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PHOSPHORUS DYNAMICS IN SOME IRISH SOILS: THE INFLUENCE OF LABORATORY DRYING, SOIL CHARACTERISTICS AND SEASON.

Presented in fulfilment
of the requirements for the degree of
Doctor of Philosophy
April 2004

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For Ruth and Brian, my parents.

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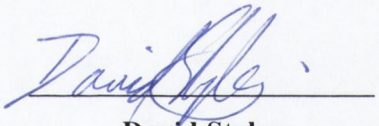

David Styles

April 2004

SUMMARY

Phosphorus (P) is a nutrient that is important in limiting biological growth in fresh waters, and desorption of P from soils is thought to be an important driver for the eutrophication of freshwater bodies. Previous studies have linked land use, soil P contents and general soil characteristics to soil P desorption. This project aims to assess the potential to use readily available soil type and agronomic soil P (Morgan P) data to predict soil P desorption - as measured by water-extractable P (P_w) and bioavailable P (P_{feo}) - for a range of Irish soils. The effects of the standard practice of sample drying prior to desorption analyses, and implications for assessing soil P desorption risk in catchment P loss models, are explored.

Dried samples of 35 soils collected from a range of soil types and land uses within the Lough Mask catchment in County Mayo were analysed for numerous soil characteristics and P sorption/desorption. Sub-samples of these samples were also maintained at the moisture content they contained during sampling (moist samples), and analysed for P desorption. Moist soil samples collected monthly from 11 sites in the Mask catchment were analysed for a range of characteristics and P sorption/desorption over a period of 12-16 months. For four of these months, representing different seasons, dried samples were subjected to the same analyses. Dried soil samples from three parent research project partners' catchments, one in N. Ireland and two in Galicia, Spain, were also analysed and compared with Mask catchments soils. Extensive stream-water chemistry data for the Mask catchment, obtained by parent research project co-workers, enabled an assessment of the relationship between soil P characteristics and water P concentrations.

Drying soil samples prior to analysis resulted in large increases in P desorption, and smaller overall increases in both P sorption and inorganic (but not total) P extracted by the Olsen reagent. Drying-induced increases in P desorption were positively associated with soil moisture and organic matter (OM) contents, and increases were proportionately greater for peat soils. Drying soils masked seasonal differences in P desorption, but not Olsen P, observed in moist soil samples.

A clear seasonal trend in Olsen-extractable P fractions in the 11 monthly-analysed soils, with winter maxima and summer/autumn minima, was attributed to biological cycling (namely, microbial P content fluctuation and plant uptake). A less clear seasonal trend was apparent for P_w, which displayed winter minima and appeared to respond rapidly to management events.

Significant, but less consistent, monthly differences in P sorption to the 11 soils were observed. Meteorological conditions during the week and month prior to sampling were significantly related to monthly variations in measured general soil characteristics (moisture content, pH and total nitrogen, but not total organic carbon) and soil P characteristics. Temporal variations in general soil characteristics were also significantly related to variations in soil P characteristics, and it appeared that grazing during or shortly before sampling increased organic P desorption. There were no clear associations between seasonal variations in laboratory soil P desorption and seasonal variations in either dissolved subsurface water P concentrations also sampled in this project, or in dissolved stream P concentrations measured for the parent research project.

Soils from the three catchments in N. Ireland and Spain all displayed similar mean Olsen P contents, but dried samples of soils from the N. Irish and Mask soils desorbed significantly more P to water than soils from the two Spanish catchments. This was probably as a consequence of significantly lower P sorption capacities.

Soil Morgan P content was nearly as good a predictor of P desorption as two separate measures of soil P saturation (DPSS) for the range of soils studied. However, moist samples of peat (>30% OM content) soil desorbed approximately one quarter of the quantity of P that moist mineral (<30% OM content) soil samples desorbed per unit Morgan P. Peat soils desorbed about half the quantity of P that mineral soils desorbed per unit DPSS. Phosphorus desorption from dried soil samples was less strongly related to various tests of soil P content, and drying samples halved the mineral/peat soil P desorption/Morgan P differential. A simple P desorption index (PDI), based on differential moist sample P desorption/Morgan P ratios for peat and mineral soils, was applied to existing maps of Morgan P content and soil type for the Mask catchment, and was found to correlate significantly with soluble stream P concentrations and area-weighted soluble P loads from the 12 subcatchments. This was despite contrasting subcatchment topography, geology, hydrology and mineral soil types. Neither subcatchment average soil Morgan P alone, nor an alternative PDI based on dried sample data, correlated significantly with soluble stream P concentrations and loadings amongst the 12 subcatchments. Therefore, it was concluded that differential P desorption from peat and mineral soils, in conjunction with Morgan P data, is an important factor in predicting catchment-scale P loss risks, but this may be obscured by the standard practice of drying soil samples prior to P desorption analyses.

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ABBREVIATIONS

Water / solutions

DOP:	Dissolved organic phosphorus
DRP:	Dissolved reactive phosphorus
MRP:	Molybdate reactive phosphorus
MUP:	Molybdate unreactive phosphorus
P_i:	Inorganic phosphorus
P_o:	Organic phosphorus
PP:	Particulate phosphorus
SS:	Suspended solids
TDP:	Total dissolved phosphorus
TP:	Total phosphorus

Soil

DPSS:	Degree of phosphorus sorption saturation in a soil
OM:	Organic matter
P_{feo}:	Phosphorus desorbed from soil to constant iron-oxide sink in solution.
Pm:	Phosphorus extracted from soil by Morgan's reagent
P_{ox}:	Oxalate extractable soil phosphorus
PSC:	Phosphorus sorption capacity of a soil
PSI:	Phosphorus sorption index of soil
P_w:	Water-extractable soil P
STP:	Soil test phosphorus e.g. Morgan P.
TEB:	Total exchangeable bases
TOC:	Total organic carbon

Organisations

EPA:	Environmental Protection Agency in Ireland
OECD:	Organisation for Economic Cooperation and Development
USDA:	United States Department of Agriculture

USEPA:	United States Environmental Protection Agency
UNFAO:	United Nations Food and Agricultural Organisation
TCD:	Trinity College Dublin
USC:	University Santiago de Compostela
UU:	Ulster University

Other

ANOVA:	Analysis of variance
ANCOVA:	Analysis of covariance
LSD:	Least significant deviation

CHAPTER 1

INTRODUCTION

1.1. Context of study

1.1.1. Phosphorus in water

Phosphorus (P) is an important limiting nutrient for biological growth in fresh waters. The US Environmental Protection Agency (USEPA) found that P was a key limiting nutrient in 90% of 479 studied lakes (Sharpley et al., 1995b). Increased algal growth rates, sometimes resulting in eutrophication, have been noticed in many fresh waters around the world over the past 50 years, and have been attributed to increasing nutrient (especially P) concentrations in these waters. In Ireland, P-driven eutrophication is the main cause of pollution in the 30% of national river channel length that is classified as polluted by the Irish Environmental Protection Agency (EPA) (McGarrigle et al., 2002). Although the percentage of river channel classified as polluted is down slightly from a 1998 peak of 33%, the length of seriously polluted channel increased from 77 km in 1994 to 112.5 km in 2000. Eutrophication refers to excessive biological growth in water bodies, and has serious ecological, economic and, potentially, health consequences. Fish die through oxygen starvation when decaying biological material uses dissolved oxygen, desirable fish species such as Salmon and Brown Trout may be replaced by less desirable species such as Pike, toxic algal blooms kill fish and are potentially dangerous to humans, reducing the amenity value of the water body and any associated economic income. Water polluted by algae is also more expensive to treat if used as a human water supply. Ireland has a number of lakes of unusually good ecological status within Europe, containing increasingly rare wild Salmon and Brown Trout fish species (McGarrigle et al., 2002; Irvine et al., 2003). These lakes are the basis for a lucrative tourism industry centred around their amenity value, fishing in particular. Ecological degradation therefore carries potentially very heavy economic costs in Ireland, providing added incentive to protect lakes from elevated P inputs.

Chlorophyll-a concentrations have been found to strongly correlate with total P (TP) concentrations in lakes, and the OECD (1982) has drawn up TP and chlorophyll-a boundaries to distinguish trophic categories (table 1.1). Whilst nitrogen (N) is also an

important nutrient in eutrophication, and may be plant-growth limiting during high summer P concentrations (Gobbelaar and House, 1995), the focus on controlling freshwater eutrophication is through managing P concentrations: potentially vast supplies of N, and carbon (C), are available to aquatic plants through fixation from the atmosphere (Sharpley et al., 1995b). In Europe, the Water Framework Directive (CEC, 2000) came into force in late 2000, and requires EU member states to legislate for the implementation of stringent new water quality targets (i.e. the elimination of water pollution by 2015). In Ireland, target P concentrations have been set at a maximum of 30 μg P l^{-1} (Clabby et al., 2002).

Table 1.1: OECD defined boundary TP and chlorophyll α concentrations for trophic categories. From OECD (1982).

Trophic category	Total P	Chlorophyll α
	μg l^{-1}	μg l^{-1}
Oligotrophic	≤10	≤2.5
Mesotrophic	10-35	2.5-8
Eutrophic	35-100	9-25
Hypereutrophic	≥100	>25

1.1.2. Phosphorus in soils

Phosphorus is the tenth most abundant element in the natural environment, constituting approximately 0.1% by weight of the Earth's upper lithosphere (Ciba, 1978). It occurs in its pentavalent state as part of the phosphate ion $[PO_4]^{3-}$, mainly in the common mineral apatite, weathering of which is the primary natural source of P release to soils. The global P cycle is therefore controlled on a geological timescale, and research on P cycling for applied purposes focuses on transformations within and between ecosystems (Tiessen, 1995). Naturally occurring P concentrations in soils are lower than in the rock from which the soils are derived as a consequence of continued weathering and preferential erosion, and leaching by ground and surface waters. Phosphorus concentrations vary widely depending on parent material and the degree of weathering: Newman (1995) suggests that weathering of soil parent material contributes 0.01 - 5 kg P ha^{-1} yr^{-1} to UK soils. On average, soils naturally contain only 0.04% P by mass, compared with 1% for potassium

(K) and 0.2% for N – the other macro-nutrient elements (Daly, 2000) - and are deficient in P with respect to levels necessary for optimum plant growth.

Phosphorus undergoes a complex series of cycles and transformations once in the soil matrix. Most interest in soil P in the past has been in relation to plant nutrition. Only a small fraction of the total P in soils is present in a form readily available to plants, and this fraction is often referred to as 'labile' P. Labile P comprises dissolved P in soil solution and P in the solid phase which is readily available for dissolution or desorption to solution. After being taken up by plant roots as inorganic P (P_i), P in plant material is then cycled back to the soil through plant decomposition or animal excrement, largely in organic form (P_o). Biological activity in the soil may also transform P_i into P_o through incorporation into microbial biomass – a process termed 'immobilisation', as it secures P in a non-available form. Whether bound in bulk organic matter (OM) or microbial biomass (immobile), or present in soluble organic complexes and colloids (labile), P_o is generally considered unavailable for immediate plant uptake, though it has been found that some simple P_o compounds may be readily plant available (e.g. Ron Vaz et al., 1993). The natural cycle of vegetation growth and decay concentrates 20-80% of total soil P in organic form (Morgan, 1997), and much of this is in the organic matter rich surface layers of the soil. Kieran-Hanley and Murphy (1973) state that, in Irish soils, 52% of total P under crop and grassland is P_o.

Conversion of P_o back to plant-available P_i is termed 'mineralisation', and is thought to occur almost exclusively via hydrolysis reactions catalysed by soil phosphatase enzymes. The balance of these reactions with immobilisation is critical in determining the amount of available P_i in solution, and is controlled by pH, temperature, total organic carbon (TOC) content, organic N content, and aeration (Tate, 1984). For example, higher temperatures have been shown to increase the rate of mineralisation (Daly, 2000). The C:N:P ratio of decomposing organic material has been found to be especially important in determining whether P is immobilised or mineralised (Tate, 1984), and McGechan and Lewis (1998) used C:N:P ratio as the major driver of a comprehensive soil P transfer model. A schematic diagram of biological P cycling is displayed in figure 5.1, and biological cycling is explored further in the associated section (5.2.1).

Inorganic P is also found in non-labile forms, usually incorporated within the structure of soil minerals, and is then referred to as occluded P. There may be some exchange between

such occluded P and labile P pools, though it tends to occur very slowly; it has been suggested that surface-adsorbed P can migrate into the structure of minerals over time under high P concentrations (irreversible sorption), and that (relatively rapid) dissolution of mineral P may contribute to solution P if P concentration becomes very low (for example, during periods of rapid plant extraction (Lookman et al., 1995; Holdford, 1988)). Figure 5.2 and section 5.2.1 contain further details on physico-chemical P cycling. Phosphorus cycling in soils has important implications for understanding diffuse P losses from different soils, and in relation to management effects and seasonal variation.

1.1.3. Phosphorus and agriculture

Phosphorus loading to freshwaters occurs from point sources such as sewage and industrial discharges, and from diffuse sources, including natural soil losses and agriculturally-derived losses. Concerted efforts to reduce point source emissions of P over the past few decades have often had relatively little impact on P concentrations in water bodies (e.g. McGarrigle et al., 2002). Smith et al. (2001) note that drastic reductions in point source emissions of P had little effect in reducing P loading to Lough Neagh in N. Ireland, and there is now a large body of evidence linking increased diffuse P losses over the past 50 years to concurrent agricultural intensification. Heathwaite (1997) estimated that 40% of external P loading to UK surface waters is from agriculture, and in Ireland Tunney et al. (2002) estimated that agriculture accounts for approximately half of P loading to surface waters. A time series for P concentrations in Lough Neagh constructed from sediment cores by Foy and Lennox (2001) indicated that the lake was mesotrophic at the end of the 19th century, with significant enrichment in P concentrations only occurring post 1950 and coinciding with the rapid expansion and intensification of agriculture. Similarly, Jordan et al. (2002) found that the rate of TP accumulation in sediment cores from Lough Friary, N. Ireland, increased steadily after c.1946, and that this increase was independent of inorganic sedimentary deposition which remained relatively constant. They concluded that these increased TP accumulation rates were consistent with increased biological productivity stimulated by increases in diffuse soluble P losses associated with concurrent agricultural intensification on this wholly-grassland catchment.

On a global scale, soil P deficiency remains a major problem (Lookman et al., 1995) and a limiting factor to increased agricultural production in large areas of the developing world

(Uexkull and Mutert, 1995). The application of mineral P fertilisers has played a crucial role in the rapid agricultural intensification that has proceeded in more economically developed countries over the past 50 years. The United Nations (UN) Food and Agricultural Organisation (FAO) estimates that in 1990 16 x 10^6 Mg of P was applied as mineral fertiliser world-wide (Tiessen, 1995). Economic incentives have tended to encourage over-application in developed countries, with the relatively low cost of fertilisers combined with agricultural policies that have directly subsidised production (e.g. the Common Agricultural Policy in the EU). This has been compounded by other factors contributing to over-application. Application rates for combined nitrogen (N), P and potassium (K) fertilizers and manures are often based on N requirements, and manure application is often determined by waste disposal pressures arising when storage capacity is reached (e.g. Carton et al., 1998). Additionally, the relative immobility of P once in the soil means that only 5 - 10% of fertilizer-applied P is taken up by agricultural crops during the first year after application: plants only extract P from soil within 2 mm of their roots (Sibbeson and Sharpley, 1997). Consequently, P is accumulating in agricultural soils, and in Ireland, where approximately four million hectares (90% of agricultural land) are dedicated to grassland agriculture, average soil test phosphorus (STP) levels (Morgan P content; see section 2.2.3) increased from 1 mg P l^{-1} soil in 1950 to 9 mg P l^{-1} in 1997 (Tunney et al., 2002). McGarrigle et al. (2002) estimate that 11-15 kg P ha^{-1} yr^{-1} are applied in surplus to requirements on agricultural land in Ireland, representing unnecessary expenditure for an industry in economic decline (average farmer income of €15, 840 in 2001 was half the industrial average wage in Ireland; Connolly, 2003). In addition to mineral fertiliser P imports to farms, P applied to fields as manure includes P from animal feeds. Animal feed was found to account for 31% of P inputs to intensive dairy farms studied by Carton et al. (1998).

As may be seen from table 1.1, the quantities of P necessary to contribute to eutrophication in fresh waters are very low, and insignificant in relation to the agronomic budgets which determine soil P application. For example, for Ireland to achieve its 20 μg P l^{-1} target concentration in salmonid waters, P losses from land need to be less than 0.25 kg ha^{-1} (Tunney, 2001). This compares with recommended P application rates of up to 60 kg P ha^{-1} yr^{-1} (Teagasc, 1998). Gibson (1997) highlighted that the annual increase in P loading to Lough Neagh of 4.5 tonnes represented just 0.5% of the 1000 kg P km^{-2} yr^{-1} applied in surplus to requirements to soils in the catchment.

1.1.4. Soil characteristics and diffuse phosphorus losses

This thesis focuses on the role of soils in diffuse P losses, with particular emphasis placed on relationships between potential P losses to water via soil P desorption and soil characteristics. Soil development, or pedogenesis, is the result of interactions between climate, parent material, relief, and biological factors occurring over time (including human influences), as identified by the Russian soil scientist Dokuchaiev (e.g. p 19, Ashman and Puri, 2002). The localised nature of many of these features results in a highly variable spatial distribution of soil types and general characteristics, with implications for the spatial distribution of diffuse P losses and land management practices.

Many soil characteristics, directly or indirectly, influence diffuse P losses from soils to water, though often in ways which are poorly quantified. For example, the capacity of a soil to bind P (its P sorption capacity; PSC) is related to concentrations of Aluminium (Al) and iron (Fe) (hydr)oxides in acidic soils (Freese et al., 1992; Lookman et al., 1995; Uusitalo and Tuhkanen, 2000). In high pH soils, it is thought that phosphate precipitates with calcium (Ca) from calcium carbonate ($CaCO_3$) to form calcium phosphate (e.g. $Ca_3(PO_4)_2$) although variable relationships have been found between PSC and carbonate content (e.g. Delgado et al., 2002; Zhou and Li, 2001). The physical structure of Fe (hydr)oxides, which tend to be most common in the clay fraction (particles <2 μm diameter) of soils, is also important in determining their capacity to sorb P, and is related to soil hydrology and aeration.

Organic matter (OM) content is another important soil characteristic involved in diffuse soil P losses. In addition to its intrinsic role in the biological P cycle (explored further in section 5.2.1), OM plays an important but poorly quantified role in P sorption/desorption reactions (explored in section 4.5.5 and 4.8.4). It is thought to both provide additional surfaces for P sorption, and inhibit P sorption onto (hydr)oxide surfaces (Morgan, 1997). Daly et al. (2001) found that peat soils (defined by > 30% OM) desorbed less P to water in laboratory experiments than mineral soils of the same Morgan P content. Organic matter also influences soil structure and hydrological characteristics, which play a crucial role in diffuse P losses from soil to water (next section). Thus, soil P sorption capacity (PSC) is related to soil pH, texture, drainage and OM content; this is explored further in chapter 4. The ability of a soil to bind applied P is critical in determining the fate of that P – especially the percentage that is lost to water.

1.1.5. Linking soil phosphorus to water phosphorus

There is a substantial body of evidence relating soil type and soil P contents (soil test P; STP) to (potential) diffuse soil P losses to water, involving laboratory desorption experiments (e.g. Daly et al., 2001; Koopmans et al., 2002; McDowell and Sharpley, 2003; Sharpley, 1995), field-scale experiments (e.g. Foy et al., 2002; Gardner et al., 2002; Haygarth and Jarvis, 1997; Pote et al., 1999b; Turtola and Yli-Halla, 1999) and catchment-scale monitoring and modelling (Daly et al., 2002; Smith et al., 1995; Withers et al., 1999; Vaithiyanathan and Correll, 1992). Tests used to determine soil P status, and the results of the above studies, are explored in more detail in the literature review for chapter 4 (section 4.2). Relating soil P losses to water quality requires an understanding of hydrological factors: soil P desorption indicates the potential for P loss to water, but in the absence of water itself, and hydrological energy, these losses will not be realised (Haygarth et al., 2000). For example, Daly et al. (2002) found that stream P concentrations were relatively higher in catchments dominated by wet soils than catchments dominated by dry soils, despite these (predominantly peat) soils desorbing less P in laboratory experiments.

The pathways of water movement are critical in determining the magnitude of P losses, as P desorbed from surface soil layers tends to be re-adsorbed onto low P subsurface soil layers from slow percolation water, whilst more rapid overland flow and (lateral) subsurface flow pathways are more efficient at transporting desorbed P. The extent to which these processes link soil (and soil P) to neighbouring surface waters is referred to as hydrological connectivity. Soil infiltration capacity and water saturation therefore play an important role in diffuse P losses, because they determine the dominant pathways of water movement. Lilly et al. (1998) developed a hydrological classification system for UK soils (hydrology of soil types: HOST) which used pedotransfer rules to predict hydrological characteristics (i.e. depth to permanent and seasonal saturation) from soil type through known characteristics associated with specific soil types (e.g. average depth to gleying or mottling). Areas of high hydrological connectivity may thus be determined from soil type data, and are termed critical source areas (CSAs) because of their susceptibility to lose soil P, especially if STP is high (Gburek et al., 2000). These CSAs may change over seasons, and over the course of individual precipitation events, leading to the concept of variable source area (VSA) (Gburek et al., 2001). Relating soil P desorption in laboratory experiments to catchment P losses therefore requires the consideration of these hydrological effects. For example, Simms et al. (2001) used a simple index approach,

where the risk of P losses from individual sites was assessed through multiplying individual risk factors (hydrology, STP and management practices) by relative weightings. Modelling of P losses is explored further in chapter 4, in which a simple ranking scheme for soil P loss risk is devised (section 4.6).

1.2. Phosphorus fractionation: nomenclature

Section 1.1.2 looked at complex P fractionation within soils. Similar P fractionation occurs in water, and has implications for the impact of P on water quality. Most phosphorus present in aquatic systems is in the form of organic P (P_o) bound in biological tissue and sediments (particulate P: PP), but also occurs in dissolved organic (DOP) and more readily available inorganic (P_i) forms. In reality, differentiation of these species is based on operational definitions which also apply to P extracted from soil in extractant solutions, and it is important to establish and understand these definitions. Note that abbreviations used for different forms of P are included in the list of abbreviations at the beginning of the thesis.

The most common method used to analyse P concentrations in solution is the ascorbic acid method. In this method, an acidic molybdate reagent is added to the test solution in the presence of a reducing agent (ascorbic acid), and forms a phosphomolybdate complex, which is then reduced to molybdenum blue. The intensity of the blue colour represents the orthophosphate $(PO_4)^{3-}$ concentration in the test solution; the P measured this way is thus referred to as molybdate reactive P (MRP), and was assumed to represent dissolved P_i. However, it has been found that the acidic conditions induced in this method encourage the hydrolysis of organic and colloid-bonded P, so MRP is actually an overestimate of dissolved P_i (Murphy and Riley, 1962; Rigler, 1968). Phosphorus that does not react with the molybdate reagent is termed molybdate unreactive P (MUP), and is calculated by subtracting MRP from total P (TP) measured after 'digestion' (oxidation) of MUP fractions to dissolved P_i.

Phosphorus fractions in water are also divided into 'dissolved' and 'particulate' P (PP), operationally defined according to whether P in solution passes through 0.45 μm diameter filters. Phosphorus that does pass through these filters is classified as 'dissolved', though it has been found to include P associated with fine colloids of less than 0.45 μm diameter

(Haygarth et al., 1997; Matthews et al., 1998), whilst P that does not pass through these filters – associated with colloids and particles greater than 0.45 μm diameter - is termed PP. Concentrations of MRP in 0.45 μm-filtered samples are thus termed dissolved reactive P (DRP), whilst P measured after digestion of 0.45 μm-filtered samples is referred to as total dissolved P (TDP). The difference between TDP and DRP (dissolved MUP) is taken to represent dissolved, predominantly organic P fractions (DOP), though also contains other forms of P, such as condensed P. Molybdate reactive P measured in digested, unfiltered samples is termed TP, and contains all of the above fractions.

The results of water P-fraction analyses must be interpreted with caution due to the operationally-defined nature of the fractions involved. There is increasing awareness that such operational definitions may deviate substantially from the physico-chemically-defined, naturally occurring fractions that they were originally assumed to represent. It is generally assumed that only dissolved P_i is readily (bio)available for phytoplankton uptake, thus making this fraction the most critical with respect to water quality. However, Rigler (1968) found that molybdate-DRP concentrations in water were 10–100 times greater than radiobiologically-traced dissolved P_i concentrations. The assumption that P in 0.45 μm filtrate actually approximates to the dissolved P fraction has also been challenged. Matthews et al. (1998) used field flow fractionation, membrane and ultra-filtration techniques to analyse runoff and drainage water, and compared the concentrations of various P fractions associated with the different colloidal size fractions. Preliminary results indicated that 1 nm – 1 μm phase colloidal material was associated with significant proportions of both organic and inorganic P. Haygarth et al. (1997) found that concentrations of MRP in soil and river waters were 50% greater in the 0.45 μm membrane-filtrates than in the <1000 molecular weight (MW) ultra-filtrates, and emphasise the distinction between chemical and physical mobility of P: P may be physically mobile (through soils) in fine colloidal material, yet remain chemically immobile. It should also be remembered that all these P fractions are in a dynamic equilibrium in natural conditions, with continuous transfer between themselves and the biology of the freshwater body. For example, low concentrations of dissolved P_i may belie rapid simultaneous transfer to (dissolution, desorption, mineralisation) and from (algal uptake) this fraction in natural lake conditions. However, laboratory analyses provide useful indications of P-related water quality, and enable objective temporal and spatial comparisons amongst waters (and soil extracts) to be made.

1.3. The BUFFER project

This study is mainly comprised of work carried out as part of the EU funded BUFFER project (contract number EVK1-1999-00094), entitled 'Key nutrient transport mechanisms important for the prediction of nutrient and phytoplankton concentrations in European standing waters'. BUFFER incorporated soil, water and sediment studies in Denmark, England, Germany, Ireland, Netherlands, N. Ireland and Spain, and aims to develop catchment scale models capable of predicting nutrient loading to lakes in varied catchments across Europe. It is hoped that the insight and final models derived from this project will be useful tools for EU member states in complying with the Water Framework Directive (CEC, 2000), which legally obliges member states to implement stringent regulatory targets for water quality (section 1.1).

The Irish contingent of the BUFFER project was based in Trinity College Dublin (TCD), and studied the water and soils of the Mask catchment in County Mayo (figure 1.1), with the specific aim of developing a nutrient budget for this catchment. Data gathered from water and soil sampling within the Mask catchment was used to develop P loss models for this catchment, and contribute to a BUFFER database used to develop a broad set of nutrient transport models for use across a range of catchments. This thesis forms a key part of BUFFER work package 4, entitled 'Nutrient mobility in soils', led by University Santiago de Compostella (USC) in Galicia, Spain. Much of the specific methodology is thus coordinated with that of USC (see section 2.2.3 for details), although the TCD component only looked at P dynamics (USC also analyses N dynamics in studied soils). The initial formal title of this study was 'Nutrient mobility in soils and the development of soil P retention coefficients for use in catchment nutrient transport models'.

1.4. Study aims

The original specific aims of BUFFER work package 4 were in the form of two separate deliverables:

Deliverable 7: 'An evaluation of the possibilities for inclusion of a retention coefficient of N and P estimated for catchment soils and which can be taken into account for use in catchment nutrient transport models'.

Deliverable 14: 'A report on the seasonal estimates of phosphorus and nitrogen fluctuation in soils with different physical structure and phosphorus saturation and their capacity to sorb and desorb phosphorus at different temperatures and water saturations'.

This study only focuses on P dynamics. The initial aim was to relate soil P chemistry, as determined in laboratory analyses, to spatial and seasonal variation in soluble P losses throughout the Mask catchment, as measured in BUFFER water sampling. The ultimate goal was to determine the extent to which readily available soil type and soil P (Morgan P) data could be used to predict spatial variation in soluble P losses to streams. Another aim, which grew in emphasis during the work, was to determine the importance of analysing soils in moist condition for P desorption. These three broad aims were pursued via the following objectives:

1) Determine the extent and implications of the standard practice of drying samples prior to P analyses, in particular in relation to:

- soil characteristics and soil type, and the impact on assessing differential soil-type desorption;
- variation in soil test P and P desorption between soils, relative to season and to each other.

2) Compare the general and P characteristics of Mask catchment soils with soils from other BUFFER partner study catchments that were analysed by this author (i.e. Friary, Fervenza and Portodemouro catchments; see section 1.6), to place Mask soils in a slightly wider context.

3) Determine the impact of land use (including specific management practices) on STP and P desorption in/from Mask catchment soils.

4) Assess the usefulness of soil P tests as predictors of potential P desorption from Mask catchment soils, in particular:

- compare different soil P tests with one another;
- determine the predictive capability of soil P tests for potential P desorption, especially Morgan P – the standard agronomic soil P test in Ireland;
- examine any influence of general soil characteristics and soil type on STP-P desorption relationships;
- assess the potential to use available data on soil type and Morgan P to predict stream P concentrations within the Mask catchment (and ultimately more generally within Ireland).

5) Quantify temporal variations in soil P dynamics over one year (2002), and relate them to potential drivers, with particular emphasis on:

- identifying any distinctive seasonal patterns;
- determining co-variation with general soil characteristics and meteorological conditions;
- determining co-variation with management practices;
- determining whether there are separate patterns of variation between different soil types and STP contents.

6) Relate soil P data to spatial and seasonal stream-water P data within the Mask catchment obtained during BUFFER stream monitoring. Attempt to bridge some of the gap between soil P and stream water by analysing P concentrations in subsurface water samples from different soils and at different depths using zero-tension samplers (section 2.4.2).

1.5. Study area

1.5.1. The lakes

There are two relatively large main lakes within the 859 km^2 western-Ireland catchment chosen for study by the Irish contingent of the BUFFER project; namely Lough Carra and Lough Mask (see figure 1.1). Lough Carra is a relatively shallow (maximum depth 20 m), marly lake with a surface area of 16 km^2, whilst Lough Mask is a relatively deep (maximum depth 60 m) lake with a surface area of 82 km^2. One of the main reasons for choosing these lakes is that they remain closer to their pristine condition than most other European lakes (e.g. TP, ± 95% C.I. from July 2001–July 2002 was 10.4 ± 1.3 $\mu g\ l^{-1}$ for Lough Carra and 12.8 ± 2.7 $\mu g\ l^{-1}$ for Lough Mask; Irvine et al. 2003). They are significantly below the 35 $\mu g\ l^{-1}$ TP concentration specified as critical for eutrophication in OECD classification (table 1.1), and are thus relatively unusual in Europe – where many lakes are seriously P-impacted. In conjunction with chlorophyll-a concentrations ranging between around 1 and 10 $\mu g\ l^{-1}$, this classifies the lakes as borderline oligotrophic/mesotrophic according to OECD classification (table 1.1). However, the low-lying limestone geology in the eastern half of catchment (section 1.5.3) ensures an adequate nutrient supply, maintaining a richer feeding ground than is common for other oligotrophic lakes - which tend to be predominantly siliceous, mountain lakes. Consequently, these lakes support large specimens of fish species often no longer found in many other lakes due to pollution. Lough Mask is especially renowned for its Brown Trout, being regarded as one of the best wild fisheries for this species in western Europe (Lough Mask Committee, 2000).

In recent years, concern has increased about water quality in these lakes. EPA surveys have indicated recent increases in Lough Mask phytoplankton concentrations and, more noticeably, elevated nutrient concentrations in some of the lakes' contributory rivers (McGarrigle et al., 2002). The largest contributory river to Mask is the River Robe (shown in figure 1.1), which drains 38% of the catchment area. EPA water quality monitoring has found a general decrease in river quality (biological Q ratings) for the river Robe since 1971, and some upper reaches of the river were recently classified as eutrophic (McGarrigle et al., 2002). Donnely (unpublished data) calculated that the Robe is responsible for 56% of the TP loading to Lough Mask. In fact, a local action group (Carra-Mask-Corrib Water Protection Group), set up by the Carra-Mask Fishing Federation, is

sponsoring legal action against the Irish Government in the European Court for alleged failure to adopt and implement the EC Dangerous Substances Directive (CEC, 1976). Phosphorus is listed as a dangerous substance to water under this directive, and declining fish catches in these lakes are being blamed on elevated nutrient levels (especially P) attributed to agricultural activities on the surrounding land. Thus, identifying key sources of P loading to these lakes, and simply increasing awareness of their ecological (and economic) importance and vulnerability, were important reasons for these lakes being chosen for study by the BUFFER project.

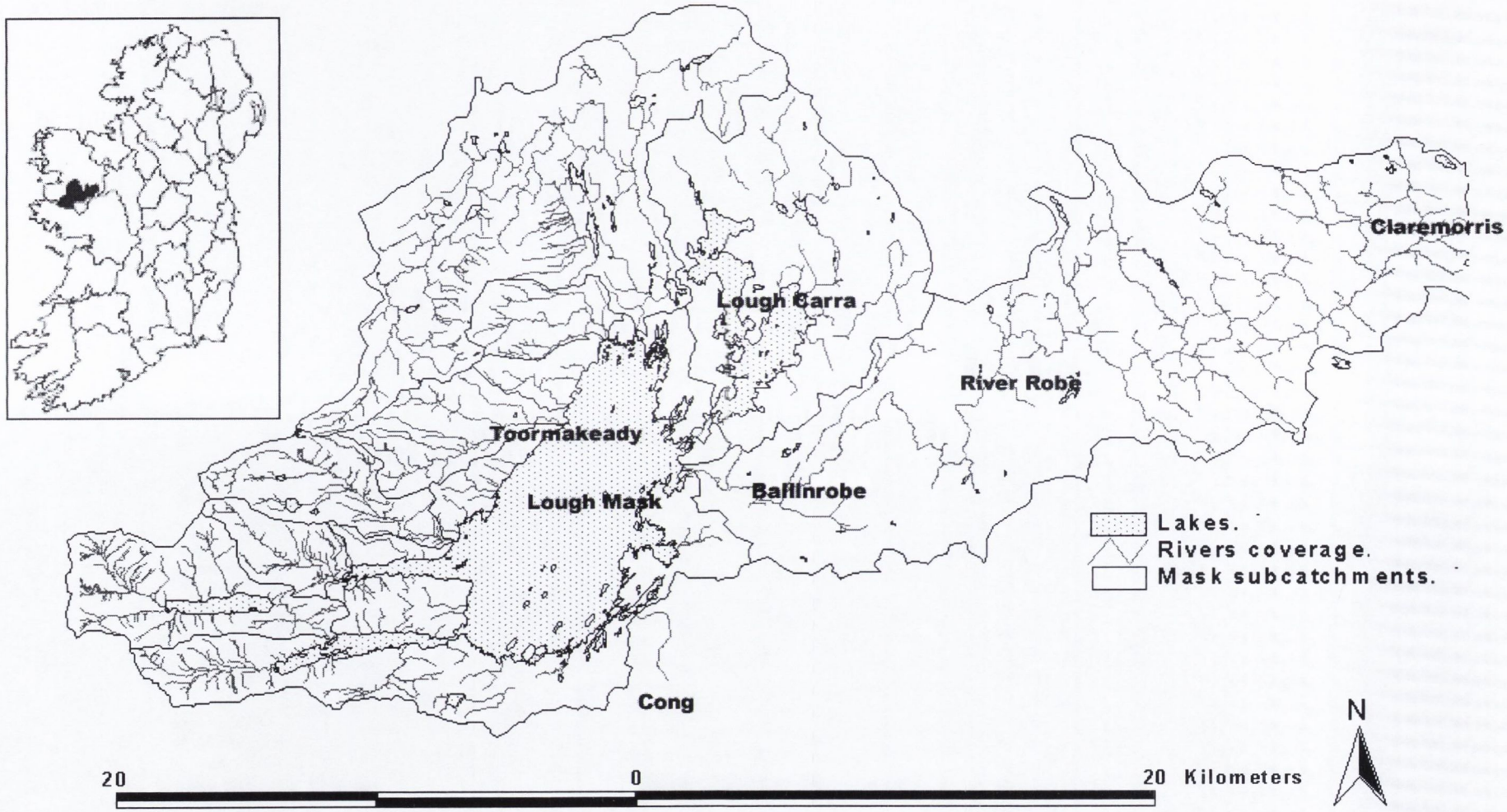


Figure 1.1: Location of the Mask catchment within Ireland (top left, inset), and the catchment outline, including the main subcatchments, rivers, and the locations of Ballinrobe, Claremorris, Cong and Toormakeady . Converted to GIS by Alice Wamaere and Dr. Ian Donohue.

1.5.2. Climate

The climate in the study area is typical of the west of Ireland, being of a temperate, maritime nature. Mean annual precipitation is relatively high, at 1143 mm in the eastern extreme of the catchment (Claremorris: 52° 48.73' N, 8° 58.29' W), and is reasonably evenly distributed throughout the year (Met Eireann data; figure 5.1 and table 5.1:). Mean annual evapotranspiration is 415 mm (Rohan 1986). Temperatures are mild throughout the year, with little deviation from the 8.9°C annual mean: increasing from a minimum monthly mean of 4.3°C in January to a maximum monthly mean of 14.3°C in July, according to climatic records from 1961 – 1990 (Met Eireann; see table 5.1). The mountainous region west of the lakes is likely to be influenced by micro-climatic effects, especially increased (orographic) precipitation induced by moist Atlantic air (brought in by prevailing westerly winds) rising over the higher ground, and lower temperatures.

1.5.3. Catchment topography and geology

Another aspect of the Carra-Mask catchment which makes it an interesting study area is the variety of topography and bedrock geology, with contrasting topography, and calcareous and siliceous geology found to the east and west of the lake respectively. Figure 1.2 is a digital elevation map, based on Ordnance Survey of Ireland (OSI) data and put into GIS format for BUFFER by Alice Wamaere. It highlights the contrast between the mountainous topography to the west of Lough Mask, with elevations up to 673 m, and the rolling lowlands to the east, mainly below 60 m. A slightly unusual aspect of the catchment worthy of note is the NW corner, where a valley runs parallel to the western shore of Lough Mask, but is separated from the lake by the Partry Mountains. Runoff water from this valley flows into the Aille river, however, thus ultimately finds its way into Lough Mask.

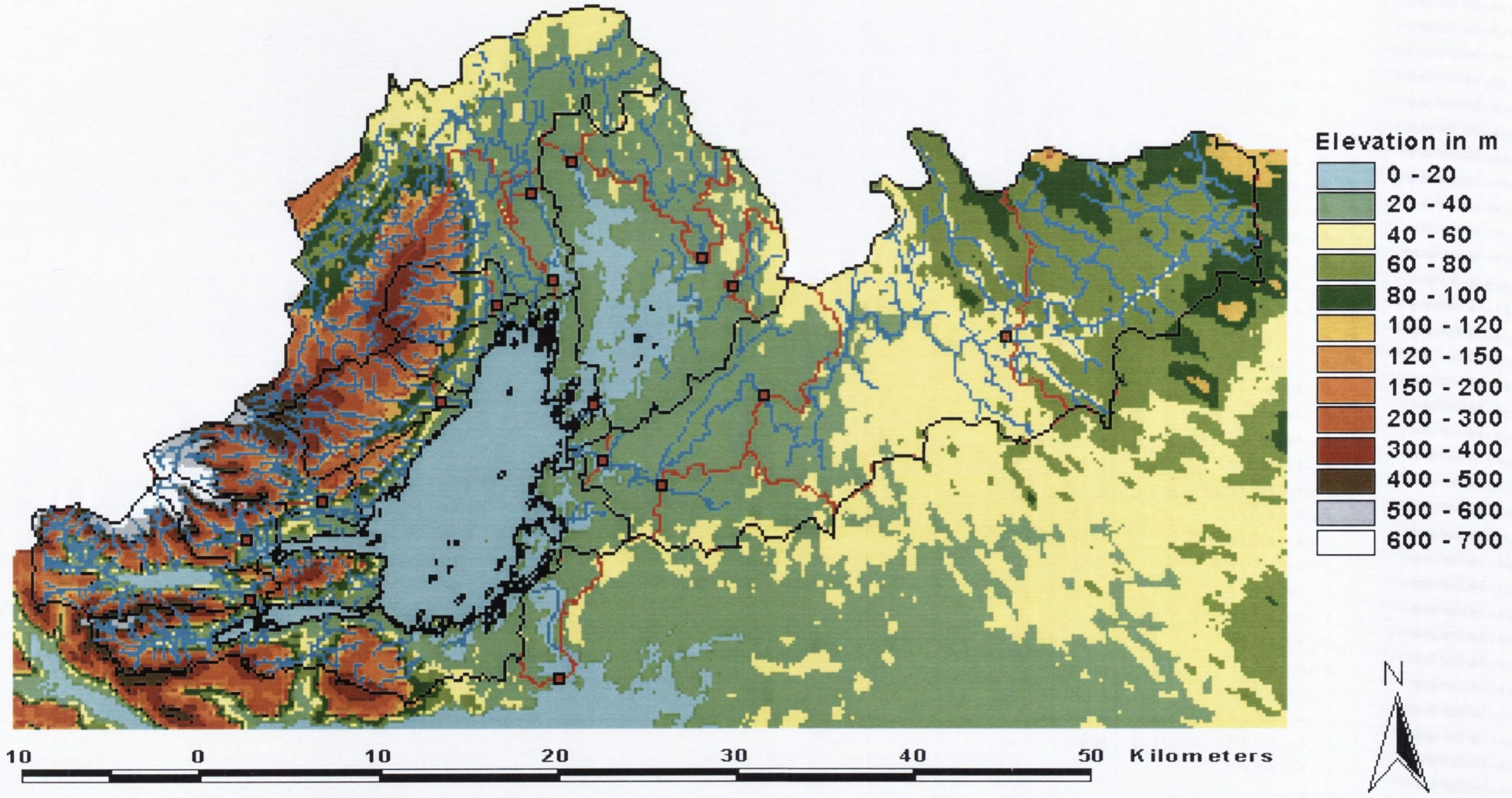


Figure 1.2: A digital elevation model of the Mask catchment, prepared by Alice Waemere using Ordinance Survey of Ireland data. Also shown are subcatchment boundaries (red lines) and BUFFER river sampling points (red boxes).

Figure 1.3 is a copy of the relevant part of the most recent Geological Survey of Ireland (GSI) bedrock geology map, at a scale of 1:100,000: Sheet 11, Geology of South Mayo (McConnell et al., 2002). It shows the varied distribution of bedrock geology in the area in and immediately surrounding the catchment, and highlights the contrasting age and rock-type of bedrock geology to the east and west of Lough Mask. East of Lough Mask is dominated almost exclusively by limestone, ranging from thick-bedded pure limestone (CO formation) in the SE of the catchment, through medium to thick-bedded pure limestone (NL formation) further north and underlying most of the River Robe catchment, to dark cherty limestone and thin shale (AS formation) extending NE from between Ballinrobe and Lough Carra, and extending north from the northern shore of Lough Carra. The area around Lough Carra is underlain by a combination of calcareous and muddy sedimentary deposits, with shale apparently underlying a significant proportion of the Lough Carra catchment (AS, Okbh, Okcr, IL and KL formations;figure 1.3). However, a large proportion of the lake itself is directly underlain by thick-bedded pure limestone (OKlc). Studies of the limestone bedrock in the east of the catchment (Coxon and Drew, 1986; Drew and Daly, 1993) found that there is substantial evidence of karstification, especially in the Cong area on the southern shores of Lough Mask, with associated implications for the hydrology of this area.

The bedrock geology directly north of Lough Mask is dominated by the TW formation, which includes red and grey sandstone, siltstone and shale. The area to the west of this, and to the west of Lough Mask itself (mainly part of the Partry Mountains), is rather more complex. This area is dominated by siliceous rocks, predominantly conglomerate sandstone (MT) and conglomerate with metamorphic clasts (DV). However, there is some variation along the western shore of Lough Mask, with additional sandstone-dominated formations (MK, KB and MP formations), small areas of the contrasting limestone-dominated TK formations, and small areas of quartz-phyric rhyolite, breccia (ER) formations. The SW corner of the catchment is underlain by particularly complex bedrock geology, though most of it is underlain by either the LG formation (a combination of greywacke sandstone, siltstone and mudstone) or the BW formation (a combination of schists, grits, metavolcanics and mylonitics). Black shale, chert, pillow lava and tuff were also found to the south of Lough Nafooey in the KK, FY and BC formations.

Figure 1.3a: Part of the key to GSI Geology of South Mayo map in figure 1.3b, including all the geological formations shown within the Mask catchment, and their age. From McConnell et al. (2002).



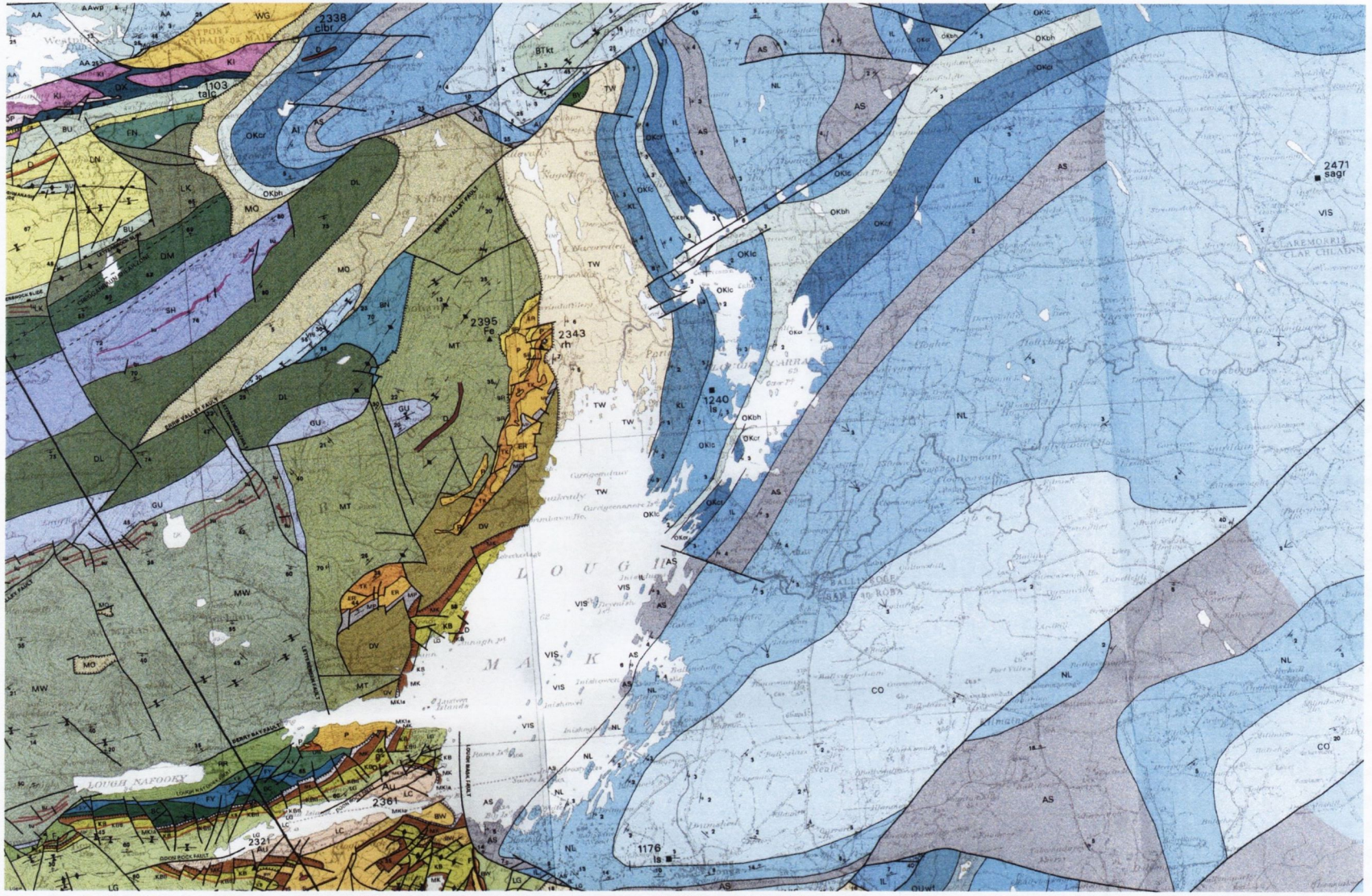


Figure 1.3b: Bedrock geology of the Mask catchment, from GSI 1:100,000 map; Geology of South Mayo map (McConnell et al., 2002).

The Quaternary geology of the catchment is mostly the result of glacial till deposited at the base of the ice-sheet, and sands and gravels deposited by melt-water from the ice-sheet of the last glaciation 18000 years ago (Drew and Daly, 1993). This results in a range of textures in soils developing on these deposits, ranging from clayey-loam brown earths to gravely sandy-loam podzolics (see section 1.5.5). The depth of Quaternary deposits varies considerably, from very shallow (< 30 cm) on the eastern shores of Lough Mask, and generally less than 1-1.5 m for the eastern half of the Robe catchment, to greater than 20 m locally, under drumlins (Drew and Daly, 1993). Alluvial deposits also occur in close proximity to some of the rivers, and slightly more extensively on the SW shores of Lough Mask.

1.5.4. Catchment hydrology

The impermeable siliceous geology (figure 1.3), steep topography (figure 1.2), and predominantly shallow or poorly drained soils (figure 1.5: next section) in the west of the catchment result in a high proportion of precipitation rapidly reaching streams as surface runoff, and thus rapid hydrological responses in subcatchments to the west of Lough Mask (and a dense stream-drainage network: figure 1.2). In such areas, stream flow is proportional to the area drained upstream, and stream chemistry is largely reflective of the surface catchment. In contrast, groundwater exchange plays an important role in the surface hydrology east of Lough Mask. Drew and Daly (1993) calculated that the downstream increase in discharge of the River Robe was proportionate to the increase in land area drained downstream for only 40% of the year. Gaining conditions, with disproportionately high flows in the lower reaches of the river, were recorded over mid-winter to late spring, whilst river bed infiltration of river water to the lowered water table resulted in a substantial (two thirds) loss of flow downstream during the summer to early autumn months. The Bulkan river (feeding into the lower reaches of the River Robe, just SW of Ballinrobe: see figure 1.1), is entirely fed by groundwater and emeges at the Cregduff springs. Such exchanges between ground and surface waters complicate the development of nutrient budgets, and may obscure relationships between stream chemistry and adjacent land characteristics.

Karstification in the SE of the catchment results in most of the effective precipitation in that area reaching groundwater as diffuse recharge or as point recharge from karst features.

This water may then feed into Lough Mask via springs, either submerged or slightly inland from the eastern shore of the lake (small rivers on the east of Lough Mask, south of Ballinrobe in figure 1.1). There is no extensive surface drainage to Lough Mask in the 200 km^2 area south of the Robe and east of the lake, although there are some springs close to the eastern edge of the lake which feed into it. Similarly, most outflow from Lough Mask into Lough Corrib occurs subterraneously, mainly along the bedding planes and some of the larger faults between the overlying pure Limestone and underlying muddy limestone of the Mask-Corrib isthmus, emerging from springs in Cong (Drew and Daly, 1993). From here, it flows down the unfinished excavated channel of the Cong canal into Lough Corrib. The SE corner of Lough Mask, becomes cut-off from the rest of the lake during the summer months when the lake level drops, and water from this part of the lake flows into Lough Corrib via karst conduit flow. However, during winter months when lake levels are high, surface flow may also occur along the full length of the Cong canal.

1.5.5. Catchment soils

Data on catchment soils were available from a number of different sources, though detailed information was patchy, with some sources only covering parts of the catchment. The only soil map available in GIS format for the whole catchment is part of The Soil Map of Ireland, with limited resolution of 1:575000 (figure 1.4). This map was compiled by Gardiner and Radford (1980), and mapping units consist of associations of soils labelled according to the dominant Great Soil Group in each association. These associations and typical soil profiles are described in an accompanying bulletin (Gardiner and Radford, 1980), which describes Great Soil Groups as "soils having the same kind, arrangement and degree of expression of horizons in the soil profile. They also have close similarity in soil moisture and temperature regimes and in base status." A more detailed map of soils in the western half of the catchment (The Soil Map of West Mayo; Kiely et al., 1974) is also referred to in this section, although it was impossible to obtain colour photocopies of the map (which was immobile, in a library) to include in the thesis. There was no accompanying report available with this map. Some additional soil data exist for the eastern side of the catchment, derived from preliminary mapping work, conducted and written by Walsh and Burke (c.1980). There was only a low resolution sketched map for half of the catchment accompanying this report, however, so it was not included in the thesis either. Further data were obtained from a report on the Corrib-Mask drainage

scheme (Walsh, 1974), which refers to the distribution of soil associations within the Mask catchment in more detail than the other reports. Included in this report is detailed information on the areal coverage of different soil types, along with additional information on parent material and drainage characteristics. It also contains some soil profile analytical data.

Walsh (1974) estimates that 47% of the catchment area is covered by lowland mineral soils, mainly east and north of Lough Mask. As indicated in figure 1.4, the majority of these (covering 40% of the catchment area) are medium-textured brown earths and grey brown podzolics. Brown earths predominate along the River Robe catchment, east of Lough Mask, becoming lighter in texture, and showing increasing signs of podzolization, towards the eastern-most edge of the catchment (Walsh, 1974). In the north-eastern most corner of the catchment, these soils showed strong-enough signs of podzolisation to be classified as degraded grey-brown podzolics and brown podzolics over a small area (Gardiner and Radford, 1980; figure 1.4). The A horizons of the medium-textured brown earths were found to typically have OM contents of 5-10%, clay contents of 18-23% and range in depth from 30-85 cm (Walsh, 1974). The A horizons of the lighter textured brown earths and brown / grey brown podzolics further east were found to contain less clay (9-17%) and OM (around 9%), and displayed greater accumulation of clay in the B-horizon than brown earths, along with some accumulation of Fe and TOC. The brown earths are considered to be excessively drained, whilst the (grey) brown podzolics are considered to be well-drained (figure 1.5).

Both Walsh (1974) and Gardiner and Radford (1980; see figure 1.4) agree that more extensive podzolisation has occurred in soils to the NE of Lough Mask, around Lough Carra, compared with the area of the Robe catchment to the south. The Soil Map of Ireland displays grey-brown podzolic dominated association 28 (which includes some gleys and peaty gleys), interspersed with basin peat, corresponding with the report of Walsh and Burke (c.1980). However, the more detailed report of Walsh (1974) also reports the presence of wet podzols and gleys on the drumlin topography, with the explanation that some of the glacial drift in this area is derived from acidic rocks such as sandstones, shales, slates and greywacke. Gardiner and Radford (1980) report that the principal grey brown podzolics in association 28 are up to 70 cm deep, contain 20-24% clay and 30-40% silt in their A horizons, and approximately 27% clay and 40% silt in their B horizons. Two soil wet podzol profiles were examined by Walsh (1974), and were

found to have A-horizons of a gravely, sandy-loam to silty-loam texture, with a high silt content of up to 56% in the B horizon. The relatively fine texture of these soils impedes their drainage, which is classed as moderate in figure 1.5.

Walsh and Burke (c.1980) reported that shallow soils, including shallow brown earths of about 30 cm depth and 'skeletal' soils, occupy patches close to the eastern shore of Lough Mask, and inland slightly to the south of Ballinrobe. This corresponds with Walsh (1974) who reported the occurrence of lithosols mainly in the vicinity of Loughs Carra and Mask, and in the Ballinrobe lowlands. These lithosols were reported to be 5-15 cm deep, with sandy-loam to loam textures, are well drained, and occupy approximately 5% of the catchment area (Walsh, 1974). These lithosols are not shown in figure 1.4, due to their patchy distribution, but a much larger area of lithosol-dominated association 4 is shown in the SW corner of the catchment. These are included in the Mountain Soil association described by Walsh (1974), which includes most of the soils west of Lough Mask and was estimated to cover approximately 20% of the catchment area. Both Gardiner and Radford (1980) and Walsh (1974) include blanket peats and peaty podzols in these associations. Wlash (1974) also included lithosols in a Valley Peat and Peaty Soil association (described later), especially close to the shores of Loughs Carra and Mask. These soils are predominately organic and 10-28 cm deep, sometimes on glacial drift or alluvial desposits. There are also very small patches of rendzina soils, where thin, high OM soils directly overlie limestone bedrock – mainly towards Cong (Kiely, 1974).

The acidic, siliceous bedrock geology, and high rainfall on the western side of the catchment have resulted in the extensive formation of gleys and podzols in this area. Gleys have formed where drainage is poor, especially in hollows or at the base of slopes, whilst better drained soils have developed into podzols due to down-profile movement of nutrients, metals, clay and OM (leaching, cheluviation, lessivage) with acidic percolating water. The Soil Map of West Mayo (Kiely et al. 1974) showed the occurrence of dry podzols north of the Owenbrin river and to the west and north of Tourmakeady on the western shores of Lough Mask. This compares with a slightly smaller area of podzol soils north of Toormakeady, and small patch south of the Owenbrin river in figure 1. According to figure 1.4, there is also an area dominated by podzols and peaty podzols in the northern half of the west side of the catchment. The Soil Map of West Mayo (Kiely et al., 1974) showed a more complicated mixture of soils to the west and north of Lough Mask, with

small patches of podzol soils interspersed amongst gleys, peats and peaty complexes. However, the soil distribution displayed in figure 1.4 does reflect the valley and low-lying area in the NW of the catchment displayed in the digital elevation model (figure 1.2): gley-dominated associations 27 and 25 include acid brown earths, peats and peaty gleys, and are found in drumlin areas dominated by acidic parent material (Gardiner and Radford, 1980). Drainage is impeded in these soils (figure 1.5) by the high clay contents (>40% in association 27), reflecting the glacial till parent material, and resulting in surface water gley formation (Gardiner and Radford, 1980). A large area, stretching along most of the western shore of Lough Mask and extending some way westwards, is also covered by gley-dominated association 21, which also includes peaty gleys.

Another consequence of the high rainfall, in combination with impermeable geology in the west of the catchment and small geological basins in the east and north side of the catchment, where the water table is often close to the soil surface, is the extensive development of peat soils. According to Walsh (1974) the Valley Peats and Peaty Soils association (excluding Mountain Soil association peats) occupies approximately 21% of the catchment. In the rolling lowlands to the east, pockets of basin (topographic) peat have formed where water and nutrient accumulation in geological basins resulted in the development and accumulation of plant material. In the mountainous area to the west there are areas of ombrogenous peat, formed as the high precipitation excess over evapotranspiration gradually sustained new and extending layers of plant growth over initial small pockets of topographic peat. There are also relatively large areas of raised bog, where rain-fed peat has continued to grow above areas of initial basin peat. Much of this raised bog has been cut over in the past, however, and Walsh (1974) estimated that 75% of the peat association soils are a combination of cut-over raised bog and fen (basin) peat. A number of basin peat profiles were examined by Walsh (1974), ranging in depth from 25-80 cm, although much of the peat mapped was observed to be greater than 1 m deep. The surface pH ranged from 5.5 to 6.4, and pockets of silty alluvial material were found in places, whilst two of the profiles were found to be underlain by calcareous marl (presumably old lake basins). Only about 5% of the peat association soils were estimated to be unexploited raised bog.

The Soil Map of Ireland (figure 1.4) shows the varied, topographically-determined distribution of the basin peat dominated association. This association occurs in

topographical basins mainly in the Carra and River Robe catchments, especially along river channels (although there are also likely to be a number of localised pockets of peat which were incorporated into the brown earth 33 association in figure 1.4). Walsh (1974) reported that peaty soils were especially prevalent along the rivers Robe and Aille, in addition to between Loughs Carra and Mask. Both Gardiner and Radford (1980) and Walsh (1974) include peaty gleys in their respective peat-dominated associations, as these tend to occur along the peripheries of the basin peats. There are also extensive areas of blanket peat shown in figure 1.4, ranging from the mid-west of the catchment to just north of Lough Mask. These are included in the Mountain Soils association of Walsh (1974) which was reported to occupy approximately 20% of the catchment area. Also included in that association are the common peaty-complexes also showing gleyic or podzolic properties (in addition to lithosols and bare rock). Figure 1.4 differentiates an area of peaty gleys amongst the blanket peats, and also a small area of peaty podzols already mentioned.

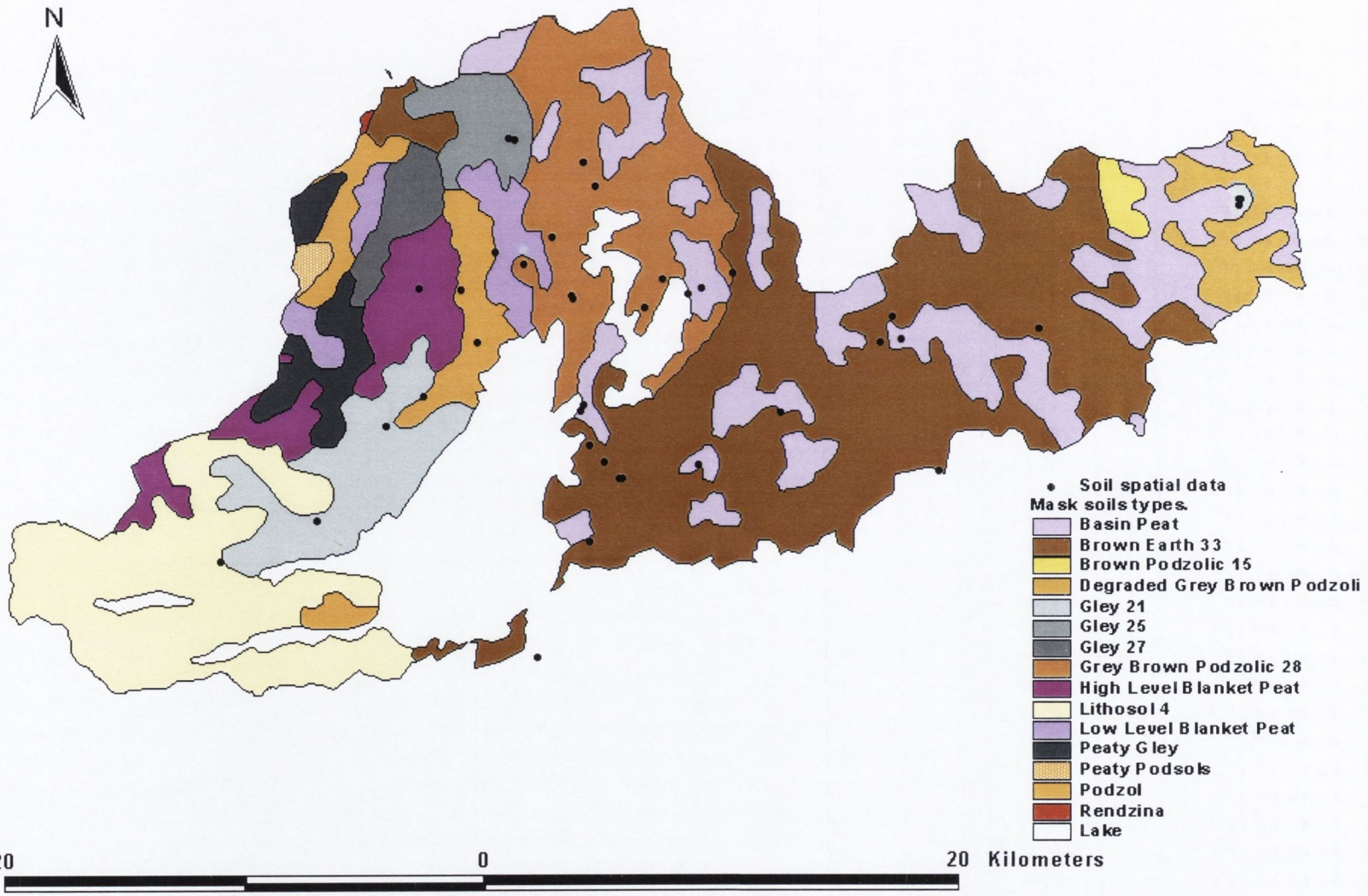


Figure 1.4: Soil associations in the Mask catchment, defined by dominant soil from The Soil Map of Ireland (Gardiner and Radford, 1980). Soil sampling locations shown as black dots.

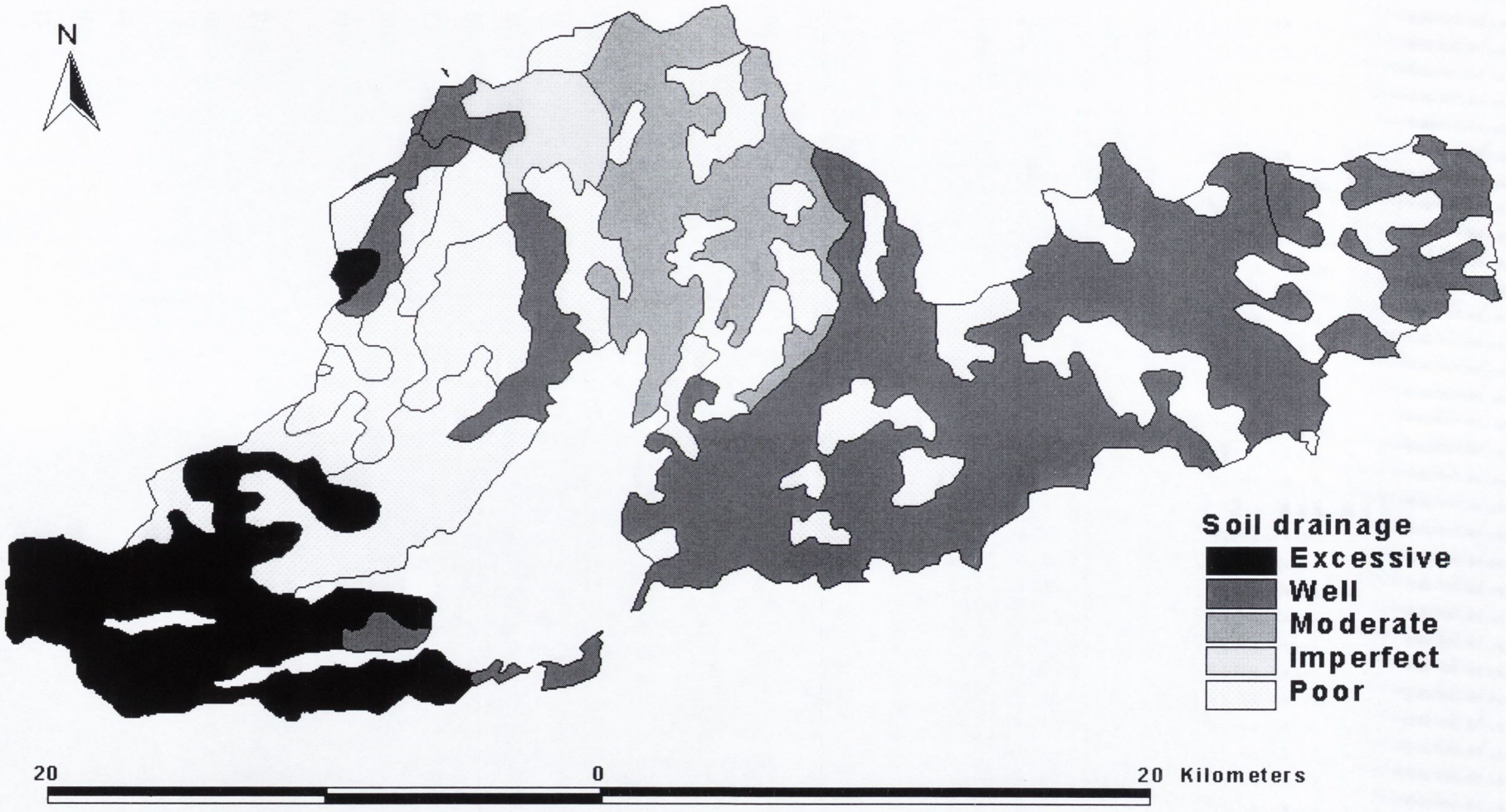


Figure 1.5: Soil drainage within the Mask catchment, based on the distribution of soil associations shown in figure 1.4.

1.5.6. Catchment land use

Figure 1.6 displays CORINE (Co-ordination of Information on the Environment) land cover distribution in the catchment. CORINE is a EU project that uses satellite imagery to estimate land coverage: therefore, land cover classes are operationally, and sometimes poorly, defined. The map displayed in figure 1.6 uses data from 1992 (the map has recently been updated, but the new version was not available to this study). The contrasting natural characteristics on the two sides of the Mask catchment are also reflected in land cover and land use. The steep topography, increased orographic rainfall and poorly drained soils on the west of the catchment are reflected in the extensive unexploited (non-dug) peat bog class that dominates the CORINE classification of land to the west of Lough Mask. Much of this land is grazed, though it is mainly used for low intensity commonage grazing, and the definition is a little misleading as this area includes mineral soils (podzols, gleys and lithosols; figure 1.4). Low productivity grasslands intersperse this unexploited land in the SW, whilst there are significant patches of 'land principally occupied by agriculture, with significant areas of natural vegetation' in the NW and along the western shores of Lough Mask. There is also a significant area of transitional woodland scrub just inland of the western shore of Lough Mask.

Land cover on the eastern side of the catchment is more fragmented, with a much lower area of unexploited peat bog and significant areas of high productivity grassland. Most of the catchment is covered by some form of grassland, with only small, isolated patches of coniferous or mixed forest, and no significant arable areas. A substantial area of this grassland is not distinguished as either low or high productivity, but is a combination of both (mixed pasture), and is distributed throughout the Robe catchment, and north of Lough Carra in particular. Estimates for County Mayo as a whole (Leonard, 1999) are that 80% of farms are dry-stock farms, 9% are dairy farms, and the area under forestry was 6% and increasing in 1999.

Population in the catchment is low, and is concentrated in the small towns of Ballinrobe, immediately east of Lough Mask, and Claremorris, in the eastern extreme of the catchment (figure 1.1). Both these towns have populations of approximately 2500. Wastewater treatment plants servicing these towns contribute relatively minor quantities of nutrients to the River Robe (comprising <5% of total annual loading of phosphorus and nitrogen; Donohue, unpublished data).

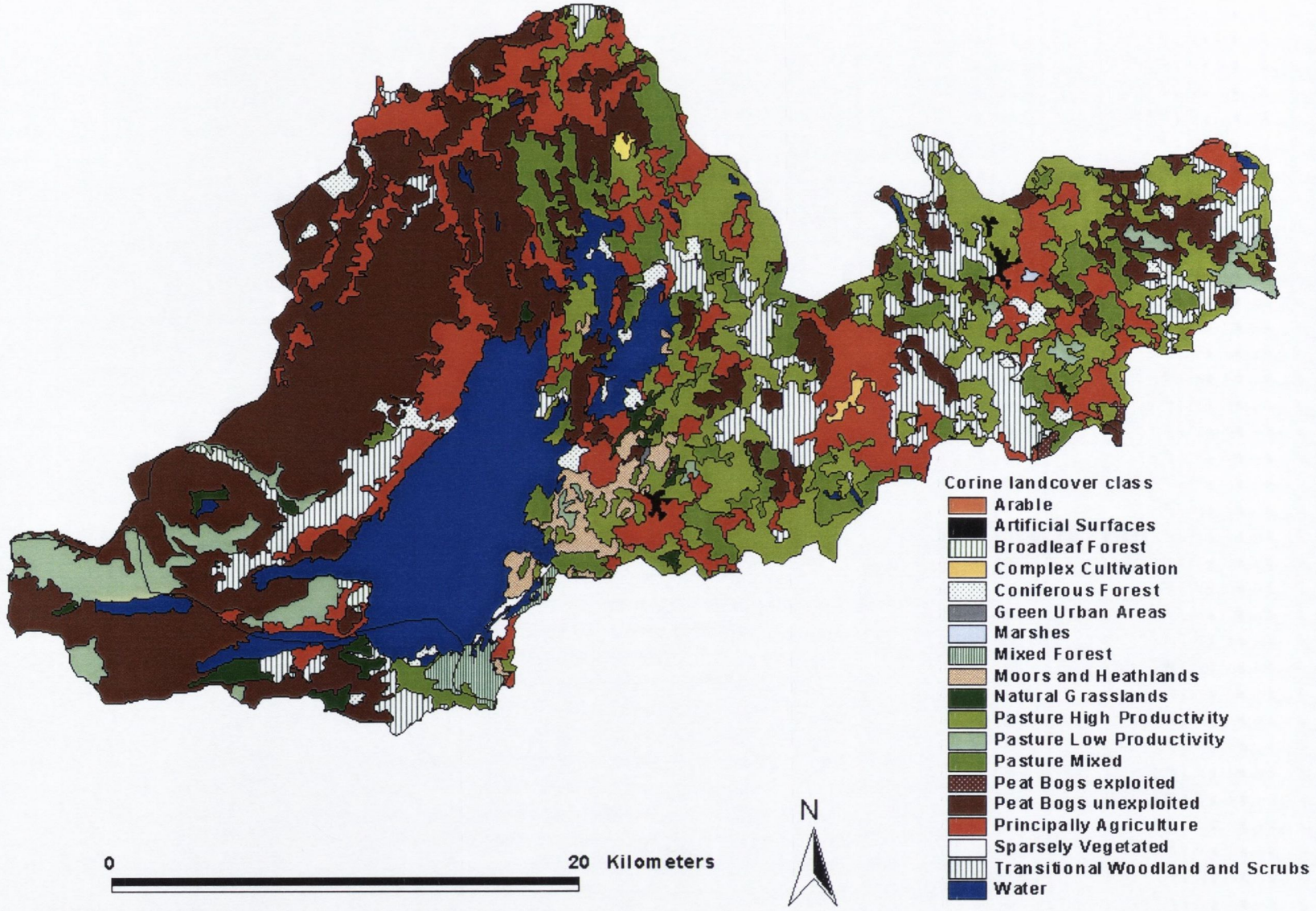


Figure 1.6: CORINE (1992) land cover classes within the Mask catchment.

1.6. BUFFER partner soils

University Santiago de Compostela (USC) was the coordinating partner for BUFFER soil analyses, and was responsible for methodology used to analyse soil samples from all BUFFER partner catchments (section 2.2.3). Soils sampled by USC were from forest and grassland land uses around the Fervenza and Portodemouro reservoirs in the mountainous region of Galicia in NW Spain. This region experiences a similar temperate maritime climate to Ireland, with slightly higher mean annual temperatures (8-12°C) and mean annual rainfall (1500 mm) (Garcia-Rodeja and Gil-Sotres, 1995) – compare with section 1.4.2. Eighteen soil samples collected by USC were sent to TCD for analyses, as were 11 soil samples from Ulster University (UU) partners in N. Ireland. These latter samples were collected from a mixture of pasture and silage soils within the small (1.01 km^2) Friary Lough catchment, County Tyrone (which falls with the large Lough Neagh catchment). This catchment is located on glacial till deposits which form a drumlin topography and overlie Carboniferous limestone and (mostly) sandstone. The Friary catchment experiences a similar climate to the Mask catchment, with mean annual rainfall of 900 mm, and a mean annual temperature of 9-10°C (Jordan, pers. comm.).

The reason that this author analysed soils from other partners was partly to distribute the soil analyses between USC and TCD, and also to enable comparison of soil P characteristics in Mask catchment soils with soils from other countries. This author had planned to analyse soils from UK BUFFER partners in Liverpool University, but soils were not sent from these partners.

1.7. Thesis structure

The thesis is divided into six chapters, including three relatively self-contained results chapters, according to the following divisions:

Chapter 1 provides a general introduction to the problem of eutrophication, the role of phosphorus and soils in eutrophication, and the reason for, and aims of, this study.

Chapter 2 explains the methods used for the selection of soil sampling sites, for sample collection, preparation and analysis, and also describes the general characteristics of the chosen soils.

Chapter 3 looks at the effect of drying soil samples, and consequences for comparing P dynamics between soils and seasons (objective 1 in section 1.4).

Chapter 4 compares Mask catchment soils to soils from the Friary catchment, N. Ireland, and the Fervenza and Portodemouro catchments in Galicia (objective 2 in section 1.4), and also looks at the effect of land use, STP, soil characteristics and soil type on P dynamics (objectives 3 and 4 in section 1.4). Soil P desorption is related to the spatial pattern of water P concentrations found in BUFFER sampling, using maps of soil type and soil P contents (objective 6 in section 1.4).

Chapter 5 looks at seasonal variations in soil P dynamics and general characteristics, relating them to meteorological conditions (objective 5 in section 1.4). Seasonal variation in subsurface water P concentrations is also touched upon, and again soil data are related to BUFFER water data (objective 6 in section 1.4).

Chapter 6 is a brief summary chapter, drawing together the overall conclusions from each of the preceding results chapters, and relating them to the original aims and objectives listed in section 1.4.

CHAPTER 2

METHODOLOGY

2.1. Sample site selection

2.1.1. The process and limitations of sample site selection

The multiple aims and objectives of this study (section 1.4) meant that the criteria used for sample site selection (defined in the following sections) were wide ranging. The fulfilment of all these criteria was limited somewhat by the difficulty of obtaining land access, partly resulting from a suspicion by some land owners of the study aims and dissemination of data relating to aspects of their land. The selection of monthly-sampling sites was aided by the local Teagasc (the Irish agriculture and food development authority) department in Ballinrobe. Teagasc initially approached a number of farmers they considered cooperative and likely to participate in the monthly field-sampling study. They also had a knowledge of the land use (intensities), and some idea of the soil types, present within different farms. However, although Teagasc are responsible for soil P testing (Morgan P), individual results are confidential and so could not be used to guide sample site selection (presently, Morgan P data over the whole country are only available on a 10 km grid scale). Unfortunately, Ballinrobe Teagasc department's jurisdiction does not extend west of Lough Mask, and only one monthly-sampling site (site 6) is in the west of the catchment. Initially, it was intended that temporal (monthly) analyses would be conducted on approximately 20 soils, to get a good indication of differences in temporal patterns amongst different soil types and land uses. However, the time taken to sieve and analyse moist soil samples in the laboratory meant that the number of monthly-analysed soils was reduced to 11. Sample site selection progressed over a number of monthly field trips to the Mask catchment in summer / autumn 2001; the catchment is 4 hours drive from the university, which meant that visits had to coincide with scheduled BUFFER water-sampling field trips.

To obtain a cross-section of soil types and land uses more representative of the whole catchment, additional sampling was conducted in March 2002 (before manure or fertiliser additions were likely to directly interfere with soil comparisons). The selection of additional sites for this sampling was conducted independently of Teagasc, in a semi-systematic nature. In total, 36 sites were sampled during this sampling run. Essentially,

general areas of extensive soil types not covered in monthly sampling were identified from figure 1.4 and we drove around these areas looking out for potential sample fields (subjectively aiming for a range of land uses; 2.1.3). Ultimately, proximity to a road and the presence of cooperative land-owners were two major influencing factors in the final selection of these sites. Time was a constraining factor as samples had to be collected over the course of two days, before driving back to Dublin for sample analyses. Another round of spatial sampling was conducted in March 2003, predominantly from the same fields (for comparative purposes), although due to some land-owners not being present to give permission, 33 sites were sampled on this occasion. Thus sample site selection was limited by available land use data, time constraints and the cooperativeness of individual farmers.

2.1.2. Scale of sampling

Issues relating to the method and accuracy of soil sampling are explored in section 2.2.1. Inherently high soil heterogeneity encourages the sampling of small plots, or the taking of replicate samples from the same sites, to ensure greater sample accuracy. However, given the time and resource constraints of this study, such sampling would have reduced the range of soil types and land uses studied, and ultimately would have reduced the real-life applicability of the results. Therefore, it was decided that soils would be analysed on a field scale: this scale provides a convenient unit of defined management practice to which results can be related, and in the west of Ireland, is not especially large (c. a few hectares on average). Ultimately, this choice of scale may compromise the accuracy of soil sample data compared with more controlled plot-experiments, but it maximises the potential applicability and representativeness of results for catchment scale P loss modelling. The use of systematic sampling should minimise problems associated with soil heterogeneity (see section 2.2.1).

2.1.3. Soil type, land use and soil P status

To determine the influence of soil type, and general soil characteristics, on P characteristics and desorption, one criterion of sample site selection was that the soils studied should be representative of the main soil types within the catchment, as previously identified in soil mapping exercises (section 1.5.4). The available maps of soil type

(including figure 1.4) were used to indicate areas where different soil types were likely to be found, although localised topographic and hydrological factors meant that individual farms / fields initially selected did not necessarily contain the soil types represented by the mapping unit for their area. A general indication of the major soil group at potential sites was obtained through a combination of observations of vegetation cover and visual inspection of either exposed areas of soil profile (e.g. the sides of drainage ditches), or, once on site, augured profiles. Table 2.6 displays the range of soil types analysed monthly (soil numbers 1–11), and to determine spatial variability (soil numbers 1–39). The dominant soil groups are represented in the monthly sampling, whilst the spatial sampling includes all the major soil groups mapped within the catchment: see section 2.3.1 for characterisation of soil types. Figure 1.4 shows the locations of all the soil sampling sites.

Soil P status and land use may vary greatly on a small (individual field) scale (beyond the resolution of available mapped data), so the selection of sites with a range of these variables was made predominantly by initial visual assessment. This was supported by a questionnaire (see appendix A) which was put to all farmers who agreed to participate in the study, asking details of land use and management. Whilst it was easy to get an immediate indication of soil type, soil P status was less easily pre-assessed, so land use (intensity) was used as a proxy for soil P status (with limited success). As with soil type, the intention of sample site selection was to cover as wide a range of soil P status and land use / land use intensities as possible. Ultimately, soil P status was not confirmed until laboratory analyses. This was a greater problem for the spatial sampling, where there was no process of preliminary analyses - as there was for monthly-sampled soils. The range of land uses and soil P status covered are displayed in table 2.5. Land use intensities are represented by estimated P applications (data on stocking density is patchy; see section 2.3.2).

2.1.4. Areas most relevant to P loss

Given that the ultimate aim of the BUFFER project was to evaluate factors most influencing the risk of P loss to water for inclusion in nutrient transport models, it was decided that study soils should predominantly be from areas and fields with other high P loss risk factors – where soil P characteristics would then be the major controlling factor of P loss. Poinke et al. (2000) found that 90% of P runoff within a Chesapeake Basin

catchment originated from only 10% of the catchment area. Such CSAs (see section 1.1.5) are usually areas where a number of P transfer risk factors combine to transfer substantial quantities of P from soil to water: namely high soil P status, high hydrological connectivity to a water course (proximity and / or preferential flow route linkages), high hydrological energy (quantity and intensity of precipitation). The influence of differing P status forms its own selection criterion (previous section), and hydrological energy from precipitation would not be expected to differ *too* substantially over the area of study (not withstanding limited topographically-induced differences; section 1.5.2). Therefore, to ensure that the hydrological characteristics of the study soils were representative of those with high P loss risk, it was decided that, where possible, soil-sampling sites should be directly adjacent to water courses. Pragmatism also played a role in this selection criterion, as choosing soil-sampling sites close to major water courses generally helped to ensure that there was not too much distance (travel time) between soil and water sample collection during tight sampling schedules. It also allowed for the possibility of higher resolution water chemistry monitoring in streams adjacent to study sites (though this was never realised). Figures 1.1 and 1.2 show the location of BUFFER soil and water sampling sites, respectively, within the catchment.

2.2. Sample collection and analysis

2.2.1. Sample collection

Soils are particularly heterogeneous, and it is notoriously difficult to obtain accurate, representative samples of a given area (e.g. Boone et al, 1999; Cameron et al., 1971; Petersen and Calvin, 1996; Starr et al., 1995). This is especially the case under grazed grassland, where nutrients are concentrated in specific, preferred areas of urination (mainly nitrogen) and defecation (nitrogen and phosphorus). For example, Addiscot et al. (1991) claim that typical daily output may be concentrated in 15% of grazing area. However, as mentioned in section 2.1.2, it was decided that, to ensure maximum efficiency of data collection, soil samples should be collected on a field scale, and resource limitations prohibited the collection of replicate samples from each field. Thus, it was decided that one composite sample would be taken from each field for both monthly and spatial sampling regimes.

The two main methods used to collect sub-samples (soil cores) to make up representative composite samples are random sampling and systematic sampling. Whilst random sampling involves the objectively random, independent selection of specific spots in a field from which cores (sub-samples) are taken, systematic sampling deliberately aims to collect cores representative of any continuous or random patterns of variation (Petersen and Calvin, 1996). By deliberately attempting to incorporate variability into the composite sample, systematic sampling requires fewer sub-samples (cores) to be taken than random sampling to achieve the same level of accuracy. However, there are particular potential problems associated with systematic sampling. For example, Petersen and Calvin (1996) warn on the danger of the interval of systematic sampling coinciding with (an integral multiple of the period of) any periodic variations present across the sample area (e.g. rows of banded fertiliser applications).

Most agronomic soil sampling is conduced in a systematic manner. For example, Teagasc recommendations for soil sampling are to take approximately twenty 10 cm deep cores at regular intervals, following a 'W' pattern across the sample field (which should be a 'uniform' area of less than 2 ha), and avoiding dung or urine patches and 'unusual spots' such as ditches, feeding areas, etc (Teagasc, 1998). This advice could lead to P loss

'hotspots' – such as poached areas (e.g. Heathwaite, 1997) - not being accounted for by sampling, although sampling high P content dung could completely obscure actual soil P concentrations. Therefore, from an environmental perspective, it seems logical to sample all areas of the field that fall within the 'W'pattern, including poached areas if these make up a significant proportion of total field area, but to avoid potentially highly contaminating fresh dung patches. This was the approach used for this study, in combination with a 2 cm diameter corer used to take approximately 25 sub-samples (cores) from each field, to make up each composite sample. Starr et al. (1995) found that, whilst there was evidence of small-scale variability in soil P concentrations, increasing sample diameters beyond 2 cm had relatively little effect on the mean and skewness of results, whilst Cameron (1971) found only a small increase in the accuracy of composite samples by increasing the number of (15 cm deep) cores bulked from 20 to 30.

Traditionally, sampling has been conducted at depths of 0-10 to 0-30cm, reflecting the rooting depth of crops, and thus nutrient extraction zone. Environmental soil testing, however, has increasingly focused on shallower sample depths of 0-1 to 0-5 cm, as this is the depth within which soil - surface runoff water interaction occurs (Sharpley et al., 1981). Turtola and Yli-Halla (1999) found that on a sandy, low P soil, flow weighted mean runoff DRP concentration increased linearly with Olsen P, anion-exchange resin P and DPSS measured at 0-5 cm depth, but not when measured at 5-25 cm depth. They suggest 'A very shallow soil sampling (<5 cm) is needed to assess P loading potential in a soil where P has been surface applied.' Teagasc experiments also found that a very close correlation (r^2 = 0.95) between P_w and Morgan P at 0-1cm depth decreased (r^2 = 0.62) when Morgan P was measured in samples collected from 0-10 cm (Teagasc, 1999). Therefore, whilst samples collected in March 2002, and over the monthly sampling regime, were collected from 0-10 cm depth to comply with BUFFER project protocol, the larger spatial dataset of soils sampled in March 2003 were collected from 0-5 cm in an effort to ensure better representation of surface soil P desorption to surface runoff.

Monthly sampling progressed from July 2001 until December 2002, but due to refinement of laboratory analytical protocol, reliable data are only available for some soils from September 2001. Additionally, on-going sample site selection (section 2.1.1) meant that data for all 11 monthly-sampled soils are available only from January 2002, providing one calendar year of seasonal data for these soils. It was initially intended to omit soil 11 from monthly sampling due to its relative inaccessibility, and the fact that soils 4 and 5 were

thought to represent mineral soils with low intensity land use and no P applications (based on farmer information). However, small quantities of manure were applied to soils 4 and 5 in February, so, after omission during that month, sampling of soil 11 resumed in March 2002.

During monthly sample collections general observations, such as whether fields were being grazed or if there was a dramatic change in weather conditions during sampling, were recorded in a sample diary (table 5.3). Ideally, to fully understand temporal variations in soil characteristics, a full record of all grazing patterns and other management practices for the duration of sampling would be required. However, because this study was conducted on fields where farmers were voluntarily allowing monthly sampling, and not on experimental farms, it was not possible in most instances to obtain detailed records of management practices. Fertiliser and lime application data rely on verbal accounts obtained periodically when land-owners were available during sampling, and it is possible that some important management practices may not have been recorded.

2.2.2. Sample preparation

Soils were stored in polythene bags placed in cool boxes prior to preparation and analysis. Standard soil analytical procedures usually involve drying soil samples prior to analyses, although this has been found to increase soil P desorption and solubilisation (e.g. Turner and Haygarth, 2001) and obscure seasonal variation in P desorption (e.g. Pote et al., 1999a). The effects and implications of soil drying are explored in detail in chapter 3. It was therefore decided that, if seasonal variations in soil P desorption were to be detected, monthly-analysed soils should be maintained at the same moisture level they were at during sampling (from here on termed 'moist samples'). Further, in order to examine the effect and implications of drying soil samples prior to analyses, monthly-collected soil samples from 4 months - selected to represent each season - were divided into sub-samples and analysed in both moist and dried condition. Samples collected for the larger spatial dataset in March 2002 were dried to compare with dried samples of other BUFFER partners, although samples collected (predominantly) from these same sites again in March 2003 were analysed in both moist and dried condition.

For moist analysis, collected soil samples were sieved through a 4 mm brass sieve within three days of collection, and homogenised (thoroughly mixed by hand). Two sub-samples of approximately 20 g of soil were taken from each sieved, homogenised sample, placed into two separate crucibles, weighed, and left in an oven at 105°C for 24 hours. The crucibles were then removed from the oven, allowed to cool in a desiccator, and re-weighed to calculate moisture loss (content). Moist soil weights corresponding to oven-dried soil equivalent weights were then calculated for each sample to ensure the correct soil-solution ratio in subsequent analyses. Meanwhile, the sieved, homogenised samples were stored at 4°C in polythene-wrapped foil trays prior to analyses within one week of sieving.

For dried-sample analysis, collected soil samples were spread out and covered in folded newspaper, and left for at least 10 days at room temperature (approximately 20°C). Dried soils were then 2 mm mesh sieved, homogenised, and stored in covered foil trays prior to analyses, usually within a month. Where samples were to be analysed for the effect of drying, soils were 4 mm mesh sieved and homogenised as per moist sample preparation, but then divided into two sub-samples. One sub-sample was stored in a sealed foil tray at 4°C as outlined above, whilst the other sub-sample was treated as an incoming sample for dried-sample analyses. Portions of air-dried soil samples were also placed in the oven to determine their moisture content above the oven-dry weight, in order to correct the expression of results; i.e. all results, for both moist and dried samples, were expressed on an equivalent oven-dry weight basis. Note that small sub-samples were taken for air-drying from all monthly-analysed samples, for analyses of total organ carbon and total nitrogen.

2.2.3. Laboratory analyses

Monthly-analysed soils were analysed for: moisture content, TOC and TN content, pH, Olsen-extractable P (MRP and TP fractions), P_w (DRP and TDP fractions), and sorption from 5 and 30 mg P l^{-1} solutions. Note that only the desorbable P fractions (P_w and P_{feo}) were analysed on both moist and dried samples of soils collected in March 2003; all other analyses of these soils were on dried samples only. The following procedures were followed for each of the analyses:

TOC and TN: Approximately 1 g of air-dried sample was weighed out into a beaker, the weight recorded, and 5 ml of double-distilled water (DDW) and 5 ml of sulphurous acid added. The beaker and its contents were then placed on a hot plate, and additional aliquots of sulphurous acid added if necessary, until effervescence subsided (this was to 'burn off' carbonate C: Verardo et al., 1990). The beakers were then left on the hot plate overnight for the samples to dry, placed in a desiccator to cool, then re-weighed in order to correct for carbonate weight loss in the final expression of TOC content. Approximately 0.05 to 0.2 g of each sample (depending on approximate TOC content) was then accurately weighed to 4 decimal places into a small tin cup, and loaded into a LECO CNS-1000 elemental analyser.

Soil pH: (Gil-Sotres, 2001). Approximately 10 g of moist soil was added to a beaker with 25 ml of DDW and the mixture stirred vigorously for one minute, then allowed to settle for half an hour. The pH was then measured using a Jenway 3030 pH meter, after 2 minutes of equilibration with the soil-solution.

Olsen P: (After Olsen et al., 1954). A 0.5M sodium-hydrogen-carbonate ($NaHCO_3$) solution was made by dissolving $NaHCO_3$ powder in DDW, and brought to pH 8.5 using sodium hydroxide (NaOH), a magnetic stirrer and a pH meter. 80 ml of this solution was then added to 125 ml polypropylene bottles containing 4 g of dry-weight equivalent soil (1:20 soil-solution ratio). The bottles were then shaken on a flat-bed shaker at approximately 120 oscillations per minute for 30 minutes. Extractant solutions were then decanted from the bottles into centrifuge tubes, centrifuged at 3500 rpm (~2200 g) for 8 minutes, and filtered through Whatman® no. 1 filter papers. 5 ml of extractant solution was made up to 50 ml in a volumetric flask, and neutralised using drops of 50% concentrated sulphuric acid (H_2SO_4) and phenolphthalein as an end-point indicator. This solution was then analysed for MRP and TP as outlined below. Due to humic colour interference during photometric analyses, sub-samples with no molybdate reagent were used as blanks for each sample (i.e. absorbance subtracted from molybdate absorbance), although this correction procedure was only initiated in January 2002. Humic interference was especially problematic for high OM soils.

P_w: (Gil-Sotres, 2001 – adaption of original P_w method of Van der Paauw, 1971). 100 ml of DDW were added to 125 ml polypropylene bottles containing 2 g dry-weight equivalent soil (1:50 soil-solution ratio). The bottles were shaken and centrifuged as per Olsen P,

prior to filtration through 0.45 μm Whatman® cellulose-acetate membrane filters, and analysed for MRP and TP in solution (operationally defined as P_w DRP and P_w TDP; see section 1.1.2 for explanation).

P sorption: (Gil-Sotres, 2001). Potassium chloride (KCl) was dissolved in DDW to produce a 0.02M KCl. A 10 g P l^{-1} stock solution of potassium di-phosphate (KH_2PO_4) was made using (oven dried) KH_2PO_4 dissolved in DDW. For each set of analyses, this solution was added to fresh 0.02M KCl solution to produce 2 solution concentrations of 5 and 30 mg P l^{-1}, and 40 ml of these 2 solutions were added to separate 125 ml polypropylene bottles containing 4 g dry-weight equivalent soil. The bottles were shaken for 24 hours, prior to centrifuging, filtration through Whatman no. 1 filter paper, suitable dilution with DDW (from no dilution to a 1:20 dilution ratio depending on concentration) and MRP analyses conducted. The P concentration remaining in solution was subtracted from the initial solution concentration to calculate soil P sorption. Sorption data from these two initial P concentrations were then applied to the Freundlich equation (see section 4.2.3) to calculate K_f values (these are an index of maximum soil P sorption capacity).

Molybdate reactive P in extracts was measured using a variation of the Murphy and Riley method deemed to be particularly suitable for soil extracts (John, 1970). Total P in soil extracts was analysed in the same way after autoclave digestion with potassium-peroxodisulphate, following Grasshoff et al. (1999). Humic acid colour interference in Olsen extracts was no longer a problem after extract digestion (Olsen TP data more reliable than Olsen P data for high OM soils). N.B.: Prior to January 2002, a different molybdate reagent was used for MRP fractions in Olsen and P_w extracts of initial monthly-collected samples, and resulted in higher proportions of P_w DRP (presumably through hydrolysis of non-molybdate reactive P compounds). In addition to the humic colour interference factor only being initiated in January 2002, this means that P_w DRP and Olsen (MR)P data are only reliable for seasonal comparison from this month onwards. P_w TDP and Olsen TP fraction procedures were unaffected, and these data are reliable for seasonal comparison.

Table 2.1 summarises the slightly complicated combination of common analyses for the different soil samples. Olsen P and P_w were measured on moist samples of monthly-collected soils (table 2.1), but were also analysed on dried samples on four occasions (January, April, August and October). Samples collected in March 2002 and March 2003 for the larger spatial datasets were analysed according to the same procedures, except that

P_w was conduced at a soil-solution ratio of 1:100 (instead of 1:50), and, for March 2002 samples, sorption from solutions containing 5 and 30 mg P l^{-1} was conducted at a 1:20 (instead of 1:10) soil-solution ratio (table 2.1). The different ratios for P_w and P sorption analyses arise from initial misinterpretation of BUFFER protocol with respect to the moisture state of soils during weighing. Dried samples of 11 soils from the Friary catchment, N. Ireland and 18 soils from the Fervenza and Portodemouro catchments in Galicia underwent identical analyses to Mask catchment soils collected in March 2002 - except they were not analysed for Morgan P. Mask catchment soil samples collected in both March 2002 and March 2003 were analysed for Morgan P according to the following methodology:

Morgan P: (after Morgan, 1941). The Morgan extractant was made up by dissolving 56 g of sodium hydroxide (NaOH) in 1.5 litres DDW, to which 144 ml of glacial acetic acid was added, and the solution made up to 2 litres. The pH was then adjusted to 4.8 using NaOH. Thirty mls of this reagent is added to 6 ml of dried soil (measured using a scoop) in glass conical flasks. The flasks were shaken at 120 oscillations per minute for 30 minutes, then the solutions were filtered Whatman® no. 2 filter papers prior to MRP analyses (Morgan, 1941).

Soils collected in March 2003 were not analysed for sorption from solutions containing 5 and 30 mg P l^{-1}. However, they were analysed for the following additional analyses accordingly:

P_{feo}: Iron-oxide impregnated paper strips were made according to the Menon (1988). One 10 x 2 cm strip was placed in each 125 ml polypropylene bottle containing 40 ml 0.02M KCl and 1 g dry-weight equivalent soil, and the bottles left shaking at approximately 80 oscillations per minute for 16 hours. The iron-oxide strips were then removed, rinsed with DDW to remove adhering soil particles, and shaken for 2 hours with 40 ml of 0.2M H_2SO_4 to extract all sorbed P. Molybdate-reactive P was then analysed in an aliquot of the H_2SO_4 solution diluted 1:5 in DDW (Daly, 2000).

PSI: (Daly, 2000). A 0.02M KCl solution containing 16 mg P l^{-1} was made using stock P solution. 50 ml of this solution was added to polypropylene bottles containing 0.5 g dry-weight soil, and the bottles were shaken at approximately 120 oscillations per minute for

24 hours to equilibrate the soil and solution. Solutions were then filtered through Whatman® no. 1 filter papers, and analysed for MRP after 1:50 dilution with DDW.

Oxalate-extractable P, Al and Fe (P_{ox}, Al_{ox} and Fe_{ox}): (Uusitalo and Tuhkanen, 2000). 0.2M oxalic acid was added to 0.2M ammonium oxalate (at a ratio of approximately 43% to 57%) to achieve a final pH of 3. 50 ml of this solution was added to 125 ml polypropylene bottles containing 1 g dried soil, and shaken at 120 oscillations per minute for 4 hours. The solution was then filtered through Whatman® no. 1 filter paper, diluted in DDW at a ratio of 1:50, and analysed for MRP as above, and Al and Fe using a Perkin Elmer Atomic Absorption Spectrophotometer.

OM content: (Allen, 1989). Approximately 1 g of oven-dry soil was accurately weighed (to 4 decimal places) and placed in a muffle furnace brought up to 550°C for 4 hours. After being left to cool in a desiccator, soils were re-weighed and percentage weight loss (OM content) calculated.

Total exchangeable bases (TEB): (Allen, 1989). 575 ml of glacial acetic acid and 600 ml of 0.88 ammonia solution were made up to 10 litres with DDW and adjusted to pH 7.0 using acetic acid or ammonia solution to produce ammonium acetate. 125 ml of this solution was then added to 250 ml polypropylene bottles containing 5 g dried soil, and shaken at 120 oscillations per minute for 1 hour. Solutions were filtered through Whatman® glass-fibre filter papers, diluted at up to 1:200 with DDW, and analysed for sodium (Na), potassium (K), calcium (Ca), Magnesium (Mg) and manganese (Mn) using a Perkin-Elmer Atomic Absorption Spectrophotometer.

Carbonate: (Allen, 1989). 40 ml of 0.5M hydrochloric acid (HCl) was added to 2 g dried soil in a glass beaker, mixed and left to stand for 1 hour. Excess acid was then titrated with 0.5M sodium hydroxide (NaOH), using phenolpthalein to indicate end point, and recording the quantity of NaOH needed.

Texture: 20 ml aliquots of 20* volume hydrogen peroxide were added to 50 g of dried (mineral) soil covered with water and heated on a hot plate to burn off OM, until reaction subsided, and the water was then evaporated off. 50 g of Calgon® were dissolved in 1 litre of distilled water and brought to pH 9 using sodium carbonate. 25 ml of this solution and 400 ml water were added to the soil in a 500 ml polypropylene container and shaken at 180

oscillations per minute for 2 hours. Individually, the bottles were emptied and rinsed with water up to the mark of a 1 litre graduated cylinder. The solution was stirred for 1 minute, left to settle and readings taken at exactly 4 minutes and 48 seconds and 5 hours with a Bouyoucos hydrometer and thermometer. Hydrometer readings (corrected for temperature) were then converted into clay and silt contents based on all clay having settled out of solution before the first reading and all silt having settled out of solution by the time of the second reading (Allen, 1989).

* The correct strength of hydrogen peroxide was not available, so more of a weaker strength solution was added. Therefore, it is possible that surprisingly low clay and silt contents noted in table 2.6 were the result of interference in the textural analyses by the high quantities of OM present in the studied soils (by flocculating with clay and silt particles). Textural data may therefore provide some comparison between soils, but may not be entirely reliable for soil classification purposes (the shallow depth of sampling may also have reduced clay and silt contents compared to average A-horizon contents).

All analyses used Analar R grade reagents and were conduced in duplicate, except P_w for monthly-analysed soils (triplicate), texture, pH, TOC and TN (no replicates). All glass and plastic ware used in analyses were thoroughly washed using DDW after every analysis, and periodically acid-washed. Filters were washed though with DDW prior to filtration of soil solution extracts. Analytical accuracy for P and other elemental concentrations in soil extract solutions was ensured for all analyses through the use of quality control (QC) standards. These QC standards were made by the laboratory technician from separate stock to calibration standards, and it was ensured that their measured concentrations always fell within an acceptable range of the true value (± 3%). Every effort was made to analyse samples exactly according to aforementioned methods. However, actual soil extraction methods were not validated using outside reference materials.

Table 2.1: Comparison of methodological differences for soils collected at different times for different purposes. Sorption refers to sorption from solutions containing 5 and 30 mg P l^{-1} only (i.e. not PSI).

Sample				Test	Ratio	Expression	Additional analyses
	No.	Depth	Condition				
Monthly	11	0-10 cm	Moist	Olsen P P_w Sorption	1:20 1:50 1:10	mg P/kg	moisture, pH, TN, TOC
March 2002	36	0-10 cm	Dried	Olsen P P_w Sorption	1:20 1:100 1:20	mg P/kg	moisture, pH, TN, TOC
Friary Fervenza Portodemouro		0-10 cm	Dried	Olsen P P_w Sorption	1:20 1:100 1:20	mg P/kg	moisture, Morgan, pH, TN, TOC
March 2003	33	0-5 cm	Moist + dried	Olsen P P_w	1:20 1:100	mg P/l	carbonate, Mn, moisture, Morgan, OM, ox.-ext. Al, Fe, P P_{feo}, pH, PSI, texture, TEB (Ca, K, Mg, Na).

2.2.4. Sample variability and accuracy

The extent and implications of sample variability were explored during monthly sample collection. From February to November 2002, one field was chosen for each sampling trip on which to conduct triplicate composite sampling. In the selected field, two composite samples were collected by following the usual 'W' pattern across the field, and another composite sample was taken by following a mirror-image 'W' pattern. These samples were then separately analysed in triplicate (for all the monthly-analyses procedures listed in the previous section) in the laboratory in order to estimate the accuracy of composite samples at representing field-scale soil characteristics. From the results, 95% confidence limits (CLs) were calculated for mean field-scale soil characteristics (table 2.2; no data for soil 4 due to oversight) according to the following equation:

$$95\%\ CL = 4.3 \times SE$$

where SE is the standard error, and is calculated from the standard deviation (SD) with Bessel's correction for small sample numbers applied (i.e. population SD = SD x square-root (n/n-1)).

As can be seen from table 2.2, estimated sample accuracy varied considerably among soils, and is very high in some instances. Replicate samples taken from soil 6 (high-level blanket peat), for example, displayed very high variability, likely to obscure any seasonal trends in soil P characteristics. For this particular soil, high variability is probably related to underlying sandy-gravel deposits which became incorporated into the bottom of soil cores where the overlying peat is shallow: thus, particularly when dried soil samples were ground for TOC and TN analyses, varying quantities of mineral material mixed into the sample resulted in highly variable results. These are reflected in apparently erratic monthly-sampling trends for this soil (see chapter 5). Olsen P is also highly variable for a number of soils (table 2.2), though variability appears to be substantially lower for the TP fraction. Humic-acid colour interference was a problem for Olsen P analyses (previous section), and may explain a substantial portion of the variability. Soil moisture content and pH displayed the lowest variability.

The effect of sample variability on inter-month comparisons was considered to be potentially particularly problematic, due to the relatively small seasonal variations expected in soil characteristics. However, despite the apparently relatively low accuracy of composite sampling for some soils, there are some surprisingly consistent trends in seasonal analyses, indicating that actual monthly sample variability may have been less than was indicated by the replicate composite samples. This could be explained by the consistent 'W' pattern used in monthly sampling, compared with the inclusion of an inverse pattern in replicate sampling; sample variability calculated from replicate samples may be over-estimates of variability associated with consistent seasonal sampling patterns. The impact of sample inaccuracy on sample representativeness of average field-scale soil characteristics is an issue for the interpretation of spatial sampling data in terms of relating soil characteristics to land use (section 4.5.2). However, it can only be qualitatively considered for these comparisons as sample variability appears to differ substantially among sites, and no sample variability data are available for most of the spatial data set.

Table 2.2: Summary results of an experiment testing the accuracy of systematic composite soil sampling. Mean values, and 95% confidence limits (CL) for field-scale soil characteristics - calculated from three composite sample replicates (collected during a different month for different soils) - are expressed for each measured parameter on each soil (except soil 4). Below each set of values, and in bold, is the CL expressed as a percentage of the mean value.

Soil	Month	Moisture	OC % weight	TN	pH	Olsen P	Olsen MUP	Olsen TP	Pw DRP mg P / kg	PwDMUP	PwTDP	Sorption
1	Nov	70±1.6	35.70±3.57	2.153±0.485	5.28+0.01	8.46±6.91	57.47±9.65	65.43±5.47	3.62±3.15	2.05±1.01	5.67±2.14	239.0±7.54
		2	**10**	**23**	**0**	**82**	**17**	**8**	**87**	**49**	**38**	**3**
2	Oct	32.4±7.7	4.70±1.03	0.398±0.078	5.17±0.13	60.96±13.46	67.12±12.03	128.07±24.17	6.06±1.49	2.43±0.34	8.49±1.69	270.1±15.7
		24	**22**	**20**	**3**	**22**	**18**	**19**	**25**	**14**	**20**	**6**
3	Jun	43.1±3.7	6.47±0.92	0.530±0.084	6.12±0.63	60.07±18.25	26.61±6.15	86.68±24.03	11.7±6.47	2.36±0.13	14.06±6.33	252.3±24.3
		9	**14**	**16**	**10**	**30**	**23**	**28**	**55**	**6**	**45**	**10**
4		-	-	-	-	-	-	-	-	-	-	-
		-	-	-	-	-	-	-	-	-	-	-
5	May	38.4±1.9	4.55±0.77	0.351±0.187	6.65±0.65	13.02±6.64	21.83±4.77	34.85±2.8	2.17±1.97	1.76±0.31	3.93±1.68	226.5±14.7
		6	**17**	**53**	**10**	**51**	**22**	**8**	**91**	**18**	**43**	**7**
6	Aug	73.2±14.8	29.56±33.68	1.272±1.786	3.89±0.59	3.04±13.19	42.29±28.13	45.34±18.82	0.55±0.15	0.60±0.30	1.16±0.44	235.8±62.5
		20	**115**	**140**	**15**	**434**	**67**	**42**	**27**	**50.0**	**37.9**	**26.5**
7	Sep	37.8±4.9	6.90±1.46	0.539±0.017	6.51±0.25	1.10±1.62	17.35±2.52	18.45±3.02	1.93±0.70	3.38±1.11	5.31±1.81	267.2±18.8
		13	**21**	**3**	**4**	**147**	**15**	**16**	**36**	**32.8**	**34.1**	**7.0**
8	Apr	34.5±3.5	3.33±1.45	0.303±0.101	7.55±0.69	25.61±4.66	21.76±4.67	47.38±7.30	3.14±0.70	2.84±0.59	5.98±0.82	255.8±6.2
		10	**44**	**31**	**9**	**18**	**22**	**15**	**22**	**21**	**14**	**2**
9	Mar	67.8±0.90			7.46±0.54	15.08±1.46	34.46±8.42	49.54±7.98	0.59±0.23	1.75±0.22	2.27±0.31	239.2±7.1
		1			**7**	**10**	**24**	**16**	**39**	**13**	**14**	**3**
10	Feb	43.86±2.71	6.39±0.22	0.590±0.000	6.57±0.72	80.56±35.20	36.57±20.52	117.12±50.49	6.99±2.39	0.84±1.27	7.83±2.99	257.1±29.3
		6	**3**	**0**	**11**	**44**	**56**	**43**	**34**	**151**	**38**	**11**
11	Jul	38.3±2.9	3.40±0.32	0.313±0.012	7.71±0.24	2.41±0.73	15.63±4.02	18.03±3.41	1.15±1.08	1.37±0.33	2.52±0.75	262.5±19.2
		8	**9**	**4**	**0**	**30**	**26**	**19**	**94**	**24**	**30**	**7**

Table 2.3 summarises and compares results from analyses of dried samples collected in March 2002 and March 2003 from 0-10 and 0-5 cm depths respectively. Results from analyses of dried samples collected from 0-10 cm depth in 2002 correlate very strongly with dried samples collected from 0-5 cm depth in March 2003. It could be construed that the reasonably close agreement between 2002 and 2003 samples from the 32 fields common to both sets of sample collection suggest reasonable sample accuracy. Significantly higher TOC, Morgan P and P_w TDP contents in the shallower 2003 samples (table 2.3) may be the consequence of OM, microbial biomass and applied P accumulation closer to the surface; in dried soil samples, microbial P content contributes to P_w TDP through cell-lyses induced P release (see section 3.6.1). It is unclear why TN contents, despite being highly correlated with TOC contents amongst samples (table 4.3), are higher in the deeper 2002 samples (table 2.3); presumably inorganic N is higher at this depth, perhaps due to a combination of leaching and higher uptake from the more densely rooted 0-5 cm depth. However, both TOC and TN are highly correlated between the years (figure 2.1).

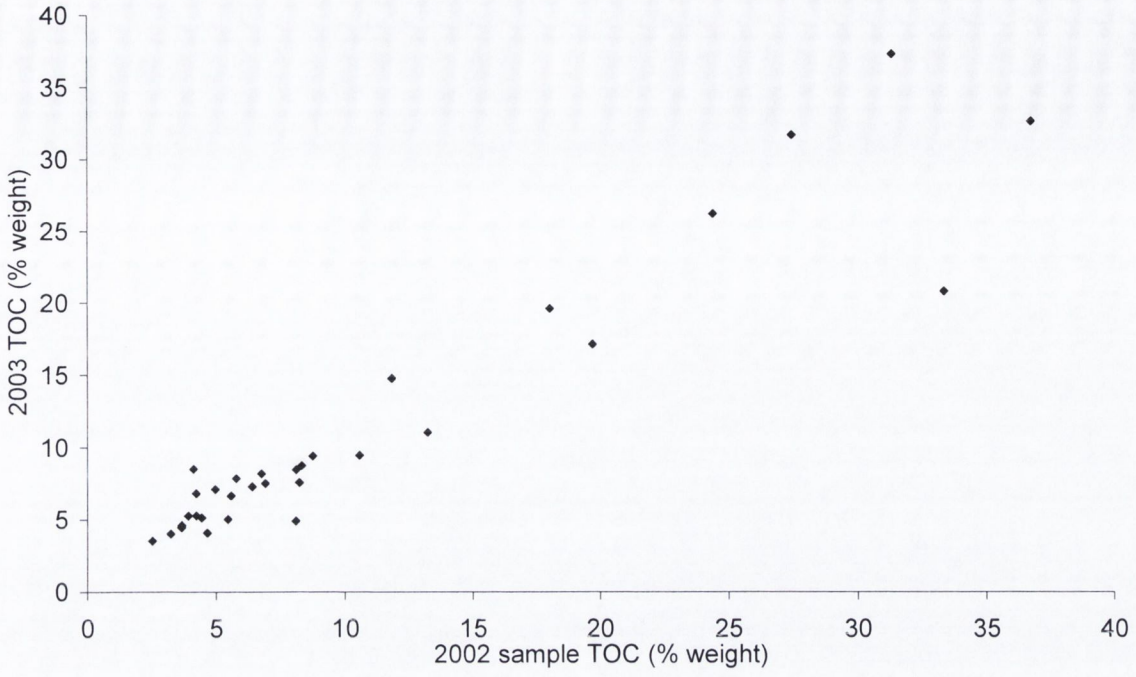
As with monthly sampling, though, samples taken in March 2002 and March 2003 were taken along a similar path across the fields (i.e. with the first leg of the 'W' pattern beginning at the field entrance), which may have reduced sample variability without improving accuracy. Additionally, composite sample variability was calculated for moist samples, which may differ from dried sample variability. Dried sample accuracy was also estimated for the 3 soils (reference numbers 2, 6 and 8) whose triplicate composite sample analyses corresponded with comparative moist and dried analyses (i.e. April, August and October 2002 samples). These data are summarised in table 2.4. Generally, variability seems greater among moist samples for soils 2 and 8, though among dried samples for soil 6. Paired *t*-test analysis indicate that there is no systematic difference between moist and dried sample variability, but the small number of samples limits any broader conclusions being made.

Table 2.3: Mean and SD values for characteristics analysed on spatial samples taken from 0-10 and 0-5 cm depth in the same fields in 2002 and 2003 respectively. Also shown are correlation coefficients (*r* and associated *p* values) and results (*t* and associated *p* values) of paired *t*-tests (on log transformed data) conducted on variables from the 2 years. n = 32.

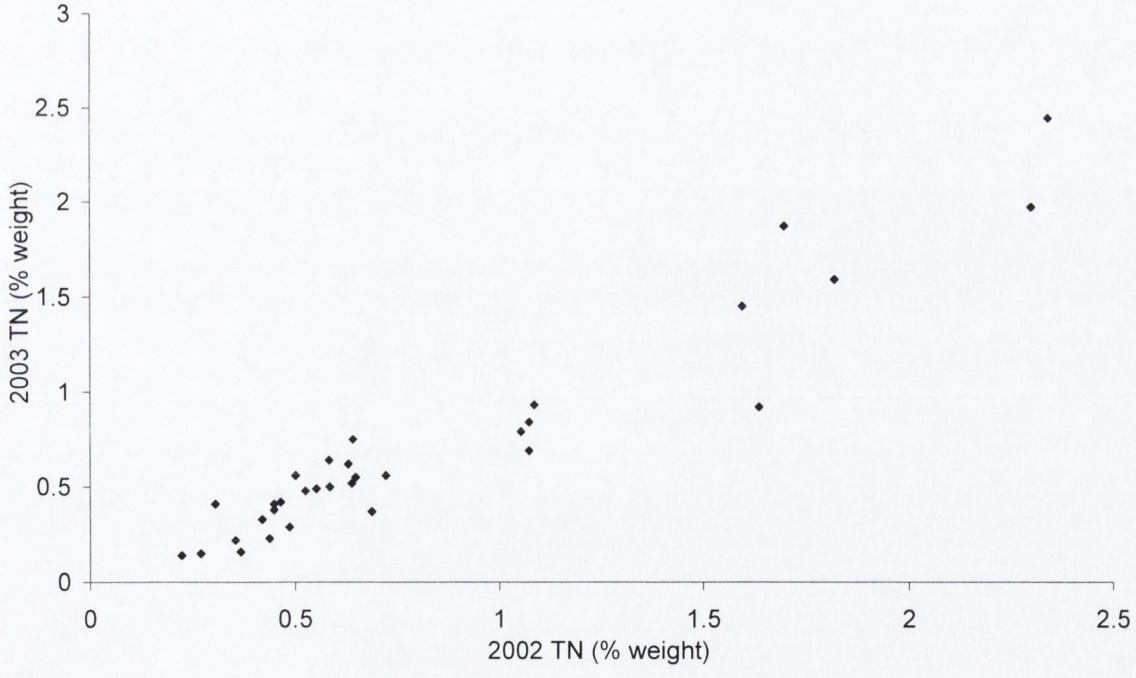
Variable	TN	TOC	pH	Pm	Olsen P	Olsen TP	P_wDRP	P_wTDP
	% weight			mg P / kg				
2002	**0.831**	**10.89**	**5.94**	**7.95**	**36.47**	**69.04**	**14.05**	**25.46**
SD	0.582	9.64	0.80	5.30	33.28	39.87	10.42	12.83
2003	**0.708**	**11.26**	**6.03**	**9.14**	**37.38**	**66.46**	**15.57**	**29.93**
SD	0.564	9.11	0.82	8.31	30.39	36.27	11.83	15.35
r	**0.96**	**0.95**	**0.92**	**0.88**	**0.9**	**0.91**	**0.87**	**0.88**
p	≤0.0001	≤0.0001	≤0.0001	≤0.0001	≤0.0001	≤0.0001	≤0.0001	≤0.0001
t	**4.69**	**2.21**	**1.55**	**0.16**	**1.07**	**0.41**	**1.82**	**3.08**
p	≤0.0001	0.0348	0.1396	0.8718	0.2932	0.682	0.0789	0.0043

Table 2.4: Mean values plus or minus 95% confidence limits (CL) for P characteristics from moist and dried samples of soils 2, 6 and 9 (expressed as a percentage of mean value in parenthesis). Calculated from triplicate composite samples for field average characteristics.

Soil	Sample	Olsen P		Olsen TP		PwDRP		PwTDP		Sorption	
		mg P / kg									
2	moist	60.96 ± 13.46	(22)	128.07 ± 24.17	(19)	6.06 ± 1.49	(25)	8.49 ± 1.69	(20)	270.1 ± 15.7	(6)
	dried	64.55 ± 6.67	(10)	115.70 ± 10.56	(9)	8.98 ± 0.74	(8)	15.49 ± 0.75	(5)	300.9 ± 2.1	(1)
6	moist	3.04 ± 13.19	(434)	45.34 ± 18.82	(42)	0.55 ± 0.15	(27)	1.16 ± 0.44	(38)	235.8 ± 62.5	(27)
	dried	15.29 ± 15.14	(99)	52.61 ± 67.67	(129)	13.77 ± 21.93	(159)	19.11 ± 33.62	(176)	304.6 ± 11.4	(4)
8	moist	25.61 ± 4.66	(18)	47.38 ± 7.30	(15)	3.14 ± 0.70	(22)	5.98 ± 0.82	(14)	255.8 ± 6.2	(2)
	dried	30.06 ± 1.41	(2)	55.21 ± 11.30	(10)	43.60 ± 1.05	(12)	11.16 ± 5.94	(17)	285.1 ± 5.94	(1)



(a)



(b)

Figure 2.1: Scatterplots showing the correlations between (a) total organic C (TOC) and (b) total N (TN) contents in soil samples collected from the same fields in March 2002 (0-10 cm depth) and March 2003 (0-5 cm depth).

2.2.5. Expression of concentrations

Jeffrey (1970) found a strong relationship between soil OM content and bulk density (BD: the dry-weight of a given volume of soil) on eighty 0-5 cm deep soil samples from a range of soil types in Australia and England:

$$BD = 1.482 - 0.6786 \log X, \qquad (r = -0.905) \quad \text{(Eq. 2.1)}$$

where BD is expressed as g/ml and X represents percentage ignition loss at 500°C (OM content). He argues that ecological comparisons are better made on a volume rather than weight basis.

Owing to the range of peat and mineral soils in this study, there is a wide range of BDs, with the consequence that expressing concentrations on a weight basis compares hugely differing volumes of soil. For example, based on OM content data presented in table 2.6 and equation 2.1, 1 kg of soil 12 represents a volume of 1.25 litres, whilst 1 kg of soil 39 represents a volume of 4.76 litres. Whilst soils of lower BD may have greater depths of soil – runoff water interaction (defined by Sharpley, 1985a), environmental interactions between soil and water are likely to approximate more to a volume basis. Therefore, where elemental concentrations are being compared between soils, especially in the development of soil P desorption indices (section 4.6), data are presented and compared on a volume basis, as calculated from Jeffrey's equation. Otherwise, concentrations are expressed as they were analysed - and according to standard practice - on a weight basis (e.g. for analysis of seasonal trends in chapter 5). The implications of, and insight from, the choice of soil elemental concentration expression is explored in relation to drying induced soil P changes (chapter 3).

2.3. Sample site characterisation

2.3.1. Soil type

It was originally intended that the 11 monthly-sampled soils would all be fully characterised by digging trial pits to get full visual and physico-chemical profile descriptions. However, farmer reluctance meant that this was not done, although trial pits were dug at 3 of the sites (soils 3, 10 and 11), and were unnecessary to classify peat soils 1, 6 and 9 (although profiles of soils 1 and 6 were naturally exposed anyway). Augered profiles of soils collected during spatial sampling in 2002 and 2003 were also briefly described (appendix A), and laboratory analyses of a reasonably wide range of general soil characteristics were carried out on 0–5 cm samples collected in March 2003 (section 2.2.3). The resulting data were used to tentatively classify soils into major soil units according to the United Nations Food and Agricultural Organisation (UN-FAO) classification system (table 2.2), following the classification key of Driessen and Dudal (1991). Based on the UN-FAO system, soils in the Mask catchment were classified into major soil groups according to a simplified system based on relevant characteristics in the following order of importance (greatest first):

Organic surface horizon – greater than 40 cm deep (less where directly above rock or rock fragments) defines histosols
Depth – less than 30 cm defines leptosols
Gleyic properties - within 50 cm of the surface defines gleysols
Subsurface OM / Fe / Al illuviation horizon – defines podzols
Subsurface clay enrichment horizon (in absence of mollic horizon) – defines luvisols
Absence of above diagnostic properties – defines cambisols

Some of these classifications involve the assessment of diagnostic properties which were not fully quantified by laboratory analyses, or which are related to subsurface horizons. In these instances, judgements were made based on the data available as to which major soil group or soil unit soils fell into. For example, the identification of mollic surface horizons involves a number of criteria related to thickness, soil structure, colour, OM content and base saturation (whether greater than 50%). There is no detailed information on soil structure, and soils were not analysed for base saturation. However, total exchangeable base (TEB) content in the top 5 cm was analysed on 2003 samples and was used as an

indicator of relative base saturation to identify soil units with mollic horizons, and major soil groups (the presence of a mollic horizon prohibits soils being classified as luvisols).

However, the UN-FAO system is not typically used in Ireland, and surface soil characteristics analysed in the laboratory may be directly used to estimate soil type. Gardiner and Radford (1980) described typical soil characteristics for Major Soil Groups, which are used to define the associations (mapping units) in which they are dominant in the Great Soil Map of Ireland, and are based on the old United States' Department of Agriculture (USDA) 1938 classification system. Daly (pers. comm., 2003) found that, for the 90 Irish grassland soils she studied, there was a good agreement between OM content in the top 10 cm and soil type, corresponding with the descriptions of Gardiner and Radford (1980). She subsequently grouped soils in her study according to OM content in the top 10 cm (Daly, 2001; table 2.5), and linked differing average laboratory P desorption characteristics of these groups to soil maps for use in reasonably successful predictive stream P concentration models (Daly et al., 2002).

Table 2.5: Organic matter (OM) thresholds used to categorise Irish grassland soils into groups representing associations of major soil groups (Daly et al., 2001; 2002).

OM content (% weight)	Principal soil types	Soil group
0 - 12	Brown earths, podzolics	S1
12 - 20	Gleys	S2
20 - 30	Peaty gleys, peaty podzols	S3
> 30	Peats	S4

Soil samples used assess the relationship between P desorption and Morgan P in this study were collected from 0-5 cm depth, and may therefore contain higher OM contents than comparable soils collected from 0-10 cm by Daly (2001). However, as indicated by the slightly higher TOC contents in 0-5 cm soil samples collected in March 2003 compared with 0-10 cm samples of the same soils collected in March 2002 (table 2.3), OM content is not hugely greater at 0-5 cm compared with 0-10 cm, and it still seems reasonable to use the same OM thresholds for simplicity. Soils were thus arranged into OM-based soil groups, as displayed in table 2.5, which were compared against the UN-FAO classifications in table 2.6.

Overall, there is general agreement between the two classifications in as far as they are comparable. Certainly both methods of classification agree on the identification of peat soils (S4 soils / histosols according to the OM-based and UN-FAO classifications respectively and shown in table 2.6), and both acknowledge the predominance of gleyic / stagnic properties in mineral soils from this catchment (reflecting the relatively high effective rainfall, poor soil drainage and seasonally high groundwater levels dominant in the catchment). However, there is some divergence of some soil characterisations according to UN-FAO soil units and OM-based soil groups apparent in table 2.6. For example, while both systems reflect the prevalence of gleyic / stagnic properties, there are some UN-FAO defined gleysols in OM-based soil group S1 (table 2.6) which is supposed to represent brown earths and podzolics only (table 2.5). In the UN-FAO classification system, subsurface soil characteristics (such as depth) and diagnostic subsurface horizons are important identifiers of soil type, and further distinctions may also rely on formative processes. For example, two soils with similar characteristics typical of periodic water saturation (e.g. mottling) may be differentiated according to whether that saturation was caused by poor drainage (stagnic properties) or high groundwater (gleyic properties). Such differentiation may be important from a soil classification perspective, but is not necessarily related to surface soil characteristics (or P desorption). Some deviation may also be attributable to management practices over time. Application of lime to soil 3 - a gleyic podzol - for example, may have encouraged OM decomposition. On a national scale, across a wider range of soil types and with a greater number of soils, agreement between OM-based soil group and UN-FAO / USDA classification systems may be expected to be closer (with more soils falling into S1 and S3 OM soil groups).

Therefore, and because of the high utility value of an easy (low data requirement) soil classification system which can easily be applied to existing national soil type data, soils in this study were grouped according to Daly (2001). This also allows for the direct comparison of P desorption indices developed from moist soil sample analyses in this study with desorption indices developed from dried soil sample analyses by Daly et al. (2001; 2002).

From table 2.6 it can be seen that there is a reasonably wide range of soil characteristics and soil types represented in this study, although all soils have relatively high OM contents (minimum 10.2%), reflecting the wet climate, shallow sample depth and years (probably decades) of surface soil OM accumulation under non-tilled pasture soils. Thus only four

soils fall into the S1 OM-based soil group, with the biggest single OM-based soil group being S2 – containing 16 soils ranging from 12 to 20% OM content (table 2.6). Organic matter differentiation between peat and mineral soils is distinct, with the highest predominantly mineral soil OM content of 27% being considerably lower than the lowest peat soil OM content of 38%, and only five soils falling into the 'peaty podzol / peaty gley' category (S3). There is a relatively wide range in soil pH, from acid peat soils (soil 6; pH 4.76) to mildly alkaline soils (soil 11; pH 7.57) for example, and carbonate contents of up to 12.6% reflect the calcareous parent material in some parts of the catchment. Iron content also varies considerably, with some very high Fe_{ox} contents in soils from the west of the catchment, again reflecting parent material. For example, high Fe_{ox} contents of 24 648 and 24 485 mg P kg^{-1} in soils 26 and 6 reflect conglomerate and sandstone bedrock geology (MT formation, with Fe deposits specified, in figure 1.3), although concentrations in these low bulk-density peat samples may also appear high due to standard expression on a weight basis in table 2.6 (see previous section). Analysed clay and silt contents appear to be relatively low for all soils (and compared with typical Major Soil Group characteristics detailed by Gardiner and Radford (1980)). This may be due to either flocculation of clay and silt with OM in particle size analyses (section 2.2.3) and / or because of the shallow 0-5 cm sample depth (erosion and translocation losses of clay from this upper layer). However, the analytical data do give an indication of relative soil textures, in conjunction with field estimations from augered samples.

Table 2.6: Summary of major soil characteristics for each soil alongside estimated soil type (soil units according to the UN-FAO classification system) and OM-based soil group (SG). Only soils on which OM analysed (collected in March 2003) displayed.

SG	Soil no.	UN-FAO Soil unit	Moist	OM	TOC %	TN	CO_3	pH	TEB meq	Fe_{ox} mg/kg	Clay	Silt %	Sand
S1	12	Dystric Gleysol	41.9	10.2	3.52	0.220	1.28	5.44	6.67	10852	10	22	68
	30	Gleyic Podzol	37.9	10.4	4.00	0.150	0.38	5.21	7.56	6727	8	8	84
	8	Haplic Luvisol	40.9	11.4	4.45	0.330	2.58	7.37	25.71	8762	7	17	76
	11	Mollic Gleysol	48.3	11.7	4.08	0.230	2.82	7.57	21.79	3889	12	20	68
S2	29	Haplic Podzol	44.8	12.3	4.60	0.140	1.16	5.14	9.17	9465	13	20	67
	5	Umbric Gleysol	45.8	13.0	5.26	0.410	2.06	6.48	17.80	5253	10	19	72
	2	Stagnic Luvisol	41.4	13.4	5.24	0.380	0.52	5.18	6.48	8771	11	26	63
	23	Gleyic Luvisol	38.4	15.1	5.02	0.290	2.08	6.35	28.81	4669	12	27	61
	31	Umbric Gleysol	52.6	15.3	8.49	0.410	0.26	5.16	6.92	4390	9	11	80
	25	Stagnic Luvisol	45.6	15.9	7.08	0.500	2.08	5.66	19.94	10187	15	30	55
	28	Gleyic Podzol	46.9	16.1	5.12	0.160	1.55	5.47	13.34	10026	11	24	65
	14	Dystric Cambisol	50.9	16.5	7.83	0.480	1.55	5.64	16.99	5589	14	23	63
	16	Mollic Gleysol	47.3	16.7	6.80	0.560	1.81	6.03	19.59	6615	10	26	64
	19	Mollic Gleysol	49.4	17.2	8.73	0.490	7.01	7.37	34.63	4460	11	13	77
	21	Stagnic Luvisol	42.0	17.2	7.28	0.620	2.35	6.49	28.21	10336	10	21	69
	15	Gleyic Luvisol	45.0	17.3	6.64	0.420	2.07	6.67	23.38	6214	12	22	66
	20	Mollic Gleysol	44.0	17.4	7.49	0.560	1.71	6.05	29.71	10598	10	24	66
	10	Gleyic Luvisol	48.7	18.1	8.16	0.640	1.04	5.65	15.52	5069	10	32	58
	4	Rendzic Leptosol	55.5	18.2	4.87	0.370	10.69	7.51	33.44	4272	10	22	68
	3	Gleyic Podzol	50.0	18.6	7.55	0.550	1.81	6.37	19.73	6520	6	22	72
	37	Mollic Leptosol	52.3	18.9	7.97	0.620	1.82	6.82	28.87	9027	10	27	63
S3	7	Rendzic Leptosol	44.8	20.4	8.43	0.519	2.52	5.85	29.91	11544	17	37	46
	27	Umbric Leptosoll	59.2	23.0	11.02	0.790	1.18	5.15	12.20	10367			
	34	Mollic Gleysol	56.2	23.2	9.44	0.840	4.50	7.08	42.87	11520	12	28	60
	18	Rendzic Leptosol	51.1	24.0	9.39	0.690	2.86	6.12	26.17	5925	10	15	75
	36	Gleyic Podzol	59.0	27.0	14.74	0.750	2.89	6.31	32.17	5875	7	15	79
S4	26	Fibric Histosol	72.0	38.0	19.60	0.930	2.68	6.02	30.29	24648			
	17	Terric Histosol	61.4	38.9	17.10	1.590	12.60	7.40	63.71	16636			
	24	Terric Histosol	62.2	47.1	26.17	1.450	4.42	5.47	49.55	7610			
	6	Fibric Histosl	76.2	50.5	20.78	0.919	0.00	4.76	10.12	24485			
	33	Terric Histosol	74.4	54.3	31.64	1.870	2.60	5.28	32.48	11038			
	1	Terric Histosol	69.9	63.2	32.57	1.970	3.38	5.08	33.80	11363			
	9	Terric Histosol	73.6	69.4	37.24	2.440	5.11	5.63	43.25	10218			
	38	Terric Histosol	69.8	73.6				5.99					
	39	Terric Histosol	72.4	75.9				6.67					

2.3.2. Land use

Land- owners of all sample fields were questioned about management practices (a copy of the questionnaire is shown in appendix A). The answers to this survey provided the data on the type of land use, type and quantity of P application, and, in some instances, approximate stocking density (table 2.7). Data obtained this way must be treated with caution for a number of reasons. Firstly, areal loading estimates of P applications were imprecise. Fertiliser application was often given as bags per field, and sometimes converted according to a visual estimate of field area, whilst slurry application was attributed an average P loading of 22 kg P ha^{-1} per application (as estimated by Teagasc, 1998), and this was arbitrarily halved in a few instances where farmers specified particularly light application. This is a problem, given the widely varying quantities of P applied in slurry applications, dependent on both the quantity of slurry applied and its P content / dilution. Constant rotation of animals between fields meant that farmers were unable to give precise estimates of average stocking density for any given field, although the type of animal that predominantly grazed specific fields was given. In some instances where farmers were unable to give estimates of stocking density, subjective judgements were made to categorise grazing into 'low' or 'high' intensities based on site assessment (e.g. the extent of poaching), although this was heavily dependent on the stage of field rotation observed during sampling. There is the additional problem that some farmers were suspicious of this study, and what the data would be used for: in some instances estimates of P application are suspected to be deliberate underestimates (a number of farmers claimed that they did not apply any P to apparently intensively used fields). These problems limit the usefulness of P application estimates, but were unavoidable given the casual nature of farmer participation.

Relating land use characteristics to soil P characteristics is complicated by relatively recent changes in management practices; the build up and decline of soil P in response to P application and off-takes occurs relatively slowly (McCollum, 1991; Power et al., 1995; Tiessen et al., 1983). This is especially problematic for sites where farmers have joined the Rural Environmental Protection Scheme (REPS). REPS is a voluntary scheme which subsidises farmers to manage land (up to 100 ha) less intensively, especially near water courses, as set out by the Department of Agriculture, Food and Rural development (2000). To receive REPS payments, various management practices must be adhered to, such as unique agri-environmental nutrient management plans devised for each farm. This is

likely to have reduced P inputs for most farms participating in the scheme, and consequently soil P contents in these farms may not correspond with current rates of application. For example, soil 10 has a relatively high Morgan P content (table 2.7), but is on a REPS participating farm and currently the farmer applies no P to this soil. Meanwhile, sites 18 and 19 both have high, identical current inputs of 59 kg P ha^{-1} a^{-1} (managed by the same farmer), but site 19 was recently reclaimed and had had only one year of P application compared with decades for site 18. Consequently, Morgan P content, whilst still high, is much lower in soil 19 compared with soil 18 (table 2.7).

Table 2.7: Land use type and estimated intensity for all study soils based on questionnaire responses about livestock units per hectare (personal estimates made in some instances, - indicates no data) and P application (assuming a 22 kg P ha^{-1} slurry application rate; 11 kg ha^{-1} if 'light' application). Also shown are soil Morgan P contents.

Soil no.	Land use	LU / ha	Fert. P	Slurry P kg/ha/y	Total P app.	Morgan P mg / l
1	cows	2	0	0	0	5.0
2	silage	2	26	0	26	8.7
3	sheep	5	22.5	22	44.5	22.4
4	silage / sheep	1	0	11	11	7.0
5	sheep	1.5	0	11	11	10.5
6	sheep	0.5	0	0	0	3.8
7	forestry	-	0	0	0	2.6
8	silage	low	0	0	0	14.9
9	cows	low	15	0	15	7.7
10	cows	low	0	0	0	14.5
11	sheep	0.5	0	0	0	2.1
12	silage / cows	-	25	22	47	2.9
13	horses	3	50	0	50	28.8
14	cows	1.5	0	0	0	5.3
15	cows	low	0	0	0	3.7
16	sheep	low	13	0	13	5.3
17	cows	0.5	0	0	0	6.6
18	cows	2	37	22	59	36.4
19	cows	2	37	22	59	19.7
20	sheep	high	-	-	0	21.9
21	sheep	2.5	37	11	48	25.0
22	cows	1	7.5	22	29.5	13.2
23	forest	-	0	0	0	1.2
24	cows	0.5	0	0	0	4.6
25	sheep	2	22	0	22	3.0
26	sheep	2	7.5	0	7.5	4.4
27	sheep	high	50	11	61	6.4
28	cows / sheep	>6	45	0	45	15.7
29	forestry	-	0	0	0	0.5
30	cows	5	15	0	15	3.2
31	sheep	low	-	0	0	11.7
32	horses	1	9	0	9	6.4
33	cows	1.5	5	0	5	6.5
34	cows	0.5	0	0	0	1.3
35	cows / sheep	1	0	0	0	0.0
36	sheep	-	7.5	11	18.5	8.4
37	silage	high	15	22	37	28.0
38	tillage	-	7	22	29	13.1
39	sheep	-	0	22	22	8.8

The forest soils (sites 7, 23 and 29) may provide a useful indication of soil P status in the absence of P applications, as no P is likely to have been applied since the trees were planted – all forest soils were found to have very low Morgan P contents (table 2.7). Site 7

is a coniferous plantation, and appeared to be the youngest forest site (with frequent disturbance of pine litter noticed during monthly sampling; table 5.3), whilst site 23 appeared to be an old, deciduous forest and site 29 a well-established mixed forest on the edge of a coniferous plantation. Additionally, soil 11 is unique in its known long-term management history, with no fertiliser application over the last 80+ years (owned by the same family, and now looked after by an 89 year old!). It is therefore a useful 'control' soil, but was only included in the final list of seasonal sample sites in March 2002 - when it was found that sites 4 and 5, initially claimed to be unfertilised, had manure applied to them. Table 2.7 shows that a relatively wide range of land use intensities is accounted for, with P application rates ranging from no P applied through to 59 kg P ha^{-1} yr^{-1}.

The difficulty of ensuring that selected sample sites represented a wide range of soil P status across the different soil types (Morgan P content determined by analysis after sample collection) is referred to in section 2.1.3. This led to the problem of a narrow range of Morgan P contents in the peat soils collected in 2003 (the highest peat soil Morgan P content was 7.7 mg l^{-1} in soil 9). Therefore, two additional peat soil samples were collected in October 2003 from fields which were selected after confirming with the land owner that they were intensively managed (soils 38 and 39; table 2.7). These soils were intended to represent higher soil P status peat soils in order to more accurately compare the Morgan P-P desorption relationships between peat and mineral soils (section 4.5.6). Only moisture content, OM content, pH and P desorption analyses were conducted on these soils (table 2.6), in order to provide sufficient data to better define the Morgan P–P desorption relationship for peat soils. Although it was not ideal to compare samples of these soils collected at a different time from samples of the other soils, it was confirmed with the farmer that no P had been applied to the soils in the preceding few months, and it was hoped that leaving collection until October (rather than earlier in the autumn or summer) would reduce the extent of any seasonal differences in P desorption (section 5.4.4). In any case, differences between soils tend to be greater than seasonal differences within the same soils; compare data in sections 4.5 and 5.4.4.

Otherwise, there is a relatively wide range of Morgan P contents amongst mineral soils, from 0.5 to 28.8 mg P l^{-1}, spanning the four Teagasc soil P indices (table 2.8). Because of the high Morgan P contents necessary to classify peat soils above Teagasc soil P index 1 (> 10 mg P l^{-1}; table 2.8), 8 of the 9 peat soils fall within this index, resulting in a high frequency of soils in this index (figure 2.2). Similarly, because soil P index 4 includes all

mineral soils above 10 mg P l^{-1}, a relatively large number of soils fall into this index. This leaves just 5 and 4 soils respectively in soil P indices 2 and 3.

Figure 2.3 displays the distribution of soil Morgan P contents within the Mask catchment, as interpolated from Teagasc sampling data, and mapped according to Daly et al. (2002) in order to test their Morgan P – based nutrient transport model. This map is used to apply the soil P desorption index (PDI) devised in section 4.6 to Mask subcatchments.

Table 2.8: Soil Morgan P ranges for the four P indices used by Teagasc to categorise soil P status.

Index	Status	Morgan P		
		Mineral	mg/l	Peat
1	Low	0.0 - 3.0		0 -1 0
2	Medium	3.1 - 6.0		11 - 20
3	High	6.1 - 10.0		21 - 30
4	Very high	>10		>30

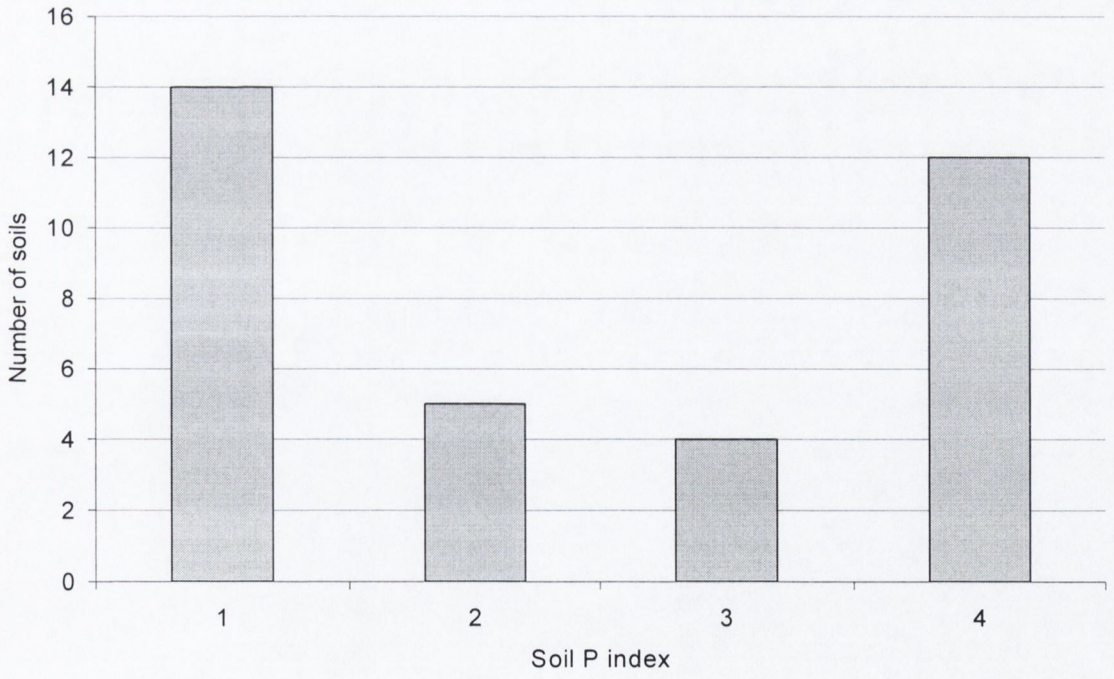


Figure 2.2: Frequency distribution for mineral soil Morgan P concentrations falling within each of the four Teagasc soil P indices (table 2.8).

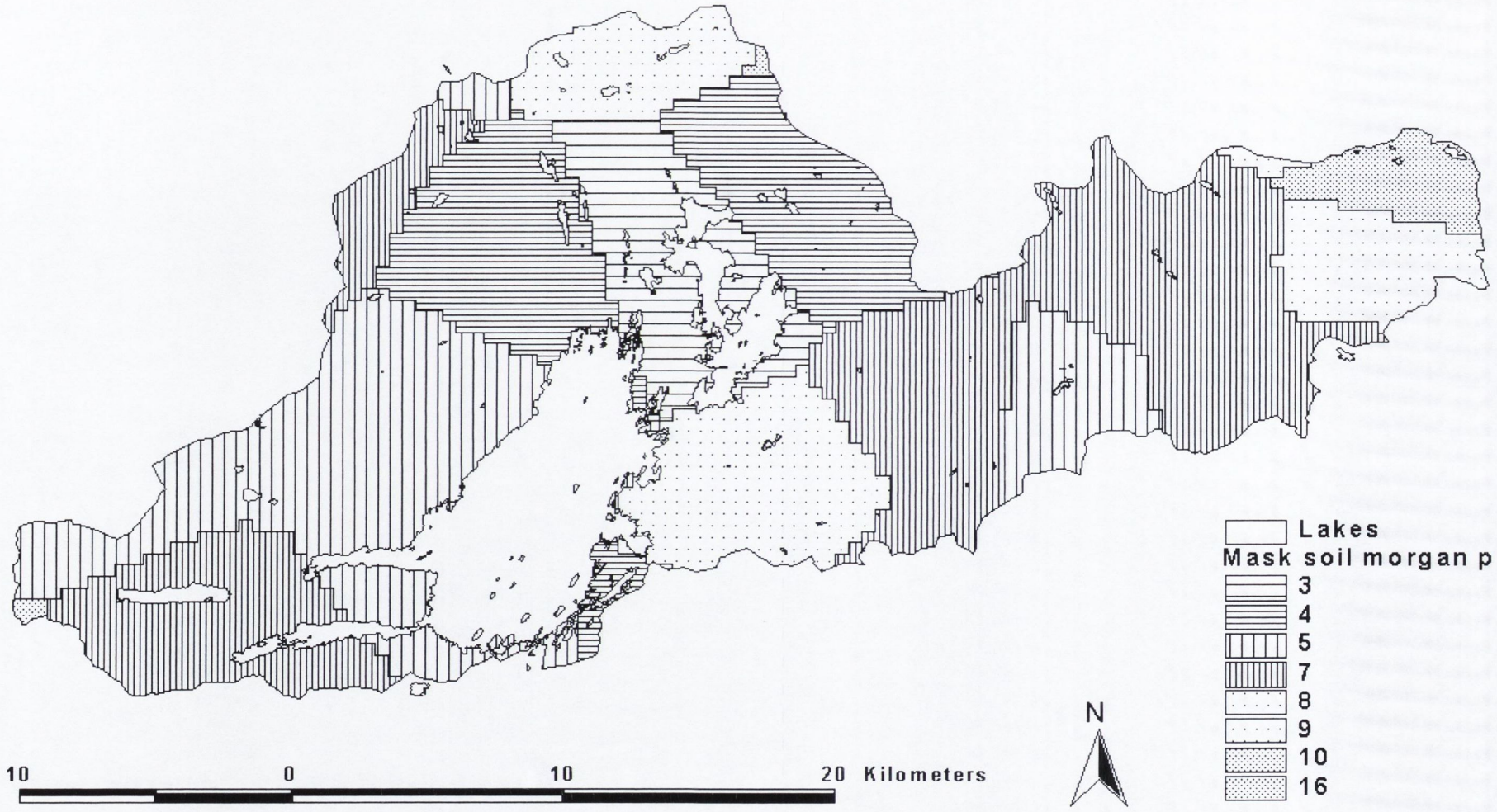


Figure 2.3: Distribution of soil Morgan P content within the Mask catchment, based on Teagasc data mapped by Daly et al. (2002).

2.4. Water data

2.4.1. BUFFER stream and lake water sampling

Water samples were collected from 14 locations on 11 rivers (see figure 1.2) throughout the catchment, incorporating all the major inflows to the lakes, and analysed by Ian Donohue for the BUFFER project. Discrete samples were collected bi-weekly from July 2001 to November 2002, and monthly from December 2002 until July 2003. Samples were analysed for, amongst other characteristics, (dissolved) MRP, TDP and TP concentrations according to methodology out-lined in Donohue et al. (submitted: see appendix C), and compatible with P_w analyses (DRP and TDP). River discharges at time of sampling were calculated from stage readings and stage-discharge relationships supplied by the EPA, and used to calculate nutirnet loads at time of sampling. These data were available to compare with soil data. Whilst this thesis focuses on soil chemistry, some comparison with water data was performed to determine the extent to which soil chemistry is important in catchment scale P losses.

2.4.2. Subsurface water sampling

In an attempt to bridge the gap between soil P characteristics and stream P concentrations, it was decided that subsurface water samples would be taken as an additional component of this research, though this was not part of the BUFFER project. In order to do this, zero-tension samplers designed to collect macro-pore flow water were constructed according to Simmons and Baker (1993): see figure 2.4. They were designed to collect water from depths of 8-21 and 51–63 cm, in order to compare data with that of Kurz (2000) who analysed P concentrations in subsurface water collected from the same depths under Irish grassland soils. Zero-tension samplers were installed by hand-augering holes into soils at 45°, and then using the same 5.5 cm diameter pipe that was used to construct the samplers to enlarge the holes to exactly the correct diameter. The zero-tension samplers were then gently forced down into the holes, where joiners of slightly wider diameter than the main body piping, used either side of the collection openings in the samplers, ensured a very tight fit and minimised the risk of surface water seepage along the outside of the samplers. Soil was compacted around the area where the zero-tension sampler broke the surface, and clay placed around edge of the samplers located in mineral soil to further minimise seepage

risk. It was particularly difficult to bore the holes in the mineral soils, especially for the deeper samplers (maximum length of over 1 m). For example, where one deeper zero-tension sampler was installed in mineral soil 10, layers of high clay and stone content were encountered and progress was very slow (other workers used tractor mounted augering screws to bore out the holes: Kurz, 2000; Simmons and Baker, 1993). Therefore, only shallow samplers were installed in one field containing mineral soil (soil 10).

The zero-tension samplers were constructed during summer 2002, and were finally installed in September 2002. It was intended that two samplers (one shallow, the other deep) be located at three locations within three fields of differing P status, to provide an indication of variation within and between fields, and between different depths. Due to the difficulties encountered installing the samplers in mineral soils, two peat soils (soil numbers 1 and 9) were chosen for comparison. Thus, three shallow and one deep sampler were installed in field 10, three shallow and three deep samplers were installed in field 1, and two shallow and two deep samplers were installed in field 9 (additional samplers intended for installation in field 9 were broken during attempted installation in other locations). Samplers were installed at locations selected randomly within the fields.

Water samples were collected from the samplers once a month, during standard soil sampling and water collection, from October 2002 until the penultimate water sampling trip in June 2003 (samplers were removed during July 2003 water sampling trip). Water was collected out of the samplers by attaching a hand held vacuum filtration unit to a pipe protruding from the sampler, sealing the top of the filtration unit, and pumping the water into the vacuum flask – if necessary, repeatedly until the sampler was empty. Simmons and Baker (1993) found that only around 50% of installed samplers collected any water (under mineral soils). In field 10, the deep sampler did not collect any water, perhaps due to the clay layer reducing vertical subsurface water movement at depth, whilst 2 of the 3 shallow samplers collected water. However, all the samplers placed in the wet peat soils collected water, although sometimes this appeared to be shallow groundwater as the vacuum flask used to collect the water could be filled repeatedly before the rate of flow slowed.

Monthly empying of zero-tension samplers was dictated by the sampling schedule, but was not ideal. Water may have been lying in the samplers for weeks prior to collection, during which time chemical and biological processes may have been occurring. For example, soil

particulates and organic debris that may have migrated into the samplers over time, bringing desorbable or soluble P with them, or sorbing P from the collecting waters. Changing pH and redox conditions could also affect chemical equilibria between colloidal or partciclate matter and collecting water. Micobial activity within the samplers could have immobilised P from the collecting waters, whilst enzymatic activity may have released P to solution. Haygarth et al, (1995) found that decreases in soil water MRP occurred very rapidly (over hours to days) after collection, and suggested that soil waters should be analysed within 48 hours of collection. Obviously, this was not the case here, although filtration through 0.45 μm membrane filters immediately upon collection was performed to minimise further cahnges after collection and prior to analysis. Only the TDP fraction was analysed in collected waters - according to the same method used for P_w extracts (section 2.2.3) – to negate the effect DOP - MRP changes.

Ultimately, high variability within fields meant that subsurface water P data were of little use in determining the effect of land use or soil P status, but they did display some apparently coherent seasonal variations; thus subsurface water P data are incorporated into the chapter dealing with seasonal variability (chapter 5, section 5.6.2).

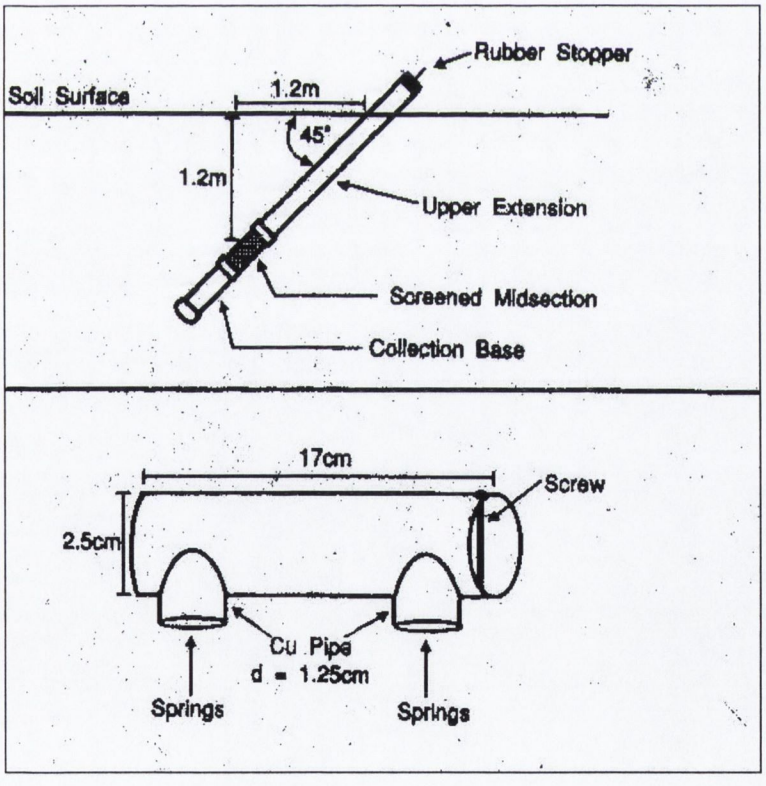


Figure 2.4: A diagram showing the design and installation of zero-tension samplers (from Simmons and Baker, 1993). See text above for installation depths used here.

2.5. Statistical analyses

Statistical analyses were performed using Microsoft Excel 2000, Data Desk version 6 and Minitab. Data were first tested for normal distribution, and, where necessary, transformed (usually logarithmically) in Data Desk for parametric analyses. The linear model function in Data Desk was used to perform analysis of variance (ANOVA), analysis of covariance (ANCOVA) and repeated measures on soil data. *Post-hoc* Least Significant Difference (LSD) tests were conducted where possible and necessary, after confirmation of significant relationships in ANOVA, ANCOVA or repeated measures analyses. Details of specific designs, including data transformations and interactions, are listed with their results. Kruskal-Wallis tests were used for more than two groups of non-parametric data. Where two sets of data were compared, either two sample or paired *t*-tests were used where data were approximately normally distributed. Mann-Whitney tests were used if at least one of the datasets were non-parametric.

Correlations between variables were conducted using Pearson Product-Moment correlation for parametric data or Spearman Rank correlation for non-parametric data. Step-wise multiple regression was performed according to Velleman (1993), by correlating the residuals of the dependent variable with all independent variables being tested for relationships. The highest correlations were selected, and visually checked for approximately normal distribution using scatter-plots, and transformed or discarded if necessary. Once included in the regression, correlations of residuals with other characteristics were up-dated and the characteristics with the highest correlation again selected, screened, and included or discarded from the regression equation depending on conformation to approximately normal distribution.

Figure 2.5 displays and describes the features of a box-plot, as used in chapter 5 to display data distributions.

Extreme values (circles) represent values which exceed the upper or lower whiskers of the



Star represents extreme outlier.

Circle represents outlier.

Horizontal bar of "T" (whiskers) is $75\%^{ile}$ + 1.5 x interquartile range (IQR)

Top of box is the 75th percentile.

The horizontal bar in the box is the median.
Base of box is the 25th percentile.

Horizontal bar of inverted "T" (whiskers) is $25\%^{ile}$ – 1.5 x IQR

boxplot, i.e. greater than $75\%^{ile}$ + 1.5, or lower than $25\%^{ile}$ – 1.5 x IQR. Extreme outliers (starbursts) represent values greater than $75\%^{ile}$ + 3 x IQR, or lower than $25\%^{ile}$ – 3 x IQR.

Figure 2.5: A description of the statistical boundaries displayed in boxplots, as used in this thesis to represent and compare data spread amongst variables (after Velleman, 1993).

CHAPTER 3

THE EFFECT OF AIR-DRYING SOIL SAMPLES ON ANALYSED PHOSPHORUS CHARACTERISTICS

3.1. Introduction

Standard preparation of soil samples prior to laboratory analysis usually involves drying the soil samples (Haynes and Swift, 1985a), either at room temperature or in an oven at temperatures usually between 30°C and 105°C. Some workers suggest that temperatures above 35°C are not recommended for P analysis due to large effects on soil physico-chemical properties (such as degredation of organo-metallic complexes) at high temperatures (e.g. Boone et al., 1999). Subsequent sieving through 2 mm mesh sieve removes rock fragments and debris of greater diameter than the coarse sand fraction, and helps homogenise the sample. Soils prepared in this manner are often stored for long periods prior to analysis. In contrast, moist soils must be kept cool (around 4°C) and analysed rapidly after collection (Chapman et al., 1997; Boone et al., 1999). They are also more difficult and time consuming to handle, so encouraging the method of soil drying where large batches of samples are analysed. However, whilst well-documented drying effects on soil N dynamics have led to the analysis of moist soil samples for inorganic N species, soil P analyses are still predominantly conducted on dried soil samples. Whilst drying soil samples has been known to have an effect on soil P measurements - especially P desorption - for some time (e.g. Bartlett and James, 1980), the issue, and its implications for understanding diffuse soil P losses, has only been focussed on relatively recently (Pote et al., 1999a; Turner and Haygarth 2001; Turner et al., 2002; Turner et al., 2003). Some of this work has aimed to identify specific mechanisms of drying-induced P release (e.g. microbial cell lysis; Turner et al., 2003). Work presented in this chapter does not aim to do this, but to establish whether any empirical relationships exist between commonly measured soil characteristics and / or season with the extent of drying-induced P release. Are there soil characteristics associated with microbial P content that could indicate the extent of drying-induced P release? Do wetter, higher OM soils display greater increases in P desorption after drying, and are increases greater in the wetter winter months than the drier summer months? The consequent implications for interpretation of soil P data, especially with respect to understanding diffuse P losses, are explored - though this is conducted more quantitatively in chapter 4.

3.2. Literature review

3.2.1. Microbial P release after drying

Bartlett and James (1980) state; "Moist soil is a delicately-poised system in a remarkably stable state of non-equilibrium. Air-drying brings about instant and major changes toward over-all equilibrium but converts some portions of the soil into highly unstable or reactive (high entropy) soil material''. It has been well documented that, immediately upon rewetting, dried soils contain much less microbial biomass than original moist soils (Stevenson, 1956; Kieft et al., 1987; Sparling et al., 1985, Turner et al., 2003; Van Gestel et al., 1991), although Mack (1962) found that drying soils had no effect on the number of viable bacterial cells. Kieft (1987), by comparing biomass released to water and KCl solution of similar osmotic potential to soil water, attributed some of this decline in biomass to the drying process itself, but most of it to the more sudden osmotic shock experienced when the soils are rewetted with water (accounting for the release of 17 – 58% of biomass C). Specifically, they hypothesise that biomass C is released to solution via both cell lyses and export of intracellular solutes from viable cells as they adjust to the change in water potential. Whilst microbial biomass constitutes only 2-3% of soil organic C, it may contain more P than overlying vegetation in temperate grasslands (Brookes et al., 1982), and is therefore an important reservoir of soil P. Consequently, biomass P has been found to contribute to substantial increases in concentrations of P in water and bicarbonate extractions from dried soils (Brookes et al., 1982; Chepkwony et al. 2001; Sparling et al., 1985; Srivastava, 1997; Turner and Haygarth, 2001; Turner et al, 2003; Turner and Haygarth, 2003). Increases in these extractable P concentrations after drying have been found to correlate well with microbial P content (Sparling et al., 1985, Turner and Haygarth, 2001, Turner et al., 2003). Sparling et al. (1985) found that bicarbonate extractable P_i increases after drying 18 soil samples correlated strongly ($r = 0.97$; $p \leq 0.05$) with P release calculated from measurements of microbial biomass decline after drying and the extractable P content of this microbial biomass, whilst Turner and Haygarth (2001) found that the increase in water extractable (similar to P_w) organic P fraction after drying 29 English and Welsh grassland soil samples was strongly related to microbial P content ($r^2 = 0.58$; $p = 1.6 \times 10^{-6}$). Detailed work on 2 Australian pasture soils found that almost all viable bacterial cells were lysed after soil drying and rewetting, and that the potential P contribution from these cells was equal to 88 and 137% of water-extractable P increase after drying. It was thought that the high latter figure may have been the consequence of a

concurrent drying-induced increase in P sorption capacity in that soil: the potential microbial P contribution was equal to 95% of water-extract MUP increase (Turner et al., 2003).

Particularly large proportional increases in water-extractable P have been found to occur after soil drying, with a 19 fold increase observed by Turner and Haygarth (2001) after 30°C drying. Kieft et al. (1987) and Van Gestel et al. (1991) suggest that soil microbes may be selectively adapted to moisture stresses in soils that experience natural wet – dry cycles, and data from Sparling et al. (1985) suggest that soils not normally exposed to moisture stress showed greater decreases in biomass after drying and rewetting. Pote et al. (1999) observed Pw increases after drying of only around 30% for Arkansas soils exposed to seasonal drying (only 4.6% moisture content during August sampling), whilst increases of 185 - 1900% have been observed from UK lowland pasture soils not normally exposed to natural drying (Turner and Haygarth, 2001). In contrast to increases in bicarbonate-extractable P, which include large P_i fraction increases (Brookes et al., 1982; Sparling et al., 1985; Srivastava, 1997; Turner and Haygarth, 2003), P_w increases are dominated by organic P concentrations in the water extracts (Turner and Haygarth, 2001; Turner et al., 2002). Analyses of the specific P fractions in soil water extracts before and after drying have found that the MUP fraction increases after drying, with significant quantities (0.132 to 0.344 μg P g^{-1}) of organic orthophosphate diester release consistent with microbial P lyses (Turner et al., 2002) as the dominant source. Additional data which may support the hypothesis that microbial P release is the dominant mechanism of P increase in some extractants after drying include the absence of any drying effect on ammonium hydroxide – lactic acid – acetic acid (ALA) extractable P (Venterink et al., 2002) and Mehlich III P (Pote et al., 1999), and oxalate- or pyrophosphate- extractable P (Haynes and Swift, 1985a). These harsh extractants are believed to be capable of extracting microbial bound P, irrespective of whether the soil has been dried.

3.2.2. Physico-chemical factors contributing to water-extractable P increase after drying

Whilst microbial cell lysis is an important mechanism of P release from soils after drying and rewetting, there are other physical and chemical processes which occur during the drying process that affect P dynamics within the soil solution matrix. Commenting on large increases (5.2 – 26.8 mg P kg^{-1}) in total bicarbonate-extractable P contents of 29 England and Wales pasture soils after drying, including large P_i fraction (Olsen P) increases (2.5 – 21.4 mg P kg^{-1}), Turner et al. (2003) concluded that physico-chemical factors other than microbial P release increase extractable P after soil drying. Van Gestel et al. (1991) conclude that lysed microbial cells made only a minor contribution to large mineralisation flushes after rewetting dried soils, whilst Nevo and Hagin (1966) studied increased nitrification rates in soil samples after drying, and found that they were not significantly lower in sterilised compared with non-sterilised samples - concluding that changes occurring in soil during drying and dried storage are independent of micro-organisms.

A number of mechanisms of drying-induced P release have been related to (non-microbial) soil OM. Substantially increased SOC concentrations have been found in extracts from dried soils (Bartlett and James, 1980; Raveh and Avnimelech, 1978; Stevenson, 1956; Van Gestel et al., 1991). It has been proposed that aggregate damage caused by soil shrinking and swelling during drying and rewetting exposes previously unexposed soil organic matter and sorption surfaces, thus potentially increasing P solubilisation and desorption (Chepkwony et al., 2001). Nevo and Hagen (1966) found a strong correlation between nitrification rate and soil surface area, proposing that increases in nitrification rate upon rewetting after drying were caused by changes in the physical structure of the organic fraction and related increase in soil surface area. Specifically, a study by Raveh and Avnimelech (1978) indicated that increased extract concentrations of SOC and dispersible organic C after drying resulted from organic micelle instability caused by the destruction of hydrogen bonds associated with the removal of water molecules during the drying process. This is succeeded by other, slower processes occurring over time of dryness. Decoiling of complex humic compounds and oxidation of newly exposed organic surfaces are thought responsible for changes in pysico-chemical characteristics which were found to continue for 10 weeks at 105°C (Raveh and Avnimelech, 1978). Bartlett and James (1980) found that organic carbon became increasingly soluble after drying, and with time of dry

storage, and Nevo and Hagen (1966) found greater increases in nitrification rates upon rewetting with increasing time of storage.

Observations of increased SOC concentrations may thus be used to infer mechanisms of P release associated with drying. However, SOC concentration increases may also actually cause some of the increases in P release upon the rewetting of dried soils. Associated with the increased microbial energy supply provided by increased SOC concentrations after drying is a rapid flush of mineralisation immediately upon rewetting (Bartlett and James, 1980; Stevenson, 1956; Van Gestel et al., 1991), which releases OM - associated P (Chepkwony et al. 2001). Also, P behaviour in the soil-solution matrix is highly dependent on redox chemistry (section 2.2.4), which elevated SOC concentrations affect. Bartlett and James (1980) note that oxidization of SOC reduces redox potential, and that this effect is dependent on the severity of drying and time of storage: different treatments affected oxidizing capacity in the following order, with the greatest effects and lowest subsequent oxidizing capacities listed first: 105°C oven-dried > air-dried 2 month stored > 40°C oven dried > field moist. It has been suggested that oxidation of the soil SOC fraction increases acidity (Raveh and Avnimelech, 1978), although some studies have found pH to increase after drying (e.g. Ross et al., 1994), probably due to other controlling factors such as increasing Ca and Mg activities (Bartlett and James, 1980). Olsen and Court (1982) noted that percentage increases in rapid soil P desorption (4-hour resin extraction) after soils were exposed to a wetting - drying cycle were significantly correlated with pH, and suggest that at higher pH, more of the P desorption sites exposed by soil drying will be of low energy and therefore desorb P more rapidly (220 hour P desorption was less affected by drying).

Further evidence that drying soil samples affects pysico-chemical P release comes from changes in extractable concentrations of metals associated with P sorption after drying. A number of studies have found increases in extractable Al, Ca, Fe, and Mn (Bartlett and James, 1980; Phillips, 1998; Ross et al., 1994), although Comfort et al. (1991) found that oxalate-, EDTA- and potassium chloride- extractable Al and Fe decreased after drying, and Haynes and Swift (1985a) found no significant increase in oxalate- or pyrophosphate-extractable Al and Fe concentrations after drying. However, Haynes and Swift (1985a) used observations of drying-induced increases in EDTA extractable Al, Fe, OM and P to suggest that drying-induced desorbable P increases may be the consequence of disruption to organo-metallic complexes associated with EDTA extractable OM. Turner et al. (2002)

found substantial increases in inositol hexakisphosphate - which usually forms strong complexes with Al, Fe and Ca compounds - after drying 5 Australian pasture soils.

Changes in soil P sorption capacity may also be important in determining P release after drying, although such changes are poorly understood. Reasons for observations of increased soil P sorption capacities after drying (Bartlett and James, 1980; Comfort et al., 1991; Haynes and Swift, 1985a) are not fully understood, and contradict the hypothesis that drying reduces P sorption capacity through increased crystallisation and reduced specific surface area of Al and Fe (hydr)oxides (Phillips, 1998). The same mechanisms that increase P desorption after drying soil samples, by exposing new (de)sorption sites, may also increase P sorption - the net effect may depend on the saturation or energy level of the exposed sites. Olsen and Court (1982) found that increases in adsorption and rapid desorption correlated strongly ($p \leq 0.01$) with each other and with CEC, taken to reflect the disruption of weak bonds and exposure of new reactive surfaces.

3.2.3. Implications for interpretation and environmental P losses

There are two ways in which data on soil drying may be interpreted regarding natural P losses: problematically and instructively. On the problem side, there are serious implications for relating laboratory measured characteristics of dried soils (especially readily desorbable P) to natural P losses from the analysed soils. Readily desorbable P from dried soil has been found to correlate well with simulated runoff P concentrations (Pote et al., 1996; Sharpley and Menzel, 1981; Sharpley, 1995), as have various methods of STP (Pote et al., 1996; Sharpley, 1995; Turtola and Yli-Halla, 1999). However, these relationships are dependent on soil characteristics, such as sorption capacity, and thus vary between soil types (Pote et al., 1996; Sharpley, 1995). The effect of soil drying on readily desorbable P release also varies among soils, related to characteristics such as microbial P content (Turner and Haygarth, 2001). Thus, drying soils will alter the observed relationships between soil test data and runoff P concentrations, with implications for interpreting the effect of STP and soil type on water P concentrations. Some STP methods have been found to be unaffected by drying (e.g. Mehlich III P - Pote et al., 1999; ALA–P - Venterink et al., 2002), although some studies have found significant increases in Olsen P after drying (Srivastava, 1997; Turner and Haygarth, 2003). In any case, relationships between standard agronomic STP tests and P_w will be changed by soil drying. Drying 5

Autralian pasture soil samples was also found to reduce the proportion of potentially bioavailable (enzyme hydrolysable) P within the dominant MUP fraction of filtered P_w extracts, from $\leq$ 65% of moist soil P_w MUP to $\leq$ 50% of dried soil P_w MUP (Turner et al., 2002). The P_w concentrations of dried soils may therefore also be less representative of potential bioavailable P loss in natural conditions.

Another problem associated with the interpretation of dried soil sample results may also have potentially instructive applications. It is thought that readily desorbable P and runoff P losses are affected by seasonal variations in soil conditions, especially moisture content (Pote et al., 1999a; see chapter 5). Drying soil samples masks seasonal variations in soil P desorption characteristics influenced by natural soil drying, as observed in moist analysed soils (Pote et al., 1999). In fact, Tate et al. (1991a) suggest that microbial biomass P acts as a seasonal buffer for soil P release, which would imply that seasonal variations in microbial P release upon drying and rewetting may actually counter natural variations in moist (field condition) soil readily-desorbable P concentrations. Seasonal changes in P desorption related to the accumulation of mineralised P during long dry periods may be masked by the flush of mineralised P that occurs upon the rewetting of dried soil samples (Bartlett and James, 1980; Stevenson, 1956; Van Gestel et al., 1991). However, drying-induced P release from different soil types may be indicative of the extent of potential P desorption from different soil types following natural soil drying events (at least for those soils that experience strong wet-dry cycles). In other words, dry soil data may provide a useful indication of maximum potential P release under extreme drying conditions, although this may be of little relevance to the humid temperate soils studied here.

3.2.4. Other limitations of soil laboratory analyses

Under natural field conditions, soil hydrology plays a crucial role in determining soil P losses, not only through its control on the pathways and efficiency of P transport, but also on the rate of P desorption related to soil physico-chemical properties. Soils exposed to prolonged water saturation may undergo reductions in redox potential, with consequences for P desorption. Some studies have found that water-logging increases extractable P concentrations (Chepkwony et al., 2001; Phillips, 1998), attributable to reduction of P-associated compounds (e.g. Fe (III) hydr(oxides)) to mobile soluble forms (e.g. Fe (II) hydroxides)). Concurrent decreases in P_w during water-logging have been attributed to

increased P sorption onto the increased surface areas of reduced amorphous Fe (II) hydroxides (Phillips, 1998), and increased concentrations of dissolved ions reducing P dissolution through a common-ion effect (Mack and Barber, 1960). However, Nair et al. (1999) observed reduced sorption capacities in spodosols under anaerobic conditions, and associated higher equilibrium solution P concentrations. Ultimately, it is extremely difficult to maintain samples at field redox potential during analysis, and changes in redox chemistry for some soils may alter their P characteristics and limit the applicability of laboratory data to field conditions, even where field-moist samples are used.

Additionally, whilst sieving soil may be practically necessary to homogenise samples, its effect on soil structure has physico-chemical and biological consequences on soil P fractionation, as indicated by changes in soil solution fractionation after sieving found by Chapman et al. (1997). Further, whilst a number of studies have noted minimal changes in some characteristics over time for soils stored at 4°C (e.g. sorption; Comfort et al. 1991), Chapman et al. (1997) found that TDP, DRP and DOP concentrations in soil water rapidly decreased with time during 4°C soil sample storage.

3.3. Methodology

This chapter deals with data from analyses of 11 monthly-collected ('seasonal sample') soils which were analysed in moist and dried form on four occasions (January, April, August and October 2002), and 33 soils collected in March 2003 ('spatial samples') which were also analysed in moist and dried form for P desorption. While July sampling would have resulted in a more orthogonal seasonal pattern, soils still apppeard relatively moist during this month, and had dried out more by August (figure 5.3b) – thus being more representative of typical drier summer conditions. The additional two peat soils sampled in October 2003 to provide extra data on peat desorption are not included in this section, as detailed soil characterisation analyses were not conducted on these soils (so drying effects cannot be compared with general soil characteristics). Details of soil site selection, and soil sample preparation and analyses are outlined in chapter 2. Note the different sample depths and soil-water ratios used in P_w analyses for seasonal (0-10 cm depth, 1:50 ratio) and spatial (0-5 cm depth, 1:100) samples.

The seasonal samples were analysed in both moist and dried form for P_w (DRP and TDP fractions), Olsen P (and TP fraction) and P sorption from solutions containing 5 and 30 mg P l^{-1} solution. Sorption from solutions of different concentrations was intended for use in determining Freundlich K_f values (see section 4.2.3), but because of low soil P loading (sorption) from the 5 mg P l^{-1} solution at the 1:10 soil-solution ratio used for monthly analysed soils (see section 2.2.3) this was not possible. Therefore, only sorption from 30 mg P l^{-1} solution was compared between moist and dried samples, and is assumed to be an indicator of P sorption potential. Phosphorus desorption from spatial samples was additionally analysed according to the P_{feo} method (section 2.2.3), which is a measure of soil bioavailable P_i (section 4.2.3). The MUP fraction of water extracts (P_wMUP) was calculated for all soils simply by subtracting soil P_wDRP from P_wTDP content, and is compared alongside P_wDRP and P_{feo} in this chapter because it may be indicative of the sources of drying-induced P release.

All concentrations are expressed on an oven-dry weight basis, and to ensure accurate comparison between moist and dried samples, moist sample Olsen-extract P contents and sorption were corrected to take account of greater volume of solution resulting from soil moisture content (not done for P_w because of high soil-water ratio and insignificant impact on results). Concentrations in the spatial samples were converted to a volume basis

according to Jeffery (1970) (see section 2.2.5). Whilst it is more appropriate to use volume basis concentrations for comparing soils of widely varying BD, especially in relation to environmental interactions (Jeffrey, 1970; see section 2.2.5), drying-induced P concentration changes are also expressed on a weight basis in this chapter. There are three reasons for this;

1) in order to highlight the effect the choice of soil concentration expression has on comparisons among soils (fitting into the methodological context of this chapter);

2) to gain some insight into mechanisms of drying-induced changes, and the importance of soil characteristics;

3) to enable comparison with drying-induced P increases recorded in the literature.

3.4. Spatial sampling results

3.4.1. Changes in desorbable P

Tables 3.1a and b show the range of changes in P desorption (P_w fractions and P_{feo}) after drying for the 33 soils collected in March 2003, expressed on a weight basis (3.1a) and volume basis (3.1b). For all but 2 soils, desorbable P fractions increased substantially after drying, with percentage change in P_w TDP ranging from –35% for soil 7 to 1010% for soil 6, and percentage change in P_{feo} ranging from –45% for soil 18 to 3378% for soil 6. Repeated measures analyses were performed on (log transformed) weight-basis P desorption. Site, sample condition (moist or dried) and fraction (P_w DRP and MUP, P_{feo}) were the independent variables, and an interactions between site and sample condition, and desorbable P fraction and sample condition, were included. These analyses confirmed that changes in desorption after drying are highly statistically significant ($F_{1,128} = 196.73$, $p \leq 0.0001$), and vary depending on site ($F_{32,128} = 1.81$, $p = 0.0111$) and desorbable P fraction ($F_{2,128} = 8.38$, $p = 0.0004$). Almost identical results are obtained when conducting the same analyses on volume-basis desorption data.

Table 3.1a: Mean and SD. of of 2 replicate analyses for water extractable P (P_w) and bioavailable P (P_{feo}) on moist and dried samples collected in March 2003, with absolute and percentage change after drying shown in brackets. Concentrations expressed on an oven-dry weight basis.

Soil	P_w DRP			P_w TDP			Pf_{eo}		
no.	Moist	Dried	Change	Moist	Dried	Change	Moist	Dried	Change
			%		mg P kg^{-1} soil	%			%
1	3.78 ± 0.37	15.72 ± 0.96	11.94 (316)	7.42 ± 0.27	43.07 ± 1.81	35.65 (480)	15.58 ± 0.18	68.51 ± 0.51	52.94 (340)
2	10.48 ± 0.20	16.09 ± 2.29	5.60 (53)	14.43 ± 0.00	38.56 ± 1.30	24.13 (167)	30.03 ± 2.84	49.09 ± 2.04	19.05 (63)
3	17.88 ± 2.54	32.70 ± 2.05	14.83 (83)	22.00 ± 2.93	60.10 ± 3.63	38.09 (173)	51.39 ± 5.17	93.24 ± 1.02	41.84 (81)
4	3.62 ± 0.59	9.05 ± 0.24	5.43 (150)	6.44 ± 0.87	38.94 ± 2.07	32.50 (505)	14.55 ± 0.68	49.57 ± 0.00	35.01 (241)
5	9.29 ± 0.91	12.37 ± 1.08	3.08 (33)	12.90 ± 1.20	30.56 ± 2.07	17.66 (137)	21.15 ± 1.47	42.31 ± 3.06	21.16 (100)
6	2.11 ± 0.03	16.63 ± 0.12	14.52 (689)	3.52 ± 0.31	39.12 ± 2.59	35.60 (1010)	0.89 ± 0.26	31.10 ± 0.00	30.20 (3378)
7	16.96 ± 0.90	7.16 ± 0.12	-9.79 (-58)	24.45 ± 0.63	15.62 ± 1.17	-8.83 (-36)	34.48 ± 3.37	36.64 ± 5.10	2.16 (6)
8	8.59 ± 1.12	10.80 ± 0.60	2.21 (26)	13.18 ± 1.18	21.53 ± 0.52	8.35 (63)	23.80 ± 1.27	38.63 ± 3.06	14.83 (62)
9	8.64 ± 1.30	24.85 ± 0.72	16.21 (188)	11.91 ± 1.13	48.31 ± 2.46	36.40 (306)	28.66 ± 4.80	61.37 ± 0.00	32.71 (114)
10	16.28 ± 1.55	25.82 ± 0.36	9.54 (59)	20.41 ± 1.61	39.51 ± 0.13	19.10 (94)	51.68 ± 1.29	93.21 ± 1.02	41.52 (80)
11	1.21 ± 0.25	3.75 ± 0.12	2.54 (211)	2.82 ± 0.10	12.28 ± 0.13	9.46 (336)	4.74 ± 0.75	16.60 ± 0.51	11.85 (250)
12	3.62 ± 0.24	7.33 ± 0.24	3.70 (102)	6.65 ± 0.40	15.38 ± 0.78	8.73 (131)	11.21 ± 0.23	24.16 ± 0.76	12.95 (116)
14	2.12 ± 0.01	11.90 ± 0.36	9.78 (462)	5.03 ± 0.54	22.66 ± 0.65	17.63 (350)	8.64 ± 2.07	45.69 ± 4.33	37.04 (429)
15	5.26 ± 0.11	7.06 ± 0.24	1.80 (34)	8.28 ± 0.50	22.48 ± 1.17	14.20 (172)	20.73 ± 1.17	25.00 ± 1.53	4.28 (21)
16	4.27 ± 1.24	10.48 ± 0.36	6.20 (145)	8.36 ± 2.75	24.61 ± 0.78	16.26 (195)	26.25 ± 1.52	42.46 ± 2.04	16.21 (62)
17	1.06 ± 0.02	4.47 ± 0.24	3.42 (322)	3.64 ± 0.18	8.62 ± 0.00	4.98 (137)	3.91 ± 0.02	19.33 ± 0.51	15.41 (394)
18	57.16 ± 1.59	61.53 ± 1.81	4.37 (8)	61.82 ± 1.46	77.50 ± 1.81	15.67 (25)	132.87 ± 0.71	72.67 ± 1.02	-60.20 (-45)
19	11.34 ± 0.16	13.43 ± 0.00	2.09 (18)	14.80 ± 0.50	26.60 ± 0.00	11.80 (80)	32.69 ± 1.10	51.95 ± 1.53	19.26 (59)
20	23.72 ± 2.55	27.98 ± 0.60	4.26 (18)	28.48 ± 2.58	38.92 ± 1.17	10.44 (37)	78.41 ± 2.56	104.36 ± 6.12	25.95 (33)
21	22.97 ± 0.87	27.57 ± 0.48	4.59 (20)	26.65 ± 0.71	40.07 ± 0.65	13.42 (50)	73.83 ± 2.84	98.57 ± 1.02	24.74 (34)
23	1.30 ± 0.28	3.27 ± 0.12	1.97 (151)	4.17 ± 0.37	11.31 ± 0.13	7.14 (171)	2.10 ± 0.00	11.22 ± 0.51	9.11 (433)
24	3.72 ± 0.74	15.60 ± 0.48	11.87 (319)	6.83 ± 1.17	27.88 ± 1.04	21.05 (308)	8.94 ± 1.74	46.50 ± 0.51	37.57 (420)
25	4.77 ± 0.18	8.06 ± 0.12	3.29 (69)	8.58 ± 0.13	19.33 ± 1.68	10.74 (125)	16.41 ± 0.40	29.59 ± 3.06	13.18 (80)
26	3.50 ± 1.17	6.48 ± 0.36	2.98 (85)	6.34 ± 1.16	17.37 ± 0.65	11.03 (174)	9.23 ± 0.58	19.50 ± 0.76	10.27 (111)
27	14.87 ± 1.14	24.80 ± 0.72	9.93 (67)	19.89 ± 0.74	44.22 ± 0.65	24.32 (122)	30.19 ± 0.23	71.32 ± 2.55	41.13 (136)
28	20.02 ± 2.39	23.77 ± 0.48	3.75 (19)	24.76 ± 2.87	35.12 ± 0.65	10.36 (42)	39.78 ± 4.23	74.86 ± 2.55	35.08 (88)
29	1.36 ± 0.24	2.45 ± 0.00	1.10 (81)	2.87 ± 0.25	7.35 ± 0.26	4.48 (156)	1.61 ± 0.25	5.01 ± 0.25	3.40 (211)
30	5.39 ± 0.47	7.47 ± 0.24	2.07 (38)	8.45 ± 0.23	14.00 ± 0.26	5.55 (66)	14.25 ± 0.61	22.77 ± 2.04	8.52 (60)
31	11.64 ± 0.15	23.05 ± 0.12	11.40 (98)	15.08 ± 0.86	32.82 ± 0.39	17.74 (118)	24.31 ± 0.69	55.56 ± 0.51	31.25 (129)
33	2.62 ± 0.73	17.78 ± 1.08	15.16 (579)	4.33 ± 0.12	34.13 ± 1.94	29.80 (688)	7.35 ± 2.95	36.04 ± 2.29	28.69 (390)
34	1.29 ± 0.37	5.31 ± 0.12	4.02 (311)	8.01 ± 1.53	22.17 ± 0.65	14.16 (177)	1.42 ± 0.02	14.85 ± 0.51	13.44 (948)
36	10.54 ± 1.24	13.49 ± 0.60	2.95 (28)	11.33 ± 2.49	27.48 ± 0.78	16.16 (143)	23.83 ± 0.69	46.88 ± 1.02	23.05 (97)
37	20.02 ± 0.11	28.46 ± 1.45	8.44 (42)	24.12 ± 0.15	47.33 ± 2.33	23.21 (96)	60.00 ± 1.76	87.50 ± 3.06	27.50 (46)

Table 3.1b: Mean and SD. of of 2 replicate analyses for water extractable P (P_w) and bioavailable P (P_{feo}) on moist and dried samples collected in March 2003, with absolute and percentage change after drying shown in brackets. Concentrations expressed on a volume basis.

Soil	Pw DRP			Pw TDP			Pfeo		
no.	Moist	Dried	Change	Moist	Dried	Change	Moist	Dried	Change
			%		mg P l^{-1} soil	%			%
1	0.98 ± 0.10	4.08 ± 0.25	3.1 (316)	1.93 ± 0.07	11.2 ± 0.47	9.26 (480)	4.05 ± 0.05	17.8 ± 0.13	13.8 (340)
2	7.51 ± 0.15	11.5 ± 1.64	4.01 (53)	10.3 ± 0.00	27.6 ± 0.93	17.3 (167)	21.5 ± 2.04	35.2 ± 1.46	13.7 (63)
3	11.1 ± 1.58	20.3 ± 1.27	9.2 (83)	13.7 ± 1.82	37.3 ± 2.25	23.6 (173)	31.9 ± 3.21	57.9 ± 0.63	26 (81)
4	2.27 ± 0.37	5.68 ± 0.15	3.41 (150)	4.04 ± 0.54	24.4 ± 1.30	20.4 (505)	9.13 ± 0.42	31.1 ± 0.00	22 (241)
5	6.74 ± 0.66	8.97 ± 0.79	2.23 (33)	9.36 ± 0.87	22.2 ± 1.50	12.8 (137)	15.3 ± 1.07	30.7 ± 2.22	15.4 (100)
6	0.69 ± 0.01	5.42 ± 0.04	4.74 (689)	1.15 ± 0.10	12.8 ± 0.84	11.6 (1010)	0.29 ± 0.08	10.1 ± 0.00	9.85 (3378)
7	10.1 ± 0.54	4.25 ± 0.07	-5.81 (-58)	14.5 ± 0.37	9.27 ± 0.69	-5.24 (-36)	20.5 ± 2.00	21.8 ± 3.02	1.28 (6)
8	6.57 ± 0.86	8.27 ± 0.46	1.69 (26)	10.1 ± 0.90	16.5 ± 0.40	6.39 (63)	18.2 ± 0.97	29.6 ± 2.34	11.4 (62)
9	2.01 ± 0.30	5.77 ± 0.17	3.77 (188)	2.77 ± 0.26	11.2 ± 0.57	8.46 (306)	6.66 ± 1.11	14.3 ± 0.00	7.6 (114)
10	10.2 ± 0.97	16.2 ± 0.23	6 (59)	12.8 ± 1.01	24.8 ± 0.08	12 (94)	32.5 ± 0.81	58.6 ± 0.64	26.1 (80)
11	0.91 ± 0.19	2.83 ± 0.09	1.92 (211)	2.13 ± 0.08	9.28 ± 0.10	7.15 (336)	3.58 ± 0.56	12.6 ± 0.39	8.96 (250)
12	2.89 ± 0.19	5.84 ± 0.19	2.95 (102)	5.3 ± 0.32	12.3 ± 0.62	6.97 (131)	8.95 ± 0.19	19.3 ± 0.61	10.3 (116)
14	1.39 ± 0.00	7.8 ± 0.24	6.41 (462)	3.3 ± 0.35	14.9 ± 0.42	11.6 (350)	5.66 ± 1.36	29.9 ± 2.84	24.3 (429)
15	3.37 ± 0.07	4.53 ± 0.15	1.15 (34)	5.31 ± 0.32	14.4 ± 0.75	9.11 (172)	13.3 ± 0.75	16 ± 0.98	2.74 (21)
16	2.79 ± 0.81	6.83 ± 0.24	4.04 (145)	5.45 ± 1.79	16.1 ± 0.51	10.6 (195)	17.1 ± 0.99	27.7 ± 1.33	10.6 (62)
17	0.43 ± 0.01	1.8 ± 0.10	1.38 (322)	1.47 ± 0.07	3.47 ± 0.00	2.01 (137)	1.58 ± 0.01	7.79 ± 0.21	6.21 (394)
18	31.2 ± 0.87	33.6 ± 0.99	2.39 (8)	33.7 ± 0.80	42.3 ± 0.99	8.55 (25)	72.5 ± 0.39	39.7 ± 0.56	-32.9 (-45)
19	7.29 ± 0.10	8.64 ± 0.00	1.35 (18)	9.52 ± 0.32	17.1 ± 0.00	7.59 (80)	21 ± 0.71	33.4 ± 0.98	12.4 (59)
20	15.2 ± 1.63	17.9 ± 0.39	2.73 (18)	18.2 ± 1.65	24.9 ± 0.75	6.69 (37)	50.2 ± 1.64	66.9 ± 3.92	16.6 (33)
21	14.8 ± 0.56	17.7 ± 0.31	2.95 (20)	17.1 ± 0.46	25.8 ± 0.42	8.63 (50)	47.5 ± 1.82	63.4 ± 0.66	15.9 (34)
23	0.89 ± 0.19	2.23 ± 0.08	1.34 (151)	2.85 ± 0.25	7.71 ± 0.09	4.87 (171)	1.44 ± 0.00	7.65 ± 0.35	6.21 (433)
24	1.29 ± 0.26	5.41 ± 0.17	4.12 (319)	2.37 ± 0.41	9.67 ± 0.36	7.3 (308)	3.1 ± 0.60	16.1 ± 0.18	13 (420)
25	3.18 ± 0.12	5.36 ± 0.08	2.19 (69)	5.72 ± 0.09	12.9 ± 1.12	7.15 (125)	10.9 ± 0.27	19.7 ± 2.04	8.78 (80)
26	1.44 ± 0.48	2.65 ± 0.15	1.22 (85)	2.6 ± 0.47	7.12 ± 0.27	4.52 (174)	3.78 ± 0.24	7.99 ± 0.31	4.21 (111)
27	8.3 ± 0.64	13.8 ± 0.40	5.54 (67)	11.1 ± 0.41	24.7 ± 0.36	13.6 (122)	16.9 ± 0.13	39.8 ± 1.42	23 (136)
28	13.3 ± 1.58	15.8 ± 0.32	2.49 (19)	16.4 ± 1.90	23.3 ± 0.43	6.87 (42)	26.4 ± 2.80	49.6 ± 1.69	23.3 (88)
29	1.01 ± 0.18	1.82 ± 0.00	0.81 (81)	2.13 ± 0.19	5.45 ± 0.19	3.33 (156)	1.19 ± 0.19	3.71 ± 0.19	2.52 (211)
30	4.28 ± 0.38	5.92 ± 0.19	1.64 (38)	6.7 ± 0.18	11.1 ± 0.21	4.4 (66)	11.3 ± 0.48	18.1 ± 1.62	6.76 (60)
31	7.9 ± 0.10	15.6 ± 0.08	7.73 (98)	10.2 ± 0.58	22.3 ± 0.26	12 (118)	16.5 ± 0.47	37.7 ± 0.35	21.2 (129)
33	0.8 ± 0.22	5.42 ± 0.33	4.62 (579)	1.32 ± 0.04	10.4 ± 0.59	9.08 (688)	2.24 ± 0.90	11 ± 0.70	8.74 (390)
34	0.72 ± 0.20	2.95 ± 0.07	2.23 (311)	4.44 ± 0.85	12.3 ± 0.36	7.86 (177)	0.79 ± 0.01	8.24 ± 0.28	7.46 (948)
36	5.38 ± 0.64	6.89 ± 0.31	1.51 (28)	5.78 ± 1.27	24.2 ± 0.40	18.4 (318)	12.2 ± 0.35	23.9 ± 0.52	11.8 (97)
37	12.3 ± 0.07	17.5 ± 0.89	5.19 (42)	14.8 ± 0.09	29.1 ± 1.43	14.3 (96)	36.9 ± 1.08	53.9 ± 1.88	16.9 (46)

Repeated measures analyses were conducted on (log transformed) actual and percentage increases against soil number and desorbable P fractions (table 3.2), in order to determine whether there were significant differences in dry-induced increases among sites and fractions. *Post-hoc* analyses were used to determine the relative size of drying-induced P increases among different fractions. Confirming the significant interaction noted between both soil and fraction with moisture condition in the initial set of repeated measures analyses, drying-induced increases are highly significantly different among soils ($p \leq 0.0001$) and among fractions ($p \leq 0.0001$), expressed either on a weight or volume basis. *Post-hoc* LSD analyses (and tables 3.3a - d) show that drying-induced desorbable P increases are greatest for the P_{feo} fraction (averaging 20.64 mg P kg^{-1}), followed by the P_w MUP fraction (averaging 10.96 mg P kg^{-1}) and P_w DRP fraction with the lowest increases (5.92 mg P kg^{-1}). Expressing soil desorbable P contents on a weight or volume basis has no effect on the significance of these differences, but *post-hoc* LSD analyses on percentage increases show that the highest relative increases in P desorption induced by soil drying are for the P_w MUP fraction (averaging 393%), followed by the P_{feo} fraction (averaging 272%) and the P_w DRP fraction again showing the lowest proportional increases (averaging 144%). Further analyses of the data show that most (mean of 62%) of the drying-induced P release to water is in the MUP from, increasing the mean contribution this fraction makes to P_w TDP from 37 to 51%.

Table 3.2: Repeated measures results (*F* and associated *p* values) dsisplaying the significance of differences among samples (site: *df* = 32, 62) and fractions (*df* = 2, 62) - listed as independent variables (IV) - for drying induced increases and percentage increases in desorbable P (P_w DRP and MUP and P_{feo} fractions). Log transformed data analysed.

Expression	IV		Increase	
			Concentration	Percentage
Weight	**Site**	*F*	**8.16**	**4.63**
		p	≤0.0001	≤0.0001
	Fraction	*F*	**94.79**	**25.71**
		p	≤0.0001	≤0.0001
Volume	**Site**	*F*	**5.73**	
		p	≤0.0001	
	Fraction	*F*	**84.76**	
		p	≤0.0001	

Tables 3.3a – d: Mean and SD. of desorbable P fractions for moist and dried samples, and their increases after drying, for all 33 soils, and separately for the 26 mineral soils and seven peat soils, expressed on a weight and volume basis.

Table 3.3a

	Moist P_wDRP		Dried P_wDRP		Increase		Increase
	mg kg^{-1}	mg l^{-1}	mg kg^{-1}	mg l^{-1}	mg kg^{-1}	mg l^{-1}	%
All	**10.04**	**6.03**	**15.96**	**9.07**	**5.92**	**3.04**	**144**
SD	10.94	6.40	11.86	7.00	5.34	2.56	172
Peat	**3.63**	**1.09**	**14.50**	**4.37**	**10.87**	**3.28**	**357**
SD	2.42	0.53	6.95	1.57	5.48	1.46	211
Mineral	**11.77**	**7.37**	**16.35**	**10.34**	**4.58**	**2.97**	**87**
SD	11.72	6.61	12.95	7.36	4.54	2.80	107

Table 3.3b

	Moist P_wTDP		Dried P_wTDP		Increase		Increase
	mg kg^{-1}	mg l^{-1}	mg kg^{-1}	mg l^{-1}	mg kg^{-1}	mg l^{-1}	%
All	**13.57**	**8.14**	**30.45**	**17.51**	**16.88**	**9.37**	**206**
SD	11.59	6.92	15.41	9.14	10.76	5.51	209
Peat	**6.29**	**1.94**	**31.22**	**9.40**	**24.93**	**7.46**	**443**
SD	2.94	0.65	14.24	3.14	12.85	3.23	313
Mineral	**15.54**	**9.81**	**30.25**	**19.69**	**14.71**	**9.88**	**142**
SD	12.28	6.89	15.97	9.01	9.24	5.92	113

Table 3.3c

	Moist P_wMUP		Dried P_wMUP		Increase		Increase
	mg kg^{-1}	mg l^{-1}	mg kg^{-1}	mg l^{-1}	mg kg^{-1}	mg l^{-1}	%
All	**3.53**	**2.11**	**14.49**	**8.44**	**10.96**	**6.33**	**393**
SD	1.39	0.99	6.55	4.08	6.60	4.04	375
Peat	**2.65**	**0.85**	**16.71**	**5.04**	**14.06**	**4.19**	**607**
SD	0.82	0.28	8.20	1.92	8.13	2.08	472
Mineral	**3.77**	**2.45**	**13.90**	**9.35**	**10.13**	**6.91**	**335**
SD	1.43	0.82	6.08	4.04	6.04	4.27	332

Table 3.3d

	Moist P_{feo}		Dried P_{feo}		Increase		Increase
	mg kg^{-1}	mg l^{-1}	mg kg^{-1}	mg l^{-1}	mg kg^{-1}	mg l^{-1}	%
All	**27.42**	**16.52**	**48.06**	**27.90**	**20.64**	**11.39**	**272**
SD	27.68	16.56	27.18	17.79	19.36	10.58	590
Peat	**10.65**	**3.10**	**40.34**	**12.16**	**29.68**	**9.06**	**735**
SD	9.18	2.04	19.38	3.96	14.11	3.47	1173
Mineral	**31.94**	**20.13**	**50.14**	**32.14**	**18.21**	**12.02**	**147**
SD	29.33	16.92	28.89	17.69	20.07	11.76	200

3.4.2. Soil type influences

Section 2.3.1 explains how soils were classified into groups representing specific soil types according to OM content, for the purpose of relating soil P desorption characteristics to mapped soil data. Due to the relatively small number of samples in some of the OM-based soils groups, soils are simply divided into the 2 most distinctive groups for the comparative purposes of this chapter; peat soils (>30% OM) and mineral soils (<30%OM). Differences in desorbable P concentrations, and increases between moist and dried samples, of peat and mineral soils are highlighted in tables 3.3a–d. Results are expressed on a weight and volume basis. All soils have a BD of less than 1 kg l^{-1}, as estimated from OM content (Jeffrey, 1970), so desorbable P values are lower when expressed on a volume basis. This is particularly noticeable for the peat soils, where increases after drying become much lower than when expressed on a volume basis. ANOVA with either (log) weight-basis increase or (log) percentage increase as the dependent variable, and (peat or mineral) soil group as the independent variable was performed on the data. Actual and percentage increases after drying were significantly higher for peat soils ($F_{1,95}$ = 4.91 and 19.47, p = 0.029 and $\leq$ 0.0001 respectively). However, when desorbable P increases were expressed on a volume basis, there was no significant difference between peat and mineral soil groups (p = 0.27).

Considering the different increases in desorption from peat and mineral soils, statistical tests were carried out to determine the implications of soil drying on differentiating between peat and mineral soil groups. ANOVA with (log) weight and volume based desorption as the dependent variable, and soil group and desorbable P fraction as the independent variables, were calculated ('All' fraction desorption in table 3.4) in order to determine whether determine whether peat and mineral soil desorption was significantly different when measured on moist or dried samples, and expressed on a weight or volume basis. They revealed that overall desorption (for all fractions) from peat soils was significantly lower than from mineral soils for moist samples expressed on a weight or volume basis (p = 0.0081 and $\leq$ 0.0001 respectively). However, for dried samples, overall desorption was only significantly (p = 0.0004) lower from peat soils when expressed on a volume basis. The same comparisons were carried out with individual ANOVA analysis for each desorbable P fraction, in order to identify the specific fractions for which differential soil-type desorption was most affected (table 3.4), and correspond with summaries of peat and mineral P desorption in tables 3.3a-d. It can be seen that none of

the desorbable P fractions are significantly different in dried samples when expressed on a weight basis; in fact, mean P_{feo} desorption from peat soils is 50 mg P kg^{-1} compared with 40 mg P kg^{-1} for mineral soils (table 3.3d), although the difference is not statistically significant ($p = 0.14$; table 3.4). Lower P desorption from peat soils (studied in more detail in chapter 4) is especially noticeable when expressed on a volume basis, due to the low BD of peat soils. Even where differences between peat and mineral soils remain significant after drying, the differential is substantially reduced. For example, mean peat P_w DRP changes from being approximately one seventh of mineral P_w DRP in moist samples to almost one half in dried samples, when expressed on a volume basis, although the difference is still significant in dried samples ($p = 0.0266$; table 3.4).

Table 3.4: ANOVA results (*F* and *p* values) for the effect of soil type (independent variable) on desorbable P fractions (dependent variables; DV) analysed in moist and dried samples, expressed on a weight or volume basis (*df* = 1,31 for each fraction, and 1, 97 for 'All'). Log transformed.

Expression	DV		Moist	Dried
Weight	P_w DRP	*F*	**4.51**	**0.01**
		p	0.0418	0.9386
	P_w TDP	*F*	**6.00**	**0.02**
		p	0.0202	0.8778
	P_{feo}	*F*	**4.02**	**0.14**
		p	0.0441	0.7101
	All	*F*	**7.32**	**0.004**
		p	0.0081	0.9506
Volume	P_w DRP	*F*	**16.21**	**5.42**
		p	0.0003	0.0266
	P_w TDP	*F*	**27.36**	**11.27**
		p	0.0001	0.0027
	P_{feo}	*F*	**13.62**	**8.98**
		p	0.0009	0.0053
	All	*F*	**29.52**	**13.27**
		p	0.0001	0.0004

3.4.3. Relationships between desorbable P fractions

Tables 3.5a and b show Pearson product moment correlation coefficients for moist and dried sample desorbable P fractions (and increases after drying) for the 33 soils collected in March 2003 against general soil characteristics, expressed on a weight and a volume basis respectively. In order to focus the correlations on relationships with increases, P_w values for soil 7 and P_{feo} vales for soil 18 were omitted from the correlations, as they showed decreases after drying (although P_w MUP from soil 7 increased slightly after drying). Desorbable P fractions, and increases after drying, were also correlated against one another in order to highlight the effect of drying on the strength of associations between these fractions and their increases. It can be seen from the table 3.5a that associations between the P_i-dominated desorbable P fractions (i.e. P_w DRP and TDP, and P_{feo}) are very strong (eg. moist sample P_w DRP compared with P_{feo}; $r = 0.95$, $p \leq 0.001$), though associations between these fractions and the presumably P_o-dominated P_w MUP fraction are weaker (e.g. moist sample P_w DRP versus P_w MUP; $r = 0.47$, $p \leq 0.05$) though still significant. Presumably in part because of the dominance of the DRP fraction in moist P_w extracts (average 63% contribution; section 4.3.1) this fraction is extremely strongly correlated with P_w TDP ($r = 1.00$), although the strength of this association weakens after drying, corresponding to a disassociation between P_w DRP and MUP fractions ($r = 0.33$, $p > 0.05$). Phosphorus desorption in dried samples remains strongly correlated with P desorption in moist samples for P_w DRP and P_{feo} fractions, but not for P_w MUP or TDP (e.g. for P_w MUP; $r = 0.18$, $p > 0.05$). P_w MUP becomes significantly positively correlated with both moisture and OM content after drying soil samples. Expressing concentrations on a volume basis has little impact on these correlations (table 3.5b).

Drying-induced desorbable P increases are not significantly related to moist sample desorption, but are significantly positively related to dried sample desorption for all fractions, most notably for P_w MUP ($r = 0.98$, $p \leq 0.001$). Percentage increases are significantly negatively correlated with moist sample desorption, but are not significantly related to dried sample P desorption (except for P_w MUP). Increases and percentage increases for all fractions are significantly positively correlated with one another, though correlation coefficients vary in strength; percentage increases for P_w DRP and P_w MUP are only just significant ($r = 0.39$, $p \leq 0.05$).

Table 3.5a: Pearson product moment *r* values for P desorption from moist (M) and dried (D) samples, and increases after drying (actual and percentage) against each other and general soil characteristics, with all concentrations expressed on a weight basis. n =32, $p \leq 0.05$ in bold.

mg kg^{-1}	MP_wDRP	DP_wDRP	Increase	% incr.	MP_wTDP	DP_wTDP	Increase	% incr.	MP_wMUP	DP_wMUP	Increase	% incr.	MP_{feo}	DP_{feo}	Increase	% incr.
MP_wDRP																
DP_wDRP	**0.92**															
Increase	-0.01	**0.38**														
% incr.	**-0.46**	-0.21	**0.56**													
MP_wTDP	**1.00**	**0.92**	-0.01	**-0.47**												
DP_wTDP	**0.77**	**0.92**	**0.53**	-0.09	**0.77**											
Increase	0.03	**0.35**	**0.85**	**0.41**	0.03	**0.66**										
% incr.	**-0.42**	-0.17	**0.57**	**0.87**	**-0.45**	0.06	**0.62**									
MP_wMUP	**0.42**	**0.37**	-0.04	**-0.35**	**0.50**	**0.36**	-0.02	**-0.49**								
DP_wMUP	0.13	0.33	**0.56**	0.16	0.14	**0.68**	**0.91**	**0.44**	0.18							
Increase	0.05	0.27	**0.58**	0.23	0.05	**0.63**	**0.93**	**0.54**	-0.01	**0.98**						
% incr.	-0.14	0.01	**0.36**	**0.39**	-0.19	0.23	**0.59**	**0.67**	**-0.57**	**0.53**	**0.65**					
MP_{feo}	**0.95**	**0.81**	0.08	**-0.53**	**0.95**	**0.63**	0.10	**-0.46**	**0.43**	0.18	0.10	-0.15				
DP_{feo}	**0.89**	**0.93**	**0.41**	-0.28	**0.88**	**0.83**	**0.41**	-0.21	**0.41**	**0.41**	**0.34**	0.01	**0.89**			
Increase	**0.38**	**0.70**	**0.76**	0.26	**0.38**	**0.78**	**0.73**	0.30	0.19	**0.60**	**0.58**	0.27	0.29	**0.69**		
% incr.	-0.33	-0.09	0.34	**0.74**	-0.34	0.05	0.32	**0.76**	-0.24	0.20	0.25	**0.49**	**-0.38**	-0.23	0.12	
Moist %	-0.19	0.08	**0.65**	**0.65**	-0.21	0.23	**0.61**	**0.67**	-0.27	**0.41**	**0.47**	**0.54**	-0.30	-0.01	**0.45**	**0.47**
OM %	-0.16	0.11	**0.66**	**0.61**	-0.17	0.25	**0.59**	**0.60**	-0.23	**0.39**	**0.44**	**0.43**	-0.23	0.03	**0.43**	**0.37**
BD	0.08	-0.17	**-0.63**	**-0.59**	0.10	-0.30	**-0.58**	**-0.56**	0.18	**-0.39**	**-0.43**	**-0.44**	0.17	-0.08	**-0.43**	**-0.38**
TOC %	-0.17	0.11	**0.67**	**0.56**	-0.18	0.22	**0.56**	**0.54**	-0.24	0.34	**0.39**	**0.39**	-0.20	0.05	**0.43**	0.26
TN %	-0.11	0.14	**0.63**	**0.51**	-0.12	0.25	**0.53**	**0.42**	-0.10	0.34	**0.36**	0.27	-0.13	0.11	**0.42**	0.16
pH	0.01	-0.17	**-0.46**	-0.24	0.02	-0.15	-0.26	-0.26	0.11	-0.05	-0.07	-0.11	0.07	-0.08	-0.28	-0.23
CO_3 %	-0.16	-0.19	-0.11	0.12	-0.16	-0.11	0.02	0.06	-0.07	0.10	0.11	0.03	-0.20	-0.14	0.02	-0.08
Clay %	-0.26	-0.32	-0.29	**0.45**	-0.26	**-0.37**	-0.34	0.28	-0.03	-0.28	-0.28	**-0.35**	-0.29	**-0.38**	**-0.40**	0.21
Silt %	-0.15	-0.09	0.18	0.25	-0.11	0.01	0.19	0.16	0.34	0.22	0.15	-0.15	0.16	0.11	-0.03	0.15
Sand %	0.20	0.17	-0.06	-0.34	0.17	0.10	-0.06	-0.22	-0.27	-0.10	-0.04	0.23	-0.04	0.03	0.14	-0.18
Na	-0.22	-0.08	0.30	**0.38**	-0.25	-0.05	0.22	**0.38**	**-0.38**	0.04	0.11	**0.49**	-0.25	-0.15	0.08	0.30
K	0.25	0.34	0.28	-0.09	0.25	**0.37**	0.29	-0.07	0.10	0.26	0.24	0.06	**0.37**	**0.41**	0.26	-0.06
Ca	-0.11	-0.11	-0.01	0.20	-0.11	-0.08	0.00	0.02	0.03	0.01	0.01	0.00	-0.09	-0.06	0.00	-0.08
Mg	0.24	**0.46**	**0.63**	**0.41**	0.22	**0.51**	**0.54**	**0.38**	-0.04	**0.36**	**0.37**	0.32	-0.04	0.15	**0.38**	0.29
TEB meq	-0.09	-0.06	0.06	0.23	-0.08	-0.03	0.05	0.05	0.02	0.05	0.04	0.03	-0.08	-0.04	0.04	-0.05
Mn	-0.11	0.05	**0.40**	**0.59**	-0.14	0.13	**0.36**	**0.71**	-0.28	0.21	0.26	**0.50**	-0.21	-0.07	0.17	0.91
Olsen P	**0.85**	**0.78**	-0.01	**-0.49**	**0.85**	**0.64**	0.00	**-0.45**	**0.42**	0.08	0.00	-0.19	**0.83**	**0.78**	0.32	-0.30
Olsen TP	**0.76**	**0.73**	0.08	**-0.40**	**0.76**	**0.61**	0.06	-0.34	**0.39**	0.10	0.03	-0.14	**0.69**	**0.70**	**0.38**	-0.21
Morgan P	**0.93**	**0.83**	-0.08	**-0.39**	**0.92**	**0.68**	-0.02	**-0.36**	**0.35**	0.09	0.03	-0.15	**0.83**	**0.72**	0.20	-0.23
P_{ox}	**0.79**	**0.70**	-0.07	**-0.46**	**0.80**	**0.57**	-0.05	**-0.45**	**0.45**	0.06	-0.02	-0.22	**0.86**	**0.76**	0.25	-0.28
PSI	**-0.44**	-0.28	0.32	**0.55**	**-0.44**	-0.20	0.20	**0.47**	-0.24	0.04	0.08	0.19	**-0.41**	-0.31	0.01	**0.40**
PSC1	**0.41**	**0.44**	0.16	-0.03	**0.41**	**0.38**	0.10	-0.07	0.24	0.08	0.04	-0.07	**0.46**	**0.45**	0.22	0.04
DPSS1	**0.79**	**0.67**	-0.16	**-0.59**	**0.80**	**0.58**	-0.03	**-0.50**	**0.45**	0.15	0.06	-0.17	**0.82**	**0.76**	0.29	**-0.40**
Fe_{ox}	-0.19	-0.12	0.16	**0.42**	-0.19	-0.08	0.10	**0.39**	-0.11	0.01	0.03	0.17	-0.18	-0.17	-0.08	**0.55**
Al_{ox}	-0.14	-0.12	0.02	0.25	-0.12	-0.20	-0.17	-0.01	0.16	-0.24	-0.28	-0.17	0.05	-0.08	-0.25	0.06
PSC2	-0.19	-0.13	0.12	**0.40**	-0.19	-0.14	-0.01	0.27	-0.01	-0.10	-0.09	0.05	-0.10	-0.16	-0.17	0.41
DPSS2	**0.90**	**0.82**	-0.05	**-0.50**	**0.90**	**0.71**	0.04	**-0.42**	**0.41**	0.18	0.10	-0.15	**0.84**	**0.81**	**0.37**	-0.34

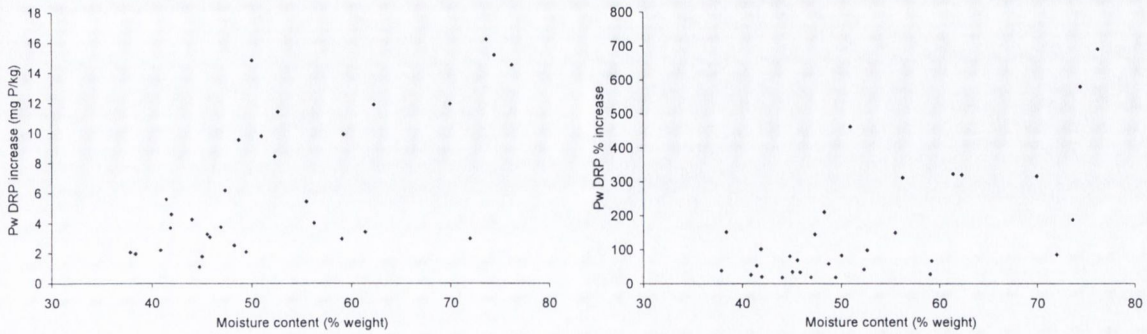
Table 3.5b: Pearson product moment *r* values for P desorption from moist (M) and dried (D) samples, and increases after drying (actual and percentage) against each other and general soil characteristics, with all concentrations expressed on a volume basis. n =32, $p \leq 0.05$ in bold.

mg l^{-1}	MP_wDRP	DP_wDRP	Increase	% incr.	MP_wTDP	DP_wTDP	Increase	% incr.	MP_wMUP	DP_wMUP	Increase	% incr.	MP_{feo}	DP_{feo}	Increase	% incr.
MP_wDRP																
DP_wDRP	**0.96**															
Increase	0.15	**0.42**														
% incr.	**-0.52**	**-0.41**	0.23													
MP_wTDP	**0.99**	**0.95**	0.15	**-0.56**												
DP_wTDP	**0.85**	**0.91**	**0.45**	**-0.46**	**0.85**											
Increase	0.18	**0.34**	**0.63**	-0.06	0.17	**0.67**										
% incr.	**-0.49**	**-0.39**	0.19	**0.85**	**-0.54**	-0.29	0.22									
MP_wMUP	**0.47**	**0.46**	0.10	**-0.54**	**0.57**	**0.46**	0.06	**-0.68**								
DP_wMUP	0.24	0.30	0.28	-0.31	0.26	**0.68**	**0.90**	0.02	0.25							
Increase	0.14	0.21	0.27	-0.20	0.14	**0.60**	**0.92**	0.18	0.03	**0.98**						
% incr.	-0.11	-0.11	-0.04	0.12	-0.17	0.12	**0.47**	**0.44**	**-0.51**	**0.47**	**0.60**					
MP_{feo}	**0.96**	**0.89**	0.28	**-0.57**	**0.95**	**0.78**	0.29	**-0.51**	**0.54**	0.33	0.21	-0.13				
DP_{feo}	**0.94**	**0.96**	**0.48**	**-0.48**	**0.93**	**0.87**	**0.45**	**-0.42**	**0.54**	**0.42**	0.31	-0.11	**0.94**			
Increase	**0.61**	**0.77**	**0.73**	-0.13	**0.60**	**0.77**	**0.62**	-0.10	**0.37**	**0.47**	**0.40**	-0.02	**0.49**	**0.76**		
% incr.	**-0.35**	-0.25	0.10	**0.74**	**-0.37**	-0.24	0.00	**0.75**	-0.33	-0.13	-0.05	0.21	**-0.37**	-0.32	-0.11	
Moist %	-0.30	-0.23	0.19	**0.65**	**-0.37**	-0.25	0.07	**0.69**	**-0.67**	-0.16	-0.01	0.34	**-0.44**	**-0.35**	-0.06	**0.47**
OM %	-0.28	-0.23	0.08	**0.61**	**-0.35**	-0.31	-0.08	**0.60**	**-0.67**	-0.29	-0.15	0.23	**-0.39**	**-0.36**	-0.19	**0.37**
BD	0.21	0.16	-0.11	**-0.59**	0.28	0.23	0.03	**-0.57**	**0.64**	0.23	0.09	-0.28	0.33	0.30	0.14	**-0.38**
TOC %	-0.29	-0.23	0.11	**0.56**	-0.36	-0.32	-0.09	**0.55**	**-0.67**	-0.31	-0.16	0.24	**-0.37**	-0.34	-0.17	0.26
TN %	-0.23	-0.18	0.11	**0.51**	-0.29	-0.27	-0.09	**0.42**	**-0.56**	-0.29	-0.17	0.15	-0.29	-0.28	-0.14	0.16
pH	0.03	-0.07	-0.34	-0.24	0.06	0.05	0.02	-0.25	0.19	0.23	0.20	-0.02	0.11	0.05	-0.07	-0.23
CO_3 %	-0.20	-0.26	-0.28	0.12	-0.22	-0.20	-0.07	0.06	-0.24	0.00	0.05	0.02	-0.24	-0.22	-0.11	-0.08
Clay %	-0.29	-0.34	-0.28	**0.45**	-0.29	**-0.48**	**-0.44**	0.16	-0.07	**-0.42**	**-0.40**	**-0.38**	-0.30	**-0.38**	**-0.39**	0.21
Silt %	-0.15	-0.09	0.16	0.25	-0.11	-0.04	0.09	0.08	0.27	0.07	0.02	-0.21	0.13	0.07	-0.06	0.15
Sand %	0.21	0.18	-0.05	-0.34	0.18	0.17	0.06	-0.11	-0.21	0.06	0.10	0.29	-0.02	0.06	0.17	-0.18
Na	-0.11	-0.17	-0.23	-0.13	-0.11	-0.15	-0.13	-0.08	-0.05	-0.05	-0.04	0.30	-0.08	-0.16	-0.26	-0.03
K	**0.40**	**0.45**	0.30	**-0.37**	**0.41**	**0.48**	0.32	**-0.35**	0.30	0.31	0.25	-0.09	**0.54**	**0.55**	**0.36**	-0.24
Ca	-0.02	-0.13	**-0.40**	-0.09	0.00	-0.09	-0.15	-0.21	0.10	0.04	0.02	-0.02	0.07	-0.02	-0.18	-0.18
Mg	**0.57**	**0.56**	0.14	-0.12	**0.55**	**0.45**	0.06	-0.19	0.17	0.04	0.00	-0.01	0.23	0.19	0.04	-0.02
TEB meq	0.03	-0.09	**-0.38**	-0.12	0.04	-0.04	-0.14	-0.24	0.13	0.05	0.02	-0.02	0.11	0.01	-0.17	-0.19
Mn	0.03	-0.09	**-0.38**	-0.12	0.04	-0.04	-0.14	-0.24	0.13	0.05	0.02	-0.02	0.11	0.01	-0.17	-0.19
Olsen P	**0.85**	**0.85**	0.26	**-0.55**	**0.86**	**0.78**	0.24	**-0.52**	**0.55**	0.28	0.17	-0.16	**0.85**	**0.87**	**0.58**	-0.32
Olsen TP	**0.75**	**0.77**	0.29	**-0.55**	**0.78**	**0.72**	0.25	**-0.51**	**0.60**	0.29	0.16	-0.19	**0.75**	**0.79**	**0.59**	-0.31
Morgan P	**0.92**	**0.91**	0.23	**-0.48**	**0.91**	**0.84**	0.28	**-0.43**	**0.44**	0.32	0.23	-0.08	**0.89**	**0.89**	**0.58**	-0.28
P_{ox}	**0.81**	**0.78**	0.13	**-0.51**	**0.83**	**0.71**	0.15	**-0.50**	**0.54**	0.23	0.12	-0.18	**0.90**	**0.86**	**0.48**	-0.30
PSI	**-0.40**	**-0.41**	-0.17	0.09	**-0.37**	**-0.45**	-0.31	-0.04	0.00	-0.28	-0.29	-0.17	**-0.27**	**-0.36**	**-0.42**	0.09
PSC1	**0.60**	**0.56**	0.05	**-0.45**	**0.62**	**0.47**	0.00	**-0.50**	**0.52**	0.09	-0.02	-0.25	**0.72**	**0.64**	0.26	-0.24
DPSS1	**0.85**	**0.83**	0.19	**-0.59**	**0.86**	**0.84**	**0.36**	**-0.50**	**0.56**	**0.46**	**0.35**	-0.08	**0.86**	**0.91**	**0.66**	**-0.40**
Fe_{ox}	-0.04	-0.11	-0.25	-0.05	-0.01	-0.19	-0.34	-0.13	0.21	-0.24	-0.30	-0.22	0.09	-0.05	-0.30	0.20
Al_{ox}	0.09	0.02	-0.21	-0.30	0.15	-0.03	-0.27	**-0.51**	**0.55**	-0.10	-0.23	-0.31	**0.36**	0.18	-0.23	-0.23
PSC2	0.02	-0.05	-0.26	-0.19	0.08	-0.13	**-0.35**	**-0.35**	**0.42**	-0.20	-0.30	-0.29	0.25	0.07	-0.30	-0.01
DPSS2	**0.93**	**0.92**	0.22	**-0.50**	**0.93**	**0.87**	0.31	**-0.43**	**0.44**	**0.36**	0.27	-0.09	**0.86**	**0.91**	**0.68**	-0.34

3.4.4. Influence of general soil characteristics

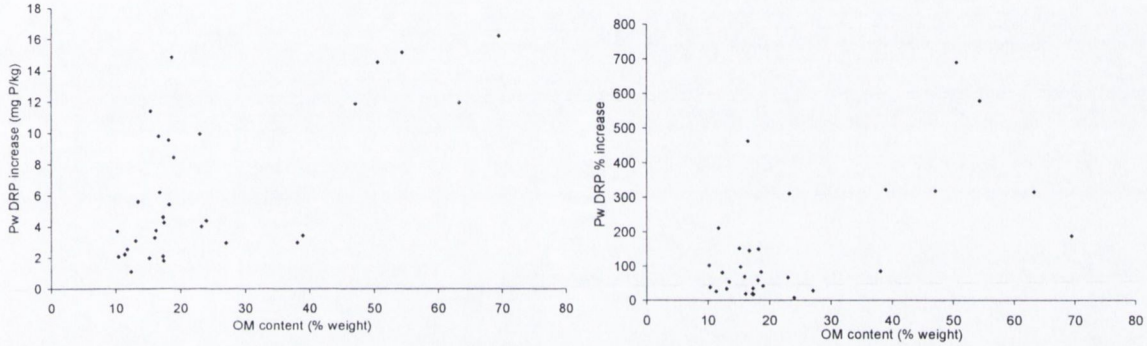
Expressing concentrations on a weight or volume basis does have an effect on correlations between desorbable P fractions increases after drying and general soil characteristics. The strongest and most consistent correlations between desorbable P increases after drying and general soil characteristics involve moisture content, which is significantly positively correlated with all desorbable P fraction actual (and percentage) increases when expressed on a weight basis, but not when expressed on a volume basis. Organic matter content is highly correlated with moisture content ($r = 0.91$, $p \leq 0.001$) and displays similar, though slightly lower, correlations with P desorption increases after drying, as do OM- associated or derived parameters such as organic C, TN and BD. Figures 3.1 and 3.2 show scatterplots of correlation between P_w increases (mg P kg^{-1}) and percentage increases with moisture content and OM respectively. Although correlations in the scatterplots appear to be increased by peat soils with high OM and high desorbable P increase in the top right corners, log-transforming the data has no effect on the correlation coefficient for actual increase, although does reduce the strength of the correlation for percentage increase (e.g. for percentage OM content, logging the data reduces r from 0.60 to 0.50, and p from $\leq$ 0.001 to $\leq$0.01).

Table 3.6 displays correlation coefficients for desorbable P fraction increases and soil moisture and OM contents when peat soils are omitted. Moisture and OM contents remain relatively strongly correlated ($r = 0.75$, $p \leq 0.001$) in mineral soils, and also remain significantly correlated with a number drying-induced desorbable P increases. Increases for the P_w MUP (and consequently also for the P_w TDP fraction) are the most closely associated with soil moisture and OM contents, whether expressed on a volume or a weight basis. Actual increases for (theoretically) inorganic P_w DRP and P_{feo} fractions are only significantly correlated with soil moisture content, and only when expressed on a weight basis.



a) b)

Figure 3.1: Scatterplots of (a) weight-basis desorbable P (P_w DRP fraction) increases and (b) percentage increases after drying compared with soil moisture contents for the 33 March 2003 collected soils ($p \leq 0.001$).



a) b)

Figure 3.2: Scatterplots of (a) weight-basis desorbable P (P_w DRP fraction) increase s and (b) (percentage increases after drying compared with soil organic matter (OM) content for the 33 March 2003 collected soils ($p \leq 0.001$).

Table 3.6: Pearson product moment *r* values for desorbable P increases compared with soil moisture and OM contents for the 26 mineral soils. Values are highlighted in bold where $p \leq 0.05$.

Expression		P_w DRP		P_w TDP		P_w MUP		P_{feo}		OM
		Increase	%incr.	Increase	%incr.	Increase	%incr.	Increase	%incr.	
Weight	Moisture	**0.44**	0.24	**0.54**	**0.41**	**0.47**	**0.51**	**0.54**	0.30	**0.75**
	OM	0.28	0.01	**0.41**	0.11	**0.40**	**0.48**	0.35	0.21	
Volume	Moisture	0.36	0.24	**0.54**	**0.41**	**0.49**	**0.46**	**0.44**	0.30	**0.75**
	OM	0.16	0.01	**0.43**	0.11	**0.44**	**0.51**	0.20	0.21	

Carbonate did not correlate significantly with any desorbable P increases after drying, whilst pH was significantly (negatively) correlated only with weight-basis DRP increase. Clay content was significantly negatively correlated with volume-based dried (but not moist) sample P_w MUP and TDP contents, and with volume-based drying-induced P desorption increases for these fractions. When concentrations were expressed on a weight basis, clay content was not significantly correlated with any soil concentrations of any desorbable P fraction, but was significantly negatively correlated with P_{feo} increase after drying. In contrast to its behaviour with the other desorbable P fractions, clay content was positively correlated with P_w DRP percentage increases. (N.B: clay content correlations were based on only 26 data points, for the mineral soils). Other general soil characteristics which were correlated with drying effects are exchangeable K and Mg. Potassium generally had inverse relationships with P desorption to those displayed by clay content. It correlated positively with P_w DRP and TDP fractions and P_{feo} in both moist and dried samples, and with drying-induced P_{feo} increases, when expressed on a volume basis. When expressed on a weight basis, it correlated only with dried sample P_w TDP content and moist and dried sample P_{feo} contents. Potassium was significantly negatively correlated with P_w DRP percentage increase after drying. However, it was not correlated with any increases or moist or dried sample Pw MUP. Exchangeable Mg concentrations were positively correlated with volume-expressed P_w DRP and TDP contents in moist and dried samples, and weight-expressed P_w DRP, MUP and TDP contents in dried samples, and weight or percentage expressed drying-induced increases in all fractions.

3.4.5. Influence of P quantity

There was relatively little difference in the strength of correlations between moist and dried sample volume-based desorbable P contents and either of the soil P saturation calculations (DPSS1 and 2). All these correlations were very strong, except for P_w MUP, and dried sample content of this fraction was not significantly correlated to DPSS when expressed on a weight basis (e.g. for DPSS2; $r = 0.18$, $p > 0.05$). However, when expressed on a weight basis, total P desorption to water (P_w TDP) from moist samples was more strongly correlated to DPSS than P_w TDP from dried samples ($r = 0.90$ compared with 0.71, for moist and dried sample desorption respectively; $p \leq 0.001$ in both instances). The impact of sample drying on P desorption-P quantity relationships is analysed in more detail in chapter 4. Both measures of DPSS displayed a trend of significant negative

correlations with percentage increases in P desorption after drying, and some positive correlations with volume-expressed increases in P desorption after drying.

The three soil P quantity measurements - Olsen P (and TP), Morgan P and P_{ox} – were highly significantly correlated with all measures of P desorption except P_w MUP content, with which they become dissociated after sample drying. Soil P quantity measurements were significantly negatively correlated with P_w DRP and TDP fraction percentage increases, and significantly positively correlated with P_{feo} increases, after drying. (N.B: Morgan P remained expressed in its standard units of mg P l^{-1} for weight correlations). Phosphorus sorption capacity as calculated from oxalate-extractable Fe and Al contents (PSC2) displayed no strong correlations with drying-induced desorbable P content increases. However, the empirical PSC1, when expressed on a volume basis, displayed significant negative correlations with P_w DRP and TDP percentage increase (r = -0.45 and -0.50 respectively, $p \leq 0.01$ in both instances). PSI was significantly positively correlated with percentage increases after drying for P_w DRP, TDP and P_{feo}.

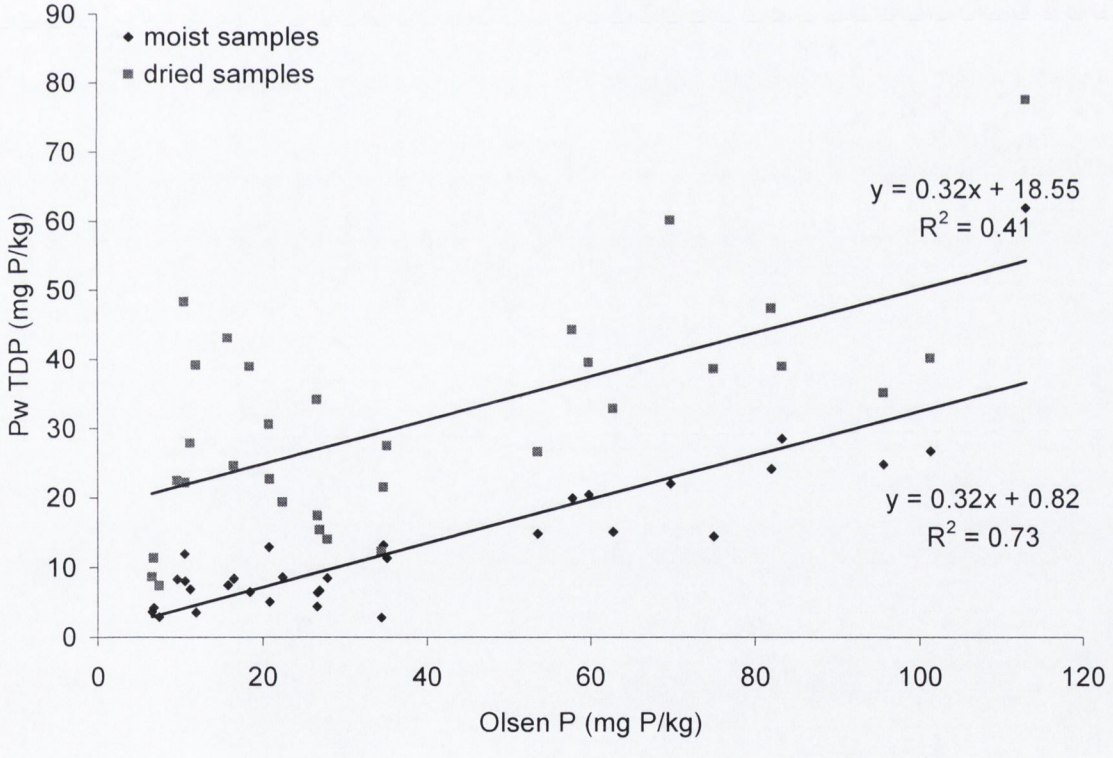


Figure 3.3: The contrasting relationships between Olsen P and P desorption (P_w DRP) from moist and dried samples ($p \leq 0.001$ in both instances).

STP-P desorption relationships most affected by drying were those with P_w TDP (tables 3.5a and b). Figure 3.3 highlights the greater scatter around the mean regression line, and the reduced relative differentiation between low and high P desorbing soils in dried compared with moist samples for P_w TDP against Olsen P content. The slopes of the 2 regression lines are identical (0.32), but the intercept is substantially higher (18.55 versus 0.82 mg P kg^{-1}), and the strength of regression much lower ($r^2 = 0.41$ compared with 0.73), for dried compared with moist samples. Section 4.4.3 analyses the relationships between P desorption and measures of STP in moist and dried samples more thoroughly.

Stepwise multiple regression analyses were conduced on desorbable P increases (table 3.7) and percentage increases (table 3.8) for each fraction, on weight and volume-expressed data, following the procedure outlined in section 2.5, again omitting soil 7 and 18 decreases in P_w and P_{feo} respectively. As noted from correlation coefficients in tables 3.5a and b, moisture content appeared to be the most important predictive characteristic for desorbable P percentage increases, although the closely related soil TOC content was slightly more strongly correlated to P_w DRP percentage increase. No other soil characteristic analysed here was correlated with residuals of P_{feo} compared with moisture content, but the inclusion of DPSS1 and exchangeable Ca as inversely related predictors improved the strength of the multiple regression equations for P_w DRP and TDP respectively, accounting for just over half of the variability between soils in desorbable P percentage increase. The inclusion of Al_{ox} content improved the strength of the predictive equation for P_w MUP so that it accounted for 35% of variance. When the same multiple regression procedure was carried out against volume-expressed soil characteristics, results were either identical of similar, so are not considered separately.

The same predictor variables remain important for P_w fraction increases when soil concentrations are expressed on a weight basis (i.e. moisture content, Al_{ox} and Ca), accounting for similar portions of variation in these increases as for percentage increase. However, P_{feo} increases appear to be related to a range of soil characteristics which together account for 70% of variation. After regression with moisture content, P saturation (DPSS2), P sorption capacity (PSC2), and pH are significant predictors of P_{feo} increase. Expressing soil concentrations on a volume basis removes moisture content (and related OM variables), and reduces the predictive power of multiple regression equations. Exchangeable Ca and Fe_{ox} content are significant predictors of volume-based P_w DRP, whilst P sorption saturation appears to be important for predicting increases in P_w MUP

and TDP (DPSS1) and P_{feo} (DPSS2). Phosphorus sorption capacity (PSC2) is also a significant predictor of P_w TDP increase expressed on a volume basis.

Table 3.7: Results of stepwise multiple regression analyses on percentage increases for each of the desorbable P fractions (MC = moisture content). Inclusion of each variable significant at $p \leq 0.05$.

Fraction	Regression equation	df	r^2
P_wDRP	-128.76 + 7.7T0C - 3.11 DPSS1	2,29	0.51
P_wMUP	-318.20 + 20.94MC - 0.086Al_{ox}	2,29	0.35
P_wTDP	-426.26 + 14.53MC - 0.42Ca	2,29	0.51
P_{feo}	-1049.85 + 25.38MC	1,30	0.20

Table 3.8: Results of stepwise multiple regression analyses on increases for each of the desorbable P fractions, for soil concentrations expressed on a weight and volume basis (MC = moisture content). Inclusion of each variable significant at $p \leq 0.05$ (*p = 0.053).

	Fraction	Regression equation	df	r^2
Weight	P_wDRP	4.56 + 0.43TOC - 0.00070Ca	2,29	0.53
	P_wMUP	1.92 + 0.33MC - 0.0019A_{lox}	2,29	0.34
	P_wTDP	17.38 + 0.42MC - 0.0023A_{lox}	2,29	0.42
	P_{feo}	17.15 + 0.90MC + 1.12 DPSS2 - 0.096PSC2 -5.86pH	3,28	0.70
Volume	P_wDRP	6.55 - 0.00074Ca - 0.00031Fe_{ox}	2,29	0.2
	P_wMUP	3.99 + 0.062 DPSS1	1,30	0.09*
	P_wTDP	11.69 + 0.081 DPSS1 - 0.057PSC2	2,29	0.20
	P_{feo}	29.08 + 0.81DPSS2 - 0.082PSC2 - 2.62pH	3,28	0.61

3.5. Seasonal sampling results

3.5.1. Water extractable P fractions

As detailed in section 2.2.3, and reiterated in section 3.3, differing soil-water ratios and sample depths for spatial and monthly samples mean that P_w data for these 2 data sets are not directly comparable. However, sample depth was the same for monthly-collected samples and samples collected in March 2002 (analysed in air-dried condition only), and soil-water ratio was the same for samples collected in 2002 and 2003. Thus, comparing these data may be indicative of the relative effects of soil-water ratio and sample depth on drying-induced P increases.

Section 2.2.4 highlights the significantly higher TOC contents (mean 11.3% compared with 10.9%; $p = 0.035$) and 1:100 P_w TDP contents (mean 29.9 compared with 25.5 mg P kg^{-1}; $p = 0.004$) in dried samples collected from 0-5 cm depth in 2003 compared with the 32 dried samples collected from 0-10 cm depth in the same fields in 2002 (though P_w DRP contents are not significantly different between the 2 occasions / depths). Comparing 1:100 P_w TDP for dried samples of soils 1-11 collected from 0-10 cm depth in March 2002 with 1:50 P_w TDP for dried samples collected from 0-10 cm depth in the same fields in April 2002 shows that significantly more P was desorbed to water at the higher soil-solution ratio used for March 2002 samples (29.4 compared with 19.5 mg P kg^{-1}; $p = 0.011$). Mean increases in P_w after drying for these 11 soils collected in March 2003 were almost double those for the same soils in April 2002 (22.6 compared with 12.9 mg P kg^{-1}, $p \leq 0.0001$) though were proportionately similar (294 compared with 331%). This could be a consequence of the higher soil-solution ratio, or just be a temporal difference, but it may reflect higher OM and microbial biomass content in the shallower 0-5 cm surface layer: P_w MUP increase after drying was also twice as high in March 2003 compared with April 2002 (15.6 compared with 7.5 mg P kg^{-1}). Thus, the influence of sample depth on soil P desorption appears small, though significant, whilst the impact of soil-solution ratio seems large, and probably accounts for most of the additional increase in March 2003 compared with April 2002 samples.

Table 3.9 compares moist and dried sample desorption for the two analysed P_w fractions over the four months they were compared, for the 11 monthly analysed soils, along with actual and percentage increases (expressed on original weight-basis). Mean moist and

dried sample P_w fraction contents over the four moths are also displayed in table 3.9, and graphically in figure 3.4). The Repeated measures analyses were performed with (log-transformed) total desorption to water (P_w TDP) analysed against site, sample condition and month, with interaction between month and sample condition. The results confirm that sample condition had a highly significant effect on P_w desorption ($F_{1,70} = 257.37$, $p \leq 0.0001$), and that this effect varied among the 4 months (seasons) that were compared ($F_{3,70} = 2.83$, $p = 0.045$). Desorbable P increased for all soils in all months, but the increases varied widely among soils, both in terms of actual values and percentage increases. Increases after drying in P_w DRP ranged from only 18% for soil 7 (the soil which showed a decrease in P_w after drying in April 2003) in August to 3434% for soil 6 in October. Repeated measures analyses were performed with P desorption increases analysed against site, fraction (P_w DRP and MUP; so as not to have overlap of P_w DRP data in P_w TDP data), and month found that whilst increases were significantly different among soils ($F_{10,73} = 10.19$, $p \leq 0.0001$), they were not significantly different between P_w DRP and MUP fractions or between months.

There was a wider range for percentage than actual increases, as the peat soils, with low moist sample P desorption, displayed some of the greatest increases. Increases after drying were greatest for high P_w soil 3 (e.g. 31.8 mg P kg^{-1} increase in January), though these translate into below average increases when expressed as a percentage of the high moist soil 3 P_w (e.g. 309% in April). When repeated measures analyses were conducted on (log-transformed) percentage increases, significant differences were found between months ($F_{3,73} = 10.51$, $p \leq 0.0001$) and fractions ($F_{3,73} = 34.37$, $p \leq 0.0001$). *Post-hoc* LSD analyses showed that percentage increases in January (mean of 634%; table 3.9) were higher than in April (mean of 330%), August (mean of 316%) and October (mean of 430%) ($p \leq 0.001$ in all instances). Otherwise there were no significant differences among the other months. P_w MUP increases were significantly greater than P_w DRP increases ($p \leq 0.0001$), although adding an interaction term between fraction and month found that differences in P_w DRP and MUP increases did not vary significantly between months (i.e. increases remained proportional for the two fractions over the different months).

Table 3.9: Mean water-extractable P (P_w DRP and TDP fraction) contents in moist and air-dried samples of soils 1-11 for the months January, April, August and October, ± SD. of three replicates (expressed on a weight basis). Changes after drying are expressed on an absolute and proportional basis (percentage increases from moist in parentheses).

Soil	Pw DRP			Pw TDP		
no.	Moist	Dried	Change	Moist	Dried	Change
			mg P kg^{-1} soil			
Jan.						
1	2.56 ± 0.26	16.98 ± 6.39	14.42 (563)	4.24 ± 0.68	28.25 ± 6.41	24.01 (566)
2	4.5 ± 0.16	8.97 ± 0.16	4.47 (99)	6.24 ± 0.36	14.77 ± 0.73	8.54 (137)
3	8.92 ± 0.71	28.1 ± 2.58	19.19 (215)	10.27 ± 0.50	42.04 ± 3.59	31.77 (309)
4	1.17 ± 0.23	8.21 ± 2.49	7.04 (603)	2.22 ± 0.64	21.45 ± 1.94	19.23 (866)
5	0.69 ± 0.10	7.8 ± 0.85	7.11 (1038)	1.74 ± 0.02	19.98 ± 4.43	18.24 (1046)
6	0.18 ± 0.03	6.25 ± 0.21	6.07 (3396)	0.61 ± 0.07	10.78 ± 0.45	10.17 (1665)
7	0.8 ± 0.02	3.33 ± 0.14	2.53 (315)	2.77 ± 0.16	10.58 ± 0..57	7.81 (282)
8	2.73 ± 0.05	4.78 ± 0.09	2.05 (75)	5.26 ± 0.09	10.38 ± 1.65	5.12 (97)
9	0.51 ± 0.03	3.14 ± 0.48	2.63 (519)	1.32 ± 0.61	11.64 ± 0.14	10.31 (779)
10	6.71 ± 1.61	16.86 ± 3.26	10.15 (151)	8.11 ± 1.54	26.13 ± 6.04	18.02 (222)
11	0.4 ± 0.19	3.98 ± 0.81	3.58 (905)	1.15 ± 0.09	12.71 ± 1.25	11.55 (1002)
Mean	**2.65**	**9.85**	**7.2 (716)**	**3.99**	**18.97**	**14.98 (634)**
April						
1	2.73 ± 0.43	10.05 ± 0.73	7.32 (268)	4.7 ± 0.50	20.71 ± 3.55	16.01 (341)
2	5.18 ± 1.58	12.14 ± 1.26	6.97 (135)	7.28 ± 1.96	21.98 ± 0.97	14.7 (202)
3	19.72 ± 2.11	30.89 ± 4.14	11.17 (57)	22.8 ± 3.03	43.6 ± 2.20	20.8 (91)
4	4.41 ± 0.68	8.77 ± 0.64	4.36 (99)	5.52 ± 0.76	21.75 ± 1.39	16.23 (294)
5	3.98 ± 0.61	8.86 ± 0.69	4.88 (122)	5.75 ± 0.81	18.98 ± 0.78	13.22 (230)
6	0.78 ± 0.26	8.17 ± 1.58	7.4 (950)	0.96 ± 0.26	13.42 ± 1.63	12.46 (1299)
7	2.01 ± 1.00	2.59 ± 0.14	0.58 (29)	5.92 ± 0.12	10.58 ± 0.62	4.66 (79)
8	3.14 ± 0.17	4.24 ± 1.02	1.1 (35)	5.84 ± 0.29	11.165 ± 1.14	5.32 (91)
9	0.99 ± 0.28	4.39 ± 0.35	3.4 (344)	2.83 ± 0.19	13.99 ± 3.48	11.16 (395)
10	8.13 ± 0.14	18.82 ± 0.62	10.69 (131)	9.22 ± 2.79	30.27 ± 2.49	21.04 (228)
11	0.74 ± 0.14	2.09 ± 0.10	1.35 (183)	1.55 ± 0.12	7.53 ± 0.40	5.99 (387)
Mean	**4.71**	**10.09**	**5.38 (214)**	**6.5796**	**19.451**	**12.871 (330)**
Aug.						
1	2.09 ± 0.14	10.41 ± 0.26	8.33 (398)	4.65 ± 0.44	18.34 ± 0.88	13.69 (294)
2	4.79 ± 0.24	7.76 ± 0.31	2.97 (62)	6.72 ± 0.23	14.2 ± 0.56	7.48 (111)
3	12.95 ± 0.33	23.89 ± 1.21	10.94 (84)	15.6 ± 0.39	36.23 ± 2.11	20.63 (132)
4	2.52 ± 0.53	5.92 ± 0.17	3.41 (135)	4.24 ± 0.55	14.34 ± 0.21	10.1 (238)
5	3.5 ± 0.17	6.21 ± 0.23	2.71 (77)	5.86 ± 0.30	13.68 ± 0.32	7.81 (133)
6	0.55 ± 0.03	13.77 ± 3.62	13.22 (2398)	1.16 ± 0.09	19.11 ± 5.54	17.95 (1554)
7	1.84 ± 0.16	2.17 ± 0.10	0.33 (18)	5.75 ± 0.21	10.22 ± 0.47	4.47 (78)
8	3.04 ± 0.10	4.13 ± 0.30	1.09 (36)	6.35 ± 0.14	10.54 ± 0.92	4.19 (66)
9	0.63 ± 0.03	4.41 ± 0.23	3.78 (597)	2.92 ± 0.16	12.78 ± 1.30	9.85 (337)
10	8.97 ± 0.52	19.67 ± 0.33	10.7 (119)	12.19 ± 0.14	32.73 ± 0.69	20.54 (168)
11	0.74 ± 0.40	2.23 ± 0.05	1.49 (203)	1.73 ± 0.76	8 ± 0.17	6.27 (364)
Mean	**3.78**	**9.14**	**5.36 (375)**	**6.11**	**17.29**	**11.18 (316)**
Oct.						
1	2.3 ± 0.05	12.26 ± 0.02	9.96 (433)	4.41 ± 0.07	26.31 ± 1.61	21.89 (496)
2	6.06 ± 0.28	8.98 ± 0.21	2.92 (48)	8.49 ± 0.33	15.23 ± 0.24	6.74 (79)
3	14.73 ± 0.19	23.65 ± 0.12	8.92 (61)	16.66 ± 0.29	33.13 ± 0.98	16.47 (99)
4	2.48 ± 0.03	8.07 ± 0.03	5.59 (225)	4.95 ± 0.09	21.44 ± 0.43	16.48 (333)
5	2.98 ± 0.16	7.28 ± 0.12	4.29 (144)	5.52 ± 0.12	16.69 ± 0.71	11.17 (202)
6	0.51 ± 0.10	18.01 ± 0.03	17.5 (3434)	0.97 ± 0.21	26.01 ± 0.36	25.04 (2577)
7	1.66 ± 0.36	2.81 ± 0.59	1.15 (69)	5.04 ± 0.16	9.87 ± 0.16	4.83 (96)
8	2.91 ± 0.23	4.19 ± 0.17	1.28 (44)	6.68 ± 0.43	11.76 ± 0.31	5.08 (76)
9	1.76 ± 0.05	7.46 ± 0.02	5.7 (325)	4.92 ± 0.28	16.76 ± 0.87	11.84 (241)
10	12.75 ± 0.83	20.57 ± 0.52	7.82 (61)	15.35 ± 0.76	31.42 ± 0.31	16.07 (105)
11	1.23 ± 0.49	1.54 ± 0.36	0.31 (25)	2.39 ± 0.26	6.5 ± 0.59	4.11 (172)
Mean	**4.49**	**10.44**	**5.95 (443)**	**6.85**	**19.56**	**13.56 (430)**

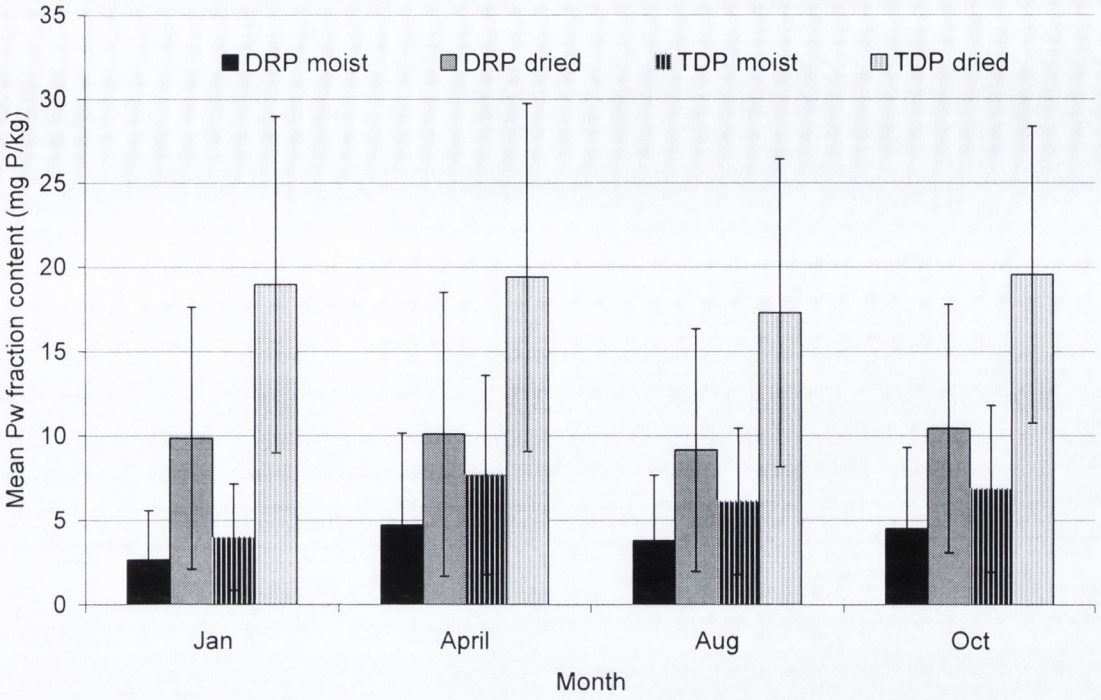


Figure 3.4: Mean water-extractable P (P_w DRP and TDP fractions) in moist and dried samples of the 11 monthly-analysed soils over the months January, April, August and October 2002. Error bars ± 1 SD.

Mean moist sample desorption appears lower in January, and also August, compared with April and October (figure 3.4). Dried sample desorption varies proportionately less, though appears to decrease slightly in August. The implications of drying soil samples for the detection of seasonal variation were analysed quantitatively by performing repeated measures analyses separately on moist and dried sample data. When P_w TDP was analysed against soil and month, moist sample desorption varied significantly among months ($F_{3,30}$ = 17.83, $p \leq 0.0001$) but dried sample desorption did not. *Post-hoc* LSD analyses revealed that, as with percentage increases, differences are confined to between January and the other months, with significantly lower P_w TDP desorption in January compared with April, August and October ($p \leq 0.0001$). The apparent dip in mean August P desorption was not statistically significant. Mean moist sample P_w TDP content in January was just over half the mean moist sample P_w TDP content in April (mean 2.65 compared to 4.71 mg P kg^{-1}: table 3.9). Repeated measures analyses found significant differences in soil moisture contents among months ($F_{3,74}$ = 25.49, $p \leq 0.0001$), and *post-hoc* LSD found that soil moisture contents were higher in January than the other three months ($p \leq 0.0001$), and also higher in April than in August ($p \leq 0.05$).

Comparing the medians and spread of values for P_w TDP over different months (figure 3.5) highlights the greater consistency of inter-site variability between months for moist samples, with similar median monthly variation to that of the mean. Of note is the fact that two soils (3 and 10) are exceptionally high compared with the other soils (April, August and October high outliers and extreme outliers) for moist samples, but these soils are not so exceptional when samples are dried due to the more even spread of higher values.

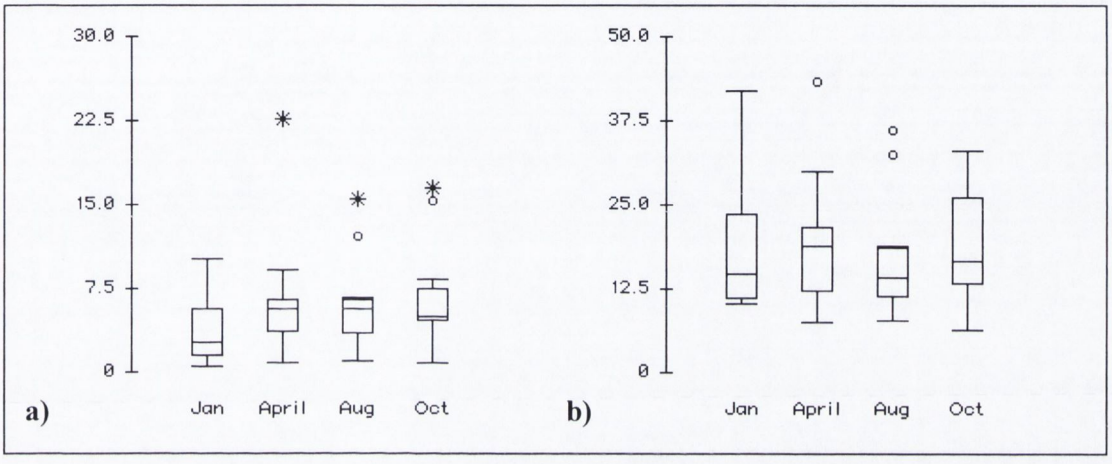


Figure 3.5: Boxplots of total water extractable P (P_w TDP) for the 11 monthly-analysed soils, from (a) moist and (b) dried samples in January, April, August and October. Y-axis is mg P kg^{-1} soil. Note the difference in scale between the (a) and (b) axes.

3.5.2. Olsen P fractions

Table 3.10 and figure 3.6 detail and summarise respectively differences in Olsen-extract P fractions between moist and dried samples. A comparison of figure 3.6 with figure 3.4 indicates that differences between moist and dried soil sample mean Olsen-extract P fraction contents were much smaller than those between moist and dried sample mean P_w fraction contents. In fact, whilst Olsen P content appeared to be slightly higher in dried samples, Olsen TP appeared to be slightly higher in moist samples overall – especially in October (mean Olsen TP content of 66.5 compared with 56.2 mg P kg^{-1}). Table 3.10 highlights the variability of drying-induced effects on Olsen-extract P contents. Actual and proportionate increases in Olsen P were greater for soils with lower Olsen P contents: i.e. soils 1, 5, 6, 7 9 and 11 all have Olsen P contents below 20 mg P kg^{-1}, and displaed consistent increases in Olsen P for all months, usually over 100% for soils 6, 7 and 11. Whilst changes after drying for the Olsen P fraction were almost exclusively increases, changes after drying for the Olsen TP fraction were mostly decreases, but there were also a number of notable increases. For example, whilst five of the soils displayed decreases (of up to 35% for soil 6) in Olsen TP after drying in January, soil 11 displayed a 59% increase, and in August, only soils 1, 5 and 6 displayed decreases after soil sample drying.

Separate repeated measures analyses were conduced on (square-root transformed) Olsen P and Olsen TP with soil, sample condition and month as independent variables, and an interaction term between month and sample condition. The results show that drying soil samples did have a significant effect on Olsen P (causing an increase; $F_{1,70} = 15.84$, $p = 0.0002$), and, despite the apparent variation in this effect among months (e.g. mean increase of 6.3 mg P kg^{-1} in January compared with 0.3 mg P kg^{-1} in October; table 3.10), there was no significant interaction between sample condition and month ($p = 0.339$). Olsen P content itself was not found to vary significantly among months ($p = 0.125$).

When data for all months are considered, sample drying had no significant overall effect on Olsen TP ($p = 0.126$), but there was a significant interaction between month and sample condition ($F_{3,70} = 3.10$, $p = 0.032$), indicating that sample drying had a different effect on Olsen TP depending on the month. Figure 3.6 suggests that this difference may be between October and the other months, and paired *t*-test analysis of moist versus dried Olsen TP content indicates that drying does have a significant impact ($t_{10} = 3.62$, $p = 0.0046$). Therefore, separate repeated measures analyses were conducted on (square-root

transformed) moist and dried sample Olsen TP against month. Both moist and dried samples showed highly significant monthly variation in Olsen TP content ($F_{3,30}$ = 13.76 and 14.12, $p \leq 0.0001$ for moist and dried samples respectively), but *post-hoc* LSD analyses indicate that there were more differences between months for moist compared with dried samples: moist sample Olsen TP was significantly different ($p < 0.05$) between all months except between April and August, whilst dried sample inter-monthly differences were limited to significantly higher ($p \leq 0.0001$) Olsen TP contents in January compared with the other three moths.

Figures 3.7 and 3.8 show that there is not much difference in the wide spread of values between moist and dried samples, for Olsen P and TP fractions respectively, although there is a more consistent pattern of monthly variation for the median and spread of Olsen TP contents in moist compared with dried samples.

Table 3.10: Mean Olsen P fraction contents in moist and air-dried samples of soils 1-11 for the months January, April, August and October, ± SD. of three replicates (expressed on a weight basis). Changes after drying are expressed on an absolute and proportional basis (percentage increases from moist in parentheses).

Soil	Olsen P						Olsen TP					
no.	Moist		Dried		Change		Moist		Dried		Change	
	mg P kg-1 soil											
Jan.												
1	8.2	±0.47	13.8	±1.12	5.6	(68)	68.6	±1.50	55.3	±5.47	-13	(-19)
2	64.6	±0.55	82.5	±0.45	17.8	(28)	153.6	±0.72	157.3	±8.77	3.75	(2)
3	85.9	±0.99	90.5	±4.96	4.6	(5)	144.1	±1.95	142.5	±3.38	-1.6	(-1)
4	34.1	±0.45	28.4	±1.02	-5.8	(-17)	66.1	±0.40	58.2	±1.56	-7.9	(-12)
5	8.5	±0.00	15.9	±2.18	7.4	(87)	46.6	±1.17	56.3	±2.97	9.64	(21)
6	0.0	±0.24	12.0	±3.52	12.0	(100)	51.7	±2.08	33.6	±0.69	-18	(-35)
7	3.3	±0.72	7.6	±0.00	4.3	(133)	24.2	±0.47	26.2	±0.52	2.03	(8)
8	32.9	±2.84	41.0	±0.20	8.1	(25)	68.0	±0.99	75.2	±1.72	7.19	(11)
9	9.2	±0.01	17.4	±0.27	8.2	(89)	64.1	±1.50	54.5	±0.04	-9.6	(-15)
10	74.9	±0.10	74.8	±2.66	-0.2	(0)	123.3	±2.83	123.5	±2.87	0.27	(0)
11	4.5	±0.00	12.2	±0.25	7.7	(174)	18.3	±0.27	29.1	±0.27	10.8	(59)
Mean	**29.7**		**36.0**		**6.3**	**(63)**	**75.3**		**73.8**		**-1.5**	**(2)**
April												
1	4.9	±0.24	11.3	±0.57	6.4	(130)	60.5	±0.62	44.2	±0.30	-16	(-27)
2	68.4	±1.77	66.8	±3.65	-1.6	(-2)	125.0	±0.41	122.5	±0.28	-2.5	(-2)
3	88.9	±1.87	80.1	±1.31	-8.8	(-10)	118.4	±1.26	117.3	±1.39	-1.1	(-1)
4	23.5	±1.73	32.4	±0.52	8.9	(38)	37.7	±0.96	53.6	±0.28	16	(42)
5	17.8	±1.78	19.7	±1.30	1.9	(11)	42.7	±1.31	46.2	±1.10	3.43	(8)
6	18.9	±7.76	10.0	±1.09	-8.9	(47)	39.4	±0.20	28.3	±1.16	-11	(-28)
7	1.8	±0.01	4.5	±0.00	2.7	(146)	17.1	±0.38	18.5	±0.00	1.42	(8)
8	26.3	±1.34	30.1	±1.22	3.8	(14)	48.2	±1.54	54.2	±2.04	5.96	(12)
9	9.5	±2.72	16.8	±0.86	7.4	(78)	40.0	±0.08	41.8	±1.82	1.85	(5)
10	60.5	±2.36	55.5	±0.52	-5.1	(-8)	96.8	±2.32	95.7	±0.83	-1.1	(-1)
11	3.1	±1.26	9.1	±0.00	6.0	(192)	19.6	±0.74	24.9	±0.55	5.24	(27)
Mean	**29.4**		**30.6**		**1.1**	**(49)**	**58.7**		**58.8**		**0.16**	**(4)**
Aug.												
1	9.1	±1.39	13.5	±0.00	4.4	(48)	71.3	±0.41	51.6	±2.08	-20	(-28)
2	49.6	±1.80	59.6	±0.25	10.1	(20)	111.4	±0.28	120.4	±0.82	9.01	(8)
3	69.2	±3.24	70.2	±0.00	1.0	(1)	105.8	±12.59	110.5	±1.10	4.7	(4)
4	13.2	±2.32	20.6	±1.05	7.5	(57)	27.3	±0.55	39.6	±0.28	12.3	(45)
5	16.2	±0.68	15.7	±0.00	-0.6	(-3)	42.0	±0.55	40.1	±0.00	-1.8	(-4)
6	3.4	±2.60	15.3	±2.05	11.9	(350)	51.8	±2.60	39.9	±1.85	-12	(-23)
7	2.6	±0.00	5.1	±0.27	2.4	(93)	17.3	±0.25	20.6	±0.56	3.33	(19)
8	24.1	±1.74	24.6	±0.25	0.5	(2)	45.7	±0.41	49.4	±0.55	3.74	(8)
9	7.4	±0.49	20.7	±0.28	13.2	(178)	37.4	±0.99	46.1	±0.91	8.71	(23)
10	64.2	±6.43	58.3	±0.78	-5.9	(-9)	96.1	±2.04	102.3	±0.55	6.2	(6)
11	3.4	±0.01	8.5	±0.76	5.1	(153)	20.7	±0.33	26.3	±1.90	5.54	(27)
Mean	**23.9**		**28.4**		**4.5**	**80.9**	**57.0**		**58.8**		**1.82**	**(8)**
Oct.												
1	8.3	±3.58	16.4	±1.30	8.1	(97)	74.3	±2.09	49.6	±0.30	-25	(-33)
2	62.5	±2.18	64.5	±12.22	2.1	(3)	131.2	±5.43	115.7	±1.78	-16	(-12)
3	71.6	±13.17	68.9	±1.92	-2.7	(-4)	121.5	±0.21	101.4	±3.00	-20	(-17)
4	51.0	±3.78	26.5	±0.24	-24.5	(-48)	42.4	±0.59	46.7	±0.27	4.32	(10)
5	15.4	±3.07	18.1	±0.24	2.6	(17)	46.7	±0.35	42.9	±0.54	-3.8	(8)
6	7.5	±5.34	15.7	±1.24	8.2	(109)	50.8	±1.75	42.7	±3.69	-8.1	(-16)
7	2.4	±0.25	8.0	±0.00	5.6	(235)	20.7	±0.28	20.1	±0.00	-0.6	(-3)
8	25.4	±0.92	28.2	±0.72	2.9	(11)	58.1	±0.91	50.0	±0.27	-8	(-14)
9	14.4	±2.06	17.5	±0.52	3.1	(21)	55.5	±1.98	34.2	±0.59	-21	(-38)
10	68.5	±0.99	58.5	±0.72	-9.9	(-14)	106.4	±0.91	93.5	±1.63	-13	(-12)
11	3.5	±0.25	10.9	±0.24	7.4	(215)	23.4	±1.03	21.1	±0.27	-2.3	(-10)
Mean	**30.0**		**30.3**		**0.3**	**(58)**	**66.5**		**56.2**		**-10**	**(-14)**

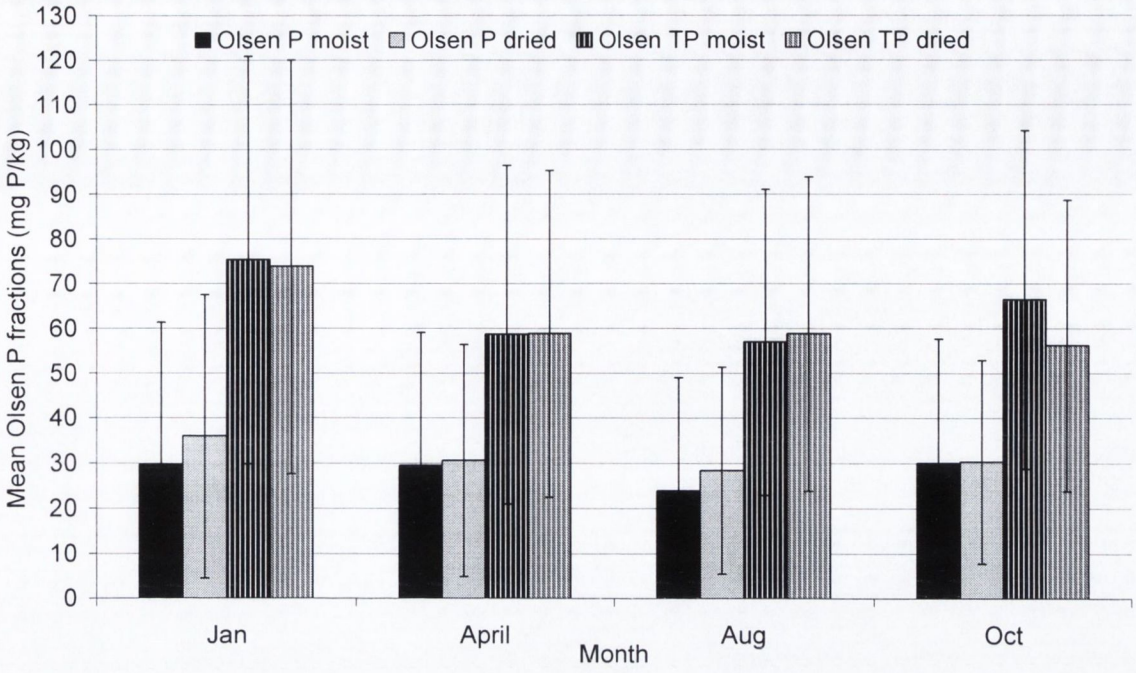


Figure 3.6: Mean Olsen P (and TP fraction) contents in moist and dried samples of the 11 monthly-analysed soils over the months January, April, August and October 2002. Error bars ± 1 SD.

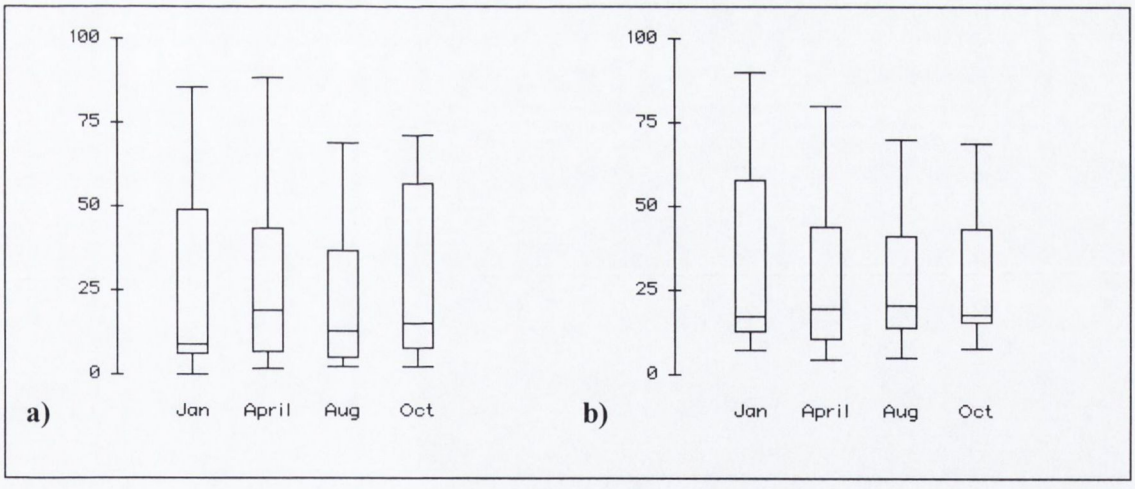


Figure 3.7: Boxplots of Olsen MRP for the 11 soils, from (a) moist and (b) dried samples, in January, April, August and October.

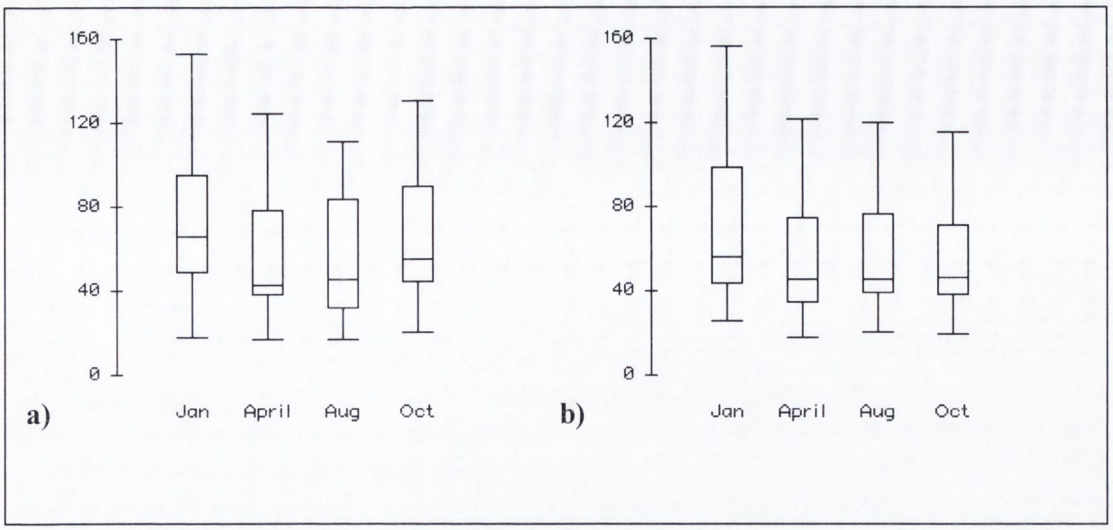


Figure 3.8: Boxplots of Olsen TP for the 11 soils, from (a) moist and (b) dried samples, in January, April, August and October.

3.5.3. Phosphorus sorption

As with Olsen P fractions, the effects of sample drying on P sorption from solution containing 30 mg P l^{-1} were not always consistent, although the general trend was for dried soils to sorb more P. It does appear from table 3.11 that the most substantial decreases after drying were for soils 4 and 11, occurring in August and October (e.g. 15 and 16% for soils 4 and 11 respectively in August). The most notable common feature to these two soils is high pH (7.51 and 7.57, respectively; table 2.6). Repeated measures analyses on sorption against soil, sample condition and month, with interaction terms between sample condition and month, confirmed that drying-induced changes in P sorption were significant ($F_{1,70} = 18.73$, $p \leq 0.0001$).

Figure 3.9 shows mean sorption by moist and dried samples in the different months, and indicates that dried samples sorbed more P in most months, though moist samples sorbed slightly more (1% on average; table 3.11) than dried samples in August. Results of the repeated measures analyses confirmed that P sorption did vary significantly with month ($F_{3,70} = 3.42$, $p = 0.022$), and that sample condition had a significant effect on this variability ($F_{3,70} = 3.20$, $p = 0.029$). Figure 3.9 and figure 3.10 show that, in contrast to Olsen TP (figures 3.7 and 3.8), dried sample P sorption displayed a more consistent monthly trend and spread of values than moist sample P desorption. It appears from figure 3.9 that dried sample sorption followed a trend of decreasing from January through April to August, and then increasing again in October. In contrast, moist sample sorption was greatest in August, followed by January, October and April

Table 3.11: Mean sorption to moist and air-dried samples of soils 1-11 for the months January, April, August and October, ± SD. of 2 replicates (expressed on a weight basis). Changes after drying are expressed on an absolute and proportional basis (percentage increases from moist in parentheses).

Soil	Sorption			
no.	Moist	Dried	Change	
	mg P kg^{-1} soil			
Jan.				
1	293.7 ±0.92	328.2 ±0.21	34.4	(12)
2	295.9 ±0.07	304.8 ±0.14	9.0	(3)
3	257.1 ±0.04	270.6 ±1.77	13.4	(5)
4	239.8 ±3.92	252.2 ±1.36	12.4	(5)
5	235.9 ±4.44	262.2 ±2.42	26.3	(11)
6	291.1 ±5.91	318.9 ±0.16	27.8	(10)
7	284.6 ±2.90	305.4 ±0.28	20.8	(7)
8	272.1 ±3.58	297.1 ±1.12	25.1	(9)
9	298.4 ±1.37	337.7 ±0.35	39.3	(13)
10	283.6 ±6.83	279.9 ±0.64	-3.7	(-1)
11	267.2 ±2.18	269.7 ±0.42	2.5	(1)
Mean	**274.5**	**293.3**	**18.9**	**6.84**
April				
1	292 ±0.23	331.3 ±0.31	39.3	(14)
2	289.3 ±0.13	286.1 ±4.17	-3.2	(-1)
3	252.9 ±3.79	263.4 ±2.56	10.4	(4)
4	210.1 ±0.33	222.5 ±1.77	12.4	(6)
5	232.3 ±1.44	249.2 ±1.06	16.9	(7)
6	293.6 ±0.47	302.9 ±2.42	9.3	(3)
7	267.1 ±0.81	302.3 ±0.89	35.3	(13)
8	263.9 ±1.07	285.1 ±1.43	21.2	(8)
9	294 ±0.31	335.3 ±0.34	41.2	(14)
10	248.7 ±4.96	271.7 ±1.20	23.0	(9)
11	277.4 ±0.99	276.8 ±0.65	-0.6	(0)
Mean	**265.6**	**284.2**	**18.7**	**(7)**
Aug.				
1	295.3 ±1.57	330.2 ±0.33	34.9	(12)
2	291.2 ±3.52	301.0 ±0.74	9.7	(3)
3	260.7 ±0.55	261.2 ±1.71	0.5	(0)
4	250.6 ±2.28	212.2 ±3.69	-38.4	(-15)
5	247.2 ±0.01	228.3 ±6.56	-18.8	(-8)
6	300.3 ±7.54	304.6 ±1.56	4.3	(1)
7	285.1 ±0.98	303.1 ±0.25	17.9	(6)
8	277.2 ±0.31	270.5 ±1.71	-6.7	(-2)
9	296.9 ±0.96	335.2 ±0.10	38.4	(13)
10	257.2 ±1.98	255.9 ±5.13	-1.2	(-1)
11	283.5 ±1.23	237.8 ±5.55	-45.7	(-16)
Mean	**276.8**	**276.4**	**-0.5**	**(-1)**
Oct.				
1	294.8 ±0.03	328.8 ±0.33	34.0	(12)
2	290.7 ±2.67	300.9 ±0.31	10.2	(4)
3	237.3 ±2.22	252.1 ±0.49	14.7	(6)
4	231.8 ±0.41	208.9 ±7.38	-22.9	(-10)
5	229 ±3.71	226.9 ±1.70	-2.1	(-1)
6	310.2 ±0.85	303.4 ±0.48	-6.8	(-2)
7	281.2 ±0.13	303.1 ±1.24	21.9	(8)
8	267.6 ±2.06	276.2 ±2.93	8.6	(3)
9	298 ±1.15	333.8 ±0.42	35.7	(12)
10	233.6 ±5.71	252.7 ±0.00	19.1	(8)
11	282.7 ±0.89	258.8 ±1.46	-23.9	(-8)
Mean	**268.8**	**276.9**	**8.0**	**(3)**

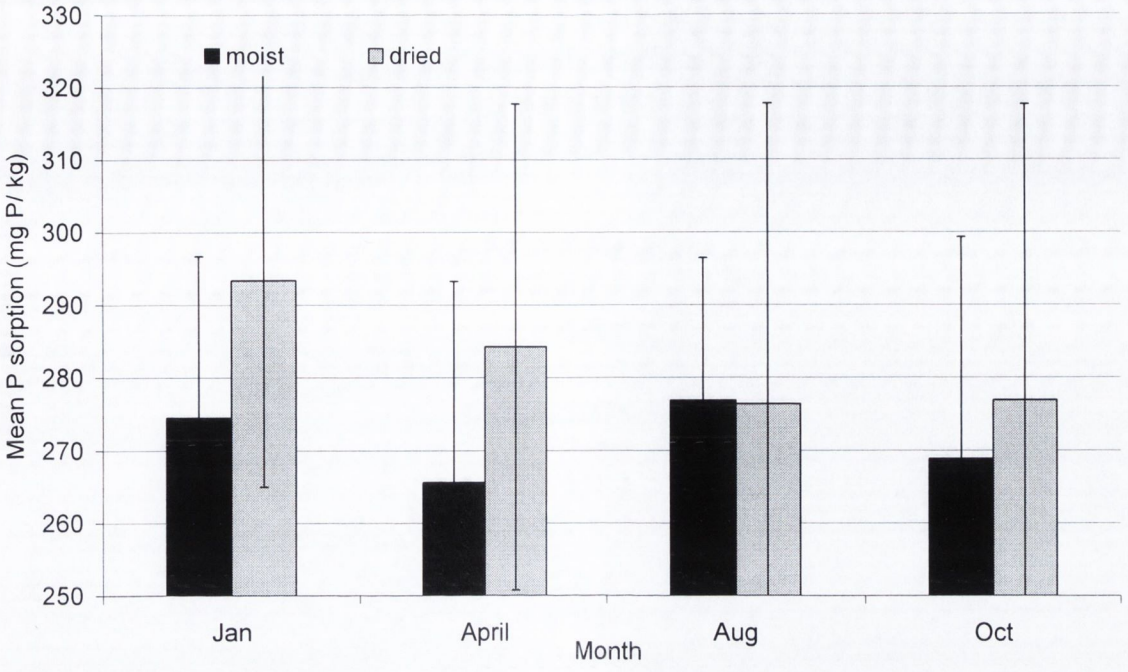


Figure 3.9: Mean sorption from solution containing 30 mg P l^{-1} to moist and dried samples of the 11 monthly-analysed soils in January, April, August and October.

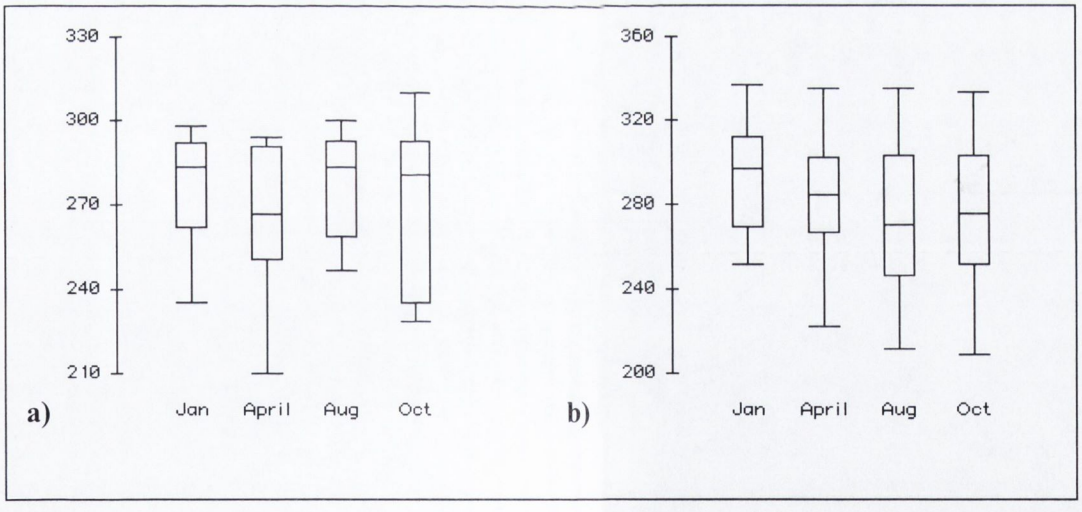


Figure 3.10: Boxplots of sorption from 30 mg P l^{-1} solution for the 11 soils, from (a) moist and (b) dried samples, in January, April, August and October.

3.6. Spatial sample Discussion

3.6.1. 'Organic' P release

Drying soil samples had profound effects on the quantity of P desorbed, resulting in up to 10 times more P being desorbed to water (by peat soil 6) in this study. The large proportionate increases in soil P_w content recorded here after drying (table 3.1a) are of a similar magnitude to those found for other pasture soils by a number of researchers (Turner and Haygarth, 2001; Turner et al. 2002), although are larger than increases found by Pote et al. (1999a) - perhaps because the soils in their study were exposed to strong seasonal drying and did not have high moisture contents when sampled (26.9 and 4.6% in May and August respectively). A large proportion of these increases were in the form of MUP (table 3.3b), and thus likely to be organic P (although some of the P_w DRP increase was also likely to be caused by organic, or other non-orthophosphate, P fractions hydrolysed during analysis; section 1.2). This is consistent with drying-induced P release resulting from microbial cell lysis, which would be predominantly (though not exclusively) in organic form. Turner et al. (2003) found that drying-induced P_w MUP increases in two Australian pasture soils corresponded with 88 and 95% of the P contained in the bacterial cells that were lysed during the process. However, the actual increases they found in soil P_w MUP content only amounted to 1.17 and 0.62 mg P kg^{-1}, compared with mean P_w MUP increases ranging from 0.96 to 27.07 mg P kg^{-1}, and averaging 10.13 mg P kg^{-1} (table3.3b) for mineral soils in this study.

Even comparison with similar soils indicates that P_w increases found in these soils were unusually high: Turner and Haygarth (2001) found water-extractable P increases ranging between 1.1 to 7.6 mg kg^{-1} after drying 29 pasture soil samples from England and Wales (though the percentage increase were similar to those in this study). Microbial P release would be expected to be high from the soils in this study for a number of reasons. Firstly, the microbial content of these soils is likely to be high, as they are high OM and moisture content pasture soils, undisturbed by tillage - probably for decades in many instances. The shallow depth of sampling also corresponds with the microbial-rich root zone of these pasture soils. Secondly, these soils do not commonly experience moisture stress, with seasonally-sustained high moisture contents (e.g. high moisture contents in samples collected throughout 2002; section 5.4.2), and therefore the microbial cells they contain are

likely to be particularly susceptible to drying-rewetting-induced lysis (Kieft et al., 1987; Sparling et al., 1985).

Despite the high P_w MUP release, and the fact that this was the dominant fraction released by drying, P_w MUP increases were proportionately less in this study compared with those found by Turner and Haygarth (2001) and Turner et al. (2002). Both the comparatively high P increases, and lower relative proportions accounted for by P_w MUP, were probably the consequence of the high soil-water ratio used here (a low soil-solution ratio of 1:4 was used in the other studies) - encouraging high P_w DRP release (Chapman et al., 1997a). Data from this study confirm that soil-solution ratios have a substantial impact on the amount of P release to water, with a 50% increase in P desorption from dried samples of the same soils analysed at 1:100 compared with 1:50 soil-water ratio (section 3.5.1). However, comparison of drying-induced P_w increases in samples of the 11 monthly-analysed soils collected in April 2002 with those for the same soils analysed at twice the soil-solution ratio in March 2003 showed that the P_w MUP fraction increases were twice as high, though accounted for a similar proportion of mean P_w TDP increase, in the March 2003 samples, despite the higher soil solution ratios. It is possible that any negative effects of soil solution ratio on the proportion of P_w MUP release were offset by higher OM and microbial biomass content in the shallower samples collected in March 2003.

Turner and Haygarth (2003) found that large increases (5.2 – 26.9 mg P kg^{-1}) in bicarbonate-extractable P after drying (from samples of the same English and Welsh pasture soils for which P_w increases were reported by Turner and Haygarth, 2001) only contained relatively small proportions of orthophosphate diesters (the main microbial P fraction), but large proportions of orthophosphate monoesters similar to whole-soil organic fraction extractions. They go on to suggest that solubilisation of OM through physical disruption of OM coatings on mineral surfaces may be responsible for most of the drying-induced bicarbonate-extractable P_o increases they noted (varying from -0.4 – 15.2 mg P kg^{-1}), consistent with large increases in SOC noted after drying (Bartlett and James, 1980; Raveh and Avnimelech, 1978; Stevenson, 1956; Van Gestel et al., 1991). This mechanism could explain the large P_w MUP increases noted in this study, which appear to increase with increasing soil-water ratio in a manner and to an extent inconsistent with exclusive release from microbial cells. Other mechanisms by which P_w MUP may be released after drying and rewetting soil samples are the disruption of soil aggregates caused by drying-induced micelle instability and oxidation of OM over time of dry storage (Raveh and

Avnimelech, 1978), and shrinking-swelling induced aggregate disruption (Chepkwony, 2001). Phosphorus associated with fine colloidal (<0.45 μm) material released during these processes is also likely to contribute to MUP concentrations measured in soil water extracts, though this may not be P_o. Significant correlations between P_w MUP increases and OM contents among soils (table 3.5a) supports the hypothesis that these mechanisms are responsible for drying-induced P release, and are examined further in section 3.6.3.

3.6.2. 'Inorganic' P release

Drying-induced increases in the P_w DRP fraction were significantly lower than increases in the P_w MUP fraction (section 3.4.1), but were substantial nonetheless – ranging from 1.10 to 16.21 mg P kg-1, with only one soil (no. 7) displaying a (substantial) decrease of 9.79 mg P kg^{-1} (table 3.1a). As referred to in section 1.1.2, the definition of DRP is an operational one, and the DRP fraction has been found to include large proportions of organic and colloidal P (Baldwin, 1998; Haygarth, 1997; Matthews et al., 1998; Rigler, 1968). Thus, a substantial proportion of drying-induced P_w DRP increase may be accounted for by hydrolysation of P_o and displacement of P_i adsorbed onto fine colloids, released by the processes listed in the above section.

Soil drying also had a substantial effect on the more rigorous P_{feo} method of measuring soil P desorption, resulting in up to 33 times more P being released (soil 6; table 3.1a), and the largest increases noted for any desorbable P faction analysed in this study (averaging 20.64 mg P kg^{-1} soil; table 3.3d). These increases were substantially greater than those found by Olsen and Court (1982) for resin-extractable P (a similar P_i method to P_{feo}) after soil drying (5 – 37%). Phosphorus desorption to a solution reflecting soil water ionic strength (0.02M KCl in this study) and a constant P sink (iron-oxide impregnated filter paper in this study) should reflect truly dissolved, and predominantly inorganic, soil P desorption potential (Van der Zee et al. 1987), though this has been questioned. Lookman et al. (1995) suggested that the adherence of particulate P to the iron-oxide strip (and subsequent hydrolysis in the acidic strip-P extraction procedure; see section 2.2.3) caused P_{feo} concentrations to overestimate rapid P desorption by to a factor of 4. Sharpley et al. (1995) also suggest that P_o may sorb onto the iron-oxide strip. Nonetheless, it seems reasonable to assume that a large proportion of, though not all, of the drying-induced P_{feo} increase represents drying-induced P_i release. The potential contribution of microbial cell lysis to

P_{feo} increase (through intra-cellular P_i release, mineralisation or sorption of P_o fractions) is likely to be minimal due to the ionic strength of the extracting solution (0.02M KCl) reducing osmotic shock, and thus the occurrence of cell lyses, during rehydration (Turner et al., 2003).

Therefore, this study shows that large quantities of P_i are released during, or as a consequence of, standard soil drying procedures for the preparation of soil samples for P analyses. There are 2 principal mechanisms which have been proposed for drying-induced P_i release after soil drying. Firstly, P_i may desorb from low energy, recently exposed (de)sorption sites (Haynes and Swift, 1985a); pH may play an important, though poorly understood, role in determining the extent of this effect (see section 3.6.5). Secondly, newly exposed and solubilised P_o may be converted to P_i during the flush of mineralisation stimulated by high SOC concentrations after rehydration of dried soils (Bartlett and James, 1980; Stevenson, 1956; Van Gestel et al., 1991). Thus, organic compounds exposed and solubilised during drying and rewetting are not only a source of solution P_o, but provide the energy for mineralisation of P_o into P_i. This mineralisation may occur during the drying process, when dried soils are stored, and after remoistening (though is likely to be limited for the 30 minute P_w extraction). Mineralisation may occur to a greater extent during the prolonged, relatively warm conditions experienced during air-drying compared to shorter oven-drying procedures, and may contribute to the high P_w DRP and P_{feo} increases noted in this study.

The large scale of drying-induced P_{feo} increases in comparison with P_w DRP increases may be partially attributable to the longer reaction time of 18 hours (compared with 30 minutes for P_w) enabling more time for P to desorb from less well exposed locations in soil aggregates and from higher energy sorption sites; after rapid initial desorption within minutes to an hour of solution contact, P desorption continues to proceed for weeks and months (Lookman et al, 1995; Maguire et al., 2001). The longer reaction time in P_{feo} analyses also allows any rehydration-induced mineralisation flushes to proceed for longer. Additionally, the constant P sink in the P_{feo} test maintains negligible P in solution (Van der Zee et al. 1987), so desorption will not slow or cease as an equilibrium concentration is approached or reached as it does in P_w extracts (theoretically maintaining a near infinite soil-solution ratio, though in practice dissolution of other compounds may hinder desorption through the common-ion effect).

3.6.3. Soil organic matter and moisture content

Strong positive correlations between OM content and desorbable P increases (table 3.1a) suggest that soil OM is particularly susceptible to drying-rewetting induced mechanisms of P release (disruption, solubilisation and mineralisation) listed in the previous sections. The fact that these correlations were stronger for P_w DRP than for P_w MUP (e.g. $r = 0.61$ compared with 0.44, $p \leq 0.001$ and 0.05, for P_w DRP and MUP percentage increases respectively against OM content) indicates that exposure of new P (de)sorption sites and SOC-related P mineralisation immediately upon rewetting are important processes for inorganic and readily-hydrolysable fractions, whilst microbial P (as opposed to soil physico-chemical properties) may be more influential on drying-induced P_w MUP release. Clay is known to form stable complexes with OM which may protect it from the effects of drying (Van Gestel et al., 1991), which could explain the significant negative correlations between clay and volume-based dried soil desorbable P, and drying-induced desorbable P increases (table 3.1b) among the 26 mineral soils.

The choice of weight or volume based expression is particularly important, and insightful, when analysing the effect of OM content on desorbable P increases. The greater volumes of higher OM soils per unit weight are likely to contain greater (potential) reactive surface areas from which P may desorb, and greater volumes of microbial biomass, and other organic compounds from which P may be released through cell lysis or solubilisation upon rewetting of dried soils. To recap on the example given in section 2.2.5, according to the method of conversion outlined in that section, 1 g of soil 12 (10.2% OM) had a volume of 1.25 ml, while 1 g of soil 39 (72.4% OM) had a volume of 4.76 ml. This OM-volume effect is removed when soil P desorption is expressed on a volume-basis (estimated from OM content itself). In fact, once overall soil BD is accounted for, high OM content soils (especially peat soils) may have lower reactive surface areas within the same volume of soil; large organic soil fibres / aggregates may have smaller (potential) reactive surface areas than fine particles in mineral soils. Thus, OM susceptibility to drying-induced P release may be counteracted by a smaller reactive surface area when soil P desorption is expressed on a volume basis, explaining the absence of correlation between OM content and volume-expressed desorbable P increases overall. However, table 3.6 shows that volume-expressed increases in P_w MUP and TDP fractions remain significantly positively correlated with soil OM content when mineral soils are considered. This could be because the susceptibility of OM to drying-induced P release remains a dominant determinant of

drying-induced desorbable P increase in these soils, and/or there may be a correlation between microbial biomass and OM content in mineral soils.

Whether all soils or just mineral soils are considered, weight-expressed and percentage increases were most strongly correlated with moisture content out of all the soil characteristics analysed (though for P_w DRP increase, TOC was slightly more strongly correlated; visual inspection of the strong P_{feo} percentage increase correlation with Fe_{ox} during stepwise multiple regression analyses showed that it was forced by an extreme outlier). Moisture content was strongly correlated with OM content ($r = 0.90$, $p \leq 0.0001$ for all soils; table 4.3), and may account for additional factors (other than OM drying susceptibility and volume effects) contributing to drying-induced desorbable P increases. For example, soils with higher moisture content may contain more microbial biomass, and this biomass may be more susceptible to the effects of drying and rewetting than that in soils with lower moisture content (Sparling et al., 1985; Kieft et al., 1987; Van Gestel et al., 1991); although this effect is likely to have been limited in these soils due to the prevailing high moisture contents (e.g. section 5.4.2). Most soils appeared to be at, or close to, saturation when sampled in March 2003, implying that moisture content was representative of pore volume, which in turn would give an indication of reactive surface area potentially affected by drying (and may conceivably also be related to microbial biomass content). It is also possible that moisture content partially reflects P flushing effects by interacting water; high P flushing would result in low moist sample desorbable P and therefore higher relative (percentage) increases after drying.

3.6.4. Soil type

Some of the correlation between OM content and P desorption increase after drying appears to be accounted for by the different behaviour of distinct high OM peat soils, as OM was not significantly correlated with P_w DRP or P_{feo} weight-expressed or percentage increases, or P_w TDP percentage increases, among mineral soils (table 3.6). Correlations between percentage increases and OM were driven partly by substantially lower P desorption from peat compared with mineral soils (tables 3.3a-d); this effect is analysed in more detail in chapter 4. Daly (2000) attributes low peat soil P desorption to biological immobilisation of P_i and humic-acid stabilisation of P_o, both of which are likely to be at least partially reversed by drying through mechanisms listed in section 3.6.1. Section 4.5.6

shows that peat soils contained significantly lower P_{ox} (p = 0.023) and Olsen P (p = 0.0008), and had significantly lower DPSS (p = 0.0016 and 0.018 for DPSS 1 and 2 respectively) than mineral soils, which may at least partially explain lower desorption (and higher relative drying induced P release) for peat soils. Volume-expressed desorbable P increases were not significantly higher for peat soils (section 3.4.2), which could also explain the absence of correlations between volume-expressed desorbable P increases and OM content in table 3.1b.

The fact that drying resulted in significantly greater weight-based desorbable P increases for peat compared with mineral soils (e.g. more than double the increase for P_w DRP) has serious implications for the understanding of desorption from these soil types in the environment. If moist samples are considered, on a weight or volume basis, then peat soils would be expected to desorb less P to a given volume of interacting surface/sub-surface water than mineral soils, but if dried samples are considered, there would be little difference in the quantity expected to be desorbed from a given weight of peat or mineral soil, though a given volume of peat soil would still be expected to desorb less. The implications of this drying-induced loss of differentiation for volume-basis P desorption will be explored in chapter 4, where P desorption indices will be determined for different soil types, but from these data it is clear that drying soils, and expressing results on a weight basis, have serious implications for the development of soil P indices for use in catchment nutrient transport models. One potential problem of expressing results on a volume basis is that the effective volume-volume soil-solution ratio in desorption analyses will vary according to soil BD, with a consequent impact on P desorption dynamics (section 3.6.1). Measuring out volumes, rather than weights, for laboratory analysis would be akward and inaccurate for soils with strong aggregate structure or high moisture contents.

3.6.5. Soil test P and P sorption

Significant negative correlations between STP and P_w DRP and TDP percentage increases were probably the consequence of strong positive correlations between STP and moist (and dried) sample desorption (table 3.1a); percentage increases were inversely related to P desorption from moist samples. Significant positive correlations between volume-expressed STP and P_{feo} increases may reflect the fact that P_{feo} - because it measures

continuous desorption over 16 hours - measures P desorbed from higher-energy and less exposed (de)sorption sites, which become exposed during and subsequent to the drying process (sections 3.6.1 and 3.6.2). Phosphorus from these sites exposed by drying is also likely to be extracted by chemical reagents used in STP analyses. Strong positive correlations between volume based measures of DPSS and P_{feo} increase (e.g. $r = 0.66$, $p \leq 0.001$ for P_{feo} increase versus DPSS2) support this; the higher the P saturation of exposed desorption sites, the greater the increase in P desorbed from these sites as they become exposed after drying.

The fact that P_{feo} is supposed to represent soil potentially desorbable P_i content is reflected by the dominance of soil P sorption characteristics found in stepwise multiple regression analyses to predict (weight and volume-expressed) drying-induced P increases (table 3.8). It appears that after the positive influence of DPSS2 was taken into account, PSC2 (used in the calculation of DPSS2) still had a negative influence on desorbable P increase (for P_{feo}, and also for volume-expressed P_w TDP). This may be because of overestimation of $P_{(ox)}$ saturation, which could be the consequence of organic-bound (as opposed to sorbed) P being solubilised during oxalate-extraction, or, more likely, it may be due to drying-induced PSC increases. Whether drying increases or decreases soil PSC is debated, and may depend both on the P saturation of newly exposed (de)sorption sites and the rate of drying - with rapid drying resulting in small crystal size and high sorption capacity, and vice versa for slow drying (Pote et al. 1999a). In this study, seasonal soil drying data suggest that, overall, drying soil samples increases PSC (section 3.7.3), and this effect may have an increasingly negative effect on soil P desorption with increasing soil PSC (potential number of sorption sites affected). The fact that PSC was not consistently significantly negatively correlated with drying-induced desorbable P increases (except weakly for volume-expressed P_w TDP increase; table 3.1b) may be due to counteracting significant positive correlations between DPSS and PSC (table 4.3) - presumably due to more fertile, higher PSC soils having higher managed P inputs. The significant negative influence of Al_{ox} on weight-expressed P_w MUP and TDP increases noted in stepwise multiple regression analyses (table 3.8) suggests that Al_{ox} may be relatively more active in soil P sorption than Fe_{ox}, and is perhaps involved in organo-metallic complexes less susceptible to drying effects than other organo-metallic complexes (e.g. involving Mg).

The inclusion of pH was also significant, as a negatively correlated predictor, in predicting the residuals remaining after regression of P_{feo} with DPSS2 and PSC2 (table 3.8), and pH

was significantly negatively correlated with weight-expressed P_w DRP increase ($r = -0.46$, $p \leq 0.01$; table 3.1a). Once the relative importance of P sorption saturation is accounted for, pH may affect drying-induced desorbable P increases either through chemical sorption / desorption equilibria, and / or through an influence on exposure of P (de)sorption sites. Increasing drying-induced desorption increase at lower pH would be consistent with OM destabilisation associated with lower pH (Raveh and Avnimelech, 1978), although would not be consistent with lower sorption energy at higher pH (Olsen and Court, 1982). Also, the increasing importance of Ca at higher pH (Ca becomes the dominant element of P sorption above pH 7) would decrease the desorption expected from (Al and Fe based) DPSS levels at higher pH, and would also explain the significant negative relationships between Ca and P_w increases found in multiple regression analyses (tables 3.7 and 3.8).

It is difficult to explain significant positive correlations between exchangeable Mg contents and desorbable P contents and their increases after drying (section 3.4.4). Magnesium is involved in soil P sorption, though to a lesser extent than Ca, and is also involved in organo-metallic complexes. Higher exchangeable Mg contents may indicate greater drying-induced organo-metallic disruption, explaining correlation with weight-expressed dried sample P desorption, and desorbable P increases. Haynes and Swift (1985a) specifically attributed extractable P release after drying to desorption caused by the disruption of organo-metallic complexes. Other potential effects of sample drying on desorbable P release may be related to redox potential decreases upon rewetting dried soils (Bartlett and James, 1980), although the consequences of this on P desorption are unclear. On one hand, sorption of P has been found to increase at redox potentials low enough to transform Fe^{3+} (hydr)oxides into Fe^{2+} hydroxides with increased sorption surface area, reducing water soluble P (Phillips, 1998), and increased concentration of ions in solution at low redox potential have been invoked for reducing P dissolution through the common ion effect (Mack and Barber, 1960). On the other hand, Nair et al. (1999) observed reduced sorption capacities in spodosols under anaerobic conditions, and associated higher equilibrium P concentrations. No redox measurements were taken in this study.

3.7. Sample drying and seasonal variation discussion

3.7.1. Water extractable P

A detailed analysis of seasonal variation in soil P fractions is conducted in chapter 5; results in this chapter focus on the implications of soil drying-induced changes for interpretation of seasonal variation.

Comparison of moist and dried samples for the 11-monthly sampled soils over months from each of the 4 seasons found that P_w increased after drying in all soils in all months. The lowest noted increase was for soil 7 P_w DRP in August (18%; table 3.9) – the same soil that displayed a decrease in P_w DRP (and consequently P_w TDP) after drying in the spatial analyses (table 3.1a). This soil has a high PSC2 (138.2 active molar concentration; table 4.2a) and a low DPSS2 (2.4%;table 4.2a), and high exchangeable Ca content and OM content for a mineral soil (20.4%; table 2.6). Thus, (de)sorption sites exposed by drying-induced processes are likely to predominantly sorb rather than desorb P. However, actual decreases in desorption after drying for spatial dataset (March 2003) analyses also appear to be because of unusually high moist sample P desorption (16.96 mg P kg^{-1} compared with 2.01 mg P kg^{-1} in April 2002; table 3.1a and 3.9 respectively). There is no obvious explanation for this. The highest relative increase in P_w after drying was again for soil 6, which displayed a 34 fold increase in P desorption (table 3.9).

Overall, the impact of drying soil samples was to mask seasonal variation in moist sample P desorption. Increases in P desorption were relatively constant among months, but percentage increases were significantly higher in January compared with the other months (averaging 634% for P_w TDP; table 3.9). These significantly higher percentage increases in January were the consequence of low moist sample P desorption in this month (significantly lower than for the other months; section 3.5.1). When dried samples were analysed, P_w was similar among months (table 3.9), and was not found to be statistically significantly different. Low P desorption in January corresponded with significantly higher moisture contents in this month compared with the other months (section 3.5.1). Magid et al. (1992) found that soil P_i was inversely correlated with soil moisture over seasons. There was a 65% increase in moist-sample P_w (TDP) between January and April (with mean values from the 11 soils increasing from 3.99 to 6.58 mg P kg^{-1} soil; table 3.9), which was not matched by an increase in mean dried sample P_w TDP content.

Mineralisation of organic P accelerates in spring as temperatures warm and the soil begins to dry, supplying plants (and water) with previously organic-bound P (Sharpley, 1985b). This is reflected in declining Olsen TP from winter into spring (section 3.5.2), and is consistent with decreasing biomass P content over the same period and into the growing season (Tate et al., 1991a). Pote et al. (1999a) also noted a substantial increase in P_w DRP between May (wet season) and August (dry season) for moist samples but not for air-dried samples, and attributed the moist sample increase to microbial cell lysis and plant tissue decomposition in the hot, dry August conditions.

In addition to possible relationships with climatic factors outlined above and in section 5.4.4, management events may also have been responsible for some dramatic moist-sample desorbable P increases between January and April (section 5.4.4). Exceptionally high stocking density (approximately 20 L.U. / ha) noted during March and April on the soil 3 field, and light manure application in February on the soil 5 field, resulted in a doubling and trebling, respectively, of moist sample P_w TDP content between January and April (increases of 12.53 and 4.01 mg P kg^{-1}; table 3.9). However, dried samples of the same soils displayed an increase of 1.56 and a decrease of 1 mg P kg^{-1}, respectively, over the same period, reflecting the absence of significant differences in P desorption among months for dried samples of these soils, and dried samples generally. Phosphorus additions in the form of fertiliser or manure are likely to be loosely bound and readily desorbable immediately after application, thus increasing moist and dried sample P desorption. Increased sorption capacity may reduce this effect in dried samples. Additionally, lower contents of microbial P and moderately labile organic P (reflected by lower Olsen TP contents), resulting from mineralisation of P in spring, may decrease the amount of P susceptible to drying-induced release in April compared with January, and thus counteract P application increases in dried sample P_w TDP.

Overall, desorbable P increases expected from mineralisation and reduced rates of hydrological flushing are likely to be masked by the release of microbial P and non-microbial organic or organic-associated P during drying and rewetting. As with spatial samples, P_w MUP increases were greater than P_w DRP increases, but there were no significant difference in the relative increase of one fraction compared with the other among months (section 3.5.1).

3.7.2. Olsen-extractable P

Results presented in section 5.3.2. show that drying soil samples did not significantly increase the total amount of P extracted from soils by the Olsen extract; in fact, it decreased the amount of Olsen TP analysed in October samples. These data conflict with those of Sparling et al. (1985) and Turner and Haygarth (2003), who found significant increases in bicarbonate (Olsen)-extractable TP after drying. Turner and Haygarth (2003) attributed significant bicarbonate-extractable P_o increases after sample drying to drying-induced physical disruption of organic coatings on mineral surfaces (see section 3.6.1), and suggested that the small contribution to drying-induced TP increases made by microbial P was because the ionic strength of the bicarbonate solution minimised rehydration-induced microbial cell lysis. In contrast, Sparling et al. (1985) attributed drying-induced bicarbonate-extractable TP increases to microbial cell lysis. Given the large drying-induced increases in P_w MUP found for soils 1-11, which, due to their scale, appear to be the consequence of both physico-chemical and biological processes, it is surprising that the same processes do not increase Olsen-extractable P - as they do in the aforementioned studies. Total P in the Olsen extract includes moderately labile P_o bound and associated with OM (Sharpley, 1985b) and (at least some) microbial P (Sparling et al., 1985; Tate et al., 1999a; Turner and Haygarth, 2003). Therefore, it is possible that the total P extracted from moist samples by the Olsen reagent is already likely to include much of the soil P vulnerable to drying-induced disruption of OM and microbial cell lysis. Mineralisation of some Olsen-extractable P_o to P_i, and subsequent sorption to dried soils of higher sorption capacity (section 3.5.3), could explain decreases in this fraction and concurrent increases in the P_i (~Olsen P) fraction (and may counteract any possible drying-induced Olsen-extractable P release).

It is more difficult to explain why there were more consistent, and overall significant, decreases in Olsen P contents after drying for October samples. It is possible that potential drying-induced P release was lower in October compared with other months. For example, lower soil microbial P contents in summer and autumn (Tate et al., 1999a) may have resulted in lower drying-induced microbial P release for August and October samples. This may have only contributed to a significant Olsen TP decrease in October due to differential drying-induced sorption effects between these 2 months (whilst drying samples was found to significantly increase sorption overall, figure 3.9 and table 3.11 indicate that this was true for October but not for August samples – which displayed a marginal

decrease in sorption). This significant drying-effect for October samples changed the monthly pattern of variation in Olsen TP between moist and dried samples slightly. Both moist and dried sample extracts reflect the decline in organic P during the growing season as it is mineralised to release P_i for plant uptake (Tate et al., 1991a), with significantly higher Olsen TP contents noted in January compared with the other months (section 3.5.2). However, dried samples did not display the same mean Olsen TP content increase in October that is displayed by moist samples, and which may reflect both reduced plant P uptake and the beginning of autumn-winter microbial P accumulation (Tate et al., 1991a).

In contrast to Olsen TP, the more consistent and statistically significant increases found for Olsen P reflect the fact that this fraction is dominated by P_i, and some labile P_o (Tate et al., 1991a), which is susceptible to drying-induced mechanisms of release. This release may include the exposure of new (de)sorption sites caused by physical disruption (Turner and Haygarth, 2003) and microbial P release (Sparling et al., 1985). However, there were also notable decreases in Olsen P for a number of soils, and monthly mean increases for the 11 soils were low (ranging from just 0.3 to 6.3 mg P kg^{-1}) compared with increases found by other studies. Turner and Haygarth (2003) found that all 29 UK pasture soils studied displayed increases in bicarbonate-P_i after drying, with an average increase of 7.7 mg P kg^{-1}, and Sparling et al. (1985) found that all but two of 18 New Zealand pasture soil samples studied displayed increases in bicarbonate-P_i, with an average increase of 10.1 mg P kg^{-1}. As mentioned in the previous paragraph, drying-induced Olsen P decreases for some soils (and the limited increases in others) may have been the consequence of concurrent increases in P sorption capacities after drying; although why this would occur to a greater extent in these soils compared with the 29 UK and 18 New Zealand pasture soil samples is unclear from the data available. One aspect that is in agreement between the aforementioned studies and this one is that increases are proportionately greater for low Olsen P soils. Relative differences in Olsen TP were less than in Olsen P (table 3.10), suggesting that the quantities of P susceptible to drying-induced release were similar, or even greater - and therefore the proportional increases greater - in lower Olsen P soils. It should be noted that there was much more humic colour interference in the analyses of MRP in moist compared with dried sample Olsen extracts, and the method used to correct for this (section 2.2.3) may have resulted in low calculated Olsen P contents in moist samples of soils where humic colouration was a particular problem – especially peat soils 1, 6 and 9.

Neither moist nor dried sample Olsen P contents displayed significant variation among the 4 months for which both moist and dried samples were analysed, although the apparently lower mean Olsen P content in August compared with the other months (figure 3.6) is consistent with the seasonal pattern of Olsen P noted in section 5.4.3 (of significantly lower Olsen P in summer compared to the other seasons). There was no significant difference in drying-induced Olsen P increases among months, although there was only a 0.3 mg P kg^{-1} increase in October (table 3.10), and there is insufficient data to conclude whether or not drying soils has implications for the interpretation of seasonal Olsen P trends.

3.7.3. Phosphorus sorption

Due to a misinterpretation of BUFFER laboratory procedures, P sorption experiments were performed at a 1:10 instead of 1:20 soil-solution ratio (sections 2.2.3 and 3.2.3), and did not load soils particularly highly with P. Therefore, sorption data do not directly indicate remaining P sorption capacity as PSI is assumed to do (see section 4.2.3), but they do give an indication of it (sorption to dried 0-10 cm April 2002 samples from 30 mg P l^{-1} P solution correlates strongly with PSI for 0–5 cm March 2003 samples; $r^2 = 0.68$, $n = 11$, $p = 0.002$). Mechanisms of aggregate disruption detailed in section 3.2.2 are likely to expose more sorption sites. This is likely to increase sorption to dried samples compared with moist samples, but the net effect of this would depend on the P saturation of the exposed sites. Pote et al. (1999a) suggest that higher sorption onto dried samples collected in May compared with August may have been due to the larger surface area of small crystals formed during the rapid air-drying process compared with the smaller surface area of larger crystals formed during slower natural drying of the August collected samples. This would explain the decrease in dried-sample sorption between January and August (table 3.11, figure 3.9), as soils became naturally drier (section 5.4.2).

The contrasting behaviour of moist samples must be related to other factors. Contrary to the effect natural soil drying appears to have on dried sample monthly P sorption variation, drier August moist samples (section 5.4.2) may be expected to sorb more P as a result of crystalline Fe compound formation during preceding warmer, drier summer months (although this effect is likely to be less pronounced than the more vigorous air-drying prior to laboratory analyses). Monthly variation in moist sample P sorption may be further

explained by interactions among a number of additional competing processes. The balance between mineralisation P_i release and plant uptake, for example, may control the quantity of weakly sorbed P, and hence remaining sorption capacity. Thus, high remaining sorption capacity in January may be the consequence of P immobilisation during this time (resulting in high Olsen TP; previous section) resulting in low saturation of sorption sites with P, whilst low remaing sorption capacity in April may be the consequence of high mineralisation rates, perhaps preceding rapid plant uptake. This effect would be amplified by management effects which increase soil P inputs during this time, such as those mentioned for soils 3 and 5 (section 3.7.1). Hydrological flushing of soil P would also act to remove weakly sorbed P, increasing remaining P sorption capacity, and would be likely to have the greatest effect on January samples (high winter effective precipitation; see section 5.4.1).

The effects of mineralisation on increasing weakly sorbed P would be obscured in dried samples, where most of the P that is likely to be mineralised during natural soil drying processes is probably mineralised during laboratory drying. This leaves the proportion of Fe crystalline sorption components formed naturally in relation to the proportion formed during laboratory drying, P applications and plant uptake, and hydrological P flushing as probable determinants of dried sample P sorption. The resulting variation looks more consistent throughout the year than moist sample variation (and is similar to Olsen TP variation), but is probably less reflective of the complicated interacting biological, chemical and physical processes affecting natural P sorption dynamics in the field.

3.8. Conclusions

The main findings of work presented in this chapter are:

- Air-drying soils clearly causes large increases in readily desorbable organic and inorganic P fractions, mainly as a consequence of mechanisms acting on soil OM (both microbial and inert).

- There was wide variation in the effect of air-drying for different soils, with implications for the development of soil-type P loss indices based on dried soil data.

- There are indications that P sorption capacity / P saturation may be important in determining the drying-induced release of readily desorbable P.

- However, much of the variation in readily desorbable P increases after drying (and the decreases noted for soils 7 and 12) remains unaccounted for, and was likely due to complex interactions between the multitude of factors known to affect P (de)sorption (pH, Eh, etc).

- Air-drying may be responsible for greater inorganic P release than oven-drying due to the longer drying period enabling more mineralisation of organic P to proceed.

- Air-drying soils masks seasonal variations in moist-sample desorbable P which are likely to be more representative of those occurring in the field.

- While Olsen P generally increased after sample drying, Olsen TP was not consistently affected, although October samples did show a significant decrease after drying.

- Phosphorus sorption was affected in a complex manner by drying, which may mask seasonal variation in complex soil P sorption dynamics.

- Although introducing another potential source of error, converting soil concentrations to a volume basis using OM content enables more representative comparison of dryings effects and natural soil-water interactions among soils.

CHAPTER 4

RELATING LAND USE AND SOIL CHARACTERISTICS TO SOLUBLE P LOSSES

4.1. Introduction

As noted in section 1.1.3, diffuse P losses from agricultural soils have been increasingly implicated in elevated surface water P concentrations and associated eutrophication (e.g., Foy et al., 1995; Smith et al., 1995; 2001). National soil test P (STP) methods are usually based on agronomic P requirements, and there is an increasing emphasis on using these tests, and developing new tests, to assess potential for P loss from soil to water. In the Republic of Ireland, there is an extensive data base for soil Morgan P contents (the standard agronomic soil P test) and these data have the potential to be included in P loss models which could be used as management tools for compliance with stringent new water quality regulations to be implemented under the EU Water Framework Directive (CEC, 2000; section 1.1.1). In order for this to be successfully achieved, understanding of the relationship between soil Morgan P concentrations and P loss to water needs to be further advanced. Recent work in Ireland has emphasised the differential effect of soil type on the relationship between Morgan P and dried soil desorption (Daly et al., 2001). The resulting soil P desorption indices were combined with soil Morgan P, soil hydrology, land management and climatological data, and incorporated into a model which displayed modest success in predicting surface water MRP concentrations for a number of Irish catchments (Daly et al., 2002).

This chapter deals primarily with data from laboratory analyses of spatial samples, and relates P desorption (P_w and P_{feo}) from moist and dried samples (previously presented in section 3.4) to land use, STP (Morgan P, Olsen P and P_{ox}) and soil P saturation (DPSS) (section 4.5.4), general soil characteristics (section 4.5.5) and, ultimately, soil type (section 4.5.6). These data, from a range of Mask catchment soil types, are then used to develop a simple soil P desorption index (PDI) based on soil type and Morgan P content, which is compared with the index devised by Daly et al. (2001). More uniquely, the impact of drying soils on the soil type / Morgan P / P desorption relationship, and consequences for the development of the soil PDI, are explored. The PDI developed in this study is then applied to stream water chemistry data for the Mask catchment, collected as part of the

wider TCD BUFFER research, in order to assess its potential for ranking soil P loadings on a subcatchment basis within the study area. Mask soils are placed in a slightly wider context through comparison with soils collected from the Friary Lough catchment, N. Ireland and the Fervenza and Portodemouro catchments in Galicia, Spain. The ultimate aim of this chapter is to assess the potential for using both land use and STP data to predict diffuse, soluble P losses from soils.

4.2. Literature review

4.2.1. Soil Test P: agronomic tests

Testing soil for its phosphorus content has been established practice for the last 150 years or so; Tunney et al. (1997) refer to early soil testing by Liebig as far back as 1872. Phosphorus has traditionally been a limiting nutrient in soils, so soil P testing has focused on quantifying plant available, or 'labile', P fractions. Tests have evolved using a variety of chemical extractants which have been found to extract quantities of P which correlate with crop responses (Williams and Knight, 1963). Extractants range from sodium hydroxide and hydrochloric acid through to distilled water, and extraction conditions vary in terms of pH, temperature, duration and soil-extractant ratio. Soil test phosphorus as measured by these tests is compared with plant response in the tested soils, and the resultant plant response curves used to interpret STP data for estimation of fertiliser application rates necessary for optimum yield-response.

In Europe alone there are over 10 commonly used STP methods (Tunney, 1997). Ireland is one of the few remaining countries to use the Morgan P test as its standard, which extracts soil P with 10% sodium acetate buffered at pH 4.8 (Morgan, 1941). Three states in the US also use this test, although others use variations of the Mehlich or Bray extraction techniques. Numerous countries have adopted the Olsen STP method (Olsen et al., 1954), including many European countries, Australia and New Zealand. This test extracts soil P using 0.5M $NaHCO_3$ at pH 8.5, and is thought to more accurately reflect P availability in calcareous soils compared with other acidic extractants (Curtin and Syers, 2001). Generally, soil P may be divided into two main fractions for the purpose of assessing plant response, but which may also be useful in assessing P loss potential: P quantity, which refers to the overall amount of labile P available in the soil, and P intensity, which refers to

the amount of directly available P maintained in soil solution. Variation in soil characteristics affecting P sorption / desorption dynamics (buffering capacity) alter the ratio of these fractions in different soils, and standard agronomic methods do not differentiate between these fractions (e.g. Holford, 1988). Indeed, complex P fractionation and cycling within soils (section 1.1.2) means that different agronomic tests extract a wide variety of combinations of different P pools, further increasing the potential soil specificity of these tests. For example, in Ireland Teagasc recommend different Morgan P levels for optimum crop response in peat and mineral soils (table 2.8, section 2.3.2). Nevertheless, the existence of extensive data sets on existing agronomic STP values and well-documented crop responses mean that there is reluctance for either standardisation of tests between countries or a move to more environmentally-oriented tests. Therefore, exploring relationships between different agronomic and environmental STP methods is potentially a useful way to use existing tests as environmental P loss indicators.

4.2.2. Olsen P compared with Morgan P

Soils in this study were analysed for both Morgan P and Olsen P to enable comparison with other Irish soils and BUFFER partners' soils, respectively (section 2.2.3). Therefore, research on the relationship between results for these two tests is reviewed here.

The use of Olsen P in N. Ireland and Morgan P in the Republic of Ireland spurred an extensive study into the relationship between these two soil tests in grassland soils of the border regions (Foy et al., 1997), in order to compare P recommendations. They found the following linear relationship for all soils studied:

$$\text{Olsen P} = 6.83 + 2.91\ \text{Morgan P} \qquad (r^2 = 0.70);$$

which was similar to the relationship found in an earlier study conducted on 100 soils from the Republic (Poulton et al., 1997):

$$\text{Olsen P} = 5.8 + 2.91\ \text{Morgan P} \qquad (r^2 = 0.67).$$

Close agreement between these two studies, which shared only 2% common data, indicates that the Morgan-Olsen relationship may be universal across Ireland. However, Foy et al. (1997) found that Olsen P contents were better predicted when a log relationship was applied to Morgan P:

$$\text{Olsen P} = 5.96\text{Morgan P}^{0.773} \qquad (r^2 = 0.76).$$

Analysis of the same data-set also found that soils with higher pH were had relatively lower Olsen P concentrations compared with Morgan P concentrations:

$$\text{Olsen P} = 30.2\ (\text{Morgan P})^{0.787}\ (10^{-0.118\text{pH}}) \qquad (r^2 = 0.77).$$

Soil pH variations have been suggested as the reason for poor correlations between Olsen and Morgan P in other studies (e.g. Reith et al., 1987) found a coefficient of variance of just 0.34 between Morgan and Olsen P values for 120 Scottish soils), and there have been a number of studies looking at the effect of pH and lime application on Olsen-extractable P (Curtin and Syers, 2001; Naidu et al., 1987; Sorn-Srivichai et al., 1984). Sorn-Srivichai et al. (1984) found that Olsen P levels in a field experiment increased as pH rose to 6.5, then rapidly decreased, following lime application, whilst exchangeable P (as measured from P^{32} isotope concentrations) increased and P_w remained relatively constant. Similarly, Curtin and Syers (2001) found that Olsen P decreased by between 3 and 7 mg P kg^{-1} per unit increase in pH. Whilst Sorn-Srivichai et al. (1984) attributed lime-induced Olsen P decreases to calcium phosphate precipitation at elevated Ca concentrations, Curtin and Syers (2001) suggest that lime-induced increases in soil sorption capacity are responsible for the effect. In contrast, Haynes and Swift (1985b) suggest that liming soils reduces their sorption capacity, and Haynes (1982) and Naidu et al. (1987) found that Olsen P values increased after lime addition. Naidu et al. (1987) suggest that preferential calcium carbonate precipitation after lime addition may competitively hinder the slower precipitation of Ca phosphate, thus leaving more in the Olsen extractant. Power (1992) found Olsen to Morgan ratios ranging between 1.81 and 9.3 for three different soil types on sites across Ireland, with the lowest ratio on a calcareous soil - consistent with the pH effects noted by Curtin and Syers (2001), Foy et al. (1997) and Sorn-Srivichai et al. (1984).

4.2.3. Soil test P: environmental tests

Van der Paauw and Sissingh (1970) tested a new water extraction method (P_w) for assessing plant available P, comparing it with P uptake and dry-matter yield of wheat and potatoes grown in 88 Dutch soils and 74 soils from Europe, the U.S.A. and Australia. They found a close correlation coefficient of 0.88 between wheat P content and P in water extracts from Australian, European and US, soils, concluding that P_w appeared to be universally applicable to all soil types. Sorn-Srivichai et al. (1988) reached the same conclusion, finding that P_w reflected both P intensity and P buffering capacity of soils. In

contrast, buffering capacity tends to affect P release from soils at given chemical extractant STP concentrations (e.g. Olsen P; Sorn-Srivichai et al., 1988). Presumably this is because water is more representative of natural soil-water (except for weak $CaCl_2$ extrcatants mentioned below), thus mimicking environmental soil P release more closely. The simplicity of P_w analysis also makes it an attractive laboratory testing procedure, and its potential to represent runoff-water desorption conditions has led to it being successfully tested as a predictor for P runoff risk (Hooda et al., 2000; Pote et al., 1996; Sharpley et al., 1981; Yli-Halla et al., 1995).

Phosphorus desorption to water has been found to vary with both time (Elkhatib and Hern, 1988; Garcia-Rodeja and Gil-Sotres, 1995) and soil-water ratio (Chapman et al., 1997; Sharpley et al., 1981). Rapid initial P desorption slows rapidly with time (dependent on the initial soil P concentration) as the quantity of weakly sorbed P decreases and solution P concentration increases. For example, Elkhatib and Hern (1988) found that P desorption to water (1:20 soil-water ratio) over a 2 hour time period was best described by a first order equation: $\ln(q_o - q) = b - k_d t$

where q = amount of P desorbed at time t, q_o = amount of P desorbed at equilibrium, and k_d is the apparent desorption rate coefficient. Chapman et al. (1997) found that P extracted in water increased from 0.42 to 4.62 mg P kg^{-1} soil as the soil-water ratio widened from 1:1.5 to 1:15.4, with the increase in extractable P being almost exclusively accounted for by MRP. Soil-water ratios vary widely (e.g. Sorn-Srivichai et al. (1988), used a 1:120 ratio) and different ratios may be used to reflect different intensities of runoff events (Sharpley et al., 1981).

Subsurface P losses are considered to be predominantly dependent on desorption equilibria between the soil and soil solution, although the depths over which these equilibria are crucial depend on the pathways of subsurface movement (e.g. Maguire et al., 2001). Consequently, environmental soil P testing to assess subsurface P loss potential uses weak electrolyte solutions (usually 0.01M $CaCl_2$; $CaCl_2$-P) representative of soil solution ionic strength (e.g. Heckrath, 1995; Hesketh and Brookes, 2000; Maguire et al., 2001; McDowell et al., 2001). Desorption to weak electrolyte solutions is less than that to water, but follows similar dynamics of decreasing rate of desorption with time (McDowell and Sharpley, 2003; Torrent and Delgado, 2001) and with decreasing soil-solution ratios (Hesketh and Brookes, 2000; Torrent and Delgado, 2001). Electrolyte solution tests tend

to be conducted at much lower soil-solution ratios than P_w in order to reflect the low soil-solution ratios in the soil matrix.

Extraction solutions of both water and weak electrolytes reach equilibrium concentrations with readily desorbable soil P, and thus underestimate the amount of P which may continue to desorb to interacting water and soil solution over the course of a prolonged precipitation event or a series of events. Another recent test developed in the Netherlands is the iron-oxide strip test method, P_{feo} (van der Zee et al., 1987), which involves shaking soils with a weak electrolyte solution (usually for 16 hours) containing (an) iron-oxide coated paper strip(s) which act(s) as a P sink and maintain(s) negligible solution P concentrations. This method is thought to extract the total readily desorbable (short-term bioavailable) P from soils (Van der Zee et al., 1987), though it has been shown that P desorption from soil to solution continues for long periods of time. Both Lookman et al. (1995) and Maguire et al. (2001) showed that P desorption to a weak electrolyte solution, in which iron-oxide strips were sequentially added and removed to maintain negligible P concentrations, increased rapidly over the first week, but continued to occur after 69 and 40 days respectively. Lookman et al. (1995) divided desorbable P into two discrete pools: a rapid desorption, readily available pool, and a slow desorption, strongly fixed pool. In theory, potential P loss to water could approach the dynamics of the strongly fixed pool under prolonged intensive precipitation or after a long sequence of precipitation events. However, Sibbesen and Sharpley (1997) note strong, linear relationships between P_{feo} and bioavailable P in surface runoff waters.

Another environmental P test originating from the Netherlands has the potential for universal application to all soil types, combining both soil P quantity and soil P sorption capacity into one expression. The degree of P sorption saturation (DPSS) uses an indicator of soil P quantity and divides it by the total capacity of the soil to sorb P (PSC) (Freese et al., 1992). In its simplest form, DPSS is calculated from one acidified ammonium oxalate extraction. The molar P (P_{ox}) concentration extracted from the soil is divided by the sum of molar Fe_{ox} and Al_{ox} concentrations multiplied by a factor (α) - representative of Fe and Al P sorption activity (e.g. Freese et al., 1992; Lookman et al., 1995; Uusitalo and Tuhkanen, 2000). This test works on the assumption that Fe and Al (hydr)oxides are the dominant species involved in P sorption in acid soils, and therefore represent P sorption capacity. The oxalate extractant also extracts Fe and Al in crystalised oxide and other mineral forms not available for P sorption, hence the α factor has typically been set at 0.5

(Freese et al., 1992; Uusitalo and Tuhkanen, 2000). The higher the ratio of P_{ox} to Fe_{ox} and Al_{ox}, the greater the degree of soil P saturation, and the more likely P is to desorb from the soil. In calcareous soils, P sorption is thought to be dominated by $CaCO_3$ (e.g. Sharpley, 1983), although varying relationships have been found between PSC and carbonate content (e.g. Zhou and Li, 2001), which may be attributable to pH effects (Barrow, 1978; Curtin and Syers, 2001).

Empirical measurements of P sorption may be used to extrapolate soil PSC, and avoid the problem of differing P sorption mechanisms and dynamics between low and high pH (calcareous) soils. One such method is the P sorption index (PSI), where the amount of P sorbed from a single high dose of P is assumed to equal the remaining P sorption capacity of the soil (e.g. Daly, 2000; Simard et al., 1994). Soil PSI may then be summed with existing (native) soil P, such as P_{ox} (presumably already occupying sorption sites), in order to determine PSC. The degree of P sorption saturation (DPSS) may then be calculated by dividing native P (e.g. P_{ox}) by PSC. Alternatively, the quantity of P desorbed from solutions initially containing different P concentrations may be applied to the Langmuir Equation to derive a PSC value (e.g. Barrow, 1978): $C/n = 1/Mb + C/M$
where C is concentration in solution, n is amount of P sorbed per unit mass, M represents PSC and b is a coefficient related to bonding energy. Some workers have applied different indices of P quantity to represent native P in the calculation of both PSC and DPSS (e.g. Mehlich 3 P; Sharpley, 1995).

Other workers have found that, over a relatively wide range of solution P concentrations, P sorption to soil increases linearly, and may be described by the Freundlich equation (e.g. Fitter and Sutton, 1975): $Logq = logK_f + nlogC,$
where q is soil sorption per unit weight, C is the solution concentration, and K_f and n are constants. K_f has been found to be correlate very strongly with PSC (Fitter and Sutton, 1975; Gil-Sotres, 1981; Zhou and Li, 2001). Soils collected in spring 2002 for this study were analysed for sorption at two different solution P concentrations, enabling the Freundlich equation to be applied to estimate the relative PSC of different soils.

Most of these environmental P tests will be compared against each other, Olsen and Morgan P, and land use factors in this chapter.

4.2.4. Phosphorus application compared with soil test P

There is an extensive body of evidence relating soil P accumulation and increasing soil P status to surplus agricultural P inputs. This evidence relates primarily land use and fertiliser P applications to agronomic STP data which, unlike environmental STP data, are extensively available and date back many years. In Ireland, mean soil Morgan P content has increased from 1 mg P l^{-1} soil in 1950 to 9 mg P l^{-1} soil in 1997, corresponding with surplus P applications over this time of 46 000 tonnes P per year nationally (Tunney et al., 1997). Nine mg P l^{-1} soil corresponds to the upper end of Teagasc soil index 3, which is designated 'high' soil P status, and is above that necessary for optimum animal production (Teagasc, 1998). Culleton et al. (1999), summarising the results of a 30 year Teagasc field trial, found that it took 30 years for soil Morgan P concentration to increase from 6 to 17 mg P l^{-1} soil at an application rate of 30 kg P ha^{-1} a^{-1}. At half this application rate, Morgan P increased only slightly (from 6 to 7 mg P l^{-1}) over the same time period. A long-term (36 year) experiment in North Carolina found STP (Mehlich 1 method) correlated strongly with P application (McCollum, 1991). Sharpley (1982) studied the effect of differing P additions (0 - 100 kg P ha^{-1}) on 20 soils, and found that P_w was linearly related to the amount of P applied. There is good evidence relating P applications to increases in Olsen extractable P (Laboski and Lamb, 2003; Power, 1995; Turtola and Yli-Halla, 1999) and water extractable P (Power, 1995; Turtola and Yli-Halla, 1999).

Data on the availability of applied P, and the influence of time after application on availability, are varied. Crop uptake and irreversible sorption, or occlusion, of P (in addition to agronomically small water losses), mean that not all fertiliser applied P remains available in the soil after application. The proportion of fertiliser applied P measurable as available P in the soil has been found to range from < 15% on calcareous soils after 30 days (Delgado et al., 2002), to 48% on a sandy soil after 3 years (Turtola and Yli-Halla, 1999). For organic P applications, or combinations of organic and inorganic applications, recovery rates range from 25% (Turtola and Yli-Halla, 1999) to 50% (McCollum, 1991). Whilst Turtola and Yli-Halla (1999) found a higher recovery rate for mineral fertiliser than organic fertiliser, other workers have suggested that organic P applications are more available than inorganic P applications. Laboski and Lamb (2003) found that swine manure application resulted in higher concentrations of Olsen P than fertiliser P applications, and that these Olsen P concentrations did not decrease with time (one to nine months) as they did after fertiliser P applications. They proposed that inositol

hexaphosphate in the swine manure displaced sorbed ortho-phosphate through preferential sorption, and that organic acids in the manure reduced overall sorption capacity, thus resulting in greater availability of organic-applied P. Similarly, in carbonate soils, Delgado et al. (2002) found that P availability after P additions was increased after humic and fulvic acid amendment – from < 15% recovery to > 40% recovery after 30 days - due to inhibition of Ca phosphate precipitation. Irreversible sorption has been proposed by a number of workers as a long-term sink for applied P (Laboski and Lamb, 2003; McCollum, 1991).

Phosphorus applications also have an effect on P fractionation within soils. Studies by Power et al. (1995) and Turtola and Yli-Halla (1999) both found that whilst P_i increased after (inorganic and organic) P applications, P_o did not increase. It has been proposed that with continuous P application, P_o reaches a maximum concentration at which the rate of immobilisation is equal to rate of mineralisation, (Power et al., 1995; Tate, 1984), although Power et al. (1995) did find that P cycling through microbial biomass was increased in soils to which P was applied (at a rate of 30 kg P ha^{-1} a^{-1}). The amount of P_o available for plants and losses to water is related to the rate of mineralisation (and other controlling factors), rather than the size of the P_o pool (Tate, 1984). It was proposed that most fertiliser applied P is initially simply reversibly sorbed onto Fe and Al (hydr)oxide surfaces, though this P may become occluded into soil particles over time. This is consistent with high P_w concentrations immediately after P applications, followed by logarithmic decline during the subsequent two weeks, as found by Sharpley (1982). An important finding by Turtola and Yli-Halla (1999) was the limited profile migration of surface-applied P: whilst STP was higher in 0 – 5 cm soil samples after P applications, it remained unchanged in 5 – 25 cm samples. Applications of lime (as mentioned in section 4.2.2) and other nutrients may also affect STP values. For example, Kabengi et al. (2003) found that P_o concentrations in cropped fields increased with N application.

4.2.5. Soil test P and P losses to water

Section 1.1.5 summarised how P concentrations in surface waters are critically dependent, not only on P desorption from adjacent soils, but on the hydrological connectivity of those soils (Haygarth and Jarvis, 1998a; Heathwaite et al., 1999). Phosphorus losses are driven by hydrological energy (Heathwaite et al., 1999), the intensity / duration of which may

determine the proportion of precipitation water moving over the soil as surface runoff or through the soil as infiltration water - and subsequently throughflow or deep percolation. Other hydrologically driven factors critical to P desorption from soils include the effective depth of soil-surface water interaction (Sharpley, 1985a), and, related to this, the soil-water ratio (Chapman et al., 1997; Sharpley et al., 1981) and duration of interaction (Elkhatib and Hern, 1988; Garcia-Rodeja and Gil-Sotres, 1995). Topography (slope), depth of the unsaturated zone, and soil infiltration capacity have a significant impact on hydrology, and therefore P losses. Season will affect the duration and intensity of rainfall events, and the depth of the unsaturated zone. This is reflected in the concept of 'variable source area' (VSA: Dunne, 1978), which refers to the changing area of overland flow generation with time during a storm event and over seasons. Furthermore, the occurrence of reducing conditions in some soils during certain times of the year will alter sorption/desorption dynamics (Nair et al., 1999).

Accurate estimation of nutrient loading from soil P concentrations may be further hindered by large incidental P losses which bypass the soil profile completely (Haygarth and Jarvis, 1998a). Haygarth and Jarvis (1997) calculated that 0.5 kg ha^{-1} of P was lost during four days in which 50 mm of rain fell six days after the addition of 16 kg fertiliser P ha^{-1} to U.K. grassland soils, and Turtola and Yli-Halla (1999) estimated that over 70% of P applied to Finnish soils over three years was removed through incidental losses. Particulate P losses will also have an influence on surface water DRP concentrations, usually through continued P desorption to the water (e.g. Gardner et al., 2002). Thus, isolating the effect of soil and STP on surface water P concentrations is a complicated process, often involving the use of computer modelling. Consequently, relationships between STP and runoff / subsurface water P concentrations have predominantly been studied through comparison of agronomic and environmental STP data or through simulated laboratory or small-scale field experiments.

Water desorbable P, $CaCl_2$-P, and P_{feo} all closely mimic natural soil-water interactions in the environment, and may reasonably be taken as directly proportional to natural soil P losses. Actual surface water P concentrations will depend on the soil-solution ratio and duration of interaction, but a number of studies have found that desorption among different soils remains relatively proportionate at different soil-solution ratios (Hesketh and Brookes, 2000; Sharpley et al, 1981; Torrent and Delgado, 2001) and over different durations (Garcia-Rodeja and Gil-Sotres, 1995; Torrent and Delgado, 2001; Maguire et al.,

2001). Whilst studies refer to differing proportions of fast and slow P release pools amongst different soils (e.g. Lookman et al., 1995), Maguire et al. (2001) found that short (1 day) and long (39 days) term desorption were closely correlated ($p \leq 0.001$). They also found that P_w (1 hour) was corelated strongly with short term P desorption ($p \leq 0.001$) and significantly correlated with long term P desorption ($p \leq 0.05$). McDowell and Sharpley (2002) conclude that runoff P losses are best predicted using short desorption times of minutes.

Strong correlations have been found between environmental STP and overland flow soluble P concentrations. Pote et al. (1999b) found a high, linear correlation between P_w and runoff DRP concentrations, which could be used to predict runoff DRP from a range of soil types when a factor accounting for soil hydrology was included. It was found that analysing soils in field-moist condition changed the slope, but not the strength ($p \leq 0.01$), of the correlation (Pote et al, 1999a). Turtola and Yli-Halla (1995) found that the DRP concentration in water extracts at a 0.4-1.0:100 soil-solution ratio corresponded with runoff DRP concentration in Finnish fields, and numerous other studies have found strong correlations between P_w and runoff DRP in simulated experiments and from field collections (McDowell and Sharpley, 2001; Sharpley et al., 1981). Soil DPSS has also been found to be a useful predictor of runoff DRP concentrations, although some studies have found linear correlations (e.g. Turtola and Yli-Halla, 1999) and others non-linear correlations (e.g. Sharpley et al., 1995). Sibbesen and Sharpley (1997) found a strong linear relationship up to 50% DPSS only. These relationships are especially important for Irish grassland soils, where dissolution of P from soil to runoff water is the principal mechanism of surface P loss and DRP is the dominant P fraction in soil runoff water, accounting for up to 75% of TDP (Tunney and O'Donnell, 2002). However, substantial P losses from soils may also occur via subsurface pathways, with DRP concentrations in subsurface water of 1.67 and 1.83 mg L^{-1} recorded by Kurz (2000) and Heckrath et al. (1995). Numerous studies have found strong correlations between $CaCl_2$-P and drainage water P from lysimeter studies (Hesketh and Brookes, 2000; McDowell and Sharpley, 2001).

Agronomic STP methods have also been found to strongly correlate with field-scale P losses. Foy et al. (2002) found that simulated runoff DRP was strongly dependent on soil Morgan P for 6 soils studied ($p<0.001$), and Kurz (2000) and Tunney et al. (2002) found correlations between Morgan P content and surface runoff DRP concentrations for Irish

grassland soils. Pote et al. (1999b) found high correlations between Olsen P, Morgan P, P_{ox} and runoff DRP concentrations, though relationships were soil specific, and Turtola and Yli-Halla (1999) also a found linear Olsen P-runoff DRP relationship. Olsen P has been found to be a useful predictor of subsurface P losses, with numerous studies indicating a 'change point' Olsen P concentration above which $CaCl_2$-P and subsurface water P concentrations dramatically increase (Heckrath et al., 1995; Hesketh and Brookes, 2000; McDowell and Sharpley, 2001; Meissner et al., 1998). Hesketh and Brookes (2000) found this change point to vary between soils, from 10 to 100 mg P kg^{-1} soil, whilst Heckrath et al. (1995) identified a change point at 60 mg Olsen P kg^{-1}. McDowell and Sharpley (2001) found a change point of 33 – 36 mg Olsen P kg^{-1}.

Less work has been done directly linking soil P desorption to stream P concentrations on a catchment scale because of the less direct linkage, and complicating variables such as hydrology.

4.2.6. Soil type

There is mixed evidence on the effect of soil type on soil P losses, and a clear distinction must be made between desorption-driven and hydrologically-driven soil type effects. Agronomic STP methods have been found to be soil specific in relation to plant P availability (section 4.2.1.), and there is evidence that they are similarly soil specific in relation to P desorption (Daly et al. 2001; Pote et al., 1999b; Sharpley, 1995). For example, Curtin and Seyers (2001) conclude that Olsen P is a poor predictor of eutrophication risk due to its highly soil-dependent relationship with P_w, and Daly et al. (2001) found that P desorption - Morgan P relationships were soil type dependent. Maguire et al. (1998) found that $CaCl_2$-P at a given Olsen P concentration increased with increasing soil OM content in 125 Irish gley soils. Soil specificity appears to be more important for longer-term P desorption (i.e. over prolonged or sequential events). Lookman et al. (1995) and McDowell and Sharpley (2003) associated short term P desorption with available P, as measured by agronomic tests such as Olsen P, but longer term P desorption to soil P sorption / desorption characteristics.

There is good evidence that P_w is capable of predicting plant-available P over a wide range of soil types (Sorn-Srivichai et al., 1988; Van der Paauw and Sissingh, 1970), and it may

be equally capable of predicting (potential) runoff P losses over a wide range of soil types (Hooda et al., 2000; Torrent and Delgado, 2001). However, low rates of hydrological runoff have been associated with low DRP concentrations in that runoff water, from soils of given STP concentration (Pote et al., 1999b; Sharpley 1985a). Pote et al. (1999b) attributed this to P 'sinking' into the soil solution matrix in low surface runoff conditions, and applied a soil hydrology factor to account for this. When this was done, P_w was linearly related to runoff P concentration over the three soil types they studied. Soil type may be used to indicate the dominant hydrological pathways occurring within a given soil, and on a catchment scale (e.g. Hydrology Of Soil Types (HOST): Dunn and Lilly, 2001; Lilly et al., 1998). Thus, assuming that environmental STP data are directly proportional to in-situ P desorption across a range soil types, they may be used in conjunction with (soil type inferred) hydrological factors as a reliable index of dissolved P loss risk. Daly et al. (2001) devised a P desorption index for soils, relating Morgan P to desorbable P for different soil types (classified according to OM content), and applied this to a P loss model predicting MRP concentrations in rivers of 35 Irish catchments. Calibration of the model involved clustering catchments according to hydrology (based on predominance of 'wet' or 'dry' soils). This hydrological clustering was found to have a greater effect on predicting river MRP concentrations than the laboratory-based P desorption index. Land use was also considered in their model, and a parameter composed of a combination of peat soil coverage and semi-natural grassland was found to be strongly negatively correlated with P desorption amongst wet catchments.

4.3. Methodology

4.3.1. Soil analyses

Site selection, soil sample treatment and laboratory analyses, and statistical data analyses were conducted as outlined in chapter 2. This chapter deals exclusively with soil characteristics and desorption from soil samples collected in 2003, except for initial comparison of dried samples collected in 2002 with soils from the Friary catchment, N. Ireand, and the Fervenza and Portodemouro catchments, Galicia, Spain (section 4.4). In order to ensure that soil data were comparable, peat soils were excluded from this comparison, as soils from the other two regions were exclusively mineral soils. Therefore, summary data for the 29 mineral soils collected from the Mask catchment in March 2002 were compared with summary data for the 11 soils from the Friary catchment, and 18 soils from the Fervenza and Portodemouro catchments. Comparison of Mask soil characteristics of dried soil samples, collected from 0-10 cm depth in 2002, with characteristics of dried soil samples collected from 0-5 cm depth in 2003, showed very little difference between these 2 sampling periods and depths (section 2.2.4), so further comparison will not be made.

As referred to in section 2.3.2, an additional two peat soil samples (numbers 38 and 39) were collected in October 2003 and analysed for Morgan P and P desorption. This was due to the limited range of Morgan P contents in peat soils, which was found to hinder the development of separate Morgan P-P desorption relationships detailed in section 4.5.6 (see section 2.3.2 for more detailed explanation). Subsequently, soil P desorption relationships were used to devise a simple P desorption index (PDI) to rank subcatchment P loss potential (see next section).

Where moist sample P desorption is compared against land use, STP contents and soil type in this chapter, soil 7 desorption values (P_w and P_{feo}) were omitted because they were considered anomalous. For example, in comparison with April 2002 (0-10 cm depth) moist sample P_w TDP content of 2.77 mg P kg^{-1} (table 3.9), March 2003 moist sample P_w TDP content was very high (16.96 mg P kg^{-1}), and decreased after sample drying. Moist sample desorption for this soil appears as an outlier in plots of desorption against STP, and is many times higher than desorption from the two other forest soils in this study. Therefore, while it is difficult to explain why moist sample desorption is so high for soil 7

(no obvious explanation such as fertiliser P application), it does not appear to be representative of this soil, and it seems reasonable to exclude it from statistical analyses where it may skew the results.

Chapter 3 compared the expression of soil concentrations on a weight or volume basis, and highlighted that the main effect was to change relationships between soil P fraction concentrations and those general soil characteristics which are not converted to volume-based expressed (i.e. pH, OM, TOC, TN, moisture and carbonate content). As proposed in section 2.2.5 and 3.8, expression of soil concentrations on a volume basis rather than on a weight basis should be more representative of natural soil-water interaction, and enable more accurate soil comparisons to be made (especially when comparing mineral and peat soils of widely differing BD). Therefore (and for the sake of brevity), this chapter compares soils on a volume basis (except for comparison with N. Irish and Galician soils: no OM content data for these soils, and peat soils omitted from this comparison). Whilst chapter 3 focused on the implications of drying soil samples, drying effects have further implications for STP- / soil type- P desorption relationships not fully explored in that chapter. Therefore, while this chapter focuses on moist sample desorption and its relationship to land use / soil variables, where relevant, implications of sample drying will continue to be referred to.

4.3.2. Land use comparisons

Section 4.5.2 of this chapter compares soil data between different land uses. To do this, data from the brief questionnaire asked of land owners when fields were sampled (section 2.3.2) were used to divide soils in three ways. Firstly, soils were divided according to vegetation cover and intensity, with the intention of relating soils to readily available land cover data in the CORINE database (see section 1.5.6). Soils were first simply divided according to grassland or forest cover, and then grassland soils further divided according to whether or not P was applied. These divisions were termed lower intensity grassland (no P application), higher intensity grassland and forest cover, and were intended to correspond with low productivity pasture, high productivity pasture and mixed forest in the CORINE database (figure 1.6).

Secondly, grassland soils were divided according to whether they were grazed or used for silage production, and grazed soils were further divided according to the predominant type of animals grazing on them, as given in farm survey data (section 2.3.2). Thus, grassland soils were divided into categories depending on cow or sheep grazing, or silage production.

Thirdly - and with some overlap of section 4.5.4 which compares Morgan P-P desorption relationships - soils were divided according to the soil P index system used by Teagasc (table 2.8, section 2.3.2). The intention of this division was to focus on the impact of management decisions (P application recommendations) based on this soil P index system. Soil P indices also offer a better reflection of land use intensity categories than current P application data, for reasons explained in section 2.3.2).

4.3.3. Comparison with water data

Discrete stream water samples were collected bi-weekly from July 2001 to November 2002, and monthly from December 2002 until July 2003. On every sampling trip, 14 water samples were collected from 12 major inflows to the lakes, and analysed for a range of chemical species, including DRP and TDP. Chemical analyses and species definitions were compatible with soil extract P analyses: both relied on 0.45 μm filtration distinction for dissolved P, and both relied on the ascorbic acid method of DRP analysis before and after acid-persulphate digestion of the non-MRP fraction (for details of water analytical methods, see Donohue et al., in press: appendix C). All DRP and TDP concentration measurements taken between December 2001 and November 2002 were then simply averaged for each sampling point in order to provide a crude average concentration for each subcatchment. Data from Observations of river stage height were applied to known discharge relationships in order to relate discharge during sampling to water chemistry. DRP and TDP concentrations were then interpolated between sampling occations for each location, and multiplied by the total flow during these two weeks as calculated from EPA continuous flow-monitoring data, to calculate annual loadings for each sampling location. Loadings were then divided by subcatchment area to provide comparable area-weighted estimates of soluble P loading during sampling for each subscatchment. The PDI, derived from soil P analyses in this study (section 4.6), was then applied to GIS maps of soil type and Morgan P concentrations for the catchment, in order to compare with subcatchment DRP and TDP concentrations and loads. This is explained further in section 4.6.

4.4. Results: Comparison with soils from N. Ireland and Galicia

Before analysing relationships between general soil characteristics, STP and P (de)sorption among Mask catchment soils, these soils will be compared with the soils from the Friary catchment, N. Ireland, and the Fervenza and Portodemouro catchments, Galicia, which were also analysed by this author. This will place Mask soils in a slightly wider context. Brief summary details of these partners' study catchments are given in section 1.5. Table 4.1 and figure 4.1 present and compare summary characteristics for these different soils.

Table 4.1 compares mean values and SD.s for general characteristics, STP and P (de)sorption in each group of Mask, Friary and Fervenza/Portodemouro soil samples. Figure 4.1 compares soil STP and desorbable P contents only. ANOVA analyses confirm that general soil characteristics were different among regions: for (log) TOC (borderline significantly different), (log) TN and pH, $F_{2,62} = 3.00$, 8.75 and 11.20, $p = 0.058$, 0.0005 and ≤ 0.0001. *Post-hoc* LSD analyses indicate that TOC content was significantly higher in soils from the Mask catchment compared with Fervenza/Portodemouro, TN content was significantly higher in Mask and Friary soils compared to Fervenza/Portodemouro soils, and pH was significantly higher in Mask soils compared with both Friary and Fervenza/Portodemouro soils. Total organic C and TN were approximately twice as high in Mask soils compared with Fervenza/Portodemouro soils (table 4.1), although average pH values were reflective of predominantly (slightly) acidic soils in all regions. Despite the exclusion of peat soils from the Mask data set, variability in these three characteristics was highest amongst Mask soils.

Table 4.1: Mean (bold) and SD. values for selected characteristics of mineral soils from the Mask catchment, the Friary catchment and the Fervenza/Portodemouro catchments. n = 29, 11, and 18 respectively.

Soils	TOC	TN	pH	Olsen P	Olsen TP	P_wDRP	P_wTDP	K_f
	% wieght			mg P / kg soil				
Mask	**6.17**	**0.552**	**6.18**	**42.60**	**71.90**	**13.93**	**23.65**	**2.263**
SD	2.65	0.222	0.78	34.68	41.47	10.96	12.71	0.320
Friary	**6.43**	**0.537**	**5.34**	**40.47**	**87.7**	**14.43**	**25.93**	**2.270**
SD	1.90	0.120	0.33	21.11	25.2	4.99	5.62	0.182
Fer./Port.	**5.38**	**0.370**	**5.11**	**41.28**	**67.1**	**5.40**	**8.66**	**2.505**
SD	2.32	0.184	0.25	34.52	41.3	4.81	5.58	0.316

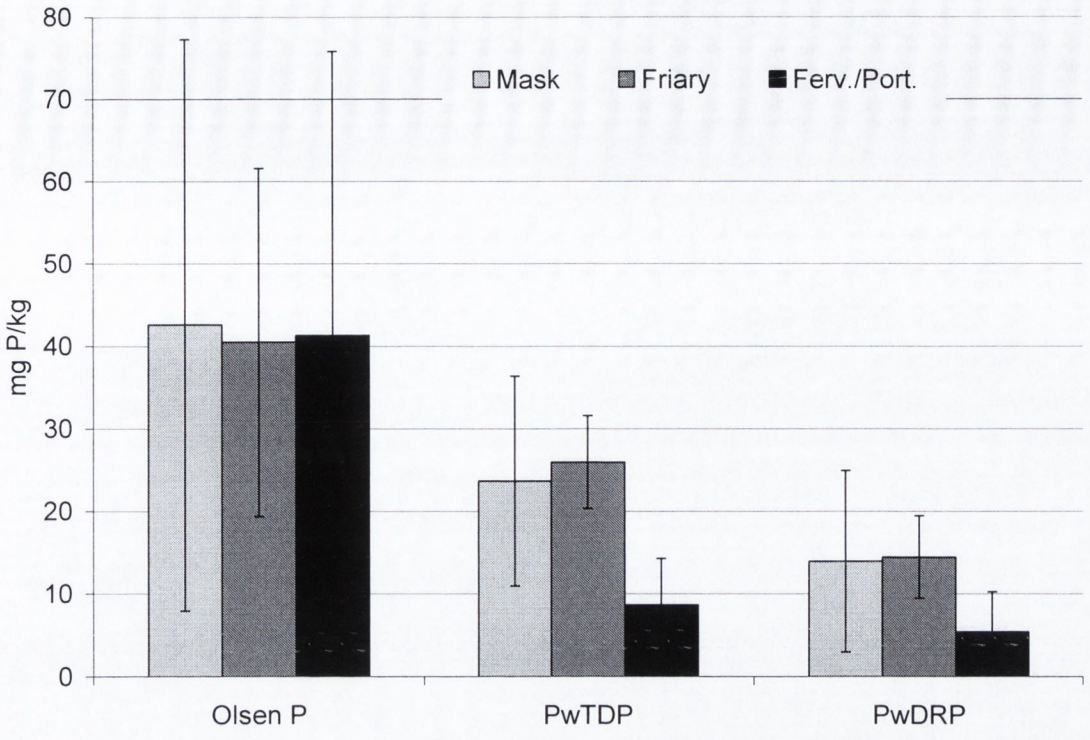


Figure 4.1: Mean Olsen P, and water-extractable P (P_w DRP and P_w TDP fraction) contents for soils from the Mask, Friary and Fervenza/Portodemouro catchments. Error bars indicate SD.

The apparently higher mean Olsen TP contents in soils from the Friary catchment (table 4.1) were not statistically significantly different to the similar mean Olsen TP contents in Mask and Fervenza/Portodemouro soils, owing to the high standard deviations within regions. Figure 4.1 shows that mean Olsen P contents (the standard measure of STP in many countries, including the UK and Spain) were almost identical for soils from the different catchments. Mean values of log K_f displayed in table 4.1 (from the Freundlich equation; see section 4.2.3) indicate that soils from the Fervenza/Portodemouro catchments had greater remaining sorption capacity than soils from either the Friary or Mask catchments (which again were similar), and the statistical significance of these differences was confirmed by ANOVA: $F_{2,62} = 4.15$, $p = 0.020$. Consequently, despite similar Olsen P contents, both (log) P_w DRP and TDP fractions (from dried samples) were significantly different among catchments ($F_{2,62} = 13.48$ and 31.64 respectively, $p \leq 0.001$). Similar P_w contents in soils from the Mask and Friary catchments (figure 4.1) were almost three times higher than those in soils from the Fervenza/Portodemouro catchments (table 4.1). Soils

from the Mask catchment displayed substantially greater variability in P_w than soils from either the Friary or Fervenza/Portodemouro catchments (SD. = 12.71, compared with 5.62 and 5.58 mg P kg^{-1} respectively). The proportion of P_w that is molybdate reactive was similar for all soils (mean of 56% for TCD and UU soils, and 62% for USC soils).

4.5. Results: Land use, soil characteristics and P (de)sorption in Mask catchment soils

4.5.1. General characteristics, soil test P and P (de)sorption in Mask soils

General soil characteristics are introduced in section 2.3.1, and land use data in section 2.3.2. Tables 4.2a and b list the mean and SE of two replicates for soil P characteristics in moist and dried samples collected in 2003. Table 4.3 displays Pearson Product Moment correlation coefficients in a correlation matrix, including all measured soil parameters, and for all soils. While the correlation coefficients displayed within it cannot be taken as a definitive guide to relationships among variables (owing to the possibility of non-linear relationships, or correlations forced by outliers), they provide a useful first indication of the main inter-variable relationships worthy of further exploration.

The different measures of P desorption were correlated very strongly with each other, especially among moist samples (Pearson Product Moment correlation r values in brackets): P_w DRP against P_w TDP (0.99) and P_{feo} (0.97) and P_w TDP against P_{feo} (0.96), $p \leq 0.0001$ in all instances. Drying samples reduced the strength of these correlations slightly, though they remained highly significant: P_w DRP against P_w TDP (0.91) and P_{feo} (0.82), and P_w TDP against P_{feo} (0.82), again, $p \leq 0.0001$ in all instances. Therefore, to simplify comparison of land uses, P_w refers to the total amount of P desorbed to water (P_w TDP), whilst inorganic P desorption is represented by P_{feo} in section 4.5.2 only. The two P_w fractions are distinguished and treated separately for relationships with STP, general soil characteristics and soil type, however (sections 4.5.4, 4.5.5 and 4.5.6).

Tables 4.2a and b (next page): Summary P characteristics for the 33 soils sampled in March, and additional two soils sampled in October, 2003. Mean values ± SD. from two replicates are shown. Units are as stated in the table headings (PSC2 is expressed as molar Fe + Al (ox) contents x 0.5). The mean and SD. for all soils are summarised at the bottom of the tables.

Soil	Pox	PSI	PSCt	PSCt 2	DPSS1	DPSS2
		mg P l^{-1} soil		molar act.	%	
1	42.9 ± 2.76	262.8 ± 1.64	305.7 ± 4.4	40.8	14.0	3.4
2	432.1 ± 3.57	556.3 ± 18	988.4 ± 21.6	124.8	43.7	11.2
3	495.8 ± 21.6	288.7 ± 15.6	784.5 ± 37.3	73.1	63.2	21.9
4	184.6 ± 1.56	104.6 ± 11.8	289.3 ± 13.4	42.2	63.8	14.2
5	154.5 ± 5.79	179.4 ± 50.2	334.0 ± 56.0	70.1	46.3	7.1
6	30.4 ± 0	369.9 ± 13.7	400.4 ± 13.7	96.9	7.6	1.0
7	110.7 ± 1.58	380.5 ± 3.74	491.2 ± 5.3	138.2	22.5	2.6
8	359.8 ± 13.3	344.1 ± 14.5	704.0 ± 27.8	109.8	51.1	10.6
9	41.2 ± 0.62	184.3 ± 20.5	225.4 ± 21.1	35.9	18.3	3.7
10	319.5 ± 7.83	225.7 ± 11.9	545.2 ± 19.7	70.7	58.6	14.6
11	160.3 ± 0	247.9 ± 14.3	408.2 ± 14.3	59.3	39.3	8.7
12	218.4 ± 7.95	461.7 ± 20.1	680.1 ± 28.0	129.0	32.1	5.5
14	154.3 ± 1.63	292.8 ± 24.8	447.1 ± 26.4	79.3	34.5	6.3
15	125.3 ± 3.41	316.4 ± 0	441.7 ± 3.4	88.6	28.4	4.6
16	178.4 ± 1.62	332.9 ± 41.1	511.3 ± 42.7	88.6	34.9	6.5
17	96.3 ± 8.03	422.0 ± 15.2	518.4 ± 23.3	108.2	18.6	2.9
18	639.8 ± 16.3	90.8 ± 10.3	730.7 ± 26.6	57.3	87.6	36.1
19	254.6 ± 4.81	198.9 ± 24.3	453.5 ± 29.1	62.8	56.1	13.1
20	834.3 ± 22.3	212.3 ± 16.1	1046.6 ± 38.5	136.8	79.7	19.7
21	916.2 ± 60.9	283.7 ± 0	1199.9 ± 60.9	129.1	76.4	23.0
23	41.5 ± 1.81	264.5 ± 47.2	306.1 ± 49.0	84.9	13.6	1.6
24	84.9 ± 64.6	267.4 ± 21.8	352.3 ± 86.4	61.2	24.1	4.5
25	184.4 ± 1.66	446.6 ± 92.2	631.1 ± 93.9	117.2	29.2	5.1
26	253.6 ± 8.16	588.2 ± 5.16	841.8 ± 13.3	140.0	30.1	5.9
27	283.0 ± 1.39	369.3 ± 24.6	652.4 ± 26.0	114.6	43.4	8.0
28	731.1 ± 14.9	365.9 ± 4.17	1097.0 ± 19.0	106.5	66.6	22.2
29	30.1 ± 1.97	526.5 ± 18.7	556.6 ± 20.7	120.8	5.4	0.8
30	161.7 ± 3.95	327.2 ± 0	488.8 ± 3.9	104.6	33.1	5.0
31	187.6 ± 0	268.1 ± 8.54	455.6 ± 8.5	58.7	41.2	10.3
33	67.4 ± 0.76	327.5 ± 7.67	394.9 ± 8.4	70.2	17.1	3.1
34	119.1 ± 4.43	388.9 ± 14	508.0 ± 18.4	130.0	23.4	3.0
36	172.5 ± 2.54	238.3 ± 28.9	410.8 ± 31.5	64.5	42.0	8.7
37	671.1 ± 4.6	218.8 ± 15.5	889.9 ± 20.1	97.1	75.4	22.4
Mean	**264.8**	**313.7**	**578.5**	**91.3**	**40.0**	**9.6**
SD	241.9	117.4	249.7	31.1	22.0	8.2

Table 4.2b: Mean and SD. of 2 replicate samples for volume-expressed STP and P desorption on moist and dried samples collected in 2003.

Soil	P app	Olsen P	Olsen TP	MorganP	P_wDRP		P_wTDP		P_{feo}	
					Moist	Dried	Moist	Dried	Moist	Dried
		mg P l^{-1} soil								
1	0	4.1 ± 1.29	12.5 ± 1.69	5.0 ± 0.19	0.98 ± 0.10	4.08 ± 0.25	1.93 ± 0.07	11.19 ± 0.47	4.05 ± 0.05	17.80 ± 0.13
2	26	53.8 ± 0.53	87.7 ± 0.19	8.7 ± 0.80	7.51 ± 0.15	11.53 ± 1.64	10.34 ± 0.00	27.64 ± 0.93	21.53 ± 2.04	35.18 ± 1.46
3	45	43.3 ± 4.76	61.1 ± 1.18	22.4 ± 2.42	11.09 ± 1.58	20.30 ± 1.27	13.65 ± 1.82	37.29 ± 2.25	31.89 ± 3.21	57.86 ± 0.63
4	11	11.6 ± 0.16	25.4 ± 0.68	7.0 ± 0.37	2.27 ± 0.37	5.68 ± 0.15	4.04 ± 0.54	24.42 ± 1.30	9.13 ± 0.42	31.08 ± 0.00
5	11	15.0 ± 0.18	32.2 ± 0.79	10.5 ± 2.44	6.74 ± 0.66	8.97 ± 0.79	9.36 ± 0.87	22.17 ± 1.50	15.34 ± 1.07	30.69 ± 2.22
6	0	3.9 ± 0.40	16.6 ± 0.18	3.8 ± 0.21	0.69 ± 0.01	5.42 ± 0.04	1.15 ± 0.10	12.76 ± 0.84	0.29 ± 0.08	10.14 ± 0.00
7	0	13.8 ± 9.55	16.7 ± 0.32	2.6 ± 0.23	10.06 ± 0.54	4.25 ± 0.07	14.51 ± 0.37	9.27 ± 0.69	20.46 ± 2.00	21.75 ± 3.02
8	0	26.5 ± 0.38	42.6 ± 1.46	14.9 ± 0.64	6.57 ± 0.86	8.27 ± 0.46	10.09 ± 0.90	16.48 ± 0.40	18.22 ± 0.97	29.57 ± 2.34
9	15	2.4 ± 0.17	6.4 ± 0.69	7.7 ± 0.03	2.01 ± 0.30	5.77 ± 0.42	2.77 ± 0.26	11.22 ± 0.57	6.66 ± 1.11	14.25 ± 0.00
10	0	37.6 ± 0.31	58.7 ± 0.68	14.5 ± 3.07	10.23 ± 0.97	16.23 ± 0.23	12.83 ± 1.01	24.83 ± 0.08	32.48 ± 0.81	58.58 ± 0.64
11	0	26.0 ± 0.99	50.4 ± 1.70	2.1 ± 0.44	0.91 ± 0.19	2.83 ± 0.09	2.13 ± 0.08	9.28 ± 0.10	3.58 ± 0.56	12.55 ± 0.39
12	47	21.5 ± 1.58	52.3 ± 0.22	2.9 ± 0.19	2.89 ± 0.19	5.84 ± 0.19	5.30 ± 0.32	12.27 ± 0.62	8.95 ± 0.19	19.28 ± 0.61
14	0	13.7 ± 0.65	29.1 ± 1.96	5.3 ± 1.19	1.39 ± 0.00	7.80 ± 0.24	3.30 ± 0.35	14.85 ± 0.42	5.66 ± 1.36	29.94 ± 2.84
15	0	6.2 ± 0.95	22.1 ± 1.39	3.7 ± 0.70	3.37 ± 0.07	4.53 ± 0.15	5.31 ± 0.32	14.42 ± 0.75	13.30 ± 0.75	16.04 ± 0.98
16	13	10.7 ± 0.32	26.3 ± 2.13	5.3 ± 0.81	2.79 ± 0.81	6.83 ± 0.24	5.45 ± 1.79	16.05 ± 0.51	17.12 ± 0.99	27.69 ± 1.33
17	0	2.6 ± 0.20	11.4 ± 1.42	6.6 ± 0.83	0.43 ± 0.01	1.80 ± 0.10	1.47 ± 0.07	3.47 ± 0.00	1.58 ± 0.01	7.79 ± 0.21
18	59	61.7 ± 1.22	76.2 ± 1.04	36.4 ± 3.75	31.19 ± 0.87	33.58 ± 0.99	33.74 ± 0.80	42.29 ± 0.99	72.51 ± 0.39	39.66 ± 0.56
19	59	34.5 ± 0.80	47.1 ± 0.87	19.7 ± 2.73	7.29 ± 0.10	8.64 ± 0.00	9.52 ± 0.32	17.11 ± 0.00	21.03 ± 0.71	33.42 ± 0.98
20	0	53.3 ± 1.75	74.5 ± 2.26	21.9 ± 2.07	15.19 ± 1.63	17.92 ± 0.39	18.24 ± 1.65	24.93 ± 0.75	50.22 ± 1.64	66.85 ± 3.92
21	48	65.1 ± 0.64	79.8 ± 0.52	25.0 ± 2.96	14.77 ± 0.56	17.72 ± 0.31	17.13 ± 0.46	25.76 ± 0.42	47.46 ± 1.82	63.37 ± 0.66
23	0	4.6 ± 0.84	13.1 ± 0.74	1.2 ± 0.08	0.89 ± 0.19	2.23 ± 0.08	2.85 ± 0.25	7.71 ± 0.09	1.44 ± 0.00	7.65 ± 0.35
24	0	3.9 ± 0.00	10.4 ± 0.28	4.6 ± 0.15	1.29 ± 0.26	5.41 ± 0.17	2.37 ± 0.41	9.67 ± 0.36	3.10 ± 0.60	16.13 ± 0.18
25	22	14.9 ± 1.15	37.2 ± 0.36	3.0 ± 0.33	3.18 ± 0.12	5.36 ± 0.08	5.72 ± 0.09	12.87 ± 1.12	10.93 ± 0.27	19.70 ± 2.04
26	7.5	10.9 ± 1.22	26.2 ± 0.11	4.4 ± 0.24	1.44 ± 0.48	2.65 ± 0.15	2.60 ± 0.47	7.12 ± 0.27	3.78 ± 0.24	7.99 ± 0.31
27	61	32.2 ± 0.97	64.5 ± 0.30	6.4 ± 0.65	8.30 ± 0.64	13.84 ± 0.40	11.10 ± 0.41	24.68 ± 0.36	16.85 ± 0.13	39.80 ± 1.42
28	45	63.4 ± 0.99	91.2 ± 1.26	15.7 ± 1.18	13.27 ± 1.58	15.76 ± 0.32	16.41 ± 1.90	23.28 ± 0.43	26.37 ± 2.80	49.63 ± 1.69
29	0	5.5 ± 1.29	17.2 ± 0.60	0.5 ± 0.02	1.01 ± 0.18	1.82 ± 0.00	2.13 ± 0.19	5.45 ± 0.19	1.19 ± 0.19	3.71 ± 0.19
30	15	22.1 ± 0.39	48.1 ± 0.43	3.2 ± 0.22	4.28 ± 0.38	5.92 ± 0.19	6.70 ± 0.18	11.10 ± 0.21	11.29 ± 0.48	18.05 ± 1.62
31	0	42.6 ± 2.18	74.8 ± 2.21	11.7 ± 1.51	7.90 ± 0.10	15.63 ± 0.08	10.23 ± 0.58	22.26 ± 0.26	16.49 ± 0.47	37.68 ± 0.35
33	5	8.1 ± 0.23	22.8 ± 0.17	6.5 ± 0.13	0.80 ± 0.22	5.42 ± 0.33	1.32 ± 0.04	10.40 ± 0.59	2.24 ± 0.90	10.98 ± 0.70
34	0	5.9 ± 0.41	18.5 ± 0.90	1.3 ± 0.13	0.72 ± 0.20	2.95 ± 0.07	4.44 ± 0.85	12.30 ± 0.36	0.79 ± 0.01	8.24 ± 0.28
36	18.5	17.9 ± 0.88	30.6 ± 0.42	8.4 ± 1.23	5.38 ± 0.64	6.89 ± 0.31	5.78 ± 1.27	24.15 ± 0.40	12.16 ± 0.35	23.92 ± 0.52
37	37	50.4 ± 1.68	66.3 ± 2.01	28.0 ± 3.58	12.32 ± 0.07	17.52 ± 0.89	14.84 ± 0.09	29.13 ± 1.43	36.93 ± 1.08	53.85 ± 1.88
38	29			13.1 ± 1.10	2.41 ± 1.68	4.16 ± 0.55	3.09 ± 1.26	6.28 ± 0.57	6.22 ± 2.46	10.85 ± 2.07
39	20			8.8 ± 0.76	2.06 ± 0.82	4.66 ± 0.63	3.12 ± 1.59	9.21 ± 2.07	2.94 ± 2.65	10.48 ± 2.47
Mean	**17**	**23.9**	**40.9**	**9.8**	**5.82**	**8.81**	**7.86**	**16.95**	**15.83**	**26.92**
SD	20	20.1	25.3	8.6	6.28	6.88	6.82	9.17	16.32	17.73

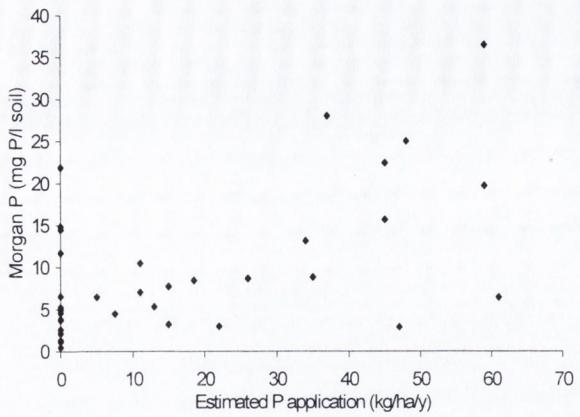
Table 4.3: A correlation matrix of Pearson Product Moment r values between all analysed soil variables and P application ($p \leq 0.05$ in bold).

	P appl.	Moist	TOC	TN	OM	Clay	Silt	Sand	BD	CO_3	pH	Na	K	Ca	Mg	TEB	Mn	Olsen P	Olsen TP	Morg. P	P_w DRP Moist	P_w DRP Dried	P_wTDP Moist	P_wTDP Dried	P_{feo} Moist	P_{feo} Dried	PSI	P_{ox}	PSC1	DPS1	Fe_{ox}	Al_{ox}	PSC2	DPS2
P app.																																	
Moist	-0.17																																
TOC	-0.21	**0.88**																															
TN	-0.18	**0.81**	**0.96**																														
OM	-0.22	**0.90**	**0.98**	**0.95**																													
Clay	-0.27	-0.12	-0.09	-0.07	-0.01																												
Silt	-0.23	-0.05	0.00	0.25	0.19	**0.59**																											
Sand	0.27	0.08	0.04	-0.17	-0.14	**-0.77**	**-0.97**																										
BD	0.18	-0.92	**-0.95**	**-0.92**	**-0.97**	-0.05	-0.26	0.21																									
CO_3	-0.06	0.27	0.22	**0.36**	0.27	0.03	-0.04	0.04	-0.32																								
pH	0.01	-0.22	-0.32	-0.17	-0.29	-0.15	-0.05	0.09	0.23	**0.62**																							
Na	-0.01	-0.19	-0.15	-0.20	-0.17	0.08	-0.12	0.07	0.17	-0.21	-0.29																						
K	0.33	-0.15	-0.26	-0.20	-0.25	-0.24	0.22	-0.11	0.18	-0.12	0.17	0.03																					
Ca	-0.11	-0.10	-0.10	0.05	-0.08	0.07	0.15	-0.13	-0.02	**0.70**	**0.87**	-0.15	0.02																				
Mg	0.08	-0.18	-0.09	-0.07	-0.07	0.31	**0.39**	**-0.41**	-0.01	-0.30	-0.23	0.13	0.06	-0.08																			
TEB	-0.10	-0.12	-0.11	0.03	-0.10	0.09	0.19	-0.16	-0.01	**0.68**	**0.86**	-0.12	0.06	**1.00**	-0.01																		
Mn	-0.03	0.32	0.13	-0.02	0.22	-0.01	-0.19	0.14	-0.20	**-0.35**	**-0.51**	0.11	-0.10	**-0.53**	-0.02	**-0.54**																	
Olsen P	**0.62**	**-0.42**	**-0.42**	**-0.39**	**-0.44**	**-0.34**	-0.15	0.21	**0.40**	**-0.30**	0.02	-0.13	**0.48**	-0.11	0.25	-0.08	-0.02																
Olsen TP	**0.61**	**-0.45**	**-0.49**	**-0.47**	**-0.51**	**-0.37**	-0.20	0.26	**0.49**	**-0.38**	-0.07	-0.08	**0.46**	-0.25	0.13	-0.23	0.05	**0.96**															
Morgan	**0.58**	-0.16	-0.15	-0.08	-0.15	**-0.43**	-0.20	0.29	0.09	-0.02	0.22	-0.25	**0.52**	0.15	0.28	0.19	-0.13	**0.80**	**0.66**														
MP_wDRP	**0.58**	-0.30	-0.29	-0.23	-0.28	-0.31	-0.15	0.21	0.21	-0.20	0.03	-0.11	**0.40**	-0.02	**0.57**	0.03	-0.08	**0.85**	**0.75**	**0.89**													
DP_wDRP	**0.57**	-0.21	-0.23	-0.17	-0.23	**-0.39**	-0.16	0.23	0.16	-0.26	-0.06	-0.18	**0.46**	-0.14	**0.46**	-0.10	0.00	**0.85**	**0.78**	**0.88**	**0.96**												
MP_wTDP	**0.58**	**-0.37**	**-0.36**	-0.29	**-0.35**	-0.31	-0.12	0.18	0.28	-0.22	0.06	-0.11	**0.41**	0.00	**0.55**	0.04	-0.10	**0.86**	**0.78**	**0.87**	**0.99**	**0.95**											
DP_wTDP	**0.55**	-0.22	-0.30	-0.25	-0.30	**-0.53**	-0.14	0.27	0.22	-0.20	0.06	-0.17	**0.49**	-0.10	0.34	-0.06	-0.05	**0.78**	**0.73**	**0.77**	**0.84**	**0.91**	**0.85**										
MP_{feo}	**0.53**	**-0.36**	-0.31	-0.23	-0.31	-0.32	-0.05	0.12	0.24	-0.19	0.09	-0.13	**0.44**	0.05	**0.50**	0.09	-0.16	**0.85**	**0.75**	**0.90**	**0.97**	**0.94**	**0.97**	**0.84**									
DP_{feo}	**0.44**	**-0.35**	**-0.34**	-0.27	**-0.36**	**-0.39**	0.06	0.07	0.30	-0.22	0.05	-0.17	**0.54**	-0.02	0.22	0.01	-0.10	**0.85**	**0.79**	**0.75**	**0.74**	**0.82**	**0.77**	**0.82**	**0.82**								
PSI	-0.11	-0.02	-0.07	-0.12	-0.07	0.33	0.29	-0.33	0.08	-0.23	-0.33	0.20	0.02	-0.31	-0.15	-0.31	0.18	-0.19	-0.07	**-0.49**	**-0.40**	**-0.42**	**-0.37**	**-0.45**	**-0.41**	**-0.38**							
P_{ox}	**0.55**	**-0.36**	**-0.35**	-0.29	**-0.35**	-0.31	0.00	0.08	0.29	-0.19	0.14	-0.12	0.58	0.09	0.24	0.12	-0.10	**0.91**	**0.83**	**0.82**	**0.81**	**0.78**	**0.83**	**0.71**	**0.86**	**0.85**	-0.18						
PSC1	**0.49**	**-0.36**	**-0.37**	-0.34	**-0.37**	-0.16	0.13	-0.07	0.31	-0.29	-0.03	-0.03	**0.57**	-0.06	0.16	-0.03	-0.01	**0.79**	**0.77**	**0.56**	**0.60**	**0.56**	**0.62**	**0.47**	**0.64**	**0.65**	**0.30**	**0.89**					
DPSS1	**0.57**	**-0.37**	**-0.43**	**-0.36**	**-0.44**	**-0.46**	-0.16	0.26	**0.37**	-0.02	0.33	-0.18	**0.53**	0.19	0.16	0.22	-0.24	**0.86**	**0.79**	**0.87**	**0.85**	**0.83**	**0.86**	**0.85**	**0.88**	**0.87**	**-0.48**	**0.88**	**0.62**				
Fe_{ox}	0.07	-0.09	-0.22	-0.24	-0.17	0.22	0.32	-0.33	0.15	-0.20	-0.15	0.20	0.24	-0.13	-0.08	-0.13	0.30	0.08	0.13	-0.12	-0.04	-0.12	-0.01	-0.21	-0.03	-0.07	**0.76**	**0.23**	**0.58**	-0.09			
Al_{ox}	0.03	**-0.55**	**-0.49**	**-0.42**	**-0.51**	**0.40**	**0.47**	**-0.50**	**0.44**	-0.27	-0.01	0.32	0.10	0.14	0.26	0.17	-0.17	0.22	0.24	-0.08	0.09	-0.02	0.15	-0.08	0.16	0.15	**0.51**	**0.31**	**0.54**	0.06	**0.57**		
PSC2	0.06	**-0.35**	**-0.39**	**-0.37**	**-0.37**	0.33	**0.42**	**-0.44**	0.32	-0.27	-0.10	0.29	0.19	-0.01	0.09	0.01	0.09	0.16	0.21	-0.11	0.02	-0.09	0.08	-0.17	0.07	0.04	**0.73**	**0.30**	**0.63**	-0.02	**0.90**	**0.88**	
DPSS2	**0.62**	-0.27	-0.31	-0.25	-0.30	**-0.40**	-0.16	0.24	0.23	-0.06	0.22	-0.23	**0.53**	0.10	0.32	0.13	-0.15	**0.88**	**0.77**	**0.93**	**0.93**	**0.92**	**0.93**	**0.87**	**0.93**	**0.81**	**-0.45**	**0.87**	**0.63**	**0.94**	-0.10	-0.05	-0.09

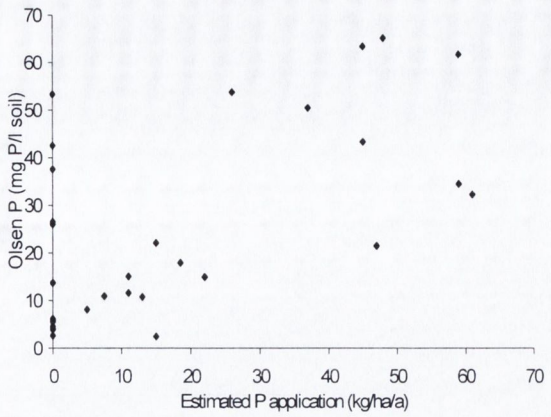
4.5.2. Relationships between soil P and land use

Table 4.3 shows that estimated P application (as recorded in land-owner questionnaires; section 2.3.2) was strongly positively correlated with both soil Morgan P and Olsen P contents ($r = 0.58$ and 0.62 respectively, $p \leq 0.001$). Estimated P application was almost as strongly correlated with moist sample P desorption ($r = 0.58$ and 0.53, $p \leq 0.001$ and ≤ 0.01 for P_w and P_{feo} respectively). Scatterplots in figure 4.2 display the wide scatter in the P application–P content relationships, especially in the range of P contents in soils with no estimated P application. Oxalate-extractable P was also positively correlated with P application ($r = 0.55$, $p \leq 0.001$), as was P saturation ($r = 0.57$ and 0.62, $p \leq 0.001$ for DPSS1 and DPSS2 respectively against P application), despite PSC1 values also being positively associated with rates of P application ($r = 0.49$, $p \leq 0.01$).

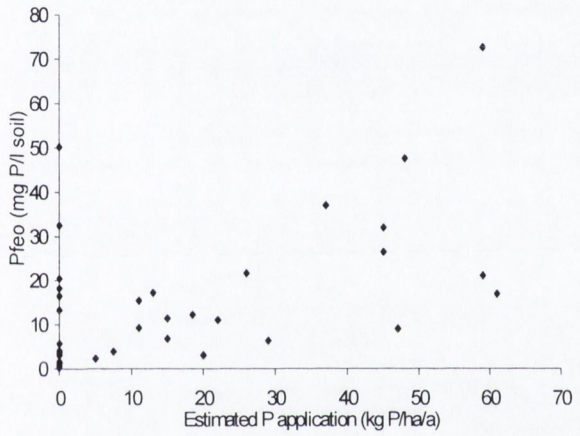
Drying soil samples increased the scatter of values for P desorption from soils (figures 4.2 b and c), but the negative impact of soil 18 on correlation with P application, as an apparent high desorption outlier, was greater among moist samples than dried samples (drying-induced proportional P_w TDP content increase for soil 18, from 33.74 mg P l^{-1} in moist samples to 42.29 mg P l^{-1} in dried samples, was relatively low; table 4.2b). Thus, correlations between dried sample P desorption and P application remained similar to those with moist samples ($r = 0.55$ and 0.44, $p \leq 0.001$ and ≤ 0.01 for P_w and P_{feo} respectively).



(a)



(b)



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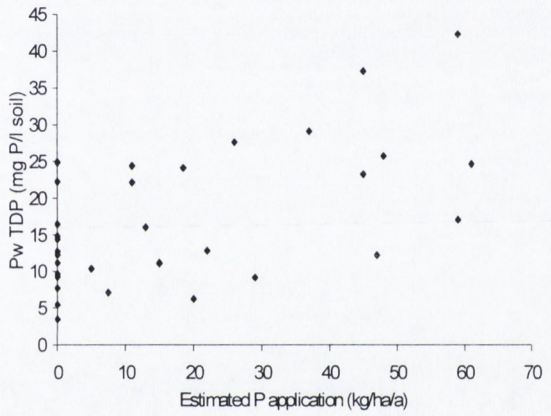

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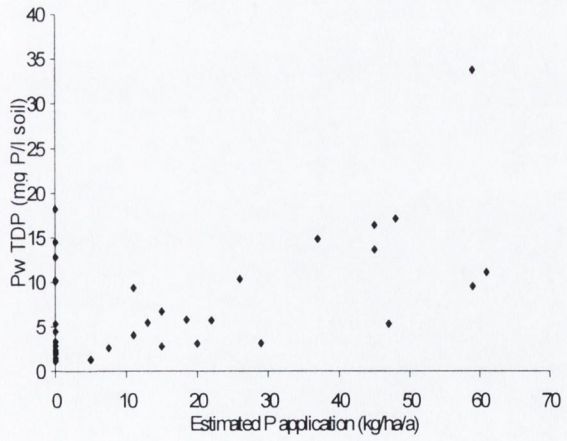

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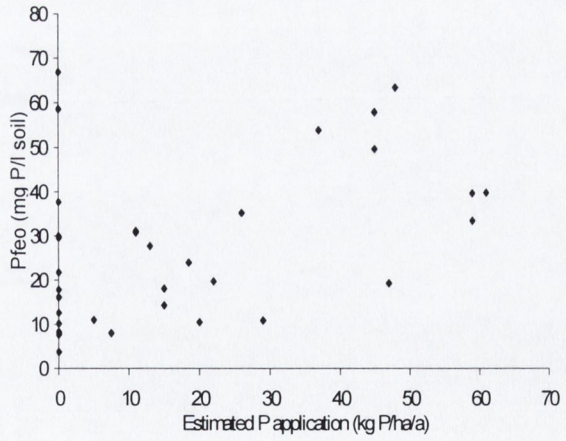


(f)

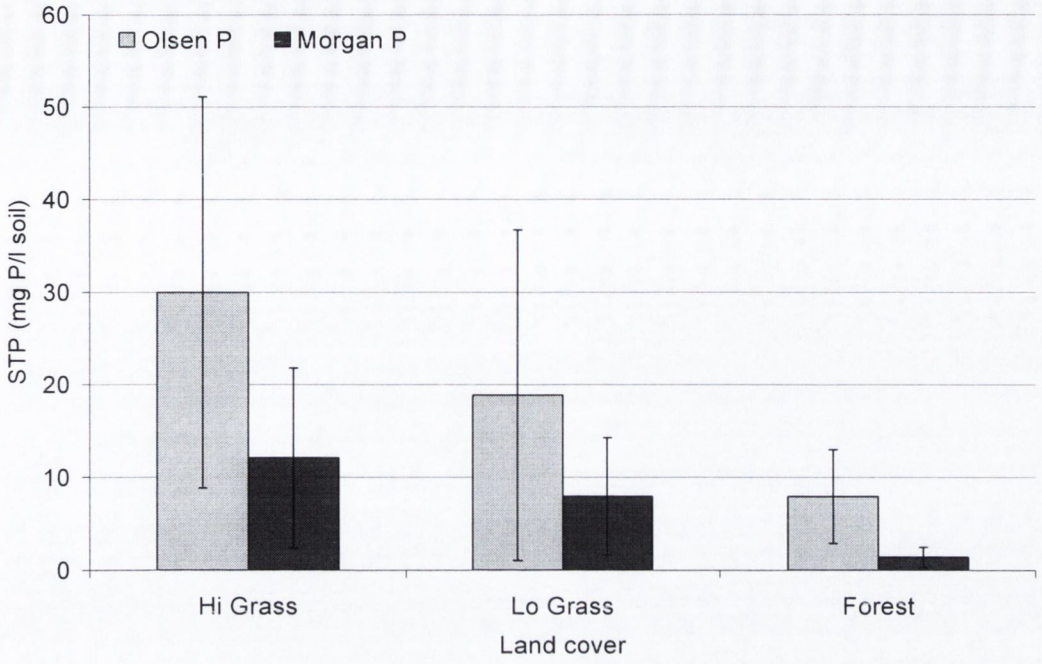
Figure 4.2: Scatterplots of (a) Olsen P, (b) Morgan P, total water-extractable P (P_w) from (c) moist and (d) dried samples, and bioavailable P (P_{feo}) from (e) moist and (f) dried samples, against estimated P application.

Soils were divided according to CORINE-compatible land cover classes (section 4.3.2). Table 4.4 summarises the results of ANOVA, with (log transformed) STP and desorbable P fractions analysed separately against land use, and these data are displayed graphically in figure 4.3. It was found that these land use divisions did have a significant influence on Morgan P (p = 0.001), although the influence on Olsen P contents was not quite statistically significant (p = 0.068) – presumably due to the high variability of Olsen P within land uses, indicated by the large SD. bars in figure 4.3. *Post-hoc* LSD analyses found that Morgan P contents were significantly lower in soils under forest cover than either lower or higher intensity grassland ($p \leq 0.01$ and 0.001 respectively; figure 4.3), but that lower mean Morgan P content in lower intensity grassland soils (figure 4.3) was not significantly different from mean Morgan P content in higher intensity grassland soils. The TP fraction in Olsen extracts was significantly different between land uses (p = 0.045), though only between higher intensity grassland and forest soil ($p \leq 0.05$).

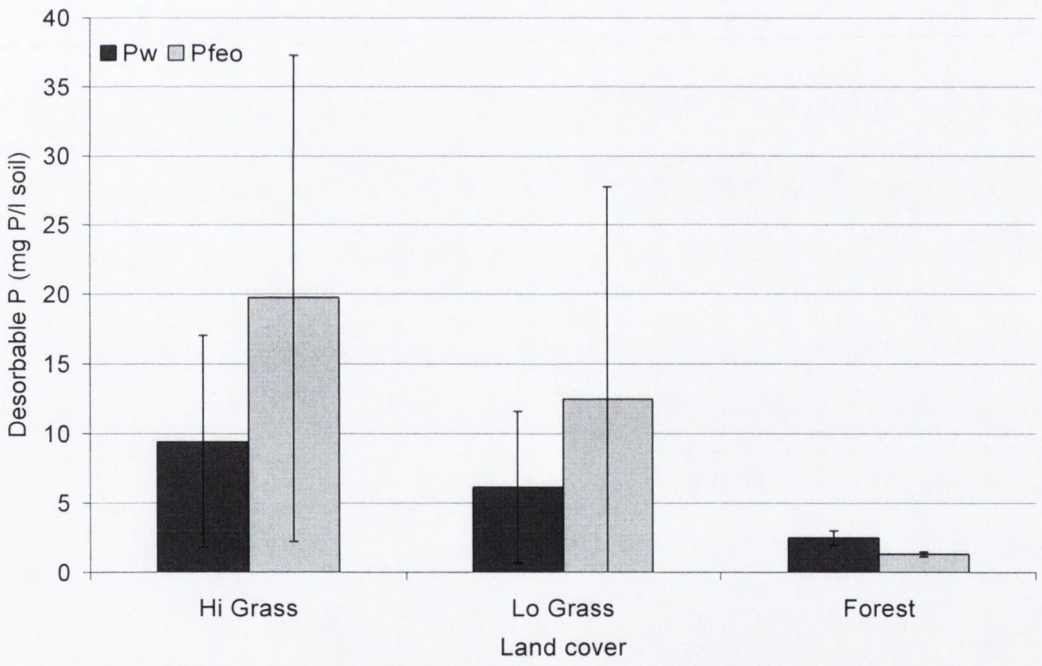
Water-extractable P was not significantly different between different land uses (p = 0.081; table 4.4) – again due to wide variability within land uses (figure 4.3) - but P_{feo} was highly significantly different between land uses (p = 0.008). *Post-hoc* LSD analyses found P_{feo} contents to be significantly higher in soils under higher intensity grassland than lower intensity grassland ($p \leq 0.05$) and forest cover ($p \leq 0.01$).

Table 4.4:Results of ANOVA analyses to determine significant differences between land use categories for (log transformed) measures of soil test P and P desorption.

Land use	*df*	*F*	*p*
Morgan P	2,30	**8.67**	0.001
Olsen P	2,30	**3.44**	0.045
Olsen TP	2,30	**2.94**	0.068
P_w	2,29	**2.75**	0.081
P_{feo}	2,29	**5.71**	0.008



(a)



(b)

Figure 4.3: Bar charts showing (a) mean Olsen and Morgan P, and (b) mean total water-extractable P (P_w) and bioavailable P (P_{feo}) for each land use category. Error bars show plus and minus one SD. from the mean; n = 18, 12 and 3 for STP, and 18, 12 and 2 for desorbable P.

Alternative methods of dividing soils according to different land use indices were explored (section 4.3.2). ANOVA analyses conducted on (log transformed) STP and P desorption data for grassland soils after dividing them according to the type of use (cow or sheep grazing, or silage) indicated that there was no difference in STP from soils under these different grassland uses. But, dividing grassland soils according to the Teagasc soil index system (see section 2.3.2) resulted in highly significant differences in desorption among the different soil indices (table 4.5). Differences in both P_w and P_{feo} were significant at the $p \leq 0.0001$ level, and figure 4.4 indicates that P desorption increased progressively with increasing soil P index. *Post-hoc* LSD analyses found that P_w differences were significant between all soil P indices except between indices 2 and 3, and P_{feo} differences were significant between all soil indices except between indices 2 and 3, and 3 and 4. Olsen P was also significantly affected by soil Morgan P index ($p \leq 0.0001$; table 4.5), with significant differences between index 4 and indices 1 and 2, and between indices 1 and 3. Figure 4.4 highlights the substantial variation in Olsen P and potential P desorption between different indices, though also shows the relatively high variation displayed by these parameters within soil P indices, which reduces the statistical significance of some differences. For example, soils in P index 4 desorbed, on average, five times more P_w and eight times more P_{feo} than index 1 soils, and approximately three times more of both P fractions than soils from index 2.

Table 4.5: Results of ANOVA analyses to determine significant differences between Teagasc soil P index categories for (log transformed) measures of soil test P and P desorption.

Soil P index	*df*	*F*	*p*
Olsen P	3,26	14.59	≤0.0001
P_w	3,26	27.08	≤0.0002
P_{feo}	3,26	18.13	≤0.0003

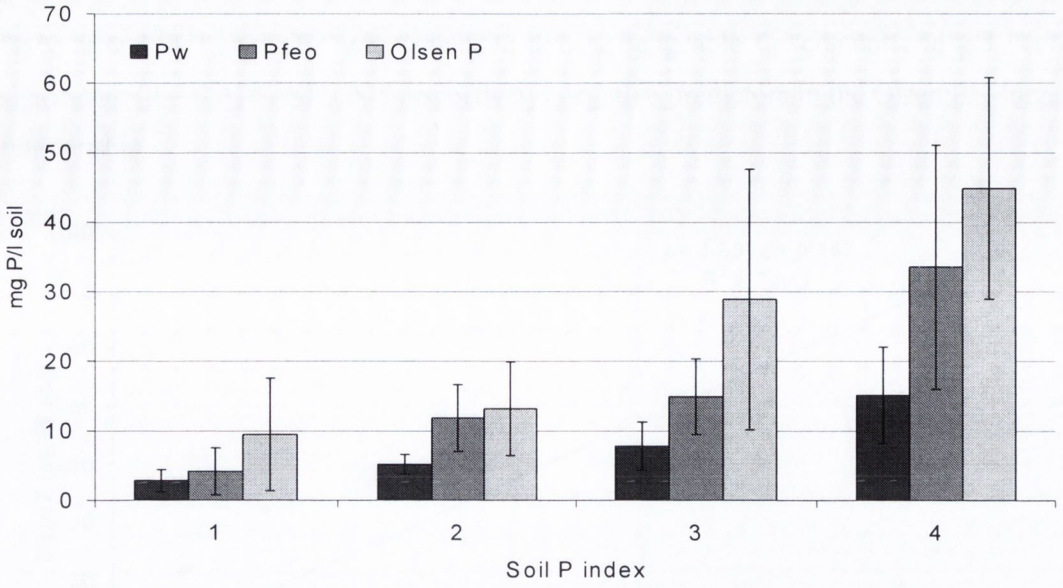


Figure 4.4: Mean values and SD. (error bars) for Olsen P, total water-extractable P (P_w) and bioavailable P (P_{feo}) in grassland soil groups divided according to Morgan P-based soil P indices. n = 11, 4, 4 and 11 for indices 1, 2, 3 and 4, respectively.

4.5.3. Relationships among different soil P tests

The various methods of P analyses in this study were all strongly correlated with one another (table 4.3). Of particular interest is the Olsen P–Morgan P relationship explored in other studies (section 4.2.2). Figure 4.5 displays a reasonably strong linear relationship between these two tests, with variation in Morgan P explaining almost 65% of the variation in Olsen P according to the following equation:

$$\text{Olsen P} = 1.83\ \text{Morgan P} + 6.14$$

This compares with the linear equation derived by Poulton et al. (1997), which accounted for 67% of the variation in soil Olsen P contents:

$$\text{Olsen P} = 2.91\ \text{Morgan P} + 5.8;$$

and the more strongly (76%) predictive, non-linear equation derived by Foy et al. (1997):

$$\text{Olsen} = 5.96\ \text{Morgan}^{0.773}.$$

Stepwise multiple regression found that, after regression with Morgan P, prediction of Olsen P residuals was best improved by the inclusion of PSC1, OM content and TEB (in that order) in a multiple regression equation:

Olsen P = 10.20 + 1.38Morgan P + 0.029PSC1 – 0.30 OM – 0.68TEB ($r^2 = 0.87$; Eq. 4.1).

Only after PSC1 and OM were included did exchangeable Ca content and pH become significant (p = 0.016 and 0.005 respectively) negative predictors in the Olsen P–Morgan P relationship.

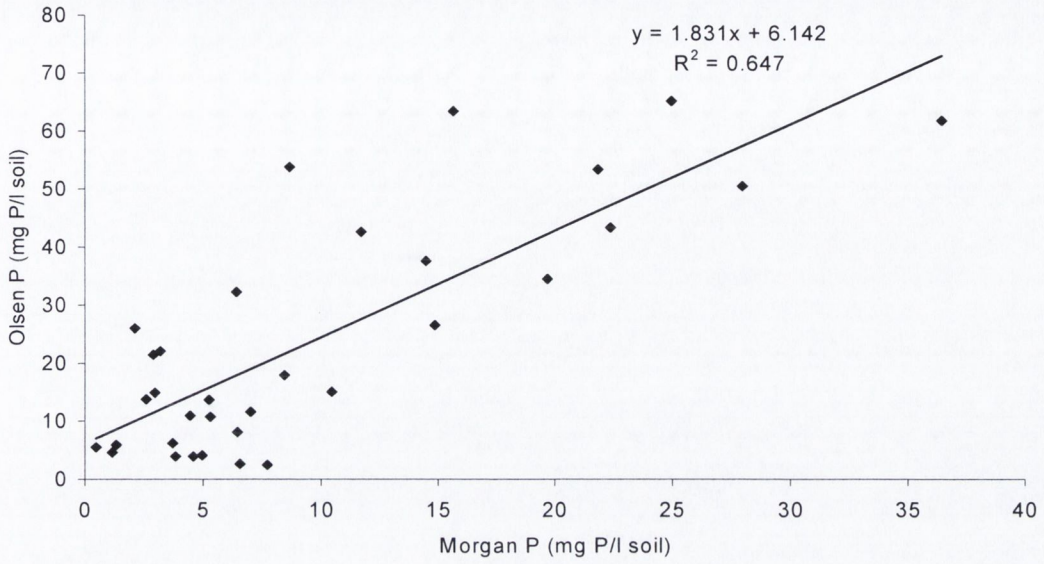
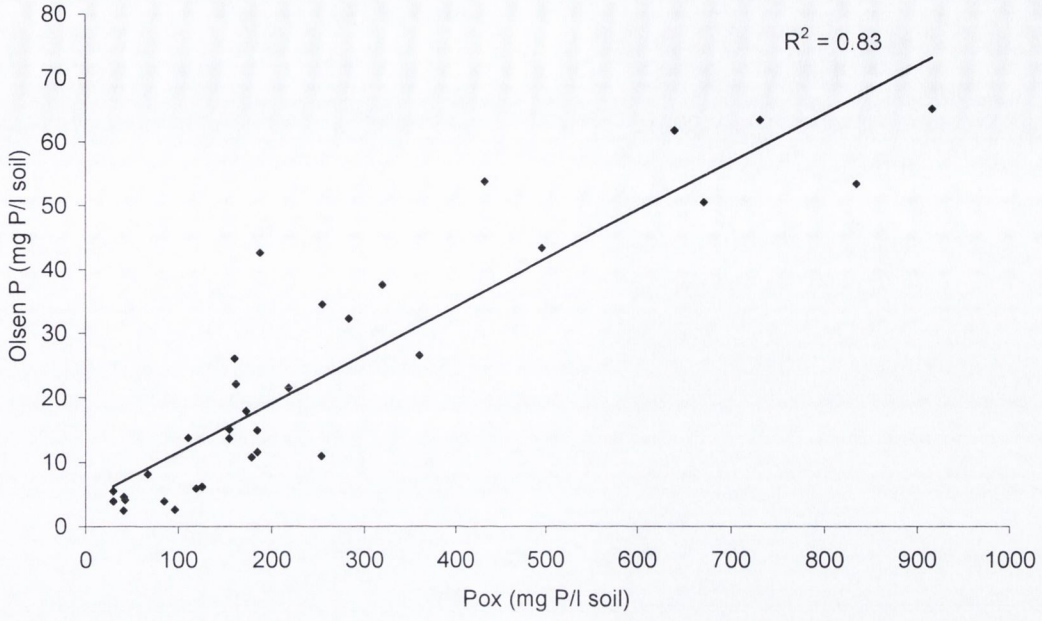
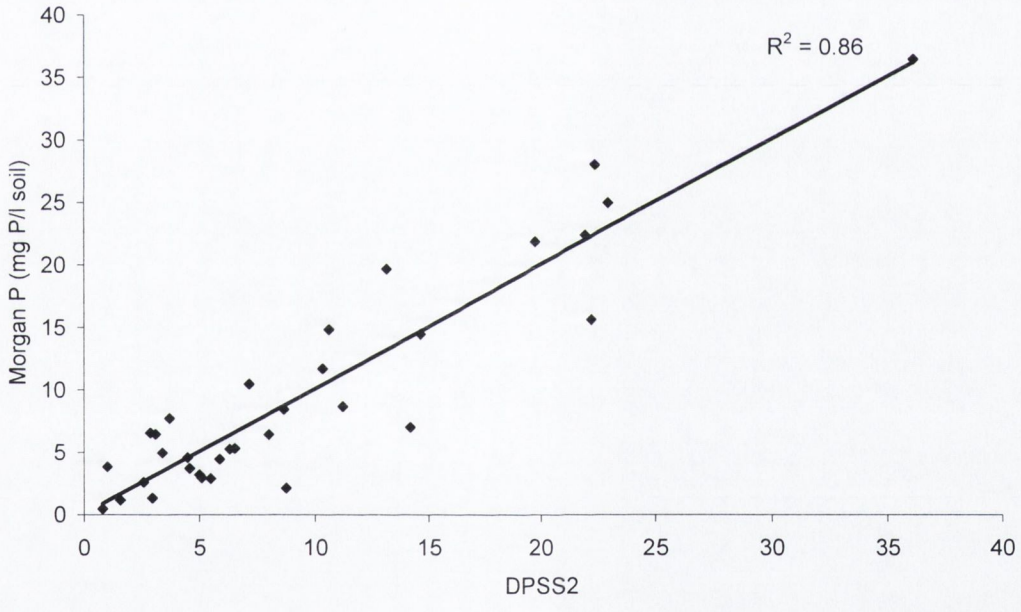


Figure 4.5: The relationship between Olsen P and Morgan P among the 33 soils collected in March 2003.

Both Olsen and Morgan P were strongly linearly associated with P_{ox} and both calculations of DPSS (table 4.3; examples given in figure 4.6). The two methods of DPSS calculation were strongly correlated ($r = 0.94$, $p \leq 0.001$; table 4.5), although the relationship was not linear (figure 4.7). There was no obvious grouping of, or deviation from the relationship, by soils with high carbonate content or pH, or OM content.



(a)



(b)

Figure 4.6: The linear relationships between (a) Olsen P and oxalte-extractable P (P_{ox}), and (b) Morgan P and the degree of P sorption saturation (DPSS2).

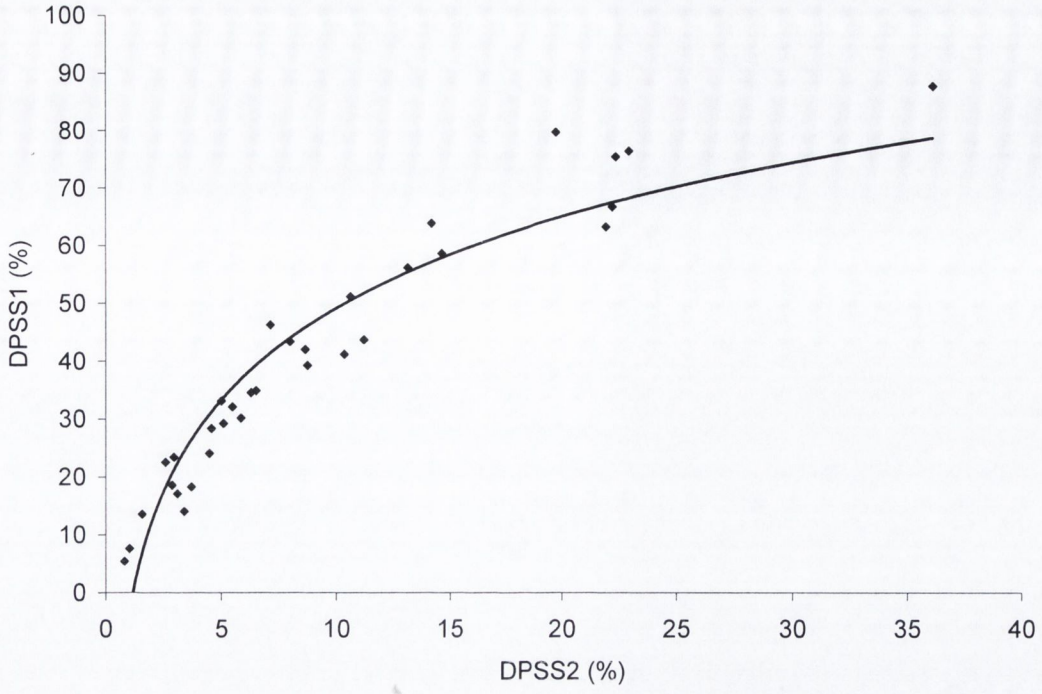


Figure 4.7: The curvilinear relationship between the two methods of degree of sorption saturation (DPSS) calculation, nearing a logarithmic line of best fit.

There was also the opportunity in this study to compare Freundlich K_f values, calculated for the 36 soil samples collected from 0-10 cm depth in 2002, with P sorption capacities calculated for the 32 samples collected at 0-5 cm depth from the same fields in March 2003. Despite these samples of the same soils being from different times and different depths, Freundlich K_f values proved to be reasonable linear predictors of PSC1 ($r^2 = 0.75$, $p < 0.001$), but not of PSC2 ($r^2 = 0.15$, $p \leq 0.05$), when P_{ox} was included in the calculation as native P. However, when native P is not included in the calculation, K_f values are less strongly related to PSC, but do account for a large proportion of variation in PSI ($r^2 = 0.57$, $p \leq 0.001$).

4.5.4. Soil test P - desorbable P relationships

All desorbable P fractions were correlated strongly with all STP methods (table 4.5) used in this study, and all STP methods appear to be good potential predictors of P desorption (table 4.6). The degree of P sorption saturation calculated from soil Al_{ox} and Fe_{ox} contents (DPSS2) was the best linear predictor of P desorption, accounting for approximately 87% of variation in moist sample P desorption (table 4.6). However, whilst P desorption (P_{feo}) was linearly related to DPSS2 (figure 4.8b), its relationship to DPSS1 is best described by a polynomial equation: the fit of the polynomial equation is slightly better than the linear line of best fit for DPSS2 (figure 4.8a). Coefficients of determination displayed in table 4.6 indicate that Morgan P was nearly as good a predictor of P desorption as DPSS2, and appeared to be a slightly better predictor of P desorption than Olsen P for moist samples, although was more affected by sample drying than Olsen P. Olsen TP was generally the least strong predictor of P desorption. P_{ox} is most strongly related to P_{feo}.

Comparison of mean desorbable P fraction contents in moist and dried samples of all soils in table 4.2b indicates that drying soil samples more than doubled mean P_w (7.86 and 16.95 mg P l^{-1} soil for moist and dried sample P_w TDP, respectively; table 4.2b), and increased mean P_{feo} by 70% (15.83 and 26.92 mg P l^{-1} soil for moist and dried samples, respectively), but also reduced the relative spread of values (e.g. SD. of 85% and 52% of the mean for P_w TDP in moist and dried samples respectively). Thus drying the samples generally reduced the predictive strength of STP methods for P desorption, sometimes substantially (e.g. P_{feo} versus DPSS2; table 4.6), mainly through increasing scatter. Figure 4.9 also shows that even where the predictive strength of soil P tests for P desorption (i.e. DPSS2 for P_w TDP) was not significantly reduced by drying, and where the slope of the relationship remained similar after sample drying (increasing from 0.74 and 0.97 in figure 4.9), the intercept was substantially increased (from 1.02 to 8.16), which implies a loss of relative difference between low and high P desorption soils after drying. Drying-induced changes in STP-P desorption relationships were similar for the other desorbable P fractions and STP methods. Only for Olsen TP was predictive power greater after drying soil samples, for P_{feo}. Overall, coefficients of determination between STP methods and P desorption were reduced less by sample drying for P_w DRP than for P_w TDP and P_{feo}.

Table 4.6: Coefficients of determination (r^2 values) between different soil test P methods and the various desorbable P fractions measured in this study. n = 34 for Morgan P, and 32 for the other tests. $p \leq 0.0001$ in all instances.

	P_w DRP		P_w TDP		P_{feo}	
	moist	dried	moist	dried	moist	dried
Morgan P	0.79	0.77	0.76	0.59	0.81	0.57
Olsen P	0.72	0.72	0.75	0.61	0.72	0.72
Olsen TP	0.61	0.6	0.61	0.52	0.56	0.63
P_{ox}	0.66	0.61	0.68	0.50	0.75	0.73
DPSS1	0.71	0.69	0.74	0.71	0.78	0.77
DPSS2	0.87	0.84	0.87	0.75	0.86	0.65

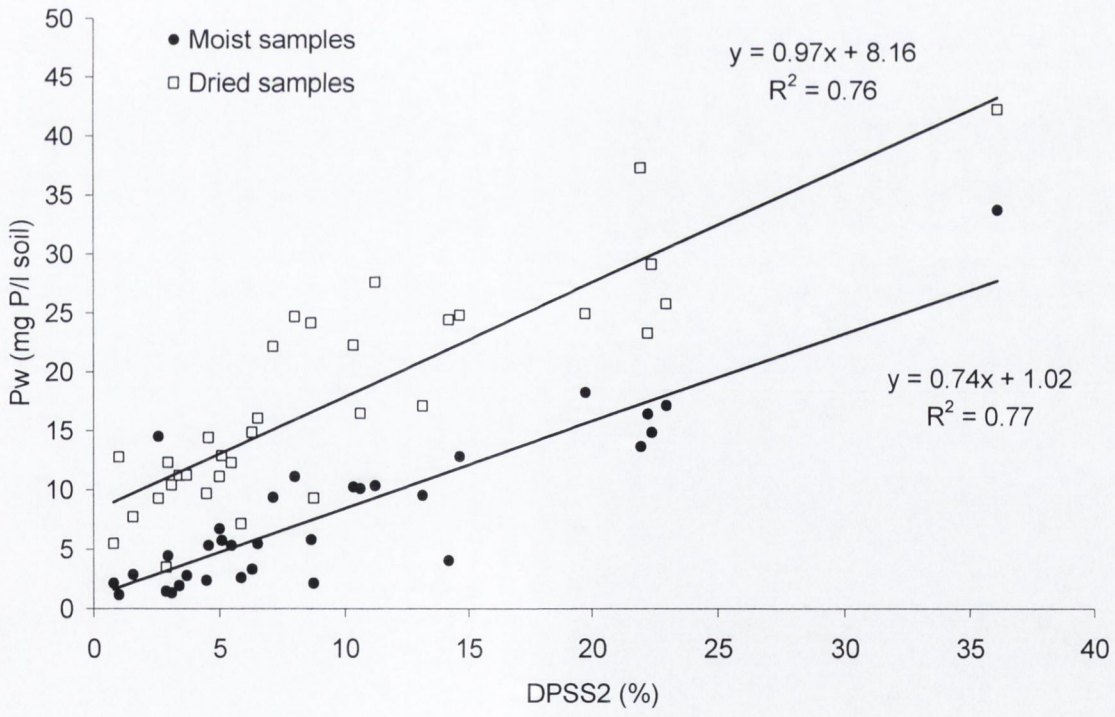
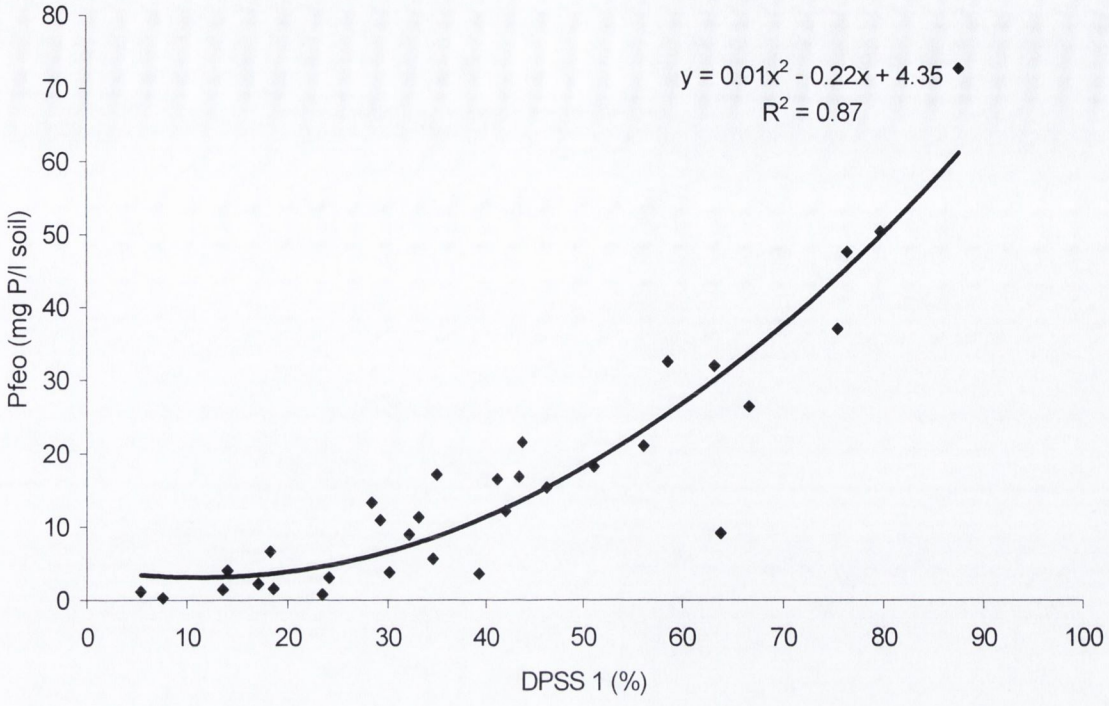


Figure 4.8: The contrasting relationships between the oxalte-calculated degree of P sorption saturation (DPSS2) and total water-extractable P (P_w TDP) for moist and dried soil samples.



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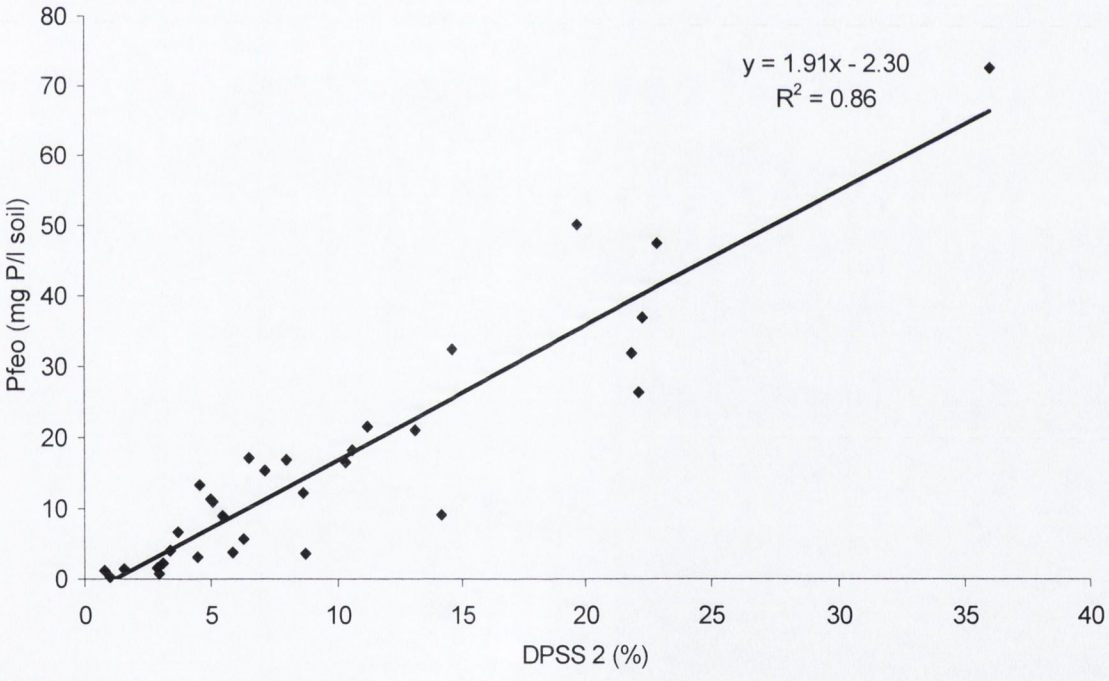
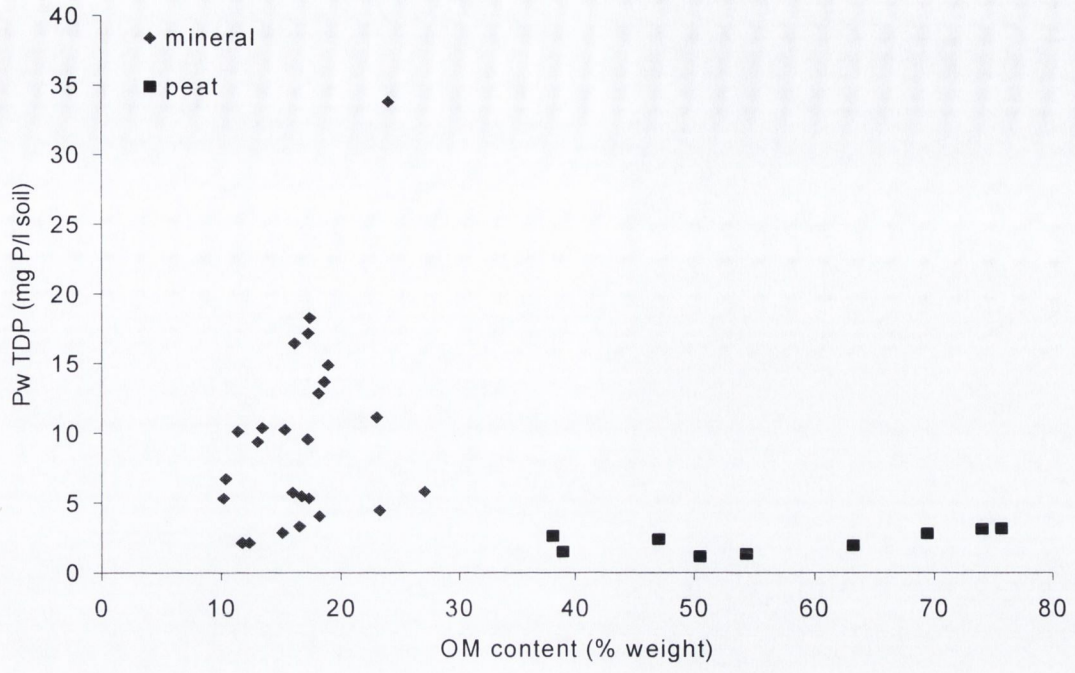


(b)

Figure 4.9: Graphs contrasting (a) the curvilinear relationship between bioavailable P (P_{feo}) and the sorption-calculated degree of P sorption saturation (DPSS1) with (b) the linear relationship between P_{feo} and the oxalate degree of P sorption saturation (DPSS2).

4.5.5. Influence of general soil characteristics on P desorption

Although the characteristics most strongly related to P desorption were those related to P quantity (previous section), some general soil characteristics were also significantly related to P desorption. Table 4.3 indicates that exchangeable potassium, for example, was significantly correlated with all the P desorption (and STP) measures. Moisture content and OM content were significantly negatively correlated with some measures of P desorption. For P loss modelling, the relationship between OM and P desorption may be important because soils have been classified into groups representative of soil types, according to OM content (Daly, pers. comm.; Daly, 2001; section 2.3.1). Figure 4.10 shows how the negative correlations between P desorption and OM content are driven by contrasting peat and mineral soil group behaviour. In fact, among mineral soils, there appears to be a slight positive relationship between P desorption and OM content, although for moist samples this proved to be boderline significant for P_w DRP only (r = 0.38, p = 0.062). However, once samples were dried, correlations became (borderline) statistically significant between P_w fractions and OM: r = 0.39 and 0.52, p = 0.053 and 0.007 for P_w DRP and TDP fractions, respectively (although P_{feo} moves further from statistically significant correlation after sample drying). Caution should be applied in reading too much into the mineral soil correlations, however, as they may be forced by high Morgan P contents (> 20 mg P/l) in mineral soils with high OM contents (i.e. soils 3, 18, 20, 21 and 37).



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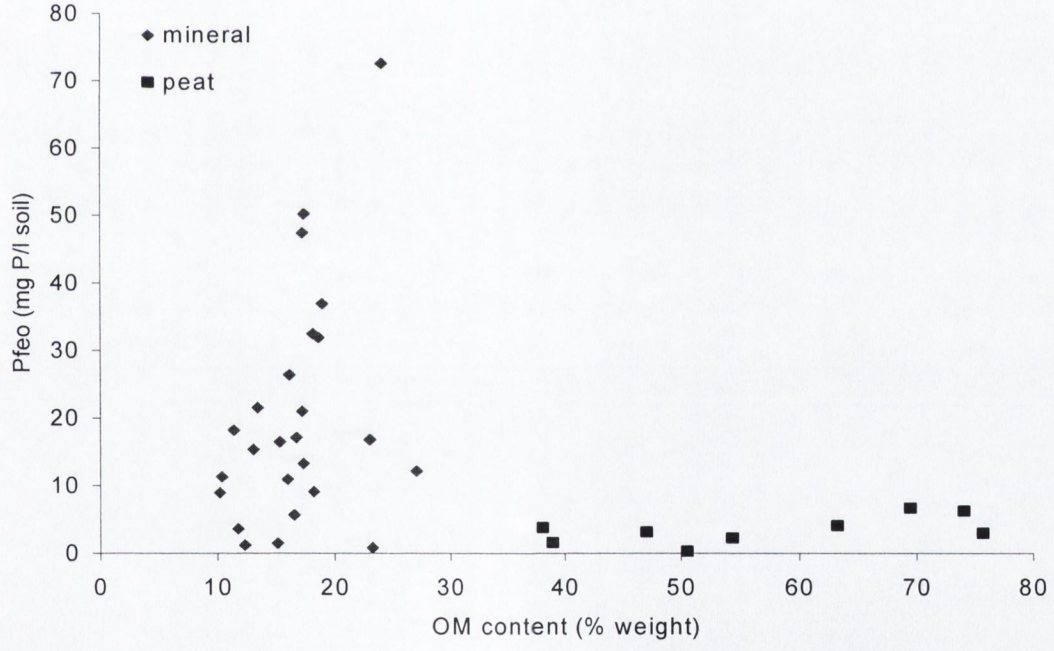


(b)

Figure 4.10: Scatterplots showing associations between organic matter (OM) content and (a) total water-extractable P (P_w) and (b) bioavailable P (P_{feo}), contrasting peat and mineral soil desorption.

Given the strong relationships between STP and P desorption, and the weak relationships between general soil characteristics and P desorption, a more instructive analysis of general soil characteristics involves looking at any significant influence they might have on STP-P desorption relationships. Stepwise multiple regression analyses were conducted to determine which characteristics affected P desorption after the strongest single predictor (DPSS2) was accounted for (table 4.7). After regression with DPSS2, residuals for the three measures of P desorption were positively correlated to Al_{ox} contents (residuals of P_w DRP against DPSS2 were also significantly positively correlated to Al_{ox}, although slightly less strongly than to exchangeable Mg content). Residuals after DPSS2 regression with P_w contents were most strongly (positively) correlated with exchangeable Mg content for both DRP and TDP fractions. Drying soil samples changed the best predictive characteristics, with exchangeable Ca content and pH becoming the strongest (negatively correlated) predictors of P_w DRP and TDP, respectively, after DPSS2 was accounted for. None of the general soil characteristics measured here improved regression between P_{feo} and DPSS2 in dried samples. Overall, the predictive power of DPSS2 and general soil characteristics was stronger for moist samples.

Table 4.7: Results of stepwise multiple regression analyses with degree of P sorption saturation (DPSS2) and the general soil characteristics most strongly correlated with residuals as predictor variables, and water-extractable P (P_w) fractions and bioavailbale P (P_{feo}) as dependent variables (DV), for both moist and dried soils. Included are available magnesium (Mg), calcium (Ca) and oxalate-extractable aluminium (Al_{ox}). Adjusted r^2 values shown ($p \leq 0.0001$ in all instances).

DV	Regression Equation	r^2
P_w DRP (moist)	$y = -5.746 + 0.662$ DPSS2 $+ 0.033$ Mg	0.90
P_w TDP (moist)	$y = -5.820 + 0.720$ DPSS2 $+ 0.029$ Mg $+ 0.0001$ Al_{ox}	0.89
P_{feo} (moist)	$y = 0.634 + 1.905$ DPSS2 $+ 0.003$ Al_{ox}	0.88
P_w DRP (Dried)	$y = 15.197 + 0.839$ DPSS2 $- 2.344$ pH	0.91
P_w TDP (Dried)	$y = 11.210 + 0.994$ DPSS2 $- 0.0014$ Ca	0.77
P_{feo} (Dried)	$y = 10.692 + 1.769$ DPSS2	0.65

As Morgan P is the standard agronomic soil P test in Ireland, the same process was repeated for residuals after regression analyses for P desorption against Morgan P, in order to find the soil characteristics with the greatest influence on the P desorption-Morgan P relationship (table 4.8). Similar characteristics appear to be important for all three measures of desorption. For moist samples, OM content and exchangeable Mg are important predictor variables, once Morgan P has been considered (although TEB content is also important for P_w DRP). For dried samples, OM content and exchangeable Ca are the dominant predictor variables. Although OM content is not the most important predictor of P_w DRP after Morgan P is considered, it is nonetheless a significant predictor variable when included in the regression. The important role of OM content in the Morgan P-P desorption is emphasised by the significance of its inclusion in regression between all desorbable P fractions and Morgan P (table 4.8). By contrast, the inclusion of OM content is not significant in regression analyses between any of the desorbable P fractions and other STP methods used in this study.

Table 4.8: Results of stepwise multiple regression analyses with Morgan P (Pm) and general soil characteristics (total exchangeable bases (TEB); exchangeable calcium (Ca) and magnesium (Mg); organic matter (OM)) as predictor variables, and water-extractable P (P_w) fractions and bioavailable P (P_{feo}) as dependent variables (DV), for both moist and dried soils (adjusted r^2 values shown, $p \leq 0.0001$ in all instances).

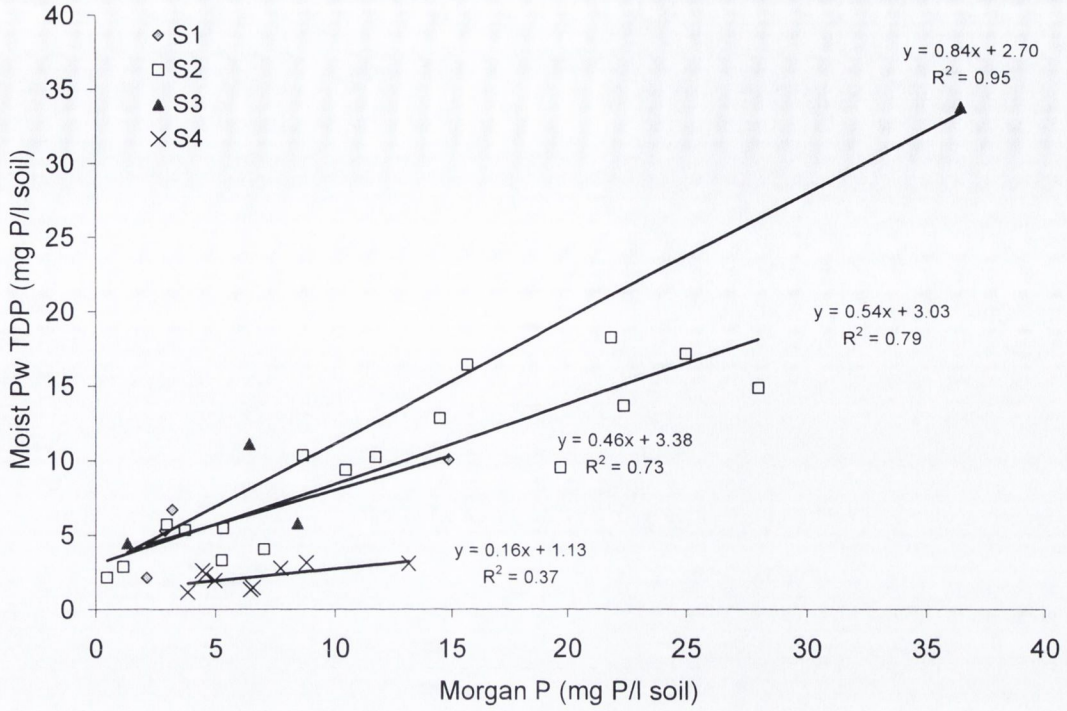
DV	Regression Equation	r^2
P_w DRP (moist)	y = -4.80 + 0.58Pm + 0.042Mg – 1.72TEB	0.89
	y = 1.16 + 0.64Pm – 0.07OM	0.83
P_w TDP (moist)	y = 2.09 + 0.60Pm – 0.092OM + 0.043Mg	0.92
	y = 3.70 + 0.67Pm - 0.10OM	0.83
P_{feo} (moist)	y = -6.23 + 1.57Pm – 0.17OM + 0.077Mg	0.89
	y = 4.62 + 1.68Pm - 0.21OM	0.87
P_w DRP (Dried)	y = 0.45 + 0.60Pm - 0.002Ca + 0.036Mg	0.92
	y = 3.87 + 0.69Pm – 0.07OM	0.81
P_w TDP (Dried)	y = 16.23 + 0.85Pm – 0.11OM – 0.002Ca	0.71
	y = 13.37 + 0.79Pm - 0.15OM	0.67
P_{feo} (Dried)	y = 20.69 + 1.50Pm – 0.31OM	0.66

4.5.6. Effect of soil group on soil test P-P desorption relationships

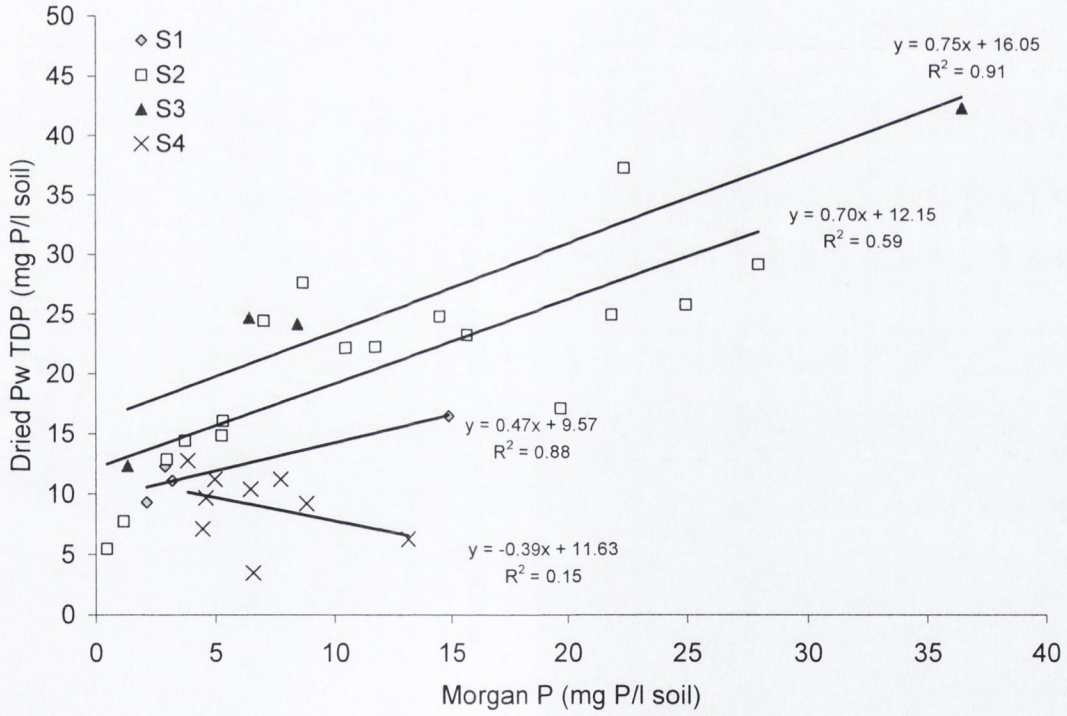
Soils were classified into groups based on OM content, according to Daly et al. (2001) – see table 2.5 and section 2.3.1. Figures 4.11 and 4.12 compare the Morgan P-P desorption relationships for each soil group, and indicate that they did differ between soil groups. ANCOVA were conducted separately on individual desorbable P fractions in moist and dried samples, with Morgan P and soil group as the independent variables, and an interaction term between them to determine if soil group had a significant influence on the Morgan P-P desorption relationship. The results are summarised in table 4.9, and confirm that differences in the Morgan P-P desorption relationshipamong groups were significant among moist samples for all desorbable P fractions, but that they were only significant for P_{feo}, and boderline significant for P_w DRP, among dried samples. Figures 4.11 and 4.12 highlight the similar lines of best fit for Morgan P-P desorption relationships among the mineral soil groups (S1-S3) when samples were analysed in moist condition, with P desorption from peat soils (S4) at given Morgan P contents being noticeably lower than from the mineral soils. Drying soil samples introduced more scatter to soil group Morgan P-P desorption relationships, and resulted in an apparent negative relationship between P desorption and Morgan P in peat (S4) soils (figures 4.11b and 4.12b).

Table 4.9: Results for interaction between Morgan P and organic matter (OM) soil group in ANCOVA, when used to predict dependent variables (DV) water-extractable P (P_w DRP and TDP), and bioavailable P (P_{feo}) in moist and dried samples.

DV	Condition	*df*	*F*	*p*
P_w DRP	moist	3, 26	7.72	0.0012
P_w TDP	moist	3, 26	3.99	0.0183
P_{feo}	moist	3, 26	3.11	0.0437
P_w DRP	dried	3, 26	2.97	0.0503
P_w TDP	dried	3, 26	1.19	0.332
P_{feo}	dried	3, 26	4.8	0.0086

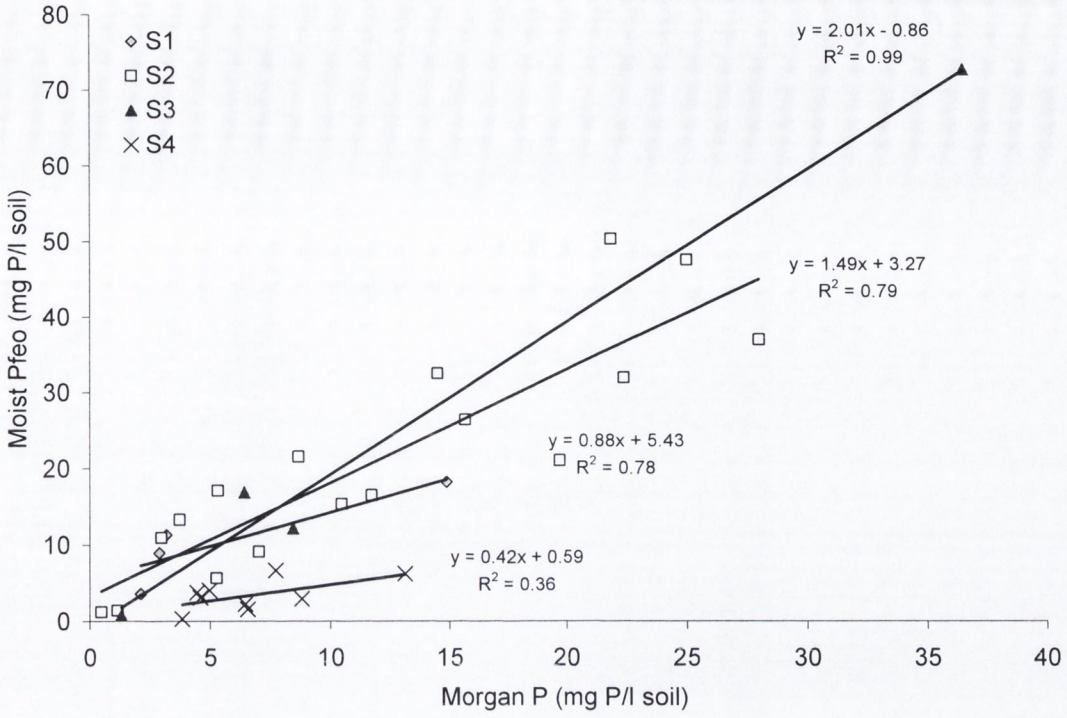


(a)

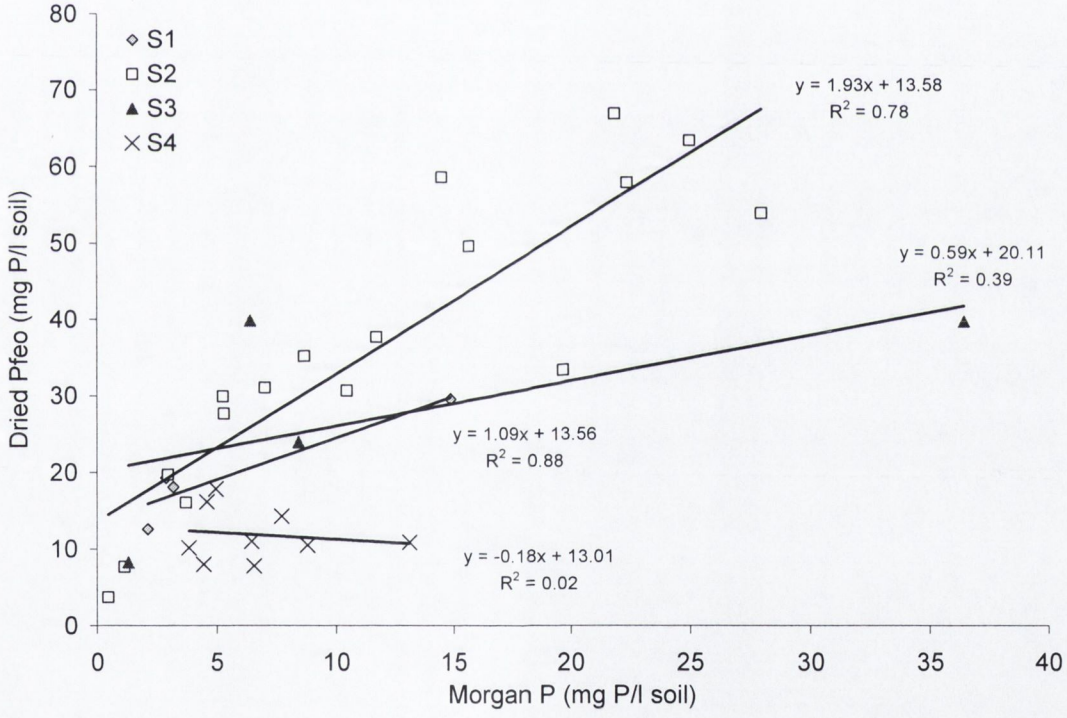


(b)

Figure 4.11: Regression lines comparing Morgan P – total water-extractable P (P_w TDP) relationships among soil groups, with P_w TDP measured on (a) moist and (b) dried samples.



(a)



(b)

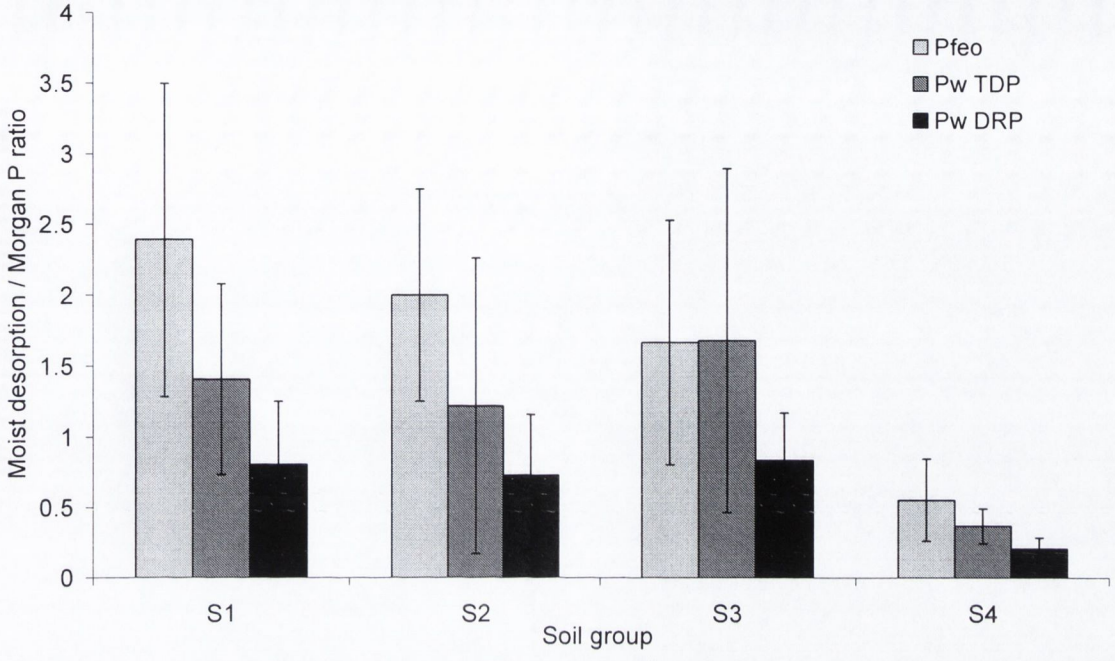
Figure 4.12: Regression lines comparing Morgan P – bioavailable P (P_{feo}) relationships between soil groups, with P_{feo} measured on (a) moist and (b) dried samples.

Unfortunately, the small number of soils in some of the soil groups (i.e. S1 and S3, with just 4 soils in each), meant that it was difficult to determine whether differences in the Morgan P-P desorption relationships were significant. It was not possible to use *post-hoc* analyses in ANCOVA to determine this. Therefore, the ratios of P desorption to Morgan P were calculated for all soils, and averaged for each soil group (table 4.10; figure 4.13a). Kruskal-Wallis analyses were conducted on these (non-parametric) ratios to determine whether significant differences existed between different soil groups. While it appears from figure 4.13 that P_{feo} / Morgan P ratios decreased progressively from low to high OM soil groups (i.e. from S1 to S4), the P_w / Morgan P ratios did not vary in such a consistent manner, and appeared highest in the high OM mineral (S3) group (especially the TDP fraction, indicating a high proportion of P_w MUP desorption / dissolution from soils in this group). However, SD values were high due to the small number of samples, and Kruskall-Wallis analyses found no significant differences in mean ratios among mineral soil groups (χ^2 = 2.43, 1.5 and 0.55, p = 0.30, 0.47 and 0.76 for P_w DRP and TDP and P_{feo} ratios respectively).

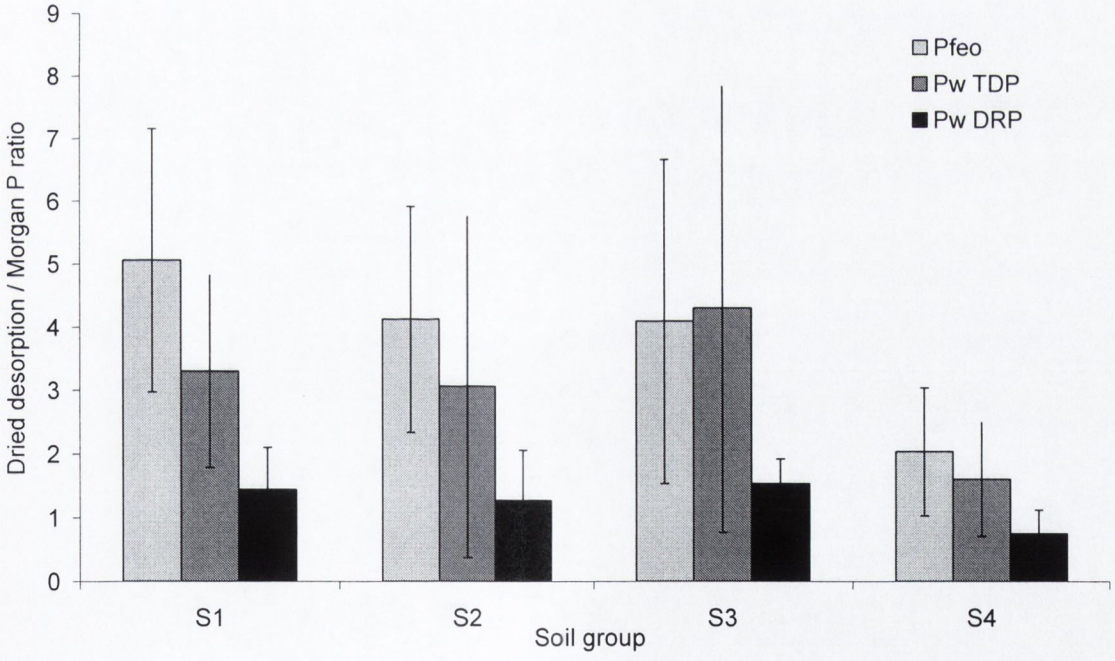
When all mineral soils were considered together as one group, and compared against peat soils, significant differences in P desorption / Morgan P ratios were found for all desorbable P fractions using the (non-parametric) Mann-Whitney *U*-test (see table 4.10). The same procedure was used to compare P desorption against DPSS2 (supposedly soil type universal; Uusitalo and Tuhkanen, 2000), and found that peat soils also desorbed significantly less P per unit DPSS2 than mineral soils (table 4.10). There were only DPSS2 data for the seven peat soils collected in March 2003, compared with these data plus those for the extra two peat soils collected in October for Morgan P (section 2.2.3 and 4.3.1). For moist samples, the quantity of P desorbed per unit Morgan P in peat soils is only about one quarter the quantity of P desorbed per unit Morgan P in mineral soils, although the soil group differential is less for DPSS2, with peat soils desorbing approximately half the quantity of P per unit DPSS2 than mineral soils.

Percentage increases in both P_w and P_{feo} caused by the drying of soils were significantly greater in peat than mineral soils (see section 3.4.2), which resulted in decreased differences in desorption between dried compared to moist samples from the two soil types. Table 4.10 shows that the quantity of P desorbed per unit Morgan P in peat compared with mineral soils increased from approximately one quarter to approximately one half after sample drying, and ratios for the two soil groups were not significantly

different for P_w TDP. Phosphorus desorption per unit DPSS2 was greater in peat compared with mineral soils, once samples had been dried, and this difference was borderline statistically significant for P_w TDP ($p = 0.061$; table 4.10).



(a)



(b)

Figure 4.13: Mean water-extractable P (P_w) and bioavailable P (P_{feo})/ Morgan P ratios for the 4 soil groups in (a) moist and (b) dried samples, with SD. bars shown. n = 4, 17, 4 and 9.

Table 4.10: Comparison of moist and dried sample P desorption / soil test P (Morgan P and degree of P sorption saturation (DPSS2)) ratios (dependent variables; DV) between peat and mineral soil groups, and the resulting index of desorption for peat compared with mineral soils. Also shown are the results of Mann-Whitney *U* tests on the significance of soil group differences. Note that peat soil n = 9 for Morgan P ratios, and 7 for DPSS2 ratios.

Sample condition	DV	Peat	Min.	Index	*U*	*p*
Moist	**P_w DRP/Pm**	**0.21**	**0.76**	0.27	**2**	**≤0.0001**
	P_w TDP/Pm	**0.36**	**1.38**	0.26	**4**	**≤0.0001**
	P_{feo}/Pm	**0.51**	**1.97**	0.27	**4**	**≤0.0001**
	P_w DRP/DPSS	**0.35**	**0.62**	0.56	**40**	**0.030**
	P_w TDP/DPSS	**0.62**	**1.00**	0.62	**38**	**0.023**
	P_{feo}/DPSS	**0.84**	**1.67**	0.50	**32**	**0.010**
Dried	**P_w DRP/Pm**	**0.75**	**1.34**	0.56	**50**	**0.014**
	P_w TDP/Pm	**1.60**	**3.30**	0.48	**90**	**0.514**
	P_{feo}/Pm	**2.03**	**4.27**	0.48	**36**	**0.002**
	P_w DRP/DPSS	**1.73**	**1.03**	1.68	**61**	**0.242**
	P_w TDP/DPSS	**3.83**	**2.37**	1.62	**46**	**0.061**
	P_{feo}/DPSS	**4.32**	**3.28**	1.32	**70**	**0.447**

Conducting two sample t-tests between peat and mineral soil groups found that peat soils contained significantly less P_{ox} ($t_{30} = 2.39$, $p = 0.023$) and Al_{ox} ($t_{30} = 2.57$, $p = 0.016$) than mineral soils, but there was no significant difference in Fe_{ox} contents ($t_{30} = 0.29$, $p = 0.77$). Phosphorus sorption capacities (PSC1 and 2) were not significantly different between soil groups (although the wide range of PSC2 values amongst the 7 peat soils displayed a

strong negative correlation with OM content; $r = 0.89$, $p \leq 0.01$). Both calculations of DPSS were lower for peat soils ($t_{30} = 3.48$ and 2.5, $p = 0.0016$ and 0.018 for DPSS 1 and 2 respectively). Olsen P contents were also lower in peat soils ($t_{30} = 3.72$, $p = 0.0008$), though differences in Morgan P contents between peat and mineral soils were only just statistically significant ($t_{31} = 2.06$, $p = 0.048$). There were no significant differences between peat and mineral soil groups for contents of any of the exchangeable bases or pH.

4.6. Relationship between soil and stream water P data

Point source inputs of soluble P in the Mask catchment were assumed to be minor, as Donohue (unpublished data) calculated that discharge into the River Robe from wastewater treatment plants servicing the main towns in the catchment (Claremorris and Ballinrobe) contributed relatively minor quantities of nutrients to the river (comprising <5% of total annual P loading). As outlined in section 4.3.3, soil P data were used to devise a simple P desorption index (PDI) based on soil group and Morgan P content:

$$PDI = mPm + cpPm$$

where m and p are the proportion of the catchment accounted for by mineral and peat soils respectively, and Pm is the average catchment soil Morgan P in mg l^{-1}, c is the ratio of peat compared with mineral desorption at a given Morgan P content. The c parameter was derived directly from laboratory analyses of moist P desorption to Morgan P ratios for peat and mineral soils summarised in table 4.10 (which were found to be similar for the three measured desorbable P fractions: 0.27, 0.26 and 0.27 for P_w DRP, P_w TDP and P_{feo} fractions respectively), and was thus set at 0.27.

This PDI was then applied to each of the 12 subcatchments within the Mask catchment, using GIS maps of Morgan P (based on Teagasc sampling data; figure 2.3) and soil association (figure 1.4), in order to create a ranking of relative soluble P loss risk. This ranking was then compared with mean DRP and TDP concentrations, and area-weighted annual DRP and TDP loads (calculated from all water sampling occasions: see section 4.3.3), using Spearman Rank correlation. The PDI ranking was significantly positively associated with mean stream concentrations of both DRP and TDP ($r_s = 0.64$ and 0.54; p <0.02 and <0.05, respectively), and with area-weighted annual loads of DRP ($r_s = 0.63$, p

<0.02). However, when a mean peat / mineral desorption ratio (*c*) of 0.5 was used, based on dried sample analyses (i.e. peat soils desorbed 56, 49 and 48% of P_w DRP, TDP and P_{feo}, respectively, per unit Morgan P content, compared with mineral soils; section 4.5.5), subcatchment PDI values were not significantly correlated with stream soluble P concentrations or loads. Similarly, average subcatchment Morgan P content itself was not significantly correlated with average annual stream P concentrations or loads.

4.7. Discussion comparing Mask soils with those from N. Ireland and Galicia.

Soils from the Friary catchment in N. Ireland and the Mask catchment in the Republic of Ireland shared similar general characteristics (table 4.1, figure 4.1), with similar high TOC and TN contents reflecting OM accumulation under common pasture-dominated land use (section 1.6), and similar cool, wet climates. The main difference between Mask and Friary catchment soils was the higher pH displayed by Mask soils, reflecting the limestone bedrock geology and calcareous glacial deposits on which many of these soils were formed, especially in the east of the catchment (figure 1.3). Soils from the Fervenza and Portodemouro catchments in Galicia were acidic, with a mean pH of 5.11, reflecting the siliceous geology and extensive weathering and leaching processes undergone by these soils in the temperate, wet Galician climate (section 1.6). Soils from all regions displayed similar, relatively high Olsen P contents. Garcia-Rodeja and Gil-Sotres, (1997) report that Galician soils are naturally deficient in P, and require high P applications of around 70 kg P ha^{-1} for agricultural production. However, the Olsen reagent may be more effective at extracting P from the acidic Galician soils compared with the higher pH (and presumably higher Ca content) Irish soils, as it is known that P precipitates with Ca at higher pH and Ca concentrations during bicarbonate extractions (e.g. Sorn-Srivichai et al., 1984; Curtin and Syers, 2001) - see also section 4.5.3. This could explain partially why P_w contents in Galician soils averaged only just over a third of those from Irish soils (which again were similar from the Mask and Friary catchments).

However, it is likely that the substantially lower P desorption from dried samples of Galician soils was more closely related to two of the analysed parameters summarised in table 4.1: TOC and Freundlich K_f values. Firstly, the lower TOC contents in Galician soils indicate lower contents of OM susceptible to drying-induced mechanisms of P release (section 3.6.3), and thus lower dried sample P_w contents, compared with Mask and Friary catchment soils. Additionally, lower TOC contents in Galician soils indicate lower OM contents and therefore higher BDs (section 2.2.5). This would have resulted in smaller volumes of these soils being analysed compared with Mask and Friary catchment soils, and thus smaller surface areas from which P desorption or dissolution could occur. Secondly, the significantly higher K_f values for Galician compared with Irish soils indicate higher sorption capacities in these soils (see section 4.5.3 for K_f - PSC comparison). This is consistent with high Fe and Al contents reported for Galician soils in other studies (e.g.

Garcia-Rodeja and Gil-Sotres, 1997), and results in P being bound more strongly to these soils, and thus less release to water.

Overall, it appears that, despite slightly different parent material, mineral soils from the two Irish catchments compared here are similar in terms of general characteristics, P contents and (de)sorption dynamics. This probably reflects similar climate and land use, and the range of soils studied in the Mask catchment (section 2.3.1) includes the most common soil types found throughout Ireland. In comparison with soils from Galicia, however (and thus presumably other acidic, high Fe and Al content soils in general), soils from the Friary Lough and Lough Mask catchment (which may be expected to be typical of many Irish mineral soils) have relatively low sorption capacities and are thus more susceptible to P losses. However, as analyses were conducted on dried soils, and high OM contents in the Irish soils are likely to have resulted in more drying-induced P release, it may be hypothesised that there is less difference in natural desorption from these soils than observed from laboratory analyses in this study.

4.8. Discussion of Mask catchment soils

4.8.1. Land use effects on soil test P and P desorption

Accumulation of STP over a number of years in agricultural soils is well documented (Culleton et al., 1999; McCollum, 1991; Mozaffari and Sims, 1994; Turtola and yli-Halla, 1999), and P inputs have been found to relate strongly to both Morgan P (Culleton et al., 1999; Power, 1995) and P_w (Sharpley, 1982; Power, 1995; Turtola and Yli-Halla, 1999). Data presented in figure 4.2 indicate that STP and potential P desorption to water were related linearly to (recent) P application data obtained in this study, but there was a high degree of scatter in the relationship. This was probably due to a combination of inaccuracies in estimates of P application used in this study, the absence of reliable stocking rate and P off-take data, and soil-specific P accumulation responses (Leinweber, 1999; Laboski and Lamb, 2003).

As detailed in section 2.3.2, estimates of fertiliser application provided by farmers were imprecise. This was primarily due to vague (and in some instances possibly misleading) estimates provided by farmers, and large assumptions about the quantity of P applied by

slurry and manure applications (which will vary depending on the intensity of spreading and dilution of the slurry). Additionally, there may be significant additional inputs (or off-takes) of P from soils depending on the intensity and timing of grazing animals. Data on grazing intensities were particularly patchy due to constant animal rotations between fields.

Even where estimates of current P application rates were accurate, there is the problem that STP includes latent soil P which may have accumuled from applications in the past, possibly under different management regimes. The effect of current land management on STP and P desorption from soils may thus be obscured by past management practices. This is especially applicable to fields where the owners reduced P inputs to comply with the voluntary REPS; see section 2.3.2. These last two points are likely to account for the wide range of Morgan P and desorbable P contents in soils with no estimated inputs (figure 4.2). Site 10, for example, is known to have been used intensively in the past, but now has no P inputs due to its owner's recent participation in REPS. Sites 18 and 19 were owned by the same farmer, and shared very high current inputs of 59 kg P ha^{-1} a^{-1}, but site 19 was reclaimed and had had only one year of recent P application compared with decades for site 18. Consequently, Morgan and Olsen P contents, while still high, were much lower in soil 19 compared with soil 18 (19.7 and 47.0 compared with 36.5 and 76.2 mg P l^{-1} respectively). These two sites were in close proximity to one another, and were of similar soil type. Thus, the higher values in soil 18 are an indication of the impact of P application on STP over a period of years. Ultimately, problems associated with relating land use and P application data to STP and P desorption need to be addressed for P loss modelling approaches which rely on these data (e.g. export coefficient models; Johnes, 1996; Johnes et al., 1996). Soil specific P accumulation and desorption responses are not usually explicitly considered in such models.

Dividing the soils according to land use intensities was complicated by recent changes in management practices and the suspected unreliability of information for some sites (section 2.3.2). The data could have been divided according to various criteria and thresholds. The methods chosen here ranged from one based on readily available land use data (CORINE-based divisions) to one based on the fundamental agricultural management intensity scale used in Ireland (the Teagasc soil P index system). The rationale for these two divisions was to assess the potential for using land use data alone to assess STP and potential soil P desorption on a catchment scale, and to assess the impact of choosing different target soil P indices on potential P desorption (this approach has some overlap

with the MorganP-P desorption relationships explored in sections 4.5.4 to 4.5.6). The third method of land use division used here involved comparing the impact of different grazing animals or silage production on grassland STP and P desorption, and found no significant differences. Observations made during monthly sampling suggest that, in practice, some fields may be grazed by a combination of animal species. Also, there was large variability in land use intensity within grazing animal and silage grass divisions. Detecting systematic differences in intensity between these different agricultural systems would require a much larger scale and more detailed land use study.

The CORINE-based classification division of soils resulted in significant differences among land use classes (table 4.5 and section 4.5.2). Unsurprisingly, the highest Olsen and Morgan P contents were under grassland to which P was applied (figure 4.3a), whilst the lowest contents were under forest cover, to which P has probably not been applied for at least the past 10 years (section 2.3.2). Section 2.3.2 details that site 7 was a coniferous plantation, and was the youngest forest site, while site 23 appeared to be an old, deciduous forest, and site 29 a well-established mixed forest on the edge of a coniferous plantation. This may explain the higher STP contents in the sample from soil 7 compared to soils 23 and 29 (table 4.2b). Mean Morgan and Olsen P were lower under grassland where there was no stated P application compared with soils where P was applied, but the difference was not significant due to the high variation in values within soils under both land use categories. Despite the small number of samples, the lower STP values in forest compared with grassland soils proved to be significant, although for Olsen P this difference was only significant with the higher intensity grassland category. Olsen P extracts a high proportion of organic P, which may be more abundant in forest soils.

As mentioned in section 4.3.1, soil 7 was removed from the forest cover P desorption figures due to its exceptional value, in relation to past values obtained during seasonal sampling and analyses of samples from that site (e.g. table 3.9), and the anomalous substantial decrease in P_w content after drying (table 4.2b). However, this did not affect the presence or absence of statistical significance for differences among land use categories. Despite following the same general trends as STP (figure 4.3b), high standard deviations meant that no significant difference was found among land use categories for P_w (table 4.5). Phosphorus application did appear to increase P_{feo} from grassland soils compared with forest soils, although lower intensity grassland and forest soils were statistically similar. Ultimately a greater number of soils would be needed to assess the

impact of different land uses more thoroughly. However, data presented here do highlight the difficulty of obtaining representative estimates of land use intensities and relating them to potential P losses, thus promoting the use of alternative approaches.

As would be expected from the strong Morgan P-Olsen P relationship explored in section 4.5.3, and the strong Morgan P-P desorption relationships explored in sections 4.5.4 to 4.5.6, there were large differences in Olsen P and P desorption among soil groups divided according to Teagasc soil (Morgan) P indices. Figure 4.4 shows that there was a clear trend of increasing soil Olsen P and P desorption with increasing soil P index. The small number of samples in soil P indices 2 and 3 restrict the conclusions that can be drawn from these data, and were probably responsible for the absence of statistically significant differences between some of the (neighbouring) soil P indices (*post-hoc* tests; section 4.5.2). However, overall differences in desorption between different indices were large, with up to 8 times more desorption (P_{feo}) recorded from soils in P index 4 compared with soils in P index 1 (figure 4.4). This emphasises the importance of target soil P index with respect to limiting potential P loss to water. Maintaining soils above soil index 3 (or index 2 in most instances) is not only unnecessary from an agronomic perspective (Teagasc, 1998), but greatly increases potential soil P loss. Relating soil P desorption to these land use intensity divisions is related to the STP-desorbable P relationships explored from here on.

4.8.2. Relationships among different soil test P methods

As expected, and found by past studies, different methods used to estimate soil plant-available P contents (i.e. Morgan, Olsen and oxalate extractable P) correlated strongly with one another (table 4.3; figures 4.5 and 4.6). The relationship between Olsen P and Morgan P in soils studied here (figure 4.5) was similar to that found in Irish grassland soils by Poulton et al. (1997); both relationships were linear and of similar strength, although Olsen P content per unit Morgan P was a little lower in this study. This could be the consequence of two factors: 1) the other studies relied on Olsen P data derived from shaking soils with the Olsen reagent for 1 hour, compared with 30 minutes in this study;

2) average soil pH may have been higher in this study, thus reducing the efficiency of P extraction by the Olsen reagent (Curtin and Syers, 2001; Foy et al., 1997; Sorn-Srivichai et al., 1984).

Soil P extraction by the Morgan reagent appeared to be disproportionately affected by soil P sorption capacity, compared with the Olsen reagent (eq. 4.1), though it is difficult to explain why this may be so. Perhaps the acidic Morgan test is more controlled by P sorption / desorption equilibria than the alkaline Olsen test, which may be more controlled by solubility factors, as implied by Sorn-srivichai et al. (1984). Equation 4.1 also indicates that OM content and TEB content had a negative impact on Olsen P relative to Morgan P extraction once the effect of PSC1 was accounted for. This could be due to greater hydrolysis of organic compounds by the acidic Morgan reagent (in proportion to the lesser amount of P extracted in the Morgan test), and the fact that TEB content was related to exchangeable Ca and Mg (the dominant base elements). TEB content may therefore indicate the risk of P precipitation at high Ca and Mg concentrations in the Olsen test (Sorn-Srivichai et al., 1984). This is supported by the fact that exchangeable Ca content was correlated almost as strongly with residuals as TEB content was. The significance of soil pH at this same stage (i.e. after the effects of PSC1 and OM content were accounted for) may be due to the same (Ca-P precipitation) reason, and indicates that pH effects were less important in this study than found by Foy et al. (1997). This could be due to the inclusion of peat soils in this study, or is perhaps a statistical consequence of the smaller number of samples compared here.

Despite the presence of some calcareous and relatively high pH soils in this study, both DPSS calculations were strongly correlated with one another (table 4.3, figure 4.7), and there was no obvious trend of deviation from the regression line by high pH soils. Values were much lower for the DPSS2 calculations (table 4.2a) due to substantially higher sorption capacities calculated from oxalate-extractable Fe and Al contents (PSC2) than from empirical PSI values (PSC1). While the PSI method of calculating PSC has been found to correlate strongly with other methods (Mozaffari and Sims, 1994; Simard et al., 1994), actual values have been found to increase as the soil-solution ratio used increases (Smilie and Quinane, 2003) and as the time of reaction (sorption) increases (Freese et al., 1992). Thus, while the soil-solution ratio used in this study was relatively high (1:100), the relatively short reaction time (24 hours) may have been responsible for low PSC1 estimates. Freese et al. (1992) used a PSI reaction time of 40 days, and found that the resulting values corresponded well with the sum of Fe_{ox} and Al_{ox} multiplied by an activity factor of 0.5, in a range of German soils. However, it could be that an activity factor of 0.5 is too high for Fe_{ox} and Al_{ox} in Irish soils. This would have resulted in the calculated PSC2

values being unrealistically high, and the DPSS2 values unrealistically low. The curvilinear relationship found between DPSS1 and 2 (figure 4.7), with DPSS1 values increasing less per unit increase in DPSS2 at high values, was the consequence of a converse relationship between PSC1 and PSC2 (i.e. lower relative increase in PSC2 values per unit increase in PSC1 values at high sorption values). This in turn may have been a consequence of either P precipitation effects at high soil P concentrations during the 24 hour PSI experiments, or greater proportions of Fe_{ox} and Al_{ox} becoming less available for sorption at higher concentrations (e.g. higher proportions may have been present as crystalline oxides at higher concentrations).

Unfortunately, comparisons of the Freundlich K_f PSC index estimates with PSC1 and 2 were not direct due to the two separate sorption experiments for the Freundlich equation only being conducted on spatial soil samples collected in March 2002 (section 2.2.3). Phosphorus sorption capacity values calculated by different methods were therefore compared for different soil samples, taken from the same fields but one year apart and at different depths (10 cm in 2002, 5 cm in 2003). Despite the probable detrimental effect of high sample variability (e.g. section 2.2.4) on correlations between analysed characteristics in these samples, the Freundlich K_f parameter showed some potential for predicting PSI, and substantial potential for predicting PSC1 (though not PSC2) when P_{ox} was included in the 'total P sorbed' expression of the Freundlich equation (section 4.4.1). However, the need for inclusion of P_{ox} contents means that K_f values remain less convenient estimates of relative sorption capacities than PSC1 estimates (which rely on just one rather than two separate sorption experiments).

4.8.3. Relationships between soil test P and desorbable P

The accumulation of readily extractable forms of P in response to P inputs has been found to vary depending on the form of application (Laboski and Lamb, 2003; Turtola and Yli-Halla, 1999), soil type (Leinweber, 1999; Laboski and Lamb, 2003) and previous P content (Power et al., 1995), although Sharpley (1982) found a linear relationship between P application and P_w. Given the problems associated with obtaining representative estimates of P application and animal inputs (section 2.3.2 and 4.8.1), it may be more reliable to use extensive existing STP data sets to predict potential soil P desorption. STP concentrations are probably good integrated indicators of management practices over time, and, depending on the specific test, may account for some of the soil type specificity in P

application – P desorption response. Additionally, as outlined in section 2.3.2, STP concentrations are used as management targets. They are thus both readily available for the prediction of potential P losses, and integral to forming management plans that may be used to reduce P loadings.

The superiority of the DPSS approach compared with other STP methods for predicting soil desorbable P contents has been found in a number of other studies (e.g. Daly et al., 2001; Hooda et al., 2000; Sharpley, 1995), and was confirmed here (table 4.6). DPSS is universally applicable to a range of soil types (Uusitalo and Tuhkanen, 2000) because, unlike most STP methods, it relates a measure of the quantity of P in a soil to the ability of that particular soil to sorb P. Despite the presence of a few calcareous, high pH soils in this study (where Ca, rather than Fe and Al, may be assumed to be the dominant P binding element), linear regression analyses (summarised in table 4.6) indicated that the oxalate-extractable Fe and Al method of calculating DPSS (DPSS2) was better at predicting P desorption than the empirical PSI method (DPSS1). This was due to the non-linearity of the DPSS1-P desorption relationship (figure 4.8a; the cause of which was explored in the previous section). A polynomial equation was found to describe an approximately equal proportion of P_{feo} than was described by the linear DPSS2 equation (r^2 = 0.87 compared with 0.86, respectively, figures 4.8a and b). Some other workers have found non-linear relationships between DPSS and desorbable P, either exponential in form or with 'change-points' where 2 straight lines of best fit with different slopes meet (Hooda et al., 2000; McDowell et al., 2001; Nair et al., 2002). Had PSI been measured on field-moist samples as desorption was, DPSS1 may have been more strongly related to P desorption.

Despite the strong predictive power and apparent soil type universality of DPSS2 for desorbable P, relationships between desorbable P fractions and DPSS2 were influenced by other soil characteristics (table 4.7). Desorption from moist samples increased with increasing quantities of Al_{ox} after the effect DPSS2 was accounted for, suggesting that Al_{ox} may be less available for P sorption than Fe_{ox}, and therefore exaggerate PSC2 (and underestimate DPSS2) calculations. The role apparently played by exchangeable Mg content in increasing P_w desorption is more difficult to explain. It appears that sample drying resulted in different soil characteristics becoming influential on the DPSS2-P desorption relationship. Exchangeable Ca and pH became negative predictors of P desorption once the dominant effect of DPSS2 was accounted for, indicating that at higher soil pH and exchangeable Ca contents, Ca may become more important in binding soil P.

Exchangeable Ca may be unexposed in soil aggregates, or bound in Ca-humic complexes (Dormaar, 1972) when soils are moist, but become exposed during soil drying due to aggregate disruption and OM dissolution (see section 3.2.2).

Unfortunately, analysing soils for DPSS is time consuming, and is not routine in Ireland. However, this study has found that the standard agronomic Morgan P test appears to account for almost as much of the variability in desorbable P as DPSS (table 4.6), despite the range of soil types analysed. The strength of the Morgan P-P desorption relationship may be attributable to a number of features of the Morgan test. In particular, the extractant used is not especially chemically aggressive (sodium acetate at pH 4.8), the soil-solution ratio is low (1:5), the contact time short (30 minutes), and the solution is analysed for MRP only. These factors combine to ensure that only P from the most readily extractable soil P fractions is measured in solution: the same fractions likely to desorb P to water and weak electrolyte (~soil water) solutions. Maintaining soils in their field (moisture) condition prior to P_w and P_{feo} analyses not only ensures that samples are more representative of field conditions, but appears to increase correlation with Morgan P (despite the fact that the Morgan P test extracts P from dried samples). The weaker correlations between P desorption and Morgan P found here for dried samples (table 4.3) were similar to those found by Daly (2000) for P_w and P_{feo} with Morgan P: 0.78 and 0.77 ($n = 90$, $p \leq 0.001$).

Olsen P appeared to explain a similar proportion of desorbable P variability to Morgan P, although the TP fraction explained less variance (table 4.6). Despite a contact time of just 30 minutes, and a soil-solution ratio of 1:20, the amount of Olsen P extracted from soils was substantially greater than that desorbed to water or the iron-oxide sink electrolyte (33 soil mean values of 23.93 compared to 8.14 and 16.52 mg P l^{-1} soil respectively). The Olsen reagent extracts P from labile hydroxy-P complexes (McDowell and Sharpley, 2003), and is likely to contain more of the organic or organic-associated P fractions released to water after drying and rewetting (section 3.7.2) than Morgan P, accounting for the smaller drying effect on the strength of the Olsen P-desorbable P correlation compared to the Morgan P-desorbable correlation. The TP fraction was approximately double the MRP fraction in the Olsen extracts, indicating that a large amount of P in these soils was bound in moderately labile organic forms (Magid and Nielsen, 1992; Tate et al., 1991a) which may become available for desorption over time (see section 5.2.3). However, much of this P is not readily available for desorption, explaining the lower predictive power of the Olsen TP compared with the MRP fraction for P desorption (table 4.6).

While other studies have noted change points – at which the slope of the relationship between STP (especially Olsen P) and desorbable P increases (Heckrath et al., 1995; Hesketh and Brookes, 2000; Mc Dowell et al., 2001) - the strong relationships noted in this study are predominantly linear (e.g. figure 4.8b and 4.9), except for P desorption compared with DPSS1 (e.g. figure 4.8a). Slightly stronger correlations between Morgan P with P_w DRP and P_{feo} than with P_w TDP (tables 4.3 and 4.6) reflect the fact that Morgan P, P_w DRP and P_{feo} theoretically extract only inorganic P, while P_w TDP includes non-molybdate-reactive (organic and condensed) P fractions. It has been suggested that P desorption proceeds from different pools depending on whether P is desorbing into water or weak electrolyte solution, and over short or longer time scales, and that the ratio of these pools to one another is soil specific (Lookman et al., 1995). However, in this study, P_w DRP and TDP fractions and P_{feo} in moist samples were strongly correlated with one another, confirming the findings of Maguire et al. (2001).

4.8.4. Effects of soil characteristics and soil group on soil test P-P desorption relationships

The results of multiple regression analyses (tables 4.7 and 4.8) suggest that a number of general soil characteristics had a significant influence on relationships between P desorption and STP. The roles of exchangeable Mg, Ca and Al_{ox} contents in DPSS2-P desorption relationships were explored in the previous section (4.8.3). Probably for the same reasons, exchangeable Mg and Ca (and TEB) are similarly involved in Morgan P-P desorption relationships displayed in table 4.8. However, the general soil characteristic with the greatest effect on P desorption after Morgan P was accounted for was OM content, which had a significant negative effect on all three fractions of soil P desorption from moist and dried samples (although moist P_w DRP was more significantly affected by exchangeable Mg and TEB contents, suggesting reactive surface area control of (de)sorption). The inclusion of soil OM content did not significantly improve the strength of regression equations between any of the other STP methods and P desorption (section 4.5.5), suggesting that Morgan P is disproportionately affected by OM content. Specifically, these results indicate that the Morgan test extracts a relatively high proportion of organic P, from high OM content soils, that is not available for desorption. This is consistent with results displayed in equation 4.1, which showed that OM content also had a negative impact on Olsen P content relative to Morgan P content, and with the large differential soil group effect on P desorption / Morgan P ratios (table 4.10). The extraction

of proportionately greater quantities of P not readily available for desorption by the Morgan test (compared with other soil P tests) may be due to the relatively small quantities of P extracted by the Morgan reagent, resulting in disproportionately large influences from drying-induced P release - which increases with soil OM content, and is higher in peat soils (section 3.4.2).

Peat soils desorbed substantially less P than mineral soils (figure 4.10), although this was partially attributable to significantly lower native P contents (e.g. Morgan P and P_{ox}: section 4.5.6), and was consistent with the findings of Daly et al. (2001). Lower concentrations of Al_{ox} and P_{ox} in peat soils (section 4.5.6) may reflect humic acid chelation of these elements, and / or lower inputs from parent material and P applications. However, Fe_{ox} contents were similar in peat and mineral soils, resulting in similar PSC2 values in these two soil groups. In combination with lower peat soil P_{ox} contents, this meant that DPSS2 values were lower in peat soils. These lower values may partially explain why only one quarter of the quantity of P was desorbed per unit Morgan P in peat compared with mineral soils: the deosprtion differential per unit DPSS2 was half that found per unit Morgan P (table 4.10). However, table 4.10 shows P desorption / DPSS2 ratios were still significantly different between peat and mineral soil groups, despite the supposed soil-type universality of DPSS2 (Uusitalo and Tuhkanen, 2000), with approximately half the quantity of P desorbed per unit DPSS2 in peat compared with mineral soils.

Despite large differences in P desorption per unit Morgan P between peat and mineral soils, and the significant negative influences of OM contents on Morgan P-P desoprtion relationships (table 4.8), the small numbers of soils in groups S1 and S3 made it impossible to distinguish statistically desorption characteristics between OM-based mineral soil groups in this study. While the general trend in P_{feo} / Morgan P ratios among the soil groups (figure 4.13) supports the finding of Daly et al. (2001), there was no such trend apparent for P_w among the mineral soil groups. Comparison of these soil groups was hindered by an apparent positive association between soil OM content and P desorption among mineral soils (figure 4.10), related to high Morgan P contents in some high OM content mineral soils (most notably soil 18; table 4.2b). A greater number of soils would need to be studied to determine if and how P desorption / Morgan P ratios differed between mineral soil groups. Ultimately, differential peat desorption was nested within the strong Morgan P-P desorption relationships (figures 4.11 and 4.12). Because Morgan P contents were lower in peat compared with mineral soils, and there were only 9 peat soil samples

compared with 24 mineral soil samples, overall Morgan P-P desorption relationships remained strong.

Daly (2000) and Iyamuremye and Dick (1996) suggest that soil OM content may be associated with higher concentrations of organic compounds which hinder and compete with P sorption onto available sorption sites. In this study, PSC1 (derived from empirical P sorption (PSI) observations), was not found to be significantly lower in peat compared with mineral soils (section 4.5.6). However, PSI was conducted on dried samples (section 2.2.3), and changes in (e.g. oxidation of) organic compounds during the drying and rewetting process may have inhibited any such effects. Assuming that organic compounds do reduce sorption, then this would result in a low proportion of P inputs to peat soils being adsorbed onto reactive surfaces, resulting in most of the P present being bound in immobilised organic form. This would explain low P desorption at given STP contents (almost all STP methods extract some organic-bound P, more especially the acidic ones such as Morgan P). It is also possible that organic compounds form complexes with P, or inhibit P desorption directly (as also suggested by Daly, 2000) through similar mechanisms to those which may inhibit sorption. One final possible reason for reduced P desorption from peat soils is that these soils are typically waterlogged, and therefore constantly experience a washout effect of any P inputs. This may be exacerbated by the inhibition of sorption by organic compounds, and maybe also through reducing conditions mobilising Fe and Al bound P.

Differential P desorption in different soil groups has important implications for understanding P loss to water, and suggests that it is important to differentiate soil types in P loss models. However, how these data should be interpreted from a management perspective is critically dependent upon the mechanisms responsible for reduced peat soil P desorption. For example, reduced peat soil P desorption (availability) is reflected in higher soil Morgan P contents used to define Teagasc soil P indices, implying that more P should be applied to these soils to increase their P status and productivity. However, from an environmental perspective, the suspected sorption hinderance and high hydrological connectivity of peat soils make them particularly susceptible to losing any P that is applied, and thus particularly unsuitable for intensive agricultural use.

4.8.5. Implications of sample drying

Drying soil samples increased scatter in, and reduced the strength of, relationships among desorbable P fractions, and between desorbable P fractions and STP methods (figure 4.2). This was the consequence of different dominant mechanisms of drying-induced P release for different desorbable P fractions (see sections 3.6.1 and 3.6.2), and the disproportionate effect of drying-induced P release on low P-desorbing soils (section 3.6.1). Different soil characteristics appear to become more important in P desorption, and in relationships between STP and P desorption, once samples are dried (especially exchangeable Ca content) (tables 4.7 and 4.8).

Reduced differentiation between high and low P desorbing soils has important implications for differentiating P desorption among soil types. Peat soils desorbed significantly less P than mineral soils when analysed in both moist and dried condition (e.g. figure 4.10, and table 3.3d), but differentiation between the two soil groups was reduced substantially after sample drying. Peat soils were especially affected by drying, not just because of their low moist P desorption, but because their high OM contents made them especially susceptible to drying-induced desorbable P increases (section 3.6.3). Thus, while P desorption / Morgan P ratios for moist-analysed peat soil samples were around one quarter of those for mineral soils, P desorption / Morgan P ratios for dried peat soil samples were around one half of those for mineral soils, and P_w TDP / Morgan P ratios were not statistically significantly different between peat and mineral soils after sample drying (table 4.10). In fact, sample drying actually resulted in more P desorption per unit DPSS2 in peat soils, although the effect was not quite statistically significant ($p = 0.061$). If moist samples are accepted to be more representative of desorption potential in the field, then drying samples reduces the differentiation in P desorption that should be attributed to peat and mineral soil groups, at given Morgan P concentrations, in P loss models.

Soil samples analysed here were collected in March, when low P mineralisation rates, wet conditions and hydrological flushing (i.e. washout effects) may have reduced P desorption compared with other months (see section 5.4.4). However, differences in peat and mineral soil P desorption from moist-analysed samples are likely to remain substantially greater than differences from dried samples, even during the summer months: natural soil drying events in the western Ireland climate are not likely to be anywhere near as extreme as laboratory drying (e.g. monthly sampled moisture contents in section 5.4.2).

4.9. Discussion of relationships between soil and water P data

Intuitively, P_w and P_{feo} should be representative of rapid runoff and longer-term soil desorbable P contents, respectively, and laboratory P desorption has been found to correlate well with P desorption on a field scale (section 4.2.5). Therefore, it seems reasonable to carry through the relationships between Morgan P and the desorbable P fractions measured here to field processes, to assess potential P release (as done by Daly et al., 2002). Despite the strong relationships between Morgan P and the different forms of P desorption found for moist soil samples here (table 4.6), and direct correlations found in other studies between Morgan P and field-scale runoff P losses (Foy et al., 2002; Pote et al., 1999b) and subsurface P losses (Kurz, 2000), Morgan P alone was not significantly correlated with subcatchment soluble P loads or mean stream concentrations measured during water sampling (section 4.6). Only when a factor to account for reduced P desorption from peat soils was included in a simple model was Morgan P significantly correlated with subcatchment soluble P loads and average concentrations during sampling. This emphasises the importance of including differential soil type effects in diffuse soil P loss models.

The measurements of average subcatchment soluble P concentrations and loads used in this study are not rigorous quantifications of average annual riverine P concentrations and loads. They are simply average riverine P concentrations measured during 25 discrete sampling occassions over one year, and annual loading calculated from the interpolation of concentrations between sampling occasions applied to continuous or frequent flow EPA monitoring data. However, sample measurements were made for a wide range of flows in each river, and are therefore likely to include soluble P mobilised and transported from soils via all potential mechanisms and pathways. Therefore, while concentrations and area-weighted loads were not corrected for flow-concentrations relationships, they should provide a reasonably robust indication of relative soluble P losses among the subcatchments studied.

That such a simple model as the PDI developed here, based only on soil P desorption characteristics, is at all correlated with soluble P losses measured during sampling across subcatchments of such contrasting typology (geology, topography and hydrology, in addition to soil type) indicates that soil P desorption is a factor which should receive heavy weighting in catchment P transport models - perhaps higher than may hitherto have seemed

appropriate based on dried soil data. This contrasts with the findings of Daly et al. (2002), who proposed that the contrasting hydrology represented by different soil types had a more important influence on determining stream MRP concentrations than differential desorption based on results of analyses on air-dried soils. In their study, it was found that 'wet' catchments (based on the dominance of 'wet' soil groups S2, S3 and S4) had significantly higher stream MRP concentrations than 'dry' catchments (dominated by 'dry' S1 group soils) under a given proportion of 'high-intensity grassland' land use, contradicting the lower laboratory desorption per unit Morgan P found from soils in groups S2, S3, and S4 in particular, compared with soils in the S1 group. However, among wet catchments, the proportion of catchment area accounted for by a combined category, incorporating the proportion of peat soil and semi-natural grassland areas (termed 'semi-peat'), was strongly negatively correlated with stream MRP concentrations - consistent with reduced desorption from peat soils. The ratios of P desorption per unit Morgan P in mineral compared with peat soils found by Daly et al. (2001), and applied to the aforementioned Daly et al. (2002) model, were similar to those found in this study for dried soil samples: i.e. S1/S4 ratios ranged from 1.5 to 2.2 depending on the soil P index, similar to the approximately two-fold higher P desorption / Morgan P ratios for dried samples of mineral compared to peat soils in this study (table 4.10). It is possible that, had the soil group differential been greater (e.g. the four fold difference found for moist samples in this study), the procedure of model development followed by Daly et al. (2002) would have been different.

A substantial proportion of variability remains unaccounted for by this simple model, which only ranks catchments according to relative risk. This may be improved with further differentiation of P desorption among mineral soil groups (if indeed such differentiation exists), which would require the analyses of a larger number of soil samples. Also, improved resolution of the existing Morgan P map (determined by a coding system used by Daly et al. (2002) to retain farm anonymity) may improve the predictive power of the PDI. Despite minimal waste-water-treatment contributions to stream P loading, septic tank point sources of stream P loading are poorly quantified, and may be a significant source of subcatchment variability in P loading. On a catchment scale, hydrological factors (connectivity and redox effects) are critical to soluble P losses. Ultimately, soil type may also be used as a proxy for such factors, as it was by Daly et al. (2002); explained in the previous paragraph. Dunn and Lilly (2001) and Lilly et al. (1998) used soil type as a proxy for the relative proportions of surface and subsurface hydrological

flow pathways (Hydrology Of Soil Types; HOST). Thus, there is the potential to use soil type data, in conjunction with STP data, in simple models accounting for both P desorption potential and hydrological P loss risk. Such models could rely on large existing databases in Ireland, and other countries, enabling P loss risk to be assessed relatively rapidly and cheaply. Implications of land management practices could be linked to these models through often well-established management practice–STP relationships analysed on different soil types for specific STP tests by agricultural researchers (e.g. Culleton et al., 1999).

4.10. Conclusions

- Estimated rates of recent P application were linearly related to STP and P desorption, but the predictive power of these estimates for potential P desorption was relatively weak due to difficulties involved in gaining reliable and representative estimates of soil P loading, and due to soil specific responses. These problems are likely to reduce the accuracy of P loss modelling based on land use data.

- Dividing the soils in this study in a manner compatible with CORINE-based land use classifications found that these classifications had a significant impact on STP (Morgan P and Olsen P) and P_{feo}, but not P_w. The choice of target soil P index will have a critical impact on soil P desorption risk.

- The relationship between Olsen P and Morgan P found for soils in this study was similar to that found in other studies. Soils with high PSC, and low OM, TEB and exchangeable Ca contents had relatively higher Olsen P compared to Morgan P contents. Soil pH did not appear to be especially important in the relationship.

- DPSS calculated from ratios of oxalate-extractable P to Fe and Al was the best linear predictor of soil P desorption, and these predictive relationships applied even to soil with high pH and exchangeable Ca contents. Al_{ox} appeared to be less available for P sorption than Fe.

- Morgan P was almost as good as DPSS at predicting P desorption, although, unlike any of the other P tests, relationships with desorbable P fractions were dependent on OM content and OM-based soil group. Peat soils desorbed significantly less P than mineral soils at given Morgan P concentrations, and differences were proportionately identical for P_w DRP and TDP fractions, and P_{feo}.

- Drying soil samples reduced the predictive strength of STP-P desorption relationships, and approximately halved the P desorption differential between peat and mineral soils. This has consequences for understanding and predicting diffuse P losses where standard air-dried soil sample data are used.

- Morgan P was a significant predictor of stream DRP loads and concentrations across subcatchments of contrasting hydrology, geology and land uses, but only once the differential desorption effect of peat / mineral soil type was accounted for. There is considerable potential for developing P loss risk models based on extensive soil type and STP data sets.

CHAPTER 5

SEASONAL VARIATION IN SOIL P DYNAMICS AND P LOSS TO WATER

5.1. Introduction

The previous chapter described how the amount of P readily desorbed to water - reflective of soil P loss potential in the field - was highly dependent on STP. High sample variability, and the interference of standard soil drying procedures in the detection of seasonal variation (Pote et al., 1999a), have limited the number of studies published on seasonal variation in soil P characteristics. However, there are a number of studies which indicate that STP, especially Olsen P (Magid and Nielsen, 1992; Tate et al., 1991a), and desorbable P (Kuo and Jellum, 1987; Pote et al., 1999a; Sharpley, et al., 1995a) vary seasonally. These variations may act to change the STP-P desorption relationship, and may have important management implications (especially regarding timing of P application for example) if P losses to water are to be reduced.

This chapter analyses the results of monthly sampling of 11 soils, with the aim of identifying common seasonal and management-specific changes in soil Olsen P, P_w, and P sorption characteristics. The soils were analysed over at least one full calendar year (2002), and some for longer. Delays in construction and installation of zero-tension samplers meant that subsurface water samples were only collected over a period of 9 months, from 12 zero-tension samplers located in fields 1, 9 and 10 (see section 2.5.2). High within field variability highlights the highly localised nature (small-scale spatial variability) of factors controlling subsurface flow P concentrations, and meant that data were of little use to compare land use / STP effects. Therefore, they were used in order to detect any seasonal trends in subsurface P losses, and results are therefore included in this chapter, for comparison with seasonal variation in soil P desorption.

The main aims of this chapter were to determine whether land management practices affected seasonal variation in general soil characteristics, STP, and P (de)sorption, and to determine whether seasonal trends in soil P desorption could be related to seasonal trends in streamwater soluble P concentrations. The following literature review explores the background of natural and management-induced seasonal patterns of P fractionation in soils, and consequent impacts on STP and desorbable P measurements.

5.2. Literature review

5.2.1. Biological cycling

Soil P is in a constantly changing equilibrium, with rapid fluxes of P between different pools. Figure 5.1 is a simple schematic displaying the main P pools and transformations involved in soil biological cycling. Biological processes may immobilise P, converting it into unavailable forms of P_o – predominantly stable humus and microbial-bound P. These processes include the uptake and incorporation of P_i by plants and microorganisms. Most P in plants is in the form of phytin (inositol phosphates), sugar phosphates, phospholipids and nucleic acids. During decomposition of plant litter, microbial and enzymate-mediated breakdown solubilises much of the P present in the latter three forms, while inositol phosphates form stable complexes with Al, Fe and Ca. Inositol phosphates thus accumulate, especially in stable humus fractions, to account for up to 50% of measureableable P_o in soils, and have been found at concentrations of 460 mg P per kg soil (Stevenson, 1994). While P incorporated into microorganisms becomes immobilised, biomass P is often rapily made available to plants through excretion, either in the form of labile P_o, or mineralised P_i: microbial biomass P is thus often also referred to as labile P. Other forms of labile P are humic and fulvic acid associated P. Much of the P present in biomass has been found to be in the form of diester P (Brookes et al., 1984). Mineralsiation from labile P_o (and dissolution from labile P_i) fractions into dissolved P_i is stimulated in the vicinity of plant roots by root-excretion of acids such as as citric, oxalic, lactic and succinic acids (Stevenson, 1994), and is mediated by phytase enzymes.

Microbial P has been found to be especially important in P cycling. Tate (1984) found the microbial P content in 21 New Zealand topsoils to range from 20-80 mg P kg^{-1} soil. Brookes et al. (1984) found that up to 24% of soil P_o was accounted for by microbial P in UK grassland soils, and they estimated that microbial P cycling in these soils proceded at a rate of 23 kg ha^{-1} yr^{-1}. Seeling and Zasoski (1993) found that soil sterilisation resulted in complete depletion of P_o over time through dissolution to permanently replenished circulating $CaCl_2$ solutions in a laboratory experiment. Microbial biomass includes a wide range of organisms. Stevenson (1994) ranks the relative numbers of microbial poulations as: bacteria > actinomycetes > fungi > algae > protozoa > nematodes, with typical numbers ranging from up to 1 billion bacteria per gram down to 50 nematodes per gram. Microbial populations may compete with, and graze on, one another, but most have evolved to act

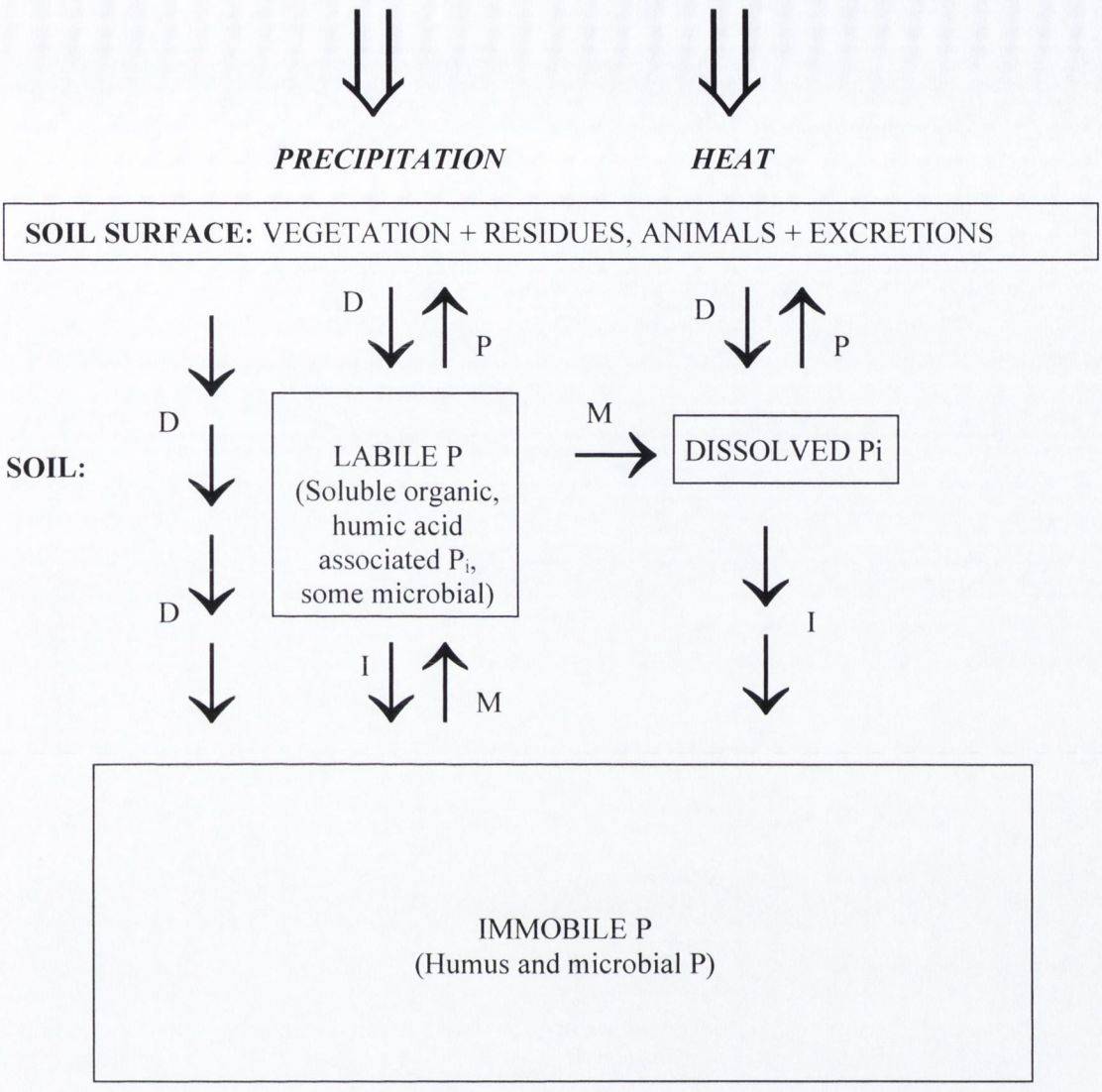
symbiotically with plants. For example, fungi develop from plant roots, and supply P extracted from an extended volume of soil to these roots. Other microbial organisms act symbiotically with plants through buffering soil available P, and result in plant and microbial activities counteracting each other in terms of P fractionation (e.g. Rubaek and Sibbesen, 1995). Earthworms and other larger animals are also important in soil P cycling, especially for their role in incorporating surface litter into the soil, and the cycling of above-ground vegetation P back into the soil through excreta.

The symbiotic relationship between plants and microbial poulations is driven by climatic factors, as indicated by the moisture and heat inputs in figure 5.1. The same conditions of wetness and warmth that encourage microbial mineralisation of organic P spur maximum plant growth and P_i uptake (Chaneton et al., 1996; Saunders and Metson, 1971; Tate et al., 1991a). Conversely, the same cool conditions under which plant growth slows and debris may accumulate encourage P immobilisation through microbial uptake (Perrott et al., 1990; Tate et al., 1991a). Thus, labile and non-labile P_o have been found to decrease over the growing season (Dormaar, 1972; Perrott et al., 1990; Sharpley, 1985b; Tate et al., 1991a). These fluxes of P through organic fractions may make very substantial quantities of P available for plant uptake. Daly (1999) noted that P_o decreased by 40% over the growing season in an Irish natural grassland soil, and Perrott et al. (1990) calculated that up to 29 kg P ha^{-1} was released from microbial P and labile P_o fractions in New Zealand grazed pasture soils over one year of study, whilst Sharpley (1985b) estimated that mineralisation contributed 20-74 kg P ha^{-1} during a growing season in a range of Texas and Oklahoma soils under different agricultural uses. Gahoonia and Nielsen (1992) studied soil directly adjacent to the root mat of a rape crop, and found that 40-46% of P uptake was apparently from less available P forms, indicating the importance of both microbial and ezymatic mineralisation. Microbial activity is influenced by a number of factors other than climatic. For example, Chauhan et al. (1979) note that C additions to soil alone may reduce soil P_i through encouraging microbial immobilisation.

Slow plant growth during cool winter conditions results in lower P uptake and the accumulation of plant debris. Perrott et al. (1990) noted a peak in earthworm activity during the autumn-winter period, and suggested that this activity incorporated plant-and animal P back into the soil as labile P_o, where it may be immobilised by the microbial population. Chaneton et al. (1996) found that the P held in surface plant debris decreased over winter and into spring. Consequently, both labile and non-labile P_o fractions have

been noted to increase over winter months. Dormaar (1972), studying Chernozem soils supporting alfalfa, found a winter increase of up to 169 mg kg^{-1} soil in total P_o, and Daly (1999) recorded a doubling of OM content at 15-25 cm depth in a non-fertilised grassland soil between late summer and December, resulting in increased P_t content. Similarly, Perrott et al. (1990) and Tate et al. (1991a) found that immobile (microbial) P_o reached maximum soil concentrations in winter, although labile P_o reached maximum soil concentrations in spring – coinciding with peaks in measured rates of soil respiration and declining soil microbial P (Tate et al., 1991a), indicating rapid soil P cycling at this time. Perrott et al. (1990) noted a secondary autumn peak in soil microbial P, stimulated by recharged soil moisture after biological-inhibiting summer soil moisture deficits. Rapid cycling of P through biomass identifies some microbial P as being in the labile pool (figure 5.1).

Some studies have related seasonal variations in soil P_o fractions, and rates of biological P cycling, to climatological patterns in temperature and precipitation. Tate et al. (1991b) found that temporal variation in climatic factors (especially rainfall) had a greater influence on soil microbial P content and activity in temperate grassland soils than P status between high and low intensity pasture fields. Perrott et al. (1990) found that potential phosphatase activity was significantly negatively correlated with soil temperature, but positively correlated with soil moisture (as was $NaHCO_3$-P_o), while potential general enzyme activities increased from spring until a November peak. Climatological variability between years also appears to affect significantly the extent and timing of soil P cycling and fractionation (Perrott et al., 1990; Shand et al., 1994; Tate et al., 1991b).



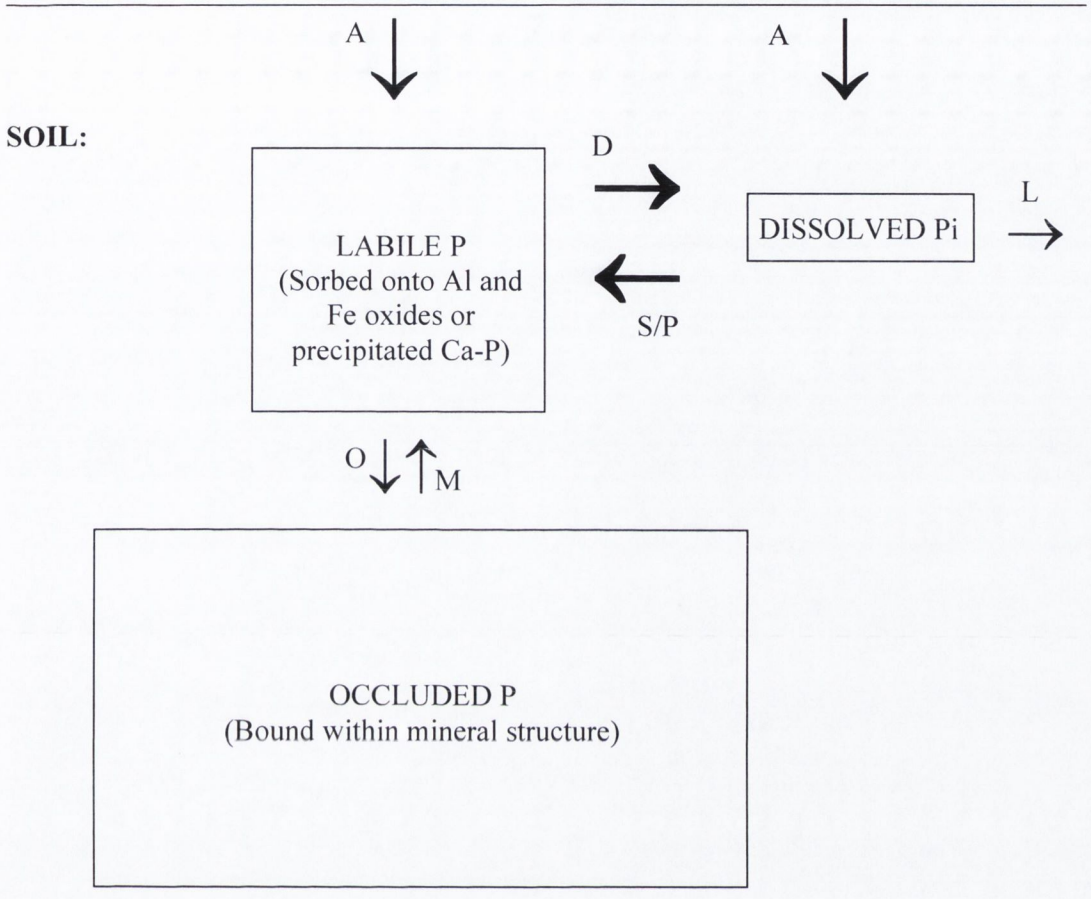
D = Decomposition (enzyme and microbial mediation) and dissolution / diffusion of animal excreted P
I = Immobilisation (microbial, fungal and earthworm uptake)
M = Mineralisation (enzyme and microbial mediation)
P = Plant (and animal) uptake / immobilisation (enzyme and fungal mediation)

Figure 5.1: A schematic diagram displaying the main drivers, transformations and fractions involved in biological soil P cycling.

5.2.2. Physico-chemical processes

Chemical processes potentially contributing to seasonal variations in soil P fraction equilibria include fertiliser P addition and physical and/or chemical mobilisation (desorption) of P_i from particulate to dissolved forms, compared with physical and/or chemical immobilisation (adsorption) of solution P_i (Rubaek and Sibbesen, 1995): see figure 5.2. Seasonal variations in these processes are not as well understood as those for biological cycling of P. Saunders and Metson (1971) noted that soil P retention (as determined by uptake of P from solution by field-moist samples) decreased as the soils dried in summer, and increased again to peak in winter. Pote et al. (1999a) also noted a decrease in P sorption from (laboratory dried) soil samples collected during the dry season compared with those collected during the wet season, and attributed this to the formation of larger Fe and Al (hydr)oxide crystals with reduced surface area for sorption during slow seasonal drying, and in the presence of less microbial biomass (compared with smaller crystals formed during rapid laboratory drying). In addition to seasonal drying processes, temperature controls the rate of chemical reactions, and Mack and Barber (1960) found that higher temperatures resulted in more P being leached out of soil, and also that temperature appeared to affect chemical species formation in laboratory incubated soils.

Bowman and Cole (1978) speculate that large proportions of non-labile P_o may in fact be P weakly bonded to organic compounds via cationic bridges, and that winter increases in available Ca noted in their Prairie study soils may encourage the formation of these bonds. Dormaar (1972) suggests that such behaviour would explain how the biomass N:P_o ratio apparently changes independently of C during winter P_o accumulation; apparently by-passing the biological mediated equilibrium. Magid and Nielsen (1992) note that seasonal changes in soil P_o and P_i fractions in Danish sandy soils were 4-40 times greater in magnitude than would be expected from N mineralisation. They suggest that P_o variation is caused by solubility changes rather than biological cycling, similarly to Blakemore (1966) who suggests that constant $CaCl_2$-P concentrations are determined by solubility products of soil P compounds. Changes in soil temperature, moisture, pH and redox potential are likely to affect the amount of P bonded with, and incorporated within, humic and fulvic acids, and may also affect the extent to which these organic acids intefere with soil P P sorption and desorption..



A = Applied fertiliser and manure P
D = Desorption from metal surfaces / dissolution from Ca phosphates (pH dependent)
L = Leaching and surface runoff losses (small)
M = Migration of occluded P to aggregate (de)sorption surfaces (slow)
O = Occlusion of sorbed P into aggregate structure (slow)
S/P = Sorption and precipitation of P to aggregate surfaces

Figure 5.2: A schematic diagram displaying the transformations and fractions involved in physico-chemical soil P cycling.

5.2.3. Soil test P variation

Agronomic data sets often provide information on long term temporal trends in soil P concentrations, as routine and research sampling usually involves collecting soils from the same fields every few years. Much less research has focused on quantifying seasonal variations in STP concentrations.

Tate et al. (1991a) found that Olsen P followed a similar trend to labile ($NaHCO_3$ extractable) P_o (and P_i) fractions in a high P status New Zealand pasture soil: declining steadily from winter through to the next autumn, before rising rapidly in autumn (both before and after P application in different years). They suggest that this increase is due to decomposition and incorporation of sheep faeces and plant residues accumulated over the summer months, and, to a lesser extent, from winter peaks in microbial P concentrations. Despite Olsen P theoretically extracting only P_i, Tate et al. (1991a) suggest that microbial P contributes up to 13% of Olsen P in winter. They found that $NaHCO_3$-P_i (very similar to Olsen P) in a similar but low P status soil followed a similar, though less pronounced pattern to $NaHCO_3$-P_i and Olsen P in the high P status soil. Seasonal variation in labile P was dominated by the P_o fraction in the low P status field. Similarly, Sharpley (1985b) found that Bray-1 STP decreased to a minimum over summer and increased to a maximum over winter in unfertilised soils. The greatest variations in Bray-1 P were, however, after fertiliser P application. In contrast, peak Olsen P concentrations in acidic brown earth soils used for root-crops, cereals and grassland were found to occur in late summer (months after P application), with minimum concentrations occurring in late winter (McDowell and Trudgill, 2000) - contradicting the pattern found by Tate et al. (1991a) under a similar temperate, maritime climate.

Watson et al. (2002) found high variability but no significant seasonal variations in Olsen P in N. Ireland grassland soils under various rates of P application. Similarly, Rubaek and Sibbesen (1995) found no seasonal variation in Olsen P in unfertilised Danish soils, but did note increases after fertiliser or manure application. In contrast, Perrott et al. (1990) recorded seasonal variations in $NaHCO_3$-P_i (very similar to Olsen P), but no peaks corresponding with P applications. Pote et al. (1999a) found that Mehlich-3 P was not significantly different in wet and dry season samples.

5.2.4. Desorbable P variation

Magid and Nielsen (1992) found that the pattern of soil solution P_i concentrations contrasted with soil P_i fractions, increasing four fold from an autumn low over a period of 6 weeks, before decreasing for the remainder of the year-long sampling period. This pattern was significantly inversely related to soil moisture content ($p \leq 0.0001$). Kuo and Jellum (1987) also noted winter maxima in P_w, which increased from low values in the early growing season, and suggest that plant uptake and pH-induced sorption changes may be responsible for this pattern. Their data showed that P_w was positively correlated with precipitation and negatively correlated with temperature. However, they analysed soils after laboratory drying, which may obscure seasonal variation in P_w (see section 2.5.1). Pote et al. (1991a) found no significant variation in P_w between dried samples collected in the wet and dry seasons, but did find that dry season P_w content in moist samples was almost twice wet season P_w content. Shand et al. (1994) also found that soil solution P concentrations from three up-land soils reached maxima in late summer and early autumn in the two years of their study. Analysing different P fractions within the soil water extracts, they noted that specific fractions displayed different seasonal trends among different soils

Saunders and Metson (1971) found that, despite plant P uptake equating to 80 mg P kg^{-1} soil in the main part of the root zone, there was little decrease in anion-exchangeable P during spring. Peaks in anion-exchangeable P and $CaCl_2$-P were noted 1-2 months after plant growth rates decreased due to soil moisture deficit, and coincided with maximum air-temperature and a decrease in soil P retention capability. They suggest that rapid cycling of soil P fractions maintains solution P_i at a relatively constant concentration. Blakemore (1966) found that the only significant variations in $CaCl_2$-P extracted from a range of lowland UK soils were after the application of fertiliser or manure P. In contrast, Garbouchev (1966) analysed soils from the same area, and found a more consistent seasonal pattern in $CaCl_2$-P and resin-exchangeable P. Whilst spring maxima were partly attributable to fertiliser P application, Garbouchev also suggests that biochemical P release was responsible for some of the increase. Decreasing growing season and increasing winter P concentrations were attributed to changing plant uptake requirements, and 're-establishing soil equilibria' over winter. Sharpley et al. (1995) found that P_{feo} was approximately three times higher in winter months compared with spring in unfertilised soils, with a gradual accumulation through the autumn. Fertilised soils showed a spring

peak in P_{feo} immediately after fertiliser application, followed by a decline over the growing season and stabilisation over the winter months. McDowell and Trudgill (2000) found a differing pattern of $CaCl_2$-P (in both moist and dried samples), noting maximum concentrations in late summer and minimum concentrations in late winter.

5.2.5. Land use effects

Probably the main direct impact of land use on seasonal P characteristics in soils is the direct application of readily available P in the form of chemical or organic fertiliser. Many studies have noted peaks in STP (Rubaek and Sibbesen, 1995; Sharpley, 1985b; Tate et al. 1991a; Watson et al., 2002), labile P fractions (Sharpley, 1985b; Sharpley, 1995; Tate et al., 1991a) and desorbable P (Blakemore, 1966; Garbouchev, 1966; Sharpley, 1985b; Sharpley, 1995) corresponding with the timing of P application, with subsequent decline over the growing season. A few of these studies suggest that P application is the only parameter that affects seasonal variations in soil P characteristics (Blakemore, 1966; Rubaek and Sibbesen, 1995). There is evidence to suggest that P application may indirectly affect longer-term seasonal P cycling in soils. Tate (1984) and Power et al. (1995) suggest that P_o accumulates with P application until it reaches a maximum threshold level. Above this level pysico-chemical processes presumably account for the fate of applied P. P applications to P deficient soils may result in more pronounced seasonal cycling of organic and available P in these soils as organic P pools increase. For example, Tate et al. (1991a) and Power et al. (1995) found large microbial P increases after sustained P application, with microbial P uptake approximately equal to plant P uptake.

However, Sharpley (1985b) and Sharpley et al. (1995a) indicate that P application actually alters the dominant processes involved in P availability, from organic cycling and phosphatase activity in unfertilised soils, to sorption / desorption reactions of P_i in fertilised soils. Similarly, Daly (1999) and Ron Vaz et al. (1993) suggest that P application suppresses biological cycling, partly through concentrating P cycling in a consequently less extensive (shallower) root zone. Daly (1999) and Heckrath et al. (1995) attribute reduced soil P contents to increased plant uptake stimulated by N application. Other studies have indicated that P application has little or no impact on the pattern or extent of P cycling. Saunders and Metson (1971) suggest that soils are able to maintain high P_i supply for plant uptake without P application through biological cycling, though maybe this is dependent

on relatively high P status achieved or maintained through past P applications. Perrott et al. (1990) noted no significant differences in biological P cycling after at least five years without P application, and Tate et al. (1991a) found that the measured microbial P 'flush' in spring was not appreciably affected by P application. Tate et al. (1991b) conclude that seasonal climatic variations have a greater impact on P cycling than P additions.

Some of the studies of seasonal soil P cycling published include comparisons between different land uses. Daly (1999) studied P and OM dynamics under grazed and fallow grassland in SE Ireland. Whilst OM content doubled at 15-25 cm depth in the non-grazed natural grassland plots between late summer and December, with a 40% decrease in P_o over the growing season, OM content remained almost constant in the soil under grazed grassland, with a small summer increase in surface OM just after a period of grazing. Others have found similar seasonal patterns in available P and P desorption between soils supporting root crops, cereals and grassland (McDowell and Trudgill, 2000) and between arable, grassland and pasture soils (Magid and Nielsen, 1992). Sharpley et al. (1995a) found similar seasonal patterns in P_{feo} and labile P in soils under native grass, sorghum, wheat and peanut. However, McDowell and Trudgill (2000) did find that forest soils behaved differently, with no noticeable seasonality in Olsen P or $CaCl_2$-P.

5.3. Methodology

Eleven soils were collected on a monthly basis for the investigation of seasonal variation, over at least the duration of 2002, and for longer in a number of instances (see section 2.2.1). These soils (reference numbers 1-11) cover a range of types (table 2.6), from a Fibric Histosol (soil 6) to a Renzic Leptosol (soil 4), and land uses (table 2.5), from silage production (e.g. soil 2) to forestry (soil 7). Moist samples of these soils were analysed for moisture content, pH, Olsen extractable MRP and TP fractions, P_w DRP and TDP fractions, and sorption from solution containing 5 and 30 mg P l^{-1}, while dried samples of the same soils were analysed for TOC and TN (as described in 2.2.3). Note that the soil-solution ratios used in P_w and sorption analyses were half those used for 'spatial' (March 2002, 2003) samples, due to misinterpretation of BUFFER protocol. Therefore, and because March 2002 spatial samples were dried prior to analyses, data here are not directly comparable to those data.

Additionally, results in this chapter are left expressed in their original weight-derived units of mg P kg^{-1}. This is for two reasons. Firstly, OM content was not measured on monthly samples (though it may have been possible to use TOC content as a reasonably reliable indicator of OM content). Therefore, and because BD is itself estimated from OM content (section 2.2.5), it is more accurate for this chapter to leave results expressed on a weight basis. Secondly, temporal rather than among-soil variation is the focus of this chapter, making soil BD differences less important. Contrasting soil BD may still be important in comparing the absolute magnitude of changes in P concentrations with timeamong soils, but not the relative changes (which determine the statistical significance of temporal trends and associations).

The impact of sample variability is potentially much greater for this chapter compared with other chapters, because samples collected at different times from each soil are assumed to accurately represent mean characteristics at each time for each soil. Estimates of (spatial) sampling accuracy determined from replicate composite sampling (section 2.2.4) are used only as a qualitative guide for analyses of individual soil trends (due to possible overestimation of variability between temporal samples).

In order to conduct statistical analyses on temporal data, and compare soil P characteristics with potential influencing factors, all soil P characteristics were listed against soil

reference number, general soil characteristics, month, season, mean temperature and mean daily effective precipitation in the month and week preceding the first day of subsequent monthly sampling (sampling usually conducted over 2-3 days), and the (recent) presence of grazing animals. Season was divided into winter (December, January and February), spring (March, April, and May), summer (June, July and August) and autumn (September, October and November). Mean temperatures in the week and month preceding sampling were calculated from averaging mean daily temperatures over the week or four weeks prior to the first day of subsequent sampling, and mean effective precipitation over the preceding month and week were calculated by dividing monthly potential evaporation figures by the number of days in that month, subtracting this from daily precipitation for each day during that month, and averaging these values for the week or four weeks preceding the first day of subsequent sampling. Meteorological data were obtained from the Met Eireann weather station in Claremorris (52 48'43.8''N, 8 58'17.4''W), in the eastern extreme of the Mask catchment (see figure 1.1). The presence of grazing animals was determined from the presence of, or evidence for the recent presence of, grazing animals as noted in the sample diary (table 5.3: see section 2.2.1 for discussion of contents).

All results, some dating back to September 2001, are displayed in graphic format. However, data gaps due to the absence of samples from a number of sites and incomplete analyses (see section 2.2.1 for details), before January 2002 mean that only data from samples collected in 2002 were analysed statistically using repeated measures analyses to determine statistically significant common trends in soil characteristics amongst all soils. *Post-hoc* least significant deviation analyses were used where discrete (e.g. month and season) independent variables were compared, and the sign of the coefficient of variation regression equation used to determine positive or negative relationships (covariation) for continuous independent variables (e.g. moisture).

Concentrations of TDP in subsurface water samples collected between October 2002 and June 2003, from 8-21 and 51–63 cm depths using zero-tension samplers, are also presented here and analysed qualitatively (see section 2.4.2 for details of sampler installation). Subsurface water samples were collected once a month from the samplers, filtered immediately through 0.45 μm membrane filters, stored at 4°C, and analysed within 3 days of collection for P_w TDP only (according to the same digestion and molybdate analyses procedures used for soil water extracts).

5.4. Soil Results

5.4.1. Meteorological and climatic conditions

Meteorological data for 2002 were obtained from the Met Eireann weather station in Claremorris. This is the only weather station within the catchment, located at: 52° 48.73' N, 8° 58.29' W and at 79 m above sea level, but may not be fully representative of conditions further west in the catchment, especially over the Partry Mountains (see section 1.5.2). Precipitation is likely to be higher, and temperatures lower, in this area (maximum height 682 m above sea level: see figure 2.2), although the relative distributions (i.e. monthly patterns) of precipitation and temperatures are likely to be similar.

Figure 5.3 displays daily meteorological conditions (mean temperature and total precipitation) for the duration of 2002, the year over which the 11 soils were sampled on a monthly basis. Monthly mean temperature and total precipitation are displayed in table 5.1, which compares them against the climatic mean averaged from meteorological data between 1961 and 1990. Monthly precipitation totals displayed in table 5.1 indicate that relatively high total precipitation was reasonably well distributed throughout 2002, though monthly totals were generally higher in the autumn and winter months than the spring and summer months: varying from 174 mm in February to 46 mm in July. Figure 5.3 indicates that significant rainfall events were frequent throughout the year, with no particularly long dry spells apparent. Temperature displayed a more progressive and marked seasonal trend, although variability was low compared to less temperate climates. Temperatures increased steadily from January to August, prior to decreasing again towards December. The lowest mean monthly temperature of 5.3°C occurred during December, while the maximum mean monthly temperature of 15.1°C occurred during August.

Comparison with average climatic data, also displayed in table 5.1, indicate that total precipitation was close to the climatic average in 2002 (1170 compared to 1143 mm climatic mean), but was less evenly distributed than the climatic average in 2002: there is a substantially greater range in 2002 monthly totals than average climatic monthly totals. In line with the general climatic trend over the past few decades, mean monthly temperatures during 2002 were almost exclusively higher than the climatic average from 1961 to 1990, and this is particularly noticeable for January and February (2002 means of 6.8 and 6.4°C compared with climatic averages of 4.3 and 4.5°C for January and February

respectively). Otherwise, the general trend in temperatures over 2002 was typical of the climatic average.

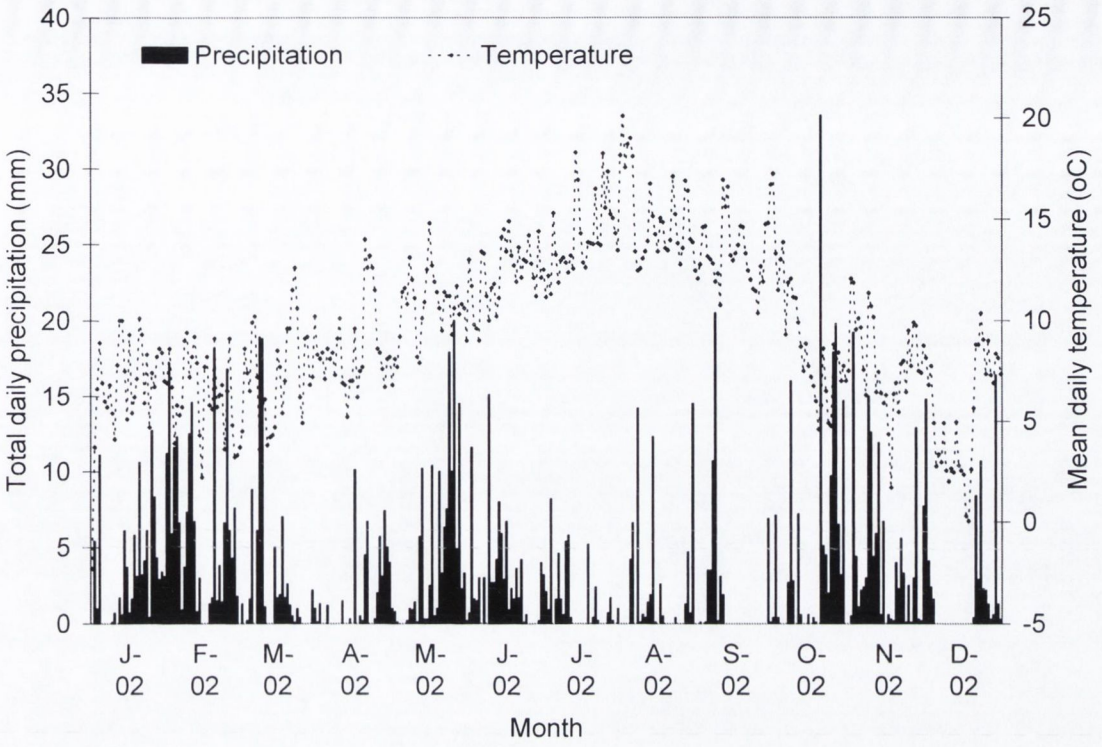


Figure 5.3: Daily total precipitation and mean temperature, recorded by Met Eireann at Claremorris meteorological station during 2002.

Table 5.1: A comparison of 1961-90 climatic data with 2002 meteorological data. (Mean) Total precipitation and daily temperature are displayed for each month.

Month	Total monthly Precipitation (mm)		Mean monthly Temperature (°C)	
	Mean for 1961-90	2002	Mean for 1961-90	2002
Jan.	120.8	111.9	4.3	6.8
Feb.	83.2	174.2	4.5	6.4
Mar.	95.5	83.1	5.9	7.3
Apr.	62.3	53.9	7.6	8.6
May	77.9	136.6	10.0	10.6
Jun.	71.1	88.8	12.6	12.0
Jul.	63.8	46.2	14.3	14.0
Aug.	96.6	66.5	14.0	15.1
Sep.	104.3	50.6	12.1	13.4
Oct.	124.6	155.2	9.8	8.9
Nov.	118.8	133.0	6.2	8.0
Dec.	124.1	70.0	5.1	5.3
Total / av.	**1143.0**	**1170.0**	**8.9**	**9.7**

5.4.2. General soil characteristics

Table 2.1 highlights the problem of wide confidence limits (CLs) in the estimation of field-scale soil characteristics from composite sample analyses, due to inherent soil heterogeneity. However, as mentioned in section 2.2.4, these estimated CLs may in fact overestimate the random variability between samples collected at different times from the same field, due to the consistent systematic sampling pattern used. Nonetheless, it is apparent that random sample variability does interfere with the identification of seasonal trends in a number of instances. For example, the sample taken from soil 6 in April appears to have an anomalously low TOC content compared with other samples from that soil (Figure 5.5a), and table 2.1 displays the very high 95% CLs estimated for characteristics of that same soil from composite sample replicates. Reasons for high CLs are explored in section 2.2.4, but for peat soil 6 are mainly related to 'contamination' with underlying mineral material where sample cores were collected from shallow patches of peat.

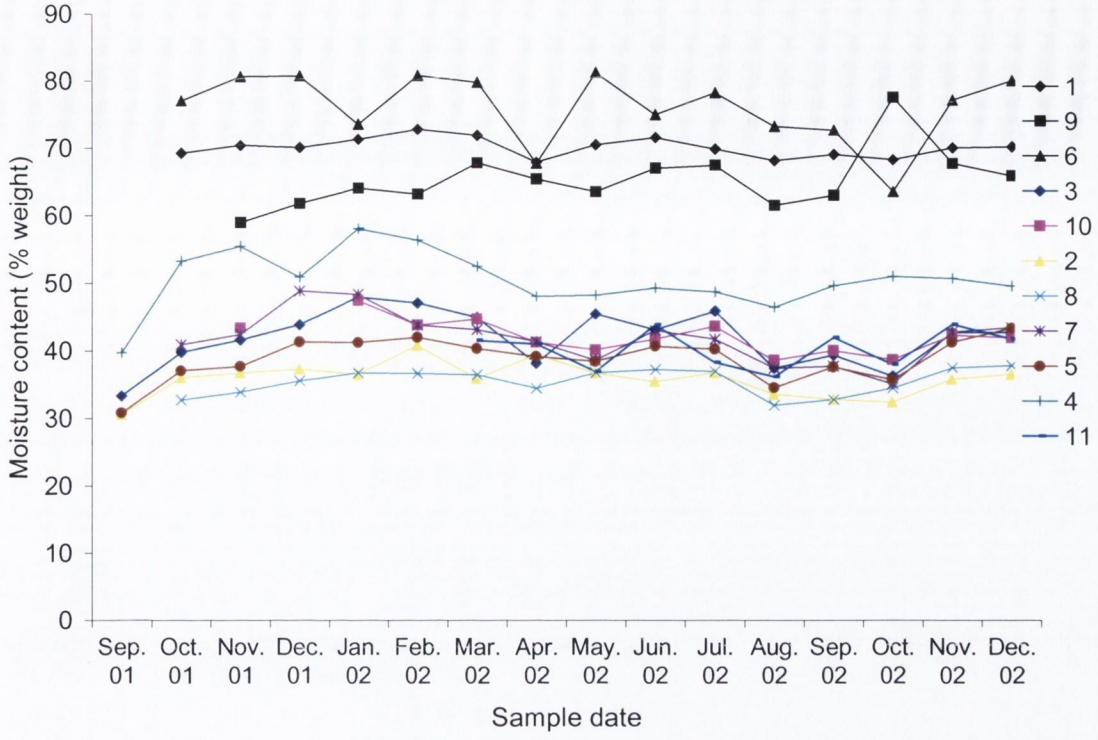
Despite the problem of sample variability for some soils, an adequate number of soils were analysed to enable repeated measures analyses on monthly samples to detect significant common trends in soil characteristics over the period studied (tables 5.2 and 5.4). Table 5.2 displays the results of repeated measures analyses on general soil characteristics (Log-transformed TN, TOC and moisture content, and pH), testing for significant differences between months and seasons, and co-variance with average meteorological conditions during the week and month prior to sampling. General soil characteristics were also analysed against soil moisture content, which may be taken as a convenient proxy for recent meteorological conditions: soil moisture contents were very strongly positively related to preceding effective precipitation, and even more strongly negatively related to preceding mean temperature (both in the preceding week and month to sampling; $p \leq 0.0001$; table 5.2).

Moisture contents in the 11 soils proved to be significantly different among months and seasons ($p \leq 0.0001$). *Post-hoc* LSD analyses indicated that seasonal differences were limited to significantly higher soil moisture contents in winter compared with summer, autumn ($p \leq 0.0001$ in both instances) and spring ($p = 0.0015$), as indicated from visual analyses of figure 5.4a. Soil TN contents followed a similar pattern to moisture contents (figure 5.4b), and were also highly significantly positively related to effective precipitation

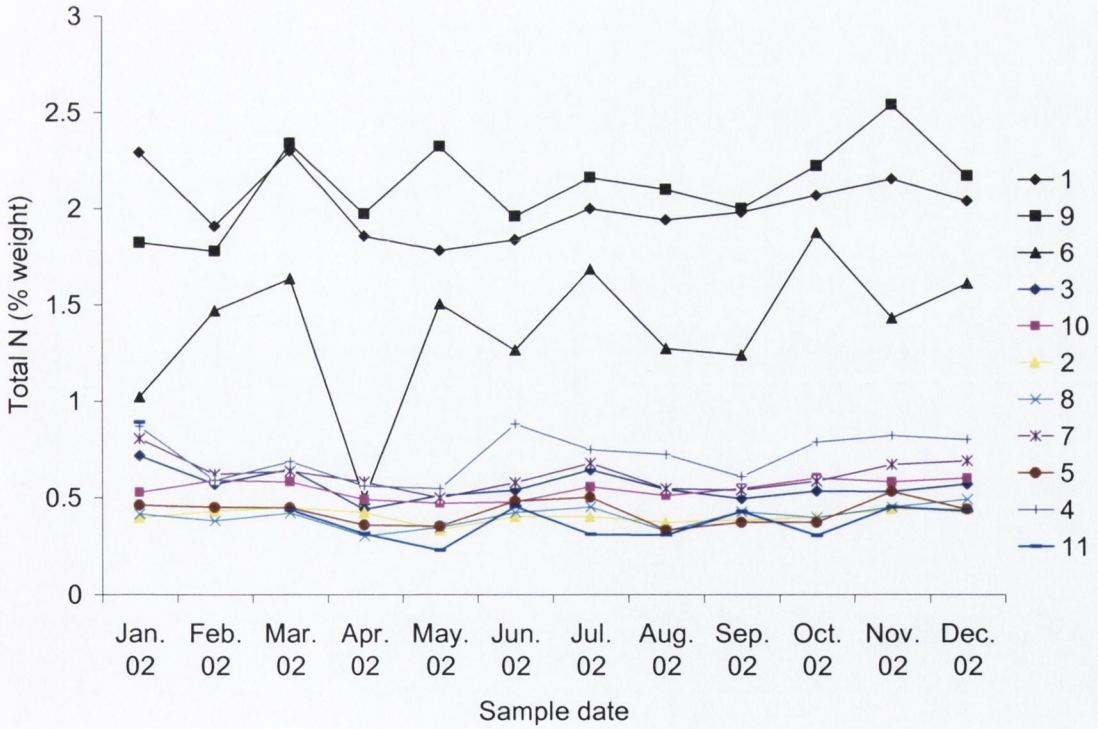
and negatively related to mean temperature in the preceding week and month to sampling. However, the relationship with preceding mean temperature was considerably less strong than with preceding effective precipitation (e.g. for the preceding month, $F_{1,118} = 5.79$ and 19.09, $p = 0.018$ and ≤ 0.0001 for mean temperature and effective precipitation). Moisture content itself is the variable that was most strongly related to TN variability in all soils ($F_{1,118} = 53.81$, $p \leq 0.0001$). However, TN seasonal variation deviated slightly from that of moisture content, with spring minima soil TN contents that were significantly lower than winter ($p = 0.0004$) and autumn ($p = 0.0104$) contents, and borderline significantly lower than summer contents ($p = 0.060$).

Table 5.2: Results (*F* values in bold, *p* values underneath) of repeated measures analyses on general soil characteristics to determine the significance of temporal variation, and co-variation with soil and climatic factors ((-) identifies negative covariance, where significant).

	df	TN	pH	Moisture	TOC
Month	11,108	**5.01**	**2.79**	**8.73**	**1.07**
p		≤0.0001	0.0031	≤0.0001	0.3945
Season	3,116	**4.80**	**6.60**	**10.97**	**0.60**
p		0.0034	0.0004	≤0.0001	0.6164
Monthly eff. precip.	1,118	**19.09**	**7.83**	**31.20**	
p		≤0.0001	0.0060	≤0.0001	
Monthly mean T.	1,118	**(-) 5.79**	**(-) 8.52**	**(-) 66.99**	
p		0.018	0.0042	≤0.0001	
Weekly eff. precip.	1,118	**28.27**	**7.01**	**30.93**	
p		≤0.0001	0.0092	≤0.0001	
Weekly mean T.	1,118	**(-) 6.05**	**(-) 6.35**	**(-) 45.98**	
p		0.0154	0.0131	≤0.0001	
Moisture	1,118	**53.81**	**1.91**		
p		≤0.0001	0.1701		



(a)



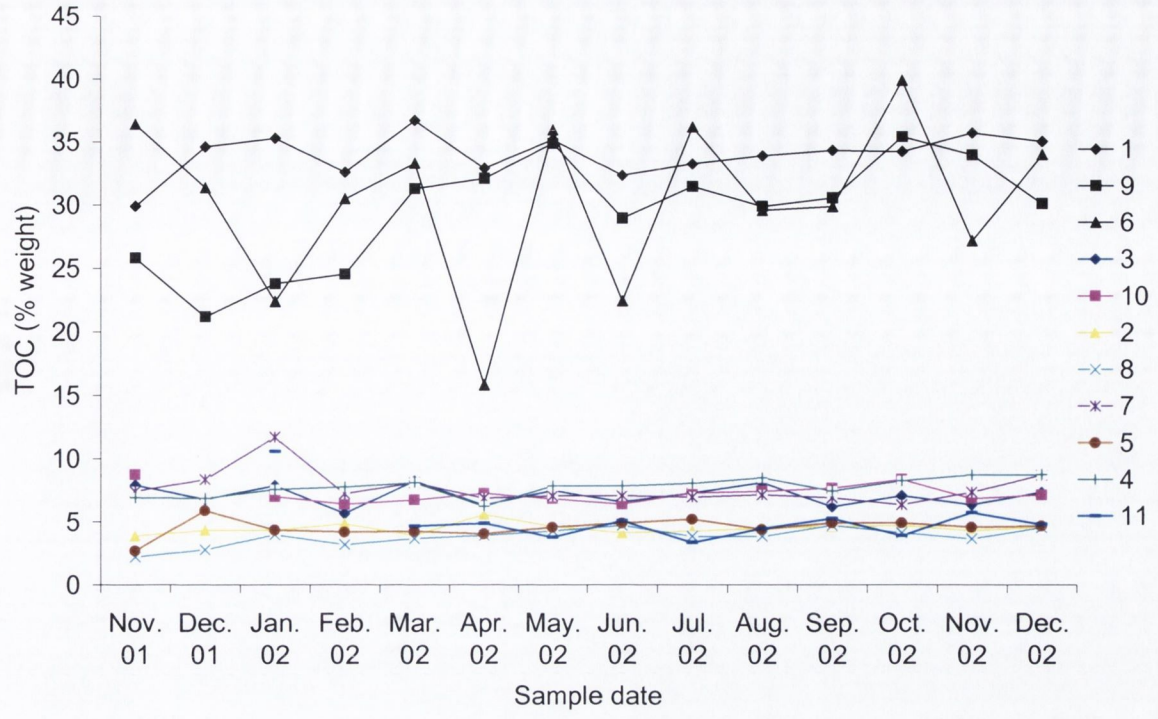
(b)

Figure 5.4: Line graphs displaying patterns of (a) moisture content and (b) total N (TN) content in monthly collected samples of soils 1-11 (peat soils 1,6 and 9 in black and listed first: then soils listed according to P status throughout).

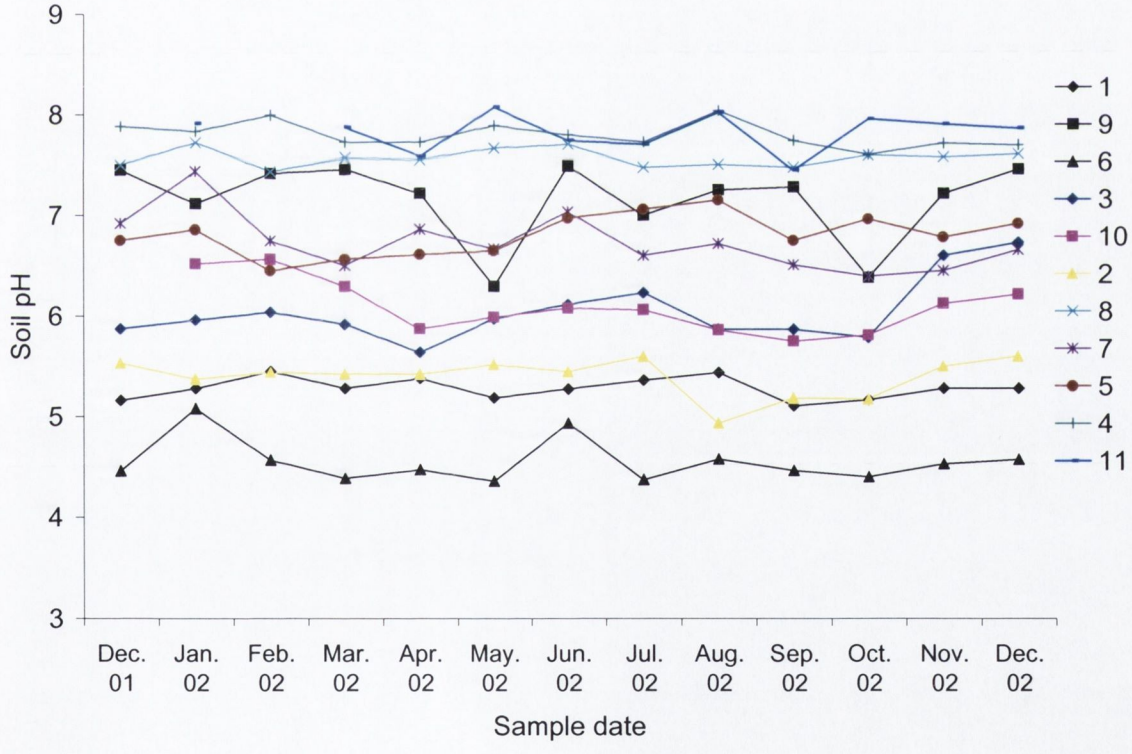
Figure 5.5a indicates that soil TOC content remained similar throughout the sampling period for the mineral soils, though varied more for the peat soils. The variation apparent in peat soil 6 appears erratic and random however, and is probably explained by high sample variability for this soil due to mineral 'contamination' as mentioned above and in section 2.2.4. Peat soil 9 displayed a more progressive pattern of variation, with lower values apparent from November 2001 to February 2002. Repeated measures analyses on TOC contents in all 11 soils found that, on average, they did not vary significantly between months ($p = 0.39$) or seasons ($p = 0.62$) (table 5.2).

It is difficult to distinguish any consistent common trends in soil pH among the 11 monthly-sampled soils from figure 5.5b, but repeated measures analyses found that it did vary significantly between months and seasons ($p = 0.002$ and 0.0003 respectively; table 5.2). Variation was significantly ($p \leq 0.01$) positively related to effective precipitation in the preceding month and week, and significantly negatively related to mean temperature over the preceding month and week ($p \leq 0.01$ and $p = 0.013$ respectively), although it was not significantly related to soil moisture content. *Post-hoc* LSD analyses indicated an unusual seasonal trend in pH, with lower values in autumn than in winter and in summer ($p \leq 0.0001$ and $p = 0.011$ respectively), and also in spring than in winter and in summer ($p = 0.0007$ and 0.049 respectively).

Repeated measures analyses were also used to test for significant relationships between the general soil characteristics which displayed significant temporal variation and the (recent) presence of grazing animals as recorded in the sample diary (table 5.3; see section 2.2.1 for details). The results were insignificant for all general characteristics except moisture content ($F_{1,118} = 4.62$, $p = 0.034$) and are therefore not displayed. *Post-hoc* LSD analyses indicated that soil moisture contents were significantly lower when grazing animals were present.



(a)



(b)

Figure 5.5: Line graphs displaying patterns of (a) total organic C (TOC) content and (b) pH in monthly collected samples of soils 1-11.

Table 5.3: Management practices on sampled fields noted on sampling occasions. Cow (C) and sheep (S) grazing – intensive in bold, *not during sampling but evidence of recently in italic* - Fertilizer application (F), recent flooding (f), lime application (L), manure application (M) and silage cut (Si). See section 2.2.1 for details of data collection.

Soil	17.08.01	16.09.01	15.10.01	17.11.01	18.12.01	21.01.02	19.02.02	20.03.02	16.04.02
1	C grazing	C grazing	No grazing	No grazing	*C grazing*	No grazing	No grazing	No grazing	No grazing
2	No grazing	Si, C grazing, F	C grazing	C grazing	No grazing	No grazing	No grazing	No grazing	No grazing
3	No grazing	No grazing	No grazing	S grazing	No grazing	No grazing	No grazing	**C + S grazing***	**C + S grazing***
4	S grazing	No grazing, L	S grazing	S grazing	No grazing	No grazing	No grazing, M	No grazing	No grazing
5	No grazing	No grazing	S grazing	S grazing	No grazing	No grazing	No grazing, M	No grazing	No grazing
6			S grazing	S grazing	S grazing	S grazing	f	S grazing	No grazing
7				Disturbance	Disturbance	Disturbance	Disturbance		
8			No grazing	No grazing	No grazing	No grazing	No grazing	No grazing	No grazing
9				No grazing	No grazing	No grazing	No grazing, f	No grazing	No grazing
10				C grazing		No grazing	No grazing	No grazing	No grazing
11						No grazing		No grazing	No grazing
Notes								*~20 L.U./ha	Rain after dryness

Soil	13.05.02	11.06.02	08.07.02	06.08.02	07.09.02	02.10.02	17.11.02	14.12.02
1	No grazing	No grazing	*C grazing*	*C grazing*	*C grazing*	*C grazing*	No grazing	No grazing
2	No grazing	No grazing	Si, F	*C grazing*	No grazing	No grazing	No grazing	No grazing
3	S grazing	S grazing	S grazing	S grazing	No grazing	No grazing, F	No grazing	No grazing
4	S grazing	No grazing	Si	S grazing	No grazing	No grazing	No grazing	No grazing
5	S grazing	S grazing	No grazing	*S grazing*	S grazing	S grazing	**S grazing**	*S grazing*
6	S grazing	S grazing	S grazing	S grazing	S grazing	*S grazing*	S grazing	S grazing
7								
8	No grazing	No grazing	Si, F	*C grazing*	*C grazing*	C grazing	No grazing	No grazing
9	No grazing	No grazing	No grazing	*C grazing*	*C grazing*	*C grazing*	No grazing	*C grazing*
10	No grazing	No grazing	No grazing	*C grazing*	*C grazing*	*C grazing*	*C grazing*	No grazing
11	No grazing	No grazing	No grazing	No grazing	No grazing	No grazing	*C grazing*	*C grazing*
Notes	Rain after dryness				Heavy rain after dryness			

5.4.3. Olsen extractable P fractions

As with general soil characteristics, seasonal patterns of Olsen extract P fractions appear to be obscured by high sample variability. However, figure 5.6 indicates that general seasonal trends were relatively consistent in pattern among all soils, and followed a similar pattern for both Olsen P and Olsen MUP fractions. Maximum Olsen P contents occurred in January (mean of 29.6 mg P kg^{-1}), and decreased over spring, remaining low (mean below 23 mg P kg^{-1}) from May through to December, except for an increase in October (mean of 26.1 mg P kg^{-1}). There was an apparent dip in September Olsen P contents common to a number of soils, and the mean content was at its lowest (19 mg P kg^{-1}) during this month. Variations in Olsen P contents generally appeared to be greater for the high Olsen P content soils (i.e. soils 2, 3 and 10). Repeated measures analyses confirmed that both Olsen P, and in particular Olsen MUP, differed significantly among months (p = 0.0012 and $\leq$ 0.0001 respectively; table 5.4) and seasons (p = 0.009 and $\leq$ 0.0001 respectively). *Post-hoc* LSD analyses indicated that Olsen P contents were higher in winter (p = 0.005), spring (p = 0.002) and autumn (p = 0.029) than in summer.

Figure 5.6 indicates that Olsen MUP (and Olsen TP) followed a similar, though more pronounced, trend to Olsen P. The main difference in seasonal variation between Olsen MUP and Olsen P was that Olsen MUP had increased more towards its peak January content by December (all soil mean of 39.5 mg P kg^{-1} in December compared with 41.7 mg P kg^{-1} in January). Olsen MUP rapidly declined to a mean of 27.7 mg kg^{-1} in April, and reached a minimum of 26.9 mg kg^{-1} in June. *Post-hoc* LSD analyses confirmed the apparent trends displayed in figure 5.6, with significant differences in Olsen MUP contents found between all seasons ($p \leq 0.05$) except between spring and summer. However, despite the greater recovery into autumn than is evident with Olsen P, Olsen MUP contents remain significantly lower in autumn than in winter, though this difference is less statistically strong (p = 0.015) than differences between other seasons ($p \leq 0.001$).

Repeated measures analyses results displayed in table 5.4 show that while Olsen P was only significantly negatively related with mean temperature over the preceding month (p = 0.009) and week (p = 0.049) to sampling, Olsen MUP was strongly negatively related to mean temperature and positively related to effective precipitation over the preceding month (p = 0.0003 and $\leq$ 0.0001 respectively) and week (p = 0.0003 and $\leq$ 0.0001

respectively) prior to sampling. Olsen MUP (but not Olsen P) was also significantly positively related to soil moisture content ($p = 0.0023$), and even more strongly positively related to soil TN content ($p \leq 0.0001$) over the year. Neither Olsen fraction was significantly related to temporal pH trends.

The similar seasonal trend in both Olsen fractions is amplified when these fractions are summed as Olsen TP (figure 5.6). Olsen TP was measured in a number of soils since September 2001, but Olsen P was not measured accurately before January 2001 due to problems with humic colour interference (see section 2.2.3). In addition, laboratory error meant that December 2001 Olsen extracts were incorrectly analysed, resulting in a data gap for that month. However, the pre-January 2002 data presented in figure 5.6 generally confirm the seasonal trend observed over 2002. The autumn increases did seem to be more sudden in 2001 than 2002, with large increases in sample Olsen TP contents between October and November.

Some deviation from the general seasonal trend by particular soils may be attributable to management practices, as opposed to deviation derived from sample variability. The impact of management practices may be qualitatively compared using data contained in the sample diary (table 5.3), which includes visual observations during sampling regarding the presence, or evidence of the recent presence, of grazing animals and accounts of fertiliser / lime applications by farmers (section 2.2.1). The (recent) presence of grazing animals was included as an independent variable in repeated measures analyses for all soil P characteristics (as it was for general soil characteristics; section 5.4.2). Results of these analyses, presented in table 5.4, indicate that the presence of grazing animals was not significantly associated with either Olsen P fraction, though was not far from being associated significantly with Olsen P ($p = 0.069$). A peak in soil 3 Olsen P content in April (figure 5.4) may be attributable to extremely intense grazing (table 5.3) on this soil during the months of March and April (the equivalent of approximately 20 livestock units per hectare were counted).

A peak in soil 5 Olsen P content in February (figure 5.6) corresponded with the light application of manure, not long prior to that sampling date, on parts of the field from which that soil was sampled. A small amount of manure was applied to a small area of field 4, but there was no corresponding increase in soil content of either Olsen P fraction. It is known that fertiliser was applied to soil 2 during mid to late July, after the first silage cut,

at a rate of approximately 26 kg P ha^{-1}, although there was only a small increase in August Olsen P. There was also a silage cut on soil 4 and 8 fields, but no fertiliser was applied to these fields. Figure 5.6 displays large decreases in Olsen P between August and September for the high P content soils 2, 3 and 10: for soil 2, this corresponded with N application. Also, some soils were sampled after heavy rainfall (20 mm) during sampling (on September 8th; see figure 5.3), following a relatively long, dry period (this rainfall was not recorded in the preceding week effective precipitation statistics, which were collated for the week prior to the *first* day of subsequent sampling). Unfortunately, there is no record of which soils were collected before and after the rainfall.

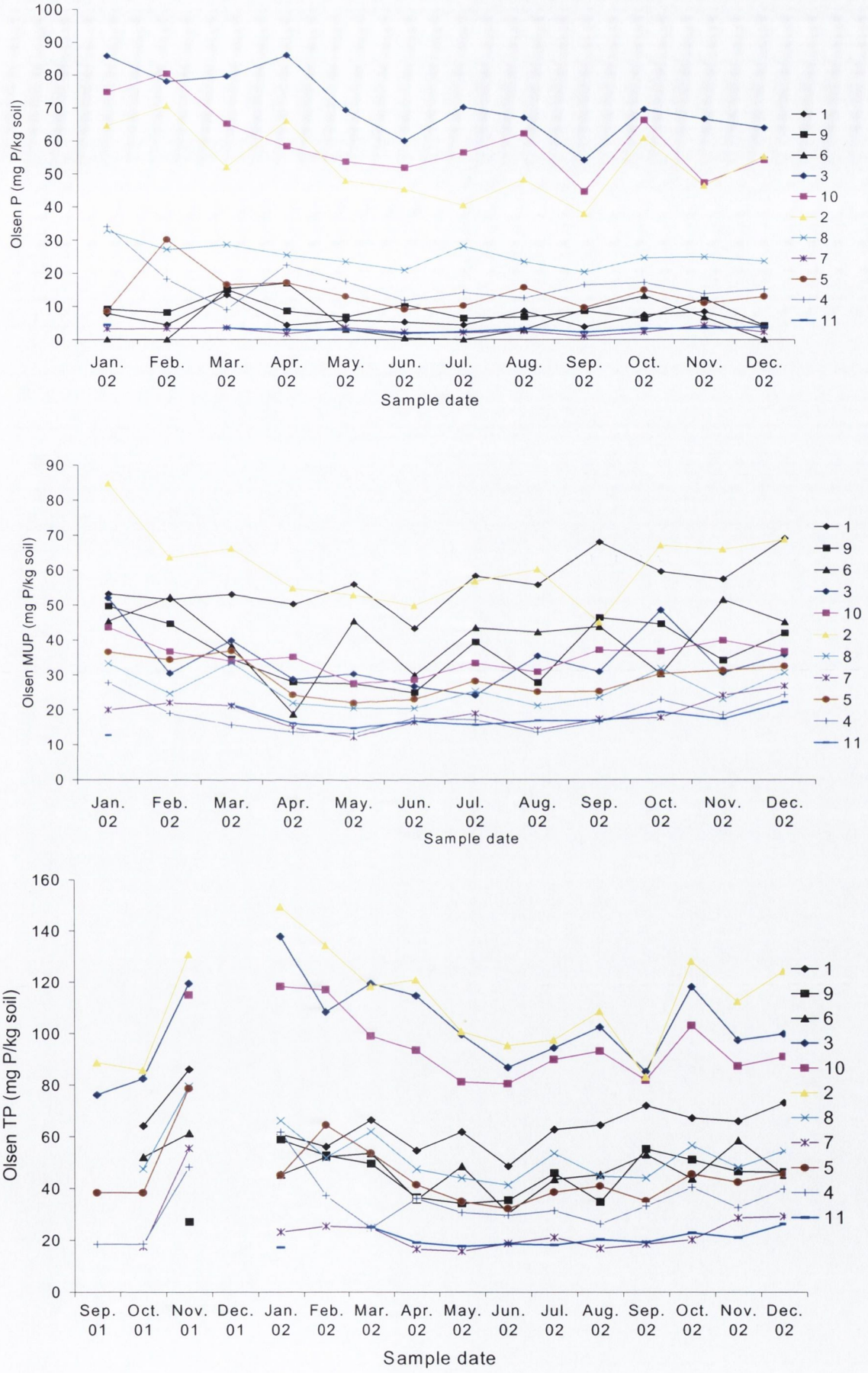


Figure 5.6: Line graphs displaying monthly variation in Olsen -P, -molybdate unreactive P (MUP) and -total P (TP) fractions for samples collected from soils 1-11.

Table 5.4: Results (*F* values in bold, *p* values underneath) of repeated measures analyses on soil P characteristics to determine the significance of temporal variation, and co-variation with general soil characteristics, climatic factors and the presence or absence of grazing animals ((-) identifies negative covariance, where significant).

	df	Olsen P	Olsen MUP	PwDRP	PwDMUP	Sorption
Month	11,108	**3.11**	**9.08**	**4.56**	**16.60**	**2.18**
p		0.0012	≤0.0001	≤0.0001	≤0.0001	0.0204
Season	3,116	**4.06**	**17.90**	**3.41**	**13.29**	**3.25**
p		0.0088	≤0.0001	0.0199	≤0.0001	0.0243
TN	1,118	**0.09**	**17.98**	**1.60**	**4.98**	**(-)9.67**
p		0.7655	≤0.0001	0.2077	0.0275	0.0023
Moisture	1,118	**0.40**	**9.74**	**2.38**	**1.41**	**(-)11.51**
p		0.5286	0.0023	0.1254	0.2371	0.0009
pH	1,118	**0.68**	**0.19**	**(-)9.02**	**0.66**	**2.37**
p		0.4016	0.6675	0.0033	0.4191	0.1267
Monthly eff. precip.	1,118	**1.31**	**12.63**	**0.69**	**0.42**	**(-)3.82**
p		0.255	0.0005	0.4092	0.5174	0.0529
Monthly mean T.	1,118	**(-) 6.99**	**(-) 13.61**	**1.61**	**10.42**	**12.78**
p		0.0094	0.0003	0.2063	0.0016	0.0005
Weekly eff. precip.	1,118	**0.69**	**17.28**	**(-) 8.19**	**0.10**	**0.84**
p		0.4064	≤0.0001	0.005	0.7472	0.3610
Weekly mean T.	1,118	**3.94**	**(-) 14.25**	**0.20**	**5.12**	**12.86**
p		0.0496	0.0003	0.6574	0.0255	0.0005
Grazing	1,118	**(-) 3.37**	**0.01**	**0.69**	**13.88**	**0.44**
p		0.0689	0.9116	0.4073	0.0003	0.5079

5.4.4. Water-extractable P fractions

Results for all water desorbable P fractions displayed high variability among months, some of which may be attributable to sample variability (table 2.1), and trends displayed in figure 5.7 appear to vary among soils. As with Olsen extractable P fractions, P_w displayed highly significant monthly variation that appeared to be greater for the MUP fraction than the DRP fraction. Figure 5.7 indicates that P_w DRP variation was dominated by high P desorption soils 3 and 10, more especially soil 3. Repeated measures analyses confirmed that both monthly and seasonal variations were significant for P_w DRP and MUP fractions, and that differences were more highly significant for P_w MUP than DRP fractions ($F_{11,108}$ =

16.60 and 4.56, $p \leq 0.0001$, respectively). It is difficult to determine a common pattern of seasonal variation for P_w DRP from figure 5.7, but *Post-hoc* LSD analyses found that soil P_w DRP contents were significantly lower in winter compared with spring ($p = 0.004$), summer (0.012) and autumn ($p = 0.027$).

Variation in P_w MUP contents was more even across all soils, with the greatest variation displayed by high P_w MUP content soil 7. A large increase in forest soil 7 P_w (TDP) between May and June was dominated by variation in the (dominant) MUP fraction, which increased from 2.5 to 6.0 mg P kg^{-1} over that month (figure 5.7). A number of soils displayed dips in September 2002 P_w content, with subsequent increases in October or November depending on the soil, followed by a general decrease into December. Figure 5.7 indicates that P_w MUP contents were lowest in winter, and increased through spring to relatively high contents during summer and autumn, although seasonal trends were obscured slightly by high inter-monthly variability. These general trends were confirmed by *post-hoc* LSD analyses which found that, as with P_w DRP contents, P_w MUP contents were significantly lower during winter than during spring ($p = 0.024$), summer ($p \leq 0.0001$) and autumn ($p \leq 0.0001$), but also that they were significantly lower during spring than during autumn ($p = 0.010$) and summer ($p = 0.0009$). As with Olsen P fractions, data for P_w DRP and MUP contents prior to January 2002 are suspected to be unreliable because of a different molybdate reagent initially used to determine DRP in water extracts (see section 2.2.3). However, comparison of reliable P_w TDP data prior to January 2002 indicate that autumn 2001 P_w (TDP) contents were relatively low (figure 5.7) compared with autumn 2002 contents, for the soils where comparison was possible.

The slightly contrasting patterns of variation in the two P_w fractions appear to be related to different soil and meteorological characteristics. Repeated measures results displayed in table 5.4 show that neither fraction was significantly related to soil moisture content, though P_w MUP was significantly positively related to soil TN content ($p = 0.028$) and P_w DRP was significantly negatively related to pH ($p = 0.003$). Neither fraction was significantly related to effective precipitation over the preceding month, although P_w DRP was significantly related to precipitation over the preceding week ($p = 0.005$). P_w MUP was significantly related to mean temperature over the preceding month ($p = 0.002$) and week ($p = 0.026$), whilst P_w DRP was not. The September dips in soil P_w DRP and P_w MUP contents (figure 5.5), noticeable for a number soils, may be attributable to the intense rainfall during September sampling (see previous section).

Repeated measures analyses against the presence or absence of grazing animals (table 5.4) found that the presence of grazing animals was significantly positively associated with P_w MUP ($p = 0.0003$), although was not significantly associated with P_w DRP ($p = 0.41$). As with Olsen P, P_w (TDP) increased substantially between February and April in soil 3 (from approximately 8 to 23 mg P kg^{-1} soil), and between January and February in soil 5 (from approximately 1.7 to 5.8 mg P kg^{-1} soil), corresponding with intensive grazing and manure application respectively in these two fields (figure 5.5). There was no immediate increase in soil 4 P_w contents following light manure application, although P_w MUP content increased substantially in this soil one month later (between February and March; figure 5.7). Both P_w DRP and MUP fractions increased simultaneously, and by similar proportions in soil 3, but in soil 5 only P_w DRP increased immediately following the manure application: P_w MUP increased from 0.84 mg P kg^{-1} in February to 1.98 mg P kg^{-1} in March, though P_w MUP varied more later in the year (reaching 4.02 mg P kg^{-1} in August). There was no peak in P_w associated with P application to soil 2 in July, although there was a peak in soil 8 P_w corresponding with the silage cut on that soil. Whilst concentrations of, and variations in, P_w DRP were greatest for the high Olsen P soils (i.e. soil 2, 3 and 10), concentrations of, and variations in, P_w MUP were equally great among high and low Olsen P soils (figure 5.7). Note that peat soils are labelled first in the graphs' keys, but after that soils are listed in order of decreasing Olsen P content, enabling visual comparison between relative Olsen P status and P_w contents and variation).

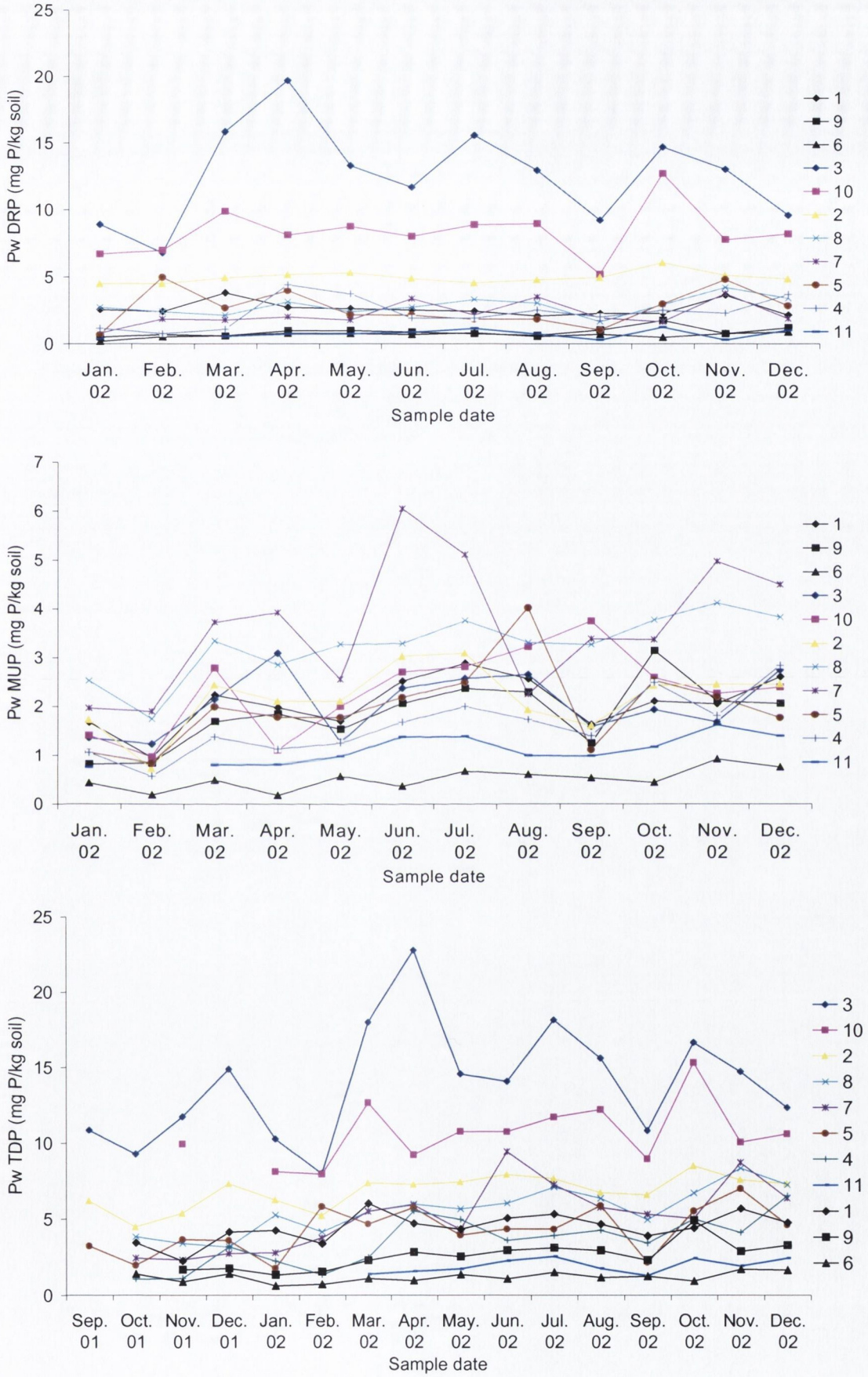


Figure 5.7: Line graphs displaying monthly variation in P_w DRP, MUP and TDP fractions for samples collected from soils 1-11.

5.4.5. Phosphorus sorption

There was no immediately obvious pattern of sorption over the study period (figure 5.8), and trends appeared to vary among soils. For example, sorption to soil 2 samples was very consistent throughout the entire sampling period, contrasting with large variation in sorption to soil 4 samples, which increased from 183 mg P kg^{-1} in December 2001 to 234 mg P kg^{-1} in August 2002. Repeated measures analyses (table 5.4) indicated that, overall, variation was significant among months ($p = 0.020$) and seasons ($p = 0.024$). Variations in sorption for all soils were significantly positively related to mean temperature over the preceding month and week to sampling ($p = 0.0005$ in both instances), and borderline significantly negatively related to effective precipitation in the preceding month ($p = 0.053$) but not week. Sorption appeared to follow an inverse trend to soil moisture ($p = 0.0009$) and TN contents ($p = 0.0023$), though was not significantly related to pH variation.

It appears from figure 5.8 that a number of soils attained high sorption capacities in summer, and this was confirmed by *post-hoc* LSD analyses which showed the only significant seasonal differences to be higher summer than spring ($p = 0.005$) and winter ($p = 0.017$) sorption. From figure 5.8, it also appears that some soils (most notably 3, 7, 9, and 10) sorbed more P in winter, with a decline in sorption into the spring months, although this was not supported by seasonal *post-hoc* analyses on data for all soils. There were no obvious defining characteristics exclusive to soils 3, 7, 9 and 10, and comparing seasonal sorption trends visually (figure 5.8) indicates that the main soil-type distinctions (peat/mineral and low/high pH) did not show specific variations.

Repeated measures analyses were conducted on low P status soils / soils receiving no P application (4, 6, 7 and 11) in order to detect any potential impact (obscuring effect) of P management practice on seasonal sorption trends. However, results from these repeated measures analyses confirmed the original results when all soils were considered. The only differences were that, in addition to seasonal differences noted above, autumn sorption was found to be significantly ($p \leq 0.05$) higher than spring and winter sorption, and covariation with preceding effective precipitation and mean temperature was stronger. The presence or absence of grazing animals was not significantly related to variation in sorption to soils. There were a few inverse relationships between sorption to specific soil samples and P_w desorption, however. Peaks in soils 3 and 10 P_w DRP in October (figure 5.7) corresponded with dips in sorption (figure 5.8), and increased soil P_w DRP between February and April

corresponded with decreased sorption over these months. Repeated measures comparison between P_w DRP and sorption revealed no significant overall relationships, however (p = 0.58).

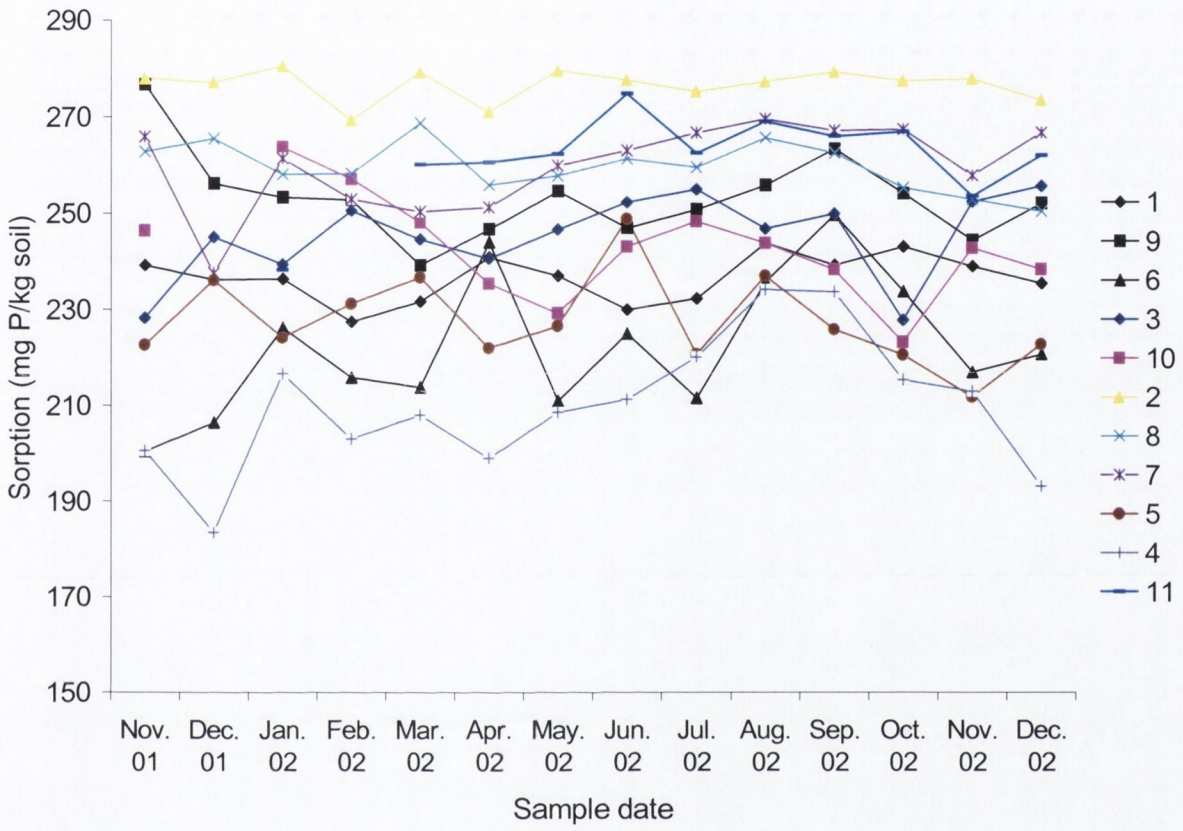


Figure 5.8: A line graph showing the variation in sorption from 30 mg P l^{-1} solution for monthly samples of soils 1-11.

5.5. Subsurface water results

5.5.1. Meterological conditions

Unfortunately, because of delays in zero-tension sampler installation, the nine months over which subsurface water samples were collected from these samplers (October 2002 until the end of BUFFER sampling in June 2003; see section 2.5.2) only had some overlap with the temporal soil sampling: while monthly soil sampling ended in December 2002, subsurface water samples were collected until June 2003. In order to determine whether seasonal trends in subsurface water P data over January to June in 2003 were likely to be influenced by similar meteorological conditions to soils analysed over the same period in 2002, meteorological data were compared between these two periods (table 5.5).

Figure 5.9 displays variation in total daily precipitation and mean daily temperature over the time period most relevant to subsurface water sample collection. The seasonal pattern is similar to that noted from figure 5.3 and table 5.1, with decreasing mean daily temperatures from September through to January, increasing again through to the end of June. Precipitation is reasonably regular throughout the sampling period, although table 5.5 shows that it was consistently, and for some months substantially, lower than precipitation during the same period in 2002. February 2003 was particularly dry in comparison with February 2002, with less than a third of the precipitation (50.8 compared with 174.2 mm; table 5.5), although February 2003 was closer to the climatic average for that month (83.2 mm; table 5.1). There was a stronger seasonal temperature fluctuation in the first six months of 2003 than 2002, with lower January and February mean temperatures in 2003 (table 5.5) steadily increasing to a higher June temperature. Overall, the first six months of 2003 were substantially drier than the first six months of 2002, but there was little difference in the mean temperature averaged for these months.

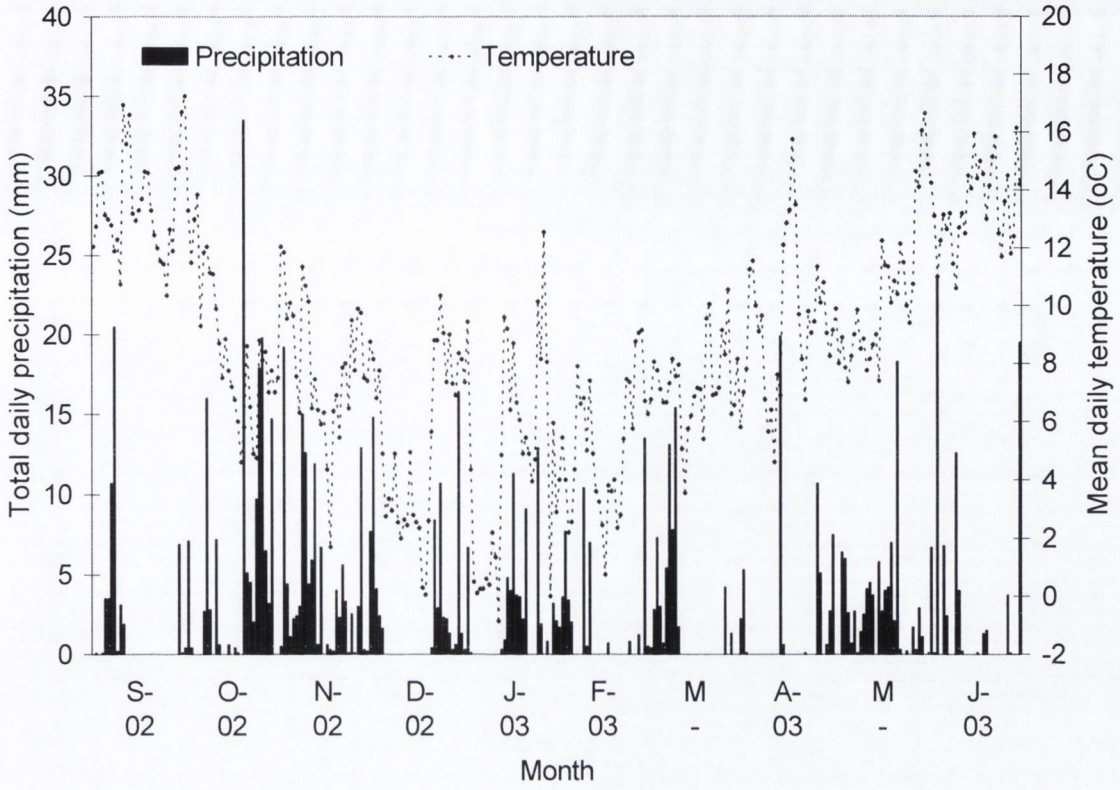


Figure 5.9: Total daily precipitation and mean daily temperatures recorded by Met Eireann at Claremorris weather station, for the period September 2002 to June 2003.

Table 5.5: A comparison of meteorological characteristics for the months of January to June, between the years 2002 and 2003.

	Total monthly Precipitation (mm)		Mean monthly Temperature (°C)	
Month	**2002**	**2003**	**2002**	**2003**
Jan.	111.9	69.3	6.8	4.7
Feb.	174.2	50.8	6.4	5.1
Mar.	83.1	65.8	7.3	7.2
Apr.	53.9	52.6	8.6	9.4
May	136.6	85.4	10.6	10.4
Jun.	88.8	82.6	12.0	13.5
Total / av.	**648.5**	**406.5**	**8.6**	**8.4**

5.5.2. Subsurface water total dissolved P concentrations

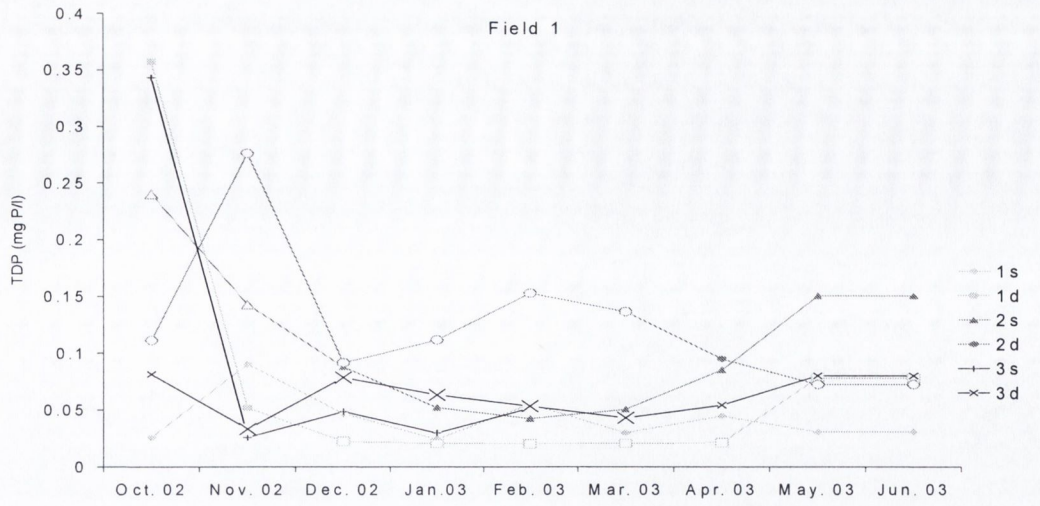
Variations in subsurface water sample TDP concentrations are displayed in figure 5.10. It is immediately clear from visual inspection of the data that temporal variations in subsurface water P concentrations differed among fields and locations within fields. This is confirmed by repeated measures analyses comparing all TDP concentrations against month, which found that there was no common monthly variation ($F_{8,90} = 0.24$, $p = 0.98$). The small number of samples, and divergent trends, makes it impossible to conduct meaningful statistical analyses to test for seasonal patterns of variation. Instead, patterns of the apparently large variations between months will be subjectively compared between fields, and with meteorological and (2002) soil P desorption data. At this point, it is worth mentioning the contrasting scale of subsurface water TDP concentrations (and consequently variations) between different locations. Highest TDP concentrations (up to 1.91 mg P l^{-1}), and magnitude of variation, were in subsurface water samples collected from zero-tension samplers at location 1 (1s and 1d) in field 9. Lowest TDP concentrations (down to below 0.005 mg P l^{-1}) were in subsurface water samples collected from location 2 (2s and 2d) in the same the same field.

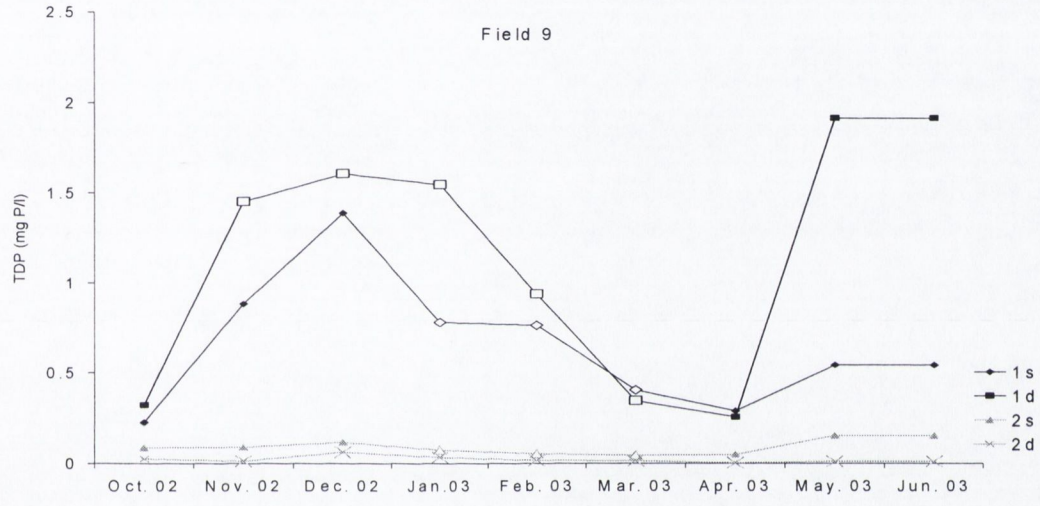
Generally, shallow and deep samples from the same locations followed similar patterns of monthly variation (even where the deep sample is suspected to be shallow groundwater). The exception to this is location 2 in field 1, where the shallow (2s) and deep (2d) subsurface water sample TDP concentrations diverged from December 2002 to May 2003: shallow sample concentrations dipped to a minimum and the deep sample concentrations peaked to a maximum in February (figure 5.10). Initial October TDP concentrations in samples 1s and 1d from field 1 were much higher than subsequent concentrations, and may have been due to 'bedding in' of the samplers (section 2.5.2), with a flush of P either desorbed from soil within the sampler, or from initial surface water seepage into it.

The two shallow subsurface water samples in field 10 displayed a similar, relatively consistent trend in TDP concentrations. They increased from October 2002 through to a February 2003 peak, before declining again until the final sample collection in June 2003. Similarly, TDP concentrations in subsurface water samples 1s, 2d and 3s from field 1 increased to February 2003, while field 9 1s and 1d sample TDP concentrations reached a peak a few months earlier in December 2002. The generally high subsurface water TDP concentrations noted over the winter months (December to February) are contrary to the

lower P_w TDP soil contents found for winter (2002) compared with the other seasons (section 5.4.4). In particular, increasing TDP concentrations between October 2002 for at least two months subsequently, in samples 1s and 1d from field 9, and in samples 1s and 2s from field 10, contrast with concurrent soil P_w TDP decreases (figure 5.7), although correspond with relatively high precipitation (figure 5.9 and table 5.1) during October and November. Other notable concurrent increases in subsurface water TDP concentrations were those between April and May for samples 1d, 2s and 3d from field 1, and 1s, 1d and 2s from field 9. These variations are closer to the general trend in soil P_w contents found the previous year, although neither soil 1 nor soil 9 themselves displayed increasing P_w TDP contents over this time. Table 5.5 indicates that precipitation was higher in April and May compared with the preceding relatively dry months, but May 2003 was much drier than May 2002.

Table 5.6 displays the data contained within the sample diary, used to note variations in management practices during soil sampling, and continued for fields 1, 9 and 10 over the duration of subsurface water sample collection. It can be seen that field 1 was not grazed at all from late autumn to early spring, while in field 9 there was no evidence of recent grazing for 3 months (February to April 2003). In field 10, there was no evidence of recent grazing during September or October 2002, or from January to March 2003. For fields 1 and 9, these periods correspond with relatively low subsurface water TDP concentrations (figure 5.10), though this is not the case for field 10.





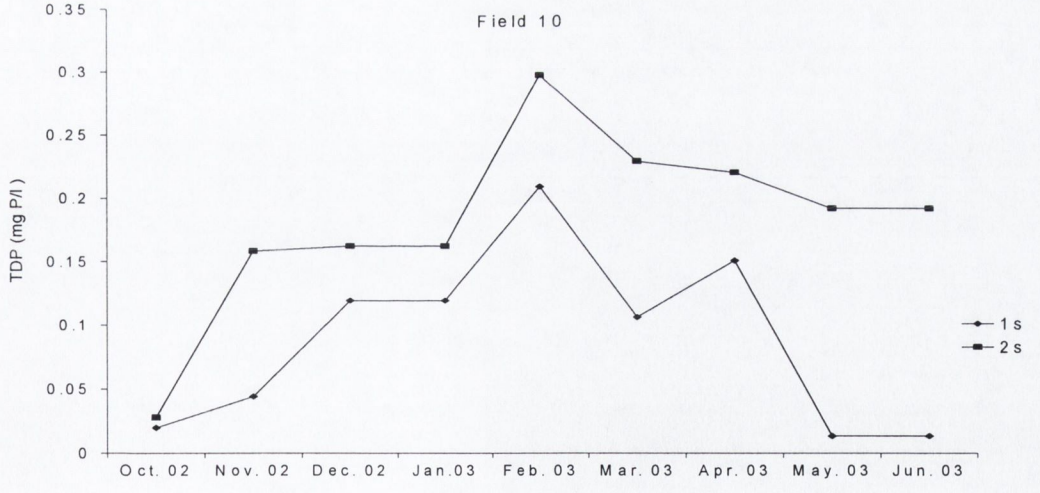


Figure 5.10: Subsurface water total dissolved P (TDP) concentrations collected at 8–21 cm (s) and 51–63 cm (d) depth from different locations (1-3) in fields 1, 9 and 10. Enlarged, hollow symbols indicate suspected groundwater.

Table 5.6: Management practices on sampled fields noted on sampling occasions. Cow (C) grazing – intensive in bold, *not during sampling but evidence of recently in italic.*

Soil	07.09.02	02.10.02	17.11.02	14.12.02	14.01.03	17.02.03	12.03.03	12.04.03	19.05.03	18.06.03
1	*C grazing*	*C grazing*	No grazing	No grazing	No grazing	No grazing	No grazing	*C grazing*	C Grazing	*C grazing*
9	*C grazing*	*C grazing*	No grazing	*C grazing*	*C grazing*	No grazing	No grazing	No grazing	*C grazing*	C grazing
10	No grazing	No grazing	*C grazing*	*C grazing*	No grazing	No grazing	No grazing	*C grazing*	*C grazing*	**C Grazing**

5.6. Relationship with stream chemistry

Seasonal variations in stream-water P concentrations within the Mask catchment are summarised in Donohue et al. (in press). Figure 5.11 is from this paper, and displays the seasonal variation in nutrient-flow relationships for different P fractions from discrete samples collected bi-weekly from July 2001 to July 2002, from the nine river sampling points located on the Lough Mask inflows (figure 1.2): Lough Carra inflows were excluded due to lack of discharge data. These nutrient-flow relationships normalise for differences in flow rates during sampling over the different seasons. However, the predetermined sampling schedule for the collection of discrete samples (section 2.4.1) meant that the range of flow rates sampled was limited for some seasons, particularly in summer when the maximum average discharge during sampling was approximately 12 $m^3 s^{-1}$ – compared with approximately 44 $m^3 s^{-1}$ in winter (figure 5.9).

Comparisons between seasons were made subjectively by comparing the different nutrient-flow relationships between seasons shown in figure 5.11, while statistical comparisons were made by testing the significance of seasonal differences in an interaction term between P concentrations (MRP, TDP and TP) and flow rates in ANCOVA. When all rivers were considered, the only significant seasonal trend recorded was for the slope of TP concentrations against river flow rates during the different seasons (ANCOVA $F = 2.63$, $p = 0.05$). TP concentrations increased most strongly with flow rate during summer, followed by autumn, spring and winter. Similar, though less strong trends, were observed for MRP and TDP concentrations (figure 5.11), although these were not statistically significant, perhaps due to insufficient numbers of high-flow events sampled during each season (especially summer). MRP concentrations (equivalent to P_w DRP; section 2.4.1) increased most strongly with flow rate during autumn months, followed by summer, winter and spring. TDP concentrations also increased most strongly with flow rates during autumn months, followed by summer, spring and winter. Thus, a qualitative comparison of statistically-unconfirmed seasonal differences in flow-normalised soluble P concentrations with seasonal variation in soil P desorption (section 5.4.4) would suggest that while low winter and high summer and autumn soil P desorption are to some extent consistent with flow-normalised soluble P concentrations during these seasons, high soil P desorption in spring is not reflected in the low flow-normalised stream P concentrations found during spring. Overall, there is no strong association between soil P desorption (or subsurface water TDP concentrations; section 5.5.2) and the possible seasonal variations in

stream-water soluble P concentrations within the Mask catchment indicated by BUFFER sampling data presented in Donohue et al. (in press).

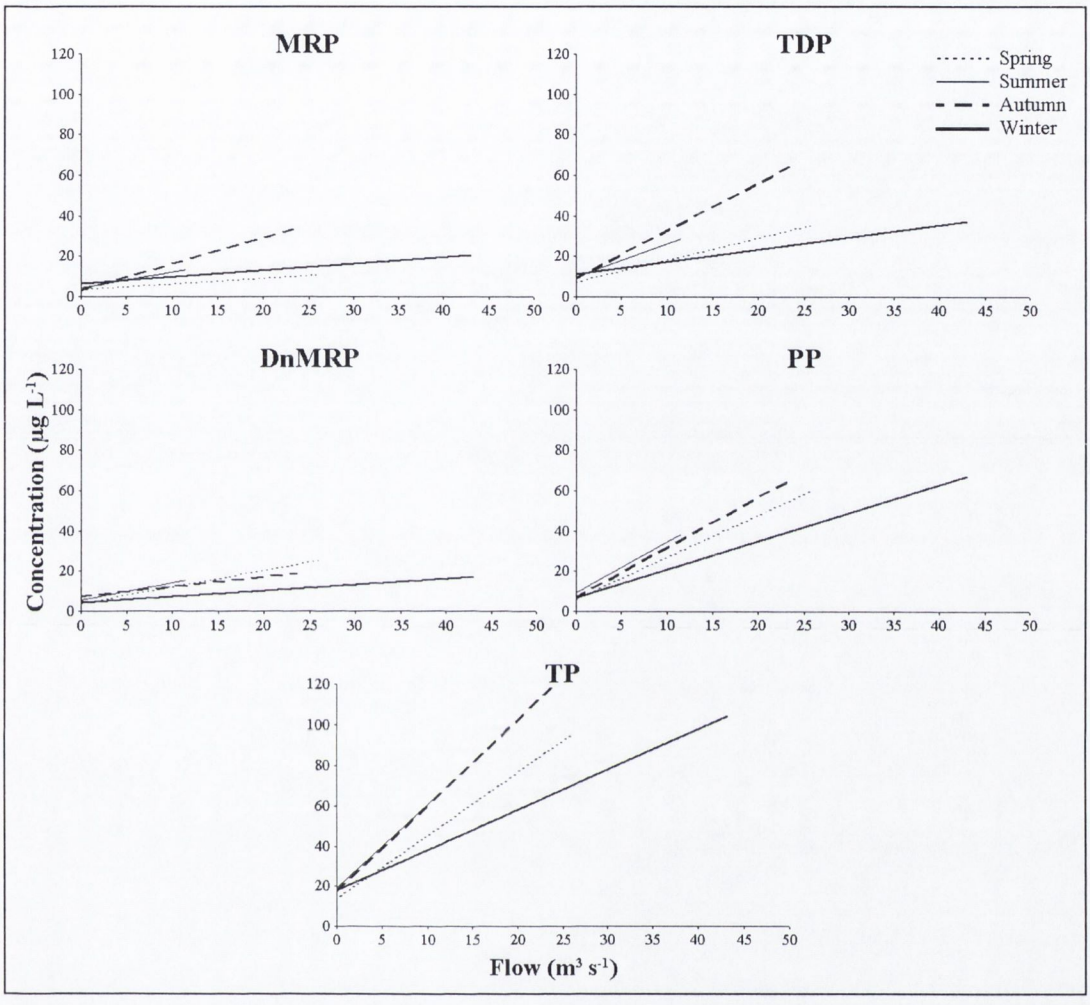


Figure 5.11: Nutrient-flow relationships for measured P fractions during each season, for all major inflows to Lough Mask sampled for BUFFER during 2001 to 2003. From Donohue et al. (submitted).

5.7. Discussion

5.7.1. Organic P cycling

Despite the absence of significant monthly or seasonal variation in soil TOC content – perhaps due to high sample variability and wide CLs, especially for the peat soils – there was a significant seasonal trend in soil TN content. Table 5.2 indicates that trend was related to a combination of antecedent temperature (negatively) and effective precipitation (positively), and was particularly strongly related to soil moisture content (itself an integrated expression of these variables). This is consistent with the pattern of variation in organic N (which forms the bulk of soil TN) that would be expected from biological cycling: i.e. accumulation/immobilisation of organic N in microbial biomass during cool, wet conditions, and mineralisation to plant available inorganic N during warmer, often drier conditions, when soil moisture is additionally depleted by high transpiration rates from growing plants. Total N reached a spring minimum, when depletion through mineralisation is at its fastest (Chaneton et al., 1996; Kuo and Jellum, 1987; Tate et al., 1991b), supplying rapid vegetation growth during this time (and perhaps just prior to spring fertiliser dressings). This pattern of immobilisation and mineralisation to and from non-labile organic fractions has also been noted for soil P in a number of previous studies (Dormaar, 1972; Daly, 1999; Perrott et al., 1990; Tate et al., 1991a), and suggests that parallel P cycling may be occurring in these soils.

Whilst the MUP fraction in soil extracts is not an accurate representation of the organic fraction, due to hydrolysis of organic P during molybdate analysis (Baldwin, 1998; Rigler, 1968: section 1.4), and the fact that it may contain other forms of P such as occluded colloidal P, it is nonetheless at least a reasonable indicator of relative P_o contents. Similarly, while soil TN content includes small amounts of inorganic N, and labile N, it is dominated by organic N, and may therefore be indicative of the balance between mineralisation and immobilisation processes affecting soil organic N contents. If rates of mineralisation and immobilisation are assumed to follow similar seasonal trends for both soil P and N, then TN variation may also be used as a proxy for the relative impact of these processes on soil organic P content. A strong, positive relationship between Olsen MUP and soil TN content (table 5.4) may be indicative that moderately labile organic P (as represented by Olsen MUP) is being controlled predominantly by rates of mineralisation and immobilisation. Olsen MUP followed a very similar, though more pronounced, trend

to soil TN content, probably reflecting the relatively labile (therefore susceptible to biological processes) nature of organic P extracted by the Olsen reagent compared with the immobile organic N that dominates soil TN contents. Both soil TN and Olsen MUP displayed strong positive relationships with soil moisture and antecedent effective precipitation, and strong negative relationships with antecedent temperature (tables 5.2 and 5.4). This would support the hypothesis that these fractions are both controlled by biological processes (predominantly micobial and enzyme-mediated decompostion and mineralisation and immobilisation through microbial and plant uptake) which in turn are known to be controlled by soil moisture and temperature (meteorological) conditions in particular. Specifically, during cool, wet autumn and winter months N and P from decaying plant debris becomes immobilised by microbial uptake, and contributes to the accumulation of transitional, labile organic P forms. During warmer spring and summer months, increased plant uptake stimulates the mineralisation of P_o and organic N, resulting in the depletion of immobile organic N (as indicated by TN depletion), immobile P_o, and labile P_o (as indicated by Olsen-extract P depletion). This is consistent with autumn-winter increases and spring summer decreases in labile ($NaHCO_3$-) P_o found in previous studies (Perrott et al., 1990; Tate et al., 1991a), found to be positively correlated with soil moisture (Perrott et al., 1990). Tate et al. (1991b) also found that rainfall was a major driver of soil microbial P content.

It has been suggested that Olsen P_o is only moderately labile (e.g. Rubaek and Sibbessen, 1992), compared with water extractable P_o, which is the most labile P_o fraction commonly measured. Labile P fractions undergo rapid cycling processes to maintain the equilibria between less labile fractions and plant uptake (Sharpley et al., 1995; Tate et al., 1991a), implying that P_w MUP is subject to more short-term variations in mobilisation and plant response than Olsen MUP. In contrast to Olsen MUP and soil TN content, P_w MUP was positively related to antecedent temperature (table 5.4), and reached a winter minimum, increasing over spring and into the summer (figure 5.4). It may be that P_w MUP content is determined by a balance between the rate of P_o mobilisation from less labile (including Olsen MUP) forms and P mineralisation. Hence a low but increasing concentration found during spring, when mineralisation is at its most rapid but when mobilisation of P_o is also increased with higher rates of biological and chemical activity. Sustained high rates of biological (i.e. microbially and enzyme-mediated decomposition and mineralisation) and chemical (i.e. solubilisation) mobilisation during the warm summer months, and low 'wash-out' rates, may explain high P_w MUP during this time. Biological immobilisation of

P during winter months increases P_o in immobile and moderately labile (Olsen MUP) P_o fractions, but probably not in the highly labile (P_w) P_o fraction. Low rates of mobilisation (both biological and chemical) from less labile fractions would be expected to result in low P_w MUP production during the cool winter months, and increased soil 'wash-out' rates of P_w MUP during the wet winter months would also result in P_w MUP depletion. The dominance of temperature in determining biological processes (the soils in this study area being adequately moist for most of year not to hinder them), or other unexplained interaction with another controlling factor, may account for the absence of significant covariation between P_w MUP and antecedent effective precipitation (table 5.4). It is unlikely that the limited drying experienced by these soils during 2002 (figure 5.4) was sufficient to induce P_w MUP release from microbial cell lyses (see section 3.2.1), and the absence of significant negative covariation with soil moisture content (table 5.3) would confirm this.

Temporal variations in the Olsen MUP fraction were substantial, with mean soil Olsen MUP increasing 14 mg P kg^{-1} (50%) between the summer minimum and winter maximum (section 5.4.3). If this fraction represents moderately labile P_o, then it highlights the strong buffering capacity of soil available P through soil P_o content. This would imply that that there is a large reservoir of P to maintain P concentrations in interacting (through or surface flow) waters throughout the year, despite plant P uptake and antecedent runoff events.

5.7.2. Inorganic P variation

Changes in the MRP fractions of Olsen and water extracts (i.e. Olsen P and P_w DRP) were also found to be significant among months and seasons (table 5.4), though patterns of change for these fractions were less pronounced and slightly different to trends in MUP fractions (sections 5.4.3 and 5.4.4). Temporal variations in both MRP fractions were not significantly related to TN, suggesting different controlling factors for these fractions. Although Olsen P did follow a similar, though less pronounced, seasonal pattern to Olsen MUP, it did not recover to the extent that Olsen MUP did through the autumn and early winter of 2002. The slower decrease in Olsen P compared with MUP over the growing season, insignificant relationship with soil moisture or antecedent effective precipitation, and significant negative relationship with temperature in the preceding month (table 5.4),

suggest that Olsen P is determined primarily by plant uptake. This is buffered by rapid mineralisation of the rapidly declining Olsen MUP fraction during spring and through the growing season, although the decline in this pool ultimately results in the delayed, gradual decrease in Olsen P. Olsen P includes organic and colloidal-associated P hydrolysed by the molybdate reagent (Baldwin, 1998; Rigler, 1968), and Tate et al. (1991a) suggest that autumn and winter increases may be the result of up to 13% microbial contribution to Olsen P content. Additionally, biological processes such as earthworm activity incorporate organic P into the soil and contribute to Olsen P accumulation over the winter months. Variation in Olsen P throughout the year, although slightly lower in absolute terms than variation in Olsen MUP, was substantial, and proportionately greater. Mean January 2002 Olsen P was 10.6 mg P kg^{-1} (56%) higher than Mean September 2002 Olsen P (section 5.4.3).

Section 3.5.2 indicated that Olsen P content increased with sample drying, and this increase may be expected to reduce seasonal variation, as it did for P_w (section 3.5.3). However, while variation in Olsen P was not found to be significant for the four months of moist-dried sample comparison, both moist and dried samples followed a similar trend to the seasonal trend in monthly-analysed moist samples noted in section 5.4.3. This would suggest that season has a substantial effect on soil Olsen P content measured in soil samples, with serious implications for the timing of sample collection for the assessment of soil P status. Relationships between (Olsen) STP and P desorption will also be affected by seasonal variations, and the divergent seasonal pattern of Olsen P (section 5.4.3) and P_w DRP (section 5.4.4) variation would imply that this effect is substantial. For example, change points (referred to in section 4.2.5) would consequently change significantly with season (although there were no change points found for STP-P desorption relationships in this study; section 4.5.4). McDowell and Trudgill (2000) found that the range of soils they studied displayed a late summer maximum and late winter minimum for both Olsen P and desorbable ($CaCl_2$) P. Similar seasonal variation for these fractions ($CaCl_2$-P followed similar patterns in both moist and dried soil samples) resulted in a relatively constant change point, irrespective of season, in their study.

It is possible that $CaCl_2$-P follows a different seasonal pattern of variation to other measures of soil desorbable P. Saunders and Metson (1971) found a similar seasonal pattern for resin P and $CaCl_2$-P to that found by McDowell and Trudgill (2000) for Olsen P and $CaCl_2$-P, and attributed it to P accumulation and low plant uptake during soil moisture

deficit conditions in summer. In contrast, results displayed here show that P_w DRP (and MUP) followed a contrasting seasonal pattern to Olsen P, with a winter minimum. Continuously high soil moisture contents (section 5.4.2) indicate that soils in this study did not dry sufficiently to impair plant growth during the study period. High inter-month variability in P_w DRP (associated with both sample variability and land use; see next section for discussion) appears to mask any further seasonal trend (figure 5.7), although P_w DRP was significantly related to some recorded meteorological variables. In contrast to P_w MUP, P_w DRP was unaffected by temperature, but did appear to be affected by effective precipitation in the preceding week, although not the preceding month (table 5.4). This suggests that readily desorbable soil P_i production may be limited by mineralisation rates, and thus its short-term concentration is probably controlled by rates of plant uptake and 'wash-out' with recently preceding precipitation (Tunney and O'Donnell, 2002). Winter minimum P_w DRP concentrations correspond with maximum effective precipitation and soil moisture saturation, and may be the consequence of 'wash-out' effects. The importance of such wash-out effects is further supported by the dips in P_w DRP contents noted for a number of soils during September sampling, some of which followed heavy rainfall (section 5.4.3 and table 5.3). Concurrent dips in Olsen P may be partially explained by such a 'wash-out' effect.

A significant negative relationship between P_w DRP and pH (table 5.4) hints that physico-chemical processes may be important in soil P_i desorption. Kuo and Jellum (1987) suggest that positive covariation between soil pH and P_w in acidic soils is caused by increased sorption as acidity increases, though in this study sorption is not significantly related to either pH or P_w DRP (table 5.4). Gahoonia and Nielsen (1992) found that localised root-induced pH decreases increased the depletion of labile P_i from the rhizosphere, although Olsen P was not significantly related to pH variation in this study. However, low spring pH (section 5.4.2) could be related to the mineralisation flush which results in the P_w DRP increase during this time (figure 5.7), and may contribute towards it - or even regulate it (Kuo and Jellum suggest that P mineralisation is biochemically controlled). Conversely, high winter pH may contribute to winter minima P_w DRP contents, in addition to 'wash-out' effects during this time. Other authors have suggested physico-chemical control of seasonal variation in desorbable P (Blakemore, 1966; Dormaar, 1972; Magid and Nielsen, 1992). Physico-chemical processes are directly impacted by manure (from grazing animals and fertiliser applications) and chemical P applications, which differ in timing between soils and make common seasonal changes difficult to discern (see next section for details).

Physico-chemical disruption of soil aggregates through natural drying (Chepkwony et al., 2001) may release a small amount of P in some of these soils during summer months, but the limited summer drying (section 5.4.2) is unlikely to have been sufficient for this release to have been substantial, and P_w DRP was not related to soil moisture content (table 5.4). Other studies mentioned in this chapter analysed laboratory-dried soils, and this may explain some of the contradictory (to this and other studies) results found in them. For example, Blakemore (1966) found constant desorbable ($CaCl_2$-) P throughout the year on dried soils (in the absence of P application) and Garbouchev (1966) found that resin and $CaCl_2$-P contents reached maxima around January and May, respectively, and reached minima around July to September. These results could be attributable to drying-induced P release masking the seasonal variation in genuinely readily desorbable P contents (section 3.7.1). However, McDowell and Trudgill (2000) found similar seasonal trends in $CaCl_2$-P analysed in both moist and dried samples.

Although the measure of sorption used here is not representative of maximum sorption capacity (as the PSI method is supposed to be; section 4.2.3) it should nonetheless provide a reasonable indication of change in remaining soil P sorption capacity. Significant seasonal variation in soil sorption was limited to relatively high summer values, and low spring and winter values. Strong positive covariation with preceding mean temperature and negative covariation with soil moisture contents (table 5.4) indicate that physico-chemical processes associated with natural soil drying may play a role in seasonal P sorption variability (preceding mean temperature is a good indicator of soil moisture status; table 5.2). Studies looking at the effects of soil drying on P sorption have reported mixed results. Pote et al. (1999a) and Saunders and Metson (1971) noted summer minima in soil P sorption. Pote et al. (1999a) suggest that microbial oxidation of Fe results in the formation of strongly-P-sorbing ferrihydrite during spring months, which may break down during exceptionally dry summer months (in Arkansas, US). In this study, such compounds may be more likely to form during the warmer, still moist summer months. Alternatively, a number of studies looking at the effect of laboratory drying on soil P sorption have found that dried soils sorb more P (Bartlett and James, 1980; Comfort et al., 1991; Haynes and Swift, 1985a). Olsen and Court (1982) suggest that aggregate disruption during drying exposes new P (de) sorption sites, and it may be possible that summer drying in the soils studied here is sufficient for this mechanism to increase summer sorption. This could explain why calcareous soil 4 displayed the most prominent summer increase in P sorption, as Fe-specific drying effects would be expected to have little impact on this high

pH, high carbonate soil (table 2.4). Ultimately, as with P_w, seasonal sorption trends were likely to have been influenced by numerous interacting factors, including short-term management effects, and changes may have been dependent on soil type: this is indicated by the widely differing ranges of P sorption by different soils found over the study period (section 5.4.5), although there was no obvious pattern attributable to specific soil characteristics.

5.7.3. Land use

It is difficult to disentangle land use from seasonal and sample variability, and management practices were not monitored in detail over the study. The most obvious and striking effects of management practices were spikes in soil P_w after intensive grazing and manure applications; most notably the effect of exceptionally intense grazing on soil 3 during March and April (figure 5.7 and table 5.3) which resulted in a trebling of P_w content in this soil over those two months (section 5.4.3). Presumably, this increase is mainly attributable to the direct dung input of P from grazing animals, though may also be the consequence of soil aggregate disruption and P release (given that areas of the field were heavily poached). Response to this intensive grazing, and to soil 5 manure application, appeared to be immediate for P_w DRP contents, and for P_w MUP content in soil 3, but a trebling in soil 5 P_w MUP content one month after manure application, and an increase in soil 4 P_w MUP content one month after manure application to part of the field, may have been a delayed response to this manure application: whilst P_i in the manure was immediately washed into the soil for subsequent desorption, it may have taken some time for mobilisation of the P_o (mainly inositol phosphate) contained in the manure. Soil 3 and 5 Olsen P contents also displayed substantial increases concurrent with P_w increases, though there were no associated increases in Olsen MUP contents (figure 5.6).

In contrast to these rapid responses to increased soil P inputs, the application of a significant quantity of fertiliser to soil 2 in July was followed by a small (perhaps insignificant) increase in the following month's Olsen P content (figure 5.6), but had no apparent effect on P_w DRP (figure 5.7). Other studies have noted a rapid decrease in desorbable P after fertiliser induced peaks (Blakemore, 1966; McDowell and Trudgill, 2000), and it is possible that August sampling missed any peak in P_w which may have occurred immediately after application, and decreased especially rapidly at this time of the

year through plant uptake or enhanced summer sorption. Thus, it appears that management events involving increased soil P inputs during wetter winter and spring conditions may have substantial and immediate impacts on runoff water and stream P concentrations, with especially large increases in the bioavailable DRP fraction. However, well-timed P applications during drier summer months may have negligible impact on runoff water and stream P concentrations during subsequent precipitation events.

Identifying residual effects of fertiliser application (STP accumulation) in terms of seasonal P variation is a little more difficult. A number of fields had no stated P application in 2002 despite having had past applications (soils 1, 8, 9, 10), and soils from these fields had relatively high P status (either Olsen or Morgan P contents; table 4.2b) for non-fertilised soils. Only one soil may be reliably taken to be representative of a non-fertilised soil: soil 11 (see section 2.3.2). This soil displayed very little Olsen P or P_w DRP variation, although showed more Olsen MUP and P_w MUP variation (figures 5.6 and 5.7), possibly suggesting maintenance of steady P_i availability throughout the year through organic cycling in non fertilised soils (Sharpley et al., 1995). However, most soils (across a range of Olsen P contents) appeared to follow a similar and well-defined seasonal pattern of Olsen P and MUP variation (figure 5.6). The magnitude of Olsen P variation was generally greater in high Olsen P soils, though Olsen MUP contents and variations appeared to be more evenly distributed across high and low Olsen P soils (section 5.4.3), countering the suggestion that P application suppresses biological cycling (Daly, 1999; Ron Vaz et al., 1993). For soil P_w in particular, while contents of, and variations in, DRP fractions were generally greater for higher Olsen P soils, contents of, and variations in, MUP fractions were not associated with Olsen P contents (figure 5.7). These findings are generally consistent with the conclusions of Sharpley et al. (1995) - that physico-chemical processes (e.g. P applications and changes in sorption capacity) dominate seasonal P variations in fertilised soils, but that biological cycling dominates seasonal P variations in non-fertilised soils. The results of this study do suggest that seasonal variations in soil P_i contents are increased by fertilisation, but that these variations occur in conjunction with large variations in P_o largely attributable to biological cycling. Biological cycling therefore has a relatively greater effect on desorption (P_w TDP) from soils of lower P status.

Intensive grazing had a large impact on both P_w DRP and TDP in soil 3, but, when statistical analyses were conducted to determine the impact of grazing animals on all soils,

the presence of grazing animals did not appear to affect P_w DRP (table 5.4). This could be because of the exceptionally intensive grazing on soil 3, and the associated poaching of the surface soil perhaps releasing P through aggregate disruption (it could also be the result of possible fertiliser application to soil 3 prior to grazing: patchy management data for this soil). However, grazing was positively correlated with P_w MUP contents when all soils were considered (table 5.4), suggesting that dung inputs, and maybe aggregate disruption, during grazing increases P_w MUP. Grazing was also significantly negatively correlated with soil moisture contents (table 5.2), presumably because animals tend to be put out to graze during drier conditions, although the strength of covariation between P_w MUP and grazing suggests that there are direct impacts on P_w MUP attributable to grazing, and it is not just the result of coincidentally similar seasonal patterns.

5.8. Relationships between seasonal variations in soil and water P data

5.8.1. Comparison with subsurface water total dissolved P variation

The lack of overlap between subsurface water P concentrations and monthly soil P data is a potential problem for relating soil P variation with subsurface water P variation directly, especially considering the deviations in meteorological characteristics between January to June 2002 and January to June 2003 (section 5.5.1). However, large within field variations in subsurface P concentrations, and in some instances patterns of variation (figure 5.10), suggest that very localised factors are responsible for the control of subsurface water P concentrations. In retrospect, it may have been better to install all the samplers at one depth, and perhaps in just two fields, to isolate and quantify the effect of season (and STP or soil type) more rigorously.

Subsurface water samples provide an indication of actual in-field desorption from soil to water, and should reflect factors such as hydrology and redox conditions, unlike potential soil P desorption measured in the laboratory. Differences in concentrations between samples collected from the same fields highlight the highly heterogeneous nature of soil P characteristics and desorption (figure 5.10). This was exemplified by subsurface water P concentrations in field 9, where subsurface water from one of the two deep samplers contained up to 1.91 mg P l^{-1}, whilst subsurface water from the other contained less than the 0.005 mg P l^{-1} detection limit at times (section 5.5.2). The former high concentration is

in agreement with Kurz (2000) and Heckrath et al. (1995), who found up to 1.67mg and 1.83 mg DRP l^{-1} respectively in subsurface waters under intensive grazing, and attributed these high concentrations to preferential flow pathways. Preferential flow pathways are formed by cracks that reach down through the soil profile, and allow surface water with P desorbed from higher P content surface soils to pass down through lower P content subsurface soils with minimum soil-water interaction, and thus minimum P readsorption. They are less likely to exist in peat soils, which tend not to dry sufficiently for cracks to form, are less resistant to water movement than mineral soils. Consequently, TDP concentrations in the deeper samplers do not appear to be consistently lower than concentrations in the shallower samplers (figure 5.10). This would suggest that spatial differences in subsurface water TDP concentrations are related to desorption or redox effects rather than the presence or absence of preferential flow pathways.

Decreasing TDP concentrations in shallower subsurface water between December 2002 and February 2003, followed by increasing concentrations between February and June 2003 (figure 5.10), reflect changes in surface soil sample P_w contents measured over the same period of 2002 (figure 5.7). Sample 2s in field 9 followed a similar pattern (though sample 1s was potentially influenced by redox conditions induced by soil saturation). Despite slightly differing meteorological conditions between the first six months of 2002 and 2003 (especially lower precipitation in 2003; table 5.6), biological control of P_w would be expected to follow similar relative trends in response to temperature variation (which was greater during 2003). Therefore, P_w contents may be expected to have followed a similar seasonal trend in 2003 compared with 2002 (perhaps smaller wash-out effect, but greater biological immobilisation effect). Varying soil desorption potential may therefore have been responsible for some of the variations in subsurface water P concentrations noted in this study. However, comparison of figure 5.10 with figure 5.7 shows that field 10 shallow subsurface water TDP concentrations contrasted with surface soil sample seasonal P desorption trends, increasing between October 2002 and February 2003 then decreasing through to June 2003 (although sample 2s remained higher in spring and into summer 2003 than it was in autumn 2002). This would suggest that factors other than soil desorbable P content are important in controlling subsurface water P concentrations. Winter peaks in mineral soil 10 subsurface water TDP concentrations may be attributable to more rapid movement of P through the soil profile (possibly through preferential flow routes) due to higher effective precipitation during winter. During the growing season, plant P uptake after rainfall may extract much of the P initially desorbed to water.

Changing redox conditions under alternating periods of soil saturation in both the shallower and deeper sampling zones at some locations may explain divergent TDP concentration trends at different depths, and deviation from patterns expected from surface soil sample desorption. For example, at location 1, field 1, higher TDP concentrations in deep compared with shallow subsurface water samples between December 2002 and April 2003 (figure 5.10) may have been due to release of soluble P in possible reducing conditions in the saturated subsoil from which the deeper samples were taken. Divergent trends during this time and up until final sample collection in June 2003 (figure 5.10), may be explained by changing redox conditions in the deeper sample zone and changing surface soil P desorption in the shallower sample zone. The small quantity of data, and contrasting seasonal patterns of variation, make it difficult to extrapolate probable consequences of varying subsurface water TDP concentrations for stream water P concentrations.

5.8.2. Comparison with temporal trends in stream quality

Comparisons of seasonal patterns in soil P desorption with stream-water P concentrations were limited in scope, and ultimately inconclusive. While the absence of statistically significant differences in relationships between dissolved stream P concentrations and stream discharge among seasons (section 5.6) could be taken to indicate that there are no seasonal differences in diffuse P losses at given flow rates, they are more likely to be the consequence of insufficient data. Accurate comparison of stream-water P concentration / discharge relationships requires a large database, including a wide range of flow rates sampled within each season. BUFFER sampling was restricted to a maximum frequency of twice per month, and figure 5.11 indicates that while the highest flow rates were sampled during winter, there were no high flow rates sampled during the summer months. This in itself is reflective of typical flow patterns, with more frequent high-flow events during winter, when extensive soil-moisture saturation results in a high proportion of precipitation reaching rivers as rapid-response surface runoff, and less frequent high-flow events in summer, when a higher proportion of precipitation infiltrates drier soils and either simply recharges soil moisture or reaches streams more slowly as throughflow (e.g. Withers et al., 1999; Haygarth et al., 2000).

Low dissolved stream-water P concentrations at given flow-rates during winter (figure 5.11) may therefore be reflective of hydrological soil P flushing during winter (e.g. Tunney

and O'Donnell, 2002), perhaps in conjunction with soil P immobilisation (section 5.8.1), and are consistent with low soil P desorption during winter reported in section 5.4.4. However, MRP concentrations measured in stream-water samples collected in spring displayed the lowest increase with discharge, in contrast to high soil P_w DRP contents measured in spring 2002 (figure 5.7). It could be that this statistically-insignificant seasonal pattern of stream-water MRP variation is not an accurate representation, but it may reflect a genuine trend of reduced stream MRP loading during spring. One possible explanation for this could be rapid biological cycling of P_i in spring (sections 5.7.1 and 5.7.2), with mineralised P taken up rapidly by growing plants, maintaining relatively high equilibrium solution P_i concentrations (and P_w DRP contents) but limiting availability to interacting overland flow and throughflow water. Additionally, high soil P_w DRP contents observed in spring 2002 could reflect continued mineralisation of soil P_o immediately after collection and/or during cold storage prior to analysis, and in the absence of plant uptake (dark conditions, and grass removed during sieving).

It is important to distinguish between stream-water P concentrations and stream P loading when making seasonal comparisons. High flow rates may result in high P loading, despite low P concentrations, during winter, and vice versa during summer (e.g. McDowell and Trudgill, 2000). In fact, soil P desorption and stream-water P loading may be causally-linked through an *inverse* relationship: i.e. higher stream P loading reflects higher soil P flushing and thus less readily desorbable P remaining in the soil (e.g. Sharpley, 1980b, Tunney and O'Donnell, 2002). A range of additional factors may mask the impact of soil P desorption on stream-water dissolved P concentrations and loading, such as P sorption/desorption reactions with newly-eroded or resuspended sediment (e.g. Avnimelech and McHenry, 1984) and biological uptake within streams. Withers et al. (1999) found that P losses varied hugely from year to year, and were highly dependent on flow rates, and suggested that TDP may have accumulated in the soil profile during drier years preceding sampling, to be washed out during subsequent high flows. Overall, time-lag effects and other complicating factors prevent any clear associations being found between seasonal patterns of soil P desorption and stream-water P concentrations, despite the relationships found by some other authors (e.g. McDowell and Trudgill, 2000; Pote et al., 1999a).

5.9. Conclusions

- For some soils, seasonal variability was obscured by high sample variability, although this problem is smaller than indicated by replicate composite sample variability - owing to the consistent pattern of sample collection. Nonetheless, powerful statistical (repeated measures) analyses were able to detect significant common trends in soil characteristics among soils.

- Large, consistent variations in MUP fractions of Olsen and P_w extracts indicate that biological cycling buffers P desorption throughout the year. P application / high soil P status does not appear to either suppress or increase this biological cycling: biological cycling is thus relatively more important in controlling P desorption from low P status soils.

- Biological cycling is driven by meteorological conditions, especially temperature and effective precipitation. Labile organic P, and organic-dominated TN, increase under cool, wet conditions as organic debris is incorporated into the soil and taken up by microboial biomass. These P and N fractions then decrease under warmer, drier conditions as they are first mobilised, then mineralised, to supply plant uptake.

- High rates of plant P_i uptake during spring and summer months deplete Olsen P over this period, whilst P mineralisation has a less well defined effect due to the inclusion of labile P_o within the soil Olsen P fraction.

- Physico-chemical processes may be important in determining P desorption, especially in high P status soils. For desorption of P_i fractions, immediately preceding effective precipitation appears to be an important controlling factor, presumably through a wash-out effect of mineralised P. Higher temperatures appear to increase desorbable P_o, either through physico-chemical solubilisation and/or biological mobilisation of moderately labile organic P. Summer sorption maxima may be controlled by soil-drying-induced exposure of new sorption sites, or (microbial-induced) formation of high sorption compounds.

- These results indicate that, despite higher plant P uptake during the growing season, more P is available for desorption to water during this period, although this P may be flushed out relatively quickly during precipitation events.

- Divergence of seasonal P_w and Olsen P variation has important implications for the use of STP as an indicator for potential P losses, for example in relation to the use of change points - which will vary with season.

- Poorly timed management events may result in large increases in P desorption, and grazing appears to increase the desorption/solubilisation of organic P.

- Subsurface water P concentrations displayed high spatial variability, and seasonal variations appear to be controlled by a combination of soil desorbable P contents, hydrology and redox conditions. The limited data here suggest that soil desorbable P contents are not a reliable indicator of spatial or temporal variation in subsurface water P concentrations.

- Limited qualitative comparison with seasonal stream-water P nutrient-flow relationships in the Mask catchment indicate that time-lags and complicating factors affect P loss routes and mechanisms, possibly obscuring any association with soil P desorption. However, this comparison was tentative due to the absence of statistical differences in nutrient-flow relationships between seasons, probably resulting from insufficient data.

CHAPTER 6

CONCLUSIONS

6.1. Main findings

The list of specific aims and objectives listed in section 1.4 have been answered in the bulleted conclusions at the end of each chapter. This short chapter aims to pull together the wok presented in this thesis, and place it in the wider context of understanding, predicting, and mitigating elevated freshwater P concentrations.

6.1.1. How useful are laboratory soil P desorption data for estimating soluble P losses on a catchment scale?

The fundamental aim of this thesis was to realate soil P desorption, as measured in the laboratory, to soluble P losses within the Mask catchment, on a spatial and temporal basis. As briefly explored in section 1.1.5, hydrological and redox factors play a crucial role in determining the magnitude of soil P losses. Soils with exceptionally high STP may not contribute much P to water courses because they are not well hydrologically connected. Much recent work on diffuse soil P losses has focussed on the importance of hydrology. The concepts of critical source areas, and variable source areas, were outlined in section 1.1.5, and are important factors contributing to soil P losses which cannot be accounted for by simple laboratory P desorption experiments: such experiments assess the potential for soil P loss. Figure 6.1 provides a simple schematic overview of the physical characteristics and factors most responsible for determing the extent of diffuse soil P losses, and highlights the importance of factors other than STP - which this study focussed on in particular.

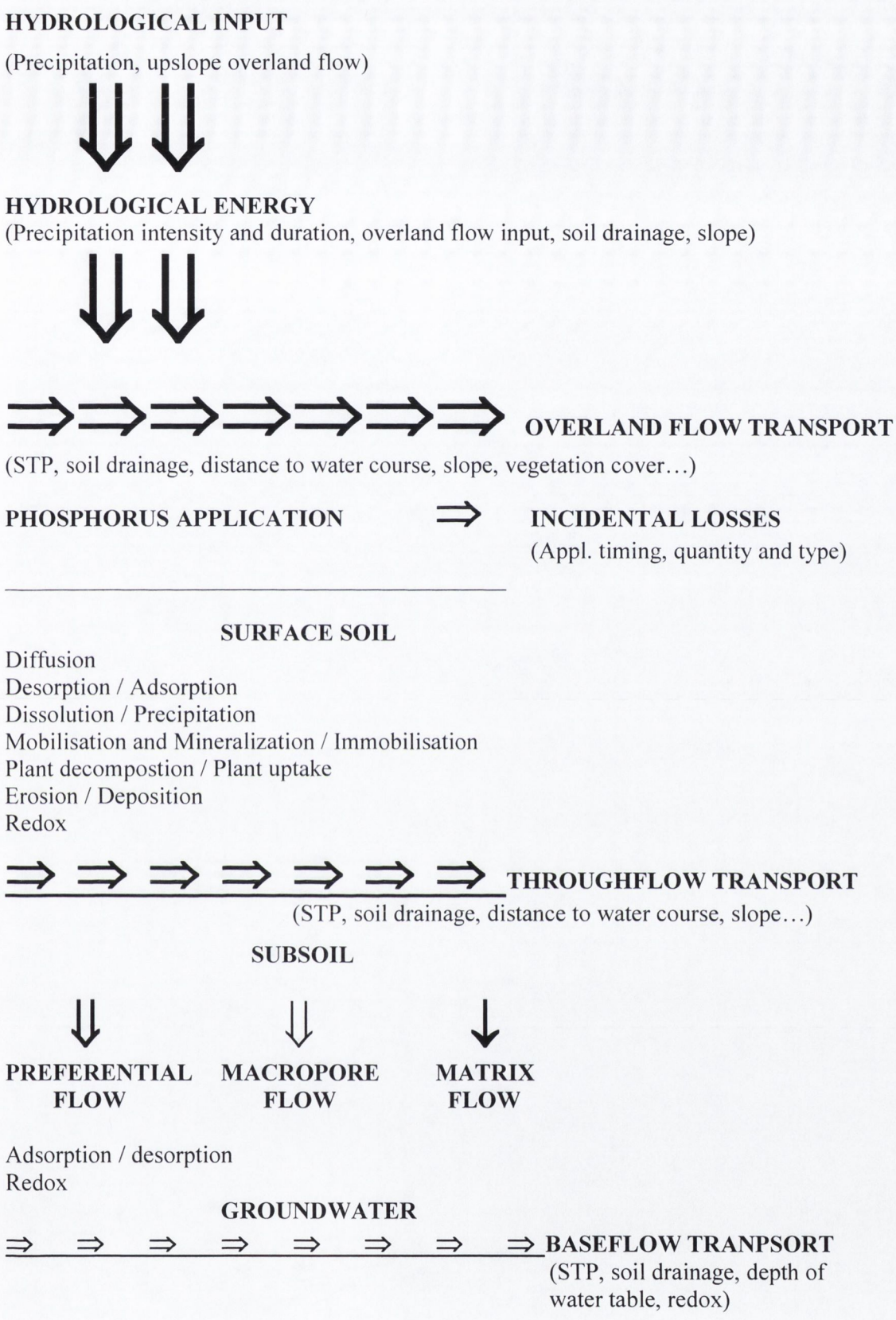


Figure 6.1: A schematic diagram displaying the major drivers and pathways of P loss to water.

Relating STP to diffuse P losses in the Mask catchment is likely to be complicated by a number of factors. As referred to in sections 1.5.4 and 5.4.1, the Mask catchment experiences a temperate, wet climate, and hydrological input and energy are relatively high throughout the catchment. However, a combination of contasting geology, topography and soil types are likely to result in varying dominant hydrological flow pathways, and thus efficiency of soil P transport to streams, thoughout the catchment. The Partry Mountains in the west of the catchment probably experience more precipitation and slightly lower temperatures (and evapotranspiration) than the low-lying eastern side of the catchment. In conjunction with the steeper slopes and impermeable bedrock geology (section 1.5.3), and thinner soils (section 1.5.5), in the west side of the catchment, this would act to increase hydrological energy in this side of the catchment relative to the east (as indicated by large areas of poor soil drainage in figure 1.5). However, there is also a large area in the SW of the catchment dominated by a combination of lithosols and freely-draining podsols, and classified as excessively drained in figure 1.5. Similarly, lithosols found along the eastern shores of Lough Mask (section 1.5.5) overlying karstic limestone, while free-draining, would have little P retention capacity. Additionally, despite deeper soils further east, a seasonally shallow water table in the eastern half of the catchment would encourage P losses through overland flow, especially in the winter months, and result in redox-induced P mobilisation (see section 3.2.4). More intensive agriculture to the north and east of Lough Mask probably results in higher incidental losses east of the Partry Mountains, although any P inputs to soils in the west of the catchment would be highly susceptible to incidental loss.

These variations in fractors important to P loss throughout the catchment may explain why average subcatchment Morgan P concentrations were not significantly related to average annual stream P concentrations or area-weighted loads, despite strong Morgan P-P desorption relationships found in this study (section 4.5.4). Morgan P data were also not of high resolution due to the area coding system used by Daly et al. (2002) (see figure 2.3), and Morgan P contents may have changed since the original data was collected in 1992 (there are suggestions that Morgan P contents north of Lough Carra may have increased due to an increase in intensive pig farming to this area). However, when differential peat-mineral soil desorption characteristics were accounted for in the simple PDI developed in this study (section 4.6), Morgan P, in association with soil type, was positively associated with average annual subcatchment stream P concentrations and area-weighted loading measured in BUFFER sampling over 2001-2002. The average annual subcatchment

stream P concentrations and area-weighted loads were themselves based on extrapolation from bi-weekly sampling (on 25 occasions), and thus may not be accurate representations of actual average annual values (especially considering most annual P loading may occur during a small number of high-flow events). The data did, however, span a wide range of flow rates, including some high-flow events, and should provide a relatively robust ranking of subcatchment P losses (which is the crucial point for the PDI; a ranking index).

The PDI was designed to be very simple, and use data available on a national level. It deliberately does not incorporate other factors (hydrological, redox, etc...) important in soil P losses. The fact that it was significantly associated with subcatchment stream P concentrations and loads, while subcatchment Morgan P alone was not, does indicate that differential soil P desorption is a very important factor in determining P losses. This is strengthened by the fact that hydrological characteristics and flow pathways associated with peat soils (saturation, overland flow dominated) would, if anything, increase P losses from these soils compared with mineral soils (as inferred by Daly et al., 2002). The PDI approach could be further developed through the inclusion of hydrological factors derived from soil type data. Thus, laboratory analysis of soil P desorption, in relation to soil type and STP, is an important and useful tool in helping to determine spatial variation in diffuse P losses to freshwaters on a (sub)catchment scale.

Using laboratory soil P desorption analyses to predict seasonal trends in stream P concentrations within the Mask catchment proved to be unsuccessful. It is clear from substantial variations in immobile, labile, and soluble P fractions either found or alluded to in this study, and associated with meterological drivers (chapter 5), that complex biological P cycling plays an important role in soil P availability and P losses to water. Essentailly, microbiological soil P cycling buffers against plant uptake requirements, and some of these requirements may be satisfied through highly targeted P release (i.e. enzyme and acid-induced mineralisation at root surfaces, and fungal transport of P to plant roots). These processes act to buffer soil solution P, and thus minimise any seasonal trends in soil P losses. The limited seasonal variations in soil P desorption found in this study (section 5.4.4) did not appear to be associated with seasonal variations in soluble stream P concentrations. This may have been due to insufficient data. For example, there were insufficient water data to statistically distinguish P-flow relationships among seasons, and soil P data were only collected on a monthly basis, during which time significant changes may have occurred (wash-out effects, etc). Variability associated with field-scale sampling

(section 2.2.4) also hindered the interpretation of some seasonal trends in soil P characteristics. Alternatively, seasonal relationships between soil P desorption and P losses to water may be completely obscured by hydrological factors and redox effects. Either way, laboratory analysis of soil P desorption does not appear, from the results of this study, to be a useful tool for determining seasonal variation in diffuse P losses. If I was to repeat this study, I would ideally sample fewer soils but more frequently, and from smaller plots, in order to get a clear picture of temporal P trends.

6.1.2. What are the implications of laboratory drying for interpreting soil P desorption data?

Drying soil samples prior to analyses resulted in huge increases (up to 3396%) in desorbable P, both for P_{feo} and P_w (sections 3.4.1 and 3.5.1) and significant increases in Olsen P (section 3.5.2) and P sorption (section 3.5.3). Desorbable P increases were positively related to soil OM and moisture contents, through mechanisms of OM oxidation, aggregate disruption, mineralisation and microbial release (section 3.6.3). Microbial biomass P, P associated with humic acids, and P incorporated within organic compounds, is particularly susceptible to drying-induced release. This resulted in peat soils displaying particularly high proportional increases in P desorption after sample drying (section 3.4.2). Consequently, the differential in moist sample peat-mineral soil desorption per unit Morgan P was reduced by half after sample drying (section 4.8.5), and resulted in an unsuccessful PDI. Soil drying thus appears to obscure important differences in desorption among soil types, and probably results in an underestimation of the importance of differential soil type desorption. Additionally, drying soil samples decreased the strength of STP-P desorption relationships, and reduced differentiation in P desorption between high and low STP soils (section 3.4.5 and 4.5.4). The standard practice of drying soil samples has probably resulted in an underestimation in the importance of STP in predicting soil P desorption and catchment-scale soluble P losses.

Drying soil samples also obscured seasonal differences in P_w (section 3.5.1), and this would lead to an underestimatation of soil P desorption as a factor influencing seasonal variations in stream P concentrations. While no clear association was found in this study between seasonal variation in soil P desorption and stream soluble P concentrations, from a conceptual perspective (figure 6.1) variations in soil P desorption throughout the year

should be an important driver of stream soluble P concentrations. At the very least, by obscuring seasonal variation in soil P desorption, drying soils would result in incorrect weightings being given to drivers of seasonal variation in soil P loss (i.e. soil P mobilisation and desorption may be lower, but hydrological energy higher, during winter compared with summer: the weighting given to hydrological energy would be lower if desorption was considered the same in both seasons, as indicated by dried sample analyses). Additionally, drying and rewetting soils solubilises and mineralises P from both labile P pools (especially portions of microbial P, P associated with organic compounds and complexes, and weakly sorbed P) and immobile P pools (especially portions of microbial P and P incorporated within organic compounds): section 3.6.1 and 3.6.2. It therefore obscures the impact and understanding of important biological cycling processes (section 5.2.1), and pysico-chemical processes (section 5.2.2), on P availability and loss-susceptibility.

In terms of instructiveness, laboratory drying of soil samples is much more extreme than that likely to be encountered to any depth by soils in the Mask catchment during natural summer drying. However, drying may be important in the surface millimetres of the soil where most desorption to overland flow and throughflow waters occurs. This effect would not have been apparent from laboratory analyses of 0-10 cm samples during monthly sampling. The extent of this effect on soil P losses will depend on a number of factors, not least the frequency with which surface drying occurs. If it is a regular annual or occurrence, then microbial populations at the soil surface are likely to have adapted over time to survive these conditions and will not relase (much) P upon rewetting. Release of P from disruption and oxidation of organic compounds and complexes would also operate during drying-rewetting cycles, but would decrease during a sequence of drying events within a short space of time. Unlike microbial P, however, physico-chemical reactions do not have the genetic "memory" that would reduce drying-induced P release in response to periodic drying. Overall, laboratory drying of soils removes them drastically from field conditions, obscuring among-soil and among-season variations in P desorption. However, where natural soil drying occurs to any appreciable extent, studying dried soil samples may be instructive of the extent and mechanisms of seasonal P release.

6.2. Recommendations

6.2.1. Analytical recommendations

The development of a simple PDI which was significantly associated with subcatchment soluble P losses in this study was critically dependent on:

1) the use of moist sample desorption data

2) expression of desorption on a volume (rather than weight) basis.

Therefore, although more time consuming and time restrictive, soil samples should be analysed in moist condition in order to detect among-soil and among-season differences in P desorption potential. The definition of "moist" used in this study was simply the moisture content during sampling, which was often field capacity. When soil samples are to be analysed for seasonal variation, analysis of soils at sampled moisture content is preferable as it minimises laboratory-induced changes in soil moisture and associated physico-chemical and biological factors. However, where soil P desorption is to be compared among soils, there is a desire for soils to be analysed at a consistent, quantified moisture content in order to standardise analyses. Conveniently, this could be gravitational moisture content. An alternative, although perhaps impracticable, solution - that would maintain genuine differences in moisture content and associated differences in P desorption among soils - would be to analyse soils collected during a specified period of the year, at sampled moisture content. Soils should also ideally be analysed on a volume basis in order to accurately compare soils of differing bulk densities – this is especially important where a mixture of peat and mineral soils are considered. Due to the difficulty of accurately measuring volumes of moist, especially wet, soils, weight-based analyses should at least be converted to volume-based expression. Finally, high sample variability indicates that where temporal variations in soil characteristics are to be studied, it may be advisable to limit the size of each sample area to a homogenous unit, rather than attempting to incorporate field-scale variability.

6.2.2. Management recommendations

Strong linear relationships between Morgan P and P desorption, and the significant correlation between the PDI and subcatchment soluble P losses, highlight the importance of regulating STP contents in order to limit diffuse soil P losses. In particular, the choice

of target soil P index has serious implications for water quality where fields are hydrologically well-connected to water courses, and in these instances environmental considerations should be prioritised. Average soil Morgan P content in Ireland is above that necessary for optimum production, and further fertiliser P application to typical agricultural soils is both economically and environmentally unsound. Despite lower P desorption from peat soils, the mechanisms responsible for this reduced desorption may in fact also lead to the rapid loss of applied P. In combination with the naturally wet status of peat soils, and thus high hydrological connectivity with water courses, this makes them unsuitable for intensive agriculture. Rapid and large increases in P_w in response to manure application and intensive grazing highlight the importance of careful timing in field management practices.

There is a clear need for a better understanding of moist sample P desorption in relation to both STP and soil type, in order to better understand, and help predict, diffuse soil P losses. Developing simple soil P desorption indices based on improved understanding of relationships between widely available STP and soil type data and soil P desorption has considerable potential as a cheap and reliable way to assess the relative risk of water P-enrichment on a subcatchment scale. Morgan P appears to be a good indicator of soil P desorption potential. Further research studying temporal variations in moist soil sample P desorption would help to quantify the impact of management practices on diffuse P losses, and could indicate optimum timing for inorganic/organic P applications and grazing in fields of high hydrological connectivity. Findings in this study highlight the importance of appropriate timing of P applications, and grazing, to minimise the potential for P to be lost to water.

6.3. Ideas for future studies

Further work needs to be conducted on moist samples to further define soil-type-specific STP-P desorption relationships, and refine the inputs to the simple PDI developed here. A parameter reflecting the different hydrological characteristics typical of different soil types could be added to the PDI, so that it maximises the information used and inferred from available soil type and STP data.

A crucial finding in this study was the extent, and distorting effect, of P release following sample drying and rewetting in desorption analyses. However, work presented in this thesis did not identify specific mechanisms of P release, which could be instructive in understanding which soils will release more P following laboratory and natural drying processes. A number of experiments could be designed to look at specific mechanisms, and should focus on a range of varying OM content soils (given that so many mechanisms of P release have been associated with OM (section 3.2.2), and OM content is a useful classification parameter):

1) Microbial versus non-microbial release. The P present in water extracts before and after sample drying could be compared using anion exchange chromatography. Microbial lysis would release predominantly diester P, while physical breakdown of organic compounds (such as plant residues and humic and fulvic acids) would release predominantly inositol (hexa)phosphate, although plant material would also include sugar phosphates, phospholipids, and nucleic acids. Drying-induced changes in P_i would represent a combination of (de)sorption site exposure, mineralisation of P_o upon rewetting, release from organo-metallic complexes, and pH-redox effects on sorption/desorption equilibria. Results from these analyses could be compared against increases in moist sample P release to water extracts after fumigation to kill microbial biomass and release P contained within them.

2) Physical aggregate disruption and release from organo-metallic complexes. The effects of drying-induced aggregate breakdown and desorption site exposure may be partly revealed by comparing desorption from moist samples with and without the presence of a non-phosphate based dispersant. The solution used to analyse desorption from non-dispersed samples would need to be made to a similar ionic strength and pH as the dispersant solution in order to correct for any pH and ionic effects on P desorption. Alternatively, pH buffers could also be applied to the dispersant solution in order to detect any pH-specic effect on P release (e.g. more P released at higher pH due to weaker sorption energy?). Anion-exchange chromatography could again be used to isolate P_i released by this process, and identify other species, such as inositol hexaphosphate, which may behave similarly. Anion-exchange chromatography and inductively coupled plasma-mass spectrometry could also be used to identify some complexes (such as humic-metallic-P complexes), and specific elements (such as Fe, Al and Ca) associated with P binding

present in dispersed moist and dried sample water extracts, to determine the extent to which these complexes and elements are degraded or made available by drying.

3) Microbial mineralisation P flush. The amount of P_i released by mineralisation flushes upon rewetting could be estimated by adding a specific microbial mineralisation inhibitor (e.g. a specific heavy metal) to water extracts of dried soil samples. The difference in P_i contents (anion-exchange chromatography) between water extracts with and without this inhibitor added could be inferred to be the microbial mineralisation flush contribution. This experiment could also be conducted using an inhibitor with the P_{feo} test, which theoretically only measures P_i. This would be cheaper and require less sophisticated equipment, but may also be less accurate due to the measurement of fine colloidal P and similar-behaving inositol hexaphosphate attached to the strips.

4) The effects of changing pH after drying could be isolated by comparing drying-induced P increases with and without the addition of pH buffers to extract solutions (water or weak electrolyte for P_{feo} analysis). A similar process could be used to determine the effect of redox changes, though would require the addition of some kind of oxidizing agent, to dried sample extraction solutions only, in order to counteract drying-induced reducing conditions in dried sample extracts.

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APPENDIX A

SUMMARY SITE AND SOIL PROFILE DESCRIPTIONS

This appendix displays data obtained on site and soil characteristics that were not displayed in the main text. All sites were characterised according to location, land use, estimated P application, area of field and brief soil descriptions based on a few augered samples. Monthly-sampled sites 1-11 were described in some additional detail. Below is an example of the questionnaire / data sheets used during soil sampling:

BUFFER sample collection

Date:

Farm Name:

Location:

GPS reference:

Number and type of livestock:

Approximate fertiliser application:

Slurry application:

Area of field:

Soil type / description:

The following pages list summary details of sampled sites and soils, including GPS grid references:

Soil

1. Partry, IM 15390, ITM 74110.

Fertiliser: None applied for past few years.

Site: Grazed grasses and rushes, heavily poached with standing surface water in poached area flat (0-2° east facing slope). See plate A1.

Soil: (Exposed profile; see plate A12).

0-25 cm: Dark brown / black, moist, crumbly peat with most roots down to 5 cm.

25-60 cm: Black, less well decomposed, moisture saturated peat.

60-100 cm: Grey-brown, less well decomposed.

> 100 cm: White-grey marl.

2. Partry, IM13910, ITM 73090.

Fertiliser: 3 bags / acre 0:7:30 NPK and 6 bags / acre N.

Site: Silage grass, south-east facing convex slope (5-15°). See plate A2.

Soil: Light brown with many fine (0.5 mm diameter) orange mottles, compact silty-loam. Higher clay content and gravely below this depth (difficult to auger).

3. Clonee, IM 12995, 74660.

Fertiliser: 1.5 bags / acre 18:6:12 NPK and slurry once per year.

Site: (Heavily) grazed grasses, poaching around gate. East facing, relatively flat at the top half of field, with concave slope at bottom end (~15°). Soils much thinner at bottom end of field. See plate A3.

Soil: (Trial pit, see plate A13).

0-45 cm: 10YR 3/3, with few mottles. Compacted, loamy, with many different sizes of stone and sparse roots to 30 cm depth.

45-60 cm: 2.5 YR 5/8. Iron-pan layer, with black deposits.

> 60 cm: Large stones.

4. Aghinish, IM 15410, 67780.

Fertiliser: Light manure application once per year.

Site: Lightly grazed grasses with some moss. Relatively flat (0-2° south facing slope). Very wet. See plate A4.

Soil: Dark grey-brown clay-loam with some gravel, shallow (10-20 cm deep) overlying limestone bedrock (outcrops nearby).

5. Aghinish, IM 15180, 67530.

Fertiliser: Light manure application once per year.

Site: Moderately grazed grasses, with concave west-facing slope (~20°) in middle of field. Hollow at bottom of field filled with water during winter months. See plate A5.

Soil: Dark-grey-brown clay-loam with some mottles and gravel, of varying depth (10-40 cm).

6. Derassa, IM 08360, ITM 73630.

Fertiliser: None applied.

Site: In Partry mountains (at elevation of 270 m). Lightly grazed (commonage land) grasses, with rushes and mosses in places. Uneven topography, with average east-south-east facing slope of 15-20°. See plate A6.

Soil: Dark brown, fibrous peat of varying depth (~10-50 cm), gravely underneath.

7. Aghinish, IM 15790, 66290.

Site: Pine forestry plantation, relatively even, flat (0-2° west-facing slope) ground. See plate A7.

Soil: Light brown clay-loam underlying ~5 cm poorly decomposed litter layer. Shallow (~10 cm).

8. Annies, IM 19980, ITM 73190.

Fertiliser: No stated P appliaction.

Site: Silage grasses, concave slope ranging in aspect from south (~12°) to west (~4°). See plate A8.

Soil: Dark grey-brown loam with dense roots to 5 cm depth, with light brown compacted loam of higher clay and gravel content underneath. Difficult to auger below 30 cm.

9. Curraboy, IM 24190, ITM 67680.

Fertiliser: 1 bag / acre 18:6:12.

Site: Moderately grazed grasses, with poaching and standing water in places (directly adjacent to Robe rive; evidence of occasional flooding). Relatively even topography, with gentle (~2-4°) west-facing slope). See plate A9.

Soil: Black, well decomposed peat to > 1 m deep.

10. Pollbaun, IM 30490, ITM 65380.

Fertiliser: None applied over past few years.

Site: Moderately grazed grasses, flat, even topography. See plate A10.

Soil: (Trial pit; see plate A14).

0-20 cm: 5 YR 3/3 sitly-loam, with massive structure and roots down to 45 cm, and fairly common small stones (5-10 mm diameter).

20-80 cm: 10 YR 5/2 mixed with 10 YR 6/4 gravely clay. Mottles. Large (5 cm diameter) red nodule (2.5 YR 5/6) and same diameter, well-rounded stones at ~30 cm depth.

11. Ballinchalla, IM 15763, ITM 62042.

Fertiliser: None applied for past 80 years.

Site: Lightly grazed natural grasses. Variable topography with north and west facing slopes of 5-12°. Small field with rock outcrops on south side, and dredged marl next to drainage ditch on north side. See plate A11.

Soil: (Trial pit; see plate A15).

0-30 cm: 7.5 YR 4/2, with few large (5-7 mm diameter) mottles of 7.5 YR 6/8. Silty loam with no stones, wet, high OM content with roots apparent down to 40 cm.

30-50 cm: 5 YR 6/1, with common large mottles (5-10 mm diameter). Sandy horizon, wet, with no stones, few roots and low OM content.

≥50 cm: 10 YR 6/2. Mixture of marl and sand.

12. Castlemargarretpark Old, IM 34672, ITM 71723.

Fertiliser: 2 hundredweight / acre 24:10:2.5 NPK, slurry once per year.

Soil: Sandy in top 20 cm, with increasing clay content, grey colour and orange mottles with depth (especially below 50 cm).

13. Tagheen, IM 28583, ITM 72283.

Fertiliser: half ton / acre 10:20 NP.

Soil: Dark brown, high OM surface horizon, loamy, friable and well-drained. Lighter orange-brown with high clay content below 50 cm.

14. Pollraddy, IM 28990, ITM 71280.

Fertiliser: No P over last 5 years, but lime and 450 lb / acre N.

Soil: Dark grey-brown loam, stony, shallow (30-50 cm cores) soil. Reclaimed.

15. Pollbaun, IM 30730, ITM 65410.

Fertiliser: No P applied over last few years.

Soil: Dark grey-brown loam, gravel and clay below 30 cm, with some orange and reddish colours. Similar to neighbouring soil 10 (see for more detailed description).

16. Clareen, IM 28019, 71109.

Fertiliser: 4 bags / acre 25:2.5:10 NPK.

Soil: Dark brown horizon to 25 cm depth, dark grey-brown below 30 cm. Wet, but better drained and with reddish surface horizon in places.

17. Friarsquater, IM 20560, ITM 65710.

Fertiliser: None applied.

Soil: Black peat to ~80 cm, light grey marl beneath.

18. Derrynacanana, IM 12629, ITM 80347.

Fertiliser: 6 bags / acre 27:5:10 NPK, slurry once per year.

Soil: Dark brown, friable sandy-loam surface horizon 5-30 cm deep, overlying black, stony horizon with higher clay content. Well-drained, with orange patches in places, but shallow (some samples < 10 cm).

19. Derrynacanana, IM 12343, ITM 80392.

Fertiliser: 6 bags / acre 27:5:10 NPK, slurry once per year: 2001 first year of application (reclaimed).

Soil: Similar to soil 18, but on level topography and moisture saturated in places, with black and orange mottles.

20. Ballintober, IM 15559, ITM 79316.

Fertiliser: No stated application, but very intensive grazing at time of sampling (and often when driving past on other sampling trips), and looked like had been applied to part of field; this part of field avoided for sample collection.

Soil: Dark brown clay-loam to 40-50 cm depth, lighter brown with some orange-tinted patches and black nodules below.

21. Baunoges, IM 16031, ITM 78219.

Fertiliser: 3 bags / acre, slurry every 2nd year. Twenty-four sheep in ~ 0.5 ha field. **Soil:** Reddish-brown sandy clay loam surface horizon, with orange clay below 70 cm. 70– 100 cm deep, well-drained but heavily poached on surface.

22. Moorehall, IM 18111, ITM 72679.

Fertiliser: 1 bag / acre low P fert., and slurry once per year.

Soil: Dark brown loamy surface horizon, with some mottles and orangey high clay content horizon below ~ 70 cm.

23. Muckloon, IM 18876, ITM 73987. Deciduous forest.

Soil: Pale grey-brown loamy surface horizon with high clay content in places, overlying higher clay content horizon below ~50 cm and with orange mottles below ~70 cm.

24. Clooncann, IM 20515, ITM 73566.

Fertiliser: None applied.

Soil: Deep (> 1 m), black peat.

25. Stonepark, IM 21771, ITM 74004.

Fertiliser: 3 bags / acre 18:6:12 NPK and 1.5 bag / acre N.

Soil: Grey-brown silty-loam surface horizon with few mottles, overlying higher clay content, paler orange horizon with some gravel.

26. Derrynamuck, IM 11790, ITM 75490.

Fertiliser: 0.5 bag acre 18:6:12.

Soil: Brown fibrous peat, very wet to depth > 1 m.

27. Derrassa, IM 10344, ITM 73512.

Fertiliser: 5 bags / acre 18:6:12 / 10:10:20 NPK, and slurry once per year for first time in 2001.

Soil: Dark brown, loamy surface horizon with few mottles, and peat in places, shallow (less than 5 cm in places).

28. Tawnagh, IM 11108, ITM 71127.

Fertiliser: 2 bags of 18:6:12 over ~0.2 ha field.

Soil: Grey-brown loamy sand surface horizon with reddish patches and some red mottles overlying a lighter grey-brown gravely sand horizon below ~10 cm, and horizon with stronger red colouration and higher clay content below.

29. Tormakeady, IM 08801, ITM 68623.

Mixed forest cover.

Soil: Reddish-brown loamy surface horizon overlying lighter coloured, sandier, horizon which has strong red colouration and higher clay content at 50-100 cm depth.

30. Killitine, IM 04280, ITM 62999.

Fertiliser: 2 bags / acre 18:6:12.

Soil: Grey-brown, silty, sandy loam surface horizon 50-100 cm deep. Bright red sand below ~70 cm depth. Some mottles.

31. Shranalong, IM 00311, ITM 61176.

Fertiliser: None stated, though grass green compared to surrounding, unfenced grassland, and bags of fertiliser on farm.

Soil: Shallow grey-brown surface horizon of varying texture overlying light grey horizon with few mottles to depth > 1 m. On slope.

32. Aghalahard, IM 13567, ITM 56766.

Fertiliser: None.

Soil: Grey-brown loam surface horizon, with higher clay content and some orange colour below. 50-70 cm cores.

33. Derrew, IM 14190, ITM 75854.

Fertiliser: 'Low' occasional applications.

Soil: Black, well-decomposed peat > 1 m deep.

34. Kilkeeran, IM 17128, ITM 64867.

Fertiliser: None applied.

Soil: Dark grey-brown silty loam surface horizon, light grey and mottled (gleyed) from ~50 cm downwards. Shallow (40-80 cm deep).

35. Creagh, IM 17005, ITM 64941.

Fertiliser: None applied.

Soil: Same profile as 34 (across the Robe river from that site).

36. Derryveeny, IM 07252, ITM 67301.

Fertiliser: 3 bags 0:7:10 NPK, 3 bags N and light slurry over 10 acre field.

Soil: Dark grey-brown loam, peaty in places, overlying podzolic profile (exposed in ditch).

37. Creagh, IM 16364, ITM 65606.

Fertiliser: 2 bags 18:6:12 and 1 bag N / acre, and slurry application once per year. **Soil:** Dark grey-brown loam up to about 25 cm, directly overlying bedrock.

38. Claremorris, IM 36255, ITM 75483 .

Fertiliser: 2 bags / ha 0:7:30 NPK and slurry application once per year.

Soil: Black, well decomposed, well-drained peat > 1 m deep.

39. Claremorris, IM 36010, ITM 74905.

Fertiliser: Slurry application once per year.

Soil: Black, well decomposed, well-drained peat > 1 m deep.

SITE PHOTOS



Plate A1: Site 1, Partry.



Plate A2: Site 2, Partry.



Plate A3: Site 3, Cloonee.

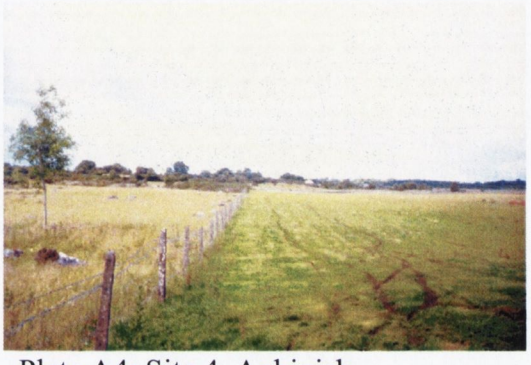

Plate A4: Site 4, Aghinish.



Plate A5: Site 5, Aghinish.



Plate A6: Site 6, Derassa.



Plate A7: Site 7, Aghinish.

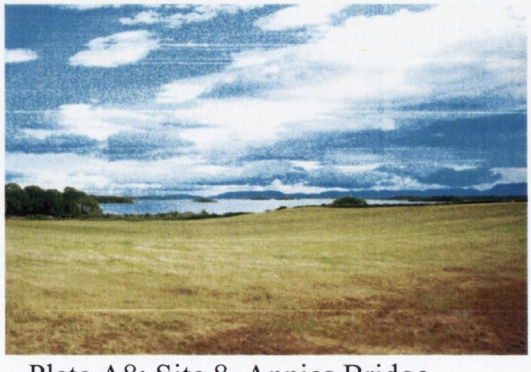

Plate A8: Site 8, Annies Bridge.



Plate A9: Site 9, Foxhill Bridge.



Plate A10: Site 10, Polbaun.



Plate A11: Site 11, Ballinchalla.

SOIL PHOTOS



Plate A12: Soil 1 exposed profile.



Plate A13: Soil 3 trial pit.



Plate A14: Soil 10 trial pit.



Plate A15: Soil 11 trial pit.

APPENDIX B

ADDITIONAL SOIL AND METEOROLOGICAL DATA

Table B1: Analytical data for dried soil samples collected from 0-5 cm depth in March 2002 from sites 1-36, including sorption from solutions containing 5 and 30 mg P l^{-1} (section 2.2.3) and Freunclick (log) K_f values calculated from these data (formula in section 4.2.3) – both with and without the inclusion of P_{ox} as native P.

Soil	TOC	TN	pH	Morgan	Olsen		Pw		Sorption		Log Freundlick K_f	
no.				P	P	TP	DRP	TDP	5 mg P	30 mg P	Excl. P_{ox}	Inc. P_{ox}
1	36.7	2.30	5.01	5.2	17.85	72.96	18.89	38.91	105.90	606.95	2.42	2.67
2	3.9	0.45	5.21	8.5	72.48	141.55	12.45	24.39	101.42	561.31	2.53	3.00
3	8.2	0.65	5.71	13.5	92.80	138.60	34.57	51.12	85.04	350.12	1.96	2.95
4	8.1	0.69	7.27	10.6	20.40	43.66	11.47	30.13	79.65	240.72	1.87	2.56
5	4.2	0.45	6.16	7.0	17.81	56.95	10.09	23.11	89.54	318.05	2.03	2.51
6	33.3	1.64	4.27	5.5	18.09	67.27	24.48	36.89	93.46	511.92	2.10	2.36
7	8.1	0.64	5.96	3.6	4.00	20.38	5.14	14.54	102.16	460.26	2.30	2.62
8	3.7	0.42	7.15	10.0	38.38	71.18	7.41	19.87	97.36	441.00	2.23	2.83
9	31.3	2.34	6.70	5.2	18.26	45.61	5.80	46.01	111.74	661.29	2.86	2.95
10	6.7	0.58	6.02	12.6	65.33	108.85	15.14	25.10	86.32	335.51	1.98	2.78
11	4.7	0.44	7.43	7.7	10.32	33.48	3.90	13.79	93.69	350.37	2.12	2.55
12	2.5	0.35	5.54	4.6	31.16	76.19	6.30	15.09	99.74	474.82	2.35	2.73
13	7.0	0.71	6.45	28.8	110.53	139.56	35.38	48.80	84.62	373.82	1.95	
14	5.8	0.53	6.35	5.2	17.56	40.20	6.91	16.32	99.80	492.30	2.34	2.69
15	5.6	0.47	6.05	6.0	24.27	48.94	10.26	18.44	96.50	404.70	2.18	2.56
16	4.2	0.50	5.76	5.9	21.96	58.13	11.51	21.76	95.49	394.70	2.16	2.64
17	19.7	1.82	7.12	0.3	13.37	32.23	5.85	17.06	107.35	629.61	2.74	2.91
18	8.7	1.07	5.96	21.2	101.16	121.90	40.86	51.76	86.71	218.71	1.96	3.10
19	8.3	0.55	7.53	8.1	39.45	56.35	9.64	19.51	75.53	346.50	1.79	2.65
20	6.9	0.72	6.62	20.2	100.64	119.64	25.00	36.40	87.61	372.46	1.99	3.15
21	6.4	0.63	6.57	21.6	107.32	132.62	30.14	42.01	85.86	373.82	1.96	3.18
22	6.7	0.48	6.58	13.2	61.63	89.24	20.15	31.70	91.67	382.43	2.08	
23	5.4	0.49	6.37	4.4	4.88	17.87	3.56	13.50	96.48	361.85	2.15	2.32
24	24.4	1.60	5.38	4.3	9.74	27.85	15.14	25.16	96.48	641.67	3.01	3.05
25	5.0	0.58	5.79	5.1	17.43	48.13	6.45	17.62	100.06	488.18	2.33	2.72
26	18.0	1.09	5.23	4.8	23.69	63.15	6.57	15.30	106.13	632.88	3.06	3.18
27	13.2	1.05	4.91	9.1	53.89	120.21	30.22	47.31	88.06	392.91	2.00	2.79
28	4.4	0.37	5.41	13.7	111.49	157.01	28.00	39.48	92.31	404.51	2.10	3.10
29	3.7	0.22	4.98	1.5	3.89	19.88	2.30	6.10	102.35	399.26	2.37	2.45
30	3.2	0.27	5.43	3.9	16.36	58.50	4.10	11.44	98.07	378.79	2.27	2.61
31	4.1	0.31	5.30	10.4	43.59	82.60	12.30	18.84	87.44	264.64	2.04	2.60
32	4.7	0.36	6.14	6.4	43.92	57.46	7.13	19.48	98.32	467.50	2.28	
33	27.4	1.70	5.38	4.8	13.16	50.71	20.11	34.63	107.04	630.70	2.76	2.91
34	10.6	1.07	6.79	4.8	9.41	28.06	5.28	15.59	104.67	607.00	2.72	2.88
35	3.0	0.33	7.93		11.82	24.71	3.74	10.83	98.02	433.54	2.26	
36	11.8	0.64	5.76	5.3	26.99	48.58	9.94	17.51	98.27	482.60	2.25	2.74

Table B2: Analytical data for dried samples collected from 0-10 cm depth during spring 2002 from the Fervenza (USC-F) and Portodemouro (USC-P) catchments in Galicia, and from the Friary catchment (UU-F) in N. Ireland. Included are sorption from solutions containing 5 and 30 mg P l^{-1} (section 2.2.3) and Freunclich (log) K_f values calculated from these data (formula in section 4.2.3) – without native P.

Soil	TOC	TN	pH	Olsen		Pw		Sorption		Log K_f
ref.				P	TP	DRP	TDP	5 mg P	30 mg P	
USC										
F1	6.2	0.57	5.14	60.28	85.09	3.74	7.74	98.83	563.58	2.62
F3	6.7	0.53	4.58	9.63	29.48	1.13	2.91	99.61	592.53	3.03
F9	7.0	0.54	5.17	60.64	89.95	7.62	10.59	98.49	550.46	2.55
F10	7.2	0.73	5.40	75.26	95.11	5.33	8.53	97.88	561.57	2.58
F12	6.8	0.45	4.76	12.84	25.22	1.58	2.13	99.18	545.37	2.56
F14	3.4	0.34	5.22	95.59	137.38	13.98	19.71	95.06	481.62	2.29
F16	8.9	0.55	5.20	88.10	109.01	12.20	16.59	97.57	562.12	2.57
F17	10.1	0.43	4.87	11.41	23.54	1.46	3.16	99.65	588.89	2.90
F19	5.7	0.37	5.30	48.51	89.00	4.02	7.49	99.11	577.60	2.73
P3	2.7	0.07	5.06	36.38	64.17	2.30	4.58	98.79	527.70	2.49
P5	4.5	0.17	5.35	4.99	16.88	1.06	3.10	99.68	584.34	2.81
P8	5.1	0.21	5.23	29.25	61.20	6.11	9.44	89.20	272.19	2.04
P10	5.7	0.33	5.44	31.75	62.31	5.62	9.75	96.45	451.76	2.29
P13	4.6	0.27	5.22	5.35	24.47	1.13	4.54	99.67	591.62	2.98
P15	2.8	0.18	5.39	15.69	42.29	4.98	9.33	95.78	354.87	2.20
P17	4.3	0.33	5.09	118.07	162.21	17.98	21.44	83.31	286.03	1.95
P18	2.5	0.16	5.48	27.11	47.85	4.35	7.61	93.96	347.59	2.16
P20	2.9	0.23	5.46	12.13	41.91	2.58	7.26	97.38	451.39	2.32
UU										
F1	6.7	0.51	5.28	31.75	85.47	13.37	25.90	95.13	406.59	2.22
F2	4.3	0.34	5.42	20.33	60.06	8.41	18.64	96.32	438.65	2.28
F3	4.9	0.41	5.12	76.33	138.13	19.64	29.08	94.95	469.97	2.27
F4	7.7	0.64	5.94	27.82	69.72	13.49	27.32	95.89	498.38	2.33
F5	10.9	0.74	5.21	17.83	76.21	5.55	14.96	99.42	581.42	2.78
F6	7.5	0.63	5.50	28.89	75.27	14.15	28.58	93.79	404.41	2.19
W1	5.5	0.51	5.20	51.72	102.90	18.10	29.48	92.79	416.79	2.17
W2	5.1	0.50	5.23	58.86	97.88	17.60	26.28	92.74	402.22	2.16
W3	4.6	0.42	5.27	64.56	110.49	15.56	25.52	94.85	422.98	2.23
W4	6.4	0.57	6.14	14.27	49.70	10.43	23.33	95.97	401.49	2.24
W5	7.2	0.64	5.31	52.79	98.81	22.42	36.11	88.85	422.25	2.09

Table B3: Daily mean temperature (°C) and total precipitation ((mm) data from Claremorris synoptic station: 52° 48.73' N, 8° 58.29' W used in sstatistical analyses of monthly-soil and subsurface water sampling data. Source: Met Eireann. Also shown total daily effective precipitation (mm) during 2002, calculated ffrom monthly-mean potential evaporation data from Connaught airport. Mean valuies of these parameters for the month and week preceding monthly soil sampling dates are highlighted.

Season	Date	Temp.	Prec.	EPrec.	Season	Date	Temp.	Prec.	EPrec.	Season	Date	Temp.	Prec.	EPrec.
Winter	1-Dec-01	4.80	1.30	1.24	Winter	21-Jan-02	9.30	3.20	3.09	Spring	15-Mar-02	4.70	5.00	4.06
Winter	2-Dec-01	4.80	4.70	4.64	Winter	22-Jan-02	5.90	4.10	3.99	Spring	16-Mar-02	8.50	1.70	0.76
Winter	3-Dec-01	7.60	25.50	25.44	Winter	23-Jan-02	8.30	6.10	5.99	Spring	17-Mar-02	7.70	1.90	0.96
Winter	4-Dec-01	6.90	3.00	2.94	Winter	24-Jan-02	4.70	0.40	0.29	**Monthly mean**		**6.12**	**4.94**	**4.13**
Winter	5-Dec-01	6.50	8.30	8.24	Winter	25-Jan-02	7.40	12.70	12.59	**Weekly mean**		**5.61**	**1.39**	**0.45**
Winter	6-Dec-01	6.70	6.60	6.54	Winter	26-Jan-02	6.70	8.30	8.19	Spring	18-Mar-02	5.40	7.00	6.06
Winter	7-Dec-01	11.60	0.50	0.44	Winter	27-Jan-02	8.20	4.30	4.19	Spring	19-Mar-02	7.00	1.70	0.76
Winter	8-Dec-01	7.20	0.10	0.04	Winter	28-Jan-02	8.60	2.90	2.79	Spring	20-Mar-02	9.60	2.60	1.66
Winter	9-Dec-01	4.40	0.00	-0.06	Winter	29-Jan-02	8.40	3.40	3.29	Spring	21-Mar-02	9.60	1.20	0.26
Winter	10-Dec-01	3.60	0.00	-0.06	Winter	30-Jan-02	7.00	3.10	2.99	Spring	22-Mar-02	11.50	0.50	-0.44
Winter	11-Dec-01	4.40	0.00	-0.06	Winter	31-Jan-02	6.90	11.20	11.09	Spring	23-Mar-02	12.60	0.10	-0.84
Winter	12-Dec-01	4.80	0.00	-0.06	Winter	1-Feb-02	8.60	17.20	16.61	Spring	24-Mar-02	10.60	1.00	0.06
Winter	13-Dec-01	5.20	0.00	-0.06	Winter	2-Feb-02	6.70	5.90	5.31	Spring	25-Mar-02	6.20	0.40	-0.54
Winter	14-Dec-01	2.50	0.00	-0.06	Winter	3-Feb-02	3.90	11.60	11.01	Spring	26-Mar-02	4.90	0.00	-0.94
Winter	15-Dec-01	0.10	0.00	-0.06	Winter	4-Feb-02	5.80	12.30	11.71	Spring	27-Mar-02	9.10	0.00	-0.94
Winter	16-Dec-01	3.40	0.00	-0.06	Winter	5-Feb-02	5.30	6.60	6.01	Spring	28-Mar-02	9.20	0.00	-0.94
Winter	17-Dec-01	3.00	0.00	-0.06	Winter	6-Feb-02	5.70	0.90	0.31	Spring	29-Mar-02	6.80	0.00	-0.94
Monthly mean		**6.59**	**3.45**	**3.38**	Winter	7-Feb-02	9.00	3.70	3.11	Spring	30-Mar-02	7.20	2.20	1.26
Weekly mean		**3.34**	**0.00**	**-0.06**	Winter	8-Feb-02	9.40	7.30	6.71	Spring	31-Mar-02	10.20	1.00	0.06
Winter	18-Dec-01	2.20	0.00	-0.06	Winter	9-Feb-02	7.20	12.50	11.91	Spring	1-Apr-02	8.30	0.10	-1.98
Winter	19-Dec-01	4.00	0.10	0.04	Winter	10-Feb-02	8.20	14.60	14.01	Spring	2-Apr-02	8.10	1.30	-0.78
Winter	20-Dec-01	2.50	0.00	-0.06	Winter	11-Feb-02	9.20	6.70	6.11	Spring	3-Apr-02	8.40	0.00	-2.08
Winter	21-Dec-01	5.60	0.80	0.74	Winter	12-Feb-02	7.90	0.80	0.21	Spring	4-Apr-02	7.10	0.00	-2.08
Winter	22-Dec-01	2.40	0.20	0.14	Winter	13-Feb-02	4.30	3.00	2.41	Spring	5-Apr-02	8.60	1.20	-0.88
Winter	23-Dec-01	3.90	1.20	1.14	Winter	14-Feb-02	2.20	0.00	-0.59	Spring	6-Apr-02	8.10	0.00	-2.08
Winter	24-Dec-01	7.10	0.70	0.64	Winter	15-Feb-02	7.70	0.00	-0.59	Spring	7-Apr-02	8.40	0.00	-2.08
Winter	25-Dec-01	3.50	1.30	1.24	Winter	16-Feb-02	8.20	0.00	-0.59	Spring	8-Apr-02	7.30	0.00	-2.08
Winter	26-Dec-01	3.20	0.60	0.54	Winter	17-Feb-02	5.80	1.30	0.71	Spring	9-Apr-02	9.10	0.00	-2.08
Winter	27-Dec-01	8.40	1.60	1.54	Winter	18-Feb-02	5.60	1.70	1.11	Spring	10-Apr-02	10.10	0.00	-2.08
Winter	28-Dec-01	4.80	0.00	-0.06	**Monthly mean**		**6.89**	**5.81**	**5.39**	Spring	11-Apr-02	6.90	1.50	-0.58
Winter	29-Dec-01	0.80	6.20	6.14	**Weekly mean**		**5.96**	**0.97**	**0.38**	Spring	12-Apr-02	6.80	0.00	-2.08
Winter	30-Dec-01	0.00	2.60	2.54	Winter	19-Feb-02	9.10	18.20	17.61	Spring	13-Apr-02	5.20	0.00	-2.08
Winter	31-Dec-01	-2.90	0.00	-0.06	Winter	20-Feb-02	5.70	1.50	0.91	Spring	14-Apr-02	7.00	0.30	-1.78
Winter	1-Jan-02	-2.30	0.00	-0.11	Winter	21-Feb-02	6.30	3.80	3.21	Spring	15-Apr-02	7.00	0.00	-2.08
Winter	2-Jan-02	3.70	5.40	5.29	Winter	22-Feb-02	6.80	1.40	0.81	**Monthly mean**		**8.25**	**0.54**	**-1.01**
Winter	3-Jan-02	6.60	1.00	0.89	Winter	23-Feb-02	3.60	6.60	6.01	**Weekly mean**		**7.44**	**0.26**	**-1.82**
Winter	4-Jan-02	8.90	11.10	10.99	Winter	24-Feb-02	6.50	16.80	16.21	Spring	16-Apr-02	9.60	10.10	8.02
Winter	5-Jan-02	6.90	0.00	-0.11	Winter	25-Feb-02	9.10	6.10	5.51	Spring	17-Apr-02	6.20	0.00	-2.08
Winter	6-Jan-02	6.00	0.00	-0.11	Winter	26-Feb-02	4.80	4.30	3.71	Spring	18-Apr-02	7.50	0.50	-1.58
Winter	7-Jan-02	5.70	0.00	-0.11	Winter	27-Feb-02	3.20	7.60	7.01	Spring	19-Apr-02	7.70	0.20	-1.88
Winter	8-Jan-02	6.80	0.00	-0.11	Winter	28-Feb-02	3.30	1.80	1.21	Spring	20-Apr-02	14.00	4.50	2.42
Winter	9-Jan-02	5.40	0.10	-0.01	Spring	1-Mar-02	3.70	0.00	-0.94	Spring	21-Apr-02	12.60	6.70	4.62
Winter	10-Jan-02	4.10	0.70	0.59	Spring	2-Mar-02	4.50	1.30	0.36	Spring	22-Apr-02	13.20	0.00	-2.08
Winter	11-Jan-02	7.80	0.00	-0.11	Spring	3-Mar-02	8.60	0.00	-0.94	Spring	23-Apr-02	12.60	0.00	-2.08
Winter	12-Jan-02	10.00	1.70	1.59	Spring	4-Mar-02	7.40	0.20	-0.74	Spring	24-Apr-02	11.50	0.30	-1.78
Winter	13-Jan-02	10.00	0.60	0.49	Spring	5-Mar-02	6.50	1.60	0.66	Spring	25-Apr-02	8.60	2.00	-0.08
Winter	14-Jan-02	7.50	6.10	5.99	Spring	6-Mar-02	9.90	8.80	7.86	Spring	26-Apr-02	8.40	5.70	3.62
Winter	15-Jan-02	5.10	3.70	3.59	Spring	7-Mar-02	10.20	0.00	-0.94	Spring	27-Apr-02	7.60	3.10	1.02
Winter	16-Jan-02	9.30	0.70	0.59	Spring	8-Mar-02	7.20	6.10	5.16	Spring	28-Apr-02	6.70	7.40	5.32
Winter	17-Jan-02	5.40	1.60	1.49	Spring	9-Mar-02	3.60	18.90	17.96	Spring	29-Apr-02	8.10	5.00	2.92
Winter	18-Jan-02	6.20	5.80	5.69	Spring	10-Mar-02	5.90	18.80	17.86	Spring	30-Apr-02	8.20	4.00	1.92
Winter	19-Jan-02	7.10	3.10	2.99	Spring	11-Mar-02	6.10	1.10	0.16	Spring	1-May-02	6.80	1.00	-1.17
Winter	20-Jan-02	10.10	10.60	10.49	Spring	12-Mar-02	3.80	0.00	-0.94	Spring	2-May-02	8.10	0.80	-1.37
Monthly mean		**5.54**	**2.33**	**2.23**	Spring	13-Mar-02	4.20	0.00	-0.94	Spring	3-May-02	7.70	0.10	-2.07
Weekly mean		**7.24**	**4.51**	**4.40**	Spring	14-Mar-02	4.30	0.00	-0.94	Spring	4-May-02	9.20	0.00	-2.17

Table B3 continued.

Season	Date	Temp.	Prec.	EPrec.	Season	Date	Temp.	Prec.	EPrec.	Season	Date	Temp.	Prec.	EPrec.
Spring	5-May-02	11.40	0.00	-2.17	Summer	26-Jun-02	12.80	0.00	-2.30	Summer	17-Aug-02	15.05	2.60	0.90
Spring	6-May-02	11.60	0.00	-2.17	Summer	27-Jun-02	12.10	0.00	-2.30	Summer	18-Aug-02	14.85	0.50	-1.20
Spring	7-May-02	10.80	0.20	-1.97	Summer	28-Jun-02	11.20	0.00	-2.30	Summer	19-Aug-02	13.55	0.00	-1.70
Spring	8-May-02	13.10	1.00	-1.17	Summer	29-Jun-02	14.40	0.20	-2.10	Summer	20-Aug-02	13.45	0.00	-1.70
Spring	9-May-02	12.00	0.90	-1.27	Summer	30-Jun-02	12.10	4.00	1.70	Summer	21-Aug-02	13.95	0.00	-1.70
Spring	10-May-02	11.10	1.40	-0.77	Summer	1-Jul-02	12.50	3.20	1.04	Summer	22-Aug-02	17.10	0.00	-1.70
Spring	11-May-02	8.20	0.10	-2.07	Summer	2-Jul-02	11.15	2.10	-0.06	Summer	23-Aug-02	15.25	0.40	-1.30
Spring	12-May-02	7.90	5.70	3.53	Summer	3-Jul-02	12.20	0.90	-1.26	Summer	24-Aug-02	13.80	0.00	-1.70
Monthly mean		**9.64**	**2.25**	**0.13**	Summer	4-Jul-02	11.30	8.20	6.04	Summer	25-Aug-02	12.75	0.00	-1.70
Weekly mean		**10.67**	**1.33**	**-0.84**	Summer	5-Jul-02	15.30	0.00	-2.16	Summer	26-Aug-02	13.55	0.00	-1.70
Spring	13-May-02	10.10	10.20	8.03	Summer	6-Jul-02	13.25	1.60	-0.56	Summer	27-Aug-02	16.90	1.30	-0.40
Spring	14-May-02	10.90	0.30	-1.87	Summer	7-Jul-02	11.85	4.60	2.44	Summer	28-Aug-02	16.40	4.70	3.00
Spring	15-May-02	12.50	0.30	-1.87	**Monthly mean**		**12.73**	**2.60**	**0.34**	Summer	29-Aug-02	14.00	0.70	-1.00
Spring	16-May-02	14.80	2.50	0.33	**Weekly mean**		**12.51**	**2.94**	**0.79**	Summer	30-Aug-02	13.85	14.50	12.80
Spring	17-May-02	12.70	10.40	8.23	Summer	8-Jul-02	12.95	1.60	-0.56	Summer	31-Aug-02	12.45	0.00	-1.70
Spring	18-May-02	11.90	0.50	-1.67	Summer	9-Jul-02	13.10	0.60	-1.56	Autumn	1-Sep-02	12.05	0.00	-1.45
Spring	19-May-02	11.40	1.00	-1.17	Summer	10-Jul-02	12.85	5.40	3.24	Autumn	2-Sep-02	12.75	0.10	-1.35
Spring	20-May-02	10.60	10.00	7.83	Summer	11-Jul-02	12.35	5.80	3.64	Autumn	3-Sep-02	14.60	0.00	-1.45
Spring	21-May-02	9.50	3.30	1.13	Summer	12-Jul-02	13.20	0.40	-1.76	Autumn	4-Sep-02	14.65	0.10	-1.35
Spring	22-May-02	11.40	6.30	4.13	Summer	13-Jul-02	12.55	0.00	-2.16	Autumn	5-Sep-02	13.15	3.50	2.05
Spring	23-May-02	11.20	7.50	5.33	Summer	14-Jul-02	18.30	0.00	-2.16	Autumn	6-Sep-02	13.00	3.50	2.05
Spring	24-May-02	11.20	17.90	15.73	Summer	15-Jul-02	16.95	0.00	-2.16	**Monthly mean**		**14.18**	**1.74**	**0.09**
Spring	25-May-02	9.30	10.00	7.83	Summer	16-Jul-02	14.30	0.00	-2.16	**Weekly mean**		**13.24**	**1.03**	**-0.46**
Spring	26-May-02	10.60	20.00	17.83	Summer	17-Jul-02	12.85	0.00	-2.16	Autumn	7-Sep-02	12.80	10.70	9.25
Spring	27-May-02	11.70	4.90	2.73	Summer	18-Jul-02	12.60	0.00	-2.16	Autumn	8-Sep-02	11.90	20.50	19.05
Spring	28-May-02	10.30	14.50	12.33	Summer	19-Jul-02	13.85	5.20	3.04	Autumn	9-Sep-02	12.30	0.20	-1.25
Spring	29-May-02	10.80	2.30	0.13	Summer	20-Jul-02	13.80	0.00	-2.16	Autumn	10-Sep-02	10.75	3.10	1.65
Spring	30-May-02	10.60	3.30	1.13	Summer	21-Jul-02	13.75	0.40	-1.76	Autumn	11-Sep-02	16.95	1.90	0.45
Spring	31-May-02	9.00	0.20	-1.97	Summer	22-Jul-02	16.50	2.40	0.24	Autumn	12-Sep-02	15.60	0.00	-1.45
Summer	1-Jun-02	13.00	0.70	-1.60	Summer	23-Jul-02	13.80	0.20	-1.96	Autumn	13-Sep-02	16.60	0.00	-1.45
Summer	2-Jun-02	11.70	11.60	9.30	Summer	24-Jul-02	13.70	0.00	-2.16	Autumn	14-Sep-02	13.20	0.00	-1.45
Summer	3-Jun-02	9.80	1.60	-0.70	Summer	25-Jul-02	18.25	0.00	-2.16	Autumn	15-Sep-02	12.95	0.00	-1.45
Summer	4-Jun-02	9.60	1.50	-0.80	Summer	26-Jul-02	15.55	0.00	-2.16	Autumn	16-Sep-02	13.30	0.00	-1.45
Summer	5-Jun-02	9.00	3.00	0.70	Summer	27-Jul-02	17.35	0.70	-1.46	Autumn	17-Sep-02	13.70	0.00	-1.45
Summer	6-Jun-02	13.40	0.00	-2.30	Summer	28-Jul-02	15.25	1.70	-0.46	Autumn	18-Sep-02	14.65	0.00	-1.45
Summer	7-Jun-02	13.30	3.00	0.70	Summer	29-Jul-02	15.05	0.20	-1.96	Autumn	19-Sep-02	14.60	0.00	-1.45
Summer	8-Jun-02	11.20	0.00	-2.30	Summer	30-Jul-02	14.30	0.00	-2.16	Autumn	20-Sep-02	13.30	0.00	-1.45
Summer	9-Jun-02	10.00	15.10	12.80	Summer	31-Jul-02	13.45	1.00	-1.16	Autumn	21-Sep-02	12.45	0.00	-1.45
Summer	10-Jun-02	11.60	2.70	0.40	Summer	1-Aug-02	18.15	0.00	-1.70	Autumn	22-Sep-02	12.00	0.00	-1.45
Monthly mean		**11.18**	**5.51**	**3.30**	Summer	2-Aug-02	20.10	0.00	-1.70	Autumn	23-Sep-02	11.55	0.00	-1.45
Weekly mean		**11.16**	**3.61**	**1.32**	Summer	3-Aug-02	17.55	0.00	-1.70	Autumn	24-Sep-02	11.45	0.00	-1.45
Summer	11-Jun-02	11.80	2.70	0.40	Summer	4-Aug-02	18.70	0.00	-1.70	Autumn	25-Sep-02	10.35	0.00	-1.45
Summer	12-Jun-02	10.20	4.20	1.90	Summer	5-Aug-02	19.00	4.20	2.50	Autumn	26-Sep-02	12.65	0.00	-1.45
Summer	13-Jun-02	11.10	8.00	5.70	**Monthly mean**		**15.26**	**1.01**	**-1.07**	Autumn	27-Sep-02	11.90	0.00	-1.45
Summer	14-Jun-02	14.10	5.90	3.60	**Weekly mean**		**17.32**	**0.74**	**-1.09**	Autumn	28-Sep-02	14.75	0.00	-1.45
Summer	15-Jun-02	14.50	2.90	0.60	Summer	6-Aug-02	18.10	6.60	4.90	Autumn	29-Sep-02	14.80	6.90	5.45
Summer	16-Jun-02	13.40	6.70	4.40	Summer	7-Aug-02	13.40	0.00	-1.70	Autumn	30-Sep-02	16.70	0.10	-1.35
Summer	17-Jun-02	14.90	0.90	-1.40	Summer	8-Aug-02	12.45	14.20	12.50	Autumn	1-Oct-02	17.25	0.40	-0.07
Summer	18-Jun-02	13.20	2.30	0.00	Summer	9-Aug-02	12.55	0.10	-1.60	**Monthly mean**		**13.54**	**1.75**	**0.34**
Summer	19-Jun-02	12.70	1.60	-0.70	Summer	10-Aug-02	13.05	0.60	-1.10	**Weekly mean**		**14.06**	**1.06**	**-0.26**
Summer	20-Jun-02	11.90	3.60	1.30	Summer	11-Aug-02	13.40	0.40	-1.30	Autumn	2-Oct-02	13.30	7.10	6.63
Summer	21-Jun-02	13.60	1.70	-0.60	Summer	12-Aug-02	13.90	1.40	-0.30	Autumn	3-Oct-02	11.50	0.40	-0.07
Summer	22-Jun-02	12.10	4.20	1.90	Summer	13-Aug-02	16.75	1.90	0.20	Autumn	4-Oct-02	13.00	0.00	-0.47
Summer	23-Jun-02	13.00	0.10	-2.20	Summer	14-Aug-02	15.15	12.30	10.60	Autumn	5-Oct-02	13.85	0.00	-0.47
Summer	24-Jun-02	12.90	0.60	-1.70	Summer	15-Aug-02	14.25	0.10	-1.60	Autumn	6-Oct-02	9.30	0.00	-0.47
Summer	25-Jun-02	14.20	0.00	-2.30	Summer	16-Aug-02	13.40	0.00	-1.70	Autumn	7-Oct-02	11.85	2.70	2.23

Table B3 continued.

Season	Date	Temp.	Prec.	EPrec.	Season	Date	Temp.	Prec.	EPrec.	Date	Temp.	Prec.
Autumn	8-Oct-02	12.05	16.00	15.53	Winter	1-Dec-02	8.15	14.80	14.74	24-Jan-03	10.15	12.90
Autumn	9-Oct-02	11.15	2.80	2.33	Winter	2-Dec-02	6.80	4.10	4.04	25-Jan-03	8.15	1.90
Autumn	10-Oct-02	11.10	0.00	-0.47	Winter	3-Dec-02	7.75	2.40	2.34	26-Jan-03	12.55	0.00
Autumn	11-Oct-02	9.90	7.20	6.73	Winter	4-Dec-02	4.90	1.60	1.54	27-Jan-03	8.05	0.80
Autumn	12-Oct-02	8.70	0.60	0.13	Winter	5-Dec-02	2.75	0.00	-0.06	28-Jan-03	0.00	
Autumn	13-Oct-02	7.50	0.00	-0.47	Winter	6-Dec-02	3.35	0.00	-0.06	29-Jan-03	5.95	3.20
Autumn	14-Oct-02	8.85	0.00	-0.47	Winter	7-Dec-02	2.95	0.00	-0.06	30-Jan-03	2.90	2.10
Autumn	15-Oct-02	7.75	0.60	0.13	Winter	8-Dec-02	4.90	0.00	-0.06	31-Jan-03	4.00	1.70
Autumn	16-Oct-02	7.20	0.00	-0.47	Winter	9-Dec-02	2.55	0.00	-0.06	1-Feb-03	5.45	3.60
Autumn	17-Oct-02	6.75	0.40	-0.07	Winter	10-Dec-02	2.00	0.00	-0.06	2-Feb-03	4.00	7.70
Autumn	18-Oct-02	6.00	0.10	-0.37	Winter	11-Dec-02	2.65	0.00	-0.06	3-Feb-03	2.20	3.40
Autumn	19-Oct-02	4.60	0.00	-0.47	Winter	12-Dec-02	2.45	0.00	-0.06	4-Feb-03	2.55	2.00
Autumn	20-Oct-02	5.80	33.50	33.03	Winter	13-Dec-02	4.95	0.00	-0.06	5-Feb-03	4.35	0.00
Autumn	21-Oct-02	8.60	5.10	4.63	**Monthly mean**		5.90	2.42	2.35	6-Feb-03	7.90	
Autumn	22-Oct-02	6.50	4.50	4.03	**Weekly mean**		3.21	0.00	-0.06	7-Feb-03	6.60	0.00
Autumn	23-Oct-02	4.90	2.00	1.53	Winter	14-Dec-02	2.80	0.00		8-Feb-03	6.80	10.40
Autumn	24-Oct-02	4.75	9.70	9.23	Winter	15-Dec-02	2.55	0.00		9-Feb-03	5.00	0.50
Autumn	25-Oct-02	8.80	17.90	17.43	Winter	16-Dec-02	2.35	0.00		10-Feb-03	7.40	7.00
Autumn	26-Oct-02	8.10	19.80	19.33	Winter	17-Dec-02	0.30	0.00		11-Feb-03	4.90	0.00
Autumn	27-Oct-02	8.40	6.50	6.03	Winter	18-Dec-02	0.05	0.00		12-Feb-03	3.60	0.00
Autumn	28-Oct-02	7.00	3.20	2.73	Winter	19-Dec-02	2.60	0.00		13-Feb-03	3.25	0.00
Autumn	29-Oct-02	7.75	14.70	14.23	Winter	20-Dec-02	5.65	0.40		14-Feb-03	2.45	0.00
Autumn	30-Oct-02	7.00	0.00	-0.47	Winter	21-Dec-02	8.80	8.40		15-Feb-03	0.75	0.00
Autumn	31-Oct-02	7.50	0.00	-0.47	Winter	22-Dec-02	8.80	2.90		16-Feb-03	3.80	0.70
Autumn	1-Nov-02	12.05	0.50	0.41	Winter	23-Dec-02	10.35	10.70		17-Feb-03	3.60	0.00
Autumn	2-Nov-02	11.85	19.20	19.11	Winter	24-Dec-02	9.05	2.30		18-Feb-03	4.00	0.00
Autumn	3-Nov-02	9.55	4.40	4.31	Winter	25-Dec-02	7.35	2.20		19-Feb-03	2.35	0.00
Autumn	4-Nov-02	10.10	1.10	1.01	Winter	26-Dec-02	9.00	1.30		20-Feb-03	2.80	0.00
Autumn	5-Nov-02	9.65	2.20	2.11	Winter	27-Dec-02	7.30	0.30		21-Feb-03	5.40	0.00
Autumn	6-Nov-02	7.55	2.40	2.31	Winter	28-Dec-02	6.90	0.60		22-Feb-03	7.45	0.00
Autumn	7-Nov-02	6.30	3.00	2.91	Winter	29-Dec-02	8.35	16.40		23-Feb-03	7.35	0.80
Autumn	8-Nov-02	11.35	15.00	14.91	Winter	30-Dec-02	8.15	1.30		24-Feb-03	5.75	0.00
Autumn	9-Nov-02	10.70	12.60	12.51	Winter	31-Dec-02	7.35	0.30		25-Feb-03	8.75	0.00
Autumn	10-Nov-02	10.15	4.40	4.31	Winter	1-Jan-03	9.45	6.70		26-Feb-03	9.05	1.20
Autumn	11-Nov-02	6.45	5.90	5.81	Winter	2-Jan-03	4.35	0.10		27-Feb-03	9.15	0.00
Autumn	12-Nov-02	7.45	11.90	11.81	Winter	3-Jan-03	0.50	0.00		28-Feb-03	6.70	13.50
Autumn	13-Nov-02	6.40	0.60	0.51	Winter	4-Jan-03	0.10	0.00		1-Mar-03	6.25	0.50
Autumn	14-Nov-02	5.90	6.70	6.61	Winter	5-Jan-03	0.25	0.00		2-Mar-03	6.75	0.40
Autumn	15-Nov-02	6.30	0.00	-0.09	Winter	6-Jan-03	0.25	0.00		3-Mar-03	8.05	2.80
Autumn	16-Nov-02	4.35	0.60	0.51	Winter	7-Jan-03	0.60	0.00		4-Mar-03	7.75	7.30
Monthly mean		7.90	7.41	7.16	Winter	8-Jan-03	0.40	0.00		5-Mar-03	7.10	3.00
Weekly mean		6.71	4.30	4.21	Winter	9-Jan-03	2.20	0.00		6-Mar-03	6.65	0.70
Autumn	17-Nov-02	1.70	0.30	0.21	Winter	10-Jan-03	1.35	0.00		7-Mar-03	6.65	5.40
Autumn	18-Nov-02	6.35	0.20	0.11	Winter	11-Jan-03	-0.85	0.00		8-Mar-03	7.30	13.10
Autumn	19-Nov-02	6.90	4.00	3.91	Winter	12-Jan-03	4.85	0.30		9-Mar-03	8.15	7.80
Autumn	20-Nov-02	5.45	2.30	2.21	Winter	13-Jan-03	9.60	0.90		10-Mar-03	7.55	15.40
Autumn	21-Nov-02	7.85	5.60	5.51	Winter	14-Jan-03	9.20	4.80		11-Mar-03	7.95	1.70
Autumn	22-Nov-02	8.00	3.30	3.21	Winter	15-Jan-03	6.40	4.00		12-Mar-03	5.05	0.00
Autumn	23-Nov-02	6.45	0.10	0.01	Winter	16-Jan-03	8.70	11.30		13-Mar-03	3.55	0.00
Autumn	24-Nov-02	9.50	2.50	2.41	Winter	17-Jan-03	6.65	3.70		14-Mar-03	5.75	0.00
Autumn	25-Nov-02	7.75	0.10	0.01	Winter	18-Jan-03	6.05	3.60		15-Mar-03	6.20	0.00
Autumn	26-Nov-02	9.90	3.00	2.91	Winter	19-Jan-03	4.90	2.20		16-Mar-03	6.85	0.00
Autumn	27-Nov-02	9.75	12.90	12.81	Winter	20-Jan-03	5.45	9.10		17-Mar-03	7.15	0.00
Autumn	28-Nov-02	7.50	0.30	0.21	Winter	21-Jan-03	4.90	0.00		18-Mar-03	7.10	0.00
Autumn	29-Nov-02	7.40	0.20	0.11	Winter	22-Jan-03	3.95	0.00		19-Mar-03	5.40	0.00
Autumn	30-Nov-02	8.75	7.70	7.61	Winter	23-Jan-03	4.70	0.00		20-Mar-03	9.55	0.00

Table B3 continued.

Date	Temp.	Prec.	Date	Temp.	Prec.
21-Mar-03	10.05	0.00	16-May-03	12.25	2.70
22-Mar-03	6.90	0.00	17-May-03	11.40	4.00
23-Mar-03	6.95	0.00	18-May-03	11.35	4.20
24-Mar-03	7.15	0.00	19-May-03	10.10	7.00
25-Mar-03	9.15	0.00	20-May-03	10.85	2.10
26-Mar-03	8.30	4.20	21-May-03	10.40	18.30
27-Mar-03	10.55	0.00	22-May-03	12.15	0.30
28-Mar-03	6.25	1.30	23-May-03	11.50	0.00
29-Mar-03	6.55	0.00	24-May-03	10.00	0.20
30-Mar-03	8.15	0.00	25-May-03	9.40	0.00
31-Mar-03	5.80	2.20	26-May-03	10.75	1.70
1-Apr-03	7.00	5.30	27-May-03	14.65	0.30
2-Apr-03	7.80	0.10	28-May-03	14.10	2.90
3-Apr-03	11.25	0.00	29-May-03	16.05	1.10
4-Apr-03	11.55	0.00	30-May-03	16.65	0.00
5-Apr-03	10.00	0.00	31-May-03	14.90	0.10
6-Apr-03	9.10	0.00	1-Jun-03	14.25	6.70
7-Apr-03	9.65	0.00	2-Jun-03	13.10	0.10
8-Apr-03	6.75	0.00	3-Jun-03	11.00	23.60
9-Apr-03	5.65	0.00	4-Jun-03	12.25	0.00
10-Apr-03	6.40	0.00	5-Jun-03	13.15	6.80
11-Apr-03	4.60	0.00	6-Jun-03	12.65	2.40
12-Apr-03	7.60	0.00	7-Jun-03	13.20	0.00
13-Apr-03	6.90	19.90	8-Jun-03	11.45	0.00
14-Apr-03	12.10	0.60	9-Jun-03	10.60	12.60
15-Apr-03	12.85	0.00	10-Jun-03	12.70	4.00
16-Apr-03	13.30	0.00	11-Jun-03	13.20	0.20
17-Apr-03	15.75	0.00	12-Jun-03	12.50	0.00
18-Apr-03	13.50	0.00	13-Jun-03	14.50	0.00
19-Apr-03	9.70	0.00	14-Jun-03	14.05	0.00
20-Apr-03	8.15	0.00	15-Jun-03	15.95	0.00
21-Apr-03	6.75	0.10	16-Jun-03	14.40	0.10
22-Apr-03	9.80	0.00	17-Jun-03	15.00	0.00
23-Apr-03	9.05	0.00	18-Jun-03	14.55	1.30
24-Apr-03	9.45	0.00	19-Jun-03	13.00	1.50
25-Apr-03	11.35	10.70	20-Jun-03	14.15	0.00
26-Apr-03	10.10	5.10	21-Jun-03	15.15	0.00
27-Apr-03	10.80	0.00	22-Jun-03	15.85	0.00
28-Apr-03	9.05	0.60	23-Jun-03	12.50	0.00
29-Apr-03	8.25	2.70	24-Jun-03	11.70	0.00
30-Apr-03	9.15	7.50	25-Jun-03	13.60	0.00
1-May-03	9.90	0.00	26-Jun-03	14.50	3.70
2-May-03	8.00	0.00	27-Jun-03	11.80	0.10
3-May-03	8.90	6.40	28-Jun-03	12.40	0.00
4-May-03	7.85	6.00	29-Jun-03	16.15	0.00
5-May-03	7.35	2.60	30-Jun-03	14.20	19.50
6-May-03	8.25	0.70			
7-May-03	9.00	2.70			
8-May-03	9.85	0.10			
9-May-03	8.50	1.40			
10-May-03	8.85	2.50			
11-May-03	7.75	4.10			
12-May-03	8.15	4.50			
13-May-03	8.65	3.70			
14-May-03	9.00	0.00			
15-May-03	7.40	5.80			

Table B4: Analytical data for moist, 0-10 cm depth monthly-collected samples from soils 1-11, in order of declining estimated land use intensity, and with peat soils first (see section 2.2.3 for analytical methodology).

Site	Season	Month	Moisture	TOC	TN	pH	P_w			Olsen			Sorp.
							DRP	DOP	TDP	P_i	P_o	TP	
1	Winter	Jan	71.4	35.3	2.29	5.28	2.56	1.68	4.24	7.9	53.1	61.0	236.3
9	Winter	Jan	64.1	23.8	1.82	7.12	0.51	0.82	1.32	9.2	49.6	58.8	253.3
6	Winter	Jan	73.6	22.4	1.02	5.08	0.18	0.43	0.61	0.0	45.3	45.3	226.1
3	Winter	Jan	48.0	7.9	0.72	5.96	8.92	1.35	10.27	85.8	52.0	137.8	239.4
10	Winter	Jan	47.5	7.0	0.53	6.52	6.71	1.40	8.11	74.9	43.5	118.4	263.7
2	Winter	Jan	36.6	4.3	0.40	5.37	4.50	1.73	6.24	64.6	84.7	149.4	280.5
8	Winter	Jan	36.8	4.0	0.41	7.72	2.73	2.53	5.26	32.9	33.2	66.1	258.1
7	Winter	Jan	48.4	11.7	0.81	7.44	0.80	1.97	2.77	3.2	19.9	23.1	261.4
5	Winter	Jan	41.3	4.3	0.46	6.86	0.69	1.06	1.74	8.5	36.5	45.1	224.1
4	Winter	Jan	58.1	7.6	0.87	7.83	1.17	1.05	2.22	34.1	27.7	61.7	216.5
11	Winter	Jan	58.0	10.6	0.89	7.91	0.40	0.76	1.15	4.4	12.6	17.1	238.2
1	Winter	Feb	72.8	32.6	1.91	5.45	2.43	0.94	3.37	4.5	51.6	56.1	227.4
9	Winter	Feb	63.2	24.6	1.78	7.42	0.70	0.84	1.54	8.2	44.6	52.7	252.8
6	Winter	Feb	80.8	30.5	1.47	4.57	0.52	0.19	0.71	0.0	52.2	52.2	215.7
3	Winter	Feb	47.1	5.7	0.57	6.04	6.78	1.22	8.00	78.1	30.3	108.5	250.5
10	Winter	Feb	43.9	6.4	0.59	6.57	6.99	0.96	7.95	80.6	36.6	117.1	257.1
2	Winter	Feb	40.8	4.9	0.43	5.44	4.50	0.72	5.22	70.8	63.6	134.4	269.3
8	Winter	Feb	36.7	3.2	0.38	7.44	2.41	1.74	4.14	27.2	24.5	51.8	258.2
7	Winter	Feb	43.8	7.2	0.62	6.75	1.86	1.89	3.75	3.4	21.9	25.3	252.9
5	Winter	Feb	42.0	4.2	0.45	6.45	4.98	0.84	5.81	30.2	34.3	64.5	231.2
4	Winter	Feb	56.4	7.8	0.59	7.99	0.76	0.57	1.34	18.3	18.9	37.2	202.9
11	Winter	Feb	*	*	*	*	*	*	*	*	*	*	*
1	Spring	Mar	72.0	36.7	2.30	5.28	3.80	2.23	6.03	13.5	53.0	66.5	231.6
9	Spring	Mar	67.8	31.3	2.34	7.46	0.59	1.68	2.27	15.1	34.5	49.5	239.2
6	Spring	Mar	79.8	33.3	1.64	4.39	0.59	0.50	1.09	15.4	38.2	53.5	213.7
3	Spring	Mar	45.0	8.2	0.65	5.92	15.87	2.13	18.00	79.7	39.8	119.5	244.6
10	Spring	Mar	44.7	6.7	0.58	6.30	9.90	2.78	12.68	65.3	33.9	99.1	248.1
2	Spring	Mar	36.0	3.9	0.45	5.42	4.94	2.43	7.37	52.1	66.2	118.3	279.3
8	Spring	Mar	36.5	3.7	0.42	7.57	2.15	3.33	5.48	28.7	33.3	62.0	268.7
7	Spring	Mar	43.2	8.1	0.64	6.51	1.78	3.72	5.50	3.6	21.1	24.7	250.4
5	Spring	Mar	40.4	4.2	0.45	6.57	2.68	1.98	4.66	16.7	36.9	53.5	236.7
4	Spring	Mar	52.5	8.1	0.69	7.72	1.10	1.36	2.46	9.1	15.5	24.6	207.9
11	Spring	Mar	41.6	4.7	0.44	7.87	0.56	0.80	1.36	3.6	21.4	25.0	260.1
1	Spring	Apr	67.9	32.9	1.86	5.38	2.73	1.97	4.70	4.4	50.2	54.6	240.8
9	Spring	Apr	65.4	32.1	1.97	7.22	0.99	1.84	2.83	8.7	27.8	36.5	246.6
6	Spring	Apr	67.8	15.8	0.49	4.47	0.78	0.18	0.96	17.1	18.6	35.7	243.9
3	Spring	Apr	38.2	6.3	0.44	5.64	19.72	3.08	22.80	86.1	28.6	114.8	240.5
10	Spring	Apr	41.3	7.3	0.49	5.88	8.13	1.09	9.22	58.4	35.0	93.5	235.3
2	Spring	Apr	39.5	5.6	0.42	5.42	5.18	2.10	7.28	66.1	54.8	120.9	271.1
8	Spring	Apr	34.5	3.9	0.30	7.55	3.14	2.84	5.98	25.6	21.8	47.4	255.8
7	Spring	Apr	41.4	6.9	0.58	6.87	2.01	3.91	5.92	1.8	14.7	16.5	251.2
5	Spring	Apr	39.2	4.0	0.36	6.62	3.98	1.77	5.75	17.2	24.1	41.4	221.9
4	Spring	Apr	48.1	6.2	0.56	7.72	4.41	1.11	5.52	22.5	13.5	36.0	198.8
11	Spring	Apr	41.0	4.9	0.31	7.58	0.74	0.81	1.55	3.0	16.0	19.0	260.5
1	Spring	May	70.5	35.2	1.78	5.19	2.63	1.68	4.31	5.9	55.9	61.8	237.0
9	Spring	May	63.5	34.9	2.33	6.30	1.00	1.52	2.51	6.8	27.3	34.1	254.6
6	Spring	May	81.3	36.0	1.51	4.36	0.78	0.58	1.35	3.1	45.3	48.5	210.9
3	Spring	May	45.5	7.5	0.51	5.98	13.30	1.25	14.55	69.4	30.2	99.5	246.6
10	Spring	May	40.2	6.8	0.47	5.99	8.77	1.98	10.75	53.7	27.4	81.2	229.2
2	Spring	May	36.7	4.7	0.33	5.52	5.32	2.10	7.42	48.0	52.8	100.8	279.6
8	Spring	May	36.8	4.3	0.35	7.66	2.40	3.26	5.65	23.6	20.3	43.9	257.8
7	Spring	May	38.6	7.1	0.50	6.67	1.77	2.54	4.31	3.7	11.9	15.6	259.9
5	Spring	May	38.4	4.6	0.35	6.65	2.17	1.76	3.93	13.0	21.8	34.9	226.5
4	Spring	May	48.2	7.8	0.55	7.89	3.74	1.23	4.97	17.5	13.0	30.6	208.4
11	Spring	May	37.0	3.8	0.23	8.07	0.75	0.96	1.71	3.0	14.6	17.6	262.3
1	Summer	Jun	71.5	32.4	1.84	5.28	2.54	2.51	5.05	5.3	43.2	48.5	229.9
9	Summer	Jun	67.0	29.0	1.96	7.50	0.89	2.05	2.94	10.6	24.8	35.4	247.0
6	Summer	Jun	75.0	22.4	1.27	4.94	0.70	0.36	1.07	0.5	29.8	30.3	224.9
3	Summer	Jun	43.1	6.6	0.54	6.12	11.70	2.36	14.06	60.1	26.6	86.7	252.3
10	Summer	Jun	41.7	6.4	0.48	6.08	8.04	2.70	10.73	51.9	28.5	80.4	243.1
2	Summer	Jun	35.5	4.2	0.40	5.45	4.89	3.02	7.91	45.4	49.7	95.2	277.7
8	Summer	Jun	37.2	4.7	0.42	7.70	2.74	3.28	6.02	20.9	20.3	41.2	261.3
7	Summer	Jun	43.0	7.1	0.58	7.04	3.38	6.04	9.42	2.3	16.3	18.6	263.0
5	Summer	Jun	40.7	4.9	0.48	6.98	2.15	2.18	4.33	9.2	22.9	32.1	248.9
4	Summer	Jun	49.3	7.8	0.88	7.80	1.92	1.67	3.59	11.9	17.5	29.5	211.2
11	Summer	Jun	43.9	5.1	0.45	7.74	0.87	1.36	2.23	2.0	16.5	18.5	274.8

Table B4 continued.

Site	Season	Month	Moisture	TOC	TN	pH	P_w			Olsen			Sorp.
							DRP	DOP	TDP	P_i	P_o	TP	
1	Summer	Jul	69.8	33.2	2.00	5.36	2.45	2.88	5.33	4.4	58.3	62.7	232.3
9	Summer	Jul	67.4	31.5	2.16	7.00	0.75	2.36	3.10	6.5	39.4	45.8	250.9
6	Summer	Jul	78.2	36.2	1.68	4.38	0.83	0.68	1.50	0.0	43.5	43.5	211.6
3	Summer	Jul	45.9	7.3	0.64	6.23	15.58	2.56	18.14	70.3	24.1	94.3	255.0
10	Summer	Jul	43.6	7.3	0.56	6.06	8.90	2.80	11.70	56.5	33.3	89.8	248.4
2	Summer	Jul	36.7	4.3	0.40	5.60	4.55	3.09	7.64	40.6	56.8	97.4	275.3
8	Summer	Jul	37.0	3.8	0.45	7.48	3.32	3.75	7.06	28.2	25.3	53.5	259.6
7	Summer	Jul	41.7	7.0	0.68	6.60	2.16	5.10	7.26	2.2	18.9	21.0	266.8
5	Summer	Jul	40.3	5.2	0.50	7.06	1.83	2.48	4.32	10.3	28.2	38.5	220.7
4	Summer	Jul	48.7	8.0	0.75	7.73	1.92	1.99	3.90	14.2	17.1	31.3	220.1
11	Summer	Jul	38.3	3.4	0.31	7.71	1.15	1.37	2.52	2.4	15.6	18.0	262.5
1	Summer	Aug	68.1	33.9	1.94	5.44	2.09	2.56	4.65	8.6	55.8	64.4	243.9
9	Summer	Aug	61.5	29.9	2.10	7.25	0.63	2.29	2.92	6.9	27.7	34.6	255.9
6	Summer	Aug	73.2	29.6	1.27	4.58	0.55	0.60	1.16	3.0	42.3	45.3	235.8
3	Summer	Aug	37.4	8.1	0.54	5.87	12.95	2.65	15.60	67.1	-3.6	63.5	246.9
10	Summer	Aug	38.6	7.4	0.51	5.86	8.97	3.22	12.19	62.3	30.9	93.1	243.8
2	Summer	Aug	33.6	4.5	0.37	4.93	4.79	1.93	6.72	48.3	60.2	108.6	277.4
8	Summer	Aug	32.0	3.8	0.33	7.51	3.04	3.31	6.35	23.5	21.1	44.6	265.7
7	Summer	Aug	37.4	7.1	0.55	6.72	3.50	2.25	5.75	2.5	14.2	16.8	269.6
5	Summer	Aug	34.6	4.4	0.33	7.15	1.84	4.02	5.86	15.8	25.1	40.9	237.1
4	Summer	Aug	46.5	8.5	0.72	8.04	2.52	1.73	4.24	12.6	13.6	26.2	234.2
11	Summer	Aug	36.1	4.5	0.31	8.02	0.74	0.99	1.73	3.3	16.9	20.1	269.1
1	Autumn	Sep	69.0	34.3	1.98	5.11	2.26	1.63	3.89	3.9	68.1	72.0	239.3
9	Autumn	Sep	63.0	30.6	2.00	7.28	1.04	1.25	2.28	8.7	46.5	55.2	263.4
6	Autumn	Sep	72.7	29.9	1.24	4.46	0.71	0.53	1.24	9.1	43.9	53.0	249.8
3	Autumn	Sep	39.3	6.2	0.49	5.87	9.22	1.59	10.81	54.2	30.9	85.2	250.0
10	Autumn	Sep	40.1	7.7	0.55	5.75	5.19	3.74	8.93	44.7	37.2	81.8	238.4
2	Autumn	Sep	32.8	4.6	0.38	5.18	4.96	1.61	6.57	38.0	45.1	83.1	279.4
8	Autumn	Sep	32.8	4.7	0.43	7.48	1.66	3.27	4.93	20.4	23.5	43.9	262.6
7	Autumn	Sep	37.7	6.9	0.54	6.51	1.93	3.38	5.31	1.1	17.4	18.5	267.2
5	Autumn	Sep	37.6	4.9	0.37	6.75	1.03	1.11	2.14	9.7	25.3	35.1	225.9
4	Autumn	Sep	49.6	7.4	0.61	7.74	2.01	1.40	3.41	16.6	16.5	33.1	233.8
11	Autumn	Sep	42.0	5.3	0.43	7.45	0.29	0.98	1.27	2.3	16.8	19.1	266.1
1	Autumn	Oct	68.3	34.2	2.07	5.17	2.29	2.11	4.40	7.5	59.6	67.1	243.2
9	Autumn	Oct	77.5	35.4	2.22	6.38	1.75	3.15	4.89	6.5	44.6	51.1	254.2
6	Autumn	Oct	63.5	39.9	1.88	4.40	0.49	0.44	0.93	13.3	30.3	43.6	233.8
3	Autumn	Oct	36.3	7.1	0.53	5.79	14.70	1.93	16.63	69.6	48.6	118.2	227.8
10	Autumn	Oct	38.7	8.4	0.60	5.81	12.71	2.59	15.30	66.3	36.8	103.1	223.3
2	Autumn	Oct	32.4	4.7	0.40	5.17	6.06	2.44	8.50	61.0	67.1	128.1	277.6
8	Autumn	Oct	34.5	4.1	0.40	7.60	2.92	3.77	6.69	24.7	31.8	56.5	255.4
7	Autumn	Oct	35.1	6.3	0.59	6.40	1.66	3.37	5.02	2.3	17.8	20.1	267.5
5	Autumn	Oct	35.7	4.9	0.37	6.97	2.98	2.53	5.51	15.0	30.4	45.4	220.6
4	Autumn	Oct	51.0	8.2	0.79	7.61	2.50	2.49	4.98	48.5	-8.2	40.2	215.4
11	Autumn	Oct	37.9	3.9	0.30	7.96	1.24	1.16	2.40	3.4	19.4	22.7	267.0
1	Autumn	Nov	70.0	35.7	2.15	5.28	3.62	2.05	5.67	8.5	57.5	65.9	239.0
9	Autumn	Nov	67.7	34.0	2.54	7.22	0.76	2.11	2.87	12.3	34.2	46.6	244.5
6	Autumn	Nov	77.1	27.2	1.43	4.53	0.77	0.92	1.70	6.8	51.6	58.4	217.0
3	Autumn	Nov	42.7	6.3	0.53	6.60	13.02	-5.45	7.57	66.7	30.7	97.4	252.5
10	Autumn	Nov	42.3	6.8	0.58	6.13	7.78	2.26	10.04	47.4	39.9	87.3	242.9
2	Autumn	Nov	35.8	4.3	0.44	5.50	5.11	9.59	14.70	46.4	66.0	112.4	278.0
8	Autumn	Nov	37.5	3.7	0.45	7.58	4.20	4.12	8.32	25.0	23.1	48.0	253.0
7	Autumn	Nov	42.8	7.3	0.67	6.45	3.74	4.97	8.71	4.4	24.2	28.5	257.9
5	Autumn	Nov	41.3	4.6	0.53	6.79	4.79	2.20	6.99	11.0	31.3	42.4	211.8
4	Autumn	Nov	50.7	8.7	0.82	7.72	2.29	1.81	4.10	13.9	18.6	32.5	213.0
11	Autumn	Nov	43.9	5.7	0.45	7.91	0.28	1.62	1.90	3.5	17.4	20.9	253.6
1	Winter	Dec	70.2	35.0	2.04	5.28	2.15	2.61	4.76	4.1	69.1	73.1	235.5
9	Winter	Dec	65.9	30.1	2.17	7.46	1.21	2.06	3.27	4.3	42.0	46.2	252.2
6	Winter	Dec	80.0	34.0	1.61	4.57	0.88	0.76	1.64	0.0	45.2	45.2	220.7
3	Winter	Dec	42.7	7.3	0.57	6.73	9.58	2.74	12.32	64.0	35.9	99.9	255.7
10	Winter	Dec	41.9	7.1	0.60	6.22	8.20	2.39	10.60	54.2	36.7	91.0	238.4
2	Winter	Dec	36.5	4.6	0.44	5.60	4.86	2.46	7.32	55.4	68.9	124.2	273.6
8	Winter	Dec	37.8	4.5	0.49	7.61	3.40	3.83	7.23	23.7	30.6	54.3	250.5
7	Winter	Dec	43.4	8.7	0.69	6.66	1.87	4.49	6.36	2.3	26.9	29.2	266.8
5	Winter	Dec	43.4	4.7	0.44	6.92	2.84	1.77	4.60	13.1	32.5	45.6	222.8
4	Winter	Dec	49.6	8.7	0.80	7.70	3.67	2.84	6.51	15.2	24.4	39.6	193.2
11	Winter	Dec	41.7	4.8	0.43	7.87	1.02	1.39	2.41	3.9	22.2	26.1	262.1

APPENDIX C

RIVER FLOW AND PHOSPHORUS ANALYSES METHODOLOGY

Methodology from Donohue et al. (in press)

3.1 Water sampling and analysis

From July 2001 to July 2003, water samples were taken from 14 locations on 11 rivers in the catchment (Fig. 1). Sampling was done biweekly until November 2002 and continued monthly thereafter. River flows at the time of sampling were calculated using well-established stage-discharge relationships for all sites except for Carra Bridge, Clooneen and Mullingar Bridge (Sites 1-3; Fig. 1), where no river gauges were installed. Flow was measured from February 2003 at these sites using an A. Ott Kempten® Z30 current meter. Water samples from each monitoring station were analysed, in triplicate, for molybdate-reactive phosphorus (MRP), total dissolved phosphorus (TDP) and total phosphorus (TP) following Murphy & Riley (1962). Samples for MRP and TDP analysis were filtered through 0.45 μm Whatman® cellulose acetate membrane filters. Samples for quantification of TDP and TP were digested following Grasshoff et al. (1999). Dissolved inorganic nitrogen (DIN, filtered through Whatman® GF/C filters) and total nitrogen (TN, digested following Grasshoff et al. (1999)) were measured from triplicate samples following Grasshoff et al. (1999) in a Bran and Luebbe® AutoAnalyzer 3. Dissolved non-molybdate-reactive phosphorus (DnMRP), particulate phosphorus (PP) and total organic nitrogen (TON) were calculated as the differences between, respectively, TDP and MRP, TP and TDP, and TN and DIN (Johnes and Heathwaite, 1992). Quality control standards were used in all analyses, and were within acceptable ranges (± 3% of target concentrations) in each case. All filtering was done immediately upon sample collection.

3.2 Statistical Methods

Spatiotemporal variability in riverine nutrient concentrations was analysed with analysis of covariance (ANCOVA), with river, site, season and flow as independent variables. Site was nested

within river and (log-transformed) flow was included as a continuous variable. Interaction terms between each of flow, river and season were included to test for spatial and temporal differences in nutrient-flow relationships. Owing to the design of these analyses, it was not possible to calculate *post-hoc* tests. Analysis of spatial and seasonal variability in river flow was analysed with analysis of variance (ANOVA), with river, season and site as independent variables. Site was nested within river. Spearman Rank correlation analyses were used to test for association between variables. The slope of the least-squares regression of flow to nutrient concentration estimated the magnitude of nutrient-flow relationships for each river, with differences between summer and winter slopes used as a metric of the extent of seasonality in nutrient-flow relationships. Slopes for Carra Bridge, Clooneen and Mullingar Bridge were not used in the seasonal analysis owing to the small number of flow measurements taken at these sites. Area-weighted nutrient loads were calculated by interpolation following Method 2 of Walling and Webb (1981) and using data from July 2001 – July 2002, reflecting the period of biweekly sampling. Hydrological loads for Carra Bridge, Clooneen and Mullingar Bridge for this period were estimated using rainfall data. All statistical tests were done with Data Desk® Version 6.

3.3 Data sources

Morphological aspects of catchments and catchment boundaries were calculated using a digital elevation model digitised from 1:50000 Discovery Series maps published by Ordnance Survey Ireland. Land cover maps were compiled from CORINE land coverage data. Digital soil Morgan P maps were provided by Teagasc and rainfall data were supplied by Met Éireann. The Irish Environmental Agency and the Office of Public Works provided river flow calculations. ArcView® Version 3.2 was used as the GIS interface.