Environmental RTDI Programme 2000–2006

EUTROPHICATION FROM AGRICULTURAL SOURCES

Seasonal Patterns & Effects of Phosphorus

(2000-LS-2.1.7-M2)

Final Report

Prepared for the Environmental Protection Agency

by

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Eutrophication from Agriculture Sources (Ref. 2000-LS-2-M2)

This study forms part of the large-scale study 'Eutrophication from Agriculture Sources' (Ref. 2000-LS-2-M2) and was funded by the Irish Government National Development Plan under the Environmental RTDI Programme 2000–2006, Phase 1. The institutions involved in the overall project included Teagasc (co-ordinator), National Universities of Ireland at Cork, Dublin and Galway, Trinity College Dublin, University of Limerick, University of Ulster, Coleraine and Met Éireann. The three groups of projects in the integrated project were as follows:

Group 2.1: Pathways for Nutrient Loss to Water with Emphasis on Phosphorus Losses

Group 2.2: Models and Risk Assessment Schemes for Predicting Phosphorus Loss to Water

Group 2.3: Effects of Agricultural Practices on Nitrate Leaching

Research in Group 2.1 sought to clarify the question of the magnitude of phosphorus losses in different farm situations and to provide an interpretation of the relative contribution of each source of agricultural phosphorus to waters in Ireland. The overall aim was to provide policy makers with a ranking of sources to enable them to introduce the most cost-effective measures to reduce or eliminate agriculture-induced eutrophication. The subprojects within this group dealt with the following topics:

- 2000-LS-2.1.1-M2: Project 2.1.1a: Soil and phosphorus
- 2000-LS-2.1.1-M2: Project 2.1.1b: Soil and phosphorus
- 2000-LS-2.1.2-M2: Project 2.1.2: Grazed pastures
- 2000-LS-2.1.3-M2: Project 2.1.3: Slurry spreading
- 2000-LS-2.1.4-M2: Project 2.1.4: Fertiliser spreading
- 2000-LS-2.1.5-M2: Project 2.1.5: Farmyards
- 2000-LS-2.1.6-M2: Project 2.1.:6 Environmental soil P test
- 2000-LS-2.1.7-M2: Project 2.1.7: Relative eutrophic effects on waterbodies

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Executive Summary

- Phosphorus is considered to be the main limiting nutrient for primary production in most freshwater systems. Long-term increases in the concentration of phosphorus have occurred in many rivers and lakes in recent decades. External supplies of nutrients to surface waters can originate from point sources, which are localised and more readily monitored and controlled, and non-point sources, which are diffuse and much more difficult to monitor and regulate. Reductions in phosphorus inputs from point sources do not always reduce phosphorus concentrations in surface waters. While internal loading from sediments may be a factor in the maintenance of phosphorus availability in these systems, diffuse losses from agricultural sources are considered the major cause.

- The export and utilisation of phosphorus show considerable temporal variation. Much of this variation is related directly and indirectly to climatic factors. Direct effects include the dominant role of rainfall in hydrology and phosphorus transport and the influence of temperature and light availability on chemical and biological cycles. Indirect effects include seasonal variations in land use and agricultural management of, particularly in Ireland, grazing patterns and slurry disposal.

- In pristine systems, the flux of phosphorus from the catchment to surface waters is mainly determined by the flow of water through the system and the underlying geology. Losses from these systems are generally low and occur by leaching over very long time periods. In general, lower phosphorus export is recorded in waters draining igneous catchments than from those with a sedimentary geology.

- Atmospheric deposition may represent a significant source of phosphorus, particularly in oligotrophic catchments. In nutrient-poor systems, concentrations in rainwater may exceed those in runoff. Seasonal differences in phosphorus load from precipitation are relatively small in areas remote from intensive agricultural activity and urban centres. In heavily fertilised agricultural areas, however, the instantaneous phosphorus load from the atmosphere may be higher during the growing season than during the winter.

- The major point source of phosphorus in urbanised areas is from municipal and industrial wastewater treatment plants. Improvements in treatment facilities required by EU regulations, and the introduction of phosphorus-free detergents, are leading to a marked reduction in phosphorus from this source. While there may be some temporal variation in the phosphorus load from these sources, there is generally no seasonal pattern.

- The contribution of diffuse agricultural sources to the overall phosphorus load increases with the percentage of agricultural land in the catchment. Although high phosphorus losses recorded from agricultural land may come from farmyards, most are attributed to the excessive accumulation of phosphorus in soils because of long-term inputs of inorganic fertilisers and manures.

- In general, the highest phosphorus losses are measured in arable systems and the lowest in forested ecosystems. Export from forested catchments may, however, increase substantially during establishment and deforestation phases and during the application of fertiliser. Tillage increases the vulnerability of soil to phosphorus losses via erosion. Losses of phosphorus from intensively managed grasslands with continuous cover can however also be significant, particularly where grazers are present or when organic manures are spread. The highest loss rates occur when an intense rainfall event follows the application of fertiliser or organic manure.

- Phosphorus loss is affected by catchment topography, geology, soil type and land use. The ability of a soil to hold phosphorus within the soil matrix may be of particular importance. Many agricultural soils in developed countries are now considered phosphorus saturated and require little or no further phosphorus fertilisation. Soil phosphorus test levels in Irish grasslands have continued to increase despite the fact that the use of phosphorus fertiliser has remained relatively constant in the period from 1990 to 1999 and is now dropping. Mineral soils in the Republic of Ireland have been found to be up to 79% phosphorus saturated. Soils with high saturation are particularly susceptible to phosphorus loss.

- The temporal variation of phosphorus loss is related to the magnitude of the pool of mobile phosphorus and the rate of transport from field to surface waters. Variation in the timing and intensity of grazing, silage making, fertiliser application and slurry spreading affects the availability of phosphorus for transport. The decline in quality of surface waters in the Republic of Ireland is most notable in areas that are characterised by intensive cattle farming or that have a high density of pig and poultry production units.

- Phosphorus transport in groundwater is often ignored in catchment monitoring. Groundwater can supply phosphorus to lakes and rivers, particularly during low flow conditions. The importance of groundwater to the overall phosphorus loading may increase in summer when rainfall and flows are low. No seasonal difference was found, however, between groundwater phosphorus concentrations in summer and winter in a survey of springs and boreholes in the Republic of Ireland.

- Surface runoff has been considered to be the dominant mode of phosphorus transport from agricultural land, particularly in areas with well-structured mineral soils. There is, however, an increasing awareness of the role of subsurface and preferential flow in the transport of phosphorus, particularly where artificial drainage systems are in place. These systems provide a direct link between the field systems and the catchment drainage network.

- High intensity/low frequency rainfall accounts for a high percentage of total phosphorus loss. Highest losses tend to occur following the first storm event after a dry period, and can be particularly high in late summer and autumn. During a dry summer, uptake of phosphorus by plants may decrease, while residues of fertiliser, slurry and cattle faecal wastes accumulate. A flush of mineralisation may occur on re-wetting, adding to soil phosphate. Losses over the winter period may decrease as the supply of potentially mobile phosphorus is exhausted.

- The literature highlights the impact of intense rainfall on the transport rate of phosphorus at a catchment scale. This rainfall is varied and unpredictable.

- Retention and release processes in rivers play a significant role in seasonal patterns of phosphorus transport. Interactions between hydrological, physical, chemical and biological processes that govern phosphorus transport are complex. Phosphorus load to receiving waters equals the total phosphorus losses from the catchment minus phosphorus retained in the drainage network.

- While factors such as light limitation and short hydraulic residence time may limit primary production in rivers and streams, many studies suggest that flowing waters are sensitive to inputs of nutrients. In general, lower chlorophyll concentrations will be measured in flowing waters than in standing waters at a similar rate of supply of phosphorus. The relationship between TP and chlorophyll *a* in flowing waters is, however, curvilinear. At higher TP concentrations, the response of algae will be limited by other factors, which include flood frequency, water column turbidity, the abrasive action of suspended sediments and inter-specific shading effects.

- Phosphorus concentrations in lakes are the result of complex equilibria between external and internal loading, and physico–chemical and biological processes in the water column. Measurements of total phosphorus include phosphorus in plankton biomass. Total phosphorus concentrations in some lakes show winter maxima and summer minima. These patterns are most apparent in eutrophic lakes. In lakes that stratify seasonally, the depletion of phosphorus in the spring and summer will often be confined to the epilimnion. However, lakes often have little seasonal variation in phosphorus concentrations, while chlorophyll concentrations vary seasonally. Many Irish lakes have highly coloured waters that influence light availability in the surface waters. In these lakes, primary production may remain low despite high inputs of nutrients. Summer peaks in total phosphorus concentrations, associated with diffuse runoff following high rainfall, have been recorded in some Irish lakes.

- Seasonal pulses in bioavailable phosphorus to lake primary producers come from either external (catchment) or internal (sediment) sources. Internal loading can be particularly important during summer when initial supplies of phosphate in the water column become depleted. The seasonal internal load is affected by variations in temperature and redox conditions, while pH, the availability of labile organic phosphorus for mineralisation, rates of biotic uptake and water column nitrate concentration may also be important. In shallow lakes, temporal variation in sediment phosphorus availability to surface waters depends on wind mixing, flushing rate and sediment disturbance. In deeper sheltered lakes, sediment phosphorus may only be available at spring and autumn overturn or during periods of mixing. Availability during summer is governed by water stability, which is temperature and wind dependent, and mixing during periods of high wind speed and/or rainfall. In most Irish lakes, wind-driven mixing can occur throughout the year.

- The effect of nutrient pulses on primary production in the receiving waters depends on the timing of the pulse, the composition of the incoming phosphorus load, the concentration of dissolved inorganic phosphorus in the water column and the lake retention time. Pulses of nutrients in late autumn and early winter have little effect in lakes with short retention times (*c*. <0.5 years). The particulate component of these pulses may contribute to the sediment phosphorus pool. The dissolved component is likely to be flushed from the system before the following spring growth period. Phosphate sorbed to the particulate load is unlikely to be released to the surface waters before sedimentation, as the dissolved inorganic phosphorus concentration of the water column will be relatively high in winter. In lakes with a longer retention time, some of the dissolved phosphorus load may contribute to the spring algal bloom.

- Even in lakes with long retention times, pulses of nutrients in spring and summer, when phosphorus limitation is often pronounced, may immediately enhance algal production. The rate of biotic uptake can vary seasonally, depending on temperature, initial nutrient availability and irradiance.

- Mathematical and conceptual models can provide an important insight into annual and seasonal dynamics of phosphorus transport and impact. This report provides an overview of the types of models that have been developed to predict and assist with management of water quality, especially with regard to the movement of phosphorus from catchments to surface waters.

- The report concludes with the identification of high risk factors for the export of phosphorus in Irish catchments, and recommendations for further studies to increase our understanding of the relationship between seasonal variation in driving variables and eutrophication of surface waters.

1 Introduction

1.1 General Introduction

Eutrophication is the nutrient-driven increase of organic matter in fresh waters (Nixon, 1995). It can lead to a suite of problems including oxygen depletion, pH variability, shifts in species composition, food-chain effects, increases in toxic algal blooms and collapse of populations of sensitive fish species (Skulberg *et al*., 1984; Champ, 1998; Smith *et al.*, 1999; Reynolds and Petersen, 2000). Although direct discharges of organic wastes may lead to eutrophication, the phenomenon is generally associated with elevated primary production linked to increased availability of a limiting nutrient. Phosphorus is considered the main limitation of primary production in most freshwater systems (Schindler, 1977; Sharpley *et al.*, 1994; Correll, 1997; Smith *et al.*, 1999), although others, e.g. nitrogen and silicon, can also be important.

Long-term increases in the concentration of phosphorus have been reported in many rivers and lakes in recent decades (Sharpley *et al*., 1994; Caraco, 1995; Gibson *et al*., 1995b; Muscutt and Withers, 1996; Bowman and Clabby, 1998; Foy and Bailey-Watts, 1998). These increases have been attributed to population increase, the use of phosphorus in detergents and the greater use of phosphorus fertilisers (Sharpley *et al*., 1994; Caraco, 1995; Nixon, 1995; Smith *et al.*, 1999). External supplies of nutrients to surface waters can originate both as point sources, which are localised and more readily monitored and controlled, and as non-point sources, which are diffuse and much more difficult to monitor and regulate (Smith *et al*., 1999). The relative contributions of these sources can differ substantially, depending upon local human densities and land use.

Reductions in phosphorus inputs from point sources in some systems in recent decades have not been associated with concurrent reductions in surface waters (Sharpley *et al*., 1994; Foy *et al.*, 1995; Heaney *et al*., 1996). Although internal loading from lake sediments may be a factor in the maintenance of phosphorus availability in these systems (Marsden, 1989; Søndergaard and Jeppesen, 1993; Søndergaard *et al.*, 1999), diffuse losses from agricultural sources are considered to be the major cause (Sharpley *et al.*, 1994; Foy *et al.*, 1995; Gibson *et al.*, 1995b; Lucey *et al.*, 1999). In the USA, runoff of nutrients from diffuse agricultural sources has been linked to the impairment of 55% of surveyed river length and 58% of surveyed lake area (Sharpley *et al*., 1994). More than 25% of 612 lakes surveyed in Northern Ireland were classed by Gibson *et al.* (1995b) as nutrient enriched. These lakes were in intensively managed agricultural catchments. In the Republic of Ireland, 19% of lakes assessed between 1995 and 1997 were classified as eutrophic (Lucey *et al*., 1999). However, even in Irish lakes with an assigned mesotrophic status, declines in fish populations have been noted (Champ, 1998). Long-term trends in the Republic of Ireland show a decline, attributed to non-point sources of phosphorus, in the length of high-quality river channel (Lucey *et al.*, 1999).

The mobilisation of phosphorus from catchments to surface waters is dependent on a number of physical, chemical and biological factors (Froelich, 1988; Sharpley *et al.*, 1994; Svendsen *et al*., 1995; Brunet and Astin, 1998; House and Denison, 1998). Many of the processes involved are, in turn, affected by geographical factors such as soil type, underlying geology and catchment typology. Superimposed on these physico–chemical, biotic and geographical influences are land use and catchment management. These factors contribute to a significant spatial variability in phosphorus export rates.

The export and utilisation of phosphorus show considerable temporal variation. Much of this is related to climatic factors and seasonal variations in land use and agricultural management; this is particularly relevant in Ireland to changing patterns of grazing, silage production and slurry disposal (Allott *et al.*, 1998). Phosphorus transport is driven directly by rainfall and the effect of temperature and light on chemical and biological cycles. The intensity and duration of rainfall is of particular importance. Peaks in phosphorus mobilisation have been related to episodic high rainfall in many studies (e.g. McGarrigle *et al*., 1993; Svendsen *et al*., 1995; Dorioz, 1996; Haygarth and Jarvis, 1996; Lennox *et al.*, 1997;

Tunney *et al*., 2000). While most rainfall in Ireland occurs during winter, high intensity rainfall is also often recorded in spring and summer. This period coincides with the maximum growth of algae and macrophytes, owing to seasonal cycles of temperature and light. Algal and macrophyte production is also influenced by lake and river hydromorphology. Summer stratification of lakes can effectively reduce the biotically active water volume, concentrate inflowing nutrients in the epilimnion, and have consequences for material lost through sedimentation to the hypolimnion and lake bottom. Stratification, anoxia and increased temperatures in the summer may also provide the conditions for internal phosphorus loading from lake sediments (Wildung *et al*., 1974; Istvanovics, 1988; Søndergaard and Jeppesen, 1993; Søndergaard *et al*., 1999).

1.2 Scope of the Study

The objective of this study was to review the literature on key factors driving temporal variability in phosphorus export from land to water and to describe the seasonal impact of that variability for the eutrophication of surface waters. The review addresses:

1. The temporal variability in phosphorus export and the main geomorphological and management factors that influence that export.

2. The effect of seasonal factors on external and internal phosphorus loads and the utilisation of phosphorus in surface waters.

3. The estimation of the impact of phosphorus loads to surface waters in relation to seasonality.

4. A summary of models that predict nutrient export at the catchment scale, with particular reference to seasonal effects.

5. Identification of high-risk factors related to catchment characteristics and seasonality.

6. Identification of the main limitations in knowledge and recommendations for further studies to increase our understanding of the relationship between seasonal variation in driving variables and eutrophication of surface waters.

1.3 Dynamics of Phosphorus

Phosphorus in water may exist in one of four broadly defined states: dissolved as an inorganic molecule readily available for biotic uptake, incorporated through sorption onto solids, incorporated within biological material, or dissolved within organic molecules of varying complexity, which may or may not be readily available for biotic use. Phosphorus exists as orthophosphate (PO_4^{3-}) in all its biologically active fractions (Reynolds and Davies, 2001). The relative proportions of its anions vary with pH. The hydrogen radicals, however, are all replaceable by metals. While orthophosphate itself is freely soluble in water, orthophosphates of the alkaline earth and transition metals are particularly insoluble. The bioavailability of phosphorus refers to 'those fractions that are readily assimilated by organisms, or can be made assimilable through the activities of organisms, and that portion which has already been assimilated' (Reynolds and Davies, 2001). The bioavailability of phosphate is reduced by adsorbtion on the surfaces of metal oxides. The sorbtion–desorbtion reactions with redox-sensitive metals such as iron and manganese are particularly important in aquatic systems. Phosphorus is a highly particle-reactive element and will often be involved in a series of sequential sorbtion/desorbtion reactions with particulate material suspended in the water column (Froelich, 1988). Where a stream or river carries a high particulate load, the balance between dissolved and particulate phosphorus pools changes continuously. Froelich (1988) described phosphate ions as 'playing hide and seek with both plankton and experimentalists'. The 'phosphate buffer mechanism' is the name given to this dynamic equilibrium (Froelich, 1988).

Kinetically there are thought to be two pools of particulate phosphorus, one that equilibrates rapidly (minutes) and that is bound to the surface of sediments, and a second that equilibrates slowly (days) and that is believed to involve solid-state diffusion within particulates. When particulates enter a waterbody, adsorbed phosphate equilibrates with the phosphate in the water. If this concentration is low, phosphorus is released from particulates to water and vice versa (Correll, 1997). Because of this, the phosphorus that is held on particles, both in suspension and in the sediment, represents a large and potentially available reservoir in excess of that dissolved in the water column. The phosphate buffer mechanism plays an important role in maintaining the phosphate concentration of some rivers, lakes and estuaries at an almost constant level (Froelich, 1988). When phosphate is consumed by primary producers, the concentration in the water column will decrease and more phosphate will be released from particulates. In contrast, a sudden increase in the phosphate concentration of the water column may result in the rapid adsorbtion of phosphate by particulates. This positive feedback has important consequences for the supply of phosphate to algae, particularly in lakes where the sediments generally contain a substantial phosphorus pool. For example, Brooks and Edington (1993) reported that the soluble reactive phosphorus (SRP) concentration in Lake Michigan remained relatively constant over a 3-year study while total phosphorus (TP) and chlorophyll concentrations showed a seasonal pattern with maximum concentrations in the summer. They hypothesised that the increased mass of TP arose from the sequestering of phosphate by algae. This, in turn, displaced the chemical equilibrium in the water column and allowed more phosphate to be released from the sediments.

Measurements of phosphorus fractions in fresh waters usually include the TP pool, the dissolved inorganic phosphorus fraction (filtered <0.45 µm) and the particulate phosphorus fraction (PP) (filtered >0.45 µm). In addition, some studies include measurements of total reactive phosphorus (TRP), total soluble phosphorus (TSP) and of dissolved organic phosphorus (DOP), while the particulate pool may also be divided into particulate organic phosphorus (POP) and particulate inorganic phosphorus (PIP). However, the viability of the division between dissolved (<0.45 µm) and particulate (>0.45 µm) phosphorus has been questioned, on the basis that a significant proportion of the material (<0.45 µm) may be associated with colloids and particulates (Heathwaite and Dils, 2000).

Although several schemes have been suggested in recent years to standardise the nomenclature of phosphorus fractions in waters (Sharpley and Pionke, 1997 (cited in Johnston *et al.*, 1997); Haygarth and Jarvis, 1999; Reynolds and Davies, 2001), there is considerable variation in the naming of these fractions in the literature. The standard method for the measurement of the dissolved inorganic phosphorus (DIP) fraction is that of Murphy and Riley (1962). However, this fraction is alternatively referred to as dissolved reactive phosphorus (DRP), dissolved phosphorus (DP), DIP, SRP or molybdate reactive phosphorus (MRP). In addition, although the measurement of dissolved inorganic phosphorus is most often performed on filtered samples (<0.45 µm), some studies use unfiltered samples. This latter measurement is generally referred to as either MRP (unfiltered) or as TRP. The use of both TP and DRP as measures of the availability of phosphorus for phytoplankton productivity has been criticised (Lean *et al.*, 1983; Bradford and Peters, 1987; Correll, 1997). The use of DRP concentrations is considered by some authors to be misleading as the turnover time of this pool is rapid and the store of particulate phosphorus is ignored (Lean *et al.*, 1983; Correll, 1997). A variable but significant proportion of the particulate phosphorus pool can be classed as available (Bradford and Peters, 1987; Correll, 1997). The use of TP concentrations is, overall, probably a more meaningful measure of phosphorus availability than DRP concentrations (Correll, 1997; Reynolds and Davies, 2001). The situation, however, is not straightforward. Bradford and Peters (1987) assessed the relationships between various phosphorus pools in lake waters and the concentration of ‘bioavailable phosphorus’, as measured by bioassays, and concluded that the TP pool is a poor correlate of available phosphorus. Their results further indicated that TRP (unfiltered, undigested, molybdate reactive) provided a better measure of phosphorus availability in oligotrophic lakes than TP, while TSP (filtered, digested, molybdate reactive) was most useful in eutrophic waters (Bradford and Peters, 1987).

Although the measurement of molybdate reactive phosphorus on unfiltered samples (TRP as described by Bradford and Peters, 1987) is not a prevalent method in the literature, it is routinely performed by the Irish Environmental Protection Agency and the UK Environment Agency. While Bradford and Peters (1987) recommend the use of TRP in nutrient-poor waters, they emphasise that turbidity can distort absorbance readings and that a blank of *each* water sample, using a modified reagent, must be included when unfiltered samples are used. This step is not generally included in monitoring programmes. Because of these limitations, the continued use of measurements of MRP on unfiltered samples to describe phosphorus availability in the total suite of conditions in Irish waters merits further consideration. In this text, units follow those used in the relevant publication. Unfiltered molybdate reactive phosphorus is referred to as MRP (unfiltered).

1.4 Seasonality in the Irish Climate

The export of phosphorus from catchments to surface waters is strongly affected by climate. Ireland has a temperate maritime climate with mild winters, cool summers and consistently humid conditions. The highest temperatures generally occur in July/August and the lowest in January/February. May generally has the highest mean hours of bright sunshine while December has the lowest (Keane, 1986). With prevalent south-westerly winds from the Atlantic, rainfall is highest in the north-west, west and south-west of the country, especially over high ground. Annual rainfall in the west between 1951 and 1980 ranged from 1000 to 1250 mm, while that in the east ranged from 750 to 1000 mm (Rohan, 1986). Highest mean monthly rainfall is usually recorded in December and January, with noticeably lower rainfall in February. July to January is normally wetter than February to June. The annual number of days with more than 1 mm of rain ('wet days') varies between about 150 per year in the drier parts and over 200 in the wetter parts of the country (Keane, 1986) (Fig. 1.1). Although the months with the highest number of wet days are in autumn and winter, high numbers also occur in the spring and summer. A similar pattern is found for days with heavy rainfall (>10 mm day^{-1}) (Fig. 1.2).

Average values of climatic parameters are, however, often less important than deviations from central conditions. In particular, the duration, number and intensity of rainfall events have a greater bearing on phosphorus losses than the total rainfall in any given month (Ryden *et al.*, 1973; Dorioz, 1996; Lennox *et al.*, 1997; Haygarth and Jarvis, 1997b; Haygarth and Jarvis, 1999). Haygarth and Jarvis (1999) considered 5 mm rain h^{-1} as a measure of high intensity/storm rainfall important for phosphorus transport, while Chambers *et al.* (2000) estimated that >15 mm rain day^{-1} caused erosive phosphorus losses from arable land, with maximum intensities of >4 mm h^{-1}. While average hourly rainfall in Ireland is quite low, short-term rates can be much higher. An hourly total of 10 mm is not uncommon, and 15–20 mm h^{-1} are expected once in 5 years. High intensity rainfall driving summer increases in phosphorus export have been recorded in Irish studies (McGarrigle *et al.*, 1993; Lennox *et al.*, 1997; Kurz, 2000; Morgan *et al.*, 2000; Irvine *et al.*, 2001). Dry

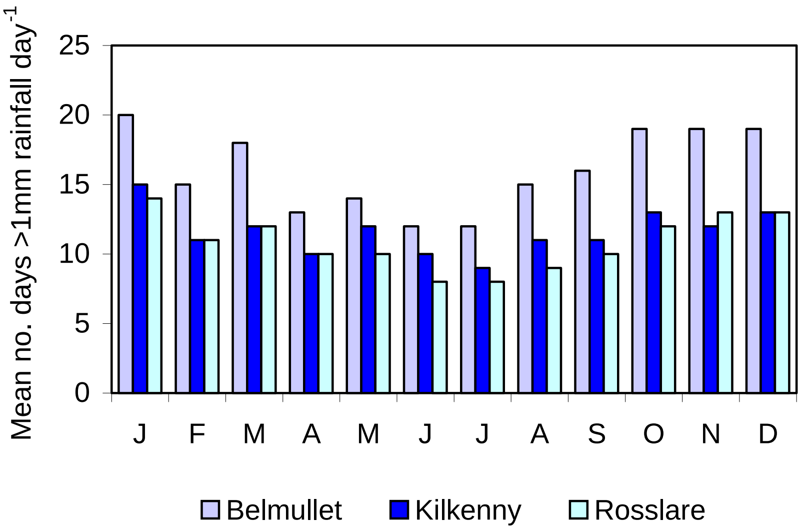

Figure 1.1. Mean number of days >1 mm rain for the period from 1961 to 1990 at Belmullet (Co. Mayo), Kilkenny and Rosslare (Co. Wexford) (Met Éireann).

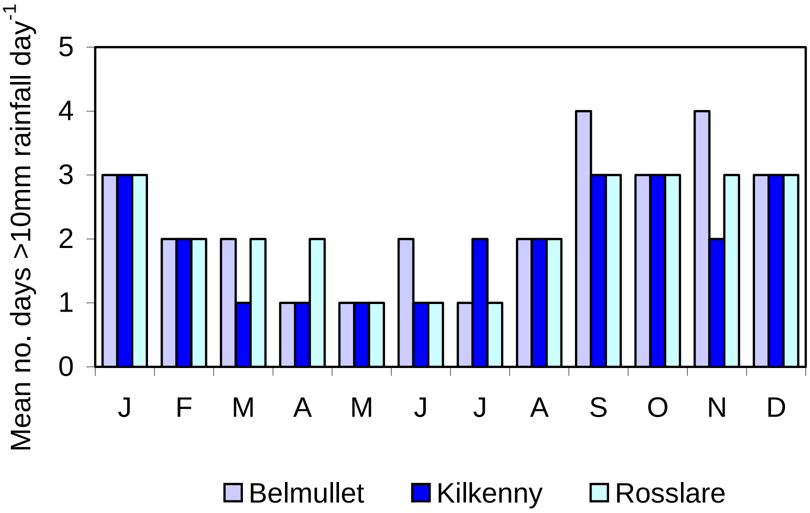

Figure 1.2. Mean number of days >10 mm rain for the period from 1961 to 1990 at Belmullet (Co. Mayo), Kilkenny and Rosslare (Co. Wexford) (Met Éireann).

periods and/or soil moisture deficit may also control phosphorus transport from catchments. During dry periods, phosphorus may accumulate in the catchment, while soil moisture deficits may affect the uptake and mineralisation of phosphorus in soil. Soil moisture deficits occur most likely between late spring and early autumn, and are greatest in July/August in soils in the eastern and south-eastern low-altitude areas, where evapotranspiration is high and precipitation is low (Keane, 1986).

2 Sources of Phosphorus

2.1 Background Sources of Phosphorus

In pristine systems, phosphorus flux from catchment to surface waters is determined mainly by water flow through the system and the underlying geology (Hobbie and Likens, 1973; Dillon and Kirchner, 1975). Losses from these systems are generally low and occur by leaching over long time periods (Sharpley and Rekolainen, 1997; Frossard *et al.,* 2000). In general, lower phosphorus export is recorded in waters draining igneous catchments than from those catchments with a sedimentary geology (Dillon and Kirchner, 1975). Dillon and Kirchner (1975) summarised published studies on phosphorus export based on geology and land use. Release rates from unpopulated forested catchments on igneous bedrock were in the order of 10 kg P km^{-2} year^{-1}, while those from a similar catchment with a sedimentary geology were up to 26 kg P km^{-2} year^{-1}. Phosphorus is released from rocks through chemical weathering. Hobbie and Likens (1973) estimated that relatively large amounts of phosphorus were added to an undisturbed catchment in the Hubbard Brook system (USA) through the weathering of rock, and that this source was the most important for undisturbed ecosystems accumulating biomass. Newman (1995) found published rates for weathering of phosphorus of 5–100 kg P km^{-2} year^{-1}, with the highest rates having been found in carbonates and rock salts. However, less direct evidence suggested that rates of up to 500 kg P km^{-2} year^{-1} could occur. Rates are higher in moist climates and a positive correlation is generally reported between water runoff and the rate of chemical weathering (Dethier, 1986). In areas underlain by calcareous rock and soil, natural washout may be influenced by the high phosphorus-binding capacity of carbonates (Gude and Gries, 1998).

2.2 Phosphorus Inputs from Atmospheric Deposition

2.2.1 Phosphorus inputs from atmospheric deposition

Atmospheric deposition may be an important source of phosphorus for both aquatic and terrestrial ecosystems (Persson and Broberg, 1985; Axler *et al*., 1994; Gibson *et al*., 1995a). While dry deposition of particulate phosphorus does occur, most phosphorus is deposited in precipitation (Newman, 1995; Yang *et al*., 1996; Hu *et al*., 1998). Sources of atmospheric phosphorus include wind erosion of soil and crustal material, pollen and plant exudates, burning of fossil fuels, and fertiliser aerosols (Newman, 1995). Inputs to surface waters include both direct inputs to lakes and rivers and deposition within the catchment. The highest loads are generally found in populated areas (Gibson *et al*., 1995a; Kelly, 1999). The estimated annual load of phosphorus from atmospheric deposition ranges from <1 kg P km^{-2} year^{-1} to >80 kg P km^{-2} year^{-1}, and mostly within the range of 10–40 kg P km^{-2} year^{-1} (Crisp, 1966; Likens *et al*., 1977; Newman, 1995; Gibson, 1997). Measuring atmospheric deposition can, however, be subject to large errors, and Newman (1995) discounts some of the higher published values. Yang *et al*. (1996) emphasise the strong episodic nature of atmospheric deposition and the need for frequent sampling.

Little information exists on the bioavailability of TP load in rainfall. Sonzogni *et al*. (1982) estimated that 25–50% of TP in wet and dry deposition in the Great Lakes area (USA) could be available. Gerdes and Kunst (1998), using algal bioassays, estimated that 26% of the TP load in rainwater in the Ilmenua catchment (Germany) was bioavailable. This was the lowest percentage bioavailability of catchment sources of phosphorus.

The importance of phosphorus loading from atmospheric deposition to lakes varies with lake trophic status. In lakes with a large point source loading and/or a catchment that includes a high proportion of agricultural land, atmospheric deposition may be a small percentage of the annual phosphorus load (Heaney *et al*., 1996; Gibson, 1997). In oligotrophic lakes, atmospheric deposition may account for a significant percentage of the annual TP load (Persson and Broberg, 1985; Gibson *et al.*, 1995a; Kelly, 1999). Seasonal differences in the phosphorus load in atmospheric deposition are relatively small in areas remote from intensive agricultural activity, and relate mainly to different rainfall rates (Gibson *et al.*, 1995a; Zhang and Mitchell, 1995; Yang *et al*., 1996; Kelly, 1999). However, owing to wind dispersion in heavily fertilised agricultural areas, phosphorus in precipitation may be much higher during the growing season than during the winter (Cole *et al*., 1990). In addition, the relative importance of inputs of phosphorus from atmospheric deposition may be greater during drier periods, when inputs via runoff are low (Cole *et al.*, 1990).

2.2.2 Irish studies on phosphorus inputs in atmospheric deposition

There are few studies of atmospheric phosphorus deposition in Ireland. Gibson *et al*. (1995a) measured an annual phosphorus load of 22 kg P km^{-2} $year^{-1}$ to an upland catchment in Northern Ireland. They considered this sufficient to explain the mesotrophic status of many upland lakes in Northern Ireland, and that concentrations of 15 µg P l^{-1} in the study lake, Loughgarve, could be entirely explained by rainfall inputs. Jordan (1997) reported mean values of 19 kg P km^{-2} $year^{-1}$ for three rural sites in Northern Ireland. These values are near the median values reported in the literature. Kelly (1999) measured phosphorus deposition in rainfall on a weekly basis, from May to September, at a remote site in the west of Ireland (Co. Mayo) and at a site in the east of the country (Co. Meath). Although total precipitation in Mayo was twice that in Meath, deposited phosphorus concentrations in Mayo were considerably lower. Annual deposition was estimated as 4.32 kg P km^{-2} $year^{-1}$ in the west but 10.65 kg P km^{-2} $year^{-1}$ in the east. These loads were at the lower end of the range reported from elsewhere in Europe and the USA. The higher deposition in Meath was attributed to the greater influence of human activity, while differences from the results of Gibson *et al*. (1995a) and Jordan (1997) were attributed to variations in meteorological conditions and higher rates of fertiliser application in Northern Ireland. Neither study reported a strong seasonal pattern. The maximum TP concentration recorded in Co. Mayo was 780 µg P l^{-1}, while concentrations of up to 1900 µg P l^{-1} were recorded in Co. Meath. These very high values may not be typical. Kurz (2000) measured DRP, TDP and TP in rainfall at Johnston Castle in Co. Wexford and reported that concentrations were generally low or undetectable. However, concentrations of TP and TDP of up to 550 and 470 µg P l^{-1}, respectively, were found occasionally. The contributions of annual phosphorus loads from precipitation to six Irish lakes with varying nutrient status were estimated by Kelly (1999) to range from 2% to 18%, with the greatest percentage contribution in the most oligotrophic lake.

Summary of background sources of phosphorus

- In pristine systems, the flux of phosphorus from the catchment to surface waters is determined mainly by the flow of water through the system and the underlying geology.
- Atmospheric deposition may represent a significant source of phosphorus to some freshwater systems, particularly in oligotrophic catchments.
- Seasonal differences in the phosphorus load in atmospheric deposition are relatively small in areas remote from intensive agricultural activity and urban centres, and relate to seasonal variation in rainfall.
- It has been suggested that the atmospheric deposition of phosphorus plays a significant role in the mesotrophic status of upland lakes in Northern Ireland.
- Estimates for the contribution to the annual phosphorus load of six lakes in the Republic of Ireland ranged from 2% to 18%, with the greatest percentage contribution in the most oligotrophic lake.

2.3 Phosphorus Inputs from Point Sources

The major point source of phosphorus in urbanised areas is from municipal and industrial wastewater treatment plants (WWTPs) (Smith *et al.,* 1999). Caraco (1995) linked the increase in the phosphorus concentration of many of the world's major rivers to an increase in the local human population. Muscutt and Withers (1996) also reported that orthophosphate concentrations in UK rivers were greatest in highly urbanised areas. Waste disposal sites, construction sites, and sources within farmyards may also make a substantial contribution to the TP load from point sources in some catchments (Foy *et al*., 1982; Hooda *et al*., 2000). While inputs of phosphorus from

WWTPs continue to account for a high proportion of phosphorus input to surface waters in many countries, improvements in treatment facilities and the introduction of phosphorus-free detergents have markedly reduced this source (Foy *et al.,* 1995). In Europe, many improvements are in response to the Urban Waste Water Directive (91/271/EEC) (CEC, 1991).

The contribution of WWTPs to the overall phosphorus load may be substantial where phosphorus removal processes have not been implemented (Foy *et al.,* 1982; Heaney *et al*., 1996; Castillo *et al.,* 2000). Foy *et al*. (1982) estimated that 54% of the SRP loading to Lough Neagh originated from sewage treatment works. Heaney *et al*. (1996) estimated that 52% of TP and 89% of SRP entering Lake Windermere originated from urban sewage treatment in the late 1980s. Castillo *et al.* (2000) reported that geology and the phosphorus loading from WWTPs were the best predictors of SRP loading in the River Raisin catchment in Michigan (USA). Improvements in phosphorus removal in WWTPs are, however, not always mirrored by improvements in phosphorus loading to receiving waters (Sharpley *et al.*, 1994; Carvalho *et al*., 1995; Foy *et al*., 1995). Foy *et al.* (1995) reported a long-term upward trend in SRP loadings in six major rivers in the Lough Neagh catchment (Northern Ireland) between 1974 and 1991, despite point source reductions.

In general, while there may be temporal variation in the TP load from WWTPs, there is no seasonal pattern (Muscutt and Withers, 1996; House and Denison, 1998; Castillo *et al.,* 2000; Neal *et al*., 2000). Data from the main sewage treatment plant in Dublin illustrate this trend (Brennan *et al*., 1994). In 1993 this plant provided only primary treatment and had a mean TP load of 1682 kg TP day^{-1}, with no overall seasonal pattern.

Summary of point sources

- The major point source of phosphorus in urbanised areas is from municipal and industrial WWTPs.
- While there may be temporal variation in the phosphorus load from WWTP sources, there is generally no seasonal pattern.
- Improvements in treatment facilities and the introduction of phosphorus-free detergents are leading to a marked reduction in phosphorus from this source.
- Improvements in phosphorus removal in WWTPs have not always been mirrored by an improvement in the phosphorus loading in the receiving waters.

2.4 Phosphorus Inputs from Agricultural Sources

2.4.1 Introduction

In undisturbed ecosystems, phosphorus is scarce and efficiently recycled (Haygarth and Jarvis, 1999). However, phosphorus losses from intensively managed agricultural land may induce eutrophication in surface waters that are linked to the field system through the drainage network. Although some losses may arise from point sources within the farmyard (Lee-STRIDE Report, 1995; Tunney *et al*., 1998; Morgan *et al.*, 2000), they are mainly attributed to the excessive accumulation of phosphorus in soils as a result of long-term inputs of inorganic fertilisers and manures (Heckrath *et al.*, 1995; Pote *et al.,* 1996; Hooda *et al*., 2000; Sharpley *et al.*, 2000; Tunney *et al.*, 2000). Diffuse agricultural sources are now considered to be the major contributor of phosphorus to surface waters in many parts of the USA (Sharpley *et al.*, 1994) and Europe (Foy *et al.*, 1995; Moss *et al.,* 1996; Tunney *et al.*, 1998; Lucey *et al.*, 1999).

Heathwaite and Dils (2000) concluded that the two key factors governing the amount and composition of phosphorus losses from agricultural land are: (1) soil biochemical processes, which control the forms of phosphorus available for transport; and (2) hillslope hydrology, which defines the transport mechanisms and pathways. Inputs to the soil phosphorus pool include plant residues, inputs from grazers, commercial fertilisers and organic manures. Many agricultural soils in developed countries, including Ireland, are now considered phosphorus saturated and require little or no further phosphorus fertilisation (Tunney, 1990; Sharpley *et al.,* 1994; Hooda *et al.,* 2000). The loss of relatively small proportions of phosphorus from agricultural soils may result in concentrations of limnological significance in surface waters (Tunney *et al*., 1998; Haygarth and Jarvis, 1999; Hooda *et al.*, 2000). High concentrations are reported in runoff and drainage water, particularly during high flow events and/or following the application of fertilisers or organic wastes (Sharpley *et al.*, 2000).

Haygarth and Jarvis (1999) reviewed phosphorus losses based on annual export coefficients from a variety of catchment studies. Although export coefficients rely on a number of assumptions, and their use requires caution, they can be useful for assessing phosphorus losses. Export coefficients also relate to the total quantity of phosphorus delivered over the annual cycle, and mask possible impacts of discrete sub-annual high-export events. Annual phosphorus export coefficients in the studies reviewed by Haygarth and Jarvis (1999) ranged from <0.01 to 620 kg P ha^{-1} $year^{-1}$. However, the latter was an extreme case related to a confined beef cattle feedlot, and typical values were *c.* 1 kg P ha^{-1} $year^{-1}$. In general, the lowest export coefficients (<0.01 kg P ha^{-1} $year^{-1}$) were from forestry and woodland catchments and from non-intensive permanent grasslands.

Export coefficients from grazed grasslands in the studies reviewed by Haygarth and Jarvis (1999) ranged from 1.8 to 3.15 kg P ha^{-1} $year^{-1}$. Gillingham and Thorrold (2000) reported rates of 0.11–1.67 kg P ha^{-1} $year^{-1}$ from sheep- and cattle-grazed pastures in New Zealand. Hooda *et al.* (2000) concluded that, while phosphorus losses in surface and subsurface runoff from livestock farming in the UK generally do not exceed 2 kg P ha^{-1} $year^{-1}$, they could be much greater from specific fields or catchments. Although these losses may not be of great economic concern, generally accounting for <5% of applied P, they are of environmental significance. Short-term phosphorus losses from grazed catchments may be of particular significance. Haygarth and Jarvis (1997a) recorded loadings of from 4 mg TP ha^{-1} h^{-1} to over 18 mg TP ha^{-1} h^{-1} in a survey of phosphorus export in a grassland catchment, with over 0.5 kg TP ha^{-1} discharged in one storm. McGarrigle *et al.* (1993) estimated that 588 kg TP entered Lough Conn (Co. Mayo, Republic of Ireland) from one catchment during heavy rainfall over a 2-day period.

Seasonal variation in the rate of phosphorus loss is related to the magnitude of soil pools, the rate of transport from field to surface waters and the timing of farming practices. Central to a framework proposed by Haygarth and Jarvis (1999) to describe diffuse phosphorus transfer from agricultural lands (Fig. 2.1) is the concept of potentially mobile phosphorus (PMP), defined as a reservoir of soil phosphorus vulnerable to loss/transfer to surface waters. Hydrology, which provides the carrier and energy for transfer, is described in the model as the single most important factor in phosphorus transfer. Temporal variability in hydrological activity is driven principally by intensity, duration and interval of precipitation. Base flow occurs during non-storm periods and comprises discharge from springs and near-stream seepage. Storm flows result in overland flow and shallow subsurface flows.

Agronomy and soil conditions control the sources of PMP and provide a means to mitigate phosphorus transfer. Land management influences phosphorus transport on three temporal levels. These are long-term changes in soil phosphorus concentration, variation over the annual cycle related to management practices, e.g. crop management and cattle movements, and short-term ‘catastrophic’ events, e.g. fertiliser or slurry application prior to rainfall (Fig. 2.1).

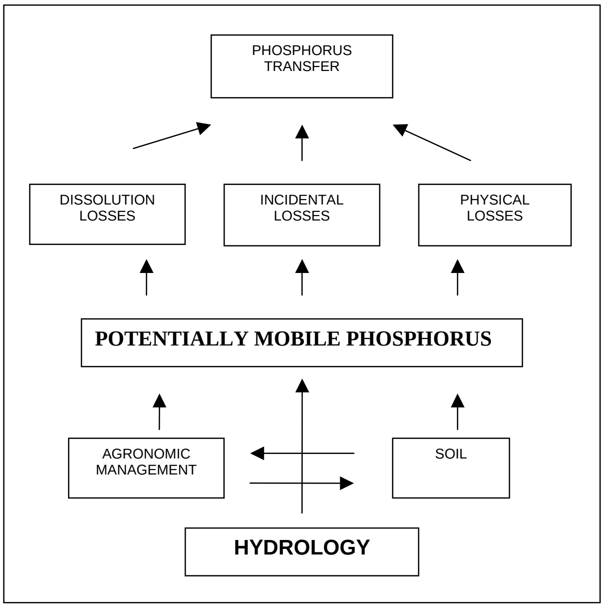

Figure 2.1. A conceptual framework describing the diffuse phosphorus transfer from agricultural lands (Haygarth and Jarvis, 1999).

The modes of phosphorus transfer described by Haygarth and Jarvis (1999) are dissolution, physical processes (e.g. erosion) and 'incidental direct losses'. The latter are defined as losses occurring soon after application of fertilisers and manures when coincident with a rainstorm. This third mode of transport is considered to be conceptually separate from the other two and is determined by unique circumstances. While dissolution will be instigated by low discharge rates associated with base flow (high frequency/low magnitude rainfall), physical transfer and incidental transfer may also be affected by low-frequency/high-intensity rainfall events. All three modes of transport contribute to overall phosphorus transfer rates.

2.4.2 Soil phosphorus pools

The concentration of total phosphorus in agricultural soils ranges from 100 to 3000 mg P kg^{-1} (Morgan, 1997; Frossard *et al.*, 2000). Most of this phosphorus is present as orthophosphate compounds. The concentration of dissolved inorganic phosphorus in the soil solution is generally low, but is replenished from the desorbtion of inorganic phosphorus held in soil particles, and through the mineralisation of organic phosphorus (Frossard *et al.*, 2000). As the capacity for a soil to hold phosphorus decreases, the concentration of phosphorus in soil water increases (Nash and Halliwell, 2000). Studies using isotopic exchange methods have shown that there is a continuum between forms of inorganic phosphorus that are immediately available, such as those present in the soil solution, and those that are present on the solid soil phase, including very slowly exchangeable forms (Frossard *et al.*, 2000). The contribution of organic phosphorus to the soil pool varies, but is generally in the range of 30–65% (Harrison, 1987; Sharpley and Rekolainen, 1997). In contrast to dissolved inorganic phosphorus, which may be held in the soil matrix, dissolved organic phosphorus is more mobile and susceptible to leaching. Dissolved organic phosphorus may make a significant contribution to the phosphorus pool in subsurface soil layers on land where animal manures have been applied.

The comparison of studies on spatial and seasonal variations in soil phosphorus is complicated by the array of methods of extraction and analysis that are in use (Tunney *et al.*, 1997). These include schemes for the fractionation of the soil phosphorus pool (e.g. Hedley *et al.*, 1982) and measures of the quantity of phosphorus that can potentially be released from soils (Olsen *et al.*, 1954; Sibbesen, 1977, 1983). Soil phosphorus sorbtion capacity and the degree of phosphorus saturation are also commonly measured. There is also considerable variation in the methods of quantifying available soil phosphorus for agricultural purposes. In the USA, Bray-1 P and Mehlich-1 P extractions are the most frequent measures of available phosphorus in soil, while in Europe, Olsen's P is used. In Ireland, Morgan's P is the most commonly used measure of plant-available phosphorus. Humphreys *et al.* (2000) found that Morgan's P and Olsen's P in soils from the Bellsgrove catchment in Co. Cavan (Republic of Ireland) were related by a non-linear equation with an r^2 value of 0.94.

Soil characteristics have an important influence on the magnitude of phosphorus losses. The ability of a soil to hold phosphorus within the soil matrix depends on particle size distribution, organic content and iron and aluminium content (Sharpley, 1995; Leinweber *et al.*, 1999; Daly, 2000). In general, sandy and organic soils have a lower capacity to bind phosphorus than those with a high clay content (Sharpley, 1995; Maguire *et al.*, 1997; Leinweber *et al.*, 1999; Daly, 2000). Maguire *et al.* (1997) reported a higher level of resin-extractable phosphorus in the silt fraction of a fertilised soil than in the sand fraction, while Leinweber *et al.* (1999) found that the risk of phosphorus leaching increased with a decrease in soil clay content. In a study of phosphorus runoff in Oklahoma (USA) soils (Sharpley, 1995), dissolved phosphorus in runoff was related to soil sorbtion capacity, with the release of phosphorus increasing as sorbtion capacity decreased. Iron and aluminium content increase the capacity of soils to bind phosphorus, while a high organic content reduces P-sorbtion capacities (Daly, 2000).

Several studies have reported a non-linear relationship between soil phosphorus, as measured by soil phosphorus tests, and inorganic phosphorus in the soil solution. The relationship has been described by a split-line model with a distinct 'change point' in slope (Heckrath *et al.*, 1995; Brookes *et al.*, 1997; McDowell and Trudgill, 2000), above which environmentally significant levels of phosphorus may be lost from the soil. Heckrath *et al.* (1995) found that concentrations of DRP and TP in drainage water were linearly related in soils with Olsen's P above *c.* 60 mg kg^{-1}. McDowell and Trudgill (2000) found a change point at *c.* 31 mg Olsen's P kg^{-1} soil in woodland, grassland and arable soils in a catchment in south Devon (UK). There was no apparent seasonal variation at this point; however, more samples lay above the change point in summer, indicating a greater risk of phosphorus loss in these soils at this time. Decreased precipitation and runoff over most of the summer lead to low loss rates, with the greatest risk of losses occurring in the first rains after a dry period.

2.4.3 Seasonal variation in soil phosphorus pools

The potential phosphorus loss from soil relates to the overall quantity of soil phosphorus and the portion of that which can be rapidly released into soil solution (McDowell and Trudgill, 2000). The magnitude and composition of soil pools reflect the combined rates of the main processes within soil phosphorus cycling. The interconversion of dissolved and particulate phosphorus involves precipitation/dissolution, adsorbtion/desorbtion and immobilisation/mineralisation (Frossard *et al.*, 2000). Several of these show seasonal cycles driven by climate, with temperature and moisture availability being particularly important for the mineralisation of organic phosphorus by the soil microbes and the uptake of dissolved inorganic phosphorus by vegetation and microbes. Further seasonal variation relates to timing of fertiliser and slurry application, livestock introduction and tillage.

Mineralisation of organic phosphorus is generally low in winter and, in response to temperature increases, high in spring and summer (Sharpley, 1985; Tate *et al.*, 1991). As temperatures rise in the spring, flushes of mineralisation occur. Increased phosphorus mineralisation rates can occur in spring even when inorganic fertiliser has been applied (Sharpley, 1995), but rates may be reduced by moisture availability. A second flush in mineralisation may occur in autumn, particularly if the summer has been dry (Magid and Nielson, 1992). The accumulation of phosphorus in plants and soil microbes has been noted in autumn when soil moisture is replenished following drought (Tate *et al.*, 1991). Inorganic phosphorus in the soil solution at that time becomes more susceptible to leaching, as vegetation growth and the uptake of phosphorus decline. Vegetation uptake of inorganic phosphorus also has a seasonal pattern, dictated by the growing cycle of the crop. In general, the highest uptake rates coincide with early summer, when light levels and temperatures are highest. Grass has its peak growth in June, but is also dependent on summer soil moisture availability (Scholefield *et al.*, 1993). Soil moisture deficit retards the growth and uptake of inorganic nutrients, until rainfall re-occurs.

In general, TP concentrations in unfertilised soils remain relatively constant over the annual cycle (Sharpley, 1985; Magid and Neilsen, 1992). However, seasonal variations in inorganic and labile phosphorus fractions have been reported for all vegetation types. High spring/summer and low autumn/winter concentrations in available inorganic phosphorus fractions have been reported by Garbouchev (1966), Gupta and Rorison (1975), Kuo and Jellum (1987), Weaver *et al.* (1988), and Magid and Nielson (1992). Garbouchev (1966) found that the concentration of resin-extractable phosphorus was greatest in the spring in both arable and grassland plots in Woburn (UK). Gupta and Rorison (1975) reported a spring peak in $CaCl_2$-extractable P in a grassland soil. Weaver *et al.* (1988) reported a similar pattern in water soluble P in sandy soils, while Kuo and Jellum (1987) noted a similar seasonal variation in water-extractable P in an arable soil.

Seasonal variation in Olsen's P in soils with root crops, cereals, grasslands and woodlands were found by McDowell and Trudgill (2000). Seasonal patterns were also noted in extractions of $CaCl_2$-extractable P in all soils, with the exception of the woodland. The pattern included late summer maxima and late winter minima. A spring increase in available phosphorus is considered to reflect temperature-driven microbial mineralisation of organic phosphorus. Increases in soil phosphatase activity have been reported during spring (Harrison, 1982; Bolton *et al.*, 1985). Some studies where no seasonal patterns in available inorganic phosphorus fractions were found (e.g. Haines and Cleveland, 1981;

Sharpley, 1985; Tate *et al.*, 1991) attributed this to a rapid turnover of this pool.

Magid and Nielson (1992) reported clear seasonal patterns in inorganic phosphorus in a sandy soil in Denmark, with the highest concentrations in spring and lowest in the autumn and winter, but no seasonal decrease in soil organic phosphorus. In contrast, a winter increase and a spring decrease of moderately labile organic phosphorus have been reported by others (Sharpley, 1985; Tate *et al.*, 1991; Fabre *et al.*, 1996). Tate *et al*. (1991) recorded an increase in labile organic phosphorus in winter in both fertilised and unfertilised pasture soils in New Zealand. In the low fertility soil, net mineralisation was strong in the spring, but net immobilisation occurred from early winter. Sharpley (1985) reported an increase in moderately labile phosphorus from summer to winter, with a decrease between winter and the following summer in both fertilised and unfertilised grassland and arable plots. Fabre *et al.* (1996) demonstrated that moderately labile phosphorus ($NaHCO_3$-organic P) increased during winter and decreased during summer in riparian forest soil. Sharpley (1985) stated that the increase in organic phosphorus in autumn and winter reflected the incorporation of inorganic phosphorus into plant and microbial biomass and the addition of fresh organic matter to the soil.

2.4.4 The influence of land use and land management practices

Variations in land use and management have an important influence on soil phosphorus status and on the magnitude and routing of phosphorus losses. Although some studies report no clear land use/phosphorus loss relationship (Svendsen *et al.*, 1995; Jordan *et al.*, 1997; Castillo *et al.*, 2000), many have reported increased diffuse phosphorus loss with an increase in percentage agricultural land (Truman *et al.*, 1993; Sharpley and Rekolainen, 1997; Allott *et al*., 1998; Tufford *et al.*, 1998; Leinweber *et al.*, 1999).

Forested ecosystems conserve phosphorus (Hobbie and Likens, 1973; Attiwill and Adams, 1993) and P exports are generally low compared with other land uses (Dillon and Kirchner, 1975; Wendt and Corey, 1980; Leinweber *et al*., 1999). Hobbie and Likens (1973) reported TP export in forested watersheds in the Hubbard Brook system (USA) as only 1% of that contained in annual leaf fall alone. Riparian forests can intercept a significant proportion of nutrients moving towards streams (Cooper *et al*., 1987; Griffiths *et al.*, 1997; Norton and Fisher, 2000). However, Norton and Fisher (2000) reported that while forest away from the stream (>100 m) in the Delmarva Peninsula (USA) acted as a TP sink, the forest closest to streams (0–100 m) acted as a TP source.

Phosphorus export from commercial forests may increase markedly during establishment and deforestation, and following fertiliser additions (Hobbie and Likens, 1973; Allott *et al.*, 1998; Nisbet, 2001). Deforestation in the Hubbard Brook system caused runoff to increase by 26% and greatly increased erosion. Studies in the UK have shown that 10% of phosphate from aerial applications can be lost over the following 3–5 years, and mainly within 6 months (Nisbet, 2001). The highest losses were from organic soils, which are characterised by low phosphorus-binding capacity. However, few studies have assessed the impact of aerial fertiliser application on the productivity of downstream standing waters. Nisbet’s (2001) review of seven Scottish data sets, in which phosphate and lake algal data were both available, indicated that fertiliser applications increased phosphate concentrations and that, in three cases, increased algal growth in receiving waters. Hobbie and Likens (1973) reported little temporal variation of TP in streams draining two Hubbard Brook watersheds. The export of phosphorus was directly related to flow. Schreiber *et al*. (2001) reported a seasonal cycle in phosphorus concentrations in streams draining pine forests in north Mississippi (USA). The greatest concentrations of all soluble phosphorus were reported in November, when litter fall was near maximum. They suggested that this phenomenon was associated with mineralisation and/or leaching of fresh litter. The lowest phosphorus concentrations occurred in February.

Higher losses of phosphorus have been reported from soils under arable cropping than for low-intensity grassland (Truman *et al.*, 1993; Sharpley and Lemunyon, 1997; McDowell and Trudgill, 2000). McDowell and Trudgill (2000) found that Olsen’s P in four land-use types in a small catchment in south Devon (UK) generally decreased in the order root crop>cereal crop>grassland>woodland. The pattern was consistent for each month in the year. Heathwaite and Dils (2000) attributed changes in land management in recent decades to the enhanced potential for phosphorus transfer. These changes include a greater proportion of land sown with winter wheat, more land drainage, an increase in winter grazing and higher livestock densities.

In general, tillage increases soil erosion (Haygarth and Jarvis, 1999), although minimum and contour ploughing can reduce the risk. Chambers *et al.* (2000) estimated that erosion from arable land comprised 18% of all phosphorus loss from agriculture in England and Wales, with three factors associated with erosive events: poor crop cover, the presence of valley floor features and the presence of compacted tramlines/wheelings. Wendt and Corey (1980) concluded that the greatest potential loss from arable land was associated with recently tilled soil and the presence of row crops, supporting the view that a move to winter cereals has increased phosphorus loss via erosion (Heathwaite and Dils, 2000).

Areas suitable for grassland farming typically have high rainfall (Haygarth and Jarvis, 1999). In Great Britain, grasslands account for 60% of total agricultural land (HMSO, 1993). In both the Irish Republic and Northern Ireland this figure exceeds 90% (Lennox *et al.*, 1997; Department of Agriculture, Food and Rural Development, 2001). Losses of phosphorus from intensively managed grasslands with continuous cover can be high, particularly where grazers are present or when organic manures are spread (Jordan and Smith, 1985; Smith *et al*., 1997; Sims *et al.*, 1998; Hooda *et al.*, 2000; Nash and Halliwell, 2000). Of four categories of land use assessed by Leinweber *et al.* (1999), grassland was found to be the most enriched in labile phosphorus. The authors suggested that, under grass, organic anions from root exudates or microbial metabolites may compete with PO_4^{3-} for adsorbtion sites. Permanent grasslands conserve organic matter and maintain high biological activity, which increases the proportion of labile phosphorus in the soil (Leinweber *et al.*, 1999).

Short-term management (i.e. fertiliser application and cattle grazing), soil moisture prior to a rain event and the intensity of rainfall may be particularly important for the release of phosphorus from grazed grasslands (Haygarth and Jarvis, 1997b). Phosphorus losses generally increase with stocking density (Schepers and Francis, 1982; Power *et al.*, 1995). Schepers and Francis (1982) found that TP and DRP in surface runoff were twice as high in grazed pasture as in ungrazed pasture. TP losses as high as 5.59 kg TP ha^{-1} $year^{-1}$ were found by Hooda *et al.* (1997) in streams draining cattle farmland in Scotland. The main phosphorus input from grazers is thought to be via faecal material (Nash and Halliwell, 2000), as concentrations of phosphorus in animal urine are generally low (Braithwaite, 1976). Haygarth *et al.* (1998) calculated that phosphorus accumulation rates (60% retention annually) in a UK dairy farm were ten times those found in a sheep farm. The largest phosphorus importation was in animal feed concentrates, of which 70% was exported to land in excreta. However, little appears to be generally known about the fate of phosphorus in dung deposited by grazers (Haygarth and Jarvis, 1997b).

Grazers may have direct interaction with stream channels. Sharpley and Syers (1979) reported that the introduction of grazers for a period of 10 h to a small catchment in New Zealand resulted in an increase in the concentration of both dissolved and particulate phosphorus (PP) in stream flow. The increase was most pronounced for PP, which increased 100-fold, and was attributed to disturbance of sediment by cattle movement and the deposition of excreta within the stream channel itself. The effect was short lived and stream-water concentrations returned to pre-grazing levels within 2 days. In a study of four arable catchments in Denmark (Grant *et al*., 1996), phosphorus losses were high in a catchment comprised partly of low-lying riparian areas used for grazing. Cattle may also poach the soil surface. This decreases infiltration in the soil and therefore increases overland flow and associated phosphorus transfer (Haygarth and Jarvis, 1999). This is particularly prevalent around gateways, drinking troughs and waterways. Heathwaite *et al.* (1990) reported that heavy grazing of permanent pasture could result in an up to 80% reduction in infiltration capacity.

In general, the increased use of fertilisers, organic manures or animal wastes increases phosphorus losses

(Lennox *et al.*, 1997; Haygarth and Jarvis, 1999; Leinweber *et al.*, 1999; Heathwaite and Dils, 2000; Hooda *et al.*, 2000). In addition, silage making may increase nutrients in surface waters (Foy *et al.*, 1994). The application of fertiliser to soil increases the rate of phosphorus cycling and the amount of phosphorus stored in the soil (Nash and Halliwell, 2000). As soil has a finite capacity to hold phosphorus (Daly, 2000), this may also lead to increased phosphorus loss from soil to water. In grazed grasslands and soils enriched with animal wastes, phosphorus accumulates in the surface layers (Sharpley *et al*., 1984; Murphy and Culleton, 1997; Humphreys *et al.*, 2000; Anderson and Wu, 2001). Downward movement of phosphorus can also occur in these soils, indicating a susceptibility to losses by leaching (Sharpley *et al.*, 1984; Eghball *et al*., 1996). Pig slurry, in particular, may lead to a high accumulation of phosphorus in soils (Carton *et al*., 1995; Anderson and Wu, 2001).

The highest loss rates from grasslands occur when an intense rainfall event follows the application of fertiliser or organic waste (Sharpley and Syers, 1979; Truman *et al.*, 1993; Lennox *et al.*, 1997; Djodjic *et al.*, 2000). After fertiliser application, Sharpley and Syers (1979) recorded a 30-fold increase in both DIP and PP concentrations in streams draining a New Zealand grassland catchment. Heathwaite and Dils (2000) reported elevated phosphorus concentrations in macro-pore flow following the addition of cattle slurry to grassland in mid-March. Leinweber *et al*. (1999) reported that increased fertiliser use generally led to increased leaching of readily soluble forms of phosphorus. The relationship found by Leinweber *et al*. (1999) was, however, not linear. Higher rates of mineral fertiliser use did not necessarily increase phosphorus leaching and the relationship varied with soil type. The highest losses from a sandy soil under grass were found with a middle fertiliser application rate (40 kg P ha^{-1}), while the highest losses from a loamy sand with crop rotation were with a low application rate (20 kg P ha^{-1}).

2.4.5 *The influence of land use and management practices in Ireland*

Of the 6.5 million ha of land in Ireland, 5 million are used for agriculture and forestry (Department of Agriculture, Food and Rural Development, 2001). About 90% of pasture and crop land is used for growing grass (Allott *et al.*, 1998; Department of Agriculture, Food and Rural Development, 2001). In Northern Ireland, grasslands represent >90% of agricultural land (Lennox *et al*., 1998). Grass, including silage, comprises 97% of cattle feed, and grass production generally exceeds demand (Culleton and McGilloway, 1995).

In the Republic of Ireland, 8% of total land area is afforested, mainly with conifers (Allott *et al.*, 1998; Department of Agriculture, Food and Rural Development, 2001). Phosphorus losses from forestry, which in some catchments represents a significant percentage of total land use (McGarrigle *et al.*, 1993), arise primarily during planting and clearing (McGarrigle *et al.*, 1993; Nisbet, 2001) and may enrich surface waters, particularly in upland catchments (Gibson, 1976). McGarrigle *et al.* (1993) found that the total amount of phosphorus leaching from plantations in the Lough Conn catchment in Co. Mayo increased steadily with increases in planted area, and was estimated to amount to 2 t P in 1991. This represented 21% of the estimated base TP load to the lake. In 1992, the planting rate was 250 ha $year^{-1}$. Cummins and Farrell (unpublished data) reported strong seasonality in MRP concentrations in two streams following combined felling and fertilising in Cloosh Valley Forest, Co. Galway. Over the period from January 1996 to December 2000, both harvesting and fertilisation were followed by an immediate rise in MRP concentrations, with subsequent and generally exponential declines of MRP, independent of season. However, in one stream with natural drainage, an annual cycle of a late summer maximum and a spring minimum occurred. An initially similar seasonal cycle in MRP concentrations was observed in a second stream following clearfelling.

The major diffuse phosphorus loss to surface waters in Ireland is from grasslands. Soil phosphorus in Irish grasslands has continued to increase despite a relatively constant use of phosphorus fertiliser in recent years (Tunney, 1997). Losses of 0.1 kg P ha^{-1} $year^{-1}$ in surface runoff from grassland with low soil P test levels in Wexford, reported by Tunney *et al*. (1997), probably represent conditions in Ireland before the widespread use of chemical fertilisers. Phosphorus export from intensively managed grassland can, however, be closer to 4 kg P ha^{-1} $year^{-1}$ and can result in considerable export to surface waters (Lee-STRIDE, 1995; Tunney *et al*., 1997; Kurz, 2000). Kurz (2000) reported an export rate of 4.8 kg P ha^{-1} $year^{-1}$ from intensively managed grassland in Co. Wexford, and 2.5 kg P ha^{-1} during August 1997, a month with high rainfall. Lennox *et al.* (1997) estimated that dissolved phosphorus accounted for more than 50% of the losses from diffuse sources in two agricultural catchments in Northern Ireland. Increases in soil phosphorus concentrations in pastures in Ireland have been attributed to both stocking and fertiliser rates (Power *et al.*, 1995). Murphy and Culleton (1997) reported increased available phosphorus in both fertilised and unfertilised grassland in Co. Wexford, in which rotational grazing had been practised over a 20-year period. Increases were found mainly in the surface layers. Humphreys *et al.* (2000) reported phosphorus accumulation in surface soils in grasslands in the Bellsgrove catchment in Co. Cavan.

The loss of accumulated phosphorus is affected by soil type and characteristics. Daly (2000) found that mineral soils in Ireland were up to 79% P-saturated. These soils are particularly susceptible to phosphorus loss. Irish soils that were considered vulnerable to phosphorus loss by desorbtion were those with elevated soil P-status and low soil P-sorbtion capacities. Soils with a higher iron and aluminium content were found to have a greater capacity to bind phosphorus (Daly, 2000).

The decline in surface water quality in Ireland is most notable in areas of intensive cattle farming or where there is a high density of pig and poultry production units (Allott *et al.*, 1998). Surface waters situated away from these areas were chiefly in the western and upland catchments and were generally of high quality. The increase in winter housing of cattle in recent years, and the disposal of the resultant wastes in particular, are probably important contributors to eutrophication (McGarrigle *et al.*, 1993; Carton *et al.*, 1995; Allott *et al.*, 1998). Silage making may also be important for phosphorus losses to surface waters, with most incidents occurring in the summer months (Foy *et al.*, 1994; Drew, 1996). Teagasc recommendations for phosphorus additions in silage production are greater than for pastures.

Allott *et al.* (1998) estimated that, in the Republic of Ireland, animals produce 29 million t of manure over the indoor winter period. Additional manure is produced by the intensive rearing of pigs and poultry. The disposal of these manures on land poses an increased risk of phosphorus loss, particularly during wet weather (Sherwood, 1980; Jordan and Smith, 1985; Carton *et al*., 1995; Lennox *et al.*, 1997; Tunney *et al*., 1998; Anderson and Wu, 2001). Pig slurry, in particular, is high in phosphorus and leads to higher rates of phosphorus accumulation in soils than does cattle slurry (Carton *et al*., 1995; Anderson and Wu, 2001). Carton *et al.* (1995) identified four opportunities for the spreading of slurry in the annual cycle in Ireland. These are in early spring, after the first silage cut, after the second silage cut and in the autumn. In practice, farmers are reluctant to spread in the early spring and summer and most slurry is spread in autumn. This may lead to phosphorus losses of several kg P ha^{-1} if heavy rain occurs (Tunney *et al*., 1998). In addition, limited storage capacity may result in slurry spreading in January or February. In Northern Ireland, Tunney *et al.* (1998) found that 39% of farms had a slurry storage capacity of less than 4 months. In these farms, the spreading of slurry is likely to occur in the early spring, when surface waters are becoming vulnerable to algal blooms. A notable deficit in slurry storage was reported in a recent study of agricultural mini-catchments in the Lough Derg and Lough Ree catchments (Kirk McClure Morton, 2001). Within the Lough Conn catchment (Co. Mayo) diffuse runoff from cattle-based agriculture was found to contribute over 60% of the total phosphorus loading to the lake in the period from 1990 to 1991 (McGarrigle *et al.*, 1993). Changes in cattle farming, including an increase in winter housing of cattle and a move from hay to silage as winter fodder, were cited as possible causes for this increase.

Summary of the effect of land use on loss of phosphorus to surface waters

- In general, diffuse phosphorus losses increase as the percentage of agricultural land in the catchment increases.

- The highest loss rates occur when intense rainfall follows the application of fertiliser or of organic waste.
- Spatial variation in the magnitude of phosphorus losses will be affected by soil characteristics, in particular the ability of a soil to hold phosphorus within the soil matrix. Soil phosphorus test levels in Irish grasslands have continued to increase despite the fact that the use of phosphorus fertiliser has remained relatively constant in recent years. Mineral soils in Ireland have been found to be up to 79% P-saturated and many are particularly susceptible to phosphorus loss.
- Seasonal variation in the rate of phosphorus losses is related to soil phosphorus pools, in the rate of transport from field to surface waters, and with farming practices. These include the timing and intensity of grazing, silage making, fertiliser application and slurry spreading.
- The decline in surface waters in the Republic of Ireland is most notable in areas with intensive cattle farming, or in areas that have a high density of pig and poultry production.

3 Transport of Phosphorus

3.1 Transport of Phosphorus in Groundwater

3.1.1 General introduction

Phosphorus transport in groundwater is generally ignored in catchment studies and monitoring programmes (Kilroy *et al*., 1999). Phosphorus in groundwater is nearly all dissolved. Because of the importance of the binding of phosphorus to sediment and soil particles, Correl (1997) considered that surface waters receive most phosphorus in surface flows. However, several studies have found that groundwater can be a source of phosphorus to lakes and rivers (Brock *et al*., 1982; Shaw and Prepas, 1989; Boar *et al*., 1995; Hagerthey and Kerfoot, 1998).

3.1.2 Groundwater studies in Ireland

In Ireland phosphorus has been overlooked in groundwater, primarily because the maximum admissible concentration for drinking waters under EU regulations (Directive 80/778/EEC) is rarely approached (Kilroy *et al.,* 1999). The EPA's Water Quality Monitoring Programme reported median MRP (unfiltered) concentrations of 17 $\mu g\ l^{-1}$ for 1995–1997 (Lucey *et al.*, 1999). Recent studies have, however, recognised the potential of groundwater phosphorus for eutrophication (Drew, 1996; Kilroy *et al*., 1999; Kilroy, 2001). Drew (1996) identified nutrients in silage and fertiliser as potential threats to groundwater quality in the Burren area. The potential for phosphorus transport to surface waters in karstic areas is much greater than in non-karstic areas because of the rapid channelling of water. Kilroy *et al*. (1999) examined data from the EPA's Water Quality Monitoring Programme and found that values in excess of >20 $\mu g\ l^{-1}$ MRP (unfiltered) were reported from 42% of sites, while values of >30 $\mu g\ l^{-1}$ MRP (unfiltered) were reported from 24% of sites. These values exceeded those outlined for MRP in the Interim Statutory Standards for Lakes and for River Waters in Ireland for moderately polluted waters (EPA, 2001).

Kilroy *et al*. (1999) reported no overall difference between summer and winter TP concentrations in a survey of springs and boreholes. Groundwater phosphorus concentrations were influenced mainly by geology and overlying subsoils. Sites located on impervious gley soils generally had less groundwater phosphorus concentrations than sites with more free-draining brown earth and grey–brown podzolic soils. Increasing well depth, overburden thickness and unsaturated zone thickness also resulted in lower phosphorus concentrations. DRP was generally the dominant fraction in these groundwaters. However, analysis of samples from karstic springs in the Robe and Fergus catchments between May 1999 and March 2000 indicated that, while TP concentrations remained relatively stable, concentrations increased by up to two orders of magnitude on occasion. The dominant fractions during these events were DOP and PP, and were probably related to local pollution events (Kilroy, 2001).

Summary of transport of phosphorus in groundwater

- The transport of phosphorus in groundwater is often ignored in catchment studies and monitoring programmes.
- Several studies have found that groundwater can be a source of phosphorus to lakes and rivers, particularly during low flow conditions. The importance of groundwater to overall phosphorus loads may increase in summer when rainfall and flows are low.
- Concentrations of phosphorus in Irish groundwater may represent a potentially important input to susceptible lakes and rivers.
- No overall difference was found between groundwater TP concentrations in summer and winter in a survey of springs and bore-holes in the Republic of Ireland.
- Concentrations of TP in groundwater in Ireland have been found to increase by up to two orders of magnitude on occasion. These probably arise from local pollution.

3.2 Transport from Field to Drainage Network

3.2.1 Introduction

Phosphorus is transported from the catchment via surface runoff, subsurface flow and leaching to groundwater. These pathways are spatially and temporally dynamic, represent a continuum, and may or may not be activated depending on factors such as antecedent moisture, topography, rainfall intensity and duration (Heathwaite and Dils, 2000). The transport of dissolved phosphorus is initiated by desorbtion, dissolution and extraction of phosphorus from soil and plant material (Sharpley and Rekolainen, 1997). All three major pathways may transport dissolved phosphorus. Particulate phosphorus includes phosphorus in organic matter and phosphorus sorbed to particles. It is transported principally by erosion and is a function of rainfall intensity and amount. Particulate phosphorus losses occur mainly in surface runoff and in subsurface flow where artificial drainage and macropores exist. While the possible importance of subsurface flow was noted by Ryden *et al*. (1973), it was believed until recently that surface runoff and erosion were the main mechanisms involved in the transport of phosphorus from agricultural land (Sharpley *et al.*, 1994; Sharpley and Rekolainen, 1997). However, while overland flow may be dominant in some systems, subsurface flow may account for a substantial proportion of total phosphorus loss (Sims *et al.*, 1998; Dils and Heathwaite, 1999; Heathwaite and Dils, 2000; Chapman *et al.*, 2001).

The loss of phosphorus from soils via all hydrological pathways is dominated by high rainfall events (Schuman *et al.*, 1973; Truman *et al.*, 1993; Sharpley *et al.*, 1994; Grant *et al.*, 1996; Heathwaite and Dils, 2000; Simard *et al.*, 2000). However, the extent of losses during these events may be masked by discrete sampling methods (Grant *et al.,* 1997; Wiggers, 1997). This can underestimate phosphorus losses in drainage water by more than 50% and in some cases by up to 120%, and reliable estimates of phosphorus losses from artificially drained catchments can only be obtained if storm events are sampled intensively (Grant *et al*., 1997).

Catchment topography influences both the magnitude of the phosphorus load and the pathways utilised. Slope length and angle increase phosphorus in runoff. Ahuja *et al*. (1982) attributed an increase in concentration with slope length to an increase in the amount of phosphorus sorbed per unit area. However, the influence of slope on phosphorus transport is dynamic. Heathwaite and Dils (2000) reported significant down-slope increases in the mean concentration of all phosphorus fractions in grassland surface runoff. Mean TP concentrations increased in the order 812, 1077 and 1455 µg TP l^{-1}, respectively, for top, middle and base hill-slope positions, which may reflect the preferential transport of phosphorus attached to fine colloidal material with deposition at the slope base.

3.2.2 Surface runoff

Large phosphorus losses in runoff have been reported from both arable (Schuman *et al.*, 1973; Burwell *et al.*, 1975; Truman *et al*., 1993) and grassland soils (Sharpley and Syers, 1979; Gillingham and Thorrold, 2000; Heathwaite and Dils, 2000; Kurz, 2000; Nash and Halliwell, 2000). The dominance of dissolved and particulate phosphorus transported in surface runoff may vary depending on land use and management. Sharpley *et al.* (1994) stated that PP can contribute 75–95% of the TP carried in surface flow and that between 10 and 90% of PP may be bioavailable.

Particulate forms tends to dominate losses in runoff from arable land (Schuman *et al.*, 1973; Burwell *et al*., 1975; Truman *et al*., 1993), while both dissolved and particulate fractions may contribute to the phosphorus loading from grazed catchments (Sharpley and Syers, 1979; Gillingham and Thorrold, 2000; Heathwaite and Dils, 2000; Nash and Halliwell, 2000). In a 3-year study of a stream draining a grazed catchment, Sharpley and Syers (1979) found that surface runoff contributed the major portion of both DIP and PP. In addition, DP represented approximately 75% of the total phosphorus load exported from the catchment. In a review of the export of phosphorus from grazing land in Australia, Nash and Halliwell (2000) reported that most phosphorus was exported dissolved in surface runoff. Heathwaite and Dils (2000) also found that dissolved forms dominated surface runoff of phosphorus (62%) from grassland in the UK and was attributed to the presence of permanent vegetation cover. In contrast, Gillingham and Thorrold

(2000) reported that particulate phosphorus accounted for most losses from sheep and cattle pasture in New Zealand. Sheep and cattle pasture in New Zealand is generally carried out in those areas with high rainfall and with steep topography, which are more prone to erosive losses. Less steep areas are used for dairying and fodder crops.

3.2.3 Seasonal losses in surface runoff

Surface runoff of phosphorus is disproportionately driven by high intensity/high magnitude rainfall because of the effect of rainfall on phosphorus sorbtion kinetics (Ahuja *et al.,* 1982). Losses of phosphorus from arable land are greatest when high rainfall coincides with low crop cover (Schuman *et al.*, 1973; Burwell *et al*., 1975; Truman *et al*., 1993). For arable land in the USA, this can be during the planting season, a time of high phosphorus application, minimal crop cover and often intense rainfall (Burwell *et al*., 1975). Schuman *et al.* (1973) reported that 80% of the annual phosphorus load in surface runoff from an arable catchment occurred during a few major storm events. This concurred with high losses reported by Truman *et al*. (1993) during high rainfall events in early spring, when ground preparation and fertiliser spreading were under way. Losses decreased as the crop canopy developed.

High spatial and temporal variability in surface runoff, related to rainfall duration and intensity, is also known from grazed catchments (Haygarth and Jarvis, 1997a, 1997b; Heathwaite and Dils, 2000). Heathwaite and Dils (2000) measured the highest concentrations (approx. 1600–1900 µg TP l^{-1}) during autumn storms following dry summer months. Phosphorus losses at those times were dominated by dissolved forms. TP concentrations, dominated by particulate forms, then declined through winter, possibly indicating exhaustion of readily mobile phosphorus. In the study by Haygarth and Jarvis (1997a), annual phosphorus losses were dominated by low frequency/high intensity rainfall events, particularly by one high intensity event in May when concentrations reached 1296 µg l^{-1} DRP and 1773 µg l^{-1} TP. When this event was excluded from the data, only 14% of TP variation during base flow was explained by discharge rate. Phosphorus export from the site was considered to be affected by the presence of cattle, both by the deposition of dung and by poaching, by the timing of fertiliser inputs and rainfall intensity. The authors also concluded that the understanding of the mechanisms of phosphorus loss under high frequency/low intensity rainfall events is still inadequate.

3.2.4 Subsurface runoff and preferential flow

Subsurface flow includes the movement of water through the soil matrix, through preferential flow pathways, i.e. soil macropores and worm burrows, and through artificial drainage networks (Stamm *et al.,* 1998; Simard *et al.,* 2000). Artificial drainage systems, together with preferential flow pathways in the soil, can form a rapid, direct hydrological link between field systems and surface waters (Stamm *et al.,* 1998; Dils and Heathwaite, 1999). The importance of subsurface flow depends on soil and catchment characteristics. Soil type, soil phosphorus concentration, antecedent soil hydrology, the ability of percolating water to mobilise soil particles and land, may all be important (Sims *et al.,* 1998; Djodjic *et al*., 2000; Hooda *et al*., 2000; Simard *et al*., 2000; Chapman *et al*., 2001). The highest loss rates occur in areas with a high water table (Grant *et al.,* 1997).

In a review of phosphorus losses in drainage, Sims *et al.* (1998) concluded that the most common agricultural situation associated with increased losses via drainage is the continuous application of organic wastes. In permanent grasslands, where the surface layer remains undisturbed, the network of macropores that enhance preferential flow will be less disturbed and will increase over time (Simard *et al.,* 2000). In addition, grasslands that are grazed or enriched with manure will have denser animal burrow and marcopore networks in summer (Estevez *et al.*, 1996), although poaching of the soil surface in winter by cattle may result in the blocking of entrances to the network. Preferential flow is enhanced in clay soils by soil cracking in dry weather.

Even in similar catchments, the extent of subsurface and preferential flow varies. Hawkins and Scholefield (1996) estimated that losses through tile drainage from a grassland catchment in the UK (0.05–0.10 kg ha^{-1} $year^{-1}$) were half the losses from surface runoff (0.10–0.22 kg ha^{-1} $year^{-1}$). However, Haygarth and Jarvis (1996) reported losses from tile drainage in another grazed grassland in the UK of 1.77 kg TP ha^{-1} $year^{-1}$, while those via surface runoff were 0.38 kg TP ha^{-1} $year^{-1}$.

Phosphorus transported in drainage comprises dissolved and particulate forms, but there is no clear indication from the literature as to which form is dominant (Dils and Heathwaite, 1999). There are some indications that PP makes a greater contribution to the TP load in this flow pathway in arable catchments than in grazed catchments. Simard *et al*. (2000) reported that PP was the main fraction of TP in tile drainage from arable land in the St Lawrence catchment (Canada). Djodjic *et al*. (2000) reported that PP accounted for between 10% and 69% of annual TP losses in four plots in an arable catchment in south-west Sweden. In contrast, the export of phosphorus in drainage from UK grassland catchments was found by Jordan and Smith (1985) and Simard *et al*. (2000) to be mainly in dissolved forms. Simard *et al*. (2000) noted that the introduction of tile drainage in poorly drained soils may reduce phosphorus transfer by increasing the infiltration capacity of the soil and so increase phosphorus adsorbtion. However, Thomas *et al*. (1997) found that inorganic phosphorus was not adsorbed during leaching through soil in Rothamsted (UK), despite the fact that the soil had a high adsorbtion capacity, suggesting a bypass of sorbtion sites as soil water is routed through preferential flow pathways.

3.2.5 Seasonal losses via subsurface runoff and preferential flow

Because phosphorus losses in subsurface and preferential flow are dependent on episodic high-flow events, they are difficult to predict (Grant *et al*., 1996; Dils and Heathwaite, 1999; Djodjic *et al.*, 2000; Chapman *et al.*, 2001). Chapman *et al.* (2001) found that PP loss through a drainage network in an arable catchment in the UK was predominantly a winter phenomenon. Grant *et al*. (1996) found that the timing of peak losses over an annual cycle varied among catchments. The highest monthly losses in drainage from two arable catchments in the south-east of Denmark were recorded in December, while the highest losses from two catchments in eastern Jutland were recorded in January and March (Grant *et al*., 1996). Overall, the highest concentrations were recorded during the first autumn storm, before the soil was waterlogged.

In a mixed agricultural catchment (Pistern Hill) in Leicestershire (UK), Dils and Heathwaite (1999) recorded loads of >300 mg TP h^{-1} in tile drainage. Between November and March, base-flow samples of tile drainage had low concentrations, i.e. 16–62 µg TP l^{-1}, which was approximately 30 µg TP l^{-1} less than the receiving stream, and was dominated by dissolved forms. In April and May, higher concentrations (mean 73 µg TP l^{-1}) in base flow were dominated by particulate forms and were attributed to new inputs from cattle grazing and fertiliser use. However, high concentrations of up to 1 mg TP l^{-1} were recorded during storm events, particularly during the first autumn storm after the summer and in February and March when there was frost. Dils and Heathwaite (1999) also reported considerable variation in phosphorus concentrations during storm events. In a December storm, dissolved phosphorus was dominant, while in a second event in February, the concentrations of dissolved and particulate phosphorus fluctuated. Dils and Heathwaite (1999) concluded that drainage systems were an effective conduit for the export of phosphorus from agricultural lands, but that the current understanding of subsurface transport is poor.

Heathwaite and Dils (2000) proposed that different hydrological pathways are characterised by distinct phosphorus ‘signatures’; the magnitude and composition of the phosphorus load transported from the Pistern Hill study depended on the discharge capacity of the flow route and the frequency with which the pathway operated. They concluded that surface runoff, although important, was spatially and temporally confined to high intensity/duration events. Subsurface flow pathways comprised groundwater, matrix, drain and macropore flows. Dissolved forms of phosphorus dominated the matrix flow. However, concentrations of TP in both the matrix and groundwater flows were generally low and contributed little to the overall load. In contrast, macropore and drain flow were important. Particulate forms dominated both macropore and drain flow. These particulates were associated with organic and colloidal phosphorus. Macropore flow at Pistern Hill had a distinct seasonal pattern, related to climate and land management. The highest concentrations occurred in the summer months when soil phosphorus levels were high as a result of fertiliser application and cattle grazing.

Concentrations remained slightly above the annual mean during autumn, and then declined gradually over winter. High autumn concentrations were attributed to the mobilisation of accumulated phosphorus from the dry summer grazing period. The winter decline was suggested to reflect the exhaustion of the phosphorus source material.

Both short-term (rainfall-induced) and seasonal variability were found in drain-flow phosphorus losses. Drain flow was continuous between September and March, low and irregular between April and May and absent between June and August. Low winter TP concentrations (mean 33 µg l^{-1}) were dominated by dissolved forms. In spring, the concentrations in base flow were double that of winter and were dominated by particulate forms. This increase was explained by land management practices including fertiliser inputs, cattle grazing and slurry spreading.

3.2.6 Effect of soil moisture deficit on phosphorus losses

A positive relationship is often reported between the quantity of nitrate leached from a soil and the magnitude and duration of a soil moisture deficit in the previous summer (Garwood and Tyson, 1977; Scholefield *et al.*, 1993). In contrast to phosphate, which may be held within the soil matrix, nitrate is readily leachable. However, many studies also report an increase in the rate of phosphorus export, following a dry period, that is not related to farm management (Haygarth and Jarvis, 1997a; Pote *et al.*, 1999; Gillingham and Thorrold, 2000; McDowell and Trudgill, 2000; Simard *et al*., 2000). This increase may be either because of phosphorus accumulation within the catchment or a direct effect of soil moisture deficit on uptake and mineralisation of phosphorus (Gillingham and Thorrold, 2000; McDowell and Trudgill, 2000).

Pote *et al.* (1999), comparing losses between wet (May) and dry (August) seasons, found twice the concentration of DRP in runoff in August (1.05 mg DRP l^{-1}) compared with May (0.57 DRP mg l^{-1}). However, runoff was significantly lower in August and, overall, season had little effect on mass loss of DRP. Haygarth and Jarvis (1997a) reported that TP losses of 464 mg P ha^{-1} in a May storm may have been related to the extent of the previous dry period. Simard *et al.* (2000), in three studies of preferential flow in soils in Canada, found high seasonal variations in TP and PP in drain water. The maximum concentrations appeared to relate to the occurrence of drought. PP was the main fraction of TP in tile drainage water after storm events following prolonged dry periods.

Gillingham and Thorrold (2000) reported increased phosphorus losses related to decreased soil moisture in several New Zealand grassland studies. Higher phosphorus concentrations were recorded in both surface and subsurface runoff in summer and autumn than in winter and spring. Explanations for this included decreased runoff during dry periods, increased mineralisation during summer, more phosphorus from plant litter and reduced phosphorus retention with decreased moisture content and increased soil redox potential. McDowell and Trudgill (2000) reported increased phosphorus losses following a dry period, and Heathwaite and Dils (2000) found that the magnitude and timing of phosphorus losses in drain flow to rainfall events depended on antecedent moisture, with a rapid response in conditions of high moisture and a delayed response with soil moisture deficit. Both preferential flow and soil moisture deficits are known to occur in the soils. Physical effects, coupled with slow plant growth, or even death during periods of low soil moisture in warmer months, can concentrate phosphorus in soil. More research is needed on the effects of soil moisture deficits on phosphorus losses (Haygarth and Jarvis, 1997a).

Summary of phosphorus transport in surface and subsurface runoff

- While surface runoff may be the main route for phosphorus export in some catchments, there is an increasing awareness of the role of subsurface and preferential flow, particularly where artificial drainage systems are in place.

- Temporal variation in phosphorus transport at the field scale is related to precipitation, with high intensity/low frequency events accounting for a high percentage of total losses of phosphorus.

- The highest phosphorus losses tend to occur following the first storm event after a dry period, with particularly high losses possible in late summer and autumn.
- During a dry summer period, the uptake of phosphorus by vegetation may be decreased, while residues of fertiliser, slurry and faecal wastes from cattle may accumulate. A flush of mineralisation may also occur on re-wetting, further increasing the soil phosphate pool.
- Losses over the winter period appear to decrease as the supply of potentially mobile phosphorus is exhausted.

3.3 Phosphorus Transport in Rivers and Streams

3.3.1 Introduction

The quantity and composition of TP entering rivers and streams reflect the combined loads of all point and diffuse sources within the catchment. In catchments with substantial point sources, dissolved forms of phosphorus generally dominate both concentrations and annual loads (Muscutt and Withers, 1996; House and Denison, 1998; Neal *et al*., 2000). In areas with a substantial diffuse input, however, the contribution of dissolved and particulate forms to the annual load can vary among catchments and over time (Sonzogni *et al.*, 1982; Kronvang, 1992; Svendsen *et al.*, 1995; Dorioz, 1996).

The rate of phosphorus transport within drainage systems depends on the catchment hydrology (Haygarth and Jarvis, 1996). It can display considerable temporal variation, with the highest loads associated with high rainfall (Verhoff *et al.*, 1982; Svendsen *et al.*, 1995; Dorioz, 1996; Kronvang and Bruhn, 1996; Cooke and Prepas, 1998; Gibson *et al*., 2001; May *et al*., 2001). In forested and agricultural watersheds in the Boreal Plain in Canada, Cooke and Prepas (1998) reported that seasonal variation in TDP export was related to traditional high summer runoff. Gibson *et al*. (2001) and May *et al*. (2001) estimated that the highest monthly TP loads occurred in the winter and the lowest loads in midsummer in the Lough Neagh catchment and in the River Cherwell, Oxfordshire (UK), respectively. The movement of phosphorus through catchments is probably similar to the "jerky conveyer belt" model described for solid particles (Newsome, 1992). Phosphorus export is characterised by an erratic, spiky pattern, governed by high intensity rainfall and the availability of mobile phosphorus (e.g. McGarrigle *et al.,* 1993; Svendsen *et al.*, 1995; Dorioz, 1996; Lennox *et al*., 1997; Pommel and Dorioz, 1997) and most export can occur in very few annual storm events (Sharpley and Rekolainen, 1997).

Retention and release processes within drainage systems regulate phosphorus transport (Behrendt, 1996; Dorioz, 1996; Pommel and Dorioz, 1997; Brunet and Astin, 1998; House and Denison, 1998). Likens (1984) considered streams and rivers as "active ecosystems exercising some degree of biotic and abiotic regulation over the timing, quantity and quality of particulate and dissolved substances moving downstream". Such regulation is related to hydrological, physical, chemical and biological cycles with both short-term and seasonal variation. It includes the deposition and mobilisation of PP and the uptake and release of DP by sediments and biota (Svendsen *et al*., 1995; Brunet and Astin, 1998; House and Denison, 1998). In general, more PP will be transported in tillage areas than grasslands (Haygarth and Jarvis, 1999; Chambers *et al.*, 2000). DP may undergo sequential sorbtion/desorbtion reactions with particulate material, changing the ratio between dissolved and particulate forms (Froelich, 1988). These processes, and the unpredictable nature of catchment hydrology, contribute to the temporal dynamics of phosphorus transport, although much more remains to be understood about phosphorus transport through catchments (Svendsen *et al.,* 1995; Johnston *et al.,* 1997).

3.3.2 The influence of catchment hydrology

Temporal variation in hydrology depends on net rates of precipitation and the balance between rainfall, runoff and input to receiving waters (Heathwaite, 1997). This balance is controlled by catchment geology, soil type, vegetation, topography and soil moisture status (Heathwaite, 1997). Intense rainfall, in particular, results in a pulse of water through the system and the rapid transport of dissolved and particulate phosphorus in surface and subsurface flow, particularly where artificial drainage systems and preferential pathways provide direct links to surface waters. In cold climates, meltwaters may contribute to high discharge rates (Kronvang, 1992; Brunet and Astin, 1998; Cooke and Prepas, 1998). Groundwater flow also increases during high flow events, particularly in karstic areas (Drew, 1996; Kilroy *et al*., 1999). The retention of phosphorus within the drainage network during high discharges may be low (Meyer and Likens, 1979).

Inverse relationships between DP concentration and flow (Kronvang, 1992; Svendsen *et al.*, 1995; Dorioz, 1996; Muscutt and Withers, 1996; House and Denison, 1997; Robson and Neal, 1997; Castillo *et al.*, 2000; Edwards *et al*., 2000) are generally attributed to a concentration effect during low flows and to dilution during high flows, most commonly in areas with significant point sources (Muscutt and Withers, 1996; House and Denison, 1997; Robson and Neal, 1997). This may result in high concentrations during dry summers. While high DP concentrations have also been associated with low flow in channels draining predominantly agricultural land (Kronvang, 1992; Muscutt and Withers, 1996; Castillo *et al.*, 2000), high phosphorus concentrations often coincide with high flow (Kronvang, 1992; Svendsen *et al.*, 1995; Dorioz, 1996; Lennox *et al.*, 1997; Pommel and Dorioz, 1997; Cooke and Prepas, 1998; Pionke *et al*., 2000). Kronvang (1992) attributed high dissolved phosphorus concentrations during periods of high flow to three phenomena: an increase in surface runoff, phosphorus desorbtion from particulate matter, and release of phosphate from interstitial water.

Although inputs of DP have often been thought to be the main contributor to eutrophication, there is increasing awareness of the role of sediment transport in catchment phosphorus budgets (Kronvang, 1992; Walling *et al.*, 1997; Webb *et al*., 2000). This takes place mainly during high flow events and is regulated by retention and release processes (Kronvang, 1992; McDonald *et al.*, 1995; Svendsen *et al.*, 1995; Brunet and Astin, 1998; House and Denison, 1998). Dorioz (1996) reported that while soluble forms of phosphorus represented more than 90% of TP during periods of low flow in a French agricultural catchment, most PP was exported during storm flow. Brunet and Astin (1998) calculated that two flood events contributed 89% of annual PP load in a stretch of the River Adour (France) and Kronvang (1992) reported that 80% of the annual POP load in a Danish arable catchment was transported during floods in 5% of the study period.

Walling *et al*. (1997) estimated that sediment-associated transport of phosphorus comprises 26–75% of annual load in UK rivers, with differences dependent on catchment soil type, land use, sediment mobilisation and potential for nutrient uptake by sediment. In four representative rivers there was limited variation in the nutrient content of suspended sediment but appreciable temporal variability. This was related to both variation in sediment properties and hydrometeorological conditions. Discharge rates, antecedent flow conditions and time of year all significantly affected the nutrient content of the sediment, particularly in relatively undisturbed catchments where point sources were of low importance. Stream bank erosion and resuspension within the river may also contribute a major proportion of PP to the annual load (Sharpley and Syers, 1979).

Soil type and agricultural practice also affect the export of PP. Sonzogni *et al.* (1982), reviewing studies on the American Great Lakes, in catchments dominated by mixed agriculture, estimated that DRP accounted for only 25% of TP on a basin-wide scale. In contrast, Cooke and Prepas (1998) reported that DRP accounted for 82% of the annual TP load in a lowland mixed agricultural catchment in the Great Plains area of the USA, an area characterised by non-erosive soils and low-lying topography. However, phosphorus concentration of mobile particulates often exceeds that of soils in catchments (Green *et al*., 1978; Kronvang, 1992; Sharpley *et al.*, 1995). Green *et al*. (1978) attribute this to the selective erosion of clay and to the adsorbtion of soluble phosphorus during transport.

Phosphorus concentrations can vary considerably between the rise and fall of storm hydrographs (Verhoff *et al*., 1982; Dorioz, 1996; House and Warwick, 1998). These changes often include hysteresis effects, with peak concentrations of phosphorus and peak flow rates temporally separated. Phosphorus during storm events in the River Swale (Yorkshire, UK) displayed ‘clockwise’ hysteresis, with higher concentrations on the rise than on the fall of the hydrograph (House and Denison, 1997). Dorioz (1996) identified two types of phosphorus export during storm flow. The first pattern followed periods of low flow. TP was maximal early in the storm hydrograph, and then decreased rapidly before maximum discharge. This pattern was suggested to reflect the flushing of particulates from the catchment. The average concentration of TP was directly proportional to the amount of phosphorus stored in the river and inversely proportional to the volume of water, reflecting a dilution of stored phosphorus. The second type of storm flow followed prolonged rainy periods. At these times, little phosphorus was stored in the river. The PP concentration increased and decreased with flow over the hydrograph, a pattern typical of erosion.

The transport of phosphorus from the catchment is affected by the extent of critical source areas most vulnerable to phosphorus loss (Heathwaite, 1997; Zollweg *et al*., 1997; Gburek *et al.,* 2000). Phosphorus export can be greatest from near streams (Tufford *et al*., 1998; Gburek *et al*., 2000; Morgan *et al*., 2000; Pionke *et al*., 2000) and those connected to the drainage system by artificial channels and preferential flow networks (Schoumans and Breeusma, 1997). According to the variable-source-area concept (Heathwaite, 1997), the area from which phosphorus is exported will contract and expand seasonally. During dry weather, the hydrologically active area will be closer to the network of rivers and streams than during wet weather, when source areas extend away and upwards, including up-slope movement.

3.3.3 Importance of high frequency sampling

Sampling intensity can be critical for the quantification of seasonal loads or the description of seasonal patterns (Verhoff *et al.,* 1982; Walling and Webb, 1985; Webb *et al*., 2000). In time-dependent sampling only a small number of samples are likely to coincide with flood conditions and maximum transport of particulate phosphorus. The dominance of dissolved phosphorus in many data sets may reflect a routine sampling regime (Muscutt and Withers, 1996). Wiggers (1997) found that the traditional collection of 18–26 samples per year underestimated phosphorus losses in Danish catchments by between 1.5 and 2.5 times compared with intensive sampling. However, storm events are often brief and unpredictable, and continuous monitoring is expensive and time consuming. Many studies compromise by intensifying sampling only during storm-flow events, using flow-proportional sampling to capture pulses of nutrients, and pooling samples taken during base-flow periods (Dorioz, 1996; Lennox *et al*., 1997; Pommel and Dorioz, 1997; Brunet and Astin, 1998; Cooke and Prepas, 1998).

Walling and Webb (1985) compared the accuracy of five methods using data from the River Exe (UK) and found a general failure to provide reliable estimates of loads, which could be underestimated by up to 50%. Many standard flux estimation procedures may produce unreliable load estimates for chemical species that have a complex storm-period behaviour or are transported in particulate-associated form, such as phosphorus. Webb *et al*. (2000) proposed a new procedure for robust ‘best estimate’ fluxes of such elements based on a detailed synthetic time series. These are then used to estimate the errors associated with flux calculation procedures, especially those resulting from differences in the timing of chemographs and hydrographs during storm events. Such a procedure could be used for catchments where detailed information on river discharge is available but where concentration data are collected less frequently.

3.3.4 Retention and release processes

Retention and release processes within the drainage system itself are important for phosphorus export (Green *et al.,* 1978; Svendsen *et al.,* 1995; Dorioz, 1996; Brunet and Astin, 1998). Retention processes include the sedimentation of particulates, adsorbtion and precipitation, trapping of dissolved phosphorus in interstitial water and biological uptake. Release processes include the scouring of particulate material during high flows, sediment desorbtion, mineralisation by sediment bacteria and the release of plant material during vegetation die-back. In rivers and streams, phosphate ions may undergo several sequential ‘spiralling’ cycles of uptake and release by particles and biota (Newbold *et al*., 1981; Correll, 1997). However, the capacity of a drainage network to retain phosphorus is limited. The quantity of DP retained in the Lac Leman basin (France) increased as weekly discharge increased, until flow rates reached 0.6 $m^3 s^{-1}$, at which point inputs equalled outputs (Dorioz, 1996).

In general, phosphorus retention within the catchment increases with catchment size (Prairie and Kalff, 1986; Behrendt and Oppitz, 2000). Retention and release processes also vary substantially along rivers depending on channel morphology, sediment characteristics and vegetation growth (Kronvang, 1992; Dorioz, 1996; House and Denison, 1997; Brunet and Astin, 1998). In rivers and streams with impoundments, sediment and particulate material may be stored temporarily or long-term (Meyer and Likens, 1979). Accumulations of terrestrial material at such impoundments can reduce the kinetic energy of water flow and further enhance storage. The presence of a flood plain and of riverine vegetation enhances particle retention (Cooper *et al*., 1987; Svendsen *et al*., 1995; Brunet and Astin, 1998). The presence of a lake upstream within a catchment may significantly affect phosphorus retention and release (Vollenweider, 1968; Kronvang, 1992; Svendsen *et al*., 1995). Svendsen *et al*. (1995) found that while in-stream phosphorus retention took place mainly in the summer, retention in the shallow Lake Sobygard (Denmark) took place only in the winter. In contrast, the lake acted as a phosphorus source in spring and summer, because of phosphorus release from the sediment. However, the summer export of phosphorus from the lake was lower during the time of peak zooplankton grazing, demonstrating the importance of in-lake biotic effects.

The quantity of PP transported during high-flow events may be affected by the preceding flow, with particular increases following prolonged dry periods (Svendsen *et al.*, 1995; Dorioz, 1996; Lennox *et al.*, 1997; May *et al*., 2001). Svendsen *et al.* (1995) reported that resuspension of stream sediment was the main phosphorus source during late-summer and early-autumn storms in lowland catchments in Denmark following dry periods. Resuspension in these streams was facilitated by weed-cutting in late summer. May *et al*. (2001) reported that the highest river discharge rates in the River Cherwell in Oxfordshire (UK) occurred in April following a major storm event.

Several studies have identified a seasonal pattern in phosphorus retention dominating in spring and summer and release dominating in autumn and winter. Brunet and Astin (1998) identified two phases in phosphorus transport over an annual cycle in a section of the River Adour (France): a retention phase during spring and summer and a mobilisation phase during autumn and winter. A similar pattern was reported for Danish (Svendsen *et al*., 1995) and UK (House and Denison, 1997) catchments. Retention and mobilisation may not be related to any single factor, but may be driven by a complex interaction of flow, temperature, vegetation growth and sediment dynamics, with the inter-conversion of particulate and dissolved phosphorus important (Brunet and Astin, 1998). In the River Adour, mobilisation of PP occurred mainly in high flows, while heavy rainfall events in winter resulted in extensive mobilisation of dissolved phosphorus stored in the riparian zone. In contrast, Lennox *et al.* (1997) found higher rates of dissolved phosphorus loss during a summer flood than winter floods in a rural catchment in Northern Ireland. They suggested that this reflected the low occurrence of summer floods, with a longer time period between events, with increased mineralisation during dry periods. The highest rates of dissolved phosphorus uptake by bottom and floodplain sediments and precipitation of phosphate with Ca, Fe and Al generally occur in spring and summer (Svendsen *et al.*, 1995; House and Denison, 1997, 1998; Brunet and Astin, 1998). Secondary calcite can form in calcareous streams, often in response to high primary production and a rise in pH from the biotic consumption of CO_2 (Green *et al.*, 1978). House and Denison (1997, 1998), in a study of a river supersaturated with calcite, found that phosphorus accumulated in sediment in spring and summer and decreased in autumn and winter. Precipitation was mainly during low-flow periods in spring and summer.

Retention of DRP was reported in all seasons from a lowland river system in Denmark, but was maximal in summer (Svendsen *et al.*, 1995). Assimilation by macrophytes was found to account for only 0.5–2% of DP uptake in the spring and summer period. Although uptake by benthic and pelagic algae was not measured, it was suggested that this process accounted for the bulk of the DP retention, together with adsorbtion by Fe and Al oxides and hydroxides. Dissolved phosphorus assimilated by algae during the growing season was exported as particulate organic phosphorus, while a large proportion of adsorbed phosphorus was exported in particulate form.

3.3.5 *The eutrophication effects of phosphorus pulses in rivers and streams*

Much of eutrophication research in fresh waters has focused on lakes and reservoirs. However, the effects of increased concentrations of nutrients in flowing waters are of increasing concern (Smith *et al*., 1999; Edwards *et al*., 2000). While light limitation and short hydraulic residence may limit primary production in rivers and streams, flowing waters are also sensitive to nutrient inputs (Soballe and Kimmel, 1987; Welch *et al.*, 1988; Correll, 1997; McGarrigle, 1998). Primary producers in rivers and streams include submerged macrophytes, emergent macrophytes, periphyton and benthic plankton. The effects of eutrophication include increased biomass, altered species composition, reduced water clarity, diel fluctuations in dissolved oxygen and pH levels and fish kills (Smith *et al.,* 1999). The effect on community structure and biological responses to nutrients is influenced by the physical and chemical gradients along the length of the channel from the headwaters (Edwards *et al*., 2000). Physical factors include slope, flow, stream length, density and the frequency of flood and drought. Chemical gradients down the length of the channel include an increase in pH, nutrient concentrations, total dissolved solids and carbon availability. Biological responses to these gradients include a downstream increase in species diversity, productivity and total biomass.

Additions of both nitrogen and phosphorus can increase primary production in flowing waters (Elwood *et al.*, 1981; Hill and Knight, 1988; Moss *et al*., 1989; Horner *et al*., 1990; Correll, 1997). Phosphorus is considered to be the main limiting nutrient (Van Nieuwenhuyse and Jones, 1996; Smith *et al.*, 1999; Edwards *et al.,* 2000). Only a small proportion of the total phosphorus load that is transported through an individual river is processed by the biomass (Petlan *et al*., 1998) and at high TP concentrations other factors limit the biotic response of algae. These include flood frequency, water column turbidity, abrasive action of suspended sediment and inter-specific shading (Horner *et al*., 1990; Peterson, 1992; Leyland, 1995; Clausen and Biggs, 1997; Edwards *et al*., 2000). Dodds *et al.* (1998) compared data from several stream ecosystems and concluded that TP concentrations below 30 mg P m^{-3} would be necessary to keep benthic algal biomass below nuisance levels of <100 mg m^{-2}. A median annual MRP (unfiltered) concentration of <30 µg P l^{-1} has been suggested as necessary to control eutrophication in Irish rivers, with stricter criteria where rivers flow into lakes (McGarrigle, 1998).

In general, at a similar phosphorus supply rate, lower chlorophyll concentrations occur in flowing than in standing waters (Soballe and Kimmel, 1987; Van Nieuwenhuyse and Jones, 1996; Edwards *et al*., 2000). Van Nieuwenhuyse and Jones (1996), on reviewing data from 292 studies, reported lower suspended algal biomass in streams in smaller catchments. They attributed this to a decrease in mean hydraulic flushing rate with increase in catchment size. A reduction in flushing might increase chlorophyll levels directly by allowing more time for algal photosynthesis, or indirectly by giving more time for dislodged benthic algae to accumulate in the water column. Changes in physical and chemical conditions along the length of a river channel affect phosphorus uptake by biota. These include a downstream increase in residence time of phosphorus and a change in the shape of the response curve between chlorophyll and TP from curvilinear to linear (Edwards *et al*., 2000). In 345 streams in the USA, Soballe and Kimmel (1987) found that algal cell abundance was related positively to both residence time and water depth, and negatively to water clarity. Edwards *et al*. (2000) considered that the quantification of phosphorus residence time within a section of river channel is essential in order to determine the contribution of phosphorus to biological demand.

Rapid increases in algal biomass in response to phosphorus addition to streams and rivers have been recorded many times (e.g. Elwood *et al*., 1981; Moss *et al*., 1989; Horner *et al*., 1990; Correll, 1997). Uptake by primary producers is greatest in spring and summer and generally coincides with periods of low flow. Where point sources are important, high concentrations of phosphorus occur because of a reduced dilution effect (Muscutt and Withers, 1996). A concurrent increase in phosphorus availability and a decrease in current velocity promote primary production (Talling and Rzoska, 1967; Kilhus *et al.*, 1975), while subsequent flood events may lead to scouring and wash-out (Tett *et al*., 1987; LaPerriere *et al*., 1989). The uptake of phosphorus by sediments is greatest in summer (House and Denison, 1997, 1998), thus decreasing phosphorus availability in the water column. The increased uptake of phosphorus by primary producers in a given section of river channel may decrease downstream nutrient availability during periods of growth and provide a subsequent export of organic phosphorus downstream during dieback. Much remains, however, to be understood about the role of other limiting factors in modifying the relationship between plant growth and phosphorus supply in flowing waters (Edwards *et al*., 2000).

3.3.6 Catchment studies in Ireland

Water quality monitoring began at a national level in Ireland in the early 1970s. In most cases, monitoring of rivers and streams has been discrete and mainly of a biological nature (Lucey *et al*., 1999), often supported with less extensive physico–chemical monitoring. Overall, there has been an increase in nutrients in Irish rivers over the last 30 years (Flanagan and Larkin, 1992; Lucey *et al*., 1999). While phosphorus export from point sources has been of importance in the past, the main impact on water quality is now attributed to an increase in phosphorus export from agricultural sources.

Several intensive studies of phosphorus losses have taken place in Irish catchments. In Northern Ireland, intensive monitoring of the Lough Neagh catchment has been in place for several decades. This monitoring has resulted in a comprehensive body of literature on phosphorus cycling (e.g. Foy *et al.*, 1982, 1995; Gibson *et al*., 2001). Phosphorus losses in the Lough Erne catchment have also been investigated (Foy *et al.*, 1993). In the Republic of Ireland monitoring has, *inter alia*, taken place in the catchments of Lough Conn (McGarrigle *et al*., 1993), Lough Leane (report in prep), the Lee (Lee-STRIDE Report, 1995), the Shannon (Kirk McClure Morton, 2001), Lough Mask (Donnelly, 2001), the Dripsey (Morgan *et al.*, 2000) and of several lakes monitored by the Fisheries Boards (Champ, 1998).

In 1997, the Irish Government launched “Managing Ireland’s Rivers and Lakes – A Catchment Based Strategy Against Eutrophication”. This strategy included Environmental Quality Objectives (EQO) for phosphorus and involved the setting of interim targets for phosphorus in river and lake waters (Department of the Environment, 1997; EPA, 2001). As part of this strategy, the government set up a number of catchment-based monitoring and management projects that included the Lough Derg and Lough Ree catchments, the Three Rivers project (Boyne, Liffey and Suir catchments) and the Lough Leane catchment. Comprehensive integrated monitoring developed for these catchments included intensive studies on a number of sub-catchments.

Studies on phosphorus transport highlight the dependence of phosphorus export on high intensity rainfall (McGarrigle *et al.*, 1993; Lennox *et al*., 1997; Tunney *et al*., 2000; Irvine *et al.*, 2001). McGarrigle *et al.* (1993) found large increases in phosphorus export to Lough Conn, Co. Mayo, in the early 1990s compared with a baseline study in the period from 1979 to 1982, and they attributed this to increased numbers of cattle housed over the winter and the subsequent increase in the quantity of organic waste spread in the catchment. McGarrigle *et al.* (1993) found that most phosphorus was lost in runoff following wet weather, particularly in the autumn, with 50% of the total phosphorus load entering over 18–25 days of the year, with one summer storm over 2 days accounting for 588 kg TP. Lennox *et al.* (1997) investigated phosphorus losses in an agricultural catchment draining into Lough Neagh and found that variation in annual losses was related to the interaction of short-term runoff events with slurry spreading or poaching of land by animals. Studies of phosphorus losses from Irish soils in Co. Cork and Co. Wexford have also found that losses were dominated by summer storms (Tunney *et al*., 2000). The highest concentrations in surface runoff in grazed grassland in Co. Wexford were partly attributed to the presence of grazing cattle on the site, although other seasonal factors were probably involved. However, the bulk of phosphorus export from the site (>2.5 kg DRP ha^{-1}) occurred during a period of heavy rainfall in August (Kurz, 2000). Phosphorus losses on a similarly managed low-P site were five times less during the same period.

Summary of phosphorus transport in rivers and streams

- The rate of transport of phosphorus within the drainage network is a function of both phosphorus availability and flow rate.
- The literature highlights the dominant influence of discrete high-intensity rainfall events on phosphorus transport. These events are by their nature varied and unpredictable.
- Retention and release processes play a significant role in the seasonal pattern of nutrient transport. The actual load is equal to the total phosphorus load minus phosphorus retained in the catchment.
- The interactions between the hydrological, physical, chemical and biological processes that govern phosphorus transport and retention are complex.

4 Phosphorus Cycling in Lakes

4.1 Lake Phosphorus Concentrations

4.1.1 Seasonal patterns in lake phosphorus concentrations

While some lakes may be nitrogen limited (Elser *et al*., 1990; Gibson *et al*., 1995b), phosphorus is generally considered to be primarily limiting in lakes (Schindler, 1977; Smith *et al.*, 1999). Phosphorus concentration occurring in a lake is the result of complex equilibria between external and internal loading, together with the physical and biological processes occurring in the water column and the sediment. The seasonal pattern of phosphorus has been documented for many lakes and can vary depending on physical, chemical and biotic processes. The literature on the subject is consequently vast, and this section can only provide a brief overview of the subject.

Some lakes show clear annual cycles of winter maxima and summer minima of TP concentrations (Bailey-Watts, 1990; Nedoma *et al*., 1993; Gibson *et al*., 1996, 2001; Heaney *et al*., 1996; Kelly and Smith, 1996; Gude and Gries, 1998). Two interlinked mechanisms govern the magnitude of the TP maxima in winter (Gibson *et al*., 1996): the magnitude of the inflowing load and the magnitude of the release of phosphorus from the sediments. Although it is possible that the summer minimum may also reflect a reduction in the input of particulate phosphorus to the lake during periods of low flow, in general low midsummer concentrations relate to biotic uptake and sedimentation of algal biomass (Guy *et al*., 1994). This seasonal pattern is, however, far from a ubiquitous phenomenon. In lakes in which sediment release rates are high, a late summer/early autumn maximum in TP concentrations may be recorded (Kelly and Smith, 1996; Søndergaard *et al*., 1999; Gibson *et al*., 2001) and in some lakes a dynamic equilibrium between sediment- and particulate-bound phosphate and the dissolved phosphorus pool keeps phosphate concentrations relatively constant over the annual cycle (Brooks and Edington, 1993; Correll, 1997). While maximum dissolved inorganic phosphorus concentrations in the surface waters of lakes are also generally found in winter, concentrations during the time of peak algal production may be below the limit of detection (Kelly and Smith, 1996; Irvine *et al.*, 2001).

The seasonal patterns in lake TP concentrations are most apparent in eutrophic lakes, where winter concentrations are well within the detectable range (Kelly and Smith, 1996; Gibson *et al*., 2001). Gibson *et al*. (2001) illustrated the main seasonal features of the TP concentrations in Lough Neagh, a large shallow eutrophic lake in Northern Ireland. The concentration at the start of the year decreased as a result of both uptake of soluble phosphorus into phytoplankton and the subsequent settling of algal cells to the bottom sediments. TP concentration remained low between April and June, then rose sharply in July and August owing to an increase in the release of phosphorus from the sediment. In autumn it dipped again slightly, owing to a combination of sedimentation and dilution by inflowing river waters. This pattern emphasises the dependence of phytoplankton on both internal and external sources of phosphorus, with the initial spring bloom highly dependent on the availability of phosphorus in the lake after the winter period. Production later in the season in Lough Neagh may depend on sediment release.

In lakes that stratify seasonally, the spring and summer depletion of phosphorus may be confined to the epilimnion (Lean *et al*., 1983; Gude and Gries, 1998) while concentrations in the hypolimnion may increase as the temperature rises (Pettersson *et al*., 1990). In the very deep Lake Constance, seasonal changes in TP concentrations are observed predominantly in the euphotic zone and in deeper layers close to sediment (Gude and Gries, 1998). In these deeper waters, an increase in TP concentrations was observed in the summer when higher temperatures increased sediment phosphorus release. Some of the phosphorus that is accumulated in deep waters may become available to primary producers in the epilimnion through entrainment and diffusion.

4.1.2 Patterns of phosphorus concentrations in Irish lakes

Many Irish lakes have highly coloured waters, which influence light availability. In these lakes, primary production may remain low, despite high nutrient inputs (Jewson and Taylor, 1978; Foy *et al*., 1993). The deterioration in water quality of many Irish lakes in recent decades has, however, been widespread, and has been attributed to increases in the availability of phosphorus, particularly from agricultural sources (McGarrigle *et al*., 1993; Foy *et al*., 1995; Champ, 1998; Lucey *et al*., 1999; Irvine *et al*., 2001).

The seasonal patterns of TP concentration in Irish lakes vary from those with high winter concentrations and early summer minima to lakes in which no seasonal pattern is apparent (Foy *et al*., 1993; Gibson *et al.*, 1996; Bowman, 2000; Gibson *et al.*, 2001; Irvine *et al*., 2001). Dissolved phosphorus concentrations in many lakes, particularly in oligotrophic lakes, may be below the limits of detection at various times of the year. Bowman (2000) reported a seasonal pattern in TP concentrations in both Lough Derg and Lough Ree, with lower concentrations during the spring and summer than during the winter. Irvine *et al.* (2001) reported seasonal TP and MRP concentrations in a survey of 32 lakes in the Republic of Ireland. The lakes surveyed ranged from oligotrophic to hypertrophic, with annual mean TP concentrations ranging from less than 7 to 530 µg TP l^{-1}. The seasonal pattern was varied. In some lakes, maximum TP was recorded in August and was attributed to an influx of TP with high summer rainfall. One shallow eutrophic lake, Lough Ramor, had high concentrations of TP throughout the summer, probably owing to sediment release. High winter concentrations of MRP were quickly depleted by algae in spring and summer. TP peaks in August, associated with high rainfall, coincided with maximum chlorophyll *a* concentrations.

In light-limited lakes, the concentration of SRP and chlorophyll *a* may be uncoupled (Foy *et al.*, 1993). Foy *et al.* (1993) found that SRP levels in the Lough Erne system were rarely depleted by spring and summer chlorophyll, and concluded that the lake was light limited rather than nutrient limited owing to its highly coloured and turbid waters. The seasonal pattern of chlorophyll *a* in the Lough Erne system included an increase from March, with maximum chlorophyll occurring in May. Concentrations then declined rapidly despite the available SRP and high sunshine levels. Maximum chlorophyll *a* levels did not coincide with minimum SRP concentrations, while a decline in TP preceded the chlorophyll increase. Irvine *et al.* (2001) also reported higher summer than winter MRP concentrations in highly coloured lakes.

Summary of seasonal patterns in TP concentrations in lakes

- The phosphorus in a lake at a given time is the result of complex equilibria between external and internal loading, together with physical and biological processes occurring in the water column and in the sediment.
- Total phosphorus concentrations in many lakes show a clear annual cycle with winter maxima and summer minima. In others there is no predictable pattern and TP concentrations may be linked to seasonal variation in precipitation. Summer peaks in TP concentration associated with high rainfall have been recorded in some Irish lakes
- Patterns in lake TP concentrations are most apparent in eutrophic lakes, where winter concentrations are well within the detectable range. Dissolved phosphorus fractions can vary owing to seasonal patterns of hydraulic discharge and uptake of phosphorus by phytoplankton. Sediment release is likely to be important for internal loads of phosphorus, particularly in shallow eutrophic lakes
- Many Irish lakes have highly coloured waters, which may impact on light availability in the surface waters. In these lakes, primary production may remain low, despite high inputs of nutrients.

4.2 Internal Cycling in Lakes

4.2.1 The role of sediments in phosphorus cycling

Lake sediments have the capacity to store and release a portion of the total particulate phosphorus load that is transported to the lake from the catchment. In addition, through sedimentation and mineralisation of dead algal material, the sediments recycle phosphorus bound up in the phytoplankton. Biological activity gradually mineralises sedimented organic phosphorus, which is then released into the interstitial water. This dissolved phosphorus may then diffuse into the water column or become bound, particularly to ferric and aluminium hydroxides, within the sediment. Sorbed phosphorus may be released in response to diffusion gradients, changing redox and temperature.

Sediment phosphorus release occurs under both aerobic and anaerobic conditions. Aerobic release (redox potential >200 mV) includes a decrease in the sorbtion of phosphate, as the pH of the water column increases, and a decrease in sediment phosphate adsorbtion with higher temperatures. Anaerobic sediment release (<200 mV) is associated with high concentrations of organic matter in the sediment and, following thermal stratification, oxygen depletion in the hypolimnion. Mortimer (1941) recognised the importance of lake sediments as a source of nutrients that are readily available for biotic uptake (Nurnberg, 1985). Release can be particularly important during summer following the depletion of phosphate in the water column and, in stratified lakes, at overturn (Wildung *et al.*, 1974; Jensen and Anderson, 1992; Kleeberg and Dudel, 1997; Søndergaard *et al*., 1999). Sediment release of phosphorus may sustain algal crops even when external sources are reduced (Marsden, 1989; Sas, 1989; Søndergaard *et al*., 1999). The importance of sediment release is greatest in shallow lakes. The disturbance of sediment through wave action and benthivorous activity may be important (Scheffer, 1998).

4.2.2 Factors controlling sediment phosphorus release

Internal phosphorus loading in any lake relates to the history of external catchment loads. Seasonal variation in internal loading is affected by climate, lake morphometry, food-web processes, temperature, pH, nitrate concentration and the availability of labile organic phosphorus for mineralisation (Istvanovics, 1988; Boström *et al*., 1988; Jones and Welch, 1990; Jensen and Anderson, 1992; Gibson *et al.*, 1996; Søndergaard *et al.*, 1999).

Internal nutrient loading, particularly in shallow lakes, is influenced markedly by wind speed and flushing rate (Jones and Welch, 1990; Søndergaard *et al*., 1999). Processes affected by wind mixing include the entrainment of phosphorus from the sediment and the mixing of water with a low phosphorus concentration down to the sediment surface. This latter process increases the concentration gradient across the sediment–water interface and promotes diffusion. Søndergaard *et al*. (1999) found that TP concentrations reported in 265 shallow lakes in Denmark were highest in summer; primarily from internal loading. Sediment profiles in the lakes suggested that internal loading may continue to have a persistent impact on summer TP concentrations for another 15 years, even if external loading were reduced.

In contrast to shallow lakes, the epilimnion in deep lakes may be isolated from the sediments during periods of thermal stratification. Sediment release may, however, make a significant contribution to the phosphorus budget in these lakes during mixing in the spring and autumn, and during brief periods of vertical mixing (Larsen *et al*., 1981; Stauffer, 1987; Soranno *et al.*, 1997). Mixing of phosphorus into the epilimnion during the summer period in deep lakes generally occurs after periods of intense rainfall. Wind mixing is also important as the driving force that couples the sediments to the water column and transports nutrients to the euphotic zone (Brooks and Edington, 1993). In very deep lakes, storms during the period of greatest stability of the water column, normally midsummer, may not result in any disturbance of the thermocline or result in mixing (Soranno *et al*., 1997). Soranno *et al*. (1997) estimated that internal loading contributed between 38% and 78% of the total phosphorus load to the epilimnion in Lake Mendota, a deep stratified lake in Wisconsin (USA). In contrast, in the very deep Lake Constance (mean depth 253 m), phosphorus entrainment from the hypolimnion was considered by Gude and Gries (1998) to make practically no contribution to the phosphorus supply in the euphotic zone. In general, because of a windy climate, only some of the deepest lakes in Ireland experience extended periods of stratification.

In temperate lakes, mineralisation of organic matter in the sediment is greatest in spring and summer when temperatures are highest (Jacoby *et al.*, 1982; Boström *et al.*, 1988; Pettersson *et al.*, 1990; Jensen and Anderson, 1992; Kleeberg and Dudel, 1997). Kleeberg and Dudel (1997), investigating the release of phosphorus from sediments in the shallow and eutrophic Lake Großer Müggelsee (Berlin, Germany), found a distinct seasonal pattern in sediment porewater and fractional phosphorus distribution, with maximum PO_4-P concentrations in the summer. This was thought to be due to microbial activity, both directly, through an increase in mineralisation with higher temperature, and indirectly, through a decrease in the redox potential of the sediment during periods of intense decomposition. Istvanovics (1988) also reported maximum release rates in summer, related to bacterial activity in surface sediments.

The release of phosphorus from sediment is also a function of pH phosphorus adsorbtion capacity. During decomposition, sediment pH decreases as CO_2 is produced by microbes. This leads to the dissolution of part of the sediment $CaCO_3$ pool, mobilising additional phosphorus to the water column, and to desorbtion of phosphorus from iron and aluminium compounds. In contrast, the co-precipitation of phosphate with calcite in the presence of photosynthesising algae may control the availability of phosphorus in the water column, particularly in hard-water areas (Hartley *et al.*, 1997). During periods of intense primary production, the pH of the water column can rise, resulting in the increased precipitation of $CaCO_3$ and the adsorbtion of phosphorus. This may account for the reductions of chlorophyll *a* observed in Canadian hard-water lakes after liming (Prepas *et al*., 1990).

High nitrate concentrations may increase the phosphate sorbtion capacity of the surface sediment by keeping iron in an oxidised state. A reduced phosphorus release at concentrations of oxidised nitrogen greater than *c.* 1 mg N l^{-1} was found in Lake Großer Müggelsee by Kleeberg and Dudel (1997). This effect was noted during periods of intense rainfall, when pulses of nitrate entered the lake. However, in some lakes increased nitrate concentrations may enhance overall microbial growth and enhance the release of phosphorus from the sediment (Jansson, 1986; Boström *et al*., 1988).

Reynolds and Davies (2001) reviewed the role of internal loading in lakes and the probability of phosphorus release from sediments. High risk factors included shallow sediments that were subject to wave action or entrainment, fine calcareous sediments poor in iron, benthic reducing conditions and a water column overstocked with benthivorous fish that physically disturb lake sediments. Low risk conditions were deep, oxic, carbon sediments, rich in iron and low in organic matter that were below entrainment, and the presence of a well-balanced fish fauna.

4.2.3 Seasonal variation in sedimentation

Particulate phosphorus that enters a lake in inflowing waters will generally be sedimented rapidly (Gude and Gries, 1998) and sedimenting planktonic material may make a significant contribution to sediment phosphorus loads in the summer (Pettersson, 2001). Particulates may adsorb or release phosphorus as they fall through the water column. The direction of these reactions will depend on the concentration of phosphate in the water column and is governed by the phosphate buffer mechanism (Froelich, 1988; Correll, 1997).

The flux of material to the lake bottom is difficult to quantify because of problems with the methodology and the resuspension of material (Dillon *et al.,* 1990; Penn and Auer, 1997). Penn and Auer (1997) investigated the seasonal variability in the rate of sedimentation and in the composition of settling particulate material in a calcareous eutrophic lake in New York (USA). They partitioned the seston total phosphorus pool into four fractions: loosely bound P, extractable biogenic P, calcium mineral P and refractory organic P. The phosphorus flux in winter (12 mg P m^{-2} day^{-1}) was *c.* 50% of the mean flux during summer and autumn (23 mg P m^{-2} day^{-1}). Extremely low concentrations of TP in seston in July were attributed to the effect of grazing by zooplankton. Following this, there was an increase in the TP content of the seston, with peak values in the autumn, attributed to both an increase in ‘extractable biogenic P’ and ‘refractory organic P’ in late September, corresponding to a decrease in the chlorophyll *a* content of the epilimnion, and to an increase in ‘loosely bound P’ in October following autumn turnover. During turnover, dissolved Fe^{2+} entrained from deeper waters became oxidised and adsorbed dissolved phosphorus from the water column, before settling to the sediment. These three phosphorus fractions represented over 85% of the TP pool. ‘Calcium mineral P’ was thought to be terrigenous in origin, with seasonal patterns related to tributary particulate loadings. In Lake Erken, a mesotrophic dimictic lake in Sweden, Pettersson (2001) found that the highest phosphorus concentrations in settling and suspended material occurred in summer. The study indicated that phytoplankton and detritus were the main source of seston in the summer, while inorganic and resuspended material were dominant during mixing periods.

Seasonal variations in sediment phosphorus concentrations and composition have been reported from many lakes (Wildung *et al.*, 1974; Jacoby *et al.*, 1982; Istvanovics, 1988; Kleeberg and Dudel, 1997). Wildung *et al.* (1974) reported a spring decrease in the concentrations of total phosphorus, inorganic and organic phosphorus in a 2-year study of a non-calcareous lake in Oregon (USA). The greatest seasonal changes were found in a bay that received agricultural runoff in early spring, with sediment concentrations of TP of 437–707 µg TP g^{-1} dw. The concentration of total phosphorus decreased at this site in late spring and early summer. Concentrations then increased in the early autumn and were quite constant until the spring. A seasonal variation in the concentration of sediment organic phosphorus was also reported. However, the concentration of inorganic phosphorus accounted for the major portion of the sediment total phosphorus pool and it was considered that the principal release was chemical in nature (Wildung *et al.*, 1974). Kleeberg and Dudel (1997) found maximum porewater PO_4-P concentrations in the summer in shallow Lake Großer Müggelsee.

4.2.4 Seasonal variation in sediment release

The highest sediment release rates of phosphorus are generally measured during summer (Wildung *et al.*, 1974; Istvanovics, 1988; Pettersson *et al.*, 1990; Jensen and Anderson, 1992; Kleeberg and Dudel, 1997), concurrent with times of maximum primary production. The period of maximum sediment phosphorus release in a non-calcareous lake in Oregon (USA) coincided with a period of exponential growth of phytoplankton (Wildung *et al.*, 1974). The spring influx of nutrients from the catchment supplied the initial pulse of phosphorus for the phytoplankton. However, the increase in sediment phosphorus release in the summer, which represented an additional supply of phosphorus to the algae, was thought to be related to algal growth, although no mechanism was suggested. No concurrent increase in water column phosphorus concentrations was observed and it was concluded that the sediment-derived phosphorus was immediately utilised by phytoplankton. During late summer and early autumn, increased sediment phosphorus concentrations were attributed to the sedimentation of algal cells and to the resorbtion of inorganic phosphorus in the sediment.

Istvanovics (1988) measured phosphorus release from sediments in Lake Balaton (Hungary). Sediments in the lake were highly calcareous and the bulk of the inorganic and exchangeable phosphorus pools were bound to calcium. The maximum release rates in the hypertrophic area of the lake were recorded in summer. Release rates from mesotrophic sediments were lower and the maximum rates occurred in the autumn. This seasonal pattern was related to bacterial numbers in the surface sediments in both areas and to a positive feedback between internal phosphorus loading and primary production.

Brooks and Edington (1993) also reported an increase in TP during the period of spring mixing and a decrease during the period of thermocline stability in Lake Michigan (USA). The spring increase in TP coincided with increased phytoplankton populations, the magnitude of which depended on solar irradiance and the duration of mixing. Internal loading from the release of SRP from sediment is important in many Danish lakes that have been heavily nutrient enriched over many decades (Søndergaard *et al.*, 1999). Jensen and Anderson (1992) showed, however, that although SRP release was the main source of phosphorus loading in four shallow Danish lakes, release rates varied through the summer and were inversely ranked according to Fe:P ratios. It was suggested that the sediment ratio of Fe:P determined the extent of free sorbtion sites for PO_4^{3-} in the sediment, while differences in sediment organic matter in the lakes also had an impact on seasonal and year-to-year variations in phosphorus release.

4.2.5 The role of sediment phosphorus release in Irish lakes

The sediment release of phosphorus has generally not been assessed in Irish lakes. Only the deepest and most sheltered lakes in Ireland experience extended periods of stratification and the flux of phosphorus from the sediment is likely to be sporadic and related to nutrient status. However, sediment release of phosphorus is considered to play an important role in the supply of phosphorus to phytoplankton in the large, shallow, eutrophic Lough Neagh (Stevens and Gibson, 1977; Gibson *et al*., 2001). A windy climate ensures that the lake is well mixed, and prolonged calm spells are rare. Annual loading from rivers to the lake was found to be between 0.7 and 1.8 g P m^{-2}, while sediment release could reach 1.4 g P m^{-2} (Gibson *et al*., 2001). Gibson *et al.* (2001) found no clear explanation for the seasonal and long-term patterns of phosphorus release in the lake. In contrast, phosphorus release from sediments in Lough Erne has been found to be low or undetectable (Foy *et al.*, 1993).

Gibson *et al.* (1996) reviewed the phosphorus cycles of 17 lakes in Northern Ireland and Scotland. All lakes were relatively shallow, with mean depths of less than 12 m, and had residence times of less than 1.25 years. They identified three patterns in internal loading based on lake morphometry and depth. In the large eutrophic unstratified lakes, such as Lough Neagh, a rapid and massive release of phosphorus occurred in the summer and was distributed throughout the water column. In small, deep lakes with an anoxic hypolimnion, such as White Lough, Co. Tyrone, phosphorus was released from the sediments at a slow rate and was confined to deeper waters, with an abrupt change in epilimnetic concentrations at autumn overturn. In the third lake type, Lough Erne, a large stratified lake with a well-flushed and oxic hypolimnion, there was no detectable release of sediment phosphorus and the TP maximum was a function of inflow concentration.

Summary of internal phosphorus loading in lakes

- Seasonal pulses in bioavailable phosphorus to lake primary producers may come from either internal or external sources.
- The supply of phosphorus from internal loading can be particularly important during summer when initial stores of phosphate in the water column may be depleted.
- Seasonal pulses in internal phosphorus loading are affected by variations in temperature and redox potential, while pH, the availability of labile organic phosphorus for mineralisation, rates of biotic uptake and water-column nitrate concentration are also important.
- In shallow lakes, temporal variation in the availability of sediment phosphorus to surface waters depends on wind mixing, flushing rate and sediment disturbance, including benthivorous fish activity.
- In deeper lakes, sediment phosphorus may only be available at spring and autumn overturn or during periods of mixing. The extent of availability during the summer months will be governed by water stability, which is temperature and wind dependent, and mixing during periods of high wind speed and/or rainfall.
- Owing to the frequent effect of wind, few Irish lakes stratify for prolonged periods.

4.3 Lake Primary Producers and Lake Phosphorus Concentrations

The seasonal pattern of phytoplankton biomass in temperate lakes is primarily dictated by light availability, with the highest rates occurring in the spring and summer. The seasonal development of phytoplankton in some waterbodies follows a bimodal pattern that includes a spring phytoplankton maximum, a clear-water phase and a second peak in mid to late summer (Sommer *et al*., 1986; Talling, 1993). Zooplankton grazing may be important for these seasonal patterns (Andersen, 1997). In many other lakes, however, nutrient enrichment may reduce or eliminate the biomass minimum in early summer, giving a unimodal pattern (Talling, 1993). The initial biomass peak in a bimodal pattern is related to light and nutrient availability in the spring (Gaedke *et al*., 1998; Lathrop *et al*., 1999). In deep lakes, the beginning of the spring bloom may also be dependent on water column stability and the subsequent decrease in the mixing depth of the surface waters. Substantial spring increases in phytoplankton in Lake Constance were found to occur only when the mixing depth for algal cells was less than 20 m (Gaedke *et al*., 1998).

The early summer minimum in chlorophyll *a* observed in many lakes (Talling, 1993; Lathrop *et al*., 1999) can result from zooplankton grazing pressure, mixing or nutrient availability. Lathrop *et al*. (1999) investigated the factors influencing early summer water clarity in Lake Mendota in Wisconsin (USA). They found that Secchi depths at this time were inversely related to the April phosphorus concentration and positively related to midsummer *Daphnia* biomass and lake stability. However, the seasonal dynamics of the biomass of grazers themselves are a function of temperature and the availability of edible algae (George *et al*., 1990; Straile and Geller, 1998). Algal development in mid to late summer may be limited by the availability of nutrients from internal cycling (Lean *et al*., 1983; Caraco *et al*., 1992; Brooks and Edington, 1993).

Seasonal patterns of inorganic nutrients in the water column reflect seasonality in both the supply of nutrients to the lake and in biological uptake. Although algae have a relatively high requirement for nitrogen, this is generally met in most lakes. In contrast, their relatively low phosphorus requirement may deplete the epilimnion of phosphorus in spring and summer (Lean *et al.*, 1983; Barbosa, 1989; Bailey-Watts, 1990; Nedoma *et al*., 1993). The classic model of Vollenweider (Vollenweider, 1968; OECD, 1982) related maximum chlorophyll concentrations to the inflowing phosphorus load. However, several criticisms have been made of the model (reviewed by Reynolds and Davies, 2001). The model ignores both the biomass of submergent and emergent macrophytes, the limitation of biomass by other nutrients or by light, and the fact that increased biomass may support an increase in higher trophic groups. This increase may in turn lead to a reduction in algal production through increased grazing pressure. In addition, the tendency for a correlation between TP and chlorophyll breaks down above *c.* 100 µg P l^{-1} (Prairie *et al.*, 1989).

Following Vollenweider (OECD, 1982), and based on the equation derived by Foy *et al*. (1992) for lakes in Northern Ireland, Tunney *et al*. (1998) estimated that, for Irish lakes with a residence time of 6 months in an area with annual rainfall of 1000 mm, eutrophic conditions would be likely when catchment phosphorus losses exceeded 0.34 kg P ha^{-1} $year^{-1}$. Where residence time was 1 year, the comparable catchment export rate would be 0.41 kg P ha^{-1} $year^{-1}$. However, generalisations such as those made by Prairie *et al*. (1989) and Tunney *et al*. (1998) are unlikely to apply to all lakes with any degree of confidence. In addition, boundaries of 'good' (oligotrophic) or 'poor' (eutrophic) need careful definition. Salmonid fish may be sensitive to even mild nutrient enrichment (Champ, 1998). In such catchments, even lower estimates for acceptable thresholds of phosphorus exports may be required, and they need further study and validation.

Positive feedback between internal loading and primary production may also play a role in the seasonal release of phosphorus from the sediments. The sedimentation of algal cells contributes to the sediment phosphorus pool (Boström *et al*., 1988), while the pH may rise during periods of intense primary production. This increase in pH may either lead to higher release rates of sorbed sediment phosphorus (Istvanovics, 1988) or to the precipitation of phosphate in the presence of excess calcite (Hartley *et al.*, 1997). The increase in algal biomass in the summer months may result in an increase in the TP concentration in lakes (Kelly and Smith, 1996; Gibson *et al.*, 2001). Other sediment–water linkages related to zooplankton community structure may also be important (Andersen, 1997). In particular, large-bodied zooplankton can extend the open-water circulation of phosphorus.

Although water column concentrations of inorganic phosphorus may be low during summer, phytoplankton production often persists. During this period, nutrient deficiency may occur (Nedoma *et al*., 1993), but internal cycling and inputs from atmospheric particulates may resupply the phosphorus requirements of primary producers (Caraco *et al*., 1992; Brooks and Edington, 1993). Luxury uptake and storage of nutrients may also contribute to algal phosphorus demands when water column concentrations are low (Sommer, 1991; Istvanovics *et al*., 1994), while motile forms of phytoplankton may access phosphorus supplies in the hypolimnion (James *et al*., 1992). In deep clear-water lakes, algae may settle at the boundary of the nutrient-poor epilimnion and the nutrient-rich hypolimnion, allowing access to nutrients by phytoplankton (Irvine *et al*., 2000). In many lakes, the equilibrium between the phosphate concentration in the water column and the particulate-bound phosphate may ensure that the concentration of phosphate in the water column remains relatively constant during peak phytoplankton production (Brooks and Edington, 1993; Correll, 1997).

Lake colour can affect the response of primary producers to phosphorus inputs (Jones, 1990). In coloured lakes, high TP concentrations are often recorded with low chlorophyll concentrations. Many Irish lakes have brown waters, generally from the input of humic material from peatland catchments (Jewson and Taylor, 1978). Such lakes often have higher phosphorus concentrations than clear lakes, but phytoplankton production may be below that predicted by the Vollenweider relationship (Jones, 1990).

Caraco *et al.* (1992) applied the concept of ‘new’ and ‘recycled’ primary production, first suggested by Dugdale and Goering (1967) for oceanic nitrogen dynamics, to the small oligotrophic Mirror Lake (New Hampshire, USA). New primary production was defined as that supported by nutrients from outside the system, while recycled primary production was supported by nutrients from within the system. The application of this concept radically altered the view of phosphorus dynamics of the lake. New production, occurring during midsummer, was 35% of total primary production. This occurred despite low stream phosphorus inputs during this period, and implied that important phosphorus sources were not being measured. Atmospheric particulates and benthic recycled nutrients were suggested to account for some of this deficit.

The effect of pulses of nutrients, from both internal and external sources, on primary production in lakes are governed by, *inter alia*, the timing of the pulse, the composition of the phosphorus load, the concentration of dissolved inorganic phosphorus in the water column, the retention time of the lake and overwinter limitations on algal growth. Pulses of nutrients in late autumn and early winter may have little effect in lakes with short retention times. The particulate component of these pulses may contribute to the sediment phosphorus pool. Phosphate sorbed to the particulate load is unlikely to be released to the surface waters before sedimentation, as the dissolved inorganic phosphorus concentration of the water column will be relatively high. In lakes with a longer retention time, the dissolved phosphorus load over the winter period can contribute to phosphorus requirements the following spring.

In all lakes, the pulses of nutrients in spring and summer (the time of greatest phosphorus depletion) will have an immediate impact (Wildung *et al.*, 1974; Stronge *et al.*, 1998; Irvine *et al.*, 2001). Using time series analysis, Stronge *et al.* (1998) found that the extent of the spring algal bloom in Lough Neagh (Northern Ireland) was highly dependent on the SRP inputs to the lake in April–June, despite the relatively long retention time in the lake (1.3 years). Spring chlorophyll concentrations were also negatively correlated with the concentration of PP in the previous summer. Pulses of available phosphorus entering lakes during periods of phosphorus limitation should have immediate impacts on algal production. Irvine *et al.* (2001) reported an increase in chlorophyll *a* in a number of Irish lakes following a pulse in external loading in August.

Summary on lake primary producers and lake phosphorus concentrations

- Seasonal pulses in bioavailable phosphorus to lake primary producers may come from either internal or external sources.

- The rate of phosphorus uptake is related to seasonal variation in temperature, initial nutrient availability and irradiance.

- Water column pH can vary seasonally with phytoplankton respiration, while the concentration of nitrate in the water column will be a function of uptake, catchment characteristics and the rainfall regime.

- Phosphorus cycles in open water can be mediated by zooplankton and fish feeding. Large-bodied zooplankton can extend periods of phosphorus recycling in open waters.

5 Water Quality Models

5.1 Review of Water Quality Models

Modelling catchment processes for the estimation of nutrient transport is a relatively new activity, having developed within the last 30 years. Much of the impetus for this development has arisen from an increasing demand for water quality as an important societal goal and the need for scientific support and validation of water and catchment management. Modelling has an enormous potential to contribute to this need, but is still very much in a development stage. This pubescence is indicated by a series of factors, including (1) the often low level of application of models in practical water quality management projects, (2) the difficulty in choosing the 'most appropriate' model, and (3) the uncertainty as to whether models can be used in a quantitative and predictive manner, or whether they are tools used only to provide comparative analyses. Many workers remain cautious about the application of models: e.g. Sharpley *et al*. (1995) state "A major limitation to model use is often the lack of detailed parameterisation data on soil physical, chemical and biological properties as well as climate, crop and tillage information. Consequently, use of many models to provide quantitative estimates of phosphorus loss … is limited. The use of many models is recommended only for comparison of relative effects of management strategies on phosphorus transfer." The aim of this section is to provide an overview of water quality models that focus on, or include, the transport of phosphorus within catchments. The first section provides a review of general issues concerning water quality modelling. In the second section, the main characteristics of a series of relevant models are given.

5.1.1 Components of water quality models

Modelling involves not just observation, description and explanation but also prediction. From the envisaged operation of a process, we should be able to predict future patterns (Ball and Trudgill, 1995). This type of description of modelling is often used to encapsulate two commonly held perspectives: that models can be used to better understand observed patterns, and that they can be deployed to provide estimates of likely outcomes, i.e. to provide a predictive capacity. The attainment of this goal is, however, not always possible, often owing to valid reasons, some of which are outlined below. A less ambitious definition is "a model is a system that reproduces important features of another system, ….is a source of data, and...involves the process of organising knowledge about a given system (where a system comprises a number of components connected to a whole)" (Warfinge, 1995).

Thus, irrespective of the expected outcomes or utility, modelling is often concerned with methods of organising knowledge about a given system, ideally carried out in an explicit manner and usually employing mathematics to quantify elements and reduce field data in a defined manner. Caveats that a model is not identical to 'reality' are normally provided, although adherents of different schools of modelling are prone to argue the pros and cons of 'abstract' compared with 'realistic' representation. Yet if a model does not mimic reality then terms such as 'too simplistic' can only be applied on account of specific characteristics or objectives. A fair evaluation of a model could be whether or not it attains its original objectives, which are often set as management goals, and may expressly include elements of simplicity or low cost of development.

The early impetus of model development for catchment processes focussed on rainfall–runoff relationships and physical aspects of water resources, including flooding. While these activities may not have considered the transfer of nutrients, they nevertheless provided insight into hydrological processes, and hence movement of solutes. The early recognition of solute–discharge relationships was in the context of overall catchment geochemical processes and the relationship between dominant bedrock composition and solute concentrations, parameterised as total dissolved solids or total conductivity.

The emphasis on the solute component of waters probably came about in response to the recognition of the environmental impact of solute transfer. The need to mitigate that impact has provided much of the impetus and funding to develop solute modelling. The first such process to gain prominence was the increased acidification in rivers and lakes linked to atmospheric pollution from industrial processes. These effects were particularly apparent in poorly buffered catchments in parts of Northern Europe and North America. In response a series of models, including BIRKENES (Lundquist, 1976, 1977) and ILWAS (Chen *et al*., 1982), was developed concerned with both episodic event modelling and the effects of long-term acidification. Importantly, these models included predictive components and attempted to simulate solute behaviour from input–output relationships within certain scenarios. They could thus assess the sensitivity of output to changes of atmospheric and catchment inputs. This was in contrast to the earlier modelling attempts which sought to describe existing hydrochemical behaviour and produce a ‘model’ that was not much more than a set of retrospective generalisations (albeit quantitative) about hydrochemical behaviour (Ball and Trudgill, 1995).

The later emergence of modelling transport of nutrients, pesticides and organic material to receiving waters, from mainly agricultural processes, was again related to a recognition of problematic driving forces within catchments. Over the last 30 years, a large number of models have addressed transport and the fate of key solutes, primarily nutrients and pesticides. A review of the literature suggests that a greater emphasis has been on modelling the fate of nitrogen than of phosphorus; the dominance of the issue of phosphorus in Ireland may be considered an exception. In the early period, the models often focussed on specific processes, which could often be distinguished by the scale at which they predominated – soil profile, field plot, hill slope and channel routing. More recently, models are increasingly combined within an integrated system, often based on GIS, to realise a more complete catchment management system, e.g. BASINS (USEPA, 1998).

It is common to distinguish water quality models on the basis of (a) spatial (units lumped or distributed) and (b) temporal (single or continuous events) precision (Maidment, 1993). However, other important criteria include the methods employed to define the magnitude of and relationships between elements in the system, in particular whether this is achieved through the implementation of the fundamentals of physics and chemistry (so-called process models) or is based on the statistical treatment of observational data (so-called empirical models) (Ball and Trudgill, 1995).

Many models can be categorised by either or both of the discrete schemes described by Maidment (1993) or Ball and Trudgill (1995). However, in other models the situation can be more complex, e.g. certain constituents are represented by detailed process mechanisms and others by data analysis. Thus, different theory and mechanisms can be applied to the hydrological, chemical and biological components of a model.

5.1.2 Resolution of model components

There is a striking range of spatial and temporal resolutions employed in water quality models, often encompassing many orders of magnitude of the measurement unit, e.g. from the soil profile to the catchment in spatial terms or from hours to years in temporal terms.

Lumped models use spatially averaged parameters and perform computations over the whole catchment or spatial unit of interest. As the within variation for the catchment increases, the model predictions may become more accurate (Pullar and Springer, 2000). However, proponents of lumped modelling approaches may hold that such an approach is meaningful in that the system of interest (catchment or other) works as a unit with collective properties that are hard to break down into smaller units, both conceptually and in the acquisition of representative data.

Distributed models are based on the discrete characterisation of model domain, frequently a catchment, into a series of smaller units. Given the prevalence of using computers in such systems, a uniform grid is normally used for computational convenience. Normally the spatial elements are modelled in two dimensions only, whether vertically to represent the soil profile or in planimetric form to represent movement and transfer towards the outlet or receiving water. Some models, particularly modern systems including SHETRAN (Abbott *et al.*, 1986), can deploy a three-dimensional representation of space, and hence high structural complexity, within the model domain. However, a conceptual gap can remain for the 'ecosystem' relevance of the selected units to represent the spatial domain in distributed models, albeit that the spatial units or cells can be small and thus allow, in theory, for the description of the modelled processes in great detail.

Leon *et al.* (2001) describe the development of a distributed water quality model that uses a 'distributed group response unit' approach, based on land cover classes for water quantity and quality modelling. This allows for fewer and larger model units than may be possible with the standard distributed model approach, where the need for in-cell homogeneity can predetermine a small cell size. This approach, they argue, has a stronger conceptual basis and is more easily transferred to remote areas, where general data availability may be poor but land cover data are available to define the response units.

Models are often categorised by whether they represent 'single events' or 'continuous time steps' (e.g. Pullar and Springer, 2000). This is taken to mean whether they are run over a comparatively short period and assess, for example, a single rainfall event (rainfall duration and drainage of rainfall from catchment), or attempt to model over a longer time period, such as a year or a seasonal crop rotation.

In a different regard, models can be classified by whether they aim to predict the change in a state variable as a function of time (dynamic) or aim to predict steady-state conditions for a given set of boundary conditions (static) (Warfinge, 1995). While dynamic models may be currently receiving most attention, static models have an established role in water quality management, e.g. in the setting of input limits to achieve the desired output conditions in critical loads and acidification studies.

Certain factors should be considered with regard to the temporal aspects of water quality models. The time step, i.e. temporal subdivisions used to solve underlying equations, should be less than the temporal resolution of the process under evaluation. Furthermore, important forcing functions, e.g. hydrologic events or seasonal uptake of nutrients, need to take account of natural variation. This may be compromised, for example, where parameters are based on annual means.

In addition to spatial and temporal resolution, the degree of model detail whereby the processes controlling the transport and fate of the constituents of interest are represented, e.g. phosphorus or nitrogen, varies greatly.

5.1.3 Models based on data analysis

Where specific processes are not explicitly evaluated, models are often based on the analysis of data considered to represent a conceptual process. It can be comparatively easy to set up and collect data for such a 'bottom–down' approach. Typically, a dependent variable, e.g. waterbody solute load or concentration, is related to driving force variables by statistical techniques.

End-member mixing analysis (EMMA) emerged from the increasing availability of soil water chemistry data from catchment studies. EMMA was proposed by Neal and Christophersen (1989) and further developed at sites in Norway, Wales and the USA. EMMA is based on the concept that stream water is a mixture of different soil water classes or end members. An end member may be identified from any area within the catchment that has been identified as contributing to stream chemistry. Different end members are considered to exhibit distinctive chemical profiles and the system is based on two assumptions. Firstly, chemical species involved are governed by fast reactions within the soil, which easily achieve equilibrium and therefore represent a constant end member for the horizon. Secondly, the end members behave conservatively, i.e. no further chemical reactions take place on the way to the stream or in the stream. The system is dynamic with regard to hydrology, and is more static with regard to chemistry, whereby the dynamics of hydrology can be determined as the relative contributions of different hydrological pathways, as identified by the end-member chemical signatures.

Export coefficient models, developed by Vollenweider (1968, 1975, 1986) and applied by, *inter alia*, Johnes and O'Sullivan (1989) and Johnes *et al.* (1996), estimate nutrient losses from catchments using simple algebraic techniques (see Section 2.4). Export coefficients are applied to information on land use, and associated stocking and fertiliser rates, to give an areal weighted estimate of catchment nutrient loss. No hydrological or chemical processes are included: the model output is simply the sum of the relative contributions from the different sources. An export coefficient approach is also employed in the AGNPS model (Young *et al.*, 1989) where N leaching rates are calculated from land-use data. Export coefficient models usually provide annual estimates of nutrient transfer. May *et al.* (2001), however, describe the development of a seasonal (monthly) estimate of phosphorus loss based on annual export coefficients normalised with respect to the relative hydraulic runoff for a particular month. This method was supported by the availability of river discharge and TP concentration data at 4-day intervals.

Moore and Philips (1999) describe the development of a Phosphorus Index for pastures based on a statistical treatment of data, where phosphorus concentrations in runoff were related to the soluble phosphorus content of manure, manure application rate, amount of phosphorus in the diet, timing of fertiliser application and soil test phosphorus levels. The potential interest of water quality management in such simple but direct analyses of data using statistical methods can be understood from the Phosphorus Index project, wherein a trend among US state and federal agencies to restrict animal manure and phosphorus fertiliser application on land where the amount of phosphorus in the soil is high was not substantiated by statistical analysis. Rather, the data suggested that other aforementioned variables exerted greater controls on phosphorus runoff than soil phosphorus levels per se. Although this work may be subject to further investigation, it highlights how a relatively simple modelling approach can generate an outcome of direct relevance to water quality management.

Following the work of Vollenweider, the annual mean in-lake concentration of TP has been predicted and/or described by a number of authors using empirical 'steady-state' models (e.g. Foy, 1992) and an estimation of lake mean depth, sedimentation of PP, and lake-flushing rates (e.g. see Section 4.3). These models are based on equilibrium conditions and, hence, are not well suited for estimating the concentrations in lakes with significant internal loading (particularly following reductions in external load). Furthermore, they do not provide any information on the seasonal aspects. Recent work to address these problems has resulted in the development of a model for shallow Danish lakes that are in the recovery phase after a reduction of external phosphorus loads (Søndergaard *et al.*, 1999, 2002). The model has only two state variables: total phosphorus in lake water (P_l) and exchangeable total phosphorus in sediment (P_s). The driving variables in the model are monthly inlet concentration of total phosphorus (P_i), the corresponding monthly water discharge (Q) and the lake water temperature (T). During the course of this review, the model was applied to three Irish lakes (Lough Leane, Lough Derg and Friary Lough) which were considered to have sufficient data for the model's use, although even then it was still necessary to use some of the Danish calculations to make it work. Furthermore, data were available for only 1 year for the Irish lakes, while the Danish model was calibrated on 16 lakes measured over 10 years. Overall, the direct application of the Danish model to the Irish lakes did not provide a reliable prediction of in-lake phosphorus because (1) the use of only 1 year's data for the Irish lakes restricted the predictive value of the model since it was not possible to consider inter-annual variations, (2) the three Irish lakes represented very different lake types and loading histories than the Danish lakes for which the model was developed, (3) the Irish lakes generally showed only minor variations in phosphorus during the season, compared with the Danish lakes for which the model was developed, where a marked and conspicuous seasonal pattern develops in most lakes, with summer total phosphorus concentrations normally exceeding winter levels by a factor of 2–3, (4) the Irish lakes (particularly Lough Leane and Lough Derg) had considerably lower phosphorus concentrations that most of the Danish lakes (yearly mean phosphorus concentration in the 16 Danish lakes ranged from 90 to 850 $\mu g\ P\ l^{-1}$) and, unlike the Danish lakes, TP concentrations were not driven by internal loading, and (5) the Irish lakes were generally much deeper and of larger area than the Danish lakes (in the 16 lakes on which it was tested, the mean depth ranged from 0.9 to 9.9 m and the lake area ranged from 5 to 662 ha). While this exercise in model 'transportation' did not provide useful predictions, it clearly demonstrated the difficulty in the application of an 'off-the-shelf' model to Irish environmental conditions. It will, therefore, be of the utmost importance that models used in Irish catchments are either developed, or validated, to account for local conditions. These, of course, may vary among catchment and waterbody typologies even in a single ecoregion.

5.1.4 Physically based process-oriented models

Physically based models attempt to quantify key processes occurring within defined spatial units. The spatial unit can be a lumped entity (e.g. a hill slope or catchment) but is more frequently dispersed (i.e. grid cell based models). Conceptually, a physically based model presupposes that conditions within the spatial unit are sufficiently well understood to allow the application of fundamental laws of science (principally from physics and chemistry) to describe the processes operating.

The basic assumption of process-oriented models is 'the law of continuity', whereby entities in each elemental volume of the model domain must either leave the volume or be retained, i.e. either diverge or accumulate (Warfinge, 1995). This is the basic principle of 'mass balance', commonly used in so-called biogeochemical models (Jorgensen, 1992). Within catchments, the physical processes that control the flux into and out of the 'elemental' volume are advection and hydrodynamic dispersion. Advection is the component of solute transport attributed to the bulk movement of the fluid. Dispersion is a mixing process, occurring as a result of mechanical mixing and molecular dispersion arising from the thermal–kinetic energy of solute particles. The principal differential equation that describes the transport of dissolved reactive constituents in saturated media is known as the advection–dispersion equation (Freeze and Cherry, 1979). In principle, the concentration and fluxes of any solute can be accounted for by the law of continuity and the advection–dispersion equation, although in practice the inclusion of even simple chemistry can lead to mathematical and programming complexities.

In distributed parameter models, the law of continuity must be made discrete, whereby the catchment is divided into a series of separate compartments and the time span of the simulation is divided into an 'appropriate' number of time steps. At a minimum, the number of equations required in a process-oriented model equals the number of components, but this applies only to systems where no chemical reactions take place. Structurally more complex models include equations to account for chemical reactions that transform one component to another; they will comprise a set of differential and algebraic equations, and the total number of equations will increase to equal the number of components plus the number of independent chemical reactions.

An attraction of process-oriented methods operating in distributed model domains is that they employ scientifically testable laws and aim to differentiate between the types and rates of processes operating at different locations. This implies a good understanding of the processes being modelled. Such models are complex but probably incorporate the greatest degree of realism and, although requiring extensive parameterisation, should require little calibration (Ball and Trudgill, 1995). It can be argued that process-oriented models can be applied with greater confidence than data analysis type models to new situations, where specific processes are not considered and the model is predicated largely on statistical relationships between data sets observed in the original catchment.

Certain issues need to be considered in the application of detailed process-oriented models. The development of an adequate body of parameter values can be complex, time consuming and expensive. Conceptually, certain issues relate to the appropriate application of, albeit scientifically sound, equations in a step-wise or deterministic sequence to estimate outcomes from the initial or allocated boundary conditions. It can be queried whether natural systems can be divided into discrete subunits in which specific processes can be quantified and, indeed, whether model subunits (usually regular grid cells) can reliably represent natural processes. How does the catchment integrate the physics and chemistry of its subsystems? Are the component processes constant within the time and space intervals chosen (within unit homogeneity)? Are all the key processes which can affect outcomes represented properly within the model? Are complex interactions, including feedback mechanisms, affected by biotic activity sufficiently determined? While natural systems often appear to have discrete subsystems, e.g. distinct soil horizons, some important phenomena such as macropore flow systems in soils or zones generating overland flow are ephemeral and may be difficult to represent within the model structure. Is there adequate theory to handle such temporal and spatial scaling issues in the structural composition of the models? These issues are recognised in the modelling community, and the testing and refinement of the components of process-oriented models are often applied to provide statistical confidence in a model. In particular, the inclusion of a stochastic element, e.g. Monte Carlo simulation, can be used to determine a range of outcomes under different conditions selected 'randomly', and to test the sensitivity of the model to changes in particular parameters.

5.2 Review of Selected Models

There is no universal commitment in practical catchment management to the use of water quality models and related techniques. The level of application varies considerably among countries and appears to be best developed in the USA. Many models have been developed over the last 30 years, often with overlapping capabilities, and not infrequently by divisions of the same organisations. There is now a general need, in the USA and elsewhere, to evaluate what has already been produced rather than, or at least in advance of, funding the development of further models. Reviews of modelling systems have been prepared by, amongst others, the Natural Resources Conservation Service of the US Department of Agriculture (NRCS, 2000) and the Water Environment Research Foundation (2000), which serves the water industry in the USA. Reviews of models are also found in textbook form, e.g. "Solute Modelling in Catchment Systems" (Trudgill, 1995). In Europe there is an increasing interest in water quality modelling, particularly arising from the quantification of catchment management required by EU Directive 2000/60/EC "Establishing A Framework For Community Action In The Field Of Water Policy" (CEC, 2000), and associated research funded under the Framework Programmes. It is apparent that a 'road map' is required to guide water quality management in the selection of appropriate modelling tools for particular studies and to prioritise further development. An interactive tool to aid model selection through a Graphical User Interface is under development by the Water Environment Research Foundation (WERF) but will only be available to subscribing members.

A list of commonly referenced models, which incorporate nutrient fate and transport elements, is given in Table 5.1 (from WERF, 2000). Table 5.2 is a summary of model descriptors, relevant to phosphorus and developed or sponsored by the USDA (NRCS, 2000). Two important models, SHE (Système Hydrologique Européen) (Abbott *et al.*, 1986) and HSPF (Hydrological Simulation Program - Fortran) (Bicknell *et al.*, 1996) are not described in Table 5.2 but should also be considered. The SHE hydrological model has been the focus of

Table 5.1. Models incorporating nutrient fate and transport elements (adapted from WERF, 2000).

Model acronym	Model name	Sponsor/developer
AGNPS-98	Agricultural Non-Point Source Pollution Modeling System – continuous version	USDA ARS
ANSWERS	Areal Non-Point Source Watershed Environmental Response Simulation	North Carolina State University
CREAMS	Chemicals, Runoff and Erosion from Agricultural Management Systems	USDA ARS
GLEAMS	Groundwater Loading Effects of Agricultural Management Systems	USDA ARS
HSPF	Hydrological Simulation Program – Fortran	USEPA; USDA
MIKE SHE	Distributed and Physically Based Modelling System for Flow, Water Quality and Sediment	UK Institute of Hydrology and Danish Hydraulic Institute
SHE/SHESED	Basin Scale Water Flow and Sediment	University of Newcastle, UK
SWAT	Soil and Water Assessment Tool	Texas A&M, USDA ARS
SWRRBWQ	Simulator for Water Resources in Rural Basins	USDA ARS

Table 5.2. Details of models sponsored by USDA which consider phosphorus (selected information extracted from NRCS (2000)).

Model attributes	AGNPS98	SWAT	APEX	EPIC	GLEAMS	REMM	SRFR	WEND
Hydrology								
Integrated climate generation	M	M	M	M		Y		
Surface water								
Overland flow	M	L	M	L	M	Y		
Channel flow	L	L	M	L	M			
Lakes	L	L	M					
Wetlands	L		M					
Estuaries			M					
Subsurface flow								
Soil moisture	M	L	M	M	M	Y		Y
Groundwater storage (aquifer)		L	M		L	Y		
Artificial drainage		L	M	L				
Lateral flow		L	M	L		Y		
Sediment								
Erosion								
Sheet and rill	M	M	M	M	M	M		
Stream bed and bank	M		M		L			
Transport								
Suspended	M	M	M		M		H	
Bed load	M		M			H	H	
Deposition	M	M	M		M		H	
Characteristics								
Particle size distribution	M	M	M		M	Y	H	
Organic/inorganic	M		M		M	M		
Yield	M	M			M	Y		
Nutrients								
Phosphorus–surface water								
Fertiliser (inorganic)	M	M	M	M	H	Y	H	L
Manure (organic)	M	M	M	M	M	Y	H	L
Dissolved/particulate	M	M	M	M	M	Y	H	L
Total P	M	M	M	M	M		H	L
Phosphorus–groundwater								
Fertiliser (inorganic)	?	?	M	M	M	Y	H	L
Manure (organic)	?	?	M	M	M	Y		L
Dissolved/particulate	?	?	M	M	M	Y	H	N
Total P	?	?	M	M	M	N	H	N
Data Requirements								
Climate								
Precipitation	Y	Y	Y	Y	Y	N	Y	Y
Temperature	Y	Y	Y	Y	Y	Y		N
Wind speed	Y		Y	Y	Y	Y		N
Humidity/dew pt/wet bulb temp	Y		Y	Y	N	Y		N
Solar radiation/sky cover/% cloud	Y		Y	Y	Y			N
Spatially distributed ?	Y	Y		N	N			N

Table 5.2 ***contd.***

Model attributes	**AGNPS98**	**SWAT**	**APEX**	**EPIC**	**GLEAMS**	**REMM**	**SRFR**	**WEND**
Landscape characteristics								
Topography	Y	Y	Y	N	Y	Y	H	N
Soils	Y	Y	Y	Y	Y	N	H	Y
Land use/landcover	Y	Y	Y	Y	Y		H	Y
Spatially distributed?	Y	Y	Y			N	M	N
Management activities								
Tillage	Y	Y	Y	Y	Y	N	L	Y
Crop rotation	Y	Y	Y	Y	Y	N		Y
Nutrient management	Y	Y	Y	Y	Y	N		Y
Conservation practices	Y	Y	Y	Y	Y	N		Y
Model Output								
Watershed mass balance								
Phosphorus		Y	Y			Y		Y
Nitrogen		Y	Y			Y		N
Lumped								
Time	Y	Y	Y	Y	Y	Y		Y
Spatial	Y	Y	Y	Y	Y	Y		Y
Distributed								
Time	Y	Y	Y	Y	Y	N		N
Spatial	Y	Y	Y		Y			N
Source tracking	Y				Y	N		N
Format								
Statistical		Y	Y	Y		Y		N
Graphical		Y				Y	Y	Y
Tabular	Y	Y	Y	Y	Y		Y	Y
GIS	Y	Y						N
Time step								
Subdaily			Y			Y	Y	N
Daily	Y	Y	Y	Y	Y	Y		N
Monthly			Y		Y	N		N
Average annual			Y		Y	N	Y	Y
Application Spatial Scale								
Point				Y	Y	N	Y	Y
Field	Y		Y	Y			Y	Y
Small watershed (<10 sq miles)	Y		Y					Y
Large watershed (10–400 sq miles)	Y	Y	Y			N		Y
River basin (>400 sq miles)		Y				Y		Y
Application Time Scale								
Continuous	Y	Y	Y	Y	Y			Y
Event	Y				Y	N	Y	N
Accumulative events	Y					Y		

L = Model element present, with a simplistic, empirical representation. M = Model element present, with a conceptual or moderately complex representation. H = Model element present, with a very detailed, sophisticated, physically based representation. ? = Model element present, complexity level unknown; Y = Yes; N = No; blank = No; - where applied.

considerable development, primarily in Europe, for many years. This includes SHETRAN (Bathurst and Purnama, 1991) and others. The SHE and derived systems comprise a structurally complex, fully distributed, physically based system in which the planimetric grid domain is divided vertically to represent surface and subsurface processes. In addition to hydrological processes, the system provides a detailed treatment of the sediment and contaminant components using the convection–dispersion equation in channel and overland flow, adsorbtion of contaminants onto sediment and soil and into immobile phases, plant uptake and recycling. The system requires extensive parameterisation but can be considered an advanced system that is receiving considerable attention. A specific phosphorus module is currently under development (M. Bruen, UCD, personal communication). The HSPF system is a comprehensive system for the simulation of watershed and water quality for both conventional and toxic organic pollutants. It is actively supported by the US EPA and is incorporated within their integrated, GIS-based, water quality management system BASINS (Better Assessment Science Integrating Point and Non-Point Sources). It has been stated that HSPF is "the only comprehensive model of watershed and water quality that allows the integrated simulation of land and soil contaminant runoff processes with in-stream hydraulic and sediment–chemical interactions" (USEPA, 2001), although it is not clear how far this has included comparison with the SHE system.

6 Conclusions

6.1 High Risk Conditions for Phosphorus Export from Grasslands

In Ireland, grasslands constitute over 90% of agricultural land. The review of the literature relating to temporal variability in phosphorus export, and the main geomorphological and management factors that influence that export, identified high risk conditions for phosphorus export from grasslands. These conditions relate to both sources and transport of phosphorus (Fig. 6.1). This review has not enabled a detailed analysis of risk, for which further research efforts are required. The assessment of risk is being addressed in projects under Group 2.2 'Models and Risk Assessment Schemes for Predicting Phosphorus Loss to Water'.

6.1.1 Phosphorus source

- **Soil:** Many agricultural soils in developed countries, including Ireland, are phosphorus saturated and require little or no further fertilisation. In Ireland, grassland soils have been found to be up to 79% saturated with phosphorus. In soils with a low phosphorus sorbtion capacity or those that are phosphorus saturated, the capacity to hold phosphorus within the soil matrix is diminished. These soils are particularly susceptible to phosphorus losses. The identification of areas within the catchment with a low capacity to hold phosphorus would aid in the control of phosphorus export.

- **Land management**: Before phosphorus can be exported from the catchment, it must be present in a mobile form. Seasonal aspects of grassland management that increase the availability of mobile phosphorus in the soil include the presence of livestock, fertiliser use, slurry spreading and farmyard discharges including silage and slurry leakage. The increases in Ireland in both winter housing of cattle and intensive rearing of pigs and poultry have dramatically increased the possibility of phosphorus build-up in soils from this source. This area has the greatest potential for control of phosphorus losses through changes in management practices.

- **Climate:** High phosphorus export rates have been reported in many studies after a prolonged dry period. This increase in losses arises from both a build-up of mobile phosphorus and the possible effects of a soil moisture deficit on mineralisation processes in the soil. Climatic factors are variable in nature and unpredictable. However, dry periods are more likely to occur in Ireland between February and June. Further research is required to qualify and predict the accumulation of phosphorus in different soil types, and the relationship with climate conditions.

6.1.2 Phosphorus transport

- **Climate:** High intensity rainfall has frequently been found to be the most important driving variable in phosphorus transport at both field and catchment scale. In Ireland, high intensity rainfall can occur in any season.

- **Link to drainage network**: The highest risk of phosphorus export may be from the critical source areas in the catchment. These include areas close to the drainage network and those linked by artificial drainage systems and preferential flow pathways, such as macropores and worm burrows. Artificial drainage systems, preferential flow pathways and karstic geology allow the rapid channelling of water to rivers and streams. The extent of the source area is variable depending on soil and geographic typology and recent rainfall. Identification of these areas could aid the control of phosphorus export.

- **River/stream**: Particulate phosphorus may be retained within the river and stream channels, particularly during dry periods. In addition, dissolved phosphorus may be retained by sediments and biota, particularly in spring and summer. The retention of phosphorus within a section of channel at these times decreases the downstream availability to primary producers. The identification of those areas of river and stream channel in which retention processes are low may be of use in the control of downstream pollution.

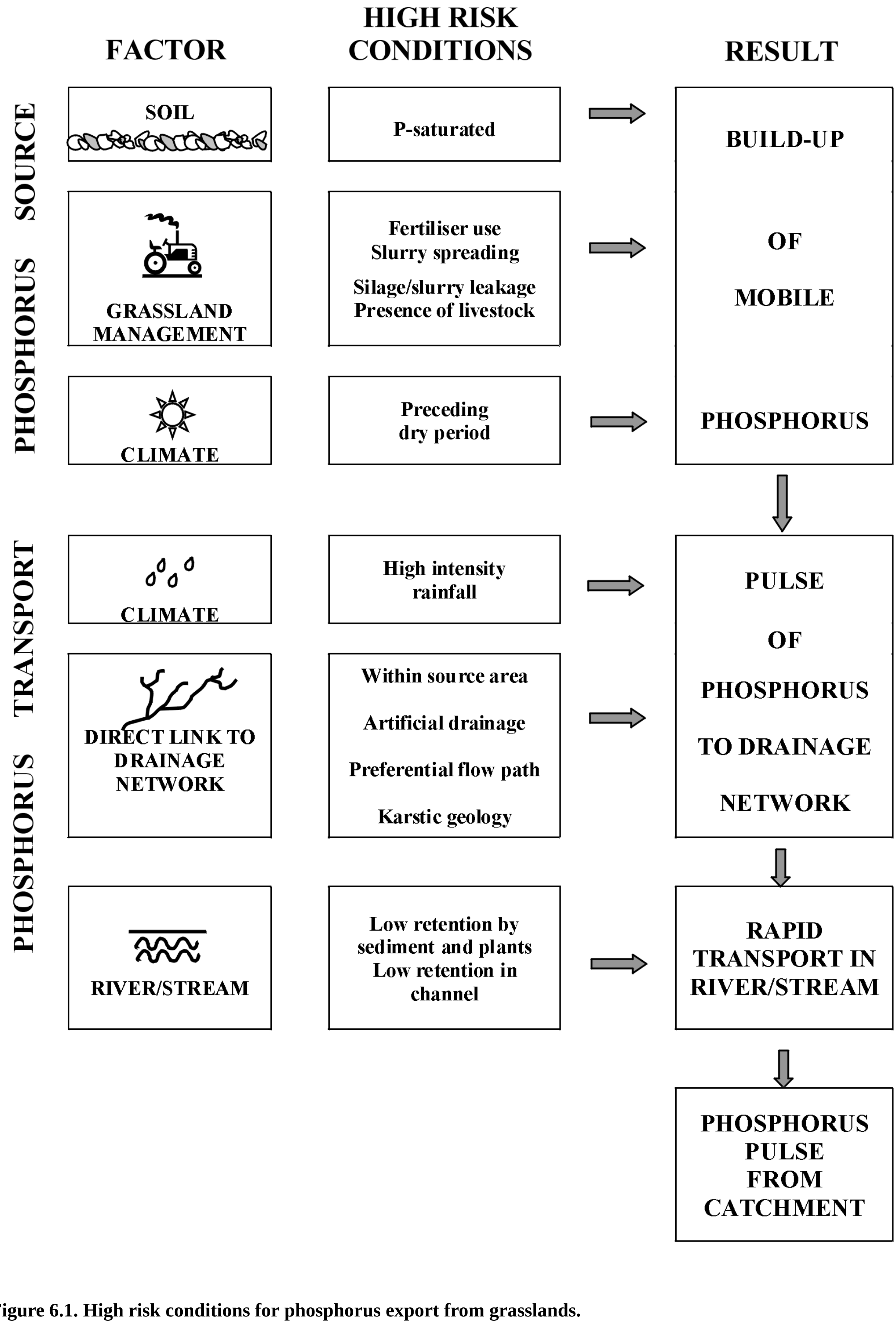

Figure 6.1. High risk conditions for phosphorus export from grasslands.

- **Lakes:** Phosphorus availability for biotic uptake in lakes varies with nutrient load, lake morphology, residence time, colour, in-lake biotic processes, sediment physico–chemistry and ambient wind conditions. All of these vary seasonally. In-lake processes have not been studied extensively across the range of Irish lake typologies, and so the application of general models linking nutrient loads and phosphorus concentrations may be frequently inappropriate. Internal cycling may play an important role in supplying the phosphorus needs of lake primary producers. While internal loads may be highest in shallow lakes, the importance of anoxic sediment phosphorus release in many Irish lakes merits further attention. Anoxia-driven internal phosphorus loading could be a future phase in the eutrophication process in Ireland as sediments continue to be loaded with externally derived phosphorus.

6.2 Gaps in the Current Knowledge and Recommendations for Further Research

This review of the literature on temporal variability in phosphorus export and the effect of seasonal factors on external and internal phosphorus loads and the utilisation of phosphorus in surface waters has identified the following areas which merit further research:

1. The continued use of measurements of MRP on unfiltered samples to describe phosphorus availability in Irish waters is open to criticism. In addition, the comparison of data from various monitoring and research studies requires a consistency in methodology. The use of measurements of MRP on unfiltered samples merits further consideration, research and debate.

2. The establishment of baseline conditions of phosphorus loss from catchments is difficult as many surface and groundwaters have undergone some eutrophication. Most relatively pristine catchments occur in the west of the country on peat soils. Whereas the measurement of phosphorus export in these catchments provides a valuable benchmark for certain catchment and water typologies, there is also a need to estimate baseline conditions in siliceous and limestone catchments. Suitable examples do exist and there is an urgent need to research these. This is, moreover, a requirement for implementation of the Water Framework Directive.

3. Little information exists on the input of phosphorus to catchments via atmospheric deposition in Ireland or on the bioavailability of atmospheric phosphorus. As this source of phosphorus can be affected by fertiliser use and has been found to be important in oligotrophic catchments, quantification of this source is needed.

4. It is likely that forestry will continue to play an important role in the Irish economy. The use of aerial fertilisation in the establishment phase of forests, and the assessment of the downstream short- and long-term effects of the use of these fertilisers requires further research.

5. Little information exists in the literature on the fate of phosphorus in the dung of grazers. As grazers are an important component of the Irish agricultural economy, research on this topic is required. Aspects of this topic are being dealt with under subproject 2000-LS-2.1.2-M2: Project 2.1.2 ‘Grazed pastures’.

6. High phosphorus losses occur when the spreading of organic wastes is followed by high intensity rainfall. However, little information exists on the extent of slurry storage capacity and temporal (and even spatial) patterns of slurry spreading in Ireland. This information is essential if the role of slurry in the eutrophication of Irish waters is to be evaluated.

7. Groundwater has been considered in the past to be less susceptible to pollutants than surface waters. Recent research has shown, however, that groundwater in Ireland can be impacted by local pollution. The downstream effects of groundwater pollution incidents merit further investigation.

8. Recent papers have indicated that artificial drainage systems play a significant role in the rapid channelling of phosphorus from the field to receiving waters. The extent of artificial drainage systems in Ireland and the impact of these systems on phosphorus losses need to be assessed.

9. Although soil moisture deficits are less frequent in Ireland than in other areas of Europe owing to the humid climate, significant soil moisture deficits are regularly recorded in many parts of the country. The effects of a soil moisture deficit on phosphorus availability in Irish soils are poorly understood and require research.

10. Little information exists on the short-term temporal dynamics of phosphorus transport in Irish streams and rivers. In particular, information on phosphorus residence times, partitioning, retention rates and biotic uptake is needed for the understanding of routing of phosphorus through Irish catchments. This is a key area of further research. The detailed temporal analysis of the data that have been collected in previous and future DELG-funded River Basin Projects is a cost-effective means of contributing to this understanding.

11. Not all areas of catchments contribute equally to the total phosphorus load. In addition, the extent of the area that is contributing phosphorus will change over time depending on the recent rainfall regime and local geography. Information on changes in the extent of the critical source area in Irish catchments is required to assess spatial and temporal patterns of phosphorus losses, and to develop tools of risk assessment to Irish fresh water from diffuse nutrient loads. Modelling subprojects in the current large-scale project may aid in this understanding.

12. Internal cycling is important for supplying the phosphorus needs of lake primary producers. In-lake cycling of phosphorus is poorly understood and dependent on a variety of physico–chemical, hydromorphological and biotic processes. The importance of anoxic sediment phosphorus release in Irish lakes merits further attention as anoxia-driven internal phosphorus loading could be a future phase in the eutrophication process as sediments continue to be loaded with externally derived phosphorus. In addition, a greater understanding is needed of the extent of stratification in Irish lakes

13. A review of the literature suggests that there has been less emphasis on the development of models specifically concerned with phosphorus than other nutrients or pollutants such as nitrogen or pesticides. This may reflect a greater concern traditionally with the fate of additives to arable and cropping systems, rather than pasture systems. However, there are several models that describe the loss of phosphorus, generally in both soluble reactive and particulate forms, which have been widely applied. A limitation to model use is often the lack of adequate parameterisation data. This is frequently cited as the main factor that can restrict model usage to the comparison of relative effects, e.g. different management strategies, rather than providing quantitative estimates of phosphorus loss under specific environmental conditions. The development of adaptable databases of, for example, soils and weather data would help to expand the application of models as quantitative assessment tools.

14. While there is clearly a management need to further understand the link between catchments and surface waters for phosphorus dynamics, the recent Water Framework Directive (2000/60/EC) appears to provide a legal requirement to do so. There is a requirement to take into account natural variation for the development of monitoring under the Water Framework Directive. In Irish catchments, this clearly should include the seasonal patterns of phosphorus movement from land to water.

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