
5 Nitrogen Cycling in Surface Waters and Lakes

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5.1 AN OVERVIEW: THE AQUATIC NITROGEN CYCLE

The rising nitrogen concentrations in streams and rivers and accelerated eutrophication of lakes and reservoirs have focused attention on the pathways and cycling of nitrogen in the aquatic system. Nitrogen is important because it controls the productivity of freshwater ecosystems, and together with phosphorus, is a rate-limiting nutrient in freshwater eutrophication.

Two factors are often taken to suggest that nitrogen is unlikely to be the controlling element in the eutrophication of freshwaters. First, nitrogen concentrations in most freshwaters are usually higher than phosphorus. Average nutrient concentrations are commonly of the order 16:1 N:P (Ryding and Rast, 1989). Second, cyanobacteria are able to fix nitrogen from the atmosphere and are not, therefore, responsive to limitations in the nitrogen supply from, for example, catchment sources. Such assumptions are an oversimplification of the processes and pathways of nitrogen cycling in aquatic systems, and do not account for factors such as the seasonal fluctuation in nutrient supply to any freshwater body from its catchment, and the ability of freshwater biota to utilise and release nitrogen and phosphorus. In this chapter, the sources, pathways and transformations of nitrogen in freshwater ecosystems will be examined, and the mechanisms by which nitrogen is involved in the eutrophication of lake systems will be identified.

Nitrogen (N) in freshwaters takes several forms, and their dynamic interrelationships can be described as the aquatic nitrogen cycle. The dominant combined N species in waters (excluding molecular N₂) are dissolved inorganic N (NH₄⁺, NO₂⁻, NO₃⁻), dissolved organic N, and particulate N, which is usually organic but can contain inorganic N. 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 freshwaters as a result of the biological decomposition of organic N.

Figure 5.1 illustrates the magnitude of the flow pathways of each nitrogen fraction within the terrestrial and aquatic systems. The importance of the terrestrial nitrogen fraction as a source of N for the aquatic system is clear. Up to 40% of the total nitrogen flux reaches the aquatic system through direct surface runoff or subsurface flow from the catchment (see Chapter 3). Consequently, the patterns of use, particularly land use, and processes of nitrogen release in the terrestrial system must, to a large extent, determine the magnitude of input to the aquatic system and the nature of the response.

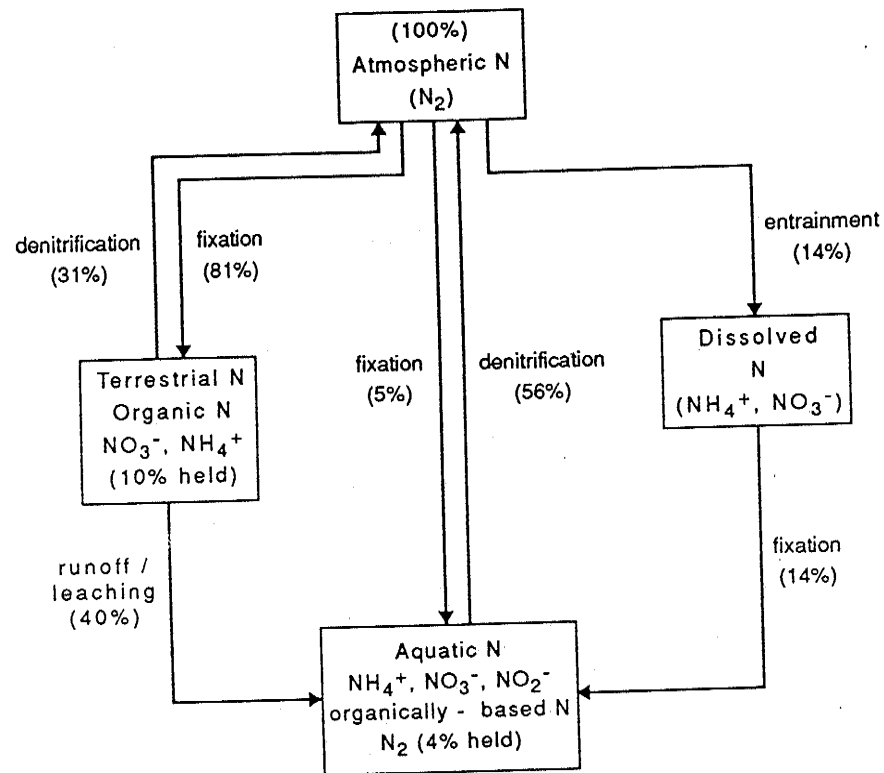


Figure 5.1 The nitrogen cycle (redrawn from Henderson-Sellers and Markland, 1987)

Figure 5.2 illustrates the nitrogen speciation in aquatic systems. The aquatic N cycle is similar in form to the terrestrial cycle, the key difference being the size of the biomass pool. In the aquatic nitrogen cycle, the biomass pool may be only one-thirtieth of the terrestrial pool (Henderson-Sellers and Markland, 1987). However, energy utilisation is more efficient so that net primary productivity may be double that of terrestrial ecosystems. Furthermore, the utilisation and turnover of nitrogen in aquatic systems is more rapid than that of terrestrial systems.

Five possible nitrogen-cycling reactions are shown in Figure 5.2. These are: fixation, nitrification, assimilation, denitrification and mineralisation or ammonification. Immobilisation may occur where there is limited O_2 but this process is usually seasonal and depends on biomass availability. Whether these reactions occur or not is largely determined by the energy required or lost during the reaction process (see Table 5.1). Actual energetics in the aquatic system must consider:

- (1) The rate of reaction;
- (2) Organic matter availability;
- (3) Partial reactions which, when taken together may constitute a thermodynamically viable process;
- (4) The energy source; and
- (5) The oxidation state of the environment.

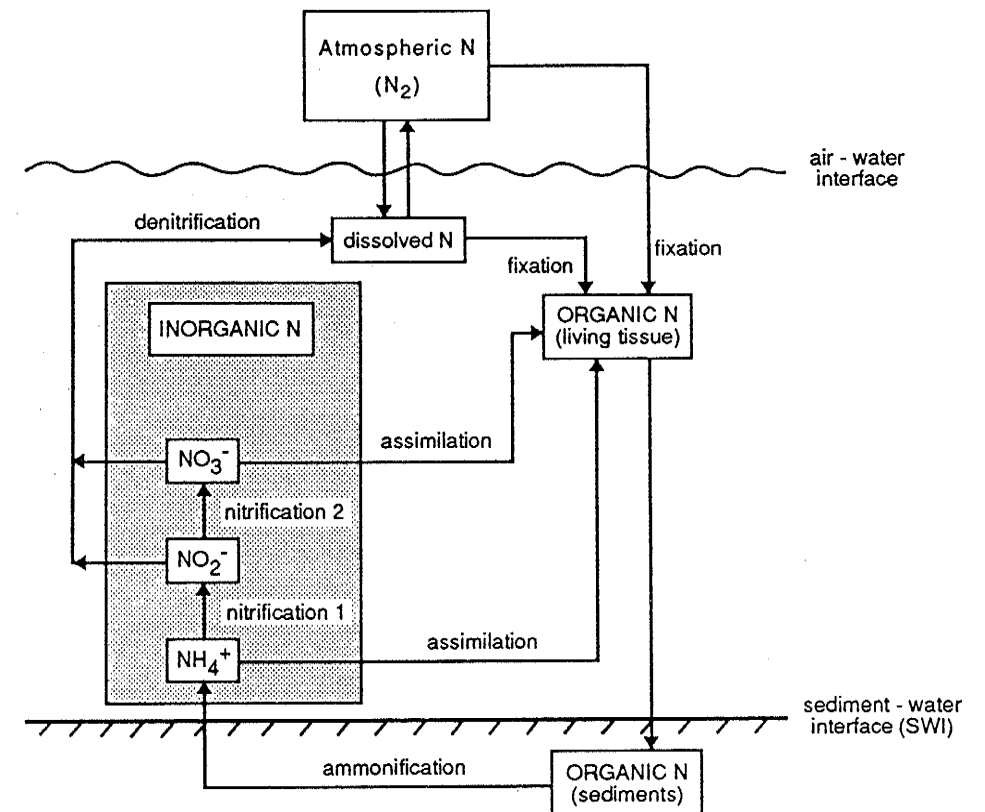
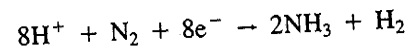


Figure 5.2 The aquatic nitrogen cycle

A further constraint on the likelihood of nitrogen transformation in aquatic systems is the supply of nitrogen. The total N in a freshwater system is less important than the rate of supply when N is a limiting factor. This can often occur in lakes in summer months (Stewart *et al.*, 1982; Van Vlymen, 1980; Heathwaite, 1989). In general, all aquatic systems have some constraints on nitrogen cycling, primarily as a result of some degree of anaerobiosis. To some extent this can be balanced by, for example, ammonium which, in the absence of cation binding sites, is more available in aquatic than in terrestrial systems. Light penetration is important in aquatic systems and may differentially affect micro-organisms and photosynthetic organisms. For example, nitrite-oxidising species are more light sensitive than ammonium-oxidising species; these differences will affect activity profiles in the water column and cause diurnal nitrogen cycling fluctuations. Table 5.2 summarises some of the factors affecting N cycling in freshwaters and these processes are examined in more detail below. The focus is primarily on lake systems, although the processes described do occur in streams and rivers but are usually at different rates.

5.1.1 NITROGEN FIXATION

Nitrogen fixation is a bacterially mediated, exergonic reduction process which converts molecular N to ammonia:



On an annual basis, total nitrogen fixation in aquatic systems rarely exceeds 20 kg N ha^{-1} (Royal Society, 1983). In general, N fixation requires adenosin triphosphate (ATP) which is generated by photosynthesis; so this process is inefficient at night. However, cyanobacteria (primarily *Anabaena*, *Aphanizomenon*, *Gloeotrichia*) can fix nitrogen directly, so do not have this diurnal limitation (Sprent, 1987). These species can form dense planktonic mats and their vertical distribution in the water column can be controlled by means of a gas vacuole. *Microcystis aeruginosa*, although an abundant bloom-forming bacterium, does not fix nitrogen.

There is still much uncertainty over the relative importance of nitrogen fixation in comparison with the total nitrogen input to lake systems from catchment sources. There is evidence to suggest that N fixation is primarily important in eutrophic lakes with large populations of cyanobacteria. Torrey and Lee (1976), for example, suggested that N fixation accounted for almost 10% of the total nitrogen load in a eutrophic North American lake.

5.1.2 ASSIMILATION OF NITROGEN IN FRESHWATERS

The importance of plankton assimilation of nitrate in freshwaters was demonstrated in Blelham

Table 5.1 Nitrogen cycle reactions: standard free energy changes

Reaction	Free energy change (kJ mol^{-1})	Process
$\text{NO}_3^- \rightarrow \text{NO}_2^-$	-142 to -161	Anaerobic NO_3 respiration
$\text{NO}_2^- \rightarrow \text{NH}_4^+$	-347 to -433	Anaerobic NO_2 reduction
$\text{NO}_3^- \rightarrow \text{NH}_4^+$	+348	$\text{NO}_2 + \text{NO}_3$ reduction
$\frac{1}{2}\text{N}_2 \rightarrow \text{NO}_2^-$	+480	N fixation
$\text{NH}_4^+ \rightarrow \text{NO}_2^-$	-229 to -338	<i>Nitrosomonas</i>
$\text{NO}_2^- \rightarrow \text{NO}_3^-$	-65 to -88	<i>Nitrobacter</i>

+ Net energy gain; - net energy loss (after Sprent, 1987).

Table 5.2 Factors affecting the nitrogen cycle in freshwater lakes

Process	Factors
Nitrogen fixation	Cyanobacteria at lake surface Photosynthetic bacteria at anoxic zone N Fixation when soluble N concentration low
Mineralisation	More important in lake sediments Rapid mineralisation when plankton biomass dominates lake (low C:N)
Nitrification	Autotrophic so NH_4^+ and O_2 dependent Seasonal variation in site: spring and autumn: at SWI; ^a summer: open water (O_2 depletion at interface)
Denitrification	Seasonal, affected by NO_3^- supply Generally occurs at SWI
Assimilation	Phytoplankton; varies with NO_3^- concentration NH_4^+ can be assimilated if available
Immobilisation	Seasonal, depends on biomass, N rapidly mineralised if sufficient O_2

^aSWI = sediment-water interface (modified from Sprent, 1987).

Tarn in the English Lake District (Preston, Stewart and Reynolds, 1980; Stewart *et al.*, 1982). The authors found that added ^{15}N -enriched sodium nitrate was removed from the water column within 14 days. The added N accumulated in the resulting *Microcystis* bloom. These results suggest that nitrogen stripping by primary producers may be an important mechanism for the removal of nitrate from freshwaters, although this depends on the ultimate fate of the nitrogen once it reaches the lake sediments because N may be available for re-release. Heathwaite and O'Sullivan (1991), for example, showed that lake sediments can store a large authigenic nitrogen fraction. The authors were able to correlate a significant peak in authigenic nitrogen in the sediments of Slapton Ley in south-west Devon, with the high nitrate load from the catchment linked to autumn rainfall following the 1976 drought.

5.1.3 AMMONIFICATION OR MINERALIZATION

Ammonium production occurs both in the water column of rivers and lakes and in their sediments. Microbial decomposition converts organic nitrogen to ammoniacal form. This process is oxygen-demanding and regenerates available nitrogen for re-assimilation by primary producers. Ammonification can result in rapid nitrogen cycling between the sediment and the water column. The rate of release of N from decomposing organic matter can be an important factor in determining nutrient limitation in freshwaters. Where N release is relatively slow, as in the example given in Table 5.3, the process of assimilation can become N-limited.

Ammonia in freshwaters can exist as the ammonium cation (NH_4^+) or as the un-ionised ammonia molecule (NH_3). High temperatures and high pH (> pH 8) encourage the conversion of ammonium to ammonia. Ammonia (NH_3) is more toxic than ammonium, and acute toxicity can occur at low concentrations. Fortunately, high concentrations of ammonia are usually only associated with wastewater discharges where biological treatment is minimum. Freshwater plants and invertebrates are more resistant to ammonia than fish. Acute toxicity data for fish suggest that lethal concentrations (96-h LC_{50}) of ammonia range from 0.3 mg l^{-1} for rainbow trout to 3.2 mg l^{-1} for mosquito fish (Ellis, 1989).

5.1.4 NITRIFICATION

Nitrification is a two-stage oxidation process mediated by the chemoautotrophic genera

Table 5.3 Inorganic N and P release in solution from decomposing plankton (after Vaccaro, 1965)

Days	Inorganic N	$\text{PO}_4\text{-P}$	Atomic N:P
0	0	24.8	0
7	12.3 ^a	24.5	1.1
17	39.3 ^a	26.0	3.3
30	43.1 ^a	32.6	2.8
48	54.0 ^b	30.4	3.9
72	57.6 ^c	30.6	4.2
87	58.0 ^c	32.2	4.1

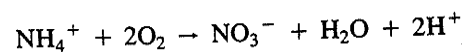
All results in $\mu\text{g l}^{-1}$.

^a $\text{NH}_4\text{-N}$.

^b $\text{NO}_2\text{-N}$.

^c $\text{NO}_3\text{-N}$.

Nitrosomonas (NH_3 to NO_2^-) and *Nitrobacter* (NO_2^- to NO_3^-). In this exothermic reaction, more energy for biosynthesis is obtained from the oxidation of NH_4^+ to NO_2^- ($-84 \text{ kcal mole}^{-1}$) than the subsequent oxidation to NO_3^- ($-18 \text{ kcal mole}^{-1}$). The net reaction is:



The oxidation of ammonia to nitrite by *Nitrosomonas* is usually rate-limiting, so nitrite is rarely present in appreciable concentrations in freshwaters. Nitrate, the end-product, is highly oxidised, soluble and biologically available.

Nitrification is oxygen-demanding and can, in some aquatic systems, create anoxic conditions. This is because *Nitrosomonas* and *Nitrobacter* are strict aerobes, requiring minimum oxygen concentrations around 2 mg l^{-1} to function efficiently. The conversion of 1 mg NH_3 to NO_3^- theoretically requires 4.56 mg O_2 . However, as this reaction is autotrophic, CO_2 may be used as the carbon source and the amount of free oxygen finally used may be less than the stoichiometric requirement at around $4.33 \text{ mg oxygen per mg ammonia}$.

The nitrifying bacteria are also pH and temperature susceptible, with an optimum pH of $8.4-8.6$ (Wild, Sawyer and McMahon, 1971) and requiring a temperature above 15°C . *Nitrosomonas* has a wider temperature tolerance than *Nitrobacter*, and the growth rate constant for these bacteria increases by approximately 10% per degree Celsius up to about 25°C . This temperature limitation suggests that optimum rates of nitrification in British rivers and lakes will be rare (Ellis, 1989). There is also evidence to suggest that the action of nitrifying bacteria at pH 7 may be reduced by as much as 50% (Krenkel and Novotny, 1980). For these reasons, nitrification in surface waters and lakes has traditionally received little attention because the population of nitrifying organisms will often be low and the reaction rate is also low compared with carbonaceous oxidation by heterotrophs. However, nitrification is important where retention times are long and temperatures high (for example, in shallow lakes in summer months). Furthermore, the discharge of nitrifying wastewater effluent to rivers and lakes will shift the balance in favour of increased nitrification.

A high rate of nitrification is essential for efficient N cycling in freshwaters, particularly as nitrate is an important substrate for denitrification (see Figure 5.2). Chemoautotrophic nitrifying bacteria are usually dominant in freshwaters and their activity is generally highest at the sediment-water interface where ammonium-N generation is maximum (Stewart *et al.*, 1982). However, in eutrophic waters in particular, nitrate generated internally through nitrification is often relatively unimportant in comparison with the nitrate load received from the drainage basin. An example for Balgavies Loch, Scotland (Stewart *et al.*, 1982), suggested that nitrification accounted for only 22% of the nitrate load entering the loch in inflowing waters. However, N production *in situ* cannot be entirely ignored as an important component of the aquatic nitrogen cycle because nitrification is often high during summer when water temperatures are high. During this period, catchment inputs are often minimum and algal utilisation of nitrogen is maximum. Nitrification during this period could be critical to the efficient cycling of nitrogen within the aquatic system.

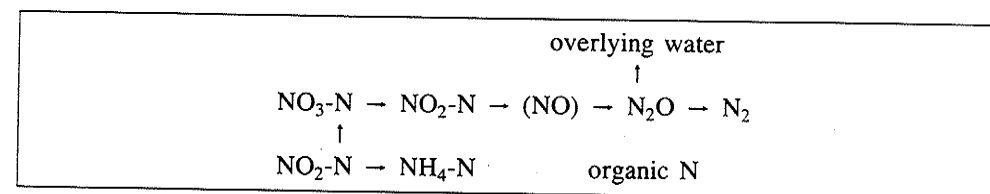
5.1.5 DENITRIFICATION

Loss of nitrate from river and lake systems can occur through denitrification or dissimilatory nitrate reduction. Denitrification is quantitatively more important, particularly in lake

sediments, and is high in summer months (Royal Society, 1983). The rate and extent of denitrification is controlled by the oxygen supply and available energy provided by organic matter. It is seen as an important mechanism in the reduction of nitrate concentrations in reservoirs, but is limited by the requirement for anaerobic conditions and a fixed bacterial carbon supply. Stewart *et al.* (1982) concluded that although denitrification rates in UK eutrophic waters were substantial, they were not sufficient to cope adequately with NO_3^- inputs from agriculture. They suggested that NO_3^- concentration in lakes are likely to continue to increase, unless inputs to the aquatic system from the terrestrial system waters are reduced, or techniques for manipulating the nitrogen cycling processes *in situ* are more effectively exploited. These mechanisms, which are examined in more detail later, may include algal-stripping or encouraging denitrification by placing nitrate-rich waters near the anoxic zone at the sediment-water interface in lakes.

5.1.6 NITROGEN CYCLING BETWEEN FRESHWATERS AND LAKE SEDIMENTS

Lake sediments and sediment deposition zones in slow-moving rivers are both important sinks and sources of nitrogen. Nitrogen in lake sediments is present mainly as organic N. Sedimentation of particulate algae is an important route whereby fixed N reaches the lake sediment. Once there, it is rapidly mineralised. Nitrate transformations in lake sediments may be the result of both preferential microbial utilisation of nitrate over ammonium and N_2 fixation by anaerobes. The overall reaction may have the following form (after Keeney, 1974):



The net result of these transformations is that a proportion of the nitrogen reaching the lake sediments will be converted to biologically available forms.

Stewart *et al.* (1982) describe the sediment-water interface as the 'engine-room' of the aquatic nitrogen cycle, and as lake sediments are generally anoxic, except in highly turbulent lakes, the processes of denitrification and nitrogen fixation dominate at the sediment-water interface. This means that several of the nitrogen pathways in lake sediments are controlled by the reduction-oxidation status at the sediment-water interface. Other factors include pH, available carbonate, available calcium and phosphorus (Keeney, 1974). Within the lake sediments, ammonification is more important, particularly in summer months when temperatures are high. Nitrogen immobilisation can be important in lake sediments in winter months.

Liao and Lean (1978) evaluated the nitrogen dynamics in the Bay of Quinte, Ontario, using limnocorrals by measuring seasonal changes in the concentrations of nitrate, ammonia and dissolved organic and particulate nitrogen in the lake waters and pore-waters of the lake sediments. They found that the seasonal changes in the nitrogen status of the lake began with a decline in particulate N in summer, which was followed by an increase in NH_3 , and finally resulting in an increase in NO_3^- throughout the winter. Their results suggest that nitrification is an essential process in nitrogen cycling in lakes. However, although the importance of

lake sediments as a net source of biologically available N was small, Liao and Lean (1978) concluded that the flux of nitrogen to and from the lake sediments was a significant component of the nitrogen cycle. This conclusion was based on nitrogen budgets for the lake, which showed that the catchment nitrate loading together with N_2 fixation were approximately equal to the net change in the total combined N in the lake water column. This suggests that denitrification at the sediment-water interface is not important. However, most of the nitrogen entering the lake system from the catchment was lost over the year, which implies that denitrification *must* be important at least for some periods of the year. The results suggest that an accurate interpretation of nitrogen cycling in lakes must be seasonally based and must incorporate the role of the lake-sediment N in the nitrogen budget. The authors also suggest that lake ecosystems are capable of compensating for low- or high-catchment nitrogen loads.

Contrary to the finding of Liao and Lean (1978), for Alderfen Broad in the Norfolk Broads, Phillips (1977) suggested that sediment was an important nitrogen source in summer because changes in the nutrient budget of the Broad could not be accounted for by changes in the nutrient load of the inflowing streams. Reductions of NO_3^- -N in the Broad in spring are thought to be the result of removal by benthic algae and planktonic material.

5.2 SOURCES OF NITROGEN IN FRESHWATERS

Nitrogen in freshwaters is derived from three key sources:

- (1) Rainfall and dry deposition;
- (2) Domestic sewage and industrial effluents;
- (3) Agricultural land.

While geochemical and topographical catchment factors will establish a regional *potential* for the nitrogen content of receiving waters, human impact can result in greater nutrient export than can natural factors. Agricultural and industrial activities usually result in *additions* to the nitrogen cycle either as inorganic and organic fertilisers or as atmospheric pollutants. A further source is domestic sewage discharge.

5.2.1 THE EVIDENCE FOR NITROGEN INCREASES IN SURFACE WATERS AND LAKES

Any examination of nitrogen sources in freshwaters, which invariably include increased inputs as a result of human activity, must start by examining the evidence for increased nitrogen concentrations in surface waters and lakes. The WHO guidelines for nitrate in drinking water are:

- (1) Recommended concentration: $< 50 \text{ mg l}^{-1} NO_3^-$
($< 11.3 \text{ mg l}^{-1} NO_3\text{-N}$)
- (2) Acceptable concentration: $50\text{--}100 \text{ mg l}^{-1} NO_3^-$
- (3) Not-recommended: $> 100 \text{ mg l}^{-1} NO_3^-$

The 1980 EC Directive is more stringent, with a guide level of $25 \text{ mg l}^{-1} NO_3^-$ and a maximum acceptable concentration of $50 \text{ mg l}^{-1} NO_3^-$ for water intended for human consumption. Current EC legislation will extend these human health considerations to environmental limits. There is no current human health legislation for ammonium in

freshwaters. Ammonium concentrations in rivers rarely exceed $0.5 \text{ mg l}^{-1} NH_4\text{-N}$ except where the sewage or industrial load is high; here concentrations may reach $2 \text{ mg l}^{-1} NH_4\text{-N}$. Instream nitrogen transformations prevent high ammonium concentration being maintained in surface waters except in polluted environments.

5.2.2 RIVERS: CONCENTRATIONS AND TRENDS

While national monitoring of nitrogen in rivers covers nitrate, and in some cases ammonium concentrations, there is a paucity of information on organic or total nitrogen concentrations. Any evaluation of the long-term trends in nitrogen concentrations in rivers is therefore only covered in part here; for further details see Chapter 10.

There are few rivers in the UK for which long-term water quality records exist. Casey and Clarke (1979) examined an 11-year nitrate record for the River Frome, UK, based on weekly nitrate samples. Their results suggest an average increase in the nitrate concentration in the Frome of $0.11 \text{ mg l}^{-1} NO_3\text{-N}$ per year. Figure 5.3 shows nitrate concentration data for five UK rivers with long-term records. The progressive increase in river nitrate concentration over the period of the records is clearly shown. All the records pinpoint the high nitrate concentration recorded in rivers following the 1976 drought.

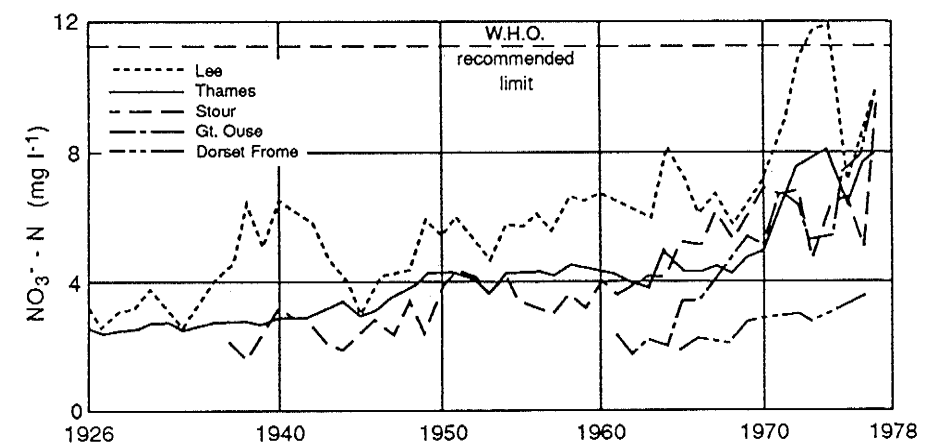


Figure 5.3 Trends in mean and annual nitrate concentration for five UK rivers (modified from Royal Society, 1983)

Figure 5.4 illustrates the 20-year nitrate record (1970–90) for a small grassland and arable catchment in south-west Devon (Heathwaite and Burt, 1991). The record was derived largely from weekly sampling with two periods of more frequent sampling (1983–5 and 1987–9), where 15-minute intervals were used during storm events and daily samples at times of low flow. The impact of the 1976 and 1984 droughts are clearly reflected in the nitrate concentration increase recorded in the autumn of those years. Over the period 1970 to 1990 a significant increase in the average stream nitrate concentration was recorded from 5 mg l^{-1} in 1970 to $8 \text{ mg l}^{-1} NO_3\text{-N}$ in 1990 (Heathwaite and Burt, 1991). Wilkinson and Green (1982) report similar nitrate concentration increases between 50% and 400% for 12 UK rivers over a 20-year period up to 1982.

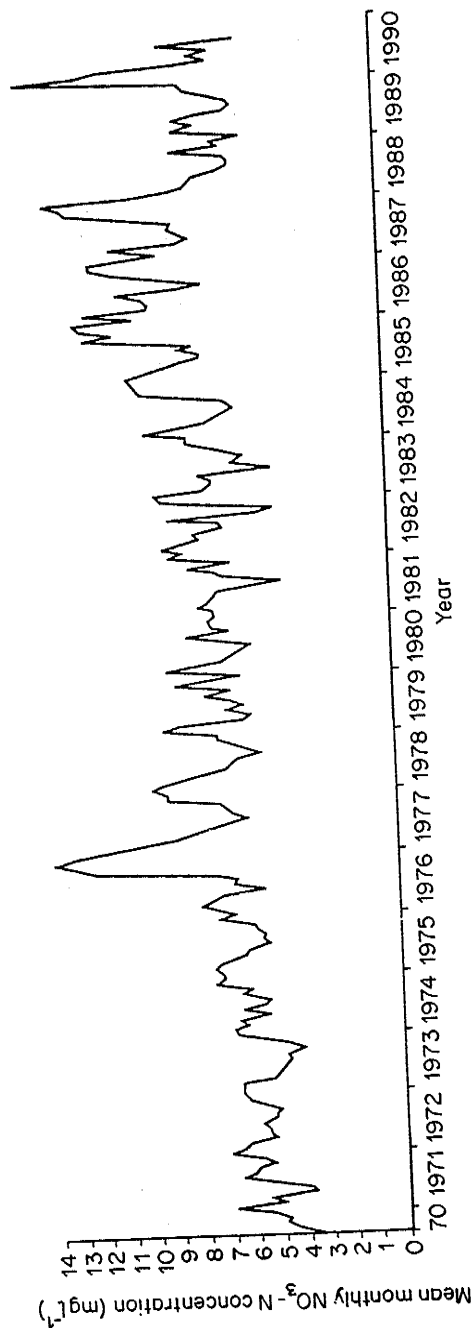


Figure 5.4 The 20-year nitrate record for the Slapton Wood catchment, Devon (after Heathwaite and Burt, 1991)

Figure 5.5 illustrates the seasonal fluctuation in stream nitrate concentration through the year for four subcatchments of the Slapton Ley catchment in south-west Devon, UK. The nitrate load is closely linked to the rainfall:runoff relationship for each subcatchment. The variation in the stream nitrate load for the different subcatchments may be accounted for by variations in catchment topography and land use (Heathwaite, Burt and Trudgill, 1989). Similar seasonal trends in stream and river nitrate concentrations have been reported by Casey and Clarke (1979) for the river Frome. Dermine and Lamberts (1987) also report seasonal variation in nitrate concentration in the Belgian Meuse which they attribute to variations in river discharge. At low discharge (less than $150 \text{ m}^3 \text{ s}^{-1}$) nitrate leaching from catchment soils increased river nitrate concentration. At higher discharges, nitrate dilution by surface runoff from the catchment lowered river nitrate concentrations. Such patterns are obviously dependent on the runoff characteristics of the catchment and antecedent soil moisture conditions (see also Chapter 10).

Models of river nutrient loads are available for the prediction of future nitrate trends in rivers — for example, the Thames Catchment Model (Onstad and Blake, 1980). This simple model has three components:

- (1) The annual mean nitrate concentration in the Thames based on the long-term nitrate record (1928+);
- (2) The catchment input based on precipitation, land use, nitrogen mineralisation rates and fertiliser application rates, denitrification and volatilisation estimates, and removal of nitrogen in crops;
- (3) A transfer component, relating (1) to (2).

Similar models are being developed for other catchments with long-term records (e.g. Johnes and O'Sullivan, 1989; Heathwaite and Burt, 1991).

5.2.3 LAKES: CONCENTRATIONS AND TRENDS

Upland lakes and reservoirs in the UK are often naturally oligotrophic; here concentrations of nitrate seldom exceed 2 mg l^{-1} (Royal Society, 1983). The dissolved organic nitrogen fraction in these lakes is normally greater than the dissolved inorganic nitrogen fraction, and primary productivity is low. The main source of organic nitrogen is catchment runoff.

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 from the catchment. High inorganic nitrogen inputs to lakes have been recorded from heavily fertilised agricultural catchments (Stewart *et al.*, 1982; Foy, Smith and Stevens, 1982; Heathwaite and Burt, 1991), and where urban effluent is discharged into the lake (Smith, 1977; Foy, Smith and Stevens, 1982; Stewart *et al.*, 1982).

The fractionation of the total N pool in lakes generally follows the pattern recorded by Stewart *et al.* (1982) in Balgavies Loch, Scotland. They found that the major N pools were dissolved inorganic N, dissolved organic N and particulate organic N. Keeney (1973) suggests the following nitrogen concentration ranges for lake waters: nitrate $0\text{--}4 \text{ mg l}^{-1}$, ammonium $0\text{--}5 \text{ mg l}^{-1}$ (higher concentrations are recorded in anoxic bottom waters and sediment interstitial waters); nitrite $0\text{--}0.01 \text{ mg l}^{-1}$ (higher in sediment interstitial waters); dissolved organic N $0\text{--}2.5 \text{ mg l}^{-1}$. Organic N often accounts for over 50% of total dissolved nitrogen in lake waters, although this is dependent on the nutrient status of the lake.

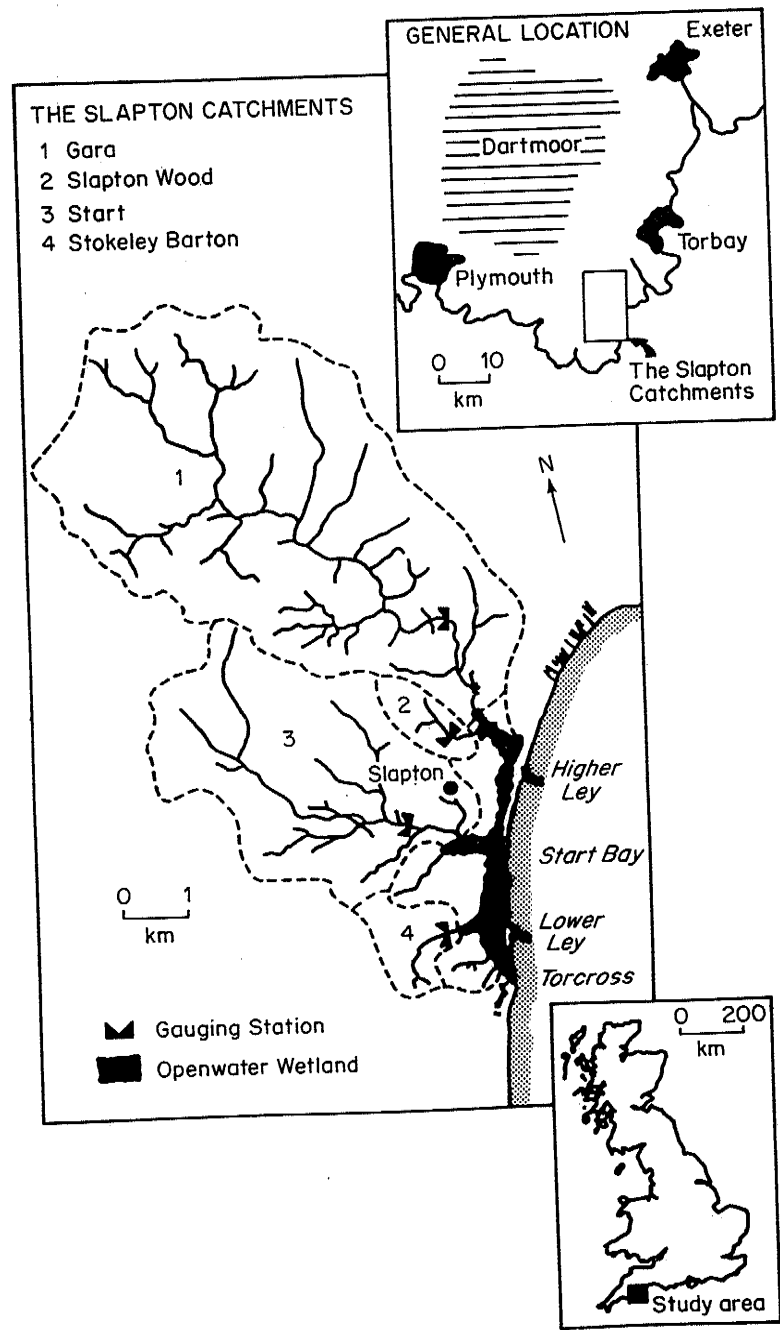


Figure 5.5 The seasonal relationship between nitrate load (kg km^{-2}) and catchment runoff for the Slapton catchments (after Heathwaite *et al.*, 1989)

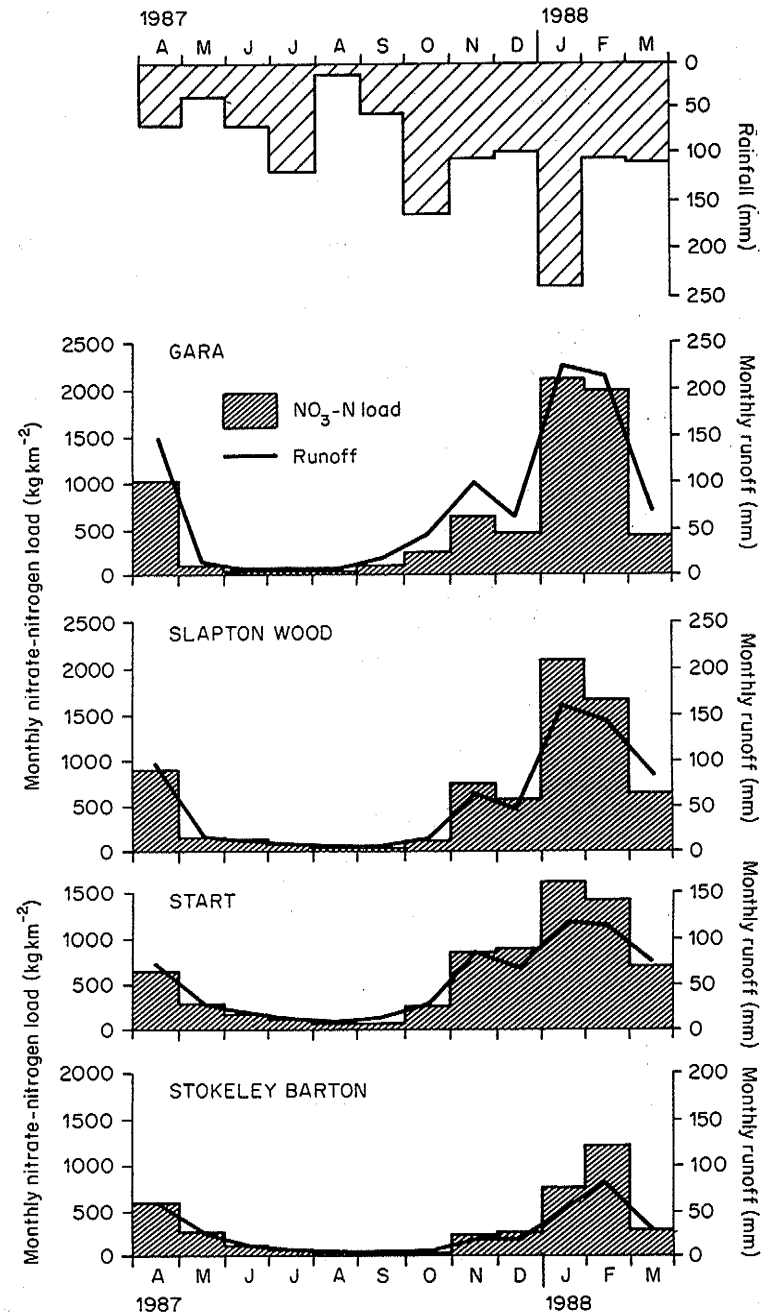


Figure 5.5 (continued)

When evaluating nitrogen cycling in lakes (and surface waters), it is important to consider seasonal fluctuations in the catchment nitrogen load and the rate of nitrogen cycling within the lake. Stewart *et al.* (1982), for example, found that the dissolved organic N pool showed little seasonal variation, whereas the dissolved inorganic pool, dominated by nitrate, shows the strong seasonal variation that has also been recorded in river systems (see, for example, Burt *et al.*, 1988; Heathwaite and Burt, 1991).

The processes and patterns of N cycling in lakes is, to a large extent, determined by the morphology of the lake and the influence of its catchment. The characteristics of lakes vary markedly from deep, oligotrophic lakes such as Loch Morar in Scotland (Maitland, 1981) to relatively shallow and commonly more eutrophic lakes such as Lough Neagh in Northern Ireland (Foy, Smith and Stevens, 1982) and Slapton Ley (O'Sullivan *et al.*, 1991) in south-west Devon. Peterson and Stewart (in Royal Society, 1983) found that the total nitrogen concentration in lakes of varying nutrient enrichment ranged from 0.51 mg l⁻¹ for Craighush, an oligotrophic Scottish lake, to 6.86 mg l⁻¹ for hypertrophic Forfar loch. The dissolved organic nitrogen fraction formed approximately 30% of total N in the oligotrophic lake and nearly 90% of total N in the hypertrophic lake, demonstrating the importance of catchment sources in nutrient-rich lakes.

Nitrogen cycling in reservoirs has also been shown to vary with catchment characteristics and upland or lowland location. In Welsh upland reservoirs, for example, nitrate concentrations are low enough to make regular monitoring unnecessary (Scott, 1975). However, in lowland reservoirs, the increase in nitrate concentration in rivers has also led to a rise in the nitrate concentration of a number of reservoirs (for example, Grafham Water Reservoir, a water supply for Anglian Water, UK (Wilkinson and Greene, 1982)). Similarly, the average annual concentration of nitrate in Farmoor Reservoir which draws water from the river Thames near Oxford has risen from 2 mg N l⁻¹ in 1961 to 6 mg N l⁻¹ in 1980. Denitrification in reservoirs is an important process by which this increased catchment nitrogen load entering reservoirs is reduced (Wilkinson in Royal Society, 1983).

5.3 MODIFICATION OF THE NITROGEN CYCLE BY HUMAN ACTIVITY

5.3.1 THE EFFECT OF LAND USE ON NITROGEN IN FRESHWATERS

Nutrient export from agricultural land, and the ultimate expression of this export in the trophic status of a waterbody, is determined both by physical parameters (for example, precipitation intensity and duration, relief, geology) and land-use modification, particularly where inorganic or organic fertilisers are added or the land is grazed (see Chapters 10 and 12). The catchment factors affecting the trophic status of a lake system are summarised in Figure 5.6, which demonstrates how the terrestrial and aquatic components of the drainage basin are linked by the transfer of sediment and solutes from land to water. Note that neither external catchment controls nor in-lake nutrient concentrations exclusively control lake productivity. The physical and biotic structure of the waterbody (for example, lake depth and flushing rate) are also important. Nitrogen input to a waterbody is also affected by the degree of biological activity in the catchment, particularly microbial and plant activity: biological nitrification and denitrification affect the nitrogen flux in the catchment.

Land use, together with the efficiency of chemical cycling and hydrological processes in the catchment, are key parameters determining the quantity of nitrogen exported from the

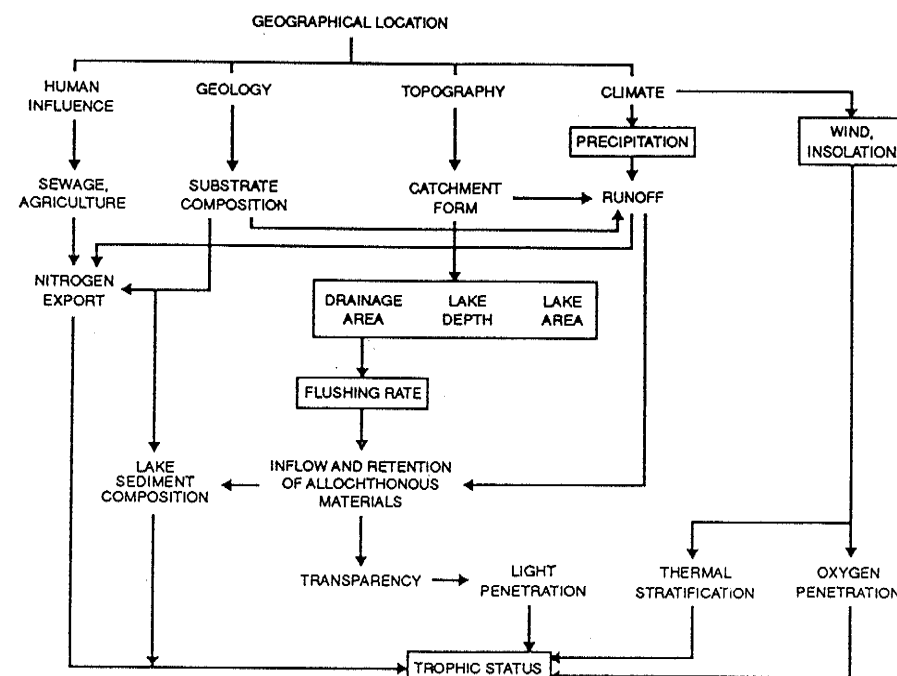


Figure 5.6 Interrelationships affecting lake trophic status (modified from Ryding and Rast, 1989)

catchment. For example, a negative correlation between nitrate input to the aquatic system and the proportion of riparian marshland or floodplains in the catchment might be anticipated because anaerobic decomposition and hence denitrification are likely to be high in waterlogged zones (see, for example, Haycock, 1991). The land-use controls given below are likely to be important in determining the magnitude of nitrogen inputs to the aquatic system:

- (1) Presence or absence of grazing animals (organic N);
- (2) Timing of ploughing and related operations;
- (3) Amount and timing of fertiliser application;
- (4) Type of manure or inorganic fertiliser used;
- (5) Extent of crop cover;
- (6) Soil type and drainage;
- (7) Quantity and frequency of fertiliser application.

Figure 5.7 indicates the range of total nitrogen loads for a number of non-point catchment sources including rural, urban and atmospheric contributions. Table 5.4 provides an estimate of the nitrogen pollution load from different non-point sources in the USA.

Forest ecosystems, for example, have a relatively low nitrogen load (Table 5.4) because most mineralised nitrogen is recycled to vegetation. However, removal of this vegetation can accelerate the export of nitrogen to surface waters. Furthermore, changes in soil temperature and moisture as a result of the removal of forest cover can accelerate nitrogen mineralisation and lead to further nitrogen losses as a result of the low potential for vegetation uptake (Likens *et al.*, 1977). Smolen (1981) examined arable non-point sources of nitrogen in a paired catchment study in Virginia. He recorded a doubling of the discharge-weighted

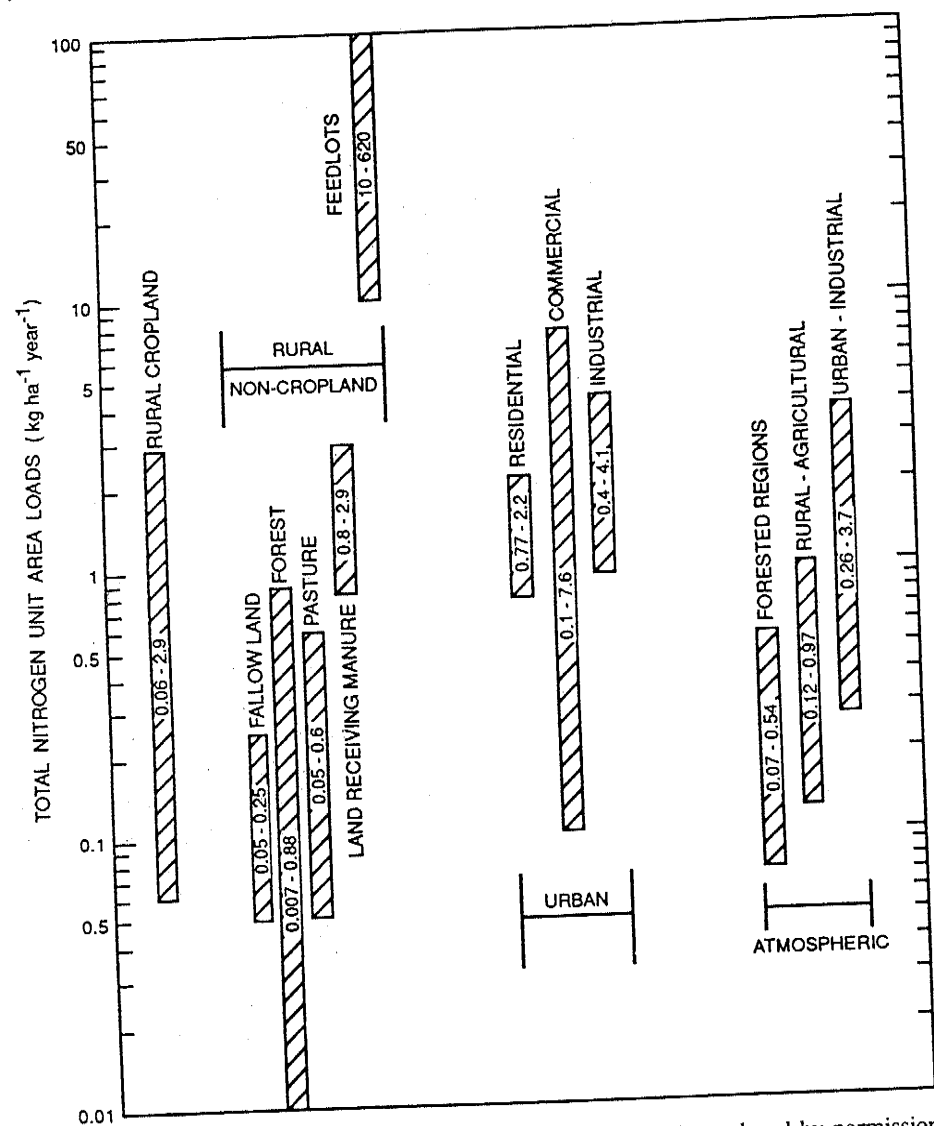


Figure 5.7 Total nitrogen loads for a range of non-point sources (reproduced by permission from Loehr, 1974)

nitrogen concentration of stream waters as a result of agricultural activity. Most of the increase in stream nitrogen was found in the soluble inorganic fraction. In comparison with arable land, nitrogen export from grassland is usually lower because grass roots rapidly exploit available soil nitrogen. Wild and Cameron (1980), for example, found that less than 10% of fertiliser applied to grassland was leached. The figure for arable land was around 15% N leached. The efficiency of fertiliser N use will depend on climatic conditions during the growing season and the timing of fertiliser application in relation to rainfall. Enhanced nitrate leaching may occur when grassland soils are ploughed.

Table 5.4 Nitrogen contribution to surface waters from non-point sources (modified from Loehr, 1974)

Non-point source	Nitrogen load ^a
Arable	4.3
Pasture	2.5
Forest	0.30
Urban runoff	0.15
Rural roadways	0.0005
Small feedlots	0.17
Landfill	0.026

^aN load in MT a⁻¹.

5.3.2 NITROGEN EXPORT FROM URBAN DOMESTIC AND INDUSTRIAL DISCHARGES

Although values for nitrogen export from urban land ranging from 1.9 to 14 kg N ha⁻¹ a⁻¹, are reported in the literature (see, for example, Loehr, 1974), detailed studies on nitrogen loads from urban areas are scarce. Urban surface water runoff can contribute a high nitrogen load to the aquatic system. The nitrogen load from urban areas will vary with the annual precipitation and the proportion of impermeable surface areas in the urban catchment. This relationship is illustrated in Figure 5.8. Surface water runoff from urban areas may contain over four times the nitrogen load of wooded ecosystems (OECD, 1982). The two key controls on non-point source nitrogen losses from urban areas are rainfall (as in rural areas) and the impermeable surface area. The relationship between these two controls is demonstrated in Figure 5.8.

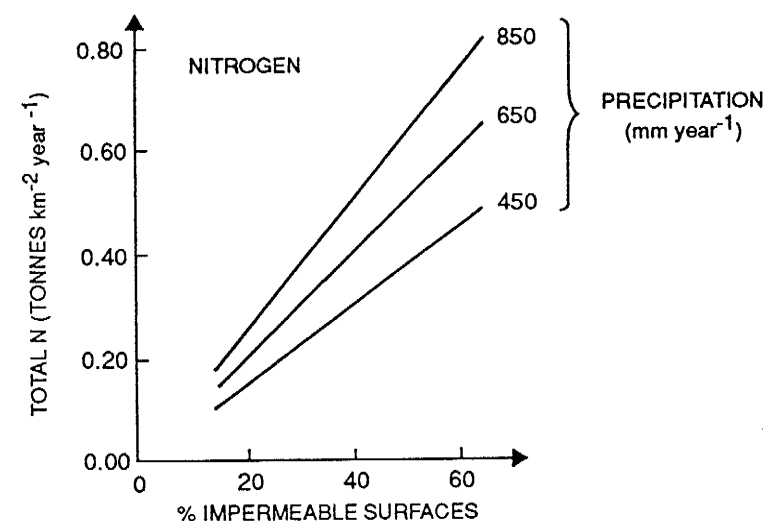


Figure 5.8 The estimated total nitrogen load from urban areas as a function of precipitation and the proportion of impermeable surfaces (redrawn from Ryding and Rast, 1989)

Point sources of nitrogen are largely associated with urban areas and, in particular, domestic sewage because nutrients in domestic and industrial wastes are rarely removed. However, important agricultural point sources do exist (for example, manure and silage waste from intensive livestock units).

The nutrient load from human waste is estimated at 10.8 g nitrogen per head per day. Nitrogen in wastewaters exists in four forms: $\text{NH}_4\text{-N}$ (50–60%), NO-N (up to 5%), $\text{NO}_3\text{-N}$ (up to 5%) and organic nitrogen (40–60%). Untreated sewage contains roughly 55 g m^{-3} total nitrogen and 25 g m^{-3} $\text{NH}_3\text{-N}$. After secondary sewage treatment, this load is reduced to between 20 g m^{-3} to 50 g m^{-3} total nitrogen, and negligible concentrations of $\text{NH}_3\text{-N}$. Moss *et al.* (unpublished) report ammonium concentrations in sewage works effluent in the Norfolk Broads ranging from $1.0\text{--}6.2 \text{ g m}^{-3}$ $\text{NH}_4\text{-N}$. The variable degree of nitrification during sewage treatment results in a wide concentration range for ammonium. Nitrate concentrations were found to fluctuate between $40\text{--}50 \text{ g m}^{-3}$ $\text{NO}_3\text{-N}$. Annual nitrogen loads to the river Brue, Norfolk, were calculated as 15 tonnes $\text{NO}_3\text{-N}$ and 0.7 tonnes $\text{NH}_4\text{-N}$ (Moss *et al.*, unpublished). Nitrate concentrations ranges for the Slapton sewage works, which discharges into Slapton Ley, a large, eutrophic freshwater lake in south-west England, are of the order $15\text{--}25 \text{ g m}^{-3}$ $\text{NO}_3\text{-N}$. Here a natural reedbed system was found to be very effective at reducing nitrate concentrations in sewage effluent to around $0.5 \text{ mg NO}_3\text{-N}$ within 10 m of the sewage works outflow (Trudgill, Heathwaite and Burt, 1990).

Table 5.5 indicates the annual nitrogen, phosphorus and BOD loads from human and animal sources, together with an estimate of the load from cropped agricultural land. Nitrogen loads from human populations are high where there is limited biological treatment of the waste. However, these nitrogen loads are small in comparison with the potential nitrogen export from livestock. This form of N-loading is primarily diffuse; the contribution to the surface water nitrogen load will depend on the transport mechanisms from the land to the stream. The diffuse nitrogen load from livestock is potentially higher than that from fertiliser-amended land (Ryding and Rast, 1989).

Table 5.5 Potential catchment nutrient loads (modified from Ryding and Rast, 1989)

Type of load	Annual population ^a equivalent		
	BOD	TN	TP
One person; no treatment	1	1	1
One person; septic tank	0.7	0.8	0.8
One person; primary treatment	0.2	0.4	0.4
One person; secondary treatment	0.1	0.3	0.1
One person; tertiary treatment	2.0	12	5.0
One livestock unit; ^b diffuse loss, manure amendment	0.5	3	0.6
One livestock unit; 6 months permanent grass, 6 months dry feed	—	9	0.5
Cropped agricultural land; ^c no organic manure, inorganic fertiliser applied	—	9	0.5

^aOne population equivalent — 54 g BOD, 13 g N, 2 g P.

^bOne livestock unit = 1 cattle/horse, 6 pigs, 14 sheep, 150 poultry.

^cAssumes N fertiliser applied at rate: 30 kg ha^{-1} cereal, 40 kg ha^{-1} roots, 80 kg ha^{-1} vegetables.

5.3.3 NITROGEN EXPORT FROM NON-POINT AGRICULTURAL SOURCES

Although point sources of nitrogen can be important, on a national scale, non-point or diffuse nitrogen sources are thought to dominate nitrogen transport pathways from terrestrial to aquatic systems (Royal Society, 1983).

5.3.3.1 Livestock and animal wastes

Livestock waste can be a valuable soil amendment because its high organic content gives it slow nutrient release characteristics and enhanced soil moisture-retention capacity. The main limitation on its value as a nitrogen fertiliser is its uneven spatial distribution together with the relatively high losses through ammonia volatilisation, particularly in warm weather. A further problem relates to trampling ('poaching') of the land surface by livestock. This can significantly reduce the infiltration capacity of the upper soil layers which can lead to high ammonium losses in surface runoff (Heathwaite, Burt and Trudgill, 1990).

The intensification of livestock production, achieved by increasing the input of allochthonous nutrients, such as artificial feed, increases the potential nitrogen load from livestock wastes. For example, the number of sheep and poultry on agricultural holdings in England and Wales doubled from 1950 to 1980. Over the same period the number of pigs trebled. Only cattle show relatively small increases (18% rise) (MAFF Agricultural statistics). Greater allochthonous inputs to the system are likely to mean greater nutrient export from the system. This is either in the form of livestock waste from intensive animal rearing units or as slurry and farmyard manure (see Table 5.5). Loehr (1974) suggests that the nitrogen load for land receiving manure is around $4\text{--}13 \text{ kg N ha}^{-1} \text{ a}^{-1}$, whereas an intensive animal rearing unit may have a potential nitrogen load as high as $1600 \text{ kg N ha}^{-1} \text{ a}^{-1}$.

Nitrogen waste from animal-rearing units is at least a *point* source of nutrient input to the aquatic system, and so *theoretically* is relatively easily controlled. Application of organic manures to land creates a *non-point* or diffuse source of nitrogen enrichment, the effect of which depends largely on timing of application and antecedent soil characteristics. Slurry application requires at least a threefold dilution for spray application to the land, which in turn creates a high runoff and nitrogen leaching potential. Unfortunately the availability of livestock waste is high in early spring following winter housing. Surface application in this period is likely to result in high runoff because the soil moisture content will be high (for further discussion see Chapter 11).

Cattle manures and slurries typically contain 1.5% N, whereas poultry manure contains up to 10% N (Royal Society, 1983). UK studies suggest that approximately 50% of the nitrogen load from cattle and 100% of the nitrogen load from sheep was directly voided onto the land (Royal Society, 1983). In England and Wales, the total nitrogen load voided in faeces and urine (739 Kt; 1978 figures) approaches that of inorganic fertilisers (924 Kt). It has been calculated that on the east coast of Scotland approximately 75% of the nitrogen present in organic manures applied to the land between November and December is lost to the aquatic system by the following March (Gostick, 1982). Organic wastes exert a high biological, chemical and nitrifying oxygen demand on the aquatic system. Furthermore, a high concentration of ammonia is toxic to many organisms (Ellis, 1989).

5.3.3.2 Inorganic fertilisers

One of the key problems with the application of both inorganic and organic nitrogen fertilisers to land is the 'balancing act' required to match crop demand to fertiliser supply. While rarely practicable on economic grounds, repeat applications also cause physical damage to the soil from farm machinery. Fertiliser applications, therefore, typically occur in large batches. This nutrient stockpile is potentially a major non-point source of nitrogen for aquatic systems.

In 1981 an average of 130 kg N ha⁻¹ was added to UK agricultural crops, with average dressings for 2–7-year grass leys of 170 kg N ha⁻¹ and permanent grassland of 97 kg N ha⁻¹ (Royal Society, 1983). At these rates, the annual application of nitrogen to agricultural land is approximately 3 Mt. The annual output of nitrogen from agricultural land in the UK can be subdivided into: crops and grass (1.4 Mt), leaching 0.3 Mt and ammonia volatilisation from livestock waste (0.5 Mt) (Royal Society, 1983). These figures suggest that an equivalent of roughly one third of the annual application of fertiliser nitrogen is lost through leaching (Foster, Cripps and Smith-Carington, 1982; Burns and Greenwood, 1982).

Nitrate leaching from agricultural land in autumn is one of the key non-point sources of stream nitrogen (see Figure 5.5 and Chapter 9). Nitrogen may be derived from unused fertiliser residues applied earlier in the year or from mineralisation of soil organic N. The relative importance of each fraction depends on factors such as crop cover, soil texture, topography and proximity to the stream, fertiliser treatment and rainfall intensity and duration. For a range of different UK soils, Macdonald *et al.* (1989) suggest that mineralisation of organic N, rather than unused fertiliser-N, is the major source of potentially leachable inorganic nitrogen in autumn.

5.4 NITROGEN PATHWAYS

The main outputs of nitrogen from the biosphere occur through the processes of denitrification and leaching. Denitrification, although representing a loss from the system, is a potentially useful process in nitrogen-enriched ecosystems because a reduction in nitrate entering the aquatic system is possible. Leaching is primarily a nitrate transfer process via subsurface water movement. Nitrogen loss through leaching from the terrestrial system is particularly important in arable soils where most soil nitrogen is present as nitrate. In forest and grassland soils, inorganic nitrogen concentrations are generally lower (Royal Society, 1983), and a larger soil ammonium fraction may exist. Furthermore, as the positively charged ammonium ion tends to be adsorbed onto soil particles, its key hydrological pathway is in association with surface runoff and erosion, rather than in subsurface flow.

5.4.1 NITROGEN TRANSFER FROM HILLSLOPE TO STREAM

In most surface waters and lakes, the catchment nitrate load dominates the total N pool for most of the year with the exception of the summer period. This means that the terrestrial system exerts an important control on N cycling in freshwaters (Stewart *et al.*, 1982; Heathwaite, Burt and Trudgill, 1989). Nitrate loading is usually highest in winter and spring and lowest in summer and early autumn. High nitrogen concentrations in early winter are a result of soil water recharge in autumn and the increase in nitrogen mineralisation that occurs when soil drying is followed by rewetting. In Slapton Ley in south-west Devon, for example,

Table 5.6 The effect of increased nitrate load on freshwater lakes (after Stewart *et al.*, 1982)

Factor	Blelham	Balgavies
Nitrate load	46	507
Primary productivity	146	136
Denitrification	38	151
Dissimilation to ammonium	7	151

All figures in kg N ha⁻¹.

the total annual nitrate load is 260 tonnes from a 46 km² arable and grassland catchment. Over 85% of this annual nitrate load is delivered between November and February. Other nitrogen sources for this eutrophic lake are negligible in comparison with the nitrate load of the inflowing waters (Heathwaite and Burt, 1991). Hill (1974) similarly found that up to 80% of the annual nitrate load of rivers in the Lee drainage basin, UK, was carried during the winter period.

In surface water and lakes, provided other nutrient and environmental factors are not limiting, primary productivity may increase as a result of increased nitrate load (Table 5.6). If other nutrients are limiting (which is commonly the case with, for example, phosphorus), denitrification and dissimilatory nitrate reduction may increase. Control of excess nitrate usually focuses, therefore, on optimising denitrification (Stewart *et al.*, 1982), often by adding a suitable carbon substrate for the denitrifying organisms. Dissimilatory nitrate reduction does not reduce the nitrate load.

The main routes for nitrogen transfer from hillslope to stream are:

- (1) Nitrate leaching to surface waters or groundwater;
- (2) Input of animal excreta at watering sites;
- (3) Surface runoff of excreta from farmyards or grazed land;
- (4) Leakage of silage effluent;
- (5) Soil erosion.

Leaching is the dominant process of nitrogen transfer from hillslope to stream owing to the high solubility of nitrate; subsurface flow is therefore the major hydrological pathway. The greatest leaching losses of nitrate from soils occur in winter months when residual nitrogen is leached below the root zone (Wild and Cameron, 1980). Depending on local stratigraphy, mobilised nitrate will enter either the surface water or the groundwater zone. A downwards migration rate in the porous sandstones and Chalk limestones of southern England has been estimated at 1 m a⁻¹. At this rate it would take 20–30 years for surface-applied nitrate to reach the water table. Therefore the doubling of nitrogen fertiliser applications in the UK in the 1960s has yet to manifest itself in some surface waters.

5.4.2 INSTREAM NITROGEN TRANSFORMATIONS

Once nitrogen enters the aquatic system, instream nitrogen transformations, as a result of both physical and chemical discontinuities in the stream, will occur. Instream nitrogen transformations are primarily concerned with the metabolic processes of the stream flora and can involve aquatic macrophytes, stream bank macrophytes, epilithic algae, micro-heterotrophs and denitrifying bacteria. Cooper and Cooke (1984), for example, found that aquatic

macrophytes accounted for 73–100% of stream biotic nitrate uptake; Howard-Williams and Downes (1984) suggest that uptake by stream bank macrophytes may be of the order of $0.9\text{--}1.5\text{ g N m}^{-2}\text{ day}^{-1}$.

Stream biota are involved not only in nitrogen uptake but also in nitrogen-transformation processes such as nitrification and denitrification, which remove N from the stream water by transferring it to the biota, atmosphere or stream sediments. Denitrification in wetlands is thought to be particularly important (Swank and Caskey, 1982; Hill and Sanmugadas, 1985). Sloey, Spangler and Fetter (1978) recorded denitrification rates up to $3.5\text{ kg N ha}^{-1}\text{ day}^{-1}$ for US wetlands during the growing season. Denitrification rates in New Zealand pastoral streams were less than $1\text{ kg N ha}^{-1}\text{ day}^{-1}$ (Howard-Williams and Downes, 1984) but were found, in some streams, to match maximum macrophyte uptake rates. Swank and Caskey (1982) suggest that rates of denitrification are positively correlated with total nitrogen and organic matter and negatively correlated with stream sediment nitrate concentrations. However, in order for denitrification to be a significant factor in removing N from wetlands, N_2 must be able to escape to the atmosphere before it is fixed as nitrate. Aerated water overlying anaerobic sediments will restrict N_2 escape, so flow in wetland systems is critical in the denitrification process.

Howard-Williams *et al.* (1982, 1988) attribute nitrate losses in New Zealand streams to macrophyte uptake. They found that in macrophyte-dominated streams, nitrate was reduced to concentrations below 5 mg m^{-3} and increases in dissolved organic nitrogen were negligible (Howard-Williams, Pickmere and Davies, 1988). Modification of stream nitrate concentrations varied seasonally, with high retention of dissolved nitrogen by macrophytes in summer. Similar seasonal trends were recorded by Hill (1979, 1988) and by Haycock (1991). However, Cooper and Cooke (1984) concluded that instream nitrogen removal occurred throughout the year.

Richey, McDowell and Likens (1985), working in the Hubbard Brook Experimental Forest, New Hampshire, did not detect nitrogen depletion where ammonium and urea were added to a stream. This, they suggest, was due to nitrogen cycling by detritus and bryophytes on the streambed, with uptake of ammonium being followed by release of nitrate, so there was no net loss of nitrogen. Wyer and Hill (1984) also found that nitrification and ammonification occurred simultaneously with nitrate reduction in laboratory experiments. In streams receiving $\text{NH}_4\text{-N}$, nitrifying bacteria are important in the conversion to $\text{NO}_3\text{-N}$ and subsequent potential losses through denitrification.

There are a number of important controls on the rate of denitrification: these include temperature, the availability of organic matter as a metabolisable energy source, the nitrate concentration in stream water overlying stream sediments and the stream flow regime and water residence time (Terry and Nelson, 1975). Hill (1988) found that nitrate removal efficiency in streams was low where the stream nitrate load was high. This was thought to be the result of shorter residence times and a higher ratio of water volume to stream sediment areas, although increased flow should increase the oxygen diffusion rate and exchange of nitrogen between organisms and water. Casey and Farr (1982) studied the effect of artificially increased flow on a chalk stream in Dorset. They suggest that, regardless of allochthonous inputs, nitrate concentrations in rivers may increase at high discharge because of the reduction in benthic denitrification at high flow. Pinay *et al.* (1990) use the concept of nutrient spiralling to explain the strong interactions between a stream and its riparian zone, where they suggest that major exchanges of matter and energy take place. Nutrient spiralling is related to the mean distance travelled by a nutrient atom during its cycle and the number of times that nutrient atom is utilised in a section of stream or river. Interactions in the terrestrial-aquatic zone

are thought to lead to changes in the recycling of nitrogen and other nutrients and, in particular, the retention of nutrients during displacement downstream. On a larger scale, Admiraal and Botermans (1989) investigated nitrogen transformations in the lower river Rhine which receives high ammonium inputs from its industrialised catchment. They found that differences in river discharge, sediment grain-size composition and the aeration and turbulence caused by shipping influenced 'in-river' nitrogen transformations and, in particular, nitrification rates.

5.4.3 NITROGEN PATHWAYS IN LAKES AND RESERVOIRS

Once nutrients enter a lake they may be recycled many times between the sediments, aquatic plants and water column. On a longer timescale, lake sediments generally form the ultimate nutrient sink, although this depends on the lake flushing rate and the nature of catchment inputs. For nitrogen, biological fixation can form a potentially significant diffuse source, particularly for eutrophic lakes.

5.4.3.1 Seasonal cycling of nitrogen compounds in lakes

In temperate lake ecosystems, nitrate concentrations show winter maxima which are independent of lake trophic status. This winter maxima arises because (1) surface and subsurface catchment inputs are high as a result of high rainfall and (2) microbial activity is low as a result of low temperatures. Lake trophic status then affects the way in which nitrogen is utilised through the spring–autumn growing season. In eutrophic lakes, and particularly in shallow lakes, the nitrate concentration drops rapidly from winter through to spring as biotic demand exceeds supply once temperatures rise (Figure 5.9). In oligotrophic lake systems, from an initially lower nitrate concentration in the water column, nitrate availability also decreases in summer. The relative decrease is less than that in eutrophic lake systems because biotic demand is lower.

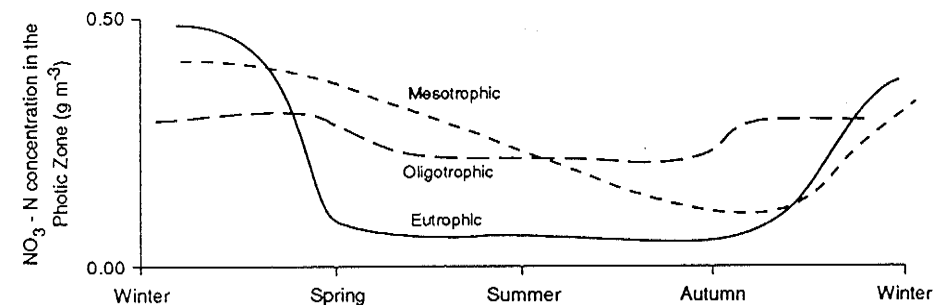


Figure 5.9 The variation in nitrate concentration as a function of lake trophic status (modified from Henderson-Sellers and Markland, 1987)

The hypothetical pattern of ammonium concentration variation in lakes is shown in Figure 5.10. Oligotrophic lakes are expected to show little variation in ammonium concentration throughout the year because lake biomass is small and the organic nitrogen store is therefore small. Mesotrophic lakes generally show an increase in ammonium concentrations at the autumn overturn, although this pattern is only found in deep, stratified lakes. Eutrophic lakes show irregular patterns of ammonium concentration fluctuation throughout the spring–autumn

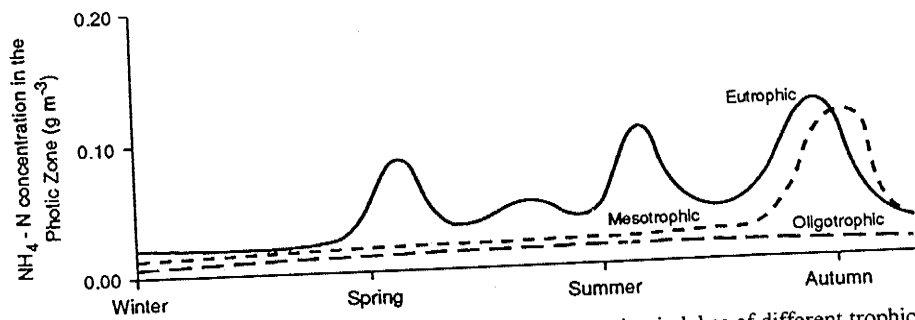
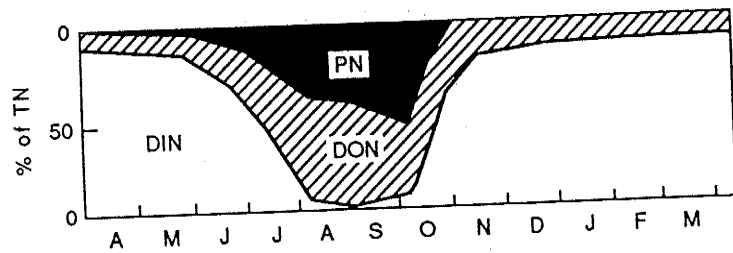
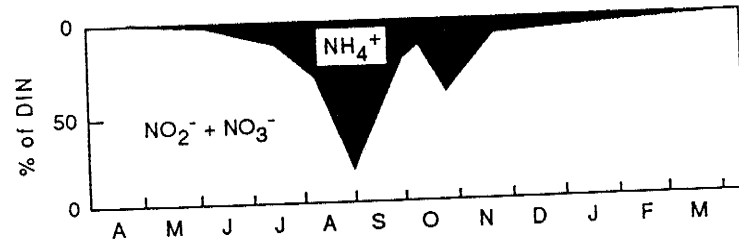


Figure 5.10 Hypothetical seasonal variation in $\text{NH}_4\text{-N}$ concentration in lakes of different trophic status (modified from Henderson-Sellers and Markland, 1987)

(a) Seasonal variation in the contribution of different N fractions to the total N concentration of a eutrophic lake.



(b) Seasonal variation in the inorganic N fraction of a eutrophic lake.



TN = Total Nitrogen
 DIN = Dissolved Inorganic Nitrogen
 PN = Particulate Nitrogen
 DON = Dissolved Organic Nitrogen

Figure 5.11 Seasonal variation in the contribution of nitrogen fractions to eutrophic Rescobie Loch, Scotland (after Peterson and Stewart, unpublished)

period. This is a consequence of the pattern of algal bloom and algal decay which is characteristic of eutrophic waters.

Figure 5.11(a) indicates the contribution of different nitrogen species to nitrogen cycling in eutrophic Rescobie Loch (Peterson and Stewart in Royal Society, 1983). It clearly illustrates the reduced contribution from dissolved inorganic nitrogen in summer which is partially balanced by the larger contribution from dissolved organic and particulate nitrogen derived

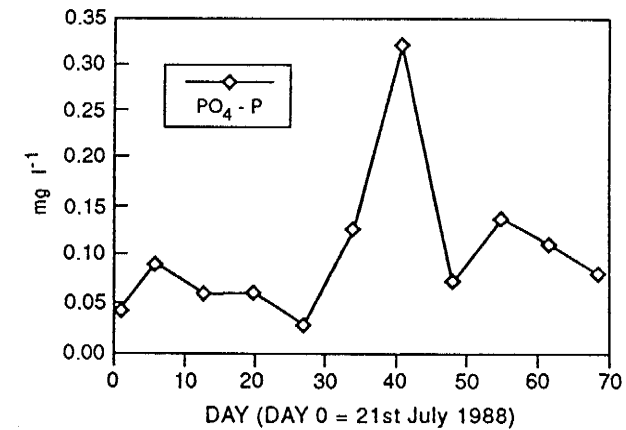
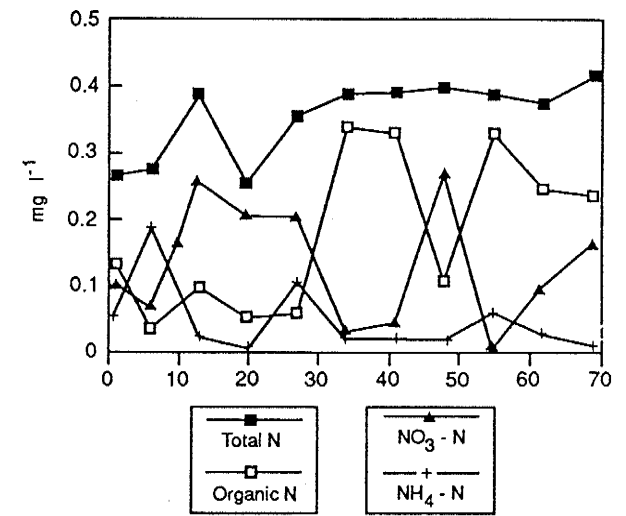
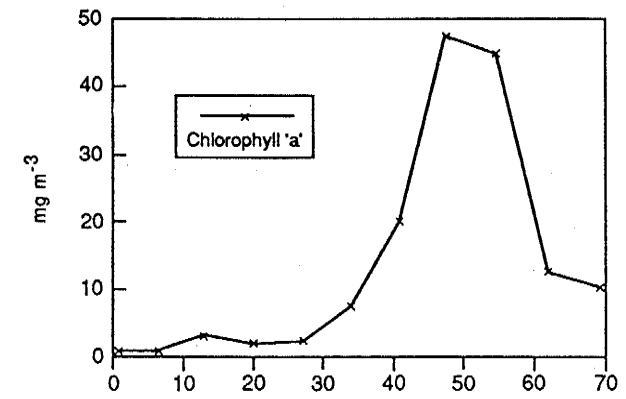


Figure 5.12 Chlorophyll 'a', nitrogen and soluble reactive phosphorus variation in Slapton Ley during an algal bloom, July to September, 1989 (after Heathwaite, 1989)

from lake biota. Figure 5.11(b) illustrates the dissolved inorganic nitrogen fractions for the same period. Nitrate dominates this fraction for most of the year, except when biotic activity is high in summer, when the concentration of ammonium in the lake waters increases.

The pattern of chemical transformations in eutrophic Slapton Ley, south-west Devon, between mid-July and mid-September are shown in Figure 5.12. Blue-green algae begin to appear in Slapton Ley in early May and remain in the water column until December. *Anabaena* are dominant in early summer and there is a shift to *Microcystis aeruginosa*, *Coelosphaerium naegelianum* and *Gloeotrichia echinulata* in autumn (Benson-Evans *et al.*, 1967; Van Vlymen, 1980). High primary productivity indicated by chlorophyll 'a' concentrations above 50 mg m⁻³ and cyanophyte blooms are evidence of eutrophication in Slapton Ley. Chlorophyll 'a' concentrations up to 330 mg m⁻³ in Slapton Ley are reported by Van Vlymen (1980).

The algal bloom represented by peak chlorophyll 'a' concentrations in September (Figure 5.12) appears to have been nitrogen-funded because it coincides with the maximum total nitrogen concentrations in the lake. Biologically available phosphorus peaks before the algal blooms, but concentrations are low during the bloom itself. The concentrations of dissolved inorganic nitrogen, which fall below 0.01 mg TON l⁻¹ in summer, suggest that Slapton Ley, for some periods, is a nitrogen-limited lake. This observation is supported by Van Vlymen (1980). More recent data for the same lake showed that, although inorganic nitrogen concentrations fell in summer, the total nitrogen concentration remained relatively constant and appeared to be maintained by a supply of organic nitrogen. However, because this form of nitrogen is less biologically available, nitrogen may still be limiting in this lake.

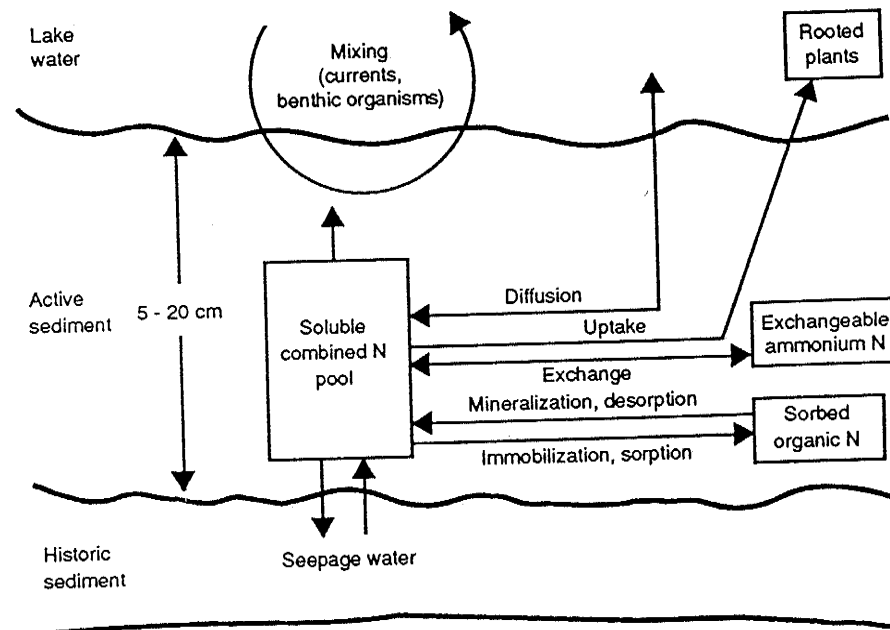


Figure 5.13 Nitrogen cycling at the sediment-water interface (after Keeney, 1973)

5.4.3.2 Nitrogen in lake sediments

Nitrogen reaches lake sediments by sedimentation, nitrogen fixation and nitrate immobilisation (Figure 5.13). Lake sediments typically contain 50–200 kg N per 10 cm sediment depth per hectare (Keeney, 1973), and are thought to act both as a sink and a source of nitrogen, depending on the N status of interstitial or overlying waters.

Readily available nitrogen in lake sediments is held in the ammonium and organic nitrogen forms present in interstitial water, and the ammonium nitrogen on the exchange complex. Diffusion and sediment mixing can release nitrogen in these forms to the water column, although, in general, denitrification is the key process. Chen and Keeney (1974), for example, showed that denitrification was a significant N sink in Wisconsin lakes. In sediment core experiments they found that 15–26% added ¹⁵N-labelled NO₃-N was immobilised to organic N and NH₄-N, the remainder being accounted for by denitrification. Chen, Keeney and McIntosh (1983) studying Lake Michigan, concluded that only 1.2% of the annual catchment nitrogen load was present in the active sediment layer of the lake. They suggested that nitrification and subsequent denitrification at the sediment-water interface was a major nitrogen sink. These nitrogen-cycling processes were, however, thought to be minor relative to the high catchment nitrogen load reaching the lake. Their study concluded that non-point nitrogen sources would be sufficient to maintain eutrophic conditions in the lake even if point sources of nitrogen were reduced.

5.5 THE ROLE OF NITROGEN IN FRESHWATER EUTROPHICATION

One of the key products of eutrophication is excess algal growth. Hayes and Greene (1984), for UK reservoirs, suggested that algal growth becomes a problem where inorganic N concentrations greater than 1.5 mg l⁻¹ and inorganic P in excess of 0.02 mg l⁻¹ are recorded. Although nitrogen is acknowledged as one of the key contributory nutrients in the eutrophication of freshwaters (see Table 5.7), most of the focus is on phosphorus inputs and phosphorus control. There are a number of reasons for this. First, nitrogen is usually derived from non-point sources, so control is difficult. Second, cyanobacteria can fix atmospheric nitrogen rendering control ineffective in some lakes, and third, phosphorus is generally viewed as the 'limiting' (and therefore controlling) nutrient. For British lakes and reservoirs, however, there is good correlation between chlorophyll 'a' concentration and nitrate (Figure 5.14), and hence a good link between lake nitrogen concentration and trophic status.

Table 5.7 Lake loading level (g m⁻² a⁻¹) for total N and total P (after Vollenweider, 1975)

Mean depth (m)	Permissible loading		Dangerous loading	
	Nitrogen	Phosphorus	Nitrogen	Phosphorus
5	1.0	0.07	2.0	0.13
10	1.5	0.10	3.0	0.20
50	4.0	0.25	8.0	0.15
100	6.0	0.40	12.0	0.80
150	7.5	0.50	15.0	1.00
200	9.0	0.60	18.0	2.00

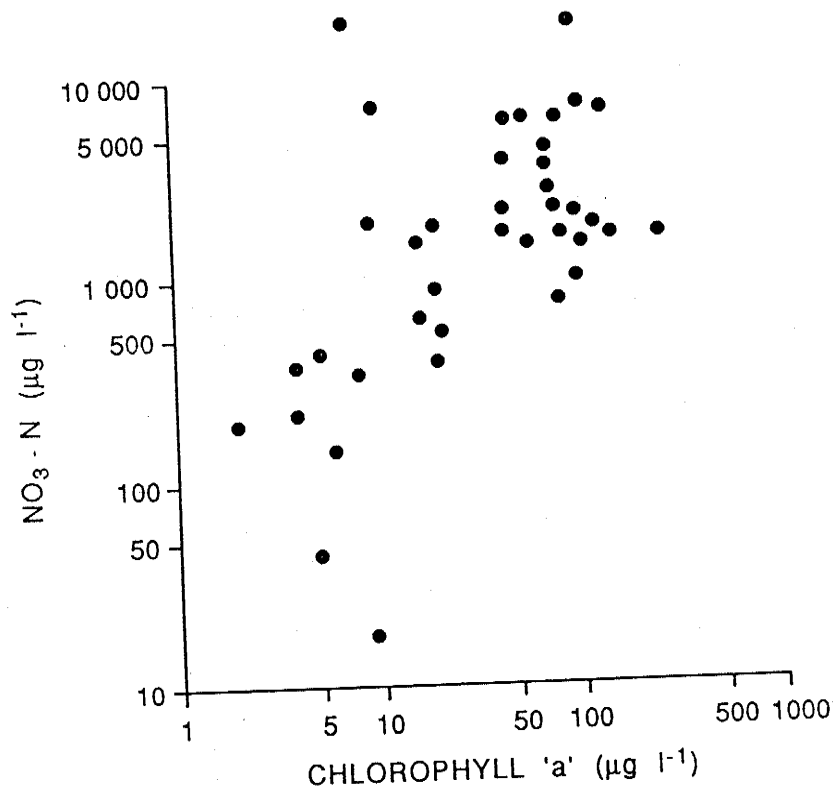


Figure 5.14 The relationship between maximum annual chlorophyll 'a' concentration and maximum $\text{NO}_3\text{-N}$ concentration in British lakes and reservoirs (after Collingwood, 1977)

Nitrogen and phosphorus concentrations tend to increase in parallel as the trophic status increases from oligotrophic through to eutrophic. The N:P ratio decreases from roughly 100N:1P in oligotrophic lakes to less than 10N:1P in eutrophic ones. This suggests a tendency for lakes to shift from phosphorus dependency towards nitrogen dependency with increasing trophic status.

5.5.1 THE TROPHIC STATUS OF FRESHWATER SYSTEMS

Lakes and reservoirs can be broadly described as ranging from oligotrophic (nutrient-poor) to eutrophic (nutrient-rich). The terms have no absolute meaning, but are valuable in reflecting the nutrient status of a waterbody. Eutrophication generally refers to standing waterbodies rather than streams or rivers, where the rate of throughput of nutrients and the rate of water movement are assumed to be too rapid for conditions characteristic of eutrophication to develop.

The identification of trophic status in freshwaters is usually based on establishing boundary values for a number of water quality criteria. Total phosphorus, chlorophyll 'a' and Secchi depth are commonly used (Table 5.8). Nitrogen, although an important determinant of the productivity of a waterbody, is normally excluded owing to the difficulty in establishing effective control strategies based on nitrogen.

Table 5.8 Water quality parameters and trophic status

Trophic category	Total phosphorus ($\mu\text{g l}^{-1}$)	Chlorophyll 'a' ($\mu\text{g l}^{-1}$)	Secchi depth (m)
Oligotrophic	< 10	< 2.5	> 6.0
Mesotrophic	10–35	2.5–8.0	6.0–3.0
Eutrophic	35–100	8.0–25.0	3.0–1.5

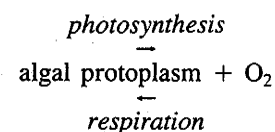
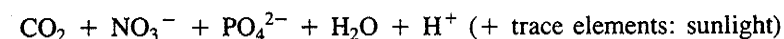
Using the OECD boundary values given in Table 5.8 (OECD, 1982), a waterbody falls into one of the three main trophic categories where no more than one of the parameters deviates from its geometric mean value by ± 2 standard deviations. Collingwood (1977) concluded that 15, 11 and 4 lakes in England, Wales and Scotland, respectively, fall into the eutrophic category on the basis of their maximum chlorophyll 'a' concentrations alone.

5.5.2 THE CONCEPT OF LIMITING NUTRIENTS: HOW IMPORTANT IS NITROGEN?

The whole-lake experiments in Canada (Schindler and Fee 1974; Schindler, 1977) confirmed the importance of phosphorus and nitrogen in lake primary productivity, previously only investigated in laboratory studies. Nitrogen is often seen as the nutrient determining lake productivity, whereas phosphorus is the nutrient limiting growth.

Phytoplankton biomass (indicated by chlorophyll concentration) in a waterbody appears to be proportional to its nutrient load up to a point, beyond which other factors such as carbon or dissolved oxygen concentration exert primary control (Sridharan and Lee, 1977; Lee, Jones and Rast, 1980). The concept of limiting nutrients in waterbodies relies on the fact that both absolute and relative quantities of essential nutrients regulate primary productivity (mainly algal biomass) in the waterbody. Therefore it is assumed that the ratio at which nutrients are taken up and used by algae reflect the relative composition of these nutrients in their cellular material. On this basis, the ratio 106C:16N:1P has become widely cited as the standard reference value for assessing the limiting nutrient in waterbodies (Ryding and Rast, 1989). Carbon is rarely limiting in freshwaters. The assumption is that control of the nitrogen or phosphorus load entering the waterbody from its catchment, or manipulation of the ratio of N:P within the waterbody, should control algal growth.

The limiting nutrient concept is based on the photosynthesis reaction. Conceptually, the reaction can be expressed as follows:



This equation suggests that several variables are involved in the reaction, so theoretically control of any one variable may offer control of eutrophication in waterbodies. Most attention has been focused on control of the external nutrient supply, partly because of the relative complexity of algal processes and partly because some macro-nutrients, particularly phosphorus, offer a *relatively* simple means of limiting nutrient control.

Table 5.9 Approximate levels of nitrogen and phosphorus limitation using N:P ratios (modified from OECD, 1982)

Total N by wt	Total P moles	Inorganic N by wt	Inorganic P moles	Limiting nutrient
< 10	22	< 5	10	N
10-17		5-12		N/P
> 17	37.6	> 12	26.5	P

There is no sharp boundary between phosphorus and nitrogen limitation (Table 5.9). Low N:P ratios favour nitrogen-fixing blue-green algae which are undesirable from a water quality perspective (Schindler, 1977). Sewage effluents, which contain a low N:P ratio because of the high concentration of soluble reactive phosphorus (SRP) released (4N:1P by weight), can shift a waterbody from phosphorus to nitrogen limitation. The N:P ratio in sewage is much lower than that of agricultural runoff, which is commonly between 30:1 and 50:1. However, seasonal variation in both the supply and uptake of these nutrients in aquatic systems complicates this simplistic pattern. Furthermore, the ratio of N:P in surface waters and lakes is not always reflected in the biota. Moss *et al.* (unpublished), for example, recorded a ratio of N:P of 26:1 by weight (64:1 by atoms) for the river Brue in the Norfolk Broads. These values are much higher than the optimum quoted for algal growth (Golteman and Kouwe, 1980). Despite these results, nitrate was often undetectable in the Brue in summer, and severe nitrogen depletion was reported in phytoplankton cells.

The 'biologically' available fraction of nitrogen and phosphorus in the lake epilimnion, rather than total nitrogen and phosphorus concentrations, are critical in funding algal blooms (Table 5.9). The biologically available fractions are: dissolved or soluble reactive phosphorus (SRP) and ammonium-N plus nitrate-N. A biologically available phosphorus concentration less than $5 \mu\text{g l}^{-1}$ and a biologically available nitrogen concentration less than $20 \mu\text{g l}^{-1}$ are usually taken to suggest phosphorus and nitrogen limitation, respectively (Ryding and Rast, 1989).

As the trophic status of a waterbody increases, the mineral nitrogen component becomes relatively more dominant. The inorganic N fraction forms approximately 60% of total N at total N concentrations less than 500 mg m^{-3} and increases to 70% at total N concentrations greater than 5000 mg m^{-3} (OECD, 1982). This trend effectively means that increasing trophic status corresponds with an increase in the 'biologically available' nitrogen fraction in a lake.

Calculation of the atomic ratio of nitrogen to phosphorus in the waterbody and comparison with the algal uptake ratio of 16N:1P is an indication of the potential growth-limiting nutrient in the waterbody. If biologically available N and P are measured in concentration units of mg l^{-1} the 16N:1P atomic reference value then corresponds to a mass ratio of 7.2N:1P. Therefore, if the N:P ratio is less than 7N:1P, nitrogen is potentially limiting because the more rapid removal of nitrogen would limit biotic growth; if the ratio is greater than 7N:1P, phosphorus is limiting. In Swedish waterbodies, Fosberg and Ryding (1980) used a ratio of less than 5N:1P to denote nitrogen limitation and greater than 12N:1P to indicate phosphorus limitation.

A major restriction on applying the concept of limiting nutrients too liberally to freshwaters is that although it is robust under steady-state conditions, it fails where the waterbody is under transient conditions (for example, where a waterbody receives intermittent inputs of phosphorus

or nitrogen). Limiting nutrients will also vary seasonally but practical use of the limiting factor concept tends to assume that a single nutrient, usually phosphorus, is limiting *throughout* the year.

Finally, different uptake and assimilation rates for different primary producers will affect the response of the waterbody to nutrient limitation. Algal populations will compete for the available nutrient resources. Smith (1983) suggested that low N:P ratios encourage dominance by blue-green algae in temperate lakes. Blue-green algae were usually absent above a total N to total P ratio greater than 29N:1P. Some species of blue-green algae are capable of 'luxury' uptake of limiting nutrients, which are stored for later use. Diatoms, for example, are superior competitors for phosphorus, but inferior competitors for nitrogen (Tilman, Kilham and Kilham, 1982). A further complication is that N_2 -fixing blue-green algae can be phosphorus-limited, while non- N_2 fixing algae can be nitrogen-limited. This can occur simultaneously in the same lake.

5.5.3 MODELLING EUTROPHICATION

5.5.3.1 Catchment-driven (nutrient load) models

The key objective of this form of model is control of eutrophication by estimating the nutrient load, particularly from non-point sources, reaching a lake from its catchment. The basis for measurement is normally the subcatchment scale. Simple models are based on steady-state nutrient loadings, whereas more realistic models attempt some subdivision of biologically available and unavailable nutrient forms. Seasonal variations in dissolved and solid-phase nitrogen and phosphorus inputs to the aquatic system may also be included.

The simplest empirical models for estimating the nutrient load to a waterbody are usually of the form:

$$A = a_0 + a_1X_1 + a_2X_2 + \dots + am^Xm$$

where A = average annual nutrient load to waterbody (kg a^{-1}),

X = catchment area (ha) for land use 1, 2... m ,

a = export coefficients (kg ha^{-1}).

The export coefficients (a) are ideally based on intensive water quality sampling in small catchments with a single predominant land use! In practice, export coefficients are usually obtained by collating published information on nutrient export from land uses covering wide geographic ranges (see, for example, Rast and Lee, 1983; Johnes and O'Sullivan, 1989; Johnes, 1990). Ryding and Rast (1989) suggest that nutrient export coefficients should be viewed primarily as a method of obtaining rough estimates of annual nutrient loads.

Coote, MacDonald and De Haan (1979) applied the simple model given above to two years of water quality data for dissolved and total nitrogen from ten Canadian agricultural watersheds. Catchment parameters included land use, fertiliser and manure application, soil erosion, slope, and soil texture. The effect of control mechanisms such as fertiliser reduction or erosion prevention can then be estimated in terms of the potential decrease in the average annual nitrogen load. The main limitation of nutrient export models is that they are usually site-specific as well as being sampling-specific. That is, the sampling interval and sampling season will be reflected in the reliability of the results. Finer resolution of nutrient loading to waterbodies requires evaluation of water and associated nutrient *fluxes* from the land surface and the soil profile. The complexity of these models depends on the required time resolution

and the extent to which biochemical processes are incorporated. The general relationships are:

$$D_{kt} = d_{kt}Q_{kt}TD_{kt}$$

where D_{kt} = dissolved nutrient loss (kg) in surface runoff or baseflow from area k in time t ,
 d_{kt} = dissolved nutrient concentration in surface runoff or baseflow (kg m^{-3}),
 Q_{kt} = surface runoff or baseflow (m^3),
 TD_{kt} = fraction of dissolved nutrients reaching the waterbody from area k .

The total nitrogen load to a waterbody in time t is computed from the sum of nitrogen losses from each catchment source. Non-point nutrient sources can be evaluated on the basis of runoff (Q_{kt}) or by including a term for erosion (X_{kt}). Baseflow nitrogen will be primarily in the dissolved inorganic nitrogen fraction. Assuming the groundwater nitrogen concentration is relatively stable, the dissolved nitrogen load can be expressed as:

$$D_k = d_k Q_{kt}$$

where d_k = dissolved nutrient concentration in groundwater from area k (kg m^{-3}),
 Q_{kt} = baseflow (m^3).

Haith and Tubbs (1981) and Haith (1982) describe a number of mechanisms for estimating non-point nutrient loads from agricultural land in the north-east United States. They found that the main limitation of the form of model given above is the transport factor (TD_{kt}) which is not easily quantified. For dissolved nutrients it is often assumed that $TD_{kt} = 1$ and that the delivery of solid-phase nutrients is equal to the sediment delivery ratio of the catchment (Haith and Tubbs, 1981).

5.5.3.2 Waterbody-driven (mass-balance) models

Based on nutrient mass balance calculations, these models are used to estimate the 'biological' response of a lake to nutrient load reductions normally using simple statistical (usually correlation or regression) parameters. Empirical waterbody models such as those of Vollenweider (1968, 1975, 1976; Rast and Lee, 1978; Ryding, 1980) are valuable in lake-eutrophication control because they are simple and are not data-demanding. In Vollenweider's 1976 model, for example, lake total phosphorus concentrations is computed from the annual areal phosphorus loading ($\text{mg m}^{-2} \text{a}^{-1}$), the annual areal water loading ($\text{m}^2 \text{a}^{-1}$), hydraulic residence time and mean lake depth. Such models are limited, however, because they do not give any indication of the processes involved or the magnitude of the various transport mechanisms responsible for delivering nutrients from land to water. Errors in predicting phosphorus concentrations, for example, can be at least $\pm 30\%$ (Ryding and Rast, 1989).

Waterbody-driven models are usually biased towards prediction of lake phosphorus concentrations. Nitrogen cycling, owing to the complexities of accounting for diffuse inputs and the possibility that nitrogen is not limiting, is not usually considered. Extensions of the basic model exist for other water quality parameters such as, chlorophyll 'a' (Dillon and Rigler, 1974; Smith and Shapiro, 1981), Secchi depth (Rast and Lee, 1978) and dissolved oxygen (Ryding, 1980; Vollenweider and Janus, 1982).

Baker, Brezonik and Kratzer (1985) developed a simple nitrogen-loading model based on the OECD-Vollenweider model (OECD, 1982) for Florida lakes which are commonly nitrogen — rather than phosphorus — limited, owing to excess P supply from phosphate-rich catchment soils. Canfield *et al.* (1983, 1984) again for Florida lake systems suggested the following

model for algal biomass prediction:

$$\log \text{chlorophyll } a = -2.49 + 0.269 \log \text{TP} + 1.06 \log \text{TN} \\ (\mu\text{g l}^{-1})$$

The model is best applied to hypertrophic lake systems ($r^2 = 0.82$ for the Florida Lake systems) and can be extended to include aquatic macrophyte infestation which also affects chlorophyll 'a' concentration.

5.5.3.3 Dynamic waterbody models

Dynamic models include some assessment of physical, chemical and biological processes within the lake system. The resolution of spatial and temporal detail is therefore greater and they are less 'site-specific'. These models usually contain:

- (1) Hydrologic and hydrodynamic characteristics;
- (2) Chemical and biological transformations;
- (3) 'Interface' terms such as input, output or exchange of material across boundaries (usually driven by (1)).

Interface terms in dynamic models are primarily concerned with the link between lake and catchment and exchange processes across both the air-water and the sediment-water interfaces, although these complex processes remain highly simplified.

The forcing variables driving dynamic models are usually external (for example, temperature or solar radiation). Hydrological components are integrated in the models and include lake flushing rate and nutrient mixing within a thermally stratified lake. The complexity of such processes usually results in an emphasis on transport rather than nutrient exchange (Shanahan and Harlemann, 1984).

Figure 5.15 illustrates the basic carbon, nitrogen and phosphorus cycles important in the

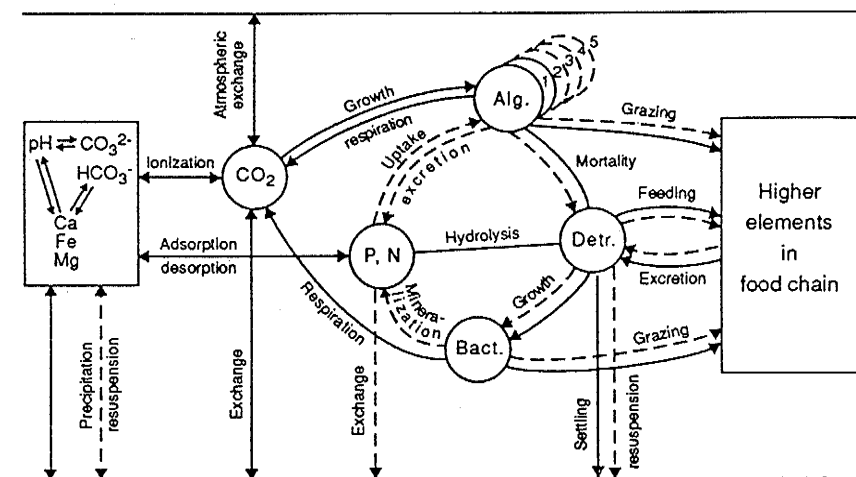


Figure 5.15 The carbon, nitrogen and phosphorus cycles involved in lake eutrophication (modified from Ryding and Rast, 1989) — = carbon; - - - = nutrients; Alg. = algae; Detr. = detritus; Bact. = bacteria; P = phosphorus; N = nitrogen; CO_2 = carbon dioxide; CO_3^{2-} = carbonate; HCO_3^- = bicarbonate; Ca = calcium; Fe = iron; Mg = magnesium

eutrophication process. To be fully effective, dynamic models need to incorporate at least some of the accepted linkages outlined in Figure 5.15. The emphasis is usually on the biological rather than the chemical component of the cycle, although DeRooij (1980) describes a dynamic model based on chemical processes in lakes.

5.5.4 NITROGEN AND THE CONTROL OF EUTROPHICATION

As discussed earlier, the main non-point sources of nitrogen are urban and agricultural runoff. Urban control mechanisms include creation of permeable surfaces in urban areas and construction of storage and detention ponds. Neither mechanism is particularly useful for nitrogen control, primarily because nitrate is highly soluble and readily leached from such devices. Agricultural control mechanisms include construction and control of manure storage facilities, attention to timing of manure and inorganic fertiliser application and the use of slow-release fertilisers. An auxiliary measure for the reduction of agricultural nitrogen transfer is the establishment of 'protection zones' or vegetative buffer strips which restrict fertiliser application close to waterbodies (see also Chapter 12). Other mechanisms of nitrogen control include the use of nitrification inhibitors such as 'N-serve' to reduce nitrate leaching losses. N-serve inhibits *Nitrosomonas* but its volatile nature means that it is difficult to incorporate into the soil.

Riparian forest 'ecotones' are acknowledged as forming natural filters against diffuse nitrogen input from agricultural land (Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985). Lowrance, Todd and Asmussen (1984) found that a riparian forest 'ecotone' in Georgia, USA, retained 68% of the diffuse nitrogen load as a result of denitrification. Chauvet and Décamp (1989) found that the nitrate concentration in groundwater varied with land use in the Garonne river catchment, France. In order of increasing nitrate concentration the authors found: woodland < pasture < orchard < fallow < cereals < market gardening < urban. However, nitrate appeared to be eliminated from groundwater *before* it reached the river *after* it had passed through the floodplain. Pinay (1986) and Pinay and Décamp (1988) examined the process of nitrate elimination from groundwater with flow towards the river system. They concluded that denitrification was responsible for allochthonous nitrate removal (Figure 5.16). Howard-Williams, Pickmere and Davies (1988) concluded that the riparian vegetation of stream channels and steam banks, together with the associated bacterial communities, were able to remove dissolved inorganic nitrogen from the stream water. The rate of removal depends on factors such as stream morphometry, discharge and season. The authors state that headwater streams are valuable for the removal of diffuse nitrogen inflow. They suggest that the grazing and watering of livestock in riparian zones should be minimised in order to maximise the nitrogen removal potential of these zones. Further discussion of riparian buffer zones is given in Chapter 12.

A simplified approach for selecting the appropriate eutrophication-control measure where nitrogen enrichment is a possible source of eutrophication is shown in Figure 5.17. The approach relies largely on external nutrient control and focuses on the nutrient status of the waterbody. Note that the starting point for control is *nitrogen* (rather than phosphorus), and some mechanisms of nitrogen control are shown in Table 5.10. Note also that it is implicit in the diagram that nitrogen will not be the limiting nutrient and that phosphorus will be the key nutrient in the *control* of eutrophication. In many eutrophic freshwaters it is not so important that phosphorus is the specific algal growth-limiting factor at a given time but rather

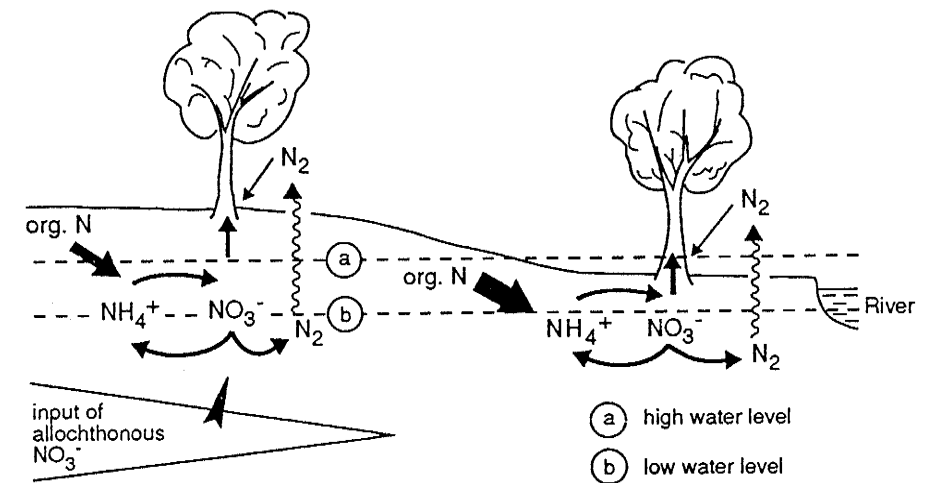


Figure 5.16 The nitrogen cycle in riparian zones illustrating the importance of denitrification in N removal (after Pinay and Décamp, 1988)

that it is *made* limiting by reducing external catchments loads or by in-lake control measures (PLUARG, 1987; Ryding, 1980; OECD, 1982).

The control of point sources of nitrogen usually focuses on sewage works discharges. One approach is to incorporate selected stages of the nitrogen cycle into the treatment process (for example, adding lime to raise the pH and volatilise ammonia). However, much nitrogen still remains in the resulting sludge which must be disposed of. Optimisation of denitrification in sewage treatment requires addition of a carbon source (for example, methanol and the creation of an anoxic environment).

Table 5.10 Methods for reducing nitrogen losses from agricultural lands (modified from United States Environmental Protection Agency, 1980)

Control practice	Description
<i>Eliminate excess use of fertiliser</i>	Cut in N leaching; cut in fertiliser cost, no effect on yield
<i>Leaching control</i>	
(1) Timing of N application	Reduction in N leaching through efficient use; inconvenient
(2) Crop rotations	Reduction in N input and erosion; not compatible with many farm enterprises
(3) Animal wastes as fertilisers	Creates non-point (slow-spreading) N source from point source
(4) Ploughing green legume crops	Reduces N fertiliser input; not always feasible
(5) Use winter cover crops	Uses nitrate, reduces percolation, reduces erosion
<i>Control of nutrients in runoff</i>	
(1) Incorporate surface applications	Decreases N in runoff; no yield effects; not always possible
(2) Control surface applications	Use when incorporation not feasible
(3) Use legumes in grasslands	Replaces N fertiliser; limited applicability; difficult to manage

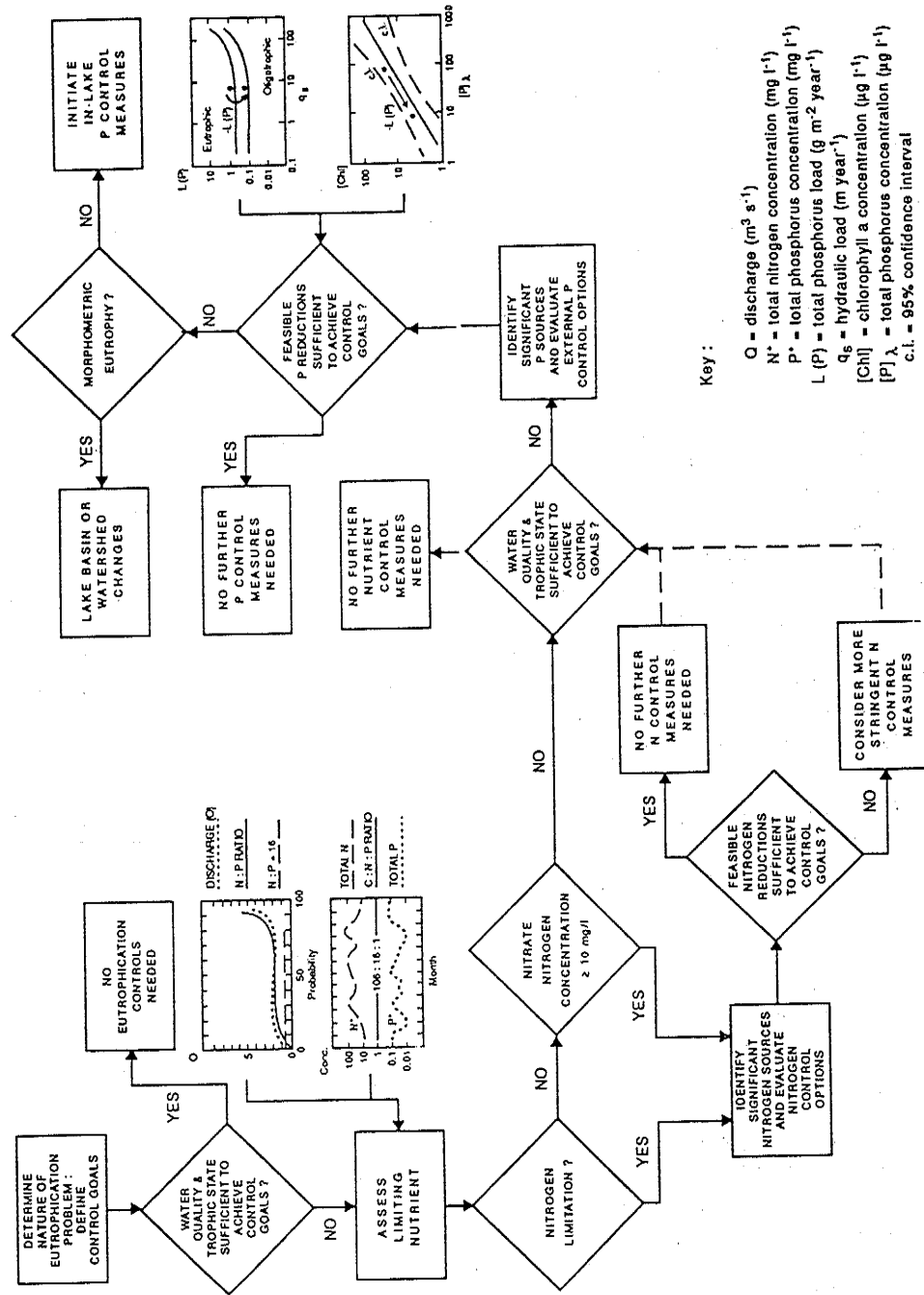


Figure 5.17 A general approach for the control of eutrophication based on nitrogen and phosphorus criteria (modified from Ryding and Rast, 1989)

Table 5.11 Water use and trophic status

Use	Trophic state	
	Required	Acceptable
(1) Drinking water	Oligotrophic	Mesotrophic
(2) Bathing	Mesotrophic	Slightly eutrophic
(3) Water sports	Mesotrophic	eutrophic
(4) Process water	Mesotrophic	Slightly eutrophic
(5) Cooling water	—	Eutrophic
(6) Irrigation	—	Strongly eutrophic
(7) Energy production	—	Strongly eutrophic
(8) Fish culture:		
salmonid	Oligotrophic	Mesotrophic
cyprinid	—	Eutrophic

5.5.5 THE NEED FOR NITROGEN CONTROL FOR DRINKING WATER

Table 5.11 indicates the variation in lake trophic status according to water use. Oligotrophic lake waters are desirable for drinking water because nitrate is potentially toxic to humans either in the form of methaemoglobinaemia in young children or through the formation of carcinogenic nitrosamines in the human gut. Control of nitrogen for drinking-water supplies may be necessary, therefore, even if it is not the limiting nutrient in the aquatic system. The problem is that land-use changes together with treatment of inflowing lake waters is much more efficient for phosphorus control than for dissolved nitrogen compounds. For example, even though measures to increase the infiltration rate of surface soils would reduce excess nitrate levels in the soil, this excess nitrate is simply passed on to the groundwater and eventually to the lake system. Nitrogen-control measures such as runoff or leaching control (see Table 5.10) are much less efficient at low temperatures. The effect of nitrogen on human health is examined more fully in Chapter 13.

5.6 CONCLUSIONS

This chapter has sought to underline some of the fundamental criteria involved in nitrogen cycling in surface waters and lakes. The sources of nitrogen for freshwater systems are examined and the implications for lake trophic status discussed. Control strategies and the implications for both natural ecosystems and human health are outlined.

Nitrogen is the key nutrient determining the primary productivity of surface waters and lakes. There is strong evidence that the concentration of nitrogen, particularly nitrate, has increased in rivers and lakes in the past 20 years. This increase is primarily the result of land-use change and agricultural intensification in the catchments of these aquatic systems. The contribution of nitrogen to freshwaters from sewage has also increased. The pathways of nitrogen transfer from the land to the stream have been discussed in this chapter and the importance of the nitrogen cycle in transforming the nitrogen export has been examined. Riparian 'ecotones' are felt to be important zones for modifying nitrogen export in the land-to-stream pathway. Instream nitrogen transformations are also viewed as critical in modifying the nitrogen load once it enters the aquatic system. In both these pathways, denitrification is the critical process governing the extent of nitrogen 'loss' from the system.

The role of nitrogen in the eutrophication of freshwaters has also been examined. It is noted that the control of nutrients to limit eutrophication normally focuses on phosphorus. However, it is not always the case that phosphorus is the limiting nutrient, and hence the controlling factor, in freshwater eutrophication. The relative importance of nitrogen and phosphorus as limiting nutrients will vary seasonally. This is particularly true of nitrogen, which is primarily dependent on catchment sources. Phosphorus is less dependent on this source and, furthermore, has a secondary source of phosphorus in lake sediments. This difference in N and P sources means that there is a high potential for nitrogen limitation in eutrophic waters when the catchment supply of nitrogen is low, that is, in summer months. The extent to which nitrogen actually becomes limiting also depends on the algal composition of lake waters. It is possible that nitrogen-fixation by blue-green algae may reduce nitrogen limitation. However, it is just as feasible that the initial dominance of blue-green algal blooms in many eutrophic waters is itself triggered by a limited nitrogen supply, which blue-greens can adapt to and exploit. More research on the role of nitrogen in freshwater eutrophication is needed if control measures are to be effective.

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