Biogeochemical and hydrological controls on phosphorus transport in a floodplain fen

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Abstract

This study investigates the biogeochemical c ontrols on the release of phosphorus (P) from riparian wetland sediments to solution, and the subsequent delivery of P to receiving waters. The research was conducted at Strumpshaw Fen, a riparian wetland in the floodplain of the River Yare in the UK. Novel mesocosm work identifies the reductive-dissolution of iron-bound P as the dominant control on P release to solution. The timing of P release to pore water and surface water is also influenced by the concentration of nitrate-nitrogen in floodwater, because redox potential is poised above the l evel n ecessary f or t he r eduction o f ferric i ron w hilst n itrate r emains i n s olution. Field-based hydrochemical monitoring confirms the findings from laboratory mesocosm work on the controls on P release to solution, and indicates that P concentrations indicative of hypereutrophic conditions may be established in the pore water and surface water of this riparian wetland. Sequential filtration establishes that the vast majority of the MRP fraction in 0.45 µm filtrates may be composed of free orthophosphate.

An investigation of hydrological connectivity between the shallow peat and (i) the underlying mineral aquifer and (ii) the adjacent open-water network is used to indicate whether P in solution might be exported from the peat in large quantities. Reliable characterisation of the hydraulic conductivity (K) of the peat deposits at Strumpshaw Fen is achieved after a thorough evaluation of the piezometer technique, and the application of a novel laboratory-based method. K is found to be relatively high, indicating a potential for substantial flows of water between the near-surface peat and the ditch network at the site, given suitable hydraulic gradients. Field-based hydrological monitoring suggests that lateral exchanges between the peat and adjacent open-water bodies are more important than vertical exchanges between the peat and the underlying mineral aquifer. It is shown that the combination of P availability and hydrological connectivity between the peat and open water, will result in bioavailable P reaching the ditch network at Strumpshaw. In the light of these findings, riparian fen wetlands should not be assumed *a priori* to be 'protectors' of the chemical and ecological quality of receiving waters, but may in fact be sources for significant quantities of P that have the potential to be exported from the fen system.

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1. INTRODUCTION TO AND JUSTIFICATION FOR THE RESEARCH

1.1 Background and justification

> "Quantification of nutrient and organic matter sources, transformations, and sinks at the catchment/floodplain scale is a major challenge in ecology" (Tockner *et al.*, 2002).

This challenge has been given a strong legislative context by the recently implemented European Union Water Framework Directive (WFD) (European Parliament, 2000), which requires management at the catchment-scale to improve the chemical and ecological quality of freshwaters. The WFD is likely to be a major driver of freshwater research over the next decade, because our understanding of nutrient and organic matter sources, transformations, and sinks at the catchment-scale remains incomplete.

Within catchments, wetlands are unique ecosystems in the continuum of terrestrial to aquatic environments (Aerts *et al.*, 1999), often at the interface between upland areas and receiving water bodies (Prior and Johnes, 2002; Reddy *et al.*, 1999). This interface has become a focus for academic and applied interest, due to the potential for wetlands to mediate anthropic impacts from upland regions before they reach economically and environmentally valuable receiving waters (Burt *et al.*, 2002). Wetlands may regulate the dissolved pollutant (including nutrient) and suspended sediment loads delivered to adjacent rivers, lakes and coastal waters. Therefore, wetlands could represent an important catchment element contributing to the improvements in the chemical and ecological quality of freshwaters required by the WFD.

The role of interfaces between pollutant source areas and receiving water bodies is of growing importance because of contemporary nutrient enrichment of surface waters (Bowes *et al.*, 2003). The process of eutrophication, usually a result of excessive

concentrations of nitrogen (N) and phosphorus (P), is *the* major source of surface water quality degradation in the United States (Carpenter *et al.*, 1998). In the UK, many surface water bodies have seen a trend of increasing N and P concentration in recent years (DEFRA 2002; English Nature, 2002), and eutrophication has been identified as a priority environmental issue (Environment Agency, 2000). Eutrophication can result in habitat loss and is a factor in the reduction of aquatic biodiversity (DEFRA, 2002; Seehausen *et al.*, 1997). There are also consequences for human use of water resources, including potentially damaging health effects, particularly associated with high nitrate levels in drinking waters (Carpenter *et al.*, 1998). Nutrient input to surface waters can come from both point and diffuse sources. The relative ease with which point sources, such as municipal sewage treatment works, can be identified and regulated has reduced the role they play in nutrient delivery to receiving waters. Instead, the focus has shifted to diffuse loads of N and P, mainly from agricultural and urban sources, because these are c urrently t he d ominant i nputs o f n utrients to s urface w aters i n m any parts o f t he world (DEFRA, 2002; Heathwaite *et al.*, 2000; Uusi-Kämppä *et al.*, 1997).

Wetlands in the riparian zone are perhaps the most obvious example of systems at the interface between upland areas and receiving waters. The definition of the riparian zone has evolved, and now includes areas of land adjacent to a channel, such that the river floodplain and the riparian zone are often taken t o mean the same thing (Burt *et al.*, 2002). The potential importance of wetlands within the riparian zone with respect to the control of diffuse nutrient loads has been recognised in recent research (e.g. Novak *et al.*, 2004; Vellidis *et al.*, 2003; Venterink *et al.*, 2003). This recognition is linked to the common conception of wetlands as sinks for nutrients (e.g. Soto-Jimenez *et al.*, 2003; Craft and Casey, 2000; Mitsch *et al.*, 1995), a concept based on the near-unique combination of chemical, physical and biological conditions found in these systems. Features such as the sedimentation of particulate matter, adsorption and precipitation of nutrient elements, and uptake by macrophytes and microorganisms, mean that wetlands may retain both N and P. In addition to net removal, wetlands may also transform nutrients from fractions that are immediately biologically available to those that require alteration before uptake and utilisation by primary producers (Reddy *et al.*, 1999). This reduces the likelihood of ecologically significant nutrient enrichment of receiving waters, i.e. nutrient enrichment that results in changes to ecosystem structure or function.

However, to assume *a priori* that riparian wetlands are nutrient sinks, protecting the environmental quality of receiving waters, is to oversimplify the complex nature of both nutrient cycling within these systems, and the delivery of solutes to receiving waters. The complexity of these processes can be highlighted using three specific examples.

Firstly, the removal of one nutrient element from water flowing into and through a riparian wetland may be dependent on factors that concurrently promote the release of a different element into solution. The reduction-oxidation (redox) conditions in wetlands can lead to the substantial removal of nitrogen, often through the reduction of nitrate to gaseous end products (Soto-Jimenez *et* al., 2003; Ross, 1995; Howard-Williams, 1985; Reddy *et al.*, 1980). The process is micobially mediated, whereby denitrifying bacteria use nitrate as a terminal electron acceptor in the absence of oxygen. A sufficient source of organic carbon, and an anaerobic environment alongside a supply of nitrate are required, characteristics met by certain wetland systems. However, the presence of anaerobic conditions has been shown to promote the release of biologically available forms of P in non-wetland environments, through the reductive-dissolution of iron-phosphate compounds. For example, early work by Patrick *et al.* (1973) demonstrated that large quantities of iron and phosphorus could be liberated under reducing conditions from strengite ($FePO_4.2H_2O$), a stable mineral under oxic conditions. Therefore, whilst representing a sink for some nutrients, wetlands may at the same time release other elements from previously biologically unavailable forms. Given this, prioritising the retention of one nutrient element over another may be necessary if optimal riparian-zone conditions are to be defined (Burt *et al.*, 2002).

Secondly, the efficiency with which a given wetland retains nutrients may vary through time. This is particularly true for P, where the capacity for retention is 'consumed' as phosphorus is input to system. The capacity is not regenerated because, unlike the cycling of N where gaseous end products are produced and subsequently released to the atmosphere, there is no obvious 'removal' mechanism for P. The production of phosphine gas under anoxic conditions presents a possible means for the escape of P from wetland sediments, but this mechanism has rarely been investigated (Soto-Jimenez *et al.*, 2003). Several studies have reported that after a period of nutrient retention, wetlands experiencing substantial phosphorus loadings may retain P less efficiently, and could potentially release phosphorus into solution (e.g. Reddy *et al.*, 1999; Craft and Richardson, 1993; Richardson, 1985). Further, to define a given wetland as a source or

sink for P requires an understanding of the different fractions of the total phosphorus load and how these fractions are cycled within the system. Novak *et al.* (2004) highlighted the potential for wetlands to represent both sink and source areas for dissolved phosphorus at different times. Whilst wetlands may be an effective sink for particulate phosphorus, their impact on loads of dissolved phosphorus is often less certain (Uusi-Kämppä *et al.*, 2000). Given that the dissolved phosphorus fraction is often equated with free orthophosphate, although sometimes incorrectly (Baldwin *et al.*, 2003; Baldwin, 1998), and that free orthophosphate is assumed to be immediately biologically available (House 2003), the net export of dissolved P from wetlands may have significant impacts upon the ecology of receiving waters.

Thirdly, physical, chemical and biological processes affecting the cycling of nutrients within wetlands are rarely considered in the context of how a system functions hydrologically (Buttle, 2002; Correll, 1997). This limits both our process understanding and our ability to interpret the wider-scale implications of chemical process findings. The lack of integrated hydrological and hydrochemical studies is despite the fact that the role of hydrological factors in wetland chemical processes has been recognised for some time (e.g. Reddy *et* al., 1995; Craft and Richardson 1993; Verhoeven *et al.*, 1990). At various scales, hydrological functioning will strongly influence the role of wetlands in nutrient cycling and delivery to receiving waters. At the larger-scale, issues such as the d egree o f h ydrological c onnectivity b etween a w etland a nd r eceiving w ater b ody will be fundamentally important to the role wetlands play in influencing nutrient and sediment loads delivered to receiving waters (Heathwaite *et al.*, 2000). Such connectivity is at the heart of how channel systems and their associated riparian zones should be perceived at the landscape level; whether the channel is 'separated' from other elements of the landscape, or 'connected' by flows across the channel-riparian zone boundary (Wiens, 2002). Hydrological factors will control soil saturation, water flow path and residence time, which in turn will determine the potential for wetlands to influence the chemical quality of water that passes through them (Burt *et al.*, 2002).

1.2   Research aim and objectives

It is notable that riparian wetlands present a particular problem when attempting to integrate these systems within catchment-scale management plans, such as those associated with the WFD. This appears to be for two main reasons. Firstly, there remain

substantial gaps in our understanding of the processes controlling nutrient cycling within riparian wetland sediments, particularly with respect to P (Novak *et al.*, 2004; Vellidis *et al.*, 2003). These gaps affect our ability to classify wetlands as sources or sinks for nutrients within a catchment. Secondly, there is little evidence in the research literature of work that investigates the degree of hydrological connectivity between wetlands and other catchment elements, and combines hydrochemical process information with hydrological connectivity to examine the implications of nutrient availability within a given wetland at different spatial scales.

Given these problems, the principal research aim for the current project can be defined as follows:

> To investigate the biogeochemical processes controlling phosphorus release from riparian wetland sediments, and to use hydrological connectivity between the wetland and other catchment elements to examine the delivery of phosphorus to receiving waters.

This will be achieved through a combination of laboratory mesocosm work and field-based hydrological and hydrochemical monitoring, in a typical riparian wetland. Five research objectives are identified that will be addressed to achieve the stated aim:

1) Characterise accurately the hydraulic properties of the near-surface sediments in a typical riparian wetland, through the development of novel methods where necessary.

2) Examine the exchange of water between the near-surface wetland sediments and deeper ground water and open water.

3) Investigate the processes involved in the sediment – pore water – surface water P dynamics, and the rates at which these processes operate.

4) Characterise the forms of phosphorus present in a typical riparian wetland sediment and examine the field-scale availability of P within the system.

5) Combine chemical process information on P availability in wetland pore water and surface water with hydrological connectivity, to examine the delivery of P to receiving waters.

1.3 Phosphorus cycling in riparian wetlands

1.3.1 A focus on phosphorus

The foci for this research are the processes controlling phosphorus retention and release in riparian wetlands, and those governing the subsequent delivery of P to receiving water bodies. Compared with nitrogen, the influence of riparian zone processes on P loads has received little attention (Vellidis *et al.*, 2003; Carlyle and Hill, 2001). This is surprising because phosphorus is a key nutrient element that may limit primary productivity in many freshwater ecosystems (House, 2003; Zhang and Oldham, 2001; Environment Agency, 2000), and wetland bacterial communities have recently been shown to be phosphorus limited (Sundareshwar *et al.*, 2003). Indeed, the occurrence of eutrophication in lakes and rivers has primarily been linked to the excessive delivery of phosphorus to these systems (Bowes *et al.*, 2003; Jordan and Rippey, 2003; Carlyle and Hill, 2001). Major sources of diffuse P include agriculture (both fertilizer and manure) and runoff from urban areas (DEFRA, 2002; English Nature, 2002; Heathwaite *et al.*, 1996). For both fertilizer and manure, the problems are related to excess application rates. Only approximately 30 % of the P applied as agricultural fertilizer in the UK is removed in produce, the remaining 70 % is either incorporated into the soil or is exported to surface waters. As a consequence, the phosphorus content of the world's agricultural soils has increased by approximately 25 % between 1950 and 1995 (Carpenter *et al.*, 1998). Therefore, not only do agricultural practices lead to export of P via runoff to surface waters, they are also rapidly 'consuming' the capacity of the world's soils to retain phosphorus. In the future, very large increases in diffuse P loads are possible, related to the growing store of phosphorus in agricultural soils and increased human pressures on agricultural practices and urban areas (Carpenter *et al.*, 1998). Given this, understanding how phosphorus is cycled within different catchment elements, including riparian wetlands, is likely to become increasingly important.

The potential for the delivery of P to receiving waters to influence the ecological quality of that water body is dependent on both the concentration in solution and also the degree of bioavailability associated with the particular form of phosphorus being delivered (Hens and Merckx, 2002). The orthophosphate ion represents the fraction of total P that is considered to be directly available and consumed by bacteria and algae (Hens and Merckx, 2002; Zhang and Oldham, 2001; Robards *et al.*, 1994), and as such

may rapidly contribute to the process of eutrophication if delivered in sufficient quantities alongside other required elements. Organic and condensed forms of P are less biologically available as they are retained within, or attached to, organic complexes/inorganic compounds (Haygarth *et al.*, 1997). They may become biologically available, but only upon transformation to free inorganic forms, which in turn is dependent on the biotic and abiotic processes acting on them in receiving waters (Reddy *et al.*, 1999; Sharpley *et al.*, 1991). Therefore, dissolved organic P and particulate P represent fractions that maintain a potential risk to ecological quality in the future. An assessment of the role of riparian wetlands with respect to the chemical quality of receiving waters must address both the concentration and the form of P present within wetland pore water and surface water.

1.3.2 Processes affecting phosphorus cycling in riparian wetlands

1.3.2.1 The influence of vegetation

One of the major processes by which nutrients may be retained in wetlands is through uptake and storage by macrophyte communities. The efficiency of these processes will depend on both the vegetation type and the associated growth characteristics (Reddy *et al.*, 1999). Much debate surrounds the relative roles of nutrient uptake from surface water and uptake from wetland pore water (Ross, 1995). The balance between the two will depend on the relative proportion of roots in the substrate and in the surface water. Floating macrophytes take nutrients directly from the water column, but represent only a short-term store of P because nutrients are returned to solution during decomposition of dead plant material (Mitsch *et al.*, 1995; Reddy *et al.*, 1995). For emergent macrophytes in non-floating wetlands, a major source of nutrients is through adsorption from the substrate rather than directly from the water column (White *et al.*, 2004). Although some species such as *Phragmites australis* Cav. (Streud.) do have 'water' roots (Howard Williams, 1985), the vast majority of the nutrient requirements of emergent macrophytes appear to be sourced from pore water (White *et al.*, 2004; Wetzel, 1990).

Seasonality in the uptake of nutrients by macrophytes has been observed, with maximum rates occurring either during initial periods of growth (e.g. Boyd and Vickers,

1971) or during the peak growing season (e.g. Wilkins, 1984). A further important seasonal aspect of the P cycle related to vegetation is the potential for internal transfers of phosphorus and other nutrients within macrophytes. Many species have the potential to transfer P from above-ground structures to roots and rhizomes at the end of the growing season before senescence, and then to utilise these stores to promote the growth of new shoots in the following spring (Reddy *et al.*, 1999). Up to 45 % of P lost from living shoots of *Typha glauca* may be transferred to root and rhizome structures (Davis and van der Valk, 1983), whilst between 35 % and 45 % of the shoot uptake of P by sedges such as *Carex lasiocarpa* Ehrh. was shown to be transferred in the same way (Richardson and Marshall, 1986). Internal transfers have been suggested as a mechanism of nutrient conservation for wetland macrophytes when external supplies of a given element are low, and may account for half of the annual flux of phosphorus through these plants (Howard Williams, 1985).

Wetland vegetation may not constitute a long-term store of phosphorus. The annual production of litter leads to complex processes of leaching and decomposition, which may return nutrient elements to wetland surface water and pore water. Vegetation material produced by the death of above-ground structures is subject to aerobic and anaerobic decomposition, depending on the hydrological conditions and the availability of terminal electron acceptors. Consequently, nutrients may be returned to the water column and refractory material deposited on the sediment surface. Over 90 % of phosphorus in the detrital material from some macrophyte species can be returned to the water column by leaching or decomposition (Reddy *et al.*, 1995). Mason and Bryant (1975) showed that, on average, 1.3-2.7 kg P ha^{-1} yr^{-1} was released to the surface water in a UK fen from decaying plant material. Richardson and Marshall (1986) suggested that around 35 % of the annual uptake of P to above-ground structures was returned to the soil litter, and of this 32 % was lost by mineralisation and leaching, equal to 0.6 kg P ha^{-1} yr^{-1}. Both Davis and van der Valk (1983) and Howarth and Fisher (1976) provide evidence suggesting that, depending on the nutrient status of the wetland, decomposition may lead to the net uptake of nutrients from surface water rather than the net return. Under nutrient-rich conditions, decomposing tissue may form a locus for the net uptake of nutrients by microorganisms from the surface water, whereas in an oligotrophic system net nutrient release to solution may occur. The death of below-ground structures such as roots and rhizomes can potentially lead to the leaching of nutrients back into pore water, and the deposition of refractory materials within the

wetland soil (Reddy *et al.*, 1999). However, the magnitude of P release from below-ground structures is likely to be far lower than from litter deposited on the sediment surface (Richardson and Marshall, 1986).

The net impact of emergent macrophyte uptake may be analogous to a 'pump' effect, whereby nutrients are transferred from the substrate to macrophyte biomass, and subsequently to surface water upon decomposition of dead plant material (Howard Williams, 1985). Alternatively, by removing nutrients from pore water, emergent macrophytes may contribute to a concentration gradient driving the diffusion of P from surface water into the pore water, thereby indirectly reducing the surface-water nutrient concentration (Reddy *et al.*, 1999).

The mineralisation of organic P is a major source of this nutrient to wetlands, and is closely linked to the decomposition of vegetation-derived detritus (Aerts *et al.*, 1999; Verhoeven *et al.*, 1990). The relatively slow rate of organic matter decomposition in wetlands means that nutrients are less rapidly liberated than is the case in many other ecosystems, although some evidence does challenge the direct positive relationship between decomposition and mineralisation rates (e.g. Verhoeven *et al.*, 1990). The rate of decomposition and mineralisation is strongly related to the chemical quality of the detritus. The existence of decay inhibitors and decay-resistant compounds in some species of wetland plant, reinforces the low rates of decomposition associated with wetland abiotic conditions (Aerts *et al.*, 1999). Perhaps the most significant abiotic factor influencing decomposition is the existence of an anaerobic compared to aerobic environment. The flooding of wetland sediments rapidly leads to oxygen depletion, because oxygen is used during aerobic respiration at a rate that cannot be sustained by diffusion from the atmosphere, given that the rate of oxygen diffusion through water is approximately 10 000 times slower than through air (Ross, 1995). Decomposition can still occur under anoxic conditions (e.g. Soto-Jimenez *et al.*, 2003) and is dependent on the action of facultative or obligatory anaerobic decomposers (Patrick and Delaune, 1972). These organisms use a suite of terminal electron acceptors in a sequence related to the degree of sediment reduction, resulting in interactions between the carbon cycle and those of nitrogen, manganese, iron and sulphur (e.g. Feijtel *et al.*, 1988; Delaune *et al.*, 1981; Patrick and Delaune, 1972).

It is conventionally assumed that carbon mineralisation rates are more rapid under conditions of aerobic rather than anaerobic oxidation of organic substrates (Baldwin and Mitchell, 2000). This is associated with a number of factors. Firstly, there is a smaller number of facultative or obligatory anaerobic decomposers than aerobic. Secondly, some important functional groups of decomposers, such as aerobic fungi and bacteria, are absent in anaerobic environments (Swift and Posner, 1972). Finally, the efficiency of the energy transfer is reduced when microbes use terminal electron acceptors other than oxygen (McLatchey and Reddy, 1998). The slower rate of organic matter decomposition under anaerobic conditions may limit the availability of nutrients in wetland systems. However, a further complicating factor exists, associated with the combination of the end products of anaerobic decomposition. Caraco *et al.* (1989) demonstrated how the interaction of ferrous iron and sulphide, produced by the utilisation of ferric iron and sulphate as terminal electron acceptors respectively, could affect the availability of phosphorus in aquatic systems. They suggest that ferrous iron and sulphide could combine to form insoluble iron sulphides in anoxic sediments. This would p revent t he r e-supply o f i ron o xides u pon a s witch t o a erobic conditions, a nd would also inhibit the formation of ferrous phosphate minerals, such as vivianite. Both factors could lead to increased availability of P for uptake by primary producers.

1.3.2.2 The impact of microorganisms

The net role for microorganisms in the retention of phosphorus by wetlands can be very substantial. Sloey *et al.* (1978), for example, suggest that approximately 60 % of the retention o f p hosphorus i n c ertain w etland s ystems c an b e a ttributed t o t he a ction o f microorganisms. However, the potential for both gross retention and release of phosphorus by microorganisms should be considered. The importance of microorganisms in the decomposition of organic matter and subsequent mineralisation and release of phosphorus was highlighted in Section 1.3.2.1. In contrast to these functions, which may lead to the release of P, microorganisms have also been shown to remove phosphorus directly from the water c olumn. Richardson and Marshall (1986) demonstrated how increased loading of P in surface water could be regulated through uptake by microorganisms, in preference to increased uptake by macrophytes or adsorption in the peat matrix. Under nutrient-enriched conditions this consumption of P, related to the formation of polyphosphate, may substantially reduce water-column

phosphorus concentration. Conversely, under more oligotrophic conditions, hydrolysis of polyphosphate may contribute P to the water column (Reddy *et al.*, 1999). Other research suggests a similar pattern of uptake and release of P through the dynamics of polyphosphate, but driven by redox conditions. Specifically, that in an anaerobic environment, P previously taken up by microorganisms under aerobic conditions through the formation of polyphosphate may be released to the water column after hydrolysis (Davelaar, 1993; Gächter and Meyer, 1993; Gächter *et al.*, 1988). In a similar manner as described for macrophyte litter in Section 1.3.2.1, the death of microorganisms results in the generation of detritus and the potential for subsequent release of P during decomposition and mineralisation.

Where there are spatial or temporal divisions between oxic and anoxic sediments, the principal source of liberated phosphorus is the anoxic zone, particularly in non-calcareous sediments where phosphorus cycling is strongly influenced by iron (Baldwin and Mitchell, 2000). Within such sediments, microorganisms play a significant role in the processes leading to P release. One important mechanism relates to the utilisation of ferric iron as a terminal electron acceptor in the anaerobic decomposition of organic material by iron-reducing bacteria. The reduction of ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}) can lead to the liberation into solution of large quantities of Fe^{2+}, and also of anions such as phosphate that were associated with Fe^{3+} prior to reduction (Pant and Reddy, 2003; Baldwin and Mitchell, 2000; Khalid *et al.*, 1977; Patrick and Khalid, 1974; Patrick *et al.*, 1973). The role that microorganisms play in this mechanism of P release has been well demonstrated (e.g. Roden and Edmonds, 1997; Lovley *et al.*, 1991). Further, the possible interaction of Fe^{2+} with other bacterially generated decomposition end products, specifically sulphide, and the consequences for P availability were highlighted in Section 1.3.2.1.

1.3.2.3 The interaction of phosphorus with wetland sediments

One of the major mechanisms by which wetland systems retain phosphorus is through providing an environment suitable for the sedimentation of organic and inorganic particulate material (Mitsch *et al.*, 1995; Howard-Williams, 1985). Processes such as the deposition of detritus from floating macrophytes or after the death of microorganisms in the water column, can contribute greater quantities of particulate

matter, and potentially P, to wetland sediments than sedimentation from inflowing waters (Reddy *et al.*, 1999). Despite this, the reduction of the sediment load in inflowing waters remains an important mechanism by which wetlands retain P. In terms of riparian systems, sedimentation may occur from water originating from both upslope inputs and over-bank flooding events from the channel (Correll, 1997). As a consequence of the lack of channelized flow through wetlands, and the interaction of flow with often dense vegetation stands, the hydraulic roughness of wetlands is often much greater than that of adjacent open-water channels. This results in decreased flow velocities and sediment transport capacity, and therefore deposition of particulate material and associated phosphorus, in both organic and inorganic forms (Uusi-Kämppä *et al.*, 1997; Hammer, 1992; Howard-Williams, 1985). However, some research suggests that a substantial proportion of the particulate phosphorus load may be bound to particles that are too small to be deposited in wetland systems (Brown *et al.*, 1981). Further, given sufficiently high flows, wetlands may actually represent source areas for nutrients due to the erosion of nutrient-enriched particulate matter from the sediment surface (Fleischer *et al.*, 1994). Following the deposition of particulate material, both biotic and abiotic processes may alter the associated P, potentially leading to subsequent release to either surface water or pore water (Reddy *et al.*, 1999), thereby reducing the potential for long-term, stable retention of P in deposited particulate material.

Phosphorus cycling within wetland sediments is further influenced by a combination of sorption/desorption and precipitation/dissolution reactions (Reddy *et al.*, 1999; Russell and Maltby, 1995; Richardson, 1985). Sorption is often perceived to be a two-stage process (House *et al.*, 1998). Initially rapid removal of P from solution is due to adsorption onto the surface of the solid phase. This can occur as chemisorption to protonated surface sites or by the replacement of surface hydroxides (Ryden *et al.*, 1972; Bache, 1964). Following this is a slower phase that may last for several hours. This second phase may continue without reaching an equilibrium, and is associated with precipitation of P, diffusion of phosphorus into the structure of the solid phase involved in the sorption process, or microbial uptake (House *et al.*, 1998; Barrow, 1983).

Sorption reactions are influenced by pH conditions. Both the charge of the P species in solution, and the surface charge on the mineral particles are pH dependent (House *et al.*, 1998). The adsorption of P from solution is also strongly related to the chemical composition of the sediment. In acid soils oxides, hydroxides and oxyhydroxides of

iron, aluminium and manganese are thought to govern P sorption. In alkaline soils calcium and magnesium are the dominant elements that react with P through, for example, the sorption of P to calcite (House, 2003; Pant *et al.*, 2002b; Pant and Reddy, 2001b; Reddy *at al.* 1999). In many cases the oxides, hydroxides and oxyhydroxides of iron and aluminium are the principal soil constituents that control the sorption of P (Freese *et al.*, 1992; Richardson, 1985; Khalid *et al.*, 1977). In some cases, iron or aluminium complexed with organic matter may be responsible for the removal of P from solution (e.g. Hens and Merckx, 2002; Shaw *et al.*, 2000; Jones *et al.*, 1993).

The propensity that metal oxides have for ion adsorption is linked to their mineralogy (Knapp *et al.*, 2002). Iron and aluminium oxides and hydroxides can exist in either crystalline or amorphous forms, with the latter being more characteristic of soils subject to periodic changes (Russell and Maltby, 1995), such as the seasonal and sub-seasonal fluctuations in the water-table position in many riparian wetland sediments. As iron and aluminium oxides and hydroxides age, they become more crystalline (Darke and Walbridge, 2000). The degree to which their amorphous or crystalline forms predominate within a given soil will have consequences for the effectiveness of P sorption. Amorphous forms of iron and aluminium are able to adsorb far greater amounts of phosphorus than crystalline forms due to their larger surface area, which exposes a greater number of reactive sites (Darke and Walbridge, 2000; Mclaughlin *et al.*, 1981). Given a role for iron in the sorption of P within wetland sediments, consideration must be given to the impact of redox conditions on P solubility (Reddy *et al.*, 1995). Under oxidised conditions, amorphous and crystalline iron oxides adsorb P. On the reduction of Fe^{3+} during the anaerobic decomposition of organic matter by iron-reducing bacteria, soluble Fe^{2+} and P can be released into solution. This may represent only a temporary release, because reduced forms of iron may readsorb P from solution or ferrous-phosphate minerals may precipitate (Roden and Edmonds, 1997). However, although the number of reactive sites for P adsorption to iron may be greater under reduced conditions, the binding energy associated with the adsorption is low, and therefore the potential for subsequent desorption remains high (Patrick and Khalid, 1974).

The potential for a given wetland sediment to retain P from inflowing waters by sorption will be governed by two main factors. Firstly, the capacity of the medium to adsorb P, which will be determined by the maximum number of sorption sites and the

level of phosphorus already retained (Reddy *et al.*, 1999). Secondly, the binding strength with which P is adsorbed to the solid phases, which will affect the potential that exists for desorption of P back into solution. The balance between these factors is described in the concept of an Equilibrium Phosphate Concentration (EPC$_0$), defined as the concentration of orthophosphate in solution in contact with natural sediment that produces no net sorption or desorption of orthophosphate over 24 hours (House, 2003). For example, under oxidised conditions, and with high soil amorphous iron oxide content, there is likely to be a low EPC$_0$, because P originally in solution will become tightly bound to the abundant solid iron phase. The balance between the EPC$_0$ and the P concentration in waters flowing into wetland systems will determine whether sorption or desorption predominates. Given a situation of low EPC$_0$ and high P concentration in inflowing waters, retention of P by sorption is likely.

Precipitation reactions involve the combination of soluble ions to form a new compound when there is an excess of these ions in solution (Stumm and Morgan, 1996). The co-precipitation of phosphorus with calcite, or the formation of calcium phosphates, may occur in the water column of wetlands, depending on concentrations of calcium and phosphorus in solution, and driven by fluctuations in pH (House, 2003; House *et al.*, 1998; House and Donaldson, 1986). Calcite precipitation, and therefore co-precipitation of P, may be inhibited by high concentrations of phosphorus or dissolved organic carbon in solution (Neal *et al.*, 2002). Other geochemical reactions are important within the sediment column. Under the anoxic conditions found in many wetland sediments, high concentrations of dissolved iron may exist in pore water. If sufficiently elevated concentrations of dissolved P also exist in the same pore water, then the precipitation of ferrous phosphate minerals may occur, one of the most common being vivianite (Fe$_3$(PO$_4$)$_2$.8H$_2$O) (House, 2003; Roden and Edmonds, 1997; Hearn *et al.*, 1983). Vivianite is likely the most stable ferrous phosphate mineral found in recently deposited sediments (Nriagu, 1972) and is therefore of particular interest in the context of long-term retention of P by wetlands. The precise mechanism involved in the formation of vivianite remains uncertain (House, 2003), and super-saturation of water with respect to the mineral does not always lead to its precipitation (e.g. Mayer *et al.*, 1999). Iron oxides that have adsorbed P from solution may become buried and later reduced. Subsequent reductive dissolution may release ferrous iron and P into solution, potentially leading to super-saturation with respect to vivianite and precipitation of this mineral (Manning, 1981). Alternatively, the formation of vivianite may occur through

the reduction of ferric deposits without the dissolution of iron and P (Nembrini *et al.*, 1983). Further questions surround the potential for vivianite to regulate the increased concentrations of pore-water phosphorus resulting from the reductive-dissolution of solid ferric iron phases (Roden and Edmonds, 1997). Sulphide, formed through sulphate reduction, may influence the role of vivianite in the control of P concentration. Factors such as the displacement of the phosphate anion from the insoluble ferrous phosphate compound by the sulphide anion, or the removal of ferrous iron from solution through the formation of insoluble iron-sulphide, may increase the concentration of P in solution (Roden and Edmonds, 1997; Caraco *et al.*, 1989).

1.3.3 Phosphorus transport in wetlands

The movement of P through wetland sediments, and the export to receiving waters, is unlikely to be directly comparable with the flow of water through the system, due to the various interactions between the different forms of P and wetland vegetation, microorganisms and sediments (Ross, 1995). The entrainment and transport of particulate phosphorus that has settled out on the sediment surface is unlikely in wetlands, except during more extreme flow events with sufficient water velocity to resuspend and transport particulate matter (Reddy *et al.*, 1999). In riparian systems, such events can be associated with over-bank flooding from the channel, and may result in the net export of P from the wetland.

Dissolved phosphorus, and P associated with suspended colloidal fractions, can be transported in both surface water and pore water. The flow of water, and associated advection of dissolved and colloidal P fractions, is driven by gradients of hydraulic head, with flow occurring from areas of higher to areas of lower head. In pore water, the translation of a potential for flow as determined by the hydraulic gradient, into actual flow, is dependent upon the hydraulic conductivity of the wetland sediment. Given a combination of high hydraulic conductivity and large hydraulic gradients, a substantial flow of water, and associated advection of solutes, may occur through wetland sediments.

Given that pore-water P concentrations are often in excess of those in the overlying water column (e.g. Pant and Reddy, 2003; Soto-Jimenez *et al.*, 2003; Fisher and Reddy,

2001), the diffusion of P from pore water into the surface water may also be an important transport mechanism in wetlands. The persistence of the concentration gradient, and its direction, will be determined in part by the renewal of the overlying water column. Given a frequent renewal with water with a low concentration of P, the gradient driving the flux from pore water to surface water may be maintained. However, where replacement of the surface water does not occur, or where the replacement water is of higher P concentration, the flux from pore water may decrease, or flux direction may reverse resulting in the diffusion of P into the wetland sediment (Moore *et al.*, 1998). In systems where redox-sensitive elements are important, simple concentration gradients of P between pore water and surface water do not guarantee the delivery of phosphorus to the overlying water column. The physicochemical conditions at the boundary between pore water and surface water may regulate the flux of P into the overlying water column (Mayer *et al.*, 1999; Moore *et al.*, 1998). Further, Fisher and Reddy (2001) and Mayer *et al.* (1999) have demonstrated how fluxes of P from pore water to overlying water may be generated by solute transport due to bioturbation or gas ebullition, in some cases the flux being at least as significant as that due to advection and diffusion.

Much previous work has suggested that the hydraulic conductivity of many wetland deposits is relatively low (see the summary in Chason and Siegel, 1986). Consequently, it is often assumed that the advection of solutes is unlikely to be as significant a transport mechanism as diffusion (Devito *et al.*, 1997). However, this ignores the potentially large differences in the hydraulic properties of wetland deposits, both between individual sites and within a given peat profile. It also fails to consider the strongly fluctuating hydrological conditions, such as water-table position, observed in many riparian wetlands, a consequence of exchanges of water with adjacent channel networks. Further, it is extremely rare to see rigorous test and analysis procedures in studies of the hydraulic conductivity of wetland sediments (cf. Baird *et al.*, 2004; Brown and Ingram, 1988), so that estimates of hydraulic conductivity and the conclusions drawn in these studies regarding the potential for water flow through wetland sediments may be in error. It is possible that the role of advection as a transport mechanism for solutes in wetland deposits, including phosphorus, has been under-estimated in previous work.

1.4 Integrating hydrological factors within studies of phosphorus cycling in riparian wetlands

Water exchanges between wetland sediments and other water bodies can have a profound influence upon the hydrological, microbiological and chemical functioning of wetland systems (Beckwith *et al.*, 2003a; Mann and Wetzel 2000; Devito *et al.*, 1997). Despite the fact that hydrological factors can influence both the processes that regulate P availability in riparian wetlands, and the delivery of phosphorus to receiving water bodies, only rarely have the linkages between chemical and hydrological processes been elucidated in previous wetlands research.

At the macro-scale, the fundamental formation and persistence of a wetland is dependent upon hydrological factors, namely the detention and/or high rate of water supply (Wheeler, 1999). The water source to a given wetland will determine many of the general chemical characteristics of the system, for example the contrast between many bogs and fens in terms of pH status, nutrient and metal contents (Aerts *et al.*, 1999). Hydrological factors also have a bearing on the processes that control the cycling of phosphorus within wetland sediments. The input of external solute loads, including P, to a wetland is dependent on hydrological connectivity between the system and i) ground water, ii) overland and sub-surface flow from upland regions, and iii) over-bank or sub-surface flow from adjacent bodies of open water. Hydrological factors such as the timing and duration of sediment submergence, and seasonal water-table range, will influence redox related reactions, which in turn may control the availability of P (Reddy *et al.*, 1995). The hydraulic properties of wetland deposits, and the nature of the hydraulic head distribution within a wetland, and between a wetland and receiving waters, will determine the residence time of water within a system, and therefore the potential for dissolved and particulate P loads to be affected by the nutrient cycling processes described in Section 1.3.2. Finally, the degree of hydrological connectivity between a riparian wetland and receiving water bodies will determine catchment-scale implications of P concentrations in wetland pore water and surface water (Heathwaite *et al.*, 2000; Hunt *et al.*, 1999). However, due to the difficulties associated with examining the cycling of P in the field, most previous research has been conducted in the laboratory (e.g. Pant *et al.*, 2002a; Newman and Pietro, 2001; Pant and Reddy, 2001b; McLatchey and Reddy, 1998). Many of these studies either make little attempt, or are unable, to translate their chemical process findings to different spatial scales, due to a

lack of consideration of hydrological factors (Wiens, 2002; Gehrels and Mulamoottil, 1989).

The emphasis for much of the hydrological research that has been conducted in freshwater wetlands has been on exchanges between wetland sediments and deeper ground water, both in terms of the hydrological and hydrochemical consequences of these exchanges (e.g. Eser and Rosen, 1999; Hunt *et al.*, 1999; 1996; Waddington and Roulet, 1997; Devito *et al.*, 1996; 1997). For example, Devito *et al.* (1997) examined how the connection between wetland sediments and ephemeral local ground-water flow systems could influence factors such as the position of the water table in the near-surface peat, and patterns of ground-water flow within the wetland deposits. In contrast to the ephemeral nature of local ground-water inputs, hydrological connection between a wetland and larger-scale regional ground-water flow is thought to produce more consistent, unidirectional inputs of ground water. These inflows have the potential to buffer the effects of short-term changes in surface-water inputs and the precipitation-evapotranspiration balance, resulting in a more stable position of the water table in the surface deposits (Devito *et al.*, 1996). However, other research has suggested that even for wetlands located in large-scale regional ground-water discharge areas, there is a potential for variation in the direction of ground-water flow through the peat stratigraphy (e.g. Hunt *et al.*, 1996). Factors such as the position of the water table, and periods of sediment submergence, will indirectly influence many of the biotic and abiotic factors affecting P cycling in wetlands.

Other research has examined the direct impact of hydrological processes on chemical cycles. Waddington and Roulet (1997) examined how patterns of ground-water flow could influence fluxes of dissolved carbon from a boreal peatland. Hunt *et al.* (1999) examined how ground-water discharge or recharge through wetland sediments could influence both the geochemical and thermal conditions found within pore water, factors clearly of importance to biogeochemical cycles such as those involving P. Eser and Rosen (1999) highlighted how the connection between wetland sediments and deeper ground water could influence wetland hydrochemical characteristics. In particular, dissolved iron concentrations within pore water were shown to be related to the direction of ground-water flow, and the possible impact of iron on the availability of phosphorus within the wetland was highlighted, although the details of this interaction were not investigated.

The scale of exchanges between wetlands and deeper ground water means that research such as that described above often examines flow patterns over several tens of metres, and is concerned with the entire depth of peat within a particular profile. Such work is unable to focus on shallow ground-water exchanges occurring within the top metre of wetland sediments. These exchanges are particularly important because the near-surface zone is the focus for biogeochemical cycling and many other processes governing wetland productivity (Mann and Wetzel, 2000). Further, the majority of research examining the interactions between wetlands and ground water has stressed the importance of seasonal and large-scale spatial variations (Drexler *et al.*, 1999). However, particularly in riparian wetlands, water exchanges occurring on a more frequent temporal scale, and at smaller spatial scales, driven by interactions with adjacent channel networks, may be important. There is clearly a need for hydrological research to refocus on water exchanges in riparian wetlands at finer temporal and spatial scales than has previously been the case. Shifting the spatial and temporal focus for hydrological research in riparian wetlands is made more difficult by the fact that our understanding of how water flows into and out of wetland sediments remains far from complete (Hunt *et al.*, 1999). Some of the barriers to increased understanding of hydrological processes in wetlands are related to the lack of thorough evaluation of data collection techniques, and insufficient scrutiny of the validity of the collected data (cf Baird *et al.*, 2004).

1.5 Justifying the current study in terms of specific research needs in riparian wetlands

Section 1.2 stated the specific research aim and objectives for this study in the context of understanding the catchment-scale role of riparian wetlands with respect to diffuse phosphorus loads. Sections 1.3 and 1.4 have highlighted the major processes that control phosphorus cycling within, and P export from, wetlands. The following discussion defines four specific research areas that will be addressed by this thesis.

1.5.1 The impact of riparian wetland sediments on the chemical quality of the water column

A considerable amount of research has focused on the impact that river- and lake-bottom sediments have on the chemical, including nutrient, quality of the water column

(e.g. House, 2003; Gunnars *et al.*, 2002; House *et al.*, 1998; Moore *et al.*, 1998; Gunnars and Blomqvist, 1997). Surprisingly little attention has been paid to the potential impact that wetland sediments may have (Fisher and Reddy, 2001), despite the fact that the prerequisite for determining the role of wetlands in P availability is an understanding of the interactions of phosphorus with the wetland sediment and overlying water column (Reddy *et al.*, 1995). It is possible that many riparian systems have accumulated a very large store of P, and that the supply of phosphorus to the water column from wetland sediments may be in excess of present-day anthropic loadings (Pant and Reddy, 2003; Fisher and Reddy, 2001; Mayer *et al.*, 1999). However, given the limited consideration of the role of wetland sediments in previous work, and accepting that the majority of research in riparian zones has focused on nitrogen transformations (Vellidis *et al.*, 2003; Carlyle and Hill, 2001), further research examining the supply of phosphorus to the water column from wetland sediments is required. This research should consider both the processes and the magnitude of P supply to the water column, and also the rates at which the processes operate.

1.5.2 Is the release of P to the water column the only potential threat to receiving water bodies from riparian wetlands?

The focus for much of the research concerning nutrient supply from sediments has been the impact on the chemical quality of the overlying water column (see references in Section 1.5.1). As the majority of such work is concerned with the possible nutrient enrichment of economically and environmentally valuable receiving waters, the focus on the overlying water column is understandable. The water column may itself be the receiving water body, as is the case for nutrient release from lake- or river-bottom sediments. Further, surface water fluxes are often extremely dynamic and may deliver phosphorus rapidly to receiving waters. Given this, the impact of the underlying sediments on the nutrient concentrations in the water column is clearly an important issue. However, in riparian systems the potential for both surface and sub-surface exchange exists (Burt *et al.*, 2002). Therefore, P in the pore water of riparian wetlands may pose a threat to the chemical and ecological quality of receiving waters, if hydrological connectivity exists between wetland sediments and receiving water bodies. The supply of P to pore water from wetland sediments is therefore of importance in its own right, rather than simply being a prerequisite for release to the overlying water column. It is possible that the processes governing P supply to pore water, the rates at

which they operate, and the factors controlling them, are different from those involved in the release of phosphorus to the water column. Yet very little previous research has considered pore-water P dynamics in the same detail as those in the overlying water column.

1.5.3 Re-focusing hydrological research in riparian wetlands

Only a limited number of previous studies have examined the hydrological flowpaths and water-table fluctuations within riparian systems (Burt *et al.*, 2002; 2001). As riparian zones are hydrological interfaces, involving the complex interaction of precipitation, ground water and surface water, understanding the hydrological processes occurring within these systems is important with respect to catchment-scale hydrological functioning (Lambs, 2000). There is a clear need for research to examine exchanges of water in the biogeochemically important near-surface wetland sediments, over a range of spatial and temporal scales (Mann and Wetzel, 2000; Drexler, 1999). Particularly in riparian wetlands, the near-surface zone may be a focus for exchanges between shallow ground water and open-water bodies, in the form of the adjacent channel network. Despite this, there has been little previous research examining the processes involved in exchanges between riparian wetlands and open-water (Schlotzhauer and Price, 1999). Further research into the exchanges of water through near-surface riparian wetland sediments is, therefore, desirable but must be coupled with a thorough evaluation of the methods used to measure or characterise such exchanges (cf. Baird *et al.*, 2004).

1.5.4 Can hydrological connectivity be used to translate the findings from hydrochemical process studies to different spatial scales?

A major challenge facing research in riparian systems is to link biogeochemical process information to larger-scale system functioning (Dahm *et al.*, 1998). With respect to phosphorus, the extent of hydrological connection between an area with *potentially* mobile P, such as riparian wetland sediments, and receiving waters will define the level of *actual* risk that should be associated with that area (Heathwaite *et al.*, 2000). However, few studies have attempted or have been able to combine chemical process findings with hydrological data, to examine whether P can be exported from riparian wetlands. This type of research represents the necessary first step towards investigating

channel systems and riparian zones as linked elements within the catchment (Tabacchi *et al.*, 1998). Given that many aspects of the hydrological functioning of riparian systems have changed due to river regulation (Baldwin and Mitchell, 2000), and that future changes associated with climate alteration are likely (Pierce, 1996; Thomas and Brandt, 1994), examining the way in which present-day hydrological functioning governs the delivery of nutrient loads to receiving waters may allow the impact of future changes to be predicted.

2. DESCRIPTION OF THE FIELD SITE

2.1 Introduction

The research reported in this thesis was conducted at Strumpshaw Fen, part of the Yare Broads and Marshes Site of Special Scientific Interest (SSSI) in the Norfolk Broads region of the UK. The Broads represent an internationally recognised wetland complex, with some 5500 hectares of Broadland protected under Ramsar designation. Strumpshaw Fen also forms an important part of the Royal Society for the Protection of Birds (RSPB) Mid-Yare Nature Reserve, a site recently designated a National Nature Reserve, and has been managed by the RSPB since the inception of the reserve in 1975.

The site is located at 52° 37' N, 1° 26' E in the northern floodplain of the River Yare, to the southeast of Brundall and approximately 10 km to the east of Norwich (Figure 2.1). The wetland complex at Strumpshaw comprises 197 hectares of open water, reedbed, carr woodland and grazing marsh within a floodplain that is generally between 500 and 1000 m wide on either side of the river. An aerial photograph in Figure 2.2 shows the wetland complex, as well as the location of the two major channel systems connected to Strumpshaw Fen; the River Yare and Lackford Run. Figure 2.2 also shows the existence of an interconnected ditch network running through the wetland, and the location of an instrumented transect used for hydrological monitoring (see Chapter 4). A railway embankment is located along the northeastern boundary of the floodplain (see Figure 2.1), at the interface between the wetland and the upland area. To the northeast of the railway the land rises relatively steeply, reaching a maximum elevation at Strumpshaw Hill (TG 353 073) of 42 m above ordnance datum (aOD), whilst more typical elevations in the upland region away from Strumpshaw Hill are between 25 and 30 m aOD.
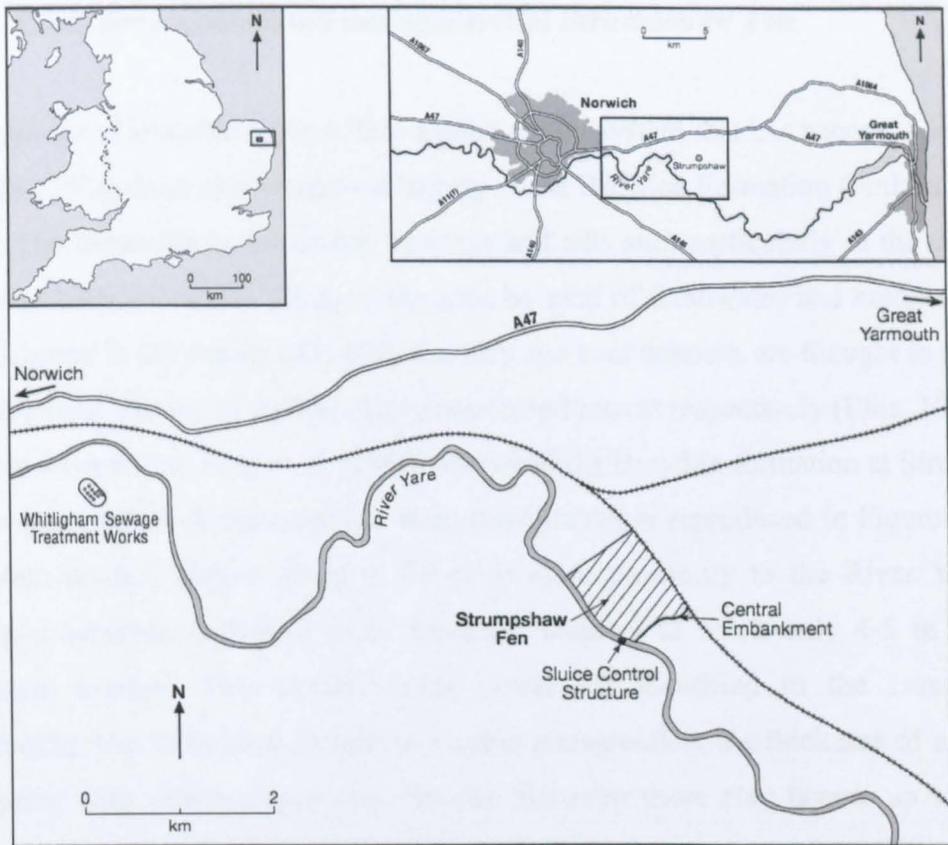
Figure 2.1 Location of Strumpshaw Fen.
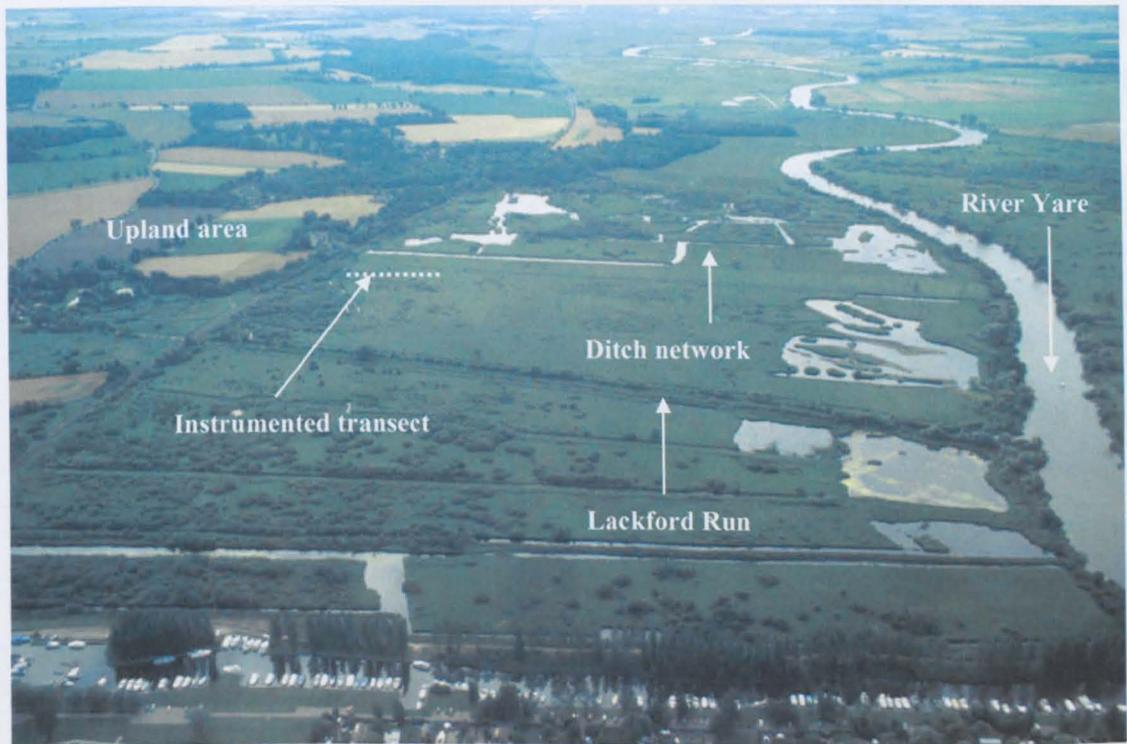
Figure 2.2 The wetland complex at Strumpshaw Fen, looking southeast.

2.2 Early development and management of Strumpshaw Fen

The majority of Broadland lies within a relict valley system that has become buried with deposits of Flandrian age, composed largely of the Breydon Formation (Arthurton *et al.*, 1994). The formation is dominated by clays and silts and, particularly in the valleys of the River Yare and many tributary streams, by peat of freshwater and brackish origin. The divisions in the stratigraphy between clay and peat deposits are thought to represent the postglacial history of marine transgression and retreat respectively (Ellis, 1965). The classical work of Lambert *et al.* (1960) described the Breydon formation at Strumpshaw Fen in some detail. A cross-section from their survey is reproduced in Figure 2.3. The formation reaches depths of up to 10 m in close proximity to the River Yare, and gradually becomes shallower away from the channel to reach only 4-5 m near the floodplain margin. Two separate clay layers are identified in the cross-section, representing two individual periods of marine transgression, the thickness of each layer decreasing with distance from the channel. Between these clay layers, up to 4 m of brushwood and mixed fen peat was deposited, whilst overlying the upper clay is 1-2 m of reed and sweet-grass peat.

The clay-peat stratigraphy described above is interrupted in the area of Strumpshaw Broad. The Broad was formed by peat digging, believed to have begun at Strumpshaw soon after the invasion and settlement of Norfolk by the Danes in 879 AD (Lambert *et al.*, 1960). The average depth of the peat diggings is 3.0-3.7 m below the ground surface. Sea level rise following the peak of the last marine regression in 700 AD led to the gradual flooding of the peat diggings and the establishment of the shallow areas of open water now known as the Broads (Ellis, 1975). At Strumpshaw it is believed that a flood in 1287 brought an end to peat digging at the site (Martin, 1987). Following the flooding of the peat diggings, a hydroserel succession leading to a gradual in-filling of the Broad would be expected. Evidence from tithe maps, Ordnance Survey maps and aerial photographs indicates that this in-filling process proceeded extremely rapidly between approximately 1800 and 1946, by which time the area of open water at Strumpshaw Broad was minimal. Evidence from sediment cores suggests that the rapid loss of open water area may be linked to increased nutrient loading to the system, as a result of open connection between the Broad and the River Yare, and consequent changes in the taxa present in Strumpshaw Broad (Moss, 1979). A summary of the
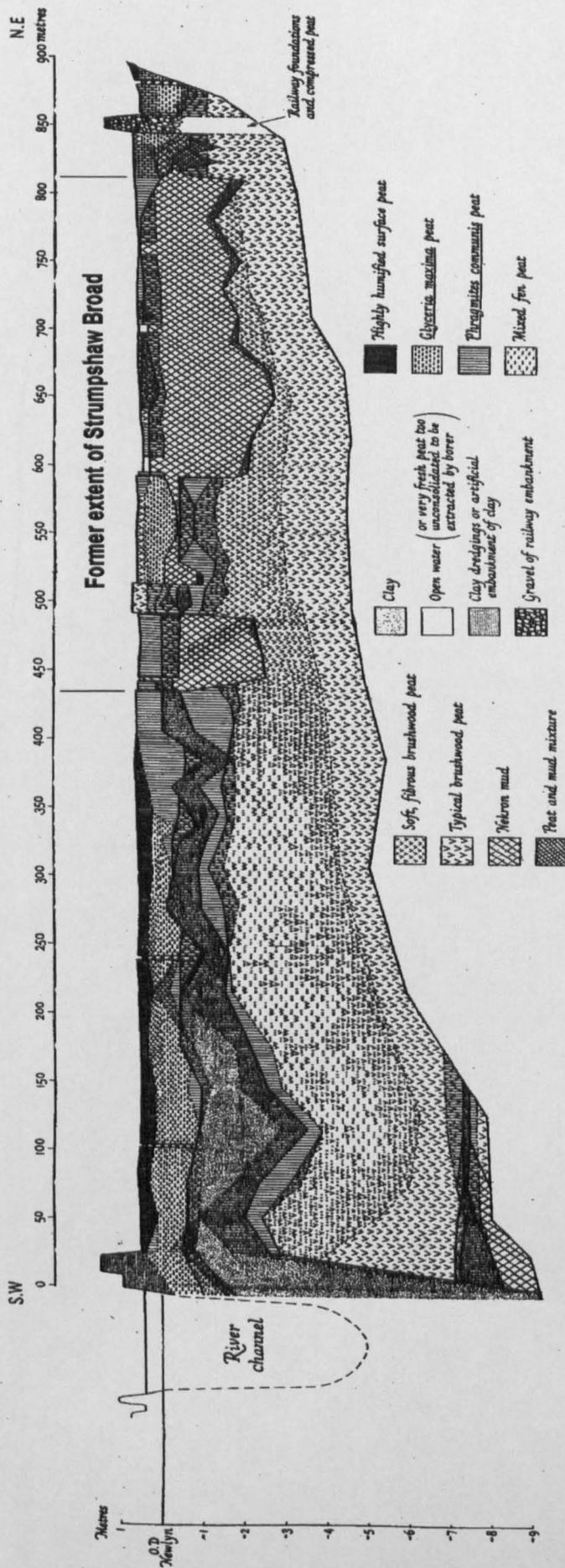
Figure 2.3 Cross-section through the Breydon Formation at Strumpshaw Fen, after Lambert *et al.* (1960).

events leading to the in-filling since *c.* 1800 is given in Table 2.1. As a consequence, the area that was formerly Strumpshaw Broad became filled with Nekron mud (high in both organic and mineral content), overlying which was a layer of 1-2 m of reed and sweet-grass peat. When the site was first leased by the RSPB in 1975 Strumpshaw Broad was approaching extinction.

During the period prior to RSPB management of Strumpshaw Fen, a number of modifications to the 'natural' state of the system had occurred, in addition to peat digging. Attempts were made to isolate the system from both the River Yare and the Lackford Run by building an embankment along the boundary of the site, and the area between the Broad and the river was drained (Martin, 1987). This ceased with a summer flood in 1916 that breached the embankments, and the previously drained area returned to rough fen (Ellis, 1965). Finally, prior to 1881 a central embankment was also constructed which now isolates Strumpshaw Fen from the drained grazing marsh immediately to the east (see Figure 2.1). Therefore, prior to 1975 clear attempts had been made to isolate the wetland complex from the River Yare and Lackford Run, although several free connections remained between the ditch network running throughout the fen and the river, and over-bank flood events could still input water to the wetland system.

2.3   The geological setting of Strumpshaw Fen

The Breydon Formation described in Section 2.2, comprising the peat and clay deposits shown in Figure 2.3, lies within a buried valley system in the location of Strumpshaw Fen. Underlying the Breydon Formation is the Yare Valley Formation, which occupies the floor of the buried valley system. The deposits of the Yare Valley Formation are composed of gravel ranging from fine to coarse, with variable amounts of fine- to coarse-grained sand, the gravel being mostly flint (Arthurton *et al.*, 1994). Approximately 4 m of the Yare Valley Formation were proved during the installation of a monitoring borehole in the aquifer underlying the Breydon Formation during the course of this PhD research (see Section 4.2.2). The buried valley system is cut directly into the Crag Group which underlies the Yare Valley Formation in the vicinity of Strumpshaw Fen, and is composed of sands sometimes with abundant shell remains, interspersed with clay layers that are in places discontinuous lenses of variable thickness. To the east and southeast of Strumpshaw Fen the Crag Group overlies

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Table 2.1 Summary of events leading to in-filling of Strumpshaw Broad since _c._ 1800 (From Moss, 1979).

DATE	NUTRIENT INPUT	EVENTS
– _c._ 1800	Low input though river relatively fertile.	Moderate bottom growing macrophytes. Clear water, marl deposition. Plankton virtually absent.
_c._ 1800 – 1900	Increased input with growth of city (Norwich).	Blanketing of low-growing macrophytes (_Chara_) with filamentous algae. Increases in epiphytes. Plankton scarce. Snails and rate of sedimentation increasing.
_c._ 1900 – 1912	Increased input with growth of city	Short transition zone as _Chara_ flora replaced by tall growing macrophytes. Water more turbid as plankton starts to increase. _Fragilaria_ and _Melosira_ varians maxima – perhaps areas of relatively macrophyte free sediment.
1912 – 1950	Increasing more rapidly with population and conversion of septic tanks to main sewerage. River organically very polluted.	Plankton increase to maximum. Aquatic plants and epiphytes in steady decline. Initially abundant tall growing macrophytes with markedly increased organic sedimentation rates but then declining. Macrophytes when present act as filter for river sediment and minimise effects of tidal flushing. Initial epiphyte maxima, snails plentiful. Marl deposition reduced.
1950 – 1974	Post-war agricultural fertilisation coupled with major increases in effluent loading. Use of phosphate detergents.	Decreasing volume of broad and increased flushing rate leads to little deposition of plankton diatoms. Loss of macrophytes complete. Inorganic sedimentation rate declines as marl source is lost but more material is washed in from river. Organic sedimentation variable and mainly of reed and river material. Sediments watery, not stabilised by macrophytes.
1974 –	Continued very high.	Much of broad a bare mud flat at low tide. Net deposit of sediment probably ceased.

Eocene deposits such as the London Clay. However, in the vicinity of the field site the Crag directly overlies the Upper Chalk, with the surface of the Chalk located some 25 to 30 m below the ground surface of the SSSI (Environment Agency, 1998). The peat towards the base of the Breydon Formation is assumed to be in hydraulic continuity with the underlying Yare Valley and Crag deposits, which in turn are believed to be in hydraulic continuity with the Upper Chalk (Environment Agency, 1998). The piezometry of the Upper Chalk indicates that regional ground-water flow is directed away from the ground-water divides, located to the northeast and southwest of the floodplain, and towards the valley axis of the River Yare (Environment Agency, 1998). To the north and east of the Strumpshaw wetland complex, where the land rises steeply, the Crag Group is overlain by various Pleistocene deposits comprising mainly Boulder Clay and glacial sands and gravels, including those of the Kesgrave and Corton formations. Figure 2.4 provides a hydrogeological section through Strumpshaw Fen and the surrounding area.
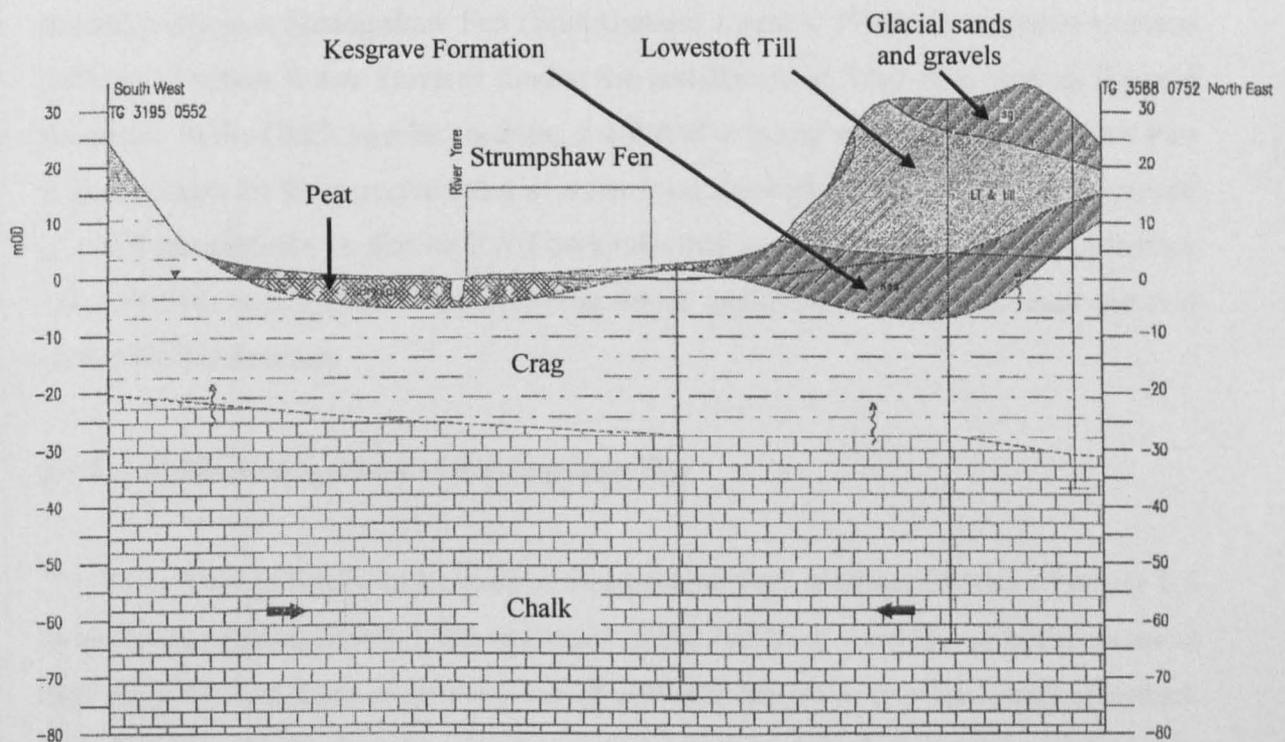
Figure 2.4 Hydrogeological cross section through Strumpshaw Fen and the surrounding area. Vertical scale 1:1000, horizontal scale 1:25 000. Arrows in the Crag and Chalk give predominant vertical and horizontal direction of groundwater flow. Reproduced from Environment Agency (2000).

2.4   The history of Strumpshaw Fen from 1951 to the present day

2.4.1   Ground-water abstraction

In 1951 two public water supply (PWS) boreholes were installed in the Chalk aquifer by Anglian Water, in close proximity to Strumpshaw Fen at grid reference TG 341 068. Abstractions by Anglian Water Services are thought to have resulted in a cone of depression forming in the vicinity of the boreholes, and consequently in the potential for water to be lost from Strumpshaw Fen via downward seepage to the Crag and Chalk, in response to the lowering of heads in these aquifers by pumping. A hydrogeological report by Martin (1987) identified that downward acting hydraulic gradients existed in the Breydon Formation at Strumpshaw Fen, supporting the conclusion that the site may be acting as a source of ground-water recharge. It is thought that prior to PWS abstraction, higher heads in the Chalk may have supported the discharge of deeper ground water into Strumpshaw Fen (Environment Agency, 1998). In response to these findings, Anglian Water Services funded the installation in 1987 of a 'Marsh Support Borehole' in the Chalk aquifer, enabling the RSPB to pump water into Strumpshaw Fen to compensate for the perceived loss of water from the wetland system as a consequence of PWS abstractions. A further PWS borehole was installed in 1992 at grid reference TG 339 074, in response to deteriorating water quality in abstractions from the two earlier PWS boreholes.

2.4.2   RSPB management of Strumpshaw Fen

The River Yare is tidally-influenced at Strumpshaw Fen, with oscillations of nearly 0.6 m observed approximately 1 km upstream of the wetland. Anaylsis of hydrochemical data suggests that there is no evidence of seawater intrusion this far inland (Haycock and Lamberth, 2000), therefore the river may be described as freshwater-intertidal in the vicinity of Strumpshaw Fen. Typical hydrochemical parameters for the River Yare are presented in Table 5.1 in Chapter 5, showing the river water to be of high pH and alkalinity, and that it is nutrient-enriched with high c oncentrations of nitrate-nitrogen and orthophosphate.

In 1975 the RSPB took control of site management. In 1978 work commenced in an attempt to isolate fully the fen from the nutrient-enriched waters in the River Yare and

Lackford Run. Figures 2.5 and 2.6 provide data showing the concentration of molybdate reactive phosphorus (MRP) in samples from these two channel systems over the period 1990-2002, illustrating the degree of nutrient-enrichment. Of particular note in these data is the significant decline in MRP concentration in the Lackford Run following the closure of Strumpshaw Sewage Treatment Works (STW) in March 1997, resulting in average MRP concentrations falling from 3.73 mg l⁻¹ P between 1990 and 1997, to only 0.24 mg l⁻¹ P between 1997 and 2002.
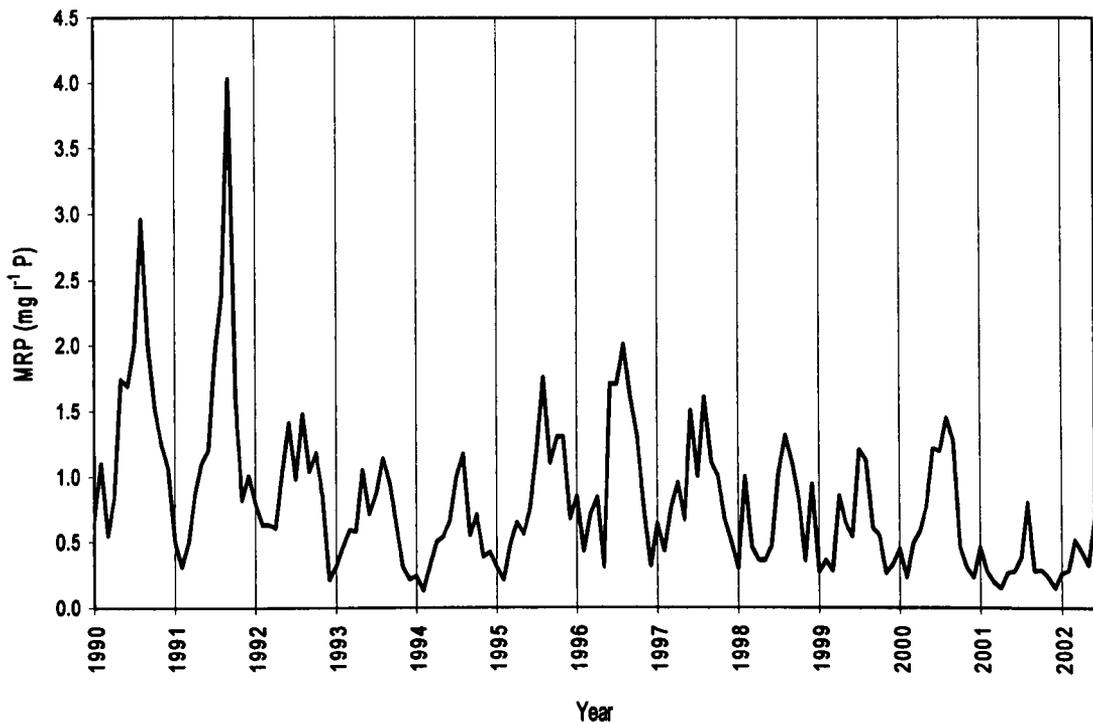
Figure 2.5 Concentrations of MRP in the River Yare, 1989-2002 (Environment Agency, unpublished data).

The main ditch channel connecting the relict Broad to the River Yare was dammed at its exit to the Yare, as were all other free connections between the ditch network and the river. The embankments running along the boundary of the fen were surveyed and modified to protect the system from an influx of river water during surge tides, and precautions were taken to reduce erosion of the banks of the River Yare caused by boat traffic. Having isolated the fen system from the river, a control structure was installed to allow manipulation of water levels within the wetland complex. A sluice was constructed in the river embankment allowing both the ingress of river water into the fen and the drainage of water from the ditch network into the Yare as required. In 1983 the relict Broad was mud-pumped to re-establish an area of open water in the location of

the original Strumpshaw Broad, and since then various areas of the pre-existing ditch network have been cleared, and new areas of shallow open water and ditch have been created. Further management including scrub clearance and reed harvesting occurs at Strumpshaw Fen.
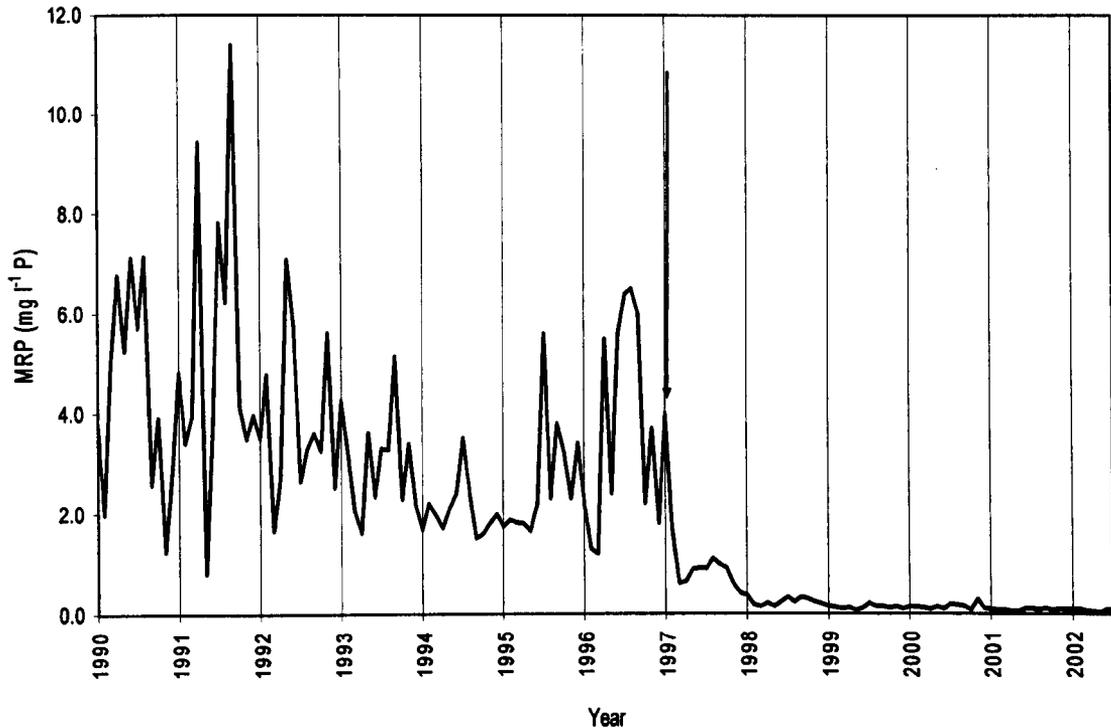
Figure 2.6 Concentrations of MRP in the Lackford Run, 1989-2002 (Environment Agency, unpublished data). Arrow indicates closure of Strumpshaw STW.

Contemporary hydrological management of the wetland complex includes the maintenance of surface inundation from late autumn/early winter through to late spring/early summer, after which evapotranspiration demand results in water tables falling below the peat surface. In some years, water from the Marsh Support Borehole may be used to maintain higher water levels and delay the time at which water levels fall below the ground surface. During mid- to late-summer, water tables may fall up to 45 cm below the ground surface.

Surface-inundated conditions are established in late autumn/early winter, either gradually due to changes in the precipitation-evapotranspiration balance, or more rapidly as a result of over-bank flooding events from the River Yare. Managed drainage of water from the ditch network into the river is used; i) after a flood event to remove eutrophic river water from the fen, or ii) to allow access to the reed beds for management personnel/machinery. Despite the attempt to isolate Strumpshaw Fen from

the River Yare, there is clearly still a potential for the input of river water to the system either during over-bank flood events or during periods when the control structure at the boundary between the fen and the river is opened.

2.5   Ecological status of Strumpshaw Fen

2.5.1   Vegetation

Much of the fen vegetation present on the site is a version of the National Vegetation Classification (NVC) type S24 *Phragmites australis – Peucedanum palustre* tall-herb fen. Other areas are type S4 *Phragmites australis* swamp with contributions from type S28 or *Phalaris arundinacea* tall-herb fen. Other areas that have been particularly affected by the input of eutrophic water from the River Yare correspond to type S26 or *Phragmites australis – Urtica dioica* tall-herb fen with *Epilobium hirsutum*, *Urtica dioica* and *Glyceria maxima* as dominants (Tickner *et al.*, 1991). Following the isolation of Strumpshaw Fen from the River Yare and Lackford Run by the RSPB, vegetation surveys have indicated a decline in *Epilobium hirsutum* and *Glyceria maxima*, two pollution-tolerant species, at the expense of an increase in *Phragmites australis*. Despite this, there has been no conclusive evidence for significant large-scale shifts in the vegetation communities at Strumpshaw Fen following the exclusion of eutrophic river water.

There is little doubt that there are substantial differences between the vegetation community present at Strumpshaw Fen today and that which would have been present in the past, which included *Cinclidium stygium* and the colourful forb-rich 'Yare Valley Fen' (Environment Agency, 1998). These shifts are probably linked to both the drying of the site due to its isolation from the River Yare, and to increased nutrient loadings to the system from the river (Environment Agency, 1998). It is recognised that these effects are difficult to separate, because drier conditions may result in increases in mineralisation and therefore nutrient availability. There is no reason to suppose that the vegetation communities present at Strumpshaw Fen, or those previously present, are/were reliant on ground-water input (Environment Agency, 1998). Reduced discharge of ground water to Strumpshaw Fen as a consequence of PWS abstraction is not thought to have had a direct impact on shifts in the vegetation community (Environment Agency, 1998). However, it is possible that reduced ground-water inflow,

coupled with the isolation of the fen from the River Yare, may have contributed to the establishment of drier conditions, and consequently to a shift in the composition of the vegetation communities. Attempts to exclude river water from Strumpshaw Fen by isolating the system from the Yare may have altered the hydrological functioning of the wetland and have contributed to the changes in vegetation community described above. In an ideal scenario, nutrient levels in the Yare would be reduced, allowing Strumpshaw Fen to be re-connected with the river, thereby re-establishing the 'natural' hydrological regime of this riparian system.

2.5.2 Aquatic macrophytes and aquatic invertebrates

Surveys of the aquatic macrophyte and aquatic invertebrate populations conducted in the late 1970s, prior to isolation of Strumpshaw Fen from the River Yare, indicated an extremely poor diversity in this polluted system, with virtually no aquatic macrophytes within the ditch network (Tickner *et al.*, 1991). Since this time there has been a recovery and diversification in the populations of aquatic species, including a recovery in pollution-sensitive species. Aquatic macrophytes including *Myriophyllum spicatum*, *Lemna minor*, *Zannichellia palustris* and *Chara* spp. recovered and were identified in both old and newly cut sections of the ditch network in the 1980s. Unfortunately, the shading of the ditch network caused by the growth of un-mown stands of *Phragmites australis* has subsequently resulted in a decline in the populations of various aquatic macrophytes (Tickner *et al.*, 1991). The diversity of aquatic invertebrates has also benefited from the improvements in water quality as a consequence of reduced water inputs from the River Yare (Blackburn, 1987).

2.5.3 Other invertebrates

A number of rare invertebrates are associated with the wetland complex at Strumpshaw Fen. Several rare species of dragonfly and damselfly are recorded at the site, including the Norfolk hawker (*Aeshna isosceles*). The swallowtail (*Papilio machaon*) is the only species of butterfly dependent on the fen for its continued existence, its larval food plant being milk-parsley (*Peucedanum palustre*). There is a good assemblage of scarce wetland Diptera, including snail-killing flies (*Sciomyzidae*) which are especially well represented (Environment Agency, 1998).

2.5.4 Birds

The Yare Broads and Marshes SSSI citation described the area as one of great ornithological interest; much of this interest now focuses on Strumpshaw Fen which is a nationally important bird site. Particularly important breeding species include bittern (*Botaurus stellaris*), marsh harrier (*Circus aeroginosus*), bearded tit (*Panurus biarmicus*), Cetti's warbler (*Cettia cetti*) and Savi's warbler (*Locustella luscinioides*), all of which are afforded legal protection under Schedule I of the 1981 Wildlife and Countryside Act, and are UK red data species (Batten *et al.*, 1990). A large number of other wetland birds breed at Strumpshaw including shelduck (*Tadorna tadorna*), teal (*Anas crecca*) and shoveler (*Anas clypeata*), alongside a diverse range of other bird species that use Strumpshaw Fen as a breeding site, for example reed warbler (*Acrocephalus scirpaceus*), sedge warbler (*Acrocephalus schoenobaenus*) and lapwing (*Vanellus vanellus*). The Yare Valley SSSI also supports nationally important numbers of passage and wintering birds including red data species wigeon (*Anas penelope*) and hen harrier (*Circus cyaneus*), alongside England's only remaining wintering flock of bean geese (*Anas fabalis*), also a red data species (Environment Agency, 1998).

2.5.5 Other vertebrates

A number of fish species have become well established within the open water habitats at Strumpshaw Fen, including roach (*Rutilus rutilus*), pike (*Esox lucius*), perch (*Perca fluviatilus*), three-spined stickleback (*Gasterosteus aculeatus*) and minnow (*Phoxinus phoxinus*). Both frog (*Rana temporaria*) and toad (*Bufo bufo*) are well established, and grass snake (*Natrix natrix*) numbers have remained steady (Tickner *et al.*, 1991).

2.6   Why does Strumpshaw Fen represent a valid research site?

The system at Strumpshaw provides a good opportunity to address a number of research needs in riparian wetland hydrology and hydrochemistry. The wetland is located at an important interface between agricultural upland areas and receiving water bodies, and may strongly influence the movement of water, sediment and solute loads between these different catchment elements. The role of riparian systems as integral parts of the wider catchment is of growing importance, because increased pressure on the environmental quality of our receiving waters is in direct conflict with legislative requirements for

improving freshwater chemical and ecological quality. Strumpshaw Fen is typical of many riparian wetlands located in the floodplains of relatively large channel systems. Similar wetlands exist throughout the Norfolk Broads along the Rivers Yare, Ant, Bure and Waveney, through northern Europe particularly in the Netherlands, France and Germany, and in north and south America (Venterink *et al.*, 2003; Bendjoudi *et al.*, 2002; Hanschke and Baird, 2001; Peck and Lovvorn, 2001; Craft and Casey, 2000; Chambers and Odum, 1990).

Strumpshaw Fen has experienced substantial and prolonged nutrient loading from adjacent eutrophic channel systems (see Figures 2.5 and 2.6), again similar to many other riparian wetlands in the floodplains of large channel systems. This loading suggests that the sediments may contain a very substantial store of nutrients, particularly phosphorus. There is only very sparse information on the impact of flooding riparian sediments on the various sediment-P fractions, and consequently on the retention/release of phosphorus (Novak *et al.*, 2004; Wright *et al.*, 2001). Investigating the processes controlling the availability of phosphorus within the sediments at Strumpshaw Fen will indicate whether 'internal' nutrient supply mechanisms are important in this, and similar, riparian wetlands.

There is a potential for hydrological connectivity between the wetland complex at Strumpshaw and i) adjacent surface water systems (ditch network and river channel), and ii) deeper ground water. Understanding the exchange of water between these catchment elements is important for understanding the hydrological functioning of riparian systems, an area of research which has only rarely been addressed (Burt *et al.*, 2002). Further, understanding hydrological connectivity between individual elements of a wetland complex, for example peat deposits and the ditch network, and between the wetland and 'external' receiving waters, is the key to understanding the export of P from wetland pore water and surface water. Research at Strumpshaw provides an opportunity to examine whether riparian wetlands have the potential to deliver P to receiving water bodies, thereby influencing the chemical and ecological quality of these waters.

Finally, site management associated with isolation of the wetland complex from adjacent channel systems and manipulation of hydrological regimes within the fen, is bound to exert an important control on the hydrological and hydrochemical functioning

of this riparian system. However, many effects of management, particularly those associated with P dynamics, are unknown or poorly-understood. Thus, research at this site may provide valuable guidance for the future management of this and similar wetlands. Pressing management issues, such as the impacts of reinstating a free connection between the river channel and the wetland complex, will be informed by this current study. Further, understanding the effects of riparian-zone management techniques with respect to nutrient supply and delivery mechanisms will be important for the successful design and implementation of catchment-scale management plans, such as those associated with the WFD.

3. DEVELOPING FIELD TECHNIQUES FOR ACCURATE CHARACTERISATION OF PEAT HYDRAULIC PROPERTIES

3.1 Introduction

Exchanges of water between wetlands and adjacent open-water bodies and between wetlands and deeper ground-water formations can have a profound effect on chemical transformations and bacterial activity in wetland sediments (Beckwith *et al.*, 2003a; Mann and Wetzel, 2000; Wheeler, 1999). The movement of water through a homogeneous porous medium, such as peat, is frequently estimated using Darcy's Law. The research conducted by Darcy established that the rate of water flow was proportional to the difference in head between two points in a porous medium, and inversely proportional to the distance between those points. Darcy also established that the quantity of flow was proportional to a coefficient, *K*, which is dependent upon the properties of both the porous medium and the liquid flowing through it (Fetter, 2001). Accepting that the volume rate of flow is also proportional to the cross-sectional area of the medium, these parameters can be combined and expressed as Darcy's Law:

$$Q = -KA\left(\frac{dH}{dl}\right) \qquad (1)$$

where Q is the water discharge ($L^3\ T^{-1}$), *K* the hydraulic conductivity of the porous medium ($L\ T^{-1}$), *A* the cross-sectional area of the medium through which flow occurs (L^2), *H* the hydraulic head (L), *l* the distance in the direction of flow (L), and *dH/dl* (-) the hydraulic gradient between two points in the porous medium. Equation (1) demonstrates that in order to examine the direction and rate of water exchange, both the hydraulic properties of the wetland sediments, and the hydraulic gradients driving flow must be considered. However, despite a recent increase in interest in water flow

processes in wetland soils, especially in northern peatlands (e.g. Drexler *et al.*, 1999; Devito *et al.*, 1997; Waddington and Roulet, 1997), data on the hydraulic properties, i.e. *K*, of wetland soils are sparse compared with data on non-wetland soils. Piezometer slug tests have been used in wetland studies to estimate *K*. Analysis of the resulting data is usually conducted with reference to the work of Kirkham (1945) and Hvorslev (1951). Hvorslev's approach assumes that the soil being tested is a rigid medium in which Darcy's law applies, and that a step change in head within the piezometer results in a log-linear recovery over time, with *K* proportional to the gradient of the log of normalised head against time (Baird *et al.*, 2004).

However, although w idely used to characterise the *K* of wetland sediments, previous work has indicated that a number of problems with the piezometer slug test may exist in peat. Several authors have suggested that Hvorslev's approach might not apply to some peat soils, because such soils often display compressible, rather than rigid, behaviour (e.g. Baird and Gaffney, 1994; Brown and Ingram, 1988; Rycroft *et al.*, 1975). Some evidence also indicates that piezometer-test *K* estimates may be substantially below 'true' values. For example, Schlotzhauer and Price (1999) show that *K* determined from piezometer slug tests was up to 5 times less than *K* estimated using a more reliable laboratory technique. This apparent ' under-estimation' of *K* during slug t ests may be related to problems of reduced rates of flow into and out of piezometers, associated with smearing of the soil around the piezometer intake (Almendinger and Leete, 1998). Further work, conducted mainly in non-wetland soils, has identified other potential problems with the piezometer technique, specifically the development of low permeability well skins resulting in progressively slower piezometer test responses (Butler and Healey, 1998; Butler *et al.*, 1996), and a dependence of test response on the mode of test initiation (insertion versus withdrawal) (Butler and Healey, 1998). In order to examine the reliability of the piezometer technique in peat, rigorous treatment of test procedures and data analysis should be conducted, as discussed in the hydrogeological literature (see, e.g., McElwee, 2002; Butler and Healey, 1998; Butler *et al.*, 1996). However, it is extremely rare to see such rigorous treatment of test and analysis procedures in studies of wetland soils (cf. Baird *et al.*, 2004; Brown and Ingram, 1988). Therefore, the major aim of the current chapter was to conduct a detailed evaluation of the piezometer slug test in peat, to assess whether it can provide reliable estimates of *K*. This work addresses Research Objective 1 identified in Section 1.2.

At the same time as the work evaluating the piezometer technique was conducted, co-workers at the Sheffield Wetlands Research Centre were developing a laboratory-based method for the determination of K in cores of bog peat, the Modified Cube Method (MCM) (see Beckwith *et al.*, 2003a). If estimates of K generated by two (or more) different techniques are in agreement at a given site, then this suggests that the data are reliable (i.e. that they accurately represent the true K). Further, given that many other authors use *either* a field or a laboratory method to characterise K, establishing the degree of similarity between K values generated by different methods is of fundamental importance if the hydraulic characteristics of individual systems are to be accurately compared. Therefore the MCM was adapted for use in the current research on fen peat, and applied alongside piezometer slug tests in Chapter 4. In the current chapter, only the details of the MCM are introduced. Restrictions associated with the UK Foot and Mouth Disease Crisis in 2001 meant that the method could not be evaluated at the same site as the piezometer technique (see Section 3.2.1).

3.2   Methodology

3.2.1   Field site and peat type

The research aimed at evaluating the piezometer slug test was conducted at Sutton Fen, a floodplain mire in Norfolk, England (52°45′N, 1°31′E). Sutton Fen was the original field site chosen in 1999 for the PhD research reported in this thesis. Unfortunately, due to Foot and Mouth Disease in the UK during early 2001, the landowner denied access to the site for a period of 9 months. Consequently, a decision was taken to abandon Sutton Fen in late 2001 and to move all further research to Strumpshaw Fen. However, prior to Foot and Mouth Disease, a series of tests had been conducted at Sutton Fen to evaluate the piezometer technique, and these tests are reported in the current chapter. Sutton Fen has extensive beds of *Cladium mariscus* L. (Pohl) and *Phragmites australis* Cav. (Streud.) in co-dominance. The beds are mown and grazed to prevent scrub invasion and they form extensive root mats. The mats are between 40 and 70 cm thick and consist of a tangled mass of rhizomes and roots with an admixture of dark brown to black well-decomposed plant material, the latter resembling a highly humified peat (see Figure 3.1). In some places the mat is 'grounded' on an underlying layer of brushwood peat; elsewhere, the mat appears to be floating, although its vertical movement is much

more limited (maximum annual movements are typically 5–10 cm) than is the case with mats that are next to lakes (e.g. Swarzenski *et al.*, 1991).
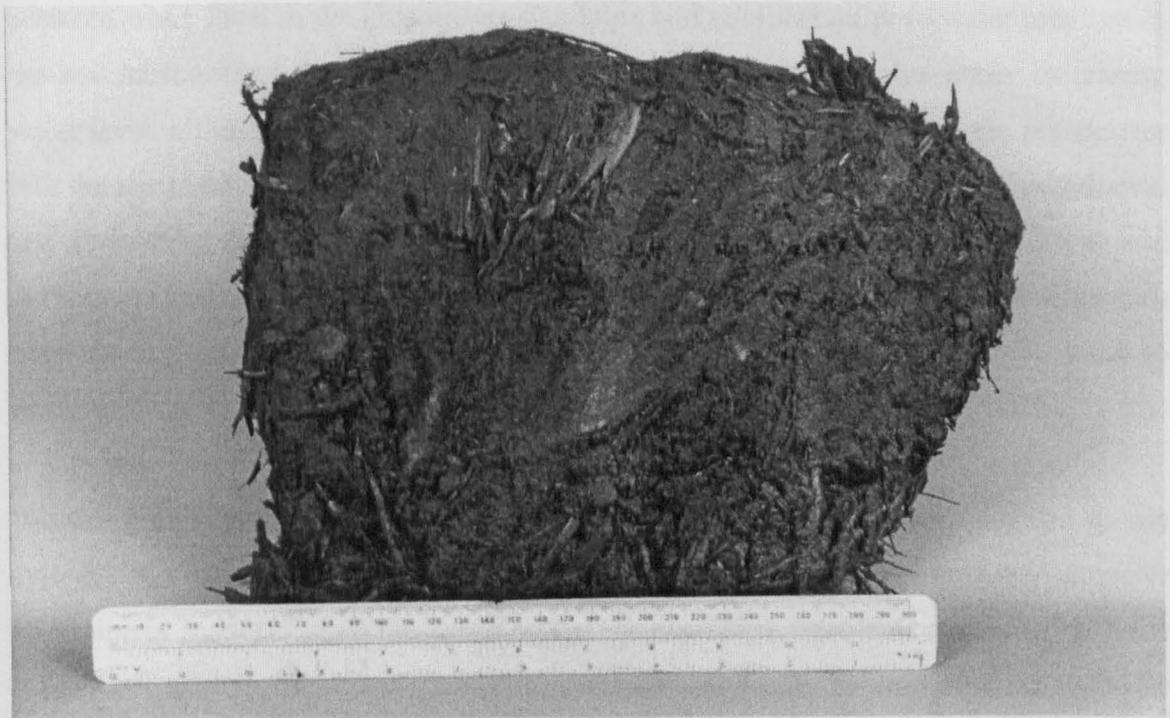
Figure 3.1 Sample of root mat taken from Sutton Fen. Note the woody material in the upper middle, middle and left middle of the sample. The ruler scale is 30 cm in length.

The term 'root mat' is used to describe a wide range of soils in wetlands that contain abundant plant roots and rhizomes. Often the wetland 'soil' consists almost entirely of roots and rhizomes in a tangled mass with an admixture of decaying organic matter. However, the term may also be used to describe an essentially mineral soil where the organic matter component is relatively small by volume (say, < 30 %) and consists mainly of living and decaying plant roots and rhizomes. The peat soil at Strumpshaw Fen differs in some respects from that at Sutton Fen, for example the near-surface peat at Strumpshaw is not 'floating' in the same way as the root mat at Sutton. However, there are sufficient similarities between the two sets of deposits (e.g. a high proportion of root and rhizome material) to suggest that the results from evaluations of piezometer slug tests on one site will apply to the other.

3.2.2 Piezometer test procedures

The piezometer test procedure involves generating a near-instantaneous head difference between water level in the piezometer standpipe and equilibrium pore-water pressure in the soil surrounding the intake of the piezometer. This can involve either increasing water level within the piezometer, an insertion test leading to flow from the piezometer into the surrounding soil, or decreasing water level within the piezometer, a withdrawal test generating flow from the surrounding soil into the piezometer. The form and duration of the recovery of water level within the piezometer to an equilibrium with pore-water pressure in the surrounding soil is observed, and subsequently used to estimate the hydraulic conductivity of the soil surrounding the piezometer intake.

Various piezometer intake designs may be used, although it is most common to use cylindrical intakes. The intake can be formed by augering an extension to a piezometer standpipe or by perforating the lower end of the standpipe. Problems can occur with the former because the intake can become distorted (especially in compressible soils) or even start to collapse. Problems can also occur with the latter if the intake is not perforated with a sufficient number of holes to allow the free flow of water between the soil and the standpipe. One way of partly avoiding this problem is to construct a filter of coarse sand or gravel around the perforated part of the intake. In this study it was felt that such a filter would be difficult to construct and seal in place, especially because most tests were conducted in late winter and spring (April and May 2000) when the surface of the fen was inundated. A new type of intake was therefore manufactured where the area of perforations exceeded 70 % but where the unperforated part of the intake still provided support for the root mat to stop it collapsing or pushing into the standpipe. Polyvinyl chloride (PVC) standpipes (outside diameter (o.d.) = 4.8 cm; inside diameter (i.d.) = 4.1 cm) were used for the tests. A 7.0 cm long intake was constructed towards the base of the tube, which was sealed at its base with a wooden cone (Figure 3.2). The piezometers were pushed into holes that had been pre-augered into the root mat. A screw auger with a diameter just less than the diameter of the PVC tubes was used to construct the holes.
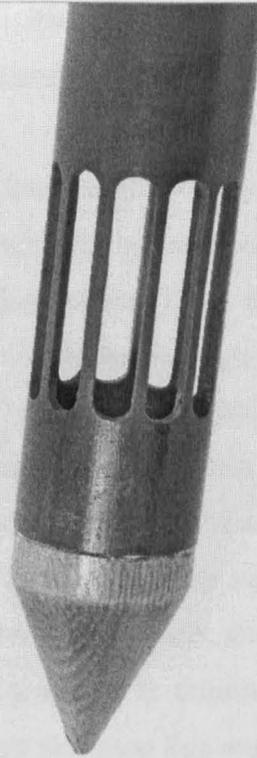
Figure 3.2 Detail of the intake design used on all piezometers at Sutton Fen. The intake is 7.0 cm in length.

After installation, all piezometers were checked, using a rod that fitted into the piezometer standpipe, to ensure that the area of tube inside the intake was not clogged with root mat debris. The water level inside the piezometer was then allowed to equilibrate with pore-water pressures around the intake. One of the reasons forwarded to explain why slug tests often give lower K estimates than other methods is the presence of a zone of low K material around the intake, caused partly by smearing during piezometer installation (Almendinger and Leete, 1998; Butler and Healey, 1998). A procedure called 'development' is usually recommended for removing this smeared material (e.g. Butler and Healey, 1998). Development involves inducing strong flows of water into the piezometer by bailing. These flows help flush material from clogged pores in the vicinity of the intake. After the initial equilibration of water level, approximately 640 cm^3 of water was bailed from each of the piezometers. Water flowing into the piezometer during bailing became somewhat turbid, which indicated that fine debris had been successfully removed from pores around the intake. Bailing was not continued to a point where the water in the piezometer became clear, because of concerns that too much development might create an artificial pore structure around the

intake. However, as reported below, the turbid water may have affected the rate of flow from the piezometers during slug insertion tests.

All piezometers were installed so that the midpoints of the intakes were 45 cm below the fen surface. Although the root mat showed some variation with depth from generally coarser to finer material, it was thought that these differences were not sufficient to warrant placing piezometers at several depths through the root mat profile. A total of 17 piezometers were placed in a 'W' arrangement within an area of 40 × 20 m. Further tests designed to elucidate other aspects of the test procedures were carried out on piezometers placed elsewhere but close to the 'W' (see Sections 3.2.3 and 3.3.3). Tests were carried out in late winter and spring, when the surface was inundated with between 5 and 30 cm of water. Piezometer water levels during slug tests can be measured manually (e.g. using electronic dipmeters) at minimum intervals of 10–20 s. It was anticipated that the K of the root mat at Sutton Fen would be high, so that such intervals would prove too large for use in these tests. One way of reducing the speed of response of the piezometer during a slug test is to use a larger diameter standpipe, but such standpipes can be difficult to install. Instead, it was decided to measure piezometer water levels automatically using a Van Essen self-logging, temperature-compensated pressure transducer ('Diver' model Dl240) with a resolution of 1 mm and accuracy for the range of pressures used in the tests of about ± 2 mm. Prior to the slug tests, the pressure transducer was programmed to log at 1 Hz and then lowered to the base of the piezometer. The water level in the piezometer was left to equilibrate with pore-water pressures around the intake. A slug consisting of PVC tubing (o.d. = 3.3 cm) filled with a ballast of saturated sand and stoppered at each end with rubber bungs was then added to the piezometer. Two lengths of slug were used, giving initial head differences in the piezometers of approximately 20 cm (shorter slug of 32.5 cm, excluding bungs) and 26 cm (longer slug of 39.9 cm). Theoretically there should be no dependence of test response on the size of the initial head difference (Butler *et al.*, 1996). After recovery, the slug was removed and the recovery to the equilibrium water level again recorded. Thus, in each piezometer, two slug tests, one involving slug insertion and one slug withdrawal, were carried out. The insertion/withdrawal of the slug typically took 1 s, although in a few tests it took 2 s. Slug withdrawal was used as well as slug insertion tests to see whether there was any difference between the two. In theory, in a rigid soil there should be no difference. A difference might indicate a problem with the test procedure or point to aspects of flow in the medium requiring closer consideration

(Butler and Healey, 1998). K is affected by changes in water viscosity related to water temperature, therefore all estimates of K from piezometer tests were standardised to 20 °C (Klute, 1965).

3.2.3 Consistency of piezometer tests

The results showed a general pattern where the head recovery after insertion was slower than that after withdrawal (see Section 3.3.1). It could be argued that such a consistent difference is due to the order in which the tests were performed (i.e. withdrawal following insertion). To investigate this problem, and assess the reproducibility of the slug tests, replicate measurements were made on three of the 17 'W' piezometers. In these instruments (Piezometers 4, 11 and 13), a slug test sequence of insertion, withdrawal, insertion, withdrawal, insertion, and withdrawal was performed. Checks were also made to see whether the 'development' of the root mat around the piezometer intake had an effect on recovery. These checks were carried out using two piezometers, named Test Piezometers 1 and 2, not in the original 'W' sample. In two further piezometers, Test Piezometers 3 and 4, the water in the instrument was replaced with 'clean' fen water. The clean water was obtained from samples of fen surface water in which organic detritus had been allowed to settle from the water column over a 24 h period. Approximately 700 cm^3 of clean water was poured rapidly into the piezometers to flush out existing 'dirty' water. Finally, tests were also done on Test Piezometers 3 and 4 to see whether the size of the initial head difference had an effect on head recovery, two slug lengths were used in these tests: one of 23.5 cm and one of 11.7 cm.

3.2.4 Data analysis

The basic theory of piezometer response during slug tests was first elucidated by Kirkham (1945) and Hvorslev (1951). Kirkham's and Hvorslev's analyses are essentially the same and assume a rigid soil (i.e. one with a constant porosity which is equivalent to a specific storage (S_s) = 0) in which Darcy's law applies. Hvorslev noted that the instantaneous discharge of water (Q) out of/into a piezometer immediately after slug insertion/withdrawal is given by

$$Q = A\frac{dh}{dt} = FKh \tag{2}$$

where A is the inside cross-sectional area of the piezometer standpipe (L^2), h is the difference in head between the piezometer and the soil around the intake, t is time (T), and F is the shape factor of the piezometer intake (L) which is a function of the size and shape of the piezometer intake and the pattern of flow around the intake. Hvorslev (1951) showed that if a new variable, the basic hydrostatic time lag, T, is defined by

$$T = \frac{Ah_0}{FKh_0} = \frac{A}{FK} \tag{3}$$

where h_0 is the initial head difference, then the change in normalised head (the head ratio) with time is given by

$$\frac{h}{h_0} = e^{-t/T} \tag{4}$$

where t is the elapsed time from the start of the test (i.e. the time since slug insertion/withdrawal) and h is the head difference at t. K can be estimated by combining Equations (3) and (4) to give

$$K = -\frac{A}{Ft}\log_e\left(\frac{h}{h_0}\right) \tag{5}$$

F for closed-bottom cylindrical intakes such as that used here can be calculated using the empirical formula of Hvorslev (1951) as modified by Brand and Premchitt (1980) (see also Brand and Premchitt, 1982):

$$F = \frac{2.4\pi d}{\log_e\left(1.2l/d + \sqrt{1+(1.2l/d)^2}\right)} \tag{6}$$

where d is the o.d. of the intake and l is the length.

It is clear from (4) and (5) that head recovery in a rigid, Darcian soil should be log-linear with K proportional to the gradient of the log of normalised head against time. If a soil displays non-rigid behaviour, i.e. the head recovery is no longer log-linear, other methods have to be used to estimate K. Non-log-linear responses are often due to compression and dilation of soil pores or contraction and expansion of 'static' gas bubbles trapped within the soil pores (Baird and Gaffney, 1994; Demir and Narasimhan, 1994; Hvorslev, 1951). Baird and Gaffney (1994) showed how Brand and Premchitt's (1982) analysis could be applied to compressible behaviour in piezometers with cylindrical intakes installed in a humified fen peat. It was anticipated that at least some of the tests at Sutton Fen would display non-log-linear behaviour because such behaviour has been reported for peats elsewhere (e.g. Baird and Gaffney, 1994; Brown and Ingram, 1988) and because it has been shown and suggested that root mats contain trapped gas bubbles (e.g. Swarzenski et al., 1991; Hogg and Wein, 1988). However, rapid piezometer recoveries due to the fibrous nature of the deposit were also anticipated, and it was not clear how far such recoveries might depart from log-linearity.

3.2.5 Applying the modified cube method (MCM) to fen peat

Originally the MCM was to be used at Sutton Fen alongside the tests evaluating the piezometer slug technique. Consistency in the K determinations made by these two separate methods would provide greater confidence that both were generating reliable data that was not prone to large amounts of error, such as would be associated with the development of low permeability well skins during piezometer testing. However, due to difficulties associated with Foot and Mouth Disease in the UK (see above) only piezometer tests were completed at Sutton Fen. However, in later work at Strumpshaw Fen both piezometer slug tests and MCM tests were conducted, and the K data generated by both techniques were evaluated (see Chapter 4). In the current chapter the background to the use of laboratory determinations of K is given, and the specifics of the MCM and its application to fen peat are discussed.

The MCM was originally developed by Beckwith et al. (2003a) for use on samples of bog peat. An intact core of peat is taken from the field using a polyvinyl chloride sampling tube and returned to the laboratory. Cubes of soil (7.5×7.5×7.5 cm) are then cut from the larger core using a sharp, smooth-bladed knife (serrated knives tend to snag and drag peat fibres during cutting, thus causing damage to a sample). The cubes are

then coated in gypsum and two opposing faces are removed. However, prolonged contact with water can weaken gypsum (Bouma and Dekker, 1981), and the material is sometimes difficult to work with. Because of these problems the original method was modified so that cubes were coated with paraffin wax (see Figure 3.3). The wax was applied by dipping successive sides of each cube into molten wax until the entire cube was encased in a *c.* 0.5-cm layer of wax. The upper and lower faces of wax were then removed using a hot knife, after which the sample was left to saturate in a container of water of similar quality to that found on the fen surface during inundation of the site. A *K* determination was then made by allowing water to flow through the cube.
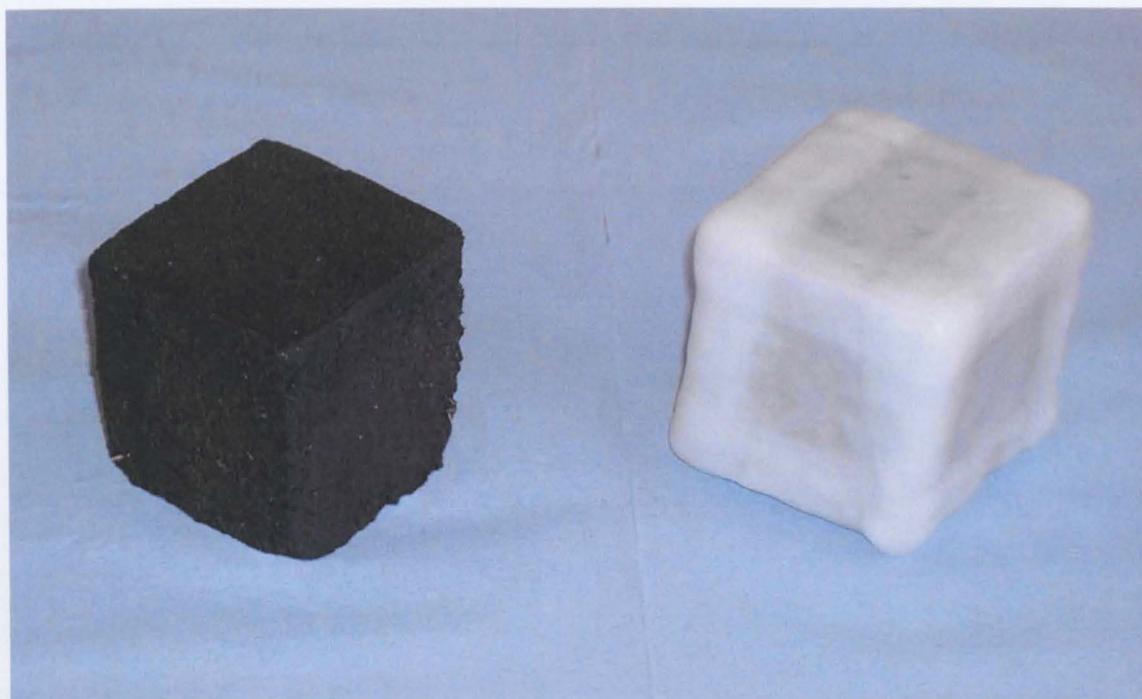
Figure 3.3 Cube of fen peat cut from a larger core, before and after coating with paraffin wax prior to *K* determination.

The MCM is thought to avoid many of the possible sources of error in other field (piezometer) and laboratory (permeameter) determinations of *K*. The core collection procedure in the MCM results in only minimal compression (typically < 2.5 % of the core length) or damage to the peat structure. When peat samples are cut to size for use in permeameter tests, smearing of the faces tends to occur. Such smearing can block larger pores in the peat and could lead to *K* being underestimated. However, in the MCM, the removal of the paraffin wax from a face removes any smeared material. This is because smeared material tends to adhere to the paraffin wax (see Figure 3.4). The

result is a 'fresh' face of peat with pore blockages removed (*cf*. Beckwith *et al*., 2003a) and a much more accurate measure of K.

Once each sample was saturated, a vertical hydraulic conductivity, K_v, test was performed as described in Beckwith *et al*. (2003a). The open faces of the cube were then dabbed dry, resealed and the cube turned through 90 ° to allow a determination of horizontal hydraulic conductivity, K_h. Repeat tests on cubes with differing peat characteristics were conducted to assess the precision of the method, and to ensure that any differences between K_h and K_v were not simply a function of the order in which the tests were conducted. To remove the potential for temperature effects, all MCM estimates of K were standardised to 20 °C, as was the case for estimates derived from piezometer tests (Klute, 1965).
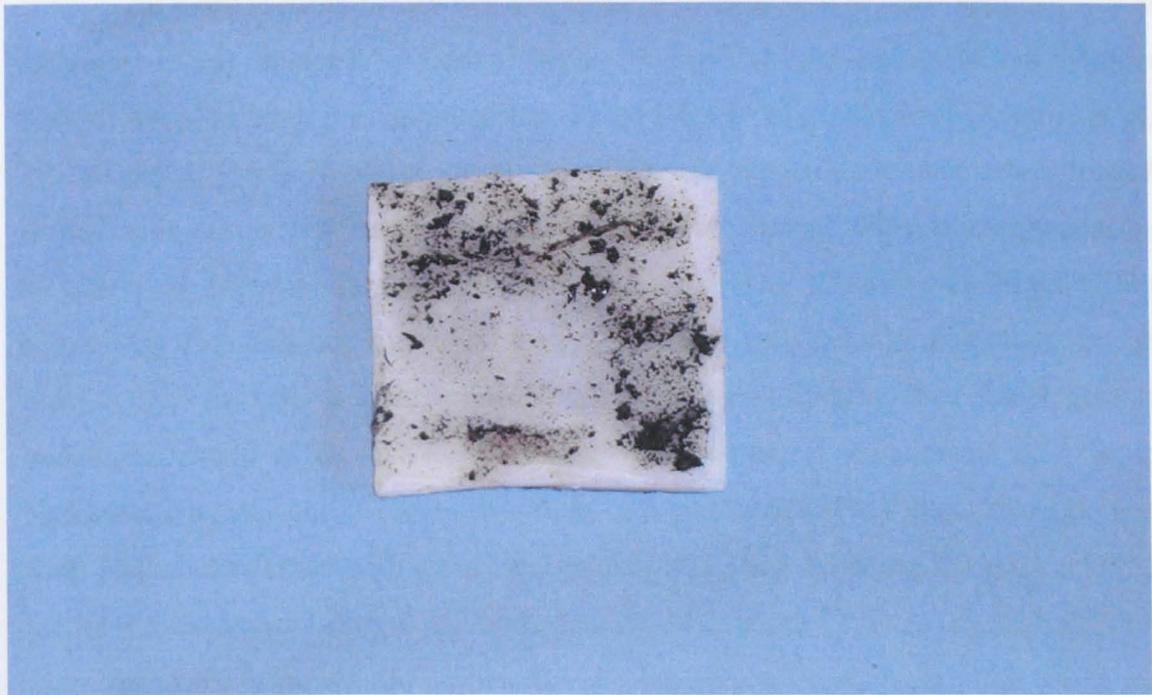
Figure 3.4 Paraffin wax removed from cube face showing adhered peat material.

Anisotropy is present in a soil when $K_h \neq K_v$. Only rarely has the anisotropy of K in peat been fully considered in studies of ground-water flow in wetland sediments, often because inadequate measurement techniques were previously available for the determination of K_h and K_v (Beckwith *et al*., 2003b). Consequently, peat has previously been assumed to be isotropic and homogeneous, or alternatively isotropic and heterogeneous. Almendinger and Leete (1998) were among the first to attempt to recognise the importance of anisotropy in peat, although there were a number of

limitations in their method for approximating the degree of anisotropy (for example the wide-scale use of averaged K_h and K_v values over the entire thickness of peat). Beckwith *et al.* (2003b) have demonstrated that the inadequate consideration of anisotropy can lead to erroneous conclusions regarding both the *pattern* of ground-water flow, because flow lines cannot be assumed to be perpendicular to lines of equipotential in an anisotropic medium, and the *rates* of ground-water flow in peat if calculated solely by combining hydraulic head gradients with piezometer-derived K values.

The first step towards a more complete consideration of the anisotropy of K in wetland sediments is the development of reliable methods to characterise both K_h and K_v. Several authors have suggested that the standpipe piezometer can be used to differentiate between horizontal and vertical hydraulic conductivity. If the piezometer has a cylindrical intake closed at its base, as in those used at Sutton Fen and in the subsequent work at Strumpshaw Fen described in Chapter 4, it is often assumed that an estimate of K_h is obtained, whereas, if the piezometer intake consists solely of the open base of the standpipe, it is assumed that an estimate of K_v is obtained (Rycroft *et al.*, 1975; Boelter, 1965). However, strictly speaking, it is impossible to obtain directional K from simple piezometer tests such as those used here (Butler, 1998). It is only possible to obtain K_h when K_v is already known and *vice versa*. Chason and Siegel (1986) recognised this problem, and noted that piezometers with cylindrical intakes provide only an *approximate* measure of K_h, whilst standpipes open at their bases give an undefined 'mean' of K_h and K_v. Similarly, from numerical experiments on a finite-element model of a soil-piezometer system, Seo and Choe (2001) found that slug tests from piezometers fitted with cylindrical intakes and analysed using Hvorslev's (1951) model (i.e. assuming isotropy and homogeneity – Equations (2) to (4) in Section 3.2.4) gave reasonable estimates of K_h when $K_h > K_v$, but only when the piezometer intake was placed centrally in a homogeneous soil layer. It has been suggested that both bog and fen peats are anisotropic, with $K_h > K_v$ (*cf.* Beckwith *et al.*, 2003a). Thus simple piezometer tests might be expected to give reasonable estimates of K_h. However, much previous evidence of anisotropy in peats is based on piezometer tests, and no independent and apparently accurate measure has been available to show whether the piezometer data are reliable and how well they approximate K_h and K_v in the field. In addition, there is considerable evidence that peats display heterogeneity even over small spatial distances (dm to m) (cf. Beckwith *et al.*, 2003a) and such heterogeneity can render piezometer estimates of K unreliable. Seo and Choe (2001) found that, where the

top or bottom of the intake was in contact with a soil layer of different K from that of the tested soil layer, Hvorslev's (1951) method could yield poor estimations of the K of the tested soil layer. This was especially true where the soil above or below the intake was of much higher K than the tested soil layer. Although it is possible within a modelled system such as that used by Seo and Choe (2001) to determine the accuracy of simple Hvorlsev-type slug tests under known conditions of heterogeneity, it is important to realise that the pattern of heterogeneity (e.g. layering within a soil) is often not known *a priori* in the field. Therefore, it would be instructive to compare the findings from field piezometer tests with accurate estimates of K_h and K_v, to provide a more complete evaluation of what piezometer slug tests in peat actually measure.

Classically, a laboratory permeameter method would be employed to determine values of K_h and K_v from core samples (e.g. Chason and Siegel, 1986; Boelter, 1965). However, the permeameter method is prone to errors associated with preferential flow along the walls of the instrument due to a poor fit with the soil, and smearing of the peat during sample preparation (Beckwith *et al.*, 2003a). These sources of error are largely avoided by the MCM, thereby producing more accurate estimates of K than other permeameter methods.

3.3 Results and discussion from the evaluation of the piezometer slug test in peat

3.3.1 Rate of recovery and differences in recovery after insertion and withdrawal

Almost all of the tests showed rapid recoveries following slug insertion/withdrawal. In every test, 90 % of the recovery to the equilibrium water level took less than 1500 s, and in many cases it took less than 300 s. Such rapid responses were expected from visual inspection of the root mat. A more striking feature of the tests was that there was a clear difference in the rate of head recovery between slug insertion and slug withdrawal, with recovery more rapid after withdrawal. This behaviour was observed in all but one of the piezometers (Piezometer 1) in the 'W' sampling frame. In one further instrument (one of the piezometers on which replicate tests were performed: Piezometer 4) this was observed in the second and third insertion–withdrawal combination, but not the first. In total, it was observed in 21 out of 23 insertion–withdrawal combinations. A typical example of such behaviour is shown for Piezometer 12 in Figure 3.5. The slug insertion

and slug withdrawal are clearly seen in Figure 3.5, as is the difference in the rate of recovery between each test. Recovery to the stable water level after slug insertion took c. 435 s and recovery after withdrawal took c. 210 s. Differences in recovery between insertions and withdrawals were evaluated by using the time taken for 90 % recovery (t_{90}) of the initial head displacement (i.e. the time at which $h = 0.1h_0$). Both the paired t-test and the Wilcoxon signed rank test for paired data were used. For those piezometers on which repeat tests were performed data from just the first insertion–withdrawal combination w ere u sed (thus n = 1 7). D ifferences i n r ecovery b etween insertion a nd withdrawal were highly significant ($p < 0.01$ for both tests). The median ratio of t_{90}-insertion to t_{90}-withdrawal was 1.90, with a minimum of 0.05 and a maximum of 7.00.
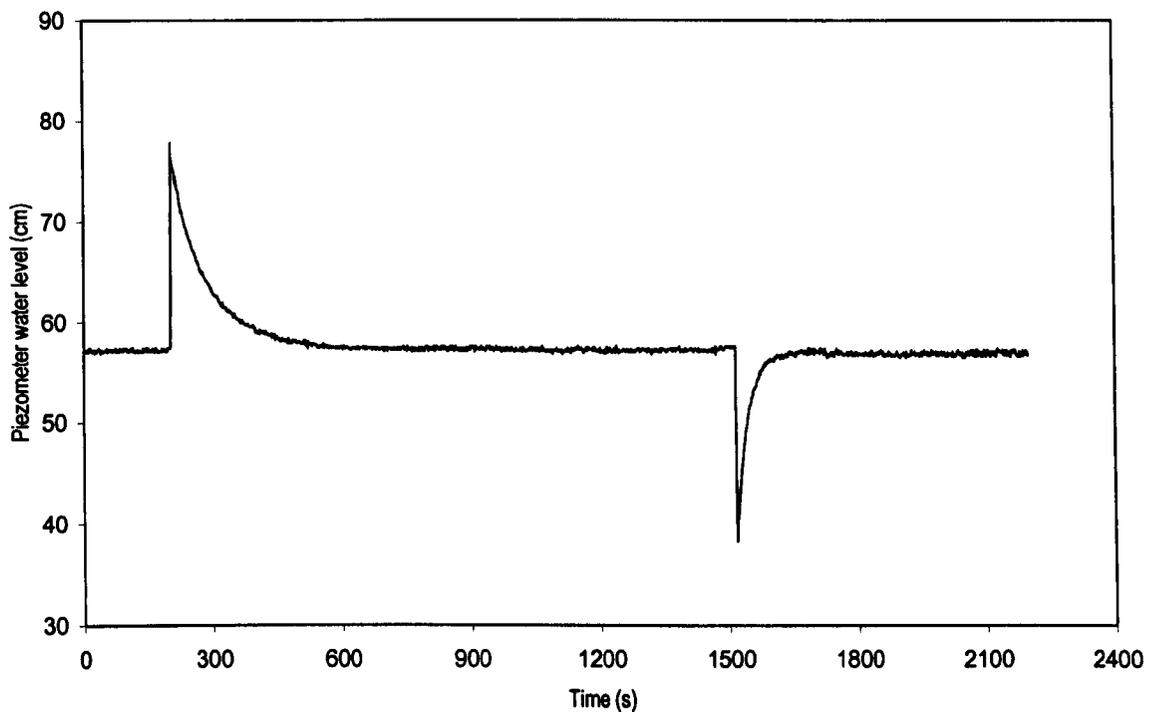
Figure 3.5 Water levels recorded by the pressure transducer during slug tests on Piezometer 12. Water levels are expressed relative to the pressure transducer.

It was noted above that repeat tests were carried out on three piezometers to check whether s uch h ysteretic behaviour was real o r w hether i t was related t o the o rder i n which the insertions and withdrawals were performed. An example of such repeat testing is shown in Figure 3.6 from Piezometer 11. The data are plotted on a common time scale with time zero representing the beginning of each test. On the morning of 10th May 2000 the slug was inserted and withdrawn. The remaining tests were performed over 24 h later but were successive, i.e. shortly after the water level from one

test had recovered the next test was performed. The sequence on 11th May was: insertion, withdrawal, insertion, and finally withdrawal.
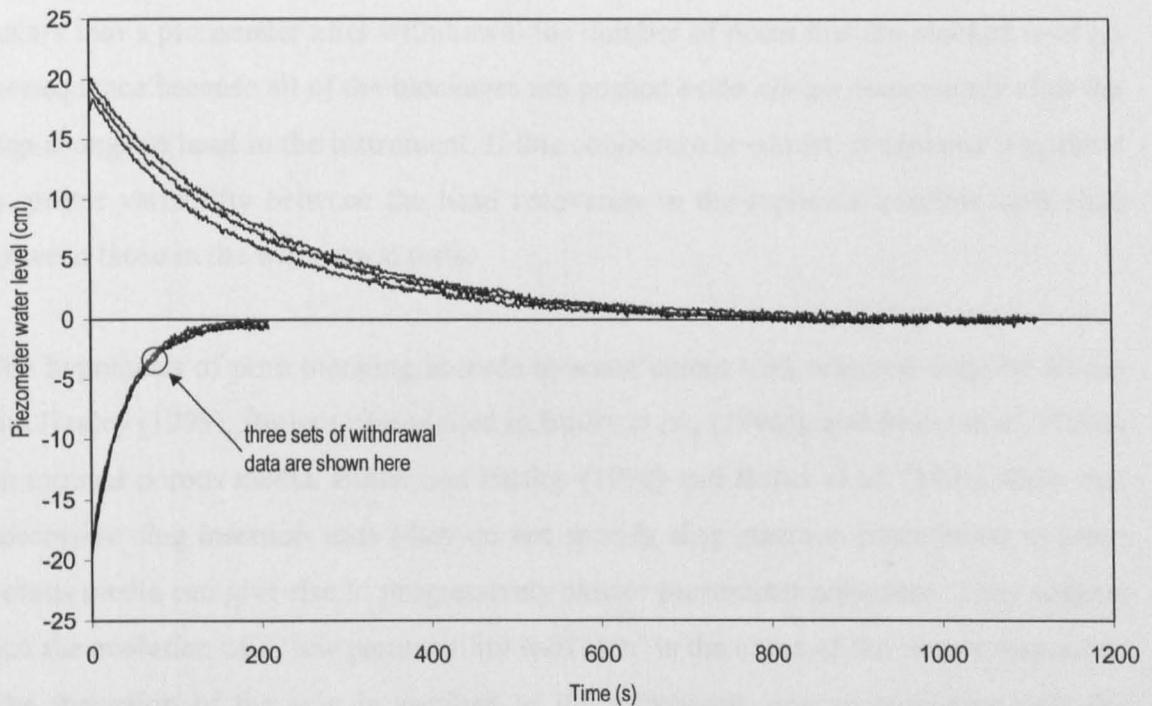
Figure 3.6 The three insertions and three withdrawals performed on Piezometer 11. Water levels are expressed relative to the stable water level between insertions and withdrawals. Insertions are shown by water levels above zero; withdrawals by levels below zero.

From Figure 3.6, it can be seen that there is a clear difference in the rates of recovery between the insertion and the withdrawal tests. It can also be seen that the patterns of water-level recovery after the three withdrawals are almost identical, whereas the patterns o f r ecovery a fter i nsertion a re m ore v aried b ut s till v ery s imilar. T hese d ata suggest that the order of test does not affect the rate or pattern of recovery, and that the test procedure produces highly reproducible but hysteretic results. Similar results to those for Piezometer 11 were found for the other two piezometers on which replicate tests were performed. The reason for the difference between recovery after insertion and that after withdrawal is not immediately obvious. However, one possibility is that during insertion, when water is flowing from the piezometer standpipe into the root mat, small p ieces o f o rganic m atter i n t he w ater i n the p iezometer c log t he ends o f p ores around the intake, causing a reduction in the rate of flow from the instrument. During withdrawal, these blockages are pushed aside or flushed into the standpipe by water flowing into the piezometer, causing recovery to be more rapid. The blocking of pore

ends during flow from the piezometer will probably be variable, i.e. different numbers of pores will be blocked in different tests and those pores that are blocked may not be blocked immediately after flow from the piezometer starts. Conversely, when flow occurs into a piezometer after withdrawal the number of pores that are blocked is of no consequence because all of the blockages are pushed aside *almost immediately* after the step change in head in the instrument. If this conjecture is correct, it explains why there is greater variability between the head recoveries in the replicate insertion tests than between those in the withdrawal tests.

The hypothesis of pore blocking accords to some extent with research done by Butler and Healey (1998), Butler (1996) (cited in Butler *et al.*, (1996)), and Butler *et al.* (1996) on mineral porous media. Butler and Healey (1998) and Butler *et al.* (1996) show that successive slug insertion tests (they do not specify slug insertion procedures) in some porous media can give rise to progressively slower piezometer responses. They suggest that the evolution of a 'low permeability well skin' is the cause of the slower responses. The formation of the skin is ascribed to the movement, and accumulation near the intake, of fine material mobilized during the introduction of the slug. The material accumulates in a manner that results in a progressive decline in near-intake permeability and, therefore, rates of test recovery with successive insertions. Successive slug insertion tests were not performed and it is impossible to confirm whether progressive changes in recovery during such testing might occur in the root mat at Sutton Fen.

Butler and Healey (1998) also observed a significant difference in the rates of recovery between slug insertions and withdrawals, with the latter recovering more rapidly than the former. They suggest that the formation of a combined bacterial/oxyhydroxide 'mat' at the piezometer intake is the cause of these differences. The mat is forced against the pores surrounding the well during insertions, leading to a reduction of flow, but is pushed back away from the pores during withdrawals, thus resulting in a more rapid recovery. No evidence for the existence of such a mat was found in the piezometers used at Sutton Fen. Yet, the pore-blocking explanation invokes exactly the same processes as the bacterial/oxyhydroxide mat explanation. That is, material is forced against the pores surrounding the intake during water flow from the piezometer, but is flushed or pushed from the pore ends during flow into the instrument. The difference

between the hypothesis given in this thesis and that of Butler and Healey (1998) lies with the material involved in the blocking of the pore ends.

3.3.2 Log-linear behaviour

Equation (4) was fitted numerically to the 'raw' head recovery data from every slug test using a least-squares minimization with T (see Equation 3) as the fitted parameter. To test for the log–linearity of recoveries runs tests (Siegel, 1956) were performed on the residuals to see whether they were scattered randomly about the best-fit line based on Equation (4). In almost all cases (44 from 46) the scatter was non-random, indicating departure from Equation (4). However, in many cases the departure was very small indeed ($r^2 > 0.998$ in 19 of the 23 withdrawal tests, and $r^2 \geq 0.999$ in 14 of the tests). Further, in 19 of the 23 insertion–withdrawal combinations the fit of the model was better for the withdrawal data than for the insertion data. Examples of typical responses are shown in Figures 3.7 and 3.8.

Figure with normalised head (log scale, y-axis from 1 to 0.1) against Time (s) on x-axis from 0 to 600. Equations shown:

$$\frac{h}{h_0} = e^{-t/188.07} \quad r^2 = 0.9990$$

$$\frac{h}{h_0} = e^{-t/104.13} \quad r^2 = 0.9993$$
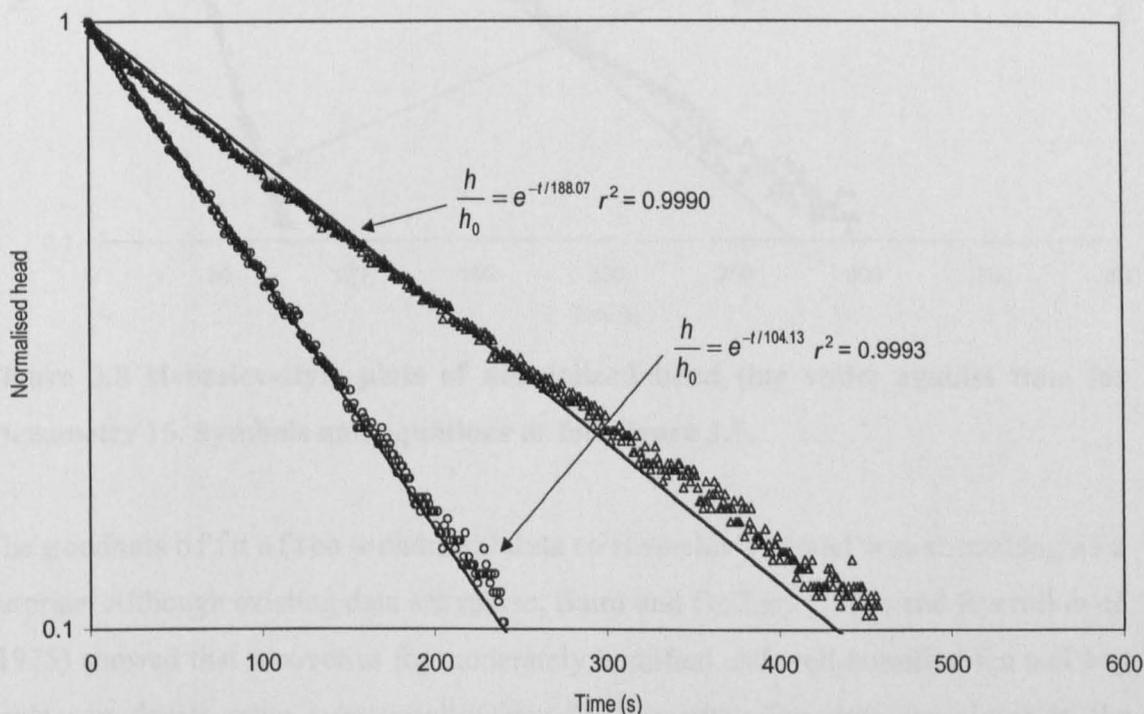
Figure 3.7 Hvorslev-style plots of normalized head (log scale) against time for Piezometer 9. Open triangles indicate recovery after slug insertion; open circles are recovery after withdrawal. The best-fit Hvorslev equations (Equation (4)) are also shown.

In Figure 3.7, which shows the results for Piezometer 9, neither test gave rise to a random distribution of residuals around the best-fit Hvorslev line (Equation (4)). However, for the recovery after withdrawal in particular, it is clear that the data are very nearly log–linear. Piezometer 9 was typical of many of the piezometers. Figure 3.8 shows the recoveries for Piezometer 15, where the scatter of the residuals for the withdrawal data was not significantly different from random (p = 0.0840), and shows again that the withdrawal data provide a closer fit to Hvorslev's model than the insertion data.

Figure with curves labelled:

$$\frac{h}{h_0} = e^{-t/118.64} \quad r^2 = 0.9977$$

$$\frac{h}{h_0} = e^{-t/32.88} \quad r^2 = 0.9992$$

Axes: Normalised head (vertical, log scale, 0.1 to 1); Time (s) (horizontal, 0 to 400).
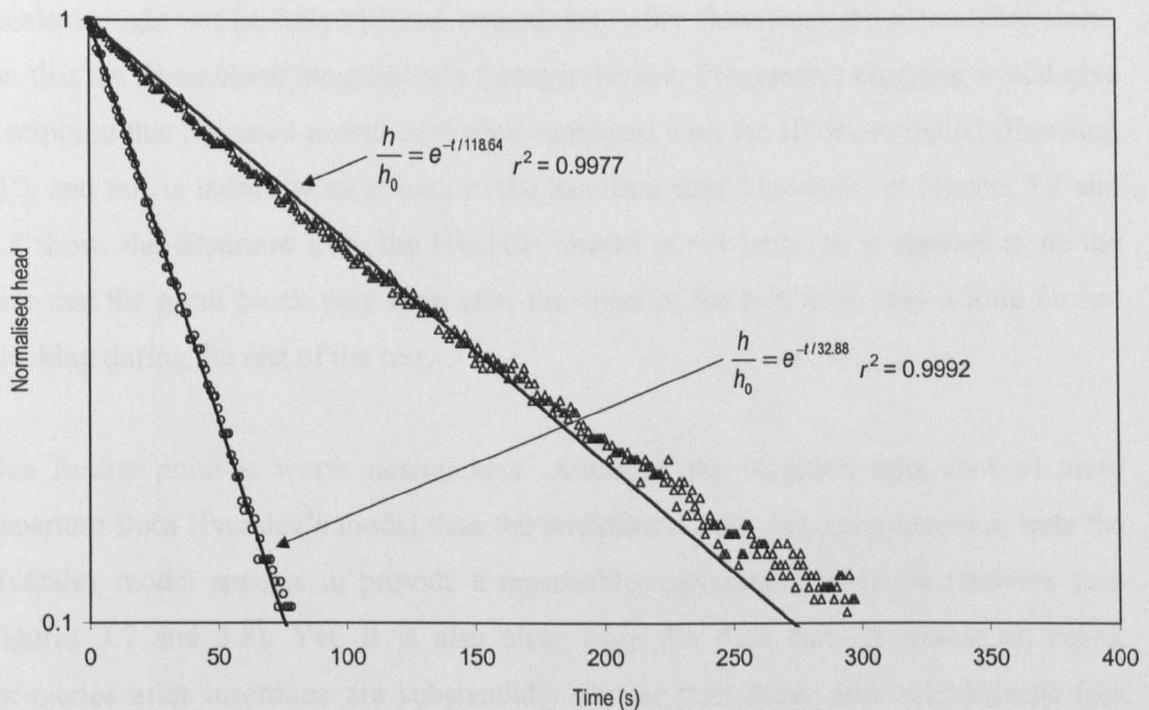
Figure 3.8 Hvorslev-style plots of normalized head (log scale) against time for Piezometer 15. Symbols and equations as for Figure 3.7.

The goodness of fit of the withdrawal data to Hvorslev's model was something of a surprise. Although existing data are sparse, Baird and Gaffney (1994) and Rycroft *et al.* (1975) showed that recoveries for moderately humified and well-humified fen and bog peats can depart quite substantially from log–linearity. The data are closer to the responses observed for poorly decomposed *Sphagnum* peat reported by Rycroft *et al.* (1975). It is possible that the approximately rigid behaviour evident in the responses is due to a stable pore structure imparted by the roots and rhizomes (which comprise the majority of the material in the root mat). If trapped biogenic gas bubbles were present in the peat, S_s would be substantially greater than zero and head recovery should, as a

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result, show pronounced departures from log–linearity. It is possible that trapped gas bubbles are not present or are rare in the root mat in late winter and early spring (i.e. when the tests took place). Gas bubble content was not measured, but ebullition of gas bubbles has been noticed when walking across some parts of the fen in late summer. Clearly, further investigations are needed on the effect of gas bubbles on the hydraulic and storage properties of the root mat.

The greater departure from log–linearity in the insertion data is consistent with the pore-blocking hypothesis. It was noted above that, during an insertion, those pores that are blocked might not be fully blocked immediately after flow from the piezometer starts, i.e. that the pores block progressively through the test. Progressive clogging would give a response that becomes slower over time compared with the Hvorslev model (Equation (4)), and this is indeed what is seen in the insertion data. However, as Figures 3.7 and 3.8 show, the departure from the Hvorslev model is not large, so it appears to be the case that the pores block very soon after the onset of the test, with only a little further blocking during the rest of the test.

One further point is worth raising here. Although the insertion tests showed more departure from Hvorslev's model than the withdrawal data, for many insertion tests the Hvorslev model appears to provide a reasonable *approximation* of the recovery (see Figures 3.7 and 3.8). Yet, it is also clear from the data that, in almost all cases, recoveries after insertions are substantially slower than those after withdrawals (see Figures 3.7 and 3.8 and Section 3.3.1). Therefore, an approximate fit to Hvorslev's model is no guarantee that a test has yielded reliable data, because the test response should not be dependent on the mode of test initiation. This highlights the need for greater scrutiny of the piezometer test procedure than has previously been the case in the majority of the wetlands literature.

3.3.3 Non-standard behaviour and the effect of development, slug size and clean water on recoveries

Further checks of the piezometer technique were performed using instruments not in the original 'W' sampling frame. Test Piezometers 1 and 2 were used to examine the influence of piezometer development on test responses. Checks of the effects of clean water and different slug sizes were performed on Test Piezometers 3 and 4, which were

installed after a period when access to the site had been refused due to Foot and Mouth Disease restrictions. The test procedures used on each test piezometer were as follows:

- Test Piezometers 1 and 2. Insertion, withdrawal, insertion, and withdrawal. Bailing and development. Insertion, withdrawal, insertion and withdrawal.

- Test Piezometers 3 and 4. Insertion and withdrawal with larger slug. Removal of pressure transducer. Data check. Reinstallation of pressure transducer. Insertion, withdrawal, insertion, and withdrawal with smaller slug. Insertion and withdrawal with larger slug. Removal of pressure transducer. Flushing with clean water. Reinstallation of pressure transducer. Insertion, withdrawal, insertion, and withdrawal with larger slug.

'Non-standard' behaviour was observed on the first insertion on Test Piezometer 1, the first insertion on Test Piezometer 3 and all of the 'dirty' water insertions on Test Piezometer 4. In all the other dirty water tests, the behaviour of the recoveries was consistent with the tests discussed earlier in this chapter. To illustrate non-standard behaviour, the insertion data for Test Piezometer 1 are shown in Figure 3.9. From Figure 3.9 it can be seen that recovery after the first insertion was initially rapid, then slowed dramatically, giving a strongly non-log–linear response. All other post-insertion recoveries took longer to reach $h/h_0 = 0.1$ and were closer to log–linearity, and all were slower than the equivalent post-withdrawal recovery (Figure 3.10).

A simple explanation for non-standard behaviour of the recovery after some insertions is not immediately obvious. Possible factors include the presence of gas bubbles, flow of water into large macropores, and stress adjustments in the root mat after installation of the piezometer. However, none of these factors can be used in a simple way to explain the observed responses, especially in Test Piezometer 1 where such behaviour occurred only once. Development does not appear to be a factor, because non-standard behaviour was also observed in two 'W' piezometers following development, in addition to Test Piezometers prior to development.
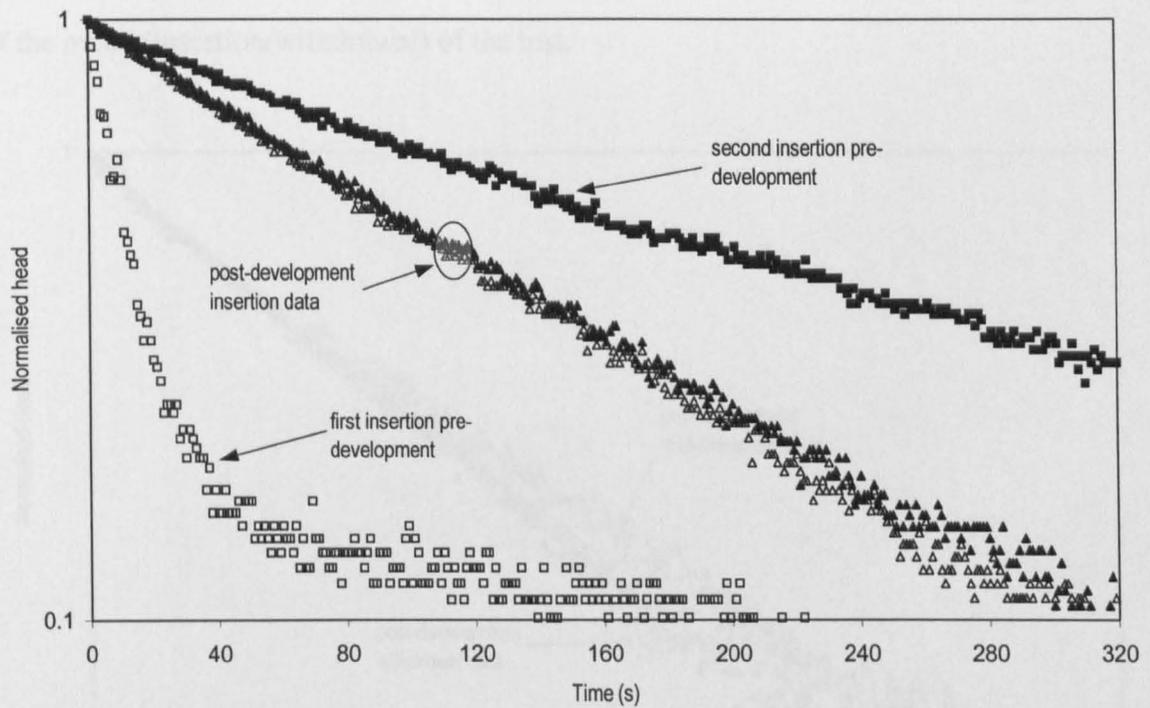
Figure 3.9 The recoveries after each insertion into Test Piezometer 1.

The effect of development on rates of recovery was somewhat difficult to assess. In Test Piezometer 2 (results not shown) the effect was negligible, with little difference between pre- and post-development responses in both insertion and withdrawal tests. The effect was clearer with Test Piezometer 1. The recoveries after the two post-development insertions were substantially quicker than the recovery after the second pre-development insertion (Figure 3.9). Similarly, although less dramatically, the post-withdrawal recoveries were more rapid after development (Figure 3.10). Thus, it appears that development does have an effect on rates of recovery. However, because of the non-standard behaviour after the first insertion in Test Piezometer 1, further work is needed on the effects of development.

Similar problems exist in interpreting the effect of slug size and clean water on rates of recovery. In Test Piezometer 4, the recoveries after every dirty water insertion were strongly non-log–linear and initially quicker than equivalent post-withdrawal recoveries. In two of the dirty water insertion tests, water levels fluctuated during parts of the recovery. Again, it was not clear what caused these features during the recovery, but they are unlikely to be due to momentum effects in the piezometer tube because the rates of recovery were relatively slow (in all cases, 90 % recovery of the initial head difference was greater than 100 s). However, all of the tests after the introduction of

clean water in Test Piezometer 4 were close to log–linear and all were similar regardless of the mode (insertion/withdrawal) of the test.
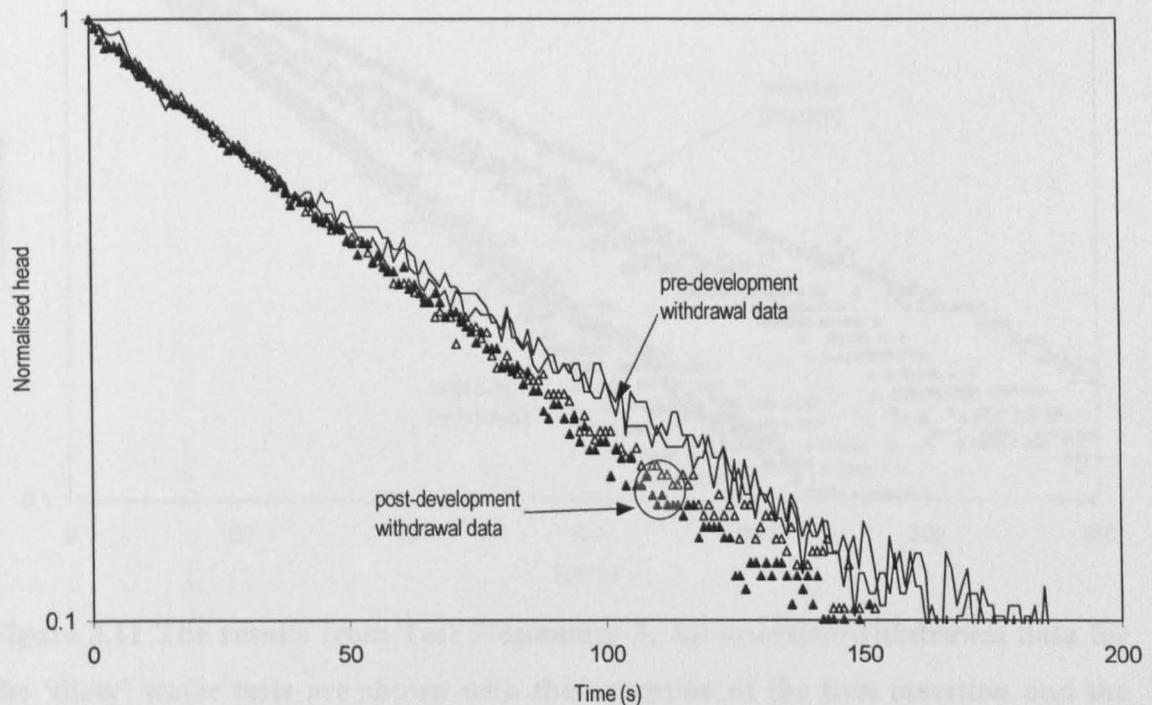
Figure 3.10 The recoveries after each withdrawal from Test Piezometer 1.

The results for Test Piezometer 3 were clearer. Apart from the first insertion, all of the data showed approximate log–linearity (see Figures 3.11 and 3.12). In Figure 3.11 it can be seen that the use of the larger slug compared to the smaller slug appears to result in slower recoveries after insertion, whereas it has no apparent effect on the withdrawal tests. These results support the suggestion made above, that differences in insertion/withdrawal behaviour are caused primarily by pore clogging. Introduction of a larger slug into the piezometer might be expected to cause more disturbance and mobilization of organic particles in the water in the standpipe and, therefore, cause more pore blocking than would occur after the introduction of a smaller slug. Also, stronger seepage forces due to a larger hydraulic gradient associated with the larger slug might be expected to result in more pores becoming clogged.

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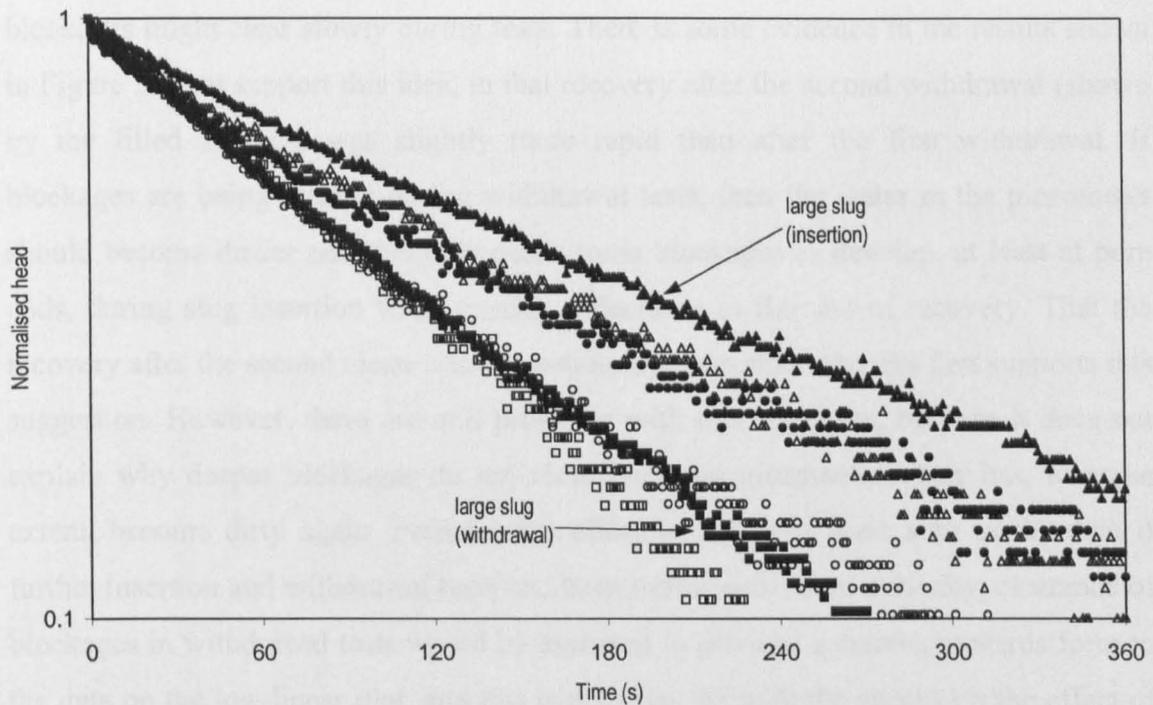
Figure 3.11 The results from Test Piezometer 3. All insertion/withdrawal data for the 'dirty' water tests are shown with the exception of the first insertion and the first withdrawal (see text for details). The filled circles and open triangles show the data from the two insertion tests using the small slug. The open squares and open circles show the data from the two withdrawal tests using the small slug. The filled triangles show the data from the insertion test using the large slug, and the filled squares are the data from the large-slug withdrawal test.

The effects of introducing clean water on the responses in Test Piezometer 3 are substantial (Figure 3.12). All of the clean water tests were done with the larger slug. The introduction of clean water has two main effects. First, all of the recoveries are more rapid than their dirty water equivalent (the dirty water results for the large slug are shown in Figure 3.12 for comparison). Secondly, the difference between recovery after insertion and recovery after withdrawal becomes much smaller. Both of these effects support to some extent the pore-clogging conjecture. With cleaner water, recoveries after insertion would be expected to be more rapid and closer to the responses after withdrawal. However, more rapid recoveries after withdrawal might not be expected. It is possible that, after the first insertion during a dirty water test, some material, rather than just blocking pore ends, enters the pores and blocks them some distance away from the pore openings in the immediate vicinity of the intake. If this were the case then such material would be expected to be more difficult to dislodge during a withdrawal test,

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resulting in a depressed rate of recovery. If clean water is introduced, then such blockages might clear slowly during tests. There is some evidence in the results shown in Figure 3.12 to support this idea, in that recovery after the second withdrawal (shown by the filled squares) was slightly more rapid than after the first withdrawal. If blockages are being cleared during withdrawal tests, then the water in the piezometer should become dirtier and this may cause some blockages to develop, at least at pore ends, during slug insertion tests, causing a decrease in the rate of recovery. That the recovery after the second clean water insertion is slower than after the first supports this suggestion. However, there are still problems with this argument, because it does not explain why deeper blockages do not recur once the piezometer water has, to some extent, become dirty again. Perhaps this effect would have been seen in the data if further insertion and withdrawal tests had been performed. More critically, clearance of blockages in withdrawal tests would be expected to produce a convex upwards form to the data on the log–linear plot, and this is not seen. As with the checks on the effect of development on rates of recovery, further tests on the effect of clean water in particular, but also slug size, are needed.
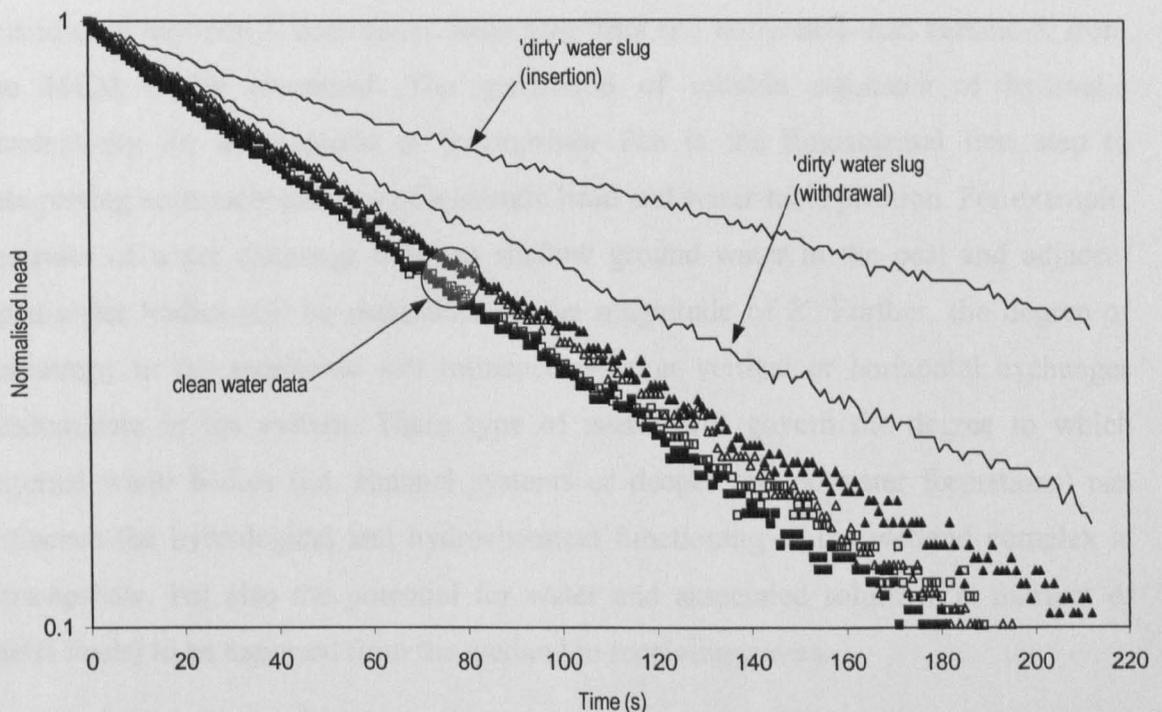
Figure 3.12 The effect of the introduction of clean water on slug test responses, Test Piezometer 3. Open triangles show the data from the first clean water insertion test. Open squares show the data from the first clean-water withdrawal test. The filled triangles and filled squares show the data from the subsequent insertion and withdrawal tests respectively.

3.4   Concluding comments

Many wetland scientists carry out slug tests rather uncritically, perhaps recording just one or two points of the recovery after slug insertion or withdrawal and applying Equation (5). It is clear from the data analysis in this chapter that uncritical use of slug tests could lead to quite large errors in the calculation of K. For example, slug insertion and slug withdrawal tests in the same piezometer can give quite different results. Although an explanation for these differences based on pore blocking by organic debris is suggested, there is still some way to go before providing unequivocal evidence for or against the pore-blocking hypothesis.

Given sufficiently detailed scrutiny of the data, piezometer slug tests can generate reliable estimates of K in peat deposits, thereby achieving Research Objective 1 identified in Section 1.2. In Chapter 4, piezometer slug tests are applied to the peat at Strumpshaw Fen, building on the developmental work reported above. The MCM is also used, to provide a direct comparison with piezometer-K values, and to allow the relationship between K determined from slug tests and horizontal- and vertical-K from the MCM to be examined. The generation of reliable estimates of hydraulic conductivity for the deposits at Strumpshaw Fen is the fundamental first step to interpreting accurately patterns of hydraulic head and water-table position. For example, the rates of water exchange between shallow ground water in the peat and adjacent open-water bodies will be dependent on the magnitude of K. Further, the degree of anisotropy in the sediments will influence whether vertical or horizontal exchanges predominate in the system. These type of issues will govern the degree to which external water bodies (i.e. channel systems or deeper ground-water formations) can influence the hydrological and hydrochemical functioning of the wetland complex at Strumpshaw, but also the potential for water and associated solutes (i.e. nutrient or metal loads) to be exported from the wetland to receiving waters.

4.   HYDROLOGICAL CHARACTERISATION OF STRUMPSHAW FEN

4.1   Introduction

Chapter 3 demonstrated that, if sufficient attention is paid to data collection and analysis protocols, apparently reliable estimates of the hydraulic conductivity (K) of fen-peat deposits can be made using piezometer slug tests. The modified cube method (MCM) was also introduced in Chapter 3 as a novel laboratory technique that could be used to indicate the reliability of K estimates and also to indicate the degree of anisotropy within a sediment. As was noted in Chapter 3, if these two independent methods for the determination of K, the piezometer slug test and MCM, generate similar K values, then greater confidence can be placed in the reliability of the data compared to a situation in which only one technique was employed, particularly if each individual method has been evaluated thoroughly and applied carefully to the peat deposits. Therefore, the first aim of the current chapter was to build on the developmental work reported in Chapter 3, and apply the piezometer method to the near-surface peat deposits at Strumpshaw Fen. The MCM was applied to the same deposits, thereby allowing an assessment to be made of the degree to which the two methods provide data that coincide. The piezometer and MCM work in this current chapter continues to address Research Objective 1 identified in Section 1.2.

The combination of reliable K data with information regarding the hydraulic gradients existing within a peat profile, enables both the pattern and the rates of water movement through the peat, and between the peat and 'external' water bodies, to be investigated through the application of Darcy's Law (see Section 3.1). The 'hydrological connectivity' between different elements of a catchment, for example a riparian wetland and the adjacent channel system, is an important concept in terms of assessing whether external water bodies can influence the functioning of the wetland system, and *vice*

versa. When strong hydrological connectivity is combined with high concentrations of environmentally s ignificant e lements i n s olution, f or e xample n utrient e lements, b oth the chemical and ecological quality of receiving waters can be threatened. This concept of 'source-plus-transport', or critical source areas, is of growing importance in the agricultural context for assessing the risk of phosphorus loss from farmed land to surface waters (e.g. Heathwaite *et al.*, 2003; 2000; Gburek and Sharpley, 1998), yet has received comparatively little attention in studies of wetland systems. Later work in this thesis (Chapters 5 and 6) examines the release of P to pore water and surface water, and the subsequent export of P from the peat. The focus for the current chapter lies solely with whether hydrological connectivity exists between the peat deposits at Strumpshaw and other catchment elements (deeper ground water and adjacent open-water bodies). To investigate this, a hydrological monitoring programme was implemented to provide data on the distribution of hydraulic head and configuration of water tables within the peat at Strumpshaw Fen. Finally, hydraulic gradients were combined with estimates of the hydraulic conductivity of the near-surface peat deposits to provide an indication of the magnitude of water exchange that can occur between the peat and receiving water bodies. These hydrological data were used to address Research Objective 2 in Section 1.2.

4.2 Methodology

4.2.1 Estimating K at Strumpshaw Fen

The background to the use of the piezometer slug test to estimate K in peat deposits was discussed in Chapter 3 (see Sections 3.2.2 and 3.2.4). The work conducted at Strumpshaw Fen followed closely the protocols described for Sutton Fen, with a number of modifications. Initial tests conducted at Strumpshaw Fen using the piezometer design described in Section 3.2.2, indicated that the rate of recovery during slug testing was likely to be slower than observed at Sutton Fen. Consequently, the piezometer design was altered so that tests recovered more rapidly. Smaller diameter polyvinyl chloride (PVC) standpipe piezometers were used at Strumpshaw Fen (o.d. = 3.3 cm, i.d. = 2.9 cm). Further, an intake of 21.0 rather than 7.0 cm length was machined at the lower end of the standpipe, which was sealed at its base with a wooden cone. The intake was of a design similar to that used in Chapter 3, with nearly 70 % of the intake open to water flow (Figure 4.1).
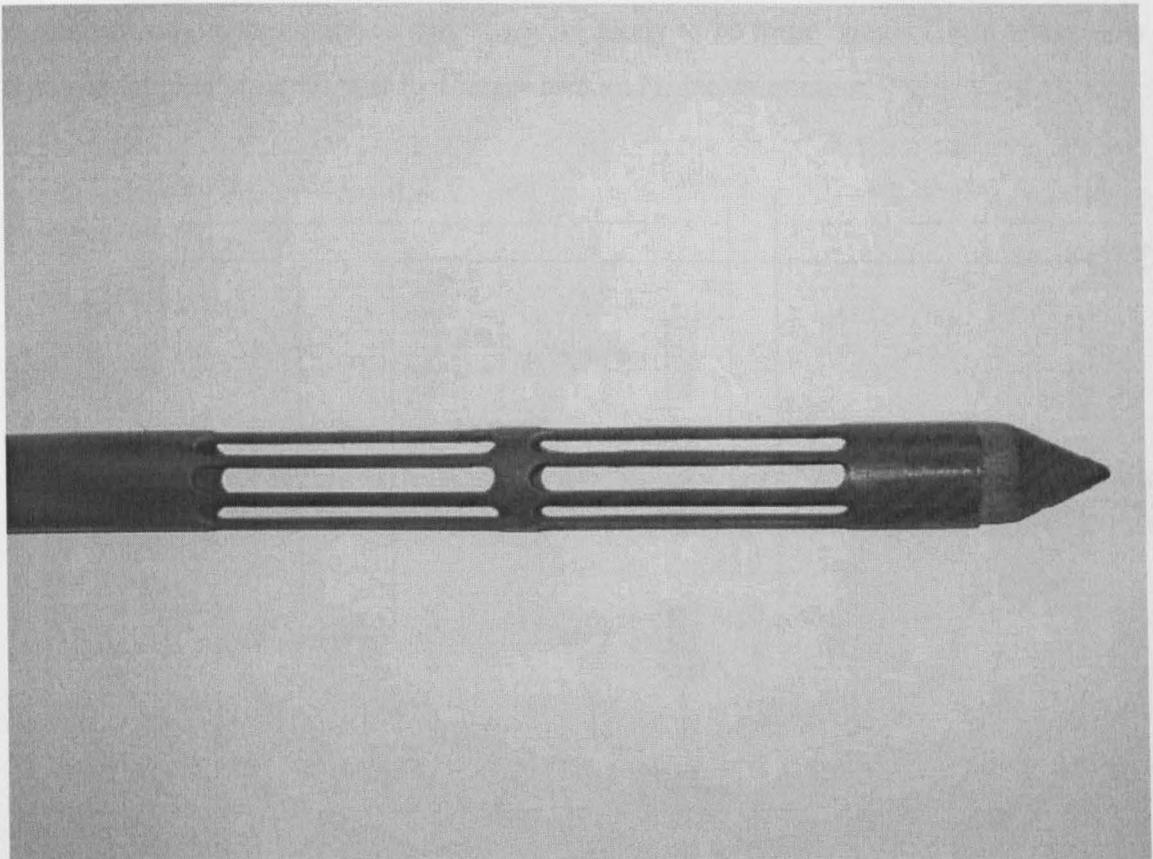
Figure 4.1 Piezometer intake design used in a ll tests conducted at S trumpshaw Fen.

The piezometers were installed in the peat using a hand screw auger of slightly smaller diameter than the outside diameter of the standpipe. Three sites at 3, 8 and 13 m from the ditch edge (subsequently referred to as locations A, B and C respectively) were positioned along a transect running perpendicular to a section of the ditch network. This transect was located within 2 m of that instrumented to record water-table configuration (see Figure 2.2 and Section 4.2.2). At each location slug tests were conducted with the intake at nominal depths of 15-36, 48-69 and 91-112 cm (subsequently referred to as depths 1, 2 and 3 respectively - see Figure 4.2). Tests were first conducted at the shallowest depth. The piezometers were then removed to allow the auger-hole to be extended before reinstalling the instruments at the middle depth and conducting further tests. This procedure was repeated for the third and final depth. The sampling design was chosen to reflect the expected foci for water exchanges at Strumpshaw Fen. Firstly, the ditch network within the wetland was expected to be an important driver of flow within the peat and therefore the hydraulic properties of the near-ditch sediments were

of particular interest. Secondly, visual inspection of the peat during hand augering indicated that the near-surface deposits were likely to be more conducive to water flow than peat at greater depth, due to a larger root and rhizome content.
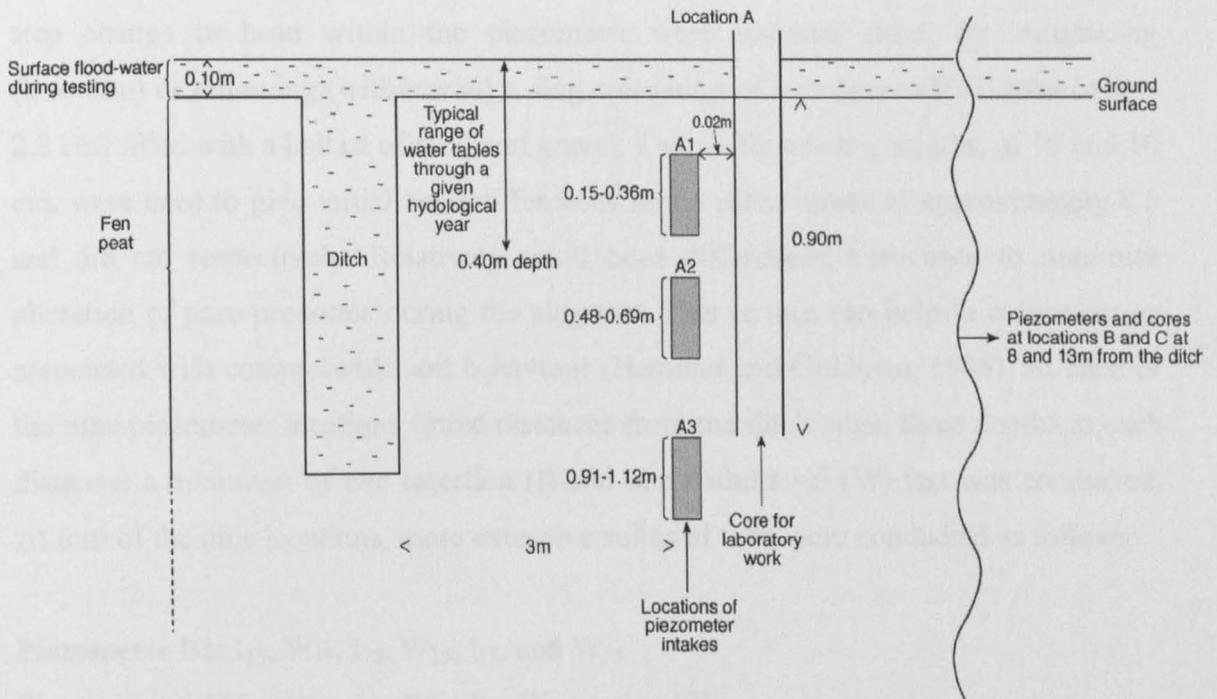
Figure 4.2 Location of piezometer positions and undisturbed core samples (not to scale).

Development of each piezometer was achieved by the removal of approximately 600 cm³ o f w ater from j ust a bove t he i ntake i n t hree s tages, a llowing e quilibration t o b e reached between each stage. The piezometers were developed in three stages at Strumpshaw Fen, rather than employing the single-stage protocol used at Sutton Fen, to reduce the size of the hydraulic gradient driving flow into the instrument. This ensured that minimal damage to the structure of the deposits surrounding the intake occurred during development, whilst maintaining a sufficiently strong flow of water into the piezometers to clear debris generated by piezometer installation and unblock any smeared pores (see Section 3.2.2). Although no direct turbidity tests were conducted on the water removed from the piezometers during development, visual inspection indicated that water removed during the third stage of development was substantially less turbid than samples collected during both the first and second stages.

Following development of the piezometer, a self-logging pressure transducer unit (In-Situ MiniTroll – for details see www.in-situ.com) with a resolution of 0.7 mm, set to record at 1 Hz, was lowered to the base of the piezometer. After allowing 1 hour for equilibration following introduction of the pressure transducer, slug tests involving a step change in head within the piezometer were initiated either by introducing (insertion) or removing (withdrawal) a slug consisting of a stoppered PVC tube (o.d. = 2.2 cm) filled with a ballast of sand and gravel. Two different slug lengths, of 15 and 10 cm, were used to give initial head differences in the piezometers of approximately 8.5 and 5.8 cm respectively. Relatively small head differences were used to minimise alteration of pore pressures during the slug test. This in turn can help to reduce errors associated with compressible soil behaviour (Hemond and Goldman, 1985). At each of the nine piezometer locations (three distances from the ditch edge, three depths at each distance) a minimum of one insertion (I) and one withdrawal (W) test was conducted. At four of the nine locations, more extensive suites of tests were conducted as follows:

Piezometer B1: I_{15}, W_{15}, I_{15}, W_{15}, I_{15}, and W_{15}.

Piezometer C1: I_{15}, W_{15}, I_{10}, W_{10}, I_{10}, W_{10}, I_{15}, and W_{15}.

Piezometer B2: I_{15}, W_{15}, I_{10}, W_{10}, I_{15} and W_{15}.

Piezometer C2: I_{15}, W_{15}, I_{15}, W_{15}, I_{15}, and W_{15}.

where the subscripts 15 and 10 refer to slug sizes of 15 and 10 cm respectively. The repeat tests using the same initial head were conducted to test for the presence of a low-permeability well skin, to determine the precision of the slug-test method, and to ensure that any differences in response between insertion and withdrawal tests within a given piezometer were not simply a function of the order in which the tests were conducted. Repeat tests using different initial heads were used to evaluate any dependence of normalised head recovery on h_0. The first and last repeats in these piezometers, e.g. B2, used the same slug size to separate a dependence on h_0 from the effects of an evolving low-permeability well skin, as suggested by Butler *et al.* (1996). Including all repeat tests, 36 individual slug tests were conducted.

If data from two independent methods coincide, then greater confidence may be placed in the reliability of the K estimates made. Further, an assessment of the degree to which K values from piezometer slug tests approximate K_h or K_v requires a precise and apparently accurate laboratory method to generate horizontal and vertical hydraulic

conductivity estimates. Ideally, exactly the same sample of peat would be used in both field piezometer and laboratory determinations of K. This is obviously not possible, but in the research at Strumpshaw Fen samples of peat for laboratory testing were collected from positions immediately adjacent to the piezometer locations. Following the completion of the final piezometer tests, cores of peat were extracted from each of the three sites along the transect using the procedures outlined in Beckwith *et al.* (2003a). A PVC sampling tube with i.d. = 10.4 cm, sharpened at one end, was driven into the peat, with the outer edge of the sampling tube no more that 2 cm from the outer edge of the piezometer tube (see Figure 4.2). The sampling tubes were driven to approximately 95 cm depth giving an undisturbed core length of 90 cm for laboratory K determination. Surface inundation of the site made extraction of deeper cores too difficult to attempt. The maximum compression during the installation of the tubes did not exceed 2.5 % of the core length. Thus it may be concluded that very little damage had been caused by the sampling process. Inspection of the samples on return to the laboratory confirmed that they were in excellent condition with no signs of damage. On return to the laboratory, K determinations were made on each of the three cores using the MCM technique described in Section 3.2.5.

4.2.2 Monitoring of water-table position and hydraulic head distribution at Strumpshaw Fen

Automatic logging together with targeted manual observations were made of hydrological variables at Strumpshaw Fen to determine the potential for water exchange between t he p eat d eposits a nd a djacent o pen-water b odies, a nd t he p eat d eposits a nd deeper ground water. The ditch network itself was monitored using an In-Situ MP Troll 8000 instrument (for details see www.in-situ.com), which recorded water level, pH, electrical conductivity (EC) and temperature at 30-minute intervals. A transect running for 100 m from a section of the ditch network into the fen interior was instrumented (see Figure 2.2 for transect location). At distances of 0.1, 1, 2, 5, 10, 25, 50 and 100 m from the ditch edge, wells were installed to 50 cm below the peat surface in pre-augered holes. The wells were constructed of PVC tubing (o.d. = 4.6 cm; i.d. = 4.2 cm), sealed at their bases, and drilled throughout their entire length, such that at least 27 % of the cross-sectional area of the tubing was open to water flow; thereby allowing changes in water-table position within the fen to be rapidly translated into changes in water level within the wells. Pressure transducers were installed to 45 cm depth within each well

and clamped in position by inserting a drilled rubber bung at the top of the well, through which the pressure transducer cable passed. All pressure transducers were wired to a Campbell CR10X logger, programmed to record the height of the overlying water column at 30-minute intervals. Data were recorded as a differential voltage measurement (mV) and were converted to centimetres of water using a linear regression equation, based on manual calibration of each individual pressure transducer prior to installation in the field. The calibration of each pressure transducer was checked again after the field monitoring programme and none had changed significantly.

At 2, 10 and 100 m from the ditch edge, piezometer nests were installed to monitor the distribution of hydraulic head through the peat profile. At each location, piezometers were installed in pre-augered holes such that the mid-point of each 5-cm long intake was at 2.5, 10, 17.5, 32.5, 102.5, 202.5 and 402.5 cm below the peat surface. For piezometers in the near-surface peat (0-35 cm) where K was expected to be higher than at greater depth due to the abundance of root and rhizome material, piezometers were constructed using slightly larger diameter PVC tubing. Piezometer standpipes and intakes at 2.5, 10, 17.5 and 32.5 cm depth had an o.d. of 2.0 cm and an i.d. of 1.6 cm, whereas for the deeper piezometers the corresponding dimensions were 1.5 cm and 1.1 cm respectively. Each piezometer intake of 5 cm was drilled to ensure that 27 % of the intake area was open to water flow. Piezometers underwent thorough development after installation, using similar procedures to those described in Section 4.2.1. Water levels in the piezometers were measured manually using an electronic dipmeter with a resolution of $< \pm 2$ mm. In addition, in August 2002 a 150 mm-diameter borehole was installed in the aquifer underlying the peat deposits. The borehole was located < 2 m from the beginning of the transect instrumented for water table and hydraulic head monitoring. The borehole was drilled to a depth of 10 m below the ground surface, with a screened section open to flow at 9.0-10.0 m below the ground surface only. The screened section was 2 m below the interface between the mineral aquifer and the overlying peat, and allowed the head in the mineral aquifer to be monitored. All observations of water-table position and hydraulic head were referenced to a common arbitrary datum.

The response-time characteristics of piezometers installed in wetland deposits are rarely considered directly, instead it is often *assumed* that instruments are in equilibrium with surrounding pore-water pressures when a reading is taken, an assumption which may lead to substantial errors (Hanschke and Baird, 2001). The efficiency of a given

piezometer, essentially the rate at which changes in pore-water pressure are reflected by changes in the water level within the instrument, is governed both by the piezometer dimensions and the hydraulic conductivity of the deposits. An extensive modelling study to assess the efficiency of the piezometers used at Strumpshaw Fen, as conducted by Hanschke and Baird (2001), was deemed to be beyond the requirements of the current research. Instead, careful consideration was given to the design of the piezometers in order to minimise the time required for the instruments to reflect a change in pore-water pressure in the surrounding deposits. Hanschke and Baird (2001) indicate that a piezometer becomes more efficient as F/A increases, where F is the shape factor of the piezometer intake (see Equation 6 in Section 3.2.4), and A the inside cross-sectional area of the piezometer standpipe. Within practical constraints, F/A was maximised for the piezometers used at Strumpshaw Fen. Piezometers at 2.5, 10, 17.5 and 32.5 cm depth had $F/A = 10.3 \text{ cm}^{-1}$, and those instruments at 102.5, 202.5 and 402.5 cm had $F/A = 18.9 \text{ cm}^{-1}$. The higher F/A for the deeper piezometers was chosen to reflect the likely lower K of these layers compared to the upper peat, based on visual inspection of the deposits during augering of the site.

4.3 Results from the determination of K at Strumpshaw Fen

4.3.1 Piezometer slug-test responses and correspondence with Hvorslev's theory

As noted above, a total of 36 piezometer slug tests were conducted in the upper 1 m of peat. For the tests on Piezometer A1, an insertion and subsequent withdrawal produced such rapid flow that an initial head difference in the piezometer could not be established. It is possible that the intake was connected to a root or rhizome network that enabled extremely rapid flows of water out of or into the piezometer in response to the introduction or removal of a slug. During augering prior to inserting the piezometer, root and rhizome material was cut at depths coincident with the subsequent position of the intake. Roots and rhizomes were found in other auger holes, but Piezometer A1 was the only one in which such 'anomalous' behaviour was observed. Consequently, the tests on this piezometer were ignored and only the remaining 34 tests are considered further.

To assess how well the responses accorded with Hvorslev's analysis, Equation (4) in Section 3.2.4 was fitted numerically to the untransformed slug test data as described in

Section 3.3.2. To test for log-linearity in the recoveries, runs tests (Siegel, 1956) were performed on the residuals between Equation (4) and the slug test data. A random and small scatter of the residuals about the best fit line suggests true log-linear behaviour; i.e., accordance with Hvorslev's analysis. In each of the 34 piezometer tests, non-random scatter was observed. However, the scale of the departure was generally apparently small ($r^2 > 0.99$ in 30 of the 34 test responses) (but see below).

Figure 4.3 shows the response in Piezometer C1 following a test initiated by withdrawal. It is clear that although the analysis of the residuals for this test suggests a systematic departure from log-linearity, the fit between the Hvorslev model and the data is extremely good. In this particular case, any error associated with a K estimate made assuming log-linear behaviour is likely to be extremely small.
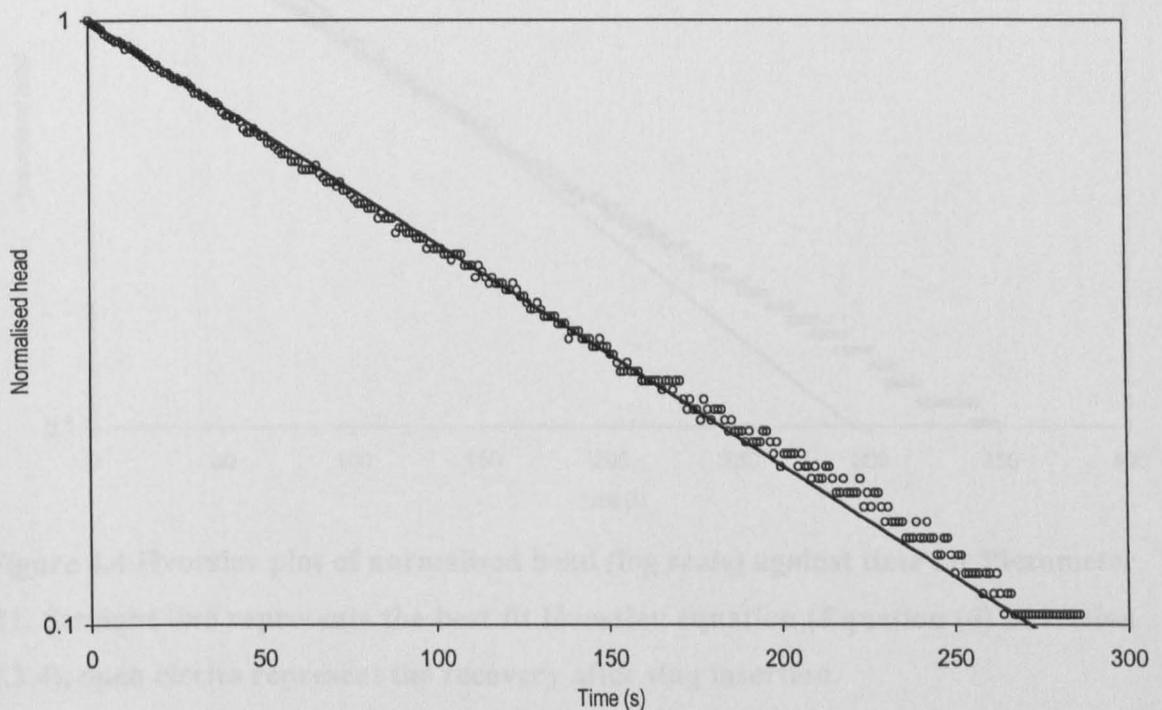
Figure 4.3 Hvorslev plot of normalised head (log scale) against time for Piezometer C1. Straight line represents the best fit Hvorslev equation (Equation (4) in section 3.2.4), open circles represent the recovery after slug withdrawal.

However, this is the only example in the 34 tests of such a good fit. In 29 of the 34 piezometer tests, a visual examination of the data supports the existence of a systematic departure from log-linearity. Figure 4.4 illustrates the recovery in Piezometer B1 following slug insertion which is typical of the 29 responses showing departure from log-linearity. Here a clear divergence of the test data from the Hvorslev model can be

seen. The recovery is more rapid at the beginning, and slower towards the end of the test, than predicated by Hvorslev's model. This pattern of departure from log-linearity is replicated in the other 28 tests, with variations only in the magnitude of departure. Thus, despite the fact that very high r^2 values imply a good fit between the test data and the Hvorslev model, the existence of clear, systematic departures from log-linearity suggest that the fit is in fact quite poor (Butler *et al.*, 1996). The form of the non log-linear response is consistent with examples of compressible peat behaviour given elsewhere (e.g. Baird and Gaffney, 1994; Brown and Ingram, 1988; Rycroft *et al.*, 1975).
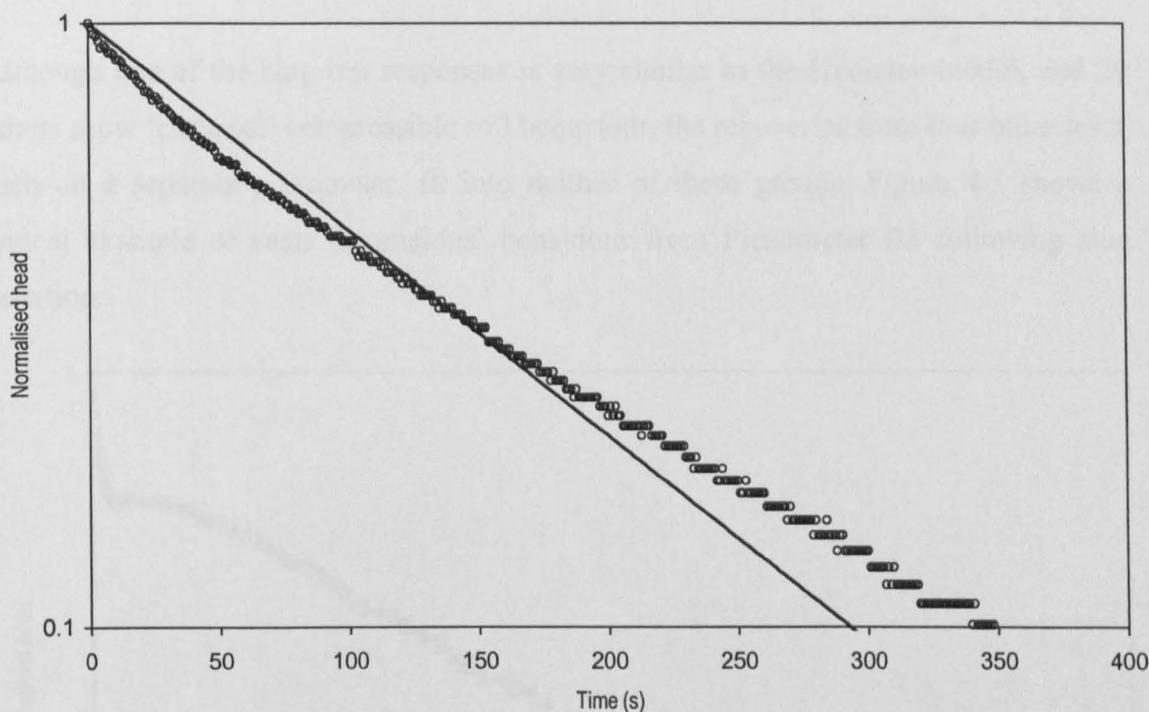
Figure 4.4 Hvorslev plot of normalised head (log scale) against time for Piezometer B1. Straight line represents the best fit Hvorslev equation (Equation (4) in section 3.2.4), open circles represent the recovery after slug insertion.

The degree of departure from the log-linear model of Hvorslev can be assessed using ratios of t_{90} to t_{50}; i.e., the times taken for 90 and 50 % recovery of the initial head difference in the piezometer. In a rigid soil, $t_{90}/t_{50} = 3.322$ regardless of the piezometer design or K of the soil (Baird and Gaffney, 1994). In a compressible medium, the ratio will consistently exceed 3.322, with higher values representing greater values of the volume compressibility of the medium (Brand and Premchitt, 1982). All 34 tests, including the withdrawal from C1 which was visually extremely near to the Hvorslev model, produced values of t_{90}/t_{50} greater than 3.322, suggesting compressible behaviour

and supporting the results of the runs tests described earlier. The five figure summary (minimum, lower quartile, median, upper quartile, and maximum) of all of the data is 3.362, 3.830, 4.298, 4.726, 12.194). In 15 of the 17 insertion-withdrawal pairs, the ratio was greater for the test initiated by slug insertion than by slug withdrawal. However, such a data summary is misleading because repeat data on single instruments are included (in effect there is 'double counting'). Applying a paired *t*-test, and its non-parametric equivalent, to the first insertion-withdrawal pair from each piezometer (n = 8) showed that there was not a significant difference ($p > 0.05$) between t_{90}/t_{50} values obtained from insertion tests and those from withdrawals.

Although one of the slug test responses is very similar to the Hvorslev model, and 29 others show 'classical' compressible soil behaviour, the recoveries from four other tests, each on a separate piezometer, fit into neither of these groups. Figure 4.5 shows a typical example of such 'anomalous' behaviour from Piezometer B3 following slug insertion.
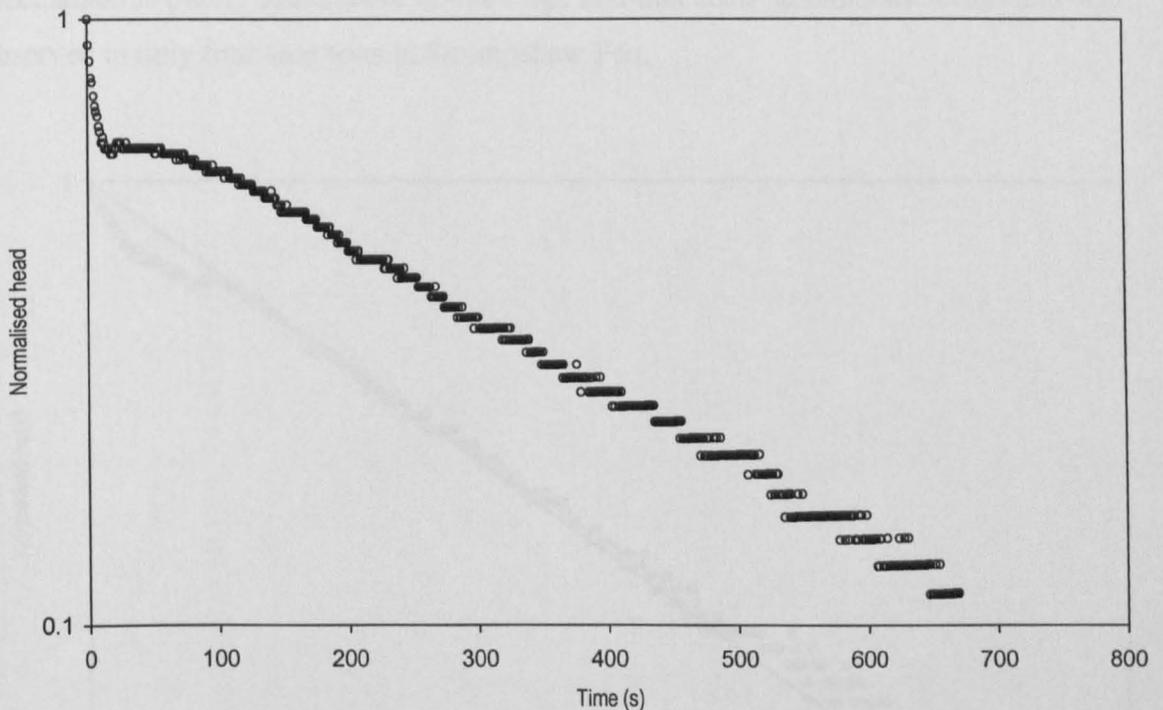
Figure 4.5 Hvorslev plot of normalised head (log scale) against time for Piezometer B3. Open circles represent the recovery after slug insertion.

The anomalous responses are characterised by a period of rapid recovery immediately following test initiation, lasting for approximately 10-30 seconds. In two of the four examples there is then a period that varies between 10 and 60 seconds when piezometer

water levels are more or less stable. Then, in all four examples, a more gradual recovery is observed, often close to log-linear in form, as can be seen in Figure 4.6 which shows data from Piezometer C3 following slug withdrawal. The form of recovery in Figure 4.6 cannot be explained by compressible soil behaviour. Indeed, it is difficult to account for this form of recovery. One possible mechanism involves the movement of biogenic gas bubbles close to the piezometer intake. Such bubbles have been observed in bog peats (see Rosenberry *et al.*, 2003; Kellner *et al.*, 2003; Beckwith and Baird, 2001), and ebullition from the peat at Strumpshaw Fen has been observed when walking across the inundated site. The mechanism requires that bubbles are mobilised by water flowing to/from the piezometer during a slug test. During this phase of bubble transport, water flow to or from the piezometer is relatively rapid. The bubbles then start to coalesce and block pores, giving the dramatic flattening of the head recovery shown in Figures 4.5 and 4.6. As coalescence continues, the bubbles grow until their buoyancy exceeds the capacity of the peat to hold them. They then move up through the peat, unblocking pores, allowing more rapid water flow and piezometer recovery. It is stressed that this mechanism is purely speculative at this stage and that such 'anomalous' behaviour was observed in only four slug tests at Strumpshaw Fen.
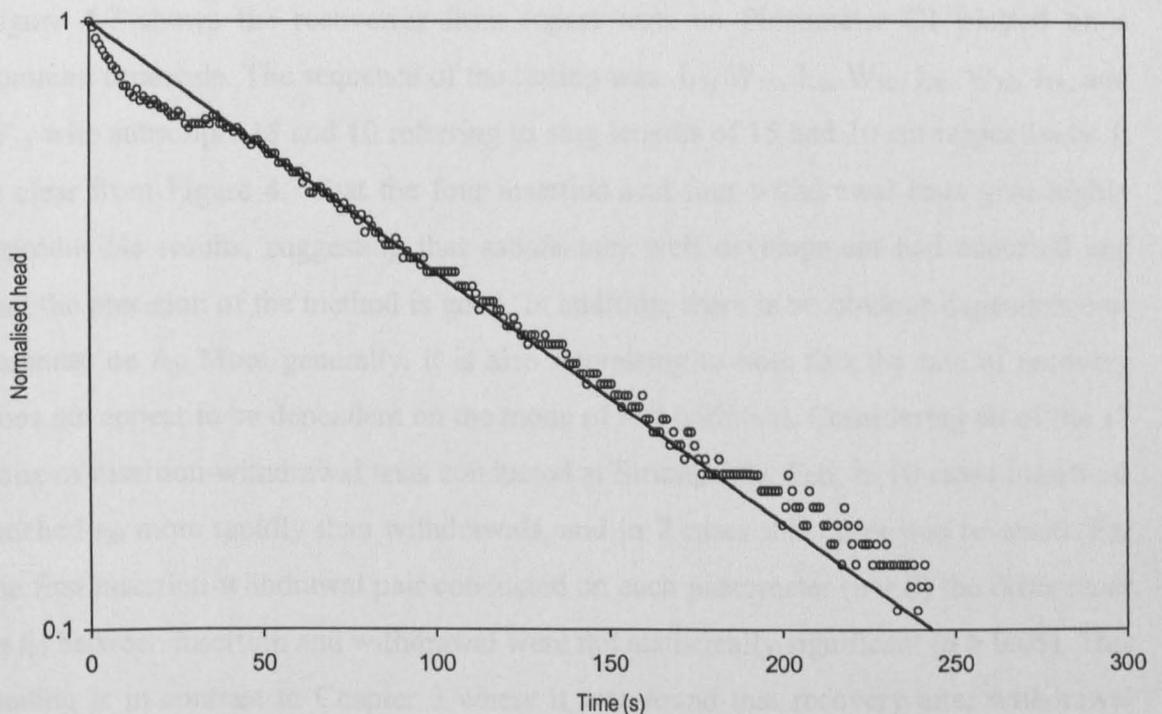
Figure 4.6 Hvorslev plot of normalised head (log scale) against time for Piezometer C3. Straight line represents the best fit Hvorslev equation (Equation (4) in section 3.2.4), open circles represent the recovery after slug withdrawal.

4.3.2 Precision of the piezometer slug test method, and dependency of head recovery on the form of test initiation and the initial head difference

On four piezometers, B1, C1, B2 and C2, repeat slug tests were conducted. The repeats involved using either the same slug size as used in the initial tests, or a combination of two different slug sizes. If repeat tests using the same initial head show progressively longer recoveries, an evolving low-permeability well skin might be the cause. Increases in the rate of recovery with successive tests might indicate that the initial development of the piezometer was unsatisfactory. Both scenarios can have important consequences for estimates of K from slug tests, but are rarely, if ever, considered in studies of wetland sediments. Butler *et al.* (1996) suggest that, in order to determine a dependence of test response on h_0, at least two initial heads, differing by a factor of two or more, should be used, with the first and last tests having similar h_0 to allow a dependence on initial head to be separated from the effects of an evolving well skin. Unfortunately, due to the depth of surface inundation on the site during the period of testing, only tests with values of h_0 that differed by a factor of $c.$ 1.5 could be conducted. Despite this, it should still be possible to identify a dependence on initial head, if one exists.

Figure 4.7 shows the recoveries from repeat tests on Piezometer C1 plotted on a common timescale. The sequence of the testing was: I_{15}, W_{15}, I_{10}, W_{10}, I_{10}, W_{10}, I_{15}, and W_{15} with subscripts 15 and 10 referring to slug lengths of 15 and 10 cm respectively. It is clear from Figure 4.7 that the four insertion and four withdrawal tests give highly reproducible results, suggesting that satisfactory well development had occurred and that the precision of the method is good. In addition, there is no obvious dependence of response on h_0. More generally, it is also interesting to note that the rate of recovery does not appear to be dependent on the mode of test initiation. Considering all of the 17 pairs of insertion-withdrawal tests conducted at Strumpshaw Fen, in 10 cases insertions reached t_{99} more rapidly than withdrawals, and in 7 cases this order was reversed. For the first insertion-withdrawal pair conducted on each piezometer (n = 8) the differences in t_{99} between insertion and withdrawal were not statistically significant ($p > 0.05$). This finding is in contrast to Chapter 3 where it was found that recovery after withdrawal was significantly quicker than that after insertion in tests in a root mat at Sutton Fen. In Chapter 3 it was suggested that blocking of pore-ends by suspended material during insertion tests resulted in slower responses compared to withdrawals. The contrast with

the results reported in Chapter 3 probably reflects the improved piezometer development procedure employed at Strumpshaw Fen. Three separate periods of flow into the piezometers at Strumpshaw Fen were generated during development (see Section 4.2.1), as opposed to only one in the work reported in Chapter 3. In addition, the total hydraulic head established during development of the piezometers at Strumpshaw Fen was nearly twice that used in the work at Sutton Fen. Both factors probably contributed to the relatively 'clean' water found in the piezometers at Strumpshaw. Although turbidity tests were not conducted, the piezometer water at Strumpshaw appeared visibly cleaner than that in the main tests performed at Sutton Fen. Such clean water would not contain much material for the blocking of pores during insertions, thereby minimising differences between responses after insertion and withdrawal. The lack of a significant difference between insertion and withdrawal tests is consistent with the results of tests reported in Chapter 3 on two piezometers flushed with 'clean' water. Finally, it is also possible that the relatively low heads used in the tests at Strumpshaw, together with the longer intakes of the piezometers, combined to minimise the pore blocking potential of any remaining particulate matter in the piezometer water.
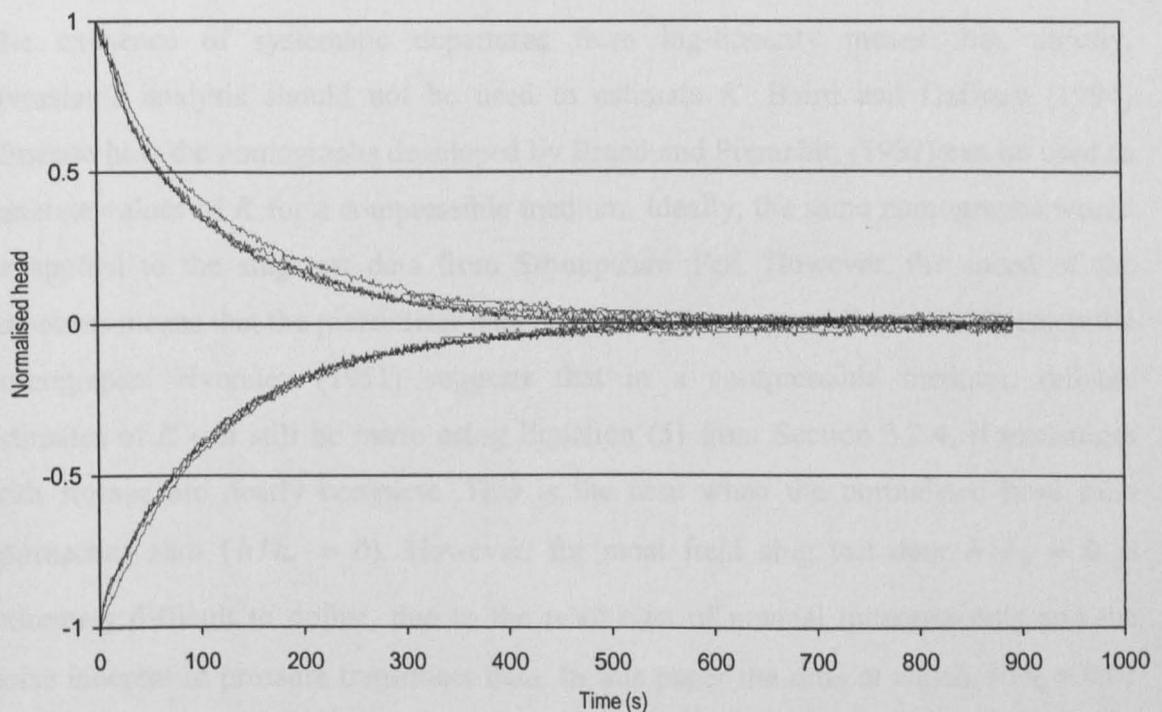
Figure 4.7 The recovery of four insertion and four withdrawal tests conducted on Piezometer C1 using two initial head differences (see text). Insertions plot as positive normalised head ratios and withdrawals as negative. Note that tests are on a common timescale.

In t he o ther t hree p iezometers o n w hich r epeat tests w ere conducted, t he w ithdrawal tests were highly reproducible suggesting there was no dependence on initial head difference. However, on two of these piezometers the insertion repeats produced successively more rapid responses. It is difficult to explain this observation. It may be that each test removed some smeared material from around the intake that was not cleared away by development, thus increasing the rates of flow from the piezometers with successive tests. However, if this were the case, the withdrawal tests would also be expected to show quicker responses with each repeat, which they did not. Settling out of suspended material in the small zone between the piezometer base and the bottom of the intake might have reduced pore-blocking between each insertion repeat, thus increasing the recovery rate. However, as discussed above, on the basis of t_{99} values for tests done on all of the piezometers there is no evidence for a general pore-blocking effect during insertions at Strumpshaw Fen, although this does not preclude the effect occurring in some instruments.

4.3.3 Estimating K from the piezometer data

The existence of systematic departures from log-linearity means that, strictly, Hvorslev's analysis should not be used to estimate K. Baird and Gaffney (1994) illustrate how the nomographs developed by Brand and Premchitt (1982) can be used to generate values of K for a compressible medium. Ideally, the same nomographs would be applied to the slug test data from Strumpshaw Fen. However, the speed of the responses means that the piezometer data lie outside the range of Brand and Premchitt's nomographs. Hvorslev (1951) suggests that in a compressible medium, reliable estimates of K can still be made using Equation (5) from Section 3.2.4, if exchanges with storage are nearly complete. This is the case when the normalised head ratio approaches zero ($h/h_0 \approx 0$). However, for most field slug test data $h/h_0 \approx 0$ is extremely difficult to define, due to the resolution of manual measurements and the noise inherent in pressure transducer data. In this paper the time at which $h/h_0 = 0.01$ (t_{99}) was used as the point at which exchanges with storage were assumed to be essentially complete.

K values were calculated using the withdrawal data. The insertion data could have been used, especially given that systematic differences between recoveries after withdrawal

and those after insertion were not found. However, as noted above, there was some variation in recovery after repeat slug insertions in some of the piezometers, suggesting the insertion data were less reliable. K values were calculated for two of the three sites at 15-36 cm (Sites B and C), and all three sites at 48-69 and 91-112 cm. Where repeat tests were conducted, data from the first withdrawal were used. The K estimates, corrected to 20 °C, are given in Table 4.1. The surface piezometers (15-36 cm) suggest a zone of relatively high K, with values greater than 1×10^{-3} cm s^{-1}. Below this zone is a layer of lower K where values drop to 10^{-4} cm s^{-1}. The deepest piezometers (91-112 cm) suggest that below the low-K layer lies peat with more elevated K.

Table 4.1 Estimates of hydraulic conductivity from piezometer tests after slug withdrawal, corrected to 20 °C.

Site	Depth (cm)	K ($\times 10^{-4}$ cm s^{-1})
A	15-36	~
	48-69	1.1
	91-112	1.8
B	15-36	11.0
	48-69	4.5
	91-112	9.2
C	15-36	16.0
	48-69	8.5
	91-112	15.0

4.3.4 *K* values obtained using the modified cube method

The results of the modified cube determinations of K for cores taken from locations A and C respectively are given in Figures 4.8 and 4.9. Core B produced similar results but is not shown. Following Beckwith *et al.* (2003a) and Chason and Siegel (1986), K values have been logged (base 10), whilst anisotropy is expressed as $\log_{10}$ (K_h/K_v). The results show that both K_h and K_v vary with depth and that three depth zones of differing K can be identified which correspond well with the zones identified by the piezometer K estimates.
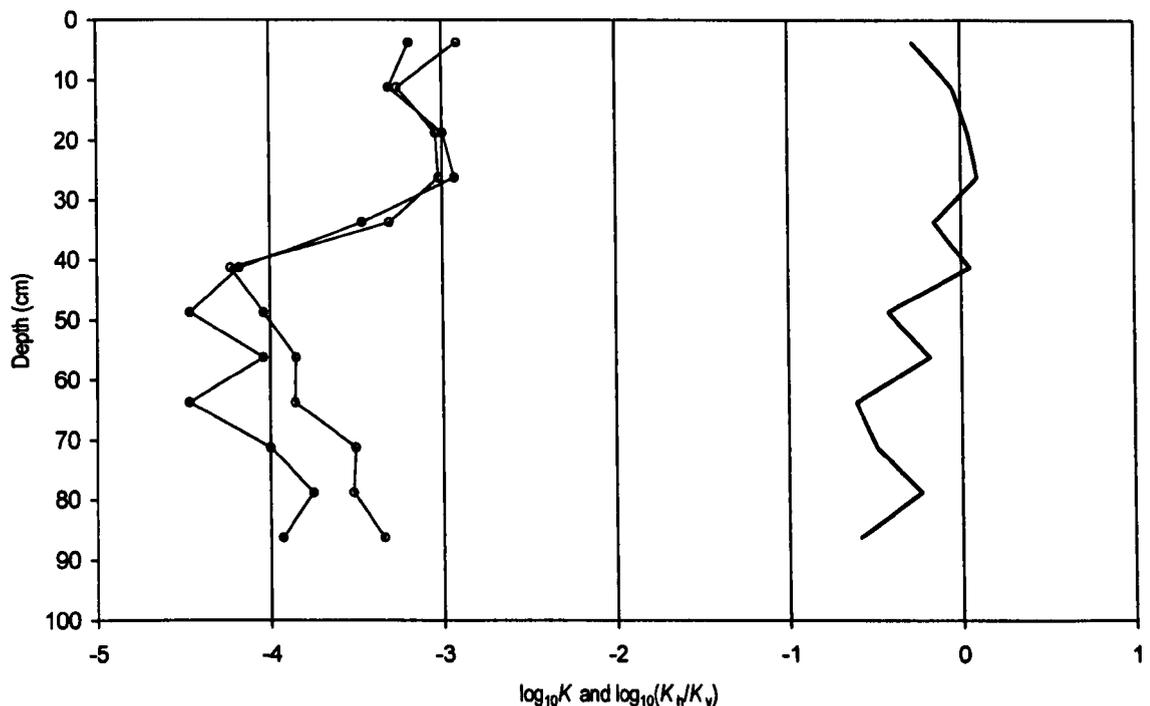
Figure 4.8 Results of modified cube determinations of *K* on Core A. Open circles are $\log_{10}K_v$, filled circles are $\log_{10}K_h$ (original data in cm s^{-1}). Solid line represents anisotropy, shown as $\log_{10}$ (K_h/K_v).

In 23 of the total of 36 cubes tested, $K_v > K_h$. As with the patterns of K_v and K_h themselves, there was a degree of depth dependency to the anisotropy. In peat from the surface to approximately 30 cm depth, either $K_v < K_h$, or else the vertical component only very slightly exceeded the horizontal (Figures 4.8 and 4.9). Below 30 cm there was more pronounced anisotropy of the form $K_v > K_h$. In the peat at Strumpshaw Fen, values of K_h/K_v reached a maximum of 1.7 in the surface layers and dropped as low as 0.1 in the deeper peat. This pattern of anisotropy was somewhat unexpected, given that previous wetland studies, albeit for bog peats, have shown that, often, $K_h \gg K_v$ (e.g.

Beckwith *et al.*, 2003a; Schlotzhauer and Price, 1999). It should also be emphasised that the magnitude of anisotropy in the peat at Strumpshaw Fen was less pronounced than observed in these other studies, for example Beckwith *et al.* (2003a) measured values of K_h/K_v up to a maximum of 10 and the mean anisotropy in their samples was 3.5.

A number of authors have suggested that the presence of root material within a peat matrix can lead to high K (e.g. Mann and Wetzel, 2000; Chason and Siegel, 1986). The surface peat at Strumpshaw Fen contains an abundance of roots and rhizomes, which could explain the relatively high K values seen in this zone. Further, observations of the peat collected in the cores suggest that root material is mainly orientated horizontally at depths between 15 and 45 cm, which could explain the observations of $K_h > K_v$. At depths of *c.* 45 cm, roots and rhizomes are much less common, which, in combination with increased bulk density, could explain the sharp decline in K seen in this zone. Below 60 cm depth, what appeared to be relict root channels were observed. These are channels where root material has decayed but left an open structure within the peat matrix through which water may readily pass, accounting for the increases in K seen at depth in the cores. These relict channels were predominantly vertically orientated, which could explain the observations of $K_v > K_h$ in the deeper peat at Strumpshaw Fen.
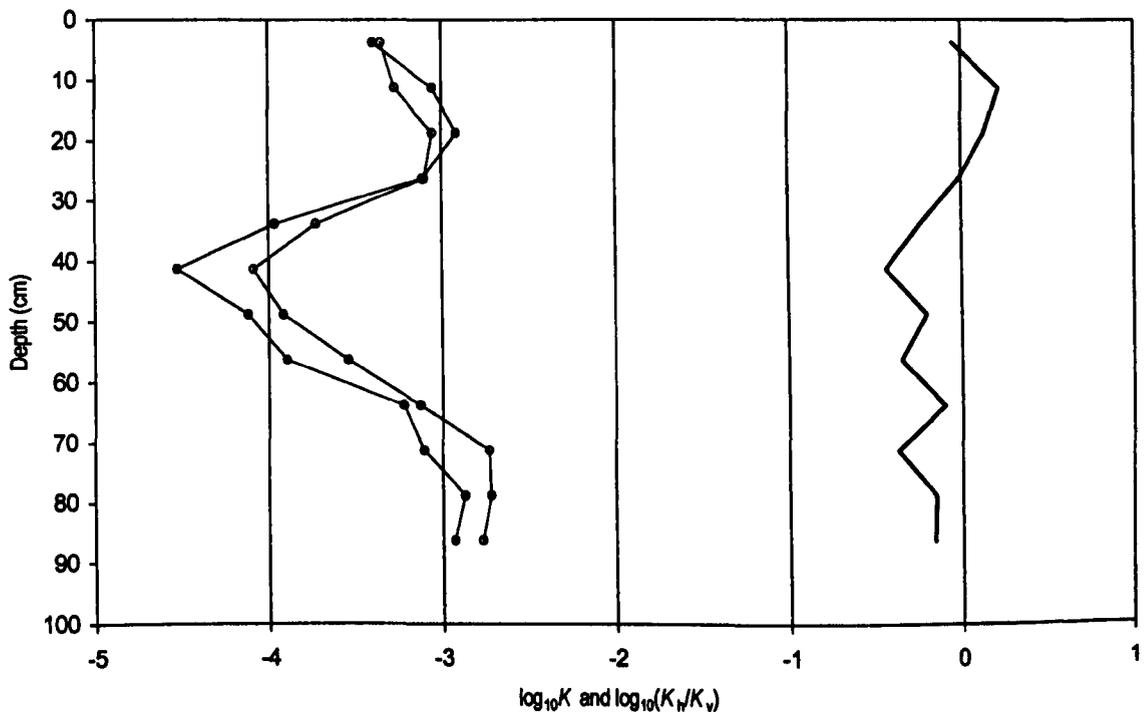
Figure 4.9 Results of modified cube determinations of K on Core C. Plotting convention as in Figure 4.8.

It is possible that the differences between K_v and K_h were simply a consequence of the order in which the tests were conducted rather than representing the true anisotropy of K. In order to test this, three cubes, covering the range of different deposits seen in the cores, were chosen for repeat testing of the form K_v, K_h, K_v, K_h, K_v, K_h, K_v, K_h. Figure 4.10 shows the results from cube 52.5-60 cm from Core C and suggests that the method is precise and that the differences between K_v and K_h are real. However, the other two cubes, which had a high root and rhizome content, showed evidence of quite poor precision, with values of K_v and K_h increasing with each repeat. This is probably due to damage to the peat associated with continued resealing and opening. The first opening of a face was found to remove only the smeared material; i.e., pores were unblocked and peat fibres were left exposed, thus providing a clean face of peat that should have yielded an accurate K estimate. Subsequent re-sealing and removal of the wax tended to pull the exposed fibres causing damage to (enlargement of) the pores within the peat. In such circumstances the results from the first test are likely to be the most accurate.
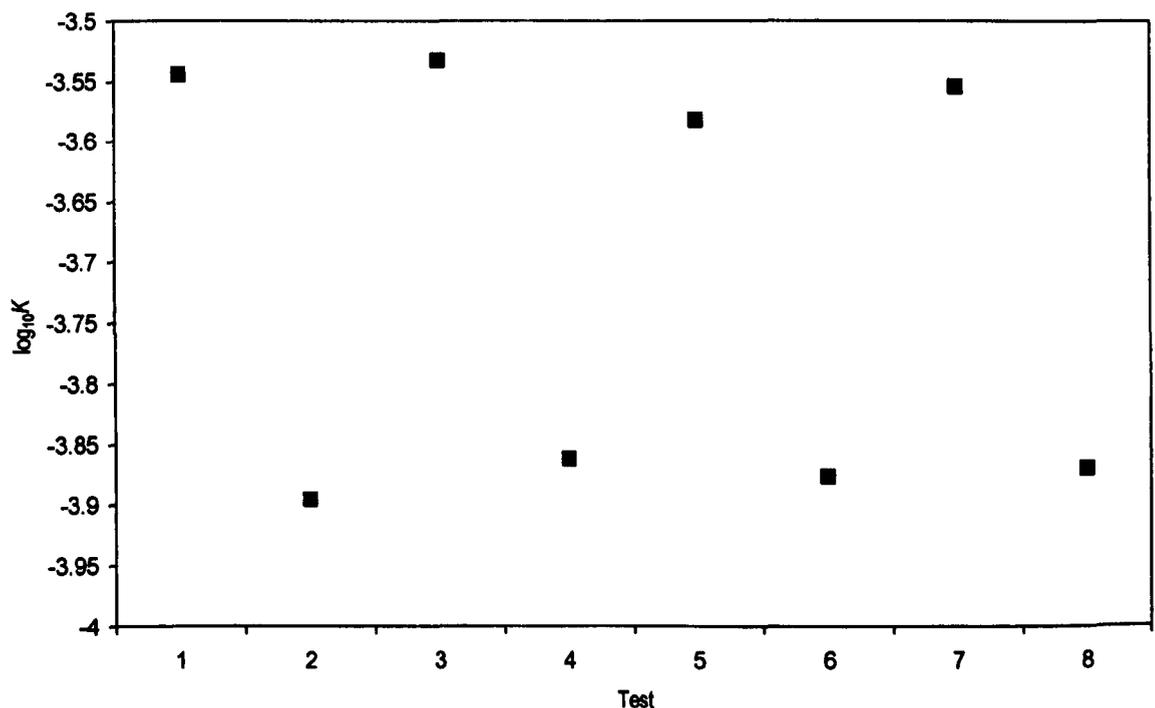
Figure 4.10 Repeat tests conducted on cube 52.5-60 cm from Core C. Note that K values are expressed as $\log_{10}$ of the original data (cm s^{-1}). Values between –3.85 and –3.9 are four determinations of K_h, values between –3.5 and –3.6 are four determinations of K_v.

4.3.5 Comparing the modified cube and slug test K estimates

Table 4.2 summarises the data from the modified cube and slug test determinations of K at depths 15-36 and 48-69 cm for locations A, B and C. The lowest piezometer depth (91-112 cm) is not compared to the modified cube method because surface inundation on the site made collection of cores to these depths impossible. However, it should be noted that the deepest cube from each location (82.5-90 cm in each case) gave K values similar to those from the deepest piezometers. The piezometer intake length of 21 cm corresponds to approximately three cubes of 7.5 cm. For each piezometer position shown in Table 4.2, the K results from the three corresponding cubes were examined. Of the K data obtained from these cubes, the minimum and maximum values for K_v and K_h are displayed for comparison.

Table 4.2 Comparison of slug test K values with K_h and K_v determined by the modified cube method. Subscript c refers to K determinations made by the modified cube method. Subscripts min and max refer to the minimum and maximum K values from the three cubes that correspond to each piezometer intake location. All values of K corrected to 20 °C.

Site	Depth (cm)	$K_{h\,min\,c}$ ($\times 10^{-4}$ cm s^{-1})	$K_{h\,max\,c}$ ($\times 10^{-4}$ cm s^{-1})	$K_{v\,min\,c}$ ($\times 10^{-4}$ cm s^{-1})	$K_{v\,max\,c}$ ($\times 10^{-4}$ cm s^{-1})	$K_{slug\,test}$ ($\times 10^{-4}$ cm s^{-1})
A	15-36	3.4	12.0	4.9	9.5	~
	48-69	0.3	0.9	0.9	1.4	1.1
B	15-36	1.2	16.0	1.2	15.0	11.0
	48-69	0.5	4.8	1.2	10.0	4.5
C	15-36	1.1	12.0	1.9	8.9	16.0
	48-69	0.8	6.0	1.2	7.5	8.5

In each case, the slug test K values lie close to the K_h values determined by the MCM. In two of the five comparisons, K determined by slug testing lies between the maximum and minimum K_h values from the MCM. In the remaining three cases, slug testing generated K values slightly greater than the maximum K_h values determined by the MCM, although only by a factor of less than 1.4. Slug test K values also correspond

quite closely to the K_v values from the MCM. Given the impossibility of measuring the K of the same volume of peat using the two methods, the similarity in the two sets of estimates is remarkable, and suggests that the slug tests generated robust K values. Although a nisotropy w as i dentified i n e ach o f t he c ubes t ested i n t he l aboratory, t he scale of the anisotropy never exceeded an order of magnitude. This is much lower than identified in other peats by Beckwith *et al.* (2003a), Schlotzhauer and Price (1999), and Chason and Siegel (1986). The data from Strumpshaw Fen compare well with the results of the numerical experiments of Seo and Choe (2001) who showed that, where $K_h > K_v$, slug tests can give good approximations of K_h. Seo and Choe (2001) also showed that, where $K_h < K_v$, slug testing will overestimate K_h. However, they found that when $K_h/K_v \geq 0.1$, as at Strumpshaw Fen, the error should not be greater than a factor of 2, corresponding well with the factor of 1.4 for the tests at Strumpshaw. Thus, given the nature of anisotropy at Strumpshaw Fen, slug tests on piezometers fitted with cylindrical intakes are likely to give reliable estimates of both K_h and K_v as shown by the data, provided, of course, that good test practice (development etc) is followed.

The MCM data suggest that the piezometer intake was in contact with layers of differing K. For example, the MCM data for Piezometer B1 suggest that over the 21 cm covered by the intake, K_h varied from 10^{-4} to 10^{-3} cm s^{-1}. Yet Table 4.2 shows that each slug test gave K values that were near to or slightly greater than the maximum K_h values determined by the MCM. This suggests that slug test K values are likely to represent higher-K layers given a situation of layered heterogeneity and an intake in contact with layers of different K, in agreement with the findings of Seo and Choe (2001). This illustrates the scale issues surrounding the use of piezometer slug tests in wetland sediments. Given the relatively small-scale heterogeneity in the sediment at Strumpshaw Fen, a smaller intake length than that used here would be needed to characterise the individual layers. Yet for much research, such small-scale heterogeneity may be less significant than the potential for water to move through the deposits at a larger-scale. Without an independent measure, as given by the modified cube method, it would be difficult to determine the extent to which slug tests provide useful estimates of K_h and K_v. However, it is possible to analyse a sediment visually (for example by looking for preferred orientations of peat fibres, roots and rhizomes and degree of decomposition) to see if anisotropy or pronounced heterogeneity of K is likely. If such an analysis suggests the potential for substantial anisotropy and/or heterogeneity, then K

is probably better estimated in the laboratory using the modified cube method. Otherwise, slug tests can be used to give a reasonably reliable indication of K.

4.3.6 *K* estimates from Strumpshaw Fen in comparison to other wetland soils

Estimates of the hydraulic conductivity of the surface 1 m of sediments at Strumpshaw Fen from piezometer slug tests and the MCM vary between approximately 1.6×10^{-3} and 3.4×10^{-5} cm s^{-1}. Reliable data against which to compare these values are sparse in wetland soils. Mann and Wetzel (2000) measured the K of surface sediments of wetland soils containing abundant plant roots using falling-head permeameters in the laboratory. In some sediment samples (samples were cylindrical, 5.1 cm in diameter and of varying lengths), from an area dominated by *Nymphaea odorata* L. and an area dominated by *Juncus effusus* L., Mann and Wetzel (2000) found that $K > 10 \times 10^{-3}$ cm s^{-1}. This figure is about an order of magnitude above that determined at Strumpshaw Fen. Baird (1997) estimated the K of a surface basin fen peat (well humified but containing roots and earthworm channels) using two methods: tension infiltrometry and laboratory permeametry. He reports K values for both methods that have a very similar range to that given in Table 4.2. The sediments studied by Mann and Wetzel (2000) and Baird (1997) were somewhat different from the deposits at Strumpshaw Fen. However, the data reported in both studies confirm that the presence of roots can lead to high K values. Finally, the Strumpshaw values are towards the top end of the range of K values reported for fen peats proper. For example, Almendinger and Leete (1998) estimated the K of calcareous fen peats using piezometer slug tests, although their exact method is not clear (they used piezometers 1.6 cm diameter with intakes 5 and 15 cm in length). They report K values in the range 2.7×10^{-5} to 9.8×10^{-3} cm s^{-1}, which they note are at the upper end of values for peats in general reported by other authors (summarized in Chason and Siegel (1986)). Given that the hydraulic conductivity o f the near-surface peat at Strumpshaw Fen appears to be relatively high, there is a potential for significant flow of water through these deposits if suitable hydraulic gradients are developed between the peat and deeper ground water or adjacent open-water bodies. The existence of such gradients forms the focus for the remaining sections of this chapter.

4.4   Using patterns of water-table position and hydraulic head to describe the potential for water exchange through the peat at Strumpshaw Fen

4.4.1   Exchange with adjacent open-water bodies

Observations o f w ater l evel i n t he d itch n etwork a nd w ater-table p osition i n t he f en, allowed an investigation to be made of the potential for two-way exchanges of water between the peat deposits and the ditch network. The findings indicated that the exchange of both surface water and pore water may occur. Rainfall, tidal pulses passing through t he d itch n etwork f rom t he R iver Y are, o ver-bank f looding e vents, m anaged control of water-table position, and summer drawdown of fen water table, all have the potential to generate water-table gradients between open water in the ditch network and pore water and surface water in the fen interior.

4.4.1.1 Rainfall

Given surface inundation at Strumpshaw Fen, no water-table gradients were developed between the fen and the ditch network during rainfall events, as water levels rose simultaneously and by the same magnitude across the entire site. However, when the antecedent water table was below the surface in the fen interior (between late July and late December during monitoring in 2002), substantial differences between water table in the fen and water level in the ditch could be generated by rainfall. Figure 4.11 shows the water-table configuration during a rainfall event over the period 9-12th September 2002 (JD 252-255).

Prior to rainfall, the water table was stable and levels in both the fen and ditch were relatively similar, at approximately 3.85 m above the arbitrary datum (AAD). During this period, the range of water-table elevation over the 10 m of transect shown in Figure 4.11 was approximately 1 cm. This likely reflects the combination of errors associated with the methods used to record water-table position (e.g. levelling error, variations in the response of individual pressure transducers), rather than a 'true' difference in water-table elevation between individual wells. This range provides a context for interpreting what represents 'significant' differences in water-table elevation during the subsequent rainfall event. Between 0630 h and 1330 h on JD 252, 21.7 mm of rainfall was delivered to the system. Although water table in the fen and water level in the ditch rose in

response to this input, the magnitude of the rise was dependent on proximity to the ditch network. Ditch water level rose from approximately 3.85 m AAD prior to rainfall, to a maximum of 3.89 m AAD by 2000 h on JD 252. Fen water table immediately adjacent to the ditch network (0.1 m) followed a similar pattern, although the rate of rise during rainfall itself was somewhat more rapid than in the ditch. At greater distance from the ditch edge, the rise in fen water table in response to rainfall was far more pronounced, reaching a maximum elevation of 3.99 m AAD at 10 m from the ditch.
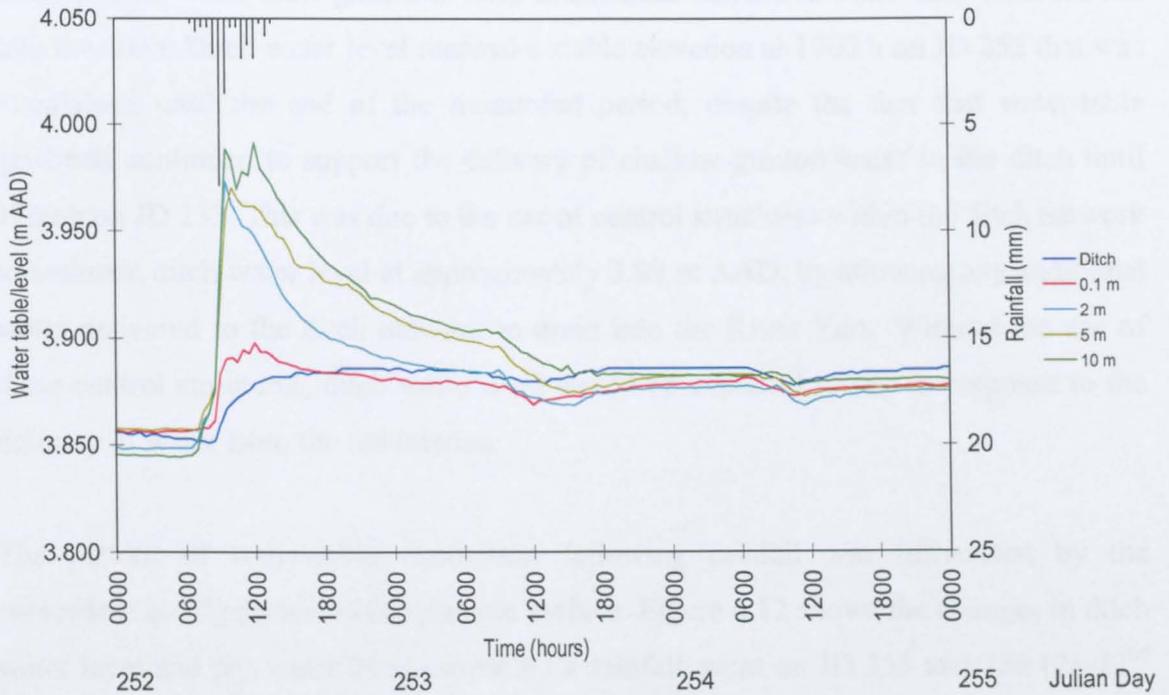
Figure 4.11 Water-table configuration during rainfall event JD 252-255.

The subsequent rate at which water table in the fen fell was also dependent on proximity to the ditch network. By approximately 1700 h on JD 252, ditch water level had reached a stable position and remained within 1 cm of this level until 0000 h on JD 255. Following the more pronounced rise during the early stages of rainfall than observed in the ditch network, fen water table at 0.1 m along the transect began to fall by 1200 h on JD 252, and by 1700 h on the same day had reached an equilibrium with ditch water level. At greater distance into the fen interior the fall in water table was slower, and the time at which fen water table returned to levels in the ditch was offset. For example, fen water table at 5 m from the ditch edge remained above the ditch water level until approximately 1200 h on JD 253. From approximately 1500 h on JD 253 to 0000 h on JD 255, fen water table and ditch water level were essentially at equilibrium, again with a range of no more that ± 1 cm along the 10 m transect.

Considering that the magnitude of water-table rise in the fen, and the subsequent rate of water-table fall were dependent on proximity to the ditch, alongside the fact that the stable fen water table that was established and maintained after 1500 h on JD 253 was essentially the same as the ditch water level, it may be concluded that the ditch network was acting as a boundary condition to shallow ground-water flow in the fen. As the specific yield of peat is clearly lower than that of open water, there was a more pronounced rise in fen water table following rainfall than in ditch water level. As a consequence, water-table gradients were established that drove water flow from the fen into the ditch. Ditch water level reached a stable elevation at 1700 h on JD 252 that was maintained until the end of the monitored period, despite the fact that water-table gradients continued to support the delivery of shallow ground water to the ditch until 1200 h on JD 253. This was due to the use of control structures within the ditch network to maintain ditch water level at approximately 3.89 m AAD, by allowing any additional water delivered to the ditch network to drain into the River Yare. Without the use of these control structures, ditch water level would be expected to rise in response to the delivery of water from the fen interior.

The pattern of water-table fluctuation following rainfall was influenced by the antecedent configuration of the phreatic surface. Figure 4.12 shows the changes in ditch water level and fen water table caused by a rainfall event on JD 355 and 356 (21-22nd December 2002). The rainfall was the first substantial input of water to the surface of the peat following a prolonged period of managed water-table drawdown (JD 319-331, see Section 4.4.1.3). The configuration of the fen water table prior to the start of rainfall at 2230 h on JD 355 reflected this history of drawdown, with ditch water level and near-ditch fen water table at lower elevation than those further into the fen interior. Between 2230 h on JD 355 and 1030 h on JD 356, 23.0 mm of rainfall was delivered to the site. The magnitude of this event was very similar to that shown in Figure 4.11, yet the rainfall was spread over 12.5 hours in Figure 4.12 as compared to only 7 hours in Figure 4.11. Consequently, the water table rose more gradually on JD 356 following rainfall, as compared to the rate of rise on JD 252.
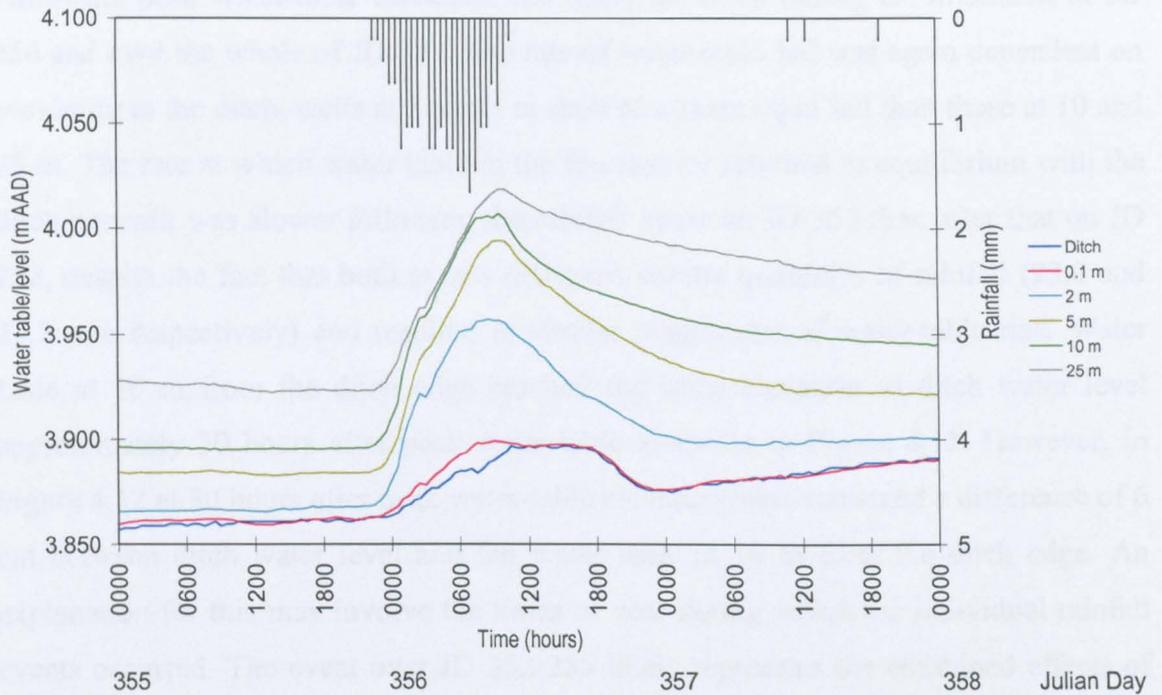
Figure 4.12 Water-table configuration during rainfall event JD 355-358.

As in Figure 4.11, the rise in water table with the delivery of rainfall on JD 355 and 356 was dependent on proximity to the ditch, with near-ditch fen water table (0.1 m) showing less pronounced rises and tracking very closely the changes in ditch water level throughout the monitored period. Following an initial rise of approximately 3 cm, ditch water level reached a plateau at 3.90 m AAD at 1030 h on JD 356, again due to the use of control structures that allowed the drainage of ditch water into the River Yare. Between 1730 h and 2230 h on JD 356, ditch water level fell by 2 cm as levels in the tidal River Yare fell, allowing further export of ditch water into the river channel. From 2230 h on JD 356 the connection between the River Yare and the ditch network was closed to prevent the ingress of nutrient enriched river water during the rising tide. Subsequently, ditch water level rose over JD 357, indicating the delivery of shallow ground water from the fen to the ditch network. Wells in the zone from 2 to 25 m from the ditch edge all indicated that water table increased by a similar magnitude in response to rainfall (approximately 10 cm), yet because of the antecedent water-table configuration the maximum elevation reached increased with distance from the ditch edge. At approximately 1000 h on JD 356, peak water-table elevation was reached in the fen, and a difference in water-table elevation of 12.5 cm existed between the fen at 25 m and the ditch.

Following peak water-table elevation, fen water table fell during the afternoon of JD 356 and over the whole of JD 357. The rate of water-table fall was again dependent on proximity to the ditch, wells at 2 and 5 m showed a more rapid fall than those at 10 and 25 m. The rate at which water table in the fen interior returned to equilibrium with the ditch network was slower following the rainfall event on JD 356 than after that on JD 252, despite the fact that both events delivered similar quantities of rainfall (23.0 and 21.7 mm respectively) and resulted in similar magnitudes of water-table rise. Water table at 10 m from the ditch edge reached the same elevation as ditch water level approximately 30 hours after peak water-table elevation in Figure 4.11. However, in Figure 4.12 at 30 hours after peak water-table elevation there remained a difference of 6 cm between ditch water level and fen water table at 10 m from the ditch edge. An explanation for this may involve the times of year during which the individual rainfall events occurred. The event over JD 252-255 likely represents the combined effects of lateral drainage of shallow ground water to the ditch network and evapotranspiration, whereas over JD 355-358 evapotranspiration was likely to be negligible leaving only lateral drainage to equilibrate fen water table with ditch water level. This hypothesis is supported by the fact that average air temperature over JD 252-255 was ~ 10 °C above that during JD 355-358. Unfortunately, a longer time series of water-table fluctuations could not be obtained beyond JD 358 to examine the continued lateral delivery of water to the ditch network, because hydrological fluctuations after JD 357 drove exchanges between the fen and ditch that were not associated with the rainfall event.

4.4.1.2 Tidal pulses

Two-way exchanges of water between the ditch network and the River Yare are possible through a control structure that connects the two systems. The principal events leading to such exchanges are the passage of tidal pulses from the River Yare through the ditch network. Such exchanges are only possible when management of the fen water table allows a free connection to exist between the channel and ditch networks. This usually occurs during late autumn/early winter, as surface-inundated conditions are re-established in the fen. An example of a single tidal pulse is shown in Figure 4.13.

The pulse is seen clearly in the record of ditch water level, beginning at 0300 h on JD 362 and reaching a peak at 0800 h on the same day, resulting in a rise in water level in the ditch of 9.7 cm to 4.00 m AAD. The pulse was transferred rapidly into near-ditch

areas of the fen by sub-surface exchange. Water table at 0.1 and 2 m from the ditch edge tracked the changes in ditch water level almost identically. At greater distance along the transect, the effect of the pulse was detectable, but the rise in water table was less pronounced, and the timing of peak water-table elevation offset from that in the ditch itself and in near-ditch wells. At 5 m, peak water-table elevation occurred at 0900 h on JD 362 and was only 2.7 cm above pre-pulse levels, at 10 m the peak was at 1230 h on the same day and the magnitude of the rise was only 1 cm. Data from the well located 25 m from the ditch edge indicated that the pulse was not transferred this far into the fen interior. During the falling limb of the pulse, the wells at 0.1 and 2 m from the ditch edge again tracked ditch water level closely. These data indicate that there was a rapid return flow of shallow ground water to the ditch network during the falling limb of the tidal pulse. Water table in wells at 5 and 10 m fell more slowly, and as a consequence the pre-pulse conditions of water-table gradients supporting the delivery of shallow ground water to the ditch network were re-established after the tidal pulse had exited the ditch network.
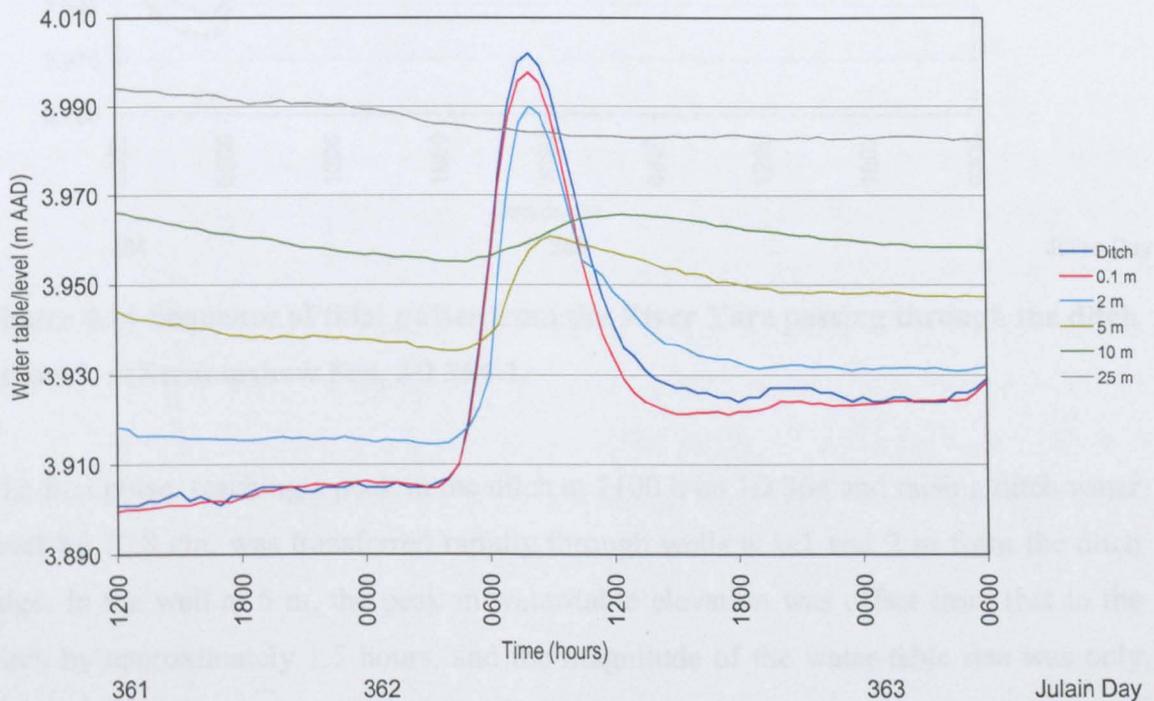
Figure 4.13 Passage of a tidal pulse from the River Yare through the ditch network at Strumpshaw Fen.

Figure 4.13 provides an example of managed exchange with the River Yare, where a single tidal pulse was allowed to pass through the ditch network. If the system were in a 'natural' state, with the ditch network freely connected to the river at several points,

then tidal pulses passing through Strumpshaw Fen would be far more frequent than is presently the case. Figure 4.14 shows a sequence of tidal pulses passing from the River Yare through the ditch network over the period 30th December 2002 to 1st January 2003 (JD 364-1), analogous to a situation of free connection between the river and the ditch network. These pulses were not managed because the ditch was freely connected to the River Yare in order to begin to flood the fen system following the summer drawdown period.
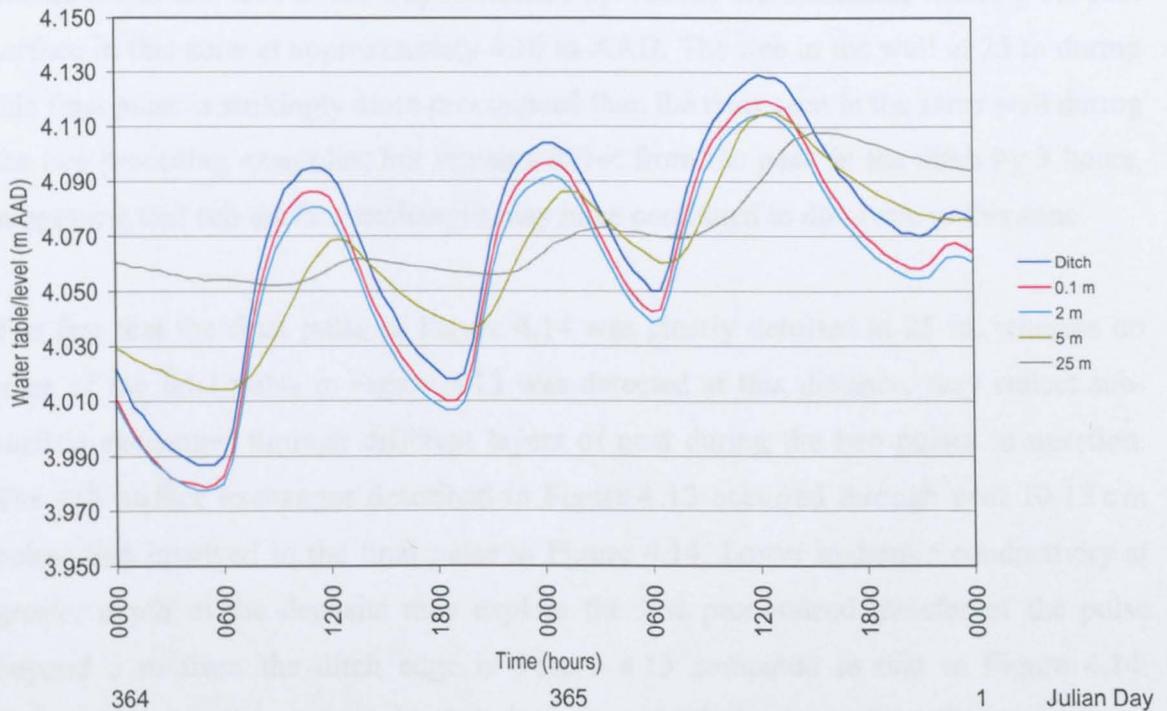
Figure 4.14 Sequence of tidal pulses from the River Yare passing through the ditch network at Strumpshaw Fen, JD 364-1.

The first pulse, reaching a peak in the ditch at 1100 h on JD 364 and raising ditch water level by 10.8 cm, was transferred rapidly through wells at 0.1 and 2 m from the ditch edge. In the well at 5 m, the peak in water-table elevation was offset from that in the ditch by approximately 1.5 hours, and the magnitude of the water-table rise was only 5.4 cm. Unlike the pulse described in Figure 4.13, that on JD 364 was observed at greater distance into the fen interior. The well at 25 m showed a small rise of 1 cm, peaking some 3 hours after the ditch. The falling limb of this pulse, and indeed the later two pulses, resulted in changes to the water-table configuration that were similar to those described previously in Figure 4.13, specifically near-ditch fen water table followed closely the fluctuation in ditch water level, whilst wells at greater distance from the ditch showed a slower rate of water-table fall. The second pulse, peaking in the

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ditch at 0030 h on JD 365 and 8.6 cm in magnitude, behaved in much the same way as the previous pulse. However, it is clear that this second pulse was transferred more efficiently into the fen interior, the well at 25 m showing a rise of some 2 cm, still offset from the ditch by 3 hours. The final pulse, peaking in the ditch at 1200 h on JD 365 and 7.9 cm in magnitude, was transferred almost fully to the well at 5 m which was offset from the ditch by only 30 minutes. The more rapid transfer of this pulse to the well at 5 m compared to that during preceding pulses may indicate the beginning of surface inundation in this area of the fen, confirmed by manual measurements locating the peat surface in this zone at approximately 4.10 m AAD. The rise in the well at 25 m during this final pulse is strikingly more pronounced than the rises seen in the same well during the two preceding examples, but remains offset from the peak in the ditch by 3 hours, suggesting that sub-surface exchanges may have continued to dominate in this zone.

The fact that the final pulse in Figure 4.14 was clearly detected at 25 m, whereas no trace of the tidal pulse in Figure 4.13 was detected at this distance, may reflect sub-surface exchanges through different layers of peat during the two pulses in question. The sub-surface exchanges described in Figure 4.13 occurred through peat 10-15 cm below that involved in the final pulse in Figure 4.14. Lower hydraulic conductivity at greater depth in the deposits may explain the less pronounced transfer of the pulse beyond 5 m from the ditch edge in Figure 4.13 compared to that in Figure 4.14. However, hydraulic conductivity data from the modified cube method (Figures 4.8 and 4.9) indicate that, compared to near-surface peat, a layer of lower K begins at a depth of approximately 25 cm below the ground surface. All of the pulses in Figures 4.13 and 4.14 involve exchanges through peat above 25 cm depth. Therefore it is impossible to provide conclusive evidence at this stage that variations in the hydraulic conductivity of the deposits are able to explain the differences in the degree to which tidal pulses are transferred into the fen interior.

Despite the implementation of hydrological management at Strumpshaw Fen designed to isolate the fen system from both the River Yare and Lackford Run due to the eutrophic nature of these two channel systems (see Figures 2.5 and 2.6), over-bank flooding from the River Yare continues to represent a significant input of water to the system. During late 2002 and early 2003, high water levels in the River Yare, combined with tidal pulses, resulted in the inundation of the floodplain and led to the re-establishment of surface-inundated conditions at Strumpshaw Fen. Figure 4.15 shows

the results of the monitoring of water table along the entire 100 m transect during the period 30th December 2002-4th January 2003 (JD 364-4).
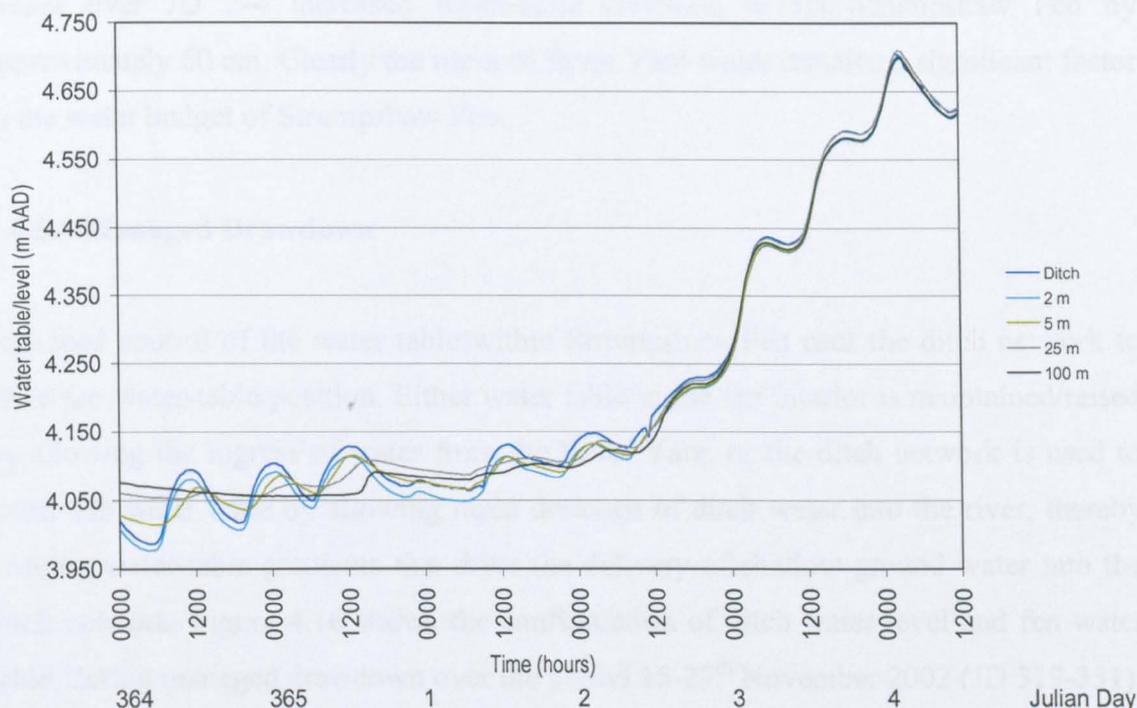
Figure 4.15 Water-table elevation during over-bank flooding from the River Yare, leading to re-establishment of surface inundation conditions.

The three tidal pulses during JD 364 and 365 were followed by two further pulses over JD 1 and 2 which continued to involve sub-surface exchange, as the magnitude of water-table rise was reduced, and the timing of peak water-table elevation offset, with increasing distance along the transect. However, the rise in water table beginning at approximately 0830 h on JD 2 was essentially simultaneous, and of the same magnitude, along the entire transect. A uniform fen water-table elevation was established after 0830 h on JD 2 and maintained throughout the rest of the monitored period, up to 1200 h on JD 4. This suggests that surface-inundated conditions were re-established during the morning of JD 2, and that subsequent water-table variations were rapidly transferred throughout the entire system by the exchange of standing surface water. Immediately prior to the re-establishment of surface-inundated conditions after 0830 h on JD 2, water-table elevation was at approximately 4.11 m AAD along the entire transect. This corresponds well with manual determinations of the position of the peat surface at Strumpshaw Fen, which indicated an elevation of between 4.05 and 4.10 m AAD, and lends further support to the conclusion that the input of floodwater from the River Yare during this period was responsible for the re-establishment of surface-

inundated conditions across the site. Further, it is important to note that the volume of water input to Strumpshaw Fen during this flood period was substantial. The four tidal pulses over JD 2-4 increased water-table elevation across Strumpshaw Fen by approximately 60 cm. Clearly the input of River Yare water remains a significant factor in the water budget of Strumpshaw Fen.

4.4.1.3 Managed Drawdown

Managed control of the water table within Strumpshaw Fen uses the ditch network to drive fen water-table position. Either water table in the fen interior is maintained/raised by allowing the ingress of water from the River Yare, or the ditch network is used to lower fen water table by allowing rapid drainage of ditch water into the river, thereby creating water-table gradients that drive the delivery of shallow ground water into the ditch network. Figure 4.16 shows the configuration of ditch water level and fen water table, during managed drawdown over the period 15-27th November 2002 (JD 319-331).
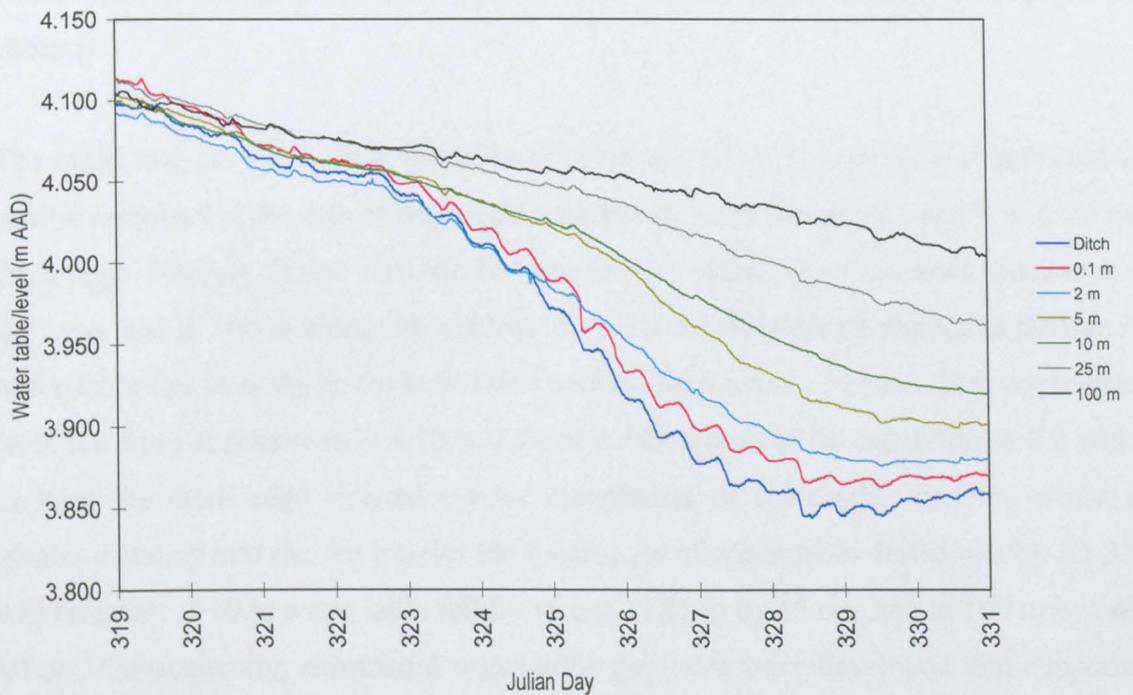
Figure 4.16 Managed drawdown of fen water tables using the ditch network as a driver, JD 319-331.

At the beginning of this period the system was inundated with a few centimetres of surface water, the position of the ground surface varying between 4.05 and 4.10 m AAD along the 100 m transect as determined from field surveys. Drawdown began with the

delivery of this surface water to the ditch network, evidenced by the uniform nature of water-table fall along the entire transect until approximately 1800 h on JD 320. After this time, water-table elevation along the transect began to diverge, with the level in near-ditch wells reflecting more closely the ditch water level, and wells at greater distance from the ditch maintaining higher water-table elevation. This pattern became particularly pronounced from JD 323 onwards. The divergence in fen water-table position indicates that, from approximately 1800 h on JD 320, the exchange between the fen and the ditch network was dominated by the sub-surface delivery of shallow ground water. Ditch water level fell rapidly in the period JD 323-328, and then remained at more stable levels until the end of the monitored period. Interestingly the connection of the ditch network to the tidal River Yare is shown clearly over this time in the form of a 'stepped' fall in the water level, particularly obvious between JD 325 and 327. The stepped decline in ditch water level involves periods of stability followed by sharp falls of approximately 2-3 cm, with periods of stable and falling water levels each lasting approximately 6 hours. This form of water-level fluctuation was also observed in the well located 0.1 m from the ditch edge, but was not transferred any further into the fen interior.

The rapid rate at which ditch water level fell from JD 323 onwards was reflected in similar increases in the rate of water-table decline in wells located 0.1 and 2 m from the ditch edge. Moving further into the fen interior, the influence of the ditch became less apparent, and at 100 m along the transect there was no discernable change in the rate of water-table fall over the entire monitored period. Between JD 319 and 328, ditch water level fell from approximately 4.10 to 3.84 m AAD, a drop of 26 cm. Wells at 0.1 and 2 m from the ditch edge showed similar magnitudes of water-table decline, whilst at greater distance into the fen interior the magnitude of water-table drawdown by JD 331 was reduced; at 10 m water table fell by 18 cm, at 25 m by 15 cm, and at 100 m by only 10 cm. Consequently, substantial water-table gradients were developed that supported the delivery of shallow ground water to the ditch network.

4.4.1.4 Sub-irrigation of the fen by the ditch network during summer drawdown

Evapotranspiration demand during the summer months can create a scenario where water-table elevation in the fen interior falls below ditch water level. Under these conditions, water-table gradients are established that indicate a potential for ditch water

to sub-irrigate the peat, thereby maintaining higher water-table elevation in near-ditch areas of the fen compared to areas further into the fen interior. Figure 4.17 shows the configuration of water table during a period of sub-irrigation by the ditch network, covering 3-7th September 2002 (JD 246-250). During this time, fen water table at 0.1 m from the ditch edge tracked almost exactly the changes in ditch water level. Water table in the wells at 2 and 5 m were at lower elevation than ditch water level, but generally by no more than 2.5 cm over the monitored period. Moving further into the fen interior, the difference between fen water table and ditch water level increased, reaching over 10 cm at a distance of 100 m. These gradients were maintained for substantial periods of time over the summer drawdown period, up to the order of a number of weeks depending on 'external' inputs of water to the system, such as from rainfall or tidal pulses, which restored water table in the fen interior to elevations equal to or above the ditch water level.
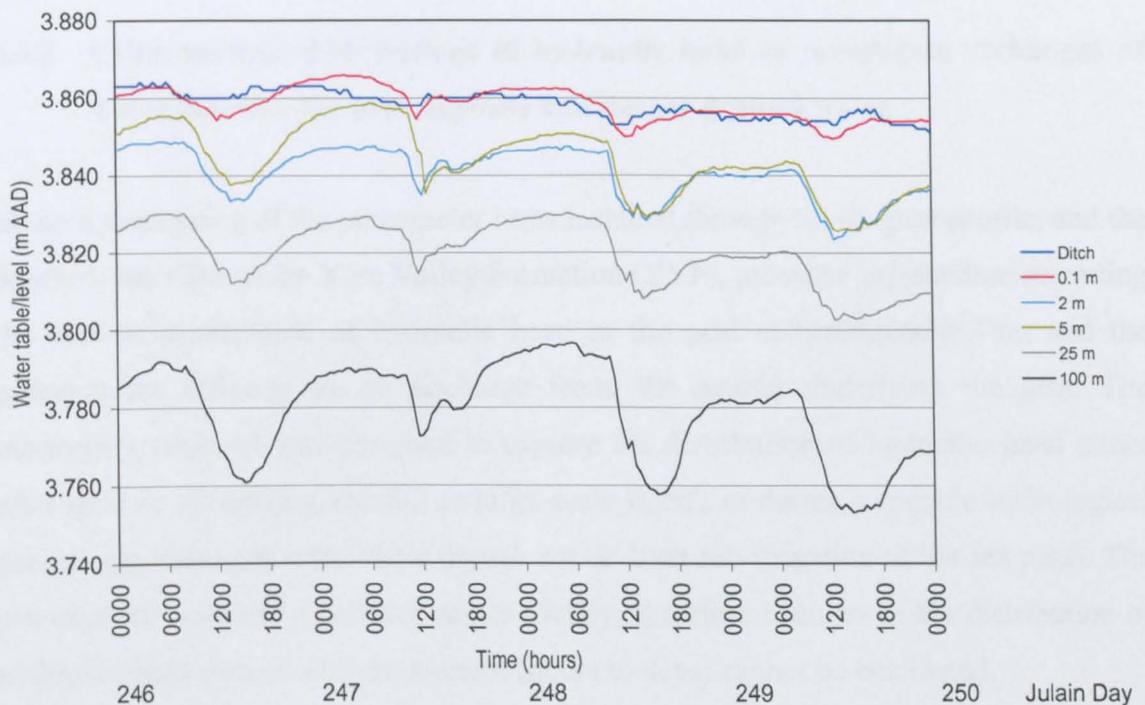
Figure 4.17 Sub-irrigation of fen peat by ditch water during summer drawdown period, JD 246-250.

An interesting feature shown in Figure 4.17 is the diurnal fluctuation in fen water-table position. These fluctuations are seen in the data throughout the summer drawdown period when water-table elevation is below the peat surface, and can reach a magnitude of up to 3 cm. The water table falls from early morning to reach minimum elevations in mid-afternoon on each day (usually between 1400 h and 1600 h). Subsequently, water

table rises over the late afternoon and through the night to reach maximum elevations in the early morning of the following day (between 0400 h and 0600 h), after which the cycle is repeated. It is possible that the fall in water table is associated with the evapotranspiration demand from the vegetation growing at Strumpshaw Fen, and that the subsequent recovery in water table is driven by recharge from the ditch network. However, the fact that water table at 25 and 100 m from the ditch shows a similar magnitude of recovery during the night as water table much closer to the ditch, suggests that recharge from the ditch is unlikely. If the ditch were acting as the source of water driving water-table recovery then water table at 100 m from the ditch edge would not be expected to fully recover from minimum daytime-elevation over a period of $\leq$ 12 hours. An alternative explanation may be related to capillary fringe effects (Gillham, 1984), although insufficient data exist to explore these water-table fluctuations more fully in this thesis.

4.4.2 Using vertical distributions of hydraulic head to investigate exchanges of water between the peat deposits and deeper ground water

Manual monitoring of the piezometer nests installed throughout the peat profile, and the borehole installed in the Yare Valley Formation (YVF), provided information regarding the vertical distribution of hydraulic head in the peat at Strumpshaw Fen, and the potential for recharge to, or discharge from, the aquifer underlying the peat. The monitoring protocol was designed to capture the distribution of hydraulic head either after specific events (e.g. rainfall or large-scale flood), or during a specific hydrological period (e.g. managed water-table drawdown or ditch sub-irrigation of the fen peat). The piezometers were not monitored automatically; therefore changes in the distribution of hydraulic head over shorter time scales (hours to days) cannot be elucidated.

Over the period during which hydraulic head was monitored at Strumpshaw Fen (April 2002 – April 2003), there was little evidence of significant vertical gradients acting within the peat profile. Considering the 4 m of deposits within which piezometers were installed, head varied by no more than 2 cm from the near-surface to the base of the profile, and frequently this difference was less than 1 cm. This was true for each of the three piezometer nests regardless of their location along the transect. The only exception to this were observations made immediately following rainfall, when head in the near-surface piezometers could exceed that in instruments in deeper peat by up to

approximately 5 cm. This may indicate a potential for recharge of ground water in deeper peat with rainfall input to the surface of the sediments. Alternatively, this observation could reflect a response time error in the piezometers used to monitor the distribution of hydraulic head at Strumpshaw Fen (Hanschke and Baird, 2001).

Data collected from the borehole at a depth of 10 m below the peat surface indicated a substantial difference between the hydraulic head in the peat and that in the underlying aquifer. Given the relatively uniform head distribution within the peat, the following comparisons with the underlying aquifer are based on head values from piezometers at 4 m depth, which are taken to be representative of head in the peat as a whole. Under surface-inundated conditions (early January to late July), head in the peat remained consistently above that in the underlying aquifer. The head difference between the peat at 4 m and the underlying aquifer at 10 m reached a maximum of over 16 cm immediately following the establishment of surface-inundated conditions in early January 2003. During subsequent sampling visits, head in the peat remained at least 10 cm above that in the underlying aquifer, and this difference was independent of location along the transect. It is possible that head in the underlying aquifer remained below that in the peat as a result of ground-water abstractions for public water supply using boreholes in close proximity to Strumpshaw Fen (see Section 2.4.1). During summer drawdown conditions, the direction of the difference was reversed, and head in the peat fell substantially below that in the underlying aquifer. Observations made on 5th September 2002 (JD 248), at near-minimum water-table elevation for the year, indicated that at 2 m from the ditch edge head in the underlying aquifer was 12.9 cm above that in the peat, whilst at 100 m from the ditch the difference reached 18.3 cm. This increase in the head difference between the peat and underlying aquifer with distance into the fen interior may reflect the sub-irrigation of near-ditch zones of the fen during the summer drawdown period (see Section 4.4.1.4), thereby maintaining higher head values than in the fen interior.

This seasonal pattern to the difference between head in the peat and in the underlying aquifer was affected by managed control of water table within Strumpshaw Fen. Observations of the distribution of hydraulic head were made on 30th November 2002 (JD 334), three days after a prolonged period of managed water-table drawdown had ceased (see Section 4.4.1.3). At 100 m along the transect, head in the peat exceeded that in the underlying aquifer by 6.2 cm. However, at 2 m from the ditch edge the direction

of the difference was *reversed*, and head in the underlying aquifer was greater than that in the peat by 12.2 cm. This is likely to reflect the far greater influence of managed drawdown at close proximity to the ditch network compared with that observed in the fen interior (see Figure 4.16). The nature of the difference between heads in the peat and in the underlying aquifer during surface inundation, summer drawdown and managed drawdown is conceptualised in Figure 4.18.

A. Surface inundation

Head in peat remains above that in underlying aquifer by at least 10 cm. Difference is independent of proximity to ditch.

B. Summer drawdown

Head in peat below than that in underlying aquifer. Difference becomes greater with distance away from ditch due to sub-irrigation of near-ditch peat.

C. Managed drawdown

Direction of difference dependent on proximity to ditch. Near-ditch zone, head in peat < in underlying aquifer, difference reversed in fen interior.

Figure 4.18 Conceptual models of the head difference between the peat and the underlying aquifer under various hydrological scenarios. Red arrows indicate the direction of the hydraulic gradient acting between the Yare Valley Formation (YVF) and the peat aquifer. Peat depth is approximately 6 m.

Observations of the hydraulic head distribution indicate that hydraulic gradients exist between the peat and the underlying aquifer, and that these gradients are variable in

direction and magnitude. However, the data also indicate that these gradients are largely not translated into actual exchanges of water between the peat and the underlying mineral aquifer. If the hydraulic gradients between the peat and the YVF were resulting in substantial flows of water between the two units, this should be reflected in the existence of a significant hydraulic gradient within the peat profile itself (Smedema and Rycroft, 1983), due to the relatively low K associated with peat as compared to other porous media. The fact that the distribution of head within the peat was essentially uniform suggests that there is little recharge to/discharge from deeper ground water in the underlying aquifer. Instead the peat appears to be a perched aquifer, with a deposit of low hydraulic conductivity likely preventing exchange between the peat and the YVF (Smedema and Rycroft, 1983).

The location and nature of this low-K deposit remains unclear. Slug tests conducted in the at 10 m depth in the YVF generated relatively high values of K (average = 9.3×10^{-3} cm s^{-1}, n = 4). Therefore it appears that either the deep peat itself, a deposit between the peat and the underlying aquifer, or a layer within the underlying aquifer at shallower depth than 10 m below ground surface, is of sufficiently low K to largely prevent the significant flow of water. Hydraulic conductivity tests were not conducted on the deeper peat (> 2.5 m) at Strumpshaw Fen. Visual inspection of the deposits during augering through the peat profile did suggest that peat at greater depth was more fully decomposed and less fibrous than the near-surface deposits. Deposits at depths below 2.0-2.5 m resembled quite well decomposed brushwood peat. Although no direct estimates of the K of these deposits are available, it is likely that hydraulic conductivity in this zone is substantially below that of the near-surface peat, and may preclude any significant flow of water. Sediment samples collected during the installation of the borehole in the Yare Valley Formation provided no evidence of the existence of clay/silt layers within this deposit. Consequently, there was no stratigraphical evidence to support the existence of potentially low-K layers within the Yare Valley Formation that would prevent vertical exchanges of water with the overlying peat deposits. However, hand augering identified a relatively substantial (~ 40 cm) layer of organic mud/fine sand at the interface between the base of the peat and the Yare Valley Formation that may have been of sufficiently low K to prevent much flow between the upper peat and the underlying mineral aquifer.

The vertical distribution of hydraulic head within the peat profile appears to support the findings from observations of water-table configuration that lateral rather than vertical exchanges of water are likely to predominate at Strumpshaw Fen. Observations of head distribution within the piezometer nests indicate that patterns of water-table configuration are transferred to hydraulic head throughout the peat profile. Under conditions of summer drawdown, Figure 4.17 shows that the ditch network may sub-irrigate the peat, thereby maintaining higher water-table elevation in near-ditch areas compared to the fen interior. The influence of the ditch under these conditions can also be observed in the distribution of head in the piezometer nests. Readings taken on 5th September 2002 (JD 248) indicate that the head in the piezometers at 2 m from the ditch edge was between 5.4 and 6.5 cm above that in piezometers from corresponding depths at 100 m from the ditch edge, presumably due to the supply of water from the ditch network. Piezometers in the nest located 10 m from the ditch edge had head values that were intermediate between those in nests at 2 and 100 m.

The impact of managed drawdown of the fen water table using the ditch network as a driver was discussed previously in Section 4.4.1.3. On 30th November 2002 measurements of the distribution of hydraulic head in the piezometer nests were made to assess the potential impact of this management technique on the vertical distribution of head within the peat. Corresponding with the water-table configuration (Figure 4.16), the head in piezometers at 2 m from the ditch edge was substantially lower than those in corresponding piezometers at 100 m. The magnitude of this difference was greatest in the near-surface peat (23.9 cm at 0.175 m depth) and decreased with depth in the profile (18.4 cm at 4 m depth). Again the piezometers in the nest at 10 m from the ditch edge had heads intermediate between those at 2 and 100 m.

Section 4.4.1.1 highlighted the potential for rainfall to generate water-table gradients that drive the lateral delivery of water from the fen interior to the ditch network. To examine the impact of rainfall events, and the subsequent water-table gradients, upon vertical distributions of hydraulic head, the piezometer nests were monitored on 16th October 2002 (JD 289). Over the preceding four days (JD 285-288) 75.8 mm of rainfall was delivered to the site, and as a result on JD 289 there were substantial water-table gradients driving the delivery of shallow ground water into the ditch network. As described above for managed drawdown, the influence of the ditch after rainfall was reflected in lower hydraulic heads in piezometers at 2 m from the ditch network,

compared to corresponding piezometers at 100 m into the fen interior. The magnitude of these differences following rainfall was less than that associated with managed drawdown, varying between 4.1 and 6.7 cm, and there was no consistent pattern to the magnitude with depth through the peat profile.

4.5 Using water-table gradients and estimates of hydraulic conductivity to estimate the volumes of water exchanged between the fen and the ditch network

The hydrological data collected from Strumpshaw Fen indicate that lateral exchanges, rather than vertical exchanges, may predominate in the peat deposits. The distribution of hydraulic head in the piezometer nests varied only slightly with depth, and any vertical gradients of head that did exist were usually exceeded by water-table gradients, generally by an order of magnitude. Further, it appears that the peat deposits are essentially isolated from the underlying aquifer in terms of water exchange, most likely because of the existence of a low-K deposit, either towards the base of the peat profile or at the interface between the peat and the Yare Valley Formation. Consequently, despite the existence of suitable hydraulic gradients, the actual recharge to/discharge from deeper ground water at Strumpshaw Fen is likely to be negligible, or at most very small. Under these conditions, the peat deposits at Strumpshaw Fen represent a perched aquifer, in which water table within the fen system is more or less hydrologically disconnected from deeper ground-water formations. Given this, and the fact that the peat represents an unconfined aquifer in which the water table forms the upper boundary to the region of flow, the Dupuit-Forchheimer approximation may be used to provide estimates of the volume of water exchanged between the fen and the ditch network under certain hydrological conditions (Fetter, 2001).

The Dupuit-Forchheimer approximation is; 1) that the hydraulic gradient is equal to the slope of the water table and is invariant with depth, and 2) that for small water-table gradients, the streamlines are horizontal and the equipotential lines vertical (Fetter, 2001). Strictly speaking, when calculating the volume of water exchanged with the ditch network at Strumpshaw Fen, the base of the ditch should represent the lower boundary to the region of flow. However, the base of the ditch is up to 2 m above the base of the peat at Strumpshaw, and consequently there may be radial flow towards the

base of the ditch through deeper peat. It is possible that peat at depths below the base of the ditch has such low K that the flow of water through these deposits is negligible. However, in the absence of direct estimates of the hydraulic conductivity of the deep peat, a correction factor was included within the Dupuit-Forchheimer approximation by multiplying the saturated thickness of the aquifer by 1.5, to account for the possibility of radial flow towards the base of the ditch. A similar approach was outlined by Smedema and Rycroft (1983) for the situation of radial flow into pipe drains.

The discharge per unit width of the aquifer can be calculated using the Dupuit-Forchheimer approximation:

$$q = Kh\frac{dh}{dx} \tag{1}$$

where q is discharge to the ditch per unit width of aquifer/length of ditch ($L^2\ T^{-1}$), K is hydraulic conductivity ($L\ T^{-1}$), h is water-table elevation above an impermeable barrier (L), and x is distance in the direction of flow (L). For the work at Strumpshaw Fen, the water-table gradient at 2 m along the transect was calculated using water-table elevation in wells located 0.1 ($h_{0.1}$) and 5 m (h_5) from the ditch edge. The lower boundary to the region of flow was taken to be the base of the ditch. The saturated thickness of the peat aquifer (equivalent to h in (1)) at 2 m in relation to the base of the ditch (h_2) was taken directly from the pressure transducer data, and included the correction factor of 1.5 as described above. Depth-weighted hydraulic conductivity values were used to describe the variation of K over the saturated thickness of the peat aquifer. The situation is conceptualised in Figure 4.19.

To calculate the depth-weighted K values the following protocol was followed. From the peat surface to a depth of 1.12 m, the hydraulic conductivity values reported earlier in this current chapter from piezometer slug tests or the MCM were applied. Where available, piezometer K values were used, whilst data from the MCM were employed for depth zones where piezometer tests had not been conducted. In either case, the average value for a particular piezometer depth or MCM cube from each of the three locations (A, B or C, see Section 4.2.1) was calculated and used in Equation (1). Considering the good correspondence between K values determined by slug tests and the MCM (see Section 4.3.5), it was felt that combining these data to give a larger-scale

view of the variation in K over the saturated thickness of the aquifer was an acceptable approach. At depths below 1.12 m, hydraulic conductivity values were generated from slug tests conducted on piezometers located 1.9 and 2.5 m below the ground surface. These data were then used to determine an average value of K for the peat between two piezometer locations, i.e. the average of the K values determined in piezometers at 1.9 and 2.5 m was used as the K value over the entire 60 cm of peat between these two depths. An overall depth-weighted K value for the saturated thickness of the aquifer was then calculated.
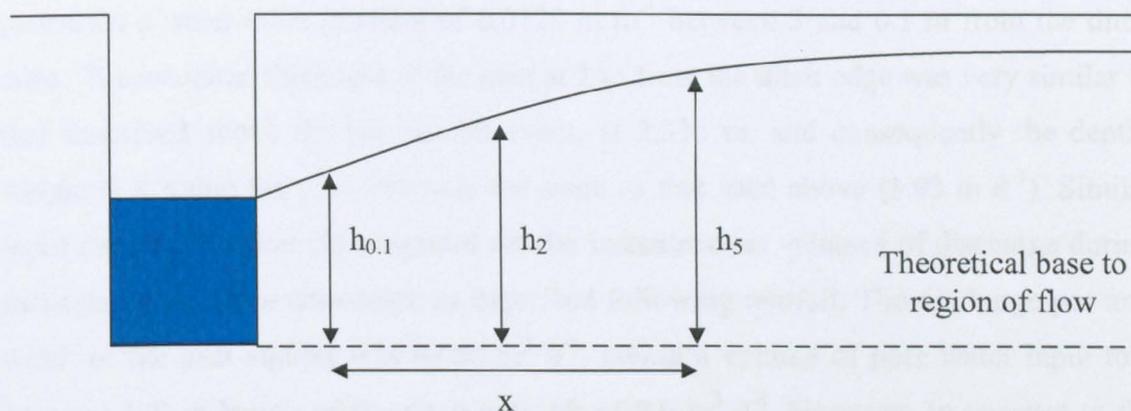
Figure 4.19 Conceptual model for applying the Dupuit-Forchheimer approximation to Strumpshaw Fen.

Two hydrological scenarios were chosen to illustrate the potential volumes of water that may be exchanged between the fen and the ditch network at Strumpshaw. Firstly the rainfall event on JD 252 described previously in Section 4.4.1.1, and secondly the period of managed drawdown of fen water tables over JD 319-331 described in Section 4.4.1.3. In both cases water-table gradients were assessed at one point in time, generally when they were near to maximum. Consequently, the discharges discussed below are towards the top end of the possible ranges over the duration of both periods of exchange.

At 1200 h on JD 252, towards the end of the input of rainfall, there was a water-table gradient of 0.0131 m m^{-1} between 5 and 0.1 m from the ditch edge. The saturated thickness of the peat at 2 m from the ditch edge was 2.348 m, with a depth-weighted K in this zone equal to 1.93 m d^{-1}. Using Equation (1), the discharge per unit width of the peat aquifer at this time was 0.089 m^2 d^{-1}. Over a nominal 100 m length of the ditch

network, this equates to a volume of pore water delivered to the ditch of 8.9 m^3 d^{-1}. It is important to note that this magnitude of discharge was maintained for only a short period of time during, and immediately following, the input of rainfall on JD 252. By 1500 h on JD 253, some 27 hours later, fen water table and ditch water level were at equilibrium. Consequently, a discharge of 8.9 m^3 d^{-1} represents an estimate of the maximum instantaneous volume of exchange between the fen and the ditch network as generated by rainfall.

By 1200 h on JD 326, managed drawdown of water table at Strumpshaw Fen had generated a water-table gradient of 0.0128 m m^{-1} between 5 and 0.1 m from the ditch edge. The saturated thickness of the peat at 2 m from the ditch edge was very similar to that described above for the rainfall event, at 2.333 m, and consequently the depth-weighted K value for this zone was the same as that used above (1.93 m d^{-1}). Similar input data to Equation (1) generated similar instantaneous volumes of discharge during managed water-table drawdown as described following rainfall. The discharge per unit width of the peat aquifer was 0.086 m^2 d^{-1}, giving a volume of pore water input to a nominal 100 m length of the ditch network of 8.6 m^3 d^{-1}. However, in contrast to the rainfall event on JD 252, this magnitude of water-table gradient was maintained for a substantial p eriod o f t ime d uring m anaged d rawdown (over 6 d ays b etween JD 3 25-331). As a consequence, very substantial volumes of pore water may have been delivered to the ditch network from the fen system during this time.

The two examples above have demonstrated how the reliable characterisation of hydraulic conductivity and water-table gradients can be combined to yield estimates of the volumes of water exchanged between the fen and the ditch network. To test the robustness of the Dupuit-Forchheimer approach, these data were compared with estimates of the volume of water discharged to the ditch made on the basis of observed changes in water-table position in the peat. The cross-sectional area between the water-table position along the instrumented transect at two points in time was calculated, and multiplied by reasonable estimates of the specific yield of peat, to determine the volume of water discharged from the fen per unit length of the ditch, described as the 'area' method below. No direct estimates of the specific yield of the deposits at Strumpshaw Fen w ere m ade. T herefore, a r ange o f t ypical v alues for p eat w as u sed (0.05 – 0.3), based on the work of Hoag and Price (1997) and Youngs *et al.* (1989).

For the rainfall event on JD 252, the volume of water estimated using Equation (1) was within the range of values calculated by the area method, depending on the choice of specific yield. With respect to managed drawdown, the area method was used to calculate the volume of water discharged to the ditch over the period 0000 h on JD 325 to 0000 h on JD 331, and compared with estimates over the same period made using Equation (1). The maximum volume calculated using the area method was 0.318 m³ per unit length of ditch, equivalent to approximately 32 000 litres along a 100 m section of the ditch network. In comparison, Equation (1) gave a volume of water discharged per unit length of the ditch of 0.398 m³, or approximately 40 000 litres along 100 m of the ditch network. This is equal to approximately 19 % of the average volume of water held in the 100 m section of the ditch network during the period JD 325-331. There is good agreement between the two methods used to calculate the volume of water discharged to the ditch network, indicating that the Dupuit-Forchheimer approach is yielding robust data, and thereby confirming the reliability of the hydraulic conductivity and water-table gradient estimates described earlier in this current chapter. That Equation (1) gives a volume that is slightly above the range calculated using the area method likely reflects inaccuracies in the K data, particularly in deposits below 1.12 m where the MCM could not be used to validate the piezometer technique, and where K values were averaged over several tens of centimetres of peat.

4.6   Concluding comments

Building on the work reported in Chapter 3, the current chapter has demonstrated that, given careful attention to data collection and analysis protocols, piezometer slug tests can generate apparently reliable estimates of the hydraulic conductivity of fen peat. The modified cube method has been shown to be a simple yet robust laboratory method for K determination. This chapter provides some of the first data that reliably compare field and laboratory methods for the determination of fen-peat hydraulic conductivity. The comparison demonstrates a remarkable correspondence between K values generated by the two methods, which lends further support to the conclusion that both techniques are providing robust data. In combination with those in Chapter 3, the data in the current chapter achieve Research Objective 1 identified in Section 1.2.

Both slug test and MCM data indicate that the near-surface deposits at Strumpshaw Fen have relatively high K, up to 10^{-3} cm s^{-1}, but that hydraulic conductivity can vary quite

substantially over relatively small spatial scales. The K data indicate that, given suitable hydraulic gradients, water may flow readily through the peat at Strumpshaw Fen. The hydrological monitoring programme reported in this chapter builds on the K data to determine whether such gradients exist at Strumpshaw. The vertical distribution of hydraulic head through the peat profile and in the underlying mineral aquifer indicates a head difference between the peat deposits and deeper ground water. During flooded conditions, downward acting gradients suggest a potential for the recharge of deep ground water from the fen system, a pattern that is reversed during summer drawdown conditions i n t he f en. H owever, t he p attern o f h ydraulic h ead w ithin t he p eat p rofile itself suggests that head is distributed in a relatively uniform way, and that consequently there is only negligible exchange between the peat and the underlying YVF. This is likely to be associated with a deposit, either towards the base of the peat or at the peat-mineral aquifer interface, which is of sufficiently low K to prevent significant water flow. The movement of water at Strumpshaw appears to be predominantly horizontal in orientation, and involves the two-way exchange of pore water and surface water from the fen with open water in the ditch network. These exchanges are event driven and can be influenced by management of the site. This work has achieved Research Objective 2 identified in Section 1.2.

The combination of relatively high K with strong water-table gradients at Strumpshaw Fen indicates that significant volumes of pore water may be delivered to the ditch network. As a consequence, the chemical quality of the fen pore water and surface water has the potential to influence the chemical and ecological quality of the receiving waters, in this case the ditch network. Further, given that the ditch network and the River Yare are connected, the chemical quality of fen pore water and surface water may influence t he s tatus o f t he a djacent c hannel sy stem i tself. O ne o f t he m ost i mportant criteria of the quality of receiving waters is nutrient status, owing to the consequences of excess nutrients in terms of eutrophication. Phosphorus is generally viewed as the main element driving eutrophication risk. Given this, and the history of high phosphorus loadings to Strumpshaw Fen (see Section 2.4.2), the following chapter examines the controls on phosphorus release to pore water and surface water at Strumpshaw. This is the first step towards assessing the hydrochemical impacts of the hydrological connectivity identified in this current chapter.

5.   PORE-WATER AND SURFACE-WATER PHOSPHORUS DYNAMICS AT STRUMPSHAW FEN

5.1   Introduction

Wetlands may represent net sources or sinks of phosphorus (P), depending on the quantity and form of P already present in the system, and the input to the system via inflowing waters (Novak *et al.*, 2004; Pant and Reddy, 2003; Soto-Jimenez *et al.*, 2003; Pant *et al.*, 2002b). Many floodplains, including those containing riparian wetlands, may have accumulated large stores of sediment-P historically due to their connection with adjacent channel systems carrying significant nutrient loads in dissolved and particulate forms (e.g. Venterink *et al.*, 2003; Owens and Walling, 2002). The release of P from riparian wetland sediments may result in the establishment and maintenance of a nutrient-enriched status within the wetland itself. Indeed, in some cases the internal supply of nutrients may even exceed current external anthropic loadings (Fisher and Reddy, 2001), particularly as environmental management often focuses on the reduction of external nutrient loads. Further, under conditions of increased internal nutrient availability, riparian wetlands may become potential source areas for the delivery of P to external receiving water bodies. This is particularly true in systems where hydrological evidence indicates a strong potential for water flow through the wetland sediments, as at Strumpshaw Fen (see Chapter 4).

Despite the potential importance of nutrient release from wetland deposits, little research has focused on the impact of wetland sediments on the chemical quality of the overlying surface water (Fisher and Reddy, 2001). More specifically, there is only very sparse information on the impact of the flooding of riparian soils on the various sediment-P fractions, and consequently on the retention/release of phosphorus (Novak *et al.*, 2004; Wright *et al.*, 2001). Further, the few studies that have been conducted in wetland systems have dealt almost exclusively with P dynamics within the overlying

surface water (e.g. White *et al.*, 2004; Pant and Reddy, 2003; Newman and Pietro, 2001). This is not surprising because surface water fluxes are extremely dynamic and may deliver phosphorus rapidly to receiving waters. However, the concentration solely on surface water neglects the potential importance of pore-water P dynamics. The release of P into overlying surface waters will be partly dependent on the phosphorus dynamics within the pore water. Further, given sub-surface hydrological connection, it is possible that P could be delivered to receiving water bodies by direct exchanges with pore water. Such exchanges may alter the nutrient status of a receiving water body without the prior need for phosphorus release to overlying surface water. Given that sediment properties relevant to phosphorus exchange processes are likely to vary with depth (Pant *et al.*, 2002b), P dynamics in the sub-surface zone require more detailed investigation than has been the case in much previous research conducted in wetlands.

The processes controlling the exchange of P between wetland sediments and the overlying water column, and between wetland sediments and pore water, and the rates at which these processes operate, remain under-researched. The long-term retention of nutrients by wetlands is often attributed to the low rates of decomposition observed in these systems, leading to the accumulation of significant quantities of organic material and associated nitrogen (N) and phosphorus (Fisher and Reddy, 2001). Low rates of decomposition are linked to both the abiotic conditions found in many wetland sediments, in particular the lack of oxygen, and also to the chemical quality of the organic material (Bridgham and Richardson, 2003; Aerts *et al.*, 1999). Despite this, one of the major sources of phosphorus in many wetlands remains the decomposition of organic matter and mineralisation of organic P (Mayer *et al.*, 1999; Ivanoff *et al.*, 1998). Decomposition in the absence of oxygen is reliant on the action of facultative or obligate anaerobic decomposers, which are dependent on a supply of terminal electron acceptors. Therefore, the release of soluble forms of P into wetland pore water and surface water may be controlled by the supply of terminal electron acceptors (McLatchey and Reddy, 1998), and in particular by the balance between aerobic and anaerobic decomposition (Fisher and Reddy, 2001).

However, research examining the role of lake bottom sediments, and some work examining the role of wetland sediments, has concluded that mineralisation of organic P, as controlled by the availability of terminal electron acceptors, is not the direct control on the exchange of phosphorus between sediments and overlying surface water

(e.g. Pant and Reddy, 2001b; Newman and Pietro, 2001; Moore *et al.*, 1998). Instead, physicochemical conditions at the interface between the sediment and overlying water column are thought to control the exchange. The interaction between iron and phosphorus, as controlled by redox status, has been identified as a possible mechanism controlling the release of P from sediments to overlying surface water (e.g. Gunnars *et al.*, 2002; Pant and Reddy, 2001b; Patrick and Khalid, 1974). Under oxic conditions, the adsorption of P by insoluble Fe^{3+} at the sediment-water interface prevents the release of phosphorus into the overlying water column. However, under reducing conditions, reductive-dissolution may release Fe^{2+} and P into solution, and these elements may subsequently be transported into the overlying water column. In some wetlands, the low mineral content of the deposits makes physicochemical control of P exchange unlikely (Moore *et al.*, 1998; McLatchey and Reddy, 1998), making it more probable that P flux into the overlying water is controlled by rates of organic matter mineralisation. However, water inputs to riparian wetlands from adjacent channel systems may carry high mineral loads (e.g. Darke and Walbridge, 2000). Consequently, the mineral content of riparian wetland sediments may be sufficiently high for P release into pore water and surface water to be physicochemically controlled. At present, few data exist to clarify the relative importance of mineralisation rate and physicochemical control in the release of phosphorus from riparian wetland sediments.

The aim of the work presented in this current chapter was to examine the exchange of phosphorus between a typical riparian wetland sediment and the overlying water column. Exchange between the sediment and pore water was also investigated, in terms of both the impact on P release to the overlying water column, and the concentration of P in the pore water itself. The research was designed to examine the processes that control these exchanges, the rates at which they operate, and whether riparian wetland sediments may act as potential sources for the delivery of phosphorus to receiving water bodies. This work addresses Research Objective 3 in Section 1.2 and also, through analysis of sediment-bound phosphorus, begins to address Research Objective 4.

5.2   Methodology

5.2.1   The collection and pre-treatment of intact fen-peat cores

The experiments described in this current chapter were conducted using intact cores of peat collected from Strumpshaw Fen. An alternative to the intact core experiment is the use of batch soil-water mixtures to examine phosphorus-soil interactions, where air- or oven-dry soil is continuously mixed with water containing different concentrations of P, often in a reactor in which variables such as pH and redox status can be controlled. From these batch experiments, information regarding features such as the potential for adsorption of P from solution, and equilibrium pore-water phosphorus concentration can be obtained (e.g. Pant *et al.*, 2002a; Pant and Reddy, 2001b; McLatchey and Reddy, 1998). Intact cores were preferred to batch experiments because they provide a closer representation of field conditions. At the field-scale, processes such as the diffusion of P through different layers of peat, the exchange of various solutes with the overlying water column, and the sediment surface area exposed to pore water, are important factors controlling the exchange of phosphorus between sediment and pore water, and sediment and overlying water (Reddy *et al.*, 1999; 1995). Batch soil-water mixture experiments are unable to realistically simulate such features, and consequently were not used in the research reported here.

Cores of the upper 50 cm of peat were collected using a polyvinyl chloride (PVC) coring device. This zone of peat encompasses the seasonal water-table range (maximum summer drawdown to approximately 40 cm below the peat surface), and is the focus for exchanges of water between the peat and the adjacent ditch network (see Chapter 4). Therefore the availability of P in this zone was of particular interest. The coring device consisted of a 75 cm length of PVC pipe of i.d. 23.7 cm. The PVC pipe was bevelled at one end to enable insertion to the desired depth without large root and rhizome material being forced into lower layers of peat, which would have damaged the internal structure of the peat core. The coring device was driven to the desired depth and then removed by digging down the outside of the device and underneath the base, thereby preventing any loss of peat from the bottom of the core on removal. Checks were made to ensure that compaction of the peat during core collection did not exceed 5 %. Emergent macrophyte material was cut so that stems did not protrude above the top of the core housing. Whilst

still in the field, the peat cores were transferred from the coring device into pre-prepared core housings (Figure 5.1).
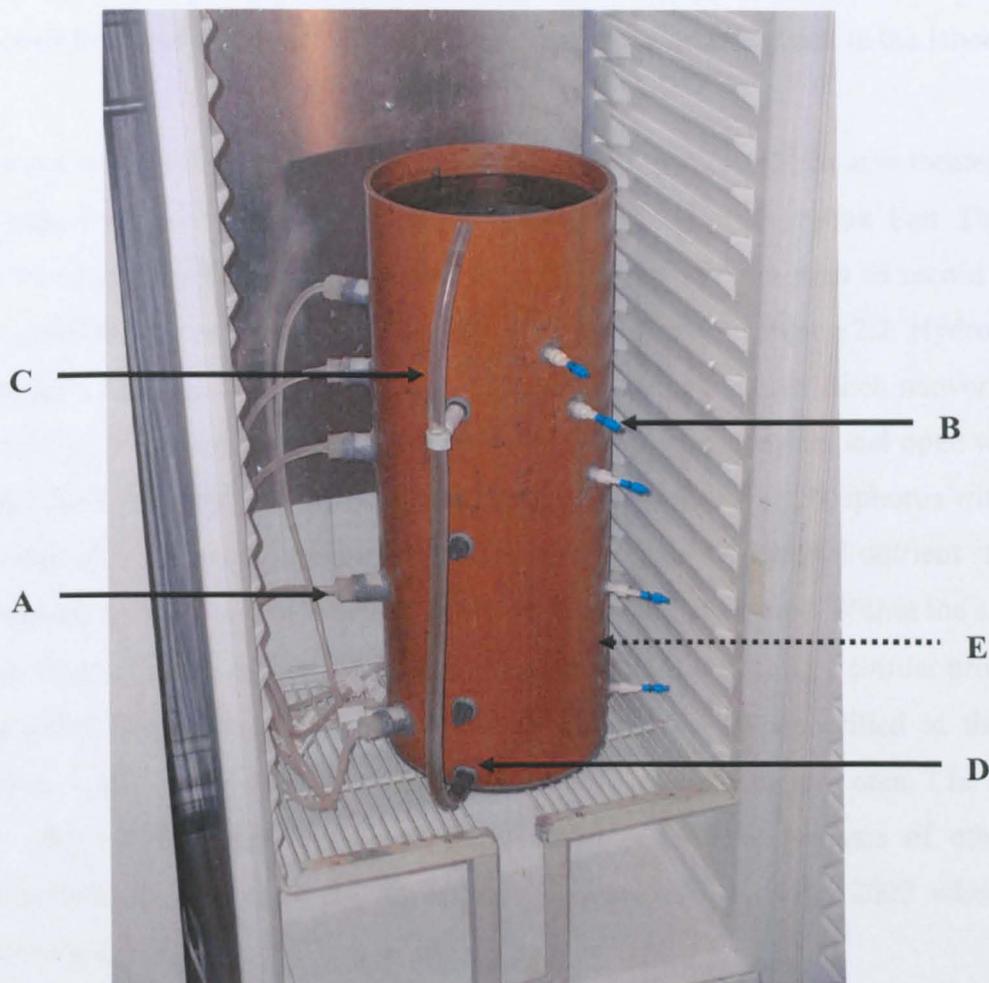
Figure 5.1 Core housing used in laboratory incubations. Sampling ports with mini piezometers installed are on the left side of the core housing (A), sampling ports on the right side (B) were not used in this study. Vertical PVC tube (C) is connected to the housing through a port at the base (D) and gives the position of the water table within the core. Peat sits on a stand within the core housing that elevates the base of the peat above this port. Water is input to/drained from an identical port on the opposite side of the housing (hidden from view, E).

Each core housing consisted of a 70 cm length of PVC pipe (i.d. = 23.7 cm), sealed at the base with a PVC plate that was attached by a PVC weld that was water- and air-tight. Each peat core sat on a perforated stand at the base of the core housing, elevating the bottom of the core 2.5 cm above the base plate. This enabled water levels within the peat cores to be easily controlled by addition or removal of water through the 'reservoir' between the base of the peat and the base of the core housing. The core housings had

each been pre-drilled with five 27 mm diameter holes with the centre-points of the holes corresponding to depths of 2.5, 10, 17.5, 32.5 and 47.5 cm below the peat surface. After transferring the cores into the housings, these holes were sealed with rubber bungs and the tops of the cores were covered with foil before transportation back to the laboratory.

Four cores were collected from random locations within a 20 × 20 m area located 10 m away from a section of the ditch network running through Strumpshaw Fen. The 20 × 20 m area included the near-ditch zone of the transect instrumented to record water-table configuration, as described in Section 4.2.2 and shown in Figure 2.2. Hydrological data suggest that this zone is strongly connected to the open-water ditch network, with the potential for two-way exchanges between pore water in the peat and open water in the ditch (see Chapters 4 and 6). Consequently, the availability of phosphorus within the sediments of this zone is of interest with respect to both the internal nutrient status of the wetland, and also the delivery of nutrients to the ditch network. Within the same 20 × 20 m area, a further nine 50 cm-depth cores were collected using a similar procedure. These cores had internal diameters of 10.2 cm and had holes drilled at the same positions in the core housing as described for the larger diameter cores. The smaller cores were used for sediment phosphorus fractionation and analysis of other peat physicochemical properties. All cores were collected during June 2003 when water tables were approximately 40 cm below the peat surface.

On returning to the laboratory, rubber bungs were removed from the holes drilled in the core housings and foil was removed from the top of the cores. Pore water was allowed to drain freely from the drilled holes and the base of the cores, and evapotranspiration was allowed to occur from the peat surface, for a period of 10 days. During these 10 days, the cores were stored in the open, and therefore subject to daily fluctuations in meteorological parameters such as air temperature and incident radiation. This was preferred to storage within the laboratory, where parameters such as air temperature were substantially different from field conditions. No significant shrinkage of the peat was observed during this time. The 10-day period was used as a standardisation period prior to the beginning of the experiments.

Towards the end of the standardisation period, peat was removed from areas next to each of the 27 mm holes drilled in the larger i.d. cores using a sharp knife. In effect, a

horizontal core of peat was removed, running 12 cm from the outer edge of the core towards the centre. Into this space was pushed a 'mini piezometer' consisting of a 15 cm long PVC tube (i.d. = 2.1 cm) sealed at its distal end. The 10 cm length of the tube nearest the centre of the peat core was perforated with holes, such that 36 % of the area in contact with the peat was drilled, and a PVC mesh was placed over the holes to prevent the ingress of peat material. Only this section of the mini piezometer was drilled to ensure that any water collecting between the outer edge of the peat core and the core housing was not incorporated in subsequent pore-water samples. The proximal end of the mini piezometer was sealed with a silicone rubber bung that was drilled with a single hole to allow a length of silicone rubber tubing to run down inside the piezometer. The tubing was clamped where it exited the mini piezometer to prevent air moving into the core. After positioning in the peat core, the mini piezometer was sealed to the core housing using silicone sealant to ensure a water- and air-tight seal. On re-flooding of the cores the clamps on the silicone tubing were released and the mini piezometer filled completely with water, excluding any air. The tubing was then re-clamped until sample collection.

5.2.2 Re-flooding of peat cores and sample collection

Two experiments were conducted, each involving the re-flooding of intact peat cores and an examination of the pore-water and surface-water phosphorus dynamics following the establishment of an overlying water column. Two of the four large cores were used in the first experiment and two in the second. In Experiment A the cores were flooded with deionised water (>18 M Ω) as a control and to allow examination of phosphorus exchanges in the absence of external loads of either P or terminal electron acceptors. In Experiment B the two cores were flooded with simulated river water. The chemical composition of the simulated water was based on analyses of samples taken from the River Yare, and was made using standard salts dissolved in deionised water (>18 M Ω) to give the final concentrations of elements shown in Table 5.1. The pH of the flooding solution was controlled by dropwise addition of either 0.1 M H_2SO_4 or 0.1 M NaOH.

Following Pant and Reddy (2003), in both experiments floodwater was introduced slowly from the base of the cores to minimise entrapment of air and leaching of phosphorus. When the cores were fully saturated, floodwater depth was adjusted to give 10 cm of standing surface water by slow addition of water directly at the surface.

Samples were collected from the surface water and each of the mini piezometers after 1, 6, 12, 24, 72, 144, 240, 360, 504 and 672 hours of flooding. In addition, in Experiment B, samples were collected immediately after standing water appeared at the sediment surface (t = 0 hours), and additional samples were collected after 1032 hours of flooding. Surface-water samples (20 ml) were collected using gas-tight syringes (Hamilton 1700 Series), which were sealed using a luer-lock cap following sample collection. For the extraction of pore-water samples, a volume of water equal to 1.5 times the volume of the mini piezometers was first removed and discarded. This ensured that the subsequent sample did not contain 'dead' water that had been in prolonged contact with the piezometer and was therefore not representative of pore water within the cores at the time of sampling. To collect a sample, the silicone tubing from the mini piezometer was connected to a conical flask. The conical flask was sealed with a bung that was drilled with two ports and fitted with two lengths of clamped silicone tubing. This arrangement allowed the flask to be purged with an inert gas (argon) prior to sample collection. Having connected the purged flask to the mini piezometer, a sample (20 ml) was collected using the pressure head in the core to drive pore water into the flask. Following sample collection, tubing clamps on the piezometer and flask were reapplied, and the head space in the flask purged again with argon to maintain an inert atmosphere prior to sample processing. The total volume of water removed during sampling (270 ml) was replaced by addition of deionised water at the surface in both experiments.

Table 5.1 Chemical composition of simulated River Yare water used in Experiment B.

Parameter	Concentration (mg l^{-1}), except pH
Cl^-	70
SO_4-S	20
PO_4-P	0.46
Ca^{2+}	100
Mg^{2+}	4
Na^+	60
K^+	6
NO_3-N	10
Total Alkalinity (as $CaCO_3$)	200
pH	7.80

In addition to the analysis of pore-water and surface-water phosphorus dynamics, changes to the sediment-P pool during flooding were also examined. At the end of Experiment B, three of the small cores that had remained drained were sectioned at 5 cm intervals and analysed using the phosphorus fractionation scheme developed by Reddy *et al.* (1998) for organic soils, alongside separate determinations of readily labile P and microbial biomass P (see Section 5.2.3.2.). A separate set of three of the smaller cores that had been subjected to the flooding period described above for Experiment B was also analysed for the same sediment-P fractions. On the remaining small cores that had been drained but not flooded, selected physicochemical properties of the peat were examined. These analyses of the sediment were conducted to provide further insight into the factors controlling pore-water and surface-water concentrations of phosphorus. All incubations of intact peat cores were conducted within constant temperature fridges set to 15 °C (± 0.1 °C). During late autumn, when re-flooding of the peat deposits typically occurs in the field, pore-water temperatures are in the approximate range of 7 to 13 °C.

5.2.3 Analytical procedures

5.2.3.1 Pore water and surface water

The processing of pore-water and surface-water samples was conducted in a glove bag under an inert N_2 atmosphere. Samples were analysed for pH using a WPA CD70 portable pH meter. Following pH determination, samples were filtered through 0.45 µm cellulose nitrate acetate (CNA) membrane filters that had been pre-conditioned with a few millilitres of each sample, the filtrate being discarded to waste. Following filtration, 10 ml of each sample was acidified to pH < 2 using 1 % v.v. 4 M H_2SO_4 and stored in argon-filled tubes. The acidified samples were analysed for Fe^{2+} using a 1,10 Phenanthroline monohydrate method, modified from the work of Stucki and Anderson (1981). Fe^{2+} and 1,10 Phenanthroline combine to form a complex with an intense red colour and an absorbance maximum at 510 nm, which was measured using a Unicam UV/Vis Spectrometer UV2 equipped with a 'Super Sipper' to inject a standard or sample into a 10 cm or 40 cm glass flow cell as appropriate. The addition of reagents to samples, and the subsequent development of the Fe^{2+}-phen complex, occurred under red light conditions, and all sample tubes were wrapped in aluminium foil. If 1,10 Phenanthroline is added to a solution containing Fe^{3+} then a ferric-phen complex may

be formed. On exposure to light with a wavelength < 500 nm, and in the presence of excess phen, this ferric-phen complex can be reduced to the Fe^{2+}-phen complex, thereby increasing the absorbance of the solution at 510 nm (Stucki and Anderson, 1981). If a determination of Fe^{2+} is being made, the photochemical reduction of the ferric-phen complex will lead to erroneously high determinations of Fe^{2+} concentration, hence the precautions described above to prevent light with a wavelength < 500 nm from reaching the samples. However, the photochemically sensitive nature of the ferric-phen complex can be used to provide a determination of Fe^{2+} and Fe^{3+} on the same sample. Having determined Fe^{2+} on solutions protected from exposure to light, the samples were exposed to direct fluorescent light for a period of 36 hours, resulting in the photochemical reduction of any ferric-phen complex. The absorbance of the solution was measured again at 510 nm after exposure to light, and any increase in absorbance compared to the Fe^{2+} assay was attributed to Fe^{3+} in solution (Stucki, 1981). No significant quantities of Fe^{3+} were found, confirming that at the pH of the samples from Strumpshaw Fen all iron was present in the ferrous form. Investigation of the 1,10 Phenanthroline method showed that when HNO_3 was used to acidify filtrates, colour development was suppressed (by 64 to 74 % in standard solutions), and that non-linear calibration curves were produced. Therefore H_2SO_4 was preferred for sample acidification.

Acidified samples were also used for the determination of major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+ and Mn^{2+}) by atomic absorption spectrometry (AAS) using a Perkin Elmer 1100B Spectrometer, having ensured that acidification of the sample resulted in no significant alteration to the concentration of these elements in solution. The remaining unacidified filtrate was stored in argon-filled tubes under a N_2 atmosphere until analysis for major anions (Cl^-, NO_3^- and SO_4^{2-}) by ion chromatography using a Dionex DX-100 ion chromatograph in conjunction with a Dionex AS40 Automated Sampler and 4400 Integrator. The same unacidified filtrate was analysed for molybdate reactive phosphorus (MRP) by automated colorimetry using flow injection analysis (FIAstar 5000). The FIA technique uses the colorimetric molybdenum blue methodology, in which orthophosphate ions react under acid conditions with molybdate to form a heteropoly acid (phosphomolybdic acid). The phosphomolybdic acid is then reduced to the coloured molybdenum blue complex by the action of stannous chloride. The molybdenum blue complex has an absorbance maximum at 720 nm, and the intensity of the colour developed is proportional to the concentration of orthophosphate in the

original sample (Foss Tecator, 2000). All sample dilutions were conducted using deoxygenated blank solutions within a glove bag filled with N_2, to prevent the oxidation of initially reduced samples.

The decision to focus on MRP, as opposed to other fractions, such as total dissolved P, was made for three principal reasons. Firstly, MRP includes the orthophosphate ion which represents the fraction of total P that is considered to be directly available and rapidly consumed by bacteria and algae (Hens and Merckx, 2002; Zhang and Oldham, 2001; Robards *et al.*, 1994). Therefore, the delivery of MRP to a receiving water body may have a rapid influence on the ecological quality. Secondly, MRP is often assumed to be highly mobile (Haygarth *et al.*, 1997). Therefore, the potential for this fraction to be transported and subsequently delivered to receiving waters may be greater than that associated with other fractions of the total P load. Finally, the role of riparian wetlands in controlling MRP concentrations is not as well understood as for other fractions such as particulate P (Uusi-Kämppä *et al.*, 2000).

5.2.3.2 Solid phase

Fractionation of the sediment phosphorus pool followed the methodology and terminology that Reddy *et al.* (1998) developed for organic soils. The top 1 cm of the cores, consisting of unconsolidated detritus, was removed. The cores were then sectioned at 5 cm intervals, major root and rhizome material removed, and fresh soils (0.5 g dry weight equivalent) were extracted with 25 ml of solution to give a dry weight to solution ratio of 1:50. The first step in the scheme was a 2 hr extraction on a continuous shaker with 1 M KCl to give loosely adsorbed P. The solutions were subsequently centrifuged at 7000 r.p.m for 15 minutes, followed by 0.45 μm membrane filtration and acidification to pH < 2 with 4 M H_2SO_4. The filtrates were analysed for MRP by FIA, and represent a readily available pool of inorganic P, termed KCl-P_i.

The residual soil was then extracted with 0.1 M NaOH for 17 hours on a continuous shaker, followed by centrifugation at 7000 r.p.m for 15 minutes, and 0.45 μm membrane filtration. The filtrates were analysed for MRP by FIA and represent inorganic P attached to oxides and hydroxides of iron and aluminium (NaOH-P_i). The filtrates were also analysed for total phosphorus following microwave digestion of samples in the presence of an acidic potassium persulphate solution (NaOH-TP). The

difference between NaOH-TP and NaOH-P_i represents organic P associated with humic and fulvic acids (NaOH-P_o).

The residual soil from the NaOH step was then extracted with 0.5 M HCl for 24 hours on a continuous shaker. Solutions were subsequently centrifuged at 7000 r.p.m for 15 minutes and filtered through 0.45 μm membrane filters prior to MRP analysis by FIA (HCl-P_i). This fraction is assumed to represent inorganic phosphorus attached to calcium and magnesium.

Finally, the residual soil from the HCl extraction was digested using the Kjedhal method, with concentrated H_2SO_4 and a selenium catalyst. The resulting solution was analysed for MRP by FIA after appropriate dilution to adjust the acid concentration. This fraction is assumed to represent highly refractory organic P and is termed residual-P_o. Some authors suggest that phosphorus in this fraction may include inorganic forms not extracted in the previous steps (e.g. White *et al.*, 2004). However, given the highly organic nature of the sediments at Strumpshaw Fen (ash content generally < 20 %), and the improbability of highly resistant forms of inorganic P existing in such sediments, such as phosphorus bound in silicate minerals, the residual-P fraction was assumed to be largely organic. The same digest procedure was also used to determine the total phosphorus content of the fresh soil, to enable a comparison with total phosphorus calculated by the sum of each P fraction from the sequential extraction procedure. Soil pH was determined on duplicate fresh soil samples from each 5 cm section using a deionised water to soil ratio (volume:weight) of 2.5:1.

Separate subsamples of each 5 cm core section were also analysed for labile organic and inorganic P, and P associated with microbial biomass following Ivanoff *et al.* (1998) and Hedley and Stewart (1982). Fresh soils (0.5 g dry weight equivalent) were extracted with 25 ml 0.5 M $NaHCO_3$ for 16 hours on a continuous shaker, followed by centrifugation at 7000 r.p.m for 15 minutes, and 0.45 μm membrane filtration. The filtrates were analysed for MRP by FIA, and TP following microwave digestion of samples in the presence of an acidic potassium persulphate solution. The MRP determination represents readily labile P_i, whilst the difference between TP and MRP constitutes readily labile P_o (Ivanoff *et al.*, 1998; Reddy *et al.*, 1998). A duplicate batch of fresh soils (0.5 g dry weight equivalent) was incubated with 1 ml of liquid $CHCl_3$ in capped centrifuge tubes for 16 hours under an extraction hood. The tubes were then

uncapped and incubated for a further 2 hours, followed by extraction with 25 ml 0.5 M NaHCO$_3$ and analysis for TP, as described above for non-CHCl$_3$-treated samples. The difference in TP between CHCl$_3$-treated and non-treated samples represents P associated with microbial biomass (Wright *et al.*, 2001; Reddy *et al.*, 1998). A recovery rate of 0.4 was used to account for the efficiency of CHCl$_3$-treatment of microbial cells, which has been shown to represent the average recovery for a wide range of soil types, including organic deposits (Walbridge, 1991; Hedley and Stewart, 1982).

As described in Section 5.2.2 the organic and inorganic P fractionation schemes were applied to both drained and flooded cores. The drained cores contained oxidised peat. In contrast, those that had been flooded were likely to be strongly reduced. Alterations to the fractionation schemes described above were made to reflect the likely anaerobic nature of the sediments from these cores. Firstly, all sectioning and pH determinations were made in a glove bag under an inert N$_2$ atmosphere. Secondly, prior to the KCl and NaHCO$_3$ extractions, pore water was removed from the peat by centrifugation of the sediment in argon-purged centrifuge tubes. Pore water was subsequently filtered through 0.45 μm membrane filters within a glove bag and the filtrate stored for MRP and Fe^{2+} analysis following suitable acidification. Analysis of pore-water samples extracted from the sediment by centrifugation at the end of Experiment B provided comparison with samples collected from mini piezometers. Thirdly, N$_2$ gas was bubbled through the KCl and NaHCO$_3$ extractants to produce deoxygenated solutions, the headspace of the centrifuge tubes used in these steps was purged with argon gas prior to shaking, and the subsequent filtering of extracts was conducted inside a glove bag filled with N$_2$.

On a further three drained cores, selected physicochemical properties of the peat were examined. Cores were again sectioned at 5 cm intervals having first removed the surface 1 cm, and then oven dried at 70 °C to constant weight. 0.5 g of oven-dry soil was then extracted with 25 ml of 1 M HCl for 3 hours on a continuous shaker, followed by centrifugation at 7000 r.p.m for 15 minutes and 0.45 μm membrane filtration. The filtrates were analysed for Ca^{2+} and Mg^{2+} by AAS and MRP by FIA. Following Roden and Edmonds (1997), separate 0.5 g sub-samples of oven-dry soil were extracted with 25 ml of 0.5 M HCl for 1 hour on a continuous shaker, followed by centrifugation at 7000 r.p.m for 15 minutes and 0.45 μm membrane filtration. The filtrates were analysed for iron by AAS. The 0.5 M HCl extraction is assumed to remove Fe^{2+} and Fe^{3+} from

amorphous and poorly crystalline phases (Tuccillo *et al.*, 1999). Finally, further sub-samples of oven-dry soil were extracted with 0.2 M acid ammonium oxalate (pH 3) for non-crystalline aluminium oxides and hydroxides following Darke and Walbridge (2000). Amorphous and poorly crystalline phases of iron and aluminium have been suggested to control the sorption of inorganic P in wetland sediments (Darke and Walbridge, 2000). Given that these phases are also prone to rapid dissolution under reducing conditions (Pant *et al.*, 2002b), their presence in wetland sediments where redox conditions can be highly variable may have important implications for P release to pore water and surface water.

5.3   Results

5.3.1   Fractionation of the sediment phosphorus pool under drained conditions

Figure 5.2 shows the distribution of total phosphorus (TP), total organic phosphorus (TP_o) and total inorganic phosphorus (TP_i) in the surface 50 cm of peat at Strumpshaw Fen. TP is the sum of TP_o and TP_i, TP_o the sum of $NaOH-P_o$ and residual-P_o, and TP_i the sum of $KCl-P_i$, $NaOH-P_i$ and $HCl-P_i$.
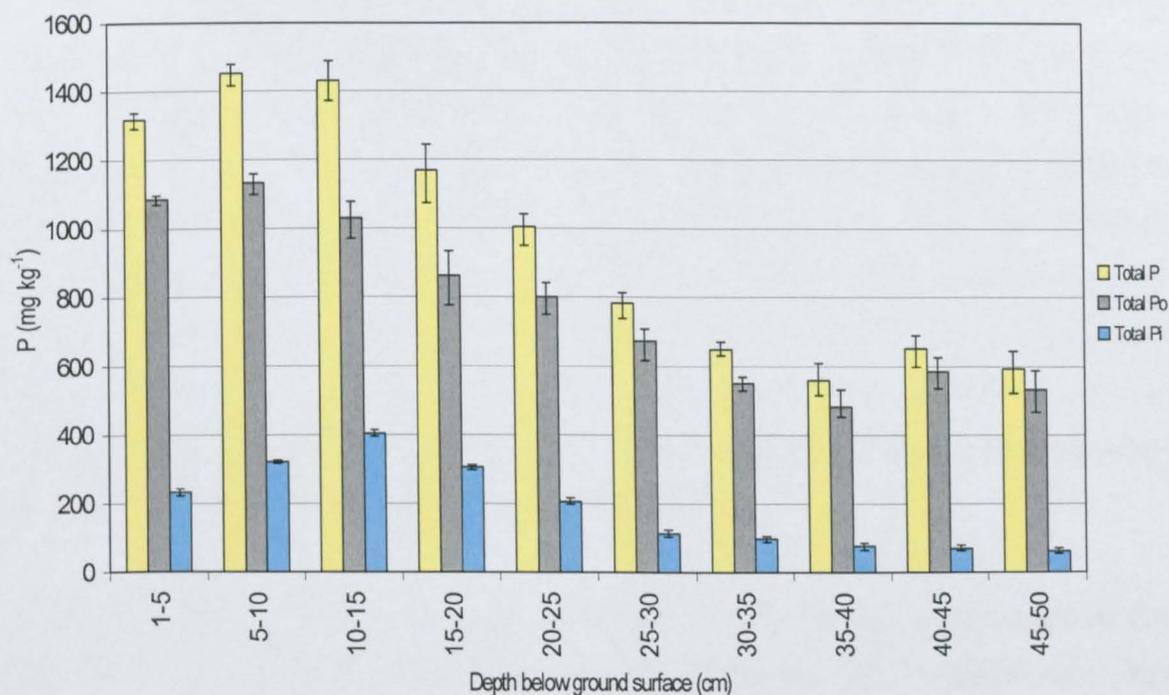
Figure 5.2 TP, TP_o and TP_i in the surface 50 cm of peat at Strumpshaw Fen. Mean values are given (n=3), error bars show the range.

The surface 15 cm of peat contained large quantities of TP, with mean values for the three cores exceeding 1200 mg kg^{-1} P. Below 15 cm depth, total phosphorus content declined substantially, until more constant levels between 550 and 650 mg kg^{-1} P were reached and maintained between 30 and 50 cm depth. Total phosphorus using the phosphorus fractionation scheme was strongly correlated with total phosphorus determined by digestion of fresh soil samples ($r = 0.98$, $p < 0.01$).

Throughout the 50 cm of peat examined, the majority of TP was present in the form of total organic phosphorus. Over the three cores analysed, between 70 and 92 % of TP at each 5 cm depth interval was present as TP_o. The pattern of TP_o content with depth matched that described for TP, with an enriched surface layer overlying peat with lower and more constant TP_o concentrations below 30 cm. There was also a clear depth dependency to the TP_i content of the peat at Strumpshaw Fen. Total inorganic phosphorus content increased with depth from the surface to reach a maximum of approximately 400 mg kg^{-1} P between 10 and 15 cm. At this depth, TP_i represented around 30 % of TP. Below 15 cm, TP_i fell rapidly to around 100 mg kg^{-1} P at 25 to 30 cm depth, followed by slower decreases towards the base of the core, reaching a minimum of approximately 60 mg kg^{-1} P (~10 % of TP) at 45 to 50 cm depth.

Table 5.2 provides more detailed information on the forms of P held in the sediment at Strumpshaw Fen. The KCl-P_i fraction, representing loosely adsorbed phosphorus that may rapidly become bioavailable (Reddy *et al.*, 1998), never exceeded 1 % of TP at any depth in any of the three cores analysed. At each depth increment, there was a relatively even split in the contributions made to TP_i by NaOH-P_i and HCl-P_i, with NaOH-P_i usually exceeding HCl-P_i, but by no more than 16 % in any of the samples analysed. The variation of NaOH-P_i and HCl-P_i with depth matched that of TP_i, with contents increasing over the first 15 cm of peat to reach a maximum of 12 to 15 % of TP between 10 and 20 cm, followed by decreases to lower contents deeper in the peat profile where HCl-P_i and NaOH-P_i represented only 4 to 6 % of TP.

The vast majority of the total organic phosphorus pool in the peat at Strumpshaw Fen was present in the highly refractory residual-P_o fraction, only released after acid digestion, which likely represents non-bioavailable forms of phosphorus (Reddy *et al.*, 1998). Between 73 and 88 % of the TP_o pool was accounted for by residual-P_o, with some indication that at greater depth a larger percentage of TP_o was present as residual-

Table 5.2 Fractionation of phosphorus held in the upper 50 cm of sediment at Strumpshaw Fen. Mean values are given (mg kg^{-1}, n = 3) with the range in parentheses.

Depth (cm)	KCl-P$_i$	NaOH-P$_i$	HCl-P$_i$	Total-P$_i$	NaOH-P$_o$	Residual-P$_o$	Total-P$_o$	Total-P
1-5	2.9 (4.2 - 1.6)	115.1 (121.5 – 107.4)	93.9 (98.7 – 89.9)	211.9 (221.7 – 201.5)	297.7 (344.1 – 263.6)	788.4 (810.2 – 749.5)	1086.2 (1095.8 – 1069.2)	1298.1 (1317.5 – 1270.6)
5-10	1.4 (2.7 – 0.4)	168.4 (178.2 – 160.6)	130.9 (149.0 – 115.1)	300.7 (315.8 – 290.4)	287.8 (314.0 – 249.2)	843.9 (890.9 – 784.2)	1131.7 (1156.9 – 1098.2)	1432.5 (1447.3 – 1414.0)
10-15	1.8 (2.6 – 0.4)	216.2 (225.4 – 207.6)	184.7 (192.1 – 177.1)	402.6 (412.5 – 395.4)	171.1 (195.3 – 129.7)	856.6 (907.3 – 774.7)	1027.7 (1076.1 – 970.0)	1430.3 (1488.5 – 1370.0)
15-20	0.5 (0.7 – 0.2)	178.1 (184.2 – 171.6)	125.9 (139.3 – 112.1)	304.5 (311.1 – 296.7)	100.1 (137.1 – 63.5)	761.7 (794.2 – 711.9)	861.7 (931.3 – 775.4)	1166.2 (1242.4 – 1072.2)
20-25	0.4 (0.8 – 0.2)	107.6 (115.5 – 98.9)	96.3 (100.1 – 89.2)	204.3 (215.4 – 198.4)	113.0 (155.2 – 79.4)	685.5 (701.1 – 670.0)	798.5 (840.5 – 749.4)	1002.8 (1039.7 – 947.8)
25-30	0.5 (0.8 – 0.2)	62.2 (66.5 – 59.7)	49.0 (55.8 – 42.3)	111.7 (122.5 – 103.1)	89.1 (99.2 – 79.2)	581.7 (628.9 – 516.5)	670.8 (708.1 – 615.7)	782.5 (811.3 – 738.2)
30-35	0.3 (0.6 – 0.1)	58.5 (62.9 – 54.4)	39.2 (43.9 – 33.0)	98.0 (103.8 – 88.0)	72.5 (80.8 – 58.7)	477.1 (495.1 – 447.4)	549.6 (566.9 – 528.3)	647.6 (670.7 – 630.5)
35-40	0.3 (0.7 – 0.1)	44.5 (47.5 – 41.7)	30.6 (36.6 – 22.0)	75.4 (84.8 – 63.8)	68.3 (76.0 – 62.6)	414.4 (454.6 – 388.6)	482.7 (530.6 – 451.2)	558.1 (608.2 – 515.0)
40-45	0.5 (0.6 – 0.4)	41.8 (48.7 – 36.8)	26.0 (29.7 – 22.4)	68.2 (78.9 – 62.8)	78.9 (89.0 – 71.1)	504.1 (549.1 – 463.0)	583.0 (625.6 – 534.1)	651.2 (688.3 – 597.2)
45-50	0.3 (0.4 – 0.1)	33.3 (37.0 – 30.1)	27.0 (32.7 – 23.9)	60.5 (69.9 – 54.2)	69.2 (75.7 – 62.7)	462.1 (516.3 – 403.5)	531.2 (585.3 – 466.2)	591.8 (642.8 – 520.4)

P_o. In the near-surface peat, residual-P_o accounted for approximately 60 % of TP. Despite the fact that absolute concentrations of residual-P_o tended to decrease with depth through the peat profile (see Table 5.2), the percentage of TP accounted for by residual-P_o increased with depth, such that at 45 to 50 cm nearly 80 % of TP was present as residual-P_o. In the surface 10 cm of peat, NaOH-P_o accounted for approximately 26 % of TP_o and 21 % of TP. Between 10 and 20 cm these percentages fell rapidly, and below 20 cm more constant NaOH-P_o contents were reached, representing around 13 % of TP_o and 11 % of TP.

Table 5.3 shows the results of $NaHCO_3$ extraction of the upper 50 cm of peat from Strumpshaw Fen. Readily labile P_i was correlated with KCl-P_i, and confirmed the existence of a very small labile inorganic P store, concentrated towards the top of the cores above approximately 15 cm depth. Readily labile P_o showed very similar patterns to P_i, both in terms of the size of the fraction and the depth-distribution. The microbial biomass store of P was relatively large in the sediments at Strumpshaw Fen, representing between approximately 6 and 9 % of TP throughout the cores. Although absolute concentrations of this fraction decreased with depth, as a proportion of TP there was little variation. Microbial biomass P content at Strumpshaw Fen corresponds well with results from nutrient-enriched peat from the Florida Everglades, where Qualls and Richardson (1995) reported that approximately 16 % of TP was present as microbial biomass P, whilst Ivanoff *et al.* (1998) reported a figure of 7 % in a flooded soil from the same region. Pant and Reddy (2001a) suggested that between 5 and 20 % of TP in wetland detritus may be present as microbial biomass P. Given that phosphorus stored in microbial biomass is considered readily labile (Ivanoff *et al.*, 1998), the substantial proportion of TP present in this form at Strumpshaw Fen suggests that it may have an important role in the release/retention of P during water-table fluctuation within the sediments.

5.3.2 Peat physicochemical properties in drained cores

Table 5.4 shows the results of pH, HCl-extractable iron (Fe) Ca, Mg, Fe and P_i, and oxalate-extractable Al analyses conducted on the peat at Strumpshaw Fen. Sediment pH values suggested that the peat varied with depth from slightly to more strongly acidic under oxidised conditions. In the surface 15 cm of peat, pH was greater than 6.1, and values up to 6.4 were recorded. Between 15 and 30 cm depth was a zone of more acidic

peat, with pH values as low as 5.5. Below 30 cm, the sediment pH increased again, reaching maximum values of 6.8 towards the base of the core. HCl-extractable Ca and oxalate-extractable Al showed equally strong depth-related patterns. Calcium content fell from around 28 mg g^{-1} Ca in the near-surface peat, to around 20 mg g^{-1} at 15 to 20 cm depth. Below 20 cm, calcium concentrations increased and exceeded 23 mg g^{-1} at the base of the core.

Table 5.3 Microbial Biomass P and NaHCO₃-extractable P in the upper 50 cm of sediment at Strumpshaw Fen. Mean values are given ($mg\ kg^{-1}$, n = 3) with the range in parentheses.

Depth (cm)	NaHCO₃ - P$_i$	NaHCO₃ – P$_o$	Microbial Biomass - P
1-5	3.1 (4.0 – 2.3)	2.0 (2.2 – 1.9)	101.4 (110.1 – 94.5)
5-10	2.0 (3.7 – 0.6)	1.7 (1.8 – 1.5)	137.5 (150.7 – 120.4)
10-15	1.9 (2.8 – 0.3)	1.5 (2.9 – 0.8)	116.7 (121.7 – 107.3)
15-20	0.8 (1.1 – 0.2)	1.0 (1.6 – 0.4)	90.1 (93.6 – 86.8)
20-25	0.6 (1.0 – 0.1)	0.8 (1.2 – 0.1)	83.0 (86.4 – 79.3)
25-30	0.4 (0.7 – 0.1)	0.2 (0.4 – 0.1)	68.4 (76.8 – 62.3)
30-35	0.2 (0.5 – 0.1)	0.4 (0.6 – 0.1)	59.1 (64.7 – 54.1)
35-40	0.3 (0.5 – 0.1)	0.3 (0.5 – 0.1)	45.6 (54.2 – 40.6)
40-45	0.2 (0.3 – 0.1)	0.2 (0.4 – 0.0)	39.9 (43.8 – 36.5)
45-50	0.3 (0.7 – 0.1)	0.2 (0.3 – 0.0)	42.6 (62.1 – 29.9)

Amorphous aluminium concentration increased through the near-surface peat from around 500 mg kg^{-1} to a maximum of approximately 1200 mg kg^{-1} at 20 to 25 cm. At greater depth, concentrations fell and reached a minimum of around 650 mg kg^{-1} at the base of the core. 1 M HCl-extractable Mg concentrations were relatively constant throughout the cores. To summarise, the peat at Strumpshaw Fen was characterised by a surface layer of some 15 cm thickness where sediment pH was near neutral, calcium

Table 5.4 Selected physicochemical properties of the surface peat at Strumpshaw Fen. Mean values are given (n = 3) with the range in parentheses. All values are mg kg^{-1}, except Ca (mg g^{-1}) and pH (-).

Depth (cm)	pH	0.2 M oxalate-Al	1 M HCl-Ca	1 M HCl-Mg	0.5 M HCl -Fe	1 M HCl-P$_i$
1-5	6.19 (6.23 – 6.15)	525.2 (605.5 – 445.7)	28.2 (30.3 – 26.3)	1550.8 (1579.6 – 1518.0)	7862.4 (8202.4 – 7415.4)	226.7 (265.0 – 199.8)
5-10	6.32 (6.40 – 6.23)	766.2 (801.5 – 735.1)	28.5 (30.0 – 26.8)	1765.6 (1806.6 – 1723.6)	10296.4 (10762.0 – 10024.6)	318.0 (355.5 – 274.1)
10-15	6.17 (6.25 – 6.1)	936.9 (956.5 – 923.9)	22.6 (24.6 – 21.1)	1743.9 (1784.6 – 1672.5)	11516.7 (13026.0 – 9828.9)	361.7 (399.5 – 342.1)
15-20	5.55 (5.57 – 5.52)	1066.0 (1145.7 – 966.6)	20.4 (21.1 – 20.0)	1662.6 (1764.6 – 1564.4)	8734.9 (9581.1 – 7749.0)	263.5 (315.3 – 208.1)
20-25	5.57 (5.75 – 5.46)	1220.1 (1248.4 – 1166.1)	21.5 (22.2 – 20.6)	1599.9 (1646.2 – 1558.9)	7165.3 (8054.7 – 5487.2)	189.7 (217.0 – 152.2)
25-30	5.90 (6.21 – 5.72)	1062.4 (1094.6 – 1023.7)	25.8 (26.5 – 25.5)	1682.7 (1712.6 – 1663.2)	6769.6 (7329.7 – 5829.4)	92.2 (97.0 – 88.7)
30-35	6.28 (6.56 – 5.99)	853.5 (941.0 – 732.1)	25.7 (26.5 – 24.9)	1517.9 (1544.8 – 1503.3)	5883.4 (5998.4 – 5755.3)	81.9 (92.4 – 71.8)
35-40	6.48 (6.64 – 6.2)	800.7 (971.2 – 665.2)	25.5 (26.5 – 24.9)	1428.2 (1487.3 – 1381.1)	5079.7 (5393.1 – 4887.1)	64.5 (77.3 – 63.8)
40-45	6.53 (6.69 – 6.29)	701.5 (869.8 – 602.3)	23.7 (25.6 – 22.6)	1239.0 (1282.9 – 1207.9)	3970.9 (4155.9 – 3731.3)	62.0 (75.7 – 67.6)
45-50	6.73 (6.81 – 6.64)	646.2 (697.5 – 589.5)	23.9 (24.4 – 23.3)	1177.9 (1203.7 – 1153.7)	3860.7 (3996.6 – 3771.1)	47.1 (70.0 – 45.1)

content was high, and aluminium concentration was low but increasing with depth. Between approximately 15 and 30 cm depth, the peat became more strongly acidic, calcium contents showed a marked decrease and aluminium a marked increase. At depths greater than 30 cm, peat pH returned towards neutrality, calcium concentration increased and aluminium content returned to concentrations similar to those in the near-surface peat.

The pattern of 0.5 M HCl-extractable Fe content with depth was strongly correlated with that described previously for TP_i ($r = 0.94$, $p < 0.01$). Concentrations of iron increased over the first 15 cm of peat to a maximum of over 11000 mg/kg Fe between 10 and 15 cm. Below 15 cm, concentrations declined steadily to reach approximately 3800 mg/kg Fe at the base of the core. Depth-patterns of 1 M HCl-extractable P_i closely matched those described for 0.5 M HCl-extractable Fe ($r = 0.94$, $p < 0.01$), with maximum values of 362 mg/kg P at 10 to 15 cm depth, falling to 47 mg/kg P at the base of the core. The relationship between total inorganic P from the phosphorus fractionation scheme, and HCl-extractable Fe and P, can be used to assess the reliability of the P fractionation scheme used in this research.
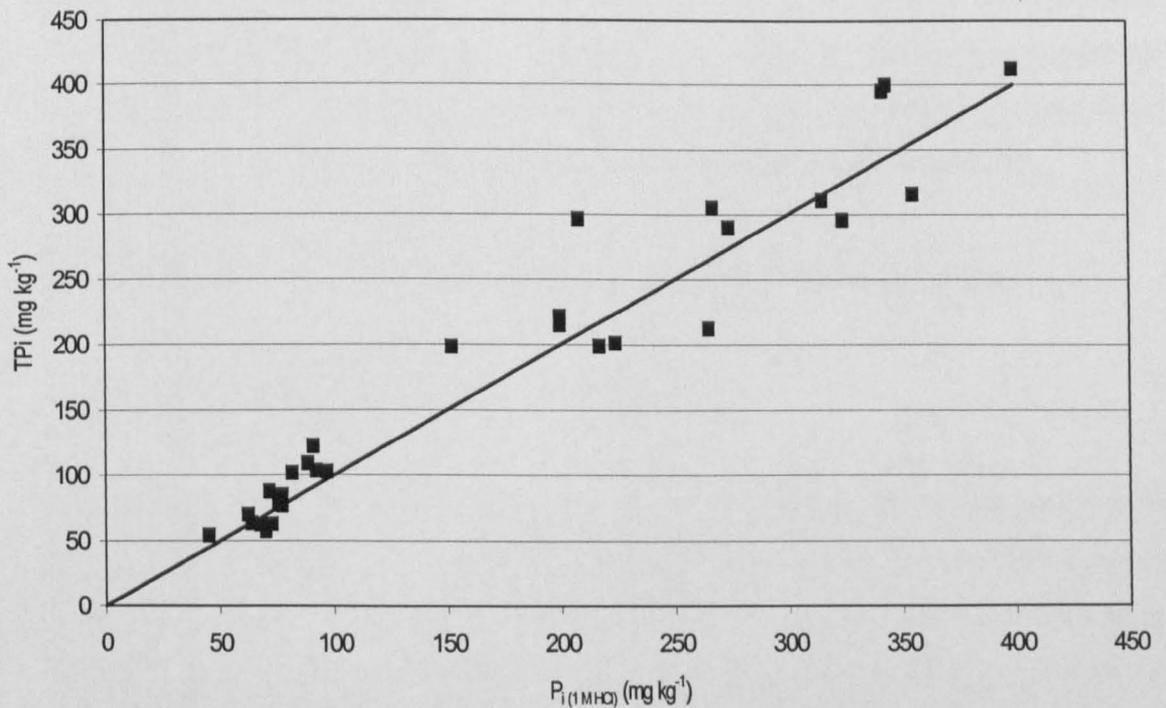
Figure 5.3 TP_i from the phosphorus fractionation scheme versus $P_{i\,(1\,M\,HCl)}$. Line gives 1:1 ratio.

One of the major concerns surrounding the use of NaOH extractions in organic soils is that hydrolysis of organic P during the sodium hydroxide step may result in erroneously high determinations of NaOH-P_i (e.g. Reddy *et al.*, 1998; Qualls and Richardson, 1995). Reddy *et al.* (1998) examined the correlation between TP$_i$ from their P fractionation scheme and P$_i$ following 1 M HCl extraction of the same soil, in order to test for the hydrolysis of organic P during the NaOH step of the fractionation scheme. Following their work, Figure 5.3 shows the correlation between these two determinants in the peat at Strumpshaw Fen ($r = 0.97$, $p < 0.01$), and indicates that TP$_i$ from the phosphorus fractionation scheme does not differ significantly from 1 M HCl-extractable P$_i$. This suggests that there is only minimal hydrolysis of organic P during the NaOH step of the phosphorus fractionation scheme.

The integrity of the fractionation scheme is further supported by a strong correlation between NaOH-P$_i$ and 0.5 M HCl-Fe ($r = 0.92$, $p < 0.01$), suggesting that phosphorus extracted during the sodium hydroxide step does indeed represent P attached to oxides and hydroxides of iron. Various authors have suggested that 0.1 M NaOH-P$_i$ may also represent phosphorus associated with oxides and hydroxides of aluminium (e.g. White *et al.*, 2004; Qualls and Richardson, 1995; Hedley *et al.*, 1982). However, no significant correlation was found in the current research between NaOH-P$_i$ and oxalate-extractable Al ($p > 0.05$), suggesting that, in the peat at Strumpshaw Fen, only a small proportion of NaOH-extractable phosphorus was previously bound to amorphous aluminium.

5.3.3 Phosphorus dynamics following re-flooding with deionised water

5.3.3.1 Surface-water and pore-water phosphorus

Figure 5.4 shows the release of MRP into the surface water of the duplicate cores following the establishment of flooded conditions in Experiment A. In both cores there was a rapid initial release of MRP into the surface water. Within 6 hours of re-flooding the cores, surface-water MRP concentrations were greater than 0.1 mg l^{-1} P. Over the first 24 hours of the experiment, the pattern of MRP release into the surface water of the duplicate cores was almost identical, with concentrations of 0.14 mg l^{-1} P reached at the end of the first day in both cores.
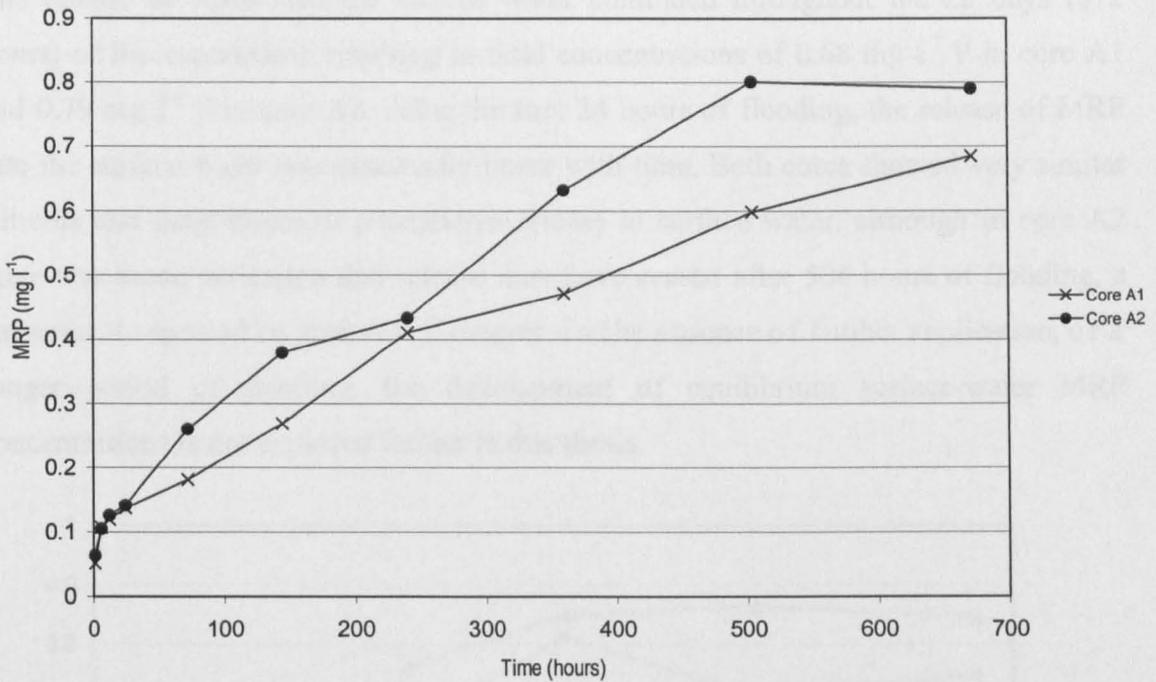
Figure 5.4 The release of MRP into surface water following flooding with deionised water.

The increasing concentration of MRP in the surface water of the cores over the first 24 hours may be a consequence of the experimental design used in the research. By flooding the cores from the base towards the surface, phosphorus may have been advected from deeper peat into the surface water. However, the transport of P from deeper peat into the surface water cannot explain why surface-water concentrations of MRP doubled between 1 and 6 hours of flooding, and continued to increase throughout the first 24 hours of the experiment. During this period there was no hydraulic gradient acting between the deeper peat and the surface water. Consequently, the advection of P from deeper sediment cannot be used to explain the observed increases in MRP concentration. Examination of pore-water MRP concentration over the first 24 hours of flooding suggests that diffusion of P from pore water into the surface water was also unlikely. For the majority of the 24-hour period, the diffusion gradient supported a movement of P from the surface water into the pore water, rather than *vice versa* (see below). A further possibility is that labile P was released into the surface water from the litter-layer on the peat surface (Pant and Reddy, 2001a; Baldwin and Mitchell, 2000; Baldwin, 1999). No attempt was made to remove this layer of undecomposed material from the cores before the experiments, in order to simulate field conditions as closely as possible.

The release of MRP into the surface water continued throughout the 28 days (672 hours) of the experiment, resulting in final concentrations of 0.68 mg l^{-1} P in core A1 and 0.79 mg l^{-1} P in core A2. After the first 24 hours of flooding, the release of MRP into the surface water was essentially linear with time. Both cores showed very similar patterns and magnitudes of phosphorus release to surface water, although in core A2 there was some indication that release may have ceased after 504 hours of flooding, a pattern not repeated in core A1. However, in the absence of further replication, or a longer period of flooding, the development of equilibrium surface-water MRP concentrations is not explored further in this thesis.
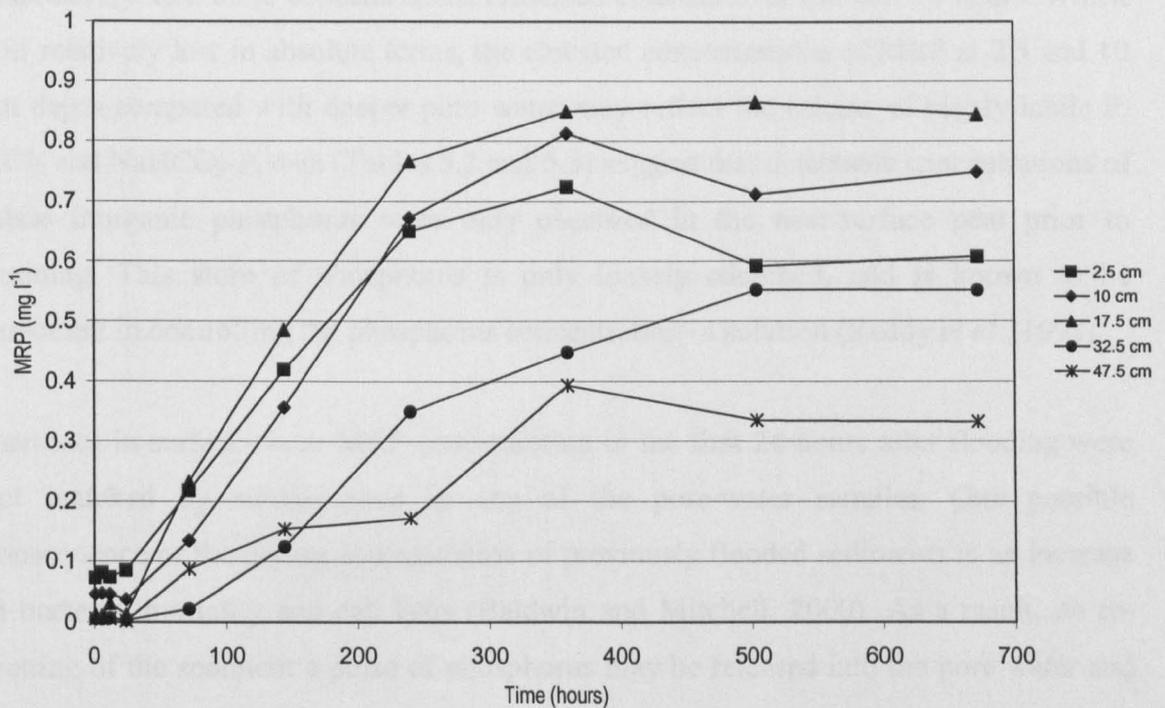
Figure 5.5 Pore-water MRP dynamics in core A1 following re-flooding with deionised water.

Pore-water phosphorus dynamics in core A1 following re-flooding with deionised water are shown in Figure 5.5. Core A2 showed very similar spatial and temporal patterns (data not shown). However, the magnitude of MRP release to the pore water of core A2 exceeded that in core A1 by up to a factor of 2.8 at the end of the experiment. This suggests that either the physicochemical properties of the peat varied quite substantially over relatively small distances, or that the processes controlling the release of MRP to pore water proceeded more efficiently in core A2 than A1. Given the consistency in the results from the three cores analysed for phosphorus fractions and other physicochemical properties (Tables 5.2 – 5.4), it is suggested that the former hypothesis

is unlikely to explain the variations observed between cores A1 and A2. Greater replication may have provided further information regarding the reasons for the different magnitudes of MRP release, however this was not possible due to practical constraints within the project design. The following discussion of pore-water phosphorus dynamics deals solely with the results from core A1.

At sample depths of 17.5, 32.5 and 47.5 cm, pore-water concentrations of MRP remained near to or below the limit of detection during the first 24 hours of flooding. Samples from 2.5 and 10 cm depth contained approximately 0.08 and 0.04 mg l^{-1} P respectively, and these concentrations remained constant over the first 24 hours. Whilst still relatively low in absolute terms, the elevated concentrations of MRP at 2.5 and 10 cm depth compared with deeper pore water may reflect the release of highly labile P. KCl- and $NaHCO_3$-P_i data (Tables 5.2 and 5.3) suggest that detectable concentrations of labile inorganic phosphorus were only observed in the near-surface peat prior to flooding. This store of phosphorus is only loosely adsorbed, and is known to be important in controlling the phosphorus concentration in solution (Reddy *et al.*, 1998).

Increases in surface-water MRP concentration in the first 24 hours after flooding were not matched by similar rises in any of the pore-water samples. One possible consequence of the drying and oxidation of previously flooded sediments is an increase in bacterial mortality and cell lysis (Baldwin and Mitchell, 2000). As a result, on re-wetting of the sediment a pulse of phosphorus may be released into the pore water and surface water, facilitating increased bacterial activity (e.g. Qui and McComb, 1996), or changes in the functioning of emergent macrophyte species such as increased primary productivity or nutrient uptake (e.g. Cui and Caldwell, 1997). In the sediments from Strumpshaw Fen there is little (if any) conclusive evidence of a phosphorus pulse being released into the pore water over the first 24 hours of flooding. This may suggest that the microbial community that exists in the sediment at Strumpshaw Fen has been selected to be able to survive periodic drying and oxidation, for example by producing drought-resistant resting stages (Baldwin and Mitchell, 2000), although the current study provides no direct evidence to support this conclusion. The possible resistance of the microbial community to periods of water-table drawdown is also shown by the lack of a significant change to the sediment microbial biomass P pool between drained and flooded conditions during Experiment B (see Section 5.3.4.3). It is unlikely that the rises seen in surface-water MRP concentration in the first 24 hours after flooding are the

result of a phosphorus pulse from lysed microbial cells, because a similar pulse is not seen in the pore-water samples. This lends further support to the hypothesis that the initial increases of surface-water MRP are related to the release of phosphorus from the plant litter on the sediment surface.

Increases in pore-water MRP concentration in each sample began between 24 and 72 hours after flooding, and continued until 360 hours, after which the samples tended to show less pronounced increases, or indeed decreases, in concentration. After 504 hours, relatively stable MRP concentrations were established in each sample. Pore-water MRP concentrations at the end of the period of flooding were highest in the sample from 17.5 cm where concentrations after 504 hours averaged 0.85 mg l^{-1} P. Towards the peat surface, pore-water samples contained progressively lower concentrations of MRP. At 10 cm depth the average MRP concentration after 504 hours was 0.73 mg l^{-1} P, whilst at 2.5 cm the average was 0.60 mg l^{-1} P. At depths below 17.5 cm there was also a progression to lower MRP concentrations: at 32.5 cm the average concentration was 0.55 mg l^{-1} P, and at 47.5 cm 0.33 mg l^{-1} P.

5.3.3.2 Evidence for concomitant release of Fe^{2+} and MRP

The temporal patterns of Fe^{2+} release into the surface water and pore water of cores A1 and A2 showed striking similarity to the patterns described above for MRP. Figure 5.6 shows the release of Fe^{2+} to the pore water of core A1. Core A2 again yielded similar temporal and spatial patterns. However, to a similar extent as described previously for MRP, the magnitude of Fe^{2+} release into the pore water of core A2 exceeded that in core A1.

Very little Fe^{2+} was released into the pore water during the first 24 hours of flooding, with concentrations throughout the core remaining only slightly above the detection limit of the method. The slightly elevated concentrations of MRP in the pore water at 2.5 and 10 cm depth over the first 24 hours of flooding (see Figure 5.5) therefore cannot be linked to spatial patterns of iron release. Between 24 and 72 hours after flooded conditions were established, substantial increases in pore-water Fe^{2+} concentration began. Fe^{2+} continued to be released into the pore water until 504 hours, after which more stable concentrations were maintained.
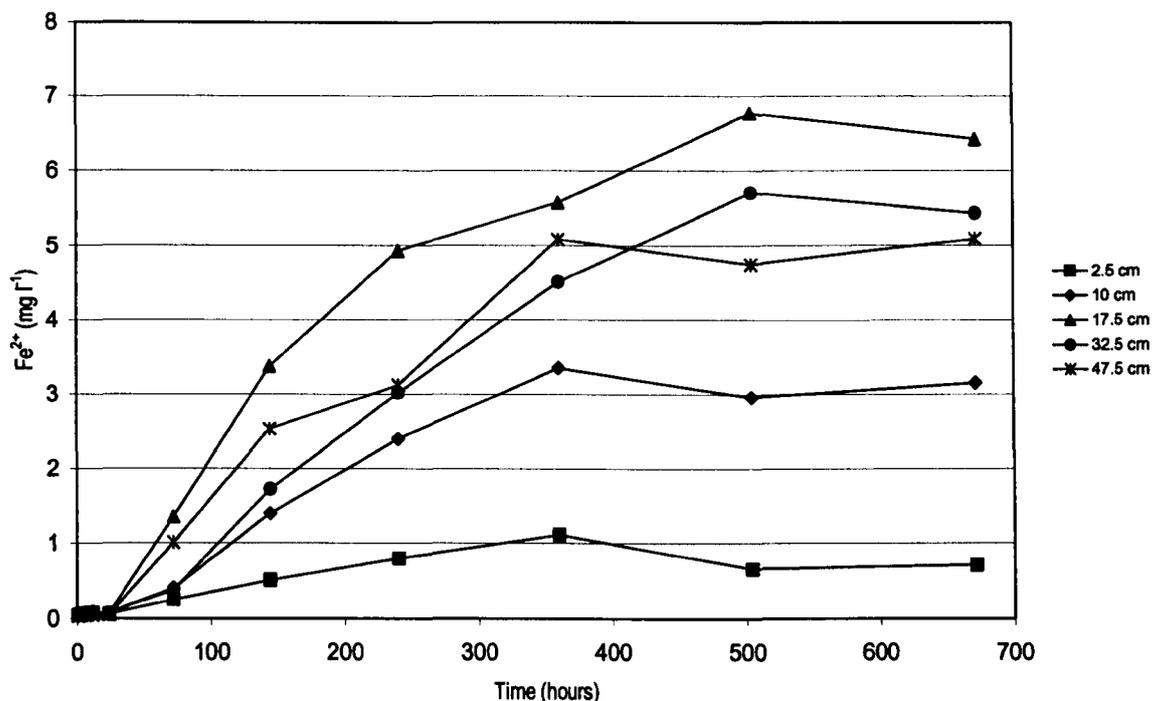
Figure 5.6 The release of Fe^{2+} into the pore waters of core A1 following re-flooding with deionised water.

This temporal pattern of Fe^{2+} release into the pore water of core A1 suggests a concomitant release of ferrous iron and MRP. Yet, the spatial pattern of Fe^{2+} concentration with depth through the core at the end of the experiment differed in some respects to that for MRP. Samples from 17.5 cm depth contained the highest concentrations of Fe^{2+} at the end of the experiment (6.4 mg l^{-1}), and also the highest MRP concentrations (0.85 mg l^{-1} P). Samples nearer the peat surface contained much lower concentrations of Fe^{2+}; at 10 cm the average after 504 hours was 3.1 mg l^{-1} and at 2.5 cm only 0.68 mg l^{-1}. Although the variation of Fe^{2+} concentration with depth in the zone from 17.5 cm to the surface matched the pattern observed for MRP, there was an order of magnitude decrease in Fe^{2+} concentration between samples at 17.5 and 2.5 cm depth, whilst MRP concentration in the same zone decreased by only a factor of 0.7. Further, samples at 32.5 and 47.5 cm depth had higher concentrations of Fe^{2+} at the end of the experiment than samples at 10 and 2.5 cm, the opposite pattern to that observed for MRP.
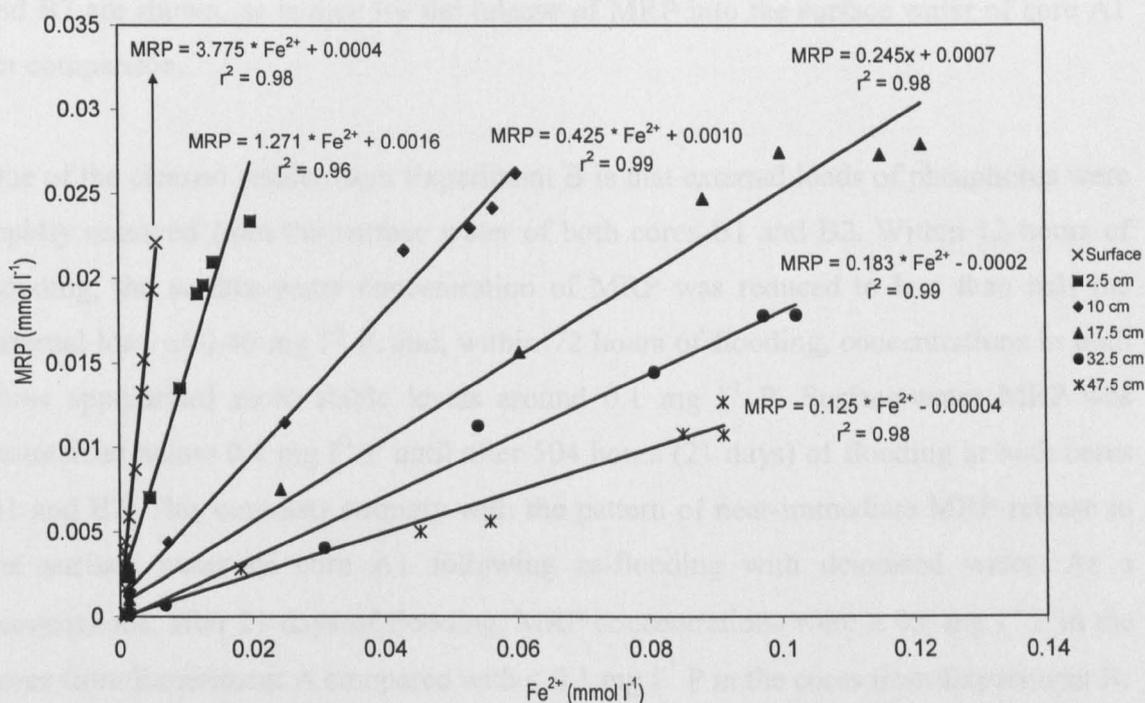
Figure 5.7 The release of Fe^{2+} and MRP into the pore water and surface water of core A1.

Figure 5.7 shows the Fe^{2+} and MRP data from all five pore-water sampling depths, and the surface water, over the duration of the flooding period for core A1. Values of $r^2 \geq$ 0.96, and the lack of systematic departures in the data from a linear relationship, indicate that the timings of Fe^{2+} and MRP release were closely correlated in all samples from this core. All regressions were statistically significant (p < 0.01). However, it is clear that the P:Fe molar ratio in pore water and surface water, represented by m in each regression equation, was not spatially consistent. There is a progression from lower P:Fe molar ratios in the pore water at the base of the core (P:Fe = 0.125 at 47.5 cm depth), to higher ratios towards the core surface (P:Fe = 1.271 at 2.5 cm depth) and into the surface water (P:Fe = 3.775).

5.3.4 Phosphorus dynamics after re-flooding cores with simulated river water carrying external loads of P and electron acceptors

5.3.4.1 Surface water

Surface-water phosphorus dynamics, following the establishment of flooded conditions with simulated River Yare water, are shown in Figure 5.8. The results from cores B1

and B2 are shown, as is data for the release of MRP into the surface water of core A1 for comparison.

One of the clearest results from Experiment B is that external loads of phosphorus were rapidly removed from the surface water of both cores B1 and B2. Within 12 hours of flooding, the surface-water concentration of MRP was reduced to less than half the external load of 0.46 mg l^{-1} P, and, within 72 hours of flooding, concentrations in both cores approached more stable levels around 0.1 mg l^{-1} P. Surface-water MRP was maintained below 0.1 mg l^{-1} P until after 504 hours (21 days) of flooding in both cores B1 and B2. This contrasts strongly with the pattern of near-immediate MRP release to the surface water of core A1 following re-flooding with deionised water. As a consequence, after 21 days of flooding, MRP concentrations were ≥ 0.6 mg l^{-1} P in the cores from Experiment A compared with < 0.1 mg l^{-1} P in the cores from Experiment B.
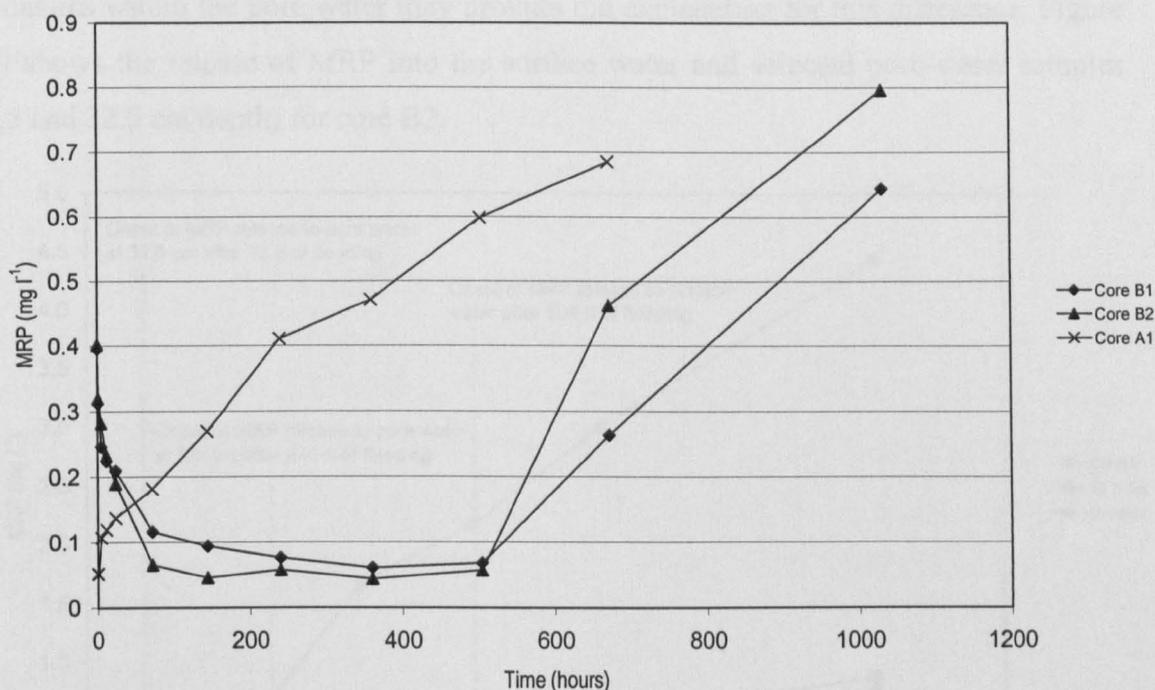
Figure 5.8 Phosphorus dynamics in the surface water of duplicate cores from Experiment B (B1 and B2) and one core from Experiment A (A1).

It is clear from Figure 5.8 that release of MRP to the surface water of cores B1 and B2 did occur after 504 hours of flooding, and that the timing of the onset of release was the same in cores B1 and B2. The magnitude of release differed somewhat between the two cores. Core B1 reached a final concentration after 1042 hours of flooding (43 days) of 0.64 mg l^{-1} P, whilst in core B2 the rise was larger and surface-water MRP

concentration in this core reached 0.80 mg l^{-1} P at the end of the experiment. Importantly, the concentration of MRP in the surface water of cores B1 and B2 at the end of the experiment exceeded the original external load supplied in the simulated River Yare water by up to a factor of 1.7. It should also be noted that the release of MRP into the surface water of both cores showed no sign of reaching equilibrium before the end of the incubation.

5.3.4.2 Pore water

The temporal pattern of MRP release to surface water after cores were re-flooded with simulated river water was quite different from that after inundation with deionised water. In particular, the timing of MRP release to surface water in Experiment B was substantially delayed compared to that in Experiment A (see Figure 5.8). Phosphorus dynamics within the pore water may provide the explanation for this difference. Figure 5.9 shows the release of MRP into the surface water and selected pore-water samples (2.5 and 32.5 cm depth) for core B2.
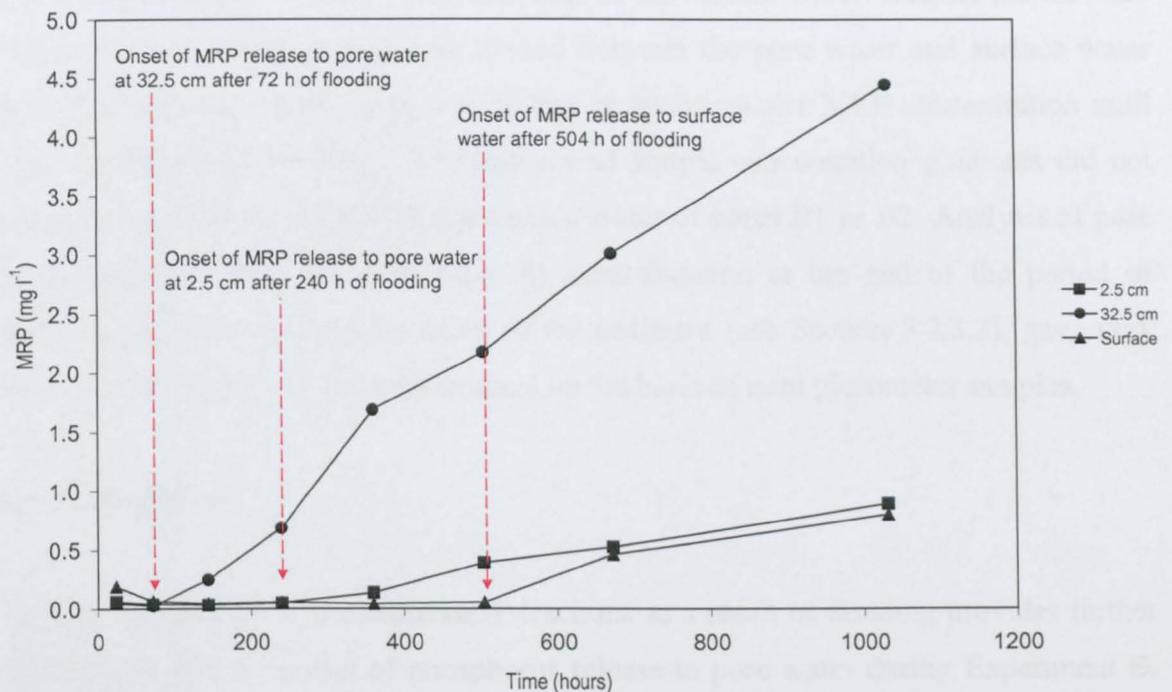
Figure 5.9 The release of MRP into the surface water and selected pore-water samples of core B2.

Samples collected between 0 and 72 hours after surface inundation suggested that relatively stable concentrations of MRP (< 0.1 mg l^{-1} P) were established in pore water after only 12 hours of flooding. In a similar manner to surface-water samples, the

concentration of pore-water MRP subsequently remained relatively constant. These concentrations were above the detection limit of the method, and were often > 0.05 mg l^{-1} P, suggesting that the microbial community at Strumpshaw Fen may not be phosphorus limited. However, whereas the onset of MRP release to surface water did not occur until after 504 hours of flooding, the release of MRP to pore water occurred earlier. There was also a clear depth-dependency to the timing of MRP release to pore water. Samples from 32.5 cm depth were the first to show increases in MRP concentration, with initial rises occurring between 72 and 144 hours after flooding. Pore-water samples from nearer the surface did not show increased MRP concentrations until later in the experiment. In core B2 at 17.5 cm MRP release began between 144 and 240 hours (data not shown), and at 2.5 cm between 240 and 360 hours. As a consequence of the different timings to the onset of MRP release to pore water and surface water, concentration gradients developed between deeper pore water and shallower pore water, and between shallow pore water and surface water. After 504 hours of flooding, the concentration of MRP in the pore-water sample from 32.5 cm depth exceeded that at 2.5 cm by 1.78 mg l^{-1} P, and pore-water MRP concentration at 2.5 cm depth was 0.33 mg l^{-1} P greater than in the surface water. Despite the fact that substantial concentration gradients existed between the pore water and surface water from 240 hours onwards, there was no rise in surface-water MRP concentration until after 504 hours of flooding. The existence of simple concentration gradients did not result in the delivery of MRP to the surface water of cores B1 or B2. Analysis of pore water extracted from sediment cores by centrifugation at the end of the period of flooding and prior to P-fractionation of the sediment (see Section 5.2.3.2), gave very similar MRP profiles to those determined on the basis of mini piezometer samples.

5.3.4.3 Sediment

Analysis of changes in the sediment-P fractions as a result of flooding provides further information on the control of phosphorus release to pore water during Experiment B. Compared to non-flooded cores, there is clear evidence that the NaOH-P_i fraction of the sediment phosphorus pool was significantly reduced during the incubation of surface-inundated cores ($p < 0.01$). Table 5.5 shows the results of NaOH-P_i analyses of the sediment from Strumpshaw Fen. NaOH-$P_{i(original)}$ represents the mean content based on analyses of three drained cores. NaOH-$P_{i(flooded)}$ is the mean content from a further set of

three cores carried through the 43 day flooding procedure before sediment P fractionation.

Table 5.5 The impact of flooding on the NaOH-P$_i$ content of surface peat from Strumpshaw Fen.

Depth (cm)	NaOH-P$_{i(original)}$	NaOH- P$_{i(flooded)}$	Change in mean content (mg kg^{-1})
1-5	115.1 (121.5 – 107.4)	83.7 (89.0 – 76.3)	-31.3
5-10	168.4 (178.2 – 160.6)	131.7 (137.6 – 120.9)	-36.7
10-15	216.2 (225.4 – 207.6)	169.3 (173.9 – 162.4)	-46.9
15-20	178.1 (184.2 – 171.6)	123.0 (132.7 – 111.3)	-55.1
20-25	107.6 (115.5 – 98.9)	50.3 (52.2 – 47.8)	-57.3
25-30	62.2 (66.5 – 59.7)	2.9 (3.3 – 2.4)	-59.2
30-35	58.5 (62.9 – 54.4)	4.0 (5.0 – 3.4)	-54.5
35-40	44.5 (47.5 – 41.7)	7.0 (9.4 – 5.5)	-37.5
40-45	41.8 (48.7 – 36.8)	6.7 (8.4 – 5.0)	-35.1
45-50	33.3 (37.0 – 30.1)	5.2 (7.1 – 3.9)	-28.0

The magnitude of the absolute change in NaOH-P$_i$ varied with depth. Maximum change was observed in the zone between 25 and 30 cm depth, where flooding resulted in a reduction in NaOH-P$_i$ content of almost 60 mg kg^{-1} compared with drained replicates. Moving towards both the surface and the base of the core from this depth, the absolute changes in NaOH-P$_i$ became smaller, reaching a minimum of approximately 30 mg kg^{-1} at the base of the core. The pattern of NaOH-P$_i$ change with depth corresponds well with the distribution of MRP in pore-water samples at the end of Experiment B (see Section 5.3.4.2). However, relatively large quantities of P remained in the NaOH-extractable fraction between 1 and 25 cm depth at the end of the incubation, indicating a

potential for continued release of P from the NaOH-fraction in this zone. Below 25 cm depth, the NaOH-fraction was almost completely depleted during the course of flooding. These findings, alongside those relating to the different timings to the onset of MRP release to pore water, suggest that a further factor must be controlling the interaction between the cycles of iron and phosphorus in these sediments, and that this factor produces a depth-dependency to the release of MRP from iron phases in the sediment during Experiment B.

Compared to $NaOH-P_i$, other sediment phosphorus fractions did not show such clear differences as a result of flooding. The $KCl-P_i$ and $NaHCO_3-P_i$ data did indicate a decrease in this labile and readily available form of sediment-bound P, particularly in the near-surface peat, but the levels were towards the detection limit of the method. The $HCl-P_i$ data showed an increase in P associated with Ca and Mg in the surface 10 cm of peat, of the order of 10 to 20 mg kg^{-1}. Between 10 and 25 cm depth, there was evidence that P was lost from the HCl-extractable fraction during flooding. Below 25 cm depth, the $HCl-P_i$ content of the peat was relatively unaffected by the hydrological regime imposed during Experiment B. Mean data for $NaOH-P_o$, representing P associated with humic and fulvic acids, suggest that this P fraction was lost from the near-surface sediments during flooding. However, mean levels at the end of Experiment B were reduced by no more than 15 mg kg^{-1} in the zone 1 to 20 cm depth relative to $NaOH-P_{o(original)}$. Below 20 cm depth there was no evidence that the $NaOH-P_o$ fraction was altered during the experiment. $Residual-P_o$ remained essentially unchanged over the course of Experiment B, supporting the hypothesis that this fraction of the soil phosphorus pool is highly refractory and unlikely to be bioavailable (White *et al.*, 2004; Reddy *et al.*, 1998). In addition, microbial biomass P remained relatively stable throughout Experiment B, in contrast to other work that has shown this fraction to be relatively labile and likely to change in response to hydrological fluctuations (e.g. Wright *et al.*, 2001; Olila *et al.*, 1997).

5.3.5 The concomitant release of Fe^{2+} and MRP and the control of the timing of MRP release in Experiment B

Analysis of changes to the sediment-P pool during the course of Experiment B, in conjunction with the findings from Experiment A, indicate that the release of MRP into the pore water and surface water at Strumpshaw Fen is controlled by the release of

phosphorus from iron-bound phases in the sediment. In Experiment A, MRP was released into all pore-water samples after a similar period of flooding (24 to 72 hours, see Figure 5.5). However, in Experiment B there was a pattern of differential timing to the release, both between pore water and surface water, and also between pore-water samples from different depths (see Figure 5.9). Any mechanism invoked to explain the release of MRP to the pore water and surface water from the sediments at Strumpshaw Fen must be able to account for the temporally uniform release in Experiment A, and the non-uniform nature of the release in Experiment B.
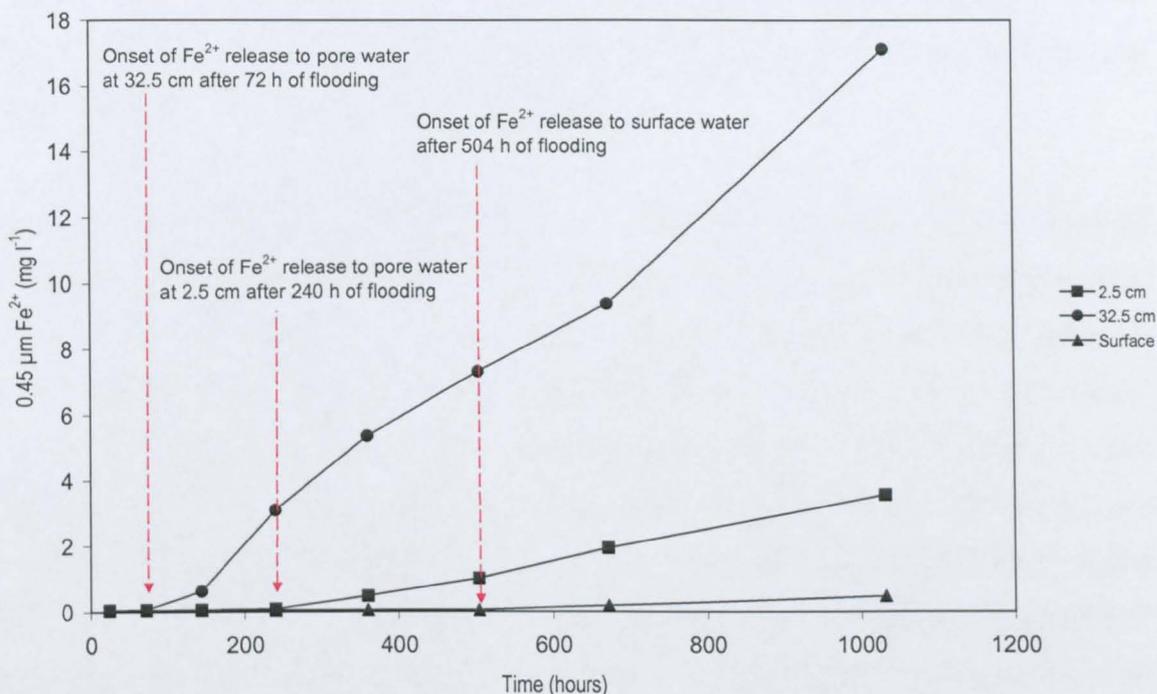
Figure 5.10 The release of Fe^{2+} into the surface water and selected pore-water samples of core B2.

Figure 5.10 shows the release of Fe^{2+} into the surface water and selected pore-water samples (2.5 and 32.5 cm) for core B2. Again, there is a striking similarity between the temporal and spatial patterns of MRP release (Figure 5.9) and those for Fe^{2+}. For the first 72 hours after flooding, the Fe^{2+} concentration in all pore-water and surface-water samples from cores B1 and B2 remained at the detection limit of the method. Between 72 and 144 hours after flooding, pore water from 32.5 cm depth in core B2 showed an increase in Fe^{2+} concentration of 0.58 mg l^{-1}, concurrent with a rise in MRP concentration in the same sample. In core B2, no other pore-water sample showed an increase in Fe^{2+} concentration between 72 and 144 hours after flooding and, equally, there was no release of MRP to any other pore-water sample between these times. Pore water from 2.5 cm depth in core B2 showed initial increases in Fe^{2+} concentration

between 240 and 360 hours after flooding, again coincident with initial rises in MRP concentration in this sample, whilst the onset of Fe^{2+} and MRP release into the surface water was delayed until after 504 hours of flooding. Concentrations of Fe^{2+} in mini piezometers at the end of Experiment B were very similar to those determined by analysis of pore water extracted from sediment cores by centrifugation. The correspondence in the timing of the onset of Fe^{2+} and MRP release was repeated in all pore-water and surface-water samples from both cores B1 and B2, and Fe^{2+} and MRP concentrations were strongly correlated in all samples ($r^2 = 0.98$, $p < 0.01$), with a dominant molar P:Fe ratio of 0.463, which, unlike samples from Experiment A, was invariant with depth in the cores. P:Fe ratios in surface-water samples from the two cores in Experiment B were 4.167 and 3.125.

The sampling protocol employed during the current research meant that the onset of MRP and Fe^{2+} release in Experiment B often occurred between samples separated by substantial lengths of time. For example, the release to the pore-water sample from 2.5 cm depth in core B2 occurred between samples collected at 240 and 360 hours, a period of 5 days. It is not possible to confirm whether MRP and Fe^{2+} were released concomitantly within the period between these sample times. However, the consistency in the patterns of MRP and Fe^{2+} release (i.e. no periods where the concentration of one increased whilst the other remained stable or decreased), and the analysis of sediment P fractions, both support a link between Fe and MRP in the sediments at Strumpshaw Fen.

Demonstrating that Fe^{2+} and MRP are concomitantly released into the pore water and surface water of cores from Strumpshaw Fen, does not directly explain why the timing of Fe^{2+} release (and thereby MRP) is apparently dependent upon depth within the peat cores in Experiment B, but independent of depth in Experiment A. Neither does it explain why the $NaOH-P_i$ fraction was almost fully depleted in deeper peat during the course of Experiment B, whilst quite large quantities of P remained in this fraction in the upper 25 cm of peat. Thermodynamically, the reduction of ferric iron through its use as an electron acceptor in the oxidation of organic carbon is less favourable than aerobic respiration, the reduction of manganese or denitrification (Christensen *et al.*, 2000). Patterns of nitrate-nitrogen (NO_3-N) consumption and manganese release (assumed to be Mn^{2+}) were examined for cores B1 and B2, in an attempt to identify the controls upon the timing of Fe^{2+} release. As expected from thermodynamic considerations, the release of Mn^{2+} to the pore water of both cores was essentially complete before Fe^{2+}

concentrations began to increase. However, the timing of the onset of Mn^{2+} release did not shown any variation with depth through the cores, and cannot, therefore, be used to explain the depth-dependency seen in the timing of Fe^{2+} release in Experiment B. NO_3-N concentration approached zero before Fe^{2+} was detected, again as expected from thermodynamic principles. In contrast to spatial patterns of Mn^{2+} release, rates of NO_3-N consumption did vary with depth in the cores. Figure 5.11 shows the concentration of NO_3-N detected in surface-water samples, and pore-water samples from 2.5 and 32.5 cm depth in core B2. The data are expressed as a normalised ratio, calculated as $C_t/C_{t=0}$ where C_t is the concentration of NO_3-N in the sample at time t, and $C_{t=0}$ is the concentration of NO_3-N in the sample at t = 0 hours. Where $C_t/C_{t=0} \sim 0$ all NO_3-N originally present in the sample at t = 0 hours was consumed, presumably through denitrification, the major mechanism for the removal of N in wetlands (White and Reddy, 1999). Because the ratio is dimensionless it allows the rates of NO_3-N consumption in different samples to be easily compared.
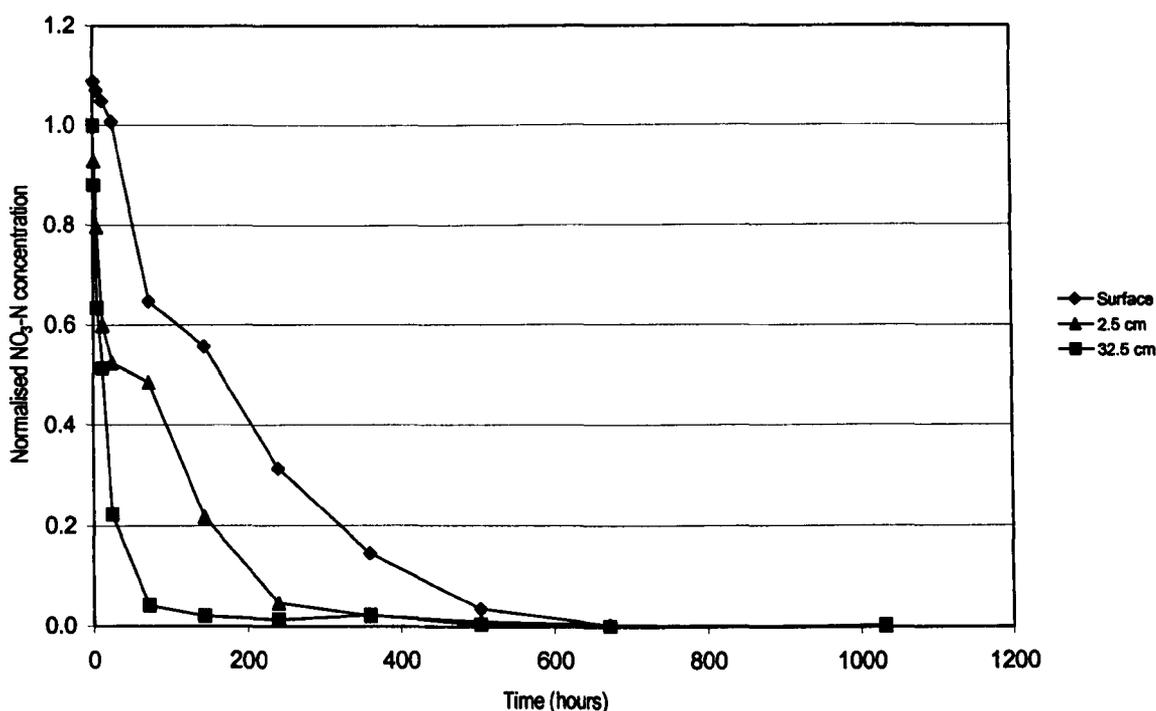
Figure 5.11 Rates of NO_3-N consumption in surface water and selected pore-water samples from core B2.

Figure 5.11 suggests the delivery of an initial pulse of NO_3-N into the surface water of core B2 (shown by normalised ratios > 1), concentrations increasing by approximately 1 mg l^{-1} NO_3-N in the first hour after flooding, a pattern repeated in core B1. Because concentration gradients within the core do not suggest that diffusion of nitrate from the

underlying sediment into the surface water occurred, it is possible that this initial increase was due to the release of nitrate from plant material on the surface of the sediment. A similar mechanism was proposed for increases in MRP concentration seen in cores A1 and A2 immediately after flooded conditions were established in Experiment A (see Section 5.3.3.1). Given that initial concentrations of NO_3-N were similar in all samples, Figure 5.11 shows that the rates of NO_3-N consumption differed between pore water and surface water, and between pore-water samples from different depths. At greater depth in the core, pore-water NO_3-N concentrations decreased at more rapid rates than in samples from nearer the sediment surface. All pore-water samples showed more rapid rates of NO_3-N consumption than surface-water samples. At 72 hours, less than 5 % of the original NO_3-N concentration remained in the pore-water sample from 32.5 cm, whilst approximately 50 % remained in the sample from 2.5 cm and 65 % in the surface water of core B2. Similar patterns were repeated in the remaining pore-water samples from core B2, and in the surface water and pore-water samples from core B1. Given that MRP and Fe^{2+} were only released into solution after NO_3-N had been consumed, the presence of nitrate-nitrogen in the flooding solution used in Experiment B is able to explain both the delayed onset of MRP release compared to samples from Experiment A, and also the differential timing of MRP release with depth in the cores during Experiment B. This interaction between the cycles of N, Fe and P is discussed further in Section 5.4.3.

5.4   Discussion

5.4.1   Enrichment of the sediments at Strumpshaw Fen

Analysis of the peat from Strumpshaw Fen suggests that a large store of total phosphorus is contained within the surface 50 cm of sediment in this system. There is no 'control' against which to compare the total phosphorus content of the near-surface peat. Sediment at greater depth was not collected due to the difficulty of extracting intact cores from deep peat, and because the focus for this research was the near-surface zone where vertical and horizontal exchanges of water are prevalent. However, comparison between the sediments at Strumpshaw Fen and other wetland and non-wetland deposits provides an indication of the degree of enrichment. The maximum total phosphorus content in the sediment at Strumpshaw Fen (~ 1450 mg kg^{-1}), lies towards the very top end of concentrations determined for organic deposits that have

been affected by nutrient loading from anthropic activities such as agricultural runoff, industrial effluent or discharge from urban areas (e.g. Soto-Jimenez *et al.*, 2003; Fisher and Reddy, 2001; Newman and Pietro, 2001; Mayer *et al.*, 1999; Reddy *et al.*, 1998), and is certainly far in excess of the TP content of peat deposits unaffected by external nutrient loading, where concentrations below 500 mg kg^{-1} are common (e.g. Wright *et al.*, 2001; Craft and Casey, 2000; Fisher and Reddy, 2001; White and Reddy, 1999). As part of the floodplain system of the River Yare, the sediments at Strumpshaw Fen bear comparison with other non-wetland floodplain deposits. In a study of 20 river systems in the UK, Walling *et al.* (2000) determined a mean TP content for floodplain sediments of 1247 mg kg^{-1} with a range of 417 to 2660 mg kg^{-1}. Owens and Walling (2002) examined the TP content of floodplain sediments of three UK rivers draining catchments with differing land uses. Catchments dominated by rural land uses had mean TP contents in floodplain sediments < 700 mg kg^{-1}, whilst in heavily industrialised and urbanised catchments, floodplain sediments contained over 4500 mg kg^{-1} TP.

It is clear that the upper 50 cm of sediment at Strumpshaw Fen contains concentrations of TP that exceed those in 'natural' wetlands, and are similar if not greater than recorded for other wetland deposits which have been exposed to significant external nutrient loading. The concentrations are also above average with respect to a number of other UK floodplain sediments from catchments of varying land use. Floodplain systems such as Strumpshaw Fen may receive inputs of water, sediment and nutrients from adjacent channel and/or upland systems, through surface and/or sub-surface exchanges (Venterink *et al.*, 2003; Hauer and Smith, 1998). A causal link may therefore exist between the elevated TP content of the surface peat at Strumpshaw Fen and the phosphorus load carried by the River Yare. The UK Environment Agency monitors the chemical quality of the River Yare. Monthly data collected by the Agency from a sample location 4.5 km upstream of Strumpshaw Fen (TG 291 062), indicate that the Yare is phosphorus enriched (see Figure 2.5). During the period March 1989 to June 2002, the average MRP concentration in the Yare was 0.84 mg l^{-1} P, with a maximum of 4.03 mg l^{-1} P (Environment Agency, unpublished data). The Environment Agency national strategy for eutrophication control proposes an annual MRP mean of 0.2 mg l^{-1} P as an interim standard for 'eutrophic' rivers (Environment Agency, 2000). Since 1989 the average MRP concentration in the River Yare has exceeded this standard by over a factor of four. Given the potential that many wetlands have to remove phosphorus from inflowing waters through a combination of biotic and abiotic processes (e.g. Soto-

Jimenez *et al.*, 2003; Craft and Casey, 2000; Mitsch *et al.*, 1995), the removal of P from phosphorus-enriched water, input to the wetland during overbank flooding events or during sub-surface exchanges with the River Yare, is likely to have contributed to the high phosphorus content in the near-surface peat. In addition to the River Yare, the input of water from the Lackford Run may also have delivered high phosphorus loads to the sediments at Strumpshaw Fen (see Figure 2.6). Between March 1989 and February 1997, MRP concentrations in the Lackford Run averaged 3.73 mg l^{-1} P. In March 1997 discharge into the Lackford Run from Strumpshaw Sewage Treatment Works (STW) ceased, and in the period March 1997 to June 2002 average MRP concentrations fell to 0.24 mg l^{-1} P (Environment Agency, unpublished data, see Figure 2.6). Despite the significant reduction in MRP concentrations in the Lackford Run following the end of direct discharge from Strumpshaw STW, average MRP concentration continues to be indicative of eutrophic conditions.

Surface-runoff from agricultural land may carry significant nutrient loads in dissolved and/or particulate form (e.g. Heathwaite and Dils, 2000; Gburek and Sharpley, 1998). Given that the majority of the upland area adjacent to Strumpshaw Fen is agricultural (Haycock and Lamberth, 2000), the input of water to the fen from this land may have contributed to the phosphorus enrichment of the near-surface peat at Strumpshaw. However, surface runoff from the adjacent agricultural land may be hydrologically disconnected from the Strumpshaw peat deposits due to the location of a railway embankment at the edge of the floodplain (see Figures 2.1 and 2.2). On the basis of the distribution of hydraulic head within the peat aquifer, it was concluded that the flow of large volumes of water between the peat and deeper ground water in the underlying Yare Valley Formation were unlikely (see Section 4.4.2). Therefore, the large-scale discharge of P-enriched ground water into the fen system is not thought to be responsible for the high TP content of the near-surface peat deposits. In addition, monitoring of the MRP concentration in samples collected from the borehole installed in the Yare Valley Formation, suggests that present-day MRP concentrations are relatively low (mean concentration < 0.06 mg l^{-1} P, n = 8). As a consequence, even if ground water was discharged into the peat at Strumpshaw it would be unlikely to contribute to the phosphorus-enriched status of the system. Therefore, although no direct evidence was collected to link historical nutrient loads delivered from the River Yare and Lackford Run to the high TP content in Strumpshaw Fen, the hydrological connection between the two channel systems and the wetland sediments suggests that

the elevated concentrations of P in the River Yare and Lackford Run are very likely to be the primary cause of the nutrient-enriched status of the near-surface peat deposits.

5.4.2   Availability of the total phosphorus store

Organic Phosphorus

Although the near-surface peat at Strumpshaw Fen is enriched with respect to TP, understanding the different forms of phosphorus held in a wetland sediment is the pre-requisite to determining the influence that the wetland system may have on the water quality of the wider catchment (Reddy *et al.*, 1995). On the basis of results from the phosphorus fractionation scheme used in the current chapter, the majority of the total phosphorus stored in the sediment at Strumpshaw Fen is in the form of organic phosphorus, either bound to humic or fulvic acids, or as residual organic P. Other research has also identified that the majority of TP may be present as organic phosphorus in wetland deposits (e.g. Mayer *et al.*, 1999; Reddy *et al.*, 1998), although a more significant role for inorganic forms has been observed in other wetland sediments (e.g. White *et al.*, 2004; Soto-Jimenez *et al.*, 2003).

Although representing a large proportion of TP, the organic phosphorus forms determined by the sequential fractionation scheme used in this research were not shown to be involved in the release of phosphorus to the surface water and pore water of intact cores during flooding. This appears to confirm that the residual-P_o fraction represents highly refractory forms of P that are not readily bioavailable over the core incubation periods used (43 days maximum), and under the conditions imposed, in this research. It is also interesting to note that there was no conclusive evidence that the NaOH-P_o content of the sediment was altered during Experiment B. Reddy *et al.* (1995) suggest that hydrolysis of this fraction of the sediment-P pool may contribute bioavailable forms of phosphorus, yet this process did not appear to be significant during flooding of the sediments at Strumpshaw Fen. In a study of the effects of prolonged flooding of organic deposits on sediment phosphorus fractions, Newman and Pietro (2001) also found the NaOH-P_o fraction to be relatively stable. Ivanoff *et al.* (1998) suggest that a distinction may be made between the moderately labile fraction of NaOH-P_o associated with fulvic acids, and the non-labile fraction associated with humic acids. Although no direct distinction was made between these two fractions in the current research, the stability of

the NaOH-P_o fraction as a whole during the period of flooding may imply a predominance of P associated with humic rather than fulvic acids. This would suggest that the near-surface peat is relatively well-humified, possibly as a consequence of the flood-dry cycles imposed on these floodplain sediments due to seasonal changes in water-table position. Such hydrologically driven changes are likely to result in alternating oxic-anoxic conditions, which have been shown to enhance rates of organic matter decomposition (Hulthe *et al.*, 1998). The existence of well-humified peat is further supported by the relatively small amounts of readily labile P_o in the sediments at Strumpshaw Fen.

Microbial biomass P represents a large store of phosphorus in the sediments at Strumpshaw Fen. Various authors have suggested that changes to wetland deposits, driven for example by fluctuating water-table position, may alter the proportion of P stored in the microbial biomass fraction (e.g. Wright *et al.*, 2001; Olila *et al.*, 1997; Qui and McComb, 1995). The drawdown of water tables and subsequent oxidation of sediments has been shown to result in a significant reduction in microbial biomass P, possibly due to the death of obligate anaerobic organisms or as a result of water stress to microbes (e.g. Pant and Reddy, 2001a; Olila *et al.*, 1997). Alternatively, under flooded conditions reductions in microbial biomass P may be linked to the death of obligate aerobic organisms or to the release of poly-P under anoxic conditions (Wright *et al.*, 2001). Under oxic conditions, and given sufficient concentrations of orthophosphate and a suitable organic carbon source, facultative anaerobes may store inorganic phosphorus in polymer form (poly-P). Under anoxic conditions, where oxidative phosphorylation is no longer possible, hydrolysis of the stored poly-P by the same bacteria results in an accumulation of inorganic P in the cell wall, which is subsequently released into solution (Khoshmanesh *et al.*, 2002; Wright *et al.*, 2001; Gächter *et al.*, 1988).

Analysis of the sediments at Strumpshaw Fen suggests that the microbial biomass P content was unaffected by the flooding regime imposed on the cores during Experiment B. There is little evidence in the literature for such stability of microbial biomass P during hydrological manipulation of wetland deposits. However, the finding is not necessarily surprising. The sediments at Strumpshaw Fen have been exposed to 'natural' flood-dry cycles since their deposition, as a consequence of their position in the floodplain of the River Yare. The resulting shifts between oxic and anoxic

conditions are likely to have resulted in the selection of a microbial community that is adapted to these fluctuations, for example the existence of facultative rather than obligate anaerobic bacteria, and bacteria that are able to form resting stages during water-table drawdown and sediment oxidation (Baldwin and Mitchell, 2000). The apparent stability of the microbial biomass P fraction in the current research suggests that the microbial community may be adapted to alternating periods of surface inundation and water-table drawdown. It is acknowledged however that the current study has not directly examined the microbial communities at Strumpshaw Fen, a potential focus for future research at this and similar riparian wetlands.

Inorganic Phosphorus

Given that the organic phosphorus store in the sediments at Strumpshaw Fen was largely unchanged during core incubations, the release of P from these deposits to surface water and pore water may be controlled by the inorganic fraction. Although relatively small in proportion to TP_o, the total inorganic phosphorus content remains substantial, reaching over 400 mg kg^{-1} in the near-surface peat. The ratio $TP_o:TP_i$ varies with depth through the cores, decreasing through the first 15 cm of peat to minimum values of 2.6, before increasing at greater depth to reach a maximum of 8.8 at the base of the cores. A number of factors may explain the apparent enrichment of the near-surface peat with respect to TP_i, compared with deeper peat. The variation with depth may reflect temporal changes in the nutrient loads input from the River Yare and Lackford Run. Increased TP_i content in the surface 15 cm of peat may be a consequence of increases in population pressure and intensity of agricultural activity in the catchments of the Yare and Lackford Run, leading to increased inorganic nutrient loads being carried in these channel systems and subsequently input to Strumpshaw Fen. Alternatively, the mineralisation of labile organic phosphorus present in the surface peat may lead to increased inorganic P concentrations (Reddy *et al.*, 1998). Finally, where phosphorus release is physicochemically controlled, certain zones in the peat profile may become enriched with inorganic P as the orthophosphate ion diffuses or is advected into oxidised sediment and is removed from solution by iron. The potential for this latter mechanism to influence the depth distribution of inorganic phosphorus will be dependent on the position of the water table within the peat profile.

The phosphorus fractionation data show that the store of labile inorganic phosphorus in the sediments at Strumpshaw Fen is generally small. This indicates that substantial, rapid release of inorganic phosphorus from this sediment pool into the pore water and surface water of the cores upon flooding is unlikely, a hypothesis confirmed by the time series of pore-water and surface-water MRP concentrations. The inorganic phosphorus pool is evenly split between HCl- and NaOH-extractable fractions. Under the relatively constant, near-neutral, pH conditions maintained during the core incubations, the HCl-P_i fraction proved to be relatively stable. Pore-water and surface-water data indicate that concentrations of dissolved Mg^{2+} or Ca^{2+} and MRP were not strongly correlated, and, consequently, that the dissolution of Ca-P or Mg-P complexes was not a dominant mechanism leading to the release of phosphorus during the core incubations (Gächter *et al.*, 1988). However, in the zone where peat pH reached a minimum of 5.6 (10-25 cm), there is evidence from the sediment phosphorus fractionation data that P may have been released from forms previously associated with calcium or magnesium. The lack of correlation between concentrations of Mg^{2+} or Ca^{2+} and MRP in pore water and surface water, may suggest that MRP released from Mg-P or Ca-P complexes was subsequently removed from solution, for example by adsorption onto iron oxyhydroxides which would still have been in oxidised form during the early stages of the core incubations. It is also evident from the P fractionation data that the HCl-P_i content of the peat increased in the zone 1 to 10 cm during the course of Experiment B. This indicates that, given a situation of substantial MRP release from the sediments, predominantly under reduced conditions in the sediments at Strumpshaw Fen, phosphorus may subsequently be removed from solution through adsorption to and/or precipitation of Mg- and Ca-P phases.

In contrast to many wetland sediments, NaOH-P_i represented a major proportion of the TP_i store. The NaOH extraction is assumed to remove phosphorus associated with aluminium and iron phases (Wright *et al.*, 2001; Reddy *et al.*, 1998). In the sediments at Strumpshaw Fen there was a very strong correlation between 0.5 M HCl-extractable Fe and NaOH-P_i in the cores under drained conditions, demonstrating the potential importance of non-crystalline iron-bound P at Strumpshaw Fen. Other research in wetland systems has suggested that the aluminium rather than iron content of the sediments is the predominant factor governing the sorption of phosphorus (e.g. Pant *et al.*, 2002b; Darke and Walbridge, 2000; Richardson, 1985). However, given the relatively low amorphous aluminium content of the sediments at Strumpshaw Fen ($\leq$

1220 mg kg^{-1}), and the fact that amorphous iron levels exceed those of aluminium by an order of magnitude in places, the importance of Fe-P is unsurprising. Such high concentrations of iron in the surface peat are likely to be the result of the input of River Yare water which carries relatively high particulate iron loads (> 18000 mg kg^{-1} Fe; Environment Agency, unpublished data). The presence of amorphous iron likely reflects the seasonal variation in water-table position within the floodplain, whereby periods of sediment submergence generate reducing conditions which inhibit the formation of strongly crystalline iron phases (Pant *et al.*, 2002b; Darke and Walbridge, 2000). Given that amorphous iron, and consequently any adsorbed ions, are prone to rapid dissolution under reducing conditions (Pant *et al.*, 2002b), the association of phosphorus with amorphous iron suggests that the exchange of P may occur between solid and solution phases, with the exchange driven by factors such as periods of sediment submergence and supply of terminal electron acceptors. These findings support those of Darke and Walbridge (2000) who found that the input of channel water could deliver mineral loads to floodplain systems, and illustrate that, in contrast to many other wetland systems, the physicochemical control of phosphorus exchanges in riparian wetlands is potentially extremely important.

5.4.3 Riparian sediments as actual sources of phosphorus

The rapid release of phosphorus into the surface water of cores during Experiment A increased MRP concentration to 0.14 mg l^{-1} P by 24 hours after flooding. During this period, the flux of phosphorus into the surface water averaged 14 mg P m^{-2} day^{-1}. The lack of hydraulic or diffusion gradients supporting the delivery of MRP into the surface water during this period, and the relative stability of organic phosphorus fractions, suggests that another source led to the release of P after the cores were re-flooded. Plant litter on the sediment surface was identified as one possibility. Phosphorus can be released rapidly (within 24 hours) when senescent macrophyte material comes into contact with surface water, and the process appears to be fundamentally abiotic (Qui *et al.*, 2002; Xiong and Nilsson, 1997). The degree to which P is released from litter will be partly dependent on the extent of litter decomposition, with less phosphorus being released into solution from increasingly well-decomposed material (Qui *et al.*, 2002). The degree of decomposition of the litter on the surface of the cores used in this current research was not assessed, but visual inspection suggested that a mixture of recently deposited senescent plant material and partly decomposed organic matter was present.

Following the initial 24 hours of submergence, the sediments continued to release phosphorus into the surface water for the duration of Experiment A, resulting in an average P flux from the duplicate cores of 2.4 and 2.8 mg P m^{-2} day^{-1} over the 28 days of the incubation. Final surface-water MRP concentrations in the two cores from Experiment A (0.68 and 0.80 mg l^{-1} P) exceeded both the interim standard for eutrophic river conditions set by the Environment Agency, and the contemporary average concentrations in the River Yare and Lackford Run (Environment Agency, 2000). These findings illustrate that the sediments at Strumpshaw Fen may act as a nutrient source to the wetland itself, even if external nutrient loadings to the site were to be reduced. More significantly, the scale of P release from the peat cores indicates that, given hydrological connection, the wetland system must be seen as a phosphorus source area, able to supply bioavailable P to receiving water bodies.

Following the re-flooding of cores with simulated River Yare water, the phosphorus concentration in surface-water and pore-water samples fell rapidly. The removal of P from solution is likely to have involved uptake by microorganisms, sorption reactions within the peat matrix, or a combination of both processes. No direct attempt was made to determine the relative roles of these processes. However, if uptake from pore water by microorganisms were the predominant mechanism, a concurrent increase in the microbial biomass P pool would be expected. The lack of a significant difference between the size of this pool prior to and after flooding (p > 0.05), suggests that microorganisms were not the major sink involved in the initial removal of P from solution. An alternative explanation involves the rapid sorption of phosphorus from pore water due to the high amorphous iron content of the sediments. Prior to re-flooding, the cores were in an oxidised state, and consequently iron in the peat is likely to have been present in the form of Fe^{3+} with a high affinity for orthophosphate ions in the water used to re-flood the cores. Sorption from pore water would develop a concentration gradient driving diffusion of P from the surface water into the sediment, where phosphorus would be removed from solution. The observed *decrease* in the sediment Fe-P pool in flooded compared to drained cores can be explained by later reductive-dissolution of iron-bound P under anoxic conditions.

Substantial releases of MRP into the surface water of intact cores during Experiment B did not occur until after 21 days (504 hours) of flooding. Between this time and the end of the experiment, a period of 22 days, fluxes of MRP across the sediment-water

interface averaged 2.62 and 3.36 mg P m^{-2} day^{-1} in the duplicate cores. Final concentrations in the surface water of the two cores (0.64 and 0.79 mg l^{-1} P) again support the conclusion that these sediments are potential sources for bioavailable P.

Few reliable data from other peat sediments exist to allow comparison with the fluxes determined for the sediment from Strumpshaw Fen. Using intact cores of peat from sites in the Florida Everglades affected by long-term nutrient loading, Fisher and Reddy (2001) determined fluxes of phosphorus to the surface water that varied between 0.04 and 6.5 mg P m^{-2} day^{-1}, depending on proximity to the source of nutrient loading and redox conditions in the surface water. Re-flooding of artificially drained peat cores taken from a constructed wetland used to remove phosphorus from the hypereutrophic Lake Apopka in the USA, resulted in average P fluxes to the overlying water of between 7.6 and 10.6 mg P m^{-2} day^{-1} depending on the duration of water-table drawdown (Olila *et al.*, 1997). Fluxes varying between 0.16 and 2.22 mg P m^{-2} day^{-1} were observed for intact cores of peat collected from the bottom of Lake Okeechobee in the USA by Moore *et al.* (1998).

Some authors have used profiles of pore-water and surface-water MRP concentration, along with diffusion coefficients, to calculate fluxes of P into surface waters on the basis of Fick's First Law (e.g. Soto-Jimenez *et al.*, 2003; Newman and Pietro, 2001). However, the potential for physicochemical control of fluxes across the sediment-water interface at Strumpshaw Fen, largely as a consequence of the high amorphous iron content of the peat, suggests that it is unlikely that MRP concentration gradients will lead directly to a flux of P into the surface water. The existence and persistence of large concentration gradients between surface water and pore water during Experiment B (see Figure 5.9), supports the conclusion of physicochemical control of phosphorus release to the surface water at Strumpshaw Fen. Further, the advection of pore water into surface water due to the action of invertebrates or as a result of gas ebullition have been suggested as potentially important mechanisms leading to the delivery of P into surface water overlying organic sediments (e.g. Fisher and Reddy, 2001; Mayer *et al.*, 1999). Although no attempt was made in the current research to identify the role of such processes, the direct measurement, rather than the calculation of P flux into the surface water, will incorporate the flux due to both diffusion and invertebrate- or gas-mediated advection of solutes.

One of the most striking findings from the current research is the importance of iron in controlling the release of P to pore water. Although the interaction between iron and phosphorus has been identified in other environments for some time (e.g. Gunnars *et al.*, 2002; Moore *et al.*, 1998; Gunnars and Blomqvist, 1997; Lovley *et al.*, 1991), very few studies have indicated a significant role for Fe-P in wetland sediments, often because of the low mineral content of many organic deposits (Moore *et al.*, 1998; McLatchey and Reddy, 1998). Yet, as the current research has shown, riparian wetland systems, due to their hydrological connection with adjacent channel systems, have the potential to receive significant mineral loads, which are subsequently incorporated within the peat matrix. In the sediments from Strumpshaw Fen the dynamics of iron, as driven by redox conditions, control P release, rather than factors such as the mineralisation of organic phosphorus. The current research represents one of the first attempts to compare directly time series of P release to surface water and pore water in a wetland sediment. Although other studies have examined in detail the patterns of P release to surface water (e.g. White *et al.*, 2004; Pant and Reddy, 2003; Fisher and Reddy, 2001), pore water has been largely ignored, except for the use of pore-water equilibrators in the field, or centrifugation of sediment cores, to provide snapshots of MRP profiles with depth to allow the calculation of fluxes across the sediment-water interface (e.g. Soto-Jimenez *et al.*, 2003; Newman and Pietro, 2001). Such studies do not provide any information regarding the shorter-term pore-water P release patterns that will both control solute fluxes into the surface water, and determine the potential for pore water to act as a source of bioavailable P to receiving waters.

In Experiments A and B, MRP and Fe^{2+} were shown to be released concomitantly into pore water, suggesting that reductive-dissolution of Fe^{3+}-P complexes under anoxic conditions released iron and phosphorus into solution. In Experiment A, the onset of Fe^{2+} and MRP release was temporally uniform in all pore-water samples and in the surface water, indicating that redox conditions throughout the core supported the reductive-dissolution of Fe-P, and that the sediment-water interface rapidly became reduced (within 24-72 hours), allowing P to be transported into the surface water. In contrast, the results of Experiment B demonstrated a temporal variability in the timing of MRP and Fe^{2+} release at different pore-water depths, and between pore water and surface water. It was shown that the external supply of NO_3-N input in the simulated River Yare water was consumed at different rates dependent on depth within the core, and that the timing of complete NO_3-N removal from solution in pore-water and

surface-water samples corresponded with the onset of Fe^{2+} and MRP release. This suggests that the presence of NO_3-N in solution poised the redox potential at a level above that required for Fe^{3+} reduction, and that only after NO_3-N had been consumed, most likely through denitrification, did the reductive-dissolution of Fe-P begin. Further, it appears that the surface water acted as a prolonged source of NO_3-N that diffused into the surface sediments maintaining the redox potential in this zone at higher levels for a longer period than in deeper sediments. This explains why substantial quantities of $NaOH$-P_i remained in the surface 25 cm of peat at the end of Experiment B, whereas in deeper peat this fraction was almost completely depleted. Given a longer incubation period, continued release of P might be expected in the zone 0-25 cm, resulting in more complete depletion of the $NaOH$-P_i pool, and higher concentrations of pore-water MRP.

The poising of redox potential at higher levels in the near-surface sediments due to the presence of NO_3-N, likely resulted in the removal from solution of MRP diffusing towards the surface from more reduced sediments at greater depth, thereby generating and maintaining concentration gradients between pore water and surface water. The removal of MRP from solution may have been caused by sorption to sediment-bound iron which would still be present in ferric form where NO_3-N remained, or by sorption of MRP to iron as both MRP and Fe^{2+} diffused into less reduced surface sediments and Fe^{2+} was oxidised. An important consequence of the control of Fe and MRP release by NO_3-N, is that external loads of nitrate can delay the release of P to surface waters. In the current research, a concentration of 10 mg l^{-1} NO_3-N in water used to flood the cores delayed the onset of MRP release to surface water by 21 days, when compared to deionised water containing no nitrate. These findings demonstrate interesting links between the cycles of N, P and Fe in riparian wetland sediments that have rarely been reported in the literature. Hydrological management of Strumpshaw Fen, involving isolation of the wetland from the input of N-enriched water from the River Yare (see Section 2.4.2) may have important consequences for the availability of P, because with reduced input of river water, rainwater that is low in nitrate will become a more dominant input to the fen.

Gächter *et al.* (1988) suggest that the simultaneous dissolution of Fe and MRP does not necessarily prove that the cycles of the two elements are coupled. Alongside other authors (e.g. Wright *et al.*, 2001; Gächter and Meyer, 1993; Boström *et al.*, 1988), they suggest that the uptake and release of P may be affected by the action of facultative

anaerobic bacteria, through the formation and release of poly-P under alternating oxic-anoxic conditions (see Section 5.4.2). Increases of MRP in solution due to release from poly-P may occur concomitantly with reductive-dissolution of iron, thereby giving the misleading impression that MRP was previously sorbed to Fe. However, in contrast to the results of Wright *et al.* (2001), flooding of the cores from Strumpshaw Fen appeared to h ave n o e ffect o n t he m icrobial b iomass s tore o f P . If t he release o f p oly-P w ere important at Strumpshaw Fen, concentrations of microbial biomass P might be expected to be lower in drained as compared to flooded cores, due to the hydrolysis of poly-P under anoxic conditions and the release of MRP into solution. The lack of such a decrease may suggest that a suitable organic substrate (for example acetate) for use by poly-P bacteria is lacking, or that under anoxic conditions nitrate- or sulphate-reducing bacteria out-compete poly-P bacteria for the available substrate at Strumpshaw Fen (Khoshmanesh *et al.*, 2002; Gächter *et al.*, 1988). The lack of conclusive evidence for MRP release from poly-P provides further support for the hypothesis that reductive-dissolution of Fe-P is the primary cause of increased pore-water MRP concentrations under anoxic conditions at Strumpshaw Fen.

Molar Fe^{2+} and MRP concentrations were closely correlated in all pore-water samples from both cores during Experiment B ($r^2 = 0.98$, $p < 0.01$). The dominant P:Fe release ratio to pore-water during the course of Experiment B equalled 0.463, and was consistent for all pore-water samples from both c ores. The results of several lines of investigation cited in Gunnars and Blomqvist (1997) suggest that the predominant P:Fe surface complexation ratio of ferric hydroxide is 0.5. Given that the reductive-dissolution of Fe-P complexes should result in the simultaneous, stoichiometric release of Fe and P (Gächter *et al.*, 1988), it is possible that MRP and Fe^{2+} were released into solution i n t he c ores f rom S trumpshaw F en d uring t he r eductive-dissolution o f f erric hydroxide under anoxic conditions. The results of core flooding with deionised water also suggested a strong correlation between MRP and Fe^{2+} in individual pore-water samples, yet the P:Fe release ratios differed with depth in the core (see Figure 5.7). No simple explanation for these results is immediately obvious. It is possible that the lack of an external load of P in the flooding solution used in Experiment A meant that Fe-P phases with stoichiometries other than approximately 0.5 were reductively-dissolved during the core incubations. The P:Fe release ratios in surface water w ere 3.846 a nd 3.448 for the duplicate cores during Experiment A, and 4.167 and 3.125 during Experiment B. Clearly these ratios are far higher than in all pore-water samples from

both Experiments A and B. This may reflect the fact that the diffusion coefficient for the orthophosphate ion exceeds that for Fe^{2+} (Li and Gregory, 1974) thereby supporting the more rapid delivery of P to the surface water than Fe, assuming that diffusion was the dominant process controlling the movement of both ions into the surface water after the sediment-water interface had become reduced.

5.5   Concluding comments

This current chapter has shown that riparian wetland sediments may contain a large store of sediment-bound phosphorus, sequestered primarily from inputs of nutrient-enriched channel water. A proportion of this store of P is in a form that may be released into pore water and surface water following flooding. The release is physicochemically controlled and involves the reductive-dissolution of Fe-P. External loads of electron acceptors other than iron, supplied in floodwater, can influence the timing of phosphorus release. The sediments at Strumpshaw Fen have the potential to act as phosphorus sources, establishing a nutrient-enriched status within the wetland even if external loads of P are reduced or removed entirely. Given hydrological connection, surface water *and* pore water from Strumpshaw Fen may deliver ecologically significant quantities of bioavailable phosphorus to receiving water bodies. This work has achieved Research Objective 3 and part of Research Objective 4 identified in Section 1.2.

A major research challenge remains to link the findings of process-based studies such as those reported in this current chapter to the larger-scale functioning of the riparian wetland system. Only by integrating information regarding the timing and magnitude of phosphorus release to solution with field-based data, such as spatial variations in hydraulic head and hydraulic conductivity, can the wider-scale implications of P release to pore water or surface water be determined. This challenge is addressed in the following chapter, by combining hydrochemical and hydrological process information to examine phosphorus availability at the field-scale and the delivery of P to receiving waters at Strumpshaw Fen.

6. TRANSLATING HYDROCHEMICAL PROCESS INFORMATION TO THE FIELD SCALE

6.1 Introduction

Chapter 5 demonstrated that concentrations of bioavailable phosphorus indicative of eutrophic conditions were released to pore water and surface water from replicate incubated sediment cores. Mesocosm studies such as those described in Chapter 5 have the advantage of being conducted under controlled, repeatable conditions, at relatively low cost (Ahn and Mitsch, 2002). However, there is uncertainty as to whether the findings of small-scale mesocosm studies are applicable to the larger field- and catchment-scales (Wiens, 2002). This uncertainty is linked to the fact that small-scale studies necessarily incorporate reduced system complexity compared to larger-scale studies, and because mesocosms introduce the effects of boundary conditions that are not observed in 'natural' systems, such as the diffusion of oxygen into sediments through the walls of laboratory cores (Ahn and Mitsch, 2002). A major challenge facing research in riparian zones is to link biogeochemical process information to larger-scale system functioning (Dahm *et al.*, 1998). This current chapter evaluates whether the information regarding P release to pore water and surface water at Strumpshaw Fen gained from laboratory core incubations translates to the field scale. Additionally, a detailed analysis of a range of pore-water samples was undertaken to provide information on the speciation of P in solution at Strumpshaw Fen. These data are used to assess the biological availability of molybdate reactive phosphorus (MRP) in solution. This work addresses the second part of Research Objective 4 identified in Section 1.2, which is concerned with the field-scale availability of P.

If it is assumed that the findings from the mesocosm studies concerning the availability of P at Strumpshaw Fen are representative of field conditions, then the near-surface (upper 50 cm) sediments are a potential source for substantial quantities of bioavailable

phosphorus. Chapter 4 demonstrated that the fen and the ditch network are hydrologically connected, and that the connection may take the form of two-way exchanges between pore water and surface water in the fen and open water in the ditch network. Further, it was shown that the magnitude of vertical exchange is likely to be small compared to lateral exchanges between the fen and the ditch network. In the current chapter the use of hydrochemical monitoring to trace these lateral exchanges is reported, providing data that are used to support to the hypothesis of hydrological connectivity between the fen and the ditch network, initially highlighted by the existence of water-table gradients reported in Chapter 4 (see Section 4.4).

It is the combination of the biogeochemical processes controlling phosphorus release to solution and hydrological connectivity, which determines the potential for the delivery of P to receiving waters. However, with respect to phosphorus, there is little evidence in the literature of research that links directly the availability of P at the process scale with hydrological connectivity between different elements of the riparian landscape. This type of research represents the necessary first step towards investigating channel systems and riparian zones as linked elements within the catchment (Tabacchi *et al.*, 1998). Therefore, a further focus of the current chapter is the integration of the findings regarding hydrological connectivity and P availability at Strumpshaw Fen, and an assessment of whether there is direct evidence at the field scale for the delivery of phosphorus to receiving waters. This work addresses Research Objective 5 identified in Section 1.2.

6.2   Methodology

6.2.1   Sampling protocol

The data reported in this chapter were generated from both the laboratory analysis of targeted pore-water and surface-water samples, and the automatic logging of hydrological and hydrochemical variables in the field. Pore-water, standing surface-water and ditch-water samples were collected from Strumpshaw Fen to examine the field-scale availability of phosphorus in the light of the findings from Chapter 5. Pore-water samples were collected from the same piezometer nests used to measure the vertical distribution of hydraulic head described in Chapter 4. The piezometer intakes of 5 cm length had mid-points at 2.5, 10, 17.5 and 32.5 cm depth, corresponding with the

location of mini-piezometers in the laboratory core incubations. Further piezometers with intake mid-points at 102.5, 202.5 and 402.5 cm depth, were sampled to examine the relationship between P availability in the near-surface pore water and that in deeper pore water.

As wetland pore water chemistry is likely to be redox sensitive (Mitsch and Gosselink, 2000), precautions must be taken to ensure that samples are protected from exposure to oxygen during collection, filtration, and determination of parameters such as pH, electrical conductivity (EC) and temperature in the field. Only rarely has the need for such precautions been explicitly considered in the design of sampling strategies used in wetland studies. For the samples from Strumpshaw Fen, a sampling protocol was developed to minimise the exposure of pore waters to the atmosphere during collection and processing. For a given sample, the protocol involved first purging the headspace between the equilibrium water level in the piezometer and the top of the piezometer standpipe with argon gas to create an inert atmosphere in contact with the sample. Whilst continuing to purge with argon, a volume of water equal to 1.5 times the volume of the piezometer was removed to waste using a peristaltic pump connected to a 12 V car battery. This ensured that 'dead' water that may have become oxidised during a long residence time in the piezometer above the intake was not incorporated in subsequent samples. Having allowed the piezometer to reach equilibrium with 'fresh' water, a sample was extracted from the piezometer. The sample passed directly into a flow-through cell developed by the Department of Civil and Structural Engineering, University of Sheffield and Waterra UK Limited. The cell allows an in-line determination to be made of pH, EC and temperature, without exposure of the sample to the atmosphere. Samples were analysed for pH and temperature using a Hanna HI-8424 combined meter, and for EC using a Hanna IP67 meter. A separate volume of pore water was then pumped into a filter unit fitted with a 47 mm diameter 0.45 µm cellulose nitrate acetate (CNA) membrane filter paper. The filter unit and filter paper were first conditioned with a few millilitres of the solution, which were discarded to waste, followed by collection of a sample. The filtrate was transferred immediately to argon-purged sample bottles. All tubing used in the collection and processing of samples was silicone rubber. The tubing, flow-through cell and filter unit, were purged for 5 minutes with nitrogen (N_2) gas prior to collection of each sample, to ensure that pore water did not come into contact with oxygen after removal from the piezometer. The combination of the flow-through cell and filtration unit allowed for in-line filtration and

determination of pH, EC and temperature (Figure 6.1). In addition to pore-water samples, samples of standing surface water and ditch water were collected, analysed for pH, EC and temperature using the same instrumentation described above, and filtered through 0.45 µm CNA membrane filters.
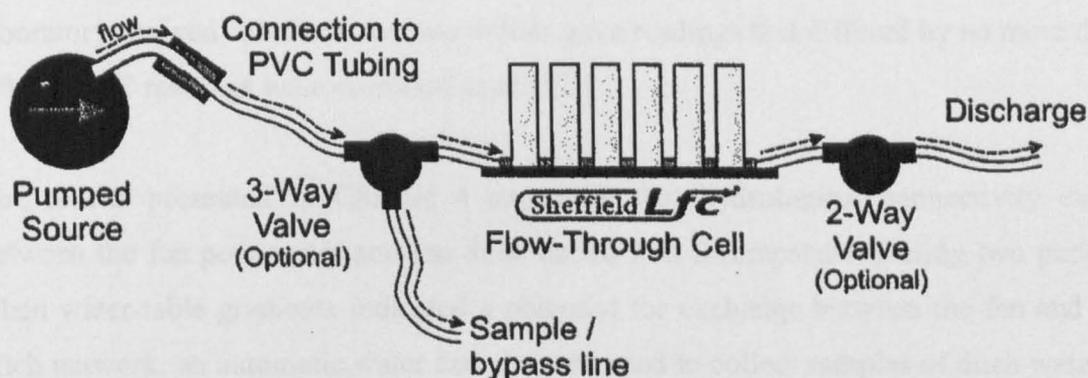
Figure 6.1 The use of a flow-through cell to collect wetland pore-water samples and simultaneously determine hydrochemical parameters.

Vertical and lateral variations in hydraulic head and water-table position between the peat deposits, deeper ground water, and the ditch network were monitored as described previously in Section 4.2.2. Hydrochemical variables, such as EC, pH and water temperature, were used to trace exchanges of water between the peat deposits and the ditch network. The EC and temperature of both the ditch water and fen pore water were recorded at 30-minute intervals using self-logging sensors. In addition, the pH of the ditch water was also recorded at the same frequency, although automatic logging of pore-water pH in the fen was not possible. The monitoring of hydrochemical parameters in the ditch was conducted using the pH, EC and temperature sensors of the same In-Situ MP Troll instrument used to record variations in ditch water level (see Section 4.2.2). The temperature and EC of the fen pore water were recorded using Campbell 247 EC/temperature probes connected to a Campbell CR10X logger. Probes were installed to depths of 50 cm below the ground surface in polyvinyl chloride (PVC) wells located at 0.1, 2, 10 and 25 m along the same transect instrumented to monitor fluctuations in fen water table. On testing the 247 probes in the field, near-instantaneous shifts in EC of > 200 μS cm^{-1} were observed. It was concluded that these shifts were errors caused by particulate organic matter becoming trapped within, and subsequently released from, the body of the probe. The particulate matter would cause significant

increases in the resistivity of the pore water within the probe, and consequently to the EC. To minimise these errors, the wells housing the 247 probes were screened with a geotextile mesh to prevent the ingress of larger pieces of organic material. Checks made in the field ensured that the EC determined in screened as compared to unscreened wells did not differ significantly ($p > 0.05$). Further tests were conducted to compare the EC readings from the MP Troll and Campbell 247 probes. In a series of field- and laboratory-derived solutions, the two probes gave readings that differed by no more than 7 %. All EC readings were corrected to 25 °C.

The results presented in Chapter 4 suggested that hydrological connectivity exists between the fen pore water and the ditch network at Strumpshaw. During two periods when water-table gradients indicated a potential for exchange between the fen and the ditch network, an automatic water sampler was used to collect samples of ditch water at 30-minute intervals. Samples taken during these two separate periods were used to determine whether there was direct evidence supporting the delivery of MRP to the ditch network. Samples were filtered through 0.45 μm CNA membrane filters in the field, no more than 6 hours after collection by the automatic water sampler, and analysed for MRP on return to the laboratory.

6.2.2 Establishing a storage protocol for wetland pore-water and surface-water samples

It is known that phosphorus speciation is highly sensitive to changes during the critical period between sample collection and analysis (Jarvie *et al.*, 2001; Haygarth *et al.*, 1995; Bull *et al.*, 1994). Several studies have highlighted that phosphorus, and in particular the fraction of total phosphorus termed MRP, may be unstable during storage (e.g. Jarvie *et al.*, 2001; Gardolinski *et al.*, 2001; Haygarth *et al.*, 1995; Bull *et al.*, 1994; Avazino and Kennedy, 1993; Lambert *et al.*, 1992; Heron, 1962). The findings from the above studies have shown that there is little consistency in the direction of concentration change, the rate of change, or the causes of change, between different samples. This is linked to the fact that the nature of water samples differs, both between sites and through time at a given site (Haygarth *et al.*, 1995). As a consequence, the production of a single storage protocol to cover all environmental samples has proved elusive (Jarvie *et al.*, 2001; German Chemists Association, 1981). Indeed, Gardolinski *et al.* (2001) indicate the importance of introducing a site-specific storage protocol

before undertaking any sampling programme for the determination of nutrients, particularly MRP. The fundamental objective of any storage protocol is to ensure that, at the time of analysis, the concentration of P within the sample remains representative of that originally present at the time of sample collection. There has been only very limited consideration of the effects of storage on the concentration of MRP in wetland samples, particularly pore water. This is surprising because the high microorganism content present in many wetland samples (Mitsch and Gosselink, 2000) increases the potential for significant changes in MRP concentration during storage. Given that the impact of storage is apparently sample dependent, and the lack of consideration in the literature of storage effects for wetland samples, tests were conducted using pore water and surface water from Strumpshaw Fen in order to provide a storage protocol for use in the current research.

6.2.2.1 Factors influencing the impact of storage on phosphorus concentrations in solution

A minimal length of time between sample collection and analysis is a desirable feature of any sampling protocol. This is best achieved through field-based analysis (e.g. Hanrahan *et al.*, 2001; Lambert *et al.*, 1992). However, for logistical and analytical reasons, this approach is not routinely employed in the analysis of environmental samples (Jarvie *et al.*, 2001; Gardolinski *et al.*, 2001; German Chemists Association, 1981). Once a period of storage is introduced, MRP concentrations may change due to: i) *removal* from solution, for example by sorption to vessel walls, or ii) *transformation* of the form in which the solute is present by biological or chemical action, for example changes between organic and inorganic forms of phosphorus driven by the action of microorganisms (Haygarth and Edwards, 2000). The extent to which these mechanisms alter the concentration of MRP in a sample is governed by a number of variables, which are discussed below.

Vessel material, size and pre-treatment

During the collection and storage of samples, the orthophosphate ion may become sorbed to the vessel walls and therefore removed from solution. This is primarily associated with anion exchange reactions, where positively charged ion-exchange sites on the vessel walls become balanced by the adsorption of negatively charged ions from

the sample (Jarvie *et al.*, 2001). Given the relatively high charge density associated with the orthophosphate ion, it has a higher affinity for adsorption to vessel walls than many other anions found in solution (Latterell *et al.*, 1974). Consequently, in samples of low ionic strength with relatively low concentrations of P, sorption losses may be particularly significant (Ryden *et al.*, 1972). However, where ionic strength increases, there is greater competition between anions for adsorption sites, and the adsorption of phosphorus may be more limited (Jarvie *et al.*, 2001). Given competition between ions, preferential electrostatic bonding will occur for counter ions that have the highest valence, smallest soluted volume and greatest polarizability, because these ions form the most stable soluble complexes (Jarvie *et al.*, 2001; Latterell *et al.*, 1974). Increasing the surface area to solution volume ratio of a sample bottle has been shown to increase the removal of MRP from solution due to sorption (Haygarth *et al.*, 1995; Latterell *et al.*, 1974). Pre-conditioning sample bottles with a small volume of the filtrate is unlikely to reduce subsequent sorption during storage, due to the relatively slow rate at which sorption from solution occurs (Ryden *et al.*, 1972).

There is little conclusive evidence in the literature regarding the impact of vessel material on the stability of MRP during storage. Haygarth *et al.* (1995) suggested that at high concentrations of MRP, PTFE vessels resulted in smaller losses over time than polystyrene or polyethylene, yet at low concentrations of MRP vessel material did not appear to be important. The degree of sorption can be influenced by a combination of vessel material and pre-treatment. Ryden *et al.* (1972) demonstrated that acid-washing of vessels, as compared to washing with deionised water, increased the amount of orthophosphate sorbed to glass containers, had little impact on the amount sorbed to polypropylene, and decreased the amount sorbed to polycarbonate. The increased sorption to the walls of acid-washed glass vessels was suggested by these authors to be a consequence of the protonation of Al-OH and Si-OH groups on the surface of the glass. Acid-rinsing of plastic bottles has been shown to reduce adsorption from solution by saturating sorption sites and killing microorganisms on the vessel walls (Clementson and Wayte, 1992). The uptake of MRP from solution by microorganisms living on vessel walls results in the removal of the orthophosphate ion from solution, in the same manner as associated with sorption reactions. Both Heron (1962) and Golterman (1970) have shown that the pre-treatment of polyethylene bottles with iodine in a potassium iodide solution can dramatically reduce the removal of MRP from solution during storage, most likely by killing microorganisms living on bottle walls. However, care

should be taken to ensure that iodine leaching from bottle walls into solution does not interfere with the analytical determination of MRP.

Filtration

The determination of the 'dissolved' phosphorus fraction requires a sample to be filtered, most commonly through a 0.45 μm CNA membrane filter (Jarvie *et al.*, 2001). In addition to this operational requirement, the filtration of samples prior to storage may aid the preservation of MRP concentrations by i) retaining microorganisms on the filter paper which may otherwise take up/release MRP from/into solution through time, and ii) removing particulate material which may also affect solution MRP concentration through sorption/desorption reactions. As a precaution against such changes, it is desirable that filtration occurs immediately after sample collection in the field, and prior to sample storage (Lambert *et al.*, 1992). Despite the potential for filtration to remove a significant proportion of the organic and inorganic particulate load, colloidal-sized organic and inorganic material is able to pass through 0.45 μm filters (Hens and Merckx, 2002). As a consequence, MRP concentration may continue to change during sample storage due to interaction with this colloidal material. The complete sterilisation of samples by filtration using pore sizes < 0.45 μm is rarely a feasible option (Avazino and Kennedy, 1993), particularly for wetland pore-water samples where the rate of filtration through papers with such small pore sizes is inordinately long.

Filtration may also directly influence the MRP concentration determined in solution. Filter papers can retain dissolved phosphorus (Tarapchak *et al.*, 1982; Schierup and Riemann, 1979), whilst Jenkins (1968) found that Millipore filters could contribute 1.3 g P per filter paper, but that rinsing of the filter could remove a substantial proportion of this phosphorus. The effective pore size of the filter may change through time with progressive blocking as material is retained on the paper, which may influence the forms of P remaining in the filtrate (Jarvie *et al.*, 2001; Lambert *et al.*, 1992). Finally, filtering a solution under pressure may cause the lysis of microbial cell walls and the destabilisation of colloids and flocs, leading to the release of MRP into solution (Lambert *et al.*, 1992; Broberg and Pettersson, 1988). Haygarth and Edwards (2000) suggest that in order to minimise the rupturing of cell walls, the pressure of filtration should not exceed 60 cm Hg^{-1} (80 kPa).

Storage conditions

Ambient temperature is a major physical variable that influences the stability of MRP during storage. Refrigeration and freezing are two widely used preservation techniques. Lower temperatures, and storage in the dark, reduce the rates at which chemical and biological processes occur, and consequently reduce the magnitude of changes to MRP concentration associated with these processes (German Chemists Association, 1981).

Freezing is generally seen as a long-term preservation technique, which may successfully stabilise MRP for a number of years in certain samples (Avazino and Kennedy, 1993). However, in other circumstances freezing has been shown to cause significant alteration to MRP concentration. Johnson *et al.* (1975) demonstrated a 33 – 78 % loss of MRP on freezing, due to the precipitation of calcite and concurrent co-precipitation or occlusion of MRP (Jarvie *et al.*, 2001). Of particular significance to studies of wetland pore water, the freezing of anaerobic samples can result in the oxidation of Fe^{2+} and precipitation of Fe^{3+}, with concurrent sorption of MRP to the iron precipitate (Avazino and Kennedy, 1993). Freezing may also rupture microbial cells, leading to the release of MRP into solution (Nelson and Romkens, 1972). Consequently, samples for MRP analysis should be filtered before freezing (Fitzgerald and Faust, 1967), although as highlighted above, 0.45 μm filtration will not exclude all organisms from solution.

Refrigeration of samples, generally at 4 °C, is often preferred for samples stored for a period of days to weeks (Jarvie *et al.*, 2001). However, the literature suggests little consistency with regards to the effect of refrigeration on MRP stability. Ryden *et al.* (1972) suggest that samples of filtered lake water show stable MRP concentrations for up to 7 days if stored at 4 °C in glass flasks. Bull *et al.* (1994) conclude that refrigeration of samples for later MRP analysis maximises the stability of this phosphorus fraction. However, refrigeration does not always prevent sample degradation. Haygarth *et al.* (1995) showed that changes in MRP concentration could occur within 48 hours in soil waters stored at 4 °C. Henriksen (1969) showed drastic reductions in MRP concentrations of refrigerated samples, whilst Johnson *et al.* (1975) suggested that significant changes in MRP concentration of stream samples could occur within half a day of refrigerated storage. Clearly, the lack of consistency between different samples with regards to the effects of both freezing and refrigeration, suggests

that prior testing is required before the treatments can be recommended (Jarvie *et al.*, 2001).

Chemical treatments

The main purpose of chemically treating a sample prior to storage is to prevent transformations of phosphorus fractions associated with the actions of microorganisms, by stopping their metabolic processes (Jarvie *et al.*, 2001). There are two main approaches, either the addition of an acid such as H_2SO_4 or HCl, or the use of a biocide such as chloroform or mercuric chloride (German Chemists Association, 1981). Again the literature provides inconsistent evidence regarding the impact of chemical treatment on the stability of MRP during storage. Henriksen (1969) showed that the addition of sulphuric acid to lake water samples collected during winter was an effective preservation technique. However, when added to summer samples, both H_2SO_4 and mercuric chloride resulted in rapid increases in MRP concentration, most likely due to the hydrolysis of organic compounds. The use of chloroform and other algicides has also been shown to result in the release of significant quantities of MRP on the death of microorganisms, with the magnitude of release dependent on the degree of mortality, and the concentration of P in the cells (Fitzgerald and Faust, 1967). Haygarth *et al.* (1995) suggested that the addition of high levels of mercuric chloride to samples could interfere with the analytical determination of MRP. The same authors demonstrated how the effectiveness of H_2SO_4 and mercuric chloride as preservation agents may vary considerably between different samples.

6.2.2.2 A storage protocol for use at Strumpshaw Fen

In light of the above discussion, and particularly as there is little consistency in the literature as to a single suitable storage protocol, a storage experiment was conducted using pore-water and surface-water samples from Strumpshaw Fen. A number of potential preservation techniques were rejected prior to the experiment. Freezing of samples was not investigated due to the potential for the diffusion of oxygen into the samples during storage, and consequent oxidation of previously reduced wetland pore-water samples, and because of the risk of P release from ruptured cells given the high microorganism content of many wetland samples (Mitsch and Gosselink, 2000). Gardolinski *et al.* (2001) demonstrated how the freezing and thawing of samples could

lead to decreased concentrations of MRP in solution, due to the formation of a precipitate, likely calcite, which co-precipitated phosphate. Samples collected from Strumpshaw Fen contained concentrations of calcium equal to or greater than those reported by Gardolinski *et al.*, suggesting that freezing of these samples could result in deterioration of MRP during storage.

A general rule in water-sample preservation is to minimize disturbance (Haygarth *et al.*, 1995) and, alongside the specific risk of P release from microorganisms upon death, the use of chemical preservation was also rejected. Investigation centred on the impacts of iodine treatment, bottle pre-washing, and storage temperature, as these were identified as the variables with the greatest potential to influence the stability of samples collected from Strumpshaw Fen. Three litres of fen pore water were collected from a piezometer at 32.5 cm depth and 0.45 μm filtered, using the procedure described in Section 6.2.1. The f iltrate w as t hen t ransferred t o sa mple b ottles a nd s ubjected t o t reatments 1 − 8 described in Table 6.1. The same treatments were applied to sample bottles filled with 0.45 μm filtrates collected from a shallow open-water area within the fen system.

Table 6.1 Treatment matrix for sample storage experiment (see text for details).

Treatment Number	Iodise	Pre-wash	Storage Temperature
1	Yes	D	4 °C
2	Yes	D + A	4 °C
3	No	D	4 °C
4	No	D + A	4 °C
5	Yes	D	Ambient Temperature (15-25 °C)
6	Yes	D + A	Ambient Temperature (15-25 °C)
7	No	D	Ambient Temperature (15-25 °C)
8	No	D + A	Ambient Temperature (15-25 °C)

Sample bottles were 30 ml high-density polyethylene, and each of the eight different bottle treatments were completed in triplicate. Half of the bottles were impregnated with iodine following the method of Mackereth *et al.* (1989), to determine whether iodine treatment reduced the uptake of MRP from solution by microorganisms living on the vessel walls. A few iodine crystals were placed inside the bottles and caps were sealed.

The bottles were then heated at 60 °C for 5 hours, after which surplus iodine crystals were removed. In order to prevent errors associated with desorption of iodine into the samples, the impregnated bottles were soaked for 24 hours in a weak Decon solution, followed by rinsing with deionised water (> 18 M Ω). Iodised and non-iodised bottles were then pre-washed either in Decon followed by rinsing in deionised water (D), or in a 10 % v.v. H_2SO_4 solution followed by Decon and deionised water stages (D + A). These treatments were designed to examine whether pre-washing with dilute acid solutions was able to reduce P removal from solution during storage by saturating sorption sites and killing microorganisms on vessel walls. Following sample collection, half of the bottles were transferred immediately to ice, whilst the remaining samples were stored at ambient temperature in the field. On return to the laboratory (< 6 hours after sample collection), those samples on ice were transferred to a refrigerator maintained at 4 °C (± 1 °C), whilst the remaining samples were stored at ambient laboratory temperature. The different temperature treatments were designed to examine both the effect of physical storage conditions within the laboratory on MRP concentration, but also whether temperature control was significant in the time between sample collection and return to the laboratory.

Samples were analysed for MRP, Cl^-, and SO_4^{2-}, 24 hours and 3, 14 and 28 days after sample collection, using the methods described in Section 5.2.3.1. Following the removal of a volume of sample from the bottles at each analysis time, the resulting headspace was purged with argon gas to prevent oxygen from entering solution and leading to the oxidation of previously reduced samples. These analysis times were chosen to reflect typical scenarios during a field-based sampling programme. Twenty four hours represents an ideal situation where samples can be collected rapidly in the field, returned to the laboratory and analysed immediately. A period of up to 3 days represents a more realistic scenario, when the logistics of travel to and from the field, sample collection protocols (see Section 6.2.1), and access to analytical equipment is considered. Periods of 14 and 28 days between sample collection and analysis were chosen to identify particularly stable elements, and to determine whether lengthy delays between sample collection and analysis caused, for example, by equipment failure, would lead to unacceptable sample degradation.

The analysis of solutions for Fe^{2+} requires that the filtrate be acidified upon collection to stabilise the iron in solution (see Section 5.2.3.1). Samples for Fe^{2+} analysis were

acidified upon collection in the field to pH < 2 using 1 % v.v. 4 M H_2SO_4, and refrigerated at 4 °C in sample bottles that had been cleaned with Decon followed by deionised water. Acidified samples were collected from the piezometer at 32.5 cm depth, and the open-water body at Strumpshaw Fen, and included in the 28 day storage experiment. These samples were analysed for total Fe, and the major cations Ca^{2+}, Mg^{2+}, Na^+ and K^+, by atomic absorption spectrometry.

6.2.3 Analysis of water samples

Samples collected to characterise the field-scale hydrochemical status of Strumpshaw Fen (see Section 6.2.1), and to assess the applicability of the findings from the mesocosm studies reported in Chapter 5 at the larger field scale, were analysed for MRP, Fe^{2+}, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, and SO_4^{2-} using the methods described in Section 5.2.3.1. In order to preserve the redox status of the pore-water samples, all dilutions were conducted using deoxygenated blank solutions within a glove bag purged with N_2. In addition, samples were stored in argon-purged tubes within the glove bag prior to analysis. Samples collected using the automatic water sampler during periods of exchange between the fen pore water and the ditch network were analysed for MRP only by FIA.

A number of authors have demonstrated that MRP determined on 0.45 µm filtrates may not be composed solely of the free orthophosphate ion (e.g. Zhang and Oldham, 2001; Shaw *et al.*, 2000; Baldwin, 1998). Colloidal material, defined as any organic or inorganic entity in the size range 1 nm – 1 µm (Buffle and Leppard, 1995), may pass through 0.45 µm filters, and P associated with this colloidal material may be released during the subsequent MRP assay (Hens and Merckx, 2002). The hydrolysis of organic- and condensed-P bonds, driven by acid or transition metal concentrations, alongside the dissolution of metal-P bonds under the acidic conditions associated with MRP analysis, may release free orthophosphate into solution, thereby leading to an overestimation of the true concentration in samples (Hens and Merckx, 2002; Baldwin, 1998). Given that the orthophosphate ion is considered to be immediately biologically available, but that organic P and P attached to inorganic particles is less bioavailable in the short term (House, 2003, Haygarth *et al.*, 1997), the speciation of P between free orthophosphate and colloidal forms is clearly important.

The use of filters with pore sizes < 0.45 μm is a simple and straightforward approach to minimise the impact of colloidal particles during the MRP assay (e.g. Shand *et al.*, 2000; Haygarth *et al.*, 1997). Hens and Merckx (2002) demonstrated that 0.025 μm filtration effectively removed all colloidal material from a range of samples, and that free orthophosphate was the only MRP species remaining in the resulting filtrate. Following their work, pore-water samples collected from Strumpshaw Fen on 25th June 2002 were filtered in the laboratory using 0.02 μm Anopore membrane filters, having been previously filtered (0.45 μm) in the field. Samples from each of the three piezometer nests, and from each depth at a given nest, were used. Filter papers were soaked for 24 hours in deionised water (> 18 M Ω) prior to use, and then positioned in Millipore Swinnex filter holders. 20 ml of deionised water was passed through each filter paper using a syringe. Analysis of the deionised water filtrates confirmed that no detectable quantities of P were released from the filter papers. A small volume (2 ml maximum) of the 0.45 μm filtered solutions was then passed through the 0.02 μm filter and stored in argon-filled tubes prior to analysis for MRP by FIA. Small volumes were used to keep filter loadings low (0.4 ml cm^{-2} maximum), in an attempt to minimise the clogging of filter papers. Triplicate aliquots of each 0.45 μm filtered solution were taken and filtered through separate 0.02 μm filters. To determine whether free orthophosphate was successfully transferred through the 0.02 μm filters, and to check for clogging, 0.45 μm solutions were spiked with standard orthophosphate solutions to final concentrations of 0.5 mg l^{-1} P, 0.02 μm filtered, and compared to non-spiked solutions. All filtration and dilution was conducted using deoxygenated blank solutions within a glove bag under an inert N_2 atmosphere.

6.3   Results from the storage of wetland pore-water and surface-water samples

Concentrations of chloride and sulphate, from both pore water and surface water, were found to be stable throughout the 28 day period of storage, and independent of the treatment applied to the sample ($p > 0.05$). Total Fe, Ca^{2+}, Mg^{2+}, Na^+ and K^+ in the acidified samples were also found to be stable during storage. Consequently, analyses for Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^- and SO_4^{2-} were conducted within 28 days of sample collection. These findings are in agreement with Bull *et al.* (1994) who suggested that cations could be stored adequately for up to 90 days, and that concentrations of Cl^- and SO_4^{2-} were also unlikely to show significant changes during storage. However, the stability of sulphate from wetland pore water during storage is perhaps surprising. Pore-

water samples extracted from the piezometer at 32.5 cm depth showed evidence of being strongly reduced, containing low concentrations of NO_3-N and SO_4^{2-}, and high concentrations of Fe^{2+}. During storage, diffusion of oxygen through the bottle walls into solution might be expected, resulting in the oxidation of samples, and, as a consequence, increases in the concentrations of sulphate with time. No evidence was found for increasing concentrations of SO_4^{2-} during the storage of samples from Strumpshaw Fen. Explanations for this observation may include i) oxygen being unable to diffuse through the bottle material, ii) low concentrations of sulphide being present in solution, for example due to the formation of insoluble iron-sulphide minerals in the field, or iii) that the kinetics of sulphide oxidation were too slow to allow significant concentrations of sulphate to develop during the course of the storage experiment. Further data would be needed to clarify the relative roles of these explanations.

Atomic absorption spectrometry (AAS) determines the total iron concentration in solution, but is unable to speciate between Fe^{2+} and Fe^{3+}. Therefore, although the concentration of total iron from the samples at Strumpshaw Fen remained stable during storage, the AAS data cannot be used to inform decisions regarding suitable storage periods for the analysis of Fe^{2+}. Unfortunately, the 1,10 Phenanthroline monohydrate methodology described in Section 5.2.3.1, that does enable the speciation of Fe^{2+} and Fe^{3+}, was unavailable during the storage experiment. However, later tests of pore-water samples from Strumpshaw Fen using the 1,10 Phenanthroline method indicated that Fe^{2+} in acidified samples stored at 4 °C was stable for up to 4 days after collection. Consequently, no samples were stored for longer than 4 days prior to analysis for Fe^{2+}.

The concentration of MRP in pore-water and open-water samples from Strumpshaw Fen was found to vary significantly both with time and with bottle treatment ($p < 0.01$). Figures 6.2 and 6.3 show the results from the storage of pore-water and open-water samples respectively. The concentration of MRP in pore-water and open-water samples across all bottle treatments at the beginning of the storage experiment differed by almost a factor of 8, averaging 3.01 mg l^{-1} P in pore water, and 0.39 mg l^{-1} P in open water. There was no evidence for a statistically significant change in the concentration of pore-water MRP between 24 and 72 hours, regardless of bottle treatment ($p = 0.57$). This was a relatively surprising finding, because much previous work has suggested that refrigeration is an important technique in the short-term preservation of water samples (e.g. Gardolinski *et al.*, 2001; Haygarth *et al.*, 1995; Bull *et al.*, 1994). Samples taken

from areas of open water did show a significant change over the study period (p < 0.05), although the direction of change (increase or decrease in MRP concentration) was not consistent across the different replicates.
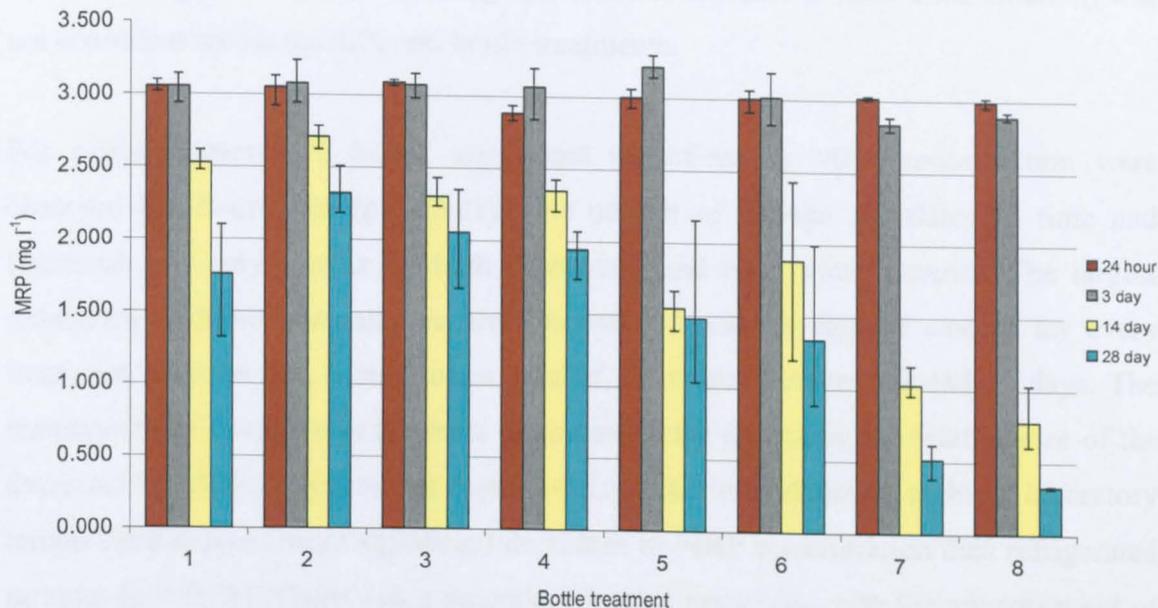
Figure 6.2 The effect of storage on wetland pore-water samples. Mean values are given for each treatment at each time of analysis (n = 3). Error bars give the range of concentrations in the triplicate samples.
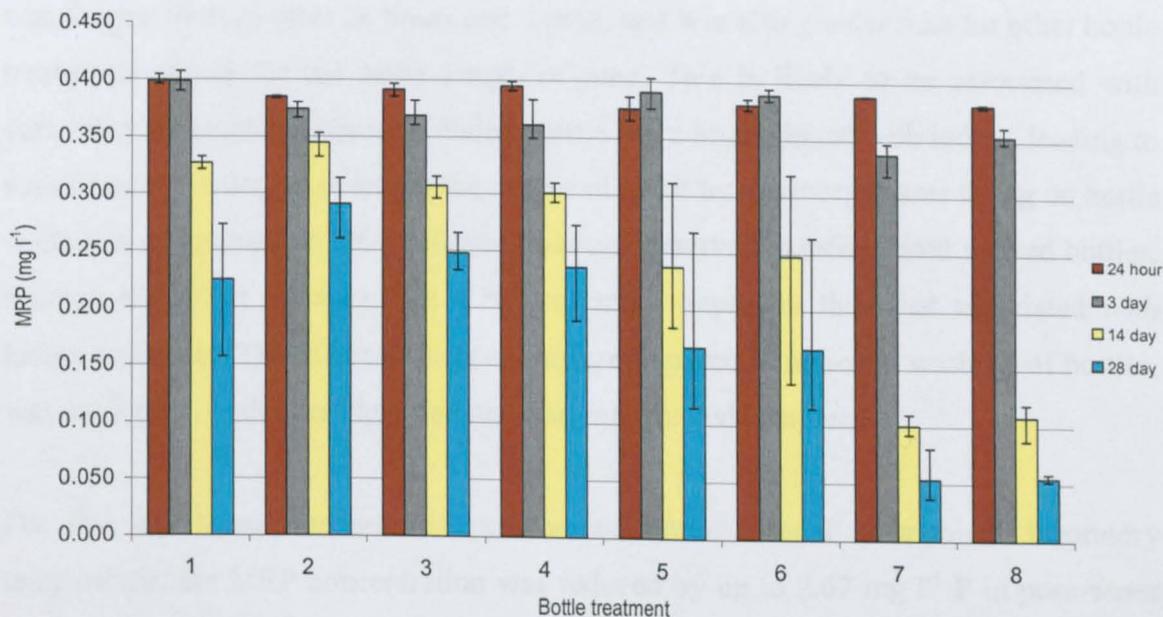
Figure 6.3 The effect of storage on wetland open-water samples. Mean values are given for each treatment at each time of analysis (n = 3). Error bars give the range of concentrations in the triplicate samples.

from areas of open water did show a significant change during the same period (p < 0.01), although the direction of change (increase or decrease in MRP concentration) was not consistent across the different bottle treatments.

For storage beyond 72 hours, significant reductions in MRP concentration were observed in all samples (p < 0.01). The pattern of change as related to time and treatment was very similar for both pore-water and open-water samples. The largest reductions in MRP generally occurred between 3 and 14 days of storage for every treatment, with further, though often smaller, decreases between 14 and 28 days. The temperature of storage was the most important factor governing the relative size of the decreases in MRP seen between 3 and 14 days. Samples stored at ambient laboratory temperature showed more significant decreases in MRP concentration than refrigerated samples (p < 0.01). There was a secondary impact associated with the pre-treatment of bottles with iodine. Iodised bottles maintained higher concentrations of MRP than non-iodised replicates, although the effect of iodine was less pronounced for samples stored in a refrigerator compared with those stored at ambient laboratory temperature.

For samples stored in iodised bottles at ambient laboratory temperature, the range of MRP concentration in the triplicate samples analysed after 14 and 28 days of storage was far greater than after 24 hours and 3 days, and was also greater than for other bottle treatments stored for the same length of time. This is likely to be associated with variability in the efficiency with which bottles were impregnated with iodine, leading to variations in the degree to which the uptake of MRP by microorganisms living on bottle walls was suppressed. A similar impact was not observed in refrigerated iodised bottles, because the effect of storage at 4 °C was more important than that associated with iodine treatment. The effect of acid-washing, compared to non-acid washing of bottles, was negligible, both in refrigerated and non-refrigerated samples.

For the worst-case scenario of non-iodised bottles stored at ambient laboratory temperature, the MRP concentration was reduced by up to 2.67 mg l^{-1} P in pore-water samples after 28 days of storage when compared to the MRP concentration determined 24 hours after collection (approximately 89 %), and by up to 0.34 mg l^{-1} P in open-water samples (approximately 86 %). In comparison, samples stored in refrigerated, iodised bottles were preserved more effectively, with reductions between 3 and 28 days of storage of 0.73 mg l^{-1} P in pore-water samples (approximately 24 % of 24 hour

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concentrations), and 0.1 mg l^{-1} P in open-water samples (approximately 25 % of 24 hour concentrations). However, time was the single most important factor governing the stability of MRP during storage. Even with the best-case scenario of storage in refrigerated, iodised bottles, samples from Strumpshaw Fen could only be stored for up to 3 days before unacceptable reductions in MRP concentration occurred, approaching 25 % of the concentration determined after 24 hours. Consequently, all further samples collected from Strumpshaw Fen were analysed for MRP within 72 hours of sample collection. Although the effect of temperature within the first 3 days of storage was found to be only minimal, the fact that the degradation of MRP beyond 3 days was exacerbated if samples were not refrigerated, suggested that samples collected from Strumpshaw Fen should be put on ice in the field and transferred to storage at 4 °C on return to the laboratory. Although refrigeration was found to be a more effective preservation method than iodine treatment, there was evidence that the degree of MRP loss between 3 and 14 days of storage was reduced, even for refrigerated samples, if bottles had been pre-treated with iodine. Therefore, samples for MRP analysis from Strumpshaw Fen were stored in iodine-treated bottles. There was no evidence that pre-washing of sample bottles with dilute acid solutions reduced MRP loss during storage, either by killing microorganisms on bottle walls or by saturating sorption sites. Therefore, acid washing was rejected in favour of Decon and deionised water steps, as described in Section 6.2.2.2.

6.4   The field-scale availability of phosphorus at Strumpshaw Fen

Pore-water samples collected from the piezometers at Strumpshaw Fen contained substantial concentrations of MRP (see Table 6.2 and discussion below), confirming the findings from Chapter 5 that the sediments are potential sources for P. Samples were collected from the field (April-July 2002) after the sediments had been submerged for several months, and during stable hydrological conditions, in an attempt to characterise the near-equilibrium availability of phosphorus. No consistent variation in the concentration of pore-water MRP was found between different piezometer nests along the sampling transect, or between different sampling dates at a given piezometer nest. However, in agreement with the laboratory core incubations reported in Chapter 5, consistent variations in the concentration of MRP were found with depth in the upper 50 cm of peat at Strumpshaw Fen. Table 6.2 shows the results of MRP analysis of samples collected from all three piezometer nests on 6th June 2002 when the system was surface-

inundated. The concentrations of MRP, and the spatial pattern of the concentrations, were similar on all other sampling dates. Also provided for comparison are the concentrations of MRP in samples from mini-piezometers at the end of both laboratory core incubations, allowing the degree to which mesocosm studies translate to the field scale to be assessed.

Table 6.2 MRP in samples collected from field piezometers on 6th June 2002, and from mini-piezometers at the end of laboratory core incubations. Mean values are given with range in parentheses (all mg l^{-1} P). For field samples, the data for each depth are from three piezometer nests located along a 100 m transect. For laboratory samples, the data for each depth are from mini-piezometers located in duplicate cores. Depths correspond to the mid-point of piezometer intakes.

Depth (cm)	MRP in field piezometer samples	MRP in laboratory Experiment A	MRP in laboratory Experiment B
2.5	1.22 (1.70 – 0.87)	1.09 (1.57 – 0.61)	0.77 (0.89 – 0.66)
10	3.66 (4.27 – 3.26)	1.29 (1.84 – 0.75)	1.21 (1.48 – 0.94)
17.5	4.55 (4.94 – 3.97)	1.61 (2.37 – 0.85)	2.29 (2.68 – 1.90)
32.5	2.79 (3.42 – 2.13)	0.79 (1.03 – 0.55)	4.00 (4.43 – 3.55)

The pattern of MRP concentration with depth in pore water from field samples corresponded closely with that determined in laboratory cores at the end of Experiment A. Concentrations increased from the surface to reach a maximum in piezometers at 17.5 cm, below which concentrations of MRP decreased. Although this pattern of depth-variation in MRP concentration was similar in field and laboratory piezometers, the absolute concentration in samples from the field consistently exceeded that in corresponding samples from Experiment A, by up to a factor of 3.5. Depth patterns of MRP from field samples also showed good correlation with those at the end of Experiment B in the zone 0 to 17.5 cm depth, again with laboratory samples containing lower absolute concentrations of MRP than field samples. However, in contrast to Experiment A, the concentration of MRP in samples from 32.5 cm depth at the end of Experiment B exceeded that in shallower samples, and also exceeded that in field samples from the corresponding depth.

A number of factors may explain the difference between concentrations of MRP in field- and laboratory-derived samples. The flooding solution used in Experiment A contained no MRP, whereas that used in Experiment B was spiked to a final concentration of 0.46 mg l^{-1} P. This lack of an 'external' source of P in Experiment A may explain the lower concentration of MRP in samples from these cores compared to corresponding field samples, given that flooding in the field often involves the input of P-enriched river water (see Section 4.4.1.2). Alternatively, the difference may indicate that equilibrium MRP concentrations were not reached during Experiment A, in contrast to field-derived samples that were collected after sediments had been submerged for several months. However, time series data (see Figure 5.5) suggest that quasi-equilibrium of MRP concentration was reached in pore-water samples in Experiment A, indicating that this was unlikely to be the explanation for the difference in MRP between samples from the field and those from the laboratory.

The fact that samples from Experiment B, except those from 32.5 cm, also had lower concentrations of MRP than corresponding field samples, despite the P-spiking of the flooding solution, likely reflects the delayed onset of P release to pore water caused by NO_3-N in the flooding solution (see Section 5.3.5). Sediment analysis revealed that substantial quantities of $NaOH$-P_i remained in the peat at depths above 25 cm at the end of Experiment B, in contrast to peat at greater depth (Table 5.5). This indicates that continued reductive-dissolution of Fe-P and associated release of MRP to pore water was possible in this zone, given a longer period of incubation. Therefore, the concentration of MRP in samples from 17.5, 10 and 2.5 cm depth might be expected to reach similar concentrations, if not exceed, that in corresponding field samples over a longer period of core incubation in the laboratory.

It is possible that the experimental procedures used in the laboratory core incubations introduced boundary effects that led to lower MRP concentration than in field samples. In particular, the diffusion of oxygen into the cores through sampling ports may have reduced the extent of reductive-dissolution of Fe-P complexes, thereby reducing the concentration of MRP in solution. Such concerns are an issue for many mesocosm studies, and may be one reason why the findings from small-scale laboratory work are not always applicable at the larger field scale (Ahn and Mitsch, 2002). However, it is felt that the effects of such boundary conditions are unlikely to have influenced the findings reported in Chapter 5. For example, the MRP concentration in samples from

32.5 cm depth at the end of Experiment B was in excess of that in the corresponding field-derived samples. This would be unlikely if oxygen were diffusing into the core through the sampling port. Given that all laboratory core housings were constructed and tested using the same protocols, it is most unlikely that every sampling port, except that at 32.5 cm depth in Experiment B, allowed oxygen to move into the core. Instead, it is much more likely that the lack of an external source of P in the flooding solution in Experiment A, and the delayed onset of MRP release associated with the presence of NO_3-N in Experiment B, were the causes of the disparities between MRP concentrations in samples from the field and those from the laboratory.

Pore-water samples were also collected from deeper piezometers with intake mid-points at 102.5, 202.5 and 402.5 cm depth, the same instruments used to monitor variations in hydraulic head (see Section 4.2.2). Piezometer nests located 2 and 10 m from the ditch edge showed similar patterns of MRP concentration on all sampling dates. Therefore, average values from both nests are discussed below. At 102.5 cm depth, MRP concentrations were lower than those in the upper peat, averaging 0.19 and 0.66 mg l^{-1} P at 2 and 10 m respectively. Further decreases in pore-water MRP concentration were observed in samples from 202.5 cm depth, averaging 0.18 and 0.13 mg l^{-1} P, and at 402.5 cm, averaging 0.08 and 0.07 mg l^{-1} P, in piezometers located 2 and 10 m from the ditch edge respectively. However, at 100 m along the transect, the decreases in MRP concentration in deeper piezometers were not as pronounced as observed in nests closer to the ditch. At 102.5 cm depth, MRP averaged 1.15 mg l^{-1} P, at 202.5 cm 0.70 mg l^{-1} P, and at 402.5 cm 0.92 mg l^{-1} P. Whilst substantially below the concentrations of MRP determined in shallower piezometers, these concentrations exceeded those from corresponding depths in nests at 2 and 10 m from the ditch edge, and by a factor of up to 10 at 402.5 cm depth.

Samples from the water column above the peat deposits were collected on three separate sampling dates, with 10 samples being taken from distances generated by random number along the instrumented transect on each visit. There was no consistent variation in surface-water MRP concentration with distance along the transect or sampling date. Analysis of these samples showed that concentrations of MRP varied between 0.20 and 0.38 mg l^{-1} P. As reported for a number of other wetlands, pore-water samples from Strumpshaw Fen contained far higher concentrations of MRP than overlying surface water (e.g. Soto-Jimenez *et al.*, 2003; Mayer *et al.*, 1999).

Pore-water samples collected on 25th June 2002 were subjected to 0.02 μm membrane filtration on return to the laboratory, and subsequently analysed for MRP. Concentrations o f M RP in 0 .02 μ m f iltrates w ere c ompared t o t hose i n samples t hat were 0.45 μm filtered in the field. There was no significant difference in the proportion of MRP in 0.45 μm filtrates that remained after 0.02 μm filtration, either between different piezometer nests or with depth at a given nest (p > 0.05 in both cases). Consequently, Table 6.3 shows the data from the piezometer nest located 2 m from the ditch only, although the findings and discussion below are also applicable to the nests at 10 and 100 m.

Table 6.3 The recovery of MRP following 0.02 μm filtration of pore-water samples collected from Strumpshaw Fen on 25th June 2002.

Piezometer depth (cm)	0.45 μm MRP[a]	0.02 μm MRP[b]	% free[c]	0.02 μm MRP with spike[d]	% recovery[e]
2.5	1.53	1.49 (1.50 – 1.48)	97.4	1.89	95.0
10	2.95	2.80 (2.81 – 2.78)	94.9	3.27	99.1
17.5	4.06	3.96 (4.00 – 3.88)	97.5	4.31	96.6
32.5	2.20	2.03 (2.04 – 2.00)	92.3	2.46	97.2
102.5	0.25	0.25 (0.26 – 0.25)	100.0	0.77	102.6
202.5	0.23	0.21 (0.22 – 0.20)	91.3	0.70	98.6
402.5	0.10	0.10 (0.11 – 0.09)	100.0	0.60	100.0

[a]filtration in the field

[b]filtration in the laboratory, mean values given (n = 3) with range in parenthesis

[c]calculated as mean 0.02 μm MRP/0.45 μm MRP

[d]0.45 μm filtrates spiked with orthophosphate to final concentration of 0.5 mg l^{-1} P, passed through 0.02 μm filters and analysed for MRP

[e]calculated as MRP analysed on 0.02 μm filtrate with spike/mean 0.02 μm MRP + 0.5

The analyses indicated that the vast majority of MRP determined in 0.45 μm filtrates was still present after 0.02 μm filtration. Between 92 and 102 % of the MRP determined on 0.45 μm solutions remained after 0.02 μm filtration, and there was little variation between the triplicate 0.02 μm filtrates (generally < ± 5 % of the mean value). The data did suggest that the concentration of MRP in 0.02 μm filtrates tended to be below that in 0.45 μm filtrates. These differences were statistically significant ($p < 0.01$). However, the magnitude was generally small, on average 96.4 % of MRP in 0.45 μm filtered solutions was present in 0.02 μm filtrates. The analyses also revealed that free orthophosphate was transferred quantitatively through the 0.02 μm filter papers, and that minimal clogging of the papers by particulate or colloidal organic and inorganic material occurred. Samples spiked with free orthophosphate showed ≥ 95 % recovery of the added orthophosphate after 0.02 μm filtration, although for the majority of samples analysis indicated that < 100 % of the spiked orthophosphate concentration was transferred through the 0.02 μm filter paper.

In Chapter 5 it was concluded that the release of phosphorus into the pore water and surface water at Strumpshaw Fen was controlled by the reductive-dissolution of Fe-P. Analysis of the Fe^{2+} concentrations in pore-water samples collected from the field piezometers at Strumpshaw Fen support a link between the cycles of iron and phosphorus in this system. Figure 6.4 shows the strong correlation found between MRP and Fe^{2+} in all samples collected from each of the three piezometer nests ($r^2 = 0.97$, $p < 0.001$). The gradient of the trend line represents the molar P:Fe ratio of the data set (0.41), which is similar to that determined on samples from Experiment B of the laboratory core incubations (0.46), and close to the dominant P:Fe ratio of P surface complexed to ferric hydroxide (approximately 0.5, Gunnars and Blomqvist, 1997). Standing surface-water samples are not included in Figure 6.4, molar P:Fe ratios in these samples varied between 1.92 and 1.75.

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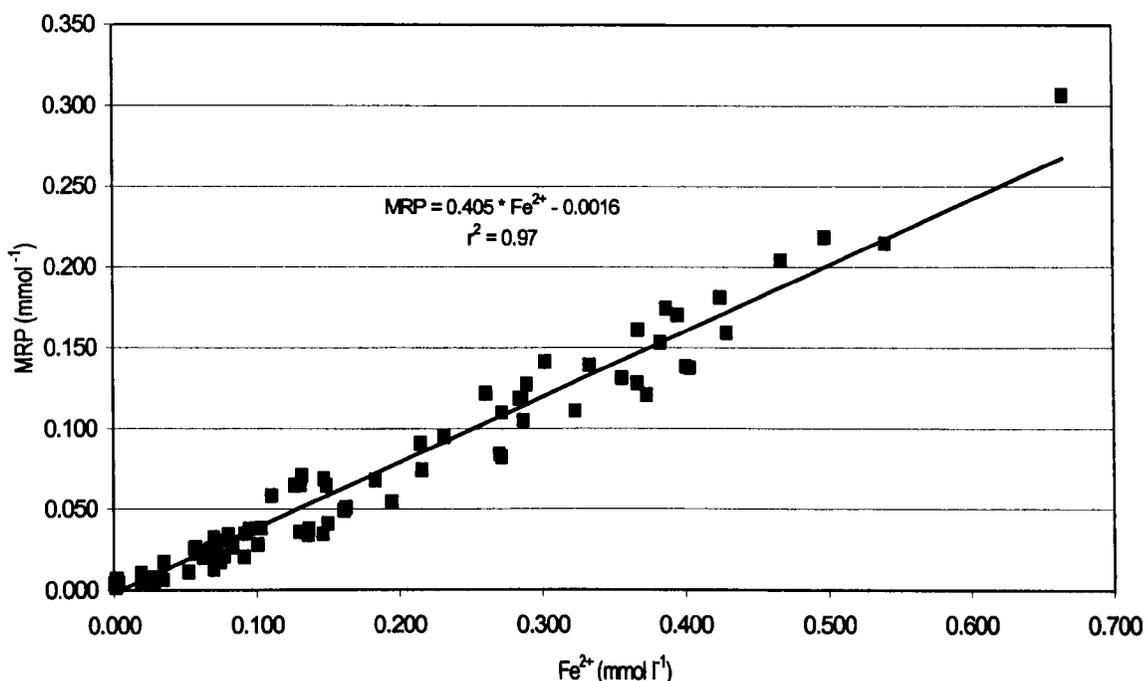
Figure 6.4 Fe^{2+} versus MRP in samples collected from field piezometers.

In the upper 50 cm of peat, the extent to which Fe^{2+} concentrations in samples from the field matched those in samples from the laboratory was very similar to that described previously for MRP. All samples at the end of Experiment A contained lower concentrations of Fe^{2+} than samples from corresponding depths in the field, and by a factor of up to 5. This was also the case for samples in the zone 0 to 17.5 cm depth at the end of Experiment B. As discussed previously for patterns of MRP, the sample from 32.5 cm depth at the end of Experiment B contained a concentration of Fe^{2+} that was in excess both of that in shallower samples from the laboratory cores, and also of that in field-derived samples from the corresponding depth.

In piezometer nests located 2 and 10 m from the ditch edge, Fe^{2+} concentration in piezometers below 32.5 cm decreased substantially, reaching average concentrations of 0.07 mg l^{-1} at 402.5 cm depth. However, again in agreement with patterns described previously for MRP, the concentration of Fe^{2+} in deeper piezometers from the nest located 100 m along the transect remained far higher than in corresponding piezometers in the near-ditch zone, with an average of over 3 mg l^{-1} Fe^{2+} present at 402.5 cm depth. Concentrations of Fe^{2+} in standing surface-water samples varied between 0.22 and 0.39 mg l^{-1}.

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Checks were made to ensure that the correlation between concentrations of MRP and Fe^{2+} were not simply caused by one element interfering with the analytical procedure used to determine the other. Serial dilution and standard addition procedures were conducted on randomly selected samples to test for interference in both the MRP and Fe^{2+} methods. All tests produced concentrations within 5 % of the expected values, and therefore interferences during analysis for these two elements were assumed to be insignificant in the samples from Strumpshaw Fen.

6.5 Using hydrochemical parameters to trace exchanges of water between the peat and the ditch network

Chapter 4 provided evidence showing that two-way hydrological connectivity may exist between the fen and the ditch network at Strumpshaw. These exchanges were often driven by specific hydrological events, such as periods of rainfall, tidal pulses passing through the ditch network from the River Yare, or the managed drawdown of fen water table. In this section, the potential for tracing these exchanges using variations in hydrochemical parameters is investigated. Hydrochemical evidence for the flow of water between the fen and the ditch network would indicate that the conclusions made in Chapter 4 on the basis of combining estimates of K with water-table gradients are likely to be reliable.

Rainfall

Rainfall has the potential to generate water-table gradients driving shallow ground water flow from the peat into the ditch network (see Section 4.4.1.1). No discernable changes in the pH or temperature of water in the ditch network were observed during periods when water-table gradients supported the delivery of shallow ground water into the ditch network. However, there were substantial fluctuations in ditch-water EC during these periods. Figure 6.5 shows the variation in ditch-water EC during 9-12th September 2002 (JD 252-255), during the same rainfall event shown previously in Figure 4.11 of Section 4.4.1.1. Water level in the ditch network and the fen water table 10 m from the ditch edge are shown, the difference between the two water elevations representing the magnitude of the water-table gradient driving flow from the fen into the ditch. The EC data recorded in the ditch network are also given, corrected to 25 °C to remove the influence of changes in water temperature.
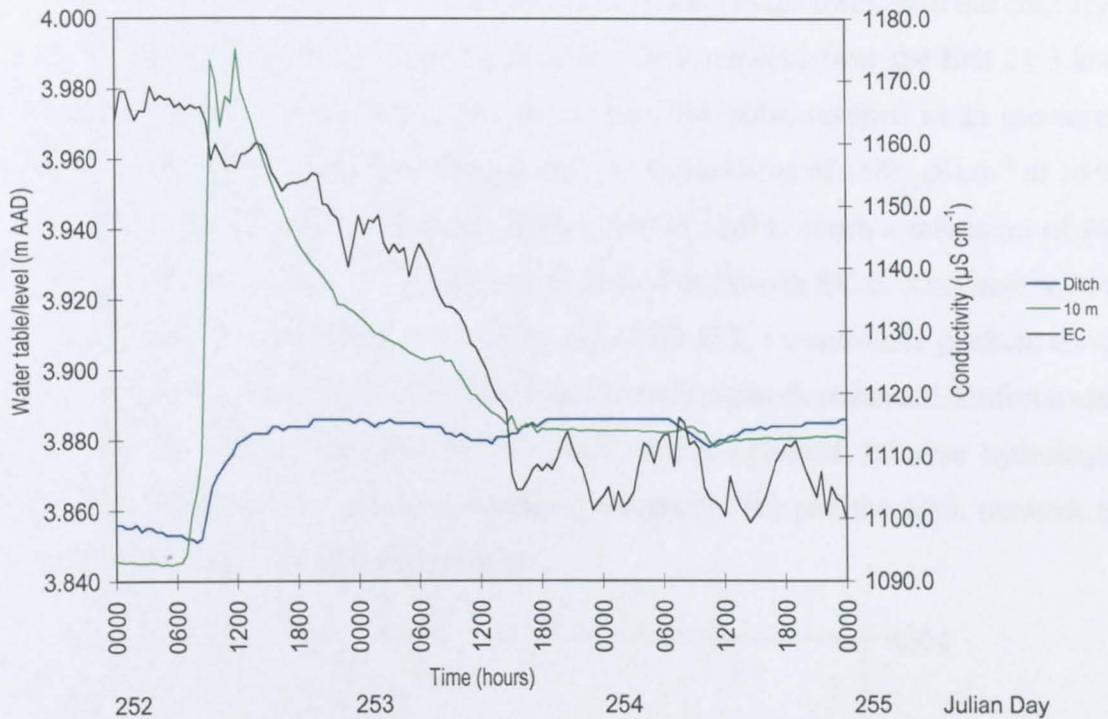
Figure 6.5 The influence of fen – ditch exchange on the EC of ditch water following a rainfall event on JD 252.

A clear decrease in ditch-water EC occurred during JD 252 and 253, and the period during which EC fell was coincident with the existence of water-table gradients between the fen and the ditch network. From maximum levels between 1165 and 1170 μS cm^{-1} prior to the beginning of rainfall, EC fell to reach a minimum of approximately 1100 μS cm^{-1} by the time equilibrium between the fen water table and the ditch water level was established, some 35 hours later. Following this equilibration (around 1600 h on JD 253), ditch-water EC remained relatively stable, with fluctuations of no more than approximately ± 15 μS cm^{-1} over the following 32 hours to the end of JD 254. These data suggest that the establishment of water-table gradients driving the flow of shallow ground water from the fen into the ditch network during rainfall may lead to the delivery of water with a relatively dilute EC signal to the ditch.

Other rainfall events appeared to result in different fluctuations in ditch-water EC. Figure 6.6 shows data collected over the period 21st-23rd December 2002 (JD 355-357), shown previously in Figure 4.12 of Section 4.4.1.1. A rainstorm event delivered 23.0 mm of rainfall between 2230 h on JD 355 and 1030 h on JD 356, and was therefore of similar magnitude to that shown in Figure 6.5. This event was the first major rainstorm following prolonged artificial drawdown of the fen water table over the period JD 319-

331 (see Figure 4.16). The data indicate that the rainfall event resulted in the delivery of an initial pulse of solute-enriched water to the ditch network over the first 11.5 hours following the start of water-table rise in the fen. The pulse resulted in an increase in ditch-water EC of approximately 180 μS cm^{-1}, to a maximum of 1588 μS cm^{-1} at 1030 h on JD 356. Following this initial rise, ditch-water EC fell to reach a minimum of 1450 μS cm^{-1} at the end of JD 357. This latter period of decline in EC is consistent with the EC pattern described in Figure 6.5. At the end of JD 357, a water-table gradient driving shallow ground-water flow from the fen into the ditch network remained. Unfortunately, a longer time series of ditch-water EC could not be obtained, because hydrological fluctuations after JD 357 drove exchanges between the fen and the ditch network that were not associated with the rainfall event.
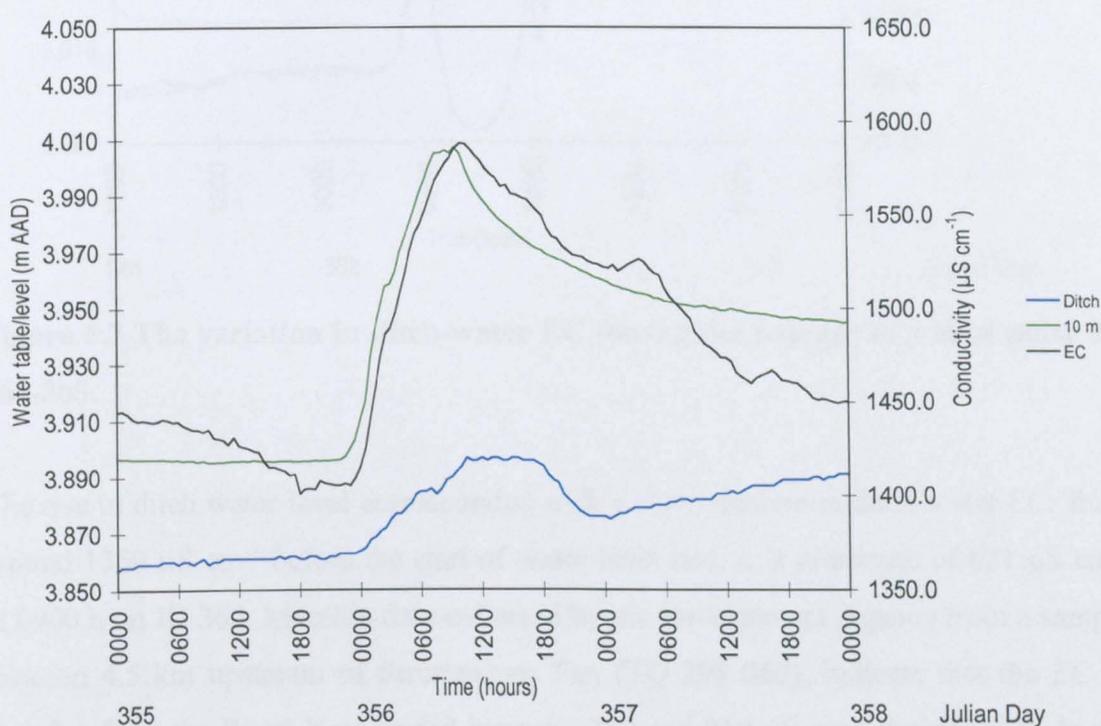
Figure 6.6 The fluctuation in ditch-water EC following a rainstorm event on JD 355 and 356.

Tidal pulses from the River Yare

Managed exchanges between the River Yare and the ditch network at Strumpshaw Fen occur through a sluice control structure (see Section 2.4.2). The potential importance of the River Yare in the hydrological functioning of Strumpshaw Fen was highlighted in Chapter 4 (see Section 4.4.1.2). Further insight into these exchanges can be gained through a consideration of their hydrochemical signatures. Figure 6.7 shows the

fluctuation of ditch-water EC during the period 27-29th December 2002 (JD 361-363), during the passage of a tidal pulse from the River Yare through the ditch network, the event shown previously in Figure 4.13.
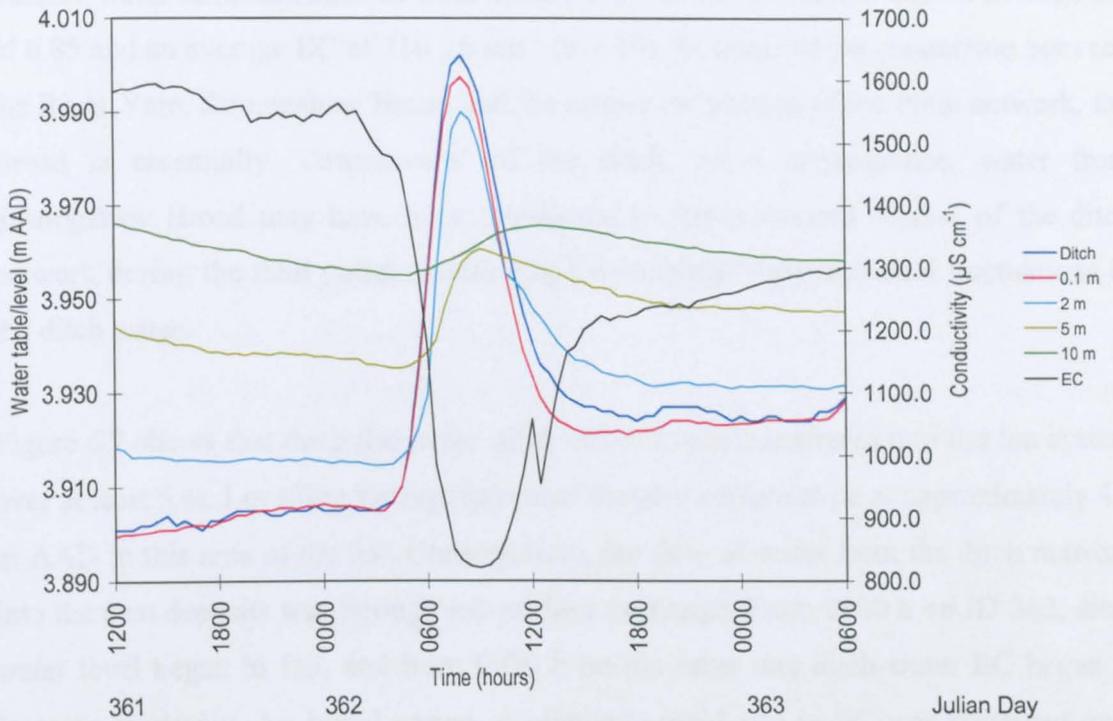
Figure 6.7 The variation in ditch-water EC during the passage of a tidal pulse JD 361-363.

The rise in ditch water level corresponded with a sharp decline in ditch-water EC, from around 1550 μS cm^{-1} before the start of water level rise, to a minimum of 821 μS cm^{-1} at 0900 h on JD 362. Monthly data collected by the Environment Agency from a sample location 4.5 km upstream of Strumpshaw Fen (TG 291 062), indicate that the EC of samples from the River Yare varied between 799 and 960 μS cm^{-1} during 2002. In the light of these Environment Agency data, the fall in ditch-water EC during the rising limb of the pulse may suggest a direct influence of water from the River Yare at this point in the ditch network. However, ditch-water pH at approximately 6.70 remained essentially unchanged during the period JD 361-363. Monthly data from the Environment Agency indicated an average pH for the River Yare during 2002 of 8.03. If water from the River Yare were directly influencing the ditch network during this tidal pulse, then a rise in ditch-water pH coincident with the rise in ditch water level would be expected. The fact that ditch-water pH remained stable suggests that water from the River Yare did not reach as far as the monitoring point during this pulse. Instead, the pulse may have been the result of the 'backing up' of water through the interconnected

Broad and ditch network at Strumpshaw Fen, as River Yare water moved into sections of the network closer to the river. The pulse was dominated by water that was of similar pH, but lower EC, to that present in the monitored section of the ditch during JD 361. Surface-water samples collected from Strumpshaw Broad on JD 356 had an average pH of 6.85 and an average EC of 716 μS cm^{-1} (n = 10). In terms of the connection between the River Yare, Strumpshaw Broad and the monitored section of the ditch network, the Broad is essentially 'downstream' of the ditch. As a consequence, water from Strumpshaw Broad may have been transferred to the monitored section of the ditch network during the tidal pulse, resulting in the observed hydrochemical fluctuations in the ditch water.

Figure 6.7 shows that the pulse in the ditch network was transferred into the fen system over at least 5 m. Levelling surveys indicated the peat surface to be at approximately 4.1 m AAD in this area of the fen. Consequently, the flow of water from the ditch network into the peat deposits was through sub-surface exchange. From 0800 h on JD 362, ditch water level began to fall, and from 0930 h on the same day ditch-water EC began to increase markedly. An initial period of relatively rapid rise in EC was sustained until approximately 1600 h on JD 362, after which time a more gradual increase in EC occurred reaching a maximum of approximately 1300 μS cm^{-1} at 0600 h on JD 363. The rapid initial rise in EC may reflect the delivery of fen pore water from zones in close proximity to the ditch network, driven by falling ditch water level. Figure 6.7 indicates that s hallow g round water w ithin 2 m o f t he d itch e dge w as s trongly coupled t o t he ditch network, with changes in ditch water level being rapidly translated into changes in fen water-table position in this zone. Water passing into and then out of the peat likely became solute-enriched as it flowed through sediments that had been oxidised for a considerable length of time prior to the ingress of the tidal pulse. The more gradual rise in ditch-water EC observed after 1600 h on JD 362 is likely to be associated with the less rapid delivery of shallow ground water from zones at greater distance away from the ditch network.

Analysis of the hydrochemical signatures of other tidal pulses suggests that it was possible for water from the River Yare to flow sufficiently far through the ditch network to influence directly the chemical quality of water at the monitoring point. Figure 6.8 shows the fluctuation in ditch water level, EC, and fen water table during the passage of a tidal pulse over the period 27-29th October 2002 (JD 300-302). From approximately

1200 h on JD 300 to 0000 h on JD 301, the ditch network drained freely into the River Yare. This resulted in the development of a water-table gradient supporting the flow of shallow ground water from the fen into the ditch network and, as a consequence, ditch-water EC rose to a maximum of 910 μS cm^{-1} at 0230 h on JD 301. The rising limb of the tidal pulse began at 0100 h on JD 301 and, as described previously in Figure 6.7, was associated with a sharp decrease in ditch-water EC, to a minimum of 820 μS cm^{-1} at 0600 h on JD 301, which coincided with maximum ditch water level. In contrast to the pulse on JD 362, observations of ditch-water pH indicated that water from the River Yare may have reached the monitored section of the ditch network during the pulse on JD 301. Ditch-water pH increased from a minimum of 7.18 at 0230 h on JD 301 to reach a maximum of 7.84 at 0700 h on JD 301, offset from maximum ditch water level by 1 hour. The maximum pH determined from monitoring of ditch water during this period was similar to the average pH for River Yare samples in 2002 determined by the Environment Agency (8.03). Ditch-water pH fell sharply during the falling limb of the pulse, returning to approximately 7.30 by 1800 h on JD 302.
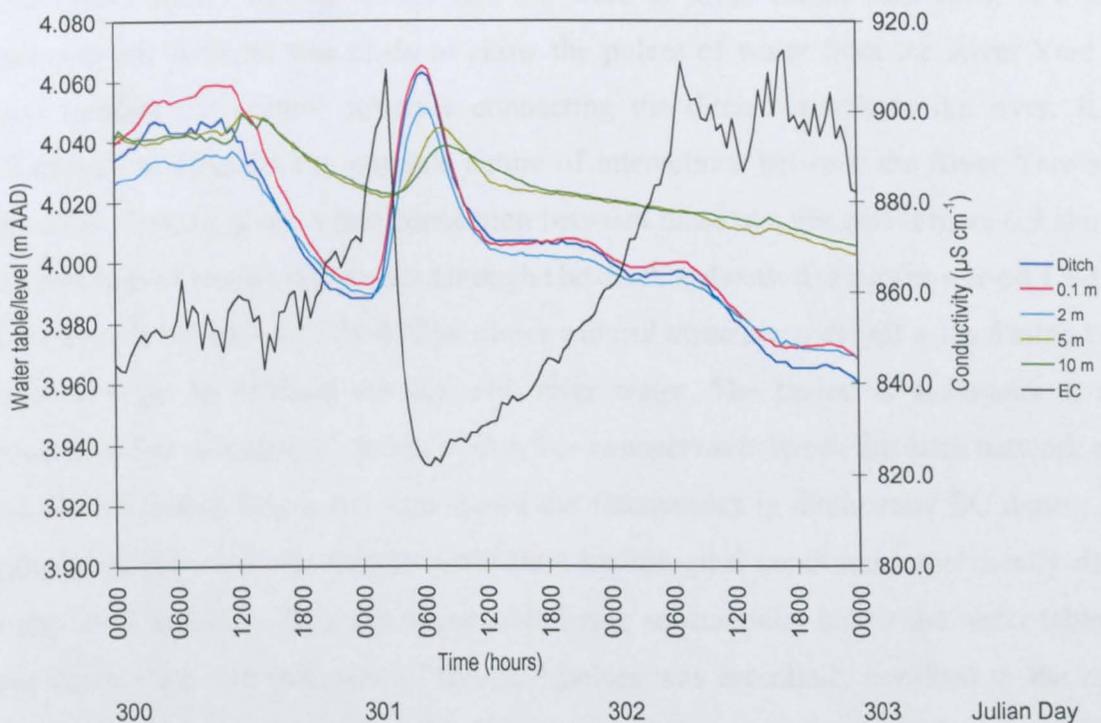
Figure 6.8 Variation in ditch-water EC during the passage of a tidal pulse delivering water directly from the River Yare, JD 300-303.

In a similar manner to the pulse shown in Figure 6.7, the pulse on JD 301 was transferred for at least 10 m into the fen through sub-surface exchange. From 0600 h on JD 301, water level in the ditch network began to fall. Until 1300 h on JD 301 the

decline was rapid, as the tidal pulse drained out of the ditch network and into the River Yare. This rapid fall in ditch water level was matched by near simultaneous falls in the fen water table for at least 2 m from the ditch edge. From 1300 h on JD 301 until the end of JD 302, there was a more gradual decline in ditch water level and fen water table, with a water-table gradient driving shallow ground water flow from the fen into the ditch network throughout this period. Coincident with the beginning of the rapid decline in ditch water level, ditch-water EC increased significantly, likely as a result of the input of solute-enriched pore water to the ditch network. The rise in ditch-water EC continued after the falling limb of the pulse had passed, indicating that the water-table gradient established between the fen and the ditch continued to result in the delivery of shallow ground water to the ditch network. Ditch-water EC rose to reach a more stable level of approximately 900 μS cm^{-1} by 0700 h on JD 302, which was maintained until the end of JD 302. The period of stable EC readings may reflect the typical EC of pore water being delivered to the ditch network during this time.

The events shown in Figures 6.7 and 6.8 were to some extent controlled, in that a management decision was made to allow the pulses of water from the River Yare to pass through the control structure connecting the ditch network to the river. It is interesting to consider the possible nature of interactions between the River Yare and the ditch network given a free connection between these two systems. Figure 6.9 shows the passage of three tidal pulses through the ditch network during the period 13-15th December 2002 (JD 347-349). The sluice control structure was left open during this time to begin to re-flood the fen with river water. The period is analogous to the situation of an unmanaged system with a free connection between the ditch network and the river channel. Figure 6.9 also shows the fluctuations in ditch-water EC during the passage of these pulses. Due to antecedent hydrological conditions, specifically ditch water level and near-ditch fen water table being substantially below the water table in the fen interior, the influence of the tidal pulses was essentially confined to the zone within 2 m of the ditch edge. Monitoring of ditch-water pH showed only minimal fluctuations during the passage of the three tidal pulses, suggesting that the pulses were not dominated by river water, at least in the monitored section of the ditch network.

The patterns of change in ditch-water EC were essentially identical to those described in Figures 6.7 and 6.8, namely a sharp decrease in EC during the rising limb of the pulse, followed by increases in EC as shallow ground water was transferred from the fen into the ditch network. The magnitude of EC change in the ditch network appeared to be dependent on the magnitude of the tidal pulse. For the second pulse, peaking at 2330 h on JD 347, the rising limb increased ditch water level by 2.2 cm with a corresponding decrease in EC of 14 μS cm^{-1}. The falling limb of this pulse decreased ditch water level by 1.7 cm, with a rise in EC of 27.6 μS cm^{-1}. This contrasts with the final pulse, peaking at 1130 h on JD 348, with a rising limb that increased ditch water level by 4.3 cm, leading to a decrease in EC of 65.2 μS cm^{-1}. The falling limb of this latter pulse resulted in a decrease in ditch water level of 3.8 cm, and a corresponding increase in EC of 69.7 μS cm^{-1}. The magnitude of the tidal pulse will determine the volume of water involved in the rising limb of the pulse, and the magnitude of the subsequent falling limb will influence the volume of shallow ground water that is transferred from the fen into the ditch network. Both factors will contribute to the size of the fluctuations observed in ditch-water EC during the passage of the tidal pulse.
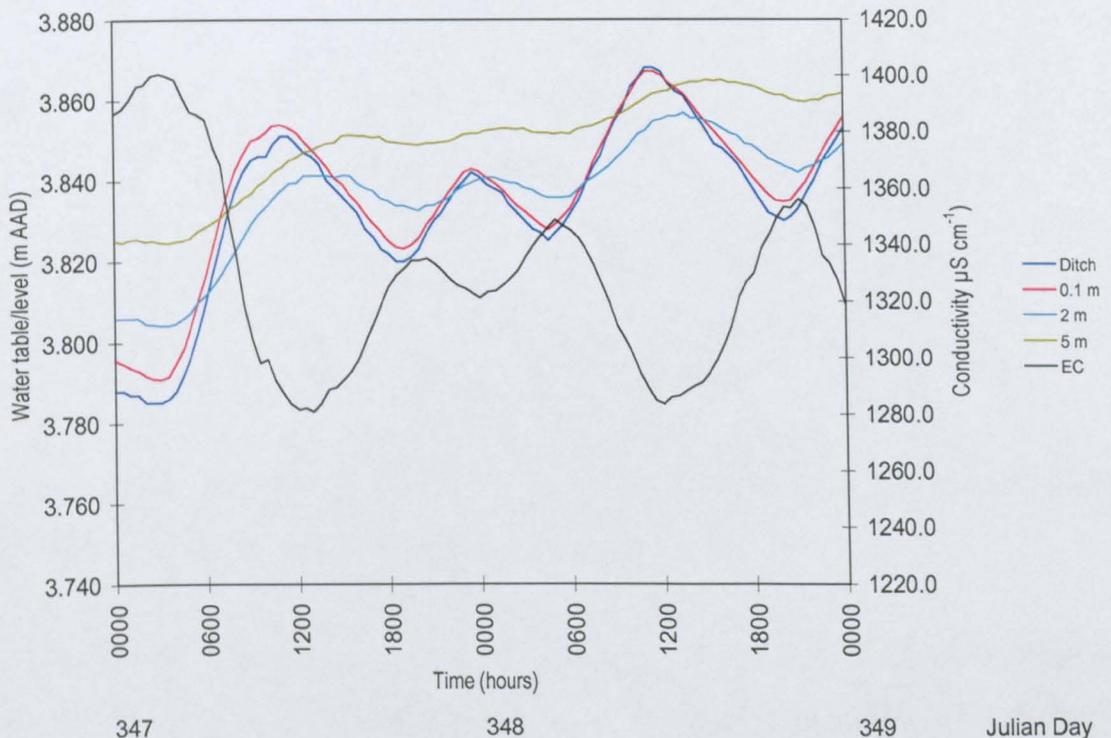
Figure 6.9 Tracing fluctuations in ditch-water EC during the passage of three tidal pulses JD 347-348, analogous to a free connection between the ditch network and River Yare.

Managed discharge

The control of fen water-table position at Strumpshaw is one of the major strategies used in the hydrological management of this floodplain wetland. The ditch network is used to manipulate the fen water table, either by allowing the ingress of river water through the ditch network and into the peat (Figures 6.7-6.9), or by lowering the fen water table by rapidly draining ditch water into the River Yare. Figure 6.10 shows the results from the monitoring of ditch water level, fen water table and ditch-water EC, during a period of managed drawdown of the fen water table. The data cover the period from 15-27th November 2002 (JD 319-331), during which time ditch water level fell from approximately 4.10 to 3.85 m AAD.
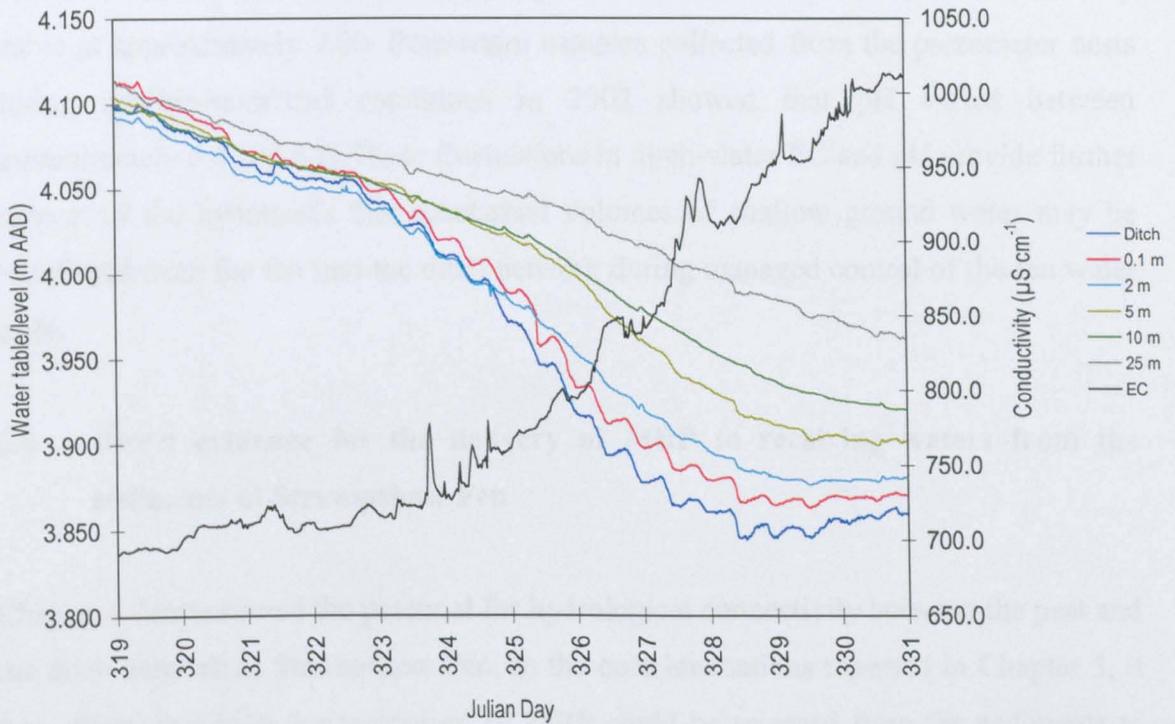
Figure 6.10 Using ditch-water EC to trace the delivery of fen pore water during managed drawdown of water tables, JD 319-331.

The hydrological details of the period of drawdown have been examined in Chapter 4 (see Figure 4.16 and associated discussion). During the input of surface water to the ditch network (approximately 0000 h JD 319 – 1900 h JD 320), ditch-water EC increased by approximately 20 μS cm^{-1} to a maximum of approximately 712 μS cm^{-1}, confirming the findings from field samples that surface water above the peat column had a typical EC of approximately 700 μS cm^{-1}. That the fen water-table elevation after 1900 h on JD 320 appears to be dependent on proximity to the ditch indicates that the

water table had fallen below the peat surface, and that sub-surface exchanges were prevalent involving the delivery of shallow ground water into the ditch network. The development of water-table gradients between shallow ground water in the fen and open water in the ditch network resulted in a substantial and prolonged increase in ditch-water EC, indicating the delivery of solute-enriched pore water to the ditch network. During the period 1900 h on JD 320 to 0000 h on JD 331, ditch-water EC increased by some 300 μS cm^{-1} to reach a maximum of over 1000 μS cm^{-1} by the end of the monitored period. Between 1200 h on JD 328 and 0000 h on JD 331, when ditch water level remained relatively constant, ditch-water EC continued to increase, indicating that the water-table gradient during that period maintained the delivery of pore water into the ditch network. Ditch-water pH fell from approximately 7.30 on JD 319 to 6.90 at the end of JD 325. From JD 326 onwards, pH in the ditch network remained relatively stable at approximately 7.00. Pore-water samples collected from the piezometer nests during surface-inundated conditions in 2002 showed that pH varied between approximately 6.4 and 6.9. These fluctuations in ditch-water EC and pH provide further support to the hypothesis that substantial volumes of shallow ground water may be transferred from the fen into the ditch network during managed control of the fen water table.

6.6 Direct evidence for the delivery of MRP to receiving waters from the sediments at Strumpshaw Fen

Chapter 4 demonstrated the potential for hydrological connectivity between the peat and the ditch network at Strumpshaw Fen. In the core incubations reported in Chapter 5, it was shown that high concentrations of MRP could be released from the sediments to pore water and surface water. Analysis of field-derived samples reported in Section 6.4 of this current chapter supported the hypothesis that the sediments at Strumpshaw Fen have the potential to act as sources for P. In Section 6.5 of this chapter it was demonstrated, through EC tracing, that the hydrological connectivity identified in Chapter 4 has the potential to deliver solute loads to the ditch network. To provide a final link between these strands of investigation, the MRP concentrations in samples from the ditch network were monitored during periods when water-table gradients supported the delivery of shallow ground water from the fen into the ditch network. Samples were collected during two separate events, the rainstorm event during JD 252-

255 (Figure 6.5) and the tidal pulse from the River Yare during JD 300-303 (Figure 6.8).

Figure 6.11 shows the variation of MRP in ditch-water samples during the period JD 252-254 that includes the rainstorm event on JD 252. It is clear that, coincident with the development of water-table gradients driving the delivery of pore water into the ditch network, concentrations of MRP rose considerably. Prior to the beginning of rainfall at 0630 h on JD 252, concentrations of MRP were consistently below 0.10 mg l^{-1} P. Concentrations of MRP rose substantially whilst water-table gradients existed between the fen and the ditch network. MRP concentration reached a maximum of 0.27 mg l^{-1} P at 0800 h on JD 253. Subsequently, MRP concentration fell gradually to a minimum of 0.19 mg l^{-1} P at the end of the monitored period at 0000 h on JD 255.
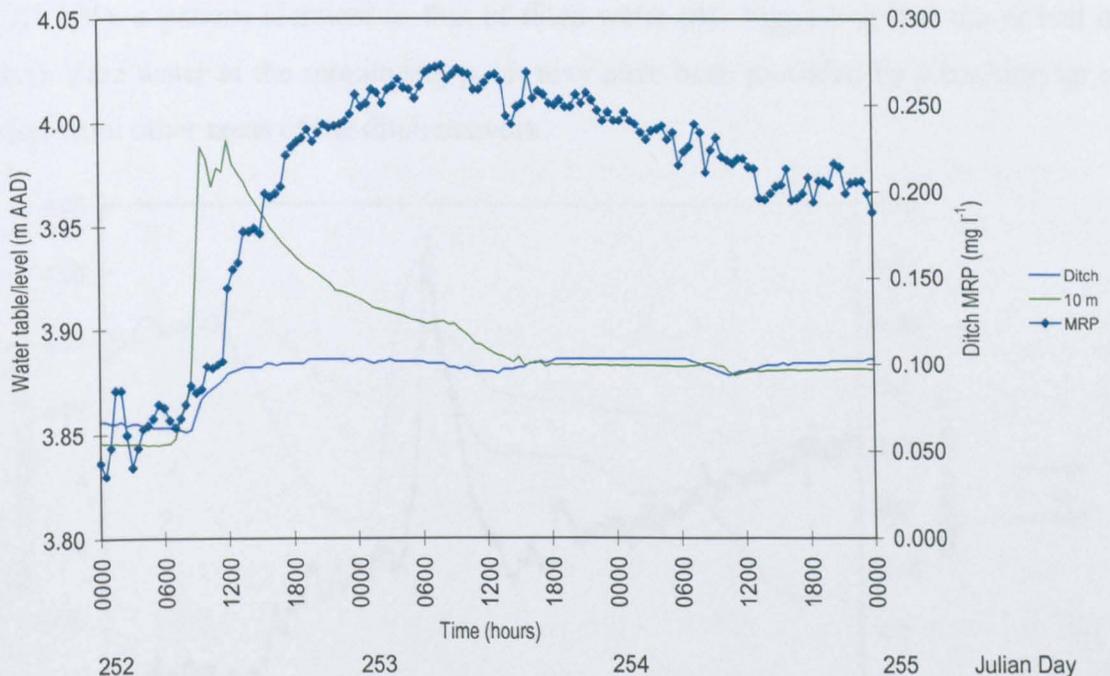
Figure 6.11 The delivery of MRP to the ditch network following a rainstorm event, JD 252-254.

Figure 6.12 shows the concentration of MRP in ditch-water samples during the passage of the tidal pulse from the River Yare during JD 301. From the beginning of the monitored period to 1200 h on JD 300, the concentration of MRP in ditch-water samples remained consistently below 0.10 mg l^{-1} P, and averaged 0.06 mg l^{-1} P. Preceding the pulse itself, there was a period of some 12 hours, from 1200 h on JD 300 to 0000 h on JD 301, when the drainage of ditch water into the River Yare led to the development of water-table gradients driving the delivery of fen pore water to the ditch

network. Coincident with the development of these gradients, the concentration of MRP in ditch-water samples increased steadily, reaching a maximum of over 0.15 mg l^{-1} P by 0000 h on JD 301. From 0100 h to 0600 h on JD 301, ditch water level rose in response to the input of water from the River Yare. Samples of ditch water indicated that the concentration of MRP in the ditch network increased rapidly during this period, reaching a maximum of 0.42 mg l^{-1} P at 0700 h on JD 301. The peak concentration of MRP in ditch samples was similar to the average MRP concentration determined in samples collected from the River Yare during the late summer and autumn of 2002 (0.52 mg l^{-1} P, n = 6) and, in combination with increasing ditch-water pH during the rising limb of the pulse (see Section 6.5), provides support to the hypothesis that water from the River Yare reached the monitoring point in the ditch network. The peak concentration of MRP was offset by 1 hour from the maximum ditch water level (0600 h JD 301), a pattern identical to that of ditch-water pH, suggesting that the arrival of River Yare water at the monitoring point may have been preceded by a backing up of water from other areas of the ditch network.
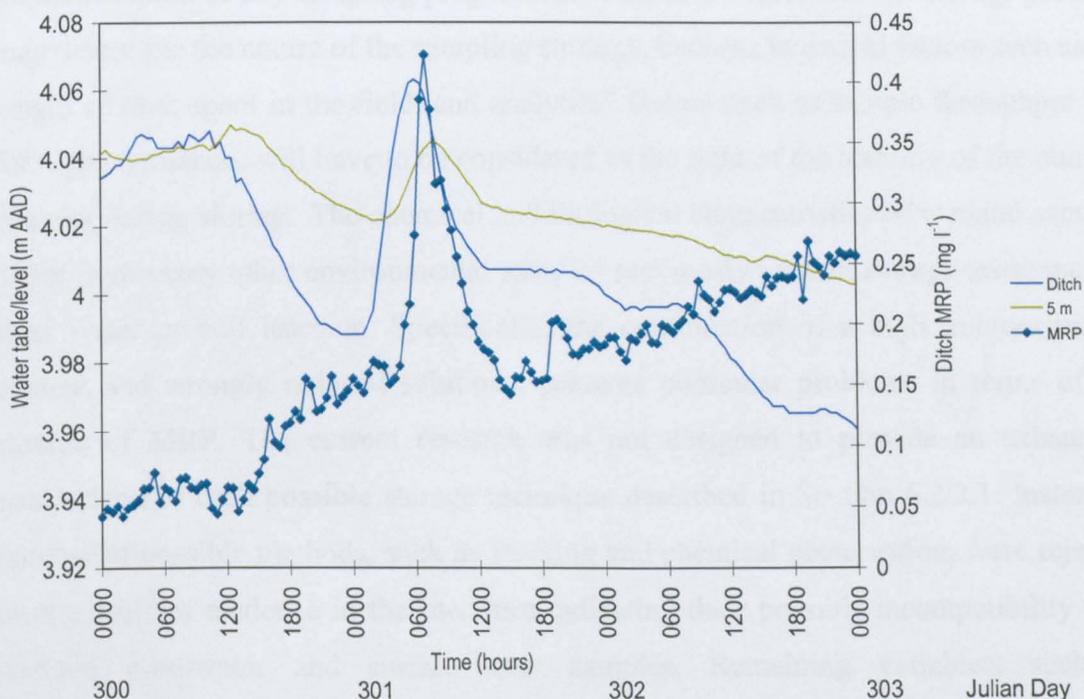
Figure 6.12 The fluctuation in ditch-water MRP concentration during the passage of a tidal pulse from the River Yare and pore water delivery to the ditch network, JD 300-302.

As ditch water level fell rapidly between 0600 h and 1330 h on JD 301, the concentration of MRP in samples collected from the ditch network also decreased

substantially as River Yare water was flushed from the ditch network, reaching a minimum of 0.14 mg l^{-1} P at 1500 h on JD 301. As the drainage of ditch water into the River Yare continued, water-table gradients driving the delivery of fen pore water to the ditch network were re-established. From 1500 h on JD 301 to 0000 h on JD 303, the concentration of MRP in ditch-water samples rose steadily, reaching 0.26 mg l^{-1} P by the end of the monitored period, as P-enriched pore water was delivered to the ditch network.

6.7   Discussion

6.7.1   The stability of MRP in wetland water samples

The data provided in this chapter represent one of the few examples of an analysis of the stability of MRP in wetland samples during storage. Gardolinski *et al.* (2001) state that it is essential to design a site-specific storage protocol for nutrients prior to the implementation of any sampling programme. Indeed, the results of the storage protocol may determine the nature of the sampling strategy, because logistical factors such as the length of time spent in the field, and analytical factors such as sample throughput rate for a given method, will have to be considered in the light of the stability of the nutrient element during storage. The chemical and biological characteristics of wetland samples differ from many other environmental samples previously used in storage tests, such as river water or soil leachate. Specifically, the combination of a high microorganism content and strongly reduced solutions, presents particular problems in terms of the storage of MRP. The current research was not designed to provide an exhaustive comparison of each possible storage technique described in Section 6.2.2.1. Instead, a number of possible methods, such as freezing and chemical preservation, were rejected on the basis of evidence in the literature indicating their possible incompatibility with wetland pore-water and surface-water samples. Remaining variables, such as refrigeration and iodine treatment, were then tested using samples from Strumpshaw Fen to develop a site-specific storage protocol.

With respect to MRP, time was the most significant factor affecting sample degradation. No sample treatment used in this study was able to prevent significant degradation in MRP concentration beyond 72 hours of storage. Therefore, sampling and analytical protocols for Strumpshaw Fen were designed to ensure MRP analysis was conducted

within 3 days of sample collection. However, beyond 72 hours of storage it was shown that both refrigeration at 4 °C, and iodine pre-treatment of bottles, had a positive effect on sample preservation. Consequently, these treatments were applied to sample bottles to guard against changes to MRP concentration in the time between collection and analysis. Other cation and anion elements were found to be more stable than MRP, and the analytical sequence used in this research was designed to reflect these findings.

6.7.2   The phosphorus status of Strumpshaw Fen at the field scale

Samples collected from Strumpshaw Fen indicated that under surface-inundated conditions phosphorus may be released from the sediments into pore water and surface water. Concentrations of MRP were indicative of exceeding thresholds at which hypereutrophic conditions might be anticipated in receiving waters, reaching almost 5 mg l^{-1} P in pore water and over 0.25 mg l^{-1} P in surface water. Only a limited number of other studies have investigated the concentrations of MRP present in wetland pore water and surface water under field conditions. Soto-Jimenez *et al.* (2003) extracted pore water by centrifugation from sediment cores collected from an intertidal marsh flat in the Chiricahueto marsh in Mexico. The system had been affected by nutrient loading through runoff from adjacent agricultural land and pore water was P-enriched, containing a maximum of 15 mg l^{-1} P in 0.8 μm filtrates from a depth of approximately 8 cm below the sediment surface. Surface-water samples from the Chiricahueto Marsh contained an average of 0.17 mg l^{-1} P as orthophosphate. Mayer *et al.* (1999) used in-situ pore-water samplers to examine profiles of P in the interstitial water below a shallow pond system in the Point Pelee Marsh, Canada. They found concentrations of MRP in 0.45 μm filtrates up to 4 mg l^{-1} P at 10 cm depth, ascribing the high P concentrations to the release of phosphorus during organic matter decomposition. Concentrations of total phosphorus in surface-water samples reported by Mayer *et al.* were approximately 0.23 mg l^{-1} P. Chambers and Odum (1990) used suction samplers to collect pore water from tidal freshwater marshes along the Chickahominy River in the USA. In 0.45 μm filtered pore-water solutions they found concentrations of MRP over 5 mg l^{-1} P, whilst in surface-water samples concentrations were generally below 0.1 mg l^{-1} P. The results from analyses of samples collected from Strumpshaw Fen are in agreement with findings from previous research indicating a tendency for concentrations of MRP in pore water to be substantially above that in surface waters, suggesting that release from the sediments is the major source of MRP in this system.

6.7.2.1 Colloidal-P and free orthophosphate in pore-water samples

Sequential filtration elucidated the speciation of P in pore-water samples from Strumpshaw Fen. Considering all samples from 25th June 2002 that were 0.02 μm filtered on return to the laboratory, over 92 % of the MRP concentration in 0.45 μm filtrates remained after filtration through 0.02 μm filter papers. Hens and Merckx (2002) provided evidence that free orthophosphate was the only MRP species present in 0.02 μm filtrates of grassland, arable, and forest soil solutions. Direct evidence that free orthophosphate was the only MRP species present in 0.02 μm filtrates of pore water from Strumpshaw Fen was beyond the scope of this study. However, speculating that the findings of Hens and Merckx are applicable to samples of wetland pore water, the data indicate that less than 8 % of the MRP present in 0.45 μm filtered solutions was colloidal. The analysis of 0.45 μm filtered samples that were spiked with free orthophosphate indicated that ≥ 95 % of added P was transferred through the 0.02 μm filter paper. However, in only 5 of the 21 samples analysed was 100 % recovery of the spiked orthophosphate observed. This suggests that either added P was rapidly bound to the colloidal size fraction and subsequently retained on the 0.02 μm filter paper, or that filter papers became clogged and did not allow free orthophosphate to pass through. Despite keeping filter paper loadings low in an attempt to minimise clogging, visual observation indicated that a green-grey gel-like material was retained on the 0.02 μm papers. If this gel clogged pores in the filter paper and prevented the transfer of free orthophosphate, then a proportion of the difference in MRP concentration between 0.45 μm and 0.02 μm filtrates may be attributed to filter paper clogging, rather than to the presence of colloidal-P. Consequently, the maximum figure of 8 % given above may be an over-estimation of the true colloidal-P content of pore-water samples from Strumpshaw Fen. However, without further analysis of the gel this conclusion remains speculative.

The finding that the vast majority of MRP in pore-water samples from Strumpshaw Fen may have been present as free orthophosphate, suggests a source of immediately bioavailable P. Although colloidal phosphorus may represent P that is potentially available to microorganisms over longer timescales (Shaw *et al.*, 2000; Jones *et al.*, 1993), only orthophosphate is considered to be directly available and rapidly consumed by bacteria and algae (Zhang and Oldham, 2001; Robards *et al.*, 1994).

The data reported in this chapter represent one of the first attempts in wetland science to examine the speciation of the fraction of total phosphorus termed 'dissolved' P, and specifically to attempt to partition the MRP concentration in 0.45 μm filtered solutions into colloidal-P and free orthophosphate. The major finding, that colloidal-P may represent only a small proportion of MRP in 0.45 μm filtered pore-water samples, contrasts with a number of other studies conducted in different environments. Hens and Merckx (2002) found that as much as 58 % of the MRP in 0.45 μm filtrates of soil solution from a grassland soil in Belgium was attached to colloidal-sized material between 0.45 and 0.025 μm in size. Baldwin (1998) determined that < 20 % of reactive P in 0.1 μm filtered samples from a eutrophic shallow lake in Australia was free orthophosphate, the remaining 80 % being the result of the hydrolysis of organic P or P attached to inorganic and organic colloids during analysis. Zhang and Oldham (2001) found that a significant proportion of the reactive P determined on 0.50 μm filtered solutions collected from a series of shallow lakes in Australia was in fact associated with the acid hydrolysis of colloidal-P.

Various authors have discussed the formation of colloidal-sized humic substance (HS)-metal-P associations (e.g. Hens and Merckx, 2002; Shaw *et al.*, 2000; Jones *et al.*, 1993). Colloidal-P may also take the form of P sorbed to Fe- or Al-oxides, in the matrix of suspended solids, or present in microorganisms (Hens and Merckx, 2002; Buffle and Leppard, 1995). The analytical conditions of the MRP assay may lead to the release of P from the colloidal fraction. The hydrolysis of organic- and condensed-P bonds driven by acid or transition metal concentrations, alongside the dissolution of metal-P bonds under the acidic conditions associated with MRP analysis, may release free orthophosphate into solution, thereby leading to an overestimation of the true orthophosphate concentration in the sample (Hens and Merckx, 2002; Baldwin, 1998).

No evidence was found to support the over-estimation of orthophosphate concentration during the analysis of pore-water samples from Strumpshaw Fen, indicating that either colloidal forms of P were largely absent from the samples, or that the conditions associated with the MRP assay did not lead to the release of orthophosphate into solution from colloidal-P. No direct attempt was made to determine the HS content of the pore water collected from Strumpshaw Fen, although visual inspection indicated a number of the samples were coloured. Given the high concentration of iron in many of the pore-water samples, it was surprising to find evidence suggesting that HS-Fe-P

associations were not abundant in the samples from Strumpshaw Fen. Hens and Merckx (2002) and Jones *et al.* (1993) suggest that as sample pH decreases, so does the predominance of colloidal-P. This was attributed to increased competition for binding sites between H^+ and Fe or Al, thereby preventing the establishment of HS-metal-P complexes, or to the instability of these complexes under low-pH conditions. However, the range of pH in the pore-water samples collected from Strumphsaw Fen during 2002 (6.75-6.44), means that low pH is unlikely to explain the apparent lack of a large colloidal-P component in the samples. None of the research described previously in the literature has dealt with the formation of HS-metal-P associations in reduced samples, such as those extracted from the piezometers at Strumpshaw Fen. The findings reported in Chapter 5, and those discussed below relating to Fe-P correlations in field-derived samples, suggest that reductive-dissolution was the major process leading to the release of MRP to pore water at Strumpshaw Fen. It is possible that reductive-dissolution of Fe-P complexes in the field maintained the majority of MRP in the form of free orthophosphate in pore-water samples. Stewart and Wetzel (1981), cited in Jones *et al.* (1993), suggested that high concentrations of dissolved calcium could inhibit the formation of HS-metal-P associations. This was attributed to the selective loss of greater molecular size dissolved humic substances, to which iron preferentially binds, with increasing c alcium concentration. Dissolved calcium concentrations in the pore-water samples collected from Strumpshaw Fen on 25th June 2002 were high, varying between 69 and 248 mg l^{-1} in the 21 samples collected, suggesting that Ca^{2+} concentrations may have been a factor inhibiting the formation of HS-metal-P colloids in pore-water samples from Strumpshaw.

Baldwin (1998) demonstrated that both commercially-available organic P compounds, and organic P in environmental samples, may be prone to hydrolysis and release of orthophosphate during MRP analysis. The data from Strumpshaw Fen, showing no significant differences between the concentrations of MRP in 0.45 μm and 0.02 μm filtrates, suggest that the hydrolysis of organic P during the analysis of pore-water samples was negligible, and are, in this respect, in agreement with the findings of Ivanoff *et al.* (1998). It is possible that the short reaction time used in the automated FIA methodology (< 10 seconds during which sample and reagents are mixed prior to measurement of sample absorbance) minimised the potential for hydrolysis of organic P during the MRP assay.

6.7.2.2 Translating laboratory mesocosm studies to the field scale

One of the aims of this current chapter was to determine if the findings from the laboratory mesocosm studies reported in Chapter 5 translated to the field scale. Specifically the availability of phosphorus, and the relationship between MRP and Fe^{2+} in pore-water and surface-water samples collected from the field was investigated, and qualitatively compared with data from the laboratory core incubations. The analysis of field-derived samples confirmed that substantial concentrations of MRP were released to, and maintained in, solution under flooded conditions at Strumpshaw Fen. By installing piezometers in the field at depths that corresponded with those used in the mesocosm work, it was possible to establish that the pattern of MRP concentration with depth in the surface 50 cm of peat that was identified during laboratory core incubations was also present at the field scale (see Table 6.2). Encouragingly, both the spatial pattern of Fe^{2+} concentration in the surface 50 cm of peat, and the strong correlation between Fe^{2+} and MRP observed during core incubations, were confirmed in field-derived samples (see Section 6.4 and Figure 6.4).

Despite this level of agreement, a number of differences were identified between samples collected at the two different spatial scales. Firstly, in the vast majority of samples, MRP and Fe^{2+} concentrations from laboratory core incubations were considerably lower than in corresponding samples collected from the field. With respect to samples from Experiment A, this likely reflects the lack of phosphorus in the solution used to flood the cores in the laboratory. This contrasts with the situation at the field scale where flooding usually involves the input of P-enriched water from the River Yare (see Section 4.4.1.2). In samples from Experiment B, the difference may reflect the fact that the presence of NO_3-N in the flooding solution delayed the onset of the reductive-dissolution of Fe-P complexes. As a consequence, insufficient time had elapsed by the end of the core incubations for P concentrations to reach the levels determined in field-derived samples collected from sediments that had been submerged for several months.

Secondly, concentrations of MRP in surface-water samples from the core incubations (0.64 to 0.80 mg l^{-1} P) were greater than observed in surface water collected from the field (0.20 to 0.38 mg l^{-1} P). This may reflect the fact that surface water became more strongly reduced during the core incubations than typically occurs under field conditions, thereby supporting increased concentrations of MRP in solution. Ahn and

Mitsch (2002) found lower dissolved oxygen concentrations and redox potential in the surface water of mesocosm wetlands (surface area 1 m^2) compared to the field scale (10 000 m^2), and suggest that this may be associated with the absence of surface turbulence, and therefore oxygen diffusion, in the surface water of their mesocosms. In the light of these findings, the concentrations of MRP reported in surface water during the core incubations (see Sections 5.3.3.1 and 5.3.4.1) may be maximum estimates, which may occur given strongly reduced conditions in surface water at the field scale. These findings highlight the importance of considering the reduced system complexity inherent in small-scale laboratory studies when attempting to translate findings to the field scale. The data reported in Chapter 5 do provide an invaluable qualitative assessment of the P status of Strumpshaw Fen at the field scale, but in absolute terms appear to have limited accuracy.

The availability of MRP in deeper pore water (below 50 cm) provides an indication of the implications of high MRP concentration in the near-surface zone. At sample sites relatively close to the ditch network (2 and 10 m), concentrations of pore-water MRP and Fe^{2+} at depths below 50 cm were much lower than in the upper 50 cm of peat (usually by at least an order of magnitude). Concentrations of MRP decreased between samples collected at 102.5 and 202.5 cm depth, and again between 202.5 and 402.5 cm, reaching less than 0.1 mg l^{-1} P towards the base of the peat profile compared with over 4 mg l^{-1} P in pore water from 17.5 cm depth. These findings indicate that, compared with the upper 50 cm of peat, that at greater depth is unlikely to contain a store of P in a form that is released to, and maintained in, solution. Despite this, concentrations of MRP over 0.2 mg l^{-1} P were still observed in samples from 202.5 cm depth in piezometer nests at 2 and 1 0 m f rom t he d itch e dge. T hese relatively h igh concentrations o f MRP a t s uch depth in the peat profile may reflect ground-water flow from the near-surface deposits into deeper peat, in response to downward-acting vertical hydraulic gradients. Although Section 4.4.2 provides little evidence to support the large-scale recharge of deeper ground water in the Yare Valley Formation with fen pore water, downward-acting vertical gradients through the peat profile were observed immediately following rainfall at the site. These gradients may have supported the movement of P-enriched near-surface pore water to greater depth in the peat profile. Alternatively, diffusion of phosphorus from the near-surface zone towards deeper peat may have resulted in P-enrichment of pore water below 1 m.

Samples collected from 102.5, 202.5 and 402.5 cm depth in the fen interior (100 m from ditch edge), contained considerably higher concentrations of MRP and Fe^{2+} than samples from corresponding depths at 2 and 10 m from the ditch edge. It is unlikely that peat at 402.5 cm depth, towards the base of the peat profile, contained a sufficiently large store of phosphorus or iron to generate MRP concentrations in pore water over 1 mg l^{-1} P and Fe^{2+} concentrations over 3 mg l^{-1}, by direct release into solution. Further, pore-water samples extracted from piezometers in the surface 50 cm of peat did not indicate that MRP or Fe^{2+} concentrations at 100 m from the ditch edge were higher than at 2 or 10 m. Therefore, if near-surface pore water is the source of the enrichment of deep pore water in the fen interior, a greater volume of water may move into the deeper peat at 100 m from the ditch edge compared to 2 or 10 m. This may be explained by the radial pattern of ground-water flow that is likely to be generated during the lateral delivery of shallow ground water to the ditch network. A radial flow pattern would produce a stronger downward-acting vertical component in the fen interior compared to the near-ditch zone (e.g. Beckwith *et al.*, 2003b; Fetter, 2001). Although the vertical flow component would remain relatively small in absolute terms, over a long time scale it would have the potential to increase the concentrations of MRP and Fe^{2+} found in deeper pore water. Alternatively, the long-term diffusion of MRP and Fe^{2+} from the near-surface may explain the elevated concentrations of these elements in deeper pore water. The vertical diffusive flux would be reduced in the near-ditch zone where lateral advection into the ditch network predominates. However, further data is needed to evaluate these hypotheses linking the concentrations of P in solution with ground-water flow patterns and diffusive fluxes.

6.7.3 Hydrochemical evidence for exchanges between the fen and the ditch network

Four principal types of water exchange between shallow ground water in the fen and open-water in the ditch network were identified on the basis of water-table gradients in Chapter 4. Firstly, rainfall rapidly generated large water-table gradients driving the delivery of fen pore water to the ditch network. Secondly, tidal pulses of water from the River Yare drove two-way exchanges of water between the fen and the ditch network. On the rising limb of the pulse, water was transferred from the ditch network into the fen, followed by the drainage of pore water into the ditch as the tidal pulse moved back into the River Yare. Tidal pulses were semi-managed events at Strumpshaw Fen, in that

the ditch network had a controlled connection to the river. However, periods analogous to free connection between the river channel and the ditch network could be identified in the data collected (see for example Figure 6.9). Thirdly, the management of fen water-table position through manipulation of ditch water level supported the prolonged delivery of fen surface water and pore water to the ditch network. Finally, water-table gradients indicating sub-irrigation of the peat by ditch water during summer drawdown conditions were observed.

The current chapter provides evidence of the hydrochemical tracing of a number of these exchanges. Different hydrochemical signatures appear to be associated with individual rainfall events, indicating the delivery of either dilute or solute-enriched shallow ground water to the ditch network. An explanation for this is not immediately obvious. It may be that the different EC signatures reflect varying volumes of pore water-dominated (solute-enriched) versus rainfall-dominated (dilute) water delivered to the ditch network in response to the water-table gradient. Alternatively, the EC patterns may reflect the history of water-table fluctuation prior to the individual rainfall event. The rainfall on JD 355 and 356 (Figure 6.6) was the first substantial input of water to the peat surface following prolonged artificial water-table drawdown over JD 319-331, which lowered the fen water table by up to 25 cm (see Figure 4.16). This period of drawdown may have contributed to the delivery of an initial pulse of solute-enriched water to the ditch network following rainfall. A number of authors have suggested that the drying of soils and sediments may lead to a large nutrient pulse being released to solution on re-wetting (e.g. Turner and Haygarth, 2001; Baldwin and Mitchell, 2000; Qui and McComb, 1995; Haynes and Swift, 1989; Salema *et al.*, 1982). In contrast, the rainfall event in Figure 6.5 followed a period of stable water-table position, where the fen water table fluctuated by no more than 1.5 cm over the 8 days prior to rainfall. However, more research is needed to examine the release of solutes to rainwater percolating through drained peat.

Hydrochemical tracing of tidal pulses from the River Yare suggested that, at a given point in the ditch network, a pulse may be dominated by river water or by water from the interconnected ditch/Broad system that was transferred through the ditch network due to the ingress of river water into near-channel sections of the fen. In terms of the delivery of water to the wetland complex, the data suggest that the River Yare has a more dynamic role to play than simply over-bank flooding events. Indeed, under a

situation of free connection between the river and the ditch network, it would be possible for river water to be input to the peat twice a day through sub-surface exchange with o pen w ater i n t he d itch, d riven b y f luctuations o f w ater l evel i n t he t idal R iver Yare. Given the location of the monitored section of the ditch network in this study, near the upland margin of the floodplain (see Figure 2.2), the findings in the current chapter demonstrate that frequent interactions between different elements of the catchment (channel system and floodplain system) can occur over a wide spatial scale, facilitated by the ditch network. Consequently, the chemical quality of the River Yare, specifically the high P concentration (see Figure 2.5), remains an important factor influencing the chemical status of Strumpshaw Fen.

Hydrological management at Strumpshaw Fen can generate substantial water-table gradients driving the delivery of surface water and pore water into the ditch network (Figure 6 .10). D uring s uch m anaged p eriods o f drawdown, d itch water i s d ischarged directly into the River Yare. Consequently, the chemical status of the ditch water, as influenced by the delivery of shallow ground water from the fen system, will have a direct impact on the chemical status of the River Yare. Combined with the findings described a bove r egarding t he m ovement o f t idal p ulses i nto the r iparian z one, t hese data illustrate the two-way nature of the interaction between the channel and floodplain systems. More specifically, the floodplain should not simply be seen as a sink area receiving inputs of water, sediment and nutrients from the channel system. Instead, the floodplain has the potential to act as a source area for the channel system, through a single point-source connection in the case of the managed Strumpshaw Fen, but through a more dispersed series of inputs under non-managed conditions. Clearly, the impact of the floodplain on the channel system will be dependent on the volume of water delivered from the floodplain relative to the volume carried by the channel system. In the case of Strumpshaw Fen, the managed connection between the ditch network and the River Yare means that the volume of water input to the river from the fen is likely to be relatively small compared with the volume of water carried by the river. Given this, the chemical and ecological effects of solutes exported from the peat are likely to be confined to the ditch network. However, this may not be the case for the floodplains of smaller rivers.

6.7.4   Direct evidence for the delivery of MRP to receiving waters

Evidence from the laboratory core incubations in Chapter 5, and from the analysis of field-derived pore-water and surface-water samples reported in the current chapter, suggests that the sediments at Strumpshaw Fen represent a source for P. Hydrological and hydrochemical monitoring has suggested that two-way transfers of water occur between shallow ground water in the fen and open water in the ditch network. The current chapter also investigated whether these source and transport factors combine to result in the delivery of MRP to the ditch network.

Figures 6.11 and 6.12 both show that significant concentrations of MRP can be delivered to the ditch network from pore water in the fen. During the rainstorm event (Figure 6.11), the MRP concentration of ditch-water samples reached a maximum of 0.27 mg l^{-1} P, reflecting the delivery of P-enriched pore water to the ditch network in response to the water-table gradients developed during rainfall. The ditch network was allowed to drain freely into the River Yare during the period shown in Figure 6.11. As a consequence, MRP in the ditch network had the potential to be delivered to the River Yare. Given that the concentration of MRP in ditch-water samples exceeded the interim standard for 'eutrophic' rivers of 0.2 mg l^{-1} P (Environment Agency, 2000), and that critical concentrations for eutrophication control of surface waters are between 10 and 20 µg l^{-1} P (Heathwaite and Dils, 2000), the delivery of ditch water to the Yare may influence the chemical and, therefore, ecological quality of the river water, although this is clearly dependent on the volume of water delivered (see above). These findings challenge the classical view of wetlands in general, and floodplain fens in particular, as buffer zones protecting the chemical and biological quality of receiving waters, and suggest that the role of floodplain fens in River Basin Management Plans, such as those associated with the EU Water Framework Directive, may need to be reviewed.

Figure 6.12 shows that tidal pulses from the River Yare can deliver high concentrations of MRP to the ditch network, which may subsequently be transferred by sub-surface exchange into the peat (see Figure 6.8). Management of Strumpshaw Fen currently focuses on over-bank flood events as the major input of River Yare water to the wetland, through embankment of the fen to isolate the system from the channel. Although this may be justified with respect to the volume of water exchanged, the present study suggests that sub-surface exchange between open water in the ditch

network and shallow ground water in the fen may continue to deliver high concentrations of MRP to the near-surface peat, the rooting zone for emergent macrophyte species at the site. Both prior to and subsequent to the passage of the tidal pulse in Figure 6.12, MRP was delivered to the ditch network from fen pore water. It is likely that this water was strongly reduced, and that MRP in solution was the result of the reductive-dissolution of Fe-P phases in the sediment (see Chapter 5). It is perhaps surprising that the delivery of pore water rich in Fe and P to the oxidised ditch environment did not result in the oxidation of Fe^{2+} to Fe^{3+}, and subsequent removal of P from solution through scavenging by precipitating ferric iron. High concentrations of total P (~ 1200 mg kg^{-1}) and total Fe (~ 24 g kg^{-1}) in samples of sediment collected from the bottom of the ditch network, suggest that the precipitation of these two elements from ditch water may occur. However, the delivery of pore water rich in HS, Fe and P to the ditch network may have resulted in the formation of HS-Fe-P colloids, which inhibit the co-precipitation of P with ferric iron, thereby maintaining P in solution (Shaw, 1994). Although no conclusive evidence was found to support the formation of such colloids in pore-water samples (see Section 6.4), these analyses were conducted on strongly reduced samples in which iron was present as Fe^{2+}. On delivery to the ditch network, Fe^{2+} may oxidise to Fe^{3+}, thereby promoting the formation of HS-Fe-P colloids. However, the fate of MRP following delivery to the ditch network was beyond the scope of this research, but would form the logical next step in work designed to determine the catchment-scale significance of phosphorus release to solution within floodplain fens such as that at Strumpshaw.

6.8   Concluding comments

The current chapter has shown that laboratory mesocosm work does provide an invaluable description of the MRP status of Strumpshaw Fen at the field scale. Spatial patterns of MRP concentration, and the correlation between MRP and Fe^{2+} release, initially identified in Chapter 5 have been reaffirmed in samples collected from the field. Speciation of MRP in 0.45 μm-filtered samples has shown that the majority of P in these filtrates may be present as free orthophosphate, rather than in colloidal fractions, indicating a source of P that is readily bioavailable. Direct evidence has been provided for the combination of source and transport factors with respect to P at Strumpshaw Fen, resulting in the delivery of MRP to the receiving ditch network. This work highlights the importance of considering both hydrological and hydrochemical

process information when attempting to determine the wider-scale implications of findings from small-scale mesocosm work. These data have achieved the second part of Research Objective 4, and all of Research Objective 5 identified in Section 1.2.

The final chapter in this study provides a summary of the major findings reported in this thesis, and attempts to conceptualise the hydrological and hydrochemical processes involved in the transfers of P at Strumpshaw Fen.

7. SUMMARY AND SUGGESTIONS FOR FURTHER RESEARCH

7.1 Introduction

This chapter presents the major findings of this study into the controls on phosphorus release from riparian wetland sediments, and the hydrological connectivity between different elements of Strumpshaw Fen, a typical managed floodplain fen complex. Section 7.2 identifies the advancements made in the understanding of the hydraulic properties of fen peat and horizontal and vertical exchanges of water within Strumpshaw Fen. Section 7.2 also looks at the biogeochemical controls on P release to wetland pore water and surface water, and the delivery of P to receiving waters through the combination of P availability and hydrological connectivity. Section 7.3 brings together the hydrological and hydrochemical strands from this thesis to produce a conceptual model describing the phosphorus transfers at Strumpshaw Fen. Finally, Section 7.4 highlights the potential importance of this study with respect to the management of this and similar riparian wetlands and identifies several areas for further research.

7.2 Major hydrological and hydrochemical findings

7.2.1 The hydraulic properties of riparian wetland sediments

This study has advanced our ability to assess a fundamental property of wetland sediments, namely the hydraulic conductivity (K). It has improved the understanding of how a commonly-used field method for the determination of K, the piezometer slug test, can be applied reliably to peat deposits. Several aspects of the piezometer test and data analysis procedures require more careful attention than has been given in many previous studies of wetland sediments. For example, pore blocking during insertion tests has

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been identified in the current research as a possible explanation for the common finding that piezometer slug tests in peat apparently underestimate 'true' K. Furthermore, 'anomalous', strongly non log-linear behaviour during some test recoveries has been described, a feature that may be associated with the action of gas bubbles within the peat matrix. That near log-linear recoveries can be gained from piezometer slug tests in peat was encouraging, given that many previous studies have highlighted compressible soil behaviour as a potential barrier to the application of these tests in wetland sediments. In addition, a novel laboratory method for K determination has, for the first time, been applied successfully to fen peat. The method provides a simple yet robust determination of both the vertical and horizontal K, which is particularly useful in peat deposits where the magnitude of anisotropy is often large (e.g. Beckwith *et al.*, 2003a; Schlotzhauer and Price, 1999).

The dual application of the piezometer slug test and the modified cube method to the peat at Strumpshaw Fen has provided one of the first reliable comparisons between field- and laboratory-based K determinations in peat deposits. Particularly encouraging was the remarkable consistency between K values determined by both techniques, providing further support to the conclusion that both are robust methods that provide accurate data. This work, reported in Chapters 3 and 4, contributed to achieving Research Objective 1 identified in Section 1.2 (to characterise accurately the hydraulic properties of near-surface peat deposits).

Tests conducted at both Sutton Fen and Strumpshaw Fen have identified deposits with K values towards the top end of the range of values determined for wetland sediments in general, up to 10^{-2} cm s^{-1}. These findings support the contention made in previous work that the presence of root and rhizome material may lead to high K (e.g. Mann and Wetzel, 2000; Chason and Siegel, 1986). That K is high in the peat at Strumpshaw indicates that, given suitable hydraulic gradients, water may flow readily through the deposits and exchange with other elements of the wetland complex. The anisotropy of K in the deposits at Strumpshaw Fen was found to be far less than often associated with bog peat, and may also be related to the orientation of roots, rhizomes and relict root channels. This study also highlights the potential for K to vary over relatively small spatial scales, reinforcing the need for greater attention to be paid to the characterisation of the hydraulic properties of wetland sediments prior to the interpretation of other hydraulic data including gradients of hydraulic head. This work completed the

achievement of Research Objective 1, and was the fundamental basis to addressing Research Objective 2 (to examine the exchange of water between near-surface wetland sediments and deeper ground water and open water). Without the advances made in this research, features such as insufficient instrument development to remove smeared peat from around the piezometer intake, or pore blocking during insertion tests, may have generated K values that were substantially lower than those reported in Chapter 4. Such low K estimates may have supported the conclusion that there was only a small potential for water exchange through the peat at Strumpshaw Fen, and that consequently shallow ground-water flow was unimportant in this system. Clearly, reliable K estimates are a fundamental requirement in the investigation of water, and therefore solute, movement in wetland sediments.

7.2.2   Exchanges of water through the peat deposits at Strumpshaw Fen

Chapter 4 examined the potential for both vertical and horizontal exchanges of water through the peat at Strumpshaw Fen. Concern has been raised previously regarding the impact of ground-water abstraction on the hydrology of Strumpshaw Fen, a concern common to many wetland systems in which ground water is perceived to be an important water source. This study has found that the direction of vertical hydraulic gradients appears to support the conclusion that abstraction from the Chalk aquifer underlying Strumpshaw Fen has generated a cone of depression in the vicinity of the wetland, resulting in ground-water recharge from surface water and near-surface pore water in the wetland. However, the distribution of hydraulic head within the peat profile was found to be relatively uniform, suggesting that although hydraulic gradients exist between the peat and the underlying mineral aquifer these are not translated into substantial volumes of ground-water flow. It is concluded that a deposit of sufficiently low K exists to minimise the flow of water between the two aquifer units. The location of this deposit is uncertain, but is likely to be either towards the base of the peat profile or at the interface between the peat and the underlying Yare Valley Formation. As a consequence, the peat should be perceived as a perched aquifer, essentially hydrologically disconnected from deeper ground-water formations in terms of the exchange of large volumes of water. In addition, it was found that during summer drawdown conditions in the fen, when evapotranspiration demand was at a maximum, hydraulic head in the underlying mineral aquifer could exceed that in the peat deposits. Again there was little evidence of ground-water flow in response to these gradients

because the distribution of head remained essentially uniform within the peat aquifer. However, it highlights the fact that the impact o f ground-water abstraction at similar sites, where the stratigraphy may not include layers of sufficiently low K to preclude substantial ground-water flow, may be temporally more complex than simply the loss of water from the wetland due to ground-water recharge.

This analysis of the vertical distribution of hydraulic head suggested that the movement of water at Strumpshaw Fen was likely to be dominated by lateral exchanges. This was confirmed by an investigation of the variation in water-table position and the horizontal distribution of hydraulic head. The current study found that the ditch network at Strumpshaw Fen, a feature common to many riparian wetlands, was an important driver of the flow o f shallow ground water in the fen. Water-table gradients supporting the delivery of surface water and pore water from the fen to the ditch network were generated during rainfall events, the falling limb of tidal pulses from the River Yare, and by managed drawdown of ditch water level. Conversely, during the rising limb of tidal pulses or during evapotranspiration-driven drawdown of the fen water table, evidence exists that indicates the transfer of open water from the ditch network to the peat deposits. Importantly, despite management efforts to isolate the fen from the river, this study has shown that both through the ditch network and through over-bank flood events, the River Yare remains an important water source at Strumpshaw, both in terms of the hydrological and hydrochemical functioning of the fen. This work, reported in Chapter 4, achieved Research Objective 2 in Section 1.2 (to examine the exchange of water between near-surface wetland sediments and deeper ground water and open water).

Through combining information regarding water-table gradients with reliable estimates of the hydraulic conductivity of the deposits at Strumpshaw Fen, this study has shown that substantial volumes of water may be exchanged between the shallow ground water in the fen and adjacent open-water systems, up to several thousand litres per day under certain conditions. As a consequence, the chemical quality of fen pore water and surface water has the potential to influence the chemical and ecological quality of the ditch environment.

7.2.3 Factors controlling the release of phosphorus from riparian wetland sediments

Sediment-bound phosphorus

This study has identified the peat deposits at Strumpshaw Fen as containing a substantial store of sediment-bound P (up to 1400 mg kg^{-1} TP), likely as a result of historical nutrient loading from adjacent channel systems. In agreement with many previous studies of wetland deposits, sequential extraction of P from the peat at Strumpshaw Fen has shown that the majority of the TP store is present in organic form. However, a substantial proportion (up to 30 %) is stored as inorganic P, and in particular the role of iron-bound phosphorus has been highlighted. This contrasts with much p revious w ork c onducted i n w etlands t hat s uggests t he l ow m ineral c ontent o f many peats means that the role of iron in P cycling may be negligible. The importance of iron at Strumpshaw Fen is a consequence of hydrological connectivity between the wetland and the adjacent river channel which carries a high particulate iron load. This work addressed the first part of Research Objective 4 in Section 1.2 (to characterise the forms of phosphorus present in a typical riparian wetland sediment).

P release from riparian wetland sediments

Chapter 5 p rovides s ome o f t he first t ime s eries o f p hosphorus r elease f rom r iparian wetland sediments to pore water and surface water, and addresses directly Research Objective 3 (to investigate the processes involved in sediment – pore water – surface water P dynamics). Core incubations using deionised water as a flooding medium showed that P was rapidly released to both pore water and surface water, reaching over 0.6 mg l^{-1} P in surface water and over 2 mg l^{-1} P in pore water by the end of 28 days of sediment submergence. These findings indicate that, given hydrological connectivity, pore water as well as surface water may pose a threat to the chemical, and therefore ecological quality of receiving waters. Phosphorus was released concomitantly with iron, providing evidence of an interaction between the cycles of these two elements in the sediments at Strumpshaw.

Further core incubations used simulated River Yare water as the flooding medium. The P load carried in this simulated river water was rapidly removed from s olution upon

contact with the peat. The timing of the subsequent release of P to pore water and surface water during these core incubations was delayed when compared to corresponding samples from the 'control' cores flooded with deionised water. Further, during incubations with simulated river water the timing of P release to pore water was dependent on depth in the core, with release near to the sediment-water interface delayed compared to samples from greater depth. This produced a concentration gradient that supported the diffusion of P into the surface water. However, the existence of a concentration gradient did not result in the immediate delivery of P to surface water, suggesting a physicochemical control on phosphorus cycling within the sediments. When P release did occur, concentrations reached up to 0.8 mg l^{-1} P in surface water and over 4 mg l^{-1} P in pore water. Phosphorus was again concomitantly released with iron, and at a consistent P:Fe molar ratio in the pore water of approximately 0.46.

Evidence of a store of iron-bound P under oxidised conditions in the sediments at Strumpshaw Fen, alongside the concomitant release of iron and phosphorus to pore water and surface water at a consistent molar ratio following sediment submergence, led to the preliminary conclusion that P release was controlled by the reductive-dissolution of iron-phosphorus complexes. The dominant P:Fe molar ratio of approximately 0.46 indicates that P surface complexed to ferric hydroxide is involved. The importance of iron within the system may also explain the removal of external loads of P from solution upon initial flooding with simulated river water, because ferric iron likely scavenged P from solution during the early stages of the incubations. Consequently, the continued input of eutrophic water from the River Yare to Strumpshaw Fen has the potential to maintain a supply of P that is retained within the peat matrix.

Evidence presented in this study highlights interactions between the cycles of phosphorus, iron and nitrogen in these riparian sediments, a feature rarely elucidated in previous wetlands research. The high concentration of nitrate-nitrogen carried by the River Yare has the potential to poise the redox potential of the sediments at levels above those necessary for iron reduction. Consequently, compared to incubations using deionised water, P release to pore water and surface water was delayed when flooding solutions carried high concentrations of NO_3-N, because all nitrate had to be consumed, likely through denitrification, prior to the onset of iron reduction and associated P release. The delayed timing of P release to pore water close to the sediment-water

interface compared to that at greater depth was due to surface water acting as a prolonged source of NO_3-N which diffused into the near-surface sediments, thereby poising redox potential at a higher level for a longer time than experienced in peat at greater depth.

Direct evidence from sediment analysis for the controls on P release

This study presents direct evidence using the sequential extraction of sediments from Strumpshaw Fen to support the hypothesis that reductive-dissolution of Fe-P complexes controls the release of phosphorus to pore water and surface water. Comparison of the NaOH-P_i content of drained and flooded sediment cores, assumed to represent iron-bound P, confirmed that flooding resulted in a statistically significant decrease in the amount of P stored in this fraction. The magnitude of the decline in NaOH-P_i was correlated with the concentrations of P in pore-water samples at the end of the incubations. In addition, other fractions of the sediment-P pool that may contribute to the release of phosphorus to solution appeared to be relatively stable. In particular, contrasting with some previous studies of wetland sediments, there was no evidence from the deposits at Strumpshaw Fen that flooding resulted in P release from microbial communities. This suggests that the microbial community at Strumpshaw may have been selected to withstand periodic fluctuations between flooded and drained conditions, as a consequence of the 'natural' seasonal water-table range under field conditions in this riparian system.

7.2.4 Combining source and transport factors to investigate solute delivery to receiving waters

Chapter 6 provides evidence showing that the eutrophic conditions established in pore water and surface water during core incubations is representative of the P status at the field scale. Analysis of samples collected from the field indicated that spatial patterns of P concentration in pore water matched those determined from laboratory mesocosm studies reported in Chapter 5. A strong correlation was also established between concentrations of iron and phosphorus in samples from Strumpshaw Fen, with dominant P:Fe molar ratios in these samples of approximately 0.41. These findings correspond well with those described previously from core incubations, and provide further support

to the conclusion that reductive-dissolution of P complexed at the surface of ferric hydroxides is responsible for P release into solution at Strumpshaw Fen.

This study provides some of the first data that attempt to speciate phosphorus in 0.45 μm solutions between 'dissolved' and 'colloidal' fractions. It was found that the majority of molybdate reactive P in samples collected from Strumpshaw Fen was < 0.02 μm, and may be composed of free orthophosphate. This finding is important with respect to the potential ecological consequences of P concentrations in pore water, because P associated with colloidal size fractions is not as readily bioavailable as the orthophosphate ion (Zhang and Oldham, 2001; Shaw *et al.*, 2000). The findings of this study contrast with much other work examining solutions rich in humic substances, iron and phosphorus, which suggests that colloidal-P may dominate. However, factors such as the strongly reduced nature of wetland pore-water samples, and the high calcium concentration in these solutions, may inhibit the formation of colloidal-P. In combination with the analysis of MRP and Fe^{2+} concentrations in field-derived samples, this work achieves the second part of Research Objective 4 (to examine the field-scale availability of P within a riparian wetland).

Chapters 3 and 4 demonstrated that the peat hydraulic conductivity and the water-table gradients developed at Strumpshaw Fen are conducive to the exchange between shallow ground water in the fen and open water in the ditch network. Chapter 6 reports attempts made in this study to provide direct evidence of the hydrochemical consequences of these exchanges, particularly in the light of findings from field and laboratory work on P release to pore water and surface water. Hydrochemical tracing using electrical conductivity signals showed that the water-table gradients generated by rainfall, tidal pulses and managed drawdown, all resulted in the delivery of shallow ground water to the ditch network that could be traced through changes in ditch-water EC. Further, on the basis of combined EC and pH tracing, it was shown that tidal pulses passing through the ditch network could take two forms, dominated either by open-water already present in the ditch/Broad prior to the pulse, or by water from the River Yare. Importantly, this finding demonstrates that the interaction between the fen and the river channel is more dynamic than just large-magnitude, low-frequency over-bank flood events, and that the chemical quality of the River Yare may continue to directly influence the fen across the entire width of the floodplain, via the ditch network.

Demonstrating the links between the hydrological and hydrochemical threads in this study, ditch-water samples were collected during periods when water-table gradients suggested the exchange of water between the fen and the ditch network was likely. These samples were analysed for P to determine if source and transport factors combined at Strumpshaw Fen to deliver phosphorus to receiving waters. It was found that the transfer of shallow ground water from the fen into the ditch network could result in substantial increases in the MRP concentration of ditch-water samples. Rainfall events and drawdown of the ditch network into the River Yare generated water-table gradients that, combined with P-enriched pore water, delivered sufficient quantities of phosphorus to the ditch network that final concentrations could exceed the interim Environment Agency guidelines for eutrophic waters (Environment Agency, 2000). Clearly, source and transport factors can combine at Strumpshaw Fen to export P from the peat matrix at sufficiently high concentrations to threaten the chemical and ecological quality of receiving waters. Tracing of the fluctuations in ditch-water EC, and direct analysis of MRP delivery to the ditch network, achieved Research Objective 5 identified in Section 1.2 (to combine chemical process information on P availability in wetland pore water and surface water with hydrological connectivity, to examine the delivery of P to receiving waters).

7.3 A conceptual model describing the interaction of source and transport factors at Strumpshaw Fen

This study aimed to conduct an integrated hydrological and hydrochemical investigation examining the factors controlling phosphorus exchange between sediment and solution phases at Strumpshaw Fen, and the potential for transport of phosphorus from the peat matrix to receiving waters. Figure 7.1 attempts to combine hydrological and hydrochemical process information in a conceptualised fen-ditch system. Hydrological events supporting the exchange of water between the fen and the ditch network are summarised in blue. On the basis of the hydrological monitoring conducted at Strumpshaw Fen, the direction of exchange is indicated by black arrows in Figure 7.1. No attempt is made to describe the volumes of water involved in the different exchanges. More work is needed before these volumes can be accurately quantified, for example the magnitude of over-bank flooding will vary substantially between individual flood events. Information contained in red describes the likely phosphorus status of water either input to the peat, or transported from the peat to the ditch network. Finally,

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Over-bank flooding from the adjacent river	P concentration is dependent on that in river water

P diffusion into the surface water, given suitably reduced conditions at the sediment-water interface

Rainfall (assuming antecedent water table below the ground surface)

| **Sub-irrigation of the peat** | Low P concentration unless preceded by the input of river water to the ditch network |

Sediment - pore-water P exchange

1) Under oxidised conditions, P is rapidly removed from solution, likely by adsorption to ferric iron in the peat.

2) Following the establishment of sufficiently reduced conditions, P may be released into solution, associated with the reductive-dissolution of Fe-P complexes.

| **Rising limb of a tidal pulse** | P concentration depends on the form of the pulse and the P concentration in river water |

Initially low P concentration in rainfall. P concentration may increase during subsequent percolation of water through the peat matrix

Fate of P following delivery to the ditch network?

a) chemical precipitation
b) formation of colloidal complex
c) consumption by microorganisms
d) export from ditch network

Flow of P-enriched pore water

P concentration depends on water residence time in the peat matrix, strongly reduced pore water is likely to be P-enriched

Managed drawdown of the fen water table

P concentration initially lower than in river water, then increasing with the input of P-enriched pore water

Falling limb of a tidal pulse

Vertical exchanges likely to be minimised by deposits of low K, despite hydraulic gradients between the peat and the underlying mineral aquifer
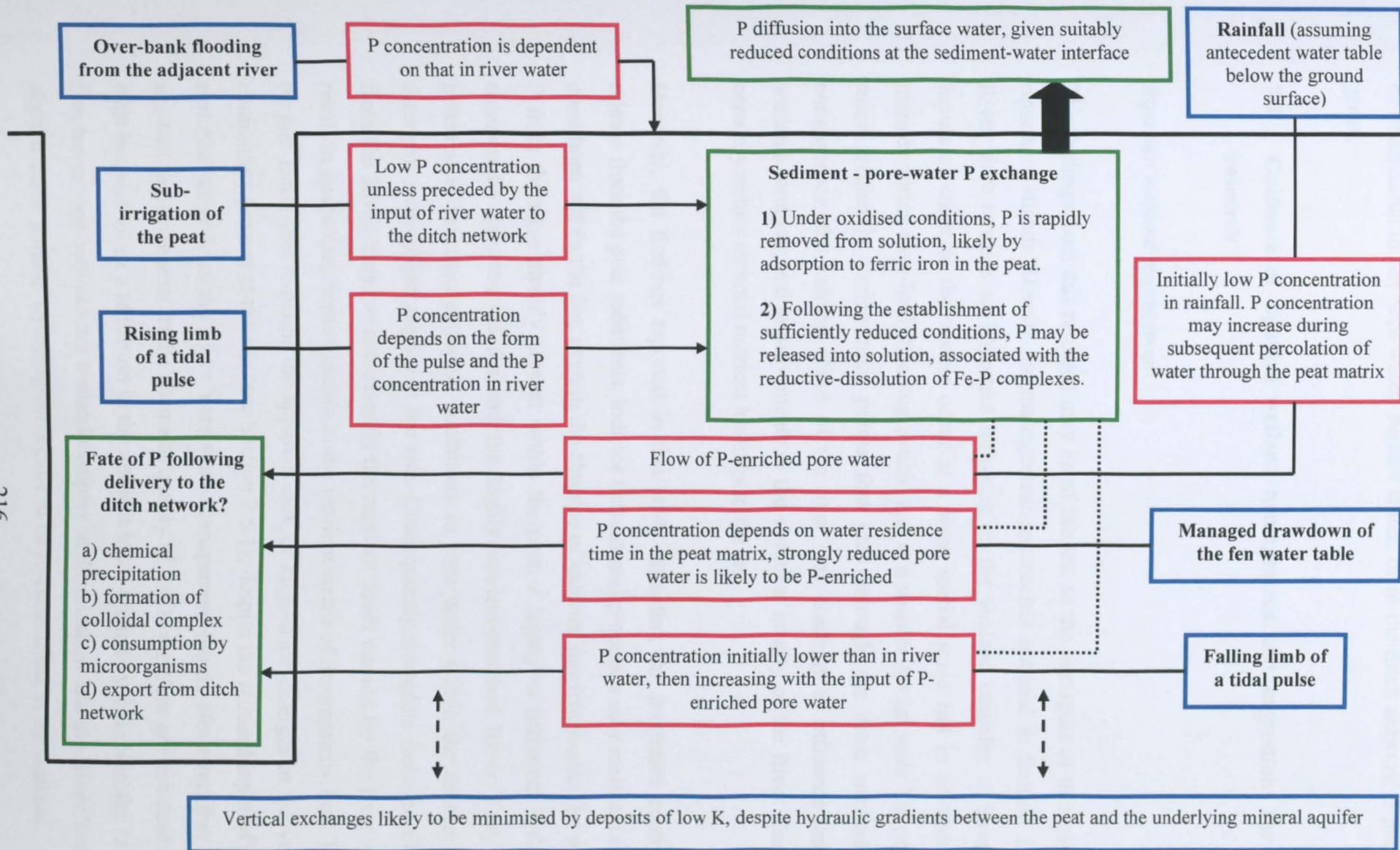
Figure 7.1 Conceptual model describing the transfers of P at Strumpshaw Fen.

biogeochemical process information regarding the factors controlling the concentration of phosphorus in fen pore water, surface water, or in the ditch network is provided in green.

7.4 Guidance of riparian wetland management and suggestions for further research

Riparian wetland management

The findings from this research may be of interest to the managers of this and similar riparian wetlands. Despite the management approaches outlined in Section 2.4.2, the River Yare remains an important influence on the wetland complex at Strumpshaw. Inputs of water to the system occur at a large spatial scale and in an uncontrolled manner during over-bank flooding events, and at a smaller spatial scale but potentially more frequently during tidal pulses that pass through the ditch network. As a consequence, the nutrient status of the river may continue to influence that of the wetland complex, and improvements in the chemical quality of the River Yare would certainly reduce external nutrient loadings to the fen.

However, the findings reported in this study regarding the processes controlling P release from the peat sediments, indicate that internal processes may maintain eutrophic conditions within the fen, even in the absence of external nutrient loads. The release of P from the store already present within the peat, a legacy of historical hydrological connectivity between the fen and the highly nutrient-enriched River Yare, has the potential to maintain eutrophic conditions in pore water within the rooting zone of emergent macrophyte species at the site. Consequently, c omplete isolation of the fen from the River Yare, or decreases in the nutrient loads carried by the river, may not result in immediate improvements in the nutrient status of Strumpshaw Fen. This may be one factor that explains the apparent lack of large-scale changes in the vegetation community present at the site (see Section 2.5.1), despite the reduced input of nutrient-enriched water from the River Yare since management began. However, this is not to say that improvements in the chemical quality of the River Yare are not desirable, not least because given a reduction in the nutrient loads carried by this river, the return of a free connection between the wetland complex at Strumpshaw and the River Yare would allow a more 'natural' hydrological regime to be re-established in the wetland.

Hydrological connectivity between the ditch network and P-enriched fen pore water means that delivery of nutrient-enriched water to the ditch network from the fen is possible at Strumpshaw. Consequently, fen pore water has the potential to influence the chemical and, therefore, the ecological quality of the ditch environment. Management techniques, such as the use of the ditch network to drive the drawdown of the fen water table, may result in the delivery of substantial volumes of eutrophic pore water to the ditch network. In addition, drainage of water from the ditch network into the River Yare has the potential to deliver P-enriched water to the river, although the impact of such delivery will be dependent upon the volume of water exported from the wetland, and is unlikely to be sufficient to influence the chemical quality of the River Yare, given that volumes of water exchanged between the fen and the river are minimised by management of Strumpshaw Fen.

This study has also indicated that there may be no 'natural' connection between the peat aquifer and deeper ground-water formations at Strumpshaw Fen, most probably because of a low K deposit either towards the base of the peat profile, or between the peat and the underlying mineral aquifer, which minimises the actual flow of water. Despite the existence of clear differences in hydraulic head between the peat and the underlying Yare Valley Formation, there is negligible evidence in this study to support the vertical exchange of water in response to these hydraulic gradients. This has important implications for assessing the impact of ground-water abstraction for public water supply on the hydrological functioning of Strumpshaw Fen. Using water abstracted from the Marsh Support Borehole from the underlying Chalk aquifer to compensate for the apparent 'loss' of water from the wetland due to ground-water abstraction (see Section 2.4.1), may in fact be introducing a source of water that was not input to Strumpshaw Fen prior to PWS abstractions. It is however recognised that the potential for water exchange with the underlying mineral aquifer may vary spatially across the entire site. The current study was based in one relatively small area of the total 200 hectare fen, because time and equipment restraints did not allow a wider-scale survey to be conducted. It is possible that the stratigraphy in the area investigated in this thesis may not be spatially continuous. For example, layers of low K that preclude the exchange of large volumes of water between the peat and the Yare Valley Formation may exist in some areas of the wetland complex but be absent in others. Further work would be needed to establish whether the entire wetland complex at Strumpshaw is apparently hydrologically disconnected from deeper ground water.

Suggestions for future research

The combined hydrological and hydrochemical investigation reported in this study has highlighted a number of areas that may provide future research interest. In terms of wetland hydrology, the anomalous behaviour of several piezometer slug tests in the deposits at both Sutton Fen and Strumpshaw Fen has been tentatively ascribed to the action of gas bubbles below the water table in these peat deposits. Very little is known about the influence of these biogenic gas bubbles on water flow in fen peat. Similar gas bubbles have been identified in bog peat (e.g. Kellner *et al.*, 2003; Rosenberry *et al.*, 2003) and preliminary work has shown that they have the potential to block water-conducting pores, thereby affecting the flow of water through bog deposits (Baird and Waldron 2003; Beckwith and Baird, 2001). Although ebullition of gas bubbles has been observed at Strumpshaw Fen when walking across the surface of the inundated site, little is known about how these gas bubbles affect the exchange of water through fen peat.

Despite the importance of hydrological processes in many of the nutrient cycles occurring in riparian wetlands, only a limited number of studies have identified the hydrological pathways operating in riparian wetlands or provided details of water-table fluctuations within floodplains (Burt *et al.*, 2002). The current study has shown that even under managed conditions, the channel system may continue to play an important role in the input of water, nutrients and sediment to the riparian zone. Given that future climate change is expected to alter the flow regime of many regulated and unregulated rivers (Gregory *et al.*, 1997; Pierce, 1996), increasing our understanding of the hydrological links between the channel and the riparian zone is fundamentally important if we are to predict the consequence of future changes in channel flow regime on nutrient cycling within riparian systems. Further work should also consider unmanaged systems where exchanges between the channel and the riparian zone are likely to be more dynamic than at Strumpshaw Fen, associated for example with twice-daily inputs of channel water to the riparian zone in tidal rivers.

In terms of the processes controlling P availability in floodplain fens, it has been shown that historically high nutrient loading can produce a situation in which the riparian zone is a source for P to the surrounding landscape. In this study, the release of P to wetland pore water and surface water, alongside the delivery of P to the ditch network, has been

demonstrated. However, the fate of P following delivery to the ditch network was beyond the scope of the current research. Future research in this area would form the logical next step in determining the wider-scale consequences of P release from wetland sediments. For example, delivery of a reduced solution containing high concentrations of humic substances, iron and phosphorus to an oxidised environment, may result in the precipitation of Fe-P or the formation of colloidal complexes involving the association of humic substances, iron and phosphorus. Both processes will have important implications for the bioavailability of phosphorus, and for the potential for P to be exported from the ditch network.

Preliminary analysis of the speciation of P in 0.45 μm filtrates has suggested a minimal role for colloidal phosphorus in pore-water samples from Strumpshaw Fen. This contrasts with much other work examining the speciation of P in samples from a range of different environments. However, the majority of previous work has been conducted using oxidised solutions. Clearly, future research in this area should expand the range of reduced solutions within which P speciation is conducted. Particularly important research questions include the mechanism apparently inhibiting the formation of colloidal-P in such samples, and the implications for the bioavailability and transportation of P within wetland pore water.

Future research should also consider how the findings reported in this study translate to the wider spatial scale. Because of time and equipment constraints, the research reported in this thesis was focused on one relatively small area of the 200 hectares of Strumpshaw Fen. This allowed the research to make significant advances in our understanding of hydrological and hydrochemical processes in riparian wetlands. However, there is a requirement to test the findings from this research in other areas of Strumpshaw Fen, and in other similar riparian wetlands. For example, the degree of hydrological connectivity between the peat and the underlying mineral aquifer, and the magnitude of phosphorus release to pore water and surface water, may vary across the site, particularly with proximity to the river channel. Replication of the research reported in this study at a greater number of locations within Strumpshaw Fen would elucidate the wider-scale applicability of the process findings reported in this thesis.

To begin to address the requirement in catchment science for both improved process knowledge and greater understanding of the wider-scale implications of this process

knowledge, this study provides an example of an integrated 'source-plus-transport' approach to environmental investigation. The implications of P release from riparian wetland sediments for the ditch environment have been assessed by combining hydrochemical process information with data regarding the hydraulic properties of the weltand sediments and the hydraulic gradients acting within them. To move from the floodplain to the catchment scale requires research in the areas described above, examining the fate of P upon delivery to the ditch network and the importance of connectivity between the ditch network and the river channel. This form of multi-scale approach will become increasingly important in future catchment research, which will be driven, in part, by the European Union Water Framework Directive, the fundamental basis of which is connectivity between different elements of the catchment.

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