction in certain environments (Burdige & Nealson, 1986). Ferrous iron (Fe^{2+}) can reduce Mn oxides at neutral pH or lower, therefore any bacteria that normally reduce iron have the potential to indirectly reduce Mn present. Microbially excreted organic acids, in addition to lowering the pH, have the ability to reduce Mn oxides. Reduction of Mn^{3+} and Mn^{4+} by a variety of organic compounds has been reported, mainly in acidic conditions where the pH was lower than 5 (Stone & Morgan, 1984; Stone, 1987a; Stone, 1987b).

The proportion of Mn reduction in soils occurring as a result of bacterial activity remains unknown. Experiments involving Fe reduction in sterile and non-sterile soil samples have shown that virtually all the reduction is biologically mediated (Lovley, 1995). Enzymatic reduction of Mn may be of lesser importance in soils, as Mn^{4+} is slightly more susceptible to reduction by simple organic acids, aromatic acids and reducing sugars than Fe^{3+}. However, it potentially accounts for a large proportion of all soil Mn reduction. Microbial reduction of Mn may not immediately result in the production of large amounts of dissolved Mn. It has been found that most of the Mn^{2+} produced from Mn^{4+} reduction in marine sediments was in the solid phase, and either absorbed onto mineral and organic matter or precipitated in the form of minerals like manganese carbonate (rhodochrosite) (Canfield *et al.*, 1993; Lovley, 1995). It is possible that a similar process occurs in soils, although the different environmental conditions and species of bacteria present mean that the mechanism and products may differ slightly. However, if formed in soils, these solid forms of Mn^{2+} may be released into solution due to the low pH and Eh common in waterlogged soils.

The type of Mn present in the soil affects the ability of bacteria to reduce it. Experiments using cultures of bacteria have shown that Mn-reducing organisms will tend to preferentially reduce the less crystalline, amorphous oxides (e.g., vernadite - δ-MnO_2) first, before attempting to reduce the highly crystalline forms (e.g., pyrolusite - β-MnO_2) (Lovley, 1991). The speed of the reduction also depends on the form of Mn oxide as well as the species of bacteria, with some species only able to reduce the crystalline oxides at a much slower rate than the amorphous types (Burdige *et al.*, 1992). There appears to be a distinct seasonality to some forms of bacterial Mn reduction, with certain species of bacteria in lake sediments found to cause extensive Mn reduction only during the summer months (Myers & Nealson, 1988).

2.3.6.2 Microbial oxidation

Microbial Mn oxidation, although not as prevalent as reduction, was observed prior to its counterpart (Gounot, 1994) and has been reported for bacteria, fungi and algae. In aquatic and sedimentary environments, bacteria are the primary catalysts for Mn oxidation (Nealson *et al.*, 1989). Bacteria that are able to oxidise Mn^{2+} belong to several common groups, including *Leptothrix*, *Bacillus*, *Micrococcus* and *Pseudomonas.* The pathways and mechanisms of bacterial Mn oxidation remain largely unknown, although several pathways involving direct and indirect oxidation have been proposed (Gounot, 1994; Nealson *et al.* 1988; Nealson *et al.* 1989) (Table 2.5).

Direct bacterial oxidation is an enzymatic reaction catalysed by specific Mn binding and oxidising proteins. The exact location of these proteins is unclear, as they have been found in both intracellular and extracellular extracts, and may vary with species. Further evidence for species-specific mechanisms of direct oxidation is provided by the different structures of Mn oxides produced, depending on the bacteria involved. One explanation for direct Mn oxidation is that bacteria use it as a defence against Mn toxicity (Ghiorse, 1984), although the exact physiological significance of Mn oxidation remains largely unknown for most groups of microorganisms (Nealson *et al.*, 1989).

Direct		**Indirect**	
Mn binding components	*Enzyme activity*	*Production of free radicals and oxidants*	*Modification of Eh*
1. Proteins	1. Mn oxidase	1. Hydrogen peroxide	1. O_2 production
2. Glycocalyxes		2. Superoxide	2. pH alteration
3. Cell wall components			a. CO_2 consumption
			b. NH_4^+ release

Table 2.5: Methods of bacterial Mn oxidation
(After Nealson *et al.*, 1989)

As with reduction, indirect bacterial oxidation can arise as a result of the interaction between Mn and excreted metabolites. Hydrogen peroxide and hydroxy radicals have been identified as two of the main oxidants involved (Nealson *et al.*, 1989). Hydrogen peroxide is able to act as both a reducer and an oxidiser in Mn geochemistry, with the latter function being favoured by high pH. Further indirect Mn oxidation can occur following alterations to pH and Eh caused by bacterial activity (Patrick & Henderson, 1980). Major changes to pH microgradients can occur because of carbon dioxide removal by bacteria, resulting in localised soil pH values of 10 or higher. Another suggested route for pH modification is the deamination of amino acids in protein-rich environments to form NH_4^+. Originally, it was thought that soil organisms able to oxidise Mn require the soil pH to be 5.5 or above for survival or for oxidation to occur (Leeper & Swaby, 1940). However, subsequent experiments indicate that microbial oxidation of Mn in acidic soils may be important at pH values as low as 3.5, though the optimum range remains between 6.0 and 7.5 (Grasmanis & Leeper, 1966).

One final consideration when dealing with microbial influence on Mn speciation is the effect of different soil microenvironments. Vastly different Eh and pH conditions, compared to those prevalent within the surrounding soil, may exist in localised areas (e.g., within individual soil peds). Therefore, there may be 'hot spots' of increased bacterial Mn reduction or oxidation within the soil.

2.3.7 Effect of soil temperature on Mn speciation

Research concerning the effect of soil temperature on Mn status provides apparently conflicting results. Some research (Takkar, 1969) has found that soil temperature is positively correlated to 'active' soil Mn concentrations, indicating that reduction increases with temperature. However, other researchers have found that increases in soil temperature result in an increase in the rate of Mn oxidation (Sparrow & Uren, 1987).

Although these results initially appear to be contradictory, they may be explained when the microbial aspect of Mn oxidation and reduction is considered. Because both processes can be biologically mediated, any change in temperature (e.g., increase) moving closer to a biological optimum for the species involved, will naturally increase the rate of metabolic activity. Whether this produces a net reduction or oxidation of soil Mn depends on other conditions in the soil and the species of bacteria present. For example, increasing the temperature of a well-aerated soil would be expected to decrease reduced forms of Mn, as the rate of microbial oxidation would increase while microbial reduction would remain negligible. However, the reverse is true for a waterlogged soil. The anaerobic conditions present would make microbial reduction of Mn possible, and the rate of reduction would be increased by any rise in temperature. This explanation was partly confirmed by Shuman (1980) who reported that extractable Mn in soil samples increased with temperature for soils held near saturation, while temperature had no effect on extractable Mn in drier soil samples. However, this study did not examine microbial activity in the soils studied, and changes in Mn availability were largely explained by chemical reduction or oxidation.

2.3.8 Effect of catalytic oxidation on soil Mn speciation

The fact that higher oxides of Mn can become involved in auto-oxidation reactions, and thus oxidise Mn^{2+}, was first shown in laboratory test-tube experiments (Nichols & Walton, 1942). The following equations (Equations 2.19 – 2.20) illustrate the processes taking place.

$MnO_2 + Mn^{2+} + H_2O \leftrightarrows Mn_2O_3 + 2H^+$ **Equation 2.19**

$Mn_2O_3 + Mn^{2+} + H_2O \leftrightarrows Mn_3O_4 + 2H^+$ **Equation 2.20**

These reactions also occur in soils (Leeper, 1947) and very small, oxidised Mn concretions have been shown to appear on soil particles, through non-microbial means, within one day of aeration (Ross & Bartlett, 1981; Wada *et al.*, 1978). Further growth of these Mn oxides is thought to occur through an autocatalytic reaction involving specific adsorption of Mn^{2+} onto the existing oxide surfaces. The precise mechanism causing the oxidation of reduced Mn remains unclear, but it is thought to involve an increase in pH, resulting from a charge-induced build up of OH^- ions near the oxide surfaces (Ross & Bartlett, 1981). Therefore, large amounts of Mn oxides within the soil should promote the formation of even more oxides through a positive feedback mechanism.

2.3.9 Summary of Mn speciation in soils

The different factors influencing Mn speciation in soils, discussed in sections 2.3.1 to 2.3.8, indicate the complexity of natural processes controlling soil Mn status. In general, soluble forms of Mn will be favoured by acidic soils and sustained periods of saturated conditions. Other important controls on Mn speciation in soils include availability of organic matter and the nature of the soil microbial community present. Although the focus of this research is on the effect soil water regime, soil type and land use have on Mn behaviour, an understanding of the many factors governing Mn speciation is of vital importance in interpreting the results.

2.4 Effect of vegetation on Mn cycling

As discussed in section 2.3.5, organic matter, particularly from decaying vegetation, can influence the state of Mn in the soil. In addition to this effect on soil Mn, vegetation also plays a vital role in the cycling of Mn in the environment. Because plants require Mn as an essential micronutrient for healthy growth, and incorporate it into several cellular structures, vegetation can act as a pool for Mn storage. This pool of Mn is effectively fixed until the plant dies, or the structure in which Mn is stored decays.

Studies of Mn occurrence in species of spruce (*Picea* sp.) have revealed that accumulation occurs within the epidermis, mesophyll and vascular tissue of the conifer needles (Godde *et al.*, 1991). The extent and location of the Mn accumulation was found to differ between trees, depending upon their state of health. Those showing severe signs of damage, attributed to the effects of environmental acidification, contained significantly less Mn in their needles than their healthier counterparts. Hodson and Sangster (1998) also suggest that mineral uptake and deposition in spruce needles is largely influenced by soil pH. Their research showed that the needles from trees grown in acidic soil contain more Mn than those from trees grown in a neutral soil. One explanation suggested for the difference in needle Mn content between the two sites was that Mn accumulation within vegetation is maximised under moderately acidic conditions, but diminishes as pH increases or decreases either side of this. Thus, the potential exists for changes in soil pH brought about by catchment acidification to indirectly influence soil Mn levels by altering the amount stored in vegetation. The effect of Mn release from vegetation on soil Mn cycling cannot be ignored, therefore the potential inputs from decaying vegetation should be considered by studies of Mn behaviour in soils.

2.4.1 Litterfall

By locking away Mn in living tissue, plants have the ability to influence the amount of Mn readily available for biogeochemical cycling. Decay of plant tissue, resulting from events such as mortality and litterfall, can therefore release large quantities of Mn into the soil. In the case of litterfall, this may occur on a seasonal basis, thereby producing increases in soil Mn at certain times of year. According to Carey & Farrell (1978), release of nutrients from litterfall is considered to be the most important source of nutrient release from trees. The land use in the catchment area studied in this research is divided approximately equally between commercial Sitka spruce (*Picea sitchensis*) plantation and open moorland dominated by heather (*Calluna vulgaris*) and deciduous grass (*Molinia caerula*). A brief review of published litterfall studies from each vegetation type is now presented.

2.4.1.1 *Molinia* litterfall

Boatman *et al.* (1975) suggested that dead *Molinia* leaves collecting in bog pools in SW Scotland were the source of elevated potassium concentrations measured in the pools during February to April. Buckets filled with water and placed level with the peat surface were used to collect any leaves blowing across the bog. Most leaves were trapped during November to March, with a maximum of 13 g dry weight per bucket collected in March. However, mineral content in the leaves was not measured, and the lack of any reported dimensions for the buckets makes it impossible to convert the quantities of leaves collected to any standardised deposition rate.

Loach (1968) studied mineral concentrations in *Molinia* leaves throughout the year and found that leaves collected from litter in winter contained only approximately 20 % of the summer mineral content of living leaves. Further work by Morton (1977) attempted to distinguish whether this loss was due to translocation back into the *Molinia* tussock, or leaching of nutrients by rainfall. Although Mn was not measured, the results of this study indicated that most of the potassium, magnesium and calcium was leached from the dead leaves by rainfall and subsequently enriched the surface of the soil.

2.4.1.2 *Calluna* litterfall

Studies of *Calluna* litterfall show that the total amount of litter produced depends upon the growth phase of individual plants. Cormack & Gimingham (1964) discovered an increasing gradient of litter production from pioneer>building>mature>degenerate growth phases (Table 2.6). They also noted a definite seasonality to the deposition, with maximum litterfall occurring in October-November and February. The amount of litter shed during these peaks was approximately 30 times greater than at other times of the year. The occurrence of two peaks in litterfall was attributed to the loss of particular structures from the plant over a relatively short time period. The autumnal peak was largely composed of short shoots shed at the end of the growing season, while the winter peak mainly comprised flowering capsules from the previous year, possibly shed during prolonged periods of frost. Therefore, although classed as an evergreen shrub, *Calluna* exhibits seasonal patterns to its litter production, which may serve to release mineral nutrients into the soil at certain times of year.

	Pioneer	Building	Mature	Degenerate
Annual litterfall[1] (kg ha^{-1} yr^{-1})	59.6[2]	73.9[2]	161.6 - 433.3[3]	393.1 - 712.4[3]

Table 2.6: Litter deposition under *Calluna vulgaris* (After Cormack & Gimingham, 1964)

[1] Air-dry weight
[2] Mean based on observations from 25 plants from 1 location
[3] Range of means, based on observations from a total of 60 plants over 3 locations

2.4.1.3 Sitka spruce litterfall

Owen (1954), Carey and Farrell (1978), Adams *et al.* (1980) and Miller *et al.* (1996) have all demonstrated the seasonal aspect of needle deposition by Sitka spruce. However, the timing of maximum litterfall and the yearly total varies between studies (Table 2.7). Unfortunately, no data concerning Mn content are presented in these studies, although analysis of other metals (potassium, calcium, magnesium) indicates that the nutrient content of needles varies throughout the year (Carey & Farrell, 1978; Miller *et al.*, 1996). Therefore Mn inputs to soil from Sitka spruce litterfall may vary temporally as a result of both the timing of maximum litterfall and the concentration of Mn contained within the litter.

Study	Location	Tree age (Years)	Mean annual litterfall (kg ha^{-1} yr^{-1})	Maximum litterfall	Maximum nutrient content of needles
Owen (1954)	Wales	30	2053	Late autumn & spring	April – May
Carey & Farrell (1978)	Ireland	34-47	5500	June - July	April – May
Adams *et al.* (1980)	Ireland	26-37	3600	June - August	March – May
Miller *et al.* (1996)	Scotland & N.England	25-30	3151	July - August	May

Table 2.7: Results from studies of Sitka spruce litterfall dynamics

Climatic conditions appear to further affect the seasonality of litterfall. Carey and Farrell (1978) found that most litter fell during the summer months when there was unusually low amounts of rainfall and high temperatures. Adams *et al.* (1980) attributed some of the heaviest litterfall to pest attacks on the trees. Attacks by the green spruce aphid (*Elatobium abietinum*) were also reported by Miller *et al.* (1996) as causing increased litterfall in summer. It is not inconceivable that a long dry summer would provide ideal breeding conditions for the pest population, thereby resulting in increased loss of needles from the trees already suffering the effects of drought stress. The climatic influence means that not only does the amount of litter produced, and therefore nutrients returned to the soil, show seasonal variation but it also varies from year to year.

In summary, nutrient cycling in vegetation is an important factor when considering catchment Mn cycling. Climatic effects on the seasonality exhibited by litterfall may serve to release a large pool of Mn into the soil during certain years. Therefore, litterfall dynamics of the major vegetation types within the study area were also investigated as part of this research.

2.4.2 Clear-felling of commercial forestry

One particular area of interest to those studying the consequences of land use and management practices on water quality in upland catchments is the effect of clear-felling forested areas on the water chemistry. The by-products from the clear-felling of commercial forestry plantations represent a massive input of decomposing litter to the soil. Decomposition of the 'brash' and root structures left behind produces a large increase in available soil minerals, which can be leached by water. Durand *et al.* (1994) noted an increase in stream Mn concentrations for 2-3 years following clear-felling of a forested catchment in Wales. Increased metal losses in runoff from recently cleared catchments are also reported by Adamson *et al.* (1987) and Titus & Malcolm (1991).

One alternative to conventional clear-felling is whole-tree harvesting, which removes both the roots and branches from the site, thus preventing a massive release of minerals from decaying vegetation (Fahey *et al.*, 1991a). Fahey *et al.* (1991b) report that nutrient leaching from the root zone of whole-tree harvested sites is less than from conventionally harvested sites in the years immediately following harvest. This is thought to arise from vegetation regrowth being suppressed by the 'brash' left behind following conventional harvesting, and therefore uptake of soil Mn by plants is lower than in whole-tree harvested areas. Because there is less Mn immobilisation in growing vegetation and greater inputs to the soil from decaying 'brash' at conventional harvest sites, there is a larger pool of soil Mn susceptible to leaching beneath them than at whole-tree harvest sites. However, concerns over the threat to soil fertility arising from large-scale removal of nutrients by whole-tree harvest and the extra expense of the technique mean that it is not widely implemented.

Soil disturbance by felling practices may be responsible for some of the increases in metal transport reported following clear-felling. The heavy machinery used for felling can disturb subsurface transport pathways, leading to alterations in soil water regime that in turn may alter soil Mn speciation. Exposure, and incorporation into organic horizons, of deep and subsurface mineral horizons caused by root and stump removal may also result in metal mobilisation. Erosion of sediment following exposure may account for some Mn removal from clear-felled sites (Heal, 2001), while the mixing of organic and mineral horizons may produce conditions favourable to the formation of soluble Mn ions.

Adamson & Hornung (1990) propose an additional mechanism for mineral loss from catchments, arising from the disturbance caused by clear-felling. Their study of drainage water chemistry following clear-felling of a Sitka spruce plantation within Kershope Forest in England identified a slight fall in pH and an increase in iron content. These changes were most marked at the wettest site investigated, and were attributed to the water table rising as a result of transpiration ceasing following clear-felling. The anaerobic conditions brought on by waterlogging were therefore believed to be responsible for promoting the formation of soluble reduced metal ions, which were then readily transported in water.

It is therefore apparent that, in addition to problems caused by acidification during their growth in certain soil types, commercial forestry plantations can have a detrimental effect on streamwater quality when they are harvested. Some estimates put the recovery time for water chemistry in clear-felled areas at decades, and possibly longer (Neal *et al.*, 1992).

2.4.3 Root exudates

In addition to playing an important role in the cycling of Mn, living plants can also directly influence the solubility of soil Mn. This is achieved through the release of specialised compounds, designed to increase Mn uptake from soils, by their root systems. These root exudates are known to include hydroxy-carboxylates, which have been shown to increase concentrations of soluble Mn on addition to MnO_2 (Hem, 1965). The mechanism of root exudate activity is believed to involve reduction of Mn at the oxide surface and subsequent complexation of the Mn^{2+} produced. Godo and Reisenauer (1980) found this 'rhizosphere effect' to be most marked in soils with a pH of 5.5 or less.

2.5 Mn distribution in the soil profile

The dispersal of Mn throughout a soil profile is thought to be closely connected to the processes of soil formation (Leeper, 1947). Factors including the weathering of minerals from parent material, release from decaying vegetation and movement of ions in solution all influence the distribution of total Mn within the soil profile.

One of the most common patterns of Mn distribution in soils is a surface accumulation from litter decomposition, a subsurface decrease as a result of leaching, and an increase at depth from weathering of parent material. This pattern of Mn distribution has been identified in organo-mineral soils from the Yorkshire Dales (Heal, 1996) and in a North American peat wetland (Walton-Day *et al.*, 1990). Weil and Holah (1989) also identified the surface build up of Mn, positively correlated with organic matter content, in the A horizons of soil profiles representing both well-drained and poorly drained members of three toposequences from the north-eastern United States.

Differences in physico-chemical behaviour mean that distinct separation of metal ions can occur in soil profiles. For example, Mn and iron can occupy discrete zones in soils depending on the prevailing soil water regime (Collins & Buol, 1970b). In freely drained soils where the ion movement is predominantly downwards, iron tends to precipitate first and so is found at shallower depths in the profile than Mn. Conversely, the reverse pattern is observed in poorly drained soils with rising groundwater, where the predominantly upward ion movement leads to Mn precipitation above iron in the profile.

Poorly drained soils within a toposequence may also potentially have less available Mn than their freely drained counterparts (Veneman & Bodine, 1982). These decreases in Mn concentrations are attributed to increased Mn mobility resulting from the reducing conditions, brought on by waterlogging, and subsequent loss of aqueous Mn^{2+} ions in solution. Moore (1973) measured total and extractable Mn levels in soil horizons of different soils from north-eastern Scotland. In this study, a slight decrease in total Mn and much greater decline in extractable Mn were evident within gleyed horizons compared to non-gleyed horizons. The topography of an area can greatly influence subsurface drainage patterns and therefore the movement of mobile Mn ions. Cassel *et al.* (2002) found that soil water Mn concentrations were greatest in soils at the base of slopes, and attributed this to subsurface flow of dissolved Mn from higher up the slope.

Therefore, it is clear that no single factor can adequately describe the distribution of Mn in soils. The percentage of soil Mn present in either reduced or oxidised, and available or fixed forms in any horizon depends on a complex interaction between several different environmental variables. Other factors directly influencing Mn concentrations in the soil profile include microbial activity and the effect of vegetation. Furthermore, antecedent soil conditions, particularly with regard to moisture content, will have a profound effect on the status and distribution of any Mn present.

When Mn distribution and behaviour in typical upland soils is considered, the influence of pH and effect of waterlogging on redox conditions will be of prime importance. The acidic nature of the organic soils commonly found throughout upland areas in the UK will tend to promote the occurrence of soluble forms of Mn. Saturated conditions prevalent in the peaty soils will also favour the production of soluble Mn ions, because of the low Eh resulting from the anaerobic conditions. Soluble Mn concentrations should also be increased because of the availability of organic matter in the soil, either directly by chelation with humic substances, or by other processes connected with the decomposition of the organic matter. One factor that could potentially prevent the mobilisation of large concentrations of Mn into soil water in some upland soils is the relative lack of mineral matter in areas of deep peat. In such expanses of deep organic soil there is often only a limited pool of soil Mn in the mineral form, thereby ensuring that soil water Mn concentrations remain low even though conditions strongly favour the production of soluble Mn. However, in areas where there are acidic, waterlogged soils containing substantial reserves of mineral Mn, the potential exists for considerable mobilisation of Mn into soil water.

2.6 Mn speciation in water

Once Mn is released from soils into soil water, throughflow processes can transport it until it reaches surface waters. This can result in either direct entry into standing water or, more commonly, incorporation into running water and subsequent transport to a lake, reservoir or the sea. Another potential pathway for Mn transport from soil water to surface water involves percolation to groundwater first, although this may not be of such importance in the upland area investigated by this research. Controls on the aqueous chemistry of Mn are similar to those influencing its form in soils. Redox reactions dependent on Eh and pH are of prime importance, their effects being modified by the residence time of Mn within different water bodies. Other factors controlling Mn geochemistry in water include autocatalysis, biotic activity (especially microbial and algal) and organic complexation.

These controls on Mn speciation are examined below, and examples of studies investigating Mn speciation in natural waters are presented.

2.6.1 Effect of Eh and pH on Mn speciation in water

Redox potential and pH affect the reversible reactions governing Mn speciation in water in a similar manner to that observed in soils (discussed in sections 2.3.3 & 2.3.4.), with oxidation of soluble Mn^{2+} to insoluble oxides favoured by high Eh and pH (Stumm & Morgan, 1996). The inverse correlation between pH and soluble Mn concentration in water is well documented (Borg, 1986; Freedman & Clair, 1987; Urban *et al.*, 1990). In general, lakes with a pH above 6 are considered to act as sinks of Mn, while acidification causes the release of Mn from lake sediments (Dillon *et al.*, 1988; Shanley, 1986; White & Driscoll, 1987). However, the kinetics of abiotic Mn oxidation in water are relatively slow, therefore Mn is likely to persist in the reduced form unless residence times in the water are long (Sung & Morgan, 1981). Laxen *et al.* (1984) observed that when the pH of water is less than 5, Mn^{2+} could remain in solution for months, possibly years. A measurable rate of abiotic reaction only occurs at pH values of 7 or greater, while between pH 5 and 7, oxidation of Mn^{2+} occurs as a largely as a result of catalysis by biota or particulate matter.

2.6.2 Effect of autocatalytic reactions on Mn speciation in water

The rapid decrease in aqueous Mn^{2+} concentrations above pH 8.5 suggests that there is also an autocatalytic function involved in the oxidation reaction. Stumm and Morgan (1996) proposed the following series of reactions involving autocatalysis:

$$Mn^{2+} + O_2 \rightarrow (slow) \rightarrow MnO_{2(s)} + 2e^- \qquad \textbf{Equation 2.21}$$

$$Mn^{2+} + MnO_{2(s)} \rightarrow (fast) \rightarrow Mn^{2+}.MnO_{2(s)} \qquad \textbf{Equation 2.22}$$

$$Mn^{2+}.MnO_{2(s)} \rightarrow (slow) \rightarrow 2MnO_{2(s)} + 2e^- \qquad \textbf{Equation 2.23}$$

Evidence for the occurrence of autocatalytic reactions involving Mn comes from the non-stoichiometric products of Mn^{2+} oxidation. Under varying alkaline conditions, a 30-90 % oxidation of Mn^{2+} was recorded, with the stoichiometry of the products ranging from $MnO_{1.3}$ to $MnO_{1.9}$. Pontér *et al.* (1990) considered autocatalytic oxidation of dissolved Mn by solid particulate Mn to be one of the factors causing a decrease in soluble Mn concentrations in the Kalix River, Sweden, during the summer months.

2.6.3 Effect of biotic activity on Mn speciation in water

The biological nature of Mn oxidation in lakes was demonstrated by Tipping (1984) who showed that the process was temperature dependent, with an optimum at 15-30°C in neutral and slightly alkaline conditions. Similar direct and indirect mechanisms for biotic Mn reduction and oxidation exist to those operating in soils (already discussed in section 2.3.6). However, in addition to bacteria, photosynthetic algae are also thought to be of considerable importance in influencing Mn status within the water column. The activity of microorganisms, particularly their effect on water Eh and pH, can cause diurnal variations in Mn concentrations (Brick & Moore, 1996). Cycles of Mn and other metals have been identified in streams, with 2-3 fold increases in concentration recorded during darkness. These are thought to arise from changes to in-stream photosynthesis and microbial respiration rates lowering dissolved oxygen and pH levels at night.

One further, somewhat different, pathway by which biotic behaviour can affect diurnal stream water Mn concentrations, proposed by Brick & Moore (1996), is that nocturnal bioturbation of stream sediments by invertebrates can release large amounts of particulate Mn into the water.

2.6.4 Effect of organic complexation on Mn speciation in water

The complexation of Mn by organic matter is not thought to play a major role in Mn transport in water. Studies investigating Mn speciation in natural waters typically show that only a small fraction of the total Mn is organically bound. Urban *et al.* (1990) reported that organically bound Mn only accounted for 3 % of the total Mn in samples from Canadian lakes. Therefore, although the timing of Mn release into surface water may occur alongside increases in water colour caused by high levels of dissolved organic carbon (Zajicek & Pojasek, 1976), the two events are thought to be largely independent of each other.

2.6.5 Studies of Mn behaviour in water

Studies of Mn in water have sought to identify factors affecting the overall Mn concentration, temporal variations in concentration, and the chemical forms involved. While the total concentration and temporal variability are relatively straightforward to record, chemical speciation and the size fractionation of Mn require the use of additional analytical techniques. The results of several studies investigating factors influencing Mn concentration and speciation in different water bodies are summarised in Table 2.8.

Study	Location	Timing of study	Type of Water	No. of Samples	Mn range ($\mu g\ l^{-1}$)	Factors influencing Mn concentration & speciation
Urban *et al.* (1990)	Canada	Dec	lakes	37	<10 – 240	pH; catchment size
Pontér *et al.* (1990)	Sweden	May-Sept	river	18	12 - 60	pH; temperature
Laxen *et al.* (1984)	England	April	rivers & streams	15	3.2 - 68	residence time
Laxen & Chandler (1983)	England	Aug	lakes & stream	13	27.7 – 2290	pH; residence time

Table 2.8: Factors influencing Mn concentration and speciation in surface waters

Some studies have employed ultrafiltration to separate Mn forms by size. The distinction between dissolved and particulate Mn is an arbitrary operationally-defined concept (Laxen & Chandler, 1983), often taken as the ability to pass through 0.45 µm filters. Other researchers have used a technique called anodic stripping voltammetry (ASV) to determine specific reduced Mn^{2+} species. ASV measures the peak current recorded during an oxidative stripping of the metal being analysed and relates this to concentration. Although able to measure very low concentrations of ions, the technique cannot differentiate between different forms of 'labile' ions (i.e. free metal ions, inorganic complexes and readily dissociable organic complexes). The technique does, however, have the advantage of being able to distinguish dissolved species from species bound to colloidal or particulate phases, regardless of size (Stumm & Morgan, 1996).

Laxen & Chandler (1983) found that manganese in the well-oxygenated surface waters of three lakes in northern England was mostly in particulate form, and retained by 0.1 µm filters. Further analysis, using a scanning electron microscope, revealed that only a few large particles with mean diameters of several µm accounted for most of the particulate Mn. The mean diameter of particulate Mn in one stratified lake was found to decrease with depth towards the thermocline. In the anoxic waters below the thermocline of this lake, essentially all Mn passed through the 0.015 µm filters used and was assumed to exist in the dissolved form. It is thought that the extended residence time in the lakes and elevated pH levels resulting from algal photosynthetic activity in the surface waters allowed oxidation of dissolved Mn^{2+} to proceed. The large particles reported would tend to arise from the effect of autocatalytic oxidation on the surface of oxidized Mn particles.

An investigation into the Mn speciation in rivers and streams in northwest England found that the soluble Mn fraction, able to pass through 0.015 µm filters, could represent between 15 and 95 % of the total Mn present (Laxen *et al.*, 1984). This wide range of values recorded appeared to be independent of water pH, alkalinity, conductivity or humic substances. Instead, the authors suggest that the dynamic conditions and short residence time experienced in the rivers result in the effective decoupling of the redox reactions between particulate and soluble Mn fractions. In this type of environment, catchment hydrogeological conditions are considered to have a greater bearing on the presence of Mn fractions than aquatic chemistry processes. The two major sources of Mn in rivers are stated as being, weathering processes producing suspended sediment, and an influx of soluble Mn^{2+} species leached from anoxic soils and groundwater.

2.6.6 Summary of Mn behaviour in water

In conclusion, the processes affecting Mn chemistry in rivers and streams are different from those operating in standing bodies of water. In running water, the forms of Mn present depend on the inputs from upstream and the surrounding catchment, which in turn depend upon the hydrogeological conditions operating within the catchment. Once Mn enters lakes, estuaries and oceans, the longer residence times encountered mean that chemical processes dominate the redox reactions governing speciation.

2.7 Metal geochemistry of upland catchments

There have been many other studies detailing the geochemical behaviour and concentration of metal ions in upland streams and soil water. Within the UK, projects at Loch Dee in Scotland (approximately 16 km from the location of this study) and Plynlimon in Wales have considerably furthered the knowledge of metal ion hydrochemistry.

2.7.1 Other studies of metal ion behaviour in upland catchments

Grieve (1990 a & b) identified distinct annual cycles of soil solution chemistry in acidic peaty soils of the Loch Dee catchment. These cycles were usually characterised by a large summer/autumn peak in iron concentrations, which was greatest following the summer drought of 1984, correlated with increases in dissolved organic carbon levels. The increase in the organic carbon content of the soil solution was attributed to formation of water soluble organic materials under the higher summer temperatures, and subsequent flushing out as the relatively dry soils were rewetted by autumn rains. Although Mn was not measured during this study, evidence for a similar summer/autumn peak in soil solution was reported by research in Yorkshire (Heal, 1996). According to this study, antecedent moisture status of the soil was found to have a major bearing on Mn concentrations in soil water, as were soil type and catchment size.

Another study based at Loch Dee calculated the hydrochemical budgets for sub-catchments with different land uses (Farley & Werrity, 1989). Spatial variability in water chemistry between sub-catchments was related to differences in afforestation and land use management practices. Stream water containing the highest Mn concentrations was found to drain from forested sub-catchments with mineral soils.

Research at Plynlimon has identified a close link between rainfall events and increased trace element losses from the catchment (Durand *et al.*, 1994). Again, this is thought to result from the flushing out, by heavy rainfall, of products formed during dry periods. These findings were in agreement with previous work in the south of France (Durand *et al.*, 1991), which reported complex fluctuations in ion concentration during storm events. In general, studies of this nature have found that the ionic concentration of stream water increases most during storm events preceded by dry conditions. Wilson *et al.* (1991) suggest that the increases in some metal concentrations, such as iron, observed in stream water during storm events may occur due to rapid release from pore surfaces by particle detachment during high water flows through the subsurface channels.

Further work, undertaken as part of the Plynlimon long-term monitoring project by Muscutt *et al.* (1990), reports that the predominant subsurface water transport pathway may alter during rainfall. Exploitation of macropore flow during storm events can flush out accumulated dry deposition and weathering products from surfaces of the previously dry channels. Further evidence of this is provided by a study in the Cairngorm mountains, which found that flow through different subsurface pathways has a great effect on water chemistry, as the composition of catchment outflow integrates the chemistry of the different soil horizons it encounters (Ferrier *et al.*, 1990). For example, organic horizons have been shown to retard Mn transport, by retaining large quantities of Mn adsorbed to soil particles, in spite of low pH values (Shanley, 1986).

It is therefore evident that, although considerable work exists detailing metal ion behaviour in upland catchments, there is a relative lack of data concerning Mn mobilisation from upland soils. Such information will be of particular benefit to the water industry, in view of current legislation concerning the quality of drinking water and the problems associated with Mn removal from water supplies.

2.7.2 Contribution of this research

The complexities of Mn geochemical cycling mean that no single study has adequately been able to account for its movement throughout an entire catchment. This research is intended to complement and extend existing studies in increasing the pool of available knowledge concerning Mn mobilisation within soils. In particular, attention is paid to the role of soil water regime in influencing soil Mn status, and the release of Mn from soil into surface waters. Accordingly, one hypothesis being tested by this research is that changes in soil water regime, resulting from rewetting of soils following a long dry period, can cause elevated concentrations of Mn in upland water supply catchments.

Although Mn movement within a catchment is highly complex and influenced by many different variables, as shown in this chapter, soil processes integrate all of these factors and provide a means of understanding the controls on Mn mobilisation. Therefore, other hypotheses investigated relate to the effects of pedology and land use on Mn release to the water supply reservoir.

It is intended to use the information gathered by this research to provide an indication of areas or water bodies most at risk from Mn mobilisation, as well as suggesting land use management strategies to limit its extent. Information of this kind is of vital importance to water supply companies concerned about water quality in existing reservoirs, or developing new ones to meet increasing public demand for drinking water.

Chapter 3: Field monitoring programme

This chapter describes the location of the experimental sites and field monitoring programme conducted during the research. The reasoning behind the choice of individual sites is presented, along with a review of the equipment installed. Finally, brief consideration is given to the expectations and intended output from these field sites.

3.1 Study location: background and characteristics

The catchment of Loch Bradan reservoir, situated in southwest Scotland (Figure 3.1), was chosen to examine the role of soil water regime, soil type and land use on Mn mobilisation from upland soils. The decision to use this catchment was based on a number of factors, including consideration of prior reservoir water Mn concentrations, surrounding land use, soil types and accessibility.

3.1.1 Previous Mn release from catchment

Situated in uplands approximately 26 km south of Ayr, Loch Bradan reservoir was managed by West of Scotland Water (WoSW – now part of Scottish Water, following the reorganisation of water authorities in April 2002) and was ideally suited to be the location of this research. During the 1990s, there were three extended periods when water from Loch Bradan reaching the nearby treatment works contained Mn concentrations considerably in excess of the 0.05 mg l^{-1} EC standard (Figure 3.2). Repeated Mn failures were a major consideration in the extensive upgrading of the treatment works in 1995, at a cost of £16 million (Little & McFadzean, 1991). The catchment is dominated by organic and organo-mineral soils, while the land use is primarily commercial conifer plantations and open moorland vegetation. This combination of soils and land use within the Bradan catchment is typical of upland sites throughout the rest of the UK. Thus there is potential for the transfer of any research findings to many similar sites.

3.1.2 Development of Loch Bradan water supply scheme

The name 'Bradan' is an Anglicisation of the Gaelic word for 'salmon', although there is no evidence to suggest the loch is particularly rich in that species of fish, and it possibly owes much to the 'Balmoralisation' of Scottish names common during the Victorian era. The current dimensions of Loch Bradan are vastly different to those at the beginning of the 20th century (Figure 3.3), as the loch has twice been enlarged in an effort to meet the rising public

Figure 3.1: Location of Loch Bradan

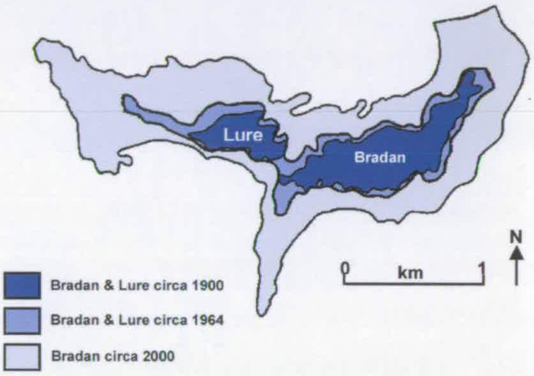


Figure 3.3: Historical growth of Loch Bradan

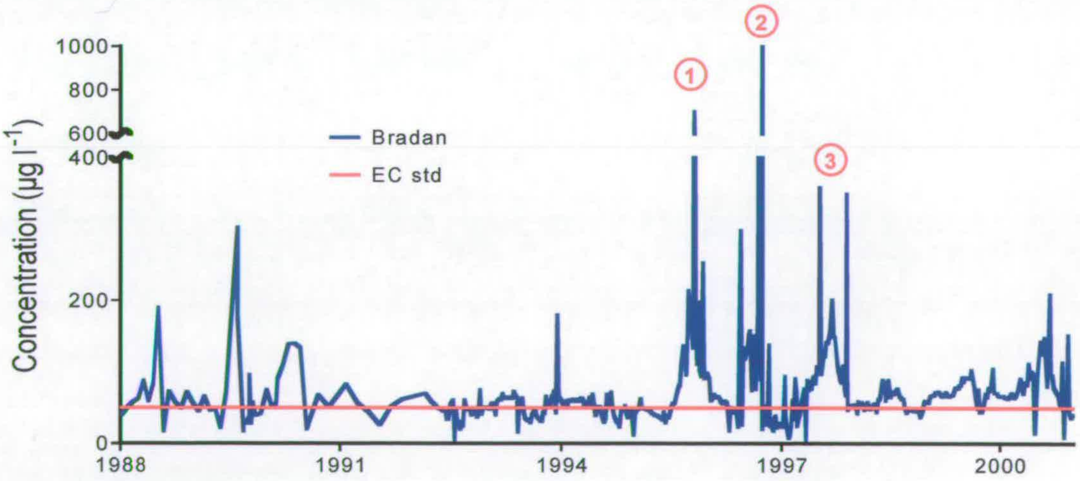


Figure 3.2: Mn concentrations in water entering treatment works from Loch Bradan, January 1988 to December 2000

Major Mn peaks in reservoir water: ① Aug-Dec 1995
② Jul-Sep 1996
③ Jul-Nov 1997

demand for drinking water in southwest Scotland. Originally, Loch Bradan and the nearby Loch Lure existed as two separate lochans surrounded by open moorland. Described by Murray and Pullar (1910), in their comprehensive bathymetric survey of Scottish lochs, as a "drift-dammed lake lying on lower Silurian greywackes and shales", Bradan was ranked 307th of the 562 lochs measured in terms of surface area. Indeed, when volume was considered, this ranking was even lower, with the shallow loch only holding an estimated 450,000 m^3 of water.

The first increase in size of Loch Bradan took place during the early 1900s, when a dam was constructed at the loch's eastern end in order to create a sizeable reservoir for supplying water to the nearby burgh of Troon. The increase in size produced a reservoir capable of holding 1,700,000 m^3 of water and supplying 9,100 m^3 per day. Although now joined to Loch Bradan, as the water level rose by 2.4 m, the smaller loch Lure still retained its identity on Ordnance Survey maps of the period.

The final increase in size of Loch Bradan, and complete incorporation of Loch Lure, occurred in 1973 following the construction of two dams by the Ayrshire and Bute Water Board. The larger of these dams was built approximately 400 m north of the original Bradan Dam across the line of the Water of Girvan. The smaller Lure Dam is described by Johnston (1974) as a saddle dam, located on the watershed at the west end of the reservoir. The building of the two dams raised the water surface by 12 m and produced a reservoir capable of providing over 100,000 m^3 of water per day for the towns of Ayr, Troon and Kilmarnock. At present, Loch Bradan is one of the 10 largest drinking water supply reservoirs in Scotland, supplying over 180,000 customers from its 19,000,000 m^3 capacity (Johnston, 1974).

Regional control of water supplies in Scotland was initiated in 1968 by the creation of regional water boards, with Loch Bradan reservoir falling under the jurisdiction of the Ayrshire and Bute Water Board. Following the reorganisation of local authority boundaries in 1975, control of the reservoir and its associated treatment works passed to the newly created Strathclyde Regional Council. Further changes to the Scottish water industry took place in 1996, with the setting up of regional water authorities, at which time WoSW assumed responsibility for all domestic water supplies in the area. This arrangement has recently (April 2002) been superseded by the creation of a single body (Scottish Water), responsible for domestic water supplies throughout the entire country.

Bradan treatment works were built at the same time as the new dams and are situated approximately 0.5 km to the north of Bradan Dam. Water supply problems, caused by the failure of conventional treatment to remove excessive Mn concentrations, resulted in extensive upgrading of the facilities during the mid-1990s. This modernisation of the Bradan treatment works, completed in 1995, saw the installation of machinery to allow Mn removal via the addition of ozone. Operating costs for the process of ozonation can be high, therefore a greater understanding of the mechanisms controlling reservoir water Mn concentration is being sought.

3.1.3 General catchment characteristics

The direct catchment of Loch Bradan covers an area of 15.5 km^2, and ranges in altitude from 300 m above ordnance datum at the reservoir to over 650 m in the hills to the south (Ordnance Survey, 1995). Additional water is brought into the reservoir via the Lure aqueduct, which drains approximately 14.5 km^2 of the neighbouring Stinchar catchment, thereby giving a total catchment for Loch Bradan of 30 km^2 (Johnston, 1974). The underlying geology is predominantly greywackes of the Blackcraig and Kirkcolm formations, with the Loch Doon granite intrusion bordering to the south and the Southern Upland Fault to the north (British Geological Survey, 1994). Much of the catchment is composed of gentle to steep hillslopes with numerous rock knolls, although expanses of level ground exist beside the reservoir.

The catchment is dominated by organo-mineral and organic soils. These typically consist of peaty podzols and peaty rankers found in shedding sites, with peaty gleys and peat in receiving sites (Bown *et al.*, 1968; Bown, 1973; Bown *et al.*, 1982). Peat in close proximity to the streams often has mineral alluvium interspersed throughout its profile. The deepest peat profiles are found in the comparatively level receiving sites surrounding Loch Bradan, where permanently saturated conditions at shallow depths have allowed organic material accumulation to depths of over 2 m.

The Forestry Commission manage the land surrounding Loch Bradan, and have established conifer plantations, predominantly of Sitka spruce (*Picea sitchensis*), over approximately 50 % of the catchment (Figures 3.4 & 3.5). These trees were planted in the 1960s and are now approaching the optimum age for harvesting. Some clearfelling operations had already taken place within the catchment prior to the study commencing, and more were evident to

Figure 3.4: Loch Bradan viewed from moorland field sites in the Ballochbeatties catchment to the southwest of the reservoir

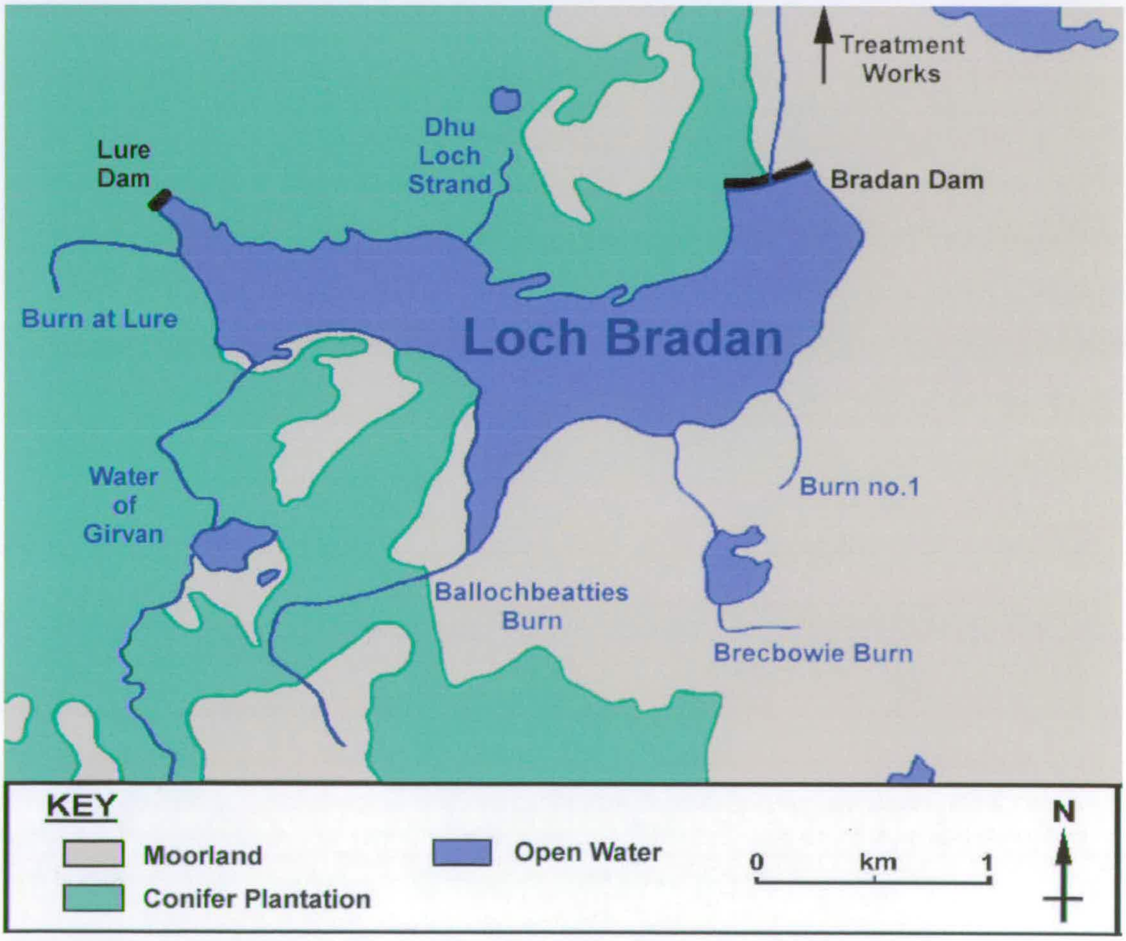


Figure 3.5: Loch Bradan map showing land use and main feeder streams

the north of the reservoir during the summer of 2000. The remaining land, deemed unsuitable for commercial forestry, has been left as moorland dominated by *Calluna vulgaris* and *Molinia caerulea*. The vegetation communities found here are typically moist Atlantic heather moor, flying bent grassland, flying bent bog and lowland blanket bog (Robertson, 1984).

3.2 Factors influencing location of field monitoring sites

In order to determine the effects of soil water regime on Mn mobilisation, a number of sites within the Bradan catchment were instrumented to monitor soil hydrological conditions and collect soil water samples. The location of these sites was of vital importance, and reflected the following criteria:

1. Sites must be in a sub-catchment from which Mn is known to originate;
2. Sites must allow comparison between major soil types in the Bradan catchment;
3. Sites must allow comparison between principal land uses in the Bradan catchment.

The following sections detail the considerations involved in selecting a sub-catchment of Loch Bradan in which to install the field monitoring sites.

3.2.1 Existing stream water Mn data

The use of existing stream water data for the Bradan catchment assumes that any stream containing large concentrations of Mn should be draining an area where Mn concentrations in soil water are equally great. WoSW provided limited data, based upon random sampling between May 1995 and May 1998, for Mn concentrations in the six main feeder streams (see Figure 3.5) supplying Loch Bradan. The results (Figure 3.6) indicate that Ballochbeatties Burn and the Dhu Loch Strand contained water with considerably greater Mn concentrations than the other four feeder streams.

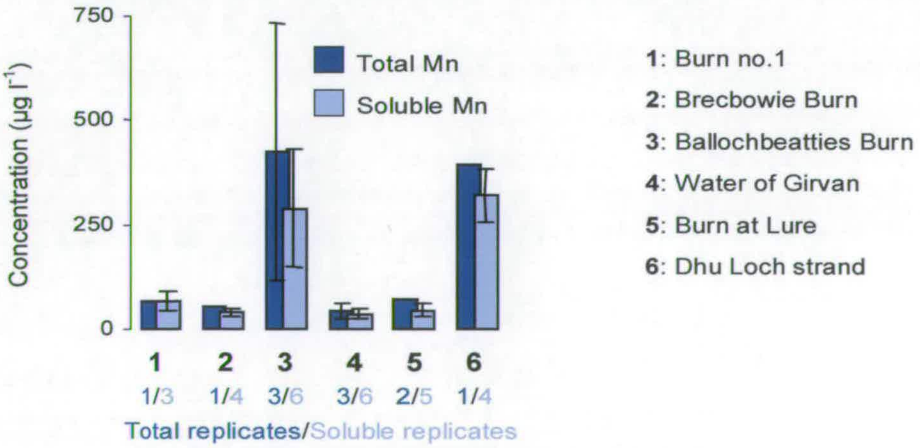


Figure 3.6: Mn concentrations in Bradan feeder streams

(Standard errors shown where data permitted)

3.2.2 Soil type and land use

The preliminary stream water chemistry data indicated that water originating from the catchments of Ballochbeatties Burn and the Dhu Loch Strand contained the greatest Mn concentrations. A site reconnaissance was undertaken in December 1998 to determine the soil types and land use surrounding the reservoir, and in particular, within these two catchments. The aim was to identify a feeder stream catchment containing a variety of soils and land uses, thereby allowing analysis of the effect soil type and land use interactions had on Mn mobilisation. Furthermore, data from a range of soil types and land uses commonly found in the UK uplands would enhance the applicability of the research work to other upland catchments.

The Dhu Loch Strand was found to drain an area predominantly composed of deep peat, while soils around Ballochbeatties Burn comprised deep peat and organo-mineral soils. Land use surrounding the Dhu Loch Strand was mainly forestry, with a small area of open moorland in the upper reaches, and an expanse of bog adjacent to the reservoir. The catchment of Ballochbeatties Burn, however, reflected the approximately equal split between forestry and moorland throughout the entire Bradan catchment.

3.3 Location and characteristics of field monitoring sites

Following examination of the data outlined above, the decision was taken to install field monitoring sites within the catchment of Ballochbeatties Burn. Not only did this place the soil water sampling sites in the catchment of a stream known to contain high Mn concentrations, but it also allowed comparisons of Mn concentrations in soil water between a number of different soil types and land uses. In addition to this, the Ballochbeatties Burn catchment was more easily accessible from the nearby road than the catchments of the other feeder streams. Therefore, the time spent moving to and from sample sites was minimised and difficulties with installing bulky equipment in remote areas were largely avoided.

The catchment of Ballochbeatties Burn covers an area of approximately 0.84 km^2 to the south of Loch Bradan. The stream rises in open moorland, at an altitude of approximately 480 m above ordnance datum, and enters Loch Bradan at the tip of the distinctive inlet on the southern side of the reservoir. Land use in the catchment is split between commercial forestry plantation and open moorland, with a small area of clear-felled land. Soils within the Ballochbeatties Burn catchment consist mainly of peaty podzols, peaty gleys and peat on the moderate slopes, while there is a large expanse of peat on the flat ground near the reservoir.

Field monitoring equipment was initially installed at six sites within the catchment of Ballochbeatties Burn on the south side of Loch Bradan (Figure 3.7) during March and April 1999. The sample sites were carefully chosen to represent both the major types of land use present (i.e. forestry and moorland) as well as enabling comparison between soil types within the moorland (Table 3.1). Although the initial intention had been to instrument a range of forest soil profiles similar to those in the moorland, this proved impossible, as the soils underlying the Sitka spruce plantation were dominated by deep peat. Where areas of peaty gley and peaty podzol soil were identified within the forest, there was evidence of large-scale damage to trees by wind-throw. This meant that there was considerable disturbance of the soil hydrological pathways at such sites, as well as a risk of damage to equipment installed there should any further wind-throw occur. In addition to this, forested areas of organo-mineral soils were usually planted with species other than Sitka spruce thereby negating any vegetation comparisons.

Land Use	Grid Reference	Altitude (m)	Site Number	Soil Type
Forest	NX4120095700	338	F1	Peat
	NX4119695704	338	F2	Peat
	NX4119295703	338	F3	Peat
Moorland	NX4140095300	390	M1	Peat
	NX4139595299	392	M2	Peaty gley
	NX4140095285	394	M3	Peaty podzol

Table 3.1: Field monitoring sample site characteristics

The three moorland sites (Figure 3.8) were located in a toposequence of soils on a north-facing slope of approximately 12°. Soil drainage became increasingly poor downhill, resulting in three different soil profiles developing over a relatively short distance. The three forest sites (Figure 3.9) were situated within Sitka spruce forest on a gentle 2° slope in an expanse of deep peat. As the forested area had been ploughed prior to planting, care was taken to install the instruments at forest sites on a surface with the least disturbance possible, in order to instrument a soil profile with a sequence of horizons typical of peat. Equipment installation at all six sites was completed by April 1999, and data were collected from then

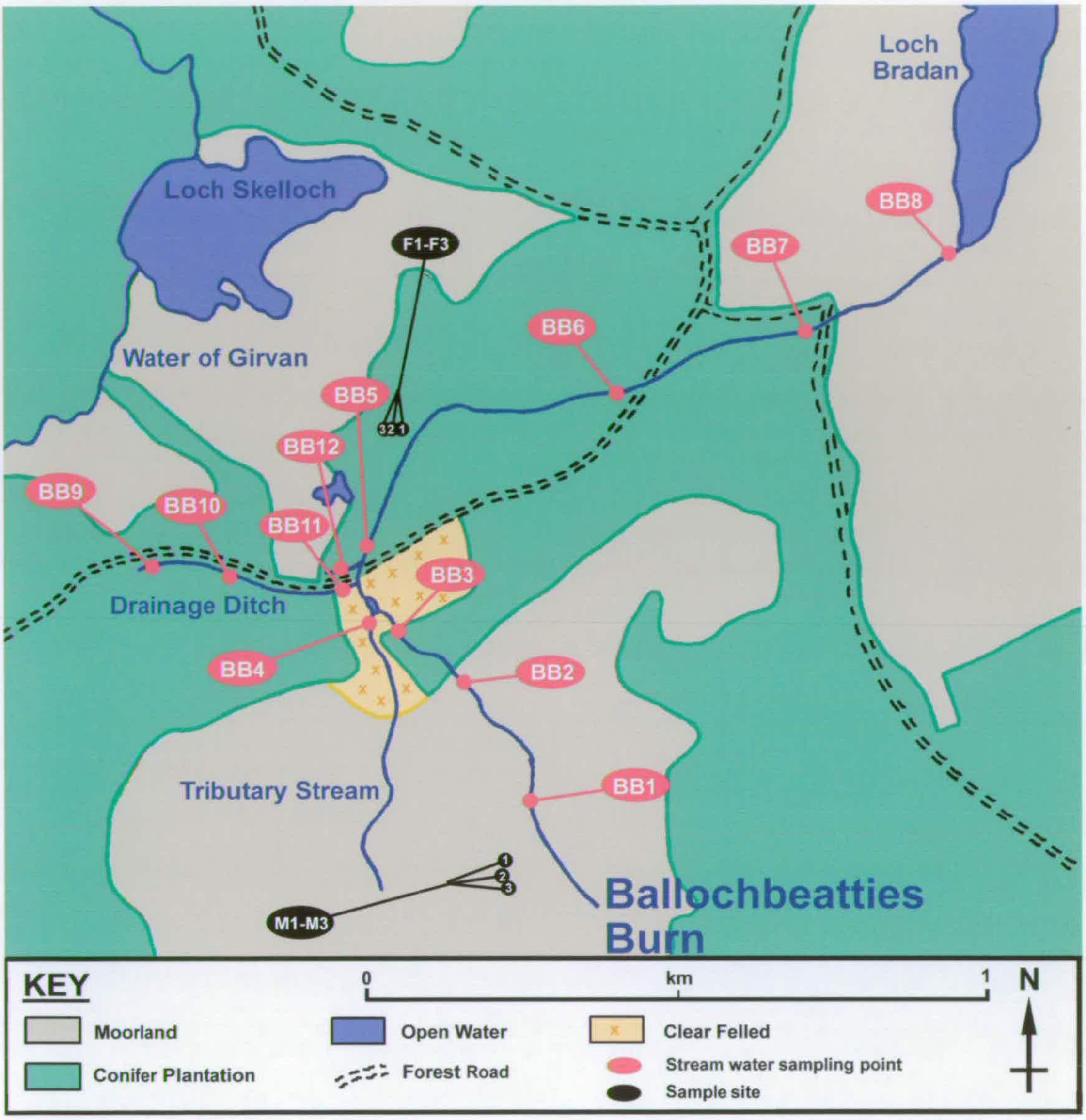


Figure 3.7: Location of sample sites and stream water sampling points within the Ballochbeatties Burn catchment

Figure 3.8: Moorland sample sites
(1=Peat; 2=Peaty gley; 3=Peaty podzol)

Figure 3.9: Forest sample site

until October 2000. This period of 18 months enabled the effect of drying conditions on soil water Mn concentrations to be investigated over two summers. A further three sites were partially instrumented in June 2000, based on the preliminary results of the field monitoring programme, and monitored for four months until the end of the field experiment. These secondary sites (described in section 3.6) served to extend the combination of soil types and land uses studied, in addition to sampling at locations identified as having high Mn concentrations in soil water (Law, 1999) after main site installation had occurred.

During the field monitoring programme, soil water samples were collected from each of the primary and secondary field sites. Volumetric water content and matric potential were also measured at the primary field sites. Stream water chemistry was monitored at 12 sampling points along the length of Ballochbeatties Burn and its associated tributaries (Figure 3.7).

3.4 Field equipment

This section describes the main types of equipment utilised during the project. The principles behind their usage, problems encountered and developmental history are all discussed. Further consideration is given to some of the similar techniques and equipment available, but not chosen for this work.

3.4.1 Suction probes

Suction probes, often also referred to as "porous ceramic cup samplers" or "tension lysimeters", are commonly employed in field studies to obtain samples of soil water *in situ*. The soil water chemistry data provided by samples obtained from suction probes installed at the study site formed a major component of this research. In all, a total of 63 suction probes were installed in the Ballochbeatties Burn catchment, representing a considerable effort both to install and sample.

3.4.1.1 Development and evolution

From their earliest appearance in scientific literature at the beginning of the 20th century (as "artificial roots"), suction probes have been used to collect samples of soil water from pre-defined depths. Following the pioneering work of Briggs and McCall (1904), Krone *et al.* (1951) further evaluated the use of ceramic cups in soil water samplers. However, it was to be a further decade before something recognisable as a "modern" suction probe appeared in the design proposed by Wagner (1962). Later workers (e.g., Bowman *et al.*, 2002; Knighton & Streblow, 1981; Wood, 1973) have suggested design modifications in order to improve aspects of reliability, ease of use, and sample contamination. Some of the more advanced designs employ remotely operated samplers with modifications to control both the amount of sample, and the rate at which it is collected (Litaor, 1988). Another alteration to suction probe design was proposed by Essert and Hopmans (1998), incorporating a suction probe and tensiometer into a single unit. Despite the many alterations and modifications to suction probe design, the probes used in this research are virtually identical to those constructed by Wagner almost 40 years ago.

3.4.1.2 Operation

Although not without their problems, suction probes are relatively cheap to construct and simple to operate. In addition to this, they offer a means of extracting soil water samples with minimal disturbance to soil profiles (Grossmann & Udluft, 1991). As they can be installed at a designated depth (i.e. within a particular soil horizon), their use is ideally suited to studies where the soils involved are heterogeneous.

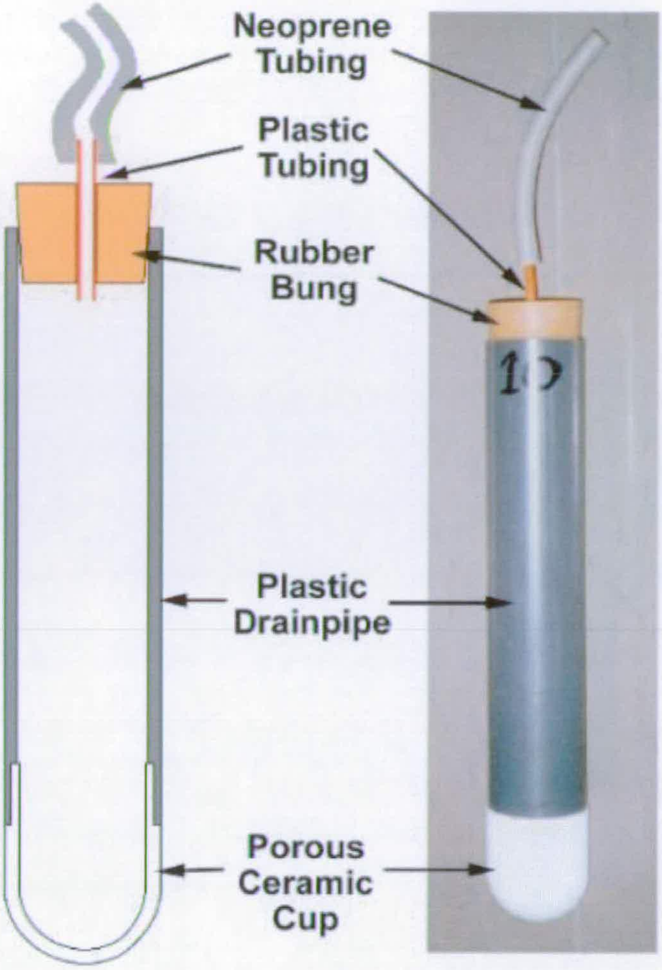
The basic principle behind the use of suction probes is the application of a negative pressure to a sealed container, attached to a porous ceramic cup buried in the soil (Figure 3.10). Simple physical laws dictate that water in the soil surrounding the cup will flow into the container for as long as the negative pressure in the suction probe exceeds the adjacent soil moisture potential (Hansen & Harris, 1975). Once collected in the suction probe, the sample can be removed using a variety of methods. These range in complexity from simply using a syringe with a length of tubing, to extensively modified suction probes containing a series of valves allowing pressurised gas to lift the sample to the surface (Wood, 1973). The evacuation method used by this research is one of the less complex techniques and is described in section 3.8.1.

3.4.1.3 Problems encountered

Given the widespread use of suction probes, it is perhaps not surprising that limitations associated with their use are well documented. Therefore, any research using suction probes requires careful design in order to reduce potential sources of error.

Representativeness of samples

Doubts exist as to how representative of the soil solution samples obtained using suction probes are. This is because soil water can exhibit large chemical differences over very small distances (Starr, 1985), and suction probes may not accurately reflect such spatial variability,



The suction probe shown in the photograph is one of the 'shallow' probes and has a 30 cm length of drainpipe attached. 'Intermediate' and 'deep' probes were constructed with 60 and 100 cm lengths of drainpipe respectively.

Figure 3.10: Design of suction probes used in this research

owing to the relatively small volume of soil from which they extract water (Barbee & Brown, 1986; England, 1974). Therefore, for example, any sampler installed next to an abnormally high source of Mn will provide samples of soil water containing far more Mn than in bulk soil water. Inaccuracies of this sort can be countered by replication, which may help smooth the variability by effectively increasing the sample volume. Further doubts over sample representativeness concern the actual source of water collected in the suction probes. The suction created in the probes can drain different sized pores, depending upon distance from the probe, the vacuum applied, the hydraulic conductivity and the soil water content (England, 1974). Therefore, because the chemistry of soil solution can vary within different sized pores (Hansen & Harris, 1975), preferential sampling of particular pore sizes will mean that the sample ionic concentration is statistically biased.

Volume sampled

The volume of soil sampled by suction probes is of vital importance when considering solute concentration throughout the soil as a whole. Studies where pedology is of importance require that samples are collected from specific soil horizons and therefore need to know the volume from which a buried probe will draw water. However, it is extremely difficult to calculate the exact zone of influence for any one suction probe, owing to the complex and changing variables involved. Warrick and Amoozegar-Fard (1977) managed to accomplish this for suction probes held at a continuous vacuum. Unfortunately, this is not a realistic assumption for most probes, as their internal vacuum falls during sample collection. When the problem was eventually solved for suction probes with a transient vacuum, their region of influence was found to be a function of probe volume (Narasimhan & Dreiss, 1986). Therefore, suction probes with a large diameter and internal volume are preferable, as they are able to sample a greater (i.e. more representative) volume of soil. However, this may not be an advantage when the suction probes are installed within a relatively thin soil horizon, as the zone of influence surrounding the ceramic cup may extend into adjacent horizons. This was one factor taken into consideration when choosing the horizons to sample within the field monitoring programme of this research. Where possible, suction probes were installed in those horizons with sufficient thickness and which satisfied the criteria of sampling the main soil horizons.

The zone of influence around a porous ceramic cup is not spherical, but deformed by the effect of gravity. Soil water from above the porous ceramic cup is drawn into the sampler under a pressure gradient defined by the sum of probe suction and gravity. Below the cup, however, this gradient is defined by the difference of probe suction and gravity. It is therefore ‘easier’ to pull water downwards from above the cup, rather than upwards from below it, so the region of influence will extend further above a porous ceramic cup than below.

Another factor affecting the zone of influence surrounding a suction probe’s porous ceramic cup is the soil water regime during the period of sample collection. As soil dries, matric potential surrounding the ceramic cup increases and so the size of the pressure gradient, along which water flows into the suction probe, decreases. Therefore, less water can be drawn into the suction probe as the soil dries and the zone of influence surrounding the ceramic cup will decrease in size. Soil hydraulic conductivity will also affect the size and shape of the area sampled. If greater hydraulic conductivity exists in any direction around a ceramic cup (i.e. anisotropic conditions), then the majority of soil water collected will come from this area. Furthermore, for probes with a falling vacuum, the source region for any sample collected will be smaller than the region of influence described by deformation of soil water. This is because, although water at the edge of the region of influence is drawn towards the suction probe, it never actually reaches the ceramic cup prior to the cessation of suction (Wu *et al.*, 1995).

An approximate maximum zone of influence was calculated retrospectively for each of the three depths of suction probe installed in the Ballochbeatties Burn catchment, based upon the volume of water they collected under saturated conditions. When the mean volume of water collected was combined with volumetric water content for a particular soil horizon, using equation 3.1, the volume of soil sampled to provide that amount of water was obtained.

$$\text{Vol. of soil sampled (cm}^3\text{)} = \text{Vol. of water collected (ml)} \times \frac{1}{\theta_V}(\text{m}^3\text{m}^{-3}) \qquad \textbf{Equation 3.1}$$

(Where θ_V is volumetric water content)

This procedure allowed the maximum zone of influence for suction probes in each horizon of the primary field sites to be estimated. The lack of volumetric water content data meant that zones of influence were not calculated for the suction probes installed at the secondary field sites. The estimated zone of influence, in conjunction with observations made during probe removal, was then used to identify any cases where sampling had potentially extended over more than one horizon. It was of vital importance to know if such cases existed, as anomalies in soil water chemistry from these points may have arisen due to the sample originating in a different horizon. Of the 54 suction probes installed at primary field sites in the Ballochbeatties Burn catchment, 12 were identified as potentially sampling soil water from more than one horizon. Nine of these were installed in the shallow (O2) horizon of the three forest sites, where the boundary with the intermediate (O3) horizon was adjudged to lie within the estimated zone of suction probe influence. The other three probes were all installed within the relatively thin intermediate (Eh) horizon of the peaty podzol at the third moorland site. In this case, the zone of influence for the suction probes was estimated to extend marginally into the O and Bh horizons above and below the Eh horizon. However, it should be noted that the bulk of the soil water collected in these 12 probes originated in the desired 'target' horizon and any water drawn from outwith this horizon would only represent a small percentage of the total volume. In addition to this, soil water originating from other soil horizons would still have been exposed to conditions within the 'target' horizon during its movement into the suction probe. Therefore, in the 12 cases where suction probe zones of influence were estimated to sample additional soil horizons, the effect on the representativeness of soil water samples may not have been as great as initially feared.

Bypass flow

Because of the relatively small volume of soil sampled, suction probes are at risk of being bypassed by flow through large diameter macropores, unless the flow is physically intercepted (Barbee & Brown, 1986). For this reason, suction probes installed in well-structured soils generally do not extract a representative solution of the mobile water phase (Hatch *et al.*, 1997). The residence time of soil water in macropores is generally shorter than in smaller pores and the surface to volume ratio far smaller. Therefore, there is less time for soil water chemistry to reach equilibrium with ions in the soil, and contact between soil particle surface and water occurs over a smaller area. The limited equilibrium time and lack of exchange sites, in comparison to smaller pores, mean that soil water from macropores may contain lower concentrations of dissolved metal ions. The extent of macropore flow in the soils surrounding Loch Bradan is unknown. However, profile pits dug at each field site failed to provide any evidence of large macropores in the soils studied.

Leaching of contaminants

According to Debyle *et al.* (1988), large quantities of cation impurities can leach into solution from porous ceramic cups. These cations, principally calcium and magnesium ions released from salts forming the ceramic cup, tend to be released in acidic conditions. In order to counteract this problem, it is recommended that ceramic cups are treated with a solution of hydrochloric acid prior to installation in the soil (i.e. to induce leaching of cations in the laboratory) and then cleaned with distilled water. Different cleaning techniques have been put forward, with the concentration of acid involved ranging from 0.001M (Hughes & Reynolds, 1988) to 8M (Wood, 1973). The ceramic cups used in this study were cleaned in accordance with the method suggested by Grover and Lamborn (1979), and subsequently recommended by Creasey and Dreiss (1988), using 1M hydrochloric acid. Treatment involved securing the suction probes (minus rubber bungs) upright above a basin and then filling them with one litre of the acid solution. Gravity caused the hydrochloric acid in the suction probes to flow through the ceramic cup pores and into the basin, removing any leachable cations. Following acid treatment, the cups were flushed with several litres of distilled water until the pH of water passing through them was close to neutral (details in Appendix D). One potential problem associated with acid cleaning is that it is thought to adversely affect ceramic cup pore size and to increase the potential for cation adsorption on cup surfaces (Hughes & Reynolds, 1988).

Adsorption of cations

The ability of ceramic cups to adsorb cations from soil solution has been noted by various sources (England, 1974; Hansen & Harris, 1975). Negatively-charged sites within the ceramic cup matrix retain positively charged ions in the soil solution as it passes through the cup pores. Unfortunately, the acid cleaning process, recommended to reduce sample contamination by leaching of cup constituents, actually increases the cation exchange capacity of the ceramic cup (McGuire *et al.*, 1992). However, adsorption should not be a problem when large volumes of soil solution are collected, as the cation exchange capacity of the ceramic cups will be fulfilled by the first few millilitres of water collected (Wood, 1974), leaving the rest of the sample unaffected. Studies have attempted to avoid this problem by allowing suction probes to 'acclimatise' in the field by discarding those samples collected immediately after installation. Hornung *et al.* (1986) and Grieve (1990b) both allowed a period of three months after installation before samples collected were analysed. Time constraints meant that samples collected from suction probes in this study were only discarded for one month after installation. However, in practice this resulted in two complete fillings of the apparatus, which was considered sufficient to remove any effects associated with the cups' cation exchange capacity. In addition to this, Mn is thought to be one of the cations least affected by adsorption (Grossmann & Udluft, 1991), while the use of suction probes with larger diameters may also reduce the effects of both leaching and adsorption (Silkworth & Grigal, 1981).

In order to test the adsorption of Mn ions by the ceramic cups used in this study, suction probes were placed in solutions of known Mn concentration, then the concentration of samples collected measured. After equipment removal from the field sites, five suction probes were randomly selected and cleaned by drawing a volume of at least two litres of distilled water into them. These probes were then used to sample standard Mn solutions of between 5 $\mu g\ l^{-1}$ and 500 $\mu g\ l^{-1}$. The solution collected during the first two fillings of the suction probe was discarded, in order to allow equilibrium to be reached at the cation exchange sites, and samples for analysis were taken from solution collected during the third filling. When analysed, samples collected from the 5 $\mu g\ l^{-1}$ standard solution contained no Mn, while those collected from the 500 $\mu g\ l^{-1}$ standard solution contained a range of concentrations from 0 to ~300$\mu g\ l^{-1}$. The most obvious explanation for the lower sample concentrations is that the ceramic cup cation exchange sites were still retaining Mn ions. The extent to which this occurred in the field is unknown. However, the presence of other cations (particularly H^+) in the soil solution would help satisfy the ceramic cups cation exchange capacity, thereby ensuring less Mn was adsorbed. Furthermore, once the suction probes attained equilibrium with the soil solution, the effect of adsorption would be negated.

Initial vacuum

The choice of initial vacuum applied to suction probes can alter the volume of sample collected and the initial rate of sample collection, although not as much as cup radius and internal sampler volume. According to Morrison and Lowery (1990), using a constant vacuum will, in general, provide samples 1.65 times the size of those collected using the same initial transient vacuum. At smaller vacuums, sample size and concentration may not be so dependent on the magnitude of initial vacuum applied. Studies have indicated that initial vacuums between -25 to -45 kPa have little effect on the volume of extracted water (Wu *et al.*, 1995), and that values of up to -40 kPa do not alter the concentration of solutes collected (Beier & Hansen, 1992). Differences in solute concentration sampled at greater vacuums may arise from the ability of the sampler to extract water from smaller diameter pores. Solution from these pores is known to have a different composition to that found in the larger pores, as the water has been in greater contact with the soil matrix over a longer period. The suction probes in this study were operated using an initial vacuum of -60 to -70 kPa similar to that used by Grieve (1990a) in similar soils within the nearby Loch Dee catchment.

Change in conditions

When water from the pores within a waterlogged soil horizon is drawn into a suction probe, it undergoes a sudden change in environmental conditions. Oxidation of redox species, such as Mn^{2+}, can occur as the solution is exposed to aerobic conditions in the probe after the anaerobic conditions prevailing in a waterlogged soil. Further complications can arise as a result of carbon dioxide degassing from water collecting in the suction probe, leading to an increase in sample pH (Litaor, 1988). Possible solutions to these problems often involve the use of an inert gas to flood the suction probe. However, the bulky equipment required and costs involved meant that these options were not practicable for this research.

Blocking of ceramic cup pores

Over time, it is possible for the ceramic cup pores to become blocked by particles of soil, organic matter and precipitates. Debyle *et al.* (1988) note that this phenomenon can seriously alter the intake rates of affected cups. Although cleaning with acid has been found to restore clogged ceramic cups, this is obviously not feasible while they remain *in situ* and can therefore only be undertaken between periods of field installation. The volumes collected by suction probes during the 18 months they were installed in the Ballochbeatties Burn catchment show no evidence of plugging, and remained relatively constant over the entire period (data presented in Appendix D). However, orange and black staining was discovered on the surface of several cups after their removal, indicating the precipitation of metal ions.

3.4.1.4 Alternative techniques

Suction probes are by no means the only method regularly employed to obtain soil moisture samples. Other techniques considered for use in this research included lysimeters, centrifugation, and guttering systems.

Lysimeters

A lysimeter consists of a hydrologically isolated block of undisturbed soil, complete with representative vegetation. Soil solution is normally collected by installing a porous ceramic plate, through which soil water can drain, at the base of the lysimeter. This allows soil solution draining through the profile under gravity to be collected for analysis. The main disadvantage with lysimeters is that they are both complex and expensive to construct and maintain (Shaw, 1994). Further disadvantages with the technique arise as a result of the disturbance to soil hydrological pathways caused by isolating the block of soil.

Centrifugation

In order to obtain soil water samples by centrifugation, samples of soil are placed in centrifuge containers and then spun at high speeds. Water is squeezed out of the soil pores as the soil is compacted and forced to the bottom of the centrifuge container, thereby allowing a soil water sample to be drawn off from the top of the tube. This technique may require the construction of specially adapted centrifuge tubes, or mixing samples with an immiscible solvent having a specific higher gravity than water prior to centrifugation (Reynolds, 1984). Sheppard *et al.* (1992) suggest that the centrifuge speed can affect the concentration of solutes collected, and should be carefully chosen for each particular ion analysed.

Law (1999) found that soil water obtained by centrifugation contains considerably more Mn than samples from the same soil horizon collected in suction probes on the same date (Figure 3.11). The work undertaken by Law, also located in the Ballochbeatties Burn catchment, collected soil water and soil samples from peat under three different land uses. The suction probes used and their mode of operation were identical to those used in this research (shown in Figure 3.10), while the centrifugation technique was similar to that described by Elkhatib *et al.* (1987). In order to extract a sample of soil water via centrifugation, 150 g of soil was placed in an unmodified centrifuge tube and spun at 13,000 rpm for 30 minutes. The resulting supernatant soil solution was transferred to a storage container until analysed. Mn concentration was determined in both centrifuged and suction probe soil water samples by inductively coupled plasma atomic emission spectrophotometry (ICP-AES).

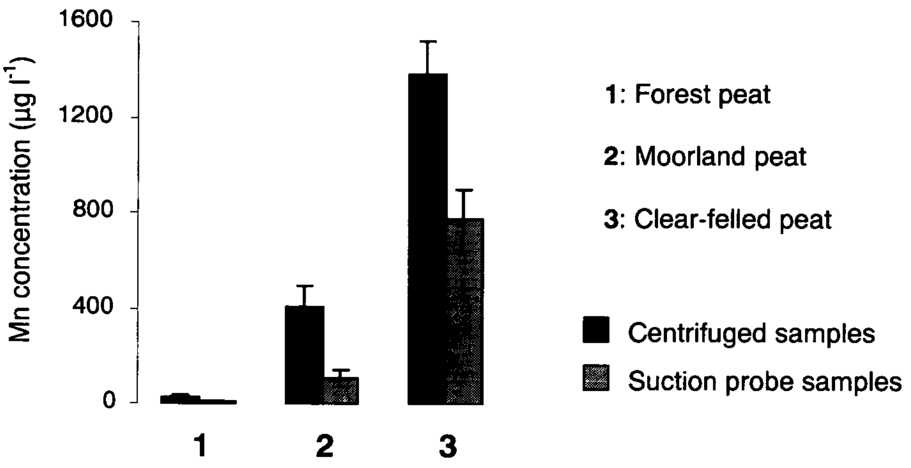


Figure 3.11: Comparison of Mn concentration (±SE) in soil water samples obtained by suction probes and centrifugation (data from Law, 1999)

This difference in Mn concentrations between techniques is thought to occur because centrifugation at high speed forces water out of smaller soil pores with different water chemistry, compared to those sampled by the suction probes, as well as having the potential to disturb solid phase Mn ions. One further serious drawback with centrifugation is that it is a destructive technique, and therefore makes it impossible to continuously monitor the same volume of soil.

Guttering

The use of guttering to collect soil samples involves installing a series of gutters in the wall of a soil pit, thus enabling flow through each soil horizon to be channelled into separate collection vessels. While this method may allow continued sampling of the same volume of soil, it can alter flow pathways within the soil and is impractical in the lower horizons of a waterlogged peaty soil, where the pit would rapidly become flooded.

3.4.2 Thetaprobes

There are several methods available for the electromagnetic determination of volumetric soil water content (θ_v), of which thetaprobes are a relatively recent addition. Although different, these techniques all measure water content indirectly by measuring the dielectric constant of the soil (ε). Because the dielectric constant of water is significantly greater than that of other soil constituents, the dielectric constant of soil depends primarily on the soil water content. Therefore measuring the dielectric constant of soil provides an accurate estimate of soil water content. A linear relationship has been found between the square root of the dielectric constant and the volumetric water content of soils (Equation 3.2) (Topp *et al.*, 1980), thereby allowing the calculation of soil volumetric water content if the dielectric constant is known.

$$\theta_v = \frac{\sqrt{\varepsilon} - a_0}{a_1} \qquad \textbf{Equation 3.2}$$

(Where a_0 and a_1 are constants depending on the particular soil type)

3.4.2.1 Development and operation

Thetaprobes were developed jointly by the Macaulay Land Use Research Institute in Aberdeen and Delta-T Devices, Cambridge. Each probe consists of a sensing head with four metal rods, a main body (housing an oscillator and transmission line) and an input/output cable (Figure 3.12). A simplified standing wave measurement is used to determine the impedance of a sensing rod array, which can then be related to the dielectric constant of the soil the probe is inserted into and thence its volumetric water content (Miller & Gaskin, 1998).

The four rods in the probe head are arranged so that they act in a similar manner to a section of transmission line, with an impedance dependent on the dielectric constant of the soil in which the rods are inserted. If the impedance of this external 'transmission line' is different

Figure 3.12: Thetaprobe

from that of a section within the probe main body, then a proportion of signal is reflected backwards, thus interfering with the incident signal. This produces a voltage standing wave along the length of the internal transmission line, the amplitude of which is related to the impedance of the probe (Miller & Gaskin, 1998). Therefore, the voltage standing wave created will change the voltage produced by the oscillator, the magnitude of alteration depending on the dielectric constant of the soil surrounding the probe rods. The thetaprobe measures the difference between the voltage at the oscillator and that reflected from the rods (Delta-T Devices, 1998). Conversion of this voltage difference (V) to dielectric constant (ε) is achieved using a third order polynomial equation (Equation 3.3).

$$\varepsilon = 1.07 + 6.4V - 6.4V^2 + 4.7V^3 \qquad \textbf{Equation 3.3}$$

Once connected to a suitable power source and datalogger, thetaprobes can be left *in situ* for long periods of time. Data from the logger can be retrieved at periodic intervals to provide a record of soil water content at the field sites.

3.4.2.2 Other systems

Capacitance probes

Capacitance probes essentially use moist soil as part of the dielectric of a capacitor (Smith & Mullins, 1991). The capacitance of the soil is measured and converted to a value for the dielectric constant. The system usually employs a probe, which is lowered down a specially designed tube inserted into the soil, thus allowing measurements to be taken at chosen depths. Capacitance probes are very sensitive to air gaps around the access tubes, therefore careful installation of the tube is vital to avoid problems (e.g., creation of air gaps by the displacement of stones when augering the hole to install the access tube). Soil shrinkage resulting from drying conditions may also create gaps around the access tube, and so capacitance probes may not accurately measure the volumetric water content during prolonged dry periods. This could be a particular problem in peaty soils, where the rate of shrinkage during drying is especially great. Due to the method of installation, water can enter the access tube at the base, thereby prohibiting the use of the probe in the flooded section. Given the nature of these problems, capacitance probes were considered unsuitable for use in the soils found in the Ballochbeatties Burn catchment.

Time domain reflectrometry (TDR)

TDR systems calculate the dielectric constant of soil by measuring the time taken for an electrical pulse to travel through a known distance of soil (Smith & Mullins, 1991). A high frequency electromagnetic pulse is passed into the soil between metal sensing rods. Part of the pulse is reflected back up through the soil from the bottom of the rods, and the time between incident and reflected pulses is used to calculate the dielectric constant. An access tube, similar to that of capacitance probes, was used in many older TDR systems, while systems are now available which use buried probes similar in design to thetaprobes. One major disadvantage with TDR systems was the need to interpret the trace produced by the electrical signal in the soil, which could prove difficult because of the extremely short timescale involved between the incident and reflected pulses. However, some newer systems are able to solve this problem by handling pulse interpretation internally.

3.4.2.3 Problems associated with electromagnetic techniques

One potential problem in attempting to determine soil water content by using electricity is the effect of solute concentration on the conductivity of water. Solutions with higher ionic concentrations will attenuate electrical signals and therefore affect the dielectric constant measured. Higher frequencies of electrical signal are less influenced by this, and thetaprobes use a signal of 100 MHz to minimise the effect (Delta-T Devices, 1998).

Care should be taken when installing probes as the presence of air pockets, stones, or plant roots adjacent to the metal rods will affect readings. This is because their dielectric constants are much smaller than that of water, altering probe readings and causing soil water content to be underestimated.

Soil spatial heterogeneity is also a problem, because of the relatively small volume of soil in which the dielectric constant is measured by any of the systems. For thetaprobes, the sensing volume approximates to a cylinder 60 mm long with a 60 mm diameter. Therefore, doubts exist over the representativeness of measurements from any single probe, especially when installed across a horizon boundary, as the different soil hydrological properties within the volume of soil measured will produce unrepresentative readings. Thetaprobes used at Loch Bradan were carefully installed in an attempt to limit the soil measured to a single horizon, although this could not be verified until the probes were excavated at the end of the study. Upon excavation, thetaprobe installation was found to have been generally successful, although air spaces were discovered around the sensing rods of one probe, the implications of which are discussed in section 4.1.2.1.

3.4.2.4 Recommendations for probe installation and use

When installing any device to measure volumetric water content, the surrounding soil should be disturbed as little as possible in order to avoid altering flow pathways within the soil. Vertical installation of thetaprobes should also be avoided, as this can result in the preferential flow of water down the probe body and subsequent ‘pooling’ around the metal sensing rods. Installation of the probes used in this study was accomplished by digging a soil pit and then inserting probes in horizontal auger holes made in the side of the pit, thereby allowing accurate placing of the thetaprobes within the desired soil horizon. Although digging a soil pit disturbed the soil profile, the sensing rods were all situated at least 20 cm upslope from the area of disturbed soil.

Finally, soil specific calibration is recommended in order to achieve the most accurate measurement of soil moisture content. For thetaprobes, calibration is thought to improve accuracy from ±5 % to ±2 % (Miller & Gaskin, 1996). To accomplish this, undisturbed soil cores were removed from the vicinity of each thetaprobe’s sensing rods once the monitoring programme was completed. These were transferred to the laboratory and used to calculate the constants given in equation 3.2, using the procedure described in Appendix D.

3.4.3 Tensiometers

Tensiometers were used to measure matric potential in the soil horizons studied in the Ballochbeatties Burn catchment. Matric potential is a measure of the force by which water is held in the soil pores, and is related to pore size. Therefore, as soil dries out, the large pores are likely to empty first leaving water in smaller pores. This results in the remaining moisture being more tightly held within the soil matrix, thereby producing an increased matric potential. Data from the 18 tensiometers installed at the field sites were intended to aid interpretation of the thetaprobe data and to characterise the field soil moisture retention characteristic for parameterisation of the soil water modelling program.

3.4.3.1 Development and operation

The first use of tensiometers to measure soil matric potential was recorded in the 1920s, but the name 'tensiometer' was not attributed to these devices until the next decade (Schmugge *et al.*, 1980). Since then, their design has remained virtually unchanged, the only major alterations being changes to the type of pressure gauge fitted and the advent of logging tensiometers.

A tensiometer consists of a liquid-filled tube with a porous ceramic cup at one end and a means of measuring pressure at the other (Figure 3.13). The tube connecting the ceramic cup to the pressure gauge can be of various lengths, depending upon the depth the tensiometer is required to be installed at. The liquid used is normally water, but an ethylene glycol-water mixture has been successfully used in colder regions to minimise frost damage.

The tensiometer shown in photograph is one of those installed in the 'shallow' horizons and has a 30 cm length of tube attached. 'Intermediate' and 'deep' tensiometers were constructed with 60 and 100 cm lengths of plastic tube respectively.

Figure 3.13: Design of tensiometers used in this research

Tensiometers are installed in a similar manner to suction probes, with the ceramic cup buried in the desired soil horizon. The ceramic cup is porous to water and solutes, but not air until pressures of -80 to -90 kPa are reached (Schmugge *et al.*, 1980). Therefore, under normal operating conditions, water can flow in or out of the tensiometer in response to matric potential changes in the surrounding soil. As the soil dries out, the increasing tension in soil pores is passed on through the tensiometer and can be read from the gauge at the surface. When soil dries out to such an extent that the matric potential exceeds the air entry value of the ceramic cup, the tensiometer fails. Failure resulting from air entry within the tensiometer occurs because any air bubbles will expand and contract with matric potential changes, thus dampening the pressure readings obtained. For this reason, it is of vital importance that the liquid used to fill the tensiometer is de-gassed.

3.4.3.2 Problems encountered

Because they consist of a water-filled tube, some of which is exposed at the surface, tensiometers are prone to the effects of water expanding or contracting with changes in temperature. Butcher *et al.* (1999) found that errors of this kind depend not on the length of tube protruding, but on the material the tubes are constructed of. Bypass flow down tubes was also found to be significant during periods of prolonged, heavy rainfall and the option of installing tensiometers horizontally was also suggested. In common with all soil monitoring equipment used in this study, soil heterogeneity can also cause problems, although matric potential is unlikely to vary on such small scales as soil water chemistry.

Readings from tensiometers installed at the field sites were not taken during extremes of rainfall or in high temperatures to minimise the effects of these conditions. However, problems were encountered with unseasonally cold temperatures causing the water in the tubes to freeze. Although the tensiometers were removed during the winter months, a period of freezing temperatures encountered during April 2000 after reinstallation damaged the pressure gauges and prevented further readings from being taken.

3.5 Field monitoring site instrumentation

At each site, nine suction probes, three thetaprobes, and three tensiometers were installed. The purpose of this equipment was to collect soil solution, record soil water content, and measure soil matric potential, respectively. This section discusses the methodology concerning selection of sampling depth and equipment installation.

3.5.1 Selection of sampling depth

The various monitoring instruments were all located at depths defined by pedology, rather than simply installing them at set depths. For each soil type studied, the three main soil horizons were selected for equipment installation, such that near-surface, subsoil and parent material horizons were instrumented at each site. A full listing of the horizons in which instruments were located is given in table 3.2. Locating the instruments according to pedology, rather than simply installing them at the same depths across all sites, allowed a better understanding of soil water chemistry and solute movement within and between soil horizons. However, to allow cross comparison between sites, these horizons will also be referred to as shallow, intermediate and deep. The suction probes were replicated within each horizon to account for spatial heterogeneity of soil water chemistry noted in other studies (Grieve, 1990b; Starr, 1985). One thetaprobe and one tensiometer were also installed in each of the horizons sampled by the suction probes. Therefore, at every site, the three most pedologically significant horizons were monitored, each containing three suction probes, one thetaprobe, and one tensiometer.

Sample Site		F1	F2	F3	M1	M2	M3
Shallow	Horizon	O2	O2	O2	O2	O2	O
	Depth	15	15	15	28	17	20
Intermediate	Horizon	O3	O3	O3	O2	Bg2	Bh
	Depth	33	25	26	47	45	30
Deep	Horizon	O3	O4	O4	O2	C(g)	Bs
	Depth	83	75	77	80	66	38

Table 3.2: Horizons sampled and approximate depths (cm) of instrumentation at primary sites

3.5.2 Description of soil profiles and instrument installation

At each field site, a soil pit was dug and the soil profile recorded (full descriptions of soil profiles are contained in Appendix C). The extent of the soil horizons listed in table 3.2 was noted and used as a guide for the approximate depth to which instrumentation was to be installed.

Suction probes

The suction probes used in this research comprised a 63 mm outer diameter porous ceramic cup (van Walt Ltd., Surrey) glued to a length of similar diameter plastic piping with a rubber bung at the other end. A hole was drilled in the centre of each rubber bung, through which a length of plastic tubing was inserted, allowing connection to a hand-held vacuum pump for creating a negative pressure inside the suction probe. Installation with minimal disturbance to the soil profile was achieved by augering a hole vertically down from the surface to the desired depth and then inserting the probe. Spoil removed during the course of augering allowed identification of each horizon in turn and therefore aided equipment installation. In mineral horizons, the fit of the ceramic cup at the base of the hole was enhanced by placing loose spoil, freshly removed from the appropriate horizon, in the hole before probe insertion. This technique was not required in the peat horizons, where the amorphous mass of organic material formed a close fit around the ceramic cup.

Tensiometers

Tensiometers installed in the Ballochbeatties Burn catchment were supplied by Soil Monitoring Engineering, Milton Keynes. They were constructed of a 25 mm porous ceramic cup attached to a similar diameter length of clear plastic tubing, with a pressure gauge attached to the top of the tubing to enable reading of soil matric potential surrounding the ceramic cup. The installation process for the tensiometers was identical to that used for the suction probes.

Thetaprobes

The pit that was dug to describe the soil profile at each site was used to install the thetaprobes, supplied by Delta-T devices, Cambridge. A screw auger was used to create horizontal holes in the side of the profile pit within the required horizons and of a slightly smaller diameter than the thetaprobe body. Thetaprobes were then carefully pushed into these holes until their sensing rods were judged to be buried in the relatively undisturbed soil at the far end. Finally, the input/output cables from the probes were connected to a datalogger and the pits back-filled with care being taken to replace soil at the appropriate depth and bulk density.

3.5.3 Instrument removal

Following completion of the field monitoring programme in October 2000, all equipment installed in the Ballochbeatties Burn catchment was removed and the sites returned to the state they were in prior to installation. As each piece of equipment was removed, a visual confirmation of the horizon sampled was made in order to identify any devices sampling multiple or incorrect horizons.

3.6 Secondary sample sites

Following a review of field results at the end of 1999, it was decided to instrument a further three sites within the Ballochbeatties Burn catchment. The decision was based on the fact that Mn concentrations in soil solution from the existing sites were lower than expected, often approaching the limits of analytical detection, and showed none of the expected seasonality. In addition to this, Mn concentrations found in stream water samples during the same period were often an order of magnitude greater than those in soil water samples. Therefore the indication was that other Mn sources existed within the Ballochbeatties Burn catchment, outwith the area sampled by the primary field sites.

One possible explanation for the very low Mn concentrations measured in soil water is that the spatial heterogeneity of soil chemical properties, coupled to the relatively small zone of soil water sampled, meant that the sites were simply missing any areas within the soil containing large concentrations of Mn. It was also felt that the expected seasonal aspect of Mn release into soil solution would be easier to identify if the concentrations in samples were greater. Therefore, three secondary soil water sampling sites (Table 3.3) were selected in the Ballochbeatties Burn catchment in an effort to locate additional sources of Mn not covered by the original sites. These secondary sites were situated in locations where high concentrations of Mn in soil water had been identified by an undergraduate research project (Law, 1999).

Land Use	Grid Reference	Altitude (m)	Site Number	Soil Type
Moorland	NX4140095305	386	M4	Peat alluvium
Forest ride	NX4112595550	342	F4	Peaty gley
Clear-felled	NX4125095540	342	CF	Peat alluvium

Table 3.3: Secondary sample site characteristics

The first site (M4) was located in a wet flush adjacent to Ballochbeatties Burn at the base of the same slope occupied by the existing moorland sites, thereby extending the toposequence of soils studied. The site had been considered during original site selection, but discounted on the grounds that the area appeared prone to flooding and soil water regime was unlikely to deviate from waterlogged even under dry conditions. A full description of the profile at this site was prohibited by the waterlogged conditions, although a peat core taken from it allowed classification of the soil as deep peat interstratified with alluvial material.

Vegetation cover at this site was almost entirely *Molinia caerulea*, forming large tussocks that gave the area a very uneven surface.

A further forest site (F4) was installed at the edge of the forest, to the south of the drainage ditch shown in Figure 3.7. This location was chosen because of the high Mn concentrations measured in water from the ditch collecting water from the area. Lack of suitable sites inside the forest meant that equipment was installed within 2 m of the Sitka spruce plantation, in a forest ride dominated by *Molinia caerulea*. The soil type was identified as a peaty gley (full profile description in Appendix C), thus allowing some comparison of soil water chemistry to be made between this site and the moorland peaty gley site.

The final secondary site sampled soil solution from the clear-felled area (CF) within the Ballochbeatties Burn catchment. Initially, the decision was taken not to place sample sites in the clear-felled land, as the soil had been heavily disturbed during the harvesting process. However, Law (1999) found that soil water samples from this area contained the greatest concentrations of Mn recorded in the Ballochbeatties Burn catchment. Equipment at this site was installed in the remains of a plantation ridge, as this was thought to provide the least disturbed profile. Prior to clear-felling, the area was covered by Sitka spruce plantation, the remains of which were visible as large amounts of decaying 'brash' nearby. However, the vegetation cover present throughout the field monitoring programme was mainly tussock-grass pasture dominated by *Deschampsia cespitosa*. The soil at this site was a deep peat containing alluvial material, similar to the secondary moorland site (full profile description in Appendix C).

Considerations over the time available for sample collection on each visit, the limited time available for monitoring and equipment availability meant that only three suction probes were installed at each of these sites, rather than the nine present in the primary sites. The probes were located in the same manner as the primary sites, with three horizons in each profile being studied (Table 3.4). Lack of equipment also prevented the use of any thetaprobes or tensiometers at these sites, so data concerning soil water regime was unavailable. However, the soil water chemistry data obtained, plus the different combinations of land use and soil type encountered, would complement data from the primary sites.

Sample Site		M4	F4	CF
Shallow	Horizon	01	O	01
	Depth	22	18	25
Intermediate	Horizon	02	Bg	02
	Depth	42	30	42
Deep	Horizon	02	Cg	03
	Depth	102	50	72

Table 3.4: Horizons sampled and approximate depths (cm) of instrumentation at secondary sites

3.7 Supplementary data

The principal data collected during the field monitoring programme came from the equipment installed at the field monitoring sites and from the stream water sampling points along the length of Ballochbeatties Burn. However, in addition to this, samples of plant litter, rainfall and throughfall were also collected during the monitoring period in order to investigate other aspects of Mn biogeochemistry within the catchment.

3.7.1 Litter collection

Litterfall from the three main types of vegetation in the Ballochbeatties Burn catchment (Sitka spruce, *Calluna vulgaris* and *Molinia caerulea*) was collected by various means during the period of study. Individual samples were analysed for total Mn and iron (Fe) content by flame atomic absorption spectrophotometry (FAAS) following a nitric/sulphuric acid digestion (method in Appendix A.5) and then the mean metal content of litter collected during that period was calculated. When combined with the bulk mass of litter collected over the same time, it was possible to estimate Mn and Fe inputs to soils from litterfall.

3.7.1.1 Sitka spruce litter

Litterfall from Sitka spruce was caught in nine litter traps, installed near the forest sample sites, over a 13-month period from September 1999 to October 2000. Litter traps were constructed of permeable cloth to allow precipitation to drain away and held in shape by a cane skeleton, forming an aperture with a surface area of 0.25 m^2 (50 cm x 50 cm) (Figure 3.14). Beneath this, the cloth was gathered together by a drawstring to form an inverted pyramid shape in which litter collected. Sample collection was achieved by releasing the drawstring and brushing the accumulated litter from the trap's base into a plastic sample bag. When possible, these litter traps were emptied on a monthly basis.

According to McShane *et al.* (1983), the dimensions of litter traps can affect the precision of forest litterfall estimates. The aperture dimensions of the litter traps used in this study were limited by available space between the closely planted conifers. However, the 0.25 m^2 surface area falls within the range of sizes used in other studies of Sitka spruce litterfall (Adams *et al.*, 1980; Hurd, 1971). The tops of the litter samplers were positioned 1 m above the ground, by mounting them on wooden stakes, in order to prevent litter on the ground from being blown into the samplers. Although the litter collected contained different parts of the trees, no attempt was made to differentiate between the constituent parts and figures reported represent a bulk analysis.

3.7.1.2 *Calluna* litter

Litter traps modified from a design described by Newbould (1967) were used to collect litterfall from the moorland *Calluna vulgaris* plants. The traps consisted of a 25 cm x 25 cm wooden frame (10 cm in height), across the base of which a plastic mesh was placed (Figure 3.15). Nine of these trays were placed under heather plants near the moorland sites from October 1999 to October 2000. Sample collection was carried out on an approximately monthly basis and achieved by lifting the trays and brushing accumulated litter into a plastic sample bag.

Figure 3.14: Forest litter trap

Figure 3.15: Moorland litter trap

3.7.1.3 *Molinia* litter

Collection of *Molinia* litter was accomplished by a different technique. At the end of 1999, nine sample plots, each 25 cm x 25 cm, were marked out in an area dominated by *Molinia* tussocks near the moorland sample sites and all dead grass removed from them. These plots were then 'harvested' in October 2000 by simply removing by hand the dead leaves that had accumulated as a result of that year's growth. Removal of the leaves in this manner was easily accomplished, as they naturally detached at the abscission point. Once collected, the dead leaves were sealed in plastic bags and transported to Edinburgh for analysis.

3.7.2 Rainfall chemistry

Metal content in rainfall was monitored on a monthly basis at two locations during the period of March to October 2000. One site was near the moorland sample sites, while the other was in the middle of a forest ride close to the forest sites. Bulk rainwater was collected in plastic bottles contained within standard Meteorological Office 15 cm diameter storage rain gauges, installed so that their rim was 30 cm from the ground surface. Samples of the collected rainwater were transferred to plastic vials for transport to WoSW laboratories for analysis of pH, colour, and total Mn and Fe content.

3.7.3 Throughfall chemistry

Samples of throughfall in the forest were obtained from another Edinburgh University research project located in the Ballochbeatties Burn catchment. The throughfall was collected in plastic guttering installed beneath the tree canopy, and samples were analysed for total Mn and Fe content in Edinburgh using graphite furnace atomic absorption spectrophotometry (GFAAS).

3.8 Data collection and analysis

Data were usually collected from field sites on a monthly basis from April 1999 until October 2000. On each sampling visit, suction probes were emptied and the vacuum reapplied, tensiometer readings recorded, data downloaded from loggers attached to the thetaprobes and stream water samples collected. The frequency of sampling visit increased to fortnightly during late summer and early autumn, to provide better temporal resolution of data at times of year associated with the changes in soil water regime thought to result in Mn mobilisation.

3.8.1 Suction probe sample collection

Evacuation of suction probes was accomplished using apparatus based on the equipment described by Wagner (1962). This consisted of a chemically inert low density polyethylene bottle, sealed with a rubber bung in which two holes were drilled and fitted with lengths of plastic tubing. The first tube was attached to a length of neoprene tubing that could be lowered into the suction probe, while the second was connected to a hand-held manual vacuum pump. Water could be quickly and easily drawn up out of the suction probe by creating a vacuum in the plastic bottle. In order to avoid contamination, the first few 100 ml of sample from each suction probe was used to rinse the equipment and then discarded. The total volume of water evacuated from each probe was recorded in order to monitor probe performance (as discussed in section 3.4.1.3) over the duration of the field monitoring programme.

Once the water had been evacuated from a suction probe into the bottle, three aliquots were transferred to labelled 60 ml plastic vials (Merck). The water sample in one vial was used for pH and colour determination, while the other two were analysed for metal content. The sample in one of the metals vials was filtered in the field using a 0.45μm syringe filter in order to remove particulate and colloidal Mn. The solution in this vial was used to determine "soluble" metals, while the other unfiltered sample was used to determine "total" metal content. Sample blanks were also run on a random basis using deionised water and in addition to this, tap water taken from a house supplied with water from Bradan treatment works was included as a random sample.

At the end of each sampling visit, samples were delivered to WoSW laboratories in Glasgow for analysis. Determination of pH and colour was carried out within 48 hours of sample collection, while samples for metals analysis were stored in the dark at low temperature until analysis could be carried out (usually within 1-2 weeks of collection). Metals analysis was undertaken using ICP-AES to provide the total and soluble concentrations of Mn, Fe and aluminium (Al) in samples. Descriptions of the analysis procedures are contained in Appendix A.8.

3.8.2 Downloading thetaprobe data

Thetaprobes at each grouping of three primary field sites (i.e. forest and moorland) were connected to a Campbell CR10x datalogger stored within a protective housing. Volumetric water content measured by the thetaprobes was recorded every hour and stored in the datalogger until retrieval during each sampling visit. Data retrieval and logger programming was accomplished using a Campbell MCR 1 memory card reader to transfer data between a 256 kb SRAM data card and the datalogger. Once back in the laboratory, the data was transferred from memory card to a computer spreadsheet for analysis.

3.8.3 Tensiometer reading

Pressure gauges on the 18 tensiometers installed were read on each sampling visit and the readings entered into a computer spreadsheet on return to Edinburgh. Unfortunately, owing to problems encountered with gauge reliability at low temperatures, data was only collected during the period April to November 1999.

3.8.4 Stream water chemistry

In addition to soil water chemistry and soil moisture content, measurements of stream water chemistry and discharge were also made in the study catchment. Stream water was sampled from a total of 12 points along the length of Ballochbeatties Burn and its tributaries on each visit. Seven sampling points were located in the main stream channel, while one was in the only natural tributary to the main burn. A further four points were in forest drainage ditches which carried water from the afforested western part of the catchment (see Figure 3.7).

Samples of stream water were collected by submerging one litre plastic bottles (supplied by WoSW) in the centre of the channel and allowing them to fill, after rinsing three times with the stream water to minimise sample contamination from the container. Two bottles were filled at each site, one for determination of pH and colour, and the other for analysis of metals. The analysis of stream water samples was carried out by WoSW, using the same techniques as the analysis of soil water samples. Filtration of the metals samples, using 0.45 µm filters, was also undertaken in the WoSW laboratory to allow the distinction between total and soluble content to be made.

3.8.5 Soil properties

Soil samples were taken in March 1999 from each horizon of the profiles excavated during installation of the field monitoring equipment. Total Mn and Fe were determined by FAAS in Edinburgh following a nitric/hydrochloric acid digestion (method in Appendix A.4). Systematic soil analyses were also undertaken by the Macaulay Land Use Research Institute. Results of the soil analyses are discussed in Chapter 4 and full descriptions of the soil profiles are given in Appendix C.

3.9 Summary of data collected

When the fieldwork phase of the research was completed, a large amount of data had been collected covering various aspects of Mn behaviour and soil hydrology. The intended applications of these data are outlined below.

3.9.1 Soil water chemistry

The measurements of soil water chemistry formed the bulk of the field research. These data were intended to determine if there was any seasonality to the Mn mobilisation identified in other studies, and to provide an indication of how this was influenced by pedology and soil water regime. The soil water samples were also analysed for Fe, Al, pH and colour to determine any association with Mn behaviour.

3.9.2 Soil hydrology

Volumetric water content and tensiometer readings were collected in order to establish if Mn mobilisation from particular soil horizons was due to changes in the soil water content within those horizons, particularly during the rewetting phase following a drying period. These data were also used to derive input data for a 1-dimensional process-based soil water simulation model (WAVE), which would be parameterised to predict the changes in soil water content in each horizon.

3.9.3 Stream water chemistry

The sampling sites along Ballochbeatties Burn provided a record of Mn inputs to the reservoir from the catchment during the study period and an indication of how closely soil water Mn concentrations were reflected in stream water. Changes in stream water chemistry could be linked to changes in soil water Mn content, and therefore indicate the relative importance of particular soil horizons in influencing reservoir water Mn concentration.

3.9.4 Mn inputs to soil

Measurement of Mn concentration in rainfall, throughfall and litterfall was undertaken to allow identification of whether any large-scale seasonal release of Mn in soil water could be explained by increased inputs from any of these sources. In addition to this, the data would be useful in helping to explain any differences in soil water Mn concentrations under different land uses.

3.9.5 Soil profiles and chemical properties

Full profile descriptions of the soil types studied in this research were used to aid the understanding of Mn behaviour within the catchment, in particular whether its potential release was associated with certain soil horizons. The chemical properties of each soil horizon were measured in order to determine if large pools of Mn existed within individual horizons and whether this was linked to Mn concentrations in soil water.

3.9.6 Data interpretation

The data collected from field monitoring sites within the Ballochbeatties Burn catchment were intended to allow interpretation of the effect soil water regime, soil type and land use had on Mn mobilisation in an upland catchment. Following completion of the field monitoring programme, data analysis was undertaken using graphical and statistical techniques, the results of which are detailed in Chapter 4.

Chapter 4: Field monitoring results

This chapter contains results and data analysis from the field monitoring programme in the Ballochbeatties Burn catchment. Analysis of samples collected from six primary field sites and the stream water chemistry sampling is discussed. Soil water chemistry of secondary field sites is then covered, followed by analysis of soil, vegetation and precipitation chemistry within the catchment. Finally, discussion and conclusions arising from the data analysis are presented.

4.1 Main field data

The six primary field sites described in Chapter 3 provided data between June 1999 and October 2000. Although instrument installation took place during April 1999, soil water collected during the first two sampling visits was discarded to allow the equipment to acclimatise at each site. The following section presents analysis of the soil water chemistry and soil hydrology recorded over this period. Data from the stream water sampling points are then discussed, followed by soil water chemistry from the secondary sample sites.

4.1.1 Soil water chemistry

Soil water collected in the suction probes described in section 3.4.1 was analysed for total and soluble Mn, Fe, and Al concentration plus pH and colour at WoSW laboratories, Glasgow. The anticipated seasonal changes in soil water chemistry were for autumnal increases in metal concentration and colour to coincide with decreases in pH. The exact sequence of events producing these effects is unknown, but the mechanisms thought to be involved have already been discussed in Chapter 2. However, the soil water chemistry at sites monitored did not follow this expected seasonal pattern.

4.1.1.1 Data overview

During the course of the field monitoring project, each primary site was sampled on 20 occasions. At each site, 9 samples were collected (3 replicates at 3 depths), resulting in a total of 54 soil water samples per sampling visit. Figures 4.1 to 4.5 show the mean values measured for each chemical determinand in soil water samples from every horizon monitored. The data are further summarised in tables 4.1 to 4.4, which include the minimum and maximum values recorded.

The mean Mn concentrations (Figure 4.1) show that soil water samples from the six primary field sites contained relatively little Mn, when compared to the maximum concentrations recorded in the reservoir water. The greatest mean Mn concentration of 33.3 $\mu g\ l^{-1}$ was recorded in the deep (Cg) horizon of the peaty gley at moorland site 2, while concentrations of close to 200 $\mu g\ l^{-1}$ were recorded in individual samples from the peaty gley (Cg) and peaty podzol (Bs) deep horizons (Table 4.1). Mn concentrations from the three forest sites appear to show a decrease with depth, possibly indicating an increase of Mn at the surface of the profile owing to leaching from vegetation. A similar trend is evident in the upper two horizons monitored in the peaty gley and peaty podzol of moorland sites two and three. However, at both these sites, soil water Mn concentrations in the deep horizon are greater than those higher up the profile. This increase with depth may be due to the presence of a larger pool of Mn in the mineral horizons at the base of the profile, resulting from weathering of parent material. The final point to note is that, in general, samples from the moorland sites appear to contain more Mn than those from the forest sites.

The distribution of mean soil water sample Fe concentrations throughout the primary field site soil profiles (Figure 4.2) followed a different pattern to Mn concentrations. No trends in Fe distribution throughout the soil profile are evident at the forest sites, although data from the moorland sites appear to indicate that the greatest concentrations are present in soil water from the shallow horizons. In addition to this different distribution pattern, the concentration of Fe present in samples was generally far greater than that of Mn. This was particularly evident in samples from moorland site one, where a maximum Fe concentration of 51.9 $mg\ l^{-1}$ was recorded (Table 4.2), approximately 1000 times greater than the corresponding Mn concentration.

The most obvious feature of the mean Al concentrations in soil water (Figure 4.3) is that the greatest concentrations in samples from the forest sites occur in the intermediate (O3) soil horizon. This distribution is not evident in the moorland soil profiles, where the greatest mean Al concentration is found in the shallow (O2) horizon of the peat at site one. Soil water samples from the deep (Bs) horizon of the peaty podzol at moorland site three appear to contain less Al than the intermediate (Eh) and shallow (O) horizons. Data in Table 4.3 show that the maximum Al concentration and greatest range of values were recorded in soil water samples from the deep (Cg) horizon of moorland site two. Soil water Mn concentrations were also greatest in this horizon and had the most variability between replicates (Table 4.1).

Soil water pH (Figure 4.4) showed distinct variation between horizons and soil types. In the forest sites, pH was greatest in the shallow (O2) horizons. However, in the moorland sites, the pH of soil water samples from all depths in the peat profile (site one) and in the intermediate (Eh) horizon of site three was considerably less than the other horizons. Soil water samples from the deep (Bs) horizon of moorland site three had the greatest pH of the moorland soils, being approximately equal to those in the shallow forest horizons. One feature of the soil water pH measurements from all the primary field sites is that they are greater than expected for organic soils, with values sometimes exceeding 8.0 (Table 4.4). This phenomenon is further discussed in section 4.3.

Figure 4.5 shows soil water sample colour from the six primary field sites. Samples from the three forest sites contained more colour than those from the moorland sites, with the exception of the shallow (O2) horizon of moorland site one. The vertical distribution of colour in soil water samples from the forest soil profiles is similar to that of Al, with the greatest concentrations found in the intermediate (O3) horizons. This similarity to Al distribution is also evident in data from moorland site one, where samples from the shallow (O2) horizon contained the most colour.

Following initial appraisal of the soil water chemistry data detailed above, time series plots were constructed to identify any temporal variations and statistical measures applied to reveal any significant trends in the data. The results of these analyses are discussed in the remainder of section 4.1.

4.1.1.2 Time series data

Figures 4.6 to 4.13 show time series graphs of the mean soil water chemistry for each site during the field monitoring programme. Where possible, points represent the mean value of all three suction probes on a particular sampling visit. However, at certain times, various suction probes did not collect a sample of soil water. This was normally attributed to soil shrinkage during dry periods resulting in a loss of suction as air spaces formed around the ceramic cup. However, on one sampling visit (20/12/99) low temperature resulted in the sample freezing inside several of the suction probes, while on another occasion the bung on one probe was found to have imploded thereby preventing sample collection. Where all three replicates were not collected, the point plotted represents the mean of two suction probes, or the only value available if two probes failed. Where no samples were collected

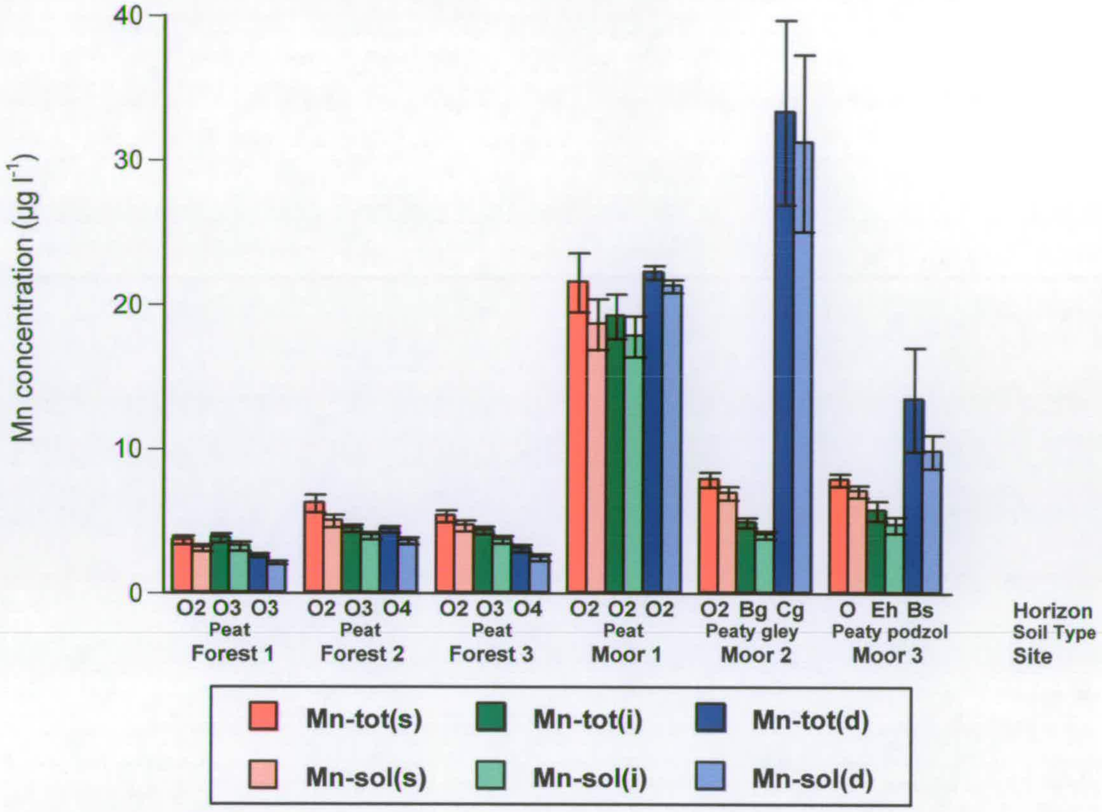


Figure 4.1: Mean Mn concentrations (±SE) of soil water samples from primary field sites

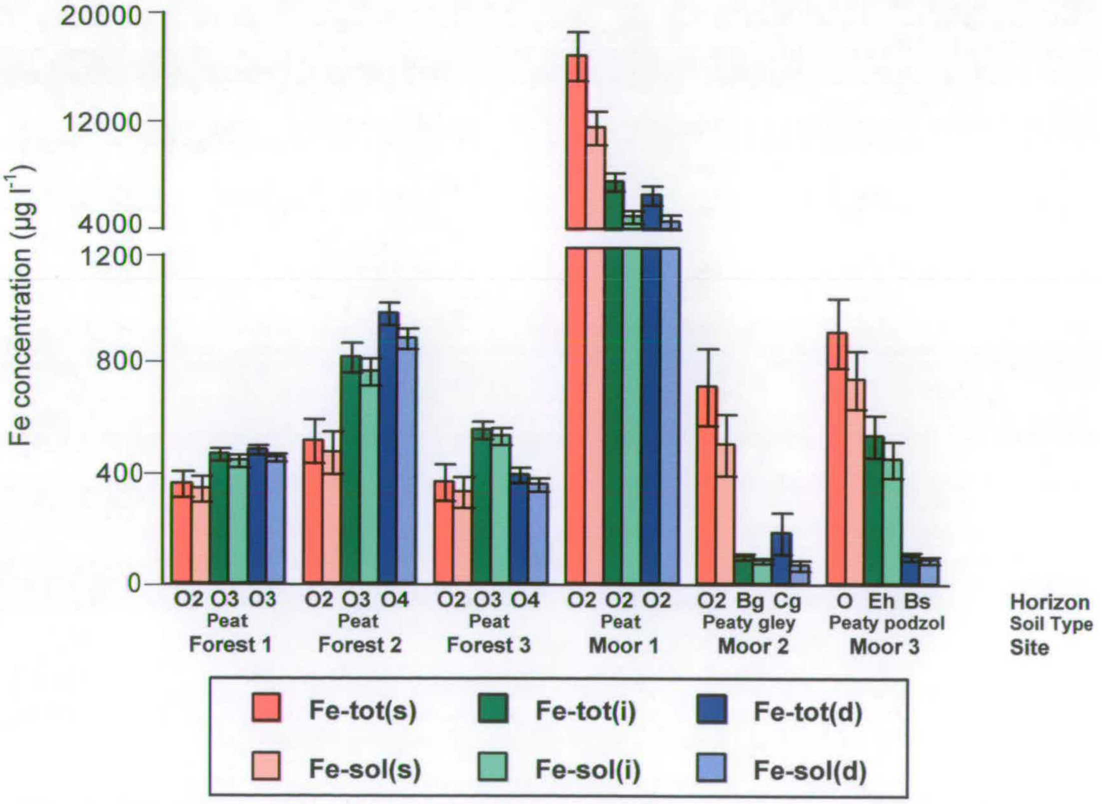


Figure 4.2: Mean Fe concentrations (±SE) of soil water samples from primary field sites

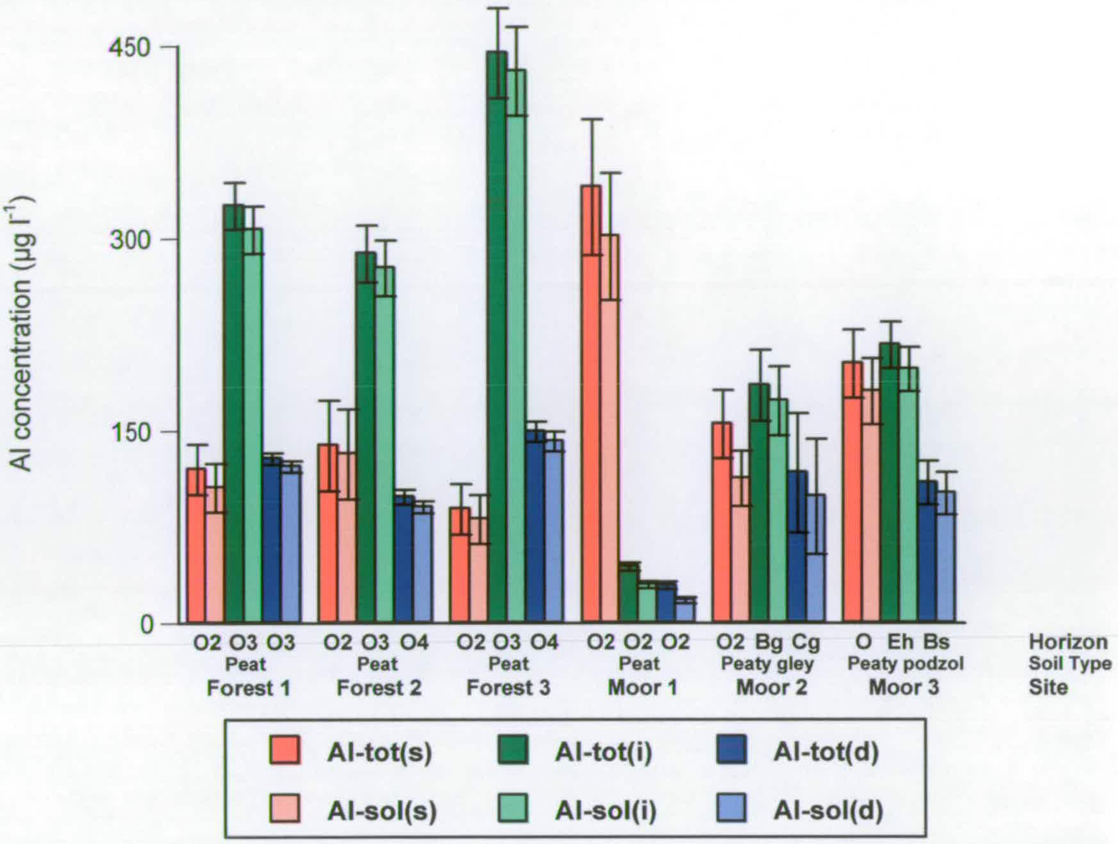


Figure 4.3: Mean Al concentrations (±SE) of soil water samples from primary field sites

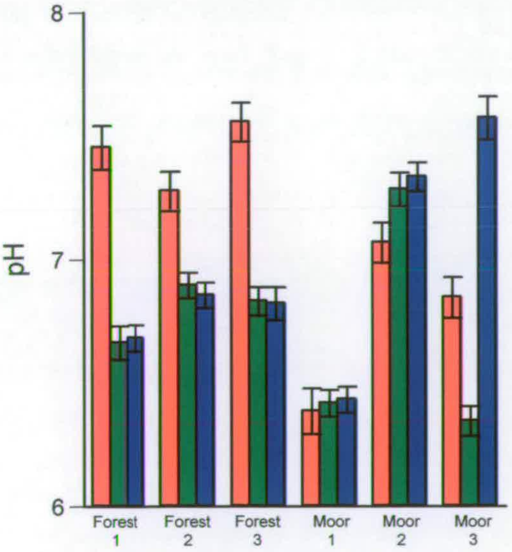


Figure 4.4: Mean pH (±SE) of soil water samples from primary field sites

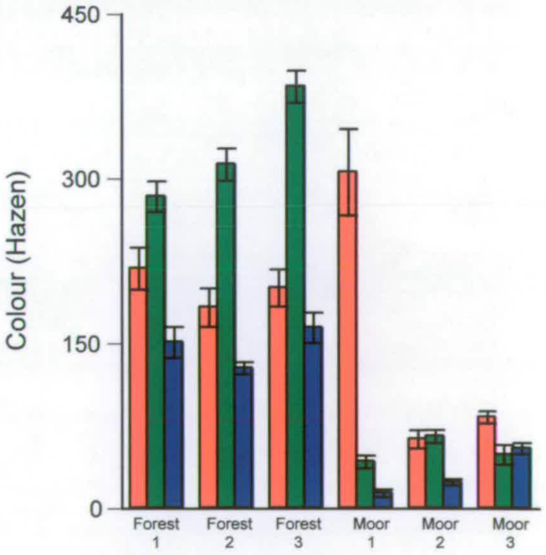


Figure 4.5: Mean colour (±SE) of soil water samples from primary field sites

Site (soil type)	Horizon		Mn-tot (µg l^{-1})				Mn-sol (µg l^{-1})			
			Mean	SE	Max	Min	Mean	SE	Max	Min
Forest 1 (peat)	O2	(s)	3.7	0.3	10	1	3.1	0.2	6	1
	O3	(i)	3.8	0.3	10	1	3.2	0.3	10	1
	O3	(d)	2.6	0.1	6	1	2.1	0.1	5	1
Forest 2 (peat)	O2	(s)	6.2	0.6	16	2	5.0	0.4	10	1
	O3	(i)	4.5	0.3	11	2	4.0	0.2	11	2
	O4	(d)	4.4	0.2	10	1	3.6	0.2	10	1
Forest 3 (peat)	O2	(s)	5.3	0.4	12	1	4.7	0.4	10	1
	O3	(i)	4.3	0.3	10	1	3.7	0.3	10	1
	O4	(d)	3.1	0.3	11	1	2.5	0.2	8	1
Moor 1 (peat)	O2	(s)	21.5	2.0	52	3	18.6	1.8	31	3
	O2	(i)	19.2	1.6	68	6	17.8	1.4	65	5
	O2	(d)	22.2	0.5	29	14	21.3	0.4	26	14
Moor 2 (peaty gley)	O2	(s)	7.9	0.5	17	2	6.9	0.5	16	2
	Bg	(i)	4.9	0.3	15	1	4.1	0.3	7	1
	Cg	(d)	33.3	6.4	195	1	31.2	6.1	193	1
Moor 3 (peaty podzol)	O	(s)	7.9	0.4	14	3	7.1	0.4	14	1
	Eh	(i)	5.7	0.7	24	1	4.7	0.6	24	1
	Bs	(d)	13.4	3.6	190	1	9.8	1.1	30	1

Table 4.1: Summary of soil water Mn concentrations from primary field sites

Site (soil type)	Horizon		Fe-tot (µg l^{-1})				Fe-sol (µg l^{-1})			
			Mean	SE	Max	Min	Mean	SE	Max	Min
Forest 1 (peat)	O2	(s)	357.7	46.5	1340	32	340.3	46.2	1266	30
	O3	(i)	464.0	22.5	899	51	441.1	22.6	895	25
	O3	(d)	480.8	16.9	992	229	452.4	14.3	801	226
Forest 2 (peat)	O2	(s)	512.3	78.9	1793	63	471.2	76.0	1759	60
	O3	(i)	811.1	53.6	1971	276	759.7	48.6	1520	267
	O4	(d)	968.1	39.8	1896	69	878.6	36.7	1836	63
Forest 3 (peat)	O2	(s)	364.6	65.7	1934	22	329.3	55.4	1492	17
	O3	(i)	551.8	31.8	1172	120	529.9	30.4	1050	108
	O4	(d)	391.0	27.2	925	67	356.6	23.5	899	62
Moor 1 (peat)	O2	(s)	16606.5	1781.3	51900	654	11388.0	1212.2	31890	75
	O2	(i)	7466.8	659.1	34810	307	4939.1	468.4	14790	131
	O2	(d)	6502.5	700.5	32650	97	4556.3	533.6	16090	81
Moor 2 (peaty gley)	O2	(s)	706.0	138.1	4750	27	499.7	110.9	4291	23
	Bg	(i)	100.1	10.9	340	11	84.9	9.3	262	10
	Cg	(d)	183.4	74.3	2939	3	68.4	18.8	938	3
Moor 3 (peaty podzol)	O	(s)	899.5	124.6	3219	18	732.7	104.8	2832	18
	Eh	(i)	530.1	75.2	2410	104	447.3	65.7	2382	92
	Bs	(d)	101.4	14.7	439	8	88.1	12.6	397	7

Table 4.2: Summary of soil water Fe concentrations from primary field sites

Site (soil type)	Horizon		Al-tot ($\mu g\ l^{-1}$)				Al-sol ($\mu g\ l^{-1}$)			
			Mean	SE	Max	Min	Mean	SE	Max	Min
Forest 1 (peat)	O2	(s)	120.1	19.5	513	10	105.7	18.9	504	7
	O3	(i)	325.5	18.2	606	32	306.8	18.5	604	31
	O3	(d)	128.4	4.5	208	22	122.2	4.4	192	16
Forest 2 (peat)	O2	(s)	138.6	35.3	897	9	131.9	35.1	897	6
	O3	(i)	288.1	22.2	881	55	276.9	21.6	867	52
	O4	(d)	98.5	5.7	270	21	90.6	4.7	161	20
Forest 3 (peat)	O2	(s)	89.0	19.7	529	9	81.1	19.1	514	7
	O3	(i)	444.3	35.1	1053	53	430.2	34.6	1052	46
	O4	(d)	149.4	7.9	226	17	141.8	7.6	225	15
Moor 1 (peat)	O2	(s)	339.8	52.9	1116	13	301.4	49.5	1052	4
	O2	(i)	44.2	3.2	120	8	30.1	2.7	84	5
	O2	(d)	29.6	3.1	107	5	17.9	2.4	85	2
Moor 2 (peaty gley)	O2	(s)	155.2	26.6	829	8	112.9	21.5	818	6
	Bg	(i)	185.5	27.7	854	8	173.3	27.0	844	8
	Cg	(d)	117.3	46.5	2452	8	98.8	44.9	2390	7
Moor 3 (peaty podzol)	O	(s)	202.2	26.5	710	7	180.7	25.8	708	1
	Eh	(i)	216.9	18.1	665	47	198.0	17.1	645	19
	Bs	(d)	109.5	17.1	499	6	101.3	16.6	472	5

Table 4.3: Summary of soil water Al concentrations from primary field sites

Site (soil type)	Horizon		pH				Colour (Hazen)			
			Mean	SE	Max	Min	Mean	SE	Max	Min
Forest 1 (peat)	O2	(s)	7.45	0.09	8.35	6.27	218.4	19.2	880	72
	O3	(i)	6.66	0.07	8.04	5.95	283.9	14.0	900	172
	O3	(d)	6.68	0.05	8.00	6.19	151.2	14.2	670	84
Forest 2 (peat)	O2	(s)	7.28	0.08	8.13	6.29	182.9	17.5	433	47
	O3	(i)	6.90	0.05	7.70	6.26	313.1	14.6	647	82
	O4	(d)	6.86	0.05	7.88	6.23	127.7	5.5	414	94
Forest 3 (peat)	O2	(s)	7.56	0.08	8.33	6.53	200.7	17.1	503	56
	O3	(i)	6.83	0.06	7.78	6.14	383.9	14.6	647	152
	O4	(d)	6.82	0.07	8.19	6.15	164.5	13.8	940	10
Moor 1 (peat)	O2	(s)	6.38	0.09	7.68	5.12	306.0	39.4	900	6
	O2	(i)	6.42	0.05	7.58	5.67	42.6	5.8	165	1
	O2	(d)	6.43	0.05	7.62	5.73	14.1	3.5	155	1
Moor 2 (peaty gley)	O2	(s)	7.07	0.08	8.41	6.00	63.0	8.3	370	17
	Bg	(i)	7.28	0.07	8.18	6.27	65.7	6.0	211	8
	Cg	(d)	7.33	0.06	8.25	6.58	24.3	2.8	97	6
Moor 3 (peaty podzol)	O	(s)	6.84	0.08	8.37	5.99	83.0	5.6	184	19
	Eh	(i)	6.34	0.06	7.78	5.61	49.1	9.0	432	14
	Bs	(d)	7.57	0.09	8.93	6.15	54.9	5.2	182	7

Table 4.4: Summary of soil water pH & colour from primary field sites

from a particular horizon, the point has been omitted. More detailed time series graphs are presented in Appendix B, showing mean, maximum and minimum determinand values for each horizon.

Time series of soil water Mn concentrations

Mn concentrations in soil water from the moorland sites appear greater and exhibit more variability than those from the forest sites (Figures 4.6 & 4.7). Closer inspection of the graphs shows that the greatest Mn concentrations occur in soil water from moorland site one (peat) and the deep horizons of moorland sites two and three (peaty gley and peaty podzol, respectively). There appears to be little difference between total and soluble Mn concentrations, indicating that most of the Mn present is in the soluble form. One notable exception to this occurred during summer 2000 in the moorland site three deep (Bs) horizon time series, where the data indicate that a large percentage of soil water Mn is in the insoluble form. No recurring seasonal peak in soil water Mn concentrations is evident from any of the sample sites, although the deep (Bs) horizon from moorland site three does display a high total Mn concentration during summer 2000. However, this release of Mn was only found in one of the three suction probes installed within the horizon, and therefore cannot be taken as representative of Mn behaviour throughout the horizon.

Time series of soil water Fe concentrations

Soil water Fe concentrations from the primary field sites are shown in Figures 4.8 and 4.9. It is important to note that concentrations on the moorland site one (peat) graph y-axis are 20 times greater than those on the other graphs. Soil water from all horizons at this site repeatedly contained far greater concentrations of Fe than samples from any of the other sites. There is also evidence of a possible late summer peak in Fe concentrations in soil water from the shallow (O) horizon of the peat at moorland site one, with large increases recorded in both 1999 and 2000. The three moorland sites appear to have greater soil water Fe concentrations in their shallow horizons, compared to intermediate and deep horizons. The reverse is true of the forest sites, where soil water Fe concentrations are generally less in the shallow horizons than in the intermediate and deep horizons. However, Fe concentration in soil water samples from the shallow (O2) horizons of forest sites two and three appears to increase over time, eventually attaining concentrations greater than in samples from the lower horizons. At all six sites, soluble Fe concentrations closely follow those of total Fe. The largest differences between the two measurements occur in the shallow horizon of moorland site one (peat), which also contained samples with the greatest Fe concentration.

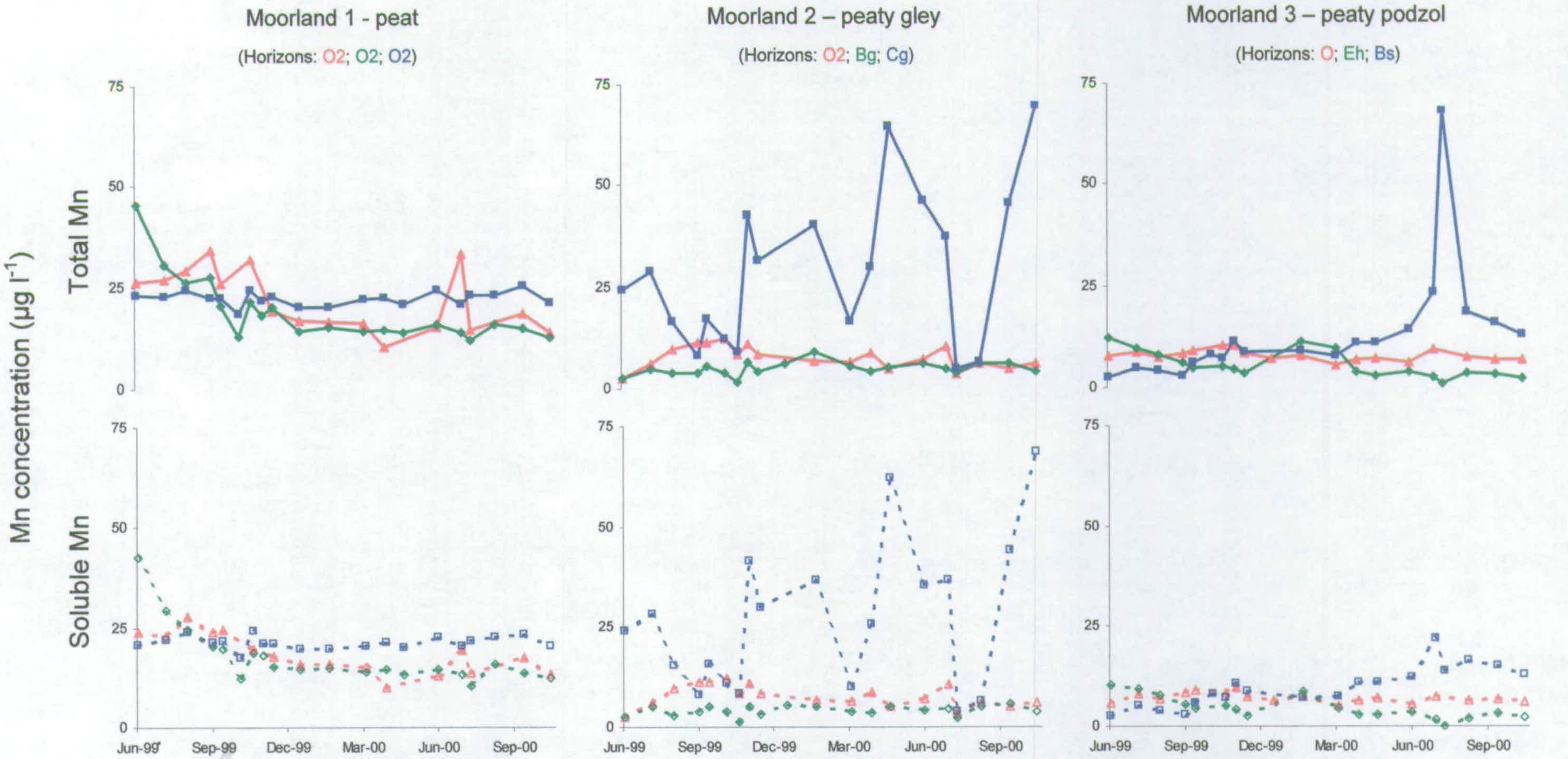


Figure 4.6: Mean soil water Mn concentrations from moorland field sites, June 1999-October 2000

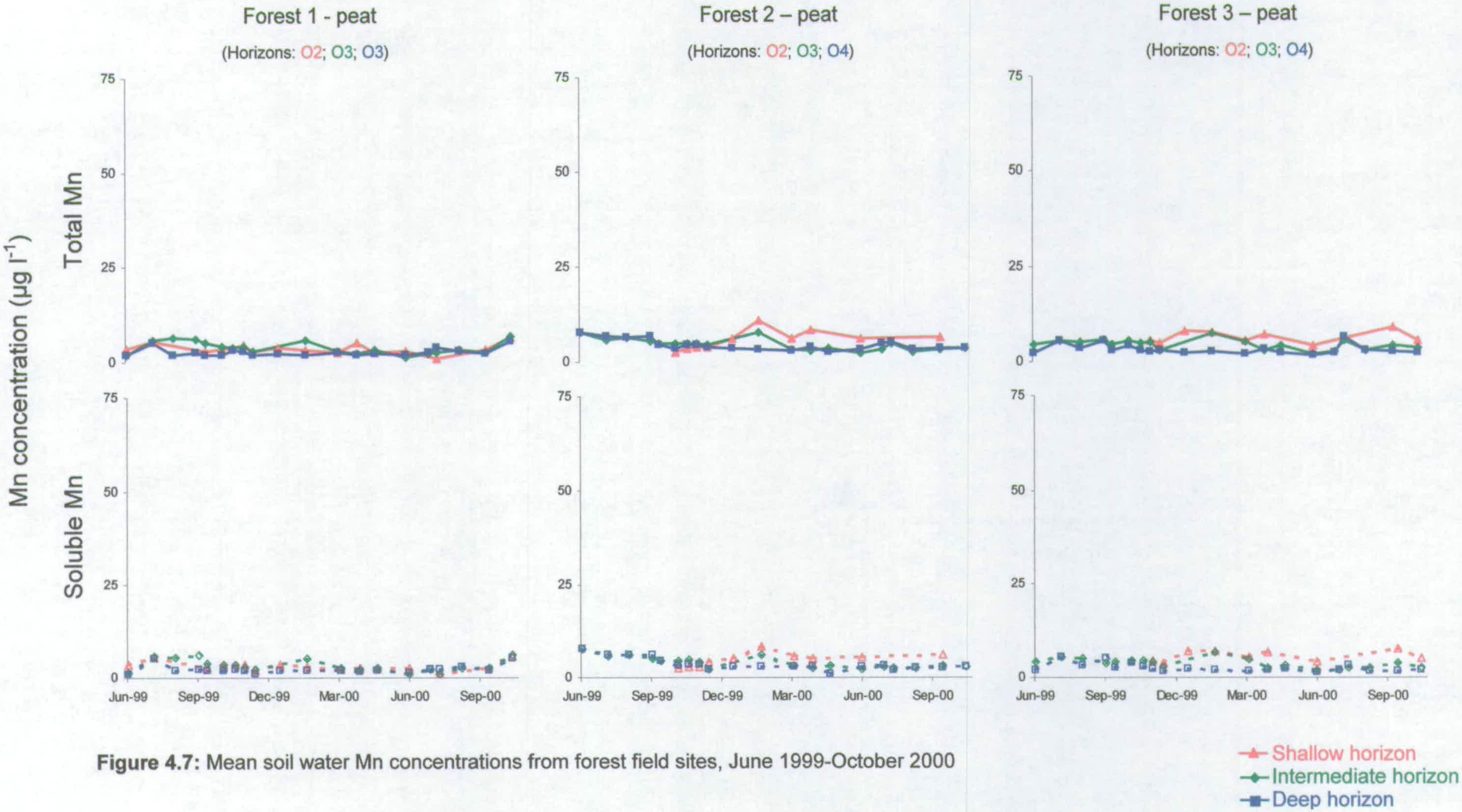


Figure 4.7: Mean soil water Mn concentrations from forest field sites, June 1999-October 2000

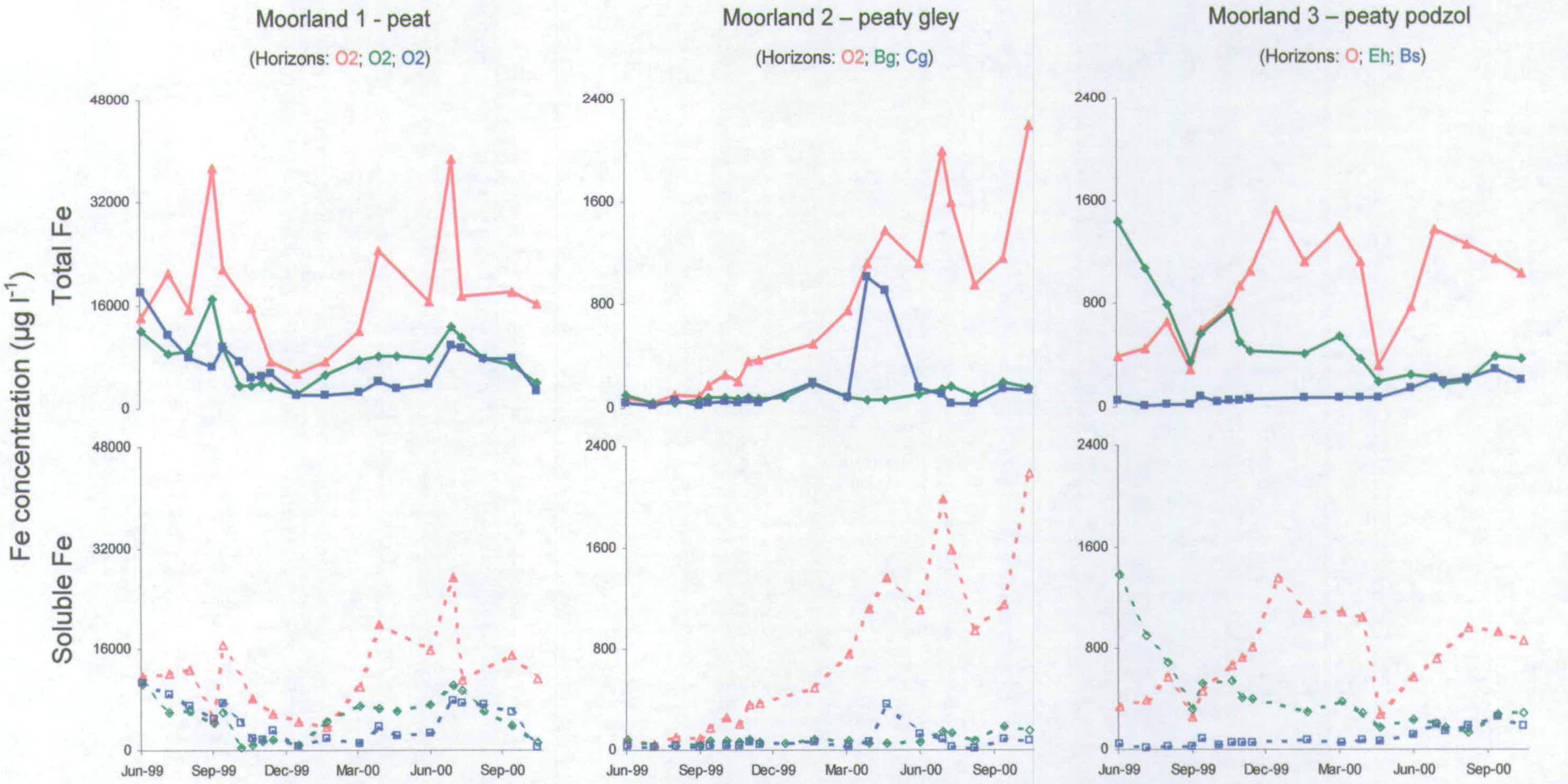


Figure 4.8: Mean soil water Fe concentrations from moorland field sites, June 1999-October 2000

NB: scale on Moorland 1 graphs' y-axis is 20x that of the other graphs

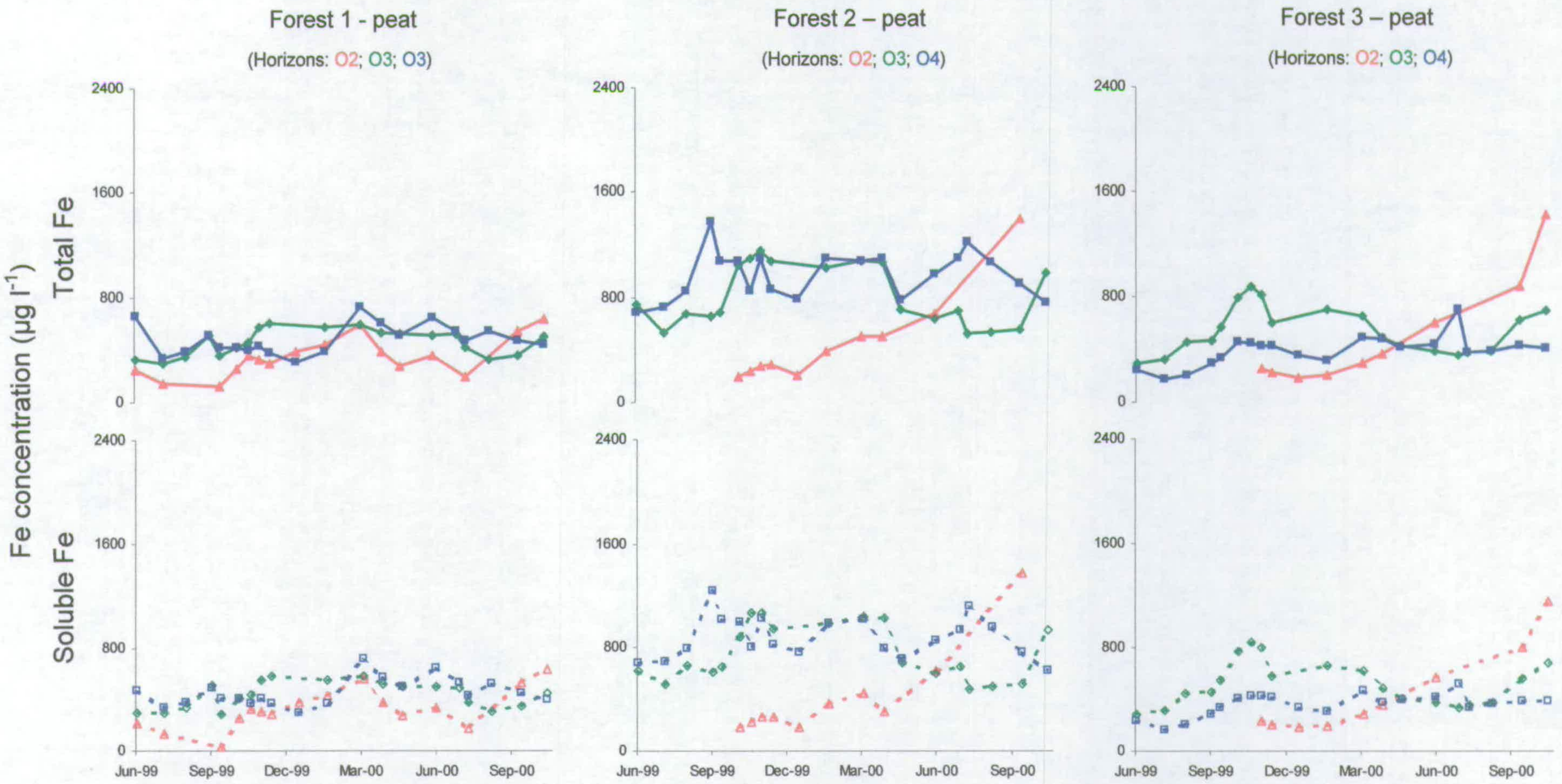


Figure 4.9: Mean soil water Fe concentrations from forest field sites, June 1999-October 2000

Time series of soil water Al concentrations

There is little difference evident between total and soluble soil water Al concentrations across all the sites (Figures 4.10 & 4.11). Concentrations in the shallow horizon of moorland site one (peat) are consistently greater than those from the lower horizons, although no such difference appears to exist at the other two moorland sites. In all three forest sites, however, the intermediate horizon soil water samples contain more Al than the shallow or deep horizons. There is also a possible seasonality apparent in the data from these intermediate horizons, with a late summer or early autumn minimum being recorded in both years.

Time series of soil water pH measurements

Analysis of pH values was complicated by the fact that the pH of samples would alter, increasing over time, during storage in the suction probes. This and other explanations for the unexpectedly great pH of soil solutions collected will be discussed in more detail in section 4.3. Therefore, the results shown in Figure 4.12 indicate relative pH trends over time, rather than absolute pH values measured. There is no obvious seasonal change in soil water pH at any of the moorland sites. However, forest site one may exhibit an increase in shallow (O2) horizon soil water pH towards the end of summer, although the timing of this is not the same in both years. Furthermore, this event is not recorded at either of the nearby forest sites (although both have incomplete records) and so may not be totally representative of soil water pH from that horizon. Other visible differences in the graphical data include the greater pH of soil water from forest shallow horizon samples, relative to the deeper horizons, although this effect disappears during the final months of monitoring. There also appears to be a correlation between pH values from the intermediate and deep forest horizons, with both rising and falling in unison, particularly during the summer of 2000. However, rapid pH changes of this nature between samples may owe more to deterioration during the time between sample collection and analysis than any environmental effects.

Time series of soil water colour measurements

The final set of graphs (Figure 4.13) show changes in colour of soil water samples during the monitoring period. For most of the horizons investigated, no seasonal changes are readily apparent, and determination of any seasonal trends may require longer time series than the 18 months of this study. However, there is a distinct winter minimum in colour of samples from the shallow (O2) horizon of the peat at moorland site one, which may also be detected in some horizons of the forest sites. Soil water from the forest peat contains more colour than the two moorland organo-mineral soils (sites two and three), or the deeper horizons of

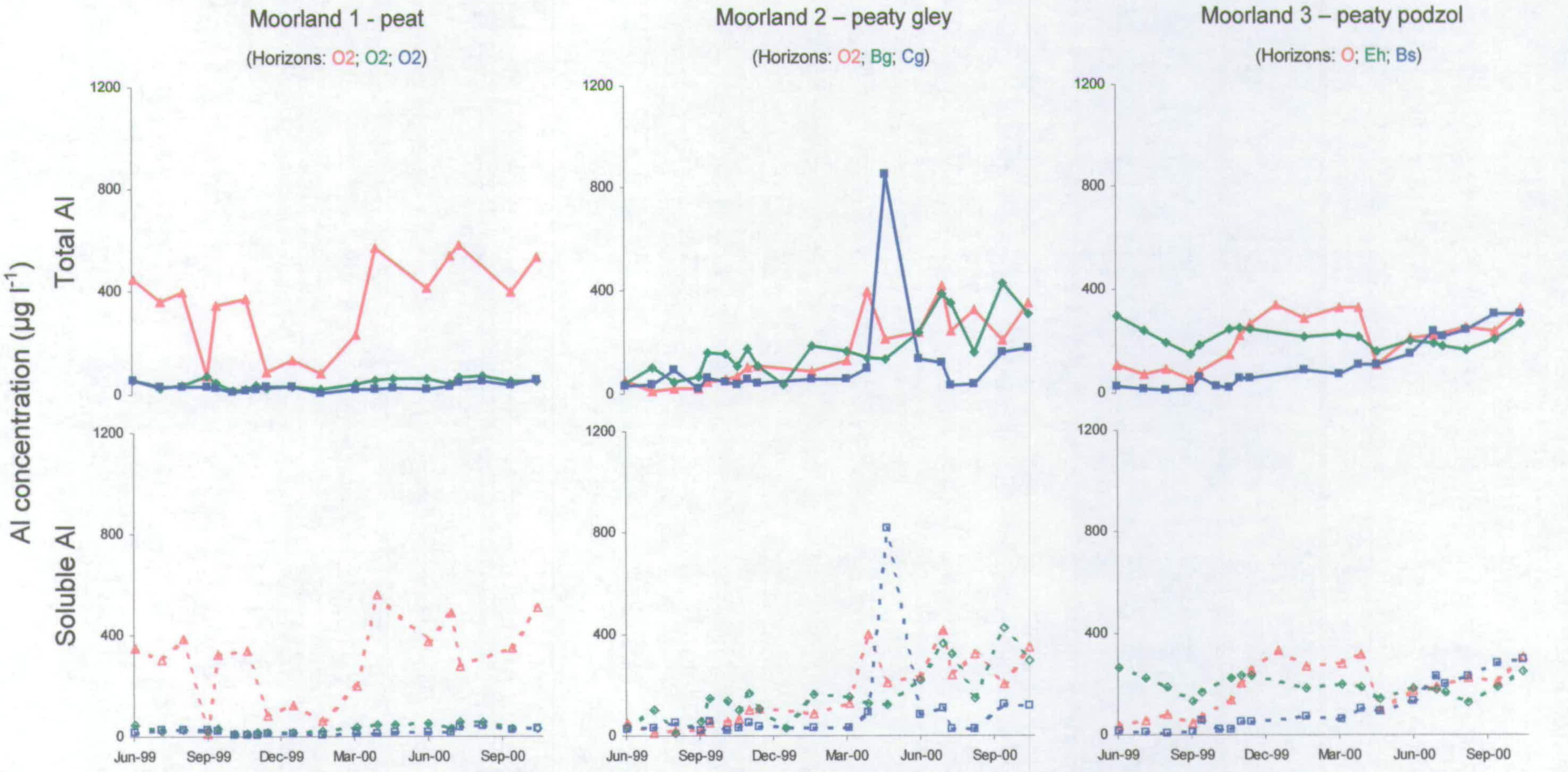


Figure 4.10: Mean soil water Al concentrations from moorland field sites, June 1999-October 2000

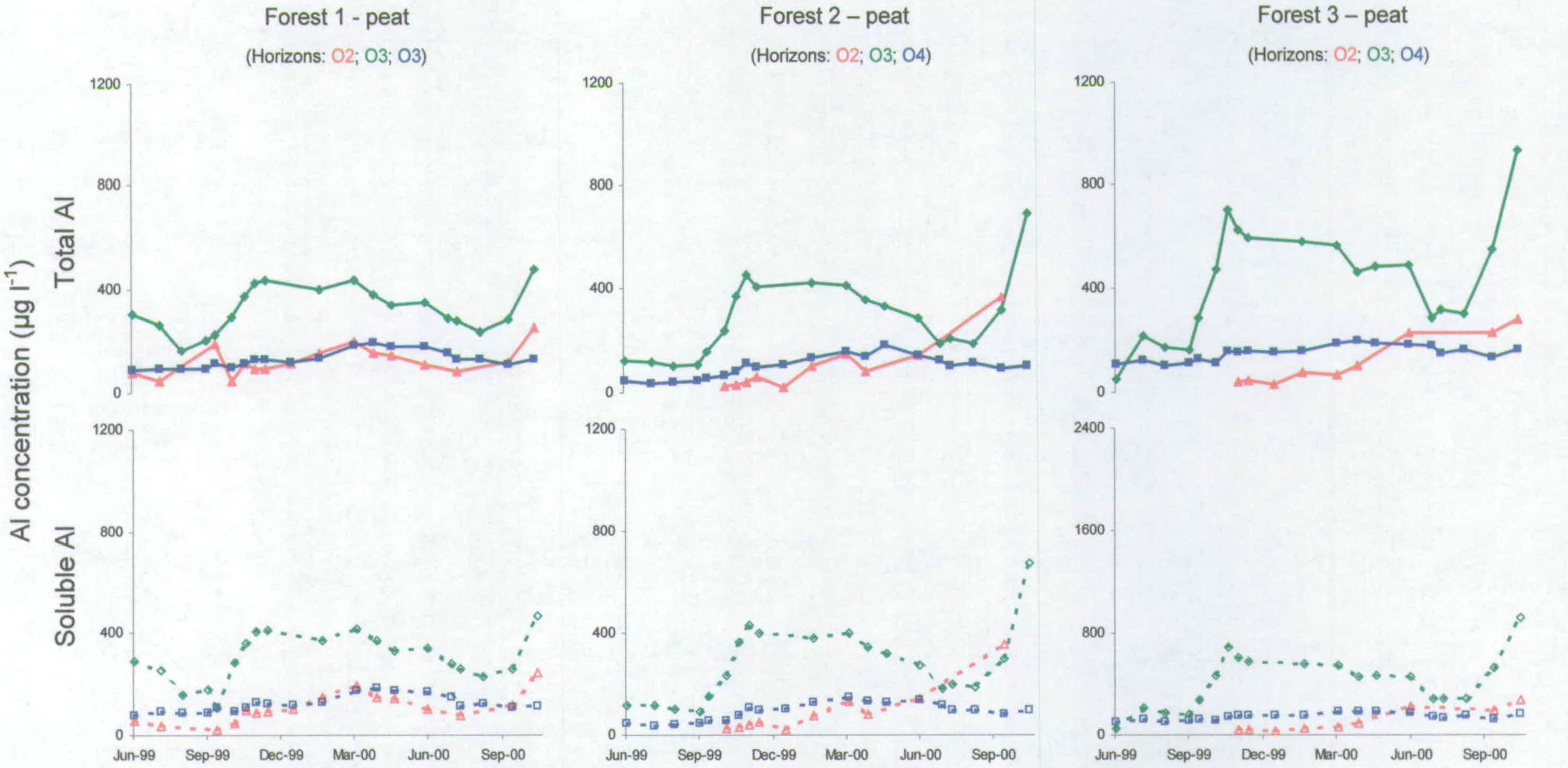


Figure 4.11: Mean soil water Al concentrations from forest field sites, June 1999-October 2000

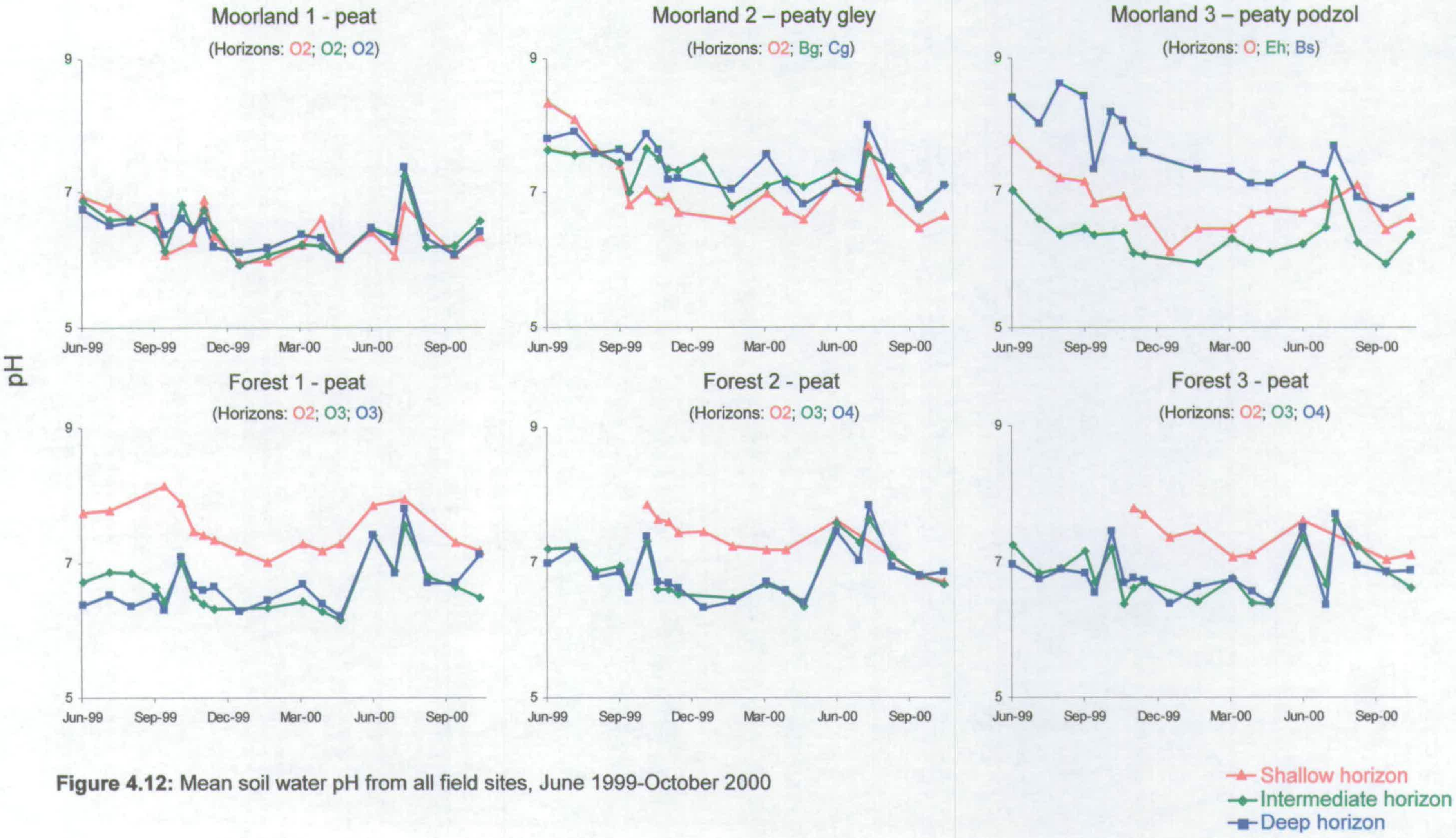


Figure 4.12: Mean soil water pH from all field sites, June 1999-October 2000

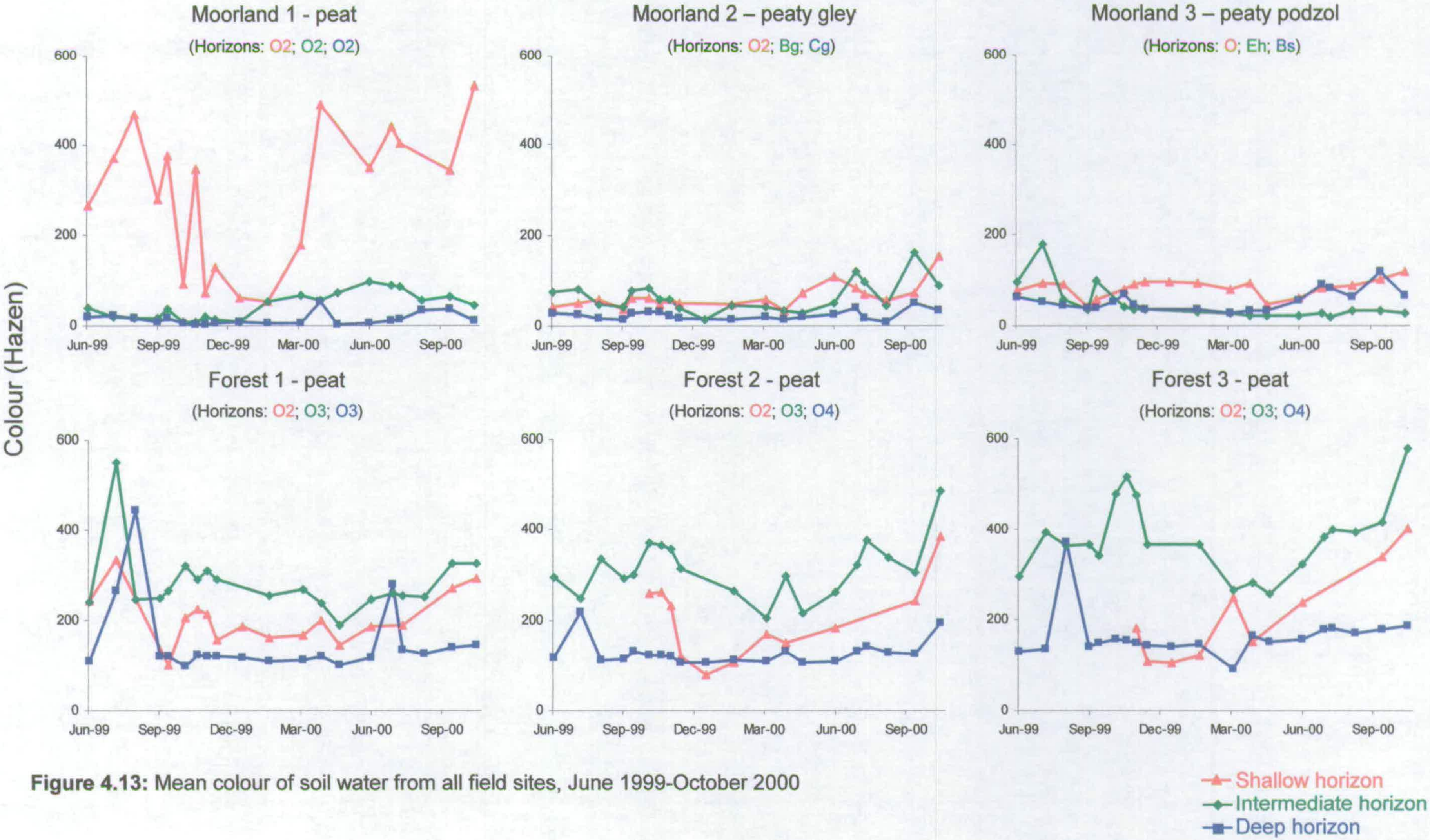


Figure 4.13: Mean colour of soil water from all field sites, June 1999-October 2000

the moorland peat (site one). However, the shallow horizon of the moorland peat provides soil water samples with colour equal to that of the forest.

4.1.1.3 Statistical analysis

Following consultation with Biomathematics and Statistics Scotland (BioSS), it was decided to use repeated measures ANalysis Of VAriance (rm-ANOVA) to further interpret the soil water chemistry data from the suction probes. As its name suggests, rm-ANOVA produces an analysis of variance for the means of repeated measurements (i.e. where the experimental design allows measurements of the same variable at different times). One distinct advantage repeated measures analysis has over other statistical methods for analysing observations from single points on several occasions (e.g., a split plot design, with each sampling visit represented by a sub-plot) is that it does not regard observations of the same subject at different times as being independent of each other. Therefore, repeated measures analysis recognises that there is likely to be a greater correlation between observations made at adjacent time points than those made further apart. Another alternative to rm-ANOVA was the use of comparable nonparametric tests (e.g., Seasonal Kendall test – Hirsch & Slack, 1984), the advantage being that such tests do not require normally distributed data and are robust in dealing with long gaps in the dataset. However, Hirsch & Slack (1984) identify problems using the nonparametric test with short datasets of less than five years. One further statistical test considered for data analysis was the use of time series analysis. However, the relatively short length of dataset was considered to favour the application of rm-ANOVA rather than time series analysis (T.Hunter, BioSS – pers.comm.).

Data preparation

The experimental design of the field monitoring project allowed a comparison of land use between the forest and moorland peats and also between soil type across the moorland sites. Soil water chemistry data was laid out in a Microsoft Excel spreadsheet with each row representing data from an individual suction probe. In addition to determinand values, each row also contained data identifying land use, soil type and soil horizon. Short gaps in the dataset of a single missing value were filled by interpolation of the data immediately before and after the missing point using equation 4.1. Where the missing data extended over more than one observation, or there was insufficient surrounding data to complete equation 4.1, the data point was treated as a missing value. Prior to analysis, data were tested for normality with the Anderson-Darling test, using the Minitab v12.1 statistical program, and any non-normal data (metal concentration and colour) were $\log_{10}$ transformed to provide normally distributed data.

$$\mathrm{Data}_{(n)} = \frac{\dfrac{\left(\mathrm{Data}_{(n-1)} + \mathrm{Data}_{(n-2)}\right)}{2} + \dfrac{\left(\mathrm{Data}_{(n+1)} + \mathrm{Data}_{(n+2)}\right)}{2}}{2}$$

Equation 4.1

Performing the rm-ANOVA

Once the spreadsheet tables were populated with data, they were imported into the Genstat 5.0 statistical program in order to carry out the analysis. The Genstat 'AREPMEASURES' procedure was used to analyse the data, with 'treatment' and 'block_structure' defined by land use, soil type and soil horizon according to the particular analysis (e.g., the effect of land use was analysed using data from the forest and moorland peat profiles, with land use set as the 'treatment' and a 'block_structure' consisting of horizons within soil type). Output from the Genstat analysis provided the variance ratio (F-value) at each level of the analysis, which was then converted to a probability, using the Microsoft Excel 'FDIST' worksheet command.

Results of rm-ANOVA

Table 4.5 shows the results of the comparisons between land use and soil type, while analysis of variation between horizons within individual soil types is presented in Table 4.6. When interpreting these results, it is beneficial to consider the graphs in Figures 4.6 to 4.13 at the same time. Comparisons between land use and soil type take into account data from all horizons simultaneously, and the p-values quoted refer to variation across all of these rather than individual horizons at similar depth.

a) Effect of land use

There are statistically significant differences in soil water chemistry between forest and moorland peats, with soil water from the moorland peat containing significantly more Mn and Fe in samples from all the horizons studied (Table 4.5) (Figures 4.6 to 4.9). However, given the relatively small concentrations of Mn and Fe found in vegetation samples (see section 4.2.2), it is doubtful whether the large differences in soil water metal concentration between forest and moorland peat arise purely because of vegetation cover. It is therefore probable that some other factor must be involved. Al concentrations from the moorland peat were only greater than the forest peat in the shallow horizon, while the opposite was found for the intermediate horizon (Figures 4.10 & 4.11). The pH of soil water from forest and moorland peats was found to differ significantly. Graphical analysis (Figure 4.12) indicates that this difference probably arises from the greater pH of samples from the forest shallow horizon. There is a highly significant ($p<0.001$) difference between the colour of samples from forest and moorland peat (Table 4.5), indicating that the overlying vegetation strongly influences soil water colour. The time series graphs of soil water colour (Figure 4.13) show that the vertical distribution of colour in forest and moorland peat was different. In the forest peat, soil water samples from the intermediate horizon contained the most colour, while in the moorland peat, the greatest amount of colour was in samples from the shallow horizon. The colouration of soil water in peaty soils is largely caused by dissolved organic matter, and is therefore a product of the extent to which decomposition of plant material in the peat has occurred, as well as vegetation type.

b) Effect of soil type

Soil type significantly affects soil water pH and the concentrations of Mn and Fe present (Table 4.5). The colour and Al concentration of soil water samples showed no significant difference between soil types. In general, Mn concentrations from the peat soil water samples were greater than those from the peaty gley or peaty podzol. However, the difference was only of the order of a few $\mu g\ l^{-1}$ and Mn concentrations in the peaty gley deep (Cg) horizon exceeded those recorded at the peat site on a number of occasions (Figure 4.6). The difference in soil water Fe concentrations between peat and the organo-mineral soils is more obvious (Figure 4.8), with soil water from the peat having concentrations at least one order of magnitude greater. This may be related to the significant ($p=0.002$) difference identified in soil water pH between the moorland soils, as the pH of soil water samples from the peat was generally less than that of samples from the peaty gley and peaty podzol (Figure 4.12). The range of Al concentrations from all studied horizons within each soil profile did not differ significantly between soil types, although the graphs (Figure 4.10) suggest greater concentrations in the peat shallow (O2) horizon. Although soil water colour was not found to differ significantly between soil types, peat shallow horizon colour values (Figure 4.13) exceed those from all other horizons studied. These observations are confirmed by the analysis in Table 4.6, which identifies variation between soil horizons for each particular soil type.

	Mn-tot	Mn-sol	Fe-tot	Fe-sol	Al-tot	Al-sol	pH	Colour
Land use	***<0.001***	***<0.001***	***<0.001***	***<0.001***	***0.019***	***0.002***	***<0.001***	***<0.001***
Soil type	***0.003***	***0.003***	***<0.001***	***<0.001***	0.282	0.144	***0.002***	0.475

Table 4.5: Repeated measures ANOVA p-values for variation of soil water chemistry resulting from land use and soil type (Land use comparison is between forest and moorland peats. Soil type comparison is between moorland peat, peaty gley and peaty podzol.)

	Mn-tot	Mn-sol	Fe-tot	Fe-sol	Al-tot	Al-sol	pH	Colour
Forest peat	*0.051*	***0.014***	***0.001***	***0.001***	***0.000***	***0.000***	***0.000***	***0.000***
Moorland peat	0.751	0.688	*0.063*	*0.052*	***0.024***	***0.036***	0.999	***0.002***
Moorland peaty gley	*0.074*	*0.063*	*0.087*	*0.092*	0.879	0.845	0.524	0.219
Moorland peaty podzol	***0.012***	***0.012***	***0.015***	***0.014***	0.119	0.111	***0.006***	0.268

Table 4.6: Repeated measures ANOVA p-values for variation of soil water chemistry between soil horizons within each site

Shading in both tables: ***$p<0.01$***; ***$p<0.05$***; *$p<0.10$*

c) Effect of horizon within forest peat

For the forest peat, almost all chemical determinands were significantly different between soil water samples from different horizons (Table 4.6). However, in the case of Mn, the extremely low concentrations and small range of values recorded at all three forest sites (Figure 4.7) mean that, although a significant statistical difference existed between horizons, the result may have no environmental significance. Of the other two metals analysed, Fe (Figure 4.9) appears to be present at greater concentration in soil water from the deeper forest peat horizons, while Al (Figure 4.11) is more prevalent in soil water from the intermediate horizon. The vertical distribution of Fe may be related to pH, as the significant ($P<0.001$) difference noted in the pH of soil water from different forest peat horizons is a result of greater pH in the shallow (O2) horizon (Figure 4.12). However, as noted earlier in section 4.1.1.2, the graph of soil water Fe concentrations shows an increase in shallow horizon concentrations over time during the field monitoring. The colour of soil water varies between forest peat horizons, with Figure 4.13 indicating that most colour is found in samples from the intermediate horizon. This matches the vertical distribution of soil water Al concentration and may indicate mobilisation of the Al by complexation with organic matter released through the process of humification in this horizon.

d) Effect of horizon within moorland peat

Mn concentrations in soil water from the moorland peat showed little variation with depth (Figure 4.6) and no statistical difference was found between horizons (Table 4.6). The graphs for both Fe and Al (Figures 4.8 & 4.10) suggest greater concentrations exist in soil water samples from the shallow (O2) horizon of this profile. However, this difference is only statistically significant ($p<0.05$) for Al, although Fe concentration differences between horizons are almost significant at this threshold. No significant difference in soil water pH between horizons was identified (Table 4.6), with changes in pH from different horizons generally following the same pattern (Figure 4.12). Colour, however, differed markedly between horizons and a statistically significant ($p=0.002$) difference was identified (Table 4.6), with the shallow horizon providing samples containing more colour than the deeper two horizons (Figure 4.13). As with the forest peat, the greatest colour and Al concentrations were measured in soil water samples from the same horizon. However, unlike the forest peat, this occurred in the shallow horizon and may indicate different degrees of humification with depth between the two peats, possibly arising because of the different vegetation present.

e) Effect of horizon within peaty gley

None of the determinands proved significantly different between horizons of the moorland peaty gley (Table 4.6). While this analysis confirms visual interpretation of the graphs for Al, pH and colour, the graphs for Mn and Fe (Figures 4.6 & 4.8) indicate differences in concentration. Graphical evidence suggests that soil water from the shallow (O2) horizon contains greater Fe concentrations than the other two horizons (Figure 4.8). Although the p-values for total and soluble Fe are not significant ($p=0.087$ and $p=0.092$) a separate rm-ANOVA of the data for this horizon alone, does indicate a significant difference in Fe concentrations as time progresses ($p<0.001$). Therefore, soil water Fe concentrations between horizons in the peaty gley soil do not differ during the initial measurements, but those from the shallow (O2) horizon increase significantly with time. This may be attributed to an environmental factor, such as progressive drying out of the soil surrounding the ceramic cup leading to sampling of smaller diameter pores, or to some aspect of equipment performance. Similarly, the graph of Mn concentrations (Figure 4.6) suggests a greater concentration in the deep (Cg) horizon soil water, which is not supported by the statistical analysis. However, the greater Mn concentrations in soil water from this horizon are largely due to samples from one suction probe. Points on the graph where the mean value decreases often represent times when this device failed to provide a sample. When the analysis was repeated without data from this suction probe, the p-value increased markedly, indicating no statistically significant difference between samples from the remaining two deep (Cg) horizon suction probes and those from the other horizons (O2 and Bg) within this profile. However, repeating the analysis and discarding points where no data were available for this probe, thereby ensuring that all observations included in the analysis were influenced by it, produced a highly significant result ($p<0.01$). Such discrepancies highlight the inherent difficulties in statistical analysis of soil water chemistry using a small number of replicates. Although the use of three replicates is comparable with other studies of soil water chemistry (e.g., Ferrier *et al.*, 1990), it is possible that increasing sampling density (e.g., Grieve, 1990a used five and seven replicates at two depths) would have provided a more representative sample of soil water, thereby increasing the confidence in the statistical analyses.

f) Effect of horizon within peaty podzol

Soil water colour and Al concentrations show no difference with depth in the peaty podzol profile (Table 4.6). However, both Mn and Fe concentrations in soil water differ significantly between horizons. The greatest Mn concentrations are found in soil water from the deep (Bs) horizon (Figure 4.6), while Fe concentration appears greatest in samples from the shallow (O) horizon (Figure 4.8). However, the increased Mn concentrations only occur towards the end of the experiment, and result from a large peak in Mn concentrations (maximum value=190 μgl^{-1}) occurring in a single suction probe during the summer of 2000. Removal of this data from the analysis resulted in no statistically significant difference in Mn concentration being identified between horizons. The pH of soil water samples from this profile varied significantly between horizons, with those from the deep (Bs) horizon being greater than the shallow (O) and intermediate (Eh) horizons (Figure 4.12), possibly because of the decreased organic matter content and increased influence of mineral weathering at depth. In addition to this, the pH of samples from the deep horizon appears to decrease during the field monitoring period, falling by approximately one pH unit from start to finish.

A summary of the graphical and statistical analysis of soil water samples is presented in Table 4.7, detailing horizons in which maximum determinand values were measured and the presence of any seasonal effects. It is evident that the three metals analysed generally exhibit different vertical distributions within the soils studied. In particular, the greatest Mn concentrations were measured in soil water from the shallow horizon of the forest peat and deep horizons of the moorland organo-mineral soils, while Fe concentrations were greatest in the forest peat deep and moorland shallow horizons. For Mn and Fe, soil water concentrations may be influenced by pH, while increased Al concentrations appear to coincide with increased colour in soil water samples.

4.1.2 Soil water regime

The thetaprobes installed at each primary field site provided a record of volumetric water content in each horizon studied. Tensiometers installed at these sites were intended to provide measurements of soil matric potential to aid interpretation of the thetaprobe data and provide data to parameterise a one-dimensional soil water simulation model. It was anticipated that any large increases in soil water Mn concentration would be preceded by a prolonged period of drying conditions followed by rewetting of the soil.

4.1.2.1 Thetaprobe data

Data provided by the thetaprobes was in the form of a signal, recorded in mV, the strength of which was related to soil wetness as described in section 3.4.2. This signal was converted to volumetric water content by using the following equation, derived from equations 3.2 and 3.3.

Determinand	Forest peat	Moorland peat	Moorland peaty gley	Moorland peaty podzol
Mn	Greatest concentrations in shallow (O2) horizons (Increase only 1-2 μg l^{-1})	No difference between horizons	Possibly greater in deep (Cg) horizon (Analysis hindered by missing data & small number of replicates)	Possibly greater in deep (Bs) horizon (Analysis hindered by small number of replicates)
Fe	Greatest concentrations in intermediate & deep horizons Increase in shallow (O2) horizons over time	Greatest concentrations in shallow horizon (Difference not significant) Possible late summer peak in shallow (O2) horizon	Greatest concentrations in shallow (O2) horizon (Difference not significant) Increase in shallow (O2) horizon over time	Greatest concentrations in shallow (O) horizon
Al	Greatest concentrations in intermediate (O3) horizons Possible late summer minimum in intermediate (O3) horizons	Greatest concentrations in shallow (O2) horizon	No difference between horizons	No difference between horizons
pH	Greatest pH in shallow (O2) horizons Possible late summer increases in shallow (O2) horizons	No difference between horizons	No difference between horizons	Greatest pH in deep (Bs) horizon Possible decrease in deep (Bs) horizon pH over time
Colour	Most colour in intermediate (O3) horizons	Most colour in shallow (O2) horizon	No difference between horizons	No difference between horizons

Table 4.7: Summary of graphical and statistical analysis of soil water chemistry data from primary field sites

$$\text{Volumetric water } (m^3m^{-3}) = \frac{(4.7V^3 - 6.4V^2 + 6.4V + 1.07) - a_0}{a_1} \qquad \text{Equation 4.2}$$

Where V is the voltage recorded by the thetaprobes, a_0 and a_1 are constants.

Calibrating the probes, by calculating the constants a_0 and a_1 for each soil horizon, using the procedure described in Appendix D, should allow an accuracy of at least ±0.02 m^3m^{-3} to be attained (Miller & Gaskin, 1998). Shrinkage, cracking and hardening of peat during the calibration procedure meant that it was difficult to obtain thetaprobe readings for the dried soil. This problem was especially severe in cores from the moorland peat site, preventing any readings being taken from the dried cores. Therefore, the data for this site were calculated with generalised values of a_0 and a_1 for organic soils, a method that is considered to have maximum errors of the order of 0.05 m^3m^{-1}. However, calibration was successfully carried out at the other five sites, allowing data to be calculated using horizon-specific values of a_0 and a_1.

Once calibrated, the data from each probe were plotted against time, along with mean values for total soil water Mn concentration, with the results from each field site shown in Figures 4.14 to 4.19. The gaps in Figures 4.14 to 4.16 were caused by datalogger failure, which resulted in no data collection from forest sites during September and October 1999.

The thetaprobe data show that the peat soils have distinctly different soil water regimes to the organo-mineral soils. In all four of the peat sites (three forest and one moorland: Figures 4.14 to 4.17), the volumetric water content remains nearly constant for the duration of the field experiment. This is not unexpected, as it is these waterlogged conditions that allow peat formation to occur in the first place. The increase in volumetric water content with depth identified at all three forest peat sites (and to a lesser extent at the moorland peat site) is as expected, and results from replacement of solid material by liquid as the degree of humification increases. However, what was unpredicted was the relative absence of any drying, even in the shallow horizon, as the summer periods progressed. Only one of the peat sites (Figure 4.15) showed any drying during the two summers of monitoring, and on neither occasion did volumetric water content fall below 75%.

Both moorland organo-mineral soils exhibited distinct wetting and drying phases in the horizons studied. This was particularly evident in the case of the peaty gley (Figure 4.18), where fluctuations of soil water regime in the shallow (O2) horizon, presumably caused by rainfall, appear to closely correspond with those in the intermediate (Bg) horizon. Furthermore, extended periods of drying in both these horizons coincide with a decrease in volumetric water content in the deep (Cg) horizon. The data from the peaty podzol thetaprobes (Figure 4.19) are similar to the peaty gley data, showing obvious fluctuations in soil water content throughout the year. There is, however, a less clear-cut relationship between volumetric water content of the shallow (O) and intermediate (Eh) horizons although events in the deep (Bs) horizon closely follow those in the intermediate. In contrast to the peat profiles, there is a decrease in volumetric water content measured with depth in the peaty podzol at moorland site three. This is presumably related to the amount of organic matter present in each horizon, with the shallow (O) horizon holding a larger volume of water than the mineral horizons beneath it.

Mean total Mn concentrations of soil water from each horizon are also plotted on the soil water content graphs, in order to highlight any changes in Mn concentration occurring during rewetting of soil following an extended dry period. However, no such change in concentrations was identified at any of the field sites. Soil water from the three forest sites contained very little Mn and the soil remained constantly wet during the monitoring period. Although soil water samples from the moorland peat site contained more Mn than the forest peats, there were no peaks in concentration, and no variation in soil moisture status. Both the peaty gley and peaty podzol profiles show fluctuations in soil moisture regime and changes in soil water Mn concentration. These increases in Mn concentration occur in the deepest horizon monitored within each profile and do not seem associated with any particular alterations in soil moisture status. Although the largest Mn concentration in the deep (Bs) horizon of the peaty podzol was recorded after several drying periods, rewetting occurred after each one without producing any other Mn peaks. It may be, however, that the timing of sample collection failed to coincide with the required conditions. Another reason may be that the drying recorded within catchment soils never occurred to the extent required to release large concentrations of Mn on rewetting.

One noticeable feature of data from both organo-mineral profiles (Figures 4.18 & 4.19) is the extremely rapid change in volumetric water content recorded in several of the horizons (peaty gley O2 and Bg; peaty podzol Eh). The effect is present throughout the year and shows no sign of any seasonal influence, with changes during the winter just as rapid as those during the summer. These sudden changes in volumetric water content are usually of 20% or greater and are complete within a matter of hours. Possible explanations for the rapid changes include: earthing problems with the datalogger; power supply problems; thetaprobe malfunction; soil hydraulic behaviour; or the presence of air pockets surrounding the sensing rods. Staff at the Macaulay Institute and Delta-t, who were responsible for developing the thetaprobes, were contacted in an attempt to identify the source of the problem. No definite cause was identified, but all electrical supply and related problems were discounted on the grounds that other thetaprobes connected to the same datalogger (e.g., moorland peaty podzol O and Bs probes) would have been similarly affected (G.Gaskin, Macaulay Institute – pers.comm.). One suggestion from staff at Delta-t was that the soil moisture status was somehow ‘flipping’ rapidly between saturation and field capacity. However, this was discounted as the volumetric water content at the drying end of one of these sudden changes was well below that expected to represent field capacity and the daily evaporation rate required to achieve this value was unrealistic. The most likely explanation for the rapid changes in measured volumetric water content was the presence of sizeable air spaces around the thetaprobe sensing rods, such that the pores would not retain moisture against the pull of gravity. If there were air spaces of a sufficient size around the sensing rods, then these would fill or drain more rapidly than the rest of the pores in the surrounding soil. The volume of water or air filling the space would therefore influence any value of volumetric water content the probe measured. For example, during a drying phase, the large space would drain quickly, leading to a rapid decrease in volumetric water content of the soil volume measured by the thetaprobe. Once the void had drained, changes in measured volumetric water content would only result from draining of the smaller soil pores, producing a more gradual decrease in volumetric water content. Such a pattern is perhaps most clearly seen in the graph of volumetric water content from the intermediate (Bg) horizon of the peaty gley at moorland site two (Figure 4.18). The discovery of an air space around the sensing rods of the thetaprobe in the shallow (O2) horizon of moorland site two, during equipment removal upon completion of the field monitoring programme, supports this theory. However, no similar gaps were found at any of the other sites, although it is possible that the thetaprobe rods intercepted macropores behind the face of the soil pit as they were pushed into the soil during installation, or that macropores were formed due to disturbance of the soil resulting from installation of equipment at the field sites. Therefore, gaps of this nature would not be discovered upon equipment removal, as the macropore lay beyond the end of the installation hole. Whatever the explanation for the anomalous behaviour, it is apparent that data from these horizons should be treated with caution.

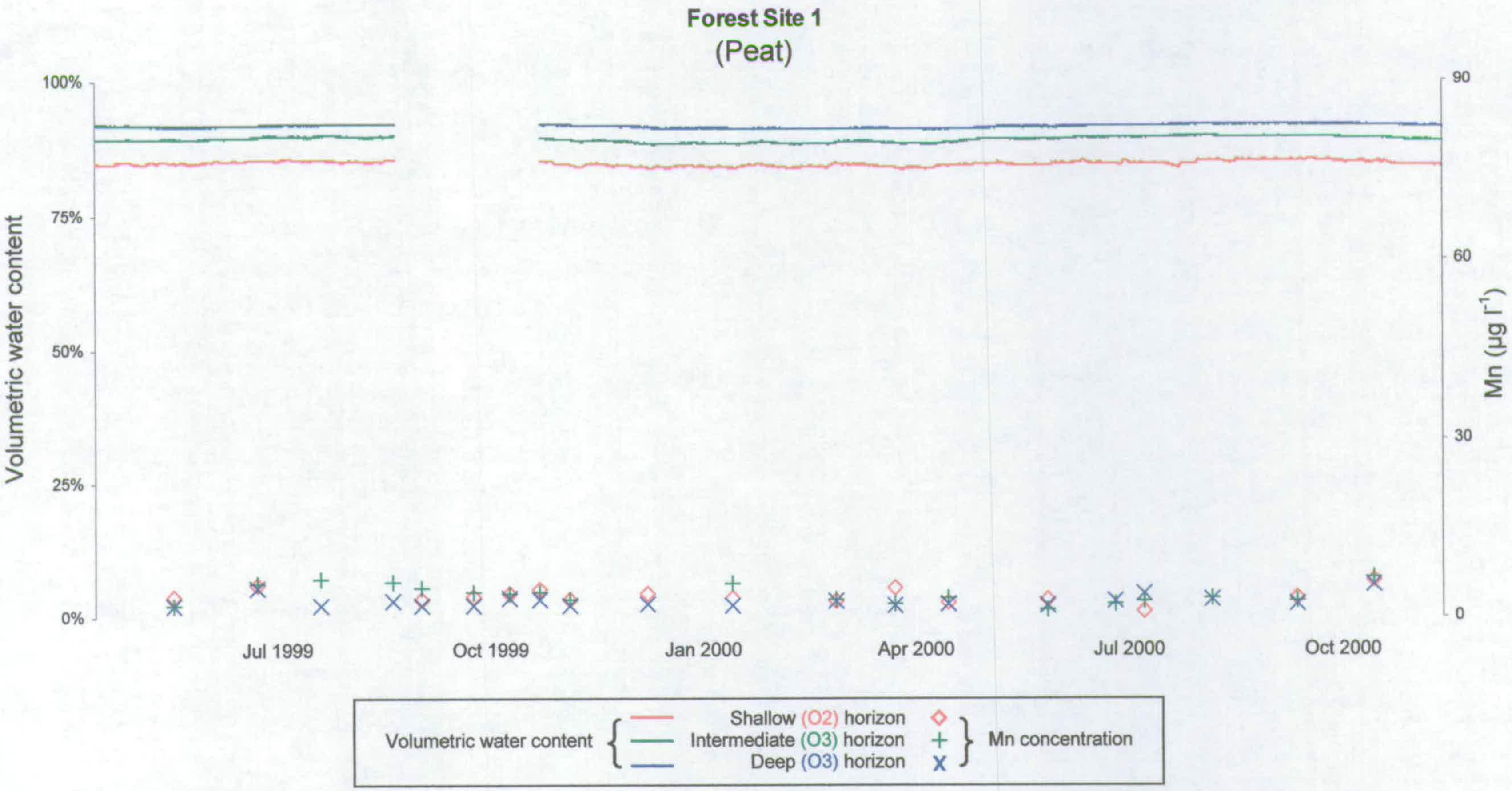


Figure 4.14: Volumetric water content and mean soil water Mn concentrations of monitored soil horizons from forest site 1 (peat)

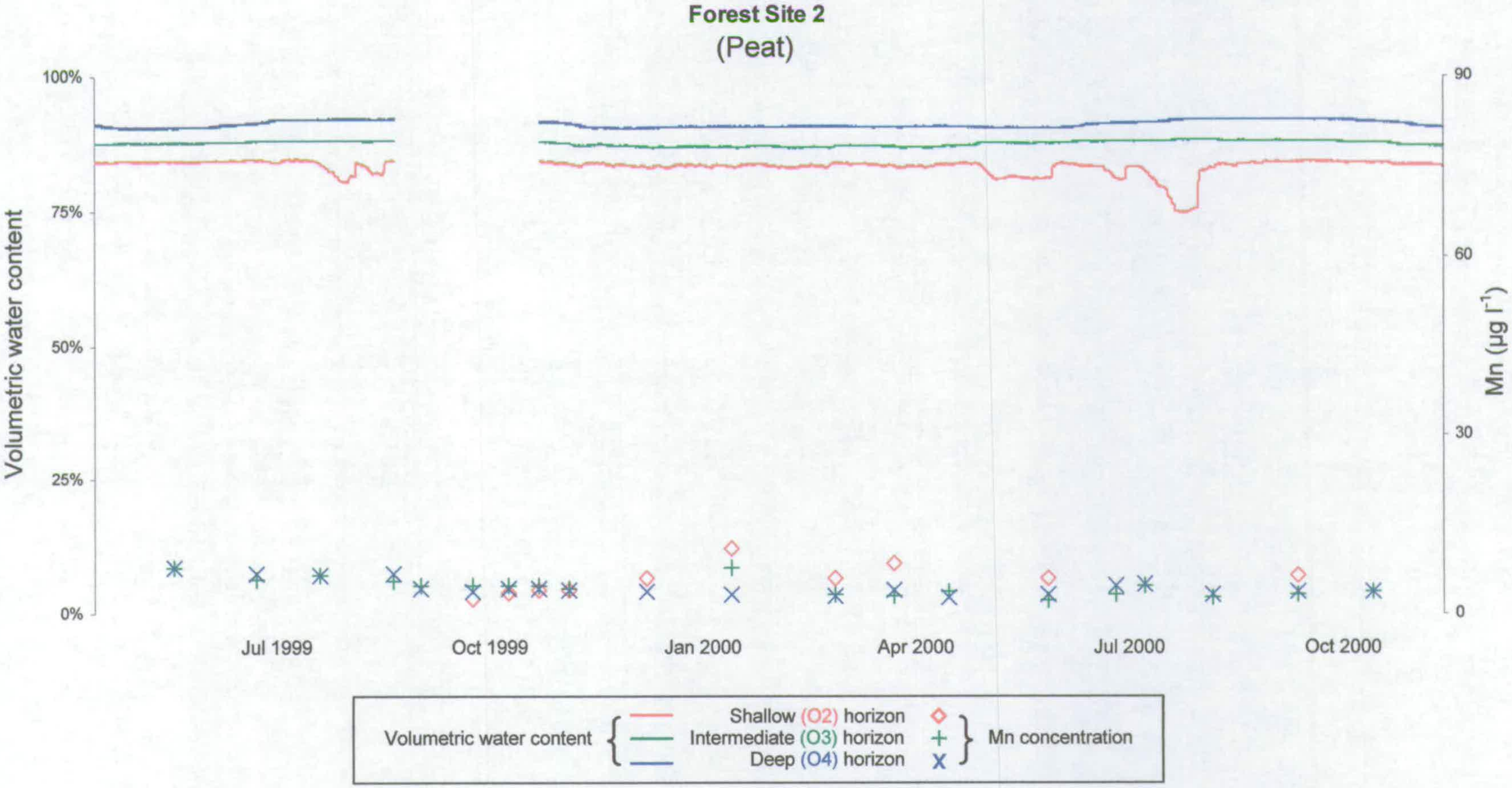


Figure 4.15: Volumetric water content and mean soil water Mn concentrations of monitored soil horizons from forest site 2 (peat)

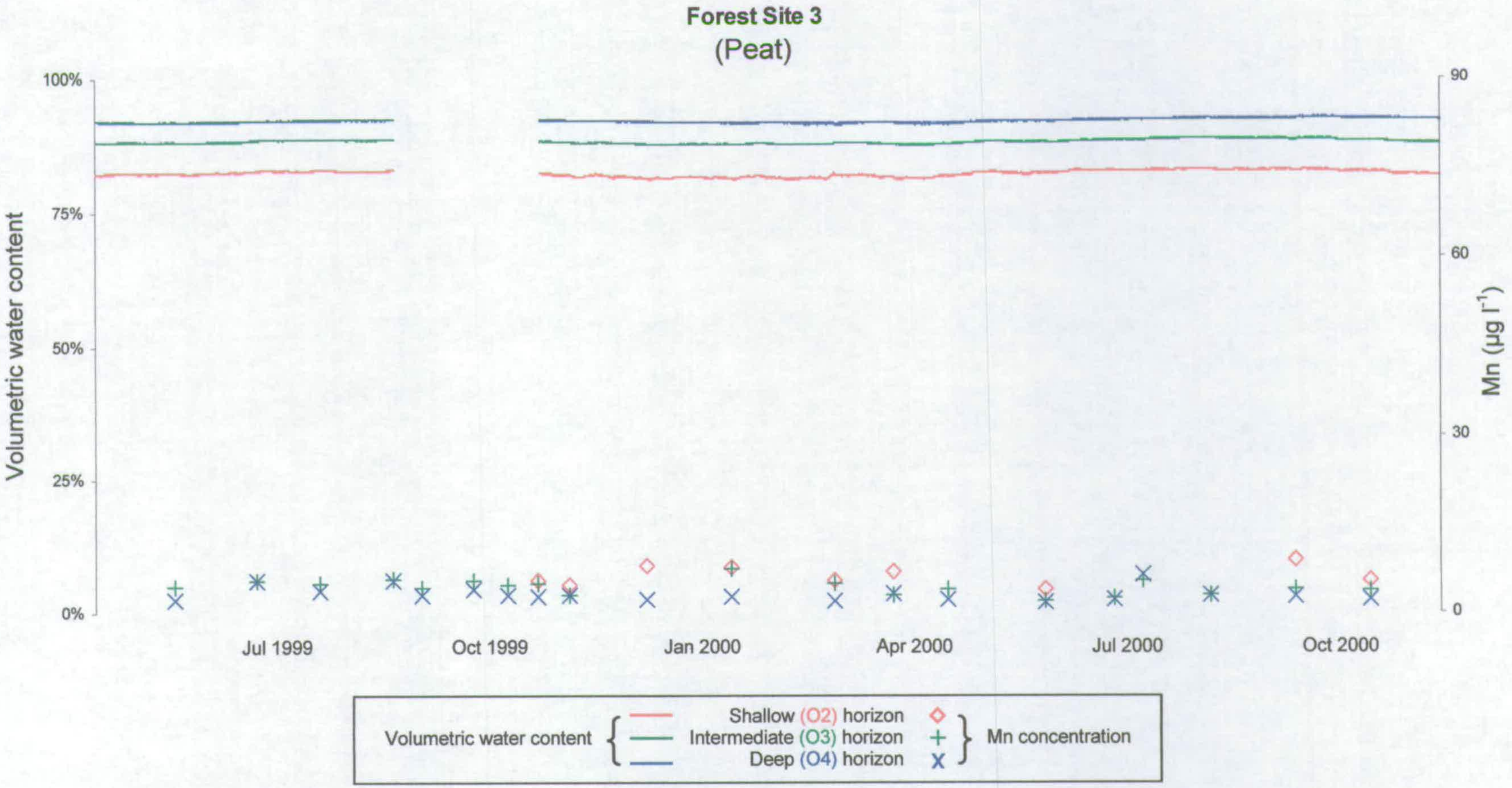


Figure 4.16: Volumetric water content and mean soil water Mn concentrations of monitored soil horizons from forest site 3 (peat)

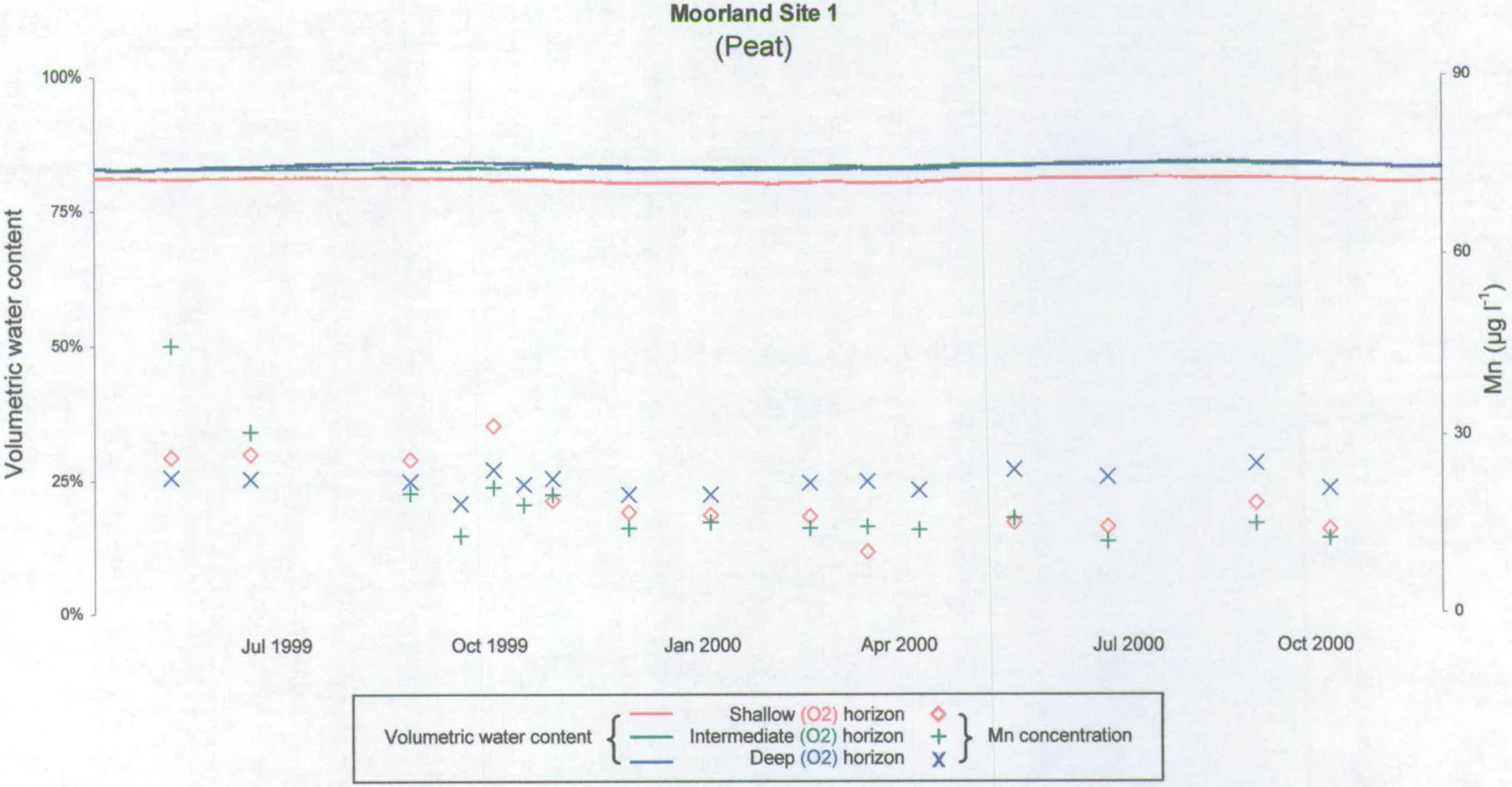


Figure 4.17: Volumetric water content and mean soil water Mn concentrations of monitored soil horizons from moorland site 1 (peat)

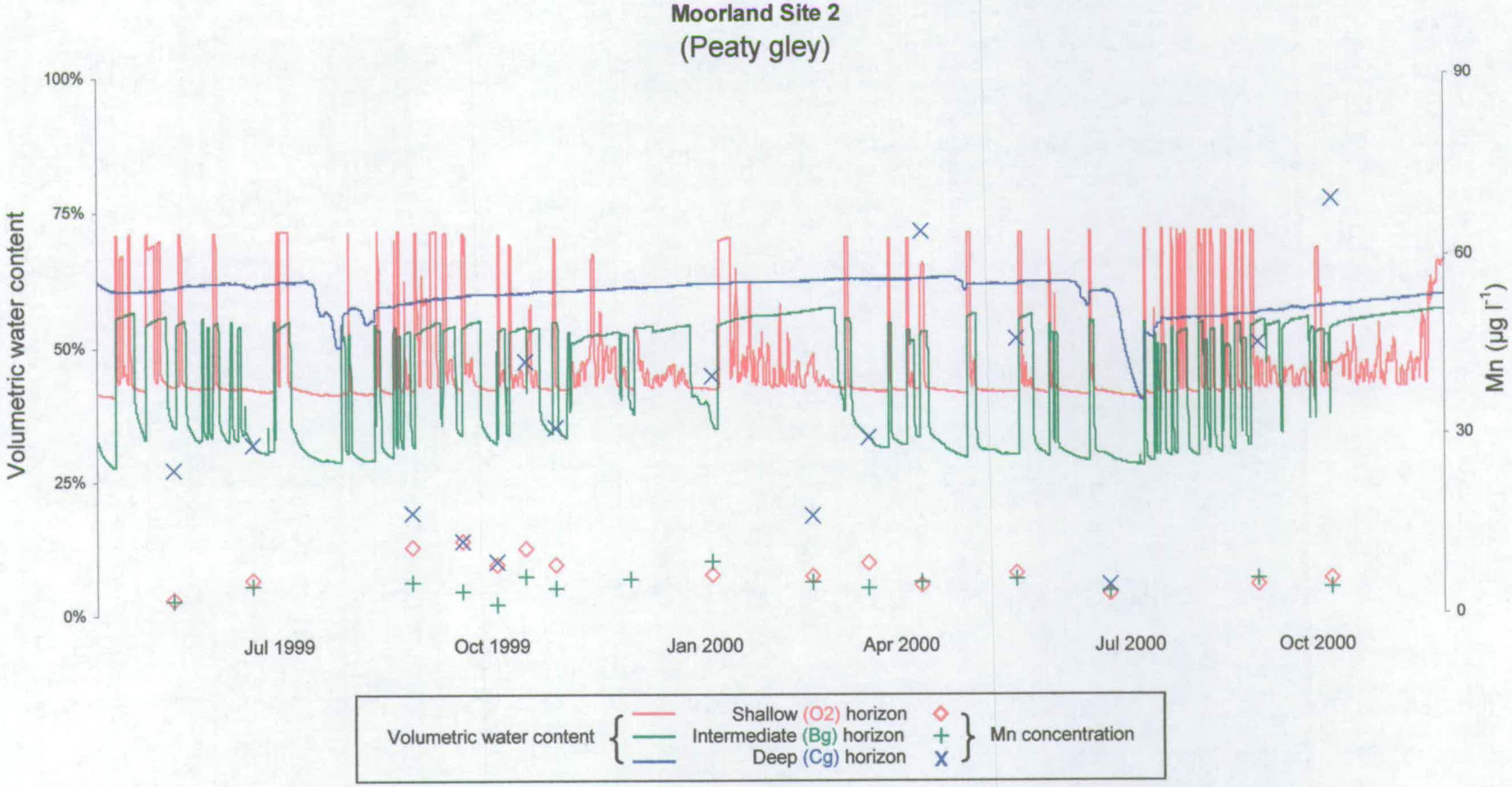


Figure 4.18: Volumetric water content and mean soil water Mn concentrations of monitored soil horizons from moorland site 2 (peaty gley)

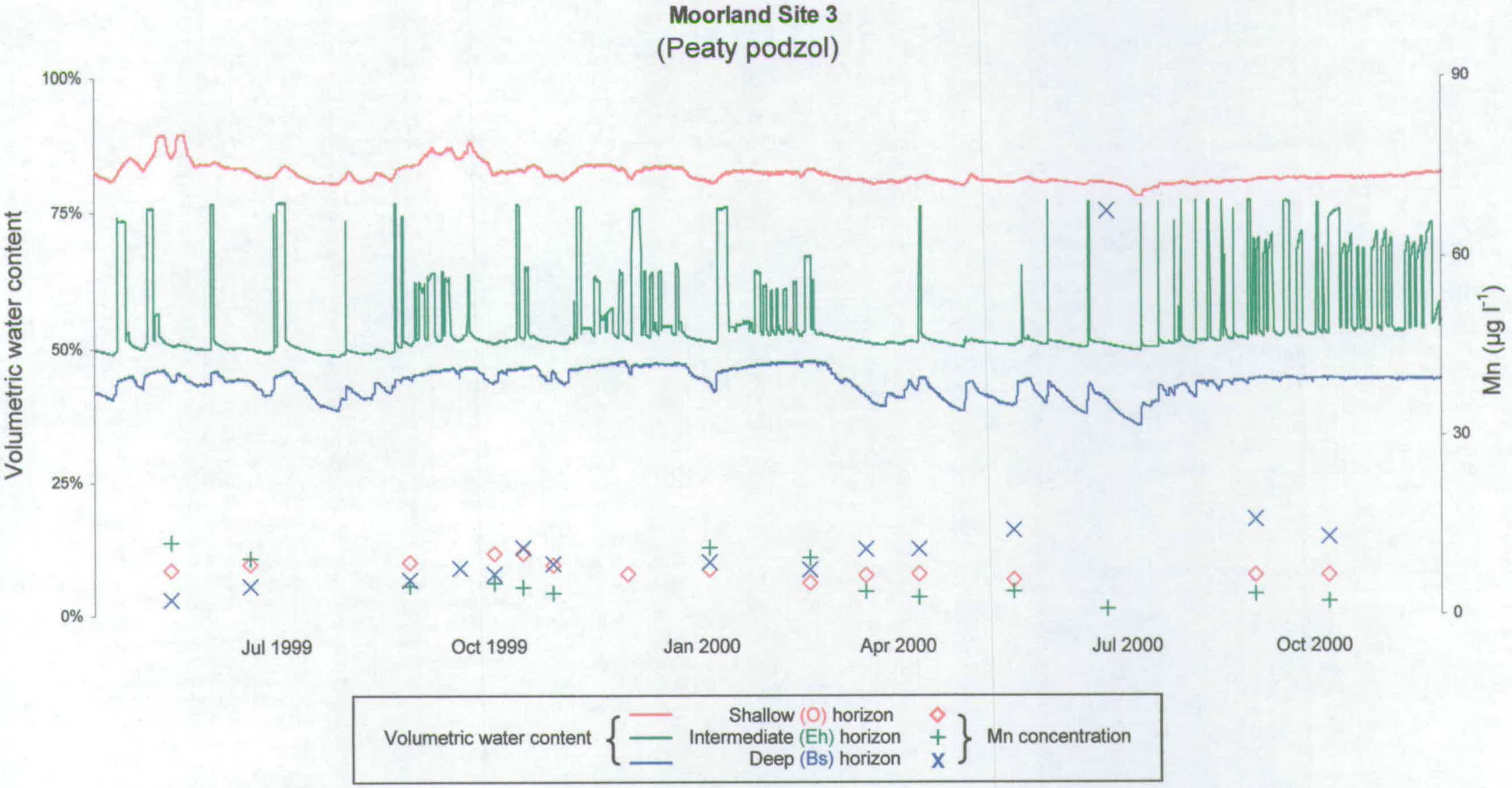


Figure 4.19: Volumetric water content and mean soil water Mn concentrations of monitored soil horizons from moorland site 3 (peaty podzol)

4.1.2.2 Tensiometer data

Tensiometer data are available for the first monitoring season, but not for the second, owing to frost damage following reinstallation after the winter in April 2000. The measurements of matric potential made prior to this event are shown in Figure 4.20, along with mean Mn concentrations of soil water samples collected at the same time. On several occasions, the tensiometers installed in the deep peats showed a positive matric potential. However, the gauges used were not designed to read in this direction and were unable to indicate the magnitude of this pressure. Therefore, these points have been arbitrarily assigned slightly positive values on the graphs in order to differentiate them from points where the gauges read zero. These positive readings were not thought to result from calibration problems, as all of the tensiometer gauges had been corrected to account for the head of water in their tubes prior to installation.

The data for the peat sites show that there is greater fluctuation in soil matric potential than in the volumetric water content recorded by the thetaprobes (Figures 4.17 to 4.19). Distinct summer drying phases, when matric potential falls as low as –60 kPa, were recorded in the shallow horizon of the forest peat. The peaty gley and peaty podzol also exhibited variation in their matric potential time series, which, in common with the peat sites, showed a decrease in soil matric potential during the summer. However, rather than being limited to the shallow horizon, the drying occurred in all horizons of the organo-mineral soils monitored, with a maximum matric potential of –80 kPa recorded in the peaty gley shallow (O2) and peaty podzol intermediate (Eh) horizons. In contrast to the other soil profiles monitored, where the largest matric potentials were recorded in the shallow horizons, the greatest drying in the peaty podzol took place within the intermediate (Eh) and deep (Bs) horizons.

The tensiometer data indicate that changes in soil matric potential were recorded in the peats during periods when little or no change in volumetric water content was recorded by the thetaprobes. For example, at forest site two a fall in volumetric water content of approximately 3-4 % (Figure 4.15) was recorded over the same period that a 40 kPa fall in matric potential was measured. This difference in the magnitude of response is due to the shape of the soil moisture release characteristic, meaning that when soils are at or near saturation, small changes in volumetric water content equate to large changes in matric potential. Therefore, matric potential may be a better measure of changes in soil water status than volumetric water content when considering the saturated peat soils. However, there

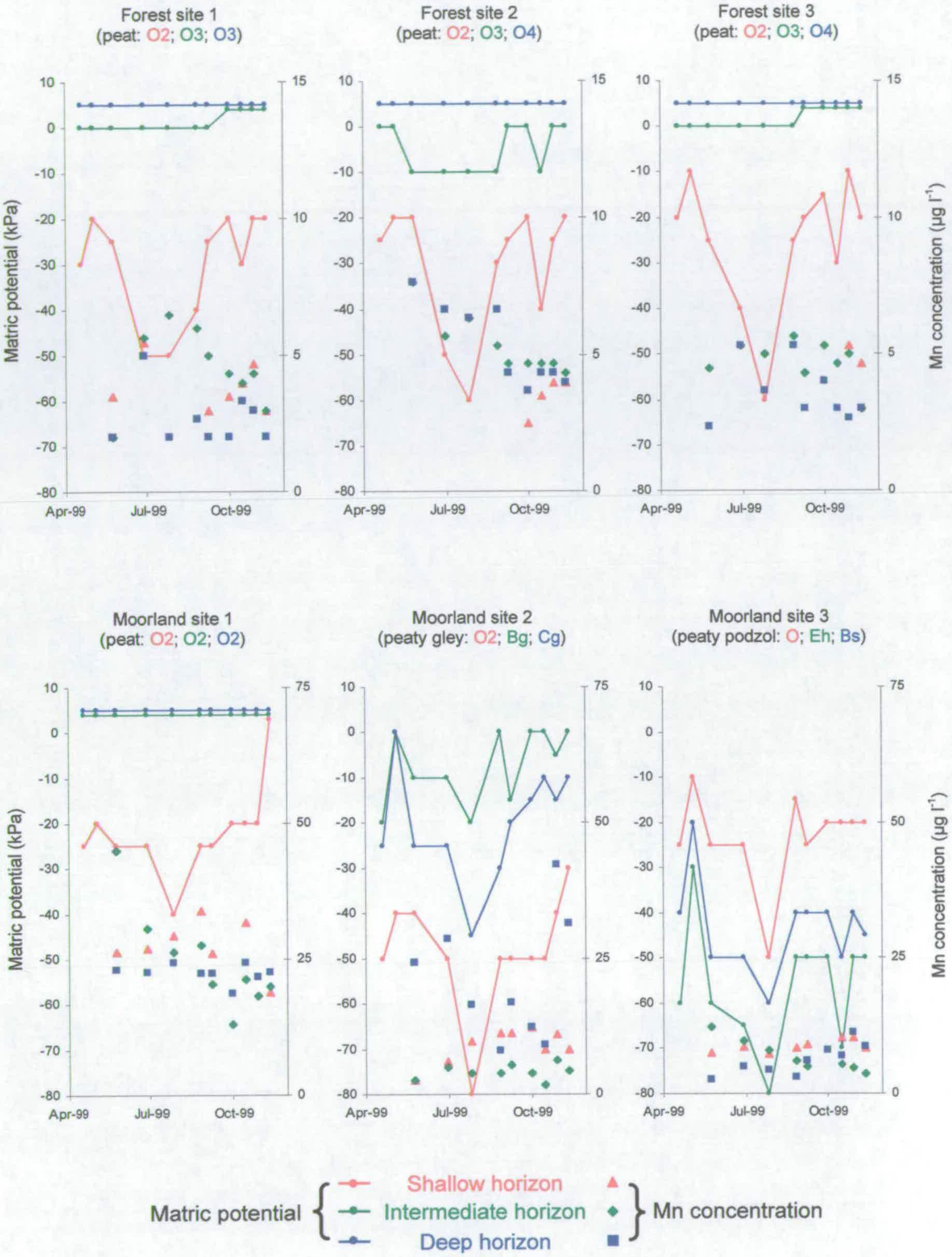


Figure 4.20: Soil matric potential and soil water Mn concentration at primary field sites, April 1999 – November 1999

N.B. Graph scale for Mn concentration differs between forest and moorland

were no increases in Mn concentration of soil water samples from any horizons during the periods immediately following rewetting as indicated by changes in soil matric potential.

4.1.3 Stream water chemistry

Water samples were collected from 12 points along the Ballochbeatties Burn drainage network on each sampling visit and analysed for the same chemical determinands as the soil water samples. It was anticipated that these would show the progression of any increases in soil water metal concentrations from catchment soils into the stream feeding Loch Bradan reservoir, thereby providing a link between soil water and reservoir water Mn concentrations.

4.1.3.1 Graphical analysis of stream water chemistry data

Data from these sampling points, the locations of which have already been described in section 3.3 and Figure 3.7, are presented in two formats. The first set of graphs (Figures 4.21 & 4.22) show mean values for all sample points, while the second set (Figures 4.23 to 4.34) show time series for each sampling point.

The relative concentrations of total and soluble metals provide an indication of how much Mn, Fe or Al was in the form of molecules greater than 0.45 μm in size. Whether this was as organic or inorganic complexes, aggregates of oxides, or simply associated with suspended sediments was not quantified. However, the data do show considerable differences between total and soluble metal concentrations, particularly in samples taken from the drainage ditches (sample points BB9-12). The difference between total and soluble metal concentrations is far greater than that observed in samples of soil water. This may indicate that the principal route for Mn transport into Loch Bradan is in the form of particulate matter suspended in stream water, rather than as free soluble ions. However, it is also likely that much of the difference between stream water and soil water total:soluble metal ratios is due to the filtering effect of the porous ceramic cups on the soil water collected.

The graphs of mean metal concentration for each sampling point (Figure 4.21) show greater concentrations in the final four points of the main channel (BB5-8) relative to the first four (BB1-4). Much of this increase may be due to the input of water from the drainage ditches (BB9-12), which enters the main channel just before point BB5. Both pH and colour (Figure 4.22) alter markedly along the length of Ballochbeatties Burn. The pH of samples decreased downstream in the main channel (BB1-8), while colour increased. Again, in the

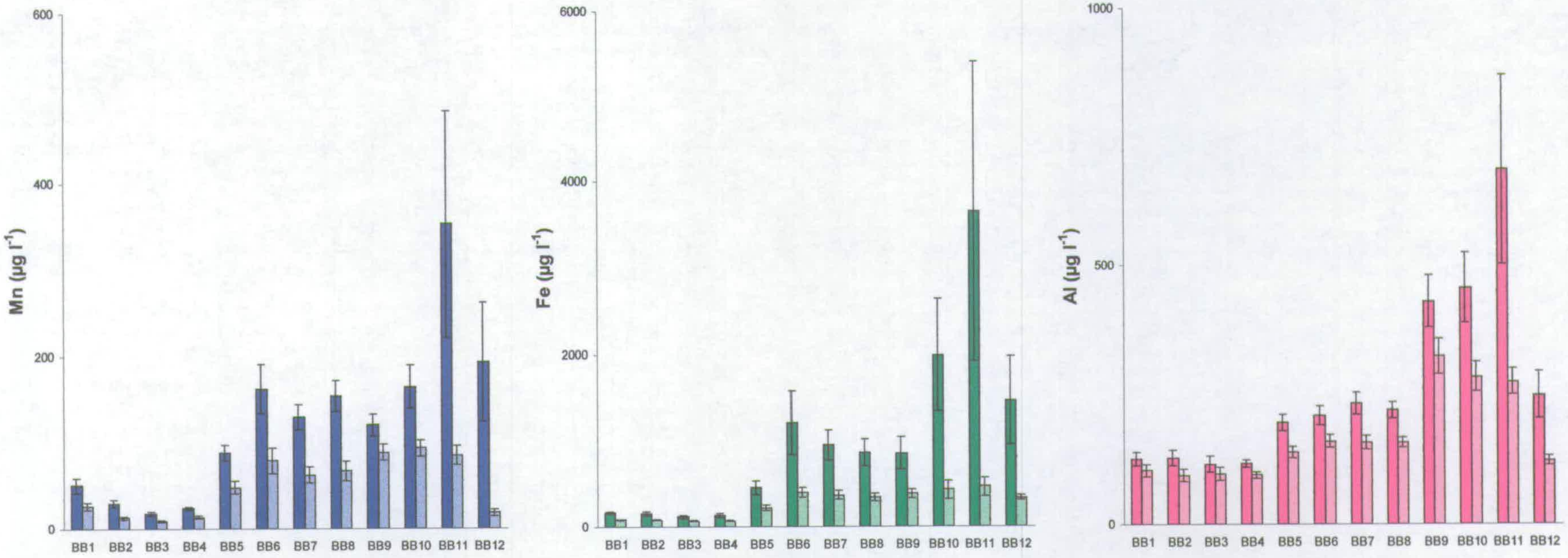


Figure 4.21: Mean (±SE) Mn, Fe & Al concentrations of stream water samples from Ballochbeatties Burn (December 1998 – October 2000) Darker bars indicate total metals, lighter bars indicate soluble metals concentration

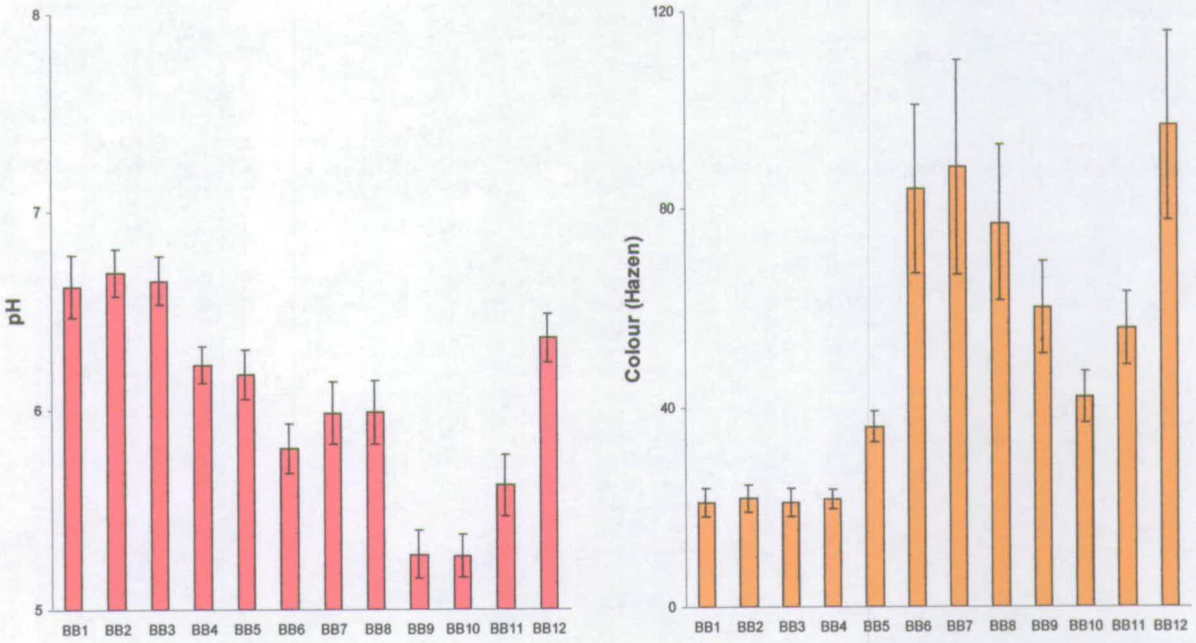


Figure 4.22: Mean (±SE) pH & colour of stream water samples from Ballochbeatties Burn (December 1998 – October 2000)

case of pH, this may partly be a result of input from the drainage ditches, although there is evidence for a fall in pH prior to this (point BB4). The largest increase in colour however, occurs between points BB5&6, when the burn flows through an area of forest planted on deep peat. One explanation for the increase in colour, and corresponding fall in pH, at this point may be the inputs of acidic organic matter from the surrounding peat.

Overall, metal concentrations in the main stream channel appear to increase downstream, whilst pH decreases and the colour of stream water samples increases. The increased afforestation of the lower reaches of the catchment may reduce pH due to acidic inputs from decaying forest litter, thus mobilising more metal ions in solution. These organic products may also increase the colour of water samples and act as chelating agents for some metal ions, thereby further increasing the degree of mobilisation. Increased metal concentrations in streams draining afforested catchments, relative to those draining moorland, have been reported by several other studies (e.g., Farley & Werrity, 1989; Heal, 2001; Neal *et al.*, 1992).

Samples from the larger of the two drainage ditches (BB9-11) were more acidic and contained more metal ions and colour than water in the main burn prior to the confluence. The relative acidity of samples from this ditch, and associated greater concentration of soluble metals, was possibly due to acidic runoff from afforested soils, as the ditch contained water draining from the largely forested western part of the catchment. Samples from the smaller drainage ditch (BB12) appear to have similar chemistry to samples from the lower reaches of the main channel. However, flow in this ditch was often negligible and therefore, the water chemistry may not be wholly representative of that found in the rest of the Ballochbeatties Burn system.

Time series graphs (Figures 4.23 to 4.34) generally suggest a summer maximum of metal concentration, associated with an increase in colour. This is most recognisable at sampling points BB7 and BB8 (Figures 4.29 & 4.30), which were situated nearest the burn's entrance to Loch Bradan. Although the stream water data appear to indicate that reservoir Mn concentrations should have increased greatly during the summers of 1999 and 2000, this was not recorded in samples of reservoir water collected at the treatment works (see Figure 3.2). There was however a slight increase in reservoir Mn concentrations towards the end of the summer in both years, although this increase occurred approximately two months after the maximum concentrations were recorded at the final point of the main stream

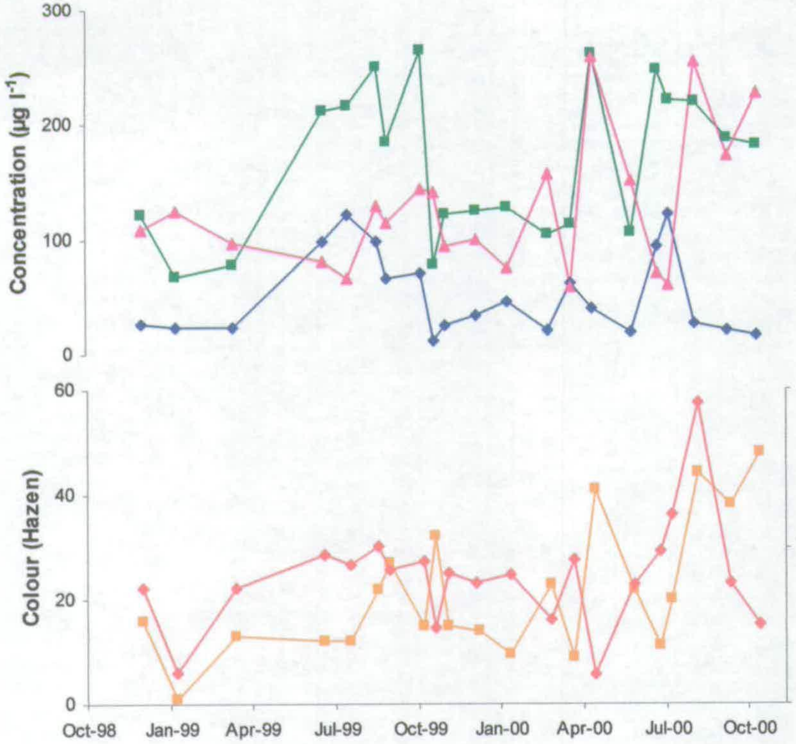


Figure 4.23: Chemistry of stream water samples from Ballochbeatties Burn point BB1

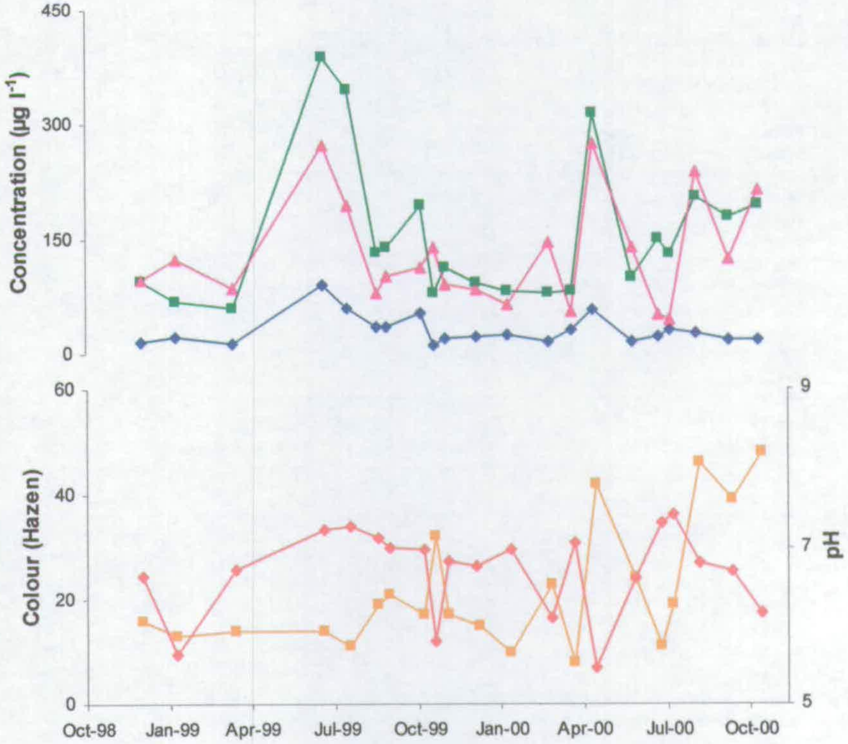


Figure 4.24: Chemistry of stream water samples from Ballochbeatties Burn point BB2

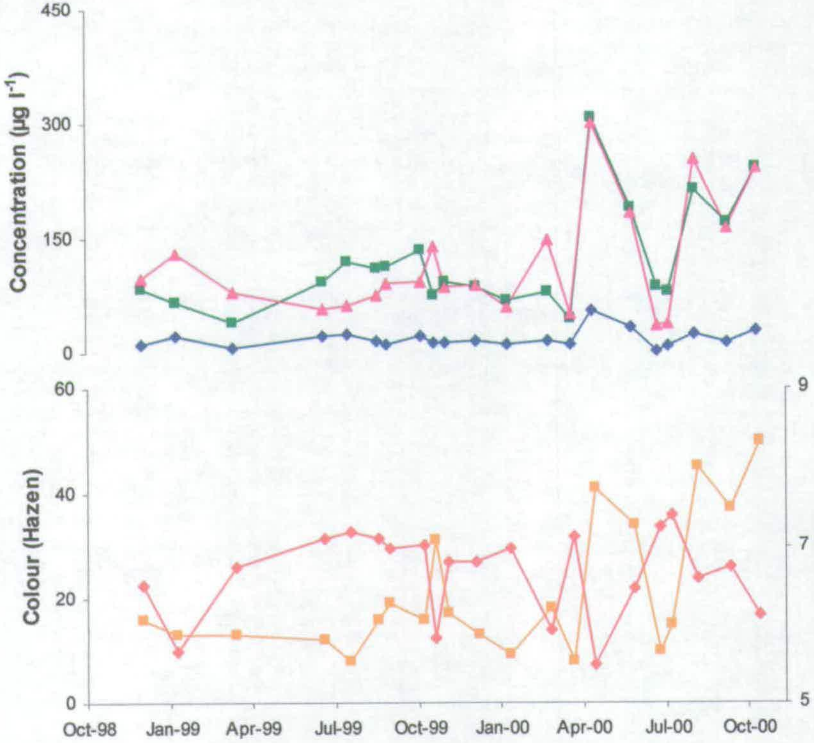


Figure 4.25: Chemistry of stream water samples from Ballochbeatties Burn point BB3

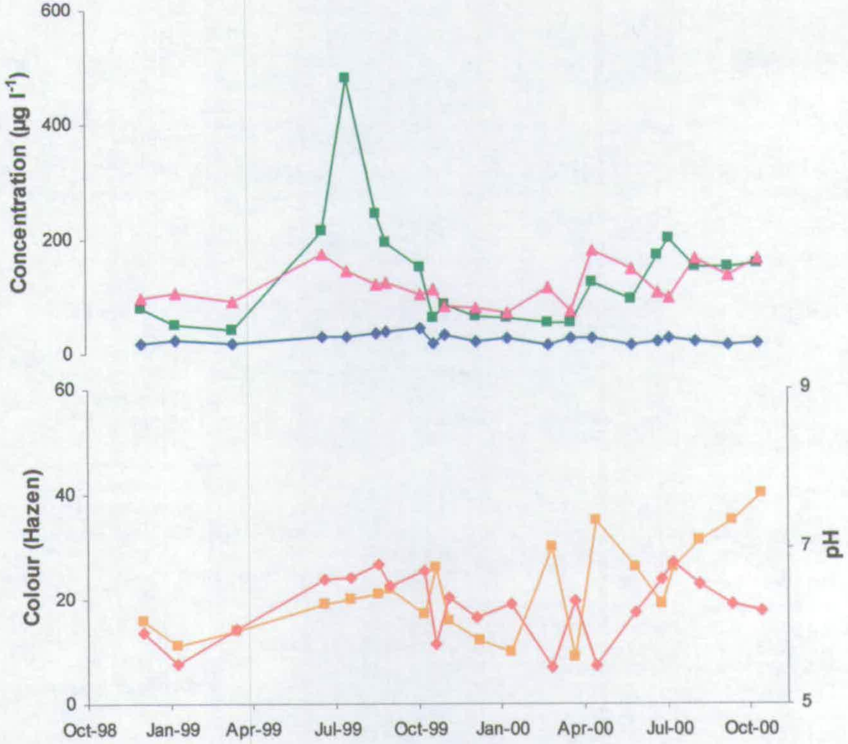


Figure 4.26: Chemistry of stream water samples from Ballochbeatties Burn point BB4

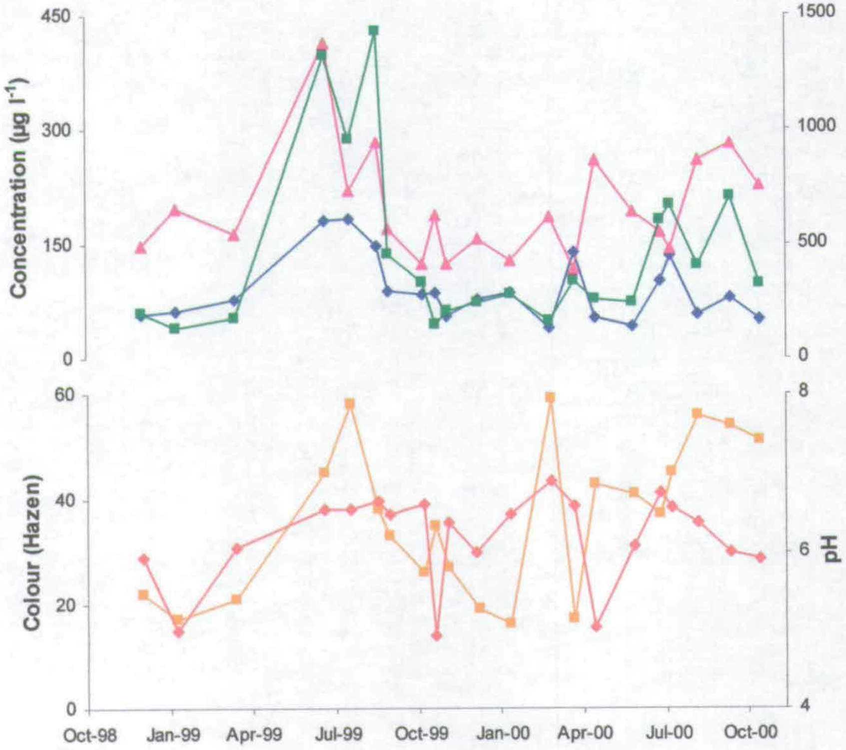


Figure 4.27: Chemistry of stream water samples from Ballochbeatties Burn point BB5

NB: Fe data plotted on second y-axis

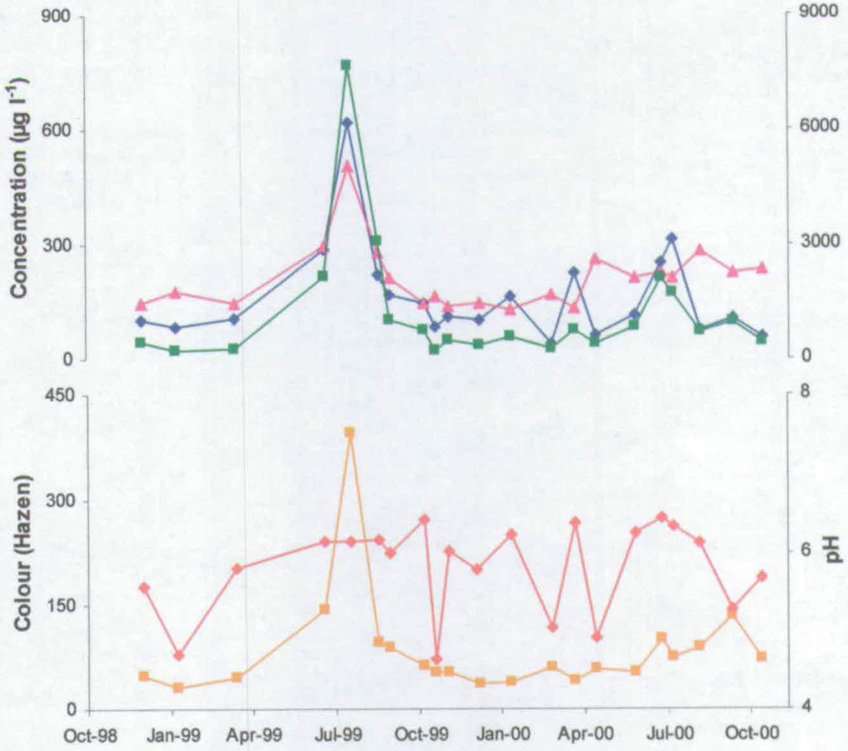


Figure 4.28: Chemistry of stream water samples from Ballochbeatties Burn point BB6

NB: Fe data plotted on second y-axis

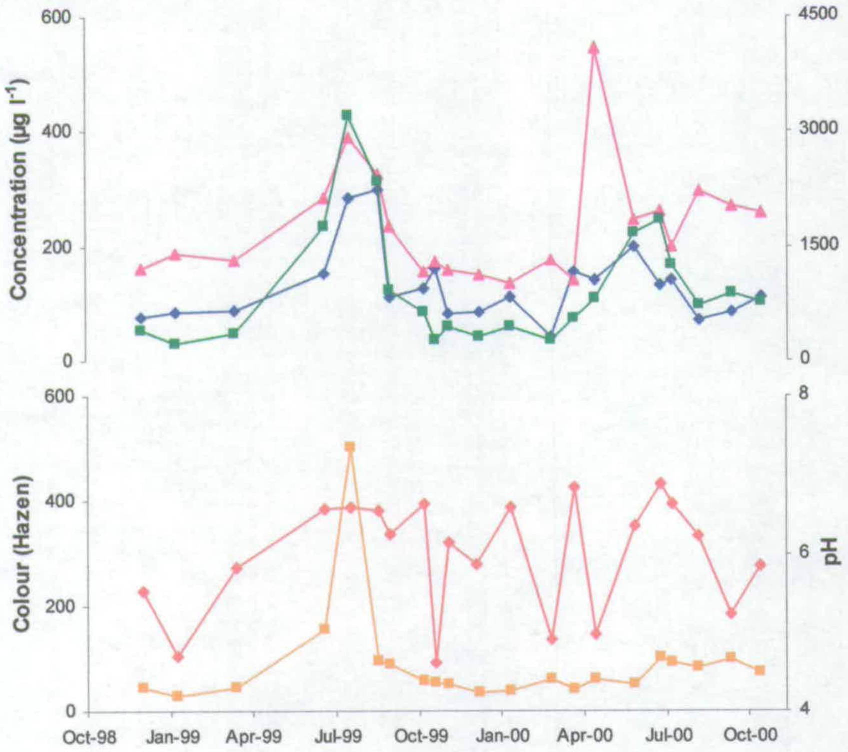


Figure 4.29: Chemistry of stream water samples from Ballochbeatties Burn point BB7

NB: Fe data plotted on second y-axis

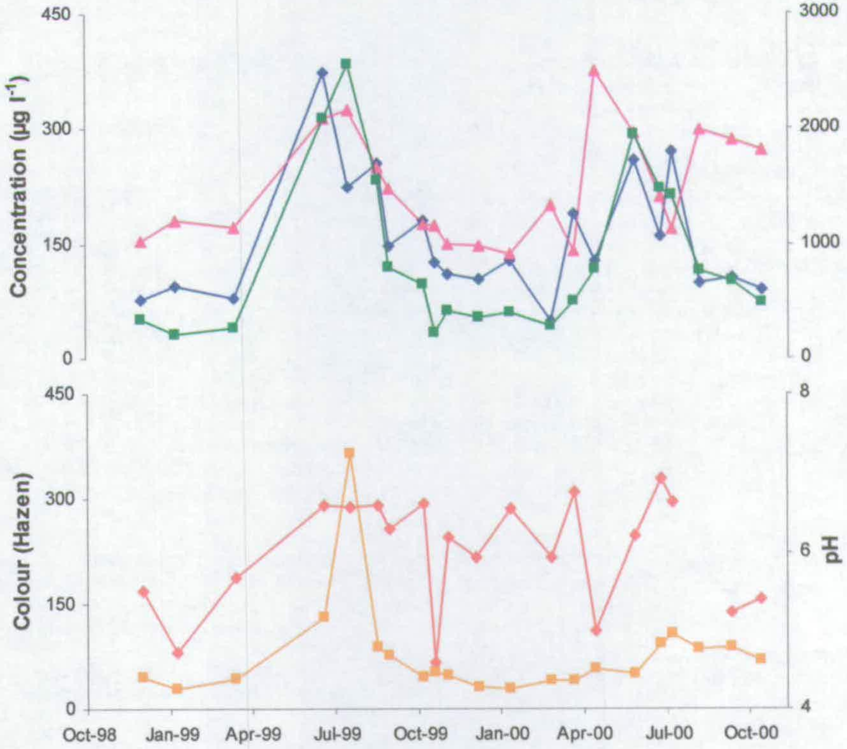


Figure 4.30: Chemistry of stream water samples from Ballochbeatties Burn point BB8

NB: Fe data plotted on second y-axis

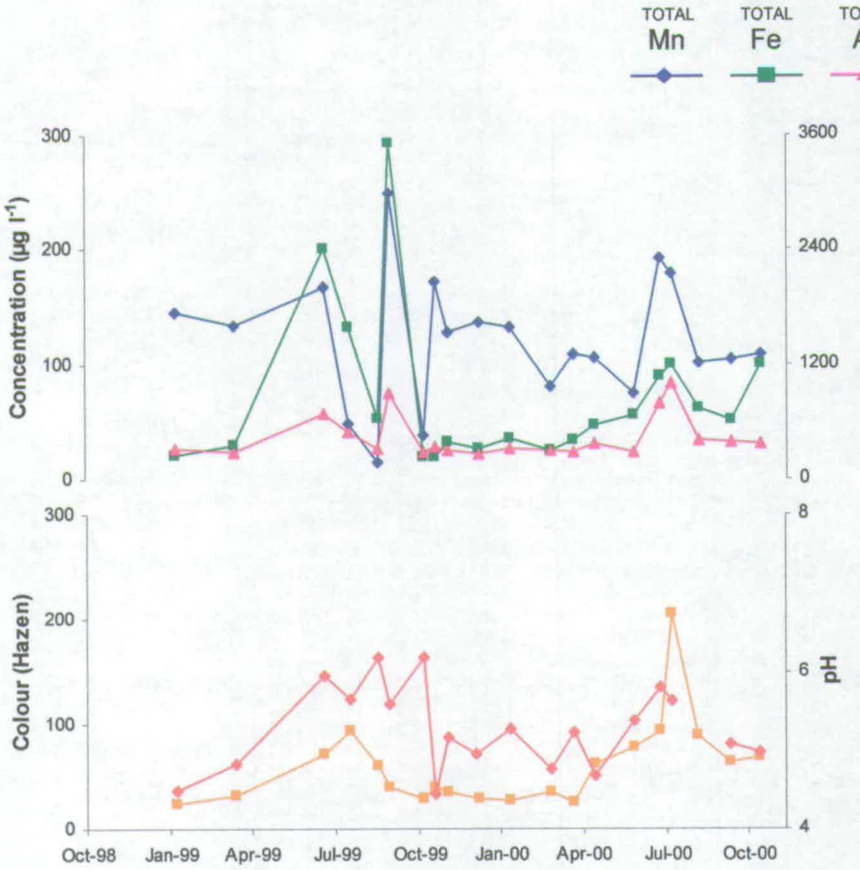


Figure 4.31: Chemistry of stream water samples from Ballochbeatties Burn point BB9

NB: Fe & Al data plotted on second y-axis

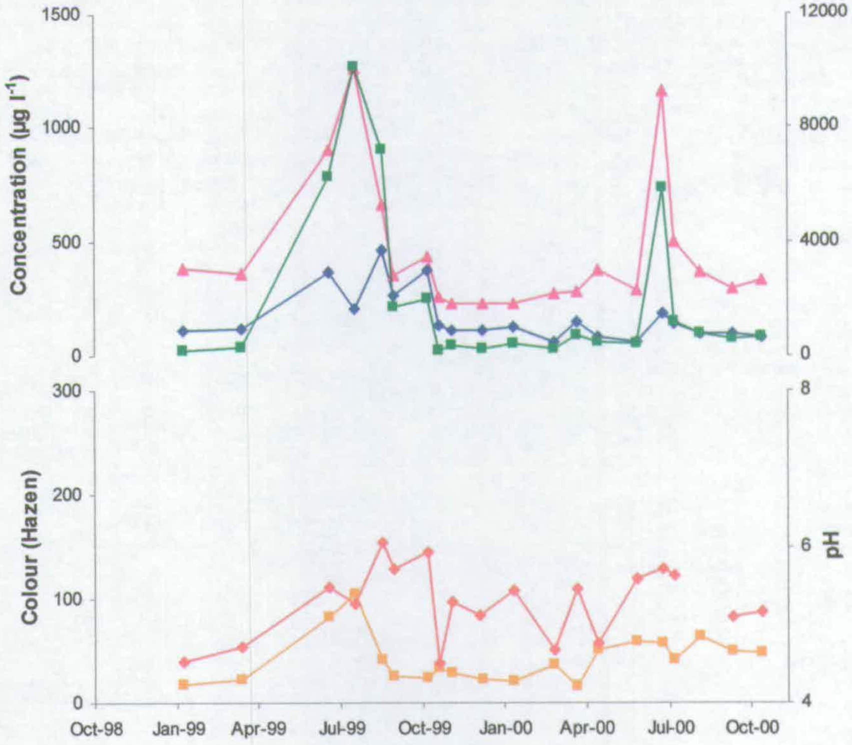


Figure 4.32: Chemistry of stream water samples from Ballochbeatties Burn point BB10

NB: Fe data plotted on second y-axis

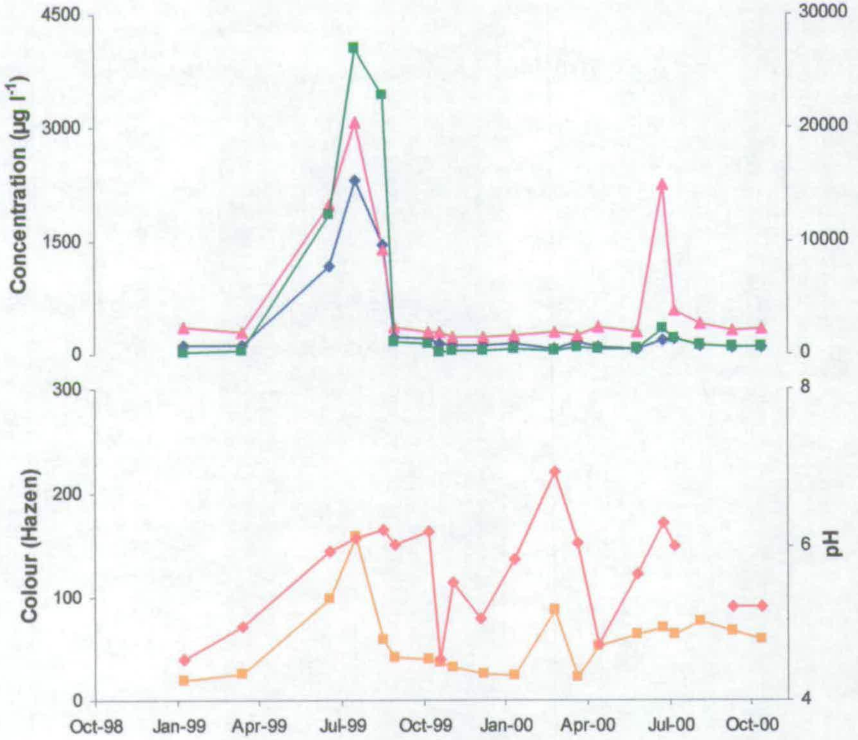


Figure 4.33: Chemistry of stream water samples from Ballochbeatties Burn point BB11

NB: Fe data plotted on second y-axis

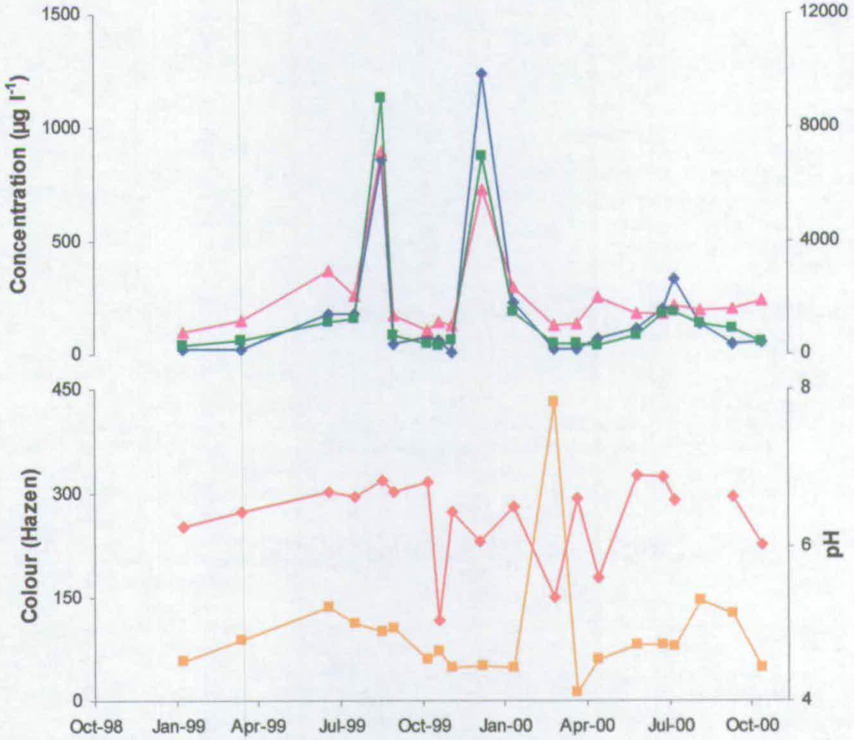


Figure 4.34: Chemistry of stream water samples from Ballochbeatties Burn point BB12

NB: Fe data plotted on second y-axis

(BB8 - Figure 4.30). It is possible that the low discharge in the burn during the period in which maximum Mn concentrations were measured meant that the actual Mn loading entering the reservoir may not have been much different to other times of year.

There appears to be an inverse relationship between pH and colour of stream water from the upper four sampling points, BB1-4 (Figures 4.23 to 4.26). On several occasions during the field monitoring programme, the first of which occurs during October 1999, there is a distinct increase in stream water colour associated with a decrease in pH. Such events may indicate different sources of runoff feeding the stream, with the organic-rich, acidic runoff originating from shallow horizons and the less coloured, less acidic runoff from deeper horizons of the moorland soils.

The stream water chemistry data also show that the Mn concentrations in stream water are generally far greater than those in the soil water samples. Aside from large peaks in the soil water data, the stream water samples often contain Mn concentrations at least an order of magnitude greater than samples collected by the suction probes. This difference is most marked when comparing soil water samples from the forest peat field sites with stream water collected nearby in Ballochbeatties Burn. In these cases, Mn concentrations in the stream water can be approximately one hundred times greater than those in the soil solution.

4.1.3.2 Statistical analysis of stream water chemistry data

Stream water chemistry data were analysed in order to determine whether any correlation existed between chemical determinands. Data for all metal concentrations, plus colour, were $\log_{10}$ transformed to provide sample populations with a distribution that approximated to the normal distribution. Table 4.8 shows the results of the correlation (Pearson product moment), performed using the Minitab v12.1 computer program.

The results in Table 4.8 show that the statistical evidence confirms the trends suggested by the graphical evidence. Metal concentrations are all significantly positively correlated with sample colour, and most are negatively correlated with sample pH. The one exception to this is total Fe, which is not significantly correlated with pH ($p=0.2$). Possible explanations for the lack of correlation between total Fe and pH include erosion events or the adsorption of Fe onto stream sediment, thereby altering the stream water Fe concentration regardless of pH. The degree of inter-correlation between metal concentrations suggests that metals are mobilised at the same time and under the same conditions. However, the strength of correlation between colour and each form of Mn suggests that, while total Mn concentration and colour in stream water show very similar responses to changes in environmental conditions, soluble Mn concentration may be influenced by slightly different processes.

	Mn-sol	Fe-tot	Fe-sol	Al-tot	Al-sol	pH	Colour
Mn-tot	**0.523**	**0.847**	**0.752**	**0.693**	**0.437**	**-0.235**	**0.528**
Mn-sol		**0.282**	**0.434**	**0.385**	**0.471**	**-0.575**	**0.179**
Fe-tot			**0.874**	**0.790**	**0.478**	-0.083	**0.719**
Fe-sol				**0.712**	**0.617**	**-0.268**	**0.772**
Al-tot					**0.823**	**-0.429**	**0.617**
Al-sol						**-0.655**	**0.558**
pH							-0.181

Table 4.8: Correlation coefficients for stream water chemistry (n=248)
(p<0.01 ; **p<0.001**; p>0.1)

4.1.4 Secondary field sites

Following analysis of the first eight months' field results, the decision was taken to partially instrument a further three soil water sampling sites within the catchment. The reasoning behind this was that samples of soil water from the existing six sites had not contained the expected high concentrations of Mn, as previously discussed in section 3.6, and contained considerably less Mn than the concentrations measured in stream water samples from Ballochbeatties Burn. The possibility existed that Mn release to stream water and thence the reservoir could be the result of mobilisation from discrete locations, rather than a general mobilisation throughout the catchment soils. In order to release large concentrations of Mn into soil water, a soil horizon must first contain an appreciable pool of Mn to be mobilised and then undergo a period when conditions favour the mobilisation. For example, if the initial sample sites had been installed in areas where there was little soil Mn, then this could mean that samples collected from them might not reflect changes in Mn status found in areas of greater concentrations. At the very least, identification of any seasonal Mn peak in soil water would be far more difficult at low concentrations. Furthermore, by partially instrumenting an additional three field sites, the number of soil and land use combinations investigated within the catchment was increased.

4.1.4.1 Site locations

The three secondary sites were installed in locations within the Ballochbeatties Burn catchment that extended the range of land use and soil type interactions studied. These were chosen based on results from Law (1999), which identified several areas in the Ballochbeatties Burn catchment with exceptionally high Mn concentrations in soil water. These data were collected after the initial site installation and so were not used to determine the location of the six primary field sites. The secondary site locations and descriptions have been previously detailed in section 3.6 and Tables 3.3 & 3.4.

4.1.4.2 Soil water chemistry

Soil water chemistry data from these secondary sites are available between June and December 2000, when the field monitoring project ended (Figures 4.35 to 4.38). The short length of the time series prevents any firm conclusions being drawn as to seasonal aspects of soil water chemistry. Gaps in the record of sample colour appear owing to the loss of samples in the WoSW laboratory, and further data are missing because of equipment failure in the forest site intermediate horizon. However, the secondary sites did provide proof that soil water Mn concentrations considerably in excess of the drinking water standard existed in the Loch Bradan catchment.

The most striking feature of the Mn graphs from the secondary field sites (Figure 4.35) is the extremely high concentrations recorded in samples from all horizons of the clear-felled site. Soil water from this site contained Mn in concentrations 100-1000 times greater than samples from the six primary field sites. Samples from the peat alluvium at moorland site four also contained greater Mn concentrations than any of the primary sites, although not as high as those from the clear-felled site. Mn concentrations in soil water from the peaty gley at forest site four were similar to those from the moorland peaty gley site.

Fe concentrations in soil water (Figure 4.36) from the three secondary field sites were far greater than those from most of the primary sites, with the exception of moorland site one. Moorland site four and the clear-felled site appear to have a similar range of Fe concentrations to moorland site one, although the maximum concentration occurs in the intermediate horizon rather than the shallow horizon. However, high Fe concentrations only occur in the shallow (O) horizon of forest site four, with samples from both the intermediate (Bg) and deep (Cg) horizons containing little Fe.

The concentration of Al in soil water from the monitored horizons of the three secondary field sites (Figure 4.37) appears similar to soil water samples from the primary sites. However, the distribution of concentrations with depth is somewhat different to the primary sites. Both moorland site four and the clear-felled site had most Al in soil water from the deep (O2 & O3 respectively) horizon, whereas the greatest Al concentrations were observed in samples from the intermediate (O3) horizons of the primary forest sites and in the shallow (O2) horizon of moorland site one.

As with the primary field sites, it is only possible to identify relative patterns in the pH of samples (Figure 4.38) because of doubts surrounding the validity of the absolute measured values. Again, the values seem to be rather high for acidic soils, and the possibility exists that sample pH altered between collection in the suction probe and analysis in the laboratory. Comparison of sample colour (Figure 4.38) between secondary and primary sites is difficult because of the considerable gaps in the secondary site records, although the range of colour seen in secondary site samples appears to be of similar magnitude to that of the primary sites.

A summary of the data for the secondary field sites is shown in Table 4.9. In general, the greatest concentrations of Mn and Fe were found in soil water samples from the clear-felled site and moorland site four. This is possibly connected with the presence of mineral material distributed throughout the peat alluvium profiles at these sites, which could act as a source of metal ions to be mobilised by processes involving the decomposition of organic matter. Another possibility is that, because both the clear-felled site and moorland site four are at the base of slopes, the high Mn and Fe concentrations may result from the accumulation of mobilised metal transported from further uphill (Cassel *et al.*, 2002). One final observation concerning the data from these three sites is that, although Mn and Fe occur in extremely high concentrations in soil water from the clear-felled site, Al concentrations from this site were similar, if not slightly lower, than those from other sites. While this may simply be a consequence of the total Al available in the soil at these sites, it could also result from a greater mobility of Al ions meaning that much of the Al present had already been mobilised from the soil and leached into surface water.

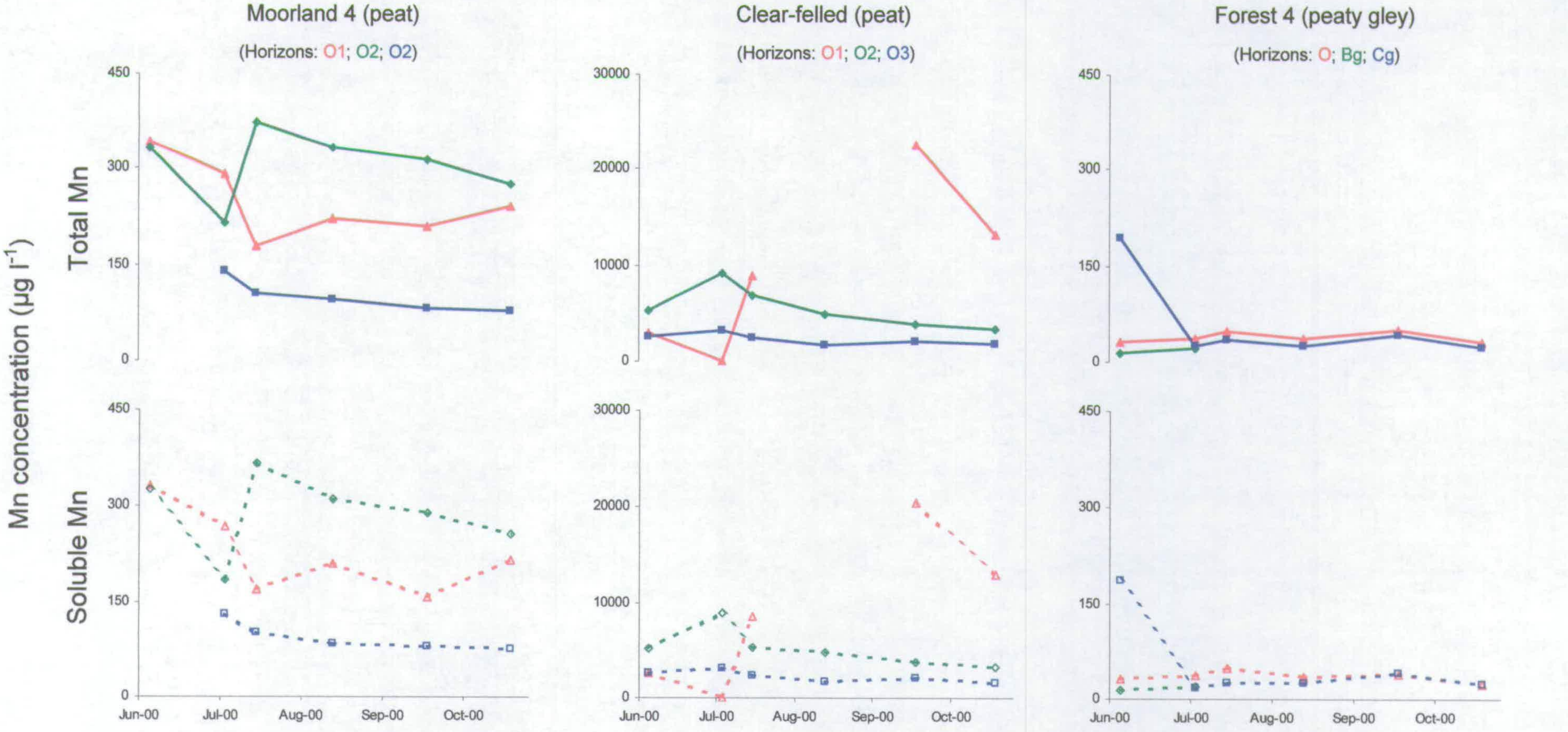


Figure 4.35: Soil water Mn concentrations from secondary field sites

N.B. Different y-axis scale for clear-felled site

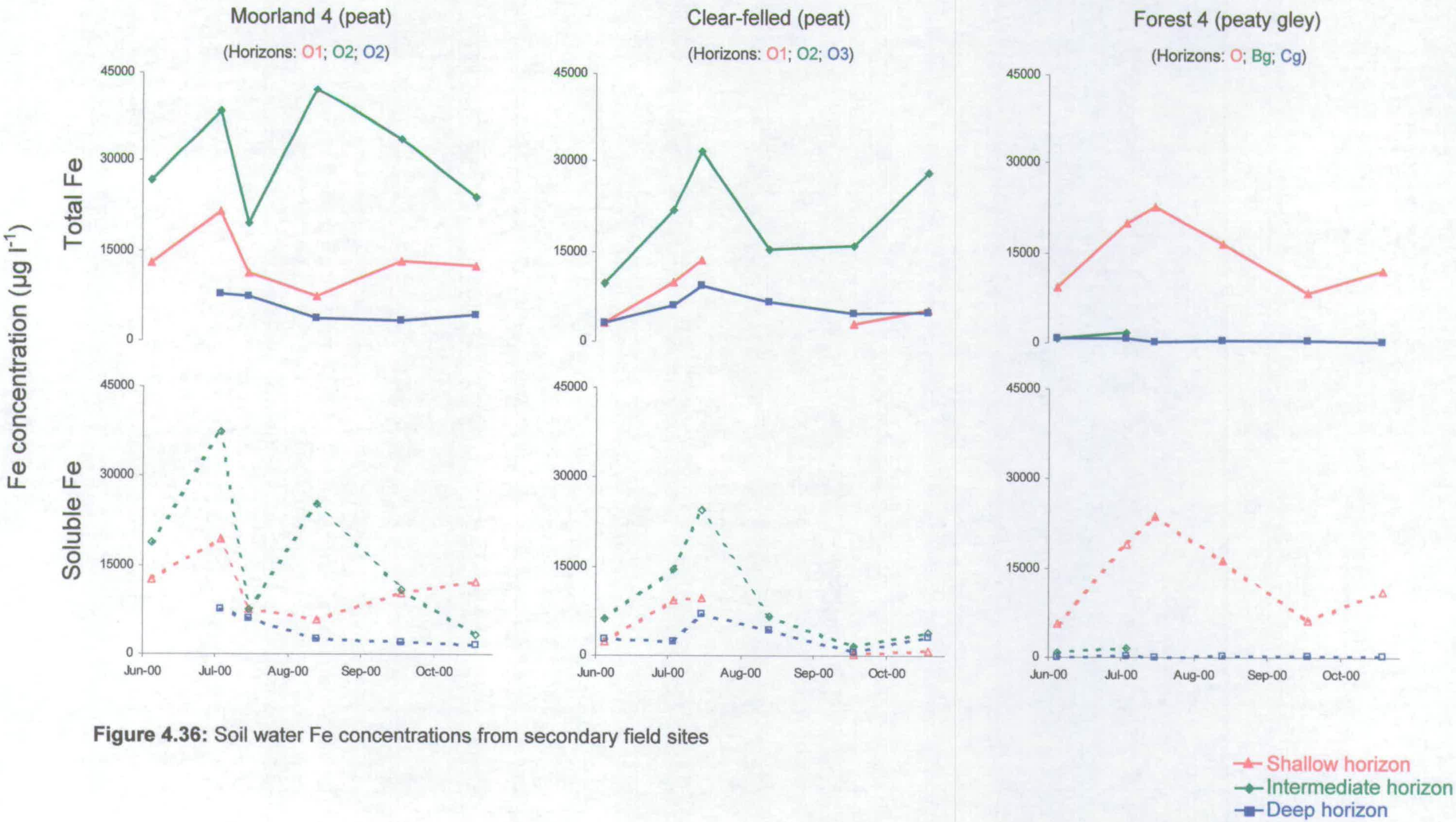


Figure 4.36: Soil water Fe concentrations from secondary field sites

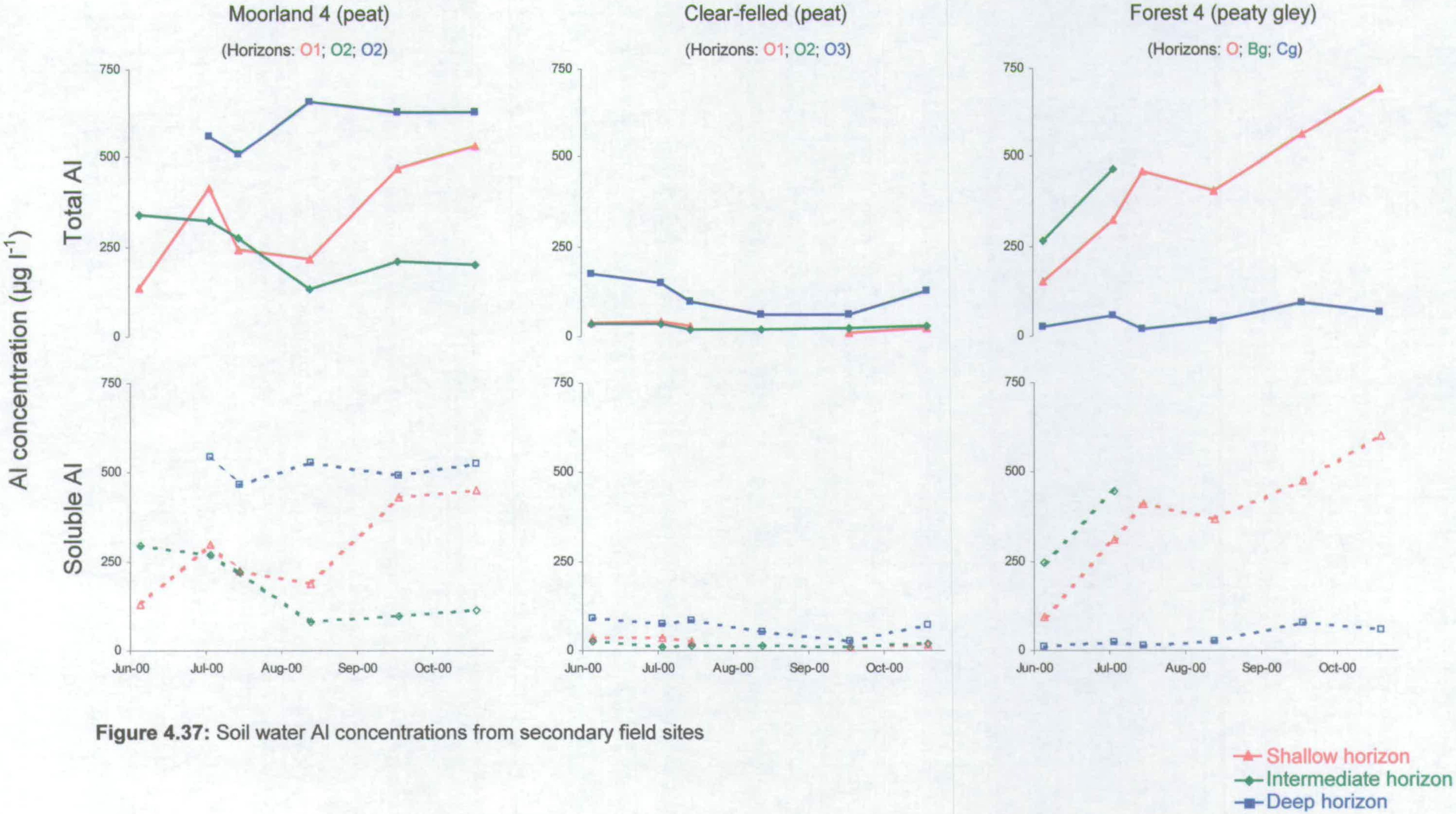


Figure 4.37: Soil water Al concentrations from secondary field sites

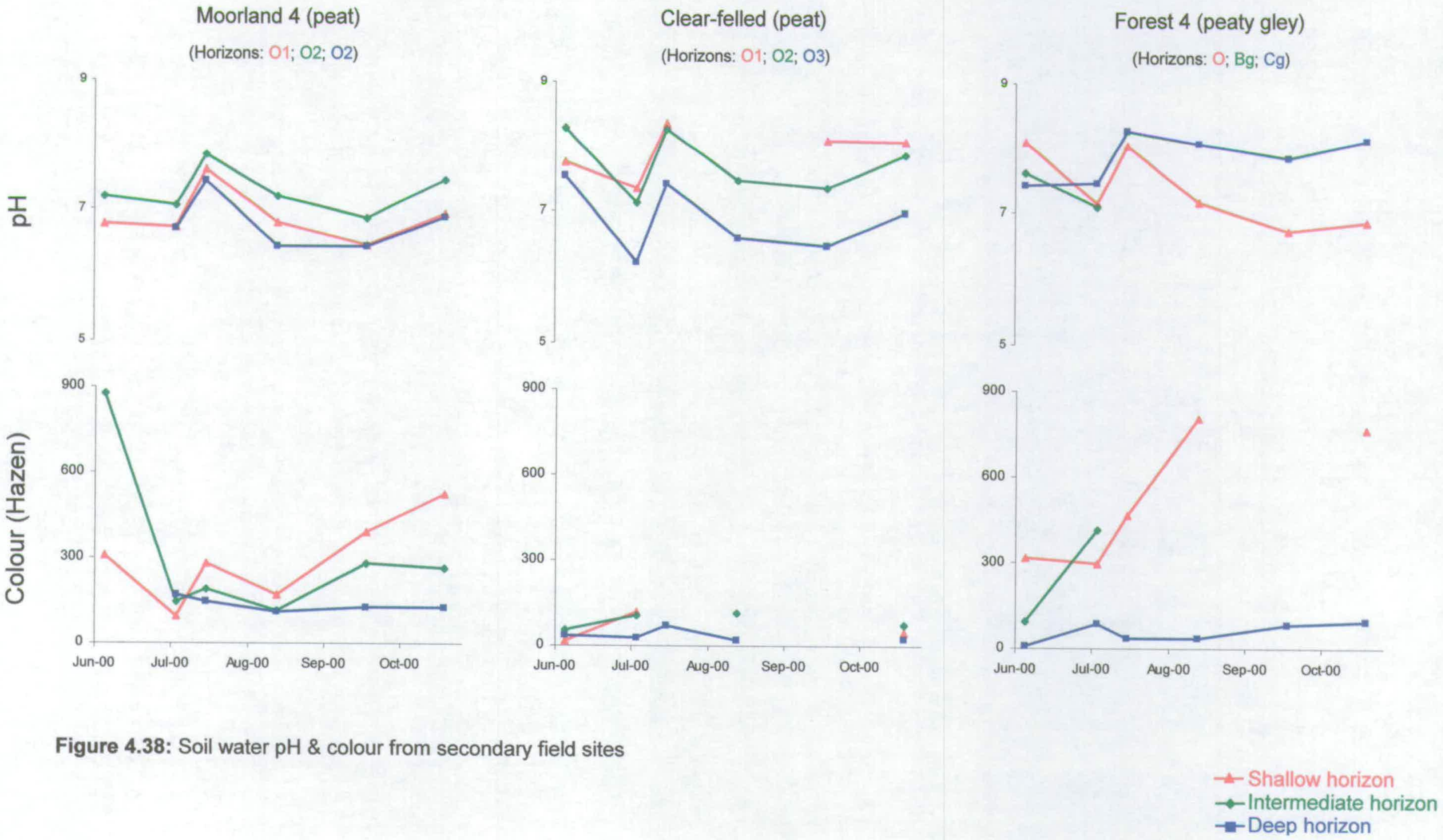


Figure 4.38: Soil water pH & colour from secondary field sites

Determinand	Moorland peat	Clear-felled peat	Forest peaty gley
Mn	Greatest concentrations in intermediate horizon Concentrations generally greater than primary sites (range ~100-400 μg l^{-1})	Greatest concentrations in shallow horizon Concentrations far greater than primary sites (maximum >20,000 μg l^{-1})	Similar concentrations to moorland site 2 (peaty gley)
Fe	Greatest concentrations in intermediate horizon Similar range of concentrations to moorland site 1 (peat)	Greatest concentrations in intermediate horizon Similar range of concentrations to moorland site 1 (peat)	Greatest concentrations in shallow horizon
Al	Greatest concentrations in deep horizon Similar range of concentrations to primary field sites	Greatest concentrations in deep horizon Similar range of concentrations to primary field sites	Greatest concentrations in shallow horizon Similar range of concentrations to primary field sites
pH	Difficult to assess No obvious difference between horizons	Difficult to assess Most acidic in deep horizon	Difficult to assess
Colour	No obvious difference between horizons Similar range of values to primary field sites	Difficult to assess Similar range of values to primary field sites	Difficult to assess Similar range of values to primary field sites

Table 4.9: Summary of graphical analysis of soil water chemistry data from secondary field sites

4.2 Supplementary field data

In addition to the data gathered from the field sites and stream water sampling sites, several other parameters believed to influence catchment Mn geochemistry were investigated during the course of the field monitoring. These included the chemical properties of soil horizons instrumented and the metal content of litterfall, rainfall and throughfall.

4.2.1 Soil horizon chemical properties

Investigation of the soil chemical properties was intended to provide an estimate of the pool of Mn present in each horizon and aid identification of the processes resulting in the mobilisation of metal ions. During the process of profile description, soil samples were collected from each horizon in the soil pits and stored in sealed plastic bags at 4°C until analysis could be carried out.

Initial sample preparation and analysis was undertaken at the Macaulay Institute in Aberdeen. In addition to particle size data, this provided measurements of soil pH (in water and $CaCl_2$), exchangeable cations, loss on ignition (LOI), and percentage nitrogen and carbon content. Air-dried samples (<2 mm fraction) of soil were then analysed in Edinburgh for total Mn and Fe, using FAAS (method in Appendix A.4). The results of all these analyses are presented in Table 4.10, with the exception of the peat at moorland site four, where the continual waterlogged conditions prohibited the digging of a profile pit and sample collection.

Correlation coefficients (Pearson product-moment) were calculated for the soil chemical properties, using the Minitab v12.1 statistical program, with the results shown in Table 4.11. In order to obtain data which were normally distributed, exchangeable cations required a $\log_{10}$ transformation of the data+1, while LOI, N%, C%, Mn & Fe data were all $\log_{10}$ transformed.

As noted by Heal (1996), soils contain greater quantities of total Fe than total Mn because of the relative concentrations present in rocks near the earth's surface, from which the metals are released to soils by weathering. The strong positive correlation between the two metals indicates that, although present in concentrations more than an order of magnitude apart, both are affected in a similar manner by processes occurring within soils. Both Mn and Fe show a strong positive correlation with soil pH and a negative correlation with LOI. Because the principal source of soil Mn in upland areas is from weathering of rocks, soil

Site	Sample depth (cm)	Horizon	pH		Exchangeable cations (meq/100g)				N%	C%	Sand%	Silt%	Clay%	LOI (%)	Mn ($\mu g\ g^{-1}$)	Fe ($mg\ g^{-1}$)
			In H_2O	In $CaCl_2$	Ca	Mg	Na	K								
Forest 1 (Peat)	1-9	O1	3.95	2.98	0.96	2.17	0.87	7.42	1.42	51.04	-	-	-	97.5	28.6	2.9
	11-17	O2	3.74	2.89	0.59	1.57	0.52	5.32	2.08	50.12	-	-	-	95.6	4.5	2.0
	35-40	O3	3.75	2.95	1.60	1.11	0.11	5.19	1.89	55.48	-	-	-	98.2	0.6	0.2
	85-90	O3	3.57	3.16	1.34	0.99	0.03	7.17	1.49	58.11	-	-	-	98.6	0.2	0.5
Forest 2 (Peat)	1-5	O1	3.95	3.03	1.74	2.02	0.96	9.55	1.38	51.28	-	-	-	96.8	8.5	0.5
	7-14	O2	3.72	2.94	0.57	1.78	0.71	6.44	2.02	49.59	-	-	-	95.5	10.5	1.9
	20-30	O3	3.70	2.88	2.85	1.65	0.20	8.17	1.76	54.35	-	-	-	98.5	5.7	0.7
	80-85	O4	4.00	3.12	1.37	1.03	0.02	7.29	1.64	58.12	-	-	-	98.7	2.8	0.8
Forest 3 (Peat)	2-8	O1	4.12	3.42	10.6	1.73	2.29	8.40	1.16	51.02	-	-	-	98.5	28.2	1.5
	15-20	O2	3.77	2.91	0.83	1.40	0.65	6.91	2.17	50.15	-	-	-	95.5	9.7	3.7
	27-33	O3	3.80	2.93	2.38	1.06	0.23	5.88	2.26	53.62	-	-	-	98.2	4.2	0.5
	70-80	O4	3.90	3.06	1.38	0.91	0.01	10.7	1.23	58.14	-	-	-	98.9	3.4	0.6
Moor 1 (Peat)	10-20	O1	4.11	3.38	3.91	1.54	2.46	5.59	0.80	45.42	-	-	-	79.0	100.2	21.7
	40-50	O2	4.68	4.00	0.84	0.32	0.10	0.98	1.60	35.16	-	-	-	62.0	64.6	25.2
	70-80	O2	5.38	4.54	0.37	0.09	0.01	0.15	0.28	6.46	-	-	-	14.8	57.5	35.8
	100-110	Cgh	5.31	4.59	0.28	0.09	0.02	0.13	0.16	3.86	64.6	30.7	4.1	10.6	169.5	80.6
Moor 2 (Peaty gley)	2-8	O1	4.16	3.27	4.35	1.66	2.57	8.53	1.19	49.59	-	-	-	95.1	24.7	4.5
	15-25	O2	4.25	3.56	0.17	0.13	0.17	0.30	0.95	18.83	-	-	-	30.7	108.0	14.3
	40-50	Bg1	5.42	4.73	0.42	0.06	0.01	0.16	0.09	2.36	70.3	25.6	4.1	6.0	135.7	89.6
	58-68	Bg2	5.57	4.88	0.28	0.06	0.01	0.13	0.03	0.82	67.6	27.4	5.1	2.9	147.2	60.6
	75-85	C(g)	5.88	5.11	0.09	0.04	0.01	0.03	0.01	0.41	75.8	18.2	6.1	2.3	204.6	13.9
Moor 3 (Peaty podzol)	12-22	O1	4.05	3.24	1.69	0.71	0.93	2.97	1.87	38.74	-	-	-	67.2	23.6	3.1
	27-32	Ehg	4.58	3.93	0.21	0.28	0.30	0.54	0.41	8.19	23.1	57.6	18.8	17.6	116.7	57.0
	34-37	Bh	4.78	4.19	0.04	0.04	0.02	0.03	0.25	5.93	62.3	28.8	8.5	13.0	60.6	43.4
	45-55	Bs(g)	5.13	4.59	0.02	0.03	0.01	0.01	0.04	1.35	80.7	13.2	6.1	4.5	141.8	120.8
	65-70	C(g)	5.14	4.55	0.03	0.03	0.01	0.01	0.04	1.18	39.0	55.7	5.3	4.2	137.3	65.3
Clear-felled (Peat alluvium)	16-26	O1	4.35	3.76	0.59	0.92	0.31	0.43	1.28	20.14	-	-	-	46.4	2929.6	31.0
	40-50	O2	4.67	4.12	0.38	0.36	0.17	0.10	0.90	15.87	-	-	-	34.0	1095.3	35.3
	70-80	O3	4.87	4.25	0.95	0.55	0.38	0.05	1.78	28.68	-	-	-	52.6	223.9	18.3
Forest 4 (Peaty gley)	10-20	O	3.97	3.31	0.75	1.54	0.31	0.53	1.49	30.67	-	-	-	58.0	84.4	6.4
	35-45	Bg	4.82	4.06	0.04	0.08	0.04	0.03	0.35	7.26	-	-	-	14.6	154.1	16.8
	55-65	Cg	5.08	4.63	0.05	0.04	0.03	0.02	0.15	2.50	-	-	-	7.4	176.3	25.2
Moor 4 (Peat alluvium)									No profile sampling because of waterlogged conditions							

Table 4.10: Soil profile chemical properties

All concentrations expressed in terms of dry weight
(- = no data available)

	Fe	pH $_{(H_2O)}$	pH $_{(CaCl_2)}$	ex Ca	ex Mg	ex Na	ex K	N%	C%	Sand	Silt	Clay	LOI
Mn	**0.848**	**0.678**	**0.692**	-0.427	-0.527	-0.071	**-0.772**	-0.478	-0.577	0.258	-0.200	-0.342	**-0.730**
Fe		**0.814**	**0.842**	**-0.605**	**-0.752**	-0.258	**-0.862**	**-0.669**	**-0.750**	-0.040	0.080	-0.109	**-0.885**
pH$_{(H_2O)}$			**0.984**	-0.575	**-0.851**	-0.437	**-0.835**	**-0.879**	**-0.919**	0.664	-0.577	-0.711	**-0.908**
pH$_{(CaCl_2)}$				**-0.598**	**-0.881**	-0.469	**-0.877**	**-0.872**	**-0.922**	0.712	-0.616	-0.767	**-0.932**
ex Ca					**0.724**	**0.750**	**0.754**	0.549	**0.666**	0.019	0.001	-0.083	**0.744**
ex Mg						**0.676**	**0.873**	**0.754**	**0.834**	-0.728	0.603	0.881	**0.920**
ex Na							0.557	0.420	0.506	-0.776	0.637	**0.962**	0.529
ex K								**0.668**	**0.795**	-0.665	0.553	0.801	**0.947**
N%									**0.975**	-0.553	0.477	0.584	**0.830**
C%										-0.525	0.444	0.582	**0.915**
Sand											**-0.978**	-0.734	-0.629
Silt												0.575	0.512
Clay													0.772

Table 4.11: Correlation coefficients for soil chemical properties (n=32)
($p<0.05$; $p<0.01$; **$p<0.001$**)

horizons containing large quantities of mineral material should also contain greater concentrations of Mn. Conversely, where the soil horizon is predominantly organic and therefore lacking a mineral component, there should be less Mn present. The positive correlation between total metal concentration and pH is probably attributable to the same phenomenon, as the pH of highly organic soils will be less than those with a substantial mineral content. There is also a significant negative correlation between total Mn or Fe and the percentage of N or C in the soil. This is not unexpected, given the relationship between both metals and LOI and is probably the result of greater total metal concentrations in mineral soil horizons, relative to organic ones.

Heal (1996) also suggested that Mn mobilisation was enhanced by the high organic matter content and waterlogged conditions found in peats. However, it should be noted that there must first be a source of the Mn present for the mobilisation to occur, otherwise Mn concentrations will be similar to those measured in the forest peat sites. At these sites (forest sites 1-3), total soil Mn concentrations are very low, with the greatest concentrations found in the shallow horizons and a general decrease with depth. This distribution of Mn in peat is well recorded (Chapman, 1964; Damman, 1978; Heal, 1996) and results from the only input of Mn coming from relatively small concentrations leaching from vegetation at the profile surface. A similar distribution of Mn is seen in the peat profile of the clear-felled site and in the organic horizons of the peat at moorland site one. However, the concentrations of Mn measured in soil samples from the clear-felled site are far greater than those at any other site. It is possible that the large Mn concentrations at this site arise as a result of leaching from the mass of decaying vegetation left behind after clear-felling, as has been recorded at other UK sites (Adamson *et al.*, 1987; Durand *et al.*, 1994; Fahey *et al.*, 1991a; Titus & Malcolm, 1991). Another explanation for the greater Mn concentrations of soil samples from the clear-felled site, compared to the three forest peat sites, is that the sediments distributed throughout the peat alluvium profile are a source of Mn not present in the forest peat sites. The distribution of Mn within the profiles of the three organo-mineral soils studied (moorland site two – peaty gley; moorland site three – peaty podzol; forest site four – peaty gley) differed from that observed in the peat profiles. In the organo-mineral soils, there was a general increase of Mn concentration with depth, which was thought to be associated with the increased incorporation of Mn-containing parent material in the horizons further down the profile.

Exchangeable cations are positively correlated with the percentage of N and C present, as well as LOI. This is possibly an indication of the influence that organic complexation has on the mobility of these cations, or that the cations are simply being released from decaying vegetation. The fact that breakdown products from decaying vegetation can chelate metal ions, thereby increasing their solubility, is well known (Dickinson & Pugh, 1974). However, the soil chemistry data from this study did not allow identification of the extent to which organic Mn complexation was occurring, and scientific opinion appears to differ concerning the importance of the process. Several studies suggest that the degree of Mn complexation by organic ligands in soil is limited (Khan, 1969; Patrick & Turner, 1968; Pohlman & McCall, 1989). In contrast, Heal (1996) describes organically-complexed Mn as being the dominant fraction in peat soils and Graham *et al.* (2002) regard complexation by humic substances as being an important process in soils of the Loch Bradan catchment.

The limited particle size analysis available, owing to the small number of mineral horizons sampled, did not indicate any statistically significant correlations with either total Mn or total Fe concentrations in the soil. A positive correlation was identified between exchangeable Mg, Na, and K with the percentage of clay, while the percentage of sand was negatively correlated with exchangeable Mg and Na. This may be an indication of metal ions present at the cation exchange sites on the clay particles, although the small number of samples for which particle size data exists prevents any definite conclusions being reached.

In conclusion, it appears that soils within the catchment are extremely varied in their chemical composition and properties, with considerable differences existing between soil horizons within the same profile. Therefore, Mn distribution in catchment soils may vary widely in three dimensions, and an understanding of its behaviour within the horizons of individual soil types is vital to predicting mobilisation from the catchment as a whole. Within the soil types of the Ballochbeatties Burn catchment investigated, the greatest concentrations of total Mn are found in the peat alluvium in the clear-felled site. Although no soil samples were collected from the peat alluvium at moorland site four, it is anticipated (on the basis of soil solution chemistry from that site) that total soil Mn concentration will also be high. Therefore, it is thought that the sediment distributed throughout the peat alluvium profiles acts as a pool of Mn, the mobilisation of which is enhanced by the waterlogged acidic conditions present in the soil and also the availability of organic matter.

4.2.2 Mn in vegetation

Living vegetation may constitute a considerable store of Mn, which can be released into the soil from the decomposition of litter or when the plant dies. Preliminary vegetation sampling studied the Mn concentration of living and dead tissue from the dominant species in the Ballochbeatties Burn catchment. Following this, regular collection of plant litter was undertaken during the field monitoring programme in order to estimate potential Mn inputs to catchment soils from litterfall.

4.2.2.1 Preliminary vegetation data

Samples of living plant tissue and decaying litter from the most abundant plant species present in the Ballochbeatties Burn catchment, collected at random during a preliminary site visit, were analysed for total Mn and Fe content to determine whether any contained greater quantities of the metals than the others. Living tissue and brash was cut from vegetation using scissors, while Sitka spruce needles were collected using a small trowel. The living tissue samples from Sitka spruce and *Calluna* were collected from areas of the plant identified as new growth, in order to enable a comparison between tissues of a similar age. Once collected, vegetation samples were placed in sealed plastic sample bags.

Vegetation samples were stored in darkness at 4°C until they could be analysed, using FAAS following a nitric/sulphuric acid digestion (procedure outlined in Appendix A.5). The results of this analysis are presented in Table 4.12.

Land use	Vegetation	Mn (mg g^{-1})	Fe (mg g^{-1})
Forest	Sitka needles (live)	0.135	0.125
Forest	Sitka needles (litter)	0.077	0.192
Forest	Sitka twigs (live)	0.135	0.187
Moorland	*Molinia caerula* [b]	0.212	0.181
Moorland	*Calluna vulgaris* [b]	1.147	0.160
Clear-felled	Brash [a]	0.043	0.260
Clear-felled	Misc. grass [a]	0.894	0.138
Clear-felled	*Sphagnum* spp.	0.051	0.081

Table 4.12: Vegetation analysis from preliminary site visits

Concentrations refer to single value, except [a] mean of two replicates [b] mean of three replicates
All values based on dry weight

The variability of Mn concentrations measured between different vegetation types was far greater than the variability in Fe. Of the living vegetation samples, the *Calluna* contained most Mn, while *Sphagnum* contained the least. Litter from Sitka spruce, in the form of needles on the forest floor and brash in the clear-felled area, contained approximately half as much Mn as living tissue. Conversely, Sitka litter samples appear to contain elevated concentrations of Fe, although the small number of samples analysed limits any statistical tests of significance.

The greater concentration of Mn found in live Sitka spruce needles and twigs, relative to litter and brash may indicate leaching of minerals from the dead vegetation, as suggested by Fahey *et al.* (1991a). However, this theory is not supported by comparison of the Fe concentrations between living and dead Sitka spruce tissue, possibly indicating that Mn is more readily leached than Fe.

4.2.2.2 Litterfall dynamics

As discussed in section 2.4.1, litterfall may play an important role in the biogeochemical cycling of metals. Therefore, an investigation into the Mn and Fe content of litter, particularly the timing of litterfall and changes in its metal concentration, was undertaken. Litter from the three main vegetation species present in the Ballochbeatties Burn catchment was sampled during the period September 1999 to October 2000, using the methods described in section 3.7.1.

Mean Mn and Fe concentrations in the three types of litter collected are displayed in Figure 4.39. A one-way ANOVA (performed using the Minitab v12.1 computer program) of this data confirms that there is no significant difference between Fe concentrations in litter from the three vegetation types ($p=0.274$). However, Mn concentrations in Sitka spruce litter are significantly less than in the *Calluna* or *Molinia* litter ($p<0.001$).

The mean litterfall from each source during the period of November 1999 to October 2000 (Table 4.13) shows that the greatest inputs of litter came from the *Molinia* and Sitka spruce. When considered in terms of metal fluxes, the data show that *Molinia* litter provides a far greater Mn input to catchment soils than Sitka spruce litter, while the Fe flux in litter from these two species is generally similar. The smallest Mn and Fe fluxes are estimated to arise from the *Calluna* litter, resulting from the relatively small rate of litterfall compared to the Sitka spruce or *Molinia*.

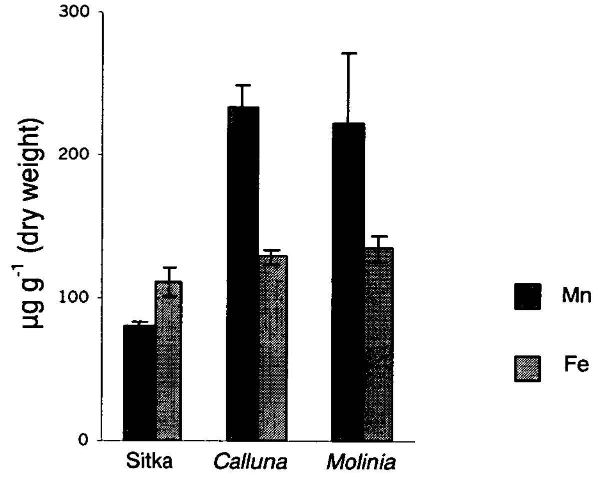


Figure 4.39: Mean concentration (±SE) of Mn & Fe in litter from major vegetation types in Ballochbeatties Burn catchment

	Annual rate of litterfall ($t\ ha^{-1}\ yr^{-1}$)	Mn flux ($kg\ ha^{-1}\ yr^{-1}$)	Fe flux ($kg\ ha^{-1}\ yr^{-1}$)
Sitka spruce	2.73	0.220	0.305
Calluna	0.61	0.142	0.079
Molinia	2.38	0.531	0.321

Table 4.13: Annual rates of litterfall (dry weight) and metal fluxes from predominant vegetation species in Ballochbeatties Burn catchment

Although no comparable deposition rates have been reported for the moorland vegetation, the rate of litterfall from Sitka spruce is within the range reported by other studies (Adams *et al.*, 1980; Carey & Farrell, 1978; Owen, 1954). Senescence in *Molinia* occurs during the autumn, and it is assumed that this is the time when leaching of metals from the dead leaves is at a maximum. Litterfall from Sitka spruce appears to have an autumn maximum (Figure 4.40), although the difference in quantity of litter collected between the two years studied is considerable. The rate of *Calluna* litterfall also peaks during the autumn, but the mass collected is considerably less than that recorded from the Sitka spruce.

The change in litter Mn and Fe concentration over time (Figure 4.41) indicates that there is little variation in Sitka spruce litter Mn concentrations throughout the year. There is possibly a late spring maximum of Mn concentrations in Calluna litter, although this is only indicated by a single data point. The concentration of Fe in Sitka spruce litter appears to exhibit a winter maximum and summer minimum, while there are no obvious seasonal changes in Fe concentrations from the Calluna litter. However, it may be that the time series are not long enough to positively identify any seasonality in the metal concentrations of the litter samples.

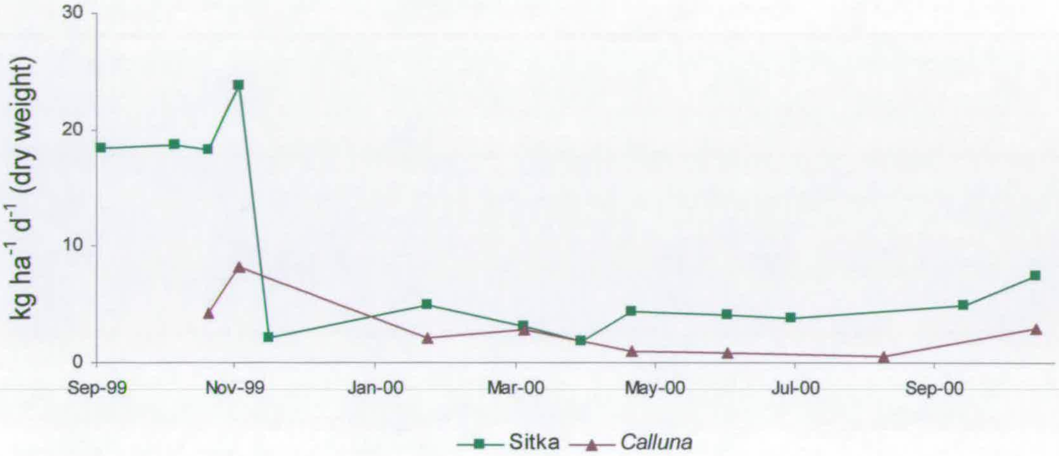


Figure 4.40: Seasonal variation in amount of litterfall from Sitka spruce and *Calluna vulgaris* in the Ballochbeatties Burn catchment
(Calculated on basis of bulk sample collected)

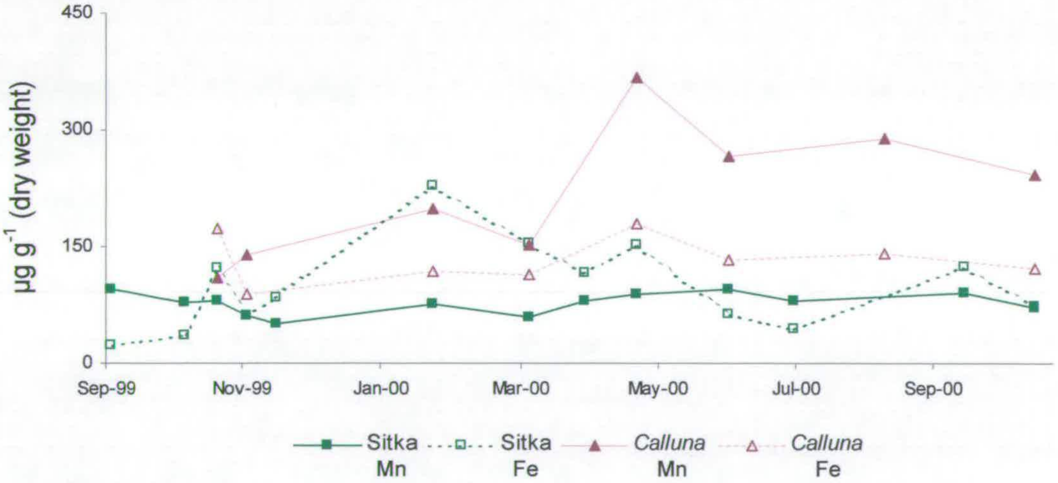


Figure 4.41: Seasonal variation in Mn & Fe concentration of litterfall from Sitka spruce and *Calluna vulgaris* in the Ballochbeatties Burn catchment
(Calculated on basis of bulk sample collected)

In conclusion, it appears that the release of Mn to catchment soils from vegetation is potentially greatest during the autumn period. As a result of its deciduous nature, areas with a high proportion of *Molinia* cover receive the largest autumn inputs of decaying vegetation.

Mn concentrations measured in litter were greatest in the *Calluna* and *Molinia*, although it is unknown whether this was caused by species-specific traits or reflects metal concentrations in the soil the plants were growing in.

4.2.3 Rainfall and throughfall

Studies indicate that rainfall percolating through a forest canopy can become greatly enriched in metal ion concentration (Adamson *et al.*, 1993; Brown & Iles, 1991; Madgwick & Ovington, 1959). The metal ions enriching throughfall can come from leaf surface deposits (wash-off of dry deposition) or internal sources (foliar leaching), with most Mn in throughfall being attributed to foliar leaching (Rea *et al.*, 2000). In order to determine the effect this aspect of Mn cycling had in the Ballochbeatties Burn catchment, Mn inputs from rainfall and throughfall were monitored at several points. Samples of rainfall accumulated in two bulk precipitation collectors, installed close to the primary soil water sampling sites, were taken on each visit. One collector was located in open moorland approximately 20 m uphill from moorland site three, while the other was located in the middle of a forest ride a similar distance from forest site three. Throughfall was collected in gutter systems below the forest canopy as part of a different study, also taking place in the Ballochbeatties Burn catchment, and was obtained from four sites in the forestry plantation. Three of the throughfall sites were in Sitka spruce forest, of which, two were located in the centre of a stand and one at the edge by a forest ride. The fourth throughfall sampling site was in the middle of a Japanese larch stand. Analysis of rainfall samples collected during the field monitoring project was carried out by WoSW, using ICP-AES to determine total Mn concentration, while throughfall samples were analysed in Edinburgh for Mn using GFAAS. None of the samples analysed were filtered, therefore the Mn concentration determined reflects both soluble and particulate forms of Mn present in the sample.

As expected, the mean Mn concentrations in samples from these six points (Figure 4.42) show that rainfall becomes greatly enriched in Mn as a result of contact with the forest canopy. Rainfall at both the forest and moorland sites contained little Mn, while most was found in throughfall from the central and roadside Sitka sites. The relatively small mean Mn concentrations of 2.3 and 2.6 $\mu g\ l^{-1}$, measured in forest and moorland rainfall respectively, are in accordance with the median Mn concentration of 5.7 $\mu g\ l^{-1}$ in rainfall from rural areas, reported by Galloway *et al.* (1982). Statistical analysis of these data, using one-way ANOVA within the Minitab v12.1 computer program, combined with the graphical evidence in Figure 4.42 confirms that the rainfall contains significantly less Mn ($p<0.001$) than throughfall at any of the sites. Rainfall Mn concentrations did not differ significantly between forest and moorland (p=0.736) and there was no statistical difference in Mn concentrations between the Sitka edge and larch throughfall (p=0.358), or between the two Sitka central sites (p=0.843). However throughfall from the Sitka central sites contains statistically more Mn than the Sitka edge or larch sites (p<0.001). Greater concentrations of ions in throughfall from beneath spruce than under larch have been reported by Adamson *et al.* (1993) and were thought to arise from the more open canopy caused by thinning practices applied to the larch. The deciduous nature of Larch may also have influenced the throughfall concentrations. It is unclear why throughfall from the Sitka edge site contained less Mn than the two Sitka central sites. One possibility is that the smaller trees at the edge site (K.Heal, pers. comm.) had a more open canopy, resulting in samples collected in the guttering being 'diluted' by rainfall passing through openings in the canopy.

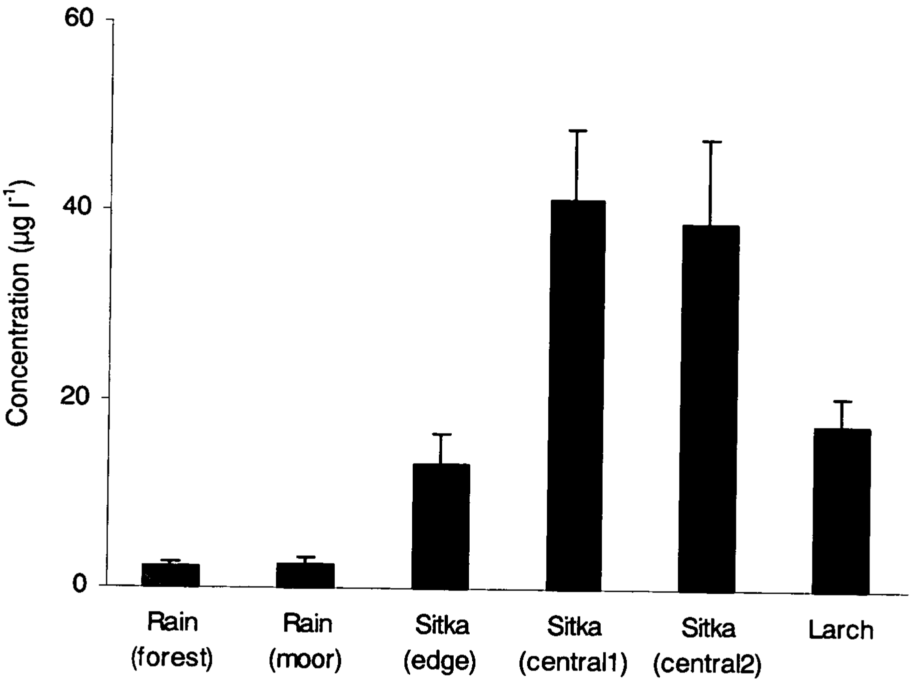


Figure 4.42: Mean (±SE) Mn concentrations in rainfall and throughfall

It is evident that although rainfall in the catchment contains relatively little Mn, leaching of Mn from vegetation surfaces considerably enriches the water as it passes through the forest canopy. The extent to which the increased Mn concentrations in throughfall influence soil water Mn concentrations in the Ballochbeatties Burn catchment is unknown. However, soil water samples from the primary forest sites had considerably less Mn concentrations than the throughfall samples. It is possible that much of the throughfall may be transported as surface runoff, rather than via subsurface flow following infiltration into the soil and therefore would not be sampled by the suction probes. Another explanation is that the sections of guttering used to collect throughfall also served as litter traps and therefore contained needles, from which 'extra' leaching of Mn would occur. Although this would result in greater Mn concentrations than in the 'natural' throughfall, it is still considered to accurately represent Mn inputs to the soil profile attributable to throughfall percolating through the litter layer of the soil (K.Heal, pers. comm.).

4.2.4 Stream sediment data

Stream sediment samples from Ballochbeatties Burn were collected during March 1999. A spade was used to collect material from the stream bed near each of the stream water sampling sites (see Figure 3.7). Samples were analysed to determine the proportion of mineral and organic matter, as well as total Mn and Fe content (using the same methods as for soil samples – see Appendix A.3 & A.4). In addition to the sediment samples, two samples were collected from the banks of the drainage ditch where metallic staining was evident (Figure 4.43). The results of all these analyses are shown in Table 4.14.

Site	% Mineral	Mn (mg g^{-1})	Fe (mg g^{-1})
Upstream of BB1	94.2	0.70	52.5
BB1	93.4	2.3	53.2
BB2	97.8	2.1	40.0
BB3	93.4	2.5	64.0
BB4	97.4	2.4	43.5
BB5	88.9	1.0	57.9
BB6	80.4	0.3	64.0
BB7	95.6	5.8	74.1
BB8	94.4	45.8	155.4
BB9	94.9	0.1	31.7
BB10	80.5	0.7	79.8
BB11	94.4	0.6	84.4
BB12	96.2	0.4	98.9
Ditch stain (orange)	46.7	1.66	284.5
Ditch stain (black)	26.4	0.1	122.8

Table 4.14: Analysis of stream sediment samples from Ballochbeatties Burn
All values based on dry weight

Figure 4.43: Drainage ditch metallic staining
(a-black stain; b-orange stain)

No statistically significant correlation was found between any of the three variables measured. In the main stream channel (sample points BB1-BB8) Mn and Fe values remained fairly constant, with the exception of the sample taken at point BB8. At this point, near to the reservoir, the sediment contained considerably greater metal concentrations. Sediment from the drainage ditches (sample points BB9-BB12) generally contained less Mn than the main channel samples. The two samples collected from the drainage ditch banks contained very high concentrations of Fe, but low Mn concentrations. The dry weight concentration and mineral content of these samples may be unreliable, owing to peat from the ditch side being collected along with the stain. The presence of the stains does, however, indicate Fe-rich soil water passing through the catchment soils and entering drainage ditches. The staining is probably caused by oxidation of soluble Fe in the soil water by atmospheric oxygen as the water flows into the drainage ditch, forming a sheet of Fe-oxide precipitates. Such an effect has also been noted occurring at the surface of stagnant pools in areas of deep peat, producing an 'oily' film at the water surface (Taylor & Patterson, 2002). The relative lack of Mn in the ditch stains does not necessarily indicate that there is no Mn mobilisation from catchment soils. This is because any Mn in the soil water is less likely to be oxidised by exposure to the atmosphere than Fe and therefore may not precipitate out on the ditch sides.

The high concentration of metals at sample point BB8 may simply result from a 'hot spot' of metals in the streambed geology, although it may also be caused by transport and deposition from mineral sources further upstream. Stream sediment samples from the same area analysed by the British Geological Survey (data supplied by WoSW) had a mean Mn concentration of 44.2 mg g^{-1} (range 1.3 – 236.3). Although these data indicate that Mn-rich sediments are found nearby (the highest concentration was found in a sample from the Water of Girvan shortly before it enters Loch Bradan), they also show that the spatial variability of Mn concentration in stream sediments is great.

Therefore, the extent to which stream sediment metal concentrations can influence water flowing into the reservoir is unknown. In general, the stream sediments analysed contained Mn concentrations at least an order of magnitude greater than in soil samples collected during the preliminary site visits. The exceptions to this were the samples from the peat alluvium soils, where there was evidence of stream sediment incorporation into the peat profile. However, given the variable nature of sediment chemistry and relatively small (in comparison to catchment soil water) contact area between water and mineral, the importance of stream sediments in determining reservoir Mn concentrations may be limited. The role of reservoir sediments is likely to be of more importance than stream sediments in this respect, and is investigated by another research project (Gavin, 1999; Gavin *et al.*, 2001).

4.3 Discussion

Mn concentrations in soil water and stream water were monitored at a variety of sites within the catchment of Ballochbeatties Burn, a feeder stream for Loch Bradan water supply reservoir. The aim was to identify if Mn was mobilised from specific soil horizons, linked to changes in soil water regime, and study its progress from soil water to stream water. Further measurements of potential Mn sources within the catchment were made in order to discern whether or not seasonal Mn release into soil water or reservoir waters could be attributed to them.

The anticipated seasonal peak in soil water Mn concentrations, or rewetting of dried soils at the start of autumn, was not apparent at any of the sampling sites. In general, soil water samples from the primary sites investigated contained low concentrations of Mn, therefore making the isolation of any seasonal peaks difficult. However, one other explanation for the absence of any Mn peak, similar to that seen in the reservoir water during the autumn of 1995, is that the soil did not experience the same drying conditions as those that would exist during a drought year. Therefore, the drying-rewetting sequence thought to be responsible for mobilisation of metal ions in soils did not occur at the field sites during the course of the monitoring programme.

Although the soil water samples showed no evidence of an autumnal Mn peak, stream water samples did show a summer peak in metal concentration and colour. Possible explanations for this include concentration of solutes because of increased evaporation, or an increase in temperature producing an increase in biotic reduction of Mn contained in sediments. Heal *et al.* (1995) also suggest that increased Mn concentrations in stream water during the summer result from changes in subsurface flow pathways to the stream channel. This theory proposes that water entering the stream during the dry summer months originates in permanently saturated regions deep within the soil profile, where the redox conditions and long residence time favour the build up of soluble Mn^{2+} ions in the soil water.

As well as the presence of an identifiable seasonal peak, the concentration of Mn recorded in stream water was often far greater than that found in soil water samples from the primary field sites. It is unknown why this difference in concentrations should occur, as the chemistry of stream water should reflect that of soil water feeding the stream. However, it is possible that certain areas of the catchment (e.g., riparian zones) have a greater effect on stream water concentration than the soils of the primary field sites. For example, assuming that the effects of base flow and preferential flow pathways were minimal, soil water from the three primary moorland field sites would pass through the riparian zone (where moorland site four was located) prior to entering the stream channel. Therefore, conditions in the riparian soil would be the last ones to influence soil water Mn concentrations before the water entered the stream. Alternatively, surface runoff containing Mn leached from vegetation, or processes occurring within the stream channel may have influenced the stream water chemistry.

The installation of secondary soil water sampling sites during the latter phase of the field monitoring programme provided samples with high concentrations of Mn. The greatest concentrations were found in soil water samples from the clear-felled site and may have been a product of the disturbance caused by the harvesting process, although high Mn concentrations were also recorded in soil water from moorland site four. Both of these sites were similar in that the soils studied were peat alluvium, containing substantial quantities of mineral deposits interspersed throughout the profile. These deposits were in the form of bands or layers of small mineral grains, and presumably resulted from deposition of sediment during times of flooding. The combination of waterlogged, acidic, peaty soil and supply of reducible metal ions in mineral form could help explain the large concentrations of Mn found in soil water samples from these sites. Although peat alluvium soils only extend over a relatively small area within the Loch Bradan catchment, their role in determining reservoir levels may be disproportionate to this as they occur in areas adjacent to streams.

The pH of soil water samples collected during the field monitoring programme was often greater than expected for organic soils. This may have been due to retention of H^+ ions by the ceramic cups, although this should only have affected the initial samples until an equilibrium condition had been reached with the cation exchange sites on the ceramic cups. Another possibility is that pH altered during the time between soil water sample collection and analysis. Although samples were analysed for pH within 48 hours of probe evacuation, the sample had often been collected within a few days of the vacuum being applied. Therefore, soil water samples were often held in the suction probes for extended periods, during which time their pH could alter as a result of exposure to atmospheric oxygen or from degassing of CO_2.

4.4 Conclusions and further work

Following analysis and interpretation of the field data, a number of conclusions can be made concerning the behaviour of Mn in the Ballochbeatties Burn catchment.

It is apparent that the distribution of Mn throughout catchment soils varies markedly between soil type and between soil horizons. The general distribution of total Mn in the deep peats has a maximum at the surface, caused by inputs from vegetation, and a decrease with depth. However, when the peat is subjected to periodic flooding from the stream, and a peat alluvium soil develops, Mn concentrations in soil water can be very high throughout the profile. The organo-mineral soils studied tend to contain most Mn in their mineral horizons, probably resulting from the weathering of parent material. The concentrations of Mn in soil water samples did not always reflect the total Mn concentration within the soil horizon. It is therefore proposed that soil horizons where reducing conditions and low pH exist in conjunction with a large supply of mineral Mn will yield soil water with the greatest concentrations of Mn. Such conditions exist in the complex peat and alluvial deposits described above, and samples from these soils contained the greatest Mn concentrations found in any soil water samples over the course of the study.

The absence of drought conditions in Ayrshire during the two summers in which equipment was installed around Ballochbeatties Burn meant that the range of soil moisture regimes encountered in the research was limited. Because the sequence of soil water regimes thought to promote Mn mobilisation involves a prolonged drying period, followed by rewetting, it is possible that conditions in the field never became dry enough to produce this effect in the soils studied, resulting in the low Mn concentrations measured. Therefore there was no enhanced mobilisation of soil Mn in autumn thought to produce the increased reservoir water concentrations observed in 1995.

The climate in Scotland does not guarantee extended drying conditions during the course of every summer. Therefore, because of the limited duration of the research project, it was decided to artificially induce drought conditions in the laboratory using a series of soil cores taken from the Ballochbeatties Burn catchment. By taking cores from the same soil horizons monitored in the field and collecting similar data from them, it was possible to extend the range of drying experienced and thus ascertain whether or not the drought conditions followed by rewetting would release Mn from catchment soils. The soil core laboratory experiments designed to achieve this are presented in the following chapter.

Finally, consideration should be given to the possibility that the measured soil solution pH values may have been too high. When compared to soil solution pH of similar upland soils reported by other studies (e.g., Grieve 1990a, 1990b), the pH values measured during the field monitoring programme of this research appear approximately 1-2 pH units greater than expected. Potential explanations for this discrepancy have already been discussed in section 4.3, and include problems associated with cation retention by the ceramic cups and degassing of CO_2 prior to sample analysis. However, such mechanisms would only account for increased sample pH over an initial period following equipment installation. The fact that soil solution pH from several sites remains consistently high throughout the field monitoring programme indicates that a further process may be occurring. It is suggested that this may involve a reaction between basic cation impurities present in the ceramic cup and the soil solution as it passes through the ceramic cup, resulting in the removal of H^+ ions from solution and a subsequent increase in the pH of soil solution samples collected. Therefore, it is recommended that these pH values be regarded as indicative of relative trends in soil solution chemistry, rather than as an absolute record.

Chapter 5: Soil core laboratory experiments

As discussed in the previous chapter, relatively wet summer conditions during the period of field data collection may explain the absence of a late summer or early autumn peak in soil water Mn concentration. Estimated summer rainfall (June-August) at the field sites (see section 6.2.3.1 for method of derivation) during 1999 was 303 mm, compared to an estimated 153 mm in 1995. Insufficient data were available to calculate the rainfall during the summer of 2000. When compared to the rainfall data since 1980, the summer of 1995 is the driest on record, receiving approximately half of the mean summer rainfall for the location (Figure 5.1). In contrast, rainfall during the summer of 1999 was approximately equal to the mean summer rainfall for the 20-year period.

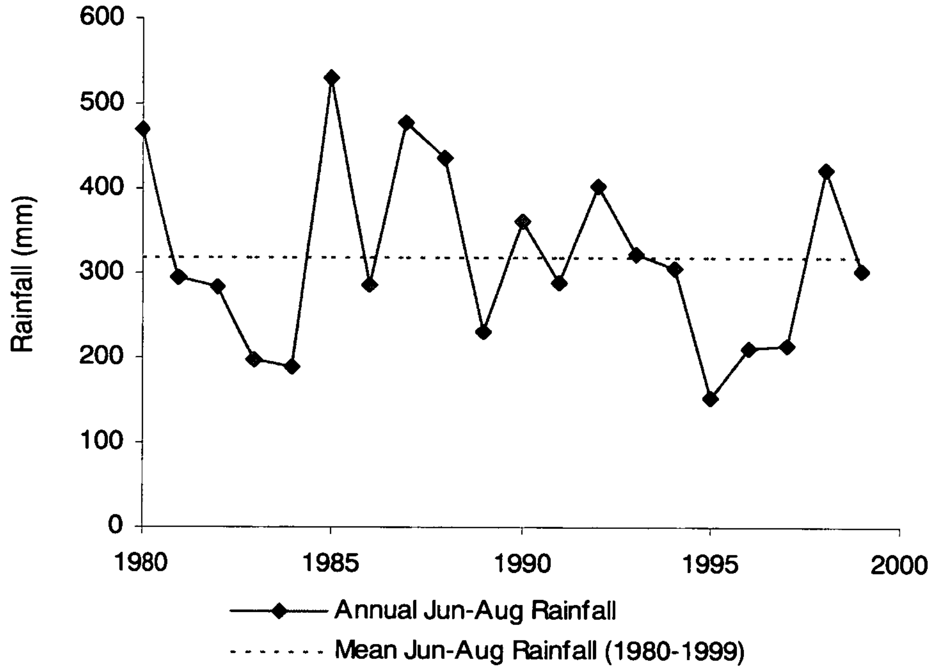


Figure 5.1: Summer rainfall at Loch Bradan 1980-1999

Investigation of the relationship between summer rainfall and summer/autumn reservoir Mn concentrations (available since 1988) was carried out using the Minitab v12.1 statistical package. Correlation analysis (Pearson product moment) indicated that there was a significant negative correlation between summer rainfall and autumn reservoir Mn concentration ($r=-0.727$, $p=0.007$, $n=12$). No correlation was found between summer rainfall and summer reservoir Mn concentrations or between summer and autumn reservoir Mn concentrations. Regression analysis of summer rainfall and autumn reservoir Mn concentration data (Figure 5.2) provided further evidence supporting the theory that dry summer conditions promote Mn release from soils during autumnal rewetting. If Mn release from soils is linked to an extended period of soil drying, it is possible that these conditions were not met during the two summers (1999 & 2000) in which field monitoring was conducted as part of this research. Therefore, in order to determine whether a drying period followed by rewetting does lead to a release of Mn from soil, laboratory experiments were conducted using soil cores to extend the range of soil water regimes experienced during the field monitoring period. The rationale, design and implementation of these experiments are detailed in this chapter, followed by the experimental results and conclusions drawn from them.

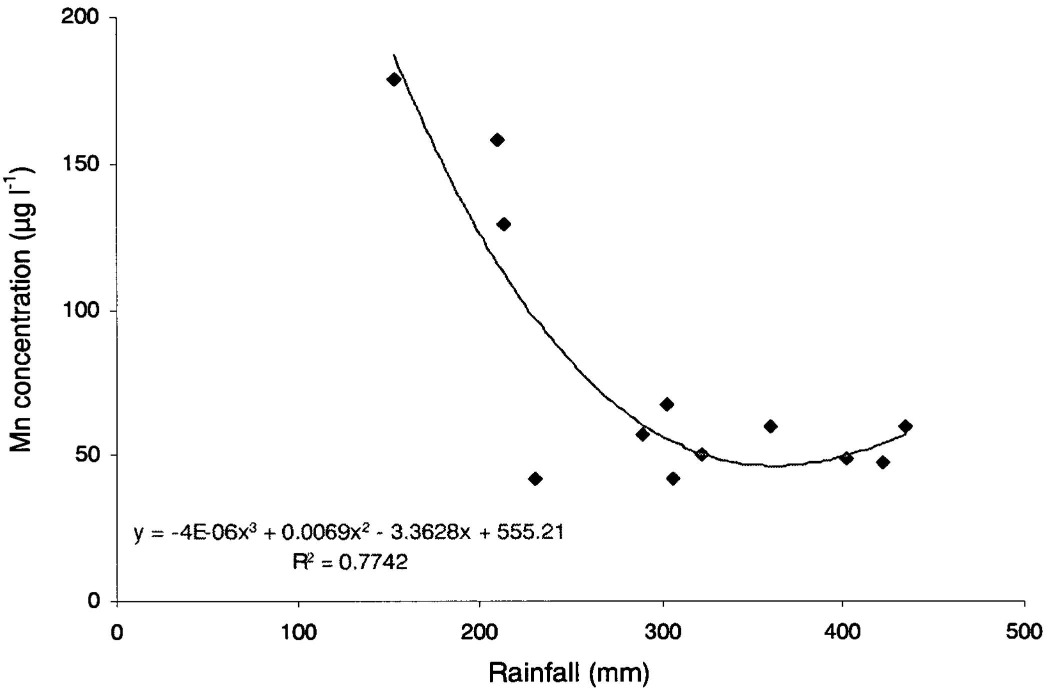


Figure 5.2: Regression analysis of summer rainfall and autumn Mn concentrations in Loch Bradan reservoir

5.1 Experimental rationale

Analysis of field data in Chapter 4 indicated that there was no identifiable seasonal peak of Mn concentration in soil water. In particular, the anticipated increase in soil water Mn concentration during autumnal rewetting following a summer soil moisture deficit was not observed. One explanation for this is that, during the period of field monitoring in the

Ballochbeatties Burn catchment, there was no prolonged build up of a summer soil moisture deficit. As explained in Chapter 2, changes in soil water regime resulting from such dry conditions are thought to promote the formation of soluble Mn ions which can be mobilised when soils are rewetted following autumn rainfall. Because summer conditions during the field monitoring programme (1999 & 2000) were considerably wetter than in 1995, the soil may not have dried out to the same extent during those years. With soils remaining wet, but not waterlogged, over the summer months, less Mn was present in the reduced form.

Therefore, the soil core laboratory experiments were designed to test the following hypotheses:

H_0: An extended period of soil moisture deficit followed by saturation produces no increase in soil water Mn concentration

H_1: Soil water Mn concentration increases during saturated conditions following an extended period of soil moisture deficit

5.2 Experimental design

The Loch Bradan rainfall data since 1980 (Figure 5.1) suggest that extremely dry summers, comparable to 1995, occur with a relatively low frequency. Since similar summer conditions were not experienced during the period of field research, it was therefore necessary to artificially induce a soil moisture deficit. In order to obtain soil water samples from catchment soils experiencing a large soil moisture deficit, soil cores were collected from the catchment and allowed to dry in the laboratory. Once sufficiently dried, the soil cores were then rewetted to saturation in order to simulate the conditions in catchment soils as evaporation rates declined during the autumn. Analysis of soil water samples collected over the experimental period provided a record of Mn concentrations as the soil dried out and was subsequently waterlogged.

Because the laboratory experiments were designed as an extension to the fieldwork, soil cores were collected from the major soil horizons of each soil type present at the primary moorland and forest field sites. A total of twelve horizons were sampled, following the same shallow-intermediate-deep strategy as the field sites (Figure 5.3).

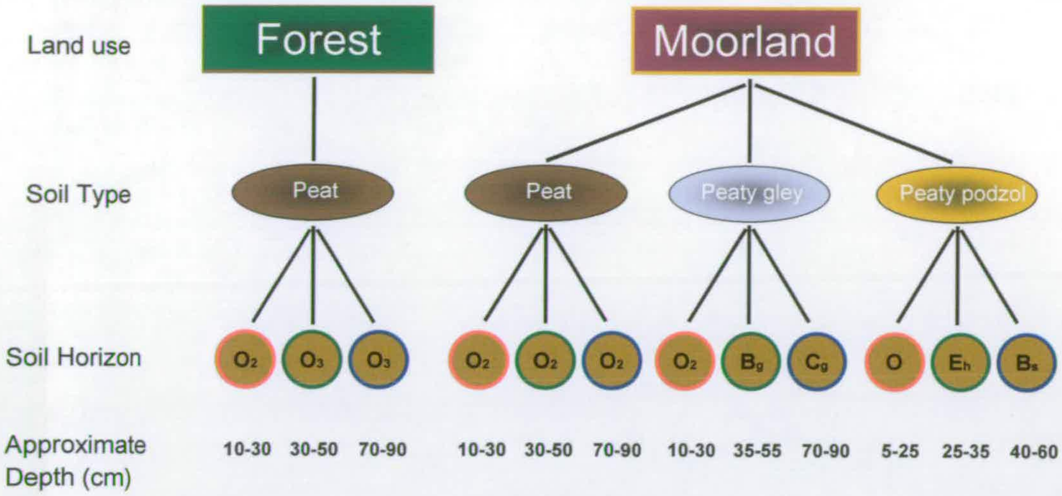


Figure 5.3: Soil horizons used in soil core experiments

Six soil cores were taken from each sample depth and randomly divided into two groups of three. The first group of cores were designated 'treatment cores' and the second group 'control cores'. The experimental procedure lasted for a period of at least six weeks, during which time the soil water regime of the treatment cores was altered to simulate an extended drying period followed by rewetting, while the control cores were kept at a constant soil moisture status (Figure 5.4).

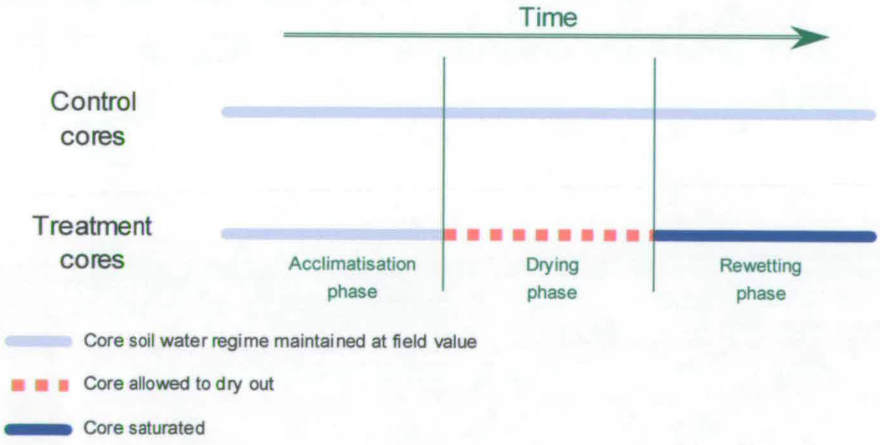


Figure 5.4: Treatment/control regime used in soil core experiments

For the first two weeks of the experiment, the treatment cores underwent an acclimatisation phase, during which the water content was maintained close to the field value at time of collection. This two-week period was designed to allow the identification of any Mn release in soil water resulting from soil disturbance during core collection, or changes in environmental conditions (e.g., temperature) during transfer to the laboratory. To achieve this, the cores were weighed each day and any weight loss (assumed to be from sample collection and evaporation of soil water) replaced with the appropriate volume of distilled water (assuming a density of 1 g ml^{-1} for water). Following the acclimatisation phase, the treatment cores were allowed to dry for a period of two weeks, during which no distilled water was added to replenish weight loss. The length of the drying phase was chosen to be consistent with the longest periods of no rainfall recorded at Loch Bradan during the summer of 1995 (the year in which an autumnal reservoir Mn peak was recorded). Once the drying phase was complete, the treatment cores were rewetted to saturation, by the addition of distilled water, to simulate the return to saturated conditions commonly experienced in the study area. Treatment cores were maintained in this saturated state for at least two weeks, in order to simulate the time between the onset of autumn rain in 1995 and the reported increase in reservoir water Mn concentrations. The control soil cores were maintained close to the field value for water content over the entire experimental period by the addition of sufficient distilled water each day to replenish weight loss.

If the theory concerning Mn release upon rewetting of dried soils is correct, soil water samples from the treatment cores should contain increased concentrations of Mn in the rewetting phase relative to their acclimatisation phase and the control cores (Figure 5.5). In order to ascertain whether this occurred in any of the soil cores, data was first visually inspected, then statistical significance of the results was determined using one-way ANOVA, repeated measures ANOVA and correlation analysis.

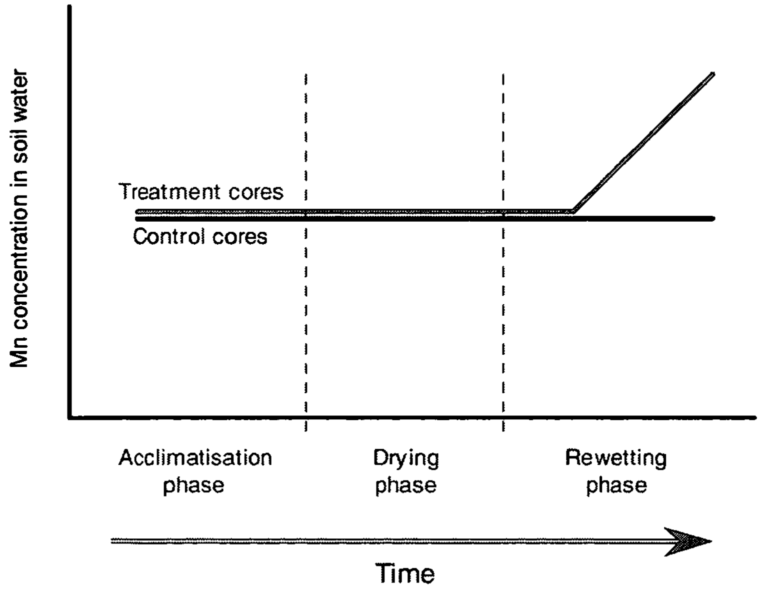


Figure 5.5: Anticipated release of Mn from treatment soil cores

5.3 Experimental methods

This section describes the processes of soil core collection and instrumentation. Details of the sampling procedure followed during the course of the experiment are also presented.

5.3.1 Soil core collection

Soil cores, 11 cm in diameter and 20 cm deep, were taken in April 2000 from locations in the Ballochbeatties Burn catchment close to the field monitoring sites. The ongoing field monitoring at this time meant that care was taken in order to avoid disturbing the existing field sites. Once the required soil profiles were located, the following collection procedure was employed at each site.

Vegetation and soil were cleared away, down to the top of the uppermost horizon to be sampled. Core rings, 20 cm long cut from 11 cm diameter plastic piping, were then placed on the exposed horizon surface and carefully pressed downwards. As the ring was gently pressed into the horizon, soil surrounding the core ring was carefully removed. This process was repeated until the core ring was filled with an undisturbed sample of soil, at which point, the collected core was freed by excavating underneath it. Excess soil was then removed from both ends of the soil core with a sharp knife, leaving the core flush with the top and bottom of the plastic ring.

Where possible, this method was used to collect single, intact cores from each horizon. However, some horizons were either too thin to fill the entire length of the core ring, or too stony to permit ring penetration. Relatively undisturbed cores were obtained from thin horizons by removing the partly filled ring at the lower horizon boundary and moving it to the surface of a fresh piece of exposed horizon. This was repeated until the 20 cm depth of core required was collected. When the horizon was too stony to permit coring, the soil cores were collected by carefully repacking soil into the core at an approximate density to the *in situ* material. Six replicates were collected from each horizon, with the exception of the intermediate (Eh) horizon of the peaty podzol, from which only three cores were obtained, as it was too thin to provide six replicates without excavating a large area of hillside and causing disturbance to the field monitoring sites. Once collected, rings containing the soil cores were wrapped in cling-film and transported back to Edinburgh, where they were stored in a darkened cold room at 4°C until required.

5.3.2 Laboratory methods

The design of the soil core laboratory experiments required that soil water from each core was sampled at regular intervals. Additionally, measurements of soil matric potential were made in order to determine the extent of drying in each core. To accommodate the necessary equipment, three holes had been drilled in a vertical line down the side of each plastic core ring prior to core collection and sealed with waterproof tape during storage. The soil adjacent to these holes was excavated to allow the fitting of two microtensiometers and a small suction probe, completing the soil core experimental apparatus (Figure 5.6).

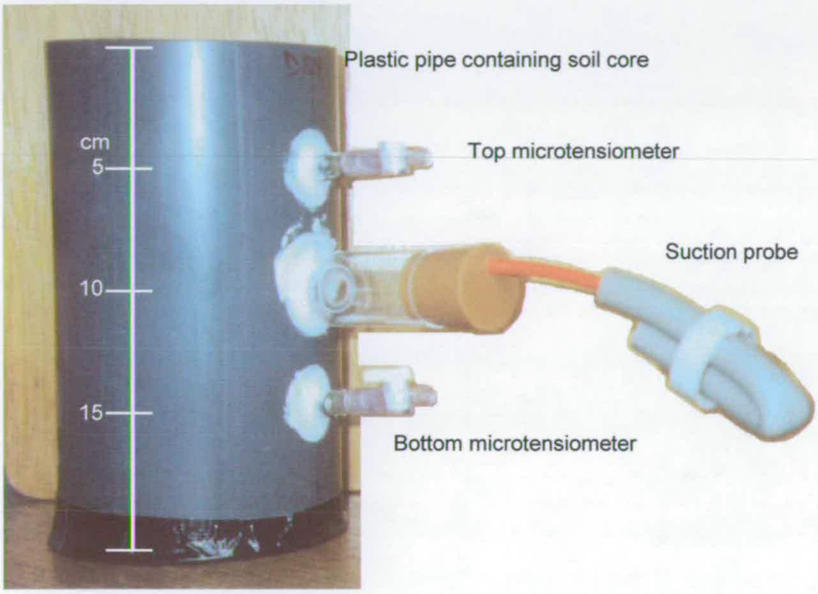


Figure 5.6: Soil core experimental apparatus

Soil removed during equipment fitting was analysed to determine soil Mn concentration, organic matter content and gravimetric water content (see Appendix A for procedures), thus providing an indication of the potential Mn pool in each soil core and two of the factors thought to influence its release into soil water. The arrangement of two microtensiometers, at the top and bottom of the core, also allowed the calculation of soil hydrological properties for the moisture retention characteristic ($\theta(h)$ relationship) using the Wind evaporation method, which were required in the soil water modelling program discussed later in Chapter 6. The base of each core was sealed with a plastic tray, inverted and held in place with silicone sealant and waterproof tape. Final waterproofing of the core was achieved by the use of sealant to close any holes around the fitted microtensiometers and suction probe.

The suction probes fitted to the soil core apparatus were constructed of a 2.5 cm diameter porous ceramic cup attached, via a 5 cm length of similar diameter Perspex pipe, to the base of a 50 ml clear plastic sample vial which acted as a sample chamber. Prior to installation, the suction probes were pre-conditioned in the same way as the larger ones installed in the field sites by flushing with 1M hydrochloric acid followed by distilled water. A rubber bung, fitted with a length of tubing in a similar manner to those used by the larger field suction probes, was used to seal the small probe and allow creation of a vacuum with a hand-held pump. The clear vials allowed a visible check of any solute collected in them, and the early identification of any malfunction in the suction probes. Periods when there was insufficient sample collection for analysis could therefore be quickly identified and measures taken to remedy this where possible (e.g., checking seals and re-applying vacuum). However, there were still periods during the drying phase when there was not enough sample collected from the treatment cores to allow analysis. In these cases, absence of sample was thought to result from matric potential in the dry soil being greater than the suction applied in the probe, or from failure of the suction probe because of air entry as the soil surrounding it cracked and shrunk.

The microtensiometers were composed of 1 cm diameter porous ceramic cups, fitted to 5 cm lengths of similar diameter plastic pipe attached to a three-way tap. Once filled with de-gassed water and inserted into the soil core, readings were taken from the microtensiometers by connecting them to a pressure gauge via a short length of plastic tubing (also filled with de-gassed water). As with the tensiometers installed at the field sites, it was important to exclude air bubbles from any part of the microtensiometer-pressure transducer system, because fluctuating bubble volumes in response to pressure changes would distort readings on the pressure transducer. When measuring matric potential, the microtensiometer tap was opened and the pressure gauge allowed a period of two minutes to reach a steady reading. Once a reading was taken, the tap was then closed to seal the microtensiometer again and the gauge transferred to the next microtensiometer to be read.

Because of equipment and time constraints, the experiment was split into four runs, each containing all the cores from an individual soil type. Soil cores were randomly arranged in the laboratory in order to minimise positioning effects that may have caused temperature fluctuations, such as proximity to a window or radiator. On the first day of an experimental run, soil cores were weighed, the soil matric potential recorded, and vacuum applied to the suction probes. Following this, further measurements were taken on a daily basis where possible. Every measurement day, the soil water was collected from the suction probes and transferred to 60 ml plastic sample vials. Next, each soil core unit was weighed and the readings from the two microtensiometers recorded, before distilled water was added to the top of the core (if required) and a vacuum reapplied to the suction probe. During the two-week acclimatisation phase at the start of the experiment, sufficient water (calculated on the basis of core weight loss) was added to maintain each core in its field moist state. Control cores were kept in this state for the entire experiment, while the soil water regime of treatment cores was manipulated by stopping water addition during the two-week drying phase then rewetting to saturation during the rewetting phase. The length of the rewetting phase was originally set to two weeks, as this corresponded to the time in 1995 between the onset of wet autumn conditions and the Mn peak in reservoir water. However, findings from the first experimental run indicated that Mn release only began to occur in the final days of this two-week period. Therefore, the duration of the rewetting phase in later experimental runs was increased in order to allow better identification of any Mn release from soil cores.

Soil water samples collected from the cores were immediately analysed for pH, using a HI9025 hand-held pH meter, and colour (as absorbance @400 nm), using a Helios Gamma spectrophotometer. Measurement of pH was intended to show whether any increases in soil water Mn concentration were associated with decreases in pH, possibly indicating one pathway by which Mn release from the Loch Bradan soils occurs. Colour was measured as it is often considered indicative of the organic carbon content of water samples, and may therefore signify the presence of organic compounds with the potential to form soluble Mn complexes. A wavelength of 400 nm is commonly used to determine organic carbon content by spectrophotometry, as the majority of compounds present absorb strongly at the red end of the visible spectrum. In theory, water containing large amounts of dissolved organic carbon should have higher values of absorbance. Samples for Mn determination were stored in darkened conditions at 4°C until analysed by GFAAS using a Pye-Unicam SOLAAR series M5 atomic absorption spectrophotometer.

5.4 Results

The following analyses were carried out on data from the soil core experiments. In addition to preliminary graphical analysis, correlation analysis was performed on the soil chemistry data from the samples removed during instrumentation of the cores. Interpretation of the soil water chemistry data was undertaken in four main stages. Firstly, a visual examination of data in time series graphs determined if any obvious patterns existed in soil water chemistry.

One-way ANOVA was then used to identify differences in soil water chemistry between treatments and also between experimental phases. This was further enhanced by the use of repeated measures ANOVA to relate differences in soil water chemistry to land use and soil properties. Finally, correlations between any of the measured soil water chemistry variables (Mn concentration, pH and colour) were identified. When complete, these analyses provided an indication of the Mn available in the soil for mobilisation, factors influencing its mobilisation and also whether there was any horizon-specific aspect to the mobilisation process.

5.4.1 Analysis of soil chemistry

Results from the chemical analysis of soil samples removed during core instrumentation are presented in Figure 5.7, showing the mean values of treatment and control cores for every soil horizon investigated in the experiment. The relative differences in chemical properties between soil types were similar to those identified following the analysis of field samples (see section 4.2.1), indicating that both peats contain less Mn than the two organo-mineral soils, but have greater organic matter and water contents. In the peaty gley and peaty podzol, soil Mn concentrations are greatest in the deeper B and C horizons where there is less organic matter and water content. This is most likely a consequence of greater amounts of Mn present in the mineral component of these horizons and may not reflect the Mn concentrations in soil water, as not all of the Mn may be readily mobilised. Statistical analysis of the soil chemistry data (Table 5.1) indicates that total soil Mn was negatively correlated with both soil organic content and soil water content. This is as expected, and again reflects the greater store of Mn in mineral horizons, compared to highly organic horizons.

	% Organic matter	% Gravimetric water
Mn	-0.974 *(<0.001)*	-0.939 *(<0.001)*
% Gravimetric water	0.973 *(<0.001)*	correlation coefficient *(p-value)*

Table 5.1: Correlation coefficients (Pearson product moment) for soil chemical analysis

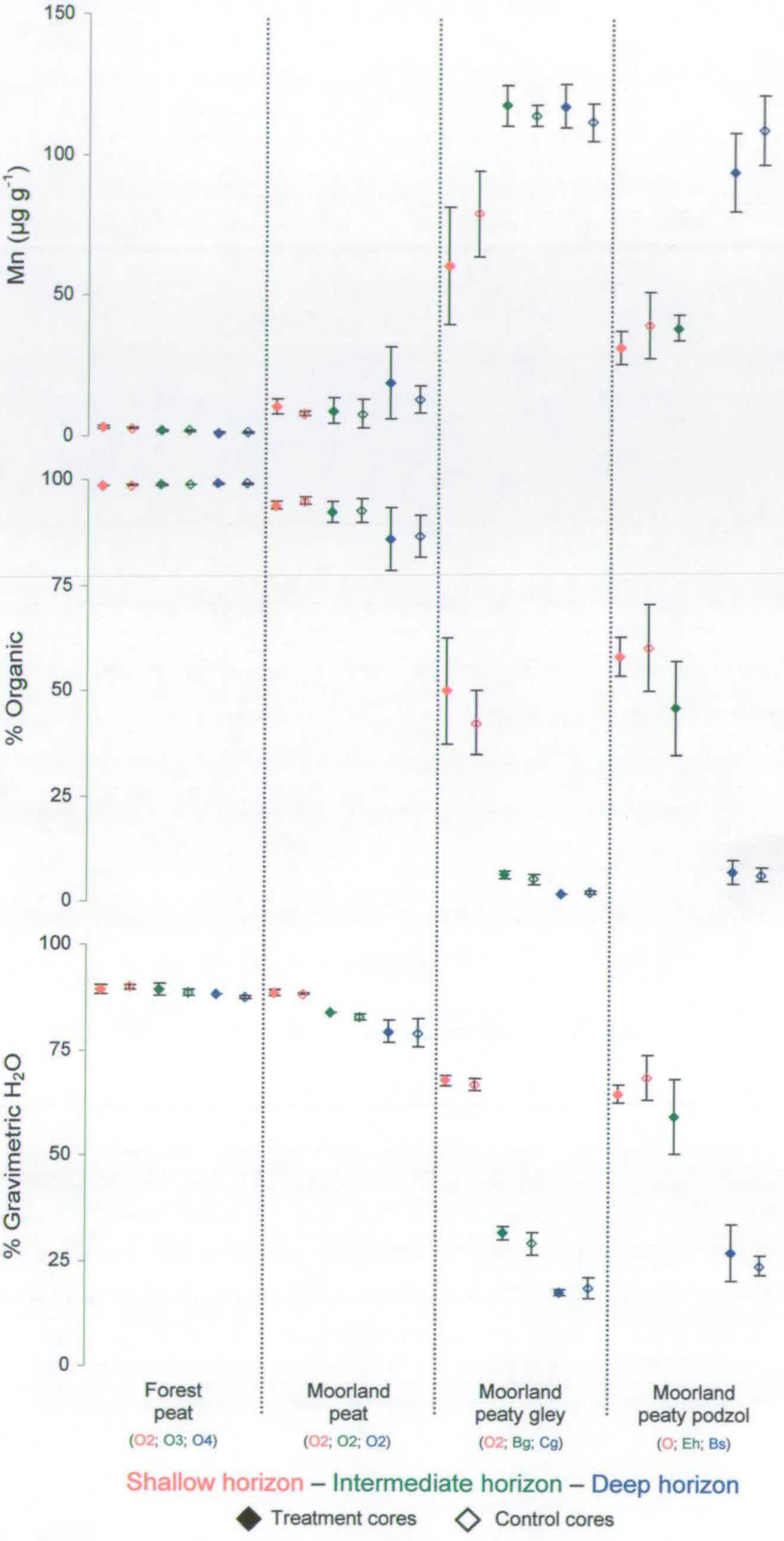


Figure 5.7: Mn concentration, organic matter content and gravimetric water content (mean of 3 replicates ±SE) of soils used in soil core experiments

5.4.2 Soil matric potential

The microtensiometers installed in each soil core provided a record of the degree to which the soil core dried out during the experiment. Data from one treatment core, selected at random, in each of the horizons instrumented are shown in Figure 5.8 to illustrate the extent of drying in each horizon. The gradual drying out of soil, followed by rapid waterlogging, can easily be seen in each graph. In contrast to this, similar matric potential graphs from control cores (Figure 5.9) were relatively constant for their entire length, indicating that soil water content was maintained near to the field levels for the duration of the experiment.

In general, the deeper horizons tended to dry out to a greater extent than shallower horizons (Figure 5.8). In the peats, this phenomenon may result from increased drying and shrinkage of those horizons with a greater degree of humification. Another point to note is that the relative difference between top and bottom tensiometer readings in the mineral horizons is often less than that observed in the organic horizons. The reason for this is possibly related to the greater hydraulic conductivity of the mineral horizons, relative to the organic ones, resulting in a more uniform drying throughout the entire core. However, it may also be due to repacking of these horizons in order to fill the cores, which may have altered their physical properties.

5.4.3 Soil water chemistry time series

The following graphs present time series of data from the four different soil and land use combinations. Data for treatment and control cores are shown as the mean of the three replicates, with standard error bars. Where no error bars are present, data were not available from all three replicate cores, while missing data points indicate failure to collect sample from any cores. Additional time series graphs are also presented, detailing the relative changes in soil water chemistry for each determinand, calculated by subtracting changes in the mean of control cores from the mean of treatment cores (Equation 5.1).

$$[\text{Mn-rel}]_{(\text{day})} = [\text{Mn-trt}]_{(\text{day})} - \{[\text{Mn-ctrl}]_{(\text{day-1})} - [\text{Mn-ctrl}]_{(\text{day})}\} \qquad \textbf{Equation 5.1}$$

Where: $[\text{Mn-rel}]_{(\text{day})}$ = relative soil water determinand value for current day

$[\text{Mn-trt}]_{(\text{day})}$ = mean of treatment core soil water determinand value for current day

$[\text{Mn-ctrl}]_{(\text{day-1})}$-$[\text{Mn-ctrl}]_{(\text{day})}$ = difference between previous day and current day's mean control core values

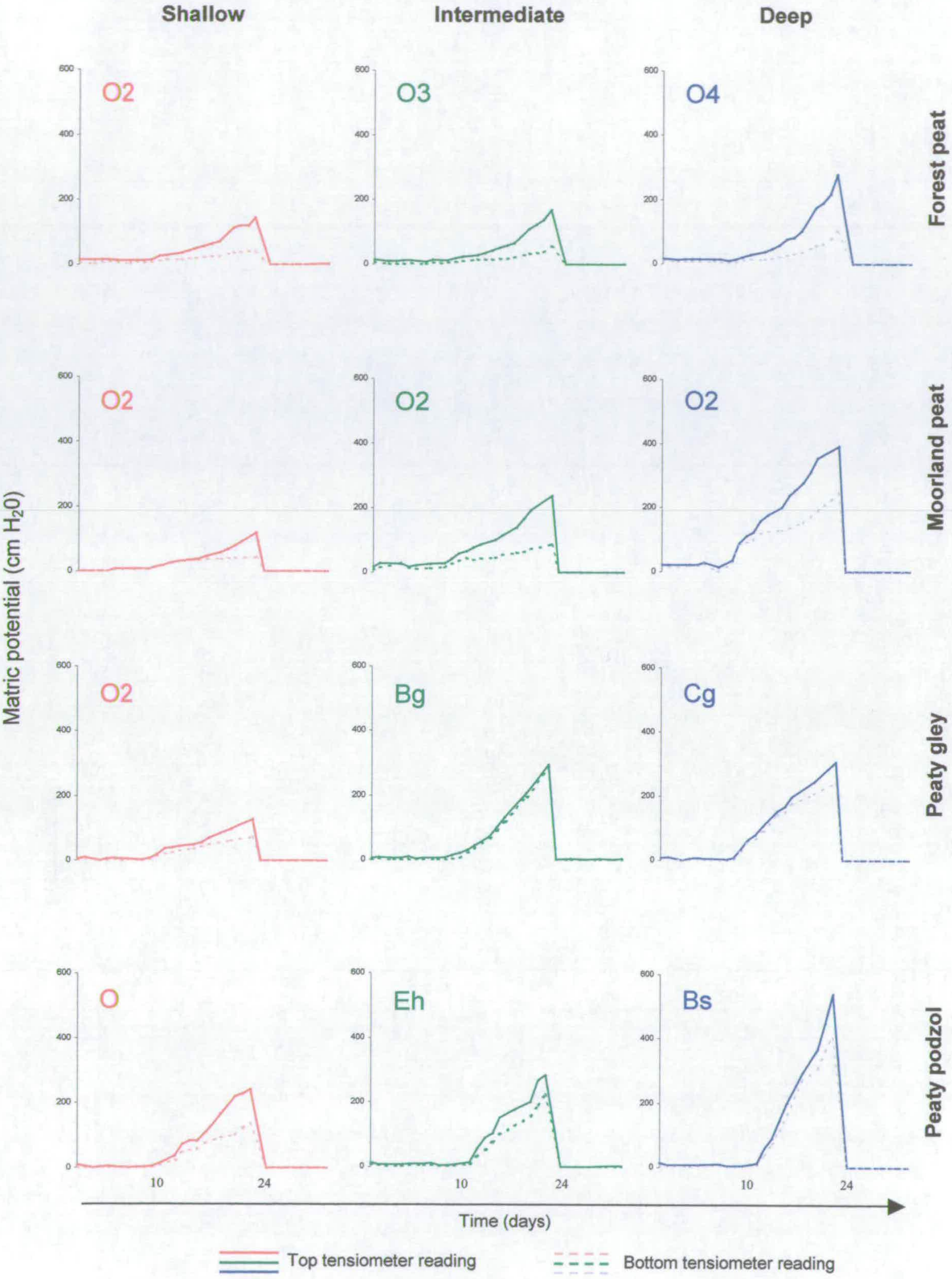


Figure 5.8: Matric potential measurements from microtensiometers installed in treatment soil cores

(In order to standardise graphs and allow better comparison of drying phases, only the 10 days before and after each horizon's drying phase are shown)

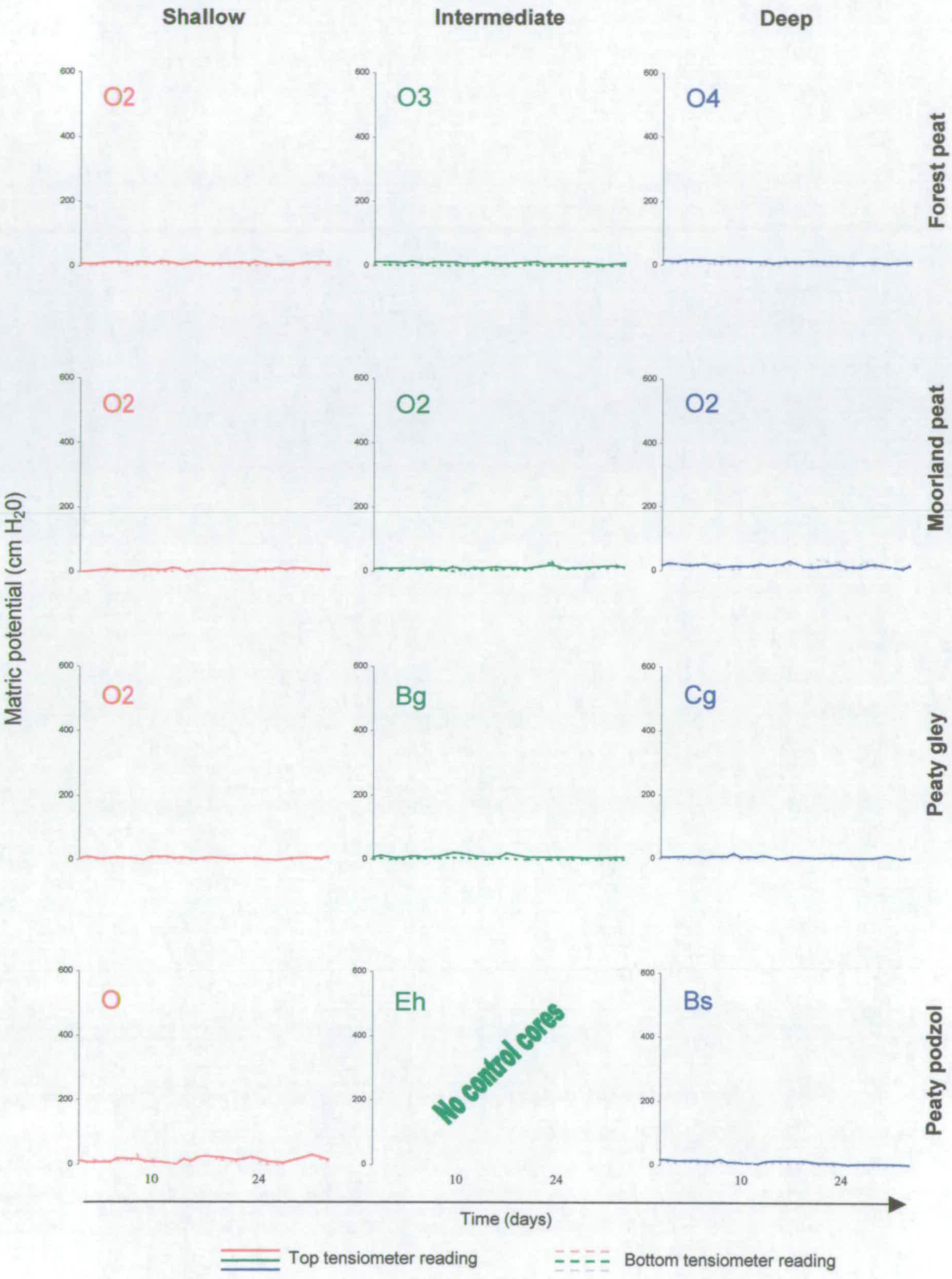


Figure 5.9: Matric potential measurements from microtensiometers installed in control soil cores

(In order to standardise graphs and allow better comparison of drying phases, only the 10 days before and after each horizon's drying phase are shown)

5.4.3.1 Mn concentrations

Figures 5.10 to 5.13 show Mn concentrations in soil water collected from the soil cores (N.B. y-axis scale differs between soil types). The most obvious feature in many of the graphs is the generally low Mn concentrations throughout the experiment. The intermediate (O3) and deep (O4) horizons of the forest peat (Figure 5.10) show very little difference between treatment and control cores, or between experimental phases. However, Mn concentrations from the shallow (O2) horizon treatment cores exhibit a decrease in magnitude during the drying phase. Data from the moorland peat cores (Figure 5.11) also show no obvious difference in Mn concentration between treatment and control cores, or between experimental phases, in the intermediate and deep horizons. The possible start of an increase in Mn concentrations is evident in the treatment cores from the shallow horizon at the end of the rewetting phase. Unfortunately, because Mn analysis took place several days after sample collection, this was not identified until after the experimental run was terminated and any sustained increase in Mn concentrations may have been curtailed. If the Mn had already been in the soluble form at the end of the drying phase, then its release into soil water should have followed rapidly upon rewetting. However, because the increase in Mn concentrations appeared to be delayed for several days after rewetting began, it is likely that changing redox conditions in the saturated soil were a major factor in the production of soluble Mn. Whether bacterial activity was involved, directly or indirectly, is unknown, as is the role of the drying phase in promoting the mobilisation. Following the discovery of this potential Mn release, the rewetting phases were extended in later experimental runs. Comparison of the two peats (Figures 5.10 & 5.11) shows that there was little difference in the soil water Mn concentrations of the intermediate and deep horizons, with both forest and moorland peat horizons containing little Mn in samples and not responding to changes in soil water regime. However, soil water samples from the two shallow peat horizons exhibit very different responses during the experiment. The time series graph of soil water Mn concentrations from the moorland peat shallow horizon shows the expected increase during the rewetting period, after little change during the acclimatisation and drying phases. In contrast to this, soil water Mn concentrations from the forest peat shallow horizon decrease during the drying phase, before returning to similar concentrations to the acclimatisation phase upon rewetting. The contrasting responses of the forest peat and moorland peat shallow horizons to changes in soil water regime may result from the different vegetation cover, as the peat forming at each site will consist of breakdown products from the decomposition of different surface vegetation and therefore may be physically and chemically different.

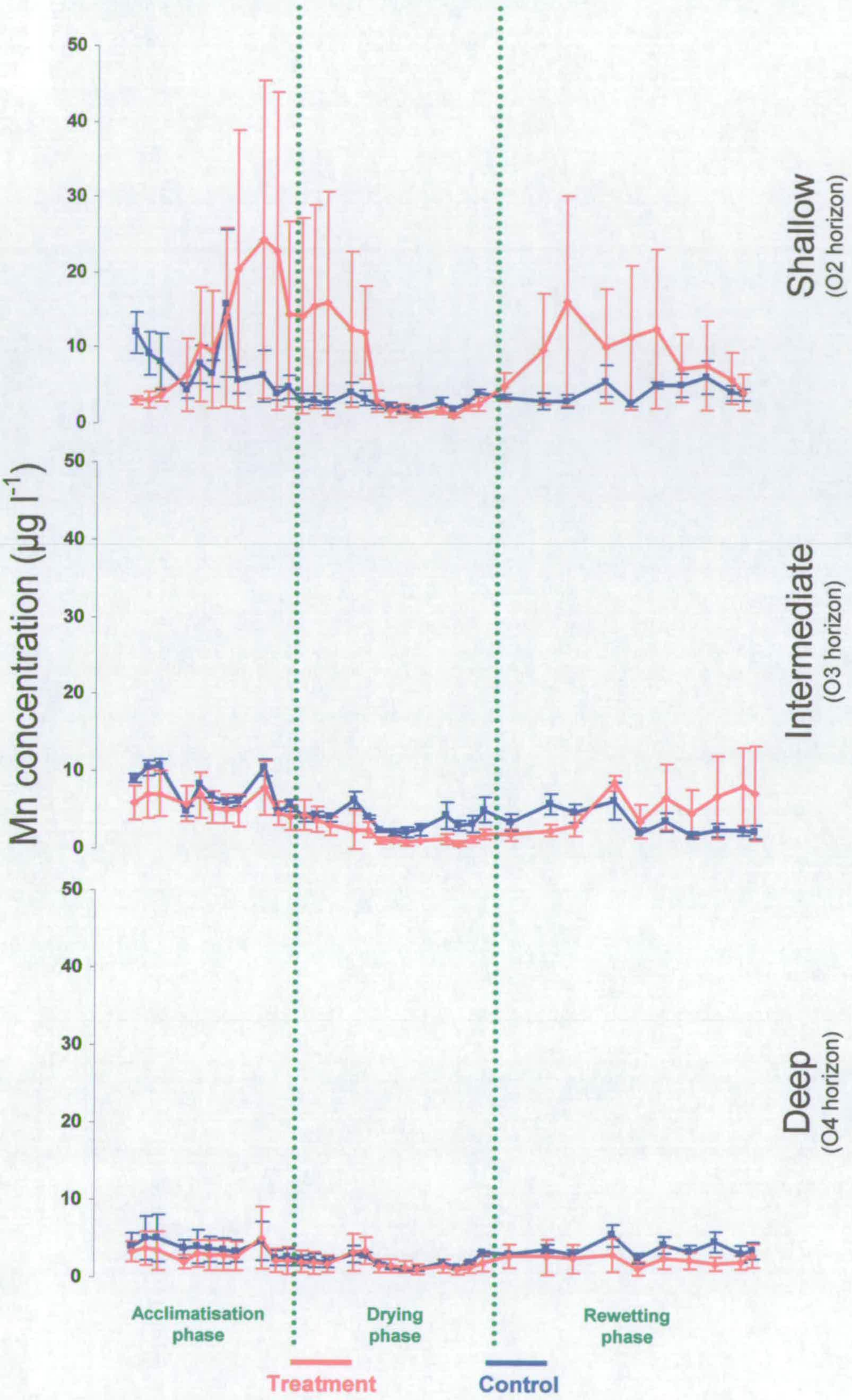


Figure 5.10: Mn concentrations (±SE) in soil water from **forest peat** soil cores

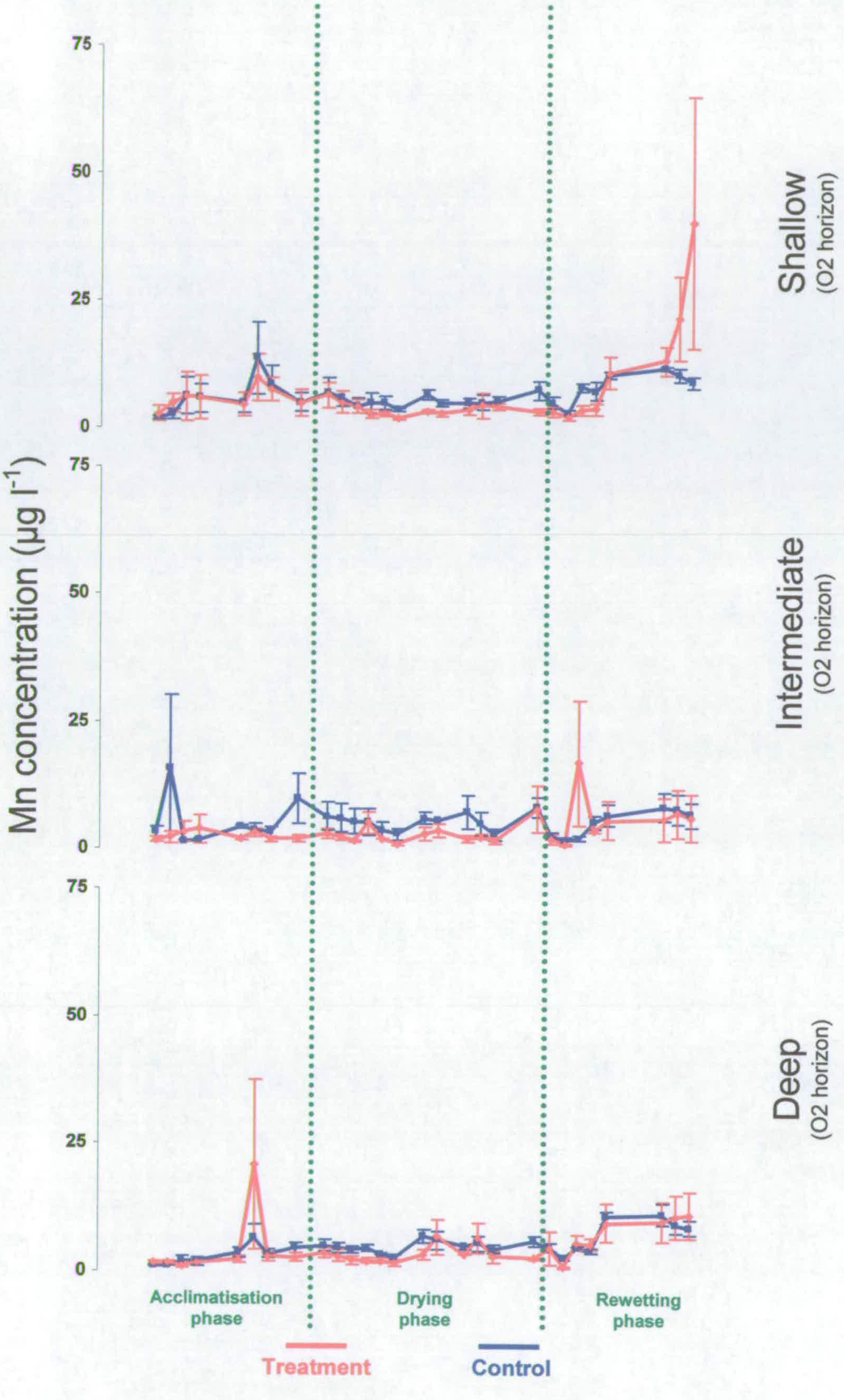


Figure 5.11: Mn concentrations (±SE) in soil water from **moorland peat** soil cores

Intermediate (Bg) and deep (Cg) horizon cores from the peaty gley (Figure 5.12) show little change in Mn concentration over the course of the experiment. However, in addition to containing more Mn, soil water samples from the shallow (O2) horizon cores have a much wider range of Mn concentrations than samples from the deeper horizons. One further point to note concerning data from the peaty gley cores is that Mn concentrations in soil water samples from the shallow (O2) horizon control cores exceed those in the treatment cores throughout the experiment. This can probably be attributed to within-horizon variability of soil water chemistry and the small sample size, rather than any experimental effects, although error bars on the time series graph indicate that the difference is greatest during the drying phase. Soil water samples from the peaty podzol horizons (Figure 5.13) contained the greatest Mn concentrations measured during the entire experiment. All three horizons show increased Mn concentration and variability between replicates of the treatment cores during the rewetting phase, compared to the preceding phases. The greatest increase in variability and concentration is found in samples from the intermediate (Eh) horizon. However, insufficient soil was collected from this horizon to allow for control cores, and any analysis is limited by this fact. The rewetting phase for the peaty podzol soil cores was extended for a further week to enable better definition of the Mn peak observed in the intermediate (Eh) horizon. In general, Mn concentrations in soil water samples from the two organo-mineral soils did not follow the pattern of total soil Mn described in section 5.4.1 with greatest concentrations in horizons containing the most mineral material. Instead, the greatest soil water Mn concentrations within these two profiles were observed in the shallow (O2) horizon of the peaty gley and the shallow (O) and intermediate (Eh) horizons of the peaty podzol. It is therefore apparent that total soil Mn alone is not a reliable indicator of potential Mn release into soil water.

The time series graphs of relative soil water Mn concentration from the treatment cores (Figure 5.14) confirm the patterns of Mn distribution suggested by analysis of the graphs in Figures 5.10 to 5.13. Increases in soil water Mn concentration during the rewetting phase are most evident in samples from the moorland peat shallow (O2) and peaty podzol intermediate (Eh) horizons. In the forest peat and peaty gley soils, the greatest soil water Mn concentrations occur in the shallow horizons throughout the experiment. Soil water samples from the peaty podzol also follow this pattern during the acclimatisation and drying phases, however this is interrupted following Mn release from the intermediate (Eh) horizon during the rewetting phase. Soil water Mn concentrations from the moorland peat exhibit little

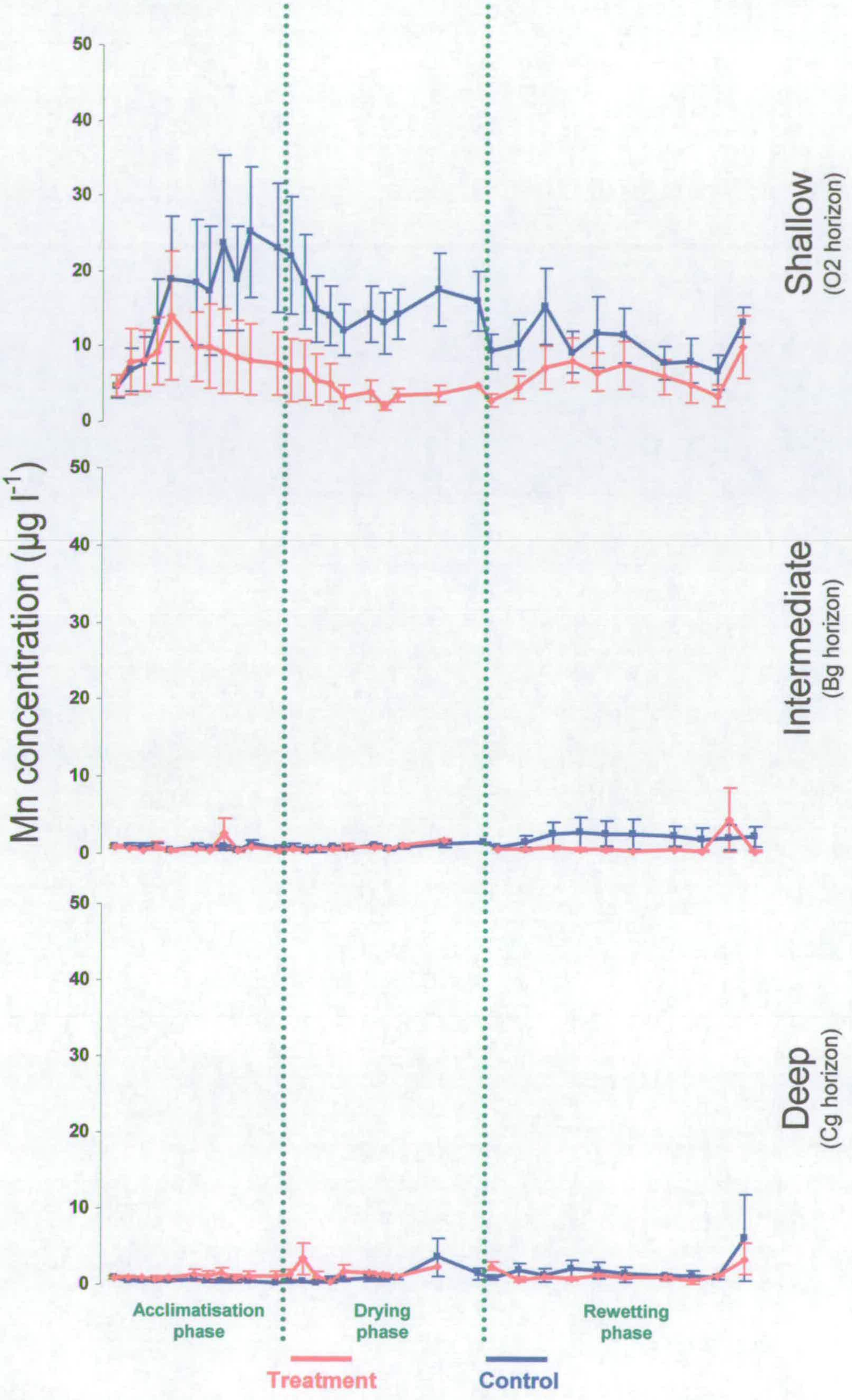


Figure 5.12: Mn concentrations (±SE) in soil water from moorland **peaty gley** soil cores

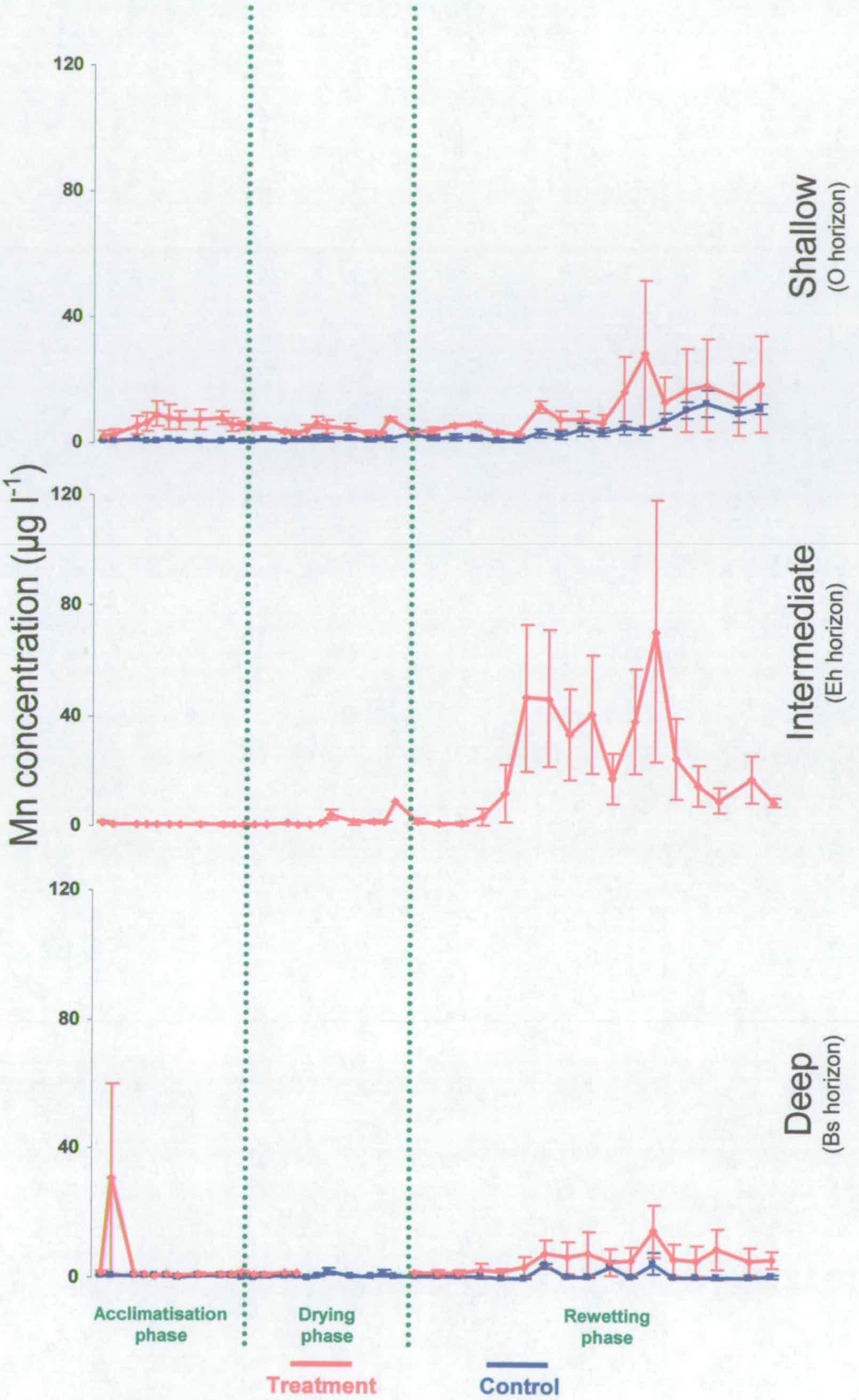


Figure 5.13: Mn concentrations (±SE) in soil water from moorland **peaty podzol** soil cores

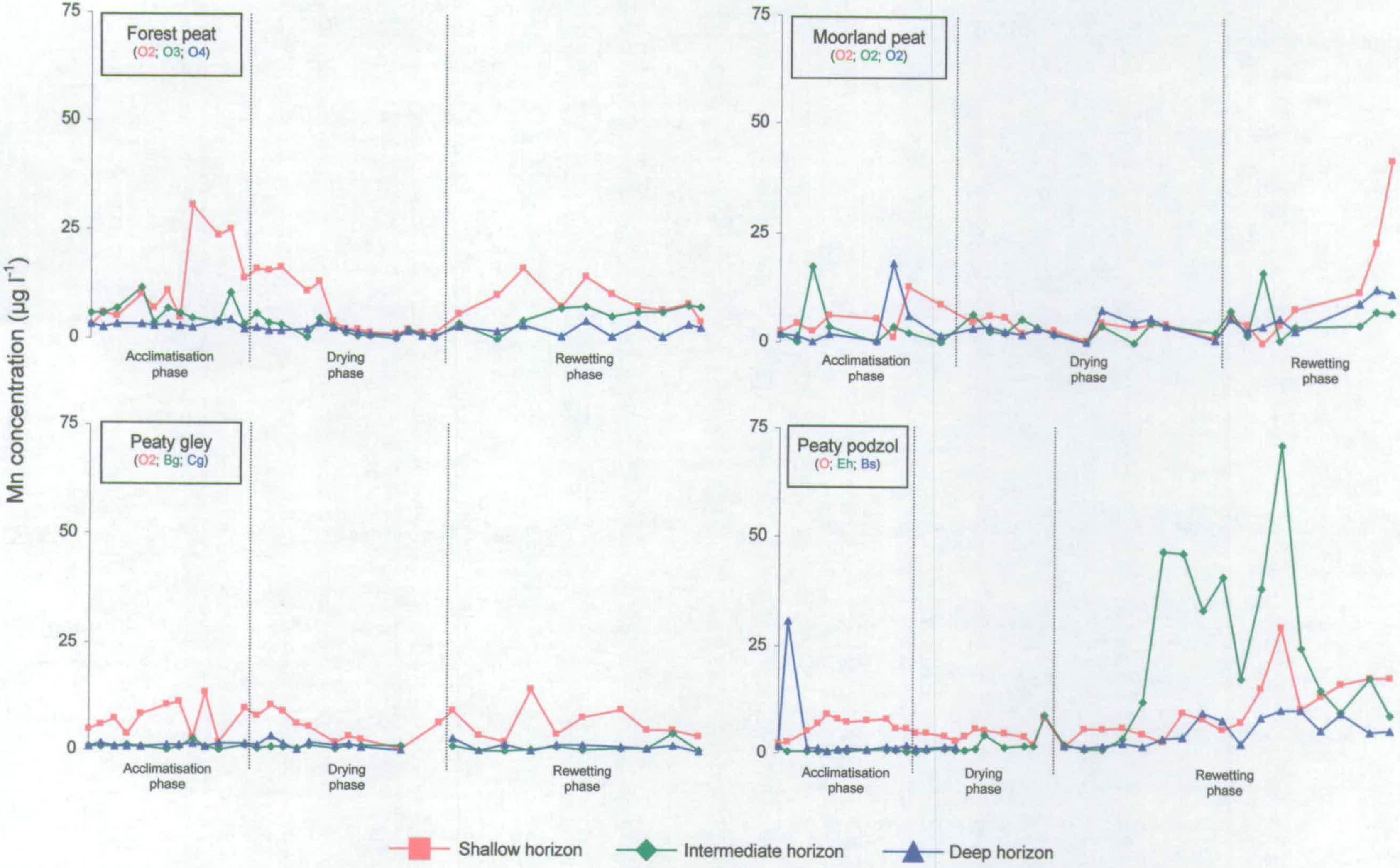


Figure 5.14: Relative Mn concentrations of soil water samples collected from treatment cores during soil core experiments

difference between horizons, until the possible emergence of the shallow (O2) horizon Mn peak at the end of the rewetting phase.

5.4.3.2 pH

Figures 5.15 to 5.18 show the pH of soil water samples collected during the experiment. There does not appear to be any great change in soil water pH resulting from the experimental procedure in most of the time series, with both treatment and control cores following the same general pattern. Samples from the treatment and control cores of the forest peat intermediate (O3) horizon (Figure 5.15) appear to have different pH values, with treatment pH exceeding control pH during the entire experiment, although this is probably due to the small number of replicates and inherent variability of soil solution chemistry. There also appears to be a decrease in pH of soil water samples from the treatment cores of all three horizons during the rewetting phase. The identification of any clear increase or decrease in soil water pH from the moorland peat soil cores (Figure 5.16) is difficult due to missing data from the treatment cores, caused by suction probes failing to collect sufficient sample for analysis during the drying phase. Treatment and control cores in all three horizons exhibit a decrease in pH at the start of the acclimatisation phase, which may be due to the release of organic acids owing to disturbance of the soil during core collection. However, another explanation for the decrease in soil water pH over the first few measurements is that H^+ ions are being retained at the cation exchange sites of the freshly cleaned ceramic cups. Therefore, until the cation exchange capacity of the ceramic cups is satisfied, the pH of soil water samples will be greater than expected. Soil water pH from all three horizons of the peaty gley cores (Figure 5.17) exhibits little difference between treatment and control cores. There may be a slight downward trend in pH over the entire experiment in samples from control cores, indicating a decrease in background pH over time. This same decrease in soil water pH is shown by samples from the peaty podzol soil cores (Figure 5.18), particularly those from the intermediate (Eh) horizon. However, this downward trend appears to be interrupted during the drying phase in samples from the treatment cores, possibly indicating an increase in soil water pH as the soil dried out.

The time series graphs of relative soil water pH (Figure 5.19) provide an indication of pH changes in soil water samples from the treatment cores during the three experimental phases. If pH during the acclimatisation phase is accepted as being relatively constant, then the general trend seen in most of the horizons is for an increase in pH during the drying phase followed by a decrease during the rewetting phase. The most noticeable exceptions to this

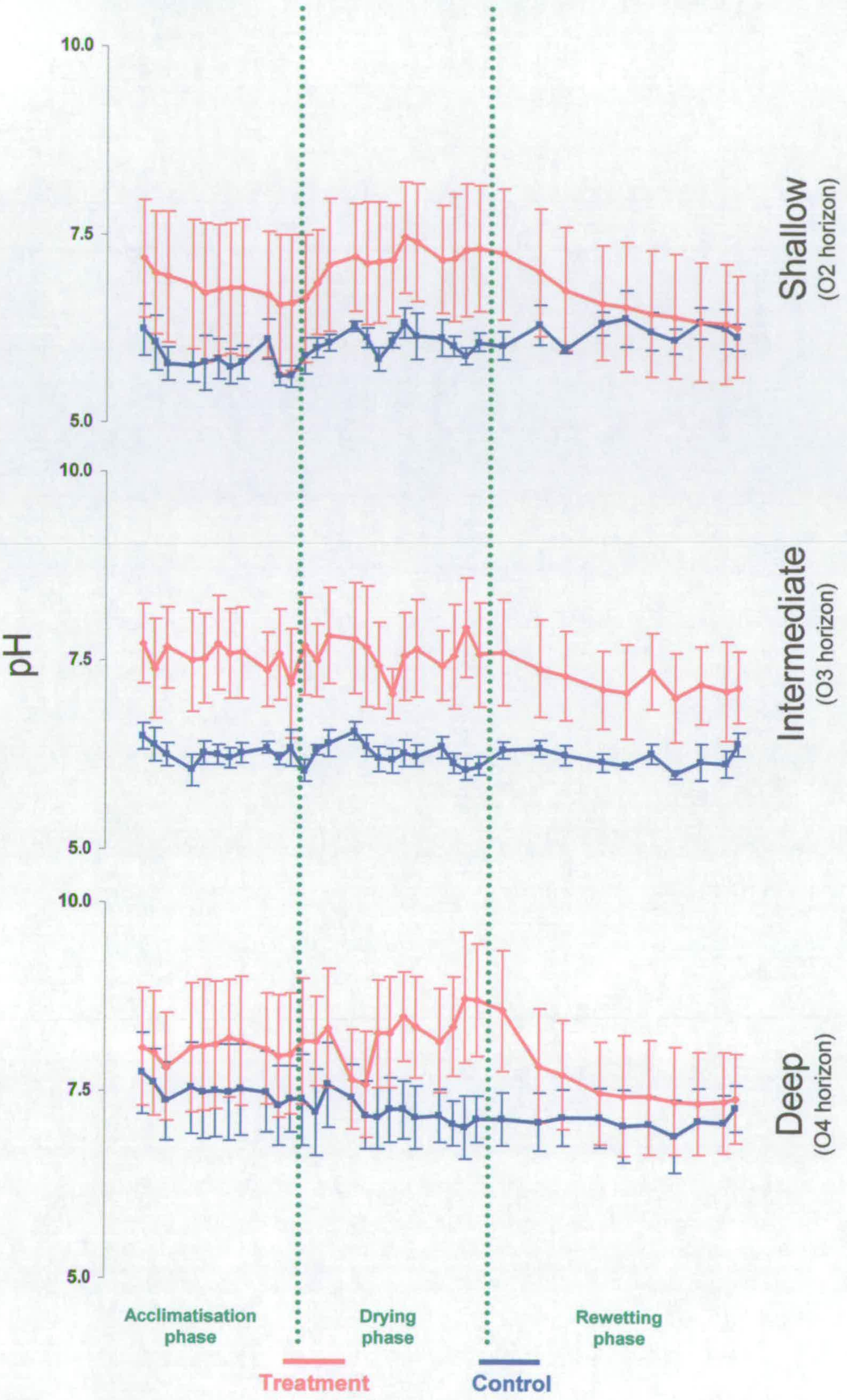


Figure 5.15: pH (±SE) of soil water from **forest peat** soil cores

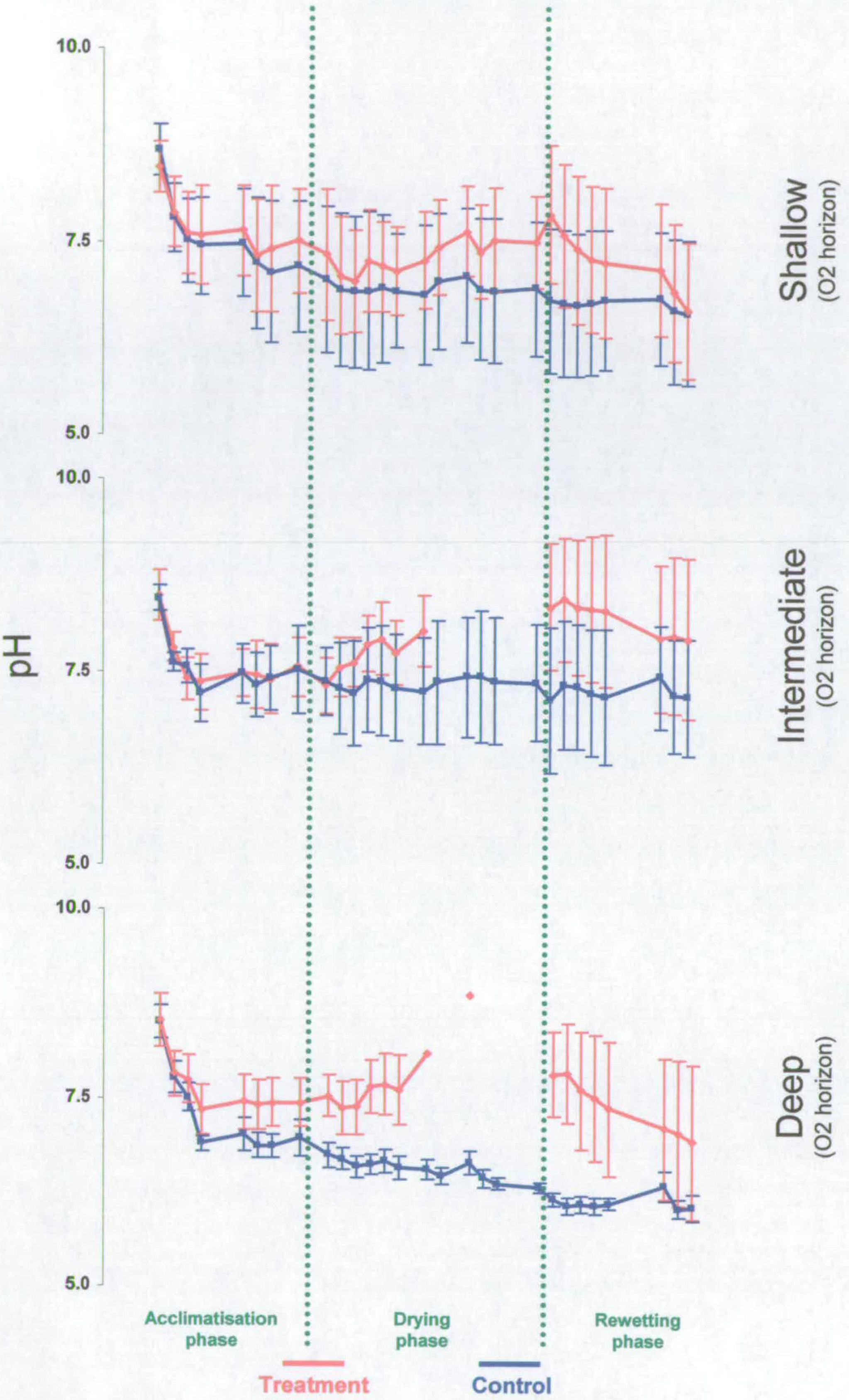


Figure 5.16: pH (±SE) of soil water from **moorland peat** soil cores

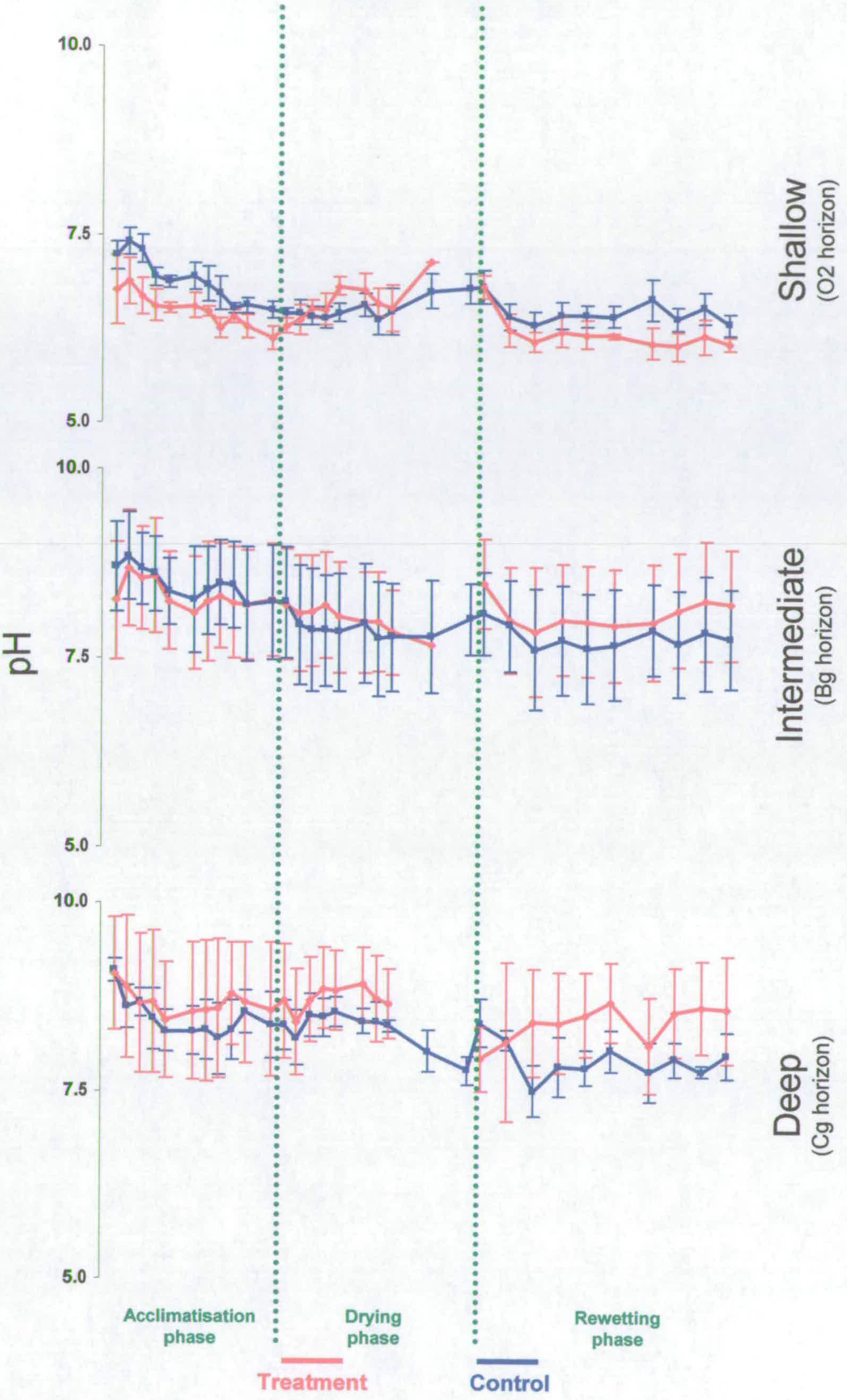


Figure 5.17: pH (±SE) of soil water from moorland **peaty gley** soil cores

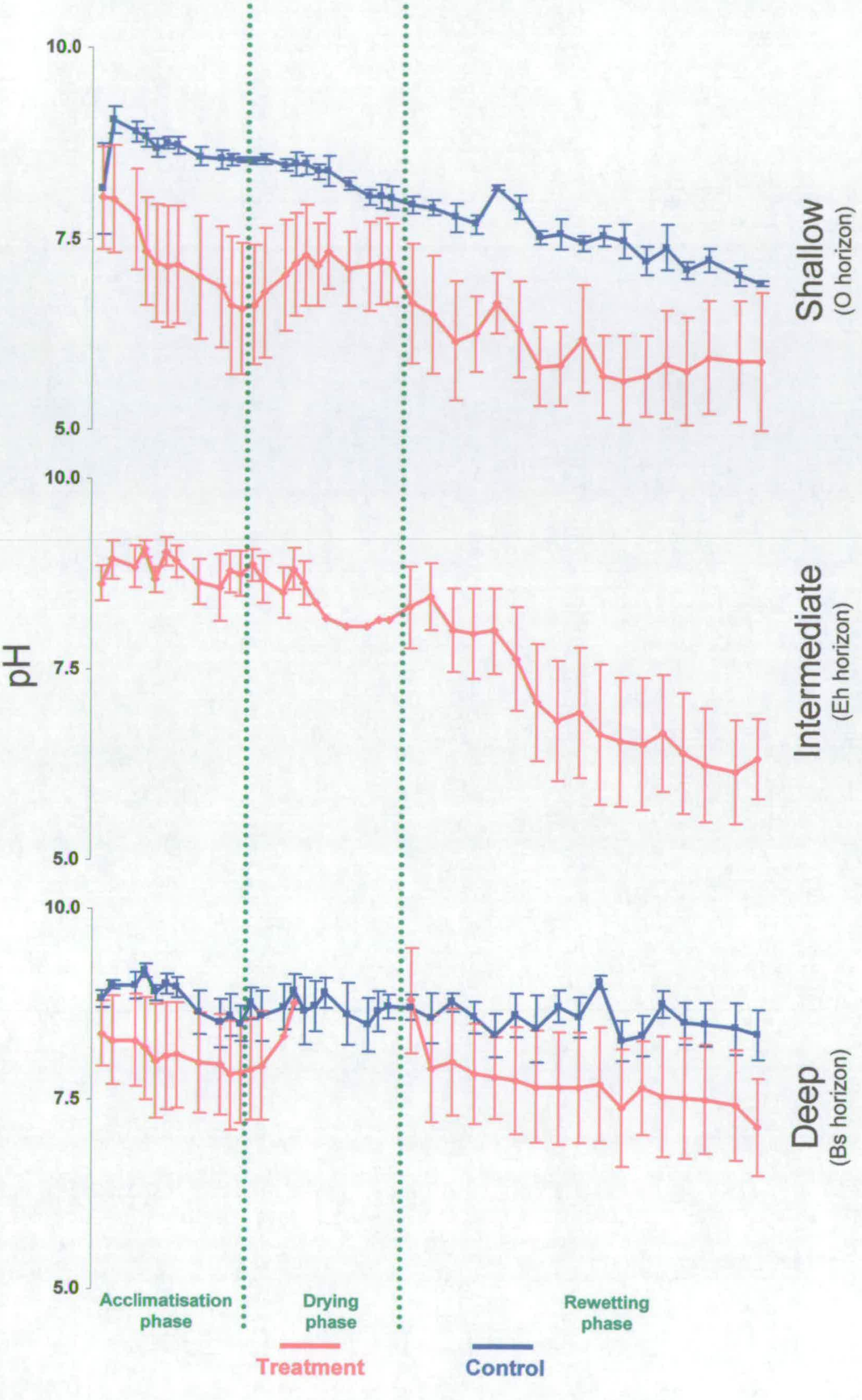


Figure 5.18: pH (±SE) of soil water from moorland **peaty podzol** soil cores

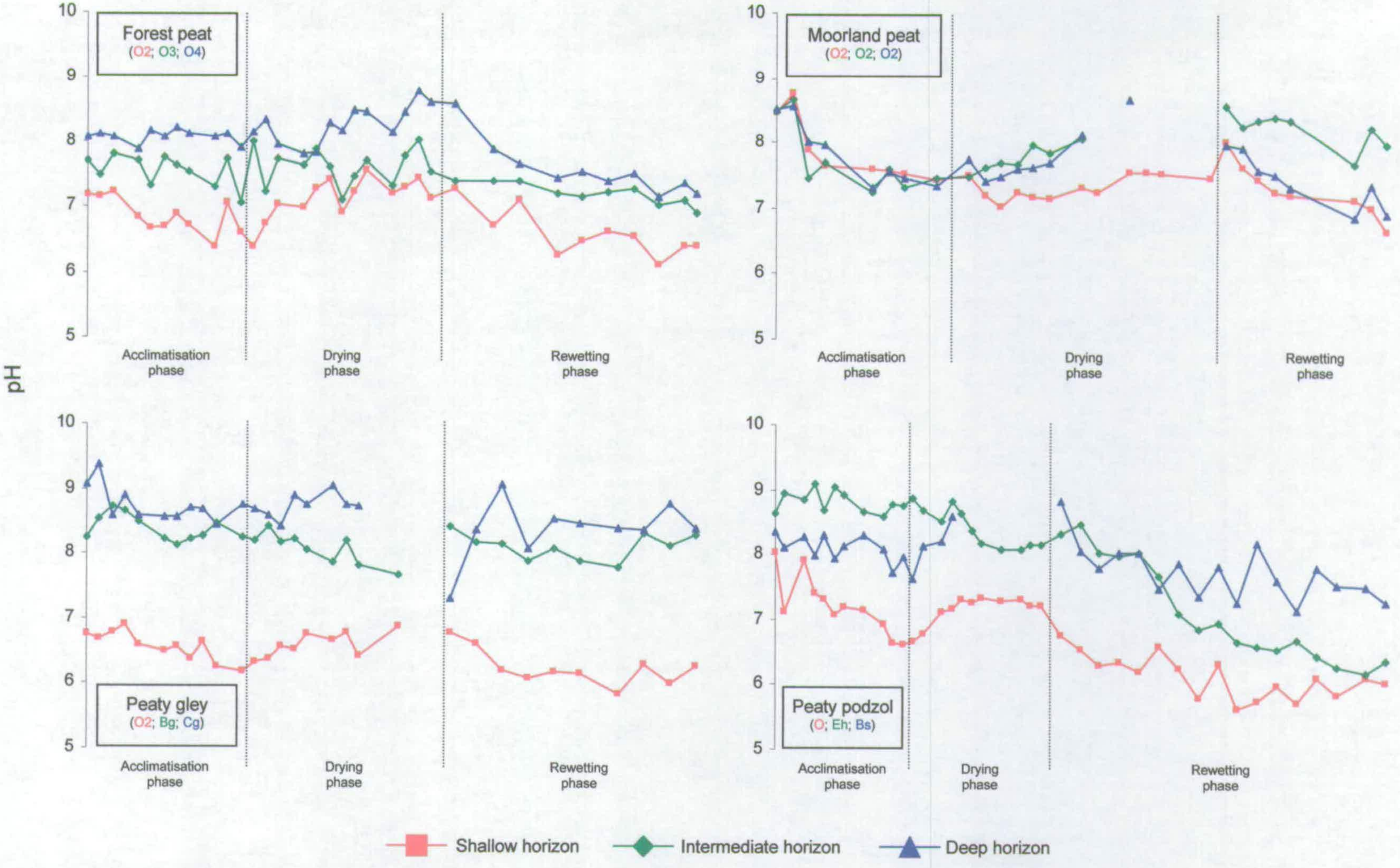


Figure 5.19: Relative pH of soil water samples collected from treatment cores during soil core experiments

are the peaty gley intermediate (Bg) and deep (Cg) horizons, which both show no change in pH upon rewetting. The decreases in soil water pH of most horizons during the rewetting phase are in accordance with the findings of several other studies (e.g., Baver, 1927; Ponnamperuma, 1972; Takkar, 1969). As discussed in section 2.3.2.1, soil water pH will tend to move towards neutral following waterlogging, resulting in pH increases for acidic and decreases for alkaline soils. Of the twelve horizons investigated, only two began the rewetting phase with soil water pH of less than neutral. Of the remaining ten horizons, eight showed a decrease in soil water pH as the rewetting phase progressed, with most approaching the 6.7 – 7.2 pH range observed by Ponnamperuma *et al.* (1966) by the time the experiment ceased.

As with the field results (discussed in section 4.3), the pH of soil water samples collected during the soil core experiments was often greater than expected for organic soils. The retention of H^+ ions by the suction probe ceramic cups may have influenced sample pH, and possibly explains the high pH of samples at the start of experimental runs (e.g., moorland peat soil cores - Figure 5.16). However, it is unlikely to have affected sample pH throughout the entire experiment, as equilibrium would have been attained between ions in solution and the ceramic cup cation exchange sites. Sample exposure to atmospheric conditions while collecting in the suction probes may also have influenced the pH of soil water. The degassing of CO_2 from water samples containing elevated concentrations of CO_2 (e.g., from microbial respiration) is known to increase sample pH following exposure to atmosphere with a relatively low partial pressure of CO_2 (Choi *et al.*, 1998; Elberling & Jakobsen, 2000). This could have altered the pH of soil water during the experiment, as samples were held in the suction probes for a period of 1-2 days prior to analysis, during which time degassing could have occurred.

5.4.3.3 Colour

Colour in soil water samples collected from the experimental cores is presented in Figures 5.20 to 5.23. One noticeable feature of the graphs is that the two peats (Figures 5.20 & 5.21) contain considerably more colour in soil water samples from their shallow horizons than any of the other ten horizons investigated. The colour of soil water samples from the forest peat shallow (O2) and intermediate (O3) horizons differs between treatment and control cores for much of the experiment. Means of the treatment and control values for soil water colour appear to diverge shortly after the drying phase begins, possibly indicating a decrease in colour of the treatment core samples. In general, there is very little colour evident in

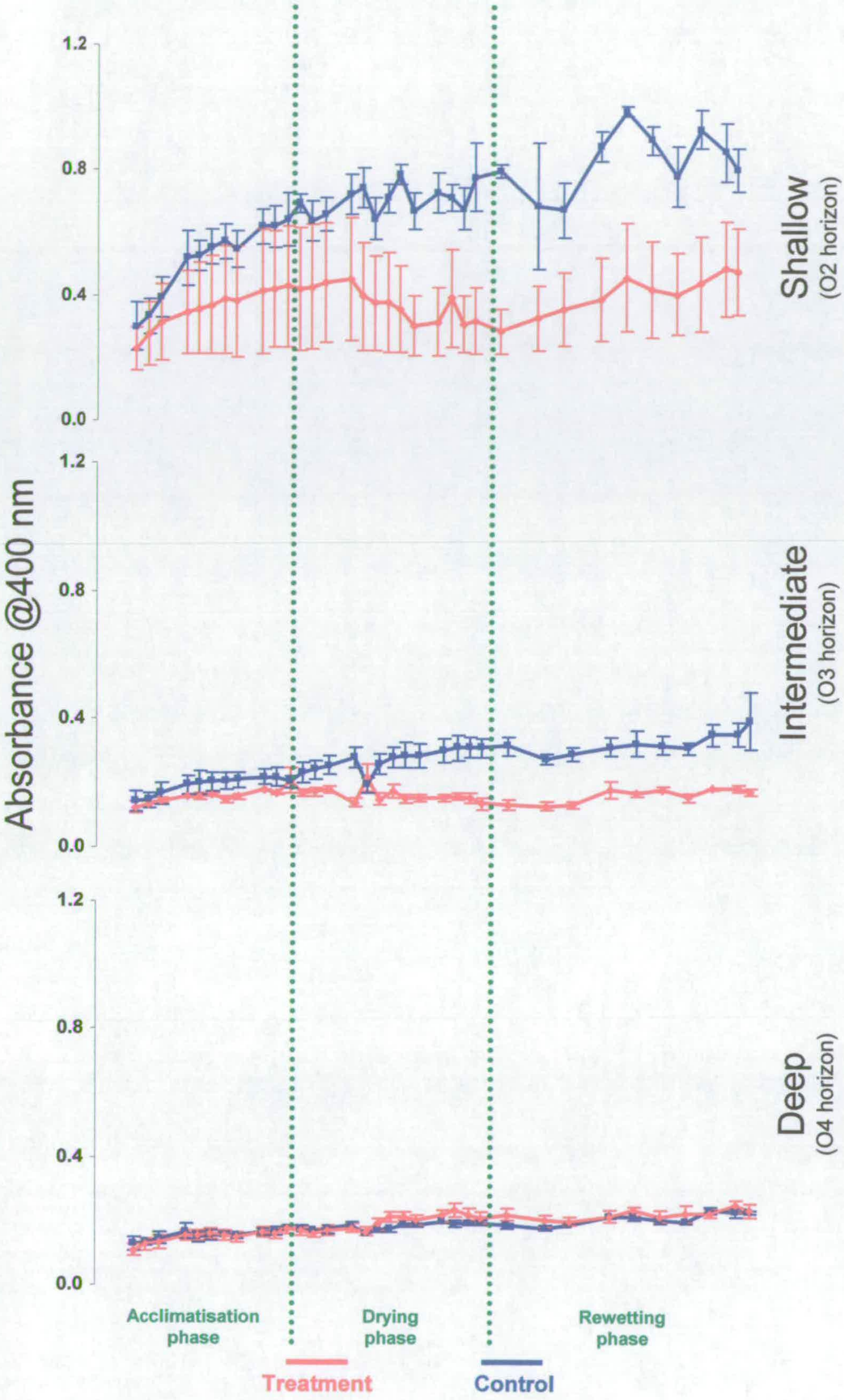


Figure 5.20: Colour (±SE) of soil water from **forest peat** soil cores

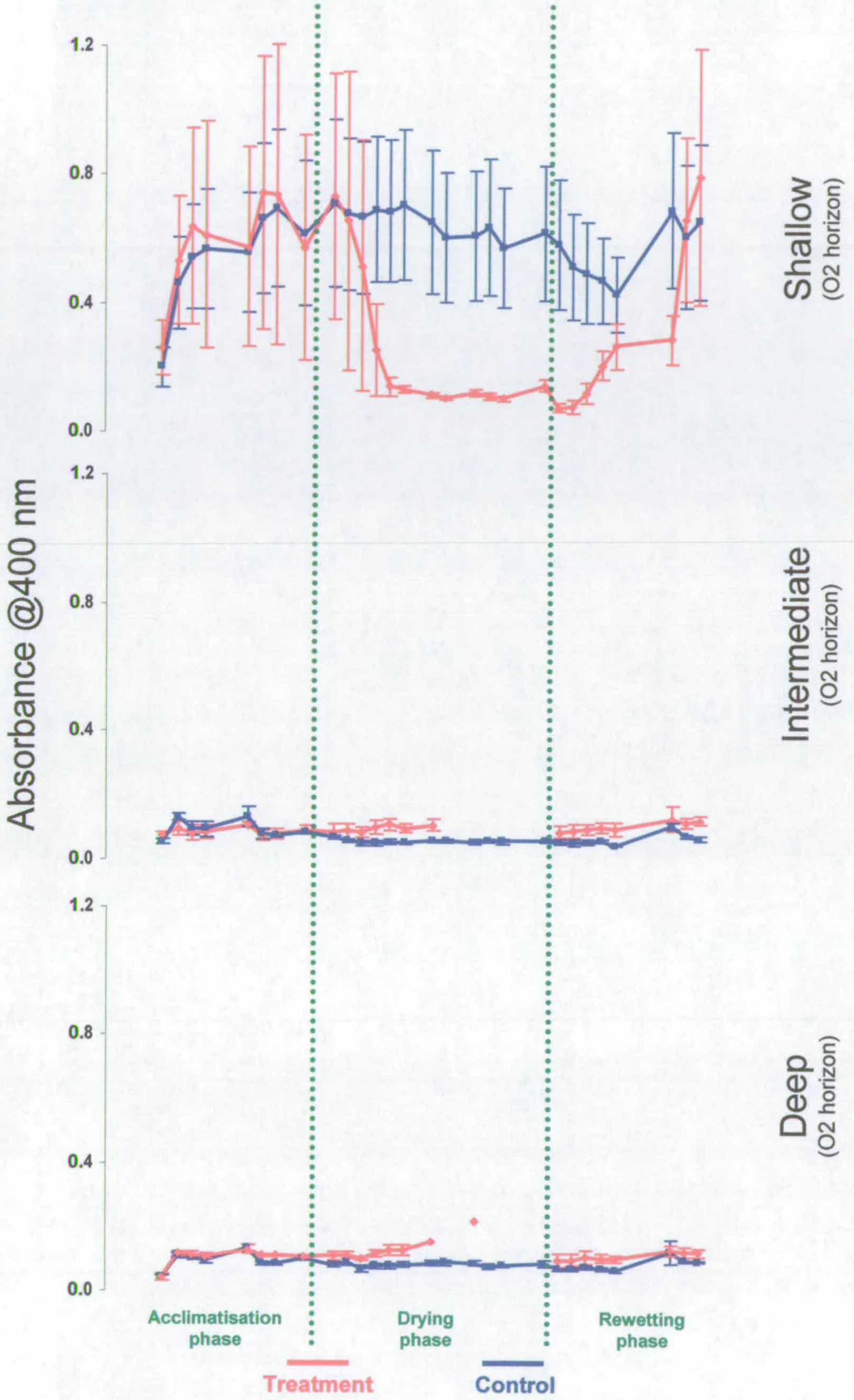


Figure 5.21: Colour (±SE) of soil water from **moorland peat** soil cores

samples from the peaty gley or peaty podzol (Figures 5.22 & 5.23). However, samples from the treatment cores of both the shallow (O) and intermediate (Eh) horizon of the peaty podzol show a marked increase in colour during the rewetting phase. This release of colour following the rewetting of dried organic soils has been reported by many other studies (e.g., Mitchell & McDonald, 1992, 1995; Naden & McDonald, 1989; Watts *et al.*, 2001). One final interesting feature is the decrease in colour of soil water samples from the moorland peat shallow horizon treatment cores during the drying phase, followed by a return to original levels during the rewetting phase (Figure 5.21). This phenomenon is also visible, albeit at a much lower magnitude, in the shallow horizon treatment cores from the peaty gley and peaty podzol (Figures 5.22 & 5.23).

Graphical analysis of the relative colour of soil water samples (Figure 5.24) confirms that samples containing the most colour were collected from the shallow horizons of the two peats. The release of colour from the peaty podzol shallow (O) and intermediate (Eh) horizons during the rewetting phase can also easily be distinguished. Within the Eh horizon rewetting phase, this release of colour is associated with a decrease in soil water pH (Figure 5.19) and an increase in Mn concentration (Figure 5.14) and may be an indication of Mn mobilisation by complexation with organic acids.

5.4.3.4 Discussion

Of the time series exhibiting any change in soil water Mn concentrations, only those from the peaty podzol (Figure 5.13) appear to coincide with changes in pH and colour. This is most obvious in the case of the intermediate (Eh) horizon, where an increase in Mn concentration during the rewetting phase is matched by a decrease in pH and increase in colour. The same pattern may occur in the shallow (O) horizon, but it is difficult to discern from the graphs alone. The final three measurements from the treatment cores of the moorland peat shallow horizon (Figure 5.11) suggest that Mn concentrations increase in conjunction with an increase in colour, however the duration and magnitude of the event may have been truncated by termination of the experiment.

In summary, graphical evidence suggests that Mn mobilisation resulting from the rewetting of soil following a drying period may only occur in certain soil horizons. Potential Mn mobilisation upon rewetting was only identified in the shallow (O2) horizon of the moorland peat and the shallow (O) and intermediate (Eh) horizons of the peaty podzol, with the greatest concentrations released from the Eh horizon. In the following sections, statistical

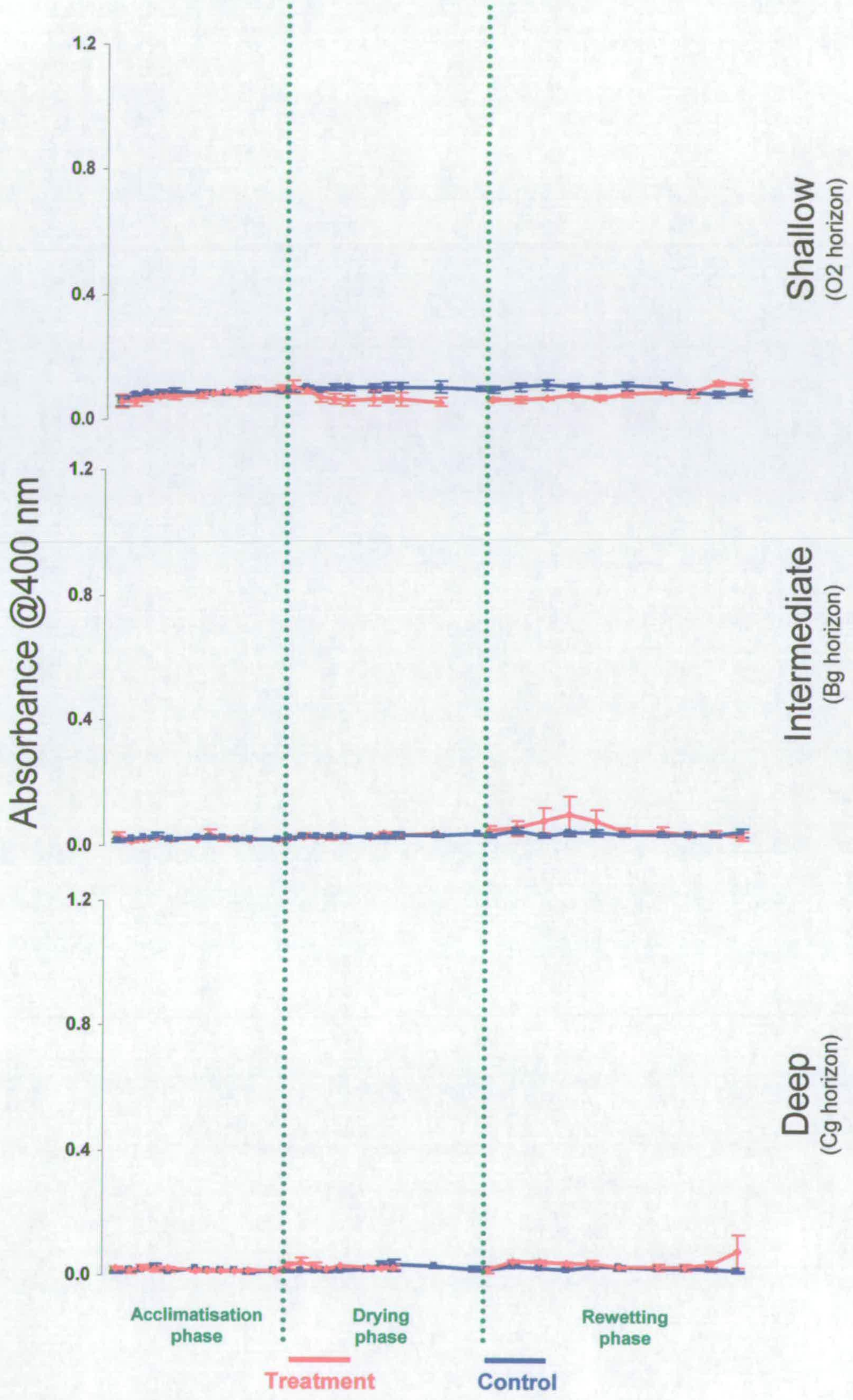


Figure 5.22: Colour (±SE) of soil water from moorland **peaty gley** soil cores

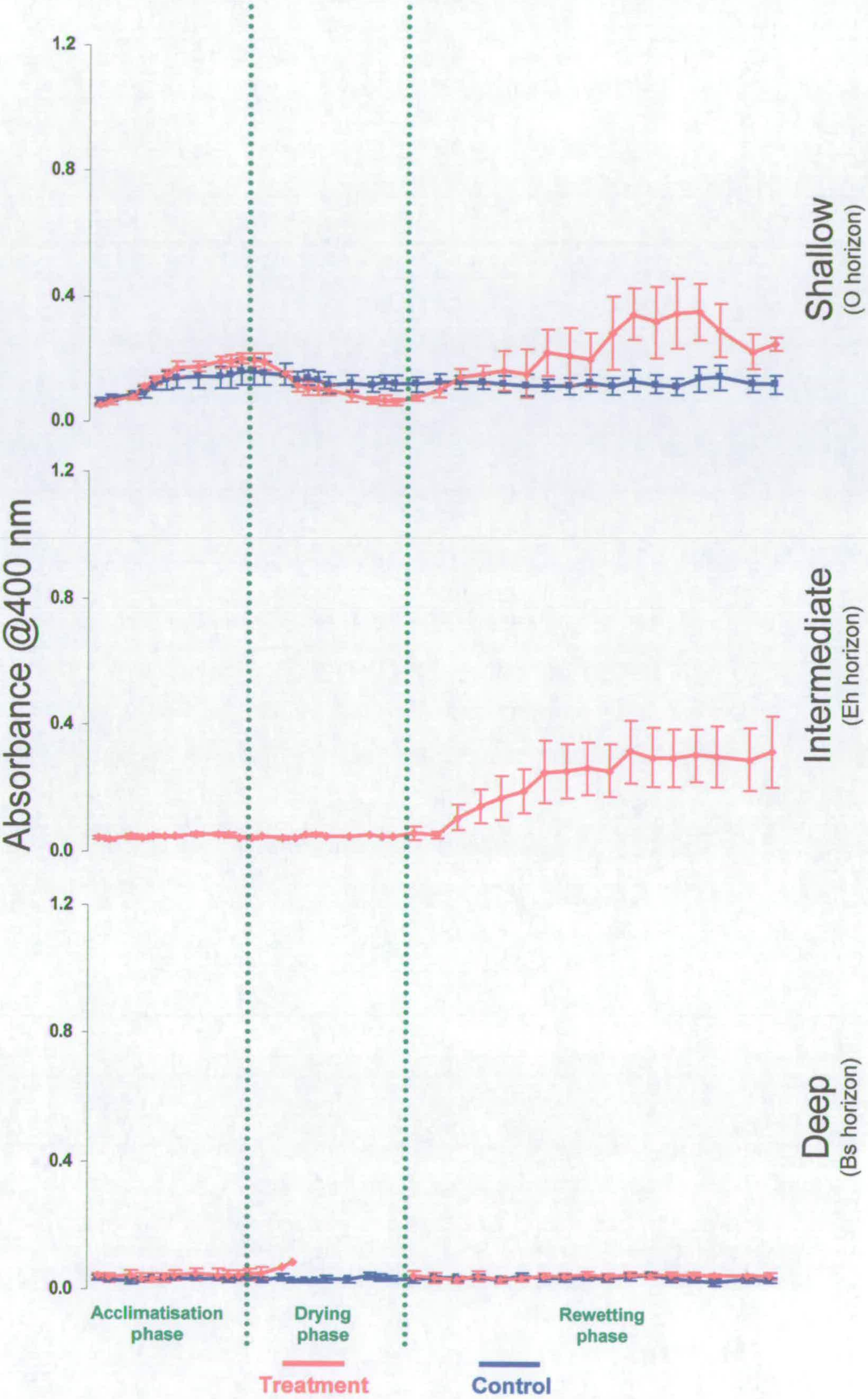


Figure 5.23: Colour (±SE) of soil water from moorland **peaty podzol** soil cores

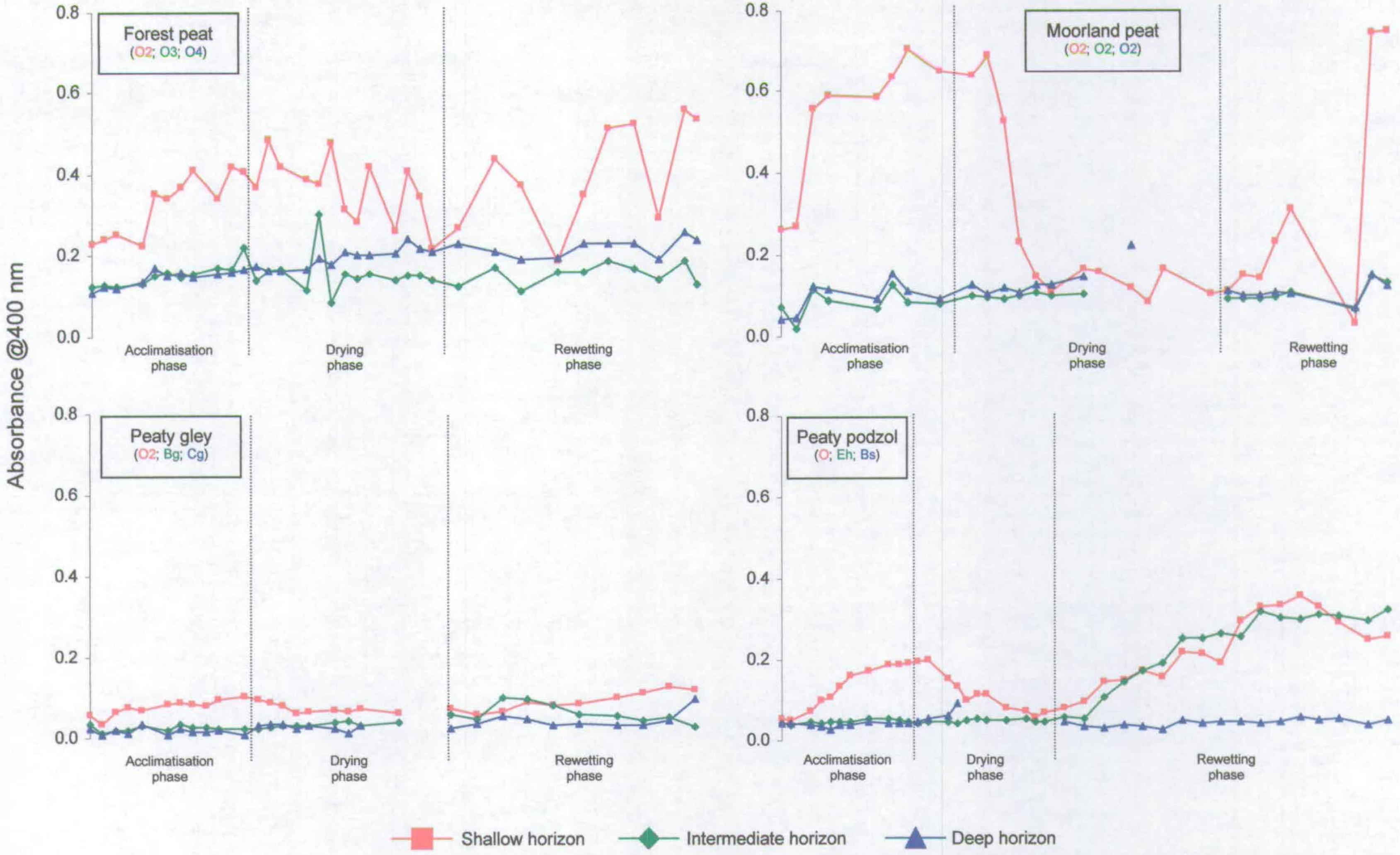


Figure 5.24: Relative colour of soil water samples collected from treatment cores during soil core experiments

analysis is applied to the soil core data in order to determine whether or not the changes identified by the graphs are statistically significant.

5.4.4 Statistical analysis: One-way ANOVA

One-way ANOVA was used to identify whether any significant differences in soil water chemistry existed between treatment and control cores within a horizon and also between experimental phases for individual horizons. For each horizon and treatment, soil water chemistry data from all three replicates were pooled according to treatment phase and used to determine a mean value for that phase. In addition to treatment and control means for each phase, the relative mean was also calculated, based upon changes observed in the control core mean values between experimental phases (Equations 5.2 & 5.3).

$\text{rel\_Mean}_{(\text{dry})} = \text{trt\_Mean}_{(\text{dry})} + (\text{ctrl\_Mean}_{(\text{acc})} - \text{ctrl\_Mean}_{(\text{dry})})$ **Equation 5.2**

$\text{rel\_Mean}_{(\text{wet})} = \text{trt\_Mean}_{(\text{wet})} + (\text{ctrl\_Mean}_{(\text{dry})} - \text{ctrl\_Mean}_{(\text{wet})})$ **Equation 5.3**

Where: rel/trt/ctrl_Mean = relative/treatment/control means
(acc)/(dry)/(wet) = acclimatisation/drying/rewetting phases

Prior to statistical analysis, carried out using the Minitab computer program (v12.1), soil water Mn concentration and colour data were tested for normality using the Anderson-Darling test. Non-normal data were $\log_{10}$ transformed in order to obtain normally distributed data. Graphical representation of the means and associated standard errors are displayed in figures 5.25 to 5.28, while tables 5.2 and 5.3 show the results of the statistical analysis.

In order for a treatment effect to be considered significant during the drying or rewetting phases, there must also be no significant difference between soil water chemistry of treatment and control cores during the acclimatisation phase. However, approximately half the horizons analysed exhibited significant differences between the treatment and control cores during the acclimatisation phase. This is probably a result of the small number of replicates and the natural variability of soil water chemistry.

Once a significant difference was identified between treatment and control cores (Table 5.2), it was checked against the differences between phases (Table 5.3). Therefore, only when treatment cores were significantly different from the control cores during the same experimental phase, and significantly different from the treatment cores during the acclimatisation phase could the horizon be said to show an effect of the drying and rewetting.

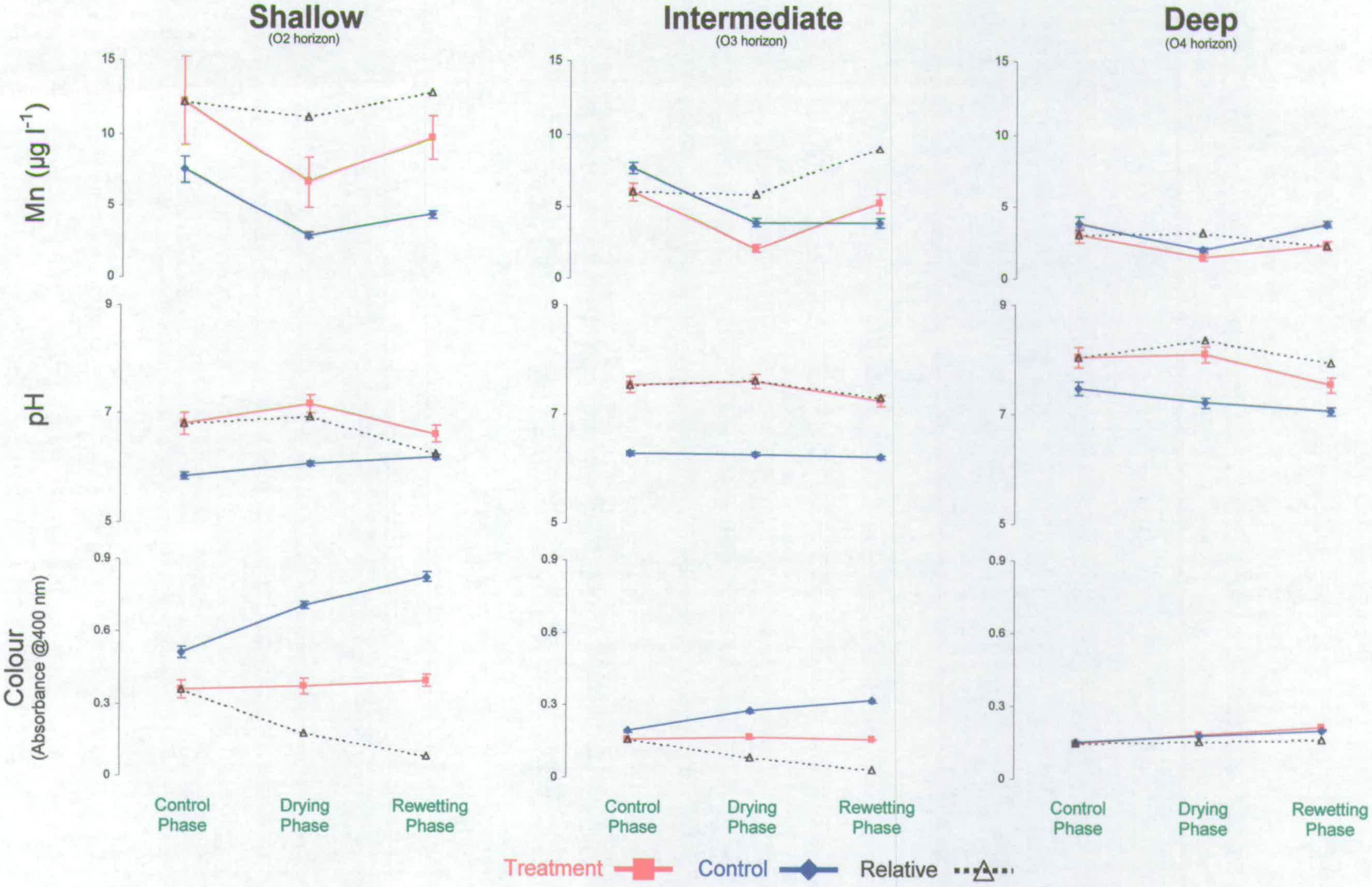


Figure 5.25: Mean values **(±SE)** for Mn concentration, pH and colour in soil water samples collected during each phase of soil core experiment from **forest peat** soil cores

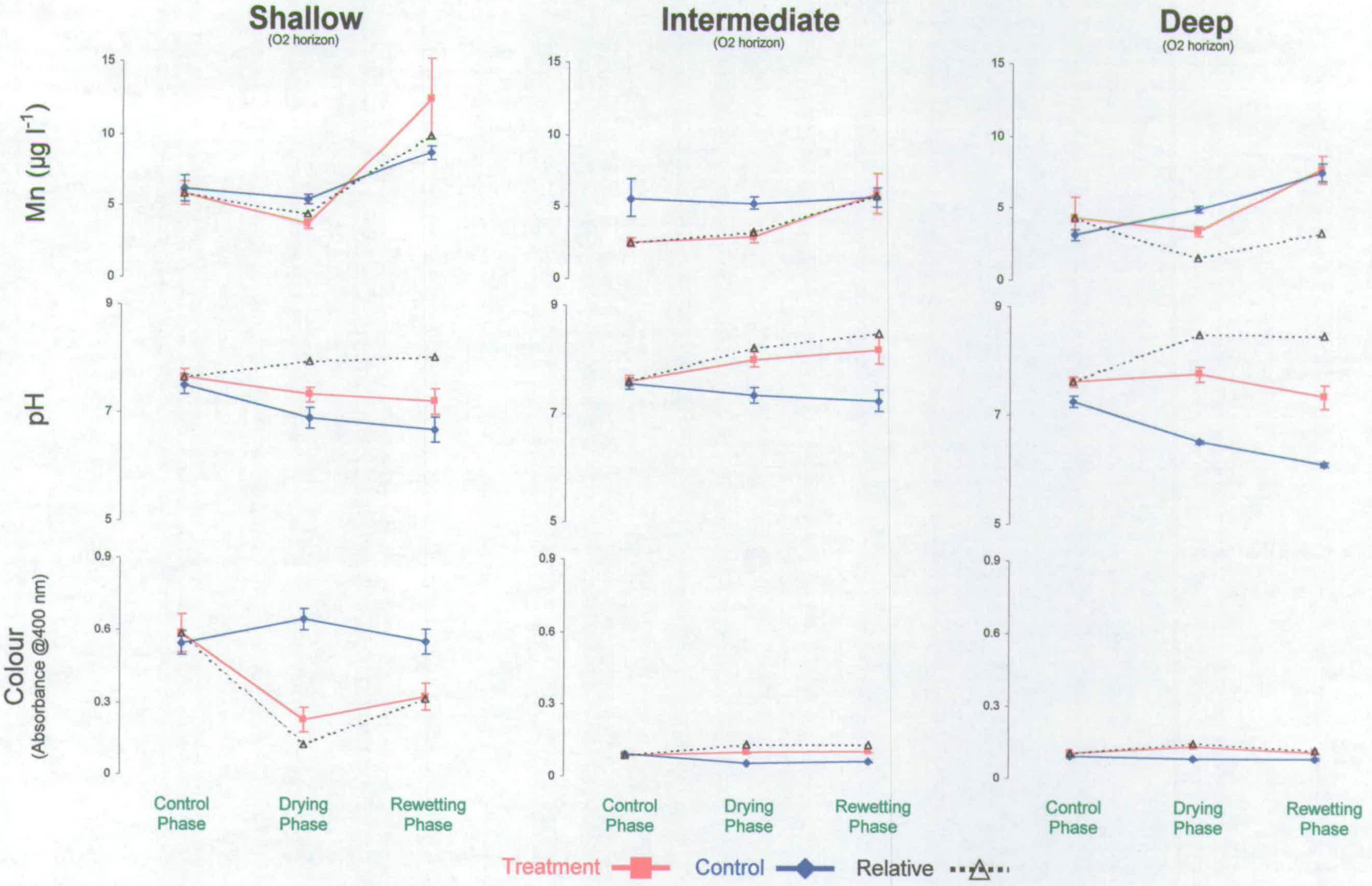


Figure 5.26: Mean values (**±SE**) for Mn concentration, pH and colour in soil water samples collected during each phase of soil core experiment from **moorland peat** soil cores

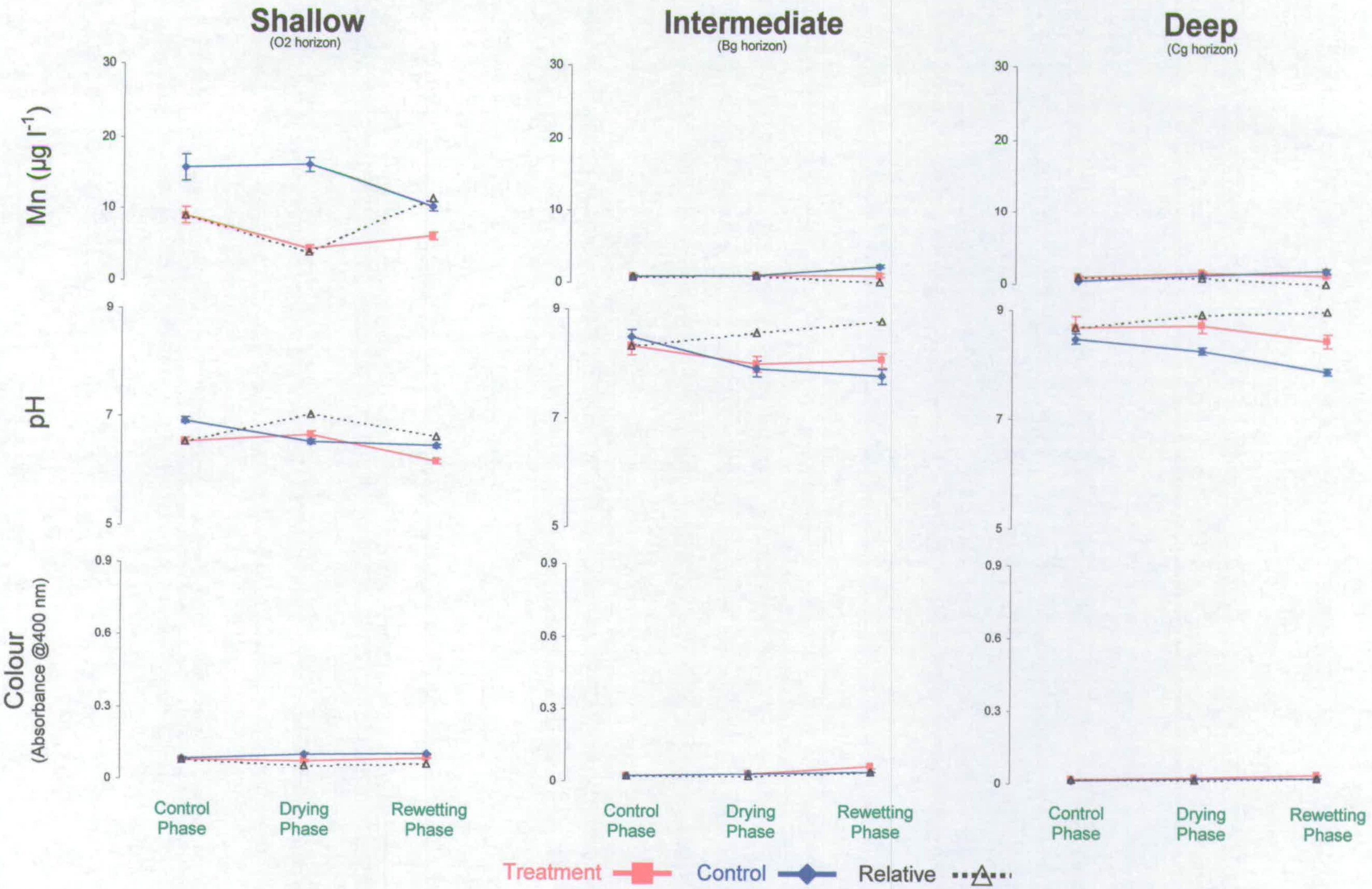


Figure 5.27: Mean values **(±SE)** for Mn concentration, pH and colour in soil water samples collected during each phase of soil core experiment from **peaty gley** soil cores

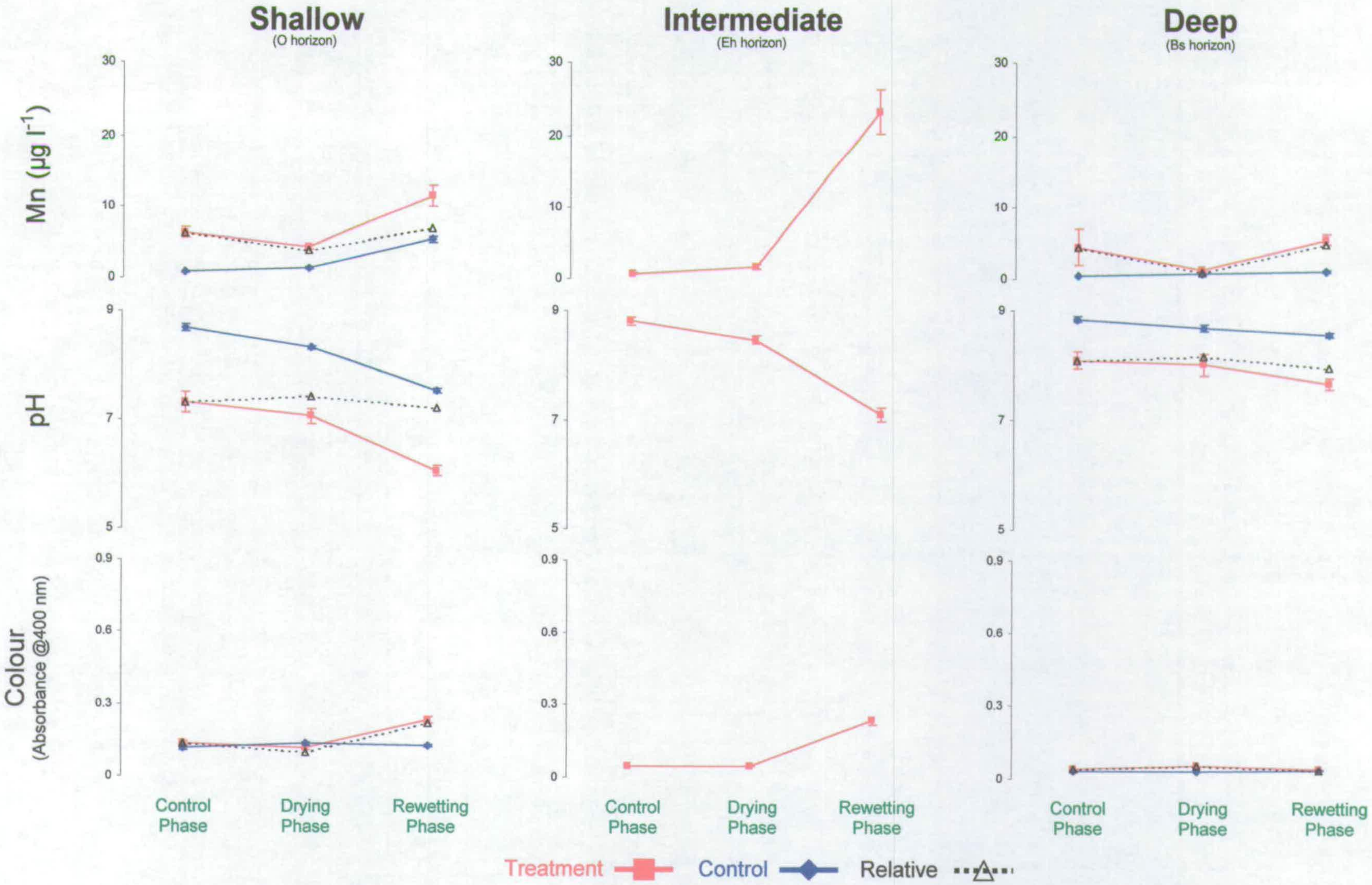


Figure 5.28: Mean values **(±SE)** for Mn concentration, pH and colour in soil water samples collected during each phase of soil core experiment from **peaty podzol** soil cores

				Acclimatisation			Drying			Rewetting		
				Mn	pH	Col	Mn	pH	Col	Mn	pH	Col
Forest	Peat	O2	Shallow	0.227	**<0.001**	**0.002**	0.057	**<0.001**	**<0.001**	0.028	0.096	**<0.001**
		O3	Intermediate	0.042	**<0.001**	**0.001**	**<0.001**	**<0.001**	**<0.001**	0.110	**<0.001**	**<0.001**
		O4	Deep	0.315	0.028	0.507	0.107	**<0.001**	0.450	**0.008**	0.045	0.089
					n=33			*n=39*			*n=60*	
Moorland	Peat	O2	Shallow	0.803	0.547	0.670	**<0.001**	0.062	**<0.001**	0.190	0.123	**0.003**
		O2	Intermediate	0.026	0.747	0.405	**<0.001**	**0.002**	**<0.001**	0.872	**0.004**	**<0.001**
		O2	Deep	0.453	**0.007**	0.033	**<0.001**	**<0.001**	**<0.001**	0.871	**<0.001**	**<0.001**
					n=39			*n=48*			*n=39*	
	Peaty gley	O2	Shallow	**0.005**	**<0.001**	0.105	**<0.001**	0.084	**<0.001**	**<0.001**	**<0.001**	**<0.001**
		Bg	Intermediate	0.766	0.478	0.584	0.508	0.675	0.499	**0.001**	0.123	**0.001**
		Cg	Deep	**<0.001**	0.363	0.162	0.284	**0.002**	0.087	0.085	**<0.001**	**<0.001**
					n=39			*n=48*			*n=60*	
	Peaty podzol	O	Shallow	**<0.001**	**<0.001**	0.112	**<0.001**	**<0.001**	0.094	**<0.001**	**<0.001**	**<0.001**
		Eh	Intermediate	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
		Bs	Deep	0.129	**<0.001**	0.036	0.018	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**0.001**
					n=39			*n=48*			*n=102*	

Table 5.2: Statistical differences between treatment and control core soil water samples from individual horizons during each experimental phase

One-way ANOVA p-values: red = treatment > non-treatment
blue = treatment < non-treatment

					Drying			Rewetting		
					Mn	pH	Col	Mn	pH	Col
Forest	Peat	O2	Shallow	Treatment	0.104	0.159	0.784	0.429	0.489	0.362
				Control	<0.001	0.003	<0.001	<0.001	<0.001	<0.001
		O3	Intermediate	Treatment	<0.001	0.716	0.359	0.418	0.105	0.835
				Control	<0.001	0.927	<0.001	<0.001	0.182	<0.001
		O4	Deep	Treatment	0.006	0.743	<0.001	0.220	0.040	<0.001
				Control	<0.001	0.105	<0.001	0.944	0.005	<0.001
Moorland	Peat	O2	Shallow	Treatment	0.006	0.118	<0.001	0.016	0.103	0.012
				Control	0.417	0.021	0.140	0.018	0.005	0.907
		O2	Intermediate	Treatment	0.416	0.017	0.019	0.013	0.022	0.009
				Control	0.808	0.256	<0.001	0.948	0.146	<0.001
		O2	Deep	Treatment	0.534	0.364	<0.001	0.071	0.230	0.336
				Control	<0.001	<0.001	0.003	<0.001	<0.001	0.087
	Peaty gley	O2	Shallow	Treatment	<0.001	0.106	0.500	0.022	<0.001	0.006
				Control	0.875	<0.001	<0.001	0.004	<0.001	<0.001
		Bg	Intermediate	Treatment	0.244	0.138	<0.001	0.487	0.239	<0.001
				Control	0.434	0.007	<0.001	<0.001	<0.001	<0.001
		Cg	Deep	Treatment	0.021	0.857	<0.001	0.232	0.320	<0.001
				Control	0.020	0.045	<0.001	0.001	<0.001	<0.001
	Peaty podzol	O	Shallow	Treatment	0.009	0.273	0.156	0.036	<0.001	<0.001
				Control	0.004	<0.001	0.059	<0.001	<0.001	0.179
		Eh	Intermediate	Treatment	0.004	0.001	0.348	<0.001	<0.001	<0.001
				Control	n/a	n/a	n/a	n/a	n/a	n/a
		Bs	Deep	Treatment	0.344	0.775	0.011	0.519	0.031	0.305
				Control	0.125	0.075	0.623	0.021	<0.001	0.022

Table 5.3: Statistical differences between soil water samples from acclimatisation phase and drying/rewetting phases *(n values same as Table 5.2)*

One-way ANOVA p-values: red = drying/rewetting > acclimatisation
blue = drying/rewetting < acclimatisation

5.4.4.1 Mn

Graphical analysis of soil water Mn concentrations (Figures 5.25 to 5.28) indicates that relative increases during the rewetting phase, compared to the acclimatisation phase, occur in five of the twelve horizons investigated. These are the forest peat shallow and intermediate (O2 and O3), moorland peat shallow and intermediate (both O2) and peaty gley shallow (O2) horizons. In addition to this, there is a large increase in soil water Mn concentrations from the peaty gley intermediate (Eh) horizon treatment cores during the rewetting phase, although the lack of control cores prevents a relative concentration being calculated. Of the six horizons where there was no significant statistical difference between treatment and control cores during the acclimatisation phase, only treatment cores from forest peat shallow (O2) horizon and the peaty podzol deep (Bs) horizon exhibit a significant increase in Mn concentrations during the rewetting phase (Table 5.2). However, when the differences between experimental phases are considered (Table 5.3), neither horizon shows a significant increase in treatment core soil water Mn concentration associated with rewetting. The only other horizon in which treatment core Mn concentrations were significantly greater than those from the control cores during the rewetting phase was the peaty podzol shallow (O) horizon (Table 5.2). However, soil water samples from treatment cores of this horizon also contained significantly more Mn than control cores during the acclimatisation and drying phases. Soil water samples from the shallow and deep (O2) horizons of the moorland peat both show a significant decrease in treatment core Mn, compared to control core Mn, during the drying phase following no significant difference during the acclimatisation phase (Table 5.2). No significant difference between treatment and control Mn concentration was detected in soil water samples from these horizons during the rewetting phase, indicating a return to parity with the control cores. Of the other horizons showing no significant difference between treatment and control soil water Mn concentrations during the acclimatisation phase, the forest peat deep (O4) and peaty gley intermediate (Bg) horizons show a significant decrease in the rewetting phase.

5.4.4.2 pH

As stated earlier, the anticipated trend during the rewetting phase was for the pH of soil water to approach neutral values as time progressed. However, the graphs of mean soil water pH of each phase (Figures 5.25 to 5.28) indicate that this was not always the case. For example, the pH of rewetting phase soil water samples from the moorland peat intermediate (O2) horizon was greater than in both the acclimatisation and drying phases. The one-way ANOVA (Table 5.2) shows that there were only four horizons where the pH of soil water samples from treatment and control cores did not differ significantly during the acclimatisation phase. Of these, the moorland peat intermediate (O2) and peaty gley deep (Cg) horizons both record a significant increase in pH of treatment cores, relative to control cores, during the drying and rewetting phases. However, when the one-way ANOVA between experimental phases (Table 5.3) is considered, only the moorland peat intermediate horizon treatment cores were found to have significantly increased pH during the drying and rewetting phases, compared to the acclimatisation phase. The other two horizons with no significant difference in soil water pH between treatment and control cores during the acclimatisation phase are the moorland peat shallow (O2) and peaty gley intermediate (Bg) horizons (Table 5.2). However, there is no significant difference identified between treatment and control core soil water pH of these horizons during the drying or rewetting phases (Table 5.2).

5.4.4.3 Colour

Colour in soil water samples from seven of the horizons investigated showed no significant difference between treatment and control cores during the acclimatisation phase (Table 5.2). Of these, no significant difference was observed in samples from the forest peat deep (O4) horizon throughout the entire experiment. The colour of soil water samples from treatment cores in peaty gley intermediate (Bg) and deep (Cg) horizons and the peaty podzol shallow (O) horizon increased, relative to the control cores, during the rewetting phase (Table 5.2). When results from the one-way ANOVA dealing with between-phase effects (Table 5.3) are considered, soil water sample colour in the peaty gley horizons increases relative to the acclimatisation phase in both drying and rewetting phases, while the colour of peaty podzol samples generally increases only during the rewetting phase. Soil water samples from treatment cores of the moorland peat intermediate (O2) horizon have significantly more colour than those from the corresponding control cores during the drying and rewetting phases (Table 5.2). Analysis of the between-phase variance (Table 5.3) shows that this is also an increase of colour in both drying and rewetting phases, relative to the acclimatisation phase. Soil water samples from the moorland peat and peaty gley shallow horizon treatment cores (both O2) contain significantly less colour, compared to control cores, during the drying and rewetting phases (Table 5.2). When between-phase effects were considered (Table 5.3), samples from the moorland peat O2 horizon treatment cores were found to contain significantly less colour during both drying and rewetting phases than in the acclimatisation phase. In contrast, samples from the peaty gley O2 horizon treatment cores showed no significant difference between the first two experimental phases and an increase in colour during the rewetting phase when compared to the acclimatisation phase.

5.4.4.4 Discussion

Overall, one-way ANOVA showed that drying or rewetting the treatment cores did not significantly affect soil water Mn concentrations, compared to control cores, in any of the soil horizons investigated. However, graphical evidence in Figures 5.25 to 5.28 suggests that relative increases in soil water Mn during the rewetting phase occur in several horizons. It is possible that pooling data from each phase in order to carry out the one-way ANOVA meant that responses observed at the end of the rewetting phase were masked by data from the rest of the phase. Therefore, application of one-way ANOVA in this manner may not be an appropriate method of statistical analysis, and should be regarded as a preliminary investigation prior to the employment of a more powerful technique to identify significant changes in soil solution chemistry during the experiment.

Another factor that could have influenced statistical analysis of the data is the extremely low concentrations of Mn measured in soil water samples from some horizons. If the concentration of Mn from such horizons was below the limits of detection for the equipment used, then the values recorded could be incorrect. The limit of detection for the GFAAS equipment was calculated using the method described in Appendix A.7 and found to be 0.012 $\mu g\ l^{-1}$ ±0.01. Therefore, even though Mn concentrations in soil water from some cores were extremely small, they were always above the limit of detection.

Only the moorland peat intermediate (O2) horizon exhibited any significant change in soil water pH as a result of the experimental procedure, with the pH of samples increasing during drying and rewetting phases. Soil water samples from treatment cores in six horizons exhibited significant changes in colour resulting from drying or rewetting during the experiment. In most of these, the trend was for soil water colour to increase during the rewetting phase (peaty gley and peaty podzol shallow horizons) or during both drying and rewetting phases (moorland peat intermediate and peaty gley intermediate and deep horizons). Such a response may have been caused by drainage of smaller diameter pores during the drying phase and the flushing out of accumulated dried organic matter from the surfaces of larger pores during the rewetting phase. However, the opposite trend was identified in soil water samples from the moorland peat shallow (O2) horizon, where the colour of treatment core soil water samples was significantly lower during the drying and rewetting phases than in the acclimatisation phase.

Statistical analysis of the pH and colour data was hampered by the apparent differences between treatment and control cores during the acclimatisation phase, combined with definite changes in control core soil water chemistry as the experiment progressed. While the initial differences between treatments can perhaps be explained in terms of soil variability and insufficient replicates, the significant changes in determinand values from control cores between phases may indicate error in experimental procedure or design.

5.4.5 Statistical analysis: Repeated measures ANOVA

As discussed in section 4.1.1.3, repeated measures ANOVA can be used to identify the causes of variation in the means of data collected from different sampling points over a period of time. Therefore, this technique was considered to be a more suitable form of statistical analysis, given the type of data collected, particularly its ability to deal with variation caused by time. Prior to analysis, data were tested for normality (using the Anderson-Darling test within Minitab v12.1) and any non-normal data were $\log_{10}$ transformed in order to obtain a closer approximation to normal distribution. Once this was achieved, all data were arranged in a suitable format within an Excel spreadsheet and imported into the Genstat 5 statistical program for analysis.

If the hypothesis concerning Mn release upon rewetting of dried soils is correct, then the expected result of the analysis would be for Mn concentrations in soil water from the treatment cores to increase significantly during the rewetting phase. If this were the case, then repeated measures ANOVA would identify the Mn release either as a treatment effect if it occurred during the whole phase, or as a treatment effect with time if it occurred as the phase progressed. Repeated measures ANOVA also reported variations between soil water samples explained by time and by land use, soil type or soil horizon. When variation is explained by time, this simply means that soil water chemistry altered over the course of the experiment, but that the variation was not caused by any of the environmental factors (e.g., land use and soil type) or by treatment effects (i.e. not the product of variation between treatment and control cores). Variation attributed to land use, soil type or soil horizon implies that the soil water chemistry of the sample sets differed significantly as a result of the different environmental factors, but was not caused by treatment effects.

5.4.5.1 Effect of land use and soil type on soil water chemistry

Comparison of the soil core experiment data for forest and moorland peat cores using repeated measures ANOVA allowed investigation of the effect of land use on soil water chemistry. Similarly, data from the three moorland soils enabled investigation of the effect of soil type on soil water chemistry. The results of these analyses (Table 5.4) generally indicate that most of the variation encountered within the data occurs as a result of changes over time during the experiment that are not associated with the drying and rewetting treatment. However, because data from each profile were combined in order to perform the analysis, it is possible that responses in individual cores or horizons are masked. The small number of replicates and the non-normal distribution of some data meant that the significance of statistical analysis using repeated measures ANOVA may have been diminished. Therefore, it was decided to adopt a probability threshold of $p<0.1$ as being weakly significant, rather than the more commonly used $p<0.05$.

Mn

There were no statistical differences in Mn concentrations, identified as arising from the treatment regime, between the three moorland soil types. However, there was a weakly significant ($p=0.056$) difference in soil water Mn concentration between forest and moorland peat cores during the drying phase, attributed to the effect of land use. There is also a significant ($p=0.018$) difference in soil water Mn concentrations of the two peats attributed to treatment effects within this phase, suggesting that the vegetation overlying the peat may be important when considering the effect of drying on soil water Mn concentration. Inspection of the relevant time series graphs (Figures 5.10 & 5.11) indicates that this difference possibly arises because of a decrease in forest peat shallow horizon soil water Mn concentration during the drying phase.

pH

The results of the repeated measures analysis for soil water pH also show a significant ($p=0.005$) difference in the response of forest and moorland peats to treatment during the drying phase. In addition to this, significant ($p<0.001$) variation resulting from treatment effects over time is detected during this phase. Similar results ($p=0.063$ for treatment effects; $p<0.001$ for treatment effects over time) are obtained from repeated measures analysis of soil water pH data from moorland and forest peats during the rewetting phase. Graphical analysis of the time series graphs (Figures 5.15 & 5.16) does not provide any obvious explanation for these differences in soil water pH between the two soil types. It is

	Acclimatisation Phase				**Drying Phase**				**Rewetting Phase**			
	1	2	3	4	1	2	3	4	1	2	3	4
Mn												
forest peat vs moorland peat	0.328	0.314	0.760	***0.029***	***0.056***	***0.018***	0.407	*0.006*	0.105	0.675	0.381	***<0.001***
peat vs peaty gley vs peaty podzol	0.438	0.370	0.381	*0.004*	0.328	0.411	0.809	***<0.001***	0.244	0.793	0.117	***<0.001***
pH												
forest peat vs moorland peat	0.266	***0.061***	0.467	***<0.001***	0.586	*0.005*	***<0.001***	*0.007*	0.591	***0.063***	***<0.001***	***<0.001***
peat vs peaty gley vs peaty podzol	0.289	0.282	0.551	***<0.001***	0.304	0.634	***<0.001***	0.169	0.705	0.999	***<0.001***	***<0.001***
Colour												
forest peat vs moorland peat	0.894	0.537	0.474	***<0.001***	0.450	***0.020***	0.180	0.300	0.450	***0.023***	0.222	***<0.001***
peat vs peaty gley vs peaty podzol	0.258	0.863	0.664	*0.003*	0.285	0.127	0.181	0.112	0.392	0.180	*0.001*	***<0.001***

Variation between soil cores explained by:-
1: Effect of land use or soil type
2: Effect of treatment
3: Time.treatment effects
4: Time

(***p<0.1***; *p<0.01*; ***p<0.001***)

n-values (acclimatisation/drying/rewetting)

	Mn	pH	Colour
Land use	(468/570/558)	(468/548/558)	(468/548/558)
Soil type	(663/764/1067)	(663/735/952)	(663/737/952)

Table 5.4: Repeated measures ANOVA analysis of soil water chemistry data during soil core experiments – variation between land use and soil type

possible that the missing data points in the intermediate (O2) and deep (O2) horizons of the moorland peat, caused by failure of suction probes to collect sufficient sample for analysis during the drying phase, influenced the statistical analysis. However, this factor did not affect data analysis from the rewetting phase, where the statistical differences were still detected. There is also a weakly significant treatment effect evident during the acclimatisation phase. This probably results from the statistically significant difference, identified by one-way ANOVA, between treatment and control cores of all three forest peat horizons, in comparison to only the deep horizon of the moorland peat (Figures 5.15 & 5.16; Table 5.2). Analysis of soil water pH from the three moorland soils indicates that significant ($p<0.001$) differences arising because of treatment effects over time exist between soil types during the drying and rewetting phases. Graphical evidence (Figures 5.16-5.18) indicates the presence of missing data during the drying phase, which may have influenced statistical analysis. However, during the rewetting phase, the significant differences may arise from the decreasing soil water pH measured in the peat and peaty podzol horizons, compared to the relatively stable pH measured in the peaty gley soil cores.

Colour

Comparison of soil water samples obtained from the forest peat and moorland peat soil cores indicates that significant variation in soil water colour, resulting from treatment regime, occurs during the drying and rewetting phases ($p=0.020$ & $p=0.023$ respectively). Time series graphs (Figures 5.20 & 5.21) show that this difference is probably the result of changes in soil water colour measured in samples from moorland peat shallow horizon cores. The only statistically significant variation in colour of samples from the three moorland soils occurs during the rewetting phase, and is associated with treatment effects as time progresses. This may be the result of increases in colour evident in the time series graphs of the peat and peaty podzol soils (Figures 5.21 & 5.23).

Summary

The repeated measures ANOVA results presented in Table 5.4 indicate that most of the variation in soil water chemistry resulting from the soil core experiments, can be explained in terms of variation over time as the experiment progressed, rather than by differences between land use and soil type. However, significant variation in all three chemical determinands measured was identified between forest and moorland peats during the drying phase, indicating that the response of soil water chemistry of peat to drying conditions was influenced by current land use. Soil water pH and colour data from the rewetting phase suggest that the soil water chemistry of peat during rewetting is also influenced by the current land use, although Mn did not appear to be affected. Differences in soil type accounted for variation in soil water pH during the drying and rewetting phases and soil water colour during the rewetting phase, with both showing a response to treatment as time progressed. There was no statistically significant variation in soil water Mn concentrations associated with soil type, although it is possible that responses within individual horizons may have been masked by undertaking analysis of pooled data from the whole profile. Following this initial analysis investigating the effect of land use and soil type on the response of soil water chemistry to drying and rewetting, further statistical analysis was undertaken to determine the extent of any responses within individual horizons.

5.4.5.2 Variation within soil type and horizon

The next stage of repeated measures ANOVA was to identify whether any differences in soil water chemistry within soil types or individual horizons could be attributed to treatment effects (drying followed by rewetting). The results of this analysis for Mn are shown in Table 5.5, with Tables 5.6 and 5.7 presenting similar data for pH and colour respectively.

Mn

Table 5.5 shows that, statistically, none of the variation in soil water Mn concentrations from the forest peat cores was found to result from drying or rewetting, and was instead all associated with effects over time during the course of the experiment. Furthermore, there was no difference in soil water Mn concentrations identified between horizons of this profile. In the moorland peat profile, treatment was found to significantly ($p=0.018$) affect soil water Mn concentrations during the drying phase. However, when individual horizons within the profile were analysed, the difference resulting from treatment was only weakly significant ($p=0.077$) in the deep (O2) horizon. The time series graph of soil water Mn concentration from this horizon (Figure 5.11) does not provide any obvious explanation for this in terms of increasing or decreasing Mn concentration. There was also a weakly significant ($p=0.068$) treatment effect related to time elapsed, from cores of the moorland peat shallow (O2) horizon during the rewetting phase. The time series graph for this (Figure 5.11) indicates that this was probably due to the increase in treatment core Mn concentration detected at the end of the rewetting phase. Mn concentrations from the peaty gley profile differed significantly between soil horizons throughout the experiment, with those from the shallow (O2) horizon being greater than the intermediate (Bg) and deep (Cg) horizons. The only cores from this soil to exhibit any variation caused by treatment were from the shallow

Mn	**Acclimatisation Phase**				**Drying Phase**				**Rewetting Phase**			
	1	2	3	4	1	2	3	4	1	2	3	4
Forest peat	0.222	0.423	0.261	0.112	0.277	0.248	0.139	***<0.001***	0.469	0.810	0.593	***0.060***
(O2) Shallow		0.851	0.267	0.464		0.894	0.397	0.179		0.737	0.406	0.475
(O3) Intermediate		0.472	0.266	***0.010***		0.173	0.324	*0.008*		0.925	0.215	0.164
(O4) Deep		0.657	0.641	0.128		0.424	0.284	*0.008*		0.293	0.310	0.622
Moorland peat	0.229	0.569	0.568	*0.002*	0.573	***0.018***	0.580	*0.005*	***0.073***	0.558	0.272	***<0.001***
(O2) Shallow		0.999	0.639	0.118		0.245	0.335	0.188		0.999	***0.068***	*0.006*
(O2) Intermediate		0.419	0.391	0.543		0.278	0.641	0.174		0.678	0.252	0.113
(O2) Deep		0.999	0.448	***0.058***		***0.077***	0.386	0.150		0.677	0.435	***0.029***
Moorland peaty gley	***<0.001***	0.678	0.332	0.123	***<0.001***	0.176	0.324	***0.048***	***<0.001***	0.126	0.657	***0.062***
(O2) Shallow		0.519	***0.031***	*0.008*		***0.038***	0.566	0.251		0.318	0.477	0.175
(Bg) Intermediate		0.737	0.448	0.239		0.478	0.165	***0.011***		0.376	0.377	0.396
(Cg) Deep		0.248	0.482	0.507		0.315	0.397	0.132		0.701	0.636	0.280
Moorland peaty podzol	*0.001*	***<0.001***	0.660	0.652	*0.004*	***<0.001***	0.445	*0.005*	0.119	***0.085***	0.333	***<0.001***
(O) Shallow		***0.032***	0.361	0.293		***0.017***	0.141	0.271		0.284	0.309	***0.068***
(Eh) Intermediate		n/a	n/a	n/a		n/a	n/a	n/a		n/a	n/a	n/a
(Bs) Deep		***0.042***	0.397	0.389		***0.085***	0.527	***0.081***		0.170	0.415	***0.060***

Variation between soil cores explained by:-
1: Effect of horizon (within soil type)
2: Effect of treatment
3: Time.treatment effects
4: Time

(***p<0.1***; *p<0.01*; ***p<0.001***)

n-values (acclimatisation/drying/rewetting)

	Whole profile	Shallow	Intermediate	Deep
Forest peat	(234/288/360)	(78/96/120)	(78/96/120)	(78/96/120)
Moorland peat	(234/282/198)	(78/96/66)	(78/102/66)	(78/90/66)
Peaty gley	(234/274/360)	(78/94/120)	(78/90/120)	(78/90/120)
Peaty podzol	(195/208/510)	(78/96/204)	(39/41/102)	(78/71/204)

Table 5.5: Repeated measures ANOVA analysis of soil water chemistry data during soil core experiments – Mn variation within soil type and horizon

horizon. However, soil water samples from the control cores contained significantly greater Mn than samples from the treatment cores during the acclimatisation phase (Table 5.2), thus indicating that the two groups could not be considered statistically similar. A significant difference in soil water Mn concentrations between horizons was also apparent in the peaty podzol profile during the acclimatisation phase, although the incomplete data set for this profile means that results should be treated with caution. Significant differences explained by treatment effects were identified in both the shallow (O) and deep (Bs) horizons during the drying phase of the experiment (Table 5.5). However, Mn concentrations in soil water samples from treatment and control cores of these horizons were statistically different during the acclimatisation phase, preventing definite conclusions being made concerning the results in the drying phase.

pH

Table 5.6 shows that the pH of soil water samples from the forest peat shallow (O2) and deep (O4) horizon cores is significantly affected by treatment as time progresses during the rewetting phase (p=0.016 and p=0.039 respectively). The time series graphs from this profile (Figure 5.15) indicate that these differences probably arise as the result of decreasing sample pH measured in treatment cores from the two horizons. There is also a weakly significant (p=0.091) treatment effect on soil water pH in the intermediate horizon during the drying phase. However, there is no obvious evidence for this in the time series graph (Figure 5.15) or corresponding one-way ANOVA (Table 5.3). Repeated measures ANOVA data from the moorland peat (Table 5.6) indicate that soil water pH of the shallow and deep (both O2) horizons was influenced by experimental regime. Significant (p=0.007) treatment effects over time were identified in the shallow horizon during the rewetting phase. Examination of the time series graph (Figure 5.16) suggests that decreasing pH in the treatment core soil water samples may have caused this. Significant variation in the deep horizon soil water samples during the drying phase was explained by treatment effects (p=0.054) and treatment effects over time (p=0.024). In this case, the time series graph (Figure 5.16) implies that treatment core soil water pH may have increased, although missing data points resulting from suction probe failure may have influenced the analysis. Soil water pH in the peaty gley cores remained unaffected by treatment throughout the experiment, although there was always a significant difference in pH between the horizons (Table 5.6). Weakly significant effects resulting from experimental regime were detected in soil water pH from the peaty podzol shallow (O) horizon cores during the drying (p=0.083) and rewetting (p=0.089) phases (Table 5.6). The variation during the drying phase is associated with treatment

pH	Acclimatisation Phase				Drying Phase				Rewetting Phase			
	1	2	3	4	1	2	3	4	1	2	3	4
Forest peat	***0.065***	***0.061***	0.208	*0.006*	0.132	***0.016***	***0.092***	*0.005*	0.231	0.141	***<0.001***	***<0.001***
(O2) Shallow		0.342	0.450	0.128		0.242	0.356	***0.084***		0.643	***0.016***	***0.073***
(O3) Intermediate		0.105	0.202	0.282		***0.091***	0.176	***0.094***		0.155	0.395	***0.047***
(O4) Deep		0.596	0.444	0.154		0.346	0.527	0.106		0.591	***0.039***	***0.017***
Moorland peat	0.914	0.586	0.345	***<0.001***	0.578	0.118	***<0.001***	*0.004*	0.417	0.170	***<0.001***	***<0.001***
(O2) Shallow		0.894	0.591	***0.046***		0.710	0.380	0.181		0.710	*0.007*	*0.002*
(O2) Intermediate		0.925	0.737	***0.055***		0.472	0.135	0.100		0.492	0.106	0.158
(O2) Deep		0.372	***0.021***	***<0.001***		***0.054***	***0.024***	***0.042***		0.225	0.105	0.125
Moorland peaty gley	*0.004*	0.781	0.488	***<0.001***	*0.002*	0.509	0.194	0.509	*0.003*	0.632	0.293	***<0.001***
(O2) Shallow		0.127	0.546	***0.048***		0.535	0.246	***0.062***		0.278	0.246	***0.012***
(Bg) Intermediate		0.871	0.538	***0.087***		0.851	0.441	0.219		0.779	0.689	0.198
(Cg) Deep		0.834	0.426	*0.009*		0.637	0.652	***0.052***		0.459	0.320	0.142
Moorland peaty podzol	***0.033***	***0.013***	0.228	*0.003*	***0.020***	***0.010***	0.417	***0.095***	***0.073***	***0.019***	***0.017***	***<0.001***
(O) Shallow		0.129	0.200	0.118		0.119	***0.083***	0.214		***0.089***	0.250	***0.010***
(Eh) Intermediate		n/a	n/a	n/a		n/a	n/a	n/a		n/a	n/a	N/a
(Bs) Deep		0.321	0.402	***0.040***		0.271	0.470	0.417		0.298	0.139	***0.020***

Variation between soil cores explained by:-
1: Effect of horizon (within soil type)
2: Effect of treatment
3: Time.treatment effects
4: Time

(***p<0.1***; *p<0.01*; ***p<0.001***)

n-values (acclimatisation/drying/rewetting)

	Whole profile	Shallow	Intermediate	Deep
Forest peat	(234/288/360)	(78/96/120)	(78/96/120)	(78/96/120)
Moorland peat	(234/260/198)	(78/96/66)	(78/85/66)	(78/79/66)
Peaty gley	(234/270/360)	(78/93/120)	(78/90/120)	(78/87/120)
Peaty podzol	(195/205/510)	(78/96/204)	(39/41/102)	(78/68/204)

Table 5.6: Repeated measures ANOVA analysis of soil water chemistry data during soil core experiments – pH variation within soil type and horizon

effects over time, and inspection of the time series graphs (Figures 5.18 & 5.19) shows an increase in pH at the beginning of the drying phase. The variation during the rewetting phase was attributed to treatment effects, and is possibly caused by the decrease in pH of treatment core soil water samples shown in Figures 5.18 & 5.19.

Colour

Results of the repeated measures ANOVA carried out on colour in the soil water samples are presented in table 5.7. The colour of soil water samples from the forest peat shallow (O2) and intermediate (O3) cores showed significant treatment-related effects during the drying and rewetting phases. However, the time series graphs of soil water colour (Figure 5.20) indicate that there was a noticeable increase in colour of samples from the control cores during this period, which may have affected the analysis. The very noticeable drop in colour evident in the moorland peat shallow (O2) horizon treatment cores during the drying phase (Figure 5.21) proved not to be statistically significant (Table 5.7). This was attributed to high variability between the control cores, particularly one core that repeatedly gave samples containing much less colour than the other two. Including data from this core in the analysis increased the standard deviation of the control core data and therefore may have prevented a significant result from being obtained when comparing control core soil water colour with the treatment cores. When the analysis was re-run without data from this core, a highly significant ($p<0.001$) difference resulting from treatment effects, caused by the decrease in colour from the treatment cores, was identified. In both the moorland peat intermediate (O2) and deep (O2) horizons, effects arising from the experimental procedure were identified during the drying phase (Table 5.7). The time series graphs (Figure 5.21) suggest that, in contrast to the moorland peat shallow horizon, the colour of soil water from these horizons increases as the soil dries. The colour of soil water samples from the peaty gley shallow horizon was affected by treatment during both the drying and rewetting phases (Table 5.7). From the time series graphs (Figure 5.22) it appears that sample colour decreases during the drying phase, before gradually returning to acclimatisation phase levels during the rewetting phase. There is also a significant ($p=0.023$) treatment effect on soil water colour of the peaty gley deep (Cg) horizon during the rewetting phase, although it is difficult to discern any definite change from the time series graph (Figure 5.22). Weakly significant treatment effects over time were identified in soil water colour from the peaty podzol shallow (O) horizon during the drying ($p=0.073$) and rewetting ($p=0.059$) phases. Analysis of the time series graph (Figure 5.23) indicates that these effects are associated with a decrease in colour of soil water samples during the drying phase followed by an increase during the rewetting

Colour	**Acclimatisation Phase**				**Drying Phase**				**Rewetting Phase**			
	1	2	3	4	1	2	3	4	1	2	3	4
Forest peat	***<0.001***	0.215	0.343	***<0.001***	***<0.001***	***0.025***	***0.026***	0.302	***<0.001***	*0.009*	0.456	***<0.001***
(O2) Shallow		0.363	0.229	*0.008*		***0.095***	0.167	0.370		***0.045***	0.387	***0.093***
(O3) Intermediate		0.254	0.372	***0.050***		***0.019***	***0.062***	0.379		*0.005*	0.437	***0.025***
(O4) Deep		0.834	0.340	***<0.001***		0.851	0.438	***0.072***		0.539	0.474	***<0.001***
Moorland peat	*0.001*	0.999	0.722	***0.027***	*0.007*	0.212	0.356	0.236	*0.001*	0.513	0.156	***0.025***
(O2) Shallow		0.999	0.663	***0.088***		0.114	0.326	0.244		0.315	0.100	***0.039***
(O2) Intermediate		0.791	0.392	***0.060***		***0.052***	***0.069***	***0.073***		0.130	0.317	***0.014***
(O2) Deep		***0.066***	0.432	*0.004*		***0.015***	***0.022***	***0.025***		0.114	0.591	0.113
Moorland peaty gley	***<0.001***	0.810	0.295	***0.059***	***<0.001***	0.256	0.257	0.343	***<0.001***	0.471	0.360	0.462
(O2) Shallow		0.543	0.369	***0.051***		***0.067***	0.325	0.523		***0.072***	***0.019***	0.259
(Bg) Intermediate		0.718	0.447	0.424		0.678	0.407	***0.060***		0.409	0.365	0.350
(Cg) Deep		0.631	0.337	0.236		0.492	0.307	0.246		***0.023***	0.353	0.482
Moorland peaty podzol	***<0.001***	0.233	0.703	*0.007*	***<0.001***	0.507	0.112	***0.017***	*0.008*	0.180	***0.015***	***0.010***
(O) Shallow		0.503	0.270	*0.005*		0.591	***0.073***	***0.010***		0.223	***0.059***	***0.049***
(Eh) Intermediate		n/a	n/a	n/a		N/a	n/a	n/a		n/a	n/a	n/a
(Bs) Deep		0.637	0.548	0.194		0.268	***0.033***	***0.066***		0.631	0.205	0.185

Variation between soil cores explained by:-
1: Effect of horizon (within soil type)
2: Effect of treatment
3: Time.treatment effects
4: Time

(***$p<0.1$***; *$p<0.01$*; ***$p<0.001$***)

n-values (acclimatisation/drying/rewetting)

	Whole profile	Shallow	Intermediate	Deep
Forest peat	(234/288/360)	(78/96/120)	(78/96/120)	(78/96/120)
Moorland peat	(234/260/198)	(78/96/66)	(78/85/66)	(78/79/66)
Peaty gley	(234/270/360)	(78/93/120)	(78/90/120)	(78/87/120)
Peaty podzol	(195/207/510)	(78/96/204)	(39/42/102)	(78/69/204)

Table 5.7: Repeated measures ANOVA analysis of soil water chemistry data during soil core experiments – colour variation within soil type and horizon

phase. The only other significant effect identified in the peaty podzol soil cores is in the deep (Bs) horizon during the drying phase, where treatment effects over time are the source of differences (p=0.033) in soil water colour between treatment and control cores. The time series graph of this data suggests that treatment core soil water colour increases as the drying phase progresses. However, samples were only collected on three occasions before suction probe failure resulted from the drying conditions, thereby limiting the extent of the analysis.

Summary

Of the twelve horizons investigated, only the moorland peat shallow (O2) horizon exhibited a statistically significant increase in soil water Mn concentrations during the rewetting phase. However, this does not disprove the theory that Mn release occurs upon rewetting following a period of drying. Instead, the data suggest that Mn release from soils is a horizon-specific event, rather than occurring throughout the entire profile. The release of Mn from the moorland peat shallow horizon occurred at the same time as a significant treatment-related decrease in soil water pH was identified. There was no significant alteration in soil water colour associated with the changes in Mn concentration and pH in this horizon.

5.4.5.3 Discussion

As with the other forms of statistical analysis used, soil heterogeneity and the small number of replicates make it difficult to draw conclusive findings, as do the absence of control cores for the peaty podzol intermediate horizon. Concentrations of Mn in soil water were only found to significantly increase as a result of treatment in the moorland peat shallow (O2) horizon, although whether this absence of Mn release is due to the problems noted earlier, or is actually representative of Mn behaviour is unknown.

Significant pH increases resulting from experimental regime were found during the drying phase in soil water samples from the moorland peat deep and peaty podzol shallow horizons. Upon rewetting, significant treatment-related effects related to decreases in soil water pH were identified in the forest peat shallow (O2) and deep (O4) horizons, the moorland peat deep (O2) horizon and the peaty podzol shallow (O) horizon. As stated in section 2.3.2.1, alterations in soil water pH during saturated conditions depend largely upon the initial pH of the soil water and tend to move towards circumneutral conditions. In each case, the mean pH of the three horizons identified as decreasing during rewetting was moving closer to 7.0 and therefore in agreement with other published work (e.g., Ponnamperuma, 1972; Takkar, 1969). What was unexpected is that the pH of soil water samples from what were considered to be acidic soils should, in some cases, be as high as pH 9. Possible explanations for this include the effect of interactions with the cation exchange sites of the ceramic cups retaining H^+ ions from the soil water collected in the suction probes, or alterations to sample pH occurring during the period between sample collection and pH measurement.

The decrease in colour observed in treatment core soil water samples from the moorland peat shallow (02) horizon during the drying phase (Figure 5.21) did not prove to be significantly explained by treatment effects when investigated using repeated measures ANOVA. However, if the consistently low readings from one control core were discarded, then a highly significant treatment effect producing a decrease in soil water colour was identified during the drying phase. If a significant difference between treatment and control core soil water samples is accepted for this horizon, then soil water samples from the shallow horizon treatment cores of the three moorland soils contain less colour than samples from the corresponding control cores during the drying phase. This is in contrast to the deep horizons of the moorland soils, where a treatment-related increase of soil water colour was noted during the drying phase. It is possible that the decrease in colour seen in the moorland soil shallow horizons may result from soil pore diameters decreasing as the highly organic cores shrank during drying. If pore diameter shrinkage reached a stage where the molecules giving rise to the colour in the soil water were too large to pass through, then these compounds would be retained in the soil as water was drawn out by the suction probe and therefore effectively filtered out of the sample. The increase in colour observed in the deeper horizons may result from sampling of different sized pores. Because the larger pores dry out first, samples collected during the drying phase should come from progressively smaller pores as time goes on, until none can be collected. Soil water in these smaller pores has a longer residence time and therefore a greater period over which dissolution of compounds from the pore walls may occur. This factor, combined with the larger surface-to-volume ratio of the smaller pores, means that soil water samples from small pores may contain greater concentrations of chemicals than the water sampled from the larger pores (Hansen & Harris, 1975). Why the cores from some horizons were affected by these mechanisms whilst others appear unaffected is unclear. It is possible that both processes occur, but that the effects of the collapsible pore mechanism can only be seen when the soil water contains enough colour arising from the presence of suitably large organic compounds. This could be explained in terms of humification, with the deep horizons possibly having undergone a greater degree of humification and therefore containing organic breakdown products with smaller molecular sizes. Therefore, as the soil dries and the diameter of water-filled pores decreases, the large organic breakdown products in the less-humified horizons are retained in the soil, while the small organic molecules in the more humified horizons are able to pass through the smaller pores.

5.4.6 Statistical analysis: Correlation

The final piece of statistical analysis undertaken on the soil core data was the calculation of correlation coefficients between the three determinands measured. The purpose of this analysis was to identify whether or not Mn concentration in soil water was related to changes in soil water pH and/or colour. Table 5.8 shows correlations (Pearson product moment) between Mn, pH and colour for each horizon and treatment regime.

5.4.6.1 Results

Soil horizons from the forest peat show strong negative correlation between Mn and colour in both treatment and control cores. However, both the shallow and intermediate horizons of the peaty podzol exhibit a significant positive correlation between Mn and colour in the treatment cores, which is not present in the control cores. The expected negative correlation between Mn and pH is identified in most of the cores, although a significant positive correlation occurs in soil water from shallow and intermediate control cores from the forest peat. Within the peats, there appears to be a negative correlation between colour and pH in the shallow horizons, which is replaced by a positive correlation further down the profile.

5.4.6.2 Discussion

As anticipated, decreasing pH was generally associated with increasing Mn concentrations in soil water, indicating the important effect that pH has on Mn mobilisation. However, this relationship is not universal, and there is a significant positive correlation between soil water Mn concentration and pH observed in the forest peat shallow (O2) and deep (O3) horizons. This may indicate some other factor controlling soil water Mn, or the correlation may simply result from the extremely small range of Mn concentrations measured in soil water from these horizons.

There appears to be a difference between forest and moorland soils in terms of the relationship between soil water Mn concentrations and colour. Significant negative correlations between Mn and colour were identified in the forest peat, while significant positive correlations were identified in the moorland soils. One possible explanation for this is that the decomposition products from different types of vegetation may be different

			Treatment cores				Control cores		
			Mn v col	Mn v pH	col v pH	n	Mn v col	Mn v pH	col v pH
Forest	Peat	Shallow	***-0.301***	***-0.220***	***-0.677***	**102**	***-0.402***	***0.229***	0.075
		Intermediate	0.122	***-0.376***	0.030	**102**	***-0.509***	***0.452***	-0.067
		Deep	***-0.456***	***-0.759***	***0.329***	**102**	***-0.304***	***-0.422***	***0.202***
Moorland	Peat	Shallow	*0.298*	***-0.238***	***-0.574***	**84**	***0.316***	***-0.407***	***-0.885***
		Intermediate	-0.091	***-0.234***	***0.545***	**84**	0.190	*-0.299*	0.184
		Deep	-0.028	***-0.287***	***0.353***	**84**	0.143	***-0.460***	-0.005
	Peaty gley	Shallow	0.034	0.134	***-0.228***	**93**	-0.025	***-0.205***	***-0.591***
		Intermediate	0.058	***-0.503***	-0.146	**93**	0.026	-0.104	0.104
		Deep	0.160	***-0.308***	0.122	**93**	***0.205***	*-0.287*	-0.181
	Peaty podzol	Shallow	***0.698***	0.008	-0.088	**117**	0.029	***-0.748***	0.111
		Intermediate	***0.693***	***-0.657***	***-0.934***	**117**	-	-	-
		Deep	-0.045	-0.134	***0.746***	**117**	0.165	0.046	***0.379***

Table 5.8: Correlation coefficients for soil water chemistry
(***$p < 0.05$*** ; *$p < 0.01$* ; ***$p < 0.005$***)

(Kaiser *et al.*, 2001; Sanger *et al.*, 1997). Therefore, the organic compounds released from decomposing moorland vegetation may have a greater ability to form soluble complexes with soil Mn than those released from the decomposing forest vegetation. There is a strong positive correlation between Mn and colour in soil water from the peaty podzol shallow (O) and intermediate (Eh) horizon treatment cores. Analysis of soil physical properties indicates that both of these horizons contain a mixture of mineral and organic matter that may provide inputs to soil water Mn and colour respectively. In addition to this, the peaty podzol deep (Bs) horizon contains substantial amounts of total Mn (~100 $\mu g\, g^{-1}$ - see section 5.4.1), which may be a potential source of mineral Mn for the whole profile. It appears that drying and rewetting in the peaty podzol shallow and intermediate horizons produces a release of both organic carbon (identified as colour) and Mn from soil, although the extent to which complexation of Mn by the organic matter occurs is unknown.

Some of the strongest correlations were found between soil water Mn, pH and colour in treatment cores of the peaty podzol intermediate (Eh) horizon. Here, increases in soil water Mn coincided with increases in colour and decreases in pH. Unfortunately, this was the horizon where there were no control cores, so the extent to which correlation resulted from drying and rewetting is unknown. In general, the findings of the correlation analysis indicate that the relationship between soil water Mn concentrations with pH and colour varies, depending upon soil horizon and land use.

5.5 Conclusions

In general, there was no difference between soil water Mn concentrations from different horizons of the organic soils, while significant differences existed between organo-mineral soil horizons. In the peaty gley and peaty podzol, soil water Mn concentrations were greater in organic horizons compared to the deeper mineral horizons. However, this is in complete contrast to the distribution of total soil Mn in these profiles, suggesting that soil water Mn concentrations in each horizon were largely controlled by factors other than the total soil Mn concentration.

Using a combination of time series graphs and statistical analysis, Mn release into soil water during the rewetting phase of the soil core experiments was identified in three horizons. These were the moorland peat shallow (O2) horizon and the peaty podzol shallow (O) and intermediate (Eh) horizons. One possible explanation for the mobilisation of Mn in these horizons is that they all contained Mn in mineral form, which would serve as a source, and a relatively large organic matter content, to facilitate mobilisation (either by complexation or by decreasing pH as decomposition occurred under saturated conditions). Although the soil samples collected from the moorland peat shallow (O2) cores for determination of soil chemical properties did not indicate this, subsequent investigation of the core upon termination of the experiment revealed the presence of at least two thin horizontal bands of mineral grains in the 20 cm depth of core. In soil horizons where there was no Mn mobilisation recorded, this might have been because there was no supply of mineral Mn (as in the forest peat), or a lack of decomposing organic matter (as in the deep mineral horizons of the moorland soils).

The small number of replicates that could reasonably be collected and processed, combined with inherent soil variability, may have affected the outcome of statistical analysis carried out on the data collected. It is therefore possible that in cases where no relationship between Mn release, soil water regime, pH and colour was statistically proven such a link might well exist.

Based upon the experience gained during the course of the soil core laboratory experiment, the following recommendations should be considered if such an experiment was to be attempted again:

1. Collection of more cores

   The provision of more replicates would not only enhance the robustness of any statistical analysis by countering the inherent variability of soil water chemistry, but it may also enable sample collection from a greater number of cores during the drying phase when suction probe failure is liable to occur.

2. Better control of soil water regime

   Rather than saturating the cores immediately following the drying phase, it may be beneficial to rewet them at a controlled rate in order to better simulate the conditions in field soils at the start of the autumn. Freeman *et al.* (1993) describe a method by which the soil water content of laboratory cores can be accurately controlled. Initially, control of soil core water content to this extent was not deemed necessary as it was the effect of continued saturation during the rewetting phase, rather than the speed at which rewetting occurred, that was being investigated. Furthermore, constraints concerning the availability, installation time and costs involved of the additional equipment required to implement the control apparatus meant that this method was not considered for use during the soil core experiments. However, if this method was adopted in any future soil core experiments, then the rate of drying and rewetting could both be controlled in order to provide a better simulation of field conditions.

3. Extension of drying and rewetting phases

   Although the drying period of two weeks matched the longest periods without rain during the dry summer of 1995, this may not have allowed the soil cores to dry out to a similar extent as the field soils during 1995. The cumulative effect of drying, resulting from several periods of dry conditions, experienced by field soils during 1995 was probably greater than that observed in the soil cores after only two weeks drying in the laboratory. In addition to this, field soils lost water by both evaporation at the top of the profile (which may have been greater than in the laboratory due to the effect of wind) and drainage at the base of the profile, while evaporation and sample collection were the only factors affecting water loss from the soil cores. Therefore, if the soil cores did not dry out to the same degree as field soils did during 1995, it is possible that the effects promoting Mn release upon rewetting did not occur to the same extent. The rewetting period, also initially set at two weeks in duration, was extended after the first experimental run, and lasted for five weeks in the final set of soil cores. Data from the experiment suggest that a period of at least 4 weeks waterlogging is required to provide proper definition of any Mn release peak occurring.

4. Extension of experimental design

   Using the current experimental design, it is impossible to ascertain whether any Mn mobilisation occurs as a result of the combined drying and rewetting treatment, or through saturation during the rewetting phase alone. It is therefore recommended that the experiment should be extended to include the effects of saturation alone, by instrumenting a series of cores that are brought to saturated conditions without having undergone the preceding drying phase.

5. Measurement of redox potential and microbial activity

   A measurement of redox potential in the soil cores as the experiment progressed could provide an indication of how changes in redox conditions as the soil dried out or was rewetted were affecting soil water Mn status. In addition to this, an estimation of microbial activity at the time (possibly by measurement of CO_2 output) and an identification of species present could be used to infer the extent of microbial Mn reduction or oxidation. These measurements would enable estimation of the processes by which Mn was mobilised in each soil horizon, thereby allowing better prediction of the occurrence and timing of any mobilisation events.

In conclusion, the soil core laboratory experiments did not provide a definitive answer to the hypotheses outlined in section 5.1, partly due to experimental design, but also to limitations in statistical techniques available to analyse such data. However, the findings of the soil core experiments suggest that the potential for Mn mobilisation, resulting from the drying-rewetting cycle investigated, varies widely between soil horizons. Horizons containing substantial amounts of both organic and mineral material were identified as releasing the greatest concentrations of Mn into soil water upon rewetting. It is hypothesised that the mineral material acts as a source of Mn, while the organic matter is involved in promoting Mn mobilisation.

At this point, it is still unknown as to how the extent of drying recorded during the soil core experiments and field monitoring programme compares with that in the field soils during 1995. Therefore, a soil water simulation model was used in order to estimate this and provide a potential link between catchment soil water regime during 1995 and the reservoir Mn concentrations. The modelling procedure and results are described in the following chapter.

As with the soil solution samples collected during the field monitoring programme, the pH of soil solution samples from the soil core laboratory experiments was often 1-2 pH units greater than might have been expected for soils of this type. When compared with the pH of soil samples collected during field site installation (Table 4.10), it is evident that soil solution samples collected using the ceramic cups are considerably greater. Therefore, it is suggested that a similar mechanism to that thought to influence the pH of samples collected in suction probes during the field monitoring programme is occurring, and that the pH values quoted in this chapter should also be regarded as indicative of relative trends, rather than absolute values.

Chapter 6: Modelling the soil water regime

Chapter six describes the procedure used to model the soil water regime of the soils studied in this project. The background and rationale to using a soil water model are presented in the first section, along with a general description of the model used. The input data required are then considered, along with details of how these data were collected. Following this, output from the model and its validation against data gathered during the field monitoring programme are presented, before discussion of the results and potential implications for catchment Mn management.

6.1 Background

Soil water simulation models are used to predict the changes in soil water regime, in response to rainfall inputs and evaporative outputs, within a specified soil profile over a set period of time. Many different models are available, often having originally been developed for specific purposes (e.g., calculating soil water transpiration rates, or nitrogen fluxes), before modification to allow more general use (Lilly, 1995). Investigating the transport of contaminants within soils is also an area that has promoted the development of soil water simulation models, for example those produced by the US Environmental Protection Agency Centre for Subsurface Modelling Support (www.epa.gov/ada/csmos/modeldescr.html). Despite their diverse origins, soil water models generally work by solving some variant of the Richards equation for water flow in an unsaturated porous medium in order to distribute water throughout soil profiles defined by the user. The majority of soil water simulation models currently available calculate water movement in one dimension (i.e. vertically within a soil profile), although some models are able to attempt this over two or three dimensions (e.g., HYDRUS-2D & SWMS_3D www.ussl.ars.usda.gov/models/; TOPOG www.per.clw.csiro.au/topog/).

6.1.1 Rationale

The principal aim of using a predictive soil water model as part of this research was to allow simulation of the soil water regime in soils of the Ballochbeatties Burn catchment during 1995. If catchment soils were predicted to dry out during the summer of 1995 to the same extent as soil cores releasing Mn in the laboratory experiment, then it could be inferred that a similar Mn release may have occurred following rewetting by autumn rainfall, leading to the increase of reservoir water Mn concentrations observed that year. Another potential application of the calibrated soil water simulation model is to enable the use of data gathered during field and laboratory experiments to predict soil moisture conditions under future climatic conditions. By combining a soil water model with Mn release data, it may be possible to predict how changes in climate, for example drier summers and wetter winters, affect soil moisture status and thence Mn mobilisation within soils of the Ballochbeatties Burn catchment.

6.1.2 The soil water simulation model - WAVE

The computer program chosen to model soil water regime as part of this research was WAVE (Water and Agrochemicals in the soil, crop and Vadose Environment), developed by the Institute for Land and Water Management, Catholic University of Leuven, Belgium. WAVE is a one-dimensional process-based model, designed to describe the transport and transformations of matter and energy within the soil, crop and vadose environment (Vanclooster *et al.*, 1994). The water transport module of the model functions by solving a modified version of the Richards equation for transient 1-dimensional vertical flow (Equation 6.1) (Vanclooster *et al.*, 1994; Radcliffe & Rasmussen, 2000).

$$\frac{\delta\theta}{\delta t} = \frac{\delta}{\delta z}\left[K(\theta)\left(\frac{\delta h}{\delta z} + 1\right)\right]$$ **Equation 6.1**

Where: θ = volumetric water content (m^3m^{-3})
z = vertical co-ordinate (cm)
t = time (day)
$K(\theta)$ = hydraulic conductivity (cm day^{-1})
h = soil water pressure head (cm)

6.2 Input data required

The input data used by any computer program is of considerable importance. There are two main categories of data required to parameterise and run the WAVE program. The first of these describes the soil profiles and defines the hydrological properties of individual horizons. These data were obtained from field and laboratory analysis of soils in the Ballochbeatties Burn catchment, combined with existing database parameters from pedologically similar horizons. The significance of accurately quantifying the soil hydraulic parameters is noted by van Genuchten *et al.* (1991), who state that these are by far the most important parameters affecting the rate by which water and dissolved chemicals move through the vadose zone. The second category was climatic data, obtained from the British Atmospheric Data Centre, primarily required in order to define water inputs to the profile from precipitation and outputs via evapotranspiration. All data were formatted in standardised text files (examples shown in Appendix E), which were then read by the computer program.

6.2.1 Soil profile data

Full descriptions of the soil profiles instrumented in the Ballochbeatties Burn catchment (contained in Appendix C) were used to define the depths and distribution of soil horizons for the WAVE soil water simulation model. WAVE allows the user to define a series of layers, analogous to soil horizons, within a soil profile (Figure 6.1). Soil layers are subdivided into compartments, each of which contains a node located at its centre where variables for the compartment are calculated using finite difference techniques. Soil compartment thickness is defined by the simulation user, although one potential limitation is that all compartments must be the same thickness. Smaller compartment thickness will increase the numerical accuracy of the program, at the expense of increased processing time. One further benefit of smaller soil compartments is that the user will be able to replicate the dimensions of the original soil profile more closely. For the purposes of this research, soil compartment thickness was set to 25 mm as this allowed accurate replication of the soil profiles without introducing excessive time delays.

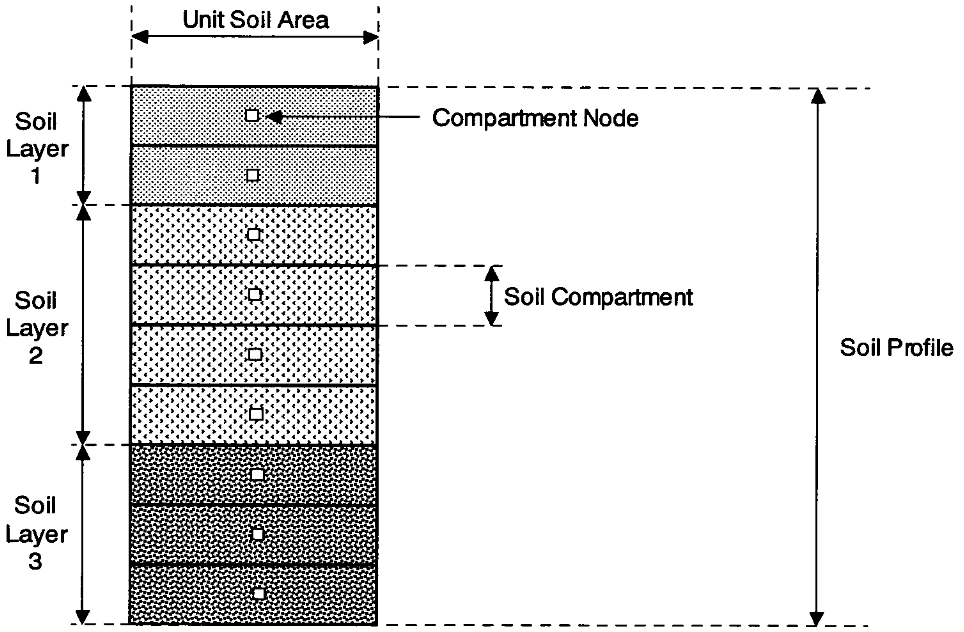


Figure 6.1: Format of soil profile data used by WAVE program (From Vanclooster *et al.*, 1994)

6.2.2 Soil hydrological properties

In order to solve equation 6.1 and model the soil water regime, the WAVE program requires parameterisation with data describing the moisture retention characteristic or $\theta(h)$ relationship and hydraulic conductivity curve or K(h) relationship for each soil layer modelled (Table 6.1). Most of these parameters were derived from data collected during the soil core laboratory experiments detailed in the previous chapter. However, where a soil horizon was not included in the soil core experiments, data were obtained from similar horizons held in the HYPRES (HYdrological PRoperties of European Soils) database (Wösten *et al.*, 1999).

Parameter	Description
Moisture retention parameters	
θ_r	Residual water content
θ_s	Saturated water content
α	Moisture retention curve shape parameter (inverse of the air entry value)
n	Moisture retention curve shape parameter (measure of slope gradient)
m	Moisture retention curve shape parameter (measure of asymmetry)
Hydraulic conductivity parameters	
K_{sat}	Saturated hydraulic conductivity
l	Tortuosity of Mualem model

Table 6.1: Soil hydraulic parameters required by WAVE program

6.2.2.1 Derivation of soil moisture retention characteristic

The moisture retention characteristic of a soil defines the relationship between soil water content and pressure head (i.e. $\theta(h)$). There are several widely used parametric models to describe the shape of the $\theta(h)$ relationship, three of which are incorporated into the WAVE computer program as part of the RETC code (van Genuchten *et al.*, 1991). The major distinction between the models available within WAVE is whether or not hysteresis is simulated. However, because insufficient data were available to adequately parameterise the hysteretic $\theta(h)$ models included in the WAVE software, the non-hysteretic van Genuchten model was used to describe the $\theta(h)$ relationship (Equation 6.2) (van Genuchten, 1980). Although hysteresis can influence the calculated soil water fluxes (Jones & Watson, 1987;

Russo *et al.*, 1989), the van Genuchten model is considered to give a suitable representation of the $\theta(h)$ relationship.

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{\left(1 + (\alpha h)^n\right)^m}$$ **Equation 6.2**

Where: θ_s = saturated volumetric soil water content (m^3m^{-3})
θ_r = residual volumetric soil water content (m^3m^{-3})
α = inverse of the air entry value (m^{-1})
n, m = shape parameters

Parameters for the $\theta(h)$ equation were calculated using the Appia 2.0 computer program (SC-DLO (now Alterra), Wageningen, Netherlands) to fit data from the soil core laboratory experiments described in Chapter 5 to $\theta(h)$ curves for each soil horizon. The Appia program works by using the evaporation method of Wind (1968) to simultaneously determine the $\theta(h)$ and K(h) relationships of a homogeneous soil sample (Halbertsma, 1996). To calculate $\theta(h)$ for a soil sample, the Wind method requires devices for measuring matric potential (e.g., tensiometers) at a minimum of two depths in the soil sample, plus a measurement of the total weight of the soil sample.

At each measurement time, the average water content of the soil sample is calculated from the average water content at the end of the experiment (determined gravimetrically) and the measured weight loss. The average water content and mean of the measured matric potentials at each measurement time are used to construct the $\theta(h)$ relationship. A smooth curve can then be fitted through the data points and used to estimate the water content in the individual compartments, based on the measured pressure head. Next, the mean of the estimated compartments' water content is compared with the calculated average water content. For each measurement time, the estimated water contents are adjusted so that their mean equals the measured average water content, resulting in a new set of estimated water contents and measured pressure heads (i.e. new $\theta(h)$ relationship) to which a smooth curve can be fitted. The procedure then repeats itself for a specified number of iterations, or until there is no significant improvement to the curve fit.

The Appia program was used to determine α, n and m parameters of the $\theta(h)$ relationship for each soil core, by fitting data from the soil core laboratory experiments to the van Genuchten model with m=1-(1/n). The two other $\theta(h)$ parameters required by WAVE for each horizon were determined by different means and used to fix the wet and dry ends of the $\theta(h)$

relationship during the Appia fitting procedure. θ_s was estimated from thetaprobe data recorded in the field, using the highest continual value recorded during the autumn and winter period when the soils were judged to be saturated. In those horizons where doubts existed over thetaprobe data (see section 4.2.2.1), the readings were still accepted as valid indications of θ_s. Although the thetaprobe response to wetting and drying in the affected horizons was greatly affected by the probable presence of macropores, the value recorded at saturation would only be slightly greater than if the probe had not intercepted a macropore. The final parameter, θ_r, which is little more than a fitting parameter to constrain the drying end of the $\theta(h)$ relationship, was taken from the HYPRES database values based on texture (procedure described in section 6.2.2.3). Once fits for all three core replicates of each soil horizon were obtained, the α, n and m values of these $\theta(h)$ curves were then used to define horizon parameter ranges for use in WAVE.

6.2.2.2 Derivation of hydraulic conductivity curve

The hydraulic conductivity curve of a soil defines the relationship between hydraulic conductivity and pressure head (i.e. K(h)). As with $\theta(h)$, many parametric models exist to describe the K(h) relationship of soils. The model used in this research was that of van Genuchten (1980), which is based on the pore size distributed conductivity model of Mualem (1976). Parameter estimation was undertaken using the Appia program, which allowed simultaneous fitting of the $\theta(h)$ and K(h) relationships with data from the soil core experiments. When this was attempted without fixing one of the two parameters required to describe the Mualem - van Genuchten model (K_{sat} and l), the program predicted excessively high values for K_{sat} (e.g., K_{sat}>100 cm d^{-1} for an organic horizon). One possible reason for this inaccuracy is that, although it performs well under slightly unsaturated conditions, the Mualem van Genuchten model does not provide a good estimate of saturated hydraulic conductivity (Vanclooster *et al.*, 1994). Therefore, K_{sat} was fixed prior to curve fitting, using an estimate of field-saturated hydraulic conductivity (K_{fs}) for each soil horizon based upon the structure contained in the profile descriptions (Appendix C). Although K_{fs} is generally less than K_{sat}, it is considered an appropriate measurement to use for studies of water movement in the vadose zone (Lilly, 1994; Schaap & Leij, 2000). Values of K_{fs} for a total of 49 combinations of primary and secondary soil structures were described by Lilly (2000). In order to obtain an appropriate value of K_{sat} for curve fitting within Appia, the structure of each horizon was matched with one of the 49 classes described by Lilly (2000) and the geometric mean of K_{fs} for these data (A.Lilly, unpublished data) used as the Appia K_{sat} value

(Table 6.2). The value of *l* derived from fitting the K(h) relationship to data from each soil core in Appia was then used to provide horizon parameter ranges for use in WAVE.

Soil type	Horizon		Structure	K_{fs} (cm d^{-1}) *
Peat (forest)	O2	(shallow)	Coarse angular blocky	4.233[1]
	O3	(intermediate)	Massive	0.835
	O4	(deep)	Massive	0.835
Peat (moorland)	O2	(shallow)	Massive	0.835
	O2	(intermediate)	Massive	0.835
	O2	(deep)	Massive	0.835
Peaty gley	O2	(shallow)	Very coarse subangular blocky	4.848
	Bg	(intermediate)	Coarse subangular blocky / Massive	1.131
	Cg	(deep)	Massive	0.835
Peaty podzol	O	(shallow)	Very coarse prismatic	0.464
	Eh	(intermediate)	Coarse platy	25.204
	Bs	(deep)	Coarse platy	25.204

Table 6.2: Field-saturated hydraulic conductivity assigned to each soil horizon on the basis of structure

* Geometric mean of values taken from Lilly (2000 & related unpublished data)

[1] No data available for structure type – value inferred from pedologically similar horizon

6.2.2.3 Use of existing database pedotransfer functions

Once the hydrological properties for each soil core were determined, parameter ranges for use in WAVE were established for all of the soil horizons studied. However, where a soil horizon present in the profile had not been sampled for use in the soil core experiments, it was impossible to derive the required modelling parameters by this method. Therefore, those horizons lacking experimental data to allow θ(h) and K(h) curve fitting within Appia were assigned parameters from the HYPRES database, using class pedotransfer values based on texture.

To calculate this, particle size distribution data from each horizon was used to classify the soil according to texture, similar to the HYPRES data (Table 6.3). Then, the class pedotransfer values for that texture (Wösten *et al.*, 1999) were adopted as the model parameters for that horizon. As stated earlier, this method was also used to derive the θ_r parameter of the $\theta(h)$ relationship for the horizons fitted within the Appia program.

Texture	% Clay	% Sand	Horizons
Coarse	<18	>65	Bg, Bh, Bs, Cg
Medium	18 - 35 or <18	>15 or 15 - 65	Ehg
Medium fine	<35	<15	
Fine	35 - 60	-	
Very fine	>60	-	
Organic	-	-	LF, O1 – O4

Table 6.3: HYPRES texture classes assigned to soil horizons

A summary of the $\theta(h)$ and $K(h)$ parameter values for each horizon modelled in the WAVE soil water simulation, including their source, is shown in table 6.4. The different methods of parameter derivation generally indicate whether a soil horizon was instrumented during the field monitoring programme and soil core laboratory experiments. However, the 2Cgh horizon at moorland site one was deemed pedologically similar to the instrumented Cg horizon at moorland site two, based on analysis of samples collected during profile description. Therefore, the parameters derived from the Cg horizon soil cores were accepted for modelling the 2Cgh horizon in WAVE as it was felt that these were more characteristic of actual soil hydrological parameters than database values. Where parameter ranges are quoted, these represent the different parameters derived from replicate soil cores using the Appia program. Section 6.3.1.1 contains a full explanation of how these ranges were used in WAVE.

6.2.3 Climate data

In order to simulate the soil water regime, the WAVE soil water model requires rainfall data (mm d^{-1}) to predict water inputs at the top of the soil profile. Other components contained within this input file are the evapotranspiration rate (mm d^{-1}) and rainfall interception by vegetation (mm d^{-1}), both of which serve to modify the water flux at the top of the profile.

6.2.3.1 Rainfall in the Bradan catchment

Records of rainfall from the Met Office station at the nearby Bradan treatment works are held in the British Atmospheric Data Centre (BADC) archives, accessible via the Internet

Peat (Forest)

	O1	O2	O3	O4
θ_r	0.010	0.010	0.010	0.010
θ_s	0.766	0.845	0.880	0.915
α	0.0130	0.0272 – 0.0357	0.0193 – 0.0243	0.0147 – 0.0170
n	1.204	1.236 – 1.314	1.372 – 1.470	1.265 – 1.303
m	0.169	0.191 – 0.239	0.271 – 0.320	0.209 – 0.233
K_{sat}	8.00	1.80	0.80	0.80
l	0.40	-5.330 – 0.334	-1.462 – 0.251	0.000

Peat (Moorland)

	O1	O2*	O2*	O2*	2Cgh
θ_r	0.010	0.010	0.010	0.010	0.025
θ_s	0.766	0.810	0.827	0.830	0.620
α	0.0130	0.0188 – 0.0211	0.0108 – 0.0156	0.0065 – 0.0093	0.0043 – 0.0049
n	1.204	1.395 – 1.682	1.365 – 1.637	1.381 – 1.438	1.639 – 1.742
m	0.169	0.283 – 0.405	0.268 – 0.389	0.276 – 0.305	0.390 – 0.426
K_{sat}	8.00	0.80	0.80	0.80	0.80
l	0.40	0.000 – 0.396	0.000	0.000	-4.106 – 0.000

* O2 horizon split to replicate field instrumentation depths (shallow; intermediate; deep)

Peaty gley

	O1	O2	Bg	Cg
θ_r	0.010	0.010	0.025	0.025
θ_s	0.766	0.725	0.570	0.620
α	0.0130	0.0103 – 0.0124	0.0051 – 0.0201	0.0043 – 0.0049
n	1.204	1.437 – 1.628	1.139 – 1.552	1.639 – 1.742
m	0.169	0.304 – 0.386	0.122 – 0.356	0.390 – 0.426
K_{sat}	8.00	0.80	1.10	0.80
l	0.40	0.000	-3.238 – 1.410	-4.106 – 0.000

Peaty podzol

	LF	O	Ehg	Bh	Bs	Cg
θ_r	0.010	0.010	0.010	0.025	0.025	0.025
θ_s	0.766	0.895	0.765	0.366	0.462	0.366
α	0.0130	0.0069 – 0.0109	0.0050 – 0.0091	0.0430	0.0035 – 0.0095	0.0430
n	1.204	1.251 – 1.295	1.261 – 1.654	1.521	1.237 – 1.292	1.521
m	0.169	0.201 – 0.228	0.207 – 0.396	0.342	0.192 – 0.226	0.342
K_{sat}	8.00	0.50	25.20	70.00	25.20	70.00
l	0.40	0.000	0.000	1.25	0.000	1.25

Table 6.4: Mualem - van Genuchten parameter values for $\theta(h)$ and $K(h)$ relationships of modelled soil profiles as input to WAVE

Parameter derivation:

1. From Appia fit of MRC & HCC with experimental data
   (Two values indicates range of parameters derived from replicates)
2. From HYPRES database - class pedotransfer function based on soil texture

(www.badc.rl.ac.uk). However, the 1999 Bradan rainfall data, required to produce model output that could be validated against thetaprobe data, contained substantial gaps. Rainfall data for the neighbouring weather stations during the same period were also missing. The nearest complete rainfall record identified was from the Auchincruive weather station, which was at a much lower altitude 25 km to the northwest and so considered unsuitable as a direct replacement for the Bradan data. Lack of a compatible, complete data set meant that rainfall for the Bradan catchment during 1999 was derived from the records of nearby stations using the weighted interpolation procedure described below.

The method used to calculate missing rainfall data during 1999 in the Loch Bradan catchment is similar to that employed by Poole (2001) to estimate daily rainfall over an 11-year period in the same catchment. Daily rainfall for Bradan was calculated from a distance and altitude weighted average, based on data from nearby weather stations with more complete records held in the BADC archive. A total of 16 stations within a 30 km radius of Loch Bradan were selected to provide data for the interpolation procedure, each being given a weighting factor based upon its distance and altitude difference from Bradan treatment works (Equation 6.4; Table 6.5). Rainfall at Loch Bradan for a single day was determined using equation 6.5, which averages the data from surrounding stations using the inverse distance and altitude weighting factor calculated in equation 6.4.

$$\text{Weighting Factor} = \frac{1}{\text{Distance Between Stations x Altitude Difference}}$$ **Equation 6.4**

$$\text{Rainfall (mm)} = \frac{\{(\text{Rain}_x \text{ x } \text{WF}_x) + (\text{Rain}_y \text{ x } \text{WF}_y) + (\text{Rain}_z \text{ x } \text{WF}_z)\ldots\}}{\sum \text{WF}}$$ **Equation 6.5**

Where: Rainfall = Predicted rainfall at Bradan treatment works
$\text{Rain}_{x,y,z}$ = Rainfall measurement for station x, y, z (mm)
$\text{WF}_{x,y,z}$ = Weighting Factor for station x, y, z

Following construction of the predicted Bradan treatment works rainfall data set, a linear regression analysis was performed against the existing partial data set of rainfall recorded at the treatment works (Figure 6.2). The R^2 value of 82.2% indicates the validity of the interpolation based on data from the surrounding weather stations. Therefore, missing daily rainfall data for Bradan treatment works were derived from the regression equation and used to create a complete rainfall data set for 1999.

Station Name	Grid Reference	Distance (km)	Altitude (m)	Weighting Factor
Garpel Burn	NX482985	5	216	0.00588
Drumjohn	NX524976	9	224	0.00427
Black Laggan	NX469777	22	235	0.00303
Kirrieroch	NX362871	14	213	0.00193
Penwhapple Reservoir	NX257969	18	202	0.00116
Patna, Blaney Avenue	NS416105	11	155	0.00096
Forrest Lodge	NX555866	17	152	0.00060
Clatteringshaws	NX554780	24	178	0.00058
Pullaugh Burn	NX544741	27	183	0.00055
Knockjarder Water Works	NS353150	18	84	0.00033
Upper Black Laggan	NX476769	23	408	0.00028
Cumnock	NS563200	24	99	0.00028
Doonholm	NS338175	21	27	0.00021
Barskimming, Burnbrae Lodge	NS476245	26	67	0.00021
Auchincruive	NS379233	25	48	0.00020
Brigton	NX361745	26	35	0.00018

Table 6.5: Weather stations and weighting factors used to supply data for Loch Bradan rainfall interpolation

(Loch Bradan Water Treatment Works: Grid Ref. = NX435993; Alt. = 250 m)

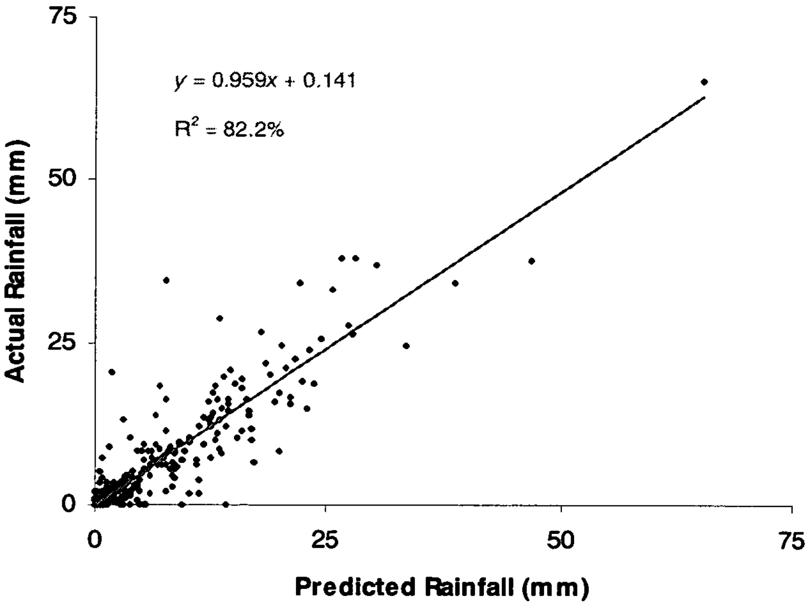


Figure 6.2: Regression analysis of predicted daily Bradan rainfall against actual rainfall

6.2.3.2 Rate of evapotranspiration

Evapotranspiration is a term used to describe the loss of water from a vegetation-covered soil to the atmosphere, combining the processes of evaporation and transpiration. The rate of evaporative water loss from an exposed soil surface depends upon incident solar radiation and wind speed, with greater moisture loss expected in hot, windy conditions. Transpiration is the process by which soil water taken in by plant roots is drawn up through the plant by the vapour gradient across the stomata-atmosphere interface and subsequently passed to the atmosphere when it reaches the stomata. It is estimated that over 90% of the water extracted from soil by plant roots is lost to the atmosphere in this way (Hillel, 1998).

The daily evapotranspiration at field sites in the Loch Bradan catchment was estimated using computer software developed at Cranfield University (Hess, 1998). This software (Reference Evapotranspiration Program) applied the Penman-Monteith method (Monteith, 1980) for calculating daily evapotranspiration rates. Input data for the program were held in the form of a text file comprising climatic variables recorded at UK Meteorological Office surface weather stations. Daily data for the input file (rainfall; maximum, minimum, dry bulb, wet bulb temperature; wind speed) were obtained from the BADC and, where possible, came from the weather station located at the Loch Bradan water treatment works. Reconstruction of these data to fill gaps in the record was accomplished by the same method as in section 6.2.3.1. Where data were not available from the Loch Bradan weather station, as in the case of dry and wet bulb temperature measurements, the dataset was entirely reconstructed using the distance-altitude weighting technique.

When run, the program produced a text file containing an estimate of the daily evapotranspiration, which was imported into a computer spreadsheet for incorporation into the WAVE input file.

6.2.3.3 Interception of rainfall

Not all of the rain falling on an area of ground actually reaches the soil surface and infiltrates into it. Substantial amounts of precipitation land on vegetation and are stored there until evaporating. The amount of rainfall that is intercepted in this way depends on a number of factors, including vegetation, wind speed and air temperature.

A maximum canopy storage value for mature heather of 2.0 mm d^{-1} has been calculated (K.Heal, pers. comm.) and this figure was used for the moorland sites where *Calluna* formed a large percentage of the vegetation cover. Therefore, if the daily rainfall was greater than 2 mm, then the estimated interception loss at each moorland site was set to 2 mm, otherwise interception was assumed to equal rainfall.

A similar figure was not available for interception by Sitka spruce forestry plantation, so a review of existing literature was undertaken to provide an estimate. Several authors have published studies of interception by Sitka spruce, detailing the interception as a percentage of total rainfall (Anderson & Pyatt, 1986; Ford & Deans, 1978; Gash *et al.*, 1980; Hudson, 1988; Johnson, 1989; Law, 1956) (Table 6.6). The percentage of rainfall intercepted by the canopy was found to be greater during the summer months. Anderson and Pyatt (1986) reported that, although the total volume of water was the same, the percentage of rainfall intercepted during April-September was 1.5 times greater than that intercepted during October-March. Studies report different findings concerning the effect of tree age on amount of interception. Anderson & Pyatt indicate that mature trees may intercept 20 % more rainfall than those at the pole stage. However, Johnson (1989) does not consider tree age to influence the percentage of rainfall intercepted and reports a mean value for a 50-year old canopy similar to that recorded at 25 to 29-year old sites. Therefore, interception of rainfall by Sitka spruce in the Ballochbeatties Burn catchment was estimated using the mean value of interception from these studies (32 % of total rainfall), as the yearly mean with a weighting modification to increase the summer interception relative to winter by a factor of 1.5 (Equations 6.6 and 6.7).

$$\text{Interception}_{(\text{Apr-Sep})} = (2 \text{ x mean interception}) \text{x} \frac{3}{5} = 38.4\ \%$$ **Equation 6.6**

$$\text{Interception}_{(\text{Oct-Mar})} = (2 \text{ x mean interception}) \text{x} \frac{2}{5} = 25.6\ \%$$ **Equation 6.7**

The resulting interception figures for moorland and forestry were then added to the computer spreadsheet forming the WAVE input file.

Study	Location	Age of trees (years)	Interception (% of total rainfall)
Law (1956)	Lancashire, England	25	38
Ford & Deans (1978)	Dumfries & Galloway, Scotland	14	30
Gash *et al.* (1980)	Kielder forest, England	27	32
	Hafren forest, Wales	29	27
Anderson & Pyatt (1986)	Kielder forest, England	25	29
		63	49
Hudson (1988)	Plynlimon, Wales	29	25
Johnson (1989)	Balquhidder, Scotland	50	28

Table 6.6: Summary of UK studies detailing interception of rainfall by Sitka spruce

6.2.4 Input files

The parameter and environmental variable data required to populate the model were contained in three text files. These files were constructed along template lines supplied with the WAVE program and discussed in the following section, with examples presented in Appendix E.

6.2.4.1 GENDATA.IN : general simulation data

The file GENDATA.IN contains general information concerning the type of simulation to be run (i.e. what factors are to be modelled) and the time period over which modelling takes place. The soil profile to be modelled is defined within this file, specifying the number of layers and compartments within each layer, along with the standard compartment size. Other factors specified (time step, maximum moisture content change, maximum balance error) govern the accuracy of the numerical solution and can be set to maximise this at the expense of computation time. The last section of the input file allows the user to define parameters concerning the production of summary tables if required.

6.2.4.2 WATDATA.IN : soil hydrological properties

The file WATDATA.IN is the largest of the three input files required to simulate soil water regime. In the first section, hydraulic parameters of the $\theta(h)$ and $K(h)$ relationship are specified for each soil layer and the simulation user is able to choose which model to apply the parameters to.

Other information contained in this file concerns plant activity, with sections detailing aspects of plant water uptake and rooting depth. Where no site-specific data were available for these parameters, they were left at the program default values. However, an estimate of rooting depth and maximum root activity was inferred by information in the soil profile description.

The user can select the bottom boundary condition for the modelled profile from a range of options. The boundary condition of soil profiles modelled in this research was set such that outflow was dependent upon the K(h) relationship, implying the natural flow of water under gravity at the base of the profile. The initial water content of soil compartments is also specified within this file. In each compartment, this was set to a figure slightly below the θ_s value for that soil layer, as this was considered to approximate soil moisture status at the simulation start date (January 1st). This initial value was chosen to reflect conditions in winter soils, where transpiration and evaporative water loss were less than hydrological inputs to the profile. By starting the simulation at this time, any inaccuracies introduced by wrongly estimating the initial moisture content were likely to be minimised prior to comparisons with measured field data (commencing April 29th) by 'balancing' of the model. The term 'balancing' refers to the time taken by the model to reproduce moisture contents that are independent of the initial user-defined values (Capehart & Carlson, 1994; Lilly, 1995).

The final section of the WATDATA.IN file deals with the variables controlling output files desired by the user. In this case, time series of predicted water content in each soil layer were selected, as these could be directly compared with measured thetaprobe values.

6.2.4.3 CLIMDATA.IN : climatic variables for model

Rainfall and other climatic data, required to solve the field water flow equation for the simulation period, are held in the CLIMDATA.IN file. Data are laid out in a table, which must have the following sequence on every line: year; month; day; evapotranspiration (mm d^{-1}); interception (mm d^{-1}); irrigation (mm d^{-1}); precipitation (mm d^{-1}); minimum and maximum temperature (°C); global radiation (J cm^{-2} d^{-1}). The irrigation field was set to zero, as this refers to anthropogenic addition of water at the soil surface to aid crop growth, which was not a factor at any of the sites. The temperature and global radiation fields were not required by the model when simulating water movement alone, so were left blank.

Once the data required had been assembled in the correct order in a spreadsheet, it was exported to a text file for use in the WAVE program.

6.3 Output from WAVE

Data output from the WAVE soil water simulation model was in the form of a text file, listing either volumetric water content or matric potential calculated at each node within the user-defined soil compartments. This file was then imported into a computer spreadsheet package in order to produce graphical and statistical analysis as required.

6.3.1 Validation against field data

Comparison of WAVE simulation data with the record of volumetric water content from the thetaprobes installed at the field sites provided a means of determining simulation accuracy. If the WAVE soil water simulation could be parameterised to predict soil water content over the same period that the thetaprobes were installed at the field sites, then the modelled water content for each profile could be validated against the value actually measured in the field.

Although the thetaprobes installed in the field were logging every hour, the validation plots of field water content were constructed using the 9 a.m. data value for each day. This was done to provide a single daily data point, against which the simulated data could be compared. The 9 a.m. value was chosen because this was the time at which rainfall and other climatic data were recorded and would therefore act as a 'start' time for each simulation 'day'.

6.3.1.1 Assessing the accuracy of simulated water content

In addition to a visual comparison of predicted and measured data, statistical techniques were used to asses the accuracy of WAVE output. Lilly (1995) considered four different statistical techniques, described by Clemente *et al.* (1994), for assessing the goodness-of-fit of a simulated soil water regime compared to measured field data. The *average error* (Equation 6.8) is simply an average of the differences between measured and predicted values. Therefore, the value of the average error may have a positive or negative sign, indicating an over or underestimation by the simulation. One considerable disadvantage with this term is that over-predictions and under-predictions can cancel each other out, thereby producing an average error of close to zero even though predicted measurements differ greatly from those observed in the field. The *standard error* (Equation 6.9) is calculated using the square of the difference between the observed and predicted data.

Therefore, although the standard error conveys no information of whether the simulation is over or under-predicting the observed values, it is not influenced by 'cancelling out' effects and reflects the true difference between observed and predicted data. The final two methods for determining goodness-of-fit are based on the average and standard errors already described. *Relative error* (Equation 6.10) can be calculated by dividing the average error by the mean of the measured values, although cancelling-out effects will still influence this value. The *coefficient of variation* (Equation 6.11) is calculated by dividing the standard error by the mean of the measured values, therefore allowing a comparison of simulation accuracy between different horizons. Accuracy of the simulation used in this research was primarily assessed on the basis of the standard error, with a target threshold based upon thetaprobe accuracy initially considered to represent an acceptable match between simulated and measured data for any given horizon. Therefore in horizons where thetaprobe calibration was possible (see section 4.1.2.1), the standard error threshold was set at 0.02, while in horizons where water content was calculated using the thetaprobe defaults it was set at 0.05.

$$\text{Average error} = \frac{\sum(\theta_p - \theta_m)}{n}$$ **Equation 6.8**

$$\text{Standard error} = \sqrt{\frac{\sum(\theta_p - \theta_m)^2}{n}}$$ **Equation 6.9**

$$\text{Relative error} = \frac{\text{Average error}}{\theta_m \bar{x}}$$ **Equation 6.10**

$$\text{Coefficient of variation} = \frac{\text{Standard error}}{\theta_m \bar{x}}$$ **Equation 6.11**

Where: θ_p = predicted volumetric water content (WAVE)
θ_m = measured volumetric water content (thetaprobe data)
n = sample number
$\theta_m\bar{x}$ = mean of measured water contents

Using Appia to fit data from each soil core replicate to the moisture retention and hydraulic conductivity curves generated one set of parameters (i.e. α, n, m, l) describing the θ(h) and K(h) relationships of that particular soil horizon in WAVE. Therefore, the three horizons from each soil profile included in the soil core laboratory experiments each had three replicate parameter sets, making a total of 27 different combinations of parameter sets for each soil type. The one exception to this was the peat profile at moorland site one, where the 2Cgh horizon was deemed to be pedologically similar to the Cg horizon of the peaty gley at moorland site two and parameterised using the same data. This resulted in four horizons of the moorland site one profile having three parameter sets and therefore a total of 81 different combinations. In order to find the best match with measured thetaprobe data, the WAVE computer simulation was run for every possible combination of horizon parameter sets. After each simulation run, predicted water content data from WAVE was imported into Microsoft Excel for comparison with thetaprobe data. To begin with, a visual inspection of the two datasets was carried out as a preliminary guide, then statistical analysis of the difference between predicted and measured water contents was undertaken using the standard error as a measure of goodness-of-fit. After every possible permutation of horizon parameter sets was modelled, the combination giving the smallest standard error when compared to the thetaprobe data was accepted as the WAVE parameters for that soil profile. Consideration was also given to using the mean of parameter replicates from each horizon to describe the $\theta(h)$ and $K(h)$ relationships in WAVE. However, it was thought that these hybrid curves would not represent actual soil hydraulic properties as well as those derived from a single source.

Initial attempts at simulating the soil water regime tended to overestimate the drying of soil, particularly towards the end of the summer (Figure 6.3). This overestimation was most evident in the two peat profiles, where thetaprobe data indicated saturated conditions for much of the year. In these profiles, the overestimation of drying was mainly attributed to the K_{sat} value of the organic horizons being too great, resulting in excess water loss from the simulated profile. In particular, the K_{sat} value of 8 cm d^{-1} from HYPRES appears large when compared to estimates from similar horizons of 0.5-0.8 cm d^{-1} (Lilly, 2000) and 0.34-1.91 cm d^{-1} (Holden *et al.*, 2001). One possible explanation for this difference is that the majority of organic soils in the HYPRES database are from mainland Europe and therefore developed under different climatic conditions to those in Scotland, resulting in peat with different hydrological properties. Therefore, K_{sat} values of the organic horizons were all decreased, based upon data from UK studies.

Holden *et al.* (2001) used tension infiltrometry to determine hydraulic conductivities for the top 20 cm of a blanket peat in the north of England, under a range of different vegetation types. While the type of vegetation decomposing to form the peat was found to affect hydraulic conductivity, the greatest influences were identified as the degree of humification evident in the peat and the depth at which measurements were made. The von Post classification of humification (recorded during description of the soil profiles) allows a link

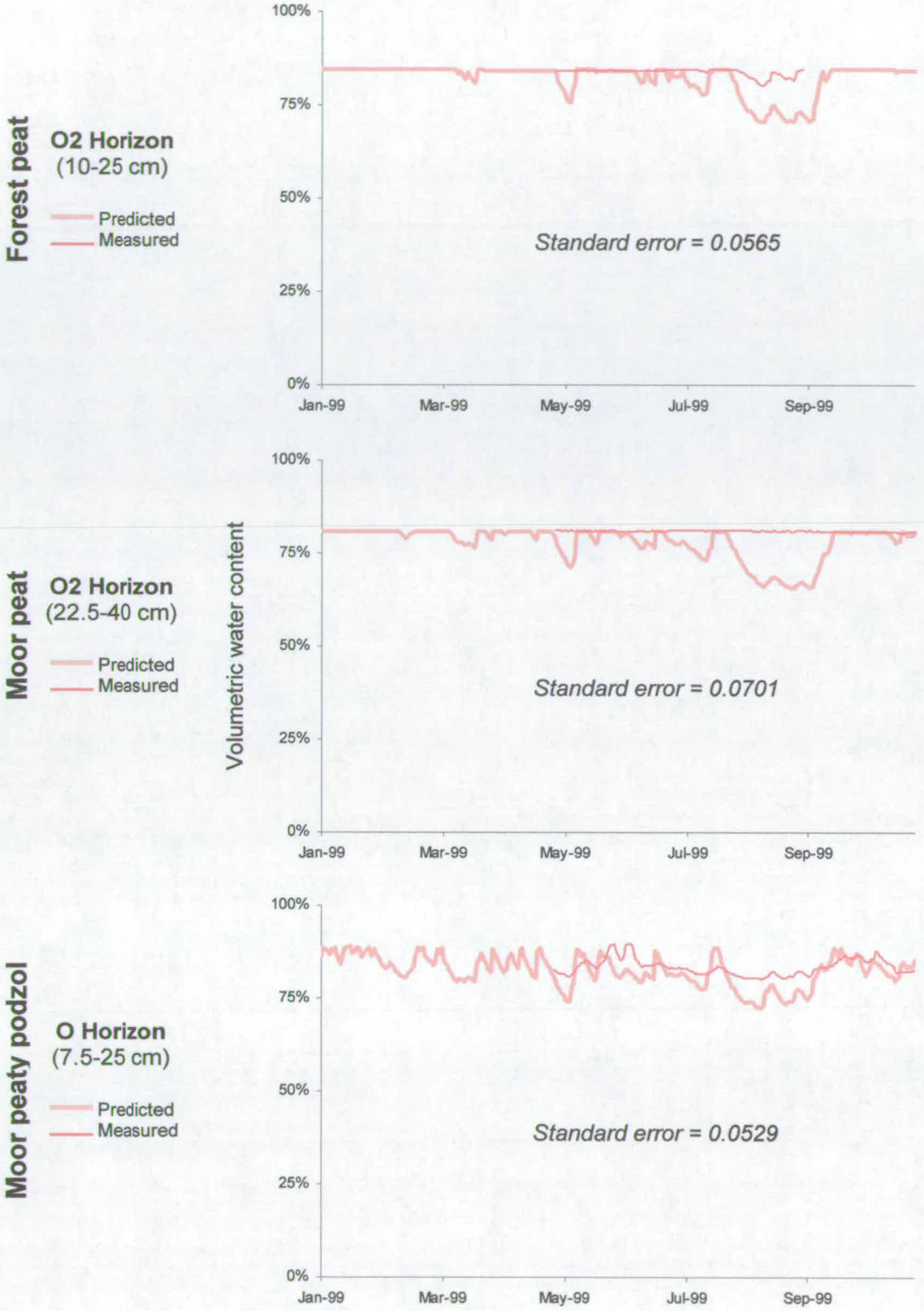


Figure 6.3: Examples of soil water simulation using HYPRES values of K_{sat} for organic horizons, compared with thetaprobe data

to be made between the peat investigated by Holden *et al.* (2001) and the organic horizons modelled in this research. Of the four vegetation types studied by Holden *et al.* (2001) (bare, *Calluna*, *Sphagnum*, *Eriophorum*), the data from the *Calluna* peat profiles was thought to be the most relevant to this research. Prior to afforestation in the 1960s, the entire Loch Bradan catchment was open moorland dominated by *Calluna* and *Molinia* (Murray & Pullar, 1910). Therefore, although the rate of peat deposition at the forest sites is unknown, only the top few cm of the forest peat profile should be derived from Sitka spruce litter, with the remainder forming from the historic moorland vegetation. In order to define more realistic hydraulic conductivity parameters for WAVE modelling, organic horizons with a similar von Post score (H1-H4) to those described by Holden *et al.* (2001) were assigned K_{sat} values based on that study's findings. Although the figures reported by Holden *et al.* (2001) are only from the top 20 cm of the peat profile, data from an earlier review of hydraulic conductivities measured in peat (Rycroft *et al.*, 1975) suggests that the hydraulic conductivity of highly humified peat found at depth in the profile can be an order of magnitude smaller than less humified deposits near the surface. Therefore, the deepest, most humified organic horizons modelled in this research (von Post H9–H10) were assigned a value of K_{sat} approximately one tenth that of the less humified (von Post H1-H4) peat. Horizons intermediate to these, in terms of humification and depth, were assigned a K_{sat} value between these figures. Table 6.7 presents a summary of the updated organic horizon K_{sat} values used in WAVE, along with an indication of their relative humification and depth.

K_{sat} (cm d^{-1})	Degree of humification (von Post)	Relative depth	Horizons
1.91	H1-H3	Shallow	Forest - O1; Moor1 - O1; Moor2 - O1
0.34	H4-H9	Shallow	Forest - O2; Moor1 - O2; Moor2 - O2; Moor3 - O
0.15	H6-H9	Intermediate	Forest - O3; Moor1 - O2
0.03	H9-H10	Deep	Forest - O4; Moor1 - O2

Table 6.7: Generation of organic horizon K_{sat} parameter for WAVE modelling, based on degree of humification

(Forest = peat; Moor1 = peat; Moor2 = peaty gley; Moor3 = peaty podzol)

When the simulation was run with the amended K_{sat} values, the extent of drying was reduced and standard errors generated by comparison of simulated and thetaprobe data were smaller, indicating a better match with measured data. Therefore, the smaller K_{sat} values were accepted in place of the HYPRES K_{sat} values, and the simulation run again for every combination of parameter sets to find the closest match to thetaprobe data.

For most of the soil horizons, the standard error difference between measured and simulated data was within the target set for 'acceptable' modelling of the soil water regime, and in several cases a standard error of <0.01 was attained. However, this proved to be unachievable for some horizons, owing to problems with the thetaprobes producing highly variable data (see section 4.1.2.1). For horizons with doubts concerning the validity of thetaprobe data, model parameters were set so as to minimise standard errors in the other horizons within the same profile, rather than to attempt modelling of the highly variable water content within that horizon. Therefore, although the standard error associated with such horizons appears large, this is an effect of the thetaprobe data and not an indication of problems concerning the soil water simulation for that horizon.

The final stage of goodness-of-fit evaluation was calculation of a correlation coefficient between measured and predicted soil water content. Once the parameters for each profile were fixed and the simulation run, the Minitab statistical package (v12.1) was used to perform the analysis. The correlation coefficient was not calculated for the moorland peat deep horizon because the simulated water content was always the same value (saturation).

The following sections (6.3.1.2 to 6.3.1.5) present results from the soil water simulation of each soil profile in detail. In addition to this, a summary of the statistical measures of simulation accuracy is contained in table 6.8.

Soil Type & Horizon			Average error	Standard error	Relative error	Coefficient of variation	Correlation coefficient
Peat (forest)	O2	(10-25 cm)	-0.0042	0.0124	-0.0050	0.0148	***0.896***
	O3	(25-35 cm)	-0.0002	0.0040	-0.0002	0.0046	-0.334
	O4	(65-90 cm)	0.0016	0.0066	0.0018	0.0073	***-0.245***
Peat (moorland)	O2	(22.5-40 cm)	-0.0050	0.0117	-0.0061	0.0145	***-0.155***
	O2	(40-80 cm)	0.0000	0.0009	0.0000	0.0011	***0.277***
	O2	(80-100 cm)	-0.0036	0.0056	-0.0043	0.0067	-
Peaty gley	O2	(10-35 cm)	0.2021	0.2208	0.4339	0.4741	0.403
	Bg	(55-70 cm)	0.1000	0.1459	0.2429	0.3543	0.267
	Cg	(70-90 cm)	-0.0127	0.0276	-0.0212	0.0461	0.440
Peaty podzol	O	(7.5-25 cm)	-0.0071	0.0270	-0.0086	0.0323	***0.645***
	Eh	(25-32.5 cm)	0.1603	0.1719	0.3037	0.3255	0.462
	Bs	(37.5-65 cm)	-0.0096	0.0173	-0.0220	0.0397	***0.758***

Table 6.8: Statistical summary of measured versus predicted water contents
Correlation analysis: $p<0.05$ (n=186)

6.3.1.2 Results of validation – peat (forest)

The forest peat is deeper than the moorland peat profile and consists of an amorphous waterlogged mass of organic material for most of its depth, with only a shallow fibrous layer at the surface. Thetaprobe data from this profile indicated that the soil was at, or near, saturation for the entire simulation period. Figure 6.4 shows the simulated water contents plotted along with measured water contents for each instrumented horizon of the forest peat profile. The standard errors of the intermediate (O3) and deep (O4) horizons where comparison between measured and predicted data was possible are less than 0.01, indicating a very good match (Table 6.8). The continually saturated conditions recorded in the field by the thetaprobes mean that there is little scope for comparing the simulation's response to wetting and drying conditions. The standard error of the shallow (O2) horizon is only marginally greater than 0.01 and also indicates a good match for the measured data. However, the simulation appears to slightly overestimate the limited amount of drying recorded by thetaprobes in the shallow horizon during the late summer, as indicated by the average error and relative error in Table 6.8.

6.3.1.3 Results of validation – peat (moorland)

There was approximately 1 m depth of peat lying on top of glacial drift at the moorland site. Again, measured field water content was near to saturation for the entire period, although this time there was no drying evident in the surface horizon during the summer months. The plot of simulated and measured water content for the moorland peat site is shown in Figure 6.5. As with the simulation of the forest peat, the intermediate and deep horizons remain at saturation for the simulation period and therefore closely match the measured data, each having a standard error of less than 0.01 (Table 6.8). In the shallow horizon, the simulation predicts a short period with three distinct drying and rewetting phases towards the end of the summer. This is similar to the prediction for the shallow horizon of forest peat profile (Figure 6.4) and results from three periods (9, 4 and 5 days in length) during July and August with no rainfall. Thetaprobe data from the shallow forest horizon appears to verify the first two of these phases, although datalogger failure meant that the record did not extend to cover the third. Assuming rainfall at both forest and moorland sites was similar, the fact that the thetaprobe trace for the moorland peat shallow horizon (Figure 6.5) does not exhibit any drying indicates that some other factor is causing the moorland peat to remain near saturation. Fipps and Skaggs (1989) report that lateral flow occurs within soils on slopes of 8.5° of greater. As the moorland soils were situated on a slope of 11-13°, it is therefore possible that water input to the moorland peat profile from upslope (and therefore not

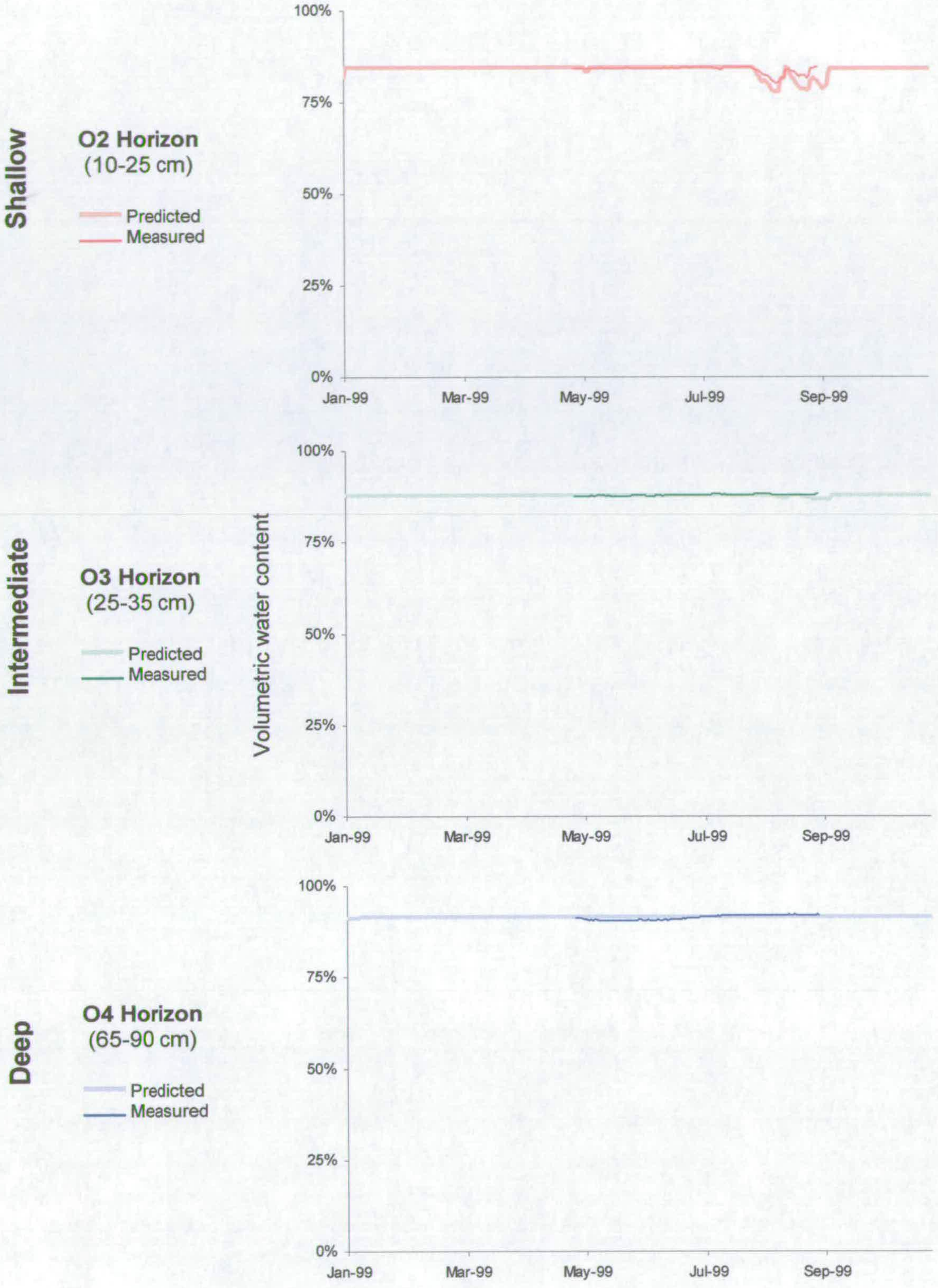


Figure 6.4: Comparison of measured water content (thetaprobe data) with predicted water content (WAVE simulation data) for **forest peat** soil profile

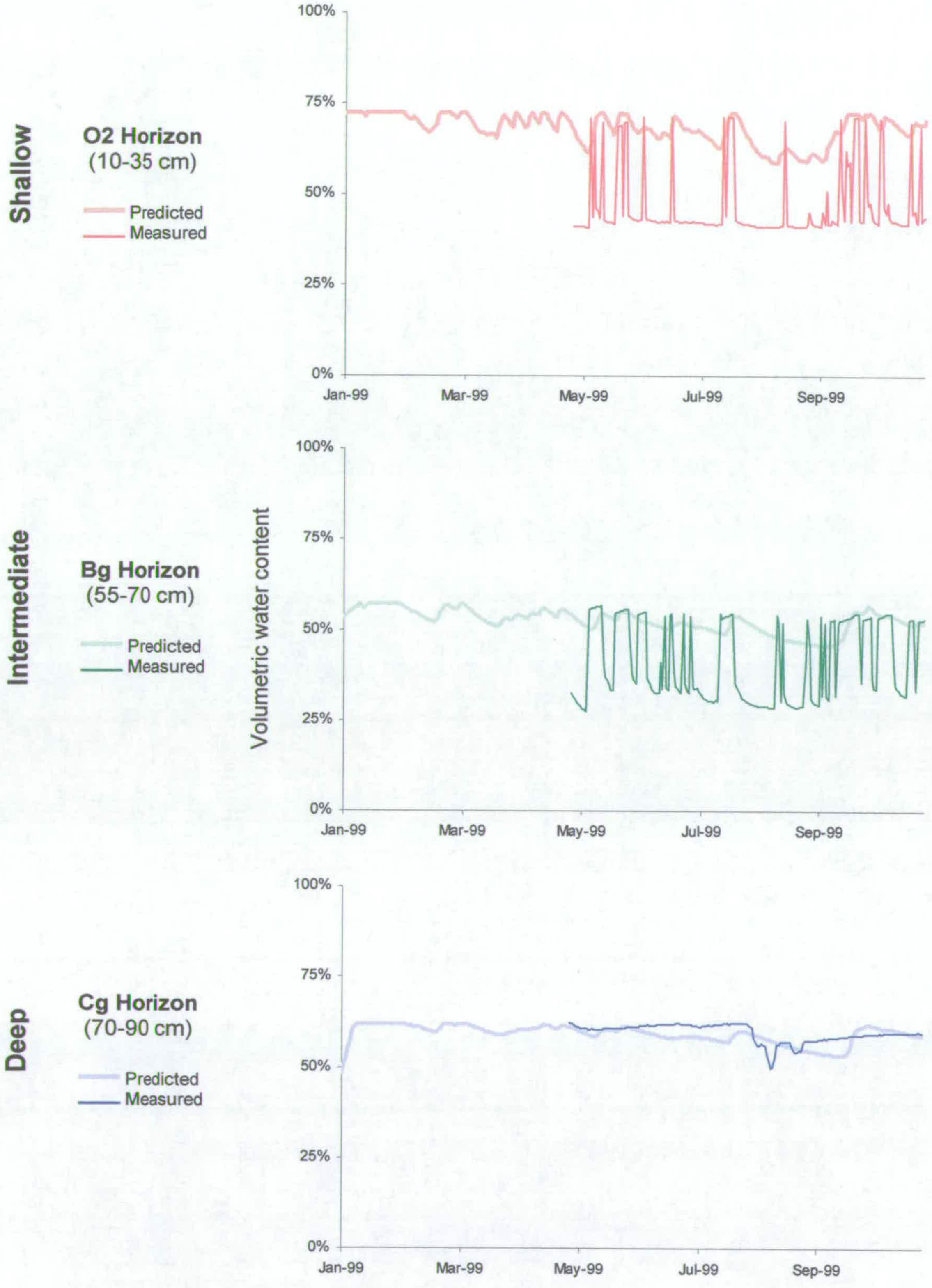


Figure 6.6: Comparison of measured water content (thetaprobe data) with predicted water content (WAVE simulation data) for **peaty gley** soil profile

layer of peat forming above mineral horizons. However, soil drainage was better than at the gley site, contributing to podzolisation within the soil profile. The plot of predicted and measured water content for each instrumented horizon of the peaty podzol profile is shown in Figure 6.7. Thetaprobe data from the intermediate (Eh) horizon was affected in a similar manner to data from the peaty gley site, with rapid changes in water content being recorded. Therefore, as with the peaty gley horizons, statistical analysis of the data is unreliable. However, both the peaty podzol shallow (O) and deep (Bs) horizon thetaprobe data showed broad fluctuations in moisture content and were considered to be realistic. The simulated shallow (O) horizon data provided a relatively good visual match for the measured data, with simulated peaks and troughs on the graph generally relating to those in the thetaprobe plot. This was also confirmed by the low standard error and high correlation coefficient (Table 6.8). However, the simulation tended to slightly over predict the extent to which the soil dried out in summer. In addition to this, the simulation also over predicted the water content following some rainfall events, while under predicting it after others. The predicted water content of the deep (Bs) horizon also provided a reasonable visual match for the thetaprobe data. However, the simulation did not reflect the fluctuations evident in the thetaprobe data and was instead relatively smooth in appearance. Considering all three horizons, it is apparent that fluctuations in the simulated soil water content become less as the depth in the profile increases. This 'smoothing' with depth was also apparent at the peaty gley site and may be caused by the one-dimensional aspect of the model, whereas the thetaprobes installed at the field sites (on a slope of 11-13°) may have recorded fluctuations in water content resulting from lateral flow. In addition to this, the profile description and data from the thetaprobe in the intermediate (Eh) horizon suggest that macropore flow possibly occurred at this site thereby producing different patterns of wetting and drying to those predicted by the model.

6.3.1.6 Summary of model validation

Simulating the soil water regime of soil type and land use combinations found in the Loch Bradan catchment provided a set of parameters, which could be used to investigate if the peak in reservoir water Mn concentrations during autumn 1995 were related to the summer soil moisture deficit. Although validation of the soil water simulation model against measured field data suggests that the method of determining model parameters was accurate, several factors should be taken into account concerning future use of this technique.

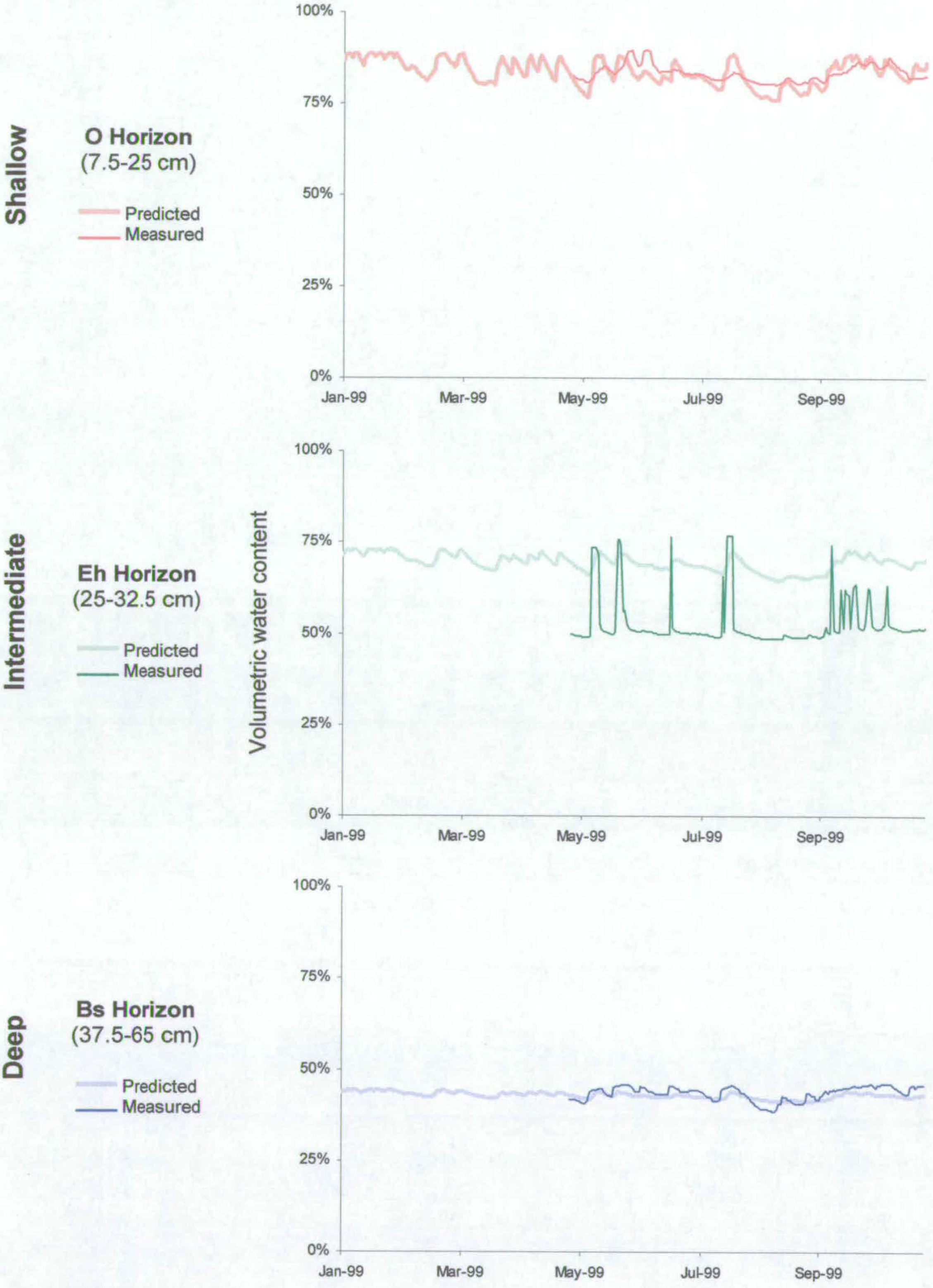


Figure 6.7: Comparison of measured water content (thetaprobe data) with predicted water content (WAVE simulation data) for **peaty podzol** soil profile

Of the twelve soil horizons in which the soil water regime was simulated, nine were found to have simulated soil water regimes closely matching the measured soil water regimes. The process of validation in the other three horizons was limited by extreme short-range variations in moisture content measured by the thetaprobes. Of the nine horizons for which model validation was carried out, five had thetaprobe plots that remained at saturation throughout the simulation period. This meant that replication of the measured data by the simulation entailed predicting a waterlogged profile, thereby limiting the scope for parameter calibration against fluctuations in soil water regime. However, the fact that the simulated profiles remained at saturation in the absence of surface ponding (prevented by input file parameters) indicates that parameterisation of the model was relatively accurate. In the remaining horizons, containing fluctuations in the measured soil water content, the simulated data matched the measured data, thus indicating that the method used for parameter derivation was successful.

Where possible, soil hydraulic parameters required by the simulation model should be derived from measurements of the soil horizons involved. Database values were used to provide ranges for approximately one third of the parameters used to populate the $\theta(h)$ and $K(h)$ models in this research. Despite the relative accuracy recorded by comparison between predicted and measured values, it is possible that parameters acquired from database and pedotransfer sources may not adequately reflect the response of the particular soils studied. The use of standardised variables for interception and evapotranspiration could also be improved by study of the particular vegetation types present. In addition to this, installation of equipment to monitor rainfall and other climatic variables may be desirable, as this would improve the simulation accuracy with respect to local weather conditions.

Finally, the limitations of using a 1-dimensional model to predict soil water movement on a slope should be considered when choosing the computer program. It is possible that lateral flow existed at certain levels within some of the soil profiles modelled in this research. Fipps and Skaggs (1989) reported that lateral flow occurred in soils on slopes of 8.5° or greater. As the moorland sites modelled in this research were situated on a slope of 11-13°, this meant the assumption made by the simulation that water flux at these sites only occurred at the base and top of the profile was invalid. Therefore it is suggested that, where profiles are located on a slope sufficient to produce lateral subsurface flow, the use of a 2-dimensional model may serve the purpose of modelling soil water regime more accurately.

Despite these limitations, the model reflected the measured moisture contents sufficiently well to allow hindcasting of the soil moisture regime in 1995.

6.3.2 Hindcasting the 1995 soil water regime

As discussed earlier (section 6.1.1), the main purpose of the WAVE soil water simulation model was to predict soil water content during 1995, the year in which the first large autumnal Mn peak was recorded in Loch Bradan reservoir water. The aim was to discover the extent to which soils within the Loch Bradan catchment dried out during that summer. When combined with Mn release data from the soil core laboratory experiments, prediction of greater drying of the catchment soils than occurred during the field monitoring period (i.e. 1999), could be used to infer that the dry summer conditions contributed to a release of Mn from catchment soils, which reached the reservoir following the onset of wetter autumn conditions.

The soil water regime for each profile was simulated for 1995 climatic conditions using the parameter values derived by model calibration against measured 1999 data. The only change to the WAVE input files was the substitution of 1995 climate data in the file CLIMDATA.IN. The 1995 climate dataset was constructed in exactly the same way as the one used for the 1999 simulation, using data accessible via the BADC website. Further minor changes were made to start and termination dates within the WAVE input files. All other model parameters were kept the same as those used on the final, calibrated run of the 1999 simulation. The WAVE program was then run for the 1995 data and the resulting predicted soil water content for each profile was plotted to allow comparison with the 1999 data (Figures 6.8 to 6.11).

6.3.2.1 Forest peat

The simulated water content of the forest peat profile (Figure 6.8) indicates that there was a greater degree of drying in the shallow (O2) horizon in 1995 than 1999. This drying period also extended for a longer time than the 1999 feature, lasting from May until the end of September. In the intermediate (O3) horizon, the 1995 simulation predicts an extended period of considerable drying from May to September, while the 1999 simulation only predicts two brief periods of slight drying in August. There is also evidence of drying in the deep (O4) horizon during the 1995 simulation, whereas the 1999 simulation remained at saturation for the entire period. Therefore, it appears that this profile would have been considerably drier during 1995 than 1999. However, Mn release data from the soil cores of this profile (see Figure 5.4) did not indicate any large-scale release of Mn into soil water following rewetting of the dried soil.

6.3.2.2 Moorland peat

Figure 6.9 shows the comparison between 1995 and 1999 predicted soil water content for the moorland peat profile. In 1999, the simulation predicted no drying in the intermediate or deep soil horizons, and only slight drying (maximum 5 % drop in volumetric water content) in the surface horizon. However, in the 1995 simulation, drying is predicted in all three horizons. This is particularly evident in the shallow horizon, where volumetric water content falls from 81 % (saturation) to 45 % during the period May-September. The results from this profile are very similar to those of the forest peat, indicating drying conditions penetrating at least 40-50 cm into the peat profile during the summer of 1995. The extent of drying in the shallow horizon during 1995 is of particular interest, as soil water samples from the soil core experiment (see Figure 5.5) showed an increase in Mn concentration shortly after the cores were rewetted. This implies that a prolonged dry period followed by return to saturated conditions can lead to Mn release at the catchment scale.

6.3.2.3 Peaty gley

The peaty gley soil profile differed from the two peat profiles modelled in that considerable fluctuations of soil water regime were predicted for 1999. However, when compared with the predicted data for 1995 (Figure 6.10) it is evident that the drying predicted in all three modelled horizons was far greater during the summer of 1995 than four years later. This is most marked in the shallow (O2) horizon, where the estimated minimum water content of 61 % in 1999 can be compared to one of approximately 20 % in 1999. However, the soil core experiment data for this profile (see Figure 5.6) did not indicate Mn release upon rewetting from any of the three horizons investigated.

6.3.2.4 Peaty podzol

As with the peaty gley, the peaty podzol was predicted to undergo repeated drying and wetting cycles during 1999. Comparison with 1995 data for this profile (Figure 6.11) also shows much drier conditions expected in all three horizons during 1995. Again, the extent of drying predicted in the shallow (O) horizon during 1995 is far greater than in 1999 (a minimum of 42 % volumetric water content compared to 76 %). The intermediate (Eh) horizon is also predicted to dry out to a far greater degree in 1995 than in 1999 (a minimum of 35 % volumetric water content compared to 65 %). This observation is of particular

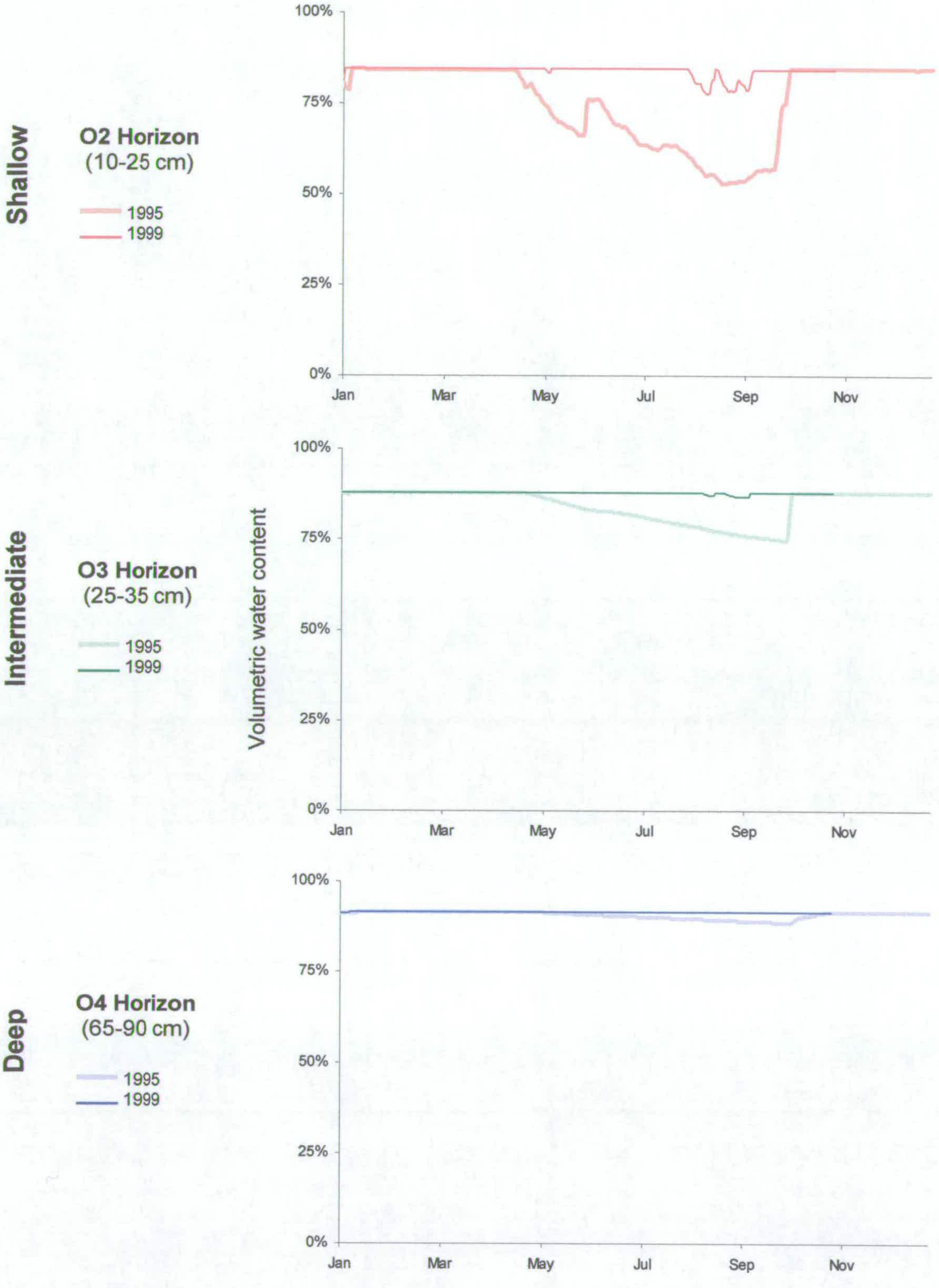


Figure 6.8: Predicted soil water content for **forest peat** soil profile during 1995 and 1999

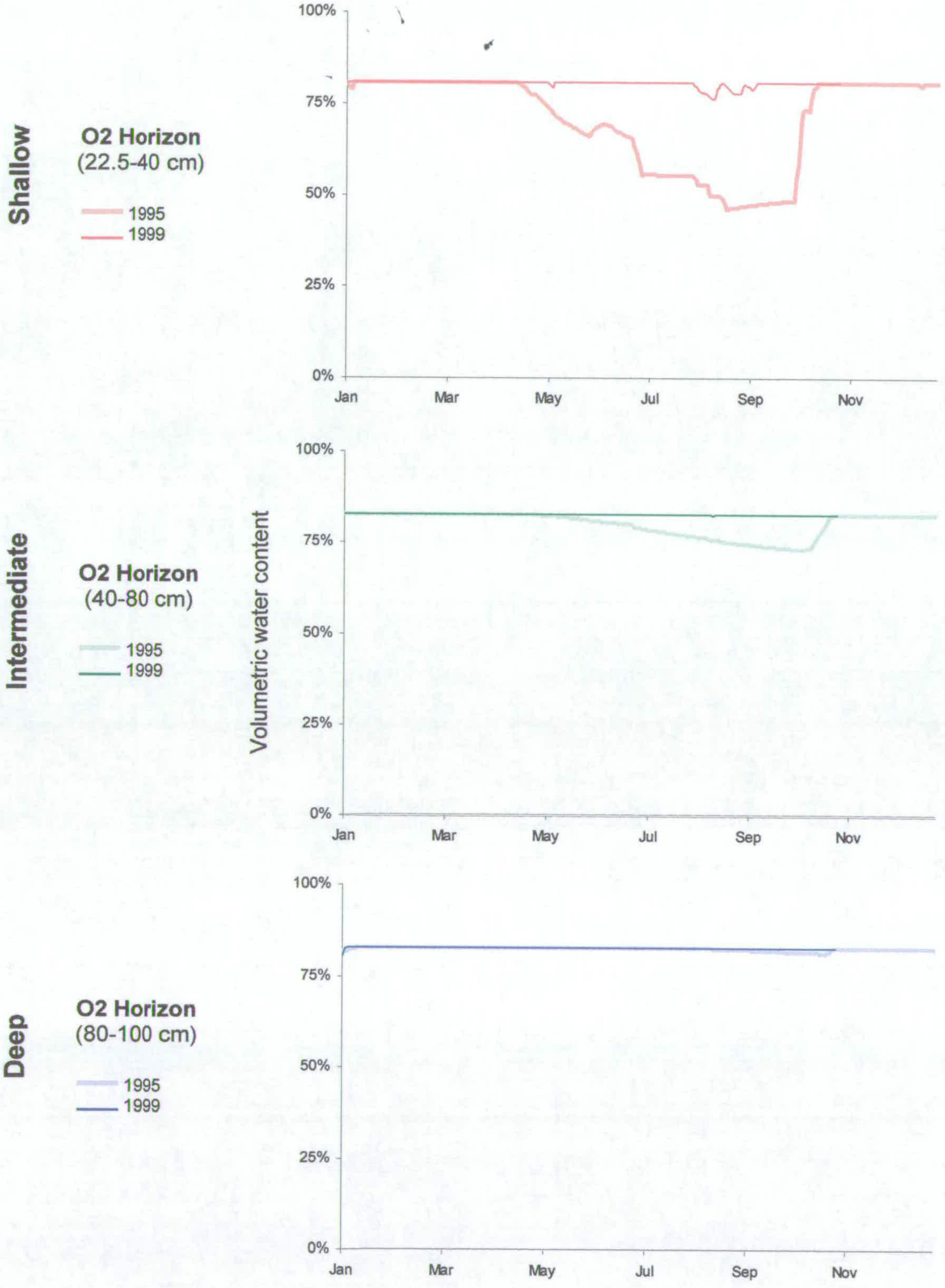


Figure 6.9: Predicted soil water content for **moorland peat** soil profile during 1995 and 1999

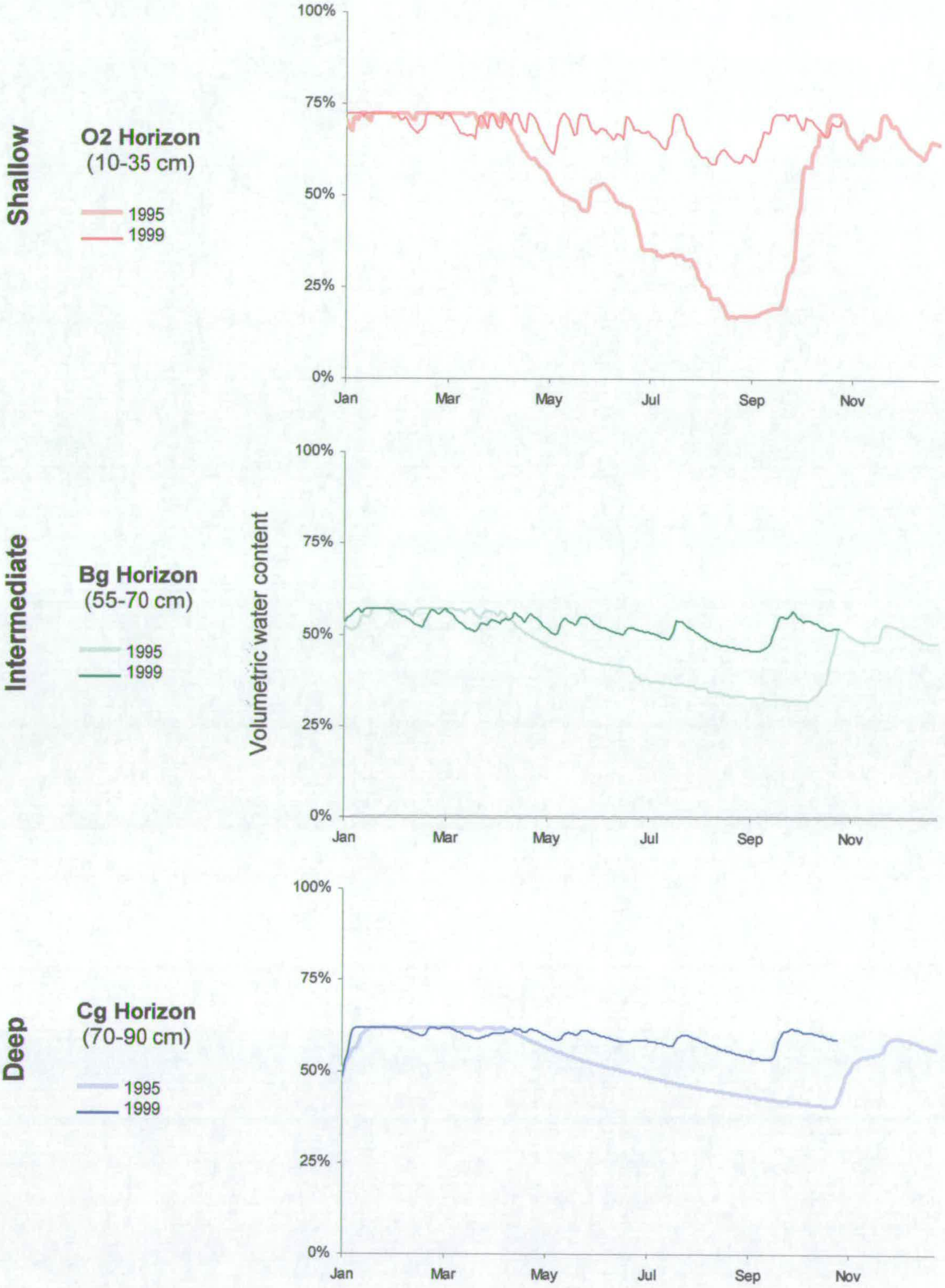


Figure 6.10: Predicted soil water content for **peaty gley** soil profile during 1995 and 1999

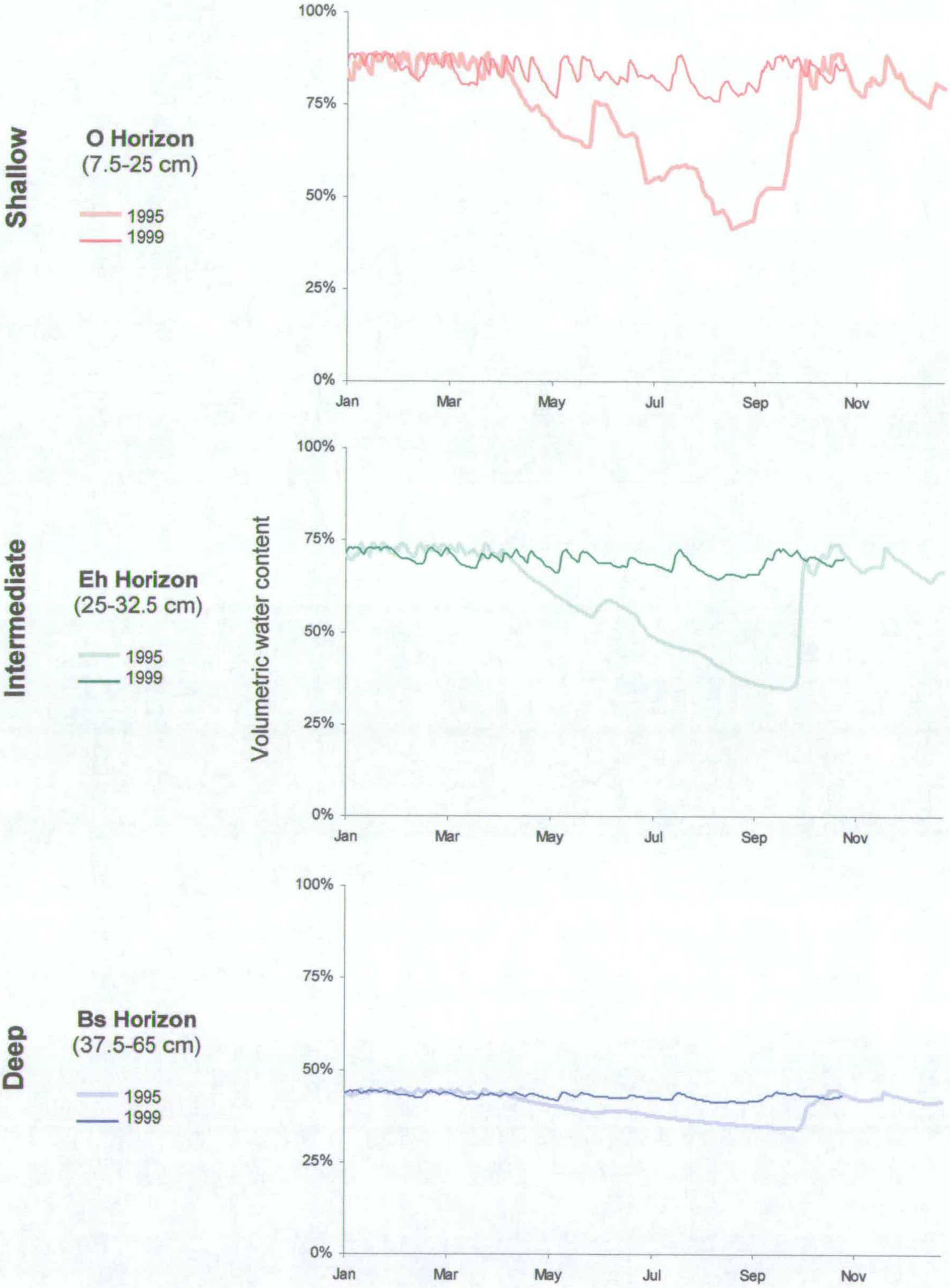


Figure 6.11: Predicted soil water content for **peaty podzol** soil profile during 1995 and 1999

importance because water samples from the Eh horizon in the soil core experiments contained the greatest concentration of Mn upon rewetting. Therefore, it is entirely possible that the changes in soil water regime in this horizon during 1995 were sufficient to induce a release of Mn in soil water similar to that observed in the laboratory experiments.

6.4 Discussion and conclusions

Simulating the moisture content of soils in the Ballochbeatties Burn catchment during 1995 and 1999 allowed a comparison of the extent to which the soils dried out in each year. Evidence from the simulated soil water regimes indicates that drying of catchment soils during summer 1995 was far greater than in 1999 (during the period when field sites were instrumented). This observation is supported by rainfall data for the two years, which show that summer (June-August) rainfall was 153 mm in 1995 compared to 303 mm in 1999 (shown in Figure 5.1). Reservoir water Mn concentrations increased during autumn 1995, reaching a peak of 702 $\mu g\ l^{-1}$, but exhibited no similar increase during 1999 (shown in Figure 3.2) the implication being that soils did not dry out sufficiently to promote Mn mobilisation. Data from the soil core laboratory experiments suggest that Mn will be mobilised from certain horizons when soils are rewetted following an extended soil moisture deficit. Drying conditions thought sufficient to promote Mn mobilisation were not recorded at the field sites during 1999 and no autumnal increase in reservoir water Mn concentrations was detected. However, WAVE simulation data for 1995, when reservoir water Mn concentrations greatly increased during the autumn, indicates that extensive drying followed by rewetting occurred in catchment soils. Calculation of soil core volumetric water content enabled a comparison to be made between the extent of drying in both simulated years and the soil core laboratory experiments. Results of this comparison for the three horizons found to release Mn upon rewetting in the soil core experiments are presented in Table 6.9.

Horizon			Volumetric water content ($cm^3\ cm^{-3}$)			
			1995	**1999**		**Soil core**
			(simulation)	(simulation)	(thetaprobe)	(calculated)
Moorland peat	(shallow)	**O2**	0.464	0.755	0.797	0.526
Peaty podzol	(shallow)	**O**	0.417	0.726	0.778	0.506
Peaty podzol	(intermediate)	**Eh**	0.349	0.623	0.485*	0.439

Table 6.9: Minimum volumetric water content ($cm^3\ cm^{-3}$) in soil horizons identified as releasing Mn upon rewetting

*Thetaprobe data from Eh horizon considered unreliable owing to possible presence of macropores

This indicates that in 1995, when reservoir water Mn concentrations greatly increased during the autumn, catchment soils were predicted to dry out to a greater degree than soil cores during the laboratory experiment. However, in 1999, when there was no large-scale autumnal increase in reservoir water Mn concentrations, catchment soils dried out to a lesser degree than the soil cores. Therefore it is possible that a threshold of soil drying exists, between the values recorded during the soil core experiments and the 1999 values, beyond which large-scale Mn mobilisation from certain horizons occurs upon rewetting.

Data from the simulation of 1995 soil water regime for the three horizons identified in the soil core laboratory experiments as releasing Mn upon rewetting were combined with reservoir water Mn concentration data (Figure 6.12). This indicates that, in catchment soils during 1995, there was an extended drying period from April until October, before a relatively rapid return to wet conditions. Approximately two weeks after this return to near-saturated conditions, reservoir Mn concentrations peaked.

Therefore, considering evidence from the WAVE simulation of soil water regime, the soil core laboratory experiments and the reservoir water Mn concentrations, it may be inferred that Mn is mobilised from catchment soils when they are rewetted following an extended drying period. This mobilisation may be of sufficient magnitude to produce greatly increased reservoir water Mn concentrations, resulting in considerable problems for domestic water supply.

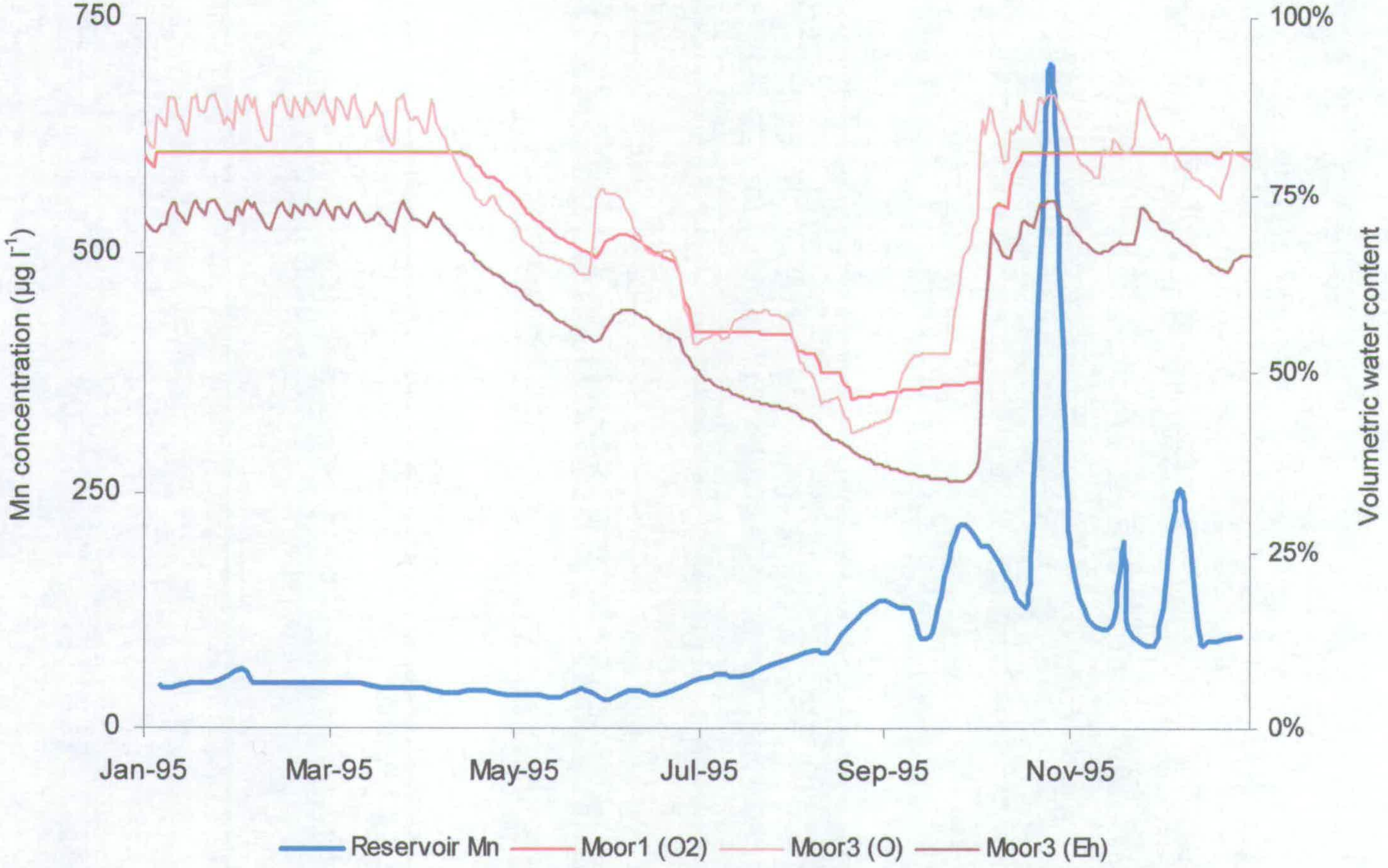


Figure 6.12: Changes in soil water regime and reservoir water Mn concentration during 1995

Chapter 7: Research findings

The aim of this research project was to investigate if soil water regime, soil type or land use influenced the extent and timing of Mn mobilisation in UK upland catchments. Within this chapter the research findings are summarised and implications for those seeking to limit the concentrations of Mn in upland drinking water supply reservoirs are discussed. In addition to this, topics for future work investigating Mn behaviour in upland catchments are also suggested.

7.1 Summary

The trace metal Mn is associated with a number of undesirable structural, aesthetic and health-related effects when present at elevated concentrations in drinking water. Many upland areas within the UK overlie rocks containing large concentrations of Mn. Over time, this Mn may be released by weathering processes from either these rocks or the soils derived from them. Insoluble forms of Mn present in soils can be mobilised into soluble forms, and therefore potentially released into surface waters. Mobilisation of Mn is governed by changes in a variety of environmental factors, soil wetness being one of the most important, and may result in large-scale release of Mn at certain times of year. Within the UK, water supply reservoirs are often situated in upland areas where Mn is present in both the soil and underlying rocks, and may therefore be at risk from such episodic Mn release. Water chemistry data indicate that excessive Mn concentrations occur in many upland water supply reservoirs, particularly during the autumn following a dry summer. Identification of the factors causing this increase in Mn concentrations will allow water authorities to take appropriate action, based upon an accurate prediction of the extent and timing of any Mn mobilisation.

One example of an affected upland water supply reservoir is Loch Bradan in southwest Scotland, where reservoir water Mn concentrations greatly exceeded the EC drinking water standard during autumn 1995. As the summer of 1995 was unusually dry compared to the mean summer rainfall recorded at Loch Bradan between 1980 and 1999 (Jun-Aug 153 mm in 1995, compared to a mean of 318 mm), it is suggested that the peak in Mn concentration during autumn 1995 was due to the extended soil moisture deficit, which resulted in Mn mobilisation from catchment soils upon rewetting, leading to an increase in reservoir water Mn concentrations. In order to test this hypothesis, field monitoring sites equipped to sample soil solution and monitor changes in soil water regime were installed within a sub-catchment of Loch Bradan reservoir. As soils and land use vary within the catchment, the potential influence of both these factors on Mn mobilisation was also investigated.

In total, 54 suction probes for collecting soil water samples, 18 thetaprobes and 18 tensiometers to monitor soil water regime were installed at six field sites. Sampling depth at each site was dictated by pedology such that the three major horizons in each soil were instrumented. At each of these primary sites, nine suction probes (three replicates at three depths), three tensiometers and three thetaprobes (one at each depth) were installed. Data from these sites were collected during 1999 and 2000, allowing investigation of Mn behaviour in catchment soils over two summer and autumn periods. Following preliminary analyses of these data, a further three sites were instrumented during 2000 in order to extended the range of soil type and land use combinations studied. Suction probes were installed at three depths in each of these secondary sites (one probe at each depth), using the same pedology-based sampling criteria as the primary sites.

Data from the field monitoring programme were analysed using graphical and statistical techniques. Initial data appraisal was carried out on time-series graphs to identify any seasonality of Mn concentrations in soil water and stream water. Following this, repeated measures ANOVA was used to identify any effects on soil water Mn concentrations arising from differences in soil type or land use. Results from the 18-month field monitoring programme did not show any seasonal Mn mobilisation from catchment soils. However, a summer Mn peak was recorded in stream water samples taken from Ballochbeatties Burn, the reservoir feeder stream in the sub-catchment investigated. This increase in stream water Mn concentration was not thought to indicate Mn mobilisation from catchment soils, and may have resulted from other factors associated with summer conditions (e.g., increased solute concentration due to greater evaporation, increased microbial activity in stream sediments, or changes in catchment hydrological pathways during the summer).

Mn concentrations in soil water samples from the six primary field sites were generally found to be an order of magnitude less than stream water samples collected at the same time, possibly indicating that stream water Mn concentrations during the field monitoring programme were controlled by processes occurring outwith these sites. However, the installation of secondary field sites during the latter part of the field monitoring programme confirmed that soil water with Mn concentrations far greater than those found in stream water existed in some catchment soils. The two field sites giving rise to soil water samples with the greatest Mn concentration were both located in peat alluvium soils. Land use (commercial forestry or open moorland) was not found to influence soil water Mn concentrations, although data from one of the secondary field sites showed that soil water from the peat alluvium soil at the clear-felled site contained the greatest concentrations of Mn recorded during the field monitoring programme. It is unknown whether this was a consequence of the clear-felling procedure, or was caused by some other factor (e.g., site location at the base of a slope resulting in accumulation of Mn in soil water draining from upslope).

The absence of an autumnal peak in soil water Mn concentrations from any of the field sites was believed to be a consequence of the relatively wet summer conditions encountered during the field monitoring programme. It is thought that, in both 1999 and 2000, the catchment soils did not become dry enough to produce any significant Mn release when rewetting occurred. Therefore, in order to test the hypothesis that prolonged and extensive drying promoted Mn mobilisation from soils upon rewetting, further laboratory-based experimental work was conducted. Soil cores were taken from the same soil type and land use combinations studied during the field monitoring programme. These cores were subjected to controlled drying and rewetting conditions in the laboratory, thus artificially inducing a soil moisture deficit and thereby extending the range of drying conditions investigated during the field-based monitoring. Analysis of data from the soil core laboratory experiments was undertaken using similar techniques to analysis of the field monitoring programme data. In addition to time series graphs and repeated measures ANOVA, one-way ANOVA was used to identify changes in soil water Mn concentration resulting from changes in soil water regime. The results of these experiments show that Mn mobilisation occurred in three of the twelve horizons investigated (moorland peat O2, peaty podzol O and Eh horizons) shortly after rewetting the dried soil. Therefore, it appears that Mn mobilisation does not occur uniformly in all soils throughout the catchment, but is confined to individual horizons within specific soil types, particularly those soils containing a mixture of mineral and organic material.

A process-based soil water simulation (WAVE) was used in order to compare the extent of drying in soils during the field monitoring programme and soil core laboratory experiments with conditions in catchment soils during 1995. Parameters for WAVE calibration describing the $\theta(h)$ and $K(h)$ soil moisture relationships for horizons at the six primary field sites were derived, using the Wind evaporation method, from data collected during the soil core laboratory experiments. Validation of the model was carried out against soil volumetric water content data from the field monitoring programme, indicating that the modelled soil water regime was a relatively good match for the measured conditions in catchment soils (statistical measures for 'goodness of fit' signifying a standard error of less than 0.02 in most cases). Once successful calibration was achieved, WAVE was used to model the soil water regime of catchment soils during 1995. This 'hindcasting' of soil water regime indicated that, during 1995, soils in the catchment of Loch Bradan did indeed dry out to a greater extent than observed during the field monitoring programme or the soil core laboratory experiments. This implies that conditions suitable for Mn mobilisation, from those soil horizons identified as releasing Mn during the soil core laboratory experiments, occurred in the Loch Bradan catchment during 1995. When considered in conjunction with reservoir water Mn concentrations observed in the autumn of 1995, there is compelling evidence to suggest that the development of a substantial soil moisture deficit during a dry summer produces conditions favouring the release of Mn shortly after rewetting occurs, thereby leading to a substantial increase in reservoir water Mn concentrations during the autumn.

7.2 Implications

EC regulations incorporated within UK law mean that water companies are required to ensure that Mn concentrations in water supplied to customers do not exceed the maximum admissible concentration of 0.05 mg l^{-1}. This can often necessitate the installation and maintenance of expensive treatment procedures designed to remove excessively high concentrations of Mn. Therefore, other means of limiting Mn concentrations in reservoir water, or methods for predicting the extent and timing of Mn mobilisation, are being sought.

The principal focus of this research, with respect to the water industry, was to investigate the influence that the environmental factors of soil type, land use and soil water regime have on Mn mobilisation from upland catchment soils. It is intended that this knowledge will be used to enable predictions of potential Mn mobilisation events, based on general catchment characteristics (soil type, land use) and climatic data (summer rainfall). For example, the data indicate that in the Loch Bradan catchment, Mn mobilisation will occur approximately two weeks after rewetting of soils following a dry summer. The findings of this research suggest that rainfall in the Loch Bradan catchment during a summer dry enough to promote Mn mobilisation will be less than 200 mm, based on reservoir water quality and climate data from the 1990s. When expressed in terms of soil water regime, it is likely that a decrease in volumetric water content of approximately 20 % relative to saturation will be sufficient to induce Mn mobilisation from affected soils upon rewetting. Therefore, planners within the water industry will be able to budget resources to either allow for increased treatment expenses during such years, or for water abstraction from unaffected reservoirs if possible. One consideration of particular importance to the water industry is how the frequency of any Mn mobilisation events will be affected by predicted changes in climate. With many climate change models currently predicting a move towards drier summers and wetter winters, data from this research may be used to investigate whether the 'return period' for Mn mobilisation in upland catchments will alter as a result.

Because this project focused upon pedology during the fieldwork, laboratory experiments and modelling, predictions of Mn mobilisation at the soil profile scale can be translated to the reservoir catchment scale. Predicted Mn mobilisation events for specific soil types can be related to conventional soil map units, thereby allowing catchment-scale risk assessment for Mn mobilisation at Loch Bradan based on information from the area soil map. The range of soils studied should also enable this predictive approach to be extended to similar upland catchments where reservoirs are located. Furthermore, the data will also aid planners within the water industry when identifying areas for the construction of new water supply reservoirs. By considering the role of soils in Mn release, it will be possible to avoid areas where there is a risk of excessive Mn mobilisation based upon the soil types present in the catchment.

7.3 Recommendations for future work

Questions raised during this research indicate that future work should take into consideration a number of recommendations. Sampling by pedology is strongly advised and care should be taken in determining the soil types present, particularly the extent of any soils where the peat has a considerable mineral component. The inclusion of a greater number of replicates would help reduce the problems of sample representativeness experienced by this study, especially in terms of soil water chemistry variability. In addition to this, the project duration should be extended in order to provide samples from at least two complete years and, if possible, last until after drought conditions are encountered.

It is also recommended that further work investigating Mn behaviour in upland catchments should consider the forms of Mn present in more detail than the soluble/total classification applied in this research. Various constraints meant that it was impractical to carry out such a detailed investigation during the course of this research project. For example, the percentage of organically-bound Mn present in soils, soil water and stream water should be determined (e.g., by using sequential Mn extractions for soils and ultrafiltration or electron spin resonance for water samples). The provision of such data may be of considerable use in determining the role of organic matter in Mn mobilisation. In particular, it will allow a greater understanding of Mn behaviour in the soils containing a mixture of organic and mineral material identified in this research as being most likely to release Mn upon rewetting.

The exact mechanism by which Mn is mobilised following the rewetting of soils in the Loch Bradan catchment remains unknown. The fact that Mn release from soil cores occurred after a period of approximately two weeks following rewetting infers that it was not already mobile at the end of the drying period. Therefore, it is suggested that conditions encountered in sufficiently dry soils will enhance chemically or microbially mediated Mn mobilisation shortly after rewetting occurs. At present, simple catchment-scale predictions of Mn mobilisation could be made on the basis of this research. However, the accuracy of such predictions could be improved by knowledge of the processes leading to Mn release from soils. To achieve this, it is suggested that future work should involve a process-based appraisal of factors influencing Mn mobilisation from organo-mineral soils undergoing drying and rewetting conditions, for example, an investigation into the extent to which microbial activity can alter soil Mn status in upland catchments. In particular, the species of bacteria capable of Mn reduction, their occurrence within different soil types, and rate of activity under changing environmental conditions should be considered. One possibility is that conditions in the dry soil during the summer result in a population increase of bacteria capable of reducing Mn. Upon a return to saturated conditions in the autumn, microbial respiration quickly outstrips oxygen supply and the facultative Mn-reducing bacteria begin to reduce the available pool of soil Mn, thereby producing a release of soluble Mn.

7.4 Conclusions

In conclusion, Mn mobilisation was shown to occur within specific upland soil horizons shortly after the rewetting of soils following an extended drying period. The Mn mobilisation did not occur in soil horizons with the most acidic pH, or from those containing the greatest concentrations of total Mn, as might have been expected. Instead, Mn mobilisation was observed in soil horizons containing a mixture of mineral and organic material. It is suggested that the mineral content serves as a source of Mn, which is mobilised by processes connected with the presence of soil organic matter during the sequence of drying and rewetting. The combined field, laboratory and modelling work in this project indicate that drying conditions in soils similar to those during the summer of 1995 will result in large-scale Mn mobilisation from the Loch Bradan catchment. When combined with soil map data, the findings of this research may also be used to indicate the risk of Mn mobilisation in other temperate upland water supply catchments.

It is recommended that future work should concentrate on identifying the processes involved and further exploring the extent of drying required to mobilise Mn from catchment soils. If undertaken, this will enable catchment managers within the water industry to provide more accurate predictions of when and where Mn mobilisation will occur and to develop better strategies to minimise the effects of mobilisation events on public water supplies.

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APPENDIX A

LABORATORY ANALYTICAL METHODS

Appendix A: Laboratory Analytical Methods

A.1 Determination of soil pH

A 10 g sample of field moist soil was weighed out and placed in a glass beaker with 25 ml of distilled water. The contents of the beaker were then stirred thoroughly with a glass rod and left to stand for 15 minutes, whereupon the suspension in the beaker was stirred once more using the glass rod. The pH of this suspension was measured by inserting the glass electrode of a calibrated pH meter into the suspension, taking care not to touch the sides of bottom of the beaker, and allowing the meter reading to stabilise. Once stable, the meter reading was recorded to one decimal place to provide a measurement of soil pH.

A.2 Determination of gravimetric soil water content

Approximately 25 g of field moist soil was weighed out into a clean, preweighed porcelain crucible (approximately 100 mm diameter). This was then placed in an oven and dried for 2 days at 60°C (a temperature of 60°C was used, rather than 105°C, because of concern about the loss of volatile compounds from the highly organic samples). The sample and crucible were then placed in a desiccating jar and allowed to cool, before being reweighed. Dry sample weight was calculated by subtracting the crucible weight from the combined dry sample and crucible weight. Gravimetric water content of the sample was then calculated using the following equation:

$$\%\ \text{Gravimetric water content} = \frac{W_1 - W_2}{W_1} * 100\% \qquad \textbf{Equation A.1}$$

Where: W_1 = Field moist sample weight
W_2 = Dry sample weight

A.3 Determination of gravimetric soil organic matter

The organic matter content of soil samples was determined using the loss on ignition method. 1 g samples of dried soil (from gravimetric water content determination – A.2) were placed in clean, preweighed porcelain crucibles (approximately 25 mm diameter). Samples were placed in the furnace at an initial temperature of 150°C and then heated slowly until the temperature reached 450°C. The furnace was maintained at this temperature for a period of six hours, after which the crucibles were removed and stored in a desiccating jar until they had cooled sufficiently to be weighed. The organic matter content of the soil samples was then determined using the following equation (assuming that loss on ignition approximates to soil organic matter):

$$\%\ \text{Soil organic matter} = \frac{W_1 - W_2}{W_1} * 100\%$$ **Equation A.2**

Where: W1 = Weight of dried soil sample
W2 = Weight of ash left after combustion in furnace

A.4 Determination of soil total metal content

A.4.1 Sample preparation

Soil samples used to determine total metal content were first sieved (<2 mm diameter) and then dried for 2 days at 60°C. Following this, 1 g of dried sample (±0.0050 g) was weighed out into a clean porcelain crucible. Samples were then heated in the furnace using the same procedure as detailed in section A.3. After ashing in the furnace, samples were stored in a desiccating jar until they had cooled.

A.4.2 Acid digestion of ashed soil samples

Crucibles containing the ashed soil samples were placed on a steam bath and allowed to heat for 5 minutes. Then, 5 ml concentrated hydrochloric acid was carefully added using a pipette and the crucibles were covered with watch glasses. After 15 minutes, the watch glasses were removed, taking care to wash any condensation collected on their underside back into the crucible using distilled water. Following this, 1 ml concentrated nitric acid was added carefully to each crucible via pipette and the crucibles left on the water bath until the liquid in them had evaporated. The residue left in the bottom of the crucibles was brought back into solution by adding 1 ml of 1:1 hydrochloric acid and gently swirling the crucible. Distilled water was then added, until the crucible was approximately half full, then the crucible was removed from the steam bath and allowed to cool slightly. The contents of the crucible were then filtered (using Whatman No. 54 filter paper) into a 50 ml volumetric flask and made up to the mark with distilled water.

A.4.3 Flame Atomic Absorption Spectrophotometry (FAAS)

Standards were prepared by diluting appropriate volumes of commercially available laboratory standards of the required metal in a volumetric flask and making the solution up to the mark with distilled water and 1:1 hydrochloric acid (so that matrix of standards was matched to samples). Approximately 5 ml aliquots of calibration standards and samples were added to test tubes, which were then loaded in sequence into the Cetac C60 automatic sampler attached to the Pye-Unicam M5 atomic absorption spectrophotometer. The spectrophotometer controls (e.g., wavelength, flame angle) were adjusted so that the signal obtained for the greatest standard concentration was an absorbance of approximately 0.800 to 1.000, in order to obtain the maximum resolution of the anticipated range of sample concentrations. Sample blanks (prepared using the acid digestion described above) were run at the same time as samples to ensure that there was no contamination from the experimental procedure. Calibration, generally using four standards, was carried out every 3-4 samples (i.e. 9-12 replicates), while the concentration of each replicate was determined from the mean of three readings. Following FAAS analysis, any samples with concentrations greater than the top standard were diluted by a factor based on their estimated concentration and then analysed again. This procedure was repeated until dilution resulted in a concentration within the range of calibration standards used. Once the FAAS analysis was complete, metal concentrations (per dry weight) of the soil samples were calculated using the following equation:

$$\text{Soil metal concentration } (\mu g\, g^{-1}) = \frac{\text{sample concentration x dilution factor x volume}}{\text{sample weight}} \text{ x } 1000 \qquad \textbf{Equation A.3}$$

Where: sample concentration = concentration determined by FAAS (mg l^{-1})
dilution factor = dilution applied during FAAS analysis (none=1)
volume = volume of sample in volumetric flask (ml)
sample weight = mass of dried soil added to crucible (g)

A.5 Determination of vegetation total metal content

A.5.1 Sample preparation

Samples of plant tissue to be analysed for total metal content were oven-dried at 60°C for 2 days and then stored in a desiccating jar until cool. Following this, the dried samples were ground in a ceramic chamber to avoid sample contamination.

A.5.2 Acid digestion of vegetation samples

Once ground, 0.1 g (±0.0050 g) of dried plant tissue was weighed into a boiling tube, with care taken to ensure that the plant tissue was not stuck to the sides of the tube. Next, 2 ml of concentrated sulphuric acid was carefully added to the sample and the tube shaken vigorously immediately afterwards to ensure that the entire ground sample reacted with the acid. A total of 1.5 ml of 100vol hydrogen peroxide was then added in two 0.75 ml stages, allowing each addition to run down the sides of the tube. After the initially violent reaction on each addition of hydrogen peroxide had died down, the tube was shaken to complete mixing of the tube contents. Once the sulphuric acid and hydrogen peroxide were added, the tubes were then transferred to a heating block, where the temperature was slowly raised to 330°C and then left for six hours. After this, the tubes were allowed to cool before the contents were filtered (using Whatman No. 54 filter paper) into 50 ml volumetric flasks and made up to the mark with distilled water. Quality control procedures were the same as those used for the digestion of soil samples, with sample blanks and three replicates of each sample prepared.

A.5.3 Flame Atomic Absorption Spectrophotometry

Calibration standards were prepared using the same procedure as in A.4.3 (this time using sulphuric acid to match the matrix of samples). Standard solutions and vegetation sample solutions were placed in test tubes, then loaded in sequence into the autosampler. The FAAS analysis was then performed in the same manner as for digested soil samples. Once the results were obtained, metal concentration (per dry weight) was calculated using the following equation:

$$\text{Vegetation metal concentration } (\mu g\, g^{-1}) = \frac{\text{sample concentration x dilution factor x volume}}{\text{sample weight}} \qquad \textbf{Equation A.4}$$

Where: sample concentration = concentration determined by FAAS (mg l^{-1})
dilution factor = dilution applied during FAAS analysis (none=1)
volume = volume of sample in volumetric flask (ml)
sample weight = mass of dried plant tissue added to test tube (g)

A.6 Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS)

GFAAS was used to determine Mn concentrations in soil water samples collected during the soil core laboratory experiments, when the concentrations were below the acceptable detection range of the FAAS analysis. Standard samples of Mn concentration were prepared as in section A.4.3 and loaded in sequence, along with the experiment samples, in the GF95 autosampler attached to the graphite furnace of the Pye-Unicam M5 atomic absorption spectrophotometer. Sample blanks and replicates were run in a similar manner to the FAAS procedure.

A.7 Limits of detection

The limits of detection for any analytical equipment can be determined by using a calculation involving the measured concentration of a sample blank (Equation A.5) (Miller & Miller, 1993).

Limit of detection = blank + (3.28 x standard deviation of blank) **Equation A.5**

When this was applied to a random selection of 20 results from the FAAS and GFAAS analysis, the limit of detection for Mn in samples was calculated to be 0.056 mg l^{-1} ±0.009 (FAAS) and 0.12 µg l^{-1} ±0.01 (GFAAS).

A.8 Water samples analysed by WoSW

Analysis of soil water, stream water and rainfall samples by WoSW was undertaken using the following procedures, depending upon the determinand required.

A.8.1 Determination of metal concentration

Metal concentrations in water samples analysed by WoSW were determined using an Inductively Coupled Plasma Optical Emission Spectrophotometer (Thermo Jarrel Ash Corporation), fitted with an Ultrasonic Nebuliser (Cetac Technologies Inc.). Prior to analysis, water samples were acidified with hydrochloric acid in order to bring all the metals present into solution.

A.8.2 Determination of pH

Water samples used for determination of pH were stored in the dark at 4°C until analysed using a Radiometer PHM95 or PHM250 pH meter. Upon removal from the storage room, samples were allowed to equilibrate with room temperature (20°C). Then, the electrodes of the pH meter were immersed in the sample until a stable reading was achieved.

A.8.3 Determination of colour

The colour of water samples was determined spectrophotometrically using a SKALAR SP100 spectrophotometer. Samples were filtered through a 0.45 µm cellulose nitrate membrane, then the absorbance was measured at a wavelength of 400 nm.

APPENDIX B

SOIL WATER CHEMISTRY TIME SERIES FROM PRIMARY FIELD SITES

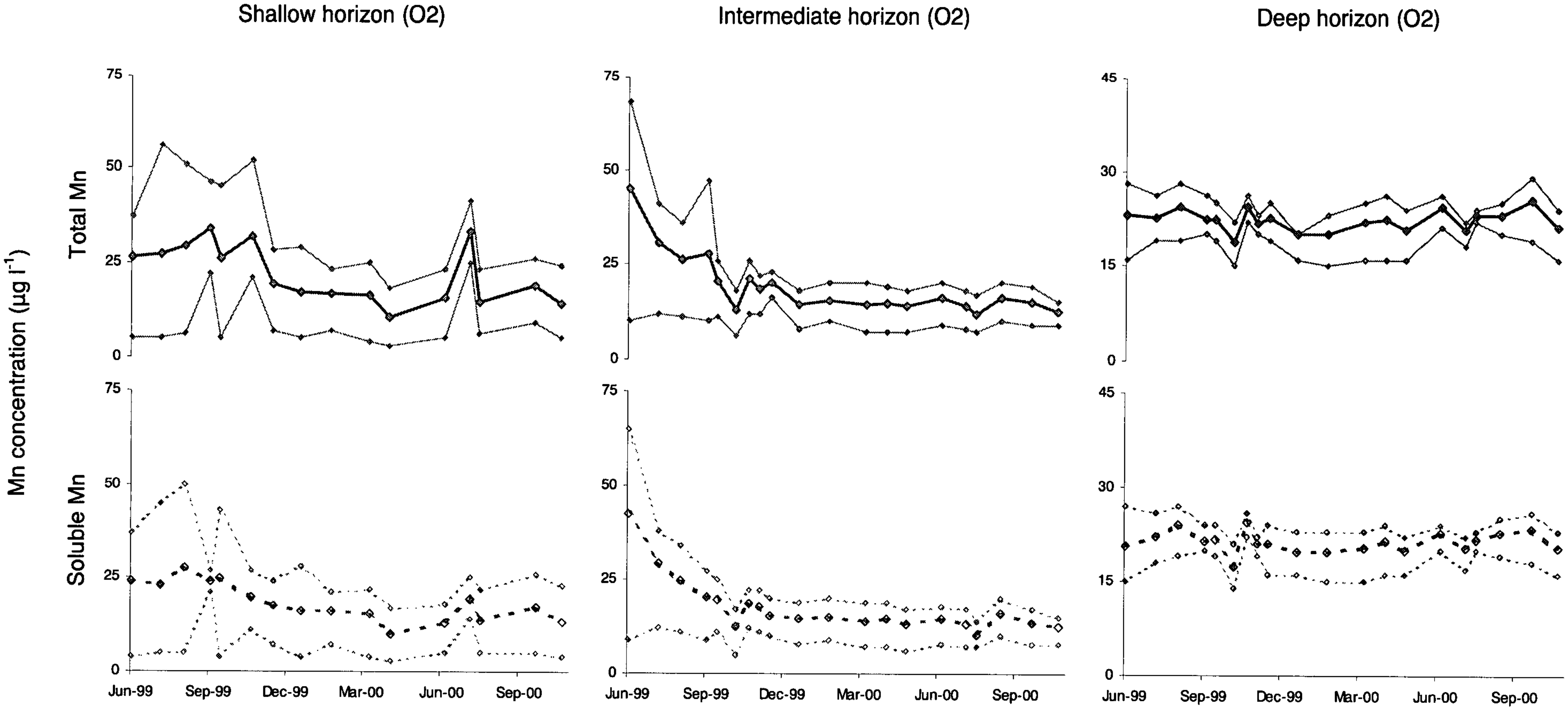


Figure B.1: Soil water Mn concentrations from moorland site 1 (peat)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. y-axis scale differs between horizons

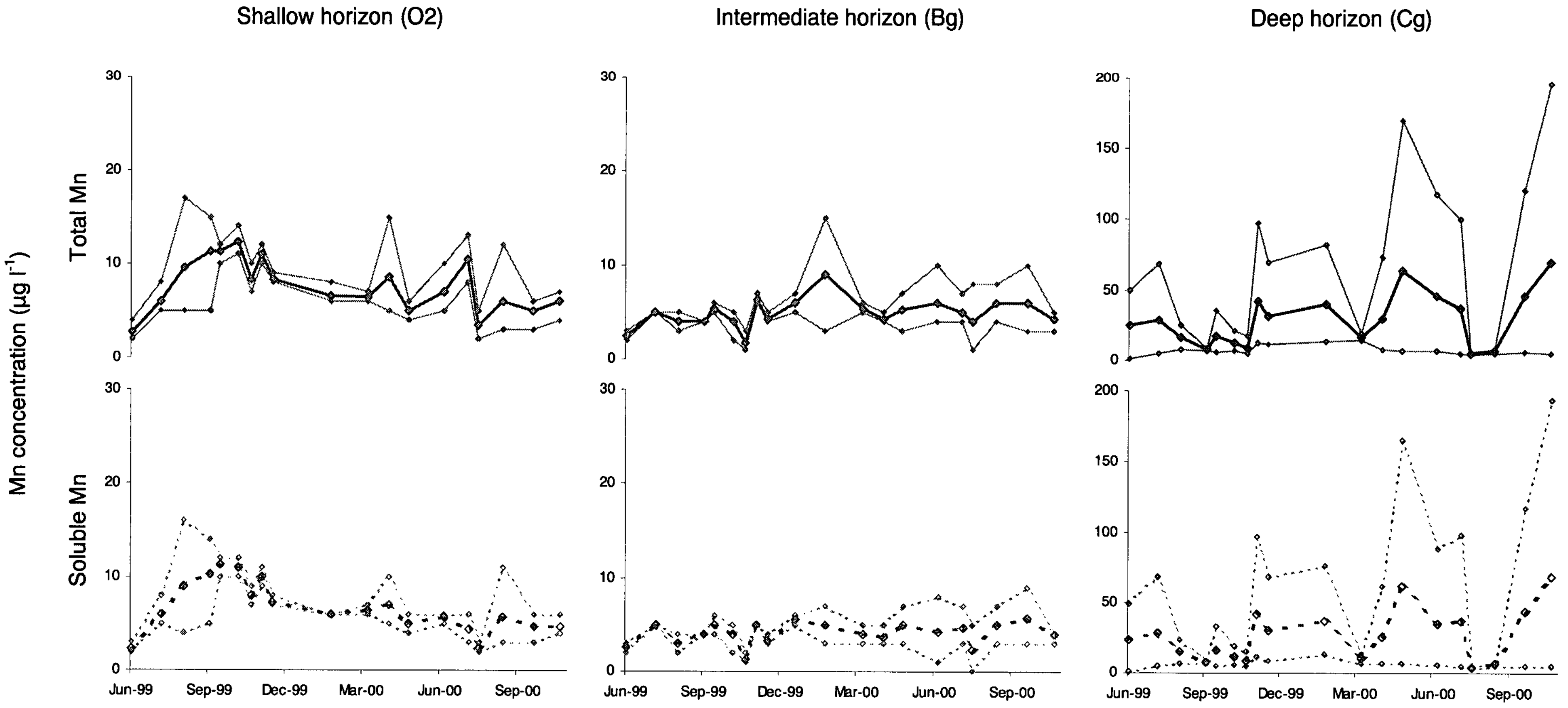


Figure B.2: Soil water Mn concentrations from moorland site 2 (peaty gley)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. y-axis scale differs between horizons

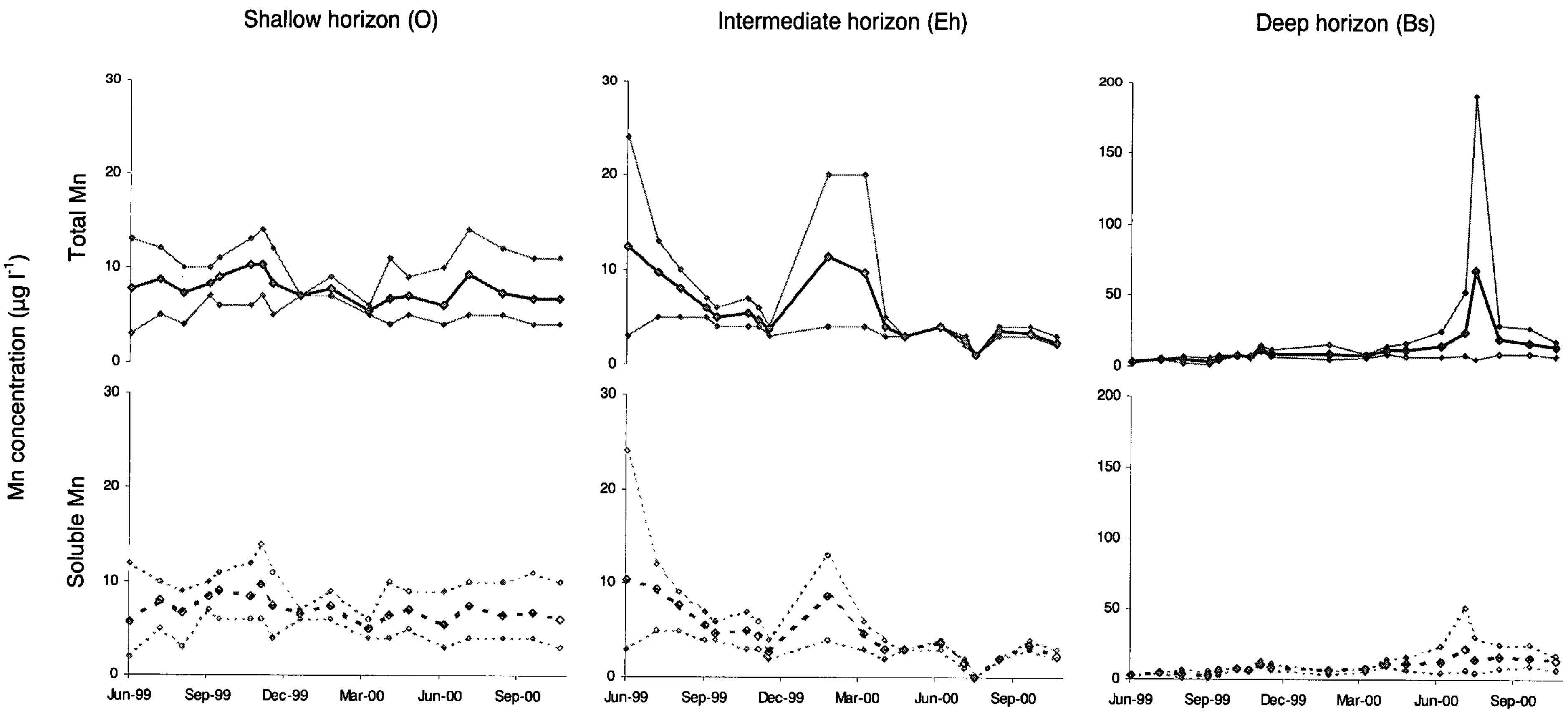
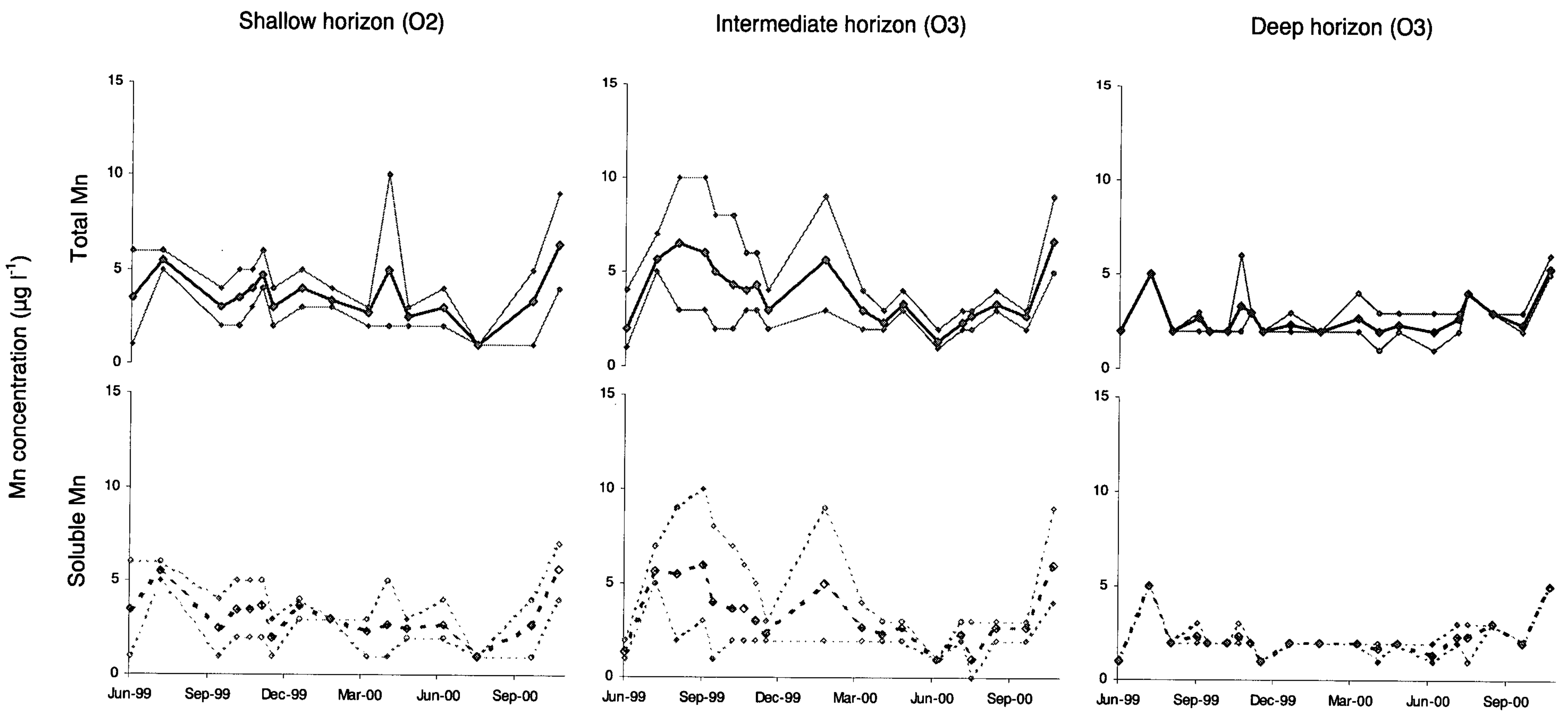


Figure B.3: Soil water Mn concentrations from moorland site 3 (peaty podzol)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. y-axis scale differs between horizons



Shallow horizon (O2)

Intermediate horizon (O3)

Deep horizon (O3)

Figure B.4: Soil water Mn concentrations from forest site 1 (peat)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations

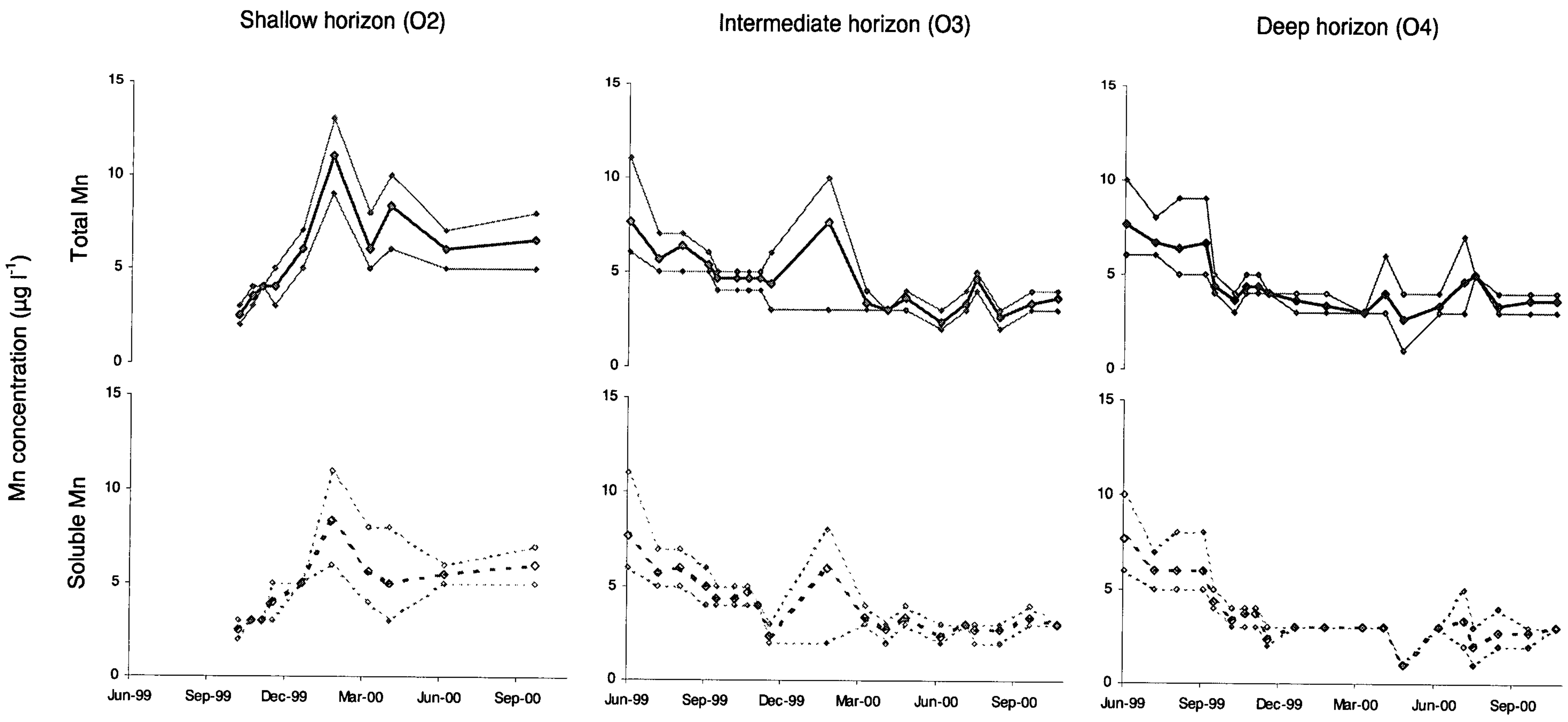


Figure B.5: Soil water Mn concentrations from forest site 2 (peat)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations

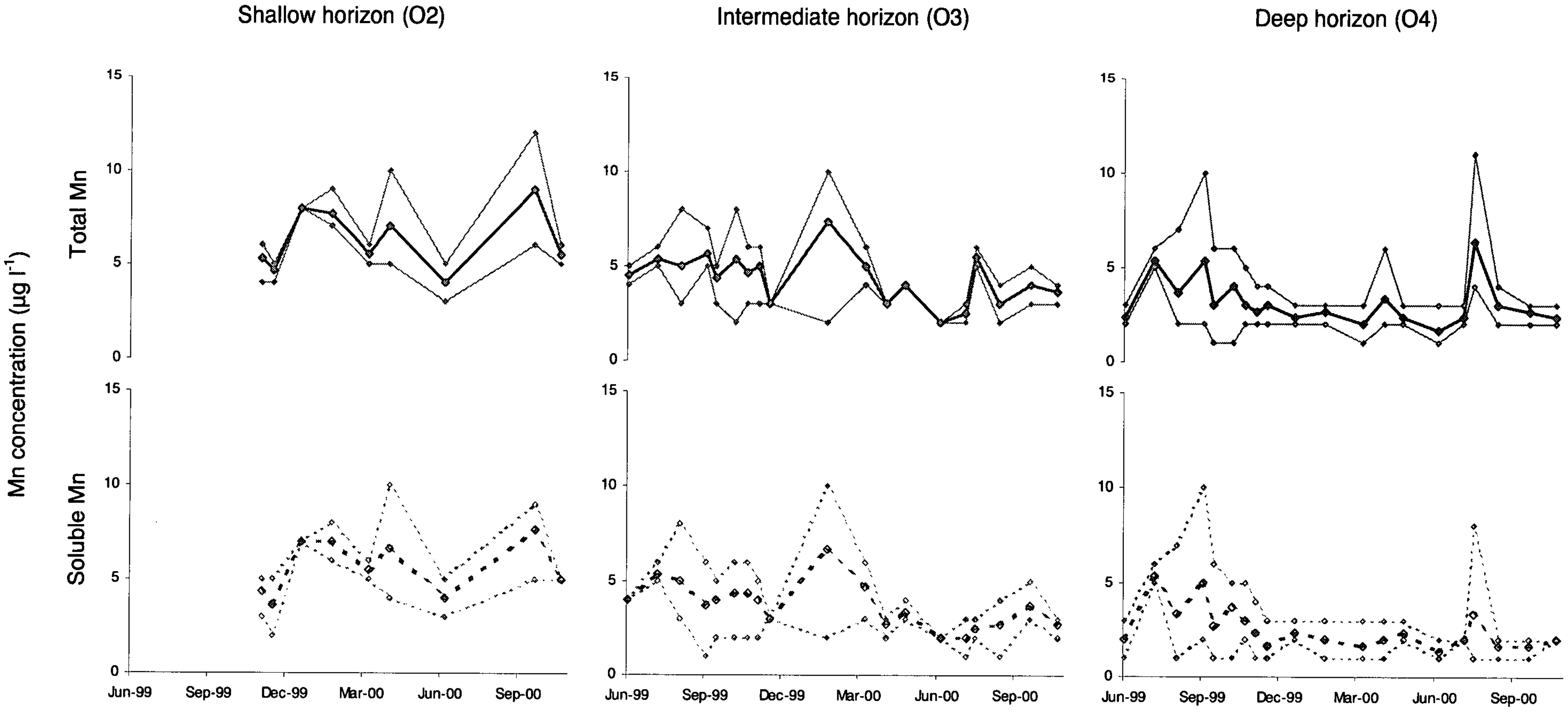


Figure B.6: Soil water Mn concentrations from forest site 3 (peat)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations

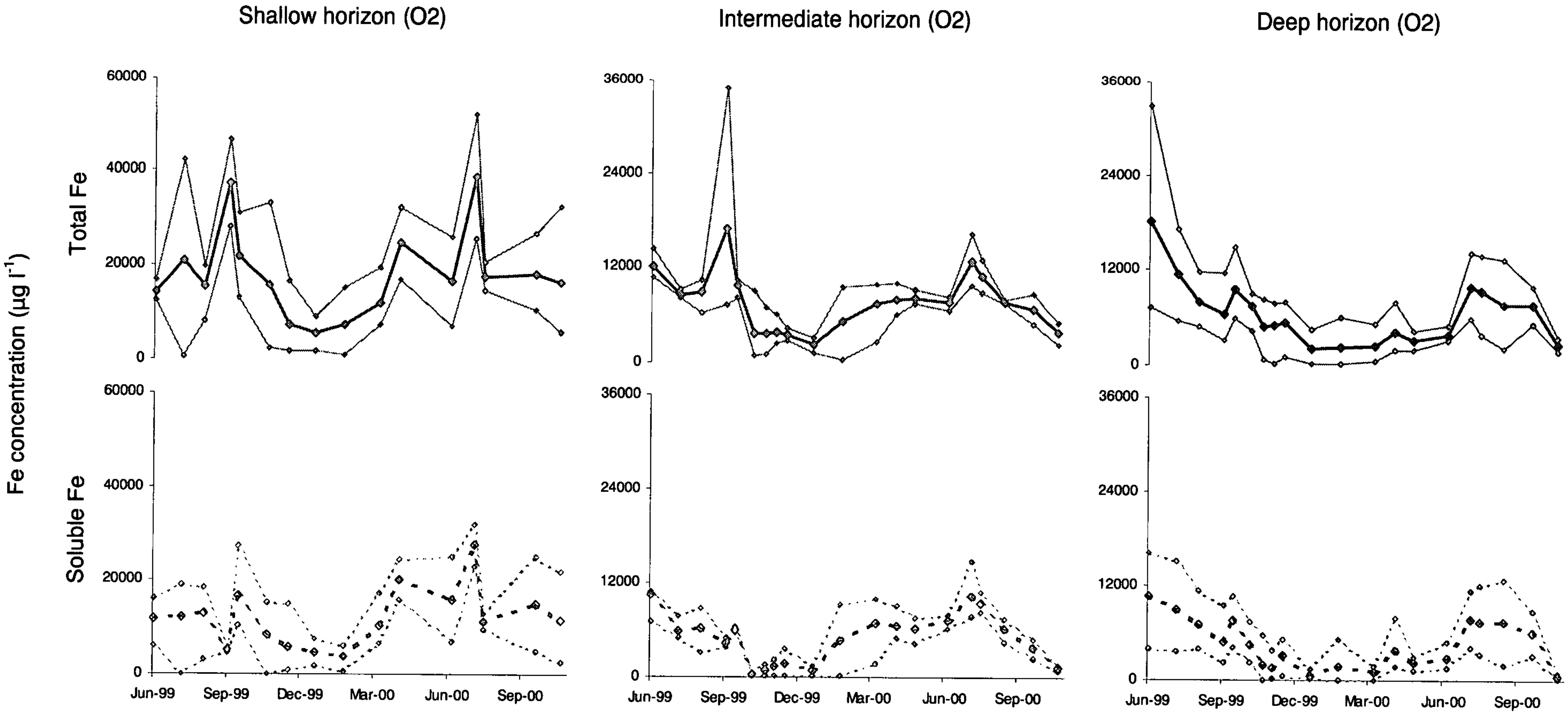


Figure B.7: Soil water Fe concentrations from moorland site 1 (peat)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. **y-axis scale differs between horizons**

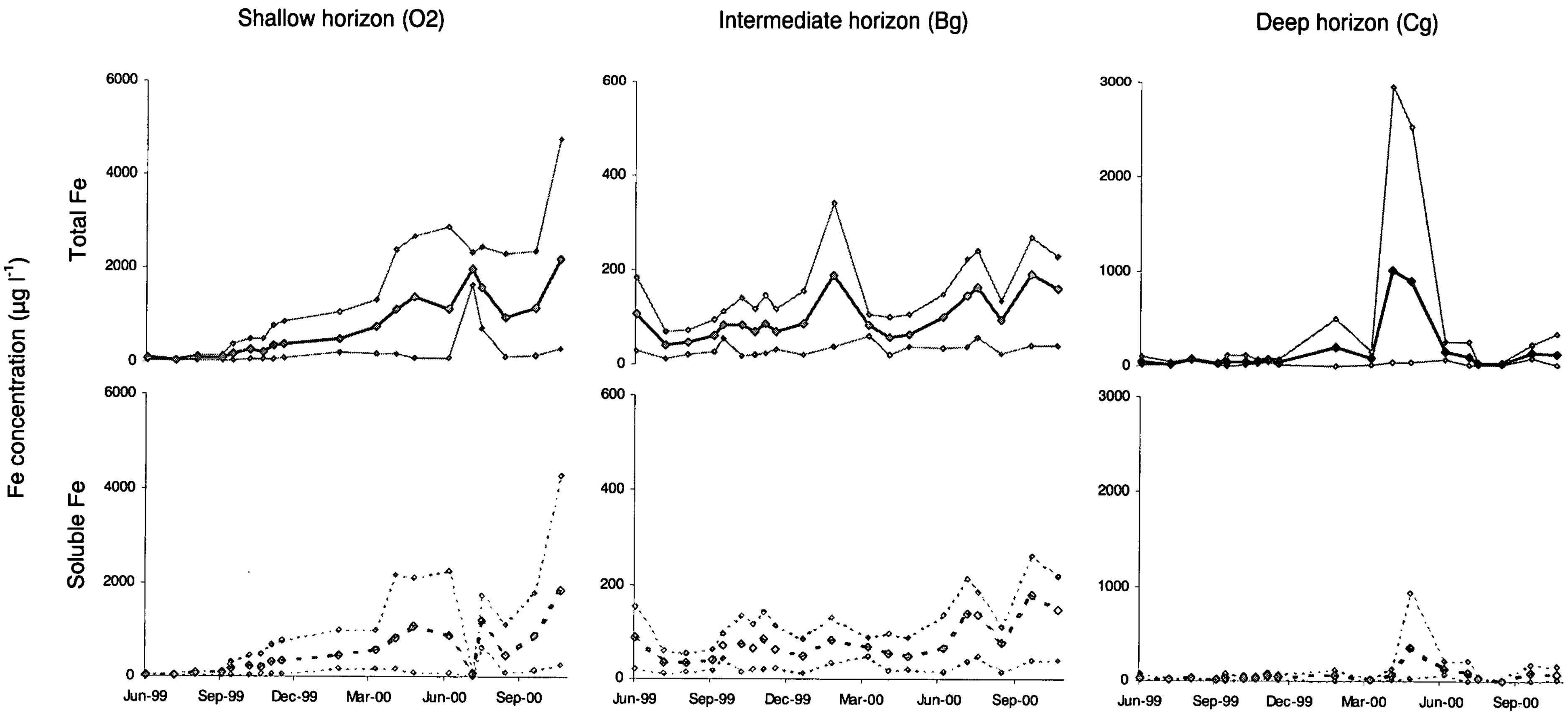


Figure B.8: Soil water Fe concentrations from moorland site 2 (peaty gley)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. **y-axis scale differs between horizons**

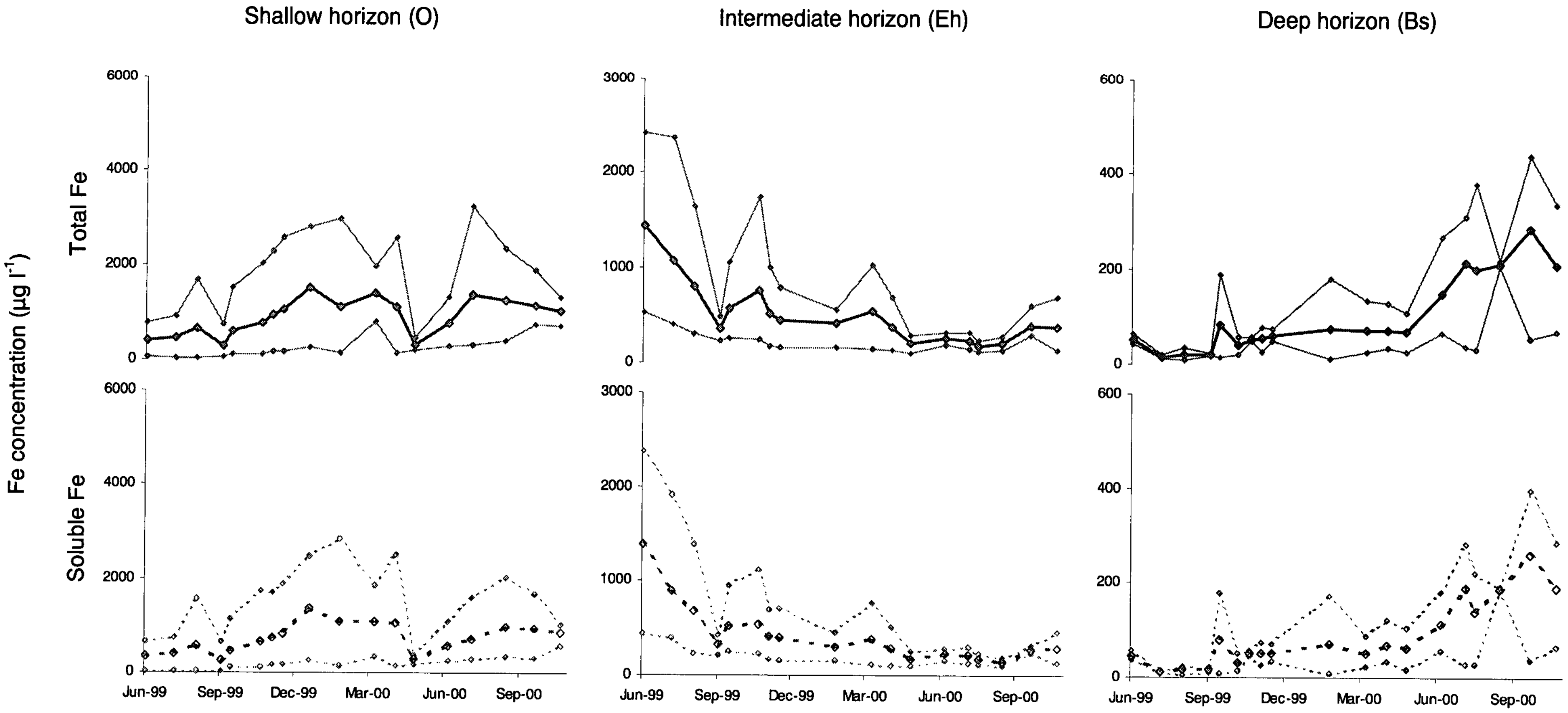


Figure B.9: Soil water Fe concentrations from moorland site 3 (peaty podzol)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. **y-axis scale differs between horizons**

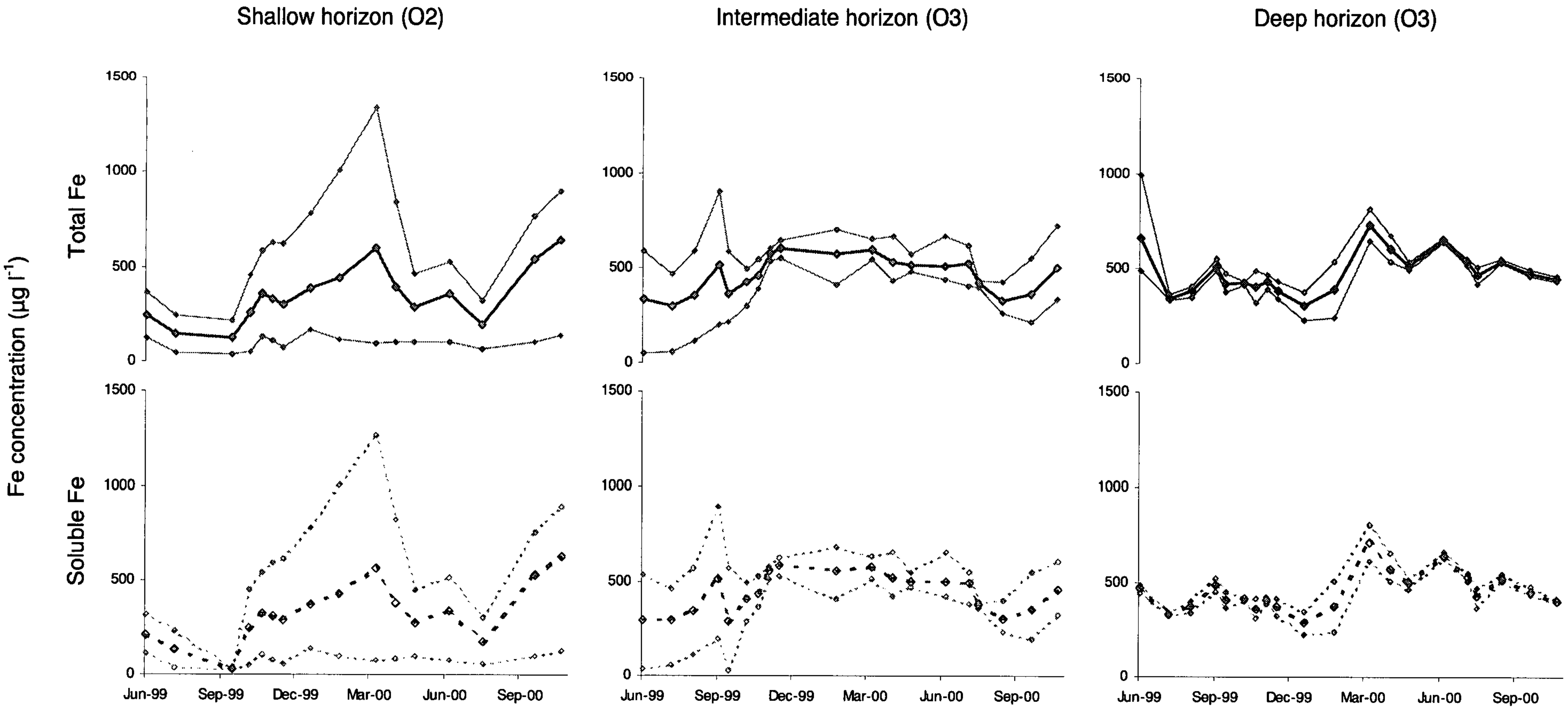


Figure B.10: Soil water Fe concentrations from forest site 1 (peat)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations

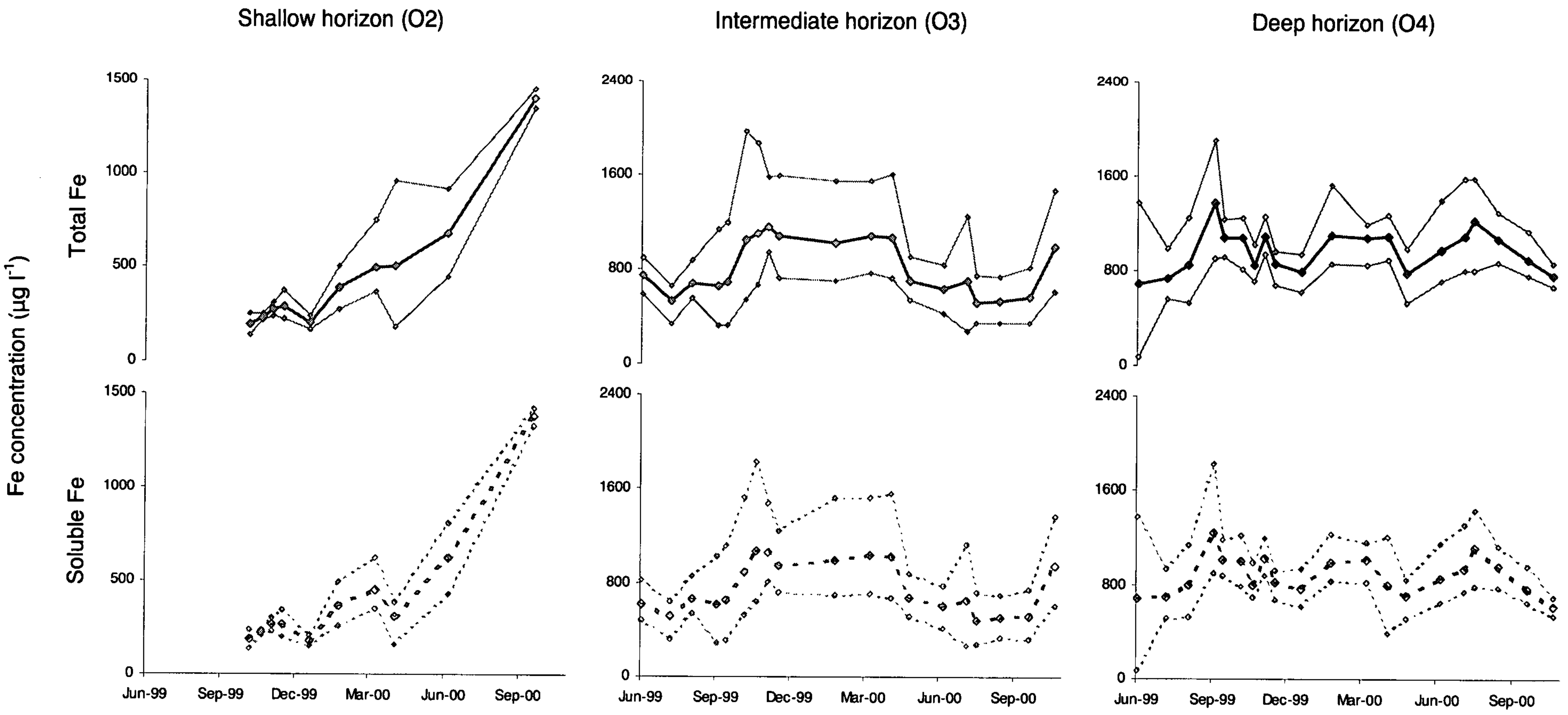


Figure B.11: Soil water Fe concentrations from forest site 2 (peat)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. **y-axis scale differs between horizons**

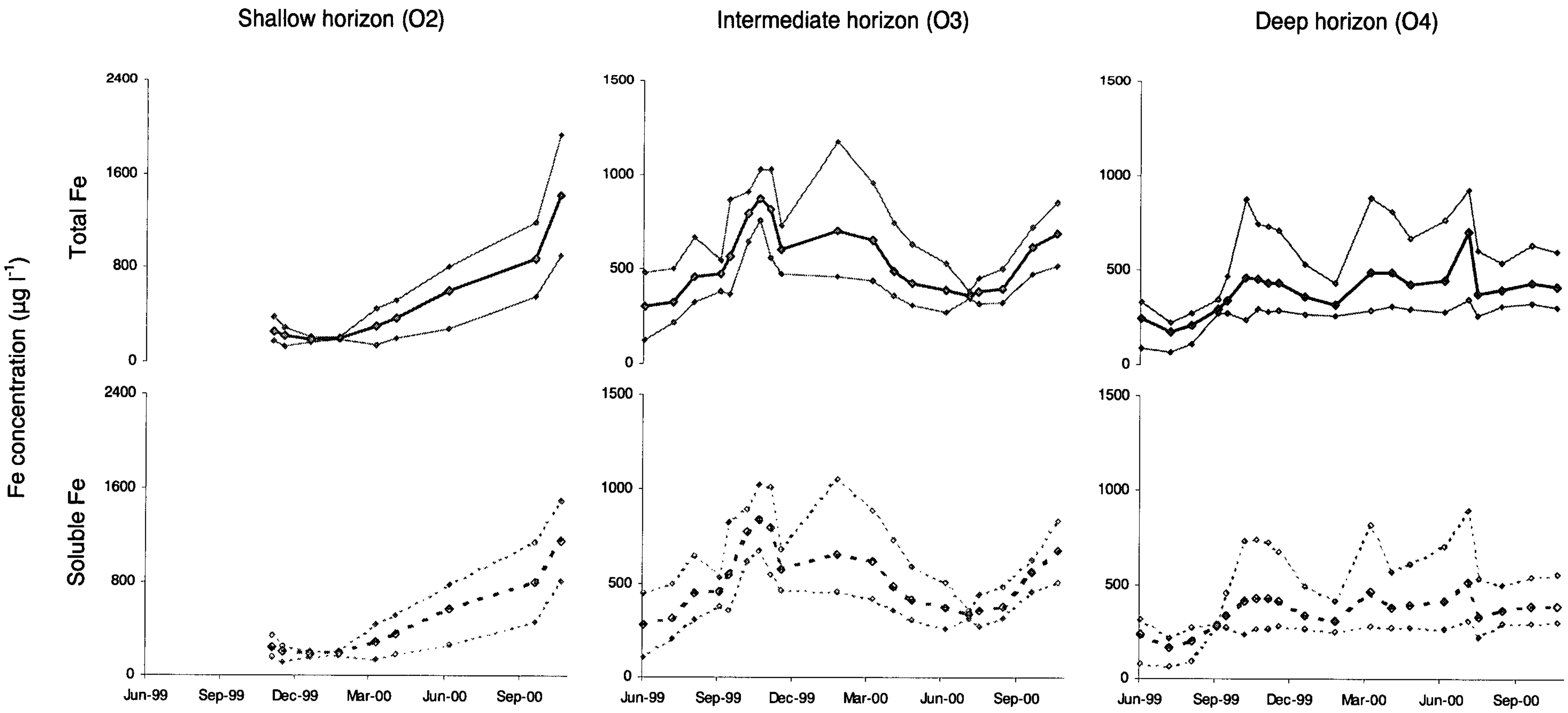


Figure B.12: Soil water Fe concentrations from forest site 3 (peat)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. **y-axis scale differs between horizons**

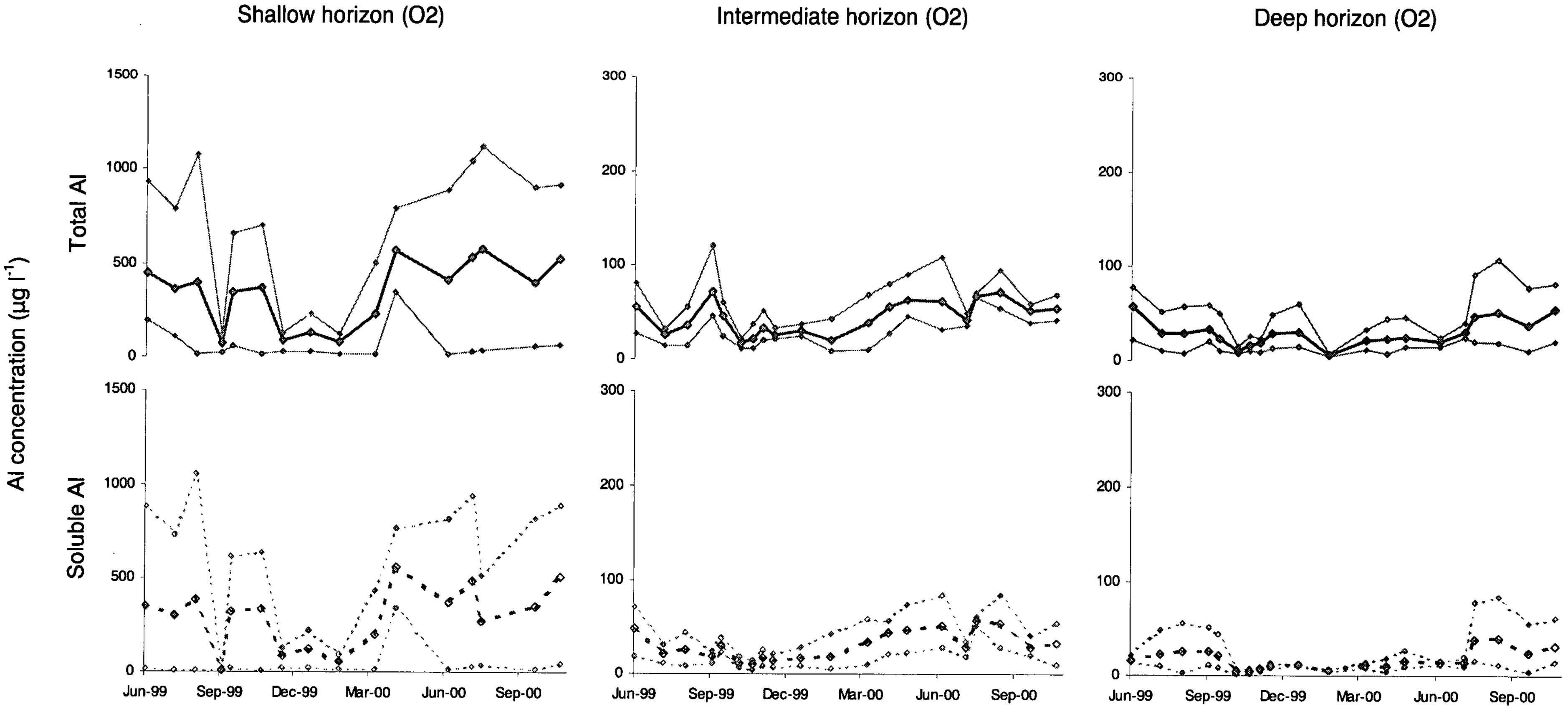


Figure B.13: Soil water Al concentrations from moorland site 1 (peat)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. **y-axis scale differs between horizons**

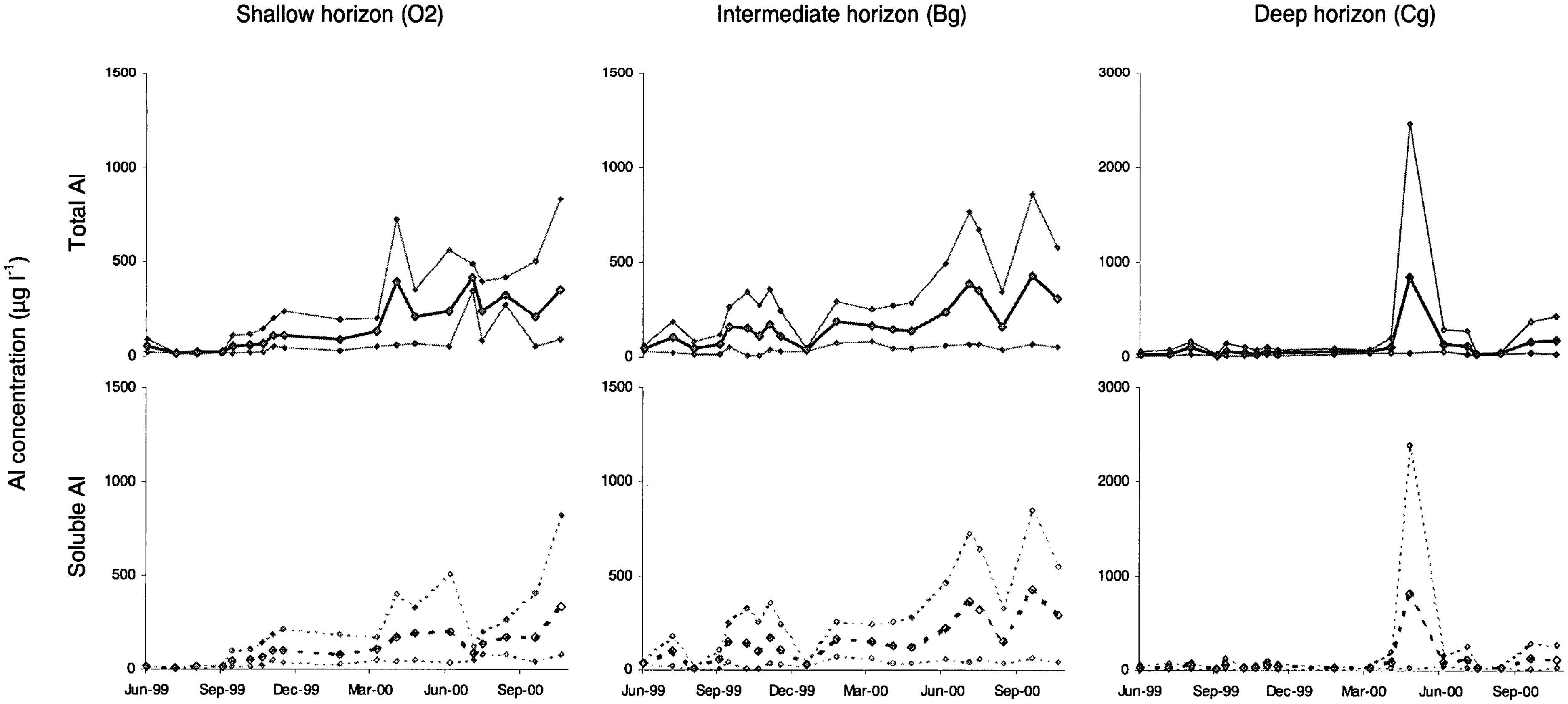


Figure B.14: Soil water Al concentrations from moorland site 2 (peaty gley)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. **y-axis scale differs between horizons**

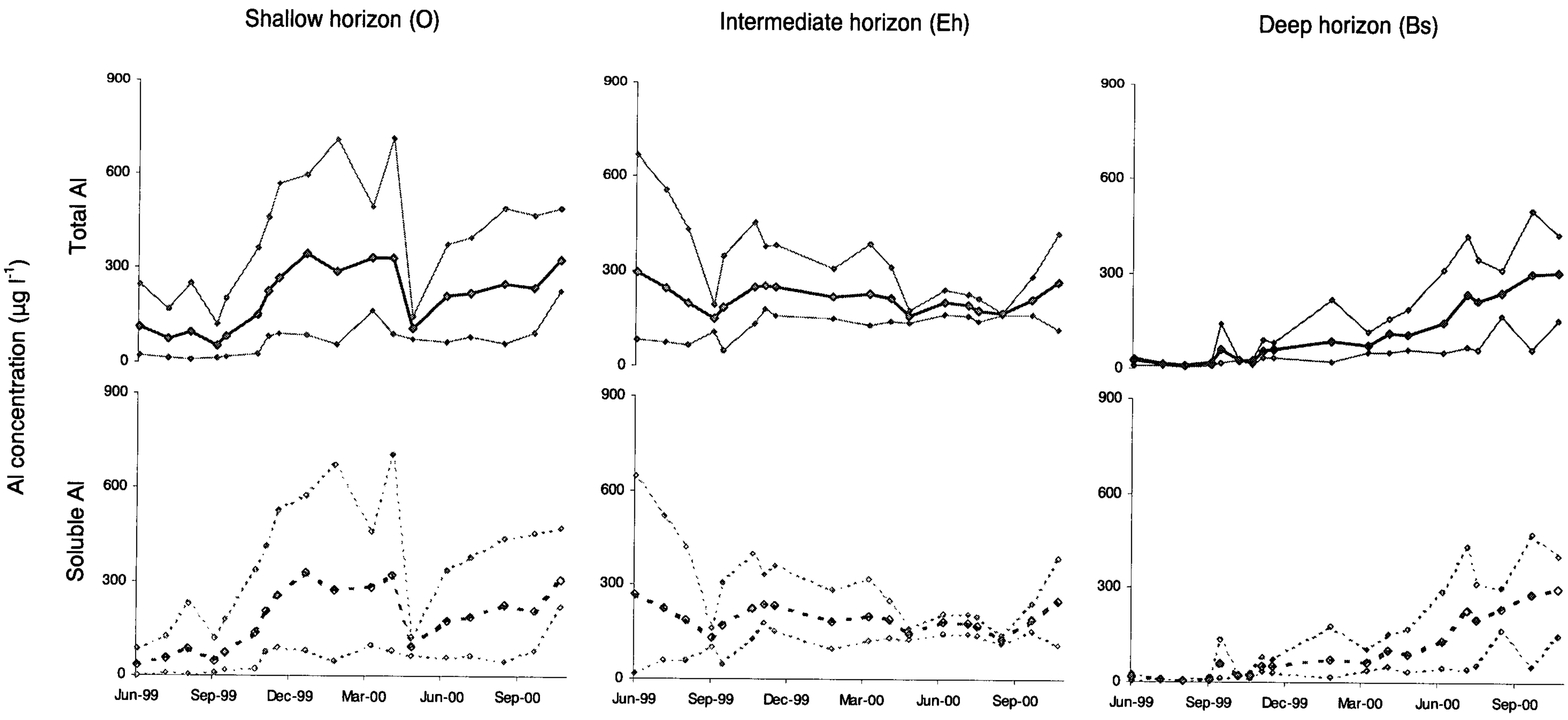
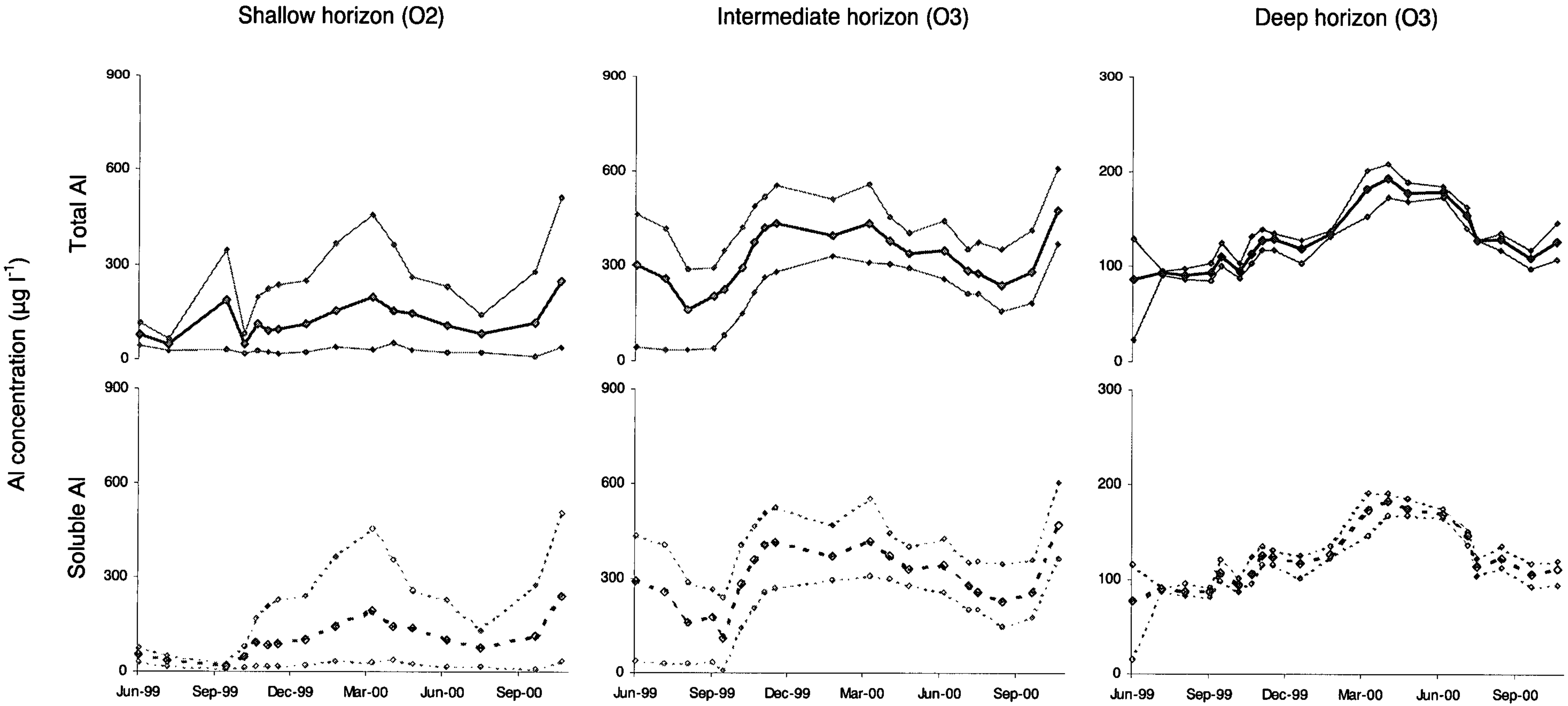


Figure B.15: Soil water Al concentrations from moorland site 3 (peaty podzol)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations



Shallow horizon (O2)

Intermediate horizon (O3)

Deep horizon (O3)

Figure B.16: Soil water Al concentrations from forest site 1 (peat)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. **y-axis scale differs between horizons**

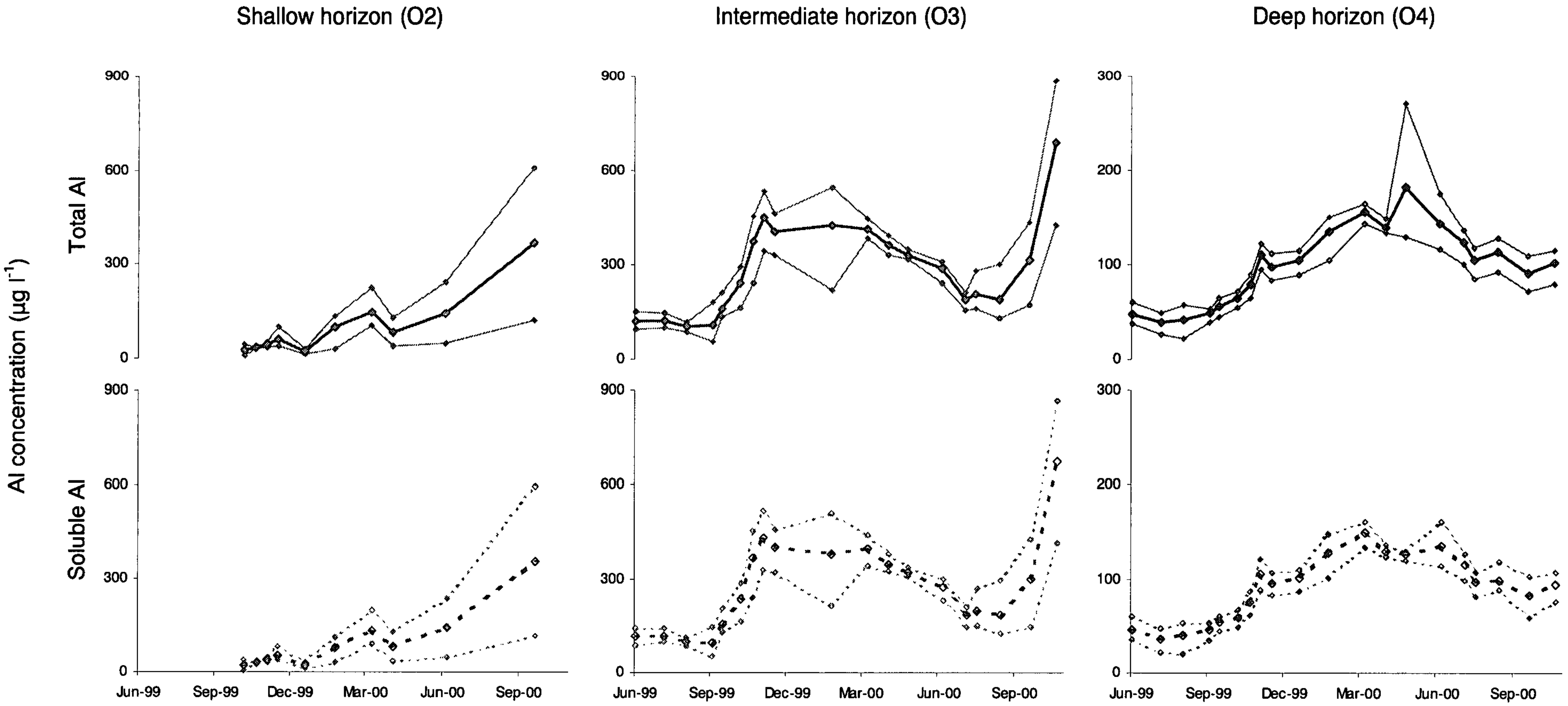


Figure B.17: Soil water Al concentrations from forest site 2 (peat)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. **y-axis scale differs between horizons**

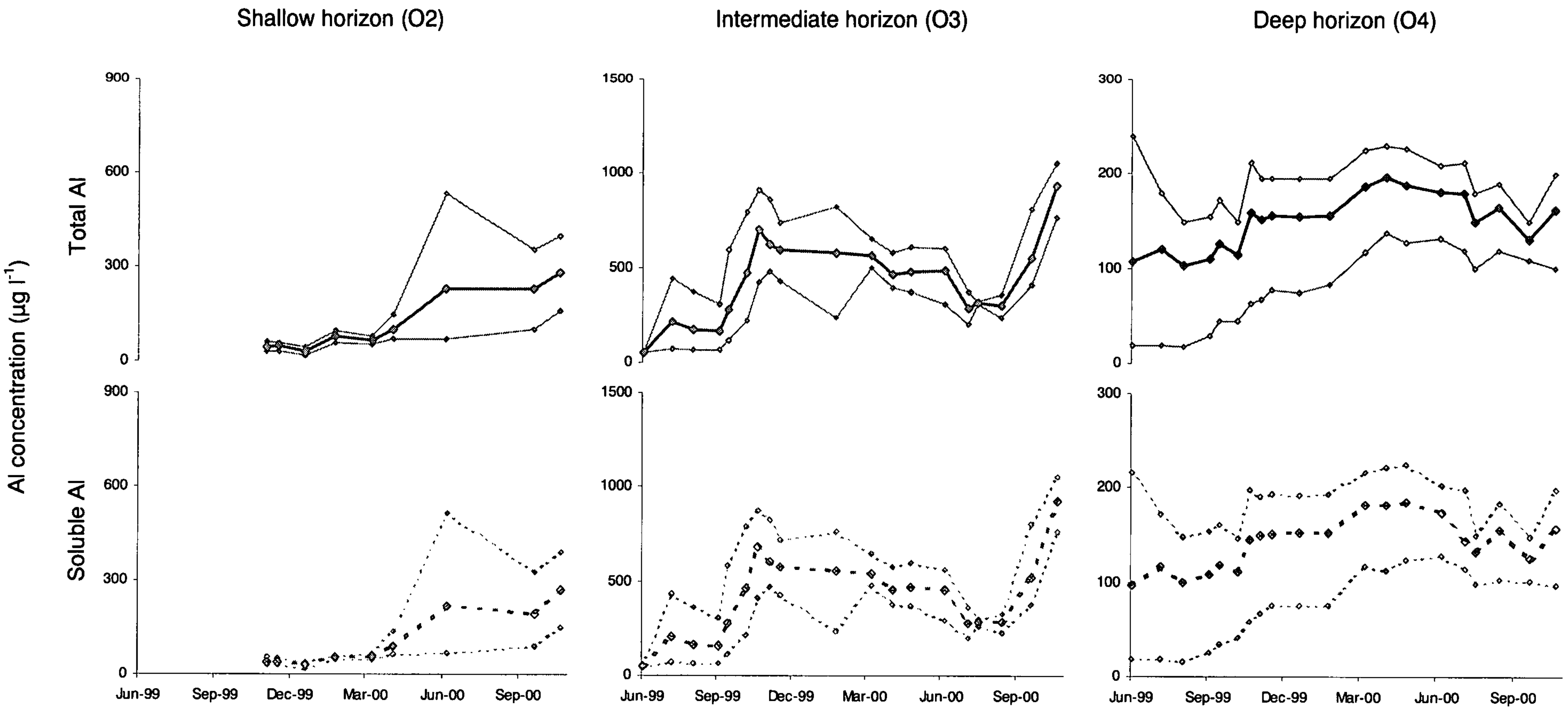


Figure B.18: Soil water Al concentrations from forest site 3 (peat)

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate concentrations
N.B. **y-axis scale differs between horizons**

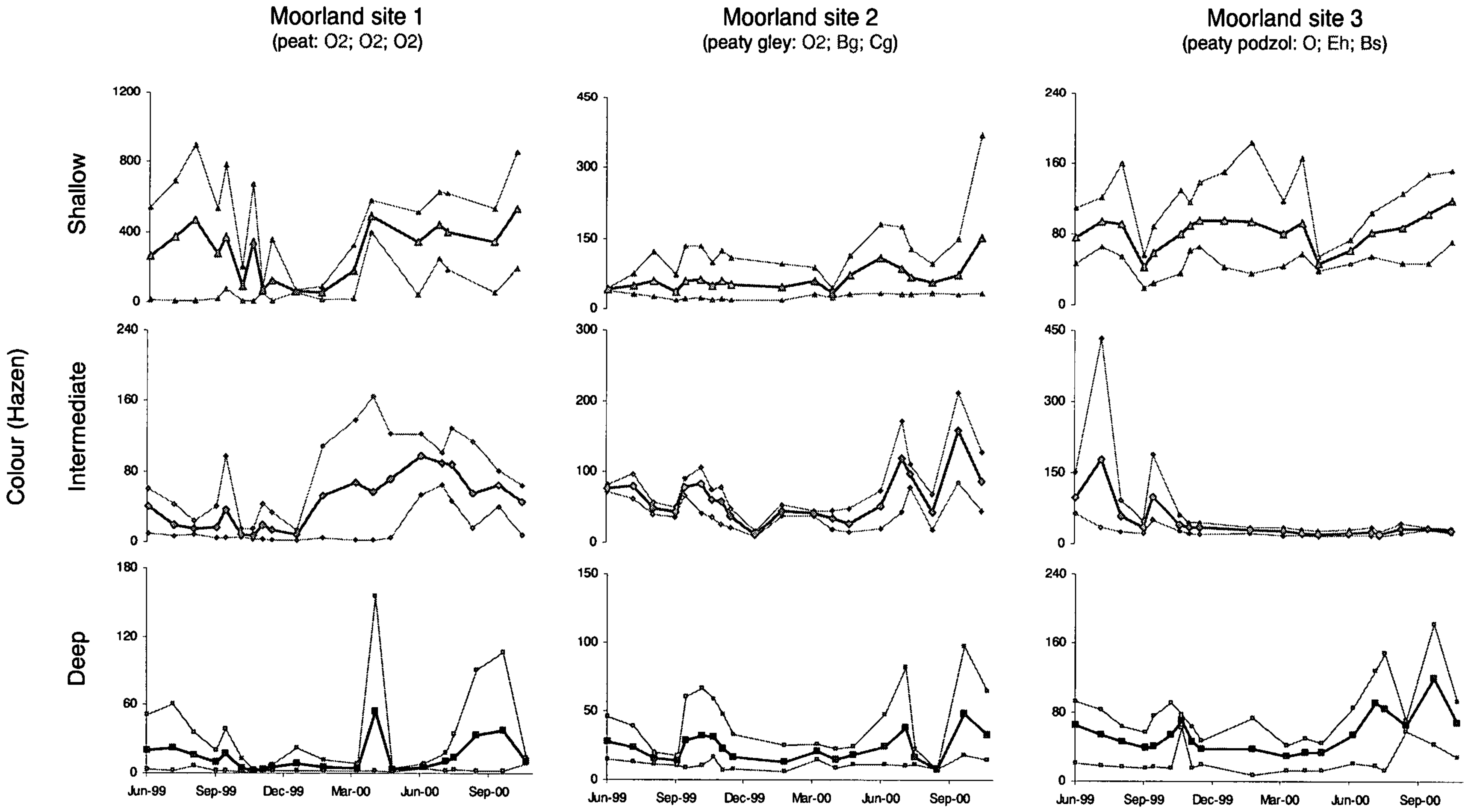


Figure B.19: Soil water colour from moorland sample sites

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate values
N.B. **y-axis scale differs between graphs**

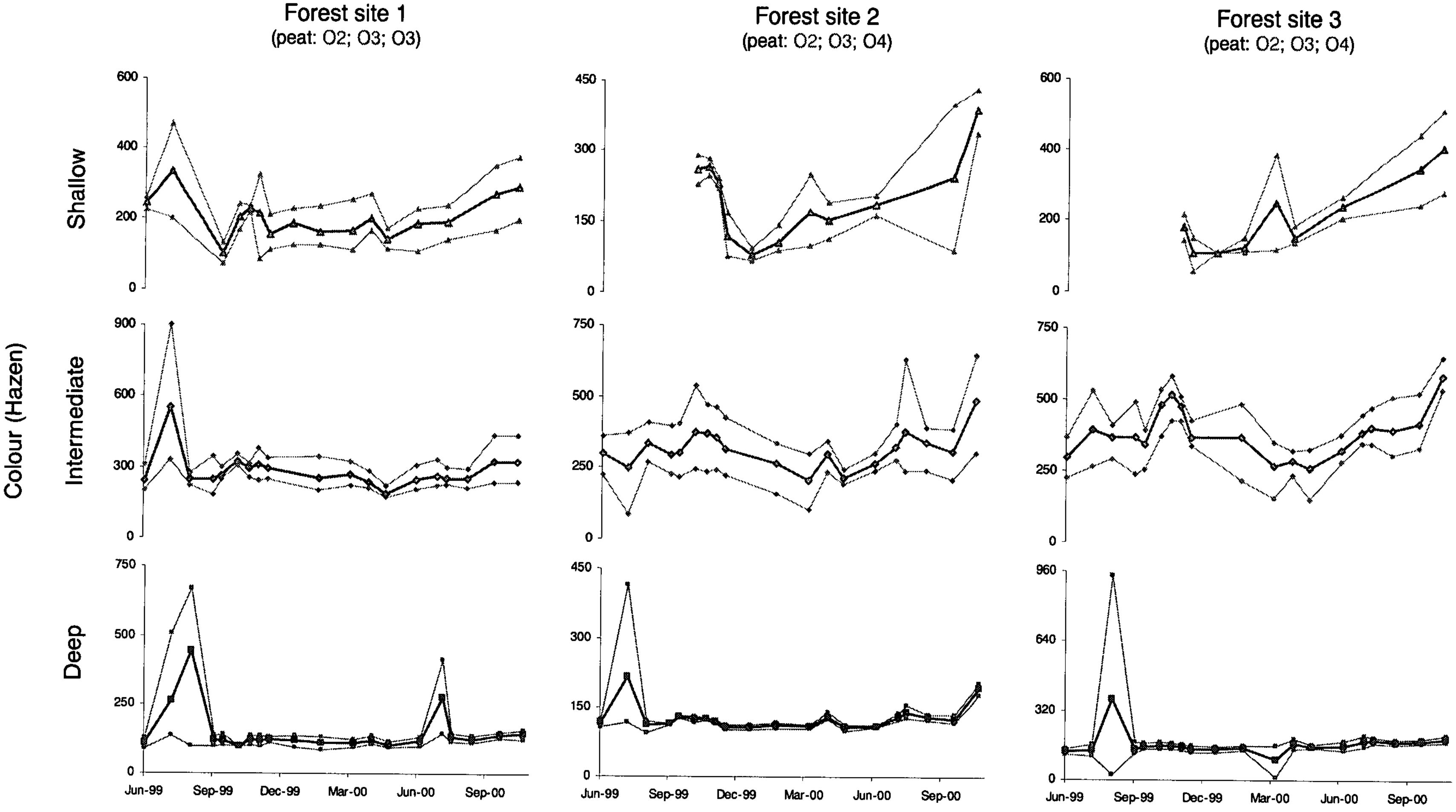


Figure B.20: Soil water colour from forest sample sites

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate values
N.B. **y-axis scale differs between graphs**

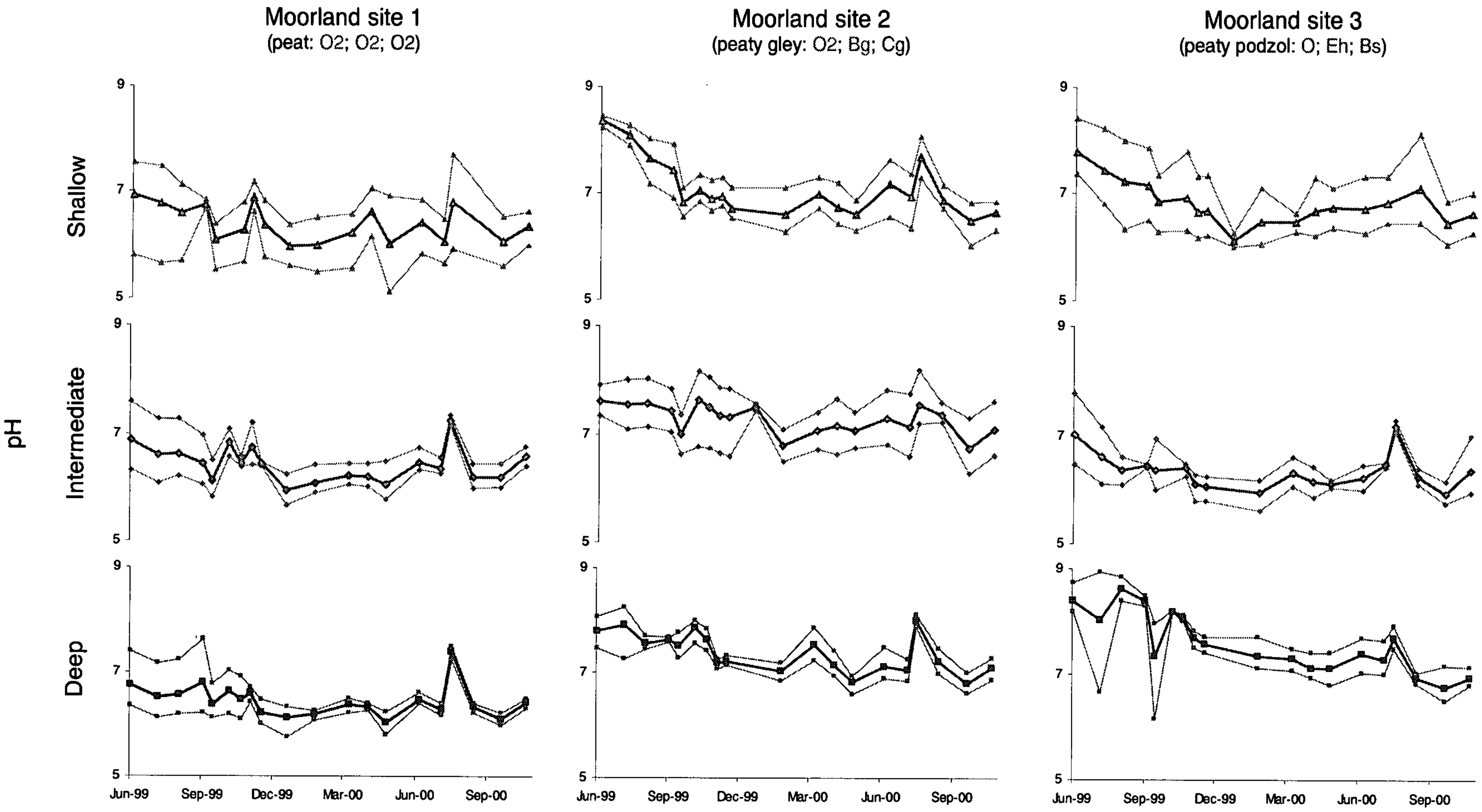


Figure B.21: Soil water pH from moorland sample sites

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate values

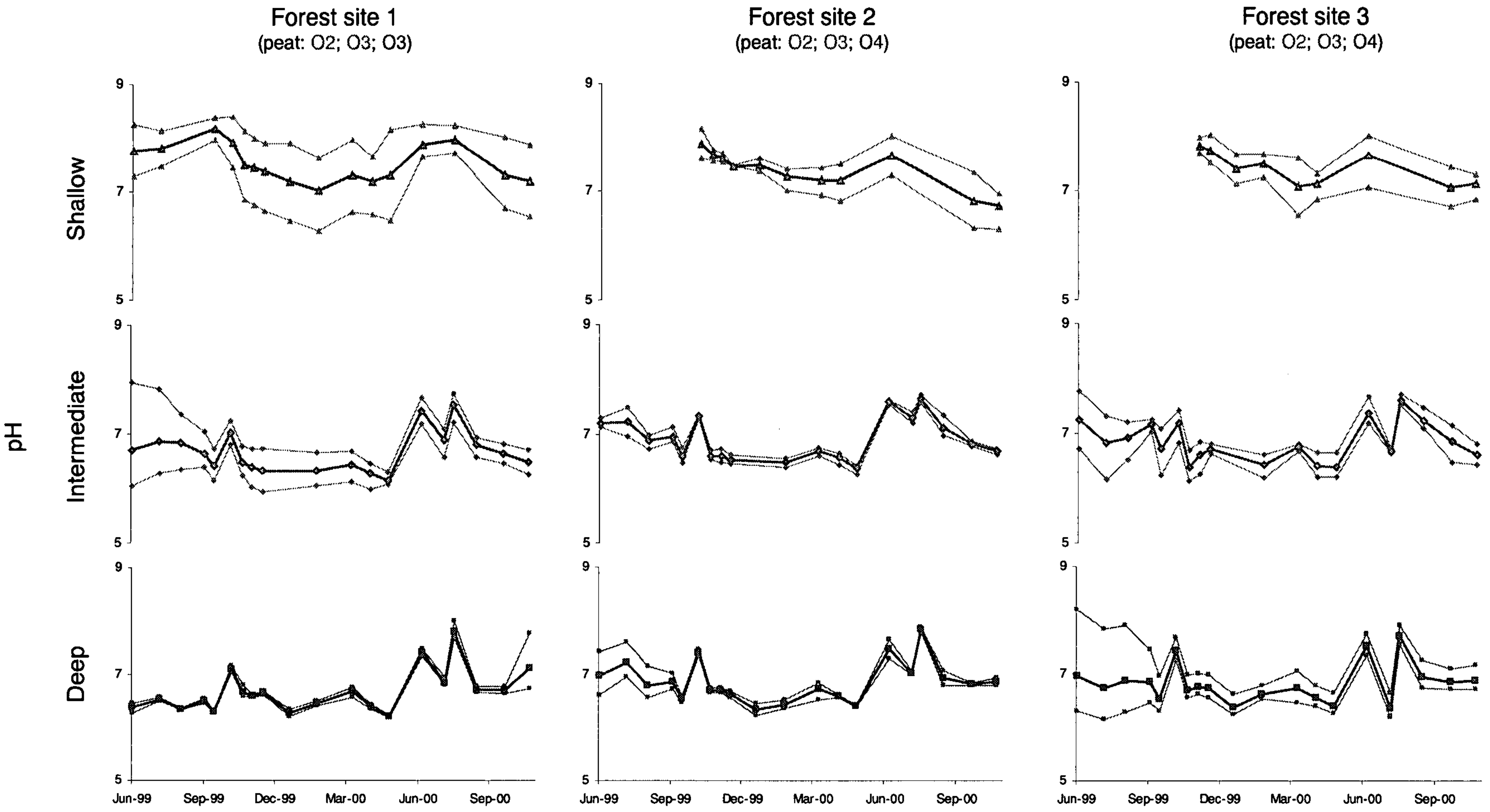


Figure B.22: Soil water pH from forest sample sites

Middle line represents mean of samples collected, upper and lower lines represent maximum and minimum replicate values

APPENDIX C

SOIL PROFILE DESCRIPTIONS

Forest Site 1

Profile name: Bradan Peat 1
Grid reference: NX4120095700
Region & District: Strathclyde, Kyle & Carrick District
Surveyor: A. Lilly
Sample date: 13-04-99
Altitude: 338 m
Slope description: 2°; straight, simple slope
Aspect & bearing: East, 81°
Rocks and boulders: No rock outcrops, no boulders
Vegetation: *Picea sitchensis* plantations (Sitka spruce plantations)
Flushing: None
Site drainage: Receiving site
Soil drainage: Very poor
Erosion: None
Association: Peat
Series: Basin peat
Parent material: Organic
Major soil subgroup: Dystrophic peat
Climate: Euoceanic perhumid southern boreal or lower oroboreal (O2P B2)
Land Capability Agri: 63W
Base of pit: Lowest horizon continues
Bulk samples: 01-09, 11-17, 35-40, 85-90 cm
Lab number range: 628042-045

O1: **0 - 10 cm**; dark reddish brown, 5YR 2/2 matrix colour; no identifiable mineral grains; fibrous; moist; weak fine platy structure; many fine fibrous and few very coarse woody roots; no stones; sharp smooth boundary.

O2: **10 - 18 cm**; black, 5YR 2/1 matrix colour; no identifiable mineral grains; amorphous; moist; moderate coarse angular blocky structure; common fine fibrous and few medium woody roots; no stones; sharp smooth boundary.

O3: **18 - 90 cm**; dark brown, 7.5YR 3/3 matrix colour; no identifiable mineral grains; amorphous; moist; massive structure; few fine fibrous roots; no stones .

Forest site 2

Profile name: Bradan Peat 2
Grid reference: NX4119695704
Region & District: Strathclyde, Kyle & Carrick District
Surveyor: A. Lilly
Sample date: 13-04-99
Altitude: 338 m
Slope description: 2°; straight, simple slope
Aspect & bearing: East, 80°
Rocks and boulders: No rock outcrops, no boulders
Vegetation: *Picea sitchensis* plantations (Sitka spruce plantations)
Flushing: None
Site drainage: Receiving site
Soil drainage: Very poor
Erosion: None
Association: Peat
Series: Basin peat
Parent material: Organic
Major soil subgroup: Dystrophic peat
Climate: Euoceanic perhumid southern boreal or lower oroboreal (O2P B2)
Land Capability Agri: 63W
Base of pit: Lowest horizon continues
Bulk samples: 01-05, 07-14, 20-30, 80-85 cm
Lab number range: 628046-049

O1: **0 - 6 cm**; dark reddish brown, 5YR 2/2 matrix colour; no identifiable mineral grains; semi-fibrous; moist; weak very coarse platy structure; few fine fibrous and few coarse woody roots; no stones; sharp smooth boundary.

O 2: **6 - 15 cm**; black, 5YR 2/1 matrix colour; no identifiable mineral grains; amorphous; moist; moderate coarse subangular blocky structure; common fine fibrous roots; no stones; sharp smooth boundary.

O 3: **15 - 33 cm**; dark reddish brown, 5YR 3/3 matrix colour; no identifiable mineral grains; amorphous; moist; massive structure; many fine fibrous roots; no stones; clear smooth boundary.

O 4: **33 - 90 cm**; very dark brown, 10YR 2/2 matrix colour; no identifiable mineral grains; amorphous; moist; massive structure; many fine fibrous roots; no stones.

Forest site 3

Profile name: Bradan Peat 3
Grid reference: NX4119295703
Region & District: Strathclyde, Kyle & Carrick District
Surveyor: A. Lilly
Sample date: 14-04-99
Altitude: 338 m
Slope description: 2°; straight, simple slope
Aspect & bearing: East, 81°
Rocks and boulders: No rock outcrops, no boulders
Vegetation: Picea sitchensis plantations (Sitka spruce plantations)
Flushing: None
Site drainage: Receiving site
Soil drainage: Very poor
Erosion: None
Association: Peat
Series: Basin peat
Parent material: Organic
Major soil subgroup: Dystrophic peat
Climate: Euoceanic perhumid southern boreal or lower oroboreal (O2P B2)
Land Capability Agri: 63W
Base of pit: Lowest horizon continues
Bulk samples: 02-08, 15-20, 27-33, 70-80 cm
Lab number range: 628050-053

O1: **0 - 10 cm**; dark reddish brown, 5YR 3/2 matrix colour; no identifiable mineral grains; semi-fibrous; moist; moderate very coarse platy structure; few very fine fibrous and few medium woody roots; no stones; sharp smooth boundary.

O2: **10 - 24 cm**; black, 5YR 2/1 matrix colour; no identifiable mineral grains; amorphous; moist; massive structure; few coarse woody and common very fine fibrous roots; no stones; sharp smooth boundary.

O3: **24 - 34 cm**; dark reddish brown, 5YR 3/3 matrix colour; no identifiable mineral grains; amorphous; moist; massive structure; many very fine fibrous roots; no stones; sharp smooth boundary.

O4: **34 - 90 cm**; dark brown, 7.5YR 3/2 matrix colour; no identifiable mineral grains; amorphous; wet; massive structure; common very fine fibrous roots; no stones.

Moorland site 1

Profile name:	Bradan Moor 1
Grid reference:	NX4140095300
Region & District:	Strathclyde, Kyle & Carrick District
Surveyor:	A. Lilly
Sample date:	14-04-99
Altitude:	390 m
Slope description:	13°; concave, complex slope
Aspect & bearing:	Northeast, 54°
Rocks and boulders:	Moderately rocky, no boulders
Vegetation:	*Erico - Sphagnetum papillosi* (Flying bent bog)
Flushing:	None
Site drainage:	Receiving site
Soil drainage:	Very poor
Erosion:	None
Association:	Peat
Series:	Blanket peat
Parent material:	Organic
Major soil subgroup:	Dystrophic peat
Rock type:	Greywacke and granite at depth
Climate:	Euoceanic perhumid southern boreal or lower oroboreal (O2P B2)
Land Capability Agri:	63W
Base of pit:	Lowest horizon continues
Bulk samples:	10-20, 40-50, 70-80, 100-110 cm
Lab number range:	628054-057

O1: **0 - 22 cm**; dark yellowish brown, 10YR 4/6 matrix colour; no identifiable mineral grains; fibrous; wet; weak very coarse platy structure; common fine fibrous and few medium woody roots; no stones; sharp smooth boundary.

O2: **22 - 100 cm**; black, 5YR 2/1 matrix colour; some mineral grains; amorphous; wet; massive structure; common fine fibrous roots; few medium subrounded and common very small angular stones: sharp irregular boundary.

2Cgh: **100 - 110 cm**; dark brown, 10YR 3/3 matrix colour with yellowish brown, 10YR 5/4 ped faces; sandy loam; no mottles; massive structure; wet; non-plastic, non-sticky; common fine fibrous roots; common medium subrounded stones and few large subrounded stones.

Moorland site 2

Profile name: Bradan Moor 2
Grid reference: NX4139595299
Region & District: Strathclyde, Kyle & Carrick District
Surveyor: A. Lilly
Sample date: 15-04-99
Altitude: 392 m
Slope description: 11°; concave, complex slope
Aspect & bearing: North-northeast, 22°
Rocks and boulders: Moderately rocky, no boulders
Vegetation: *Carici binervis - Ericetum cinereae* (Moist Atlantic heather moor)
Flushing: None
Site drainage: Receiving site
Soil drainage: Poor
Erosion: None
Association: Ettrick
Series: Dochroyle
Parent material: Till
Major soil subgroup: Peaty gley: ground-water gleying
Rock type: Greywacke and granite
Climate: Euoceanic perhumid southern boreal or lower oroboreal (O2P B2)
Land Capability Agri: 63W
Base of pit: Lowest horizon continues
Bulk samples: 02-08, 15-25, 40-50, 58-68, 75-85 cm
Lab number range: 628058-062

O1: **0 - 10 cm**; black, 5YR 2/1 matrix colour; no identifiable mineral grains; fibrous; wet; weak very coarse platy structure; few medium woody and common very fine fibrous roots; no stones; sharp smooth boundary.

O2: **10 - 36 cm**; black, 5YR 2/1 matrix colour; no identifiable mineral grains; amorphous; moist; strong very coarse subangular blocky structure; many fine fibrous roots; no stones; gradual wavy boundary.

Bg1: **36 - 56 cm**; brown, 10YR 5/3 matrix colour with many fine distinct sharp dark brown, 7.5YR 4/4 mottles; sandy loam; very weak coarse subangular blocky structure tending to massive; very moist; friable; common fine fibrous roots; common very small subangular and common medium subangular stones; clear smooth boundary.

Bg2: **56 - 70 cm**; yellowish brown, 10YR 5/4 matrix colour; with abundant fine prominent sharp yellowish red, 5YR 5/8 mottles; sandy loam; very weak very coarse platy structure; moist; firm; weakly indurated; few fine fibrous roots; common very small subangular and common medium subangular stones; sharp smooth boundary.

Cg: **70 - 90 cm**; yellowish brown, 10YR 5/4 matrix colour with few fine distinct sharp yellowish red, 5YR 5/6 mottles; loamy sand; massive structure; very moist; firm; no roots; many very small subangular and common medium subangular stones.

Moorland site 3

Profile name:	Bradan Moor 3
Grid reference:	NX4140095285
Region & District:	Strathclyde, Kyle & Carrick District
Surveyor:	A. Lilly
Sample date:	15-04-99
Altitude:	394 m
Slope description:	13°; convex, complex slope
Aspect & bearing:	Northeast, 34°
Rocks and boulders:	Moderately rocky, slightly bouldery
Vegetation:	*Carici binervis - Ericetum cinereae* (Moist Atlantic heather moor)
Flushing:	None
Site drainage:	Normal
Soil drainage:	Moderate
Erosion:	None
Association:	Ettrick
Series:	Auchrae
Parent material:	Till
Major soil subgroup:	Peaty podzol
Rock type:	Greywacke and granite
Climate:	Euoceanic perhumid southern boreal or lower oroboreal (O2P B2)
Land Capability Agri:	63S
Base of pit:	Solid rock
Bulk samples:	12-22, 27-32, 34-37, 45-55, 65-70 cm
Lab number range:	628063-067

LF: **0 - 7 cm**; dark reddish brown, 5YR 3/2 matrix colour; no identifiable mineral grains; fibrous; wet; very weak very coarse platy structure; few fine fibrous roots; no stones; sharp smooth boundary.

O: **7 - 26 cm**; dark brown, 7.5YR 3/2 matrix colour; no identifiable mineral grains; amorphous; wet; strong very coarse prismatic structure; many fine fibrous and few medium woody roots; no stones; sharp smooth boundary.

Ehg: **26 - 33 cm**; black, 5YR 2/1 matrix colour; humose loamy sand; no mottles; weak coarse platy structure; moist; friable; common fine fibrous roots; few very small subangular stones; clear smooth boundary.

Bh: **33 - 38 cm**; dark brown, 7.5YR 3/2 matrix colour; humose sandy loam; no mottles; weak medium subangular blocky structure; moist; friable; common very fine fibrous and few fine fibrous roots; no stones; sharp wavy boundary.

Bsg: **38 - 65 cm**; yellowish red, 5YR 4/6 matrix colour with yellowish brown, 10YR 5/6 ped faces; loamy sand; no mottles; weak coarse platy structure; slightly moist; firm and weakly cemented; few fine fibrous roots; common small subangular and common medium subangular stones; sharp irregular boundary.

Cg: **65 - 70 cm**; yellowish brown, 10YR 5/6 matrix colour with common medium prominent clear strong brown, 7.5YR 5/6 mottles; loamy sand; mottles; massive structure; slightly moist; friable; no roots; no stones.

Forest Site 4

Profile name: Bradan Ride
Grid reference: NX4112595550
Region & District: Strathclyde, Kyle & Carrick District
Surveyor: A. Lilly
Sample date: 27-04-00
Altitude: 340 m
Slope description: 7°; convex, complex slope
Aspect & bearing: North, 10°
Rocks and boulders: No rock outcrops, no boulders
Vegetation: *Juncus squarrosi – Festucum tenuifoliae* (*Molinia* grassland)
Flushing: None
Site drainage: normal
Soil drainage: Poor
Erosion: None
Association: Ettrick
Series: Dochroyle
Parent material: Moraine
Major soil subgroup: Peaty gley: ground-water gleying
Rock type: Greywacke
Climate: Euoceanic perhumid southern boreal or lower oroboreal (O2P B2)
Land Capability Agri: 63W
Base of pit: Lowest horizon continues
Bulk samples: 10-20, 35-45, 55-65 cm
Lab number range: 666522-524

LF: **0 - 3 cm**; dark reddish brown, 5YR 2/2 matrix colour; no identifiable mineral grains; semi-fibrous; wet; weak medium platy structure; few coarse fleshy and common medium fibrous roots; no stones; sharp smooth boundary.

O: **3 - 30 cm**; black 5YR2/1 matrix colour; no identifiable mineral grains; amorphous; wet; very weak coarse angular blocky structure; many very fine fibrous roots; common medium fleshy roots; sharp smooth boundary.

Bg: **30 - 51 cm**; dark yellowish brown, 10YR 3/4 matrix colour with few fine faint sharp dark brown, 7.5YR3/4 mottles and dark greyish brown 10YR4/2 ped faces; sandy silt loam; weak coarse subangular blocky structure tending to weak medium subangular blocky structure; very moist; friable; many fine fibrous and few medium fleshy roots; many medium subangular and few large angular stones clear smooth boundary.

Cg: **51 - 75 cm**; greyish brown, 10YR 5/2 matrix colour with few fine distinct sharp brownish yellow, 10YR 6/8 mottles and brown, 10YR 5/3 ped faces; sandy silt loam; massive structure; very moist; friable; few fine fibrous roots; common small subangular and common medium subangular stones.

Clear-felled site

Profile name:	Bradan Clearfell
Grid reference:	NX4125095540
Region & District:	Strathclyde, Kyle & Carrick District
Surveyor:	A. Lilly
Sample date:	27-04-00
Altitude:	339 m
Slope description:	1°; straight, simple slope
Aspect & bearing;	North-northwest, 284°
Rocks and boulders:	No rock outcrops, no boulders
Vegetation:	*Deschampsia cespitosa* dominant (tussock-grass pasture); Formerly *Picea sitchensis* (Sitka spruce) plantations
Flushing:	Slightly flushed
Site drainage:	Receiving site
Soil drainage:	Poor
Erosion:	None
Association:	Peat
Series:	Basin peat
Parent material:	Organic
Major soil subgroup:	Dystrophic peat
Climate:	Euoceanic perhumid southern boreal or lower oroboreal (O2P B2)
Land Capability Agri:	63W
Base of pit:	Flooded
Bulk samples:	16-26, 40-50, 70-80 cm
Lab number range:	666519-521

LF: **0 - 8 cm**; dark yellowish brown, 10YR 4/4 matrix colour; no identifiable mineral grains; fibrous; moist; weak medium platy structure; common fine fibrous and few very coarse woody roots; no stones; sharp wavy boundary.

O1: **8 - 29 cm**; black, 5YR 2/1 matrix colour; some mineral grains; sandy peat; fibrous; moist; moderate very coarse subangular blocky structure; common very fine fibrous and few very coarse woody roots; no stones; clear smooth boundary.

O2: **29 - 58 cm**; very dark brown, 105YR 2/2 matrix colour; some mineral grains; amorphous; moist; moderate very coarse subangular blocky structure; few very fine fibrous and few medium woody roots; no stones; clear smooth boundary.

O3: **58 - 102 cm**; dark yellowish brown, 10YR 3/4matrix colour; some mineral grains; amorphous; wet; massive structure; few very fine fibrous roots; no stones.

APPENDIX D

EQUIPMENT CALIBRATION AND MONITORING

Appendix D: Equipment calibration and monitoring

D.1 Thetaprobe calibration

Following equipment removal from the field monitoring sites, soil-specific calibration was carried out for each thetaprobe in order to improve measurement accuracy from ±0.05 m^3m^{-3} to ±0.02 m^3m^{-3}.

Cores (8 cm deep, 11 cm diameter) of relatively undisturbed soil were taken from the same soil horizons investigated during the field monitoring programme using the coring technique described in Section 5.3.1. Each soil core was wrapped in cling-film immediately after collection to prevent water loss, and then stored in a darkened room below 4°C until used in the calibration procedure.

To obtain soil-specific calibration for the thetaprobes, the following procedure was followed for each soil horizon. First, the weight (W_W) and volume (L) of each soil core were measured. Next, the thetaprobe was inserted into the field-moist soil core and the probe output recorded (V_W). The square root of the dielectric constant for the field-moist soil ($\sqrt{\varepsilon_W}$) was calculated using equation D1.

Each soil core was then completely dried (i.e. $\theta=0$) in a fan oven at 60°C and the weight of the dry core measured (W_0). Thetaprobe output was measured (V_0) and the square root of the dielectric constant for the dry soil ($\sqrt{\varepsilon_0}$) was then calculated using equation D1. This equals the first calibration constant, a0.

$$\sqrt{\varepsilon} = 1.07 + 6.4V - 6.4V^2 + 4.7V^3 \qquad \textbf{Equation D1}$$

The volumetric water content of the original sample (θ_W) was calculated, using equation D2. The second calibration constant, a1, was then obtained by substituting the values for $\sqrt{\varepsilon_W}$, $\sqrt{\varepsilon_0}$ and θ_W in equation D3.

$$\theta_W = \frac{(W_W - W_0)}{L} \qquad \textbf{Equation D2}$$

$$a1 = \frac{\sqrt{\varepsilon_W} - \sqrt{\varepsilon_0}}{\theta_W} \qquad \textbf{Equation D3}$$

The soil-specific constants obtained using the above procedure are detailed in Table D.1. In several organic horizons, it proved impossible to insert the thetaprobes into the dried soil and therefore no reading was taken. In such cases, no soil-specific constants were calculated and the thetaprobe data interpreted using the default constants for organic soil.

Site	Constants	Horizon					
		Shallow		Intermediate		Deep	
Forest 1	a0	(O2)	1.38	(O3)	1.25	(O3)	1.29
(Peat)	a1		6.45		6.06		5.87
Forest 2	a0	(O2)	1.38	(O3)	1.25	(O4)	1.29
(Peat)	a1		6.40		6.36		6.00
Forest 3	a0	(O2)	1.38	(O3)	1.25	(O4)	1.29
(Peat)	a1		6.63		6.38		6.04
Moor 1	a0	(O2)	-	(O2)	-	(O2)	-
(Peat)	a1		-		-		-
Moor 2	a0	(O2)	1.40	(Bg)	1.76	(Cg)	1.73
(Peat)	a1		7.67		7.51		5.68
Moor 3	a0	(O)	1.36	(Eh)	1.45	(Bs)	1.66
(Peat)	a1		6.08		7.22		7.96

Table D.1: Soil-specific constants for thetaprobe calibration

D.2 Suction probe preparation

Prior to installation, all suction probes were cleaned with dilute acid and distilled water in order to remove any impurities that may have contaminated samples collected. During the first stage of cleaning, the suction probes were placed in clamp stands and suspended over a plastic basin. Rubber bungs were removed from the top of the suction probes and one litre of 1M hydrochloric acid poured into the empty probes. The acid was allowed to drain under gravity through the porous ceramic cup into the basin, before being discarded. Following this, the suction probes were immersed in distilled water and a vacuum of approximately -70 kPa applied to them. The suction probes were left to fill overnight and emptied the following day. This process was repeated until the pH of water collecting in the suction probes was approximately neutral, thereby indicating that all of the acid had been washed out of the equipment. Figure D1 shows the changes in pH of water collected in the suction probes during the cleaning process.

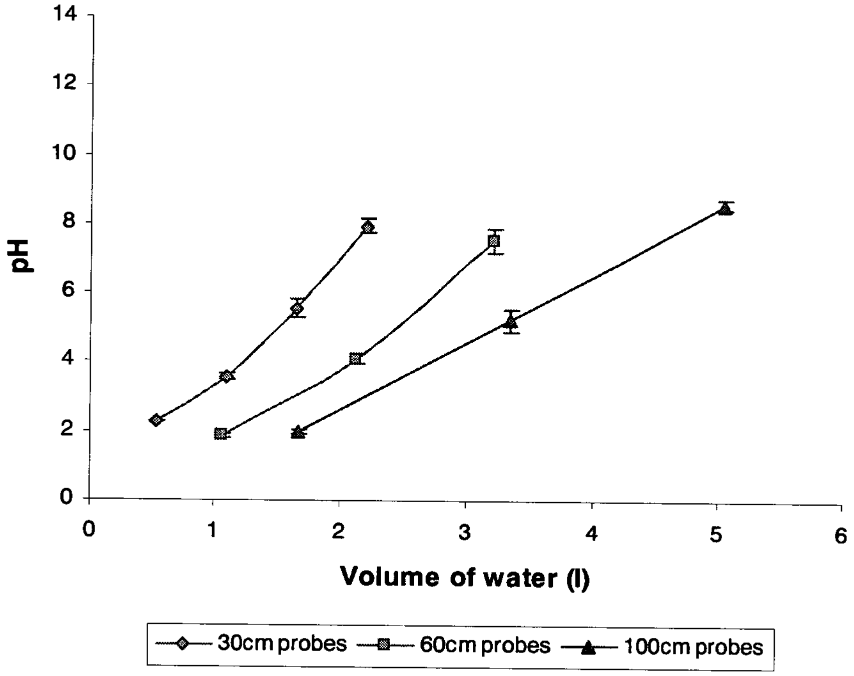


Figure D1: pH (±SE) of water collected in suction probes during cleaning process
(Data points represent the mean value for all probes of a particular size)

The data in Figure D1 indicate that the acid was flushed out of all suction probes within 3-4 filling cycles. However, it is unknown if the pH of water collected would continue to increase beyond the final values measured with additional treatment. As discussed in section 3.4.1.3, the increase in pH above neutral may result from retention of H^+ ions at cation exchange sites on the ceramic cups. It is therefore likely that an equilibrium between H^+ ions in solution and the cation exchange sites would be attained, after which the pH measured would be that expected for distilled water.

D.3 Suction probe volume monitoring

The volume of water collected in suction probes during the field monitoring programme was recorded in order to identify whether suction probe performance was impaired by plugging of pores in the ceramic cups. Figure D2 shows the mean volume of water collected in the three sizes of suction probes at each site during the field monitoring programme.

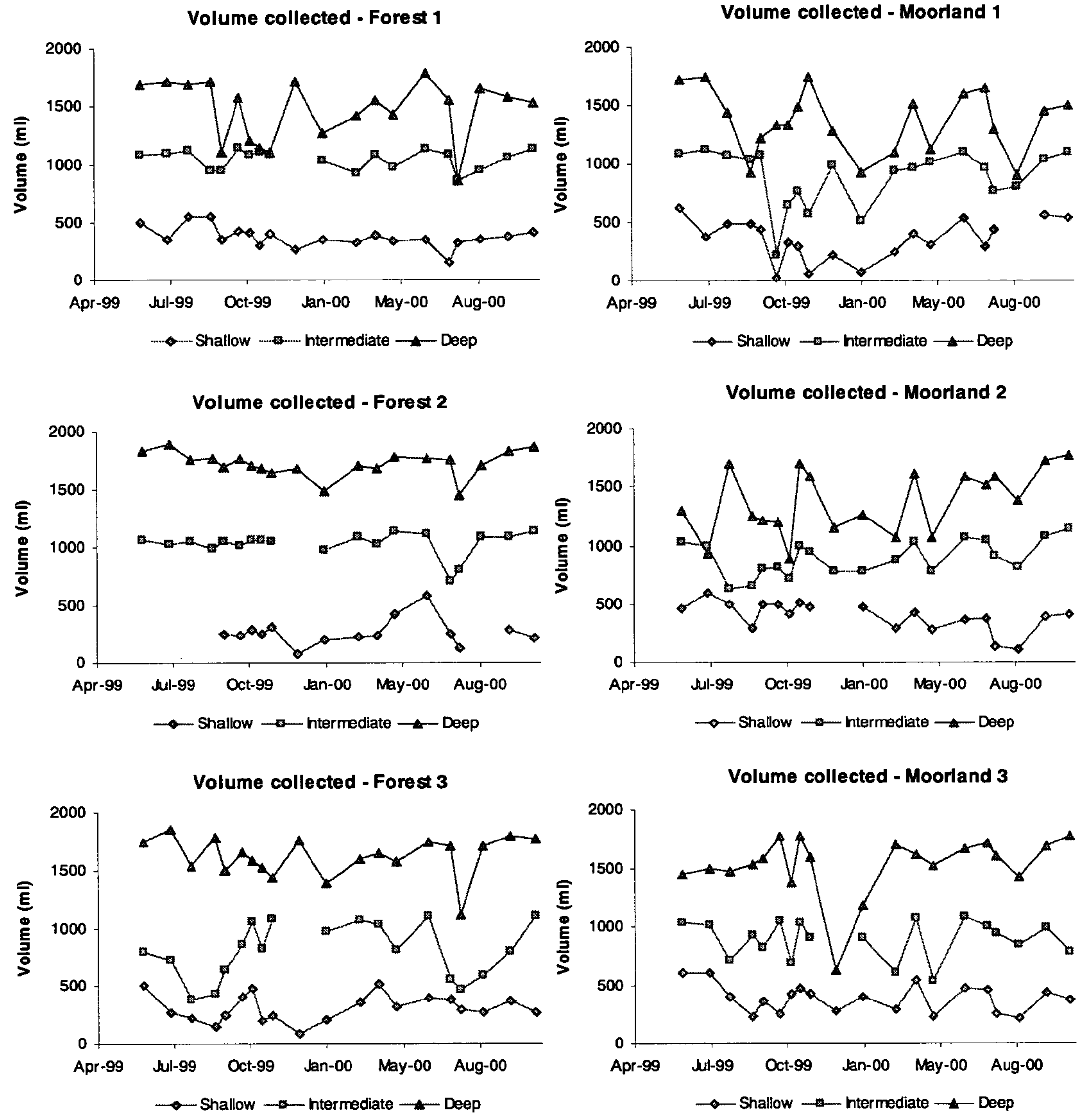


Figure D2: Volume of soil water collected in suction probes at primary field sites
(Data points represent the mean value for all probes of a particular size)

As expected, the larger volume suction probes (i.e. longer length of plastic pipe) collected the greatest volumes of water. Short duration decreases in volume collected are apparent during dry periods when soil matric potential was greatest. In the case of the deep suction probes, the volume of soil water collected also decreased when the sampling regime changed from monthly to fortnightly. On these occasions, there was insufficient time for the suction probes to fill completely between sampling visits. Aside from these examples, there was no obvious decrease in the volume of water collected over the course of the field monitoring programme. Therefore it is concluded that plugging of ceramic cup pores did not influence suction probe performance.

APPENDIX E

SAMPLE WAVE INPUT FILES

```
C ***********
C CLIMDATA.IN
C ***********

C  SPECIFY THE CLIMATOLOGICAL DATA
C  IF NITROGEN IS MODELLED THEN SPECIFY MIN AND MAX TEMPERATURES
C  IF SUCROS IS USED THEN SPECIFY MIN, MAX TEMPERATURES AND GLOBAL RADIATION
C  ELSE SKIP LAST THREE COLUMNS

C Yr     M       Day      ET0      Precip   Irrig    Intercept  Min Temp Max Temp   Glob Rad
C                         (mm)     (mm)     (mm)    (mm)       C        C          (J/CM2/Day)
C --------------------------------------------------------------------------------------------

1999     1       1        1.6      6.45     0       2.0
1999     1       2        2.2      30.10    0       2.0
1999     1       3        2.2      7.40     0       2.0
1999     1       4        4        9.30     0       2.0
1999     1       5        3.6      3.20     0       2.0
1999     1       6        0.2      10.60    0       2.0
1999     1       7        1.2      6.20     0       2.0
1999     1       8        1.6      15.70    0       2.0
1999     1       9        3        0.10     0       0.1
1999     1       10       3.2      0.00     0       0.0
1999     1       11       1.4      0.00     0       0.0
1999     1       12       0        11.20    0       2.0
1999     1       13       0        14.60    0       2.0
1999     1       14       1.2      10.20    0       2.0
1999     1       15       0.6      24.70    0       2.0

*        *       *        *        *        *       *
CLIMATE DATA CONTINUES…   16/01 to 15/10
*        *       *        *        *        *       *

1999     10      16       0        0.00     0       0.0
1999     10      17       0        0.00     0       0.0
1999     10      18       0        0.00     0       0.0
1999     10      19       0        0.00     0       0.0
1999     10      20       1        0.00     0       0.0
1999     10      21       9.6      0.00     0       0.0
1999     10      22       3.4      9.20     0       2.0
1999     10      23       2.8      3.66     0       2.0
1999     10      24       3.8      11.92    0       2.0
1999     10      25       1.6      4.94     0       2.0
1999     10      26       2.2      0.41     0       0.4
1999     10      27       3        0.33     0       0.3
1999     10      28       3.8      6.73     0       2.0
1999     10      29       0        0.66     0       0.7
1999     10      30       0        4.26     0       2.0
1999     10      31       5.8      8.26     0       2.0
ET
```

WAVE input file:
CLIMDATA.IN

WAVE input file: GENDATA.IN

```
C **********
C GENDATA.IN
C **********

C SIMULATION TYPE
C TTTTTTTTTTTTTTT
 - ARE THERE PLANTS? (Y/N) ........................................: Y
 - IF THERE ARE PLANTS, WILL SUCROS BE USED? (Y/N) .................: N
 - IS TEMPERATURE MODELED? (Y/N) ...................................: N
 - ARE SOLUTES MODELED? (Y/N) ......................................: N
 - IS NITROGEN MODELED? (Y/N) ......................................: N

C SOIL PROFILE DEVELOPMENT
C TTTTTTTTTTTTTTTTTTTTTTT

 - COMPARTMENT SIZE (MM) ...........................................: 25
 - NUMBER OF SOIL LAYERS ...........................................: 6
C
C- NUMBER OF COMPARTMENTS FOR EACH SOIL LAYER
C  LR  NO_OF_COMPARTMENTS
C  --  -----------------
   1    3
   2    7
   3    3
   4    2
   5    11
   6    2
ET

C IF MODELING SOLUTES (NITROGEN) OR HEAT TRANSPORT SPECIFY BULK DENSITY
C LR  BULK_DENSITY
C       KG L-1
C --  ----------

C SIMULATION TIME VARIABLES
C TTTTTTTTTTTTTTTTTTTTTTTTT

 - START OF CALCULATIONS  (Y M D) ..................................: 1999 01 01
 - END OF CALCULATIONS (Y M D) .....................................: 1999 10 31
C NEXT TWO DATES ARE ONLY INPUT IF THERE ARE PLANTS
C IN CASE THE CROP GROWTH IS MODELED THE FIRST DATE IS THE EMERGENCE DATE
 - PLANTING OR EMERGENCE DATE (M D) ................................: 01 01
 - HARVEST  DATE (M D) .............................................: 10 31

C PARAMETERS CONCERNING THE NUMERICAL SOLUTION
C TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT

 - THE MAXIMUM TIME STEP (DAY) ( > 0.001 DAY) ......................: 1
 - THE MINIMUM TIME STEP (DAY) ( < 1 DAY) ..........................: 0.1
 - THE MAX. ALLOWED MOISTURE CONTENT CHANGE (CM3 CM-3)(0.002<.<0.05): 0.05
 - THE MAXIMUM ALLOWED BALANCE ERROR(0.00001< < 1.) (CM3 CM-3DAY-1).: 0.01

C PARAMETERS CONCERNING PRINTING
C TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT
C - STOP THE PROGRAM WHEN THERE ARE RANGE ERRORS IN THE INPUT? (Y/N): Y
C - IS THE TIME INCREMENT BETWEEN THE PRINTING OF THE SUMMARYTABLES
C   LISTING THE DIFFERENT STATE VARIABLES CONSTANT? (Y/N) ..........: Y
C   IF "YES"
C    GIVE THE TIME INCREMENT (DAY) (INTEGER)........................: 30
C   IF "NO"
C     1) GIVE THE NUMBER OF DATES THERE IS A SUMMARY TABLE..........:
C     2) GIVE THE DATES AT WHICH THE SUMMARY TABLE MUST BEPRINTED
C     M  D
C     -- --
C - SPECIFY ISD, THE BOTTOM COMPARTMENT OF THE TOP LAYER FOR WHICH THERE IS
C   OUTPUT IN THE SUMMARY FILES  ...................................: 2

C - COMPARTMENT RANGES FOR THE TIME SERIES FILES
C    1) NUMBER OF COMPARTMENT RANGES FOR THE TIME SERIES FILES .....: 6
C    2) GIVE THE UPPER AND LOWER COMPARMENT FOR EACH RANGE
C    UPPER     LOWER
C    -----     -----
      1          3
      4         10
     11         13
     14         15
     16         26
     27         28
ET
```

```
C***********
C WATDATA.IN
C***********


C HYDRAULIC PROPERTIES
C TTTTTTTTTTTTTTTTTTTT

 - INPUT FROM EXTERNAL FILE WATPAR.WP? (Y/N) ...............: N
 - MULTIPOROSITY (Y/N?)                  ...................: N

C IF YOU ARE USING MULTIPOROSITY MODELS FOR THE HYDRAULIC PROPERTIES,
C SKIP THIS SECTION AND GOTO THE MULTIPOROSITY SECTION

C SINGLE POROSITY
C ---------------

 - MOISTURE RETENTION CHAR (MODEL NR) (INTEGER) ............: 1
C  MODELS AVAILABLE
C   MOISTURE RETENTION CHARACTERISTIC MODEL           NUMBER
C    NO HYSTERESIS:
C     VAN GENUCHTEN   SE = 1/(1+(ALPHA*H)**N1)**M         1
C             WITH      SE = (WC-WCR)/(WCS-WCR)
C    HYSTERESIS:
C     MUALEM UNIVERSAL MODEL BASED ON MUALEM MODEL II     2
C     MUALEM MODEL II                                     3

 - HYDRAULIC CONDUCTIVITY MODEL (MODEL NR) (INTEGER) .......: 5
C  MODELS AVAILABLE
C   HYDRAULIC CONDUCTIVITY MODEL                      NUMBER
C    GARDNER(POWER)  K = KSAT/(1+(BH)**N2)                1
C    GARDNER (EXPON) K = KSAT*E**(ALPHA2*H)               2
C    GILHAM          K = A*WC**N2                         3
C    BROOKS&CORREY   K = KSAT*SE**((2+3*LAMBDA)/LAMBDA)   4
C    MUALEM          K = KSAT*SE**L*((1-SE**(1/M))**M)**2 5

C MOISTURE RETENTION PARAMETERS FOR EACH SOIL LAYER
C ---------------------------------------------------------
C  LR   WCR    WCS    ALPHA    N      M                        (MODEL 1)
C  LR   WCR    WCS    ALPHAW   N      M                        (MODEL 2)
C  LR   WCR    WCS    ALPHAD   ND     MD   ALPHAW    NW     MW (MODEL 3)
   1   0.010  0.775   0.0425  1.375 0.273
   2   0.010  0.895   0.0075  1.225 0.184
   3   0.050  0.765   0.0055  1.575 0.365
   4   0.050  0.366   0.0430  1.521 0.342
   5   0.078  0.462   0.0075  1.250 0.200
   6   0.078  0.445   0.0121  1.407 0.289
ET

C IN CASE OF A HYSTERESIS MODEL GIVE THE MAXIMUM RELATIVE CHANGE
C IN PRESSURE HEAD  (-) ELSE SKIP ..........................:

C HYDRAULIC CONDUCTIVITY PARAMETERS FOR EACH SOIL LAYER
C ----------------------------------------------------
C LR  KSAT   B      N      (GARDNER POWER FUNCTION)
C LR  KSAT   ALPHA         (GARDNER EXPONENTIAL FUNCTION)
C LR  KSAT   N             (GILHAM)
C LR  KSAT   LAMBDA        (BROOKS AND CORREY)
C LR  KSAT   L             (MUALEM)
C    (CM/DAY)
  1  45.0   0.4
  2   0.7   0.4
  3  25.2   0.74
  4  31.0   1.25
  5  25.2   1.25
  6   0.8   1.25
ET
```

```
C MULTIPOROSITY MODELS
C --------------------
C - IF MULTI POROSITY MODEL IS ASSUMED, MOISTURE RETENTION IS DESCRIBED
C   WITH A SUM OF DIFFERENT VAN GENUCHTEN EQUATIONS (DURNER, 1994) AND
C   THE HYDRAULIC CONDUCTIVITY WITH MUALEM'S GENERAL MODEL (MUALEM, 1976).
C - SPECIFY FOR EACH LAYER
C    NR_POR      = NUMBER OF POROSITY CLASSES          (-)
C    WCR         = RESIDUAL MOISTURE CONTENT          (M3/M3)
C    WCS         = SATURATED MOISTURE CONTENT         (M3/M3)
C    L           = TORTUOSITY FACTOR OF THE MUALEM MODEL
C    KSAT        = SATURATED CONDUCTIVITY            (CM/DAY)
C   SPECIFY FOR EACH POROSITY CLASS
C    W(NR_POR)    = WEIGHT FACTOR FOR EACH PARTIAL MRC
C    ALFA(NR_POR)= INVERSE AIR ENTRY VALUE FOR EACH PARTIAL MRC
C    N(NR_POR)    = N FOR EACH PARTIAL MRC
C    M(NR_POR)    = M FOR EACH PARTIAL MRC
C  IN THE FOLLOWING ORDER
C   NR_POR  WCR  WCS  L KSAT
C    W(1) ALFA(1) N(1) M(1)
C    ..........
C    W(I) ALFA(I) N(I) M(I)

C WATER UPPER BOUNDARY CONDITIONS
C TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT

 - INPUT FROM EXTERNAL FILE WATUBC.WU? (Y/N) ................: N

 - GIVE THE MINIMUM ALLOWED PRESSURE HEAD AT THE SURFACE (CM): -1.E+07
 - MAXIMUM PONDING DEPTH (MM)...............................: 5


C PLANT WATER UPTAKE ASPECTS
C TTTTTTTTTTTTTTTTTTTTTTTTTT

 - INPUT FROM EXTERNAL FILE WATCROPWC? (Y/N) ...............: N

C KC-FACTORS
C ----------
C - IF THE CROP GROWTH MODEL IS USED
C    DO YOU WANT TO USE USE DVS UNITS FOR CROP STAGES? (Y/N).:
C   ELSE
C    DON'T ANSWER THE PREVIOUS QUESTION  (ONLY DATES ARE POSSIBLE)
C - NUMBER OF DATES OR DVS..................................: 1
C   NOTE IN CASE OF BARE SOIL, PUT KC EQUAL TO 1
C    DATES (M D) OR DVS  KC
C    -- --               --
     01 01               1.1
ET

C - IF THERE ARE NO PLANTS SKIP THIS SECTION
C   AND GO TO THE BOTTOM BOUNDARY SECTION

C INACTIVATION OF THE ROOTS NEAR THE SURFACE DUE TO SENESCENCE
C ------------------------------------------------------------
  - DATE WHEN ROOTS START TO BECOME INACTIVE    (M D) ........: 10 31
  - DATE WHEN ROOTS REACH THEIR MAX INACTIVITY (M D) ........: 10 31
  - DEPTH ABOVE WHICH  THERE IS NO WATER UPTAKE (MM) ........: 10

C LEAF AREA INDEX AND ROOTING DEPTH
C ---------------------------------
C - IF THE CROP GROWTH IS MODELED SKIP THIS SECTION
C   AND GOTO 'THE WATER SINK TERM VARIABLES'

C - SPECIFY A TIME SERIES OF LAI VALUES (ONE VALUE = CONSTANT)
C   M  D  LAI (M2/M2)
C   -- -- -----
    01 01 0.50
ET

C - SPECIFY A TIME SERIES OF EFFECTIVE ROOTING DEPTH (ONE VALUE = CONSTANT)
C   M  D  DRZ (MM)
C   -- -- --------
    01 01  650
ET
```

```
C WATER SINK TERM VARIABLES
C -------------------------
C - IS THE RELATION BETWEEN THE REDUCTION FACTOR OF THE
C   ROOT WATER UPTAKE (ALPHA) AND THE PRESSURE HEAD LINEAR? (Y/N).: N
C - SPECIFY THE VALUE OF THE PRESSURE HEAD BELOW WHICH THE ROOTS
C   START TO EXTRACT WATER FROM THE SOIL (CM) ....................: -10
C - SPECIFY THE VALUE OF THE PRESSURE HEAD BELOW WHICH THE ROOTS
C   START TO EXTRACT WATER OPTIMALLY FROM THE SOIL (CM) ..........: -50
C - SPECIFY THE VALUE OF THE PRESSURE HEAD BELOW WHICH THE ROOTS CAN NO
C   LONGER EXTRACT WATER OPTIMALLY
C                               AT A HIGH EVAPORATIVE DEMAND (CM).: -2000
C                               AT A LOW  EVAPORATIVE DEMAND (CM).: -2000
C - THE VALUE OF THE PRESSURE HEAD AT WHICH THE WATER
C   UPTAKE BY THE ROOTS CEASES (WILTING POINT) (CM) ..............: -16000
C - IS THE FUNCTION BETWEEN THE POTENTIAL ROOT WATER UPTAKE
C   AND DEPTH LINEAR ? (Y/N) .....................................: N
C     - IF "YES" SPECIFY THE PARAMETERS OF THE EQUATION
C      SMAX=ARER+BRER*ABS(DEPTH IN MM)
C       1 ARER (INTERCEPT) (DAY-1) ...............................:
C       2 BRER (SLOPE)  (DAY-1 MM-1) .............................:
C     - IF "NO" INPUT MAXIMAL ROOT WATER UPTAKE FOR EACH COMPARTMENT
C      COMP  SMAX
C            (DAY-1)
C      ----  ------
         1    0.013
         3    0.033
        10    0.033
        15    0.023
        26    0.000
ET

C WATER BOTTOM BOUNDARY CONDITION
C TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT

C - INPUT FROM EXTERNAL FILE WATBBC.WB? (Y/N)........................: N
C - IS THE GROUNDWATER LEVEL INPUT (MM)? (Y/N)   ....................: N
C    M  D  GWL
C          (MM)
C    -- -- ------


C - IS THE FLUX FROM THE SATURATED ZONE INPUT? (Y/N)................: N
C   IF THE FLUX FROM THE SATURATED ZONE IS INPUT THEN SPECIFY
C   - THE INITIAL GROUNDWATER LEVEL (MM)(REAL)......................:
C   - THE FLUX
C      M  D  FLUXSAT
C            (MM DAY-1)
C      -- -- ----------
C - IS THE FLUX FROM THE SATURATED ZONE CALCULATED? (Y/N)...........: N
C   IF THE FLUX FROM THE SATURATED ZONE IS CALCULATED AS
C   A FUNCTION OF THE GROUNDWATER LEVEL,THEN SPECIFY
C   - THE INITIAL GROUNDWATER LEVEL (MM)............................:
C   - THE PARAMETERS OF THE EQUATION
C     FLUX=AREL*EXP(BREL*ABS(GROUNDWATER LEVEL))
C       - AREL (MM DAY-1)...........................................:
C       - BREL (MM-1)...............................................:
C - IS THE PRESS. HEAD OF THE BOTTOM COMPARTMENT INPUT? (Y/N).......: N
C    M  D  PH
C          (CM)
C    -- -- ------
C - IS THE FLUX AT THE BOTTOM OF UNSATURATED ZONE ZERO? (Y/N).......: N
C - IS THE PROFILE DRAINING FREELY? (Y/N)...........................: Y
C - IS THERE A LYSIMETER BOTTOM BOUNDARY CONDITION? (Y/N)...........: N
```

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C WATER INITIAL VALUES
C TTTTTTTTTTTTTTTTTTTT

C - INPUT  FROM EXTERNAL FILE WATINIT.WI? (Y/N).......................: N
C - SHOULD THE PRESSURE HEAD (CM) AT EACH NODAL POINT BE CALCULATED
C   IN EQUILIBRIUM WITH THE INITIAL GROUNDWATER TABLE ? (Y/N)........: N
C   - IF "YES" THEN SKIP THIS SECTION
C      AND GOTO  SECTION 'WATER PRINTING CONTROL'
C     ELSE
C       CONTINUE
C - IS THE PRESSURE HEAD AT EACH NODAL POINT INPUT? (Y/N) .......... : N
C   - IF "NO"
C      GIVE THE INITIAL MOISTURE CONTENT (CM3 CM-3) FOR EACH COMPARTMENT
C     ELSE
C      GIVE THE INITIAL PRESSURE HEAD (CM) FOR EACH COMPARTMENT
C      COMP   PH OR MC
C            (CM OR CM3 CM-3)
C      --    --------
       1     0.740
       2     0.740
       3     0.740
       4     0.890
       5     0.890
       6     0.890
       7     0.890
       8     0.890
       9     0.890
      10     0.890
      11     0.750
      12     0.750
      13     0.750
      14     0.360
      15     0.360
      16     0.450
      17     0.450
      18     0.450
      19     0.450
      20     0.450
      21     0.450
      22     0.450
      23     0.450
      24     0.450
      25     0.450
      26     0.450
      27     0.450
      28     0.450
ET

C WATER PRINTING CONTROL
C TTTTTTTTTTTTTTTTTTTTTT

 - DETAILED ITERATION HISTORY (WAT_HISTOR.OUT)? (Y/N) ................: N
 - SUMMARY FILE (WAT_SUM.OUT)? (Y/N) .................  ......... .....: Y
 - CUMULATIVE TERMS OF THE WATER BALANCE (WAT_CUM.OUT)? (Y/N) .........: N
 - EVAPOTRANSP. AND GROUND WATER TABLE LEVEL (WAT_ET.OUT)? (Y/N)......: N
C TIME SERIES
 - PRESSURE HEAD        (PH.OUT)? (Y/N) ..............................: N
 - WATER CONTENT        (WC.OUT)? (Y/N) ..............................: Y
 - CUM. ROOT EXTRACT (CRTEX.OUT)? (Y/N) ..............................: N
```

WAVE input file:
WATDATA.IN