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THE IMPACT OF AGRICULTURE ON DISSOLVED NITROGEN AND PHOSPHORUS CYCLING IN TEMPERATE ECOSYSTEMS

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Although most research has focussed on inorganic nutrient forms of nitrate (NO_3^-) and phosphorus (PO_4^{3-}) in runoff and receiving waters, nitrogen loss from agricultural land can also occur in organic and ammonium-nitrogen form; phosphorus losses, although often dominated by particulate transport, may occur in soluble organic and inorganic form. Furthermore, fluxes between different species may take place during transport from the land to the stream and as a result of in-stream, in-river or in-lake transformations. Knowledge of the spatial and temporal variation in all nitrogen species and phosphorus fractions in a drainage basin is therefore essential if the wider environmental significance of elevated nutrient concentrations in natural waters are to be assessed. This paper reviews recent work on N and P losses from agricultural land and presents some results from two intensive agricultural catchments: Slapton, Devon and the river Windrush catchment in the Cotswolds.

KEY WORDS: Particulates, soluble fractions, phosphorus, nitrogen, organics, agriculture.

INTRODUCTION

The increasing intensity with which land is used for crop production, and the extent of land use change in lowland Britain in particular, is reflected in long-term increases in the nutrient concentration of many rivers and lakes (see for example, Casey *et al.*, 1993; Foster *et al.*, 1985; Heathwaite, 1993; Meybeck *et al.*, 1989; Roberts and Marsh, 1987; Royal Society, 1983). Unfortunately, because nutrients such as nitrogen and phosphorus reach surface waters from a primarily diffuse or non-point agricultural source areas, it is difficult to identify clearly the assumed link between land use, fertiliser application and stream water quality (Casey and Clarke, 1976; Dermine and Lamberts, 1987). This limitation is compounded by the over-emphasis in many studies of nitrogen and phosphorus transport, on the dissolved inorganic nutrient fraction. Lewis and Saunders (1989) suggest, that compared with inorganic constituents, relatively little information is available on the transport of dissolved organic material by rivers. This is largely a result of the relatively minor contribution the dissolved organic fraction makes to the total dissolved load, and the perception that this means that dissolved organic forms are less important when interpreting the nutrient dynamics of freshwater systems. Nitrogen (N) and phosphorus (P) concentrations in natural waters consist of both soluble (dissolved) and particulate forms. Dissolved organic nitrogen and phosphorus are generated from the nitrogen and phosphorus content of the organic matter of plant and organic biomass residues. Dissolved inorganic N and P are released through mineralization (N and P) and nitrification (N). The soluble fraction is generally considered to be bioavailable, although particulate-associated nutrients have *potential* bioavailability. For example, it is

thought that around one-third of the phosphorus associated with suspended sediment is biologically available (Ryding and Rast, 1989). Various chemical interactions occur between dissolved solutes and the solid constituents of soil as a result of sorption, exchange and precipitation reactions. Johnson and Cole (1977) suggest that the order of leaching from agricultural soils is: $\text{NO}_3^- > \text{NO}_2^- > \text{NH}_4^+ > \text{organic N} > \text{PO}_4^{3-}$.

The concentration of N and P in agricultural runoff depends on the interaction of a wide range of variables such as land use, fertiliser application rate, soil type and the hydrological flow pathway linking the land to the stream. Identification of the relative importance of these, and other environmental features, in characterising water quality requires quantification of the variation in *all* N species and P fractions. Climate and land use influence the *total* nutrient load exported from a catchment, not just the inorganic nutrient fraction. Furthermore, downslope and in-stream nutrient transformations may change the chemical forms of N and P.

Examination of published results on nitrogen speciation and phosphorus fractionation in runoff from agricultural land and on their relative concentrations in receiving waters reveals a paucity of information on organic or total nutrient concentrations. Whilst national monitoring of nitrogen in rivers covers nitrate, and in some cases ammonium, concentrations (Heathwaite and Burt, 1991; Foster and Crease, 1974; Foster, 1976; José, 1989; Betton *et al.*, 1991), there is virtually no evidence of long term changes in total nutrient concentrations and even less information on the dissolved organic load. This means that where increases in the concentration of nitrate in many UK rivers are claimed (Edwards and Thornes, 1973; Casey and Clarke, 1979; Burt *et al.*, 1988) it is not always possible to elucidate whether this is the result of an absolute increase in the concentration of nitrate in the river or a relative change in the proportions of the various nitrogen forms present as a result of, for example, land use changes in the catchment.

In rivers, rapid variations in the concentration of dissolved nutrients and suspended sediment may occur during storm events. It is normally assumed that the chemical quality of the river water is determined by the routes taken by runoff to the river. That is, there is a close link between the terrestrial and the aquatic systems. This assumption ignores the effects of changing discharge on the watercourse and in particular the metabolic processes of the stream flora. As solutes enter a stream they are transported downstream, and subjected to further physical, chemical and biological processes in addition to those encountered as they move through the agricultural landscape. Some of these in-stream processes are depicted in Figure 1. They include physico-chemical sorption type reactions between the solute and the streambed. Biological processes such as heterotrophic and autotrophic uptake and release of dissolved nitrogen and phosphorus, and macrophyte egestion of particles, are also important. The denitrification process may form a significant pathway for nitrogen loss (Hill, 1979). In-stream nutrient transformations involving stream biota result in both nutrient uptake and nutrient transformation. The rate of change and resulting nutrient forms appear to be a function of discharge (Casey and Farr, 1982; Hill, 1988). The interpretation of in-stream nutrient transformations requires an evaluation of the size and rate of variation in the different nitrogen and phosphorus pools. Casey and Farr (1982) base their conclusions on the dissolved inorganic nutrients (NO_3^- and PO_4^{3-}) alone. Their results are therefore limited because without N speciation and P fractionation, it is not possible to determine whether the variations observed were the result of absolute changes in the amounts leaving the catchment or were the result of relative changes in the forms of N and P within the stream as a result of changes in stream discharge.

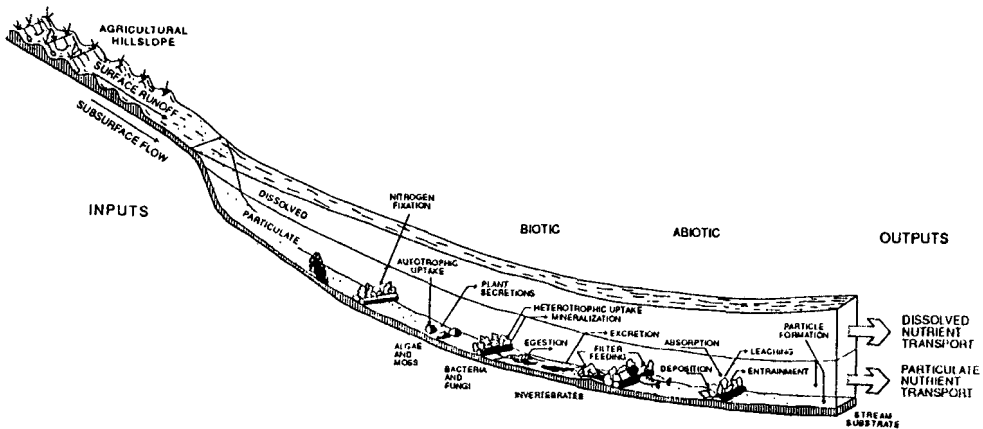


Figure 1 Some processes that can potentially affect solute dynamics within headwater streams (modified from Swank, 1986).

NITROGEN SPECIATION AND PHOSPHORUS FRACTIONATION IN FRESH WATERS

Nitrogen in runoff from agricultural land takes several forms. The dominant combined N species (excluding molecular N_2) are dissolved inorganic N (NH_4^+ , NO_2^- , NO_3^-), dissolved organic N and particulate N, which is predominantly organic in nature. Organic nitrogen usually exists either as an integral part of protein molecules or in the partial breakdown of these molecules, for example, peptides, urea and amino acids. Ammoniacal N is usually present in fresh waters as a result of the biological decomposition of organic N.

Phosphorus transport from agricultural land to receiving waters is generally thought to occur in particulate form (Olness *et al.*, 1975; Johnson *et al.*, 1976). The erosion of particulate material is particle-size selective, with organic-rich clay and silt-sized fractions being removed preferentially; this means that the soil particles with the maximum concentration of particulate nutrients are transported first. Particulate P may be (i) bound to organic matter, (ii) incorporated in mineral (e.g. apatite) phases or (iii) adsorbed to hydrated non-crystalline oxides, especially iron. The latter is generally thought to be the bioavailable fraction (Sonzogni *et al.*, 1982; Thomas *et al.*, 1991), although organically-bound phosphorus may be quantitatively more important and can form up to 90% of total phosphorus in soils. Phosphorus release in a bioavailable inorganic form occurs through mineralization. Organic phosphates may react with iron and aluminium in acid soil to become insoluble. The amount of organically associated phosphorus in forest and grassland soils usually exceeds that of arable soils. Organic phosphorus, present in soil solution, can reach concentrations twenty times that of the dissolved inorganic fraction (Harrison, 1987). This means that phosphorus can be lost from agricultural systems in organic form in both surface and subsurface runoff (Sharpley and Syers, 1976; Sharpley *et al.*, 1976; Duffy *et al.*, 1978); although the former pathway is quantitatively more important. Under some conditions, organic phosphorus can be more mobile and more intensively leached than inorganic phosphorus (Hoffman and Rolston, 1980; Castro and Rolston, 1977). The addition of organic manures or excreta from grazing animals generally

increases the mobility of soil organic P (Harrison, 1987). Phosphorus in dissolved form can be removed by absorption through plant roots and adsorption to soil particles. Adsorption, desorption or dissolution of particulate or dissolved phosphorus as it is transported from agricultural land to the stream depends on the relative concentrations of phosphorus in agricultural runoff and in the stream. For example, particulate P may be desorbed where it enters a stream with a low dissolved P concentration. Marston (1989) suggests that the rate of desorption will be in direct proportion to the exchange surface area of the stream sediments. However, other important parameters such as pH, redox status and the presence of competing anions will also influence the likely reactions that phosphorus will undergo on entering a stream.

The wider environmental impact of increasing nutrient concentrations in rivers and lakes needs to take account not only of the dissolved inorganic nutrient fraction, which is relatively easy to monitor, but also the contribution from particulate and organic forms. These nutrient forms, although they may not be 'available' to aquatic organisms at the time of sampling, may become available downstream or within the lake water column as a result of nutrient transformations within the aquatic system. This was recognised, for nitrogen at least, by the Department of Environment (1986) report: *Nitrate in Water*, which suggested that:

"The rates at which the various organic and inorganic nitrogen compounds interchange in fresh waters are still not known these fluxes need to be compared in high and low nitrate waters along with exchanges between water in sediment, and seasonal differences" (paragraph 5, page 67, DoE, 1986).

For nitrogen, it is usually assumed that particulate nitrogen transport from agricultural land is low and most of the nitrogen is transferred in dissolved inorganic form as nitrate (Kissel *et al.*, 1976). The proportion of phosphorus transported in the particulate fraction is usually much higher (see above). Sommers (1975) reports particulate P losses from arable land between 50 and 70% of the total P removed for a study of the Black Creek catchment in Indiana. Lewis and Saunders (1989) fractionated the total soluble N and P load of the Orinoco River in South America. They found that the concentration of dissolved inorganic and organic N and P showed strong seasonal trends, with greater seasonal variation for inorganic rather than organic components. Nitrate in particular, was found to be more seasonally variable than other nitrogen species or phosphorus fractions. All soluble organic elements appeared to be strongly controlled by discharge. Thus their concentration increased as discharge increased. The same was found for the particulate fraction. In contrast, the dissolved inorganic fraction, and nitrate especially, showed strong dilution effects at high river discharge. This suggests that biological as well as physical controls are important in governing the transport of nitrate from the catchment to the river. Sloane (1979) and Richey *et al.* (1985) similarly report an increase in the concentrations of dissolved organic nitrogen (DON) with increasing discharge in headwater streams. This, they suggest, is a result of the decreased contact time between the stream water and the stream bed which in turn reduces the rate of oxidation of dissolved organic nitrogen to nitrate. The net effect is a rise in the concentration of DON.

For agricultural catchments, some authors, notably Schuman *et al.* (1973), Olness *et al.* (1975) and Johnson *et al.* (1976), suggest that particulate transport of nitrogen and phosphorus in surface runoff from agricultural land may be more important than previously thought. In their studies in the USA, particulate transport accounted for

67–97% of total P losses and up to 92% of total N losses. Unfortunately, they did not examine subsurface hydrological pathways, which resulted in an over-emphasis of the importance of overland flow as the main delivery mechanism for nutrients reaching surface waters. Weiskel and Howes (1991) suggest that this omission is characteristic of many nutrient transport studies. The groundwater flow pathway has rarely been quantified because direct measurement in the field is difficult; nutrient loading models are typically used to obtain estimates of groundwater nutrient fluxes (Teal, 1983; Valiela and Costa, 1988). For phosphorus, the groundwater flow pathway contributes mostly dissolved (and therefore bioavailable) phosphorus to a water body, but concentrations are usually low (Ryding and Rast, 1989).

The studies cited above pin-point the need to identify the relative flux of all nitrogen species and phosphorus fractions from agricultural land to receiving waters. However, the routine chemical analysis of freshwater samples has in the past focussed only on inorganic determinands: nitrate (NO_3^-) or total oxidisable nitrogen ($\text{NO}_3^- + \text{NO}_2^-$), ammonium (NH_4^+) and soluble reactive phosphate (PO_4^{3-}). This is probably because of: (i) the relative ease of measurement of these determinands and (ii) the assumption that inorganic nutrient forms are the key fractions available to organisms in fresh waters. This can be misleading where, for example, organic nitrogen provides an important reserve of available nitrogen in a river but only the concentration of nitrate is monitored. It is well known that the concentration of nitrate in a river decreases in summer as a result of reduced catchment influx and increased biotic uptake, but Johnes (1990), for example, showed that the nitrate decrease was often balanced by an increase in the concentration of organic nitrogen. Other studies, notably conducted by limnologists who have traditionally considered both P fractions and N species in standing waters (see for example: Vollenweider, 1968, 1975; Dillon and Rigler, 1974; Schindler *et al.*, 1974; Vollenweider and Kerekes 1981) have demonstrated the importance of rates of interchange and flux between different forms of nitrogen and of phosphorus in fresh waters (e.g. Ryding and Forsberg, 1979; Stevens and Stewart, 1982).

The transformations between different nitrogen species and phosphorus fractions both during transport along a hillslope hydrological pathway or within the aquatic system once the 'nutrient parcel' enters the stream, have been investigated by Lee *et al.* (1989), Owens *et al.* (1989), Pinay *et al.* (1990) and Heathwaite (1993). Such transformations are part of the *dynamic* nature of these key nutrient elements. Figure 2 illustrates this point further by using the potential transformations of phosphorus as an example. Assuming that P is mainly present in insoluble (particulate P) form in the soil, the initial transport process may begin with erosion, involving detachment (particulate P) and/or dissolution (dissolved P). The initial P transport is controlled by soil (organic matter, soil texture and structure) and hydrological (rainfall: runoff ratio) factors. As P is transported down the hillslope, it is unlikely to remain in the same fraction owing to modification by further physical (sediment deposition, P adsorption) and biological (P assimilation) reactions. Thus even if we know the form in which P was initially transported, this is not necessarily the same form in which P enters the stream. It is essential, therefore, if water quality planning is to be effective, that we know the magnitude and the rate of transformation of all the component parts of the nitrogen and phosphorus cycles, both within the agricultural system and within the stream.

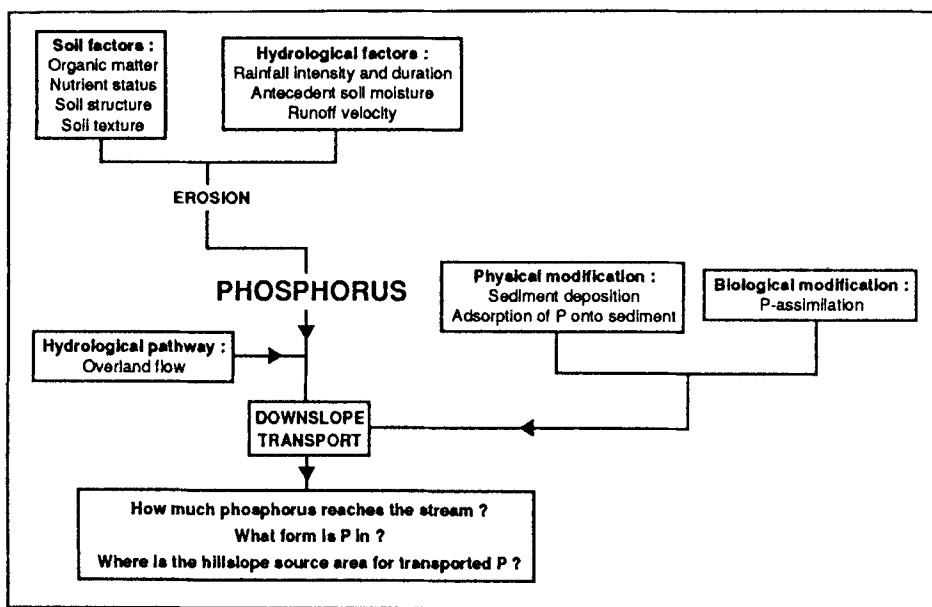


Figure 2 Processes influencing phosphorus transport and transformation along a hillslope hydrological pathway (after Heathwaite and Burt, 1991)

AGRICULTURAL LAND USE AND NITROGEN AND PHOSPHORUS LOSSES

Land use, together with the efficiency of chemical cycling and hydrological processes in the catchment, are key parameters determining the quantity of nutrients exported from the catchment. The land use controls given below are likely to be important in determining the magnitude of nutrient inputs to the aquatic system:

1. presence or absence of grazing animals
2. timing of ploughing and related operations
3. amount and timing of fertilizer application
4. type of manure or inorganic fertilizer used
5. extent of crop cover and root activity.

Land use practices influence the amount of nitrogen and phosphorus reaching surface waters and lakes. For example, cultivation alters soil structure and the rate of microbial breakdown of organic matter, releasing a potentially leachable nitrogen source (Skjemstad *et al.*, 1988; McEwen *et al.*, 1989; Dowdell *et al.*, 1983). Ploughing grassland, leaving ground bare after an arable crop has been removed, and excessive cultivations (e.g. re-seeding grass leys) make a significant contribution to nitrate leaching from agricultural land. Ploughing of permanent grassland can release up to 4000 kg N ha⁻¹ (Whitmore *et al.*, in press) and ploughing of temporary grass, 100–200 kg N ha⁻¹ depending on the length of ley (Darby *et al.*, 1988). Livestock farming also has a potentially high nutrient loading, especially where it is based on dairying or pig farming. Dairy farming, which uses large volumes of water and has

a high production of organic waste, results in a large volume of slurry which must be stored when application to land during winter months is restricted.

Nutrient transport in runoff from agricultural land uses may vary in both amount and form. The main routes for nutrient transfer from hillslope to stream are: (i) leaching to surface waters or groundwater (mainly NO_3^-), (ii) input of animal excreta at watering sites, (iii) surface runoff of excreta from farmyards or grazed land, (iv) leakage of silage effluent, and (v) soil erosion. It is commonly held that inorganic N will be the dominant nitrogen species in runoff from arable land, whereas organic nitrogen and ammonium-nitrogen are the major nitrogen species in grassland runoff (Webb and Walling, 1985; Heathwaite *et al.*, 1990). The presence of grazing animals will also be important. In England and Wales, the total nitrogen load voided in faeces and urine (739 kt; 1978 figures) approaches that of inorganic fertilisers (924 kt) (Royal Society, 1983). Ryden *et al.* (1984) showed that nitrate leaching below a grass sward grazed by cattle was nearly six times greater than that from a cut sward and exceeded nitrate losses normally observed on arable land.

The value of nitrogen speciation of water samples is shown by the nitrogen budget studies of Meyer *et al.* (1981) and Triska *et al.* (1974) which demonstrated the importance of biota in transforming inflows of particulate and dissolved (organic and inorganic) nitrogen to outflows of dissolved (inorganic) nitrogen for headwater streams. Johnson and Reynolds (1977), Likens *et al.* (1977) and Richey *et al.* (1985) found that the export of nitrogen from headwater streams in northeastern United States is dominated by nitrate; dissolved organic nitrogen concentrations are generally low ($<0.05 \text{ mg N l}^{-1}$) for most of the year. Nitrogen budgets for the Hubbard Brook Experimental Forest indicated that in-stream transformations (primarily biological oxidation) of nitrogen inputs could account for 12–25% of the nitrogen exported as nitrate during winter and spring. Richey *et al.* (1985) found that dissolved nitrogen was retained within the stream system from summer through to autumn, with 82% of this retention due to NO_3^- , 8% due to NH_4^+ and 10% to dissolved organic nitrogen. This retention was a temporary transformation and storage mechanism within the stream that occurred prior to nitrogen export as NO_3^- during winter and spring.

THE EFFECT OF FERTILISER ADDITIONS ON N AND P TRANSPORT AND TRANSFORMATION FROM AGRICULTURAL LAND

The addition of inorganic and organic fertilisers to agricultural land is a key factor influencing the amount of nutrients reaching streams and rivers. For nitrogen, fertiliser 'wastage' occurs through denitrification, volatilisation and leaching of nitrogen compounds. Phosphorus losses are largely associated with the transport of particulate material, although the importance of dissolved organic and inorganic losses have not been studied widely. The addition of phosphate as an inorganic fertiliser may increase the organic phosphorus content of surface soils (Harrison, 1987) but appears to be dependent on soil organic matter content and pH. Nitrogen equivalent to 30–50% of the fertiliser nitrogen applied may be lost to the atmosphere through denitrification, whilst up to 30% may be lost through leaching (Frissel and Van Veen, 1982; Jenkinson, 1982; Stewart and Rosswall, 1982). Powlson *et al.* (1987) found that soils with a long history of nitrogen fertiliser application generally had a large mineralisable nitrogen fraction which could form a potentially large leachable nitrate source given the right environmental conditions (warm, moderately wet soils). There is, however,

no simple relation between fertiliser application and nutrient loss. Factors such as climate, soil type, soil drainage, fertiliser timing and application rate and the presence of grazing animals, all influence nitrogen leaching losses (Armstrong, 1984; Armstrong and Garwood, 1991; Garwood *et al.*, 1980; Ryden *et al.*, 1984).

LOSSES OF NITROGEN AND PHOSPHORUS FROM AGRICULTURAL LAND: SOME RESULTS CONDUCTED AT DIFFERENT SCALES OF INVESTIGATION

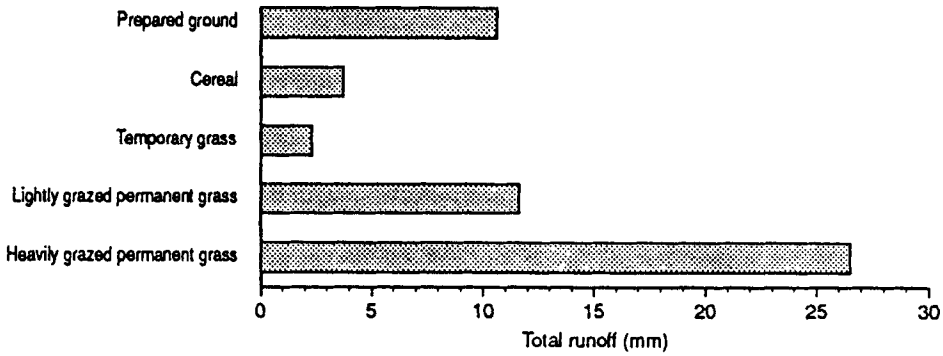
1. Nutrient losses in surface runoff at the hillslope scale

Nitrogen speciation and phosphorus fractionation in surface runoff were examined for a number of different land uses in the Slapton catchment, southwest Devon. The nutrient export from the hillslope plots are shown in Figure 3. The total surface runoff (mm) from each land use type is also shown. The results are mean values derived from duplicate 4-hour rainfall simulation runs on each land use. For total nitrogen, the concentration in surface runoff ranged from 0.6 mg l⁻¹ for prepared ground (ploughed and rolled; no vegetation cover) and lightly grazed permanent grass, to 5.2 mg l⁻¹ for heavily grazed grassland. Nitrogen was below the level of detection of the analytical technique for temporary grass and cereal land use (Heathwaite *et al.*, 1990). For total phosphorus, the concentration in surface runoff ranged from 0.4 mg l⁻¹ for cereal and prepared ground to 9.4 mg l⁻¹ for the heavily grazed permanent grassland.

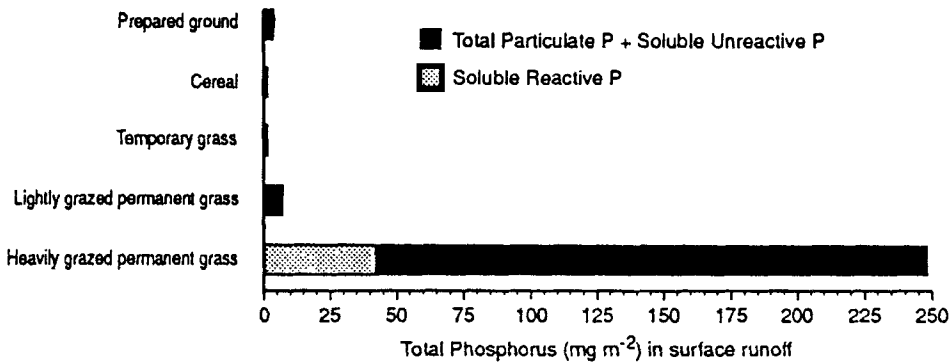
The key pattern to emerge relates to the high nutrient loading from the heavily grazed permanent grassland. Where the surface vegetation cover is removed through over-grazing or poaching, and the inputs of animal excreta are high, the total nitrogen and total phosphorus load in surface runoff is correspondingly high; ammonium was found to constitute over 90% of the total nitrogen load. This is in contrast to the lightly grazed permanent grassland where most N appears to be transported in the organic fraction (particulate + dissolved), although the magnitude of N delivery is considerably lower. Nitrogen delivery in surface runoff from cereal crops and temporary grassland was negligible. The total phosphorus delivery from lightly grazed pasture was markedly lower than from heavily grazed grassland. Cereal, temporary grassland and bare ground show similar rates of total phosphorus delivery, all being lower than those observed for heavily grazed permanent grassland. Less than 20% of the total phosphorus delivery was in soluble reactive form. Most of the total phosphorus load was transported in the unreactive (soluble unreactive phosphorus + particulate phosphorus) fraction. There appears to be a strong association between phosphorus and sediment delivery from grazed land. The suspended sediment load in runoff from the heavily grazed permanent grassland was nearly thirty times greater than the runoff from lightly grazed permanent grassland and nearly double that from prepared ground from which, as the vegetation cover was absent, high sediment delivery was anticipated.

At the small (hillslope) scale of these experiments, the results highlight the importance of the livestock density in grassland areas as a key control of both the total nutrient loading and the form of that load. For nitrogen, inputs of animal excreta appear to have elevated the ammonium-nitrogen loading; whereas for phosphorus, poaching and the subsequent removal of the vegetation cover appear to have increased the contribution from particulate phosphorus to the total load in surface runoff. The total nutrient load in surface runoff from land use plots which are not grazed or have a relatively low stocking density (less than 8 livestock per hectare) is markedly lower than that of the heavily grazed grassland.

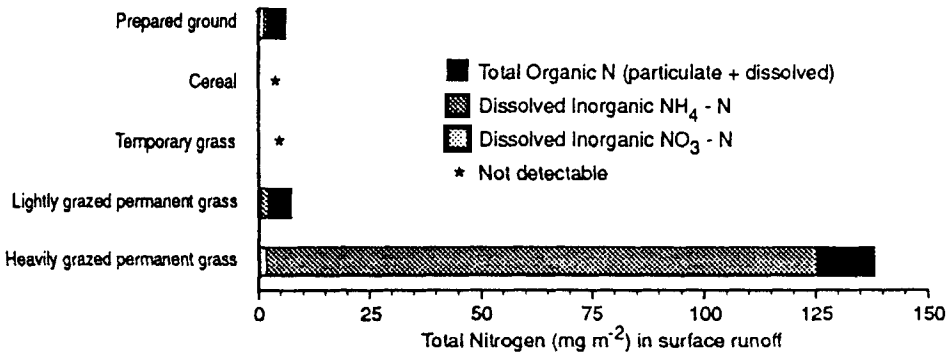
(a) TOTAL SURFACE RUNOFF FOR DIFFERENT LAND USES



(b) PHOSPHORUS FRACTIONATION IN SURFACE RUNOFF FROM DIFFERENT LAND USES



(c) NITROGEN SPECIATION IN SURFACE RUNOFF FROM DIFFERENT LAND USES



(results are means of two runs on each land use)

Figure 3 Nitrogen speciation and phosphorus fractionation in surface runoff from different land uses, Slapton, Devon (after Heathwaite *et al.*, 1990)

2. Subsurface runoff of N and P from high nutrient export crops in experiments conducted at the sub-catchment scale

Heathwaite and Johnes (in press) examined the mean monthly concentrations of nitrogen species in subsurface runoff from a high nutrient export crop—oilseed rape (*Brassica napus*); some of their results are reproduced in Figure 4. For the dissolved inorganic nitrogen species, maximum stream concentrations were associated with either hydrological factors, so that peak nitrate concentrations are correlated with the period of maximum rainfall and subsurface runoff, or with biological factors, where the concentration of nitrite, which is maximum in August, may be linked to the mineralisation of organic nitrogen within the stream. The concentration of organic nitrogen also rises to a maximum during the summer months; this may be the result of the uptake of bioavailable N and its subsequent release as organic nitrogen as a result of decay and decomposition. During the summer period, the total organic nitrogen concentration is almost double that of nitrate in subsurface runoff. This result highlights the relative importance of organic nitrogen as a constituent of the total nitrogen load in subsurface drainage. The concentration of ammonium in subsurface runoff appears to be linked to fertiliser additions to the rape crop which are largely in the form of urea (46% N as NH_4^+).

3. Nitrogen speciation in surface waters at the catchment scale

A strongly seasonal pattern in the concentration of the different nitrogen species was recorded by Johnes (1990) and Heathwaite and Johnes (in press) for the river Windrush in the Cotswolds. Similar seasonal trends have been reported by Lewis and Saunders (1989) and Richey *et al.* (1985). Dissolved inorganic nitrogen species (NO_3^- and NO_2^-) were found to be highly correlated with the seasonal variation in discharge. The nitrate concentration in the river reaches a peak in winter when the average discharge is maximal, whereas nitrite has its peak in summer, when flow and dissolved oxygen concentrations in the river are lowest. The concentration of dissolved inorganic ammonium follows a similar trend to the pattern of suspended sediment delivery to the river. The organic nitrogen fraction constituted almost 40% of the total annual nitrogen load, although it did not have a strongly seasonal pattern. There was an increase in the relative contribution from organic nitrogen to the total nitrogen load in a drier year.

At the catchment scale, the speciation of the total nitrogen load for the river Windrush confirms the assumption that nitrate—which has traditionally been the focus of aquatic nitrogen studies—is the dominant species contributing to the total annual nitrogen loading. This is largely because the highest nitrate concentrations coincide with periods of high river discharge during the winter. However, organic nitrogen is an important secondary constituent of the total nitrogen load, and since nitrogen may undergo rapid inter-specific cycling, both within the hillslope hydrological pathway and within the stream, organic nitrogen may be an important component of nitrogen enrichment in riverine systems.

4. Nutrient forms and the trophic status of waterbodies: the impact of N and P losses on receiving waters

Nutrient enrichment of the aquatic ecosystem, which can often be linked to agricultural intensification in the surrounding catchment, alters the trophic status of the

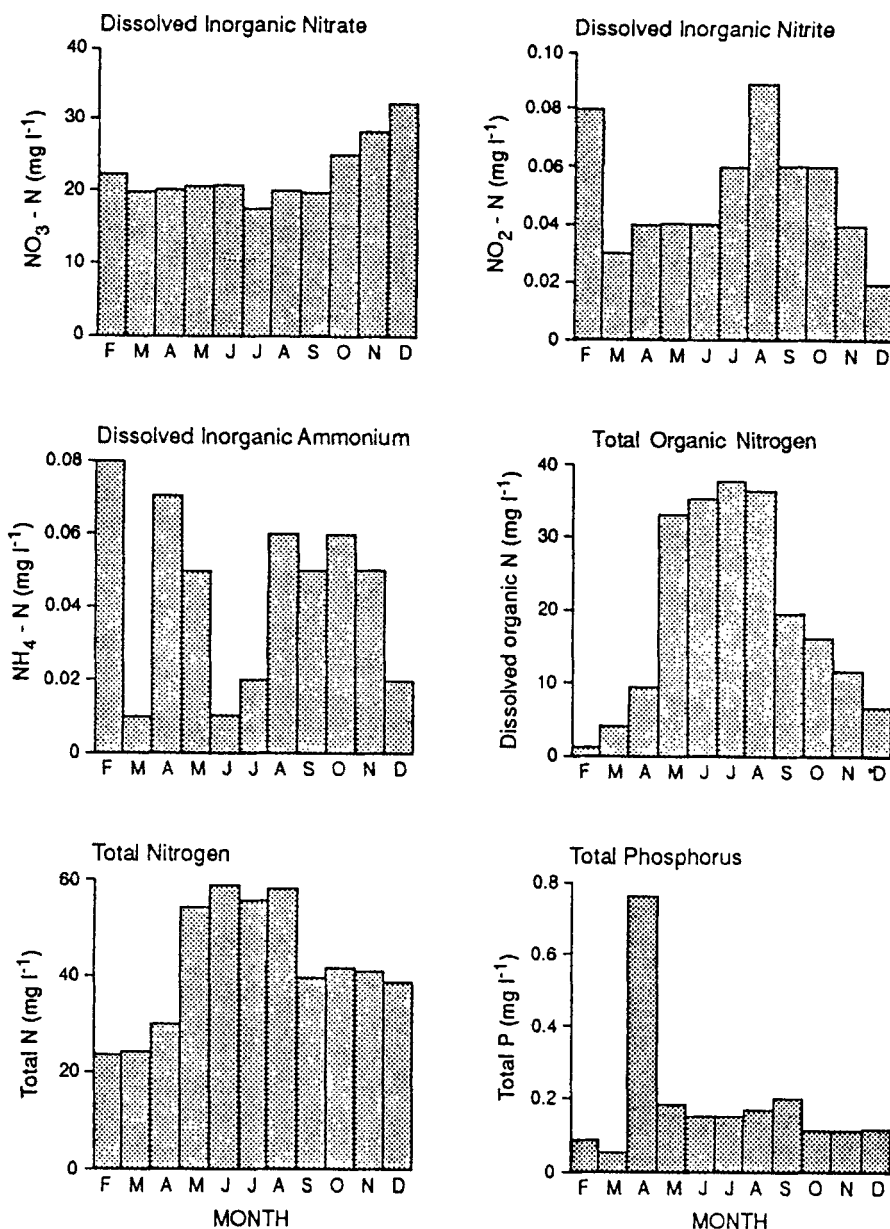


Figure 4 Nitrogen speciation in runoff from a high nutrient export crop: oil seed rape, Windrush catchment, Cotswolds (after Johnes, 1990).

receiving waters. Depending on the trophic status of the waterbody, organic N may account for over 50% of total dissolved nitrogen in lake waters; dissolved organic N is commonly in the range 0–2.5 mg l⁻¹ with dissolved inorganic N in the range 0–4 mg l⁻¹ for NO₃⁻-N and 0–5 mg l⁻¹ for NH₄⁺-N (Keeney, 1973). Stewart *et al.*

(1982) found that the dissolved organic nitrogen pool in lakes showed little seasonal variation, unlike the dissolved inorganic pool which was dominated by seasonal variations in the supply of nitrate. However, the reduced contribution from dissolved inorganic nitrogen in summer may be partially offset by the larger contribution from dissolved organic and particulate nitrogen derived from lake biota. A similar pattern has been observed in rivers (Johnes, 1990; Heathwaite and Johnes, in press, and see above).

Upland lakes and reservoirs in the UK are often naturally oligotrophic; here concentrations of nitrate seldom exceed 2 mg l^{-1} and the dissolved organic nitrogen fraction is normally greater than the dissolved inorganic fraction. The main source of organic nitrogen is catchment runoff, often derived from peat-rich soils. In eutrophic lakes, the proportion of inorganic to organic nitrogen dissolved in the water column usually increases, largely as a result of high nitrogen export (as nitrate) from the catchment. This trend means effectively that increasing trophic status corresponds with an increase in the 'biologically available' nutrient fractions in a lake. High inorganic nitrogen inputs to lakes have been recorded from heavily fertilised agricultural catchments (Stewart *et al.*, 1982; Foy *et al.*, 1982; Heathwaite and Burt, 1991), and where urban effluent is discharged into the lake (Foy *et al.*, 1982; Stewart *et al.*, 1982).

CONCLUSIONS

Traditionally, studies of nitrogen and phosphorus losses from agricultural land have focussed only on inorganic nutrient forms of nitrate (NO_3^-) and phosphorus (PO_4^{3-}) in runoff and receiving waters (e.g. Wild and Cameron, 1980; Powlson *et al.*, 1987; McGill and Myers, 1987; Marston, 1989). Some research has illustrated the *dynamic* nature of nitrogen speciation and phosphorus fractionation balances in natural waters and the role of organic nitrogen and particulate phosphorus in contributing to the total nutrient loading on a waterbody (Heathwaite *et al.*, 1990; Johnes, 1990; Ryding and Forsberg, 1979; Stevens and Stewart, 1982). It is clear that nitrogen losses from agricultural land can also occur in organic and ammonium-nitrogen forms; phosphorus losses, although often dominated by particulate transport, may occur in soluble organic and inorganic form. Knowledge of the spatial and temporal variation in all nitrogen species and phosphorus fractions in a drainage basin is essential if the wider environmental significance of elevated nutrient concentrations in surface waters is to be assessed (Johnes and Heathwaite, 1992; Heathwaite and Johnes, in press). This is because nutrient fluxes between different species may change during transport from the land to the stream and as a result of in-stream, in-river or in-lake transformations once the 'nutrient parcel' has entered the aquatic system. The results discussed above highlight the importance of organic nitrogen and unreactive phosphorus as components of the total nutrient load in fresh waters, and the temporal and spatial variability in the rates of interchange between nutrient species. In designing research programmes to examine the links between the agricultural land and the water quality of receiving waters it is important to consider the whole range of nutrient forms that may be present.

References

- Armstrong, A.C. (1984) The hydrology and water quality of a drained clay catchment, Cockle Park, Northumberland pp. 153–168 in Burt, T.P. and Walling, D.E. (Eds) *Catchment Experiments in Fluvial Geomorphology*, Geobooks, Norwich.
- Armstrong, A.C. and Garwood, E.A. (1991) Hydrological consequences of artificial drainage of grassland. *Hydrological Processes*, **5**, 157–174.
- Betton, C., Webb, B.W. and Walling, D.E. (1991) Recent trends in NO₃-N concentration and loads in British rivers. *IAHS publication* **203**, 169–180.
- Burt, T.P., Arkell, B.P., Trudgill, S.T. and Walling, D.E. (1988) Stream nitrate levels in a small catchment in south west England over a period of 15 years, 1970–1985. *Hydrological Processes*, **2**, 267–284.
- Casey, H. and Clarke, R.T. (1976) The seasonal variation in dissolved reactive phosphate concentrations in the River Frome, Dorset, England, pp. 257–265 in *Monitoring to Detect Changes in Water Quality Series* (Proceedings of the Budapest Symposium), IAHS publication No. 157.
- Casey, H. and Clarke, R.T. (1979) Statistical analysis of nitrate concentrations from the river Frome (Dorset) for the period 1965–1976. *Freshwat. Biol.*, **9**, 91–97.
- Casey, H. and Farr, I.S. (1982) The influence of within-stream disturbance on dissolved nutrient levels during spates. *Hydrobiologia*, **92**, 447–462.
- Casey, H., Clarke, R.T. and Smith, S.M. (1993) Increases in nitrate concentrations in the River Frome (Dorset) catchment related to changes in land use, fertiliser applications and sewage input. *Chemistry and Ecology* (in press).
- Castro, C.L. and Rolston, D.E. (1977) Organic phosphate transport and hydrolysis in soil: theoretical and experimental evaluation. *J. Soil Science Soc.*, **41**, 1085–1092.
- Darby, R.J., Hewitt, M.V., Penny, A., Johnston, A.E. and McEwen, J. (1988) The effects of increasing length of ley on the growth and yield of winter wheat. *Rothamsted Report 1987 Part I*, 101–102.
- Dermine, B. and Lamberts, L. (1987) Nitrate nitrogen in the Belgian course of the Meuse River—fate of the concentrations and origins of the inputs. *J. Hydrol.*, **93**, 91–99.
- Department of Environment (1986) Nitrate in Water. *Department of Environment Pollution Paper* **26**, 104 pp. HMSO.
- Dillon, P.J. and Rigler, F.H. (1974) The chlorophyll-phosphorus relationship in lakes. *Limnol. Oceanogr.*, **19**, 767–773.
- Dowdell, R.J., Crees, R. and Cannell, R.Q. (1983) A field study of effects of contrasting methods of cultivation on soil nitrate content during autumn, winter and spring. *J. Soil Science*, **34**, 367–380.
- Duffy, P.D., Schreiber, J.D., McClurkin, D.C. and McDowell, L.L. (1978) Aqueous- and sediment-phase phosphorus yields from five southern pine watersheds. *J. Environ. Qual.*, **7**, 45–50.
- Edwards, A.M.C. and Thornes, J.B. (1973) Annual cycle of river water quality: a time series approach. *Water Res. Res.*, **9**, 1286–1295.
- Foster, S.S.D. (1976) The vulnerability of British groundwater resources to pollution by agricultural leachates. *M.A.F.F. Technical Bulletin*, **32**, 68–91.
- Foster, S.S.D. and Crease, R.I. (1974) Nitrate pollution of chalk groundwater in East Yorkshire—a hydrogeological appraisal. *J. Inst. Water Eng.*, **28**, 178–194.
- Foster, S.S.D., Geake, A.K., Lawrence, A.R. and Parker, J.N. (1985) Diffuse groundwater pollution: lessons of the British experience. *Memoirs of the 18th Congress of the International Association of Hydrogeologists*, Cambridge, 168–177.
- Foy, R.H., Smith, R.V. and Stevens, R.J. (1982) Identification of factors affecting nitrogen and phosphorus loading to Lough Neagh. *J. Environ. Management*, **15**, 109–129.
- Frissel, M.J. and Van Veen, J.A. (1982) A review of models for investigating the behaviour of nitrogen in soils. *Phil. Trans. Roy. Soc., London*, **B296**, 341–349.
- Garwood, E.A., Salette, J. and Lemaire, G. (1980) The influence of water supply to grass on the response to fertiliser nitrogen and nitrogen recovery, pp. 59–65 in: Prins, W.H. and Arnold, G.H. (Eds) *Proc. Int. Symp. Europe Grassland Federation on role of nitrogen in intensive grassland production*, Pudoc, Wageningen.
- Harrison, A.F. (1987) *Soil Organic Phosphorus: A Review of World Literature*, C.A.B. International, Wallingford, UK, 257 pp.
- Heathwaite, A.L. (1993) Nitrogen Cycling in Surface Water and Lakes, pp. 99–140 in: Burt, T.P., Heathwaite, A.L. and Trudgill, S.T. (Editors) *Nitrate: Processes, Patterns and Management*. John Wiley and Sons Ltd.

- Heathwaite, A.L. and Burt, T.P. (1991) Predicting the effect of land use on stream water quality. *IAHS publication* **203**, 209–218.
- Heathwaite, A.L., Burt, T.P. and Trudgill, S.T. (1990) The effect of agricultural land use on nitrogen, phosphorus and suspended sediment delivery to streams in a small catchment in south west England, pp. 161–179 in: Thornes, J.B. (Editor) *Vegetation and Erosion*, Wiley.
- Heathwaite, A.L. and Johnes, P.J. (in press) The chemical composition of nitrogen and phosphorus losses in runoff from agricultural land. *Journal of Applied Ecology*.
- Hill, A.R. (1979) Denitrification in the nitrogen budget of a river ecosystem. *Nature*, **281**, 291–292.
- Hill, A.R. (1988) Factors influencing nitrate depletion in a rural stream. *Hydrobiologia*, **160**, 111–122.
- Hoffman, D.L. and Rolston, D.E. (1980) Transport of organic phosphate in soil as affected by soil type. *J. Soil Science Soc. of America*, **44**, 46–52.
- Jenkinson, D.S. (1982) An introduction to the global nitrogen cycle. *Soil Use and Management*, **6**, 56–61.
- Johnes, P.J. (1990) An investigation of the effects of land use upon water quality in the Windrush catchment. Unpublished DPhil Thesis, Oxford University, UK.
- Johnes, P.J. and Heathwaite, A.L. (1992) The simultaneous determination of total nitrogen and total phosphorus in freshwaters using a microwave digestion procedure. *Water Research*, **6**, 1281–1287.
- Johnson, D.W. and Cole, D.W. (1977) Anion mobility in soils: relevance to nutrient transport from terrestrial to aquatic ecosystems. *EPA Ecological Research Series EPA-600/3-77-068*, Corvallis, Oregon, US Environmental Protection Agency.
- Johnson, A.H. and Reynolds, R.C. (1977) Chemical character of headwater streams in Vermont and New Hampshire. *Water Res. Res.*, **13**, 469–473.
- Johnson, A.H., Bouldin, D.R., Gayette, E.A. and Hedges, A.M. (1976) Phosphorus loss by stream transport from a rural watershed: quantities, processes and sources. *J. Environ. Qual.*, **5**, 148–157.
- José, P. (1989) Long-term nitrate trends in the River Trent and four major tributaries. *Regulated Rivers: Research and Management*, **4**, 43–57.
- Keeney, D.R. (1973) The nitrogen cycle in sediment-water systems. *J. Environ. Qual.*, **2**, 15–27.
- Kissel, D.E., Richardson, C.W. and Burnett, E. (1976) Losses of nitrogen in the Blackland Prairie of Texas. *J. of Environ. Qual.*, **5**, 288–292.
- Lee, D., Dillaha, T.A. and Sherrard, J.H. (1989) Modelling phosphorus transport in grass buffer strips. *Journal of Environmental Engineering*, **115**, 409–427.
- Lewis, W.M. and Saunders, J.F. (1989) Concentration and transport of dissolved and suspended substances in the Orinoco River. *Biogeochemistry*, **7**, 203–240.
- Likens, G.E., Bormann, F.H., Pierce, R.S. and Eaton, J.S. and Johnson, N.M. (1977) *Biogeochemistry of a Forested Ecosystem*. New York, Springer-Verlag, 148 pp.
- Marston, R.A. (1989) Particulate and dissolved losses of nitrogen and phosphorus from forest and agricultural soils. *Prog. Physical Geography*, **13**, 234–259.
- McEwen, J., Darby, R.J., Hewitt, M.V. and Yeoman, D.P. (1989) Effects of field beans, fallow, lupins, oats, oilseed rape, peas, ryegrass, sunflowers and wheat on nitrogen residues in the soil on the growth of a subsequent wheat crop. *J. Agric. Science*, **115**, 209–219.
- McGill, W.B. and Myers, R.K.J. (1987) Controls of dynamics of soil and fertiliser nitrogen, pp. 27–38 in: Follett, R.F. *et al.*, (Editors) *Soil fertility and organic matter as critical components of production systems*. *Soil Science Society of America and the American Society of Agronomy*, Madison, USA.
- Meybeck, M., Chapman, D. and Helmer, R. (1989) *Global Freshwater Quality: A First Assessment*. Global Environmental Monitoring System/UNEP/WHO, 360 pp.
- Meyer, J.L., Likens, G.E. and Sloane, J. (1981) Phosphorus, nitrogen and organic carbon flux in a headwater stream. *Arch. Hydrobiology*, **91**, 28–44.
- Olness, A., Smith, S.J., Rhoades, E.D. and Menzel, R.G. (1975) Nutrient and sediment discharge for watersheds in Oklahoma. *J. Environ. Qual.*, **4**, 331–336.
- Owens, L.B., Edwards, W.M. and Van Keuren, R.W. (1989) Sediment and nutrient losses from an unimproved, all-year grazed watershed. *J. Environ. Qual.*, **18**, 232–238.
- Pinay, G., Décamp, H., Chauvet, E. and Fustec, E. (1990) Functions of ecotones in fluvial systems, pp. 141–170 in: Naiman, R.J. and Décamp, G. *The Ecology and Management of Aquatic-Terrestrial Ecotones*. Parthenon, Paris.
- Powelson, D.S., Brookes, P.C. and Christensen, B.T. (1987) Measurement of soil microbial biomass provides an early indication of changes in total soil organic matter due to straw incorporation. *Soil Biol. Biochem.*, **19**, 154–164.
- Richey, J.S., McDowell, W.H. and Likens, G.E. (1985) Nitrogen transformations in a small mountain stream. *Hydrobiologia*, **124**, 129–139.
- Roberts, G. and Marsh, T. (1987) The effects of agricultural practices on the nitrate concentrations in the surface water domestic supply sources of Western Europe. *IAHS publication* **164**, 365–380.

- Royal Society (1983) *The Nitrogen Cycle of the United Kingdom: A Study Group Report*. The Royal Society, London, 264 pp.
- Ryden, J.C., Ball, P.R. and Garwood, E.A. (1984) Nitrate leaching from grassland. *Nature*, **311**, 50–54.
- Ryding S.-O. and Forsberg, C. (1979) Nitrogen, phosphorus and organic matter in running waters: studies from six drainage basins. *Vatten*, **1**, 46–58.
- Ryding, S.-O. and Rast, W. (1989) (Editors) *The Control of Eutrophication in Lakes and Reservoirs*, Man and the Biosphere Series, Volume 1, Parthenon Publishing Group, France, 314 pp.
- Schindler, D.W., Welch, H.E., Kalff, J., Brunskill, G.J. and Kritsch, N. (1974) Physical and chemical limnology of Char Lake, Cornwallis Island (75° N lat.). *J. Fish. Res. Bd. Canada*, **31**, 585–607.
- Schuman, G.E., Burwell, R.E., Piest, R.F. and Spomer, R.G. (1973) Nitrogen losses in surface runoff from agricultural watersheds in Missouri Valley loess. *J. Environ. Qual.*, **2**, 299–302.
- Sharpley, A.N. and Syers, J.K. (1976) Phosphorus transport in surface runoff as influenced by fertiliser and grazing cattle. *New Zealand J. Sci.*, **19**, 277–282.
- Sharpley, A.N., Syers, J.K. and O'Connor, P.W. (1976) Phosphorus inputs into a stream draining an agricultural watershed. I: Sampling. *Water, Air, Soil Pollut.*, **6**, 39–52.
- Skjemstad, J.O., Vallis, I. and Myers, R.K.J. (1988) Decomposition of soil organic nitrogen, pp. 134–144 in: Wilson, J.R. (Ed) *Advances in Nitrogen Cycling in Agricultural Ecosystems*, CAB International, Wallingford, UK.
- Sloane, J. (1979) Nitrogen flux in small mountain streams in New Hampshire. M.S. Thesis, Cornell University, Ithaca, NY.
- Sommers, L.E. (1975) Nutrient contribution to the Maumee river. *EPA Ecological Research Series EPA-905/9-75-007*. Corvallis, Oregon: US Environmental Protection Agency.
- Sonzogni, W.C., Chapra, S.C., Armstrong, D.E. and Logan, T.J. (1982) Bioavailability of phosphorus inputs to lakes. *J. Environ. Qual.*, **11**, 555–563.
- Stevens, R.J. and Stewart, B.M. (1982) Concentration, fractionation and characterisation of soluble organic phosphorus in river water entering Lough Neagh. *Wat. Res.*, **16**, 1507–1519.
- Stewart, W.D.P. and Rosswall, T. (1982) The Nitrogen Cycle. *Phil. Trans. Roy. Soc. London*, **B296**, 299–576.
- Stewart, W.D.P., Preston, T., Peterson, H.G. and Christofi, N. (1982) Nitrogen cycling in eutrophic freshwaters. *Phil. Trans. Roy. Soc. London*, **B296**, 491–509.
- Swank, W.T. (1986) Biological control of solute losses from forest ecosystem, pp. 85–140 in: Trudgill, S.T. (Editor) *Solute Processes*, John Wiley and Sons Ltd.
- Teal, J.M. (1983) (Editor) *The Coastal Impact of Groundwater Discharge: An Assessment of Anthropogenic Nitrogen Loading in Town Cove, Orleans, M.A.*, Final Report, Woods Hole Oceanographic Institute, Woods Hole, Massachusetts.
- Thomas, R.L., Santiago, S., Gandais, V., Zhang, L. and Vernet, J. (1991) Forms of particulate phosphorus and the sediment carbon/nitrogen ratio as indicators of phosphorus origins in aquatic systems. *Can. J. Water Pollut. Res.*, **26**, 433–451.
- Triska, F.J., Sedell, J.R., Cromack, K., Gregory, S.V. and McCorison, F.M. (1974) Nitrogen budget for a small coniferous forest stream. *Ecological Monographs*, **54**, 119–140.
- Valiela, I. and Costa, J. (1988) Eutrophication of Buttermilk Bay, a Cape Cod coastal embayment: Concentrations of nutrient and watershed nutrient budgets. *Environ. Management*, **12**, 539–551.
- Vollenweider, R.A. (1968) *Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorus as factors in eutrophication*. Technical Report DAS/CSI/68.27, Environmental Directorate, OECD, Paris, 154 pp.
- Vollenweider, R.A. (1975) Input-output models with special reference to phosphorus loading concept in limnology. *Schweiz. Zeit. Hydrol.*, **37**, 53–84.
- Vollenweider, R.A. and Kerekes, J.J. (1981) Background and summary results of the OECD cooperative programme on eutrophication. Appendix 1 in: *The OECD Cooperative Programme on Eutrophication* Canadian contribution (compiled by L.L. Janus and R.A. Vollenweider), Environment Canada Scientific Series 131.
- Whitmore, A.P., Bradbury, N.J. and Johnson, P.A. (in press) The potential contribution of ploughed grassland to nitrate leaching. *Agriculture, Ecosystems and Environment*.
- Webb, B.W. and Walling, D.E. (1985) Nitrate behaviour in streamflow from a grassland catchment in Devon, UK. *Wat. Res.*, **19**, 1005–1016.
- Weiskel, P.K. and Howes, B.L. (1991) Quantifying dissolved nitrogen flux through a coastal watershed. *Wat. Res. Res.*, **27**, 2929–2939.
- Wild, A. and Cameron, K.C. (1980) Soil nitrogen and nitrate leaching, pp. 35–70 in: Tinker, P.B. (Ed) *Soils and Agriculture*, Blackwell, Oxford.