ENVIRONMENT AGENCY

# Eutrophication Control via Nutrient Reduction in Rivers: Literature Review

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EA - Anglian Water Quality

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# ABBREVIATIONS AND ACRONYMS

| | |
|---|---|
| AAI | Algal Abundance Index |
| BMWP | Biological Monitoring Working Party |
| CCA | Canonical Correspondence Analysis |
| LOIS | Land Ocean Interaction Study |
| MRP | Molybdate Reactive P |
| MTR | Mean Trophic Rank |
| NVZ | Nitrate Vulnerable Zone |
| PME(ase) | Phosphomonoester(ase) |
| PP | Particulate P |
| PTV | Pollution Tolerant Valves |
| RIVPACS | River Invertebrate Prediction and Classification System |
| RTSI | River Trophic Status Indicator |
| SRP | Soluble Reactive Phosphate-P |
| SSSI | Site of Special Scientific Interest |
| STW | Sewage Treatment Works |
| SWQO | Statutory Water Quality Objective |
| TDI | Trophic Diatom Index |
| TP | Total P |
| UWWTD | Urban Waste Water Treatment Directive |

# EXECUTIVE SUMMARY

1. A overview is presented of the literature on nutrients and rivers, with the emphasis on information useful in the UK on eutrophication control via reduction in nutrients. It is recommended that catchments should each have their own eutrophication management plan and that this should focus on diffuse and small point sources as well as the major point sources.

2. Diffuse sources, including small point sources, make an important nutrient input to many rivers; this has probably often been underestimated, especially for phosphate.

3. Where diffuse (and small point) sources of nutrients to a river are important, the catchment plan should target those stretches of stream and river which make the greatest contribution and the data should be integrated to a Geographical Information System database. It is important to focus effort on the key sites.

4. Storm events have an important influence on nutrient loads, both by enhancing inputs from diffuse sources and by mobilizing bed sediment. In catchments subject to marked variation in flow, sampling programmes for water chemistry should take extreme events into consideration.

5. The problem of long-term buildup of phosphate needs to be considered when assessing the management of buffer zones and also wetland sites used for nutrient stripping.

6. Buffer zones have many environmental advantages, but seem unlikely to be adopted widely by farmers without some form of financial incentive.

7. Weed cutting and dredging should both be considered as possible means of nutrient removal; both involve the need to find a site for dumping the material without recontaminating drainage to the river.

8. It is unrealistic to assume that a procedure for sampling and analysis of water and chlorophyll which has been designed for routine pollution monitoring will prove suitable for assessing long-term changes, including those where improvements related to the Urban Waste Water Treatment Directive have been made to a sewage treatment plant. It is suggested that there is a need for a critical assessment of the Environment Agency's procedure for sampling, storage and analysis of water, particularly in the case of phosphate.

9. More detailed understanding is needed of the process of denitrification in rivers, wetland treatment systems and buffer zones, both to enhance nitrate removal and to minimize that component of the process which terminates in nitrous oxide.

10. Ongoing biological monitoring of eutrophication should be done using phototrophs, though information from macroinvertebrates and other animals may prove useful for assessing old datasets where there is no information for phototrophs.

11. Algae are the most useful phototrophs for assessing changes in nutrient conditions, because they respond relatively quickly to change. A system based on

diatoms appears to cover most of the present needs for a trophic index, but nevertheless a system should also be developed which takes into account a wider taxonomic range.

12. Rooted macrophytes can also provide valuable information, but care should be taken to allow for a probable lag in response to decreases in ambient phosphate because of accumulation of phosphate in sediments and in the plant biomass. This applies both to the initial datasets used to establish the trophic index and observations made during a period of nutrient decrease.

13. Although either N or P are almost always considered to be the key nutrients in eutrophication studies, the possibility should be borne in mind that vitamins might influence the biomass of some algae such as *Cladophora*.

14. Considerable care is needed when designing a sampling programme for the use of plankton chlorophyll *a* as an indicator of eutrophication in large rivers, because of marked short-term and seasonal changes.

15. Sites of Special Scientific Interest are likely to be especially vulnerable to eutrophication, so it is important that algae are considered in any assessment of the status of these sites.

## KEY WORDS

**River, eutrophication, nutrients, nutrient control, nitrogen, phosphorus, point source, diffuse source, water chemistry, sediment, alga, macrophyte, Urban Waste Water Treatment Directive**

# 1 INTRODUCTION

## 1.1 Aims of review

The aim of this document is to provide a review of literature and current research in eutrophication control and nutrient reduction in rivers.

The following topics are considered:

* Monitoring the sources, levels, movement, availability and forms of nutrients in water
* Modelling and monitoring of nutrient movement from land to water
* Assessing the extent and impact of other (non-point and small point) sources of nutrients
* Consideration of flow, nutrient load and nutrient concentration data accuracy and relevance
* General river eutrophication studies
* Movement of nutrients through the food web
* Biological monitoring programmes and interaction between biota and nutrients
* Techniques and technology employed to reduce nutrient levels in sewage effluent.

## 1.2 Perspective on eutrophication

The literature on eutrophication is so extensive, that it is helpful to have some perspective on earlier research when considering modern studies. Until recently the majority of studies have dealt with lakes, especially in the case of phosphate. Truly quantitative studies on the role of nutrients in eutrophication followed from the increasing concern during the 1960s with problems in large lakes, such as Lake Erie. The increasing occurrence and awareness in the latter part of the 1960s of blue-green algal blooms in many lakes and reservoirs led to a simple target for water quality: keep the level of phosphate in the water below that likely to lead to lead to nuisance blooms. This became still more important during the late 1970s and 1980s as water managers came to realize how often these blooms are toxic (Bell & Codd, 1994).

In the case of river studies, research and management was often focussed on organic effluents originating from point sources. There was, however, considerable interest in the UK during the 1960s and early 1970s in problems of shallow rivers due to growths of *Cladophora*. Most of the specific cases appear to have been tackled on an *ad hoc* basis rather than attempts being made to draw up the types of general guidelines produced for standing waters. This is reflected in the fact that data on phosphate for many UK rivers have until quite recently often been fragmentary and sometimes unreliable; this often contrasts with the more detailed records for some N fractions obtained because of their relevance to assessing the quality of sewage effluents.

Eutrophication is considered here as both the phenomenon of increasing nutrient levels and the effects which result from them. However, as information on the biological effects of eutrophication is not always available, it is useful to have some chemical guideline when checking the literature. Harper (1994), in a survey of one year's data for P levels in mesotrophic rivers in the Anglian Region, considered sites with mean values of < 0.1 mg $L^{-1}$ P as clearly mesotrophic and 0.10 - 0.25 mg $L^{-1}$ P as probably mesotrophic. Sites with 0.25 mg $L^{-1}$ P and over were eutrophic. Because of errors inherent from use of only year's data, a value of 0.2 mg $L^{-1}$ P was suggested as the mesotrophic-eutrophic boundary for a more accurate dataset. However, this is considerably higher than the limits suggested by authors for some other regions. For instance, based on a study of 800 sites in Ireland over a 3-year period, McGarrigle (1993) concluded that river eutrophication begins to be a problem when median annual MRP (molybdate reactive phosphate) exceeds 0.03 mg $L^{-1}$ P in unfiltered water. Based on this criterion, 22% total of 3000 km channel length surveyed in Ireland was classified as eutrophic (McGarrigle *et al.*, 1992).

The recent stimulus in interest in nutrient eutrophication in rivers, especially that due to phosphate, has several origins. Many serious problems due to oxygen depletion resulting from sewage and major industrial effluents entering non-tidal rivers have been tackled successfully, thus making the public more aware of other problems. The EC directive on Urban Waste Water Treatment (EEC, 1991a) helped to raise awareness of the need to develop targets for nutrient levels in rivers. This in turn led initially to attention being focussed mainly on major point sources of nutrients, but, as further point source control becomes less cost-effective, attention will increasingly be directed towards the contribution of agricultural non-point sources (Sharpley & Rekolainen, 1997). This has in turn increased awareness of how much there is still to learn about such non-point sources. The literature quoted in the articles in the book edited by Tunney *et al.* (1997), which was based on a conference in 1995 at Wexford, Ireland, shows much of what is available on this subject has been published during the 1990s. The Abstracts of an OECD sponsored workshop held in Belfast in June 1998 reached the authors too late to be integrated fully into this review, but several papers are mentioned which make important points not covered elsewhere. This book (Foy & Dils, 1998) includes extended abstracts for 98 talks, the majority of which are directly relevant to the present report.

There were 27 EC Council Directives relevant to community water legislation in the period 1973-1991 (see Mariën, 1997, and **Section 3.5**); next to the UWWTD, the directive on *Nitrates from Agricultural Sources* (EEC, 1991b) is the most relevant to the present review. Within the UK, the control of nitrate loss from agriculture to certain categories of water body is considered in combination with the Water Resources Act 1991 (Sections 94 and 95), which deals with the establishment of nitrate sensitive areas (Ball, 1993).

Preparation of this report has made it clear to the authors that there is huge body of literature, some of which is widely quoted, some of which appears to have been largely ignored. The journal *Hydrobiologia* has published various symposia on phosphate, which are an important source of information e.g. *Hydrobiologia* Volume 170 in 1988, titled *Phosphorus in Freshwater Ecosystems*, and Volume 364(1) in 1997/98, titled *Sediment-Water Interactions 8*. A number of topics require more detailed and critical review than has been possible here. We have also pointed out aspects where it seems surprizing that further information appears to be lacking.

## 1.3 Major nutrients and key processes influencing their dynamics

These introductory notes are intended to highlight key aspects for non-specialists and inevitably simplify complex topics. Some of the important aspects for river chemistry are described in more detail later. Mainstone *et al.* (c. 1993) also provide useful background for anyone without specialist knowledge of phosphorus chemistry.

### 1.3.1 Nitrogen

The predominant form of soluble combined nitrogen in the aerobic aquatic environment is usually nitrate, which is replaced by ammonium at low Eh values ("redox potential": Stumm & Morgan, 1981); interconversions between nitrate and ammonium result from microbially driven processes under particular redox conditions rather than the result of a simple chemical equilibrium. All nitrate salts are highly soluble; the positive charge of the ammonium ions favours binding to cation exchange surfaces such as clay minerals. However, this is a weak association and both ammonium and nitrate are readily leached from soil by rainfall. Due to the dissociation of ammonium ions to $NH_3$ at high pH, $NH_3$ loss to the atmosphere becomes increasingly more important at pH values above about 9.0. Organic N compounds derived from soils, especially peaty ones, are sometimes quantitively important in river water. Various microbial processes (nitrogen fixation, nitrification, denitrification and dissimilatory nitrate reduction) are involved in the nitrogen cycle.

### 1.3.2 Phosphate

Soluble phosphate may exist as inorganic ions or organic molecules. Due to the low solubility of many phosphate compounds under oxic conditions and at higher pH values, inorganic phosphate often exists in colloidal form or associated with small particles. In practice the soluble fraction is therefore usually defined operationally, as the phosphate passing through a particular size of filter. However, part of the 'soluble reactive phosphorus' or 'molybdate reactive phosphorus' (MRP) in soil solutions and water may, in fact, be bound to particle and colloidal material (Haygarth *et al.*, 1997). (In this review the terminology for the various fractions is mostly that used by the authors of the particular papers quoted. In most cases the terms 'soluble phosphate' and 'filtrable phosphate' are interconvertable.)

The main elements controlling the solubility of inorganic phosphate are Ca, Mn and Fe. Under anoxic conditions, which in turn lead to a reduction in Eh , Mn IV and Fe III are reduced to MnII and FeII and associated phosphate is usually released into solution.

Organic phosphates are mostly derived from the breakdown of biological material and require enzymatic activity to release inorganic phosphate.

# 2 SOURCES OF NUTRIENTS

## 2.1 Introduction

The principal point sources of nutrients are sewage and industrial effluent, while the principal diffuse sources are atmospheric deposition and agriculture. The more recent literature often comments on the relative contribution of point and diffuse sources of nutrients entering rivers, but it is not always clear how reliable are the data for diffuse sources. There is also some ambiguity as to exactly what should be considered as a point source and what as a diffuse source, because many inputs from terrestrial sources such as urban runoff and agriculture often consist largely of numerous mini-point sources rather than truely diffuse sources like atmospheric deposition. However we follow the majority of the literature in including mini-point sources such as field drains as diffuse sources. Such diffuse sources almost certainly account for most of the combined N entering UK rivers (Wright *et al.*, 1991; MacDonald *et al.*, 1994).

In the case of P, the literature (e.g. Harper, 1992) indicates that point sources account for most of the P entering rivers. However, diffuse sources can also be important, particularly in areas with intensive agriculture coupled with low flow rates (Muscutt & Withers, 1996), and Edwards and Withers conclude (1998) that an increasing proportion of P reaching surface waters appears to be derived from agricultural land.

A booklet published by the Soap and Detergent Industry Association (1989) quoted the following values for P output to surface waters in the UK (in t $yr^{-1}$): industrial, 3,000; sewage effluents, 56,000; manure/slurry, 26,000; silage, 2,000; soil runoff, 18,000). Part of the contribution from manure and silage eventually reaches rivers as diffuse sources. A recent estimate (Smith *et al.*, 1998) of manure added annually to UK agricultural land is 119,000 t, of which 66,000 t are to applied arable land and 53,000 t to grassland. If the two sets of data collected about a decade apart can be combined, they suggest that almost one-quarter of the P added to land as manure reaches the rivers.

## 2.2 Atmospheric sources and climate

Combined N from the atmosphere reaches soils and vegetation as both dry and wet deposition, principally as nitrate and $NH_4$-N. A major source of the latter is $NH_3$ emissions, especially from livestock, which were highlighted in a 1994 report for the Department of the Environment (cited from ENDS Report 238, 1994). This report suggests that calculating critical loads for N will be difficult, but in principle all effects such as eutrophication, acidificiation and fertilization should be considered, and protective action based on the most sensitive factor. Detailed maps of ammonia emissions have been prepared for all Europe (Buijsman *et al.*, 1987; Asman, 1992). In the UK (ENDS Report 238, 1994), ammonia emissions from farms contributed as much N deposition as $NO_x$ releases from industry and vehicles. N deposition across most of the UK exceeds 5 kg $ha^{-1}$ $yr^{-1}$, and in parts of Wales, Cumbria and the South Pennines is more than 30 kg $ha^{-1}$ $yr^{-1}$. In terms of the mass balance, however, the atmosphere contributed only about 10 % of the total in areas of intensive agriculture in Denmark (Kronvang *et al.*, 1995), although the percentage value could be much higher in areas without artificial additions of fertilizer.

Recent studies in southern Norway have assessed the impact of acidification and climatic change on nutrient levels. In the Bjerkreim river catchment, N inputs are an important acidifying component (Henriksen *et al.*, 1997). N inputs must be reduced substantially in order to reach non-exceedance of critical loads in the runoff waters, with a 80% reduction being required in the most sensitive subcatchment. This and another large catchment were also assessed with respect to the impact of climatic fluctuations and possible long-term changes in climate on nutrient mobilization in soils (Hessen *et al.*, 1997). Climatic patterns strongly affect the seasonal runoff patterns, and long-term climate change could result in mobilization of huge stores of organic N as a result of increased mineralization. The various changes would be expected to increase the N : P ratio of upland streams and rivers, thus enhancing the already marked P limitation shown by these ecosystems.

The atmospheric P load is generally low in comparison to loads from other sources (Holtan *et al.*, 1988), although it may be significant for oligotrophic catchments (Gibson *et al.*, 1995). The latter authors reported an input of 22 kg P $km^{-2}$ $yr^{-1}$ for an upland catchment on the Antrim Plateau, Northern Ireland. Comparison with literature data (e.g. Beltman *et al.*, 1993) showed that this was near the median value. P outputs to an upland lake were more or less balanced by inputs from rain, in contrast to combined N, where outputs were very much less than inputs. We have been unable to find further literature to establish whether this important conclusion applies widely in upland areas of the UK.

## 2.3 Sewage and industrial effluents

The properties of sewage effluents and other types of wastewater are treated in various standard texts; Gray (1989) provides a useful source of information for biologists, including a huge bibliography. N in wastewaters derived from human or animal sources exists as proteins, amino-acids, urea, ammonia and, if sufficient time has been left during treatment for oxidative steps, nitrate. Silage liquor is especially rich in N, containing up to 2.5 g $L^{-1}$ N (Gray, 1989). The better the quality of the effluent from a STW or other source, the more the N is converted to inorganic molecules.

Phosphorus is present in sewage as orthophosphate, polyphosphate and organic phosphate, but after secondary treatment, about 80% of the total P in a final effluent is orthophosphate (Gray, 1989). Conventional secondary treatment removes about 40-50% of P, leaving about 1 kg person$^{-1}$ $yr^{-1}$ in the resulting effluent (Harper, 1992); it also enhances the hydrolysis of detergent-derived polyphosphate to orthophosphate. The input of effluents from STWs may be expected to decrease the N : P ratio in river water, unless special measures have been introduced to remove phosphate (**8.1**). Tertiary treatment of effluents to Loch Leven reduced P inputs by 8 t between 1985 and 1995, which represents 40% of the TP loading to the loch in 1985 (Foy & Bailey-Watts, 1998). In spite of decreased TP loadings from point sources to two major rivers flowing into Lough Neagh (Main and Ballinderry), MRP loading had increased due to diffuse sources increasing at annual rates of 1.9 and 2.3 kg P $km^{-2}$.

## 2.4 Urban runoff and storm sewer overflows

Good estimates of the contribution made by urban runoff to total nutrient budgets in catchments are difficult to obtain, largely because this source tends to be intermittent in nature and also highly variable between catchments. Important factors include the proportion of catchment area that is impermeable (buildings, roads etc) and whether or not there are separate storm drains and foul sewers. Significant sources of nutrients in the urban environment include urban erosion (N + P), lawn fertilizers (N + P), animal populations (N + P), leachate from leaves (mainly P) and petroleum additions (mainly P). The traditional view (e.g. Mance, 1981) is that urban runoff is not a serious problem in UK rivers; although there is evidence that this may be over-optimistic. Wiebel *et al.* (1964) measured a phosphorus load from urban runoff of 2.8 kg $ha^{-1}$ $yr^{-1}$ in a small catchment in Cincinnati, Ohio, compared with 30.2 kg $ha^{-1}$ $yr^{-1}$ in raw sewage. Assuming that about half of the P in raw sewage is removed during treatment, then urban runoff contributed about one-fifth of the total. This particular catchment had separate storm drains and foul sewers and Weibel (1969) estimated that these measurements would be three times higher if the catchment had a system of combined sewers. Generalisations are difficult, not just because of catchment factors, but also because of variations in the effectiveness of the hydraulic design in each case. The literature includes situations where urban runoff was unimportant compared to other sources (Emery *et al.*, 1975; Sager & Wiersma, 1975) and where urban runoff was significant (Kluesener & Lee, 1974; Baumann & Kelman, 1971). However, Wiebel (1969)'s figures, though dated and higher than reported in some other cases (e.g. Ellis, 1986), suggest that the contribution of urban runoff to the total nutrient load in rivers should not be disregarded.

The peak TP concentration typically occurs on the rising limb of a storm hydrograph (the 'first flush' effect) as accumulated materials are washed into storm drains (Kluesener & Lee, 1974). An exception to this pattern was shown by Cordery (1977). A consequence of the 'first flush' effect is is that routine chemical monitoring programmes may underestimate the contribution of storm sewers and detailed sampling around storm events will be required if more accurate evaluations are required. Kelly (1998b) noted the abundant growth of *Cladophora* upstream of some major STWs and attributed this to intermittent inputs of nutrients to the river from urban runoff and storm overflows.

## 2.5 Agriculture

The type and intensity of agriculture influences the quantity of fertilizer which it is economic to apply to the land. Inorganic N is added as soluble nitrate or ammonium salts and leaching is faster from well drained than heavy soils. This leaching, in turn, increases the demand for N from crops grown on light soils. Kronvang *et al.* (1995) quoted a net N input 84 % higher in sandy catchments in Denmark, compared to loamy catchments. The amount of N removed in crops was similar in both cases, but N leaching from the soil was more than twice as high in the sandy soils.

N is perceived as the principal limiting nutrient for crop production. Harper (1992) commented that the use of P in fertilizers, in contrast to N, has remained relatively static in the UK since the 1940s, but has increased in some other countries, such as Ireland. Tunney *et al.* (1997) state that the reason for this difference between the UK and Ireland is unclear, but is apparently leading to an even greater build-up of P in soils of Ireland.

Nevertheless, the majority of farms in the UK add more P to land than is removed in produce, thus creating an overall P surplus in soils, the size of which differs between different types of farming (Edwards & Withers, 1998); particularly high values (> 20 kg $ha^{-1}$) are associated with intensive livestock production and lower values (< 10 kg $ha^{-1}$) with arable farms. In another estimate, Haygarth *et al.* (1998b) calculated that grasslands in the UK receive an annual P surplus of about 24 kg $ha^{-1}$. This surplus must either be immobilized in the soil or move towards water.

Inorganic phosphate is readily fixed and prevented from leaching by precipitation with Ca, Fe and Al, or adsorption to clays and other soil particles (Frossard *et al.*, 1995), although the proportion of inorganic P which escapes binding and ultimately drains towards water is sometimes quantitatively important (see **3.2**). Organic P accounts for a substantial proportion of the P in soil systems, typically between 29-65%, but up to 90% in some organic soils (Harrison, 1987). This fraction includes both soluble and insoluble components. Dissolved organic P and dissolved condensed P can exceed the amount of molybdate reactive P in the soil water of grasslands (Ron-Vaz *et al.*, 1993; Shand *et al.*, 1994) and a forested catchment in North Carolina (Qualls *et al.*, 1991). The highly insoluble phytates of Al, Fe and other elements or adsorbed to their compounds are a quantitatively even more important form of organic P in some soils (Turner & Haygarth, 1998). Despite the large quantities of soil organic P, dissolved organic P appears to be controlled by biological production rather than solubility (Chapman *et al.*, 1997).

## 2.6 Nutrients and environmental legislation

The legal basis for eutrophication control is outlined in the Eutrophication Control Strategy (Environment Agency, 1996) and is summarized in Table 2.1. Apart from the UWWTD and Nitrates directives, most legislation only enables indirect control of eutrophication, and the onus is on the Agency to create an unambiguous case. Many of the issues raised later in this report will influence the ability of the Agency to make such cases and several of the conclusions highlight the individuality of each catchment. The value of legislation enabling indirect control will depend upon the Agency developing a suite of widely-applicable methods that allow appropriate data to be collected and analyzed with sufficient rigour.

The UWWTD provides clear guidance on emission standards for N and P from major STWs once qualifying criteria have been established. These include the identification of 'sensitive areas' (freshwaters which are eutrophic or which may become eutrophic if protective action is not taken): a task which has proved to be a major intellectual challenge for the Agency since 1991 partly because the directive is itself vague about the definitions of eutrophication. Whilst the directive has proved useful for raising the profile of eutrophication as an issue, the UWWTD has many flaws, including the criterion of 10,000 population equivalent as the lower limit for a 'qualifying discharge'. This has inevitably focussed attention on STWs serving large towns, usually in lowland areas. Many of the 27 rivers designated as SSSIs flow through predominantly rural areas served by a series of smaller STWs and are not affected by the UWWTD.

The Nitrates Directive uses a similar form of wording to the UWWTD to establish 'Polluted Waters (Eutrophic)' for rivers with very high (> 50 mg $L^{-1}$) nitrate concentrations. Land draining to these waters is designated as Nitrate Vulnerable Zones (NVZs) and restrictions will be imposed upon farming within these areas to limit nitrate losses. It has recently been suggested (ENDS Report, 1997) that the N content of sewage may also need to be controlled in such zones. The definition of NVZs is similar to that of Nitrate Sensitive Areas (NSAs), established under the 1991 Water Resources Act. Not surprisingly, the agricultural lobby is unenthusiastic about both NSAs and NVZs and, as a result, only a small area is covered by NVZs at present (Wilson *et al.*, 1996).

A general policy of agricultural 'extensification' has been pursued within the EC, partly to counteract surpluses (butter mountains etc) and budgetary problems; however, these policies also provide opportunities for environmental improvements (Wilson *et al.*, 1996). Within the UK this policy was pursued via the 1986 Agriculture Act which provided support for less-intensive agriculture in 'Environmentally Sensitive Areas' (ESAs) and the 1988 Set Aside Regulations which allowed farmers in all areas (not just ESAs) to remove land from production. This not only reduces the overall nutrient input but provides opportunities for the establishment of nutrient buffer zones (**Section 8.2**). The financial incentives provided as part of the scheme serve as a 'carrot' to complement the 'stick' of legal controls implemented via the Nitrates Directive.

Statutory Water Quality Objectives (SWQOs) are legally binding targets for water quality set by the Agency. SWQOs will relate to the "uses" made of the water. At present, only the 'River Ecosystem' is used, although a further category, "Special Ecosystem" has been proposed for waters of high conservation value. Wilson *et al.* (1996) criticise the River Ecosystem scheme as a tool for eutrophication control as it permits BOD readings to be ignored if high algal levels are responsible. It also uses 1990 as a baseline for maintaining water quality, although this drought year had particularly poor water quality. The proposed Special Ecosystem class is potentially more valuable as it is designed with conservation goals in mind, and sets stringent targets for P. These include an "initial" target level of 0.2 mg $L^{-1}$, followed by phased reductions to a level appropriate to that river type. For clay and alluvial lowland rivers this is 0.1 mg $L^{-1}$: an order of magnitude less than is measured at present in many such rivers.

In response to this variety of legislation the Agency has proposed (Environment Agency, 1996) site-specific Eutrophication Control Action Plans (based upon procedures for Blue-green Algae Action Plans) although the Eutrophication Control Strategy recognises the potential for "complex and emotive" conflicts of interest between different water users. An Action Plan manual is under development, with details of consultation mechanisms, data requirements, cost-benefit frameworks and modelling tools relevant to nutrient control.

The forthcoming Council Directive Establishing a Framework for Community Action in the Field of Water Policy (the 'Framework Directive') will also provide new obligations for the monitoring and control of eutrophication. The overall purpose of this Directive is to establish a framework for the protection of Community waters which, for surface fresh water, estuaries, coastal waters and groundwater:

1. prevents further deterioration and protects and enhances the status of aquatic ecosystems and, with regard to their water needs, terrestrial ecosystems; and,
2. promotes sustainable water consumption based on a long-term protection of available water resources.

A key element in the directive is the identification of "high ecological status" (i.e. the ecological status not significantly influenced by human activity) and "good ecological

status" (i.e. significantly influenced by human activity, but which nevertheless has a rich, balanced and sustainable ecosystem). This latter criterion should be achieved in all surface waters by 31 December 2010. Ecological status, for rivers, includes biological, hydromorphological and chemical and physico-chemical parameters. Annex V lists the biological parameters as:
Composition and abundance of aquatic flora
Composition and abundance of benthic invertebrate fauna
Composition, abundance and age structure of fish fauna.
A summary of the requirements relevant to this report are given in **Appendix I** and it is clear from this that the influence of nutrients on rivers will be important for determining their ecological status. From the wording of Annex V, it would appear that a stretch of river deemed to be a "sensitive area" under the terms of the UWWTD is, *ipso facto*, only of 'fair quality' in the terms of the Framework Directive. Several of the issues raised in **Chapter 7** are relevant to the Framework Directive

Table 2.1. Legislation of major relevance to eutrophication control in freshwaters. (From Environment Agency, 1996). See also Mariën (1997).

| Legislation | Comment |
|---|---|
| **UK** | |
| Water Resources Act 1991 | Several aspects relevant to eutrophication, including provision for establishment of Nitrate Sensitive Areas, issuing of consents to discharge and Statutory Water Quality Objectives |
| Environment Act 1995 | Supplements powers of Water Resources Act 1991. Agency required to 'form an opinion of the general state of pollution in the environment', which provides a rationale for raising awareness of problem areas such as nutrients and eutrophication |
| Wildlife and Countryside Act 1981 | Provides English Nature with powers to control potentially damaging operations in Sites of Special Scientific Interest. Such operations may include eutrophication. |
| Agriculture Act 1986 | Establishment of 'Environmentally Sensitive Areas' within which less-intensive farming practices are supported. |
| Set Aside Regulations 1988 | Opportunities exist to exploit set-aside land for nature conservation and buffer zones. This and Agriculture Act 1988 both implement aspects of Common Agricultural Policy. |
| **EC** | |
| Urban Waste Water Treatment Directive (91/271/EC) | Control of nutrient emissions from large STWs discharging into 'sensitive areas' |
| Nitrates Directive (91/676/EC) | Control of pollution from nitrates into "Polluted Waters (Eutrophic)". Primarily relevant to agricultural runoff, but may also apply to point sources within these areas. |
| Habitats Directive (92/43/EC) | Designation of Special Areas of Conservation in which rare and endangered habitats and species must be protected. Nutrient control requirements if conservation status of SAC affected by eutrophication. |
| Freshwater Fish Directive (78/659/EC) | Guideline (rather than imperative) standards for different nutrients in designated waters |
| 'Framework Directive' | Not yet in force. See Table |
| Common Agricultural Policy | Several aspects relevant to eutrophication control, including Set Aside Regulations (1988). |
| **International Commitments** | |
| 2nd North Sea Conference (1987) | States bordering North Sea agreed 50% reduction of inputs of problem substances, including nutrients, between 1985 and 1995. No firm commitment by UK |
| Convention on Biological Diversity and Agenda 21 (Rio, 1992) | Action to achieve sustainable development. Establishment of 'UK Biodiversity Action Plan' to prevent loss of species and habitats. |

## KEY COMMENTS: SOURCES OF NUTRIENTS

i) Point sources of nutrient entry to UK rivers are in general more important than diffuse sources for P, while the converse is true for N. (Diffuse sources often include mini-point-sources.) There are, however, wide differences depending on region, catchment and position down any particular river.

ii) The atmospheric contribution of combined N is in general much more important than that of P. However, atmospheric input of P may be important in upland unfertilized regions, though the available data are sparse.

iii) An upland soil in Northern Ireland has been reported to accumulate much of the N contributed from the atmosphere, but apparently does not accumulate the P. However, there is much evidence for long-term increases of P in fertilized agricultural soils, especially grasslands. Although the values are high in the UK, they are even higher in Ireland.

iv) The contribution of storm sewers to total nutrient load may be significant in some circumstances, but this needs to be evaluated for each catchment. It is worth examining the broad relationships between characteristics of urban catchments to see if total nutrient load can be modelled by an export-coefficient type of approach.

v) The EU directives most relevant to eutrophication in rivers are the Urban Waste Water Treatment Directive and the Nitrates Directive. The Framework Directive is also likely to become increasingly important. Relevant schemes which can provide financial help for indirect improvement of river water quality are the construction of buffer zones as a form of set-aside land and the establishment of environmentally sensitive areas, where less intensive farming is encouraged.

vi) The sampling strategies related to the Urban Waste Water Treatment Directive need to bear in mind the potential role of storm sewers in the vicinity of a 'Qualifying discharge'. It may be necessary to sample upstream of urban areas in order to estimate the contribution of urban runoff to total nutrient load and the biological resoponse.

vii) Other legislation (e.g. Habitats Directive) requires the Agency to create an unambiguous case that eutrophication is causing a problem. Techniques for creating these cases may be addressed via Eutrophication Control Action Plans.

# 3 NUTRIENT MOVEMENT FROM LAND TO RIVERS

## 3.1 Introduction

Most P reaching rivers is derived from point sources such as major STWs (Harper, 1992; Kinniburgh *et al.*, 1997), when catchments are considered as a whole. However, there are many situations, particularly in headwater areas of major catchments or in areas of low population density where diffuse sources may be significant. The precise importance of agriculture as a source of nutrients entering a river within a particular catchment depends upon the relative intensities of human settlement and agriculture, as well as the type of agriculture. Some of the topics covered in Section 3 are dealt with further in Section 4 for particular UK rivers investigated in the LOIS programme.

In a catchment in Sweden where 71% of the land area was used for agriculture, 84% of the P load in 1988 was derived from agriculture (Krug, 1993). This represented a seven-fold increase over the situation in 1960 - a figure only partially explained by increased fertilizer applications. Similarly, the N load increased four-fold between 1960 and 1988, whilst the rate of fertilizer application only doubled. For both nutrients, other factors (e.g. tillage practices, loss of buffer zones, changes in drainage patterns) must also have been important.

Studies on UK streams and rivers (Foy *et al.*, 1995) have confirmed the importance of agricultural sources of nutrients at a local level. However, Foy and Bailey-Watts (1998) conclude that the problems of interpreting river P concentration without reference to flow and the lack of information on how point sources have changed make it difficult to attribute apparent trends in P in UK freshwaters as due to changes in diffuse P inputs.

## 3.2 Diffuse sources

### 3.2.1 Land use and disturbance

Assessment of the relative contributions of different types of land use in catchments in England and Wales to diffuse N and P sources has been made by made using export coefficient modelling (Johnes, 1996; Johnes & Heathwaite, 1997; McGuckin et al., 1998). A combination of such modelling with pilot scale experimental studies was applied to a 1.5 $km^2$ subcatchment of the River Lugg (an ADAS experimental station) (Johnes & Hodginson, 1998). The authors concluded that the scope of such a model is at present only applicable to small areas, as it can only simulate total P export on an annual basis and is incapable of prediction over shorter time scales. They stressed the need for development of process-based models as a prerequisite for the development of management strategies to reduce non-point P load on water bodies.

Disturbance of land tends to enhance nutrient losses to rivers compared with undisturbed catchments. For instance, in a recent study in Denmark (Kronvang *et al.*, 1995), losses of total N from agricultural land were between 7 and 14 times greater than from undisturbed catchments, leading to concentrations in receiving streams up to six times greater. In the case of P, more was contributed by loamy than sandy ones (Kronvang *et al.*, 1995). In the UK, high rates of nutrient runoff mirror the increased use of slurry and artificial fertilizers, rather than farmyard manure (Harper, 1992). Activities associated with forestry can also have an important influence on nutrient runoff. In the case of the Hubbard Brook catchment in eastern USA, there was a 60-fold increase in nitrate concentations in streams draining a clearfelled block of forest (Bormann *et al.*, 1968). In the UK, forestry tends to be confined to poorer soils, which in lowland areas are often heathlands with naturally high leaching rates. Leaching of nutrients may be expected to decrease as the trees become established, although when the trees are felled the rate of N input will again increase.

### 3.2.2 Physical and chemical factors

Physical features of the land surface can have an important effect on nutrient loss, especially the slope. Typically, a steeper slope leads to a relatively greater loss of phosphorus than nitrogen, as it favours particulate runoff. Bank erosion can contribute to the particulate load in a river and an ongoing study at the University of Birmingham has shown a marked seasonal difference between upstream and downstream sites on the Swale - Ouse system: bank erosion at upstream sites mostly results from freeze-thaw cycles and hence occurs in winter, whereas that downstream results mostly from floods (Lawler *et al.*, 1998). The subject of nutrient inputs to rivers resulting from storm events is discussed in **Section 4.1.**

The relative contributions of groundwater and surface runoff may have a marked effect on the nutrient composition of water entering a river, because the two sources may differ greatly. This may influence not only the relative proportions of N and P, but also the proportions of different forms of N. In a study in the Chesapeake Bay catchment, USA, nitrate in stream water was positively correlated with the proportion of base flow relative to storm flow in streams (on an annual, flow-weighted basis), whilst organic nitrogen (e.g. urea) was negatively correlated (Jordan *et al.*, 1997). It was concluded that discharge of nitrate was influenced most by groundwater flow, whilst that of organic nitrogen most by surface runoff.

The insoluble nature of P means that it is typically most abundant in surface horizons. Improvement in soil drainage was found to reduce transfer of P to water (Haygarth *et al.*, 1998a), presumably through aeration and increased likelihood of sorption in lower horizons. Conversely, waterlogging, leading to anoxic conditions, can enhance the rates of loss of phosphate from soils due to reduction of Mn and Fe and hence solubility of their phosphates (Holtan *et al.*, 1988). Presumably the reoxidation of the Mn and Fe on entering streams or draining through river banks leads to the reprecipitation of much of this phosphate (in association with 'iron oxide' flocs), but quantitative data appear to be lacking.

Powlson (1998) outlines key changes in the understanding of the routes by which P can move from agricultural soils to water. Considerably more P than had been realized can move through soils to reach field drains and then surface waters. This is because the phenomenon of by-pass flow occurs in a wider range of soils than previously thought, so more of the P leaving topsoil escapes adsorption in the low P subsoil than was previously thought likely. This mechanism of loss is significant when topsoil P concentration exceeds a certain value known the 'change point', which varies betweeen soil types. The intensification of agriculture, especially intensive animal production, with the associated disposal of slurry, has increased the likelihood of more soils reaching such a concentration.

There is also now a greater recognition of soil erosion and surface runoff as mechanisms of P transport; again, the disposal of slurry over limited areas is almost certainly increasing the importance of this pathway.

The influence of soil chemical factors on P transfer is summarized in Table 3.1.

Table 3.1. Theoretical examples of how soil factors may affect risk of inorganic P transfer to watercourses. (Modified from Haygarth, 1997).

| Factor | Effect | Risk of transfer |
|---|---|---|
| High P status | Large pool of potentially transferable P | high |
| High Ca, Al or Fe status | Precipitation of P, reduced chance of transfer to soil solution | low |
| Waterlogged - reducing conditions | P precipitated with Fe under oxic conditions becomes mobilized | high |
| High organic matter status | P immobilized | low |
| Lime added - increased pH | > pH 6 P sorbed or precipitated | low |
| | pH 5 - 6 | high |
| | < pH 5 P sorbed or precipitated to Fe and Al oxides | low |
| High clay content | Poor vertical drainage, high chance of surface runoff | high |
| | High P sorptive capacity | low |

Organic P can form a large proportion of the total P in runoff from the land, being transferred through both surface and subsurface pathways (Haygarth & Jarvis, 1997; Turner & Haygarth, 1998). Transfer of organic P through subsurface pathways is especially important, because of its mobility in the soil compared to inorganic P (Chardon *et al.*, 1997). However, the levels of dissolved organic P appear to be controlled by biological production rather than solubility (Chapman *et al.*, 1997).

### 3.2.3 Ratio of nitrogen to phosphorus in agricultural contributions to eutrophication

Any factor, such as the angle of slope of cultivated fields, which tends to enhance the loss of one element versus the other (see above) will lead to a shift in the N:P ratio in the water. The relatively high N content of most waters derived from agricultural drainage may have a direct effect on eutrophication in coastal areas, where N is more likely to be the nutrient limiting primary productivity. The extent to which this is significant will of course depend on processes in the downstream river and estuary, which have themselves have a marked effect on the N : P ratio of water reaching the sea. High levels of agricultural N will also have an indirect effect on eutrophication in freshwaters by maintaining a higher N : P ratio than would otherwise be expected following P additions.

### 3.2.4 To what extent is runoff from agriculture likely to influence decisions made during implementation of the UWWTD?

Provisions within the UWWTD for nutrient removal apply only to STWs with a p.e. > 10,000. There is therefore usually a considerable upstream stretch of UK rivers to which the Directive does not apply, although there may be considerable nutrient inputs from agriculture as well as, in most cases, several works with a capacity < 10,000 p.e. Nutrients from both these sources will contribute to the total load and the concentration of nutrients in a river.

Whilst generalizations are difficult, the study of nutrient loads in streams feeding Lough Neagh makes (Foy *et al.*, 1995) salutary reading. P reduction was installed at nine STWs in the Lough Neagh catchment during 1981 and a drop in P concentrations was observed. However, in subsequent years, P concentrations gradually increased until, by 1988, they had reached the levels experienced before phosphorus removal was installed. The underlying reasons for these increases is not known for certain, but Foy *et al.* (1995) present data showing that there had been an increase in background P of about 1.5 kg $km^{-2}$ $yr^{-1}$ across all the subcatchments draining into Lough Neagh. In view of the uniformity of land use in the catchment as a whole, this suggests that agricultural practices are the cause, rather than increases from point sources. The impact of these increases on the biological manifestations of eutrophication has apparently not been measured.

## 3.3 Seasonal patterns

Nitrate concentration in UK rivers tends to be highest in winter, reflecting the high runoff during this period due to rainfall. This pattern was observed both in the upper, unmanaged portions of the Dee catchment in Scotland, and in the predominantly agricultural areas further down the valley (MacDonald *et al.*, 1994). Other factors which may influence these trends include the seasonal cycle of fertilizer application and shifts towards autumn-sown crops, encouraging fertilizer applications at this time.

The seasonal pattern of P concentration in most rivers is the opposite to that for N, with maximum concentrations in summer, rather than winter (Casey & Clarke, 1986; Muscutt & Withers, 1996; MacDonald *et al.*, 1995). These studies indicate an inverse relationship between P concentration and flow for a given river, suggesting a relatively constant input of P to the system, which is simply diluted by increased volume of water. However, if loads, rather than flows, are considered, then low frequency, high intensity events are responsible for a high proportion of the TP load entering watercourses from the land (**4.1**), particularly if such events follow fertilizer applications (Haygarth & Jarvis, 1996, 1997).

Marked increases in P were found in streams in the peaty catchment of Upper Teesdale (Northern Pennines) for a short period in spring, with concentrations reaching two to three orders of magnitude higher than than those during much of the rest of the year (Livingstone & Whitton, 1984). At least half, sometimes more, of this enhanced P was dissolved organic, suggesting the that it had been mobilized by biological activity in soils of the catchment. It seems likely that some streams of the Swale catchment also receive short periods of high P concentration in spring, though P is otherwise very low (Christmas & Whitton, 1998a). No such seasonal surge was found in the small lake on the Antrim Plateau studied by Gibson *et al.* (1995).

## KEY COMMENTS: NUTRIENT MOVEMENT FROM LAND TO RIVERS

i) Several studies of particular catchments indicate that the relative contributions of P from point sources originating from sewage treatment plants and diffuse agricultural sources may be shifting, with the former decreasing and the latter increasing. In the case of Lough Neagh, a decrease in the former is now more than compensated for by the latter i.e. P concentrations are still rising.

ii) The relative contributions of groundwater and surface runoff may influence not only the relative inputs of N and P, but also the relative inputs of different nutrient fractions, such as nitrate versus organic N.

iii) Nitrate concentration in UK rivers tends to be highest in winter, reflecting the high runoff at this season. The seasonal pattern of P concentration in most rivers is the opposite of that for N, indicating a inverse relationship between P concentration and flow.

iv) Upland streams and the unpolluted upper parts of rivers in the Northern Pennines tend to have ecosystems which are P limited for much of the year, though they may receive short periods of high phosphate in spring.

# 4. RELATIONSHIPS BETWEEN FLOW, NUTRIENT LOAD AND NUTRIENT CONCENTRATION

## 4.1 Introduction

Riverine exports of nutrients from terrestrial systems are of major concern because of the eutrophication of coastal waters. However, estimates for export are often only very approximate, both because of the lack of data for many rivers and the difficulty of interpreting the data that are available. It is probably for the latter reason that some water management bodies appear to have been slow to publish overall assessments of river loads, as is apparently the case for the Rhine - Meuse system (W. Admiraal, pers. comm.). Past estimates of loads transported from the east coast to the North Sea should be treated with caution.

Other key problems are the design of the sampling programme to obtain data on nutrient concentrations and the statistical treatment of the raw data to be integrated into overall estimates. The latter topic is the focus of a research study at the Department of Geography, University of Exeter (Dr B. Webb). Underestimates of P transported in rivers due to the statistical bias introudced when employing log-log regression equations are evaluated by Lennox and Smith (1998). Kinniburgh *et al.* (1997) use a modelling approach for the River Thames to integrate data from routine P measurements to obtain load estimates. They point out that the model takes account of average concentrations, since this was the criterion set in Department of the Environment methodology (1993).

A routine sampling programme for water chemistry may provide information of use for biologists, because it is the ambient concentrations which influence growth of algae and other phototrophs. However, it is unsatisfactory for estimating total annual nutrient loads transported downstream. It is generally accepted that storm events can be responsible for major inputs of nutrients, though there are only a moderate number of detailed quantitative studies. Sudden increases in nitrate concentration occur during storm events, especially if these follow prolonged dry periods (Johnes & Burt, 1993). Surface runoff and and drainage waters may contain very high contents of suspended solids (> 1 g $dm^{-3}$) and particulate P is usually much greater than MRP under these conditions (House *et al.*, 1998).

Some details of the factors leading to nutrient input to rivers have been given in Section 3. More detailed studies where modelling of the data has been incorporated for predictive purposes have been made for predominantly agricultural catchments in several parts of Europe. In an examination of the causes of year-to-year variation in nitrate concentrations in the rivers flowing to Lough Neagh, Stronge *et al.* (1997) developed a multiple regression model, which explained 74% of the variation of nitrate concentrations for the period 1974 to 1994. The independent variables incorporated into the model were efficiency of fertilizer usage, previous summer rainfall, sun hours in winter and rainfall for the period January to June. Based on worst case scenario, employing the extreme values for these climatic variables and the least fertilizer efficiency ratio, the predicted nitrate concentration is only 4.4 mg $L^{-1}$ N, which is well below the EC maximum admissible level of 11.3 mg $L^{-1}$ N for drinking water.

Changes in suspended solids and particulate P were reported by Kronvang *et al.* (1997) for the long-studied Gelbaek Stream in Denmark over a two-year period. In both cases losses mainly occurred during infrequent storm events. In comparison with intensive storm sampling, infrequent (fortnightly) sampling underestimated annual transport during the two study years by 24 and 331%, respectively, for suspended solids, and by 86 and 151 %, respectively for particulate P. Stream bank/bed erosion was considered to be the major diffuse source of suspended solids and particulate P in both years.

The results from a study over a one-year period in the River Deel, Co. Mayo, Ireland, were used to develop a model relating discharge and MRP to rainfall (McGarrigle, 1993). It was suggested that the use of such an approach permits the rapid build-up of a picture of the effectiveness of any particular sampling regime and its likely accuracy in assessing the true situation in the river. The necessary calculations could be carried out with the aid of a spreadsheet such as Lotus 123 or Microsoft Excel.

Drought is another factor to be considered. A study (Boar *et al.*, 1995) of analytical and flow data for the River Nar, East Anglia, showed that dissolved inorganic P was retained increasingly over a 4-year period when drought conditions were prevalent. Biological uptake by higher plants was probably responsible for most of the DIP which was retained.

## 4.2 LOIS studies

### 4.2.1 Introduction

The LOIS programme sponsored by the Natural Environment Research Council has provided especially detailed studies relating flow, nutrient loads and nutrient concentrations for various rivers in eastern England and Scotland, so these will be used to comment on various aspects. The raw data on the chemistry of water and sediments obtained during this study are included in a CD-ROM to be published in 1998 (contact: R. Moore, Institute of Hydrology). Many of the papers on rivers resulting from the LOIS programme have been published in two special volumes of Science of the Total Environment (1997, vol. 194/195; 1998, vol. 210/211). A third volume is due for publication in March 1999.

A detailed analysis of nutrient data collected under the LOIS core programme from September 1993 to December 1996 was presented by Jarvie *et al.* (1998). They refer to 15 sites on 12 rivers (Tweed and Humber tributaries). These are some key points.

**Total N** consists overwhelmingly of total dissolved N in all the rivers studied, though there was a relatively lower proportion of particulate N in the urban/industrial rivers to the south of the region. **Nitrate** shows a strong negative relationship with flow on the urban and industrial rivers, indicating the dominance of point sources. In contrast, the rivers draining the more rural and agricultural catchments (Tweed, Swale, Ouse, Derwent) exhibit a positive relationship between nitrate concentration and flow, reflecting diffuse agricultural runoff sources. **Nitrite and ammonium** exhibit predominantly negative relationships with flow in most rivers, indicating the importance of point sources, even within the more rural northern rivers. **Particulate N** exhibits a positive but poor relationship with flow in all rivers.

**Soluble reactive P** exhibits strong dilution with increasing flow in all the rivers, indicating the dominance of point sources, even in the rural and agricultural areas. **Dissolved hydrolysable P** shows no discernable patterns concentration with flow.

**Average N : P ratios** are highest in the agricultural rivers, where the mean ratio is typically > 20. (The ratio is based on total dissolved inorganic N to total dissolved P, using values based on mass.) For the urban and industrial rivers, mean N : P ratios are typically < 11. The mean N : P ratio at all sites is higher under storm flow than baseflow conditions. During stormflow, nitrate concentrations increase as a result of mobilisation of diffuse sources, while P concentrations decrease, presumably as a reult of dilution of point source inputs.

### 4.2.2 Tweed

The water quality of the Tweed was assessed more fully by Robson and Neal (1997). Point source inputs are important for phosphate, while diffuse agricultural sources are particularly important in lowland agricultural areas for nitrate and phosphate. Detailed colour maps show the relative contributions of different sources to nitrate and ammonium. Many determinands show striking seasonal variations. For nitrate, phosphate, silicate and oxygen, the seasonal variations are greatest on small lowland streams draining arable areas. The concentrations of a number of determinands (e.g. phosphate) decrease with rise in flow and in general such determinands are likely to have either ground water sources or significant point sources (as with phosphate). Determinands which rise with flow (e.g. nitrate, ammonium, silica) may have sources from the upper soils and from near surface runoff or mobilisation of the sediments; groundwaters carry comparatively lower concentrations of these nutrients. Contributions from sewer overflows at high flows are not significant in this predominantly rural catchment.

Data for nitrate were considered in particular detail. A basic empirical regression model was investigated for nitrate and found to be able to explain regions variations in terms of land use and soil type. Histograms are presented for concentration, average load and load per unit area at sites down the main river and six tributaries. Three variables relating to land use explain 93% of the total variation in nitrate concentration. These are: tilled land; mown/grazed grass; soils which have a macoporous structure overlying shallow groundwater. However, the authors stressed that great care would be needed for these results to be extrapolated to other regions, so details of the estimated regression coefficents were not included. A large number of variables were considered in the regression, so it is possible that one or more of the above were selected due to coincidental correlation rather than a causal effect. Nevertheless, the authors suggested that their simple type of approach may provide a means of estimating how stream water quality will respond to future changes in land use.

### 4.2.3 Swale - Ouse system

More detailed studies have also been made on one of the Humber tributaries, the Swale-Ouse system. Analysis of long-term datasets from August 1993 to April 1995 were made by (House *et al.*, 1997) together with further long-term data and three 100-h periods of intensive monitoring (House & Warwick, 1998). Point sources entering the main river and major tributaries were a major contribution to TP concentrations during low-flow conditions in spring and autumn, while the lower PP concentrations occurred under these conditions. The highest PP concentrations were associated with the highest discharges. Nevertheless, there was a low correlation between river discharge and PP concentration (House *et al.*, 1997). Most of the PP export occurred during a few major storms. The first major storms in autumn led to the resuspension of deposited sediment accumulated over the summer and a general scouring of the river bed. This suspended material contained a greater concentration of P than material in winter storms.

Nitrate concentration was more influenced than P by diffuse inputs and previous weather conditions. Although nitrite concentrations generally increased with river flow, the changes were less marked than for nitrate. Ammonium also increased in the main river during high-flow conditions. All nutrients showed hysteresis in the concentration - discharge relationship during a a major storm, which indicates the importance of diffuse sources. The effect was consistent with a depletion of nutrients during the falling limb of the hydrograph (House & Warwick , 1998).

## KEY COMMENTS: RELATIONSHIPS BETWEEN FLOW, NUTRIENT LOAD AND NUTRIENT CONCENTRATION

i) Data on N and P annual loads transported by UK rivers are likely often to be unreliable, perhaps including earlier estimates of loads to the North Sea. This is because routine sampling programmes for water chemistry tend to underestimate transport during major storm events. This may also have led to underestimates of annual nutrient loads removed from some agricultural areas.

ii) The Land Ocean Interaction Study programme sponsored by Natural Environment Research Council and supported by the Environment Agency has now produced a major database on chemistry of water and sediments for the Tweed and the Humber tributaries covered extended periods within 1993-1997. The data are available on CD-ROM (obtainable from the Institute of Hydrology) and much of the data have been / will be published in three double volumes of Science of the Total Environment.

iii) Analysis of data for the Tweed (by A.J.Robson and C.Neal) showed that seasonal variations for nitrate, phosphate, silicate and oxygen were greatest on small lowland streams draining arable areas. Besides nitrate, ammonium and silicate also increased with a rise in flow.

# 5 NUTRIENT FORMS AND DYNAMICS

## 5.1 Water column

### 5.1.1 Introduction: problems related to analysis

Accounts of the various N and P fractions which can be measured by straightforward analytical methods are given in texts such as that published by American Public Health Association (1992), while the Standing Committee of Analysts (1980) "blue" book on phosphorus analysis includes a detailed flow diagram of the procedures used to characterize various particulate and dissolved forms of phosphate. The main soluble forms in which N and P occur in the water column are summarized in Section 1.2. Physical, chemical and biological processes can all be important in determining the distribution of N forms between soluble and particulate phases. Physical and physico-chemical processes include solution, precipitation, adsorption and ion-exchange. Phosphorus measurements in particular are influenced markedly by the procedure used for filtration, because there is probably often a continuum between phosphate in true solution, through colloidal forms to particles of various sizes.

If samples are not analyzed immediately, there are various potential errors. Lambert et al. (1992) report a study on possible changes in four P fractions during storage of two lake water samples at 4° C. Total P remained unchanged after 4 h, but decreases (25 - 54%) occurred in total dissolved P, total reactive P and dissolved reactive P. Nutrient stability studies by House and Warwick (1998) showed that, although nitrite had considerable stability, both ammonium and P fractions were less stable. These nutrients must be analyzed as soon as possible after sampling to avoid changes caused by processes in solution and interactions of soluble compounds with colloids and suspended material during storage. The forms and amounts of N and P are both potentially subject to microbial activity and further studies are needed on the rates at which nitrite can be oxidized in stored water samples. If the water has been sterilized successfully by filtration, then only organic P should be influenced by biological activity (see below). The 0.45 µm filters in widespread use should remove all (or rarely, almost all) bacteria; however, there have been reports in the microbiological literature that not all types of membrane are fully reliable. (We have been unable to find a recent and critical evaluation of the various types of membrane.)

We have not seen any critical assessment of the accuracy and precision of measurements of N and P determinands made by the Environment Agency. However, a study made at the University of Durham suggests that it is important to establish the reliability of measurements, if data are to be used for assessment of long-term changes. As the NRA had agreed in 1995 to analyze a set of water samples in relation to a particular project at the same time as NERC's LOIS programme was conducting an interlaboratory comparison of N and P measurements, the opportunity was taken to split 36 samples for simultaneous analysis by NRA and the other laboratories. The values supplied by the NRA for 33 samples fitted closely to the measurements by the other laboratories, but those for the other 3 (ammonia or phosphate) differed markedly.

We suggest that the approach to water chemical analysis used by the Environment Agency for routine monitoring should be reconsidered for purposes such as monitoring long-term change, the status of a stretch of river designated as a SSSI or downstream of a major improvement to a STW. As far as possible, such measurements should be made within a few hours of collection or, if this not practical, then special precautions should be introduced such as filtration and storage as near to 0° C as possible without risk of freezing. Similar care is needed with storage of samples for chlorophyll *a* analysis (**7.1**), which should be filtered to remove as many grazers as possible without also removing phototrophs and stored at about 8 °C in the dark. In the case of chlorophyll, in particular, it is important that analyses are carried out locally.

Preservatives are sometimes used with water samples stored for nutrient analysis, especially marine samples, but we have been unable to find a critical assessment of this procedure for a wide range of types of water.

Another problem with the routine procedures used by the Environment Agency is that the detection limits are too high for nutrient determinands at some sites. Although this is seldom likely to occur in eutrophic environments, it is important when establishing long-term data for less nutrient-rich states. This problem occurred with the CORE data collected within the LOIS programme, when values often fell below the detection limits (similar to Environment Agency limits) at some middle river sites, such as the Swale at Catterick. (This problem was only rectified half way through the LOIS study.) This makes it difficult to comment on the variability of data for particular determinands and impossible to assess the impact of high flows. Such data on variability is important, for instance, for quantifying loads transported from agricultural catchments under flood conditions and for sites on rivers designated as SSSIs.

Biological removal of nutrients from river water may occur due to planktonic or benthic organisms. The most detailed literature on nutrient removal is for benthic algae and this has been reviewed by Mulholland (1996), though this includes only a few reports on the ambient rates of nutrient uptake (see below). In the case of rooted plants, the literature is also sparse on the relative contributions of uptake by submerged leaves and roots in the sediments (**7.2**).

### 5.1.2 Nitrogen

In addition to the loss of $NH_3$ to the atmosphere when the pH rises above 9.0 (**1.2**), nitrate and ammonium are both removed by biological accumulation by bacteria, algae, bryophytes and higher plants. It seems likely that the majority of organisms removing combined N from the water column utilize nitrate and ammonium, but there are few satisfactory data.

Parts of the nitrogen cycle may occur in the water column or associated with benthic communities. For instance ammonia is likely to be oxidized to ammonium at values for $Eh_{7.0}$ above about + 180 mV; this probably mostly takes place due to bacteria attached to particles. Nitrification (oxidation of nitrite to nitrate) is also likely to be important where nitrite is released to well-oxygenated water. It seems likely that the occurrence of this process in stored samples is sometimes reponsible for nitrite concentrations being underestimated, because microbial oxidation has taken place by the time the analysis is made.

Recent studies from Germany (Werner, 1991) and Northern Ireland (Smith *et al.*, 1995) have reported concentrations of nitrite in rivers of 100 - 200 $\mu g\ L^{-1}$ N, values which greatly exceed the European Union nitrite guideline of 3 $\mu g\ L^{-1}$ N for rivers supporting salmonid fisheries (EEC, 1978). Reports of nitrite accumulation appear to be linked to large inputs of agricultural N (Kelso *et al.*, 1997), though only 40% of the nitrite in Northern Ireland rivers originates directly from land drainage, with the remainder originating from sediment - water interface transformations of N substrates from point sources (Smith *et al.*, 1995). Studies by Kelso *et al.* (1997) indicate that this nitrite originates by dissimilatory nitrate reduction in anoxic sediments (see below).

No evidence for denitrification was found in the water column of the freshwater tidal Yorkshire Ouse, in spite of a relatively high content of suspended solids (García-Ruiz *et al.*, 1998b). However, there have been several reports of denitrification taking place in benthic algal communities (mostly *Cladophora*); the various studies assume the occurrence of anoxic or near anoxic microenvironments within the mats, but there are few measurement to support this. Nevertheless, Duff *et al.* (1984) reported denitrification rates up to 1.3 mmol $NO_3\ m^{-2}\ d^{-1}$ in intact periphyton communities dominated by *Cladophora* in a N-rich northern California stream. Considerably higher rates have been reported at the base of algal communities in N-rich Danish streams (e.g. Nielsen *et al.*, 1990). Most of the authors noted that denitrification rates were considerably higher during the night than during the day, suggesting that low oxygen conditions are more prevalent when photosynthetic oxygen production ceases.

Benthic nitrogen-fixing blue-green algae are abundant some upland streams, such as *Rivularia* in Upper Teesdale (Livingstone & Whitton, 1984) and *Stigonema* in some soft-water streams of the Lake District. The presence of these long-lived organisms is usually assumed to indicate periods during the year when N limitation (as opposed to P limitation) is important. Such blue-green algae, which can be recognized by the presence of heterocysts (nitrogen-fixing cells) were absent from streams in the Swale-Ouse catchment (Whitton & Lucas, 1997). Heterocystous blue-green algae often occur in the plankton of lakes with much more P-rich water and occasionally in the plankton of rivers, However, they appear to be absent in the benthos of downstream river sites. This strongly suggests that nitrogen fixation is unimportant or does not occur in the benthos of downstream sites.

### 5.1.3 Phosphorus

The key features of inorganic chemistry are known quite well and summarized clearly by Hutchinson (1957). For instance, the relative contributions of inorganic phosphate are influenced by pH, with $H_2PO_4^{2-}$ predominant at low pH. Precipitation of phosphate may be important when MnII or FeII are released from peaty drainages or pumped mine water and then oxidized when they encounter oxygenated river water. Water draining heavy metal wastes is also likely have very low concentrations of soluble inorganic phosphate due to the low solubility of heavy metal phosphates. Phosphate co-precipitation on calcite may be enhanced by algal photosynthesis (Hartley *et al.*, 1997).

The fraction of the river water passing through a 0.45 µm membrane (see above) may include a range of molecules in the colloidal size range, even if they though they are included analysis in the MRP (molybdate reactive P) fraction. Haygarth *et al.* (1997) report on a study of two river and two soil waters, where the water was fractionated into <

0.45, < 0.22, < 0.1 and < 0.025 µm fractions and also into < 10,000 and < 1000 molecular weight fractions. There was evidence that some of the MRP occurs in quite large molecules, raising the question how much of this phosphorus is available to algae. For instance, the concentration of MRP in the < 1000 molecular weight fraction was singificantly less than in the < 0.45 µm fraction.

The phosphate fraction released by acid digestion (usually persulphate) of soluble phosphate is treated as organic phosphate in standard analytical procedures. However, it may consist of organic molecules such as phosphodiesters (Paul *et al.*, 1991) and phosphomonoesters (Boon, 1993) released during biological degradation or complex interactions between phosphate and other organic molecules such as humic acids. The phosphoesters may be hydrolyzed by phosphatases (phosphodiesterases and phosphomonoesterases). If the enzymes are in solution, any phosphate released should be added to the inorganic phosphate pool (Klotz, 1991). At least in the case of blue-green algae, only phosphomonoesterases are released into the environment; phosphodiesterases are retained by the organisms (Whitton *et al.*, 1991). If the enzymes are associated with the surfaces of organisms, some will be accumulated by the organism, but probably in some cases also a part released to the water column. These changes may be quantitatively important in water samples stored for more than a few hours.

Organic phosphate typically forms a higher proportion of the soluble phosphate pool at upstream sites (e.g. Christmas & Whitton, 1998a) and may be the predominant form. Studies on upland streams which neglect the organic phosphate fraction should be regarded as of limited value. Organic phosphate is probably especially important to organisms in chemical regimes which favour precipitation of inorganic phosphate and some algae are characteristic of such environments (e.g. *Draparnaldia* and *Microthamnion*: BAW, unpublished data). However, the majority of algae and mosses appear to be able to utilize organic phosphate when inorganic phosphate is limiting.

Further downstream soluble inorganic phosphate usually exceeds soluble organic phosphate, though the latter needs to be considered when assessing long-term changes in ambient phosphate. With respect to this, one likely future change should be monitored. There has recently been much interest in adding phytases (one type of phosphomonoesterase) to the feed for chickens (Lynch & Caffrey, 1997; Oloffs *et al.*, 1998), pigs (Han *et al.*, 1997) and cattle (Metcalf *et al.*, 1996). Although this should lead to a considerable reduction of P in manures (Han *et al.*, 1997), it is likely to lead to a considerable increase in phosphatase activity in water draining areas of intensive poultry and pig-farming, and hence more rapid breakdown of part of the organic phosphate fraction in the water.

## 5.2 Bed sediments

### 5.2.1 Nitrogen

Those parts of the nitrogen cycle favoured by low oxygen conditions are important in the bed sediments. Denitrification, which was thought until the early 1980s to be an anoxic process is now known to proceed optimally under microoxic rather than anoxic conditions. Denitrification could in fact be detected in sediments of a relatively fast-flowing upland stream of the Swale-Ouse system (Pattinson *et al.*, 1998), but the rate (per unit area of sediments) increased by almost three orders of magnitude on passing downstream. Key factors found to favour denitrification were organic content of the sediments and nitrate concentration of sediment water. There is almost certainly a wide variety of organisms involved in denitrification in river sediments, but relatively little is known of the contribution of different species under different conditions or the effect of environmental factors, including possible toxic substances. (A new project is being planned by R.V.Smith at Belfast on the diversity of river sediment organisms involved in the nitrogen cycle.)

Denitrification converts nitrate to nitrous oxide or nitrogen gas. Almost certainly the former is more important at higher ambient oxgyen concentrations, though there are few data. However, it is clear that nitrous oxide can at times represent a considerable proportion of the nitrate removed in river sediments; for instance, values for sediments in the R. Wiske, Yorkshire, sometimes exceed 50% (García-Ruiz *et al.*, 1998a). Experimental studies on the influence of various factors showed that, while the addition of various organic substrates to sediment cores had no effect on denitrification rate, it did lead to a significant decrease in the proportion of nitrous oxide formed as a result of nitrate reduction. Presumably an increase in the organic content of sediments led to a reduction in oxygen concentration. This shows how complex may be the effects of making changes such as an improvement in the quality of a sewage effluent, which the present results suggest might actually lead to an increase in nitrous oxide release to the atmosphere (see also **8.1**). In view of the fact that nitrous oxide is considered to be one of the three principal "greenhouse" gases, further quantitative information is needed for river sediments.

Kelso *et al.* (1997) concluded that the high nitrite concentrations found in summer in the six major rivers of the Lough Neagh catchment, Northern Ireland, probably resulted from dissimilatory nitrate reduction in the sediments, the process which ultimately leads to formation of $NH_4^+$. Experimental studies showed that maximum concentrations of nitrite (up to 1.4 mg $L^{-1}$ N) were found in sediments deeper than 6 cm associated with a high concentration of metabolizable carbon and anoxic conditions. The authors commented that sediments from the algal blooms provide elevated carbon concentratons as an energy source, while at the same time the release of $OH^-$ resulting from photosynthesis elevates the pH.

### 5.2.2 Phosphorus

The insolubility of many inorganic phosphates means that there is often a tendency for sediments (suspended or bed) to accumulate particulate phosphate (see above). Many phytates, the most abundant form of particulate organic phosphate in soils, are also highly insoluble, so material removed by erosion will also tend to be deposited in river sediments. During high flows, particles may be redistributed, but at downstream sites net removal of P by this process may be limited. Some P may also be expected to be released into solution, such as when Mn and Fe 'oxides' are reduced under anoxic conditions or when phytates are mobilized by phytases, and hence potentially to the water column.

A series of studies related to P have been conducted in recent years on interactions between the water column and sediments by the River Laboratory of the Institute of Freshwater Ecology (W.A.House: see Appendix II), which deal with aspects of P deposition and release. Kinetic studies on the influx of SRP (soluble reactive P) to stream sediment showed a marked contrast between the fast uptake of P by suspended sediment, which may subsequently be deposited in bed sediment, and the much slower direct uptake by bed sediment, due to the rate-limiting diffusional transfer across the sediment-water interface (House *et al.*, 1995a). Further experiments (House *et al.*, 1995b), using an experimental channel with a characterized bed sediment together with its fauna, showed the importance of water velocity and hydrodynamics in controlling the transfer rates. The values for several parameters calculated from the experiments were used to estimate the SRP flux to sediment over a distance up to 5 km downstream from a point input of SRP.

House and Denison (1997) investigated processes leading to input and loss of SRP from sediments downstream of a STW effluent in a hardwater river, the Great Ouse, near Brackley, Northamptonshire. (The study was based on samples taken during one preliminary survey and subsequently once for each of four seasons.) In spring and summer, P concentrations in sediments increased immediately downstream of the main input and then decreased on passing downstream. The effect was consistent with a large uptake of P to bed sediment and associated vegetation. Seasonal changes in sediment composition were consistent with the deposition of calcite, either abiotically or associated with algal biofilms in the sediment. There was a high correlation between total P and Ca in sediments, particularly at sites furthest from the STW. However, the equilibrium phosphate concentrations of the surface sediments did not respond quickly to the higher concentrations of dissolved P found in summer. Similar kinetic studies will be needed on a range of rivers with diverse chemistries and flow regimes before it is possible to make general predictions on P uptake and release by sediments.

The influence of rooted macrophytes on P mobilization and losses is largely unknown. Obvious questions that need to be answered are what percentage of P in the green shoots is returned in the autumn to rhizomes or tubers in the sediments and how much P is lost from the plants during the growing season due to mechanical or grazing losses. Because of all the uncertainties, it is difficult to predict the time-scale of changes in sediment P composition when aqueous P levels are reduced as a result of improvements in effluent quality or agricultural management. However, it is suggested that P loss may be much slower than P gain as a result of eutrophication, especially if submerged macrophytes play a major role at a site. It seems likely that by far the most effective way of reducing P loads in the sediment would be to remove submerged macrophytes at the height of the growing season, preferably by physical removal from the river rather than herbicide treatment. Any biomass removed must be dumped well away from the river, perhaps by incorporating it into a composting system.

## KEY COMMENTS: NUTRIENT FORMS AND DYNAMICS

i) More care is needed in the storage and analysis of water samples where the data are required for assessing long-term change rather than for routine monitoring purposes. The sampling and analytical protocol for the two different requirements should be separated.

ii) Recent studies in Germany and Northern Ireland have shown nitrite concentrations in river water which exceed the European Union nitrite guideline for rivers supporting salmonid fish by such a wide margin that their potential toxicity to other organisms should be considered. Studies in Northern Ireland by R. V. Smith and colleagues indicate that both land drainage and transformations at the sediment - water interface are important sources of this nitrite.

iii) Denitrification in river sediments is an important process leading to loss of nitrate. It occurs under low oxygen conditions, rather than the anoxic conditions suggested in older textbooks. Providing fine sediments are present, the process can be quantitatively important even in well oxygenated, relatively fast-flowing rivers.

iv) Removal of nitrate by denitrification can lead to the formation of nitrous oxide (one of the three most important 'greenhouse gases') and/or nitrogen gas. The factors favouring formation of nitrous oxide rather than nitrogen are poorly understand, but it seems probable that denitrification proceeds all the way to nitrogen under lower oxygen conditions.

v) Kinetic studies by W.A.House and colleagues on phosphate uptake by sediments have shown a marked contrast between the rapid uptake of soluble reactive phosphate by suspended sediment and the slow direct uptake by bed sediment. This suggests that much of the P-rich components of bed sediment may be derived from formerly suspended phosphate-rich sediment.

vi) The influence of rooted macrophytes on P mobilization and losses is largely unknown, but it is suggested that their presence may slow the rate of overall loss of P from a site when aqueous phosphate concentrations have decreased as a result of improved effluent quality from a sewage treatment works.

# 6 BIOLOGICAL IMPACTS OF NUTRIENTS

## 6.1 General features

### 6.1.1 Benthic community

Increased nutrient concentrations affect the biota of a river in many different ways and it is likely that all trophic levels are affected either directly or indirectly. The marked changes in benthic algal communities which may be evident on passing down a river system are likely often to be influenced by downstream increases in nutrient concentrations. The greater variability of nutrient concentrations at some upstream sites is also likely to be important. In the case of upland streams and upstream stretches of main rivers in the UK, many species such as bryophytes and the longer-lived algae, which are often common here (e.g. *Lemanea*), probably encounter marked variation in nutrient levels during their growth cycles.

It is has long been known that high nutrient levels can lead to dense growths of filamentous algae in rivers. For instance, the study by Butcher *et al.* (1937) showing that nutrient enrichment led to mass growths of *Cladophora glomerata* in the River Tees, England, has been followed by many further studies on nuisance growths of *Cladophora* (see Whitton, 1970; Dodds, 1991). A detailed record of long-term changes has been made for a 90-km long stretch of the River Wear, where there 70 more 0.5-km lengths with this alga present in 1996 than 1966 (Whitton *et al.*, 1998).

Unfortunately, it is seldom clear whether N or P has been the more important nutrient in enhancing growths of *Cladophora*. Much of the older literature tended to assume that increases in P had been the key factor at particular sites, but with little critical evaluation of the data. Circumstantial evidence that *Cladophora* and other submerged plant growths may reach sufficient biomass to cause P limitation of growths further downstream was provided by Jarvie *et al.* (1998), based on an assessment of detailed water chemical records for river sites in east coast rivers of the UK. One mid-river site (on the Ure) showed that 44% samples had an aqueous N : P ratio by mass > 24. Comparison of the records for the "growing season" (April to September) with the "dormant season" showed that the high ratios were associated with the former, even when allowance was made for differences in flow regime at different seasons. The authors suggested that the conspicuous plant growths in this stretch of river may have been responsible for reducing aqueous phosphate levels during the growing season and thus shifting the ratio of N : P in the water.

A further problem with assessing which factors are likely to bring about increases in *Cladophora glomerata* is that the alga requires several other nutrients, which are almost always overlooked. These are silicate, thiamine and probably also vitamin $B_{12}$ (Moore & McLarty, 1975). Circumstantial evidence that vitamins might occasionally be important comes from observations at a site in New Zealand where mass growths of *Oedogonium* (which probably does not require an external source of vitamins for growth) were largely replaced immediately downstream of a very small sewage effluent by mass growths of *Cladophora* (B.A.W., unpublished data).

In addition to *Cladophora*, three other large algae are at times especially abundant in lowland rivers in the UK. *Enteromorpha flexuosa* can form large masses of tubular thalli in summer, but overwinters as small attached filaments, so presumably requires the presence of some firm substrates. The summer forms are usually free-floating or intermingled with submerged vegetation, but in the shallow, fast-flowing R. Lyne (Northumberland), many thalli remain attached to the rocks (B.A.W., unpublished). There is some evidence that this alga was rare or absent in the earlier part of this century at sites where it is now sometimes abundant. For instance, the thorough account by Butcher *et al.* (1937) of the Skerne and Tees in the 1930s indicates that it was absent then; however, it was frequent by the mid-1960s. Marine forms of *Enteromorpha* (predominantly *E. intestinalis*) can form nuisance growths in estuaries downstream of rivers with very high nitrate, such as the Ythan, which was the subject of study by the former North East River Purification Board (ENDS Report 253, 1996).

*Vaucheria sessilis* is best known from slow-flowing drainage ditches and small streams in lowland areas such as East Anglia, but is sometimes as abundant and conspicuous as *Cladophora* in fast-flowing rivers e.g. Wear.

*Hydrodictyon reticulatum*, the water-net, has until recently mostly been known in the UK from shallow lakes and slow-sand filters, though it was abundant in the lower Tweed in the mid-1970s. However, there are many records of its very recent invasion into lowland rivers round the UK, including the Tyne, Wear (Whitton *et al.*, 1998) and Swale (Whitton & Lucas, 1997).

The distribution in rivers of *Cladophora glomerata*, *Enteromorpha flexuosa* and *Vaucheria sessilis* to ambient water chemistry all suggest that these are strongly favoured by high levels of nutrients, even if it is difficult to establish the relative importance of N and P. Although *Hydrodictyon reticulatum* is probably also favoured by eutrophication, it seems likely that a recent series of summers with long periods of low flow may have been the key factor leading to its spread in rivers. The alga apparently overwinters by spores rather than attached structures like the other three algae, so it may take several months of low flow for a large population to develop.

The response of filamentous algae to nutrients may be influenced by current speed. It has been known since the studies of Whitford and Schumacher (1961, 1964) that P uptake is strongly enhanced in some algae at higher speeds. However, it has been shown (Borchardt, 1994) for *Spirogyra fluviatilis* that there is also a higher P demand for growth at higher speeds. The response by individual species may therefore be complex.

Rooted macrophytes sometimes also form growths which are sufficiently dense to cause a nuisance and where eutrophication is thought to be the cause. Emergent weeds have to be cut annually in a number of nutrient-rich slow-flowing rivers in the UK (e.g. Wiske, Yorkshire) and fully submerged plant material is also sometimes removed from much faster rivers. There appear to be relatively few publicised accounts of eutrophication and the formation of nuisance growths of submerged macrophytes in rivers, though Thomas (1976) does this for *Ranunculus fluitans* in the upper Rhine.

As described in more detail in 7.2, it is difficult to comment on the relative importance of nutrients in the water column and in bed sediments on rooted macrophytes. Some of the literature up the late 1980s is reviewed in the report by Mainstone *et al.* (c. 1993). Haslam (1978) suggested that the amount of cuticle on submerged leaves may be important in determining the extent of nutrient uptake from water and made general comments on the extent of cuticle development in various species. She also pointed out that fragments of plants such as *Myriophyllum spicatum* and *Ranunculus* species may survive for some time by taking up nutrients from water, but only thrive when they become anchored. However, the literature may provide information which is apparently conflicting even for individual species. For instance, Spink *et al.* (1993) reported increased growth of *Potamogeton pectinatus* in experimental channels at the expense of *Ranunculus penicillatus* ssp. *pseudofluitans* at high (0.2 mg $L^{-1}$ P) concentrations compared to a control (0.04 mg $L^{-1}$ P). In contrast, Peltier and Welch (1969) concluded that the growth of *Potamogeton pectinatus* was little affected by concentrations of aqueous P.

### 6.1.2 Phytoplankton

The phytoplankton is typically dominated by a few groups, especially centric diatoms and motile and non-motile green algae. Blue-green algae are occasionally quantitatively important in the phytoplankton of UK rivers such as the Great Ouse during periods combining low flow and high temperature (Marker & Collett, 1997; Rose & Balbi, 1997).

The relationship between phytoplankton abundance and nutrients is difficult to define, and the literature can appear contradictory. In the case of rivers such as the Nene and Great Ouse, concentrations of N and P are sufficiently high that they are unlikely to limit primary productivity (Rose & Balbi, 1997). Variations in phytoplankton population density between years at particular sites on large downstream or slow-flowing rivers is much more likely to reflect hydrological differences (Ibelings *et al.*, 1998), especially if the onset of the spring bloom is delayed by high flows (Marker & Collett, 1997).

Decreases in silicate concentration in spring at about the time of maximum populations of centric diatoms have been recorded for downstream sites on larger or more slow-flowing rivers by a number of authors. Almost certainly such decreases are due to growth of the diatoms. Most authors have concluded that a reduction in Si led to limitation of diatom growth e.g. Rhine and Loire (Admiraal *et al.*, 1993) and Trent (Skidmore *et al.*, 1998). Modelling of the Seine basin (Garnier *et al.*, 1995) has also indicated that Si, but not P, can limit the standing crop here. In the case of the Thames (Lack, 1971) and Great Ouse (Marker & Collett, 1997), the authors also found drops in Si levels, but concluded that these did not limit diatom growth. The latter authors regarded 1 mg $L^{-1}$ Si as low, so perhaps the differing interpretions reflect differences in the extent to which Si is reduced relative to other nutrients or other environmental variables. The literature probably needs to be reassessed critically and detailed studies are needed to quantify the changes taking place at the time of peak populations.

If Si limitation does occur for periods of some days, it seems likely this will lead to a relative increase in other groups of algae such as small non-motile greens. Si limitation would not necessarily lead to limitation of the phytoplankton population as a whole by P or another nutrient, though the possibility should not be excluded. For the purposes of river management, an indication of a threshold Si : P ratio (akin to Redfield Ratio for C : N : P: Tett *et al.*, 1985) would be helpful. At 15 °C, diatoms dominate in Lake Superior at Si : P ratios approximately > 20 (Kilham *et al.*, 1986); however, cellular Si : P varies considerably between diatom species (Tilman & Kilham, 1976) and further study is needed if the impact of P removal on phytoplankton dynamics in lowland rivers is to be understood.

In temperate rivers, the summer months are often characterized by "clear phases", when flow is low and nutrients, temperature and light are abundant. Top-down control by zooplankton usually plays a significant role in phytoplankton dynamics during this period (e.g. Billen *et al.*, 1994; Kobayashi *et al.*, 1996). The principal groups of zooplankton are rotifers, ciliates and, to a lesser extent, cladocerans and copepods. It has been reported that the density of zooplankton in rivers is less than lakes with similar chlorophyll concentrations (Basu & Pick, 1996), but a more comprehensive assessment of the data is needed before this can be treated as a generalization. Three recent studies have shown the importance of the zebra mussel, *Dreissena polymorpha*, in North American rivers. For instance, Basu and Pick (1997) estimated that it could filter about 40% of the total volume of water in summer in the Rideau River, Canada.. In the UK, Skidmore *et al.* (1998) have suggested that the large numbers of *Unio* dredged from sediments in the Trent at Cromwell indicate that this may be quantitatively important in loss processes here.

Billen *et al.* (1994), in their model of phytoplankton dynamics in the Seine basin, found that inclusion of zooplankton in the model could not explain all the features of algal development in the summer and added a further term, "lysis" to account for factors such as fungal, bacterial and viral pathogens, in order to obtain a more realistic simulation. Further factors which need to be considered as possible controls on phytoplankton densityare grazing by fish fry and settling due to reduced turbulence.

### 6.2 Sites of conservation value

English Nature has selected 27 rivers as SSSIs, although it is recognised that several of these are deteriorating due to the impact of effluents, abstraction and adjacent land management (English Nature, 1997). Strangely, in view of their importance as indicators of the nutrient status of a river, algae have apparently been ignored in the selection of these sites. A series of "targets" for orthophosphate has been proposed by English Nature and the Environment Agency for different river types, yet many of the SSSI rivers already exceed even the "initial" target of 0.2 mg $L^{-1}$ P (which will be followed by phased reductions to levels appropriate to the river type). The value of this guideline is confused, because it is unclear whether the concentration refers to orthophosphate or P. In some cases, installation of tertiary treatment has reduced phosphate levels (e.g. Moors River - English Nature, 1997), yet in others (e.g. River Beault - Muscutt & Withers, 1996) the situation may be more complicated with both point and diffuse sources contributing to the problem.

A study (Carvalho & Moss, 1995) of 102 freshwater SSSIs identified 79 as having symptoms of eutrophication, of which 40 had possible problems with sewage effluent, 14 had proven or possible problems with farm wastes and four had proven or possible problems with septic tanks. Other causes included fish or bird communities, landfill effluents and sediment release. Diffuse pollution from agriculture was not discussed. However, only three of the sites were running waters and the authors pointed out several other inadequacies of their dataset. The relative contributions of point and diffuse sources to the nutrient budgets of these catchments can only be determined by detailed studies on a case-by-case basis and further work is clearly needed.

Any nutrient increase of groundwaters emerging as a spring is likely in most cases to have a received a substantial contribution from diffuse agricultural sources. This can pose problems where the water is used for growing watercress beds. This may also apply to some SSSIs. One of the present authors (BAW) is in receipt of a grant from Northumbrian Water to investigate eutrophication at a pond SSSI in Co. Durham and a preliminary overview of possible causes suggests that nutrient enrichment of the underwater springs supplying the water for this pond may be a factor.

## KEY COMMENTS: BIOLOGICAL IMPACTS OF NUTRIENTS

i) Marked variation in nutrient concentrations is an important factor in the ecology of upland streams.

ii) Data on aqueous N : P ratios at different seasons and under various flows may provide a means of assessing when submerged plants remove sufficient phosphate to have a significant effect on the water chemistry.

iii) The macro-algae, *Cladophora glomerata*, *Enteromorpha flexuosa* and *Vaucheria sessilis*, are all ones which respond positively to eutrophication. It is less clear how important this is a factor for the alga *Hydrodictyon reticulatum* (water-net), which has invaded many UK rivers in recent years.

iv) In spite of many studies on mass growths of *Cladophora* in rivers, it is seldom clear which, if any, nutrient is a limiting factor for growth at a particular site. The requirement of this alga for one of more vitamins is almost always overlooked.

v) The relative contributions of water and sediments to nutrient supply for submerged macrophytes is unclear and probably differs between species, though the literature mostly indicates that sediments are the more important.

vi) Phytoplankton in downstream stretches of UK rivers often shows a marked peak in population density in late spring, the population usually consisting largely of small centric diatoms. A number of studies in the UK and rivers on mainland Europe have reported a sharp fall in aqueous silicate at the time, though authors differ in whether or not they consider silicate availability to become a limiting factor for growth at this time.

vii) English Nature has selected 27 rivers as SSSIs. Although minimizing the impact of eutrophication is likely to be important at a number of these sites, algae, the organisms which respond most unambiguously to the nutrient status of a site, have been neglected in the assessment of these sites.

# 7 BIOLOGICAL MONITORING PROGRAMMES RELATED TO NUTRIENTS

## 7.1 Introduction

Primary producers have been the preferred organisms for monitoring eutrophication in rivers because their response to inorganic nutrients is more direct than that of most other groups of organisms. In addition, excess growths resulting from eutrophication may themselves be a considerable nuisance (7.1). It is helpful, however, to recognise which changes in other components of the biota are also characteristic of eutrophication. This aim of this chapter is to review briefly how the various components of the biota are affected by elevated nutrient concentrations, and to examine the present and future of monitoring based on each group. The implications of the Framework Directive are described in **Section 2.6**.

## 7.2 Benthic communities

### 7.2.1 Filamentous algae

There are many reports for rivers of temporal or spatial increases in attached filamentous algae being large enough to cause a nuisance and there is often sound evidence that these result from nutrient increases. Because of this, a number of researchers have proposed practical methods which depend on their being a relationship between amount of alga and concentrations of nutrients in the water at a particular site. Quantitative measurement of biomass, usually assessed as chlorophyll *a* (Marker, 1976), is possible. However, its value for routine monitoring is questionable, because of the many other factors which influence it besides nutrients, such as seasonal changes, floods and grazing (Biggs & Lowe, 1994; Allen, 1995). These problems could probably be overcome in part by a frequent enough sampling programme, but this is not only very time-consuming, but difficult to standardize because of the practical difficulties of removing samples.

In order to avoid the difficulties of fully quantitative sampling, Marsden *et al.* (1997) described an approach based on relatively simple observations at a site and developed during some years of practical experience of monitoring rivers in the Forth Basin, Scotland. Their Algal Abundance Index was defined as follows:

$$\mathrm{AAI} = \frac{2(\text{No. of abundant records}) + \text{No. of common records}}{\text{number of site visits}} \times 100$$

The abundance / cover is assessed on a semi-quantitative scale of "abundant", "common", "present", "rare" or "none". The relationship between this index and P is crude: although high values of the AAI indicate high nutrient levels, low values can occur for a variety of reasons, such as the lack of suitable substrata. Nonetheless, when used in conjunction with chemical data, it does allow the trophic limits of streams in the catchment to be defined (Table 1). Moreover, it is simple enough to be included as a part of routine invertebrate sampling in the catchment and thus allows a larger number of streams to be screened than would be possible if full macrophyte surveys or diatom samples were required. A similar scale of *Cladophora* abundance was developed by Marker and Bolas (1982), but no advice on sampling programme or interpreting the data were provided.

More ambitious algal survey techniques have also been developed which still avoid quantitative sampling of biomass Typically, these involve an estimate of percent cover of macroscopically-obvious algal growths in a predetermined length of river, followed by microscopic examination of samples of each type of growth and semiquantitative estimates of abundance. In the UK methods were developed by Holmes and Whitton (1981) and refined by Kelly and Whitton (1994). Similar methods have been developed independently in Austria (Pipp & Rott, 1996), Scandinavia (Jarlman *et al.*, 1996) and the USA (Porter *et al.*, 1993). However, whilst survey methods are generally well-developed, tools for data interpretation are less so, although the Scandinavian method permits different water qualities to be distinguished (see Lindstrøm, 1996, for practical example) and methods for using these techniques to evaluate ecological integrity are under development in Austria (Pipp & Rott, 1996).

A number of rivers in N-E. England and S-E Scotland have been surveyed by recording the presence or absence of particular species within defined 0.5-km lengths all down the river. If the species concerned are ones usually considered to indicate eutrophication, such as *Cladophora glomerata* and *Enteromorpha flexuosa*, then the number of records can be used to assess the trophic state of the long lengths of river. For instance, *Cladophora glomerata* was present in 70 more 0.5-km lengths of the 90-km long stretch of river surveyed in 1996 than 1966, suggesting a considerable increase in ambient nutrient concentrations over the period. However, even with *C. glomerata* some caution is needed, because the recent success of the alga may also have been influenced by other factors such as a decrease in aqueous zinc from mining activities.

The floating algal mats which occur in many rivers, particularly those dominated by blue-green algae, also tend to be associated with lowland, nutrient-rich stretches. The mats develop initially over bottom sediments, but it is unclear whether their growth better reflects the ambient water or the sediments.

### 7.2.2 Diatoms

The taxonomic composition of benthic diatom communities has been widely used for monitoring water quality. The initial development of a quantitative approach was largely due to R. Patrick, who used artificial substrates placed in the river (Patrick *et al.*, 1954; Patrick, 1973) and put particular emphasis on taxonomic diversity to interpret the extent of pollution. However, the majority of indices developed since that of Descy (1979) have used populations taken from substrates already growing at a site and interpret the data based on the relative proportions of species present at the site. The tendency to share the same basic principles of sample collection has made it easier to compare results from different studies and authors (Kelly *et al.*, 1998).

Until the 1990s most of the indices provided measures of general water quality and so may be considered a special modification of the saprobien system. However, with the advent of the UWWTD (EEC, 1991), several countries in Europe have started to apply these methods to monitor nutrients (Table 2). Two trends are apparent. The first has been to assume that the strong relationship between values of indices of "general" water quality and phosphorus fractions in the water is evidence that these indices monitor eutrophication alongside other forms of pollution. The other has been to develop specialised indices specifically for monitoring nutrients under particular circumstances. Kelly (1998b) argues that the latter is a more scientifically-rigorous approach, but that it is important to define the performance characteristics of the method in question. In particular, phosphate concentrations are likely to be correlated with other variables associated with organic pollution and it is important that the influence of these on the index is understood.

The **Trophic Diatom Index** (TDI: Kelly & Whitton, 1995; Kelly, 1998a) uses the relative proportions of benthic diatom taxa to assess phosphate concentrations in rivers, but also requires a second value, the percentage of pollution tolerant valves (% PTV), to be calculated. When % PTV is high, then interpretation of the TDI in terms of nutrients alone requires caution. Ideally, the TDI might be extended further to separate the effects of combined nitrogen and phosphate, but at present there is too little information on the physiological ecology of individual species of diatoms to guess whether this will ever be a worthwhile practical approach. It would be valuable to obtain data from sites combining high combined N with low phosphate or low combined N with high phosphate.

There is now a quite a lot of information about the range of nutrient concentrations over which the TDI is valuable for monitoring purposes. At present, the upper limit of sensitivity of the TDI is about 1 mg $L^{-1}$ P, when related to a programme of sampling under low flow conditions in summer (Kelly, 1998). Further refinements of the TDI (e.g. by inclusion of more taxa) may lead to greater sensitivity at lower concentrations, but seem unlikely to extend the range higher. Regional differences in geographical characteristics and in the ways in which European directives are implemented.means that complete standardization of the indices is not realistic. It is better to strive for harmonisation between national approaches (Prygiel *et al.*, in press).

McCormick and Cairns (1996) have pointed out the potential value of slides of river diatom populations archived in museums to achieve partial reconstruction of historical conditions, as has been done for various types of water in The Netherlands by van Dam and Mertens (1993). It would be useful to check as many such slides as possible from the UK using the TDI.

A further possibility is to use nutrient-enriched substrata as an *in situ* bioassay. For this, agar containing different combinations of nutrients is employed as an artificial substratum (typically in Petri dishes attached to a baseplate in a factorial arrangement). Both species composition and biomass can be estimated and differential colonization between the control and experimental treatments provides insights into the nature of the limiting nutrients. This technique has been used widely as an experimental tool (e.g. Chessman *et al.*, 1992; Biggs & Lowe, 1994) and may well be a valuable tool for situations where more information is required than can be provided by a community-based index alone.

### 7.2.3 Macrophytes

Methods for surveying macrophyte communities have been developed in several countries but in most cases these are designed only to describe the vegetation rather than to infer water quality. Two countries have gone on to develop indices: UK and France. The UK approach was modified from a survey method originally designed for assessments for conservation purposes ("Method B" in Standing Committee of Analysts, 1987), development of which started in the 1960s (Whitton & Buckmaster, 1970) and was refined during the 1970s (Holmes & Whitton, 1977). The Standing Committee of Analysts (1987) also included an index for relating the "plant score" to water quality, developed by J.P.C. Harding in north-west England. This, along with an earlier trophic index developed by Newbold and Holmes (1987) provided a foundation for the development of the Mean Trophic Rank (MTR: Holmes, 1995). A further stage of development towards a predictive tool (PLANTPACS) is currently underway. It will be important to ensure that the database used to establish this (or to refine the MTR) are obtained from sites which are more or less in equilibrium with their environment, rather than ones which are shifting in response to eutrophication or nutrient abatement.

In France a survey method, based on 50-m stretches, along with an index of general water quality, has been developed by Haury *et al.* (1996), following earlier evaluations of macrophyte indices (Haury & Peltre, 1993) including Harding's Plant Score and that of Newbold and Holmes (1987). Precise details of methodology in published papers are sparse, but the survey method appears to be broadly similar to the UK method, whilst the index (l'indice du Groupement d'Intérêt Scientifique) has a formula very similar to that of the MTR. Meanwhile, Robach *et al.* (1996) developed a "reference system" to indicate the degree of eutrophication in rivers in north-east France. This system provides separate scales at low nutrient concentrations for low pH, circumneutral and alkaline waters. Robach *et al.* (1996) describe different macrophyte communities as indicating certain combinations of nutrients and pH/alkalinity. It is not yet sufficiently refined for widespread use, but it represents a new and interesting approach that deserves further study, although, from a UK perspective, any future PLANTPACS ought to recognise similar distinctions.

The practical use of macrophyte-based indices has raised many questions about exactly what is being measured by a complex community of organisms which derives nutrients from both water and sediment, and for whom nutrients are but one *of a range of selective pressures. Anthropogenic pertubations such as weed cutting and boat traffic are recognised as confounding factors for interpretation of the MTR (Holmes, 1996). Kelly (1998b) argues that other components of a sewage discharge besides P might influence the macrophyte flora, and therefore that, especially at very high nutrient concentrations, the relationship between an index and P may not be a direct "cause and effect". Hynes (1960), for example, comments, with respect to the preference of *Potamogeton pectinatus* for organically-polluted water, that "..doubtless excessive silting of the stream bed favours its development". Holland and Harding (1984) comment similarly on the decrease in abundance of the moss *Rhynchostegium riparioides* and the corresponding increase in abundance of *Amblystegium riparium* downstream of a paper mill which produced an effluent with a high BOD, but low in nutrients. However, Spink *et al.* (1993) observed that growth of *Potamogeton pectinatus* increased in experimental channels at the expense of *Ranunculus penicillatus* ssp. *pseudofluitans* at high (0.2 mg $L^{-1}$ P) concentrations compared to a control (0.04 mg $L^{-1}$ P). These data do not necessarily contradict Hynes's (1960) observations, but provide evidence that, at moderate nutrient concentrations, competition for nutrients may be one factor determining community structure. Significantly, F.H.Dawson (pers. comm.) has found an inflection point on a graph of MTR values throughout England and Wales plotted against P concentrations at about 1 mg $L^{-1}$ P, the same concentration as for the TDI.

A further complication facing macrophyte-based over algal-based indices is that many macrophytes can potentially derive nutrients from the sediment as well as direct uptake from the water (Denny, 1972; Chambers *et al.*, 1989; see also **6.1**). The significance of sediments as a source of nutrients is poorly known and is likely to vary from species to species. Studies on *Phragmites australis*, for example, have demonstrated that the rhizome : shoot ratio decreases at nitrate concentrations greater than 6 mg $L^{-1}$, which in turn affects the physical stability of reedbeds (Boar *et al.* 1989). In contrast, macrophytes such as *Elodea* and *Callitriche obtusangula* derive more of their nutrients from the water (Robach *et al.*, 1995). From the point of view of spatial reconnaisance studies, such as have been performed using the MTR in the UK, the source of nutrients may not be important. However, the existence of two separate, but linked, "pools" of nutrients, each exerting influence on species in different ways, may complicate an understanding of the way in which macrophyte communities will change in response to a decrease in nutrients. A faster response may be expected in a river where the dissolved pool is larger than the sediment pool. One consequence of this might be that two rivers with apparently similar nutrient concentrations may react in quite different ways. One possible route for refinement of macrophyte indices may be the inclusion of functional attributes of the macrophyte vegetation into the index. Such an approach is presently been explored and developed as the River Trophic Status Indicator model (RTSI: Murphy & Ali, 1998). Pilot tests have shown the RTSI to perform slightly better than the MTR at sites in Scotland.

There are few data on the likely rate of response of the macrophyte community to a change in nutrient concentrations and the problem with most short-term studies is that it is difficult to distinguish "real" changes from "natural" year-on-year variations. Work on the Norfolk Broads has suggested that the process may be quite slow, although the winter floods scouring away nutrient-enriched sediments in rivers (House *et al.*, 1997) may make the expensive sediment removal episodes required in the Broads (see Phillips, 1992) unnecessary. As well as removing sediments, such floods may also scour away not only old growths of *Cladophora* and other macroalgae, but also rhizomes and turions in sediments and free substrata for recolonisation.

Peltre *et al.* (1993) studied a river in the Meuse basin in France before and after a phosphoric acid discharge was removed and noted no change in macrophytic vegetation after one year. Presumably a longer time period is required, particularly for perennial species which may store sufficient nutrients in rhizomes or similar structures to initiate growth the following spring. Quite how long is required is unclear, and indeed it may be that riverine communities, like those of the Broads, need to be regarded not as a gradual continuum through changing trophic states, but as two stable equilibria, in which case effecting the change will require finding those factors necessary to trigger the "flip" from one state to the other. There are sufficient unknowns for the careful monitoring of all aspects of the ecology of rivers downstream of sensitive areas to be essential if these rivers are to be effectively managed.

## 7.3 Phytoplankton

Quantitative sampling of phototrophic communities in rivers has largely been restricted to the phytoplankton. The quantity and composition of river phytoplankton communities is measured as chlorophyll *a* concentration or by cell/filament/colony enumeration by many water management bodies. Chlorophyll is typically estimated on filtered samples and thus may underestimate picoplankton, which may also be overlooked during direct enumeration unless special precautions are followed. It is of course important to know the chlorophyll concentration of water removed for purposes such as the supply of a storage reservoir. However, the brief overview above (7.1) is sufficient to indicate that long-term datasets are needed if chlorophyll concentration is to be used to assess the condition of the river and that, even then, they may be of limited use for commenting on the nutrient status of the water.

A consequence of this assessment of the literature is to call into question the current criteria for assessing eutrophication issued by the Department of the Environment. The chlorophyll *a* concentration in the water column of a river is clearly subject to a number of forces, of which nutrients are but one. Seasonal variations in chlorophyll raise doubts about the statistical validity of the criterion of an "annual mean concentration" of > 0.025 mg $L^{-1}$ chlorophyll *a*, while year-to-year differences at the time of the spring population maximum suggest that using the other criterion, an annual maximum of > 0.1 mg $L^{-1}$, is also questionable. Whilst there is almost certainly value in using phytoplankton biomass as a measure of eutrophication in rivers, more work is clearly needed in order to define this relationship more precisely. It is also important to establish a suitable frequency for sampling, in view of the influence of short-term fluctuations in biomass on interpretation of results (Kiss *et al.*, 1996).

Although the nutrient concentrations in downstream rivers are often high enough that there are few, if any, falls in the phytoplankton standing crop which can be attributed directly to changes in nutrients, the most abundant species are not always the same. For instance, Ibelings *et al.* (1998) concluded that while many of the most abundant species were the same in the Netherlands Rhine and the Meuse, the occurrence of the diatom *Skeletonema subsalsum* was a feature of the Rhine and of the green algae *Neodesmus danubialis, Micractinium pusillum* and *Pseudotetrastrum punctatum* in the Meuse. These were interpreted as features related, respectively, to the high salinity of the Rhine and specific riverine conditions of the Meuse. Although the authors did not speculate about the latter, possibilities include physical and nutrient regimes of upstream zones permitting the persistence and development of the characteristic species.

It may thus be possible to resolve differences between rivers in response to nutrients not only on the basis of chlorophyll concentration (Søballe & Kimmel, 1987; Basu & Pick, 1996), but also the community composition (O'Farrell, 1994). As biomass estimates are subject to so many other influences, the latter may hold more potential, yet has been the subject of relatively few studies.

The use of Generalized Linear Modelling (GLM) in conjunction with Canonical Correspondence Analysis (CCA: Ruse & Love, 1997) is an attempt to make sense of the complicated dynamics of populations in a manner that may enable rpredictions to be made. Yet in this study (based on data from the River Thames) silicate and nitrate were the only nutrients to make significant contributions to the first two CCA axes. This situation might change if a less nutrient-rich river or a range of rivers were included in the CCA. In the short term, a shift in emphasis from studying the ecology of the entire phytoplankton community to more detailed autecological studies of individual genera or species may provide the most effective approach to understanding the likely effects of a change in nutrient regime.

## 7.4 Animals

An increase in primary production in a river due to eutrophication will change the relative proportions of energy derived from various sources within the river. The proportion derived from photosynthesis will increase, whilst that from detritus and coarse and fine organic matter will decrease. One likely effect of eutrophication therefore may be a change in the relative proportions of invertebrate functional groups. That the number of grazers increases has been shown in several studies (e.g. Biggs & Lowe, 1994; Allen, 1995) and, similarly, numbers of filter feeders such as *Dreissena polymorpha* might respond to increased availability of phytoplankton (Basu & Pick, 1997). Whilst direct grazing on macrophytes is usually assumed to be insignificant (Allen, 1995), their decay will generate "coarse particulate organic matter" which may be locally important as a food source for "shredders" during certain times of the year. As current invertebrate monitoring within the Agency often depends merely upon the presence or absence of invertebrate families, such trends may be difficult to detect from existing data.

Further analysis of macroinvertebrate data may be worthwhile because the historical record of invertebrates is, in many Regions, stronger than for macrophytes and diatoms. In those Regions where data on abundance and/or specific composition are held, it would be useful to process the information for storage on computer file in order to look for possible long-trm trends. Even where this information is not available, it is still possible to ask worthwhile questions. Does the probability of detecting "grazer" families increase in eutrophic rivers? Are more "grazer" families found in such circumstances? Are any broad patterns of invertebrate functional groups apparent between the major RIVPACS classes, in a way that can be readily related to nutrient levels?

There are a large number of possible interactions between riverine fish and macrophytes and algae, leading to many possible implications of eutrophication on the fish community. No adult fish in UK rivers are herbivores, although plants may form part of the diet of several, particularly cyprinids (Maitland, 1972). Many other cyprinids lay their eggs amongst macrophytes. Factors that affect the distribution of macrophytes in a river might as a consequence affect the distribution of cyprinids, particularly at the margins of their present ranges within rivers. Salmonids, by contrast, lay their eggs in river gravels and are able to move even thick growths of benthic diatoms in order to prepare the redds (D.T. Crisp, pers. comm.). Other species, such as *Esox lucius*, use macrophyte beds to hide from potential prey species.

High rates of daytime photosynthesis as a result of increased primary production are accompanied by high rates of respiration at night, which can deplete the oxygen concentration sufficiently for oxygen-sensitive species such as salmonids to be killed. Similarly, photosynthesis can raise the pH of river water to lethal levels. The relative roles of algae and macrophytes in such incidents is often difficult to establish. Larval stages tend to be more sensitive but there risk assessments are difficult due to large numbers of variables involved (Bowburn Consultancy, 1997). Although blue-green algal toxins can contribute to fish kills (Rogers *et al.*, 1994), there is at present no evidence of a fish kill that is attributable to these, rather than to factors such as the oxygen regime.

The role of fish in controlling eutrophication through biomanipulation and "top down" control has been studied extensively in lakes (see Harper, 1992, for references). It is reasonable to assume that such processes also work in rivers, although there have apparently been no studies. If zooplankton were shown to be controlling phytoplankton density during the summer, then an increase or decrease in abundance of a planktonivorous fish might influence chlorophyll *a* concentrations. In the River Great Ouse, rotifers represent the main food for young cyprinids (Bass *et al.*, 1997), whilst juvenile trout in the Tees feed on ostracods and small Cladocera (D.T. Crisp, pers. comm.). However, as the chlorophyll concentration in rivers is usually lower than for a lake of comparable P status (Basu & Pick, 1996) and zooplankton density is usually less in a river than would be expected in a lake of comparable algal abundance (Pace *et al.*, 1988). If these two studies are typical, then the degree of top-down control that can be exerted is clearly limited; however, more work is clearly needed.

Carvalho and Moss (1997) point to the role of bottom-feeding cyprinids (especially carp) as contributors to eutrophication in standing waters, by disturbing bottom muds in their search for food, and releasing nutrients into the overlying water. Again, such effects have not been studied in running waters but should not be excluded. This, along with the previous point, suggest that stocking policies might need to be reviewed if the maximum benefits from nutrient removal are to be obtained.

Certain planktonic rotifers have been considered to be characteristic of eutrophic conditions (Winner, 1975), raising the possibility of using the zooplankton community as a monitor of nutrient status. However, the literature quoted by Winner is largely based on the saprobien system, so critical studies are needed to establish which factors are involved. In addition, use of zooplankton has the additional problem of a lag in response of the grazer to its food (or predator to its prey). The relationship between zooplankton species composition and trophic status (which in turn affects numbers and types of phytoplankton) appears to be much better understood for lakes than for rivers (see Harper, 1992, and Allen, 1995, for references).

## 7.5 Bioassays

The Algal Assay Procedure developed by the US Environmental Protection Agency (EPA: Miller *et al.*, 1978) to assay the growth potential of planktonic algal strains in standing waters has also been applied to rivers. The organism used initially, *Selenastrum capricornutum*, grows well under a wide range of ambient chemistry, though it may be necessary to isolate local strains for assays, if the river water chemistry differs markedly from the media recommended by the US EPA for bioassays (Whitton & Kelly, 1995).

Assays on the response of phototrophs to nutrient additions have also been adapted such that they can be carried out *in situ*. This means that the results integrate events over some days rather than the quality of one particular water sample. Such assays are more suited to testing likely responses to future eutrophication than future nutrient decreases, though they can still be helpful for the latter. Various types of practical method have been tested, all involving some means of ensuring slow release of the nutrients; these include use of porous flower pots, slow-release fertilizer granules and agar blocks containing different combinations of nutrients. In the last case the agar is typically held in a number of petri dishes attached to a baseplate with a factorial arrangement. Both species composition and biomass can be estimated and differential colonization between the control and experimental treatments provides insight into any possible limiting nutrient (Chessman *et al.*, 1992; Biggs & Lowe, 1994).

Another approach is to analyze the nutrient composition and/or carry out enzyme assays on submerged plant material taken from a site in order to establish whether it is likely to be limited by either N or P. For instance, assays of surface phosphatase activity of filamentous algae and mosses have considerable potential for monitoring the nutrient status of an aquatic site (Whitton, 1991). Providing the ambient phosphate levels are not too high, there are marked positive correlations between surface phosphomonoesterase (PMEase) activity of the green alga *Stigeoclonium*, the presence of multicellular hairs and the N : P ratio of the water (Gibson & Whitton, 1987). The PMEase content of 2-cm apices of shoots of the mosses *Fontinalis antipyretica* and *Rhynchostegium riparioides* decreased on passing from the headwaters of the Swale - Ouse system down the main river, reaching baseline levels of activity by the time the river had reached a site with a mean of 0.16 mg $L^{-1}$ filtrable reactive $PO_4$-P (Christmas & Whitton, 1998a). Further research on this topic is currently being carried out at Durham supported by an Environment Agency contract.

## 7.6 Conclusions

Practical monitoring of eutrophication in the UK is already underway, using indices such as the AAI, MTR and TDI, as well as chlorophyll *a* concentration (Table 7.1). The three indices are new tools for the monitoring biologist's armoury and much remains to be learnt about the response of these communities to eutrophication (Kelly, 1998b). It is also clear that the relationship between chlorophyll$_a$ and nutrients is not straightforward and more work is required here if robust predictions are to be based on these data. However, other components of the biota are also affected by eutrophication. For some groups (e.g. zooplankton), data from rivers is sparse and concepts derived from studies on lakes have had to be extrapolated (with caution) to rivers.

Table 7.1 Current status of various methods for monitoring nutrients in the UK.

| Objective | Method | Stage of development |
|---|---|---|
| Quick screening of many sites | AAI | *Operational* (in Scotland). May require modification for use in England and Wales |
| Intermediate level evaluations of nutrient impacts | TDI | *Operational*, ongoing minor improvements |
| | MTR | *Operational* |
| Confirmation of role of nutrients | Nutrient-enriched substrata | Requires further development |
| | Phosphatase assays | Under development |

The MTR and TDI have been used for spatial reconnaisance studies in England and Wales (Harding & Kelly, 1998) and values produced by these indices assessed alongside chemical and other biological evidence. It is important to stress that for correct diagnoses to be made values of these indices need to be used in conjunction with nutrient data, as well as information on community composition. An increase in the index itself does not represent "proof" of eutrophication, but rather the index is an expression of community structure that permits spatial and temporal comparisons to be made. Neither the MTR nor TDI links "cause" and "effect" and were this required, then further development of bioassay techniques will be required. Nutrient-enriched substrata and the phosphatase assay are two techniques that may have particular value as they can be performed *in situ* or on organisms removed from the river, rather than on laboratory cultures.

The next stage of eutrophication monitoring in UK rivers is to examine the effects of nutrient removal as the first tranche of designations become operational. The rates at which different components of the biota are likely to respond will vary (Table 7.2).

Table 7.2 Typical rate of response of various monitoring methods likely to occur in response to a reduction in aqueous nutrient concentrations.

| | days | weeks | months | years |
|---|---|---|---|---|
| Water chemistry | + | | | |
| Sediment chemistry | | | + | + |
| Attached algal community | | + | + | |
| Diatoms | | + | + | |
| Submerged vascular plants | | | + | + |
| Benthic macro-invertebrates | | | + | + |
| Phytoplankton | | + | | |
| Zooplankton | | + | + | |
| Fish | | | + | + |
| Phosphatase assay with moss | | + | + | |
| Phosphatase assay with *Stigeoclonium* | + | + | | |

Macrophyte and macroalgal growths, for example, may require winter floods to scour away old growths and open up the habitat for new invaders. Such floods will also be important for moving nutrient-rich sediments downstream (House *et al.*, 1997) and the establishment of new macrophyte communities may depend upon the rates at which this happens.

The outcome of competition can be predicted from theories of ecological competition, the outcome of which may be the complete exclusion of one or other species or mutual coexistence (see Harper, 1977). If P concentration was the resource gradient that determined such competition, then the outcome would translate into a changed abundance of both species, which would be reflected in a new value for an index such as MTR or TDI. A further possibility is that the change in P concentration shifts, in the short term at least, the focus of competition from P to a different factor. Assuming that the post-stripping concentration of P still permits some growth of the species that was dominant at the pre-stripping concentration, then the fact that it occupies most of the physical space within the habitat may preclude a new equilibrium between the two species being attained. The rate at which other species can invade will therefore depend upon the rate at the formerly dominant species is removed. However, even if P is the primary resource gradient determining species composition (a precondition of indices such as the MTR and TDI: Kelly, 1998b), it is unlikely to be the only factor at work and it is better to conceive of a species' niche as an 'n-dimensional hypervolume' (Krebs, 1978) within which many variables will exert an influence. As density-dependent factors such as grazing are known to control benthic algal biomass under some circumstances (Biggs & Lowe, 1994), it is equally plausible that the dominant organism in a community will be resistant to grazing as well as being adapted to the ambient P concentration. Such is the case with the benthic diatom *Cocconeis placentula* (Jacoby, 1987; Rosemund *et al.*, 1993). Therefore, grazing pressure may determine the rate at which space becomes available for species to invade. Iserentant and Blancke (1984) demonstrated a similar effect, albeit for organic pollution rather than eutrpohication, for benthic diatoms transplanted between polluted and control sites in Belgium. The same basic scenario, albeit with different variables, could be rewritten for macrophytes and other organisms. If the rate of such factors is low, relative to the total numbers of the dominant organism, then the rate of change will depend upon the intensity of catastrophic density independent events such as winter storms.

Some of the comments in this section (7) are treated more fully or with a different perspective in a review in the journal Hydrobiologia (Kelly & Whitton, 1998).

## KEY COMMENTS: BIOLOGICAL MONITORING PROGRAMMES RELATED TO NUTRIENTS

i) Primary producers are the preferred organisms for monitoring eutrophication in rivers because their response to inorganic nutrients is more direct than that of most other groups of organisms.

ii) A fully quantitative approach to sampling natural benthic communities of phototrophs is too time-consuming for routine purposes. A relatively simple semi-quantitative approach (Algal Abundance Index) has been developed by M.W. Marsden and colleagues for rivers in the Forth Basin and something like this could be adapted for comparative surveys of rivers in other regions. More ambitious survey methods for more fundamental studies have been developed recently in a number of countries: it is as yet uncertain whether these methods are likely to evolve towards a more standardized approach that can be used in many different regions.

iii) The use of diatom communities from rock or other surfaces to assess river water quality has gradually evolved towards the development of indices, which reflect nutrient conditions in the water, rather than a combination of nutrients and other factors such as Biological Oxidation Demand. One of these indices, the TDI (Trophic Diatom Index), is currently being tested or put to practical use at a number of sites in the UK

iv) The use of macrophytes as indicators of nutrient status has been systematized by the introduction of the MTR (Mean Trophic Rank). This has already shown its practical use in comparative surveys made for monitoring purposes. However, the speed with which the plant community reflects permanent changes in ambient nutrients is unclear, so the use of the MTR for assessing improvements related to the UWWTD will need careful evaluation.

v) The chlorophyll content of both benthic and phytoplankton communities has at times been used as an index of eutrophication, with the latter being specifically recommended by the Department of the Environment. However, the amount of chlorophyll recorded from either type of community is influenced by so many factors that it requires a large number of samples to provide statistically worthwhile comparisons.

vi) The river fauna may also reflect the nutrient chemistry, but the effect is usually sufficiently indirect to make it not worthwhile to use animals in preference to phototrophs. An important exception is where it is desired to evaluate past changes, because there is often much more old data for macroinvertebrates than phototrophs.

vii) Several types of bioassay may be used to give further information about nutrient status at a site. Assays which integrate the variability in composition of river water are particularly useful. These can be done for measuring the response of *in situ* communities to nutrient additions or by removing biofilms, algae or bryophytes from a site and carrying out assays of enzyme activities which reflect the nutrient status of the organism. For instance, assays of surface phosphatase activity may be used to assess P limitation in upstream populations, though it is at present unclear how widely downstream populations show obvious P limitation.

# 8 TECHNIQUES AND TECHNOLOGY EMPLOYED TO REDUCE NUTRIENTS ENTERING RIVERS

## 8.1 Point sources

### 8.1.1 Introduction

The principle that the quantities of limiting nutrients entering a catchment can be controlled is central to legislation such as the UWWTD, as well as to other exercises to reverse eutrophication (e.g. Norfolk Broads: Phillips, 1992). The technology employed therefore depends upon the correct identification and principle sources of the limiting nutrient, followed by the correct selection, design and use of an appropriate technology. This needs to include an appreciation of the likely variations in load that the plant is likely to encounter, as well as the environmental factors which affect the perfomance of the system under consideration.

The technologies available for tertiary treatment leading to nutrient removal are presented here under five headings, of which only the first two are at present widely used in the UK on the type of STW affected by the UWWTD.

### 8.1.2 Chemical precipitation

Chemical precipition of phosphate is achieved using iron, aluminium or calcium salts. Of these, aluminium is the most effective, but is expensive and is linked to concerns about Alzheimer's disease. Calcium is rarely employed due to the large quantities of sludge that are produced. Iron salts are the most commonly employed, at ratios of about 1 : 1 to 1 : 1.5 Fe : P, with up to 98% P being removed (Clark *et al.*, 1997). This is a very adaptable technique, and the iron salts can be added at any stage of treatment to activated sludge or trickling filter processes. This makes it ideal for experiments, where data are required to justify investment (as for studies on STWs discharging to the Rivers Nene and Great Ouse: Rose & Balbi, 1997). There may be additional benefits to the quality of the effluent through the precipitation and settling of other solids. However, the possible toxicity of Fe to benthic organisms needs to be assessed.

### 8.1.3 Enhanced biological phosphorus removal

This is usually a modification of the activated sludge process in which two activated sludge tanks are operated in sequence, with an anerobic stage, which permits denitrification and "luxury" uptake of phosphate, followed by an aerobic stage where nitrification occurs and phosphate and combined nitrogen are removed through growth. This technology, and a number of variants, is being researched intensively at present and has the advantage of controlling N and P simultaneously. Problems include:
i) temperature dependence of microbial activity, which recues effectiveness during cold weather (Marklund & Morling, 1994);
ii) the need, under some circumstances, to add short chain fatty acids (e.g. from fermentor liquor) to achieve maximum P removal (Upton *et al.*, 1996);
iii) excessive aeration during the anerobic stage caused by high rainfall (Brdjanovic *et al.*, 1998). Occasionally the water from ponds is used for irrigation rather than release to the

river, as with the anaerobic ponds introduced to prevent P from dairy wastes in central Florida (Havens *et al.*, 1996) reaching rivers.
Both chemical precipitation and enhanced biological phosphorus removal produce large quantities of nutrient-rich sludge which needs to be removed from STWs. At present, about 15% of this is spread on land, although the feasibility of using this sludge as a source of P for the detergent industry is also being examined (ENDS Report, 1997)

### 8.1.4 Microfiltration

Microfiltration of effluents from secondary treatment is being examined primarily as a means for removing pathogens such as *E. coli* and *Salmonella*, but is also effective for nutrient removal (Dittrich et al., 1996).

### 8.1.5 Immobilization

Systems based upon immobilized algae have been tested in Hong Kong (Tam *et al.*, 1994). Here, algae such as *Chlorella vulgaris* are trapped on alginate beads and packed into columns over which raw or semi-treated sewage are poured.

### 8.16 Oxidation ponds and artificial streams

A variety of tertiary systems have been introduced or tested where ponds or lagoons of standing water are encouraged to grow planktonic algae, or sometimes also other phototrophs. These bring about several types of improvement in the quality of the effluent, including nitrification and phosphate removal similar that the aerobic stage of enhanced biological removal mentioned above, except that the oxygen is supplied by photosynthesis rather than aeration. Such systems are better suited to climates warm enough to permit considerable activity throughout the winter. The following general comments therefore largely apply to warmer countries than the UK, such as southern USA.

Oxidation ponds have been in practical use in many countries since the 1960s and have apparently sometimes had moderate success in the UK, such as the large system of ponds associated with Rye Meads STW near Stevenage. There is a very large literature on the design and management of oxidation ponds, with some of the most important papers originating over a long period from the research group of W.J. Oswald at the Berkeley campus of the University of California (e.g. Nurdogan & Oswald, 1995). Practical problems for their use in the UK include not only the fact that they operate poorly in winter, but also the requirement for a large area.

The **algal turf scrubbers** described by Craggs *et al.* (1996) are artificial streams, 152 m × 6.7 m with a gentle slope over which effluent from secondary treatment flows. The stream was colonized naturally by a mixture of epilithic algae, including blue-green algae, diatoms and green algae and a strainer at the bottom removed any sloughed-off debris. This system removed about 50% of the P and, like other biological systems, is strongly temperature dependent. One consequence of the short residence time is that the system also appeared to be less effective at night.

All of the systems at or beyond the pilot stage rely upon an equilibrium between nutrient load in the effluent and the availability of sites upon which the chemical or biochemical reactions occur. There are, therefore, risks of pulses of particularly nutrient-rich water or excessive quantities of raw effluent overloading a system. Such risks can be minimized by the design of the plant and its control mechanisms. A further problem with biological systems is that pulses of toxins can kill the organisms responsible for nutrient removal.

### 8.1.7 Wetland systems without open water

Since the mid-1980s, the use of various types of wetland system lacking open water to improve effluent quality have been tested in many countries, including the UK. Natural wetlands have no doubt aided the clean-up of organic wastes for many centuries, but modern systems appear to have been introduced initially as much to remove toxic materials as nutrients. However, their potential role to remove nutrients is clear, with impressive values quoted in the literature, such as efficiencies up to 90% for N removal (Cooper, 1990). Some countries appear to have particularly ambitious plans. For instance, as part of an announcement of plans to reduce N exports by 50%, Sweden has recognized that wetlands can play a pivotal role in achieving this goal (Jansson *et al.*, 1994). The approach has been adopted widely in the UK for small STWs, but apparently not yet for works covered by the UWWTD.

The methodology introduced in the 1980s has become known as **root zone treatment** (RZT), although this may give a slightly false impression of the processes involved. Emergent macrophytes such as *Phragmites australis*, *Phalaris arundinacea* and *Typha latifolia* in the UK, and also other *Typha* spp. and *Schoenoplectus* spp. in other countries, are grown on artificial wetlands. *Phragmites* grows in more oxygenated sediments than *Typha*. Nutrient removal occurs through a number of pathways, including denitrification in microoxic parts of the sediments, enhancements of aerobic processes such as nitrification in the vicinity of the rhizosphere and direct uptake by the plants. Between 79 and 93% of P and 65 and 92% of nitrogen was removed from dairy farm wastewaters in one study (Tanner, 1996; Tanner *et al.*, 1995). This technology is widely used for STWs treating small settlements, as well as for agricultural wastes and has positive effects on many aspects of the effluent including BOD and parasite eggs (Mandi *et al.*, 1996). However, such systems are substantially less effective in the winter, with P removal rates falling to 28% and N removal to 27% in one study in Connecticut (Newman & Clausen, 1997).

RZT, if correctly designed and once established at a site, is a low maintenance, high efficiency system that has considerable potential for treating wastes from small settlements and farms. However, some cutting of above-ground parts is likely to become essential in the long run as P levels increase in the ecosystem. The economics of the process would in fact be improved if the wetlands could be planted with an economic crop, and the feasibility of systems based on 'unconventional' forage crops or, alternatively, a system similar to RZT known as overland flow are being investigated (Debusk *et al.*, 1995; Turner *et al.*, 1994). A further option is that RZT could be incorporated into agricultural subsidy systems as a type of 'set-aside'. The inherent sustainability of RZT makes the system very attractive to environmentalists, although it is possible that the impact of large artificial wetlands might be regarded as aesthetically undesirable in some regions and their long-term sustainability has not been assessed thoroughly.

There is apparently no review in the literature which makes a really critical comparison of the many studies. In most cases it is essential to read the original papers in order to understand all the practical details before assessing how valuable a method would be if adopted widely. Few of the authors consider the problems of how such wetland systems can be used over periods of many years. However, the following are a few recent studies in various countries which raise important points to be considered wherever it is planned to construct wetlands for nutrient removal. They include ones where most of the N removed was apparently trapped in plant biomass and at least one where it was almost entirely due to microbial reduction of nitrate.

The properties of beds of a bulrush, *Schoenoplectus validus*, and unplanted gravel-bed wetlands to remove N and P from dairy parlour wastewater were compared at Hamilton, New Zealand (Tanner *et al.*, 1995). As theoretical wastewater retention time increased from 2 to 7 days, mean reduction of total N increased from 48 to 75% in the planted wetlands and from 12 to 41% in the unplanted wetlands. In the planted wetlands, mean annual removal rates of total N (0.15 - 1.4 g $m^{-2}$ $d^{-1}$) and total P (0.13 - 0.32 g $m^{-2}$ $d^{-1}$) increased gradually with the rate of mass loading, whereas the unplanted wetlands showed a marked decline in removal of both N and P at high loadings. Net storage by plants in the first year of monitoring accounted for between 3 and 20% of the greater N removal and between 3 and 60% of the greater P removal in the planted wetlands.

Another study (Tanner, 1996) from the same research group at Hamilton tested the use of beds with eight different species, including the same bulrush as previously and also three species which grow in the UK (*Phragmites australis*, *Glyceria maxima*, *Juncus effusus*). The maximum values for accumulation by plants of 135 g $m^{-2}$ N and 18.5 g $m^{-2}$ P accounted for about 30% of that supplied in wastewaters. Mean removal of total N ranged from 65 - 92%, showing a significant positive correlation with plant biomass. Mean removal of total P ranged from 77 - 91%.

Twelve much larger wetland systems in Estonia, which had been established over a 6-year period, were compared for their ability to remove BOD, total N and total P from wastewaters (Mander & Mauring, 1997). The systems tested included a sand/plant filter, a *Phalaris arundinacea* slope and an aquatic macrophyte ditch. The sand/plant filter system showed a poor performance with respect to N, whereas the output of the *Phalaris* system was always lower than the recommended limits ($BOD_5$ < 10 mg $L^{-1}$; total N < 10 mg $L^{-1}$; total P < 2 mg $L^{-1}$). The outputs of the bioditch were high and extremely variable. All the results showed that compared to other seasons the winter performance was not reduced. this rather surprizing result differs with some other observations in the literature, especially for BOD and total N.

### 8.1.8 How to get nitrate removal without forming nitrous oxide?

There is a need to assess whether nitrous oxide formation during denitrificaton is quantitatively important, but relatively few reliable data exist. Mengis and Schulthess (1996) concluded that a planned introduction of N removal in Swiss sewage treatment plants would contribute less than 1% of total nitrous oxide emissions in Switzerland. They estimated this the total amount from Swiss STWs to be 9-30 t N $yr^{-1}$. Nitrous oxide emissions from lakes amount to less than 3% of total emissions in Switzerland. Nevertheless the authors warned that increasing N pollution could lead to increased nitrous oxide emissions from lakes. They did not supply data for rivers, presumably because most rivers in Switzerland are relatively fast-flowing.

There are apparently no overall estimates for nitrous oxide emissions from UK STWs. However, it may eventually prove that yhe increasing introduction of wetland systems and buffer zones to enhance nutrient removal is a more important source of nitrous oxide than well-managed STWs. A study by Freeman *et al.* (1997) shows both the considerable potential for nitrate removal by wetlands, but also the need for detailed studies before the systems are put into operation. Nitrate and nitrous oxide fluxes were measured in a series of peat-accumulating wetlands near Plynlimon, mid-Wales. Diversion of water inflows caused a 200% increase in nitrate release and > 95% decline in nitrous oxide emission over a 2-week period. The responses were attributed to the onset of drier and more aerobic conditions causing aerobic mineralization and nitrification plus the absence of denitrification.

A similar problem of trying to maximize nitrate removal without enhancing nitrous oxide production during denitrification, or nitrite formation as a step in dissimilatory nitrate reduction, faces all attempts to optimize nitrate removal within river ecosystems. In view of the economic importance of this topic, it seems strange how few studies have been made to understand and, hopefully, resolve the problem. However, the study on River Wiske sediments by García-Ruiz *et al.* (1998a: see **5.2**) suggests that there may be ways of maximizing nitrate removal while minimizing nitrous oxide production. One obvious solution would be to ensure that nitrate-rich water passes through, or in close contact with, sediments which are organic-rich and nearly anoxic. However, this would conflict with the desire to improve oxygen concentrations in the river water, unless the water was reoxygenated before entering the river.

## 8.2 Diffuse sources

In view of the importance of agriculture as a source of diffuse nutrient inputs to rivers, any long-term answer must rest heavily on methods of minimizing inputs and loss from agricultural systems. There are a considerable variety of approaches towards this, especially for P (Catt *et al.*, 1998; Withers & Jarvis, 1998), many of which lie outside the direct scope of water management. For instance, Castle *et al.* (1998) list a number of recommendations for future agricultural practices at the level of individual farms. Heathwaite (1997) describes a number of problems and solutions which are more directly related to rivers. Where livestock is grazed on riparian land, there is virtually no buffer between the land and the stream. Runoff from grazed riparian areas may contain high concentrations of P, especially around feeding and watering areas. Consequently riparian land needs to be carefully managed to control P losses. Management options include the introduction of riparian buffer zones of various widths and designs and the control of fertilizer and livestock inputs close to such zones (Heathwaite, 1997). These all have economic implications for the farmer. The *Code of Good Agricultural Practice* (MAFF, 1991) recommends a 10-m buffer strip between agricultural land and a watercourse, though this was not mentioned in a subsequent publicity booklet on *The Environment* distributed by MAFF (1993). Flint (1998) reports on a scheme in Scotland in which demonstration sites are set up on farms to show relatively simple methods of enhancing riparian habitats which eventually lead to the establishment of tall vegetation i.e. the first step towards a buffer zone.

Heathwaite (1997) describes a series of experiments with 10-m buffer strips and shows how effective they can be, provided subsurface hydrological pathways are relatively unimportant. It is clear that the success of a buffer zone depends on the mechanisms by which P moves from land to river (Muscutt *et al.*, 1993). Buffer zones are in some respects a compact and highly managed version of the wetlands considered in **8.1** for treatment of effluents from point sources, though usually considerably drier than the wetland communities developed for stripping nutrients.

The information booklet on *Buffer Strips* distributed by the Environment Agency (1996) deals largely with riverain strips to reduce agricultural pollution. It states that strips may be 5 - 30 m wide and reports that experiments have shown that nearly all nitrate is removed form water which passes through buffer strips at depths of less than 30 cm via a combination of denitrification and plant uptake. Nitrate is removed within the first 10 m of flow within the strip and in some cases all nitrate can disappear with 2 m. For buffer strip to be effective at reducing nitrate pollution in headwater streams, the bulk of the water movement must be through the near-surface soils, a situation which is thought to be uncommon. Where soils are wet and 'anaerobic' (i.e. anoxic) the bulk of water movement is likely to be overland flow. However, buffer strips can reduce land run-off by increasing infiltration of rainwater into soils. The booklet also states that an advantage of buffer strips is to provide organic matter to watercourses. However, we are unaware of any critical assessment of the advantages of encouraging *in situ* organic production by primary producers in lowland streams in the UK (presumably mainly in spring and summer) versus input from bankside vegetation (presumably mainly in autumn).

There are apparently no detailed guidelines on setting up buffer zones in the UK, presumably because of wide differences in hydraulic and soil conditions influencing movement of nutrients from fields to the river, and also wide differences in river bank morphology and river flow regime and chemistry. However, several papers provide further useful information. The effectiveness of buffer zones generally deteriorates with time (Withers & Jarvis, 1998) without careful management to avoid , for instance, sediment build-up on the leading edge of a grass buffer zone (Dillaha & Inamdar, 1997). Buffer zones should be targeted at source areas which contribute the most loss, such as ephemeral and first-order streams, where the ratio of land area to stream length is low (Withers & Jarvis, 1998). Studies on cost effectiveness (Prato & Shi, 1990) or which consider overall economic aspects (Hayward & Muscutt, 1995; Dillaha & Inamdar, 1997) suggest that buffer zones are likely to have a negative effect on farm finances, so are only likely to be adopted widely where the overall environmental benefits are clear and where the farmer is offered a financial incentive.

If N removal depends largely on denitrification, the buffer zone can be expected to operate indefinitely, apart from the problem of nitrous oxide emission (8.1) and the fact that it will be less effective in winter due to lower temperatures. There appear to be few data on the rate of transfer of nitrate through a buffer zone, but presumably the wider the zone the slower the transfer, so broader zones should be encouraged if it is important to ensure that nitrate reduction occurs in winter as well as summer. It may even be speculated that rates of denitrification will increase with time, as the microbial populations at a particular site become adapted to the local environment.

The long-term situation for P removal is the opposite to that for N. If the buffer zone is working effectively, P concentrations in the soil will increase with time, unless some means is found to remove it from the system, such as harvesting and removing some of the vegetation. In addition, the effectiveness of buffer zones in reducing diffuse P loss is less clear than for N (Uusi-Kämppä *et al.*, 1997). Uusi-Kämppä *et al.* (1998) concluded from studies in Finland and Norway that buffer zones and wetlands reduces losses of particulate

P and total P, but that retention of dissolved P is not very effective and may actually increase. Withers and Jarvis (1998) concluded that the reduction in flow as surface runoff enters a buffer zone (or waterbody used as a barrier) allows deposition of the suspended sediment load and increased opportunity for soluble P to be adsorbed by the soil and/or taken up by the vegetation. In practice, the reduction in flow may be insufficient to allow sedimentation of finely suspended clay particles and associated P, with the result that reductions in particulate P loads are less than those in sediment loads (Withers & Jarvis, 1998). The slightly different conclusions reached by these two groups of authors shows the need for further research to determine the effectiveness of buffer zones and wetlands to diminish the P load passed to rivers.

It may be expected that the more the buffer zone resembles a wetland community, the greater will be its ability to remove nitrate. Species of flowering plant which are sensitive to high nutrient levels are unlikely to thrive in buffer zones, so they cannot be considered as potential nature reserves for rare flowering plants, even if they can act as sites for riverside animals or corridors for animal movement. For instance, it seems unlikely that the alder (*Almus glutinosa*) with its nodules of nitrogen-fixing actinomycete, would thrive here, although we have been unable to find any report of experimental studies related to this. Conversely, it seems probable that at least some of the flowering plants which have become so successful on river banks in the past half-century are ones which respond especially well to eutrophication, though this factor appears to be neglected in current studies of plant invaders. *Impatiens glandulifera* seems likely to be a species whose success has been aided greatly by nutrient eutrophication, presumably from field drainage and increased levels in river water. If this species accumulates P to a high level, it should be relatively easy to design buffer strips to permit its growth and subsequent removal annually at the time of maximum growth (August).

A rather different approach is to enhance clean-up processes within the river. The planned restoration of the lowermost 18 km of the Skern river system in Denmark provides a good example (Andersen & Svendsen, 1997); the authors state that this is the largest river restoration project in Europe. It will involve re-meandering the river to its former course and the creation of a shallow lake and ponds. As a consequence of retention in different areas of the lower river system, it is estimated that transport of suspended solids and total P in the river will be reduced by 37% and 20%, respectively. Data on N are quoted from another report (Svendsen & Hansen, 1997). The reduction in N load due to the restoration project (increased denitrification and cessation of cultivation) is estimated to be 270 - 600 t $yr^{-1}$ N, corresponding to 5 - 12% of the annual riverine load.

Based on studies in the USA, Pionke *et al.* (1997) and Daniel *et al.* (1997) have emphasized the importance not only of local decisions about management to reduce transfer of nutrients from agricultural land to rivers, but also the need to consider the catchment as a whole. Pionke *et al.* (1997) report detailed studies on two small catchments to establish the controls on loss of 'bioavailable phosphorus', which include hydrological, erosion, chemical and P-useage controls from critical source areas within the catchments. They use the data to establish models and then to discuss which remediation strategies are likely to be most effective.

Daniel *et al.*'s (1997) account focusses on how to consider priorities for a large catchment. The approach is broadly the same as Pionke *et al.*'s in that it quantifies the inputs of particular parts of the system (in this case, sub-basins) and targets those likely to be responsible for the particular nutrients causing problems. For instance, if P in runoff is the problem, the programme targets sub-basins largely responsible for surface run-off. The article gives accounts and references to a number of such studies relating to N or P. Although Daniel *et al.* did not say it explicitly, this sort of approach demands detailed catchment models for N and P, perhaps using GIS (Geographical Information System). It also requires full use by water management of all the available agricultural information within a catchment. There may be sufficient information about fertilizer loading in the catchments of some Yorkshire rivers on the LOIS database to make this approach feasible now. It would also seem to offer much scope for an area with intensive agriculture, such as much of the Anglian Region.

## KEY COMMENTS: TECHNIQUES AND TECHNOLOGY EMPLOYED TO REDUCE NUTRIENTS ENTERING RIVERS

i) Chemical precipitation of phosphorus and 'enhanced biological phosphorus removal' are quite widely used on the type of sewage treatment works affected by the Urban Waste Water Treatment Directive, while beds of emergent macrophytes are increasingly being used to treat wastes from smaller sewage treatment works. The latter system has become widely known as 'root zone treatment' (RZT), though a variety of processes may be involved in nutrient removal. Although many trials have been reported or are underway, there is considerable scope for further optimization of these systems, including their incorporation into treating effluents from larger sewage treatment plants.

ii) Other tertiary systems developed for treatment of point source effluents appear to have only limited potential use in the UK, though the best systems operating in warmer climates should be kept under review, in case there are ways in which they can be modified for use here.

iii) The reduction of nutrient inputs from diffuse agricultural sources is only likely to succeed with close collaboration between MAFF and the Environment Agency. In order for reduction to be large enough to have an obvious impact on a river, careful targetting is required of the key sites within a catchment where nutrients move from land to streams and rivers. If nutrient control is especially important, such as where the water eventually reaches a lowland reservoir, it will almost certainly require a combination of detailed data on the distribution of nutrients within the catchment (using Geographical Information System) and the use of export coefficient models to predict the stretches most important in nutrient transfer between land and water.

iv) The simplest approach to reducing nutrient transfer from land to water is the construction of a buffer zone, which may be 5 - 30 m wide. In most situations it should be possible to design a zone which will indefinitely remove most of the nitrate, apart from very cold periods. The effectiveness of buffer zones for long-term removal of phosphate is less clear and it will probably require careful design and management for this to be fully effective. The conservation value of such strips for the flora should not be exaggerated, because it is likely that in many cases species characteristic of eutrophic conditions will dominate, such as the giant balsam (*Impatiens glandulifera*).

v) Unfortunately, the introduction of buffer zones is likely to have a negative economic effect on farming, so they will probably only be adopted widely as part of set-aside or similar schemes.

# RECOMMENDATIONS

1. More attention should be paid to diffuse sources, including small point sources, since they make an important input of nutrients to many rivers, which has often been underestimated, especially for phosphate.

2. Catchments should be considered individually, each with their own eutrophication action plan. This could then be incorporated into any overall management plan for the catchment.

3. Where diffuse (and small point) sources of nutrients to a river are important, the catchment plan should target those stretches of stream and river which make the greatest contribution and the data should be integrated to a Geographical Information System database. It is important to focus effort on the key sites.

4. Storm events have an important influence on nutrient loads, both by enhancing inputs from diffuse sources and by mobilizing bed sediment. In catchments subject to marked variation in flow, sampling programmes for water chemistry should take extreme events into consideration.

5. The problem of long-term buildup of phosphate needs to be considered when assessing the management of buffer zones and also wetland sites used for nutrient stripping.

6. Buffer zones have many environmental advantages, but financial incentives are required if they are to be adopted widely by farmers.

7. Weed cutting and dredging should both be considered as possible means of nutrient removal; both must be conducted with ecological understanding of possible harmful side-effects and both involve the need to find a site for dumping the material without recontaminating drainage to the river.

8. There is a need for a critical assessment of the Environment Agency's procedure for sampling, storage and analysis of water, particularly in the case of phosphate and chlorophyll. It is recommended that the processing of samples for more research-oriented studies, such as assessing long-term changes, should be separated entirely from that used for routine monitoring programmes.

9. More detailed understanding is needed of the process of denitrification in rivers, wetland treatment systems and buffer zones, both to enhance nitrate removal and to minimize that component of the process which terminates in nitrous oxide.

10. Ongoing biological monitoring of eutrophication should be done using phototrophs, though information from macroinvertebrates and other animals may prove useful for assessing old datasets where there is no information for phototrophs.

11. Algae are the most useful phototrophs for assessing changes in nutrient conditions, because they respond relatively quickly to change. Although a system based on diatoms appears to cover most of the present needs for a trophic index, a system should also be developed and tested which takes into account a wider taxonomic range.

12. Rooted macrophytes can also provide valuable information, but care should be taken to allow for a probable lag in response to decreases in ambient phosphate because of accumulation of phosphate in sediments and in the plant biomass. This applies both to the initial datasets used to establish the trophic index and observations made during a period of nutrient decrease.

13. Although either N or P are almost always considered to be the key nutrients in eutrophication studies, the possibility should be borne in mind that vitamins might influence the biomass of some algae such as *Cladophora*.

14. Considerable care is needed when designing a sampling programme for the use of plankton chlorophyll *a* as an indicator of eutrophication in large rivers, because of marked short-term and seasonal changes.

15. Sites of Special Scientific Interest are likely to be especially vulnerable to eutrophication, so it is important that algae are considered in any assessment of the status of these sites.

16. The Environment Agency should conduct more assessments of their own records on nutrients in rivers; it is important to ensure that old records are not lost and time should be allocated for staff so that at least part of any assessment can be done by 'in-house' studies.

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# memorandum

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**EUTROPHICATION CONTROL VIA NUTRIENT REDUCTION IN RIVERS: LITERATURE REVIEW**

Please find enclosed a copy of the above report, produced for Anglian Region by Brian Whitton and Martyn Kelly of the University of Durham. This study was undertaken as a means of getting an up to date view of the state of knowledge regarding river nutrients, their control and the monitoring of impacts. The work follows on from that undertaken on the rivers Nene and Great Ouse in Anglian Region, which investigated the impact of trial nutrient removal at a number of key sewage treatment works.

If you require additional copies of the report then please contact David Balbi at the Agency Office in Spalding.

A copy of the Executive Summary is due to appear in a Scottish Natural Heritage newsletter in the near future.

Yours sincerely

Sarah.

**Sarah Chadd**
**Regional Environment Scientist**

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## APPENDIX I UK and EC legislation most relevant to nutrients and UK rivers.

Normative definitions of ecological status classifications for rivers required by the 'Framework Directive'

| Element | High Quality | Good Quality | Fair Quality |
|---|---|---|---|
| General | No evidence, or only very minor evidence, of anthropogenic impacts on biological communities, and the physico-chemical and physical environment. | Detectable but low-level impacts on biological communities and the physico-chemical and physical environment | Significant impacts on biological communities and their physico-chemical and physical environment. |
| | Composition and abundance of the biota reflect that normally associated with the ecotype under undisturbed conditions. | Biota shows signs of disturbance but deviates in terms of survival, reproduction and development only slightly from that normally associated with ecotype under undisturbed conditions. | Biota deviates moderately from that normally associated with the ecotype under undisturbed conditions |
| Phytoplankton | Species composition and abundance correspond totally or nearly totally to the type-specific conditions. | No accelerated growth of algae and higher forms of plant life as to produce an undesirable disturbance to the balance of organisms present in the water and to the quality of water . | Species composition and abundance show significant/moderate effects of impacts (e.g. eutrophication) due to anthropogenic activities. |
| | Average biomass and/or chlorophyll *a* concentration are at type-specific levels corresponding to the type-specific nutrient levels | | Average chlorophyll *a* concentration is significantly different from the type-specific natural levels. |
| Macrophytes and phytobenthos | Species composition and abundance correspond totally or nearly totally to the type-specific conditions. | Only slight changes in species composition and abundance compared to type-specific conditions. No significant changes (increase or decrease) in macrophytic and phytobenthic biomass due to anthropogenic activities (e.g. nutrient input) | Species composition and abundance differ significantly from type-specific conditions. Significant/moderate changes (increase or decrease) in macrophytic and phytobenthic biomass due to anthropogenic activities (e.g. nutrient input) |
| | No changes (increase or decrease) in macrophytic and phytobenthic biomass due to anthropogenic activities | Photosynthetic community is not interfered with by bacterial tufts/coats due to anthropogenic activities. | Phytobenthic community is interfered/displaced by bacterial tufts/coats due to anthropogenic activities. |

# APPENDIX II Research groups in the UK with particular interest in nutrients and rivers

(This list is far from comprehensive, but includes many of those whose work is quoted in the review)

**Prof. T. P. Burt** *Department of Geography, University of Durham, Durham DH1 3LE*
email t.p.burt@durham.ac.uk
On-going programme of nitrate-related research, establishing the importance and relevance of leaching studies at the hillslope and catchment scale by identifying the linkage between flow processes and nutrient transport. Analysis of long time series of nitrate concentrations in river water have provided a context for research projects investigating links between land use change and water quality. Most recently, involved in studies of nitrate buffer zones, funded by MAFF and EC.

**Dr F. H. Dawson** *Institute of Freshwater Ecology, The River Laboratory, East Stoke, Dorset BH20 6BB* email fhd@wpo.nerc.ac.uk
Macrophytes and plant communities in rivers:
1. Role in environmental assessment, including Mean Trophic Ranking system, habitat requirements and effects of eutrophication on communities.
2. Ecology and control of native and introduced species.
3. Advice on construction on rivers and wetlands, including quality assessment of biota.
4. Development and surveys for Environment Agency River Habitat Surveys.

**Dr D. M. Harper** *Department of Zoology, University of Leicester, Leicester LE1 7RH*
email dmh@knighton.u-net.com
General studies on eutrophication, nutrients in rivers, macroinvertebrates

**Dr A. L. Heathwaite** *Department of Geography, University of Sheffield, Sheffield*
Catchment studies and nutrient pathways to rivers

**Dr N.T.H. Holmes** *Alconbury Consultants, The Almonds, 57 Ramsey Road, Warboys, Ramsey, Cambridgeshire PE17 2RW*
Development of trophic index based on macrophytes (Mean Trophic Rank)

**Dr W.A. House** *Institute of Freshwater Ecology, The River Laboratory, East Stoke, Dorset BH20 6BB* email WAH@wpo.nerc.ac.uk
1. Role of river-bed sediments in the release of P following reductions of sewage discharges. (DETR)
2. Development of a phosphate selective electrode for monitoring P in waters and sediments. (Leverhulme)
3. Exports of P in large river catchments and comparison of point and diffuse inputs-mainly seasonal effects. (MAFF)
4. Development of methods to assess the P status of river and lake sediments (NERC)

**Dr M.G. Kelly** Bowburn Consultancy, 11 Monteigne Drive, Bowburn, Durham DH6 5QB email 101327.2514@compuserve.com

Ongoing development of Trophic Diatom Index (including training and Quality Assurance aspects). Also completed Agency-funded project on benthic algal mats in 1997 and is involved in development of standard European methods. Interested in all aspects of relationship between nutrients and algae in rivers.

**Prof. B. Moss** *Applied Ecology Research Group, School of Biological Sciences, Derby Building, University of Liverpool, Liverpool L69 3BX* email brmoss:liv.ac.uk
(with Dr D. Stephen, Dr D. McKee, Dr J.W. Eaton, Dr R.T. Leah, Dr A.Gill)

Research on nutrient flows in river/lake systems, use of models to predict nutrient delivery on a river/cathment basis, influence of climate change on these processes, canal systems, impact of fish on nutrient/productivity relations, restoration and rehabilitation of freshwater systems from nutrient loading.

**Dr K. J. Murphy** Division of Environmental & Evolutionary Biolog, yGraham Kerr Building, University of Glasgow, Glasgow G12 8QQ email k.murphy@bio.gla.ac.uk

Studies of functional relationships between river vegetation and river trophic status. Fieldwork in UK and overseas; collaboration includes with SEPA (Scotland). The aim is to develop multiple regression models of river P status (and other water physico-chemistry variables) using functional attributes of river plants as predictor variables (together with suite of other predictor variables). Such models have an interesting potential as the basis for novel bioindicator systems for river water quality.

**Dr C. Neal** *Institute of Hydrology, Wallingford, Crowmarsh Gifford, Wallingford, Oxon OX10 8BB* email c.neal@univxa.nerc-wallingford.ac.uk
(with Dr H. Jarvie)

1. Relationship between nutrient fractions and flow in various rivers, including the Wear.
2. Nutrients in River Kennet.

**Dr R. V. Smith** *Agricultural and Environmental Science Division, Agriculture and Food Science Centre, Newforge Lane, Belfast BT9 5PX* email r.v.smith@qub.ac.uk
(with J.S. Bailey, R.H. Foy, S.D. Lennox and others)
The general objectives are:

1. To acquire fundamental understanding of nutrient dynamics in soil-plant-water-air systems by process studies;
2. To quantify existing inputs of agricultural pollutants to soil, water and air by monitoring;
3. To identify the factors causing pollution of soil, water and air by interrogation of acquired databases;
4. To evaluate management strategies for decreasing pollution of soil, water and air.

**Dr B. W. Webb** *Department of Geography, University of Exeter, Rennes Drive, Exeter EX4 4RJ* email b.w.webb@exeter.ac.uk
Evaluation of the reliability of river load data:

1. Assessment of the effects of different sampling modes and frequencies and flux calculation algorithms on the accuracy and precision of estimates of sediment, particulate-associated and dissolved transport in fluvial systems;

2 Nutrient cycling in drainage basins including the effects of land drainage and woodland buffering on N loss and the role of sediment-associated transport in nutrient flux;
3. Water quality dynamics and trends including seasonal and storm-period chemical behaviour and long-term changes in physical and chemical water quality.

**Dr B. A. Whitton** *Department of Biological Sciences, University of Durham, Durham DH1 3LE* email b.a.whitton@durham.ac.uk

1. Phosphatase methodology for monitoring **P** status of rivers (Environment Agency: E. Clegg, Northumbrian Region).
2. Phosphorus and changes in the submerged vegetation of a highly calcareous pond (Northumbrian Water in liaison with English Nature).
3. Relationship between nutrient fractions and flow in the Wear (with C. Neal).

# INDEX

(Major nutrients and other items which occur throughout the review are not listed here)