PHOSPHORUS AND RIVER ECOLOGY

Tackling sewage inputs

ENGLISH NATURE

ASIANTAETH YR AMGYLCHEDD
ENVIRONMENT AGENCY

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Tackling sewage inputs

March 2000

Prepared on behalf of English Nature

and the Environment Agency

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Front cover: Water-crowfoot beds *Ranunculus peltatus* in the upper reaches of the River Lambourn SSSI. Photograph by David Withrington

Contents

Summary of key messages

This document has been produced to help place decisions concerning the control of phosphorus loads to rivers on an objective and consistent footing. A number of key messages need to be emphasised.

- Phosphorus dynamics in rivers are complex, involving both rapid and slow transformations within and between the water column, sediment and biota. Current monitoring programmes can only give insights into small parts of the overall picture.
- The aquatic plant community is the foundation for a healthy and diverse riverine ecosystem, providing food, shelter and breeding habitat for a wide range of animal species. Phosphorus enrichment in rivers can degrade the plant community by altering the competitive balance between different aquatic plant species, including both higher plants and algae. This has consequences for the whole ecosystem.
- Phosphorus enrichment at concentrations up to 200 - 300 $\mu g\ l^{-1}$ soluble phosphorus, and probably beyond, has great potential to increase the growth rates and standing crop of algal communities in a river, including phytoplankton, epiphytes, benthic forms and filamentous algae.
- Natural phosphorus concentrations in river water are likely to lie below 30 $\mu g\ l^{-1}$ in most cases, with background concentrations (admitting a small amount of human influence) somewhat higher than this. Increasing soluble phosphorus concentrations from background levels to 200 - 300 $\mu g\ l^{-1}$ and above therefore constitutes an important mechanism for the decline of submerged higher plants. Phosphorus concentrations in both the water column and the sediment can be important.
- To promote healthy riverine plant communities and the wide range of animal species dependent on them, phosphorus concentrations should be reduced to as near background levels as possible. The risk of adverse effects declines as phosphorus concentrations approach background levels, such that any incremental reduction should be seen as a positive step towards trophic restoration.
- Continuous point sources of phosphorus, dominated by sewage treatment works, have a highly important influence on levels of bioavailable phosphorus in the water column through the growing season. It is important to tackle point sources *comprehensively* so that reductions in phosphorus concentrations are maximised during this critical time of year.
- Diffuse sources of phosphorus, particularly from agriculture, are a major contributor to phosphorus levels in riverine sediments. This phosphorus can be utilized by benthic algae and rooted plants and can also be released into the water column by a variety of processes. As point sources are brought under control, the contribution from diffuse sources becomes increasingly important.
- An integrated programme of control, involving proactive action on both point and diffuse sources, is typically required to bring phosphorus levels in the water column and sediment down to near background levels.
- The complex nature of competition within plant communities and the interaction of nutrient enrichment with many other man-made impacts means that the ecological benefits accruing specifically from a phosphorus reduction programme cannot be stated with any certainty. This makes the development of a business plan for investment a difficult process and requires that a more pragmatic, precautionary approach is taken to evaluating the need for investment in phosphorus removal.
- Numerous techniques are available for removing phosphorus from effluent streams, producing concentrations in the final effluent down to below 1 $mg\ l^{-1}$ Total Phosphorus. A range of site-specific factors needs to be considered when selecting the most appropriate technique, but biological removal is favoured from an environmental perspective. On smaller works there is no real alternative to chemical dosing unless the effluent can be routed to a larger site. Where chemical treatment is required, calcium dosing has a number of environmental advantages over iron dosing.
- A lack of immediate ecological benefits from phosphorus stripping should not be interpreted as a lack of progress towards ecological restoration. A long-term perspective and an integrated approach to river enhancement is required to bring about stable and lasting ecological benefits.

- Phosphorus recovery from the waste stream for reuse in agro-industrial applications is feasible when biological removal or calcium dosing is employed. Recovered phosphorus is an attractive raw material for agricultural fertilisers and there is therefore great potential to reduce the mass-transfer of phosphorus into UK catchments by replacing imported rock phosphate with recovered material. This tackles eutrophication problems at their true source.
- Where phosphorus is not recovered, enriched sludge needs to be applied to agricultural land in accordance with the phosphorus requirements of the soil and crop in order to avoid long-term accumulation in catchment soils. This will inevitably mean application over larger areas of land per unit volume of sludge.

Rationale of this document

Eutrophication is one of the largest problems facing the ecology of freshwaters in the UK and elsewhere. The nutrient status of many lakes and rivers has increased dramatically over the past 50 years in response to increased collection and discharge of domestic wastes, increased loadings to collection systems (including the use of phosphate detergents), and widespread agricultural intensification. The importance of phosphorus in lake eutrophication is widely accepted, but there is more debate over the role of phosphorus in rivers and what steps should be taken to control its effects.

With the strong national and international obligations towards eutrophication control (Box 1), coupled with the more positive stance of the UK Government and the mechanism of the water industry's Asset Management Planning (AMP) process, there are now important opportunities to restore the nutrient status of rivers that have suffered from modern urban and rural pressures. To make the most of these opportunities, it is vital that the uncertainty surrounding phosphorus in rivers is minimised by providing objective and easily digestible information on its behaviour, effects and control.

The Environment Agency has recently produced a eutrophication strategy (Environment Agency 2000), covering all surface waters in England and Wales. It seeks to target monitoring and control effort through risk assessment procedures, and then assign environmental targets against which to monitor the effectiveness of control programmes. In the first instance, targets for freshwaters will be based on phosphorus concentrations, but ecological targets are likely to be included in the future. This document aims to build on this foundation in relation to rivers by providing relevant technical information that facilitates the local decision-making process in a nationally consistent way.

The information presented here is relevant to a wide audience but is primarily aimed at headquarters and local staff in English Nature and the Environment Agency and at staff in water companies and Government Departments involved in developing phosphorus removal programmes. The main objectives of the document are to:

- provide information on the behaviour and effects of phosphorus in the riverine ecosystem;
- discuss factors obscuring the effects of phosphorus;
- raise awareness of the importance of phosphorus control;
- clarify the contribution that can be made by phosphorus-stripping.

Whilst English Nature and the Environment Agency have common concerns about all rivers in England, the principal statutory focus of English Nature is on rivers designated specifically for their nature conservation interest. There is an established network of riverine Sites of Special Scientific Interest (SSSIs), some of which have been additionally designated as Special Areas of Conservation (SACs) under the EC 'Habitats' Directive. The riverine SSSI series comprises the best examples of the range of river types found in England, whilst riverine SACs contain the best English examples of riverine habitats and species of European importance. Many rivers would benefit from phosphorus control, but a minimum requirement should be to tackle phosphorus loads to these priority rivers comprehensively, in order to minimise detrimental impacts but also to provide demonstration studies that can be used to guide similar activity on other rivers. The Environment Agency has additional duties towards sensitive areas designated under the Urban Waste Water Treatment Directive, which provide a further focus for their eutrophication strategy.

Box 1. Key obligations and pressures driving phosphorus control in rivers.

There are statutory obligations and strong political pressures for greatly increased emphasis on the control of phosphorus levels in UK rivers. It is important to note that phosphorus control is not only relevant to the ecology of the river itself, but also to any static waterbodies or wetlands that are fed by the river. The proposed EU Water Framework Directive provides an important new impetus for the general control of phosphorus, and also gives a strong focus on priority areas, particularly Special Areas of Conservation (SACs) under the EU 'Habitats' Directive, Sites of Special Scientific Interest (SSSIs) under the Wildlife and Countryside Act 1981, and 'sensitive areas' under the 'Urban Waste Water Treatment' (UWWT) Directive. In 1998, the government announced an extensive programme of improvements that it expects the water industry to undertake by 2005 (DETR 1998), including measures to protect specified designated sites from the adverse effects of effluent discharges to rivers (Environment Agency 1998). This is the first major step in bringing phosphorus levels under control in UK rivers.

Some of the pressures for control outlined below are specific to phosphorus, whilst others require the more general management of anthropogenic influences to protect river ecology. Amongst these anthropogenic influences, eutrophication is a primary consideration.

Obligation/pressure	Relevant requirements
Proposed EC Directive (25/02/97) establishing a framework for community action in the field of water policy - ***the proposed Water Framework Directive.***	To reach and/or maintain at least 'good' ecological status in all surface waters, and to comply with any standards/objectives for EC 'Protected Areas'*, by the year 2010.
EC Directive 91/271/EEC concerning urban waste water treatment - ***the Urban Waste Water Treatment (UWWT) Directive.***	To identify 'sensitive areas' and to install appropriate treatment facilities for phosphorus and/or nitrogen removal at sewage treatment works serving more than 10,000 'population equivalents'.
EC Directive 92/43/EEC on the conservation of natural habitats and of wild fauna and flora - ***the Habitats Directive.***	To maintain or restore the 'favourable conservation status' of specified natural habitats and species of wild fauna and flora, through a range of measures including the designation of Special Areas of Conservation.
EC Directive 79/409/EEC on the conservation of wild birds - ***the Birds Directive.***	To protect and where necessary enhance populations of specified bird species (including many wetland species), through a range of measures including the designation of Special Protection Areas and the control of pollution.
The 1981 Wildlife and Countryside Act	To protect the national network of Sites of Special Scientific Interest as representative examples of the habitats, flora and fauna of the UK. The network includes a series of riverine SSSIs in England and Wales.
The Rio Convention on Biological Diversity	Through the UK Biodiversity Action Plan, to conserve and where possible enhance populations and natural ranges of priority native species, the quality and range of priority habitats, and the biodiversity of habitats where this has been degraded.
UK Government programme of improvements to the aquatic environment (DETR 1998).	The water industry to implement a range of improvement measures between 2000 and 2005, including the upgrading of sewage effluents discharging into specified riverine SSSIs or rivers feeding wetland SSSIs.

Note: Each EC Directive is brought into UK law by statutory 'Regulations' which have not been detailed here.
* 'Protected Areas' include those designated under the EU UWWT, Habitats and Birds Directives.

Question 1. How can phosphorus enrichment affect riverine wildlife?

A healthy submerged plant community is vital to the nature conservation value of a river. Apart from being of conservation importance in its own right, it provides essential resources for a range of animal species, associated with feeding, shelter and breeding. Dependent animals include invertebrates such as blackfly larvae, caddis-fly larvae and gastropod molluscs, which either filter-feed or graze algae off plant leaves and stems. Many fish species use submerged beds of higher plants as a spawning substrate, with the beds then becoming essential refuge and feeding habitat for juveniles. Bird species may graze plant shoots or feed on resident invertebrates, often utilising both food sources. Water-crowfoot (*Ranunculus* spp.) beds and associated plant and animal species are of particularly high nature conservation importance, being scheduled as a priority habitat under the EC 'Habitats' Directive (92/43/EEC). Plant communities characteristic of other river types, such as the moss floras typical of many upland watercourses and the diverse plant associations of sluggish lowland rivers, are also of high nature conservation importance in terms of their contribution to the overall diversity of riverine plant assemblages nationally.

Of the major plant nutrients, phosphorus is typically in shortest supply in rivers and other freshwaters and so generally has the greatest potential to limit plant growth (Box 2). Increasing phosphorus availability can affect the growth rates and standing crop of individual plant species (algae and higher plants) and consequently the competitive balance within riverine plant communities. Such changes can have knock-on consequences for animal species dependent on riverine plants. In addition, changes in the plant community can lead to severe nocturnal sags in dissolved oxygen (due to plant respiration) that stress the most sensitive animal species and may result in mortality. In upland streams and rivers, the entrapment of fine particles by excessive growths of epilithic algae exacerbates siltation problems, leading to spawning difficulties for species such as Atlantic salmon.

The behaviour of phosphorus in river catchments is complex, being delivered from a variety of sources in different forms and undergoing numerous biological and physico-chemical transformations once in the river network. Phosphorus can be taken up by plants from either the water column or sediment, whilst it can also be removed from the water column by sediment uptake (settlement, adsorption and microbial uptake) or released by the sediment into the water column (resuspension, desorption and microbial decomposition). It is important for anyone involved in developing phosphorus control strategies to have a basic understanding of the principal sources of phosphorus and the highly dynamic nature of riverine phosphorus cycling between the water column, sediments and biota. Appendix A provides information on the different forms of phosphorus that can be determined in the laboratory, whilst Appendix B gives a brief account of phosphorus entry into, and behaviour in, the river environment. It is worth spending time reading these before continuing with the main text.

There are four principal ways in which elevated phosphorus levels can affect riverine plant communities:

1. by increasing higher plant growth rates and thereby creating a large standing stock that regrows rapidly following management;

2. by the encouragement of higher plant species whose growth rates are geared to higher nutrient levels, thereby altering species composition/balance;

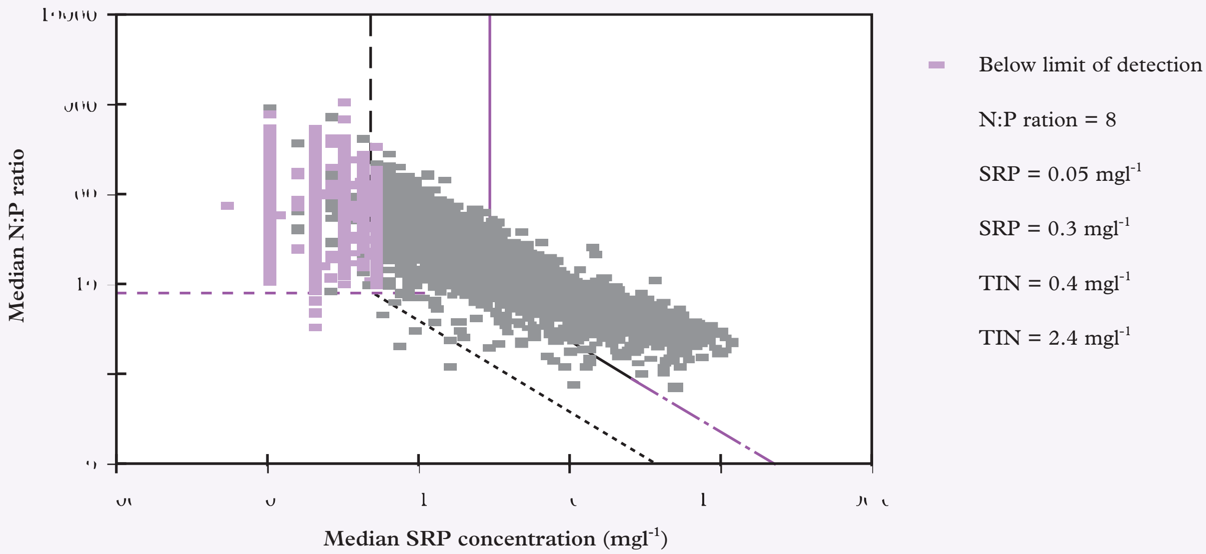
3. by the encouragement of epiphytic, epibenthic, filamentous and planktonic algae, thereby reducing the amount of light reaching the leaves and stems of higher plants and shifting community balance towards shade-tolerant species and ultimately algal dominance;

4. by reducing rooting depth and thereby making higher plants more susceptible to being ripped out of the substrate under high river flows.

Box 2. Nitrogen and phosphorus limitation of riverine plant growth in England and Wales.

Whether nitrogen or phosphorus availability actually limits plant growth in a river depends on many factors, including light intensity, current velocity and the availability of other major and trace plant nutrients. However, an assessment can be made of which of these two major nutrients *may* be limiting growth purely from consideration of their relative and absolute availabilities. The graph below (modified from Mainstone *et al.* 1995) plots the median N:P ratio (using Total Inorganic Nitrogen, TIN, and Soluble Reactive Phosphorus, SRP) against the median SRP concentration for over 5000 sites on rivers across England and Wales (1990-92 inclusive). It has been divided up into 5 zones on the basis of a threshold N:P ratio (broadly equating to the dividing line between phosphorus and nitrogen limitation), SRP concentrations (where the likelihood of phosphorus limitation of algal growth might be considered to change), and Total Inorganic Nitrogen (TIN) concentrations (which are plotted as a function of the N:P ratio and SRP thresholds).

The graph indicates that, at SRP concentrations at which phosphorus might conceivably be limiting growth, N:P ratios are nearly always above 8 and typically well above this value. This means that nitrogen is invariably surplus to plant requirements relative to phosphorus in such situations, strongly supporting the view that phosphorus is most likely to be limiting growth in rivers. The low N:P ratios at very high SRP concentrations are mainly due to the dominance of phosphorus inputs from sewage treatment works, which produce effluents with very low ratios.



Zone 1 - P likely to be limiting
Zone 2 - P may be limiting for part of the growing season
Zone 3 - Neither N or P likely to be limiting
Zone 4 - N likely to be limiting
Zone 5 - N may be limiting for part of the growing season

For any of these mechanisms to operate in response to artificially enhanced phosphorus concentrations, background levels of phosphorus in the river have to lie below concentrations that trigger an effect. If this is not the case, no effect of increasing phosphorus levels above background concentrations can be expected.

Mechanisms (1), (2) and (4) are probably dependent upon phosphorus levels in both the sediment and the water column, whilst mechanism (3) acts largely through phosphorus uptake from the water column. This said, benthic forms of algae will receive phosphorus from the sediment as well, whilst epiphytes can derive at least some of their requirements from the host plant. Enhanced standing crops of benthic algae may be important to the success of seed germination and seedling growth in rooted plants and so should not be overlooked as a potential mechanism of effect.

Little detailed work has been undertaken on the role of phosphorus in the competition between different higher plant species, but somewhat more is known about the risks from mechanism (3) due to extensive work on algal growth rates at varying levels of ambient soluble phosphorus (see Box 3). The main point from such work is that phosphorus has the potential to greatly affect the growth rates and standing crop of riverine algal communities at water column concentrations up to 200-300 $\mu\ l^{-1}$ and probably beyond. Increases in riverine concentrations to such levels are consequently extremely important in the battle for dominance within the plant community.

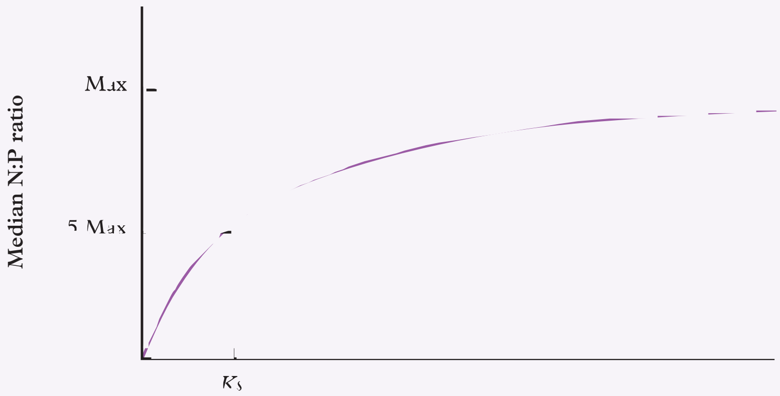
It is important to set the issue of algal growth rates and standing crop into the wider context of competition between submerged rooted plants and algae. Extensive work has been undertaken in lakes on the eutrophication process, and it is useful to see what parallels can be made with rivers. Current thinking (Box 4) views phosphorus availability as a fundamental driving force in the competitive balance between submerged higher plants and phytoplankton in lakes, dictating the probability of shifts occurring between relatively stable macrophyte-dominated and phytoplankton-dominated states. The influence of phosphorus operates over a wide range of concentrations, up to and probably beyond 1 mg l^{-1} total phosphorus.

The environmental conditions in the lower reaches of impounded rivers are very similar to those in lakes, with relatively long residence times allowing abundant phytoplankton growth, and comparisons are therefore very direct. The theory might also be tentatively applied to the balance between higher plants and filamentous/epiphytic/epibenthic algae in swifter-flowing rivers (with algal grazers such as crayfish and gastropods replacing zooplankton in feed-back processes). Indeed, the role of epiphytes and filamentous algae in shifting the competitive balance away from higher plants may be critical in all freshwater bodies, including lakes and sluggish rivers (Phillips *et al.* 1978). Filamentous algal problems are typically more observable in rivers, but it is important to note that epiphytic algal growth can constitute a large proportion of the total primary production. One detailed study on the River Itchen at Otterbourne concluded that epiphytes, which were mainly diatoms attached to brook water-crowfoot (*Ranunculus penicillatus* subsp. *pseudofluitans*), were actually the principal primary producers in that section of river (Shamsudin and Sleigh 1995).

Application of the basic principles of current lake theory to rivers would extend considerably the range of concentrations over which phosphorus is influential in rivers, and make any reduction in riverine phosphorus concentrations towards background levels an important contribution to the maintenance/restoration of higher plant communities. Importantly, the much more disturbed nature of rivers, in terms of both natural flow variations and river maintenance/engineering operations, provides many more opportunities for algal populations to gain dominance under enriched conditions.

Box 3. The effect of phosphorus on algal growth rates.

Two basic equations can be used to describe nutrient-limited growth by algae. The Monod equation relates growth rate to external nutrient concentrations, while the Droop equation relates growth rate to intracellular nutrient stores (Kilham and Hecky 1988). The Monod model describes simple Michaelis-Menten kinetics, and includes a half saturation coefficient, Ks, the external nutrient concentration at which half of the maximum growth rate is achieved (see figure below). Ks values are often cited to support the idea that the growth rate of the algal community as a whole is only limited at P concentrations of <10 μg l^{-1}. Reported Ks values for individual species range between 1 and 364 μg l^{-1} (Reynolds 1984), such that at any concentration within this range some species will be growing at their maximal rate. It is self-evident that the growth of individual species may be limited at concentrations substantially greater than 10 μg l^{-1}. Substantial increases in growth are possible even above the Ks value of a species, as is evident from the figure below.



The Monod model of plant growth kinetics

Algae which dominate at high phosphorus concentrations appear to have high Ks values and are out-competed at lower concentrations by algae with low Ks values. They are sometimes, but not always, faster-growing than those which dominate at lower concentrations. In any case, higher algal standing standing crops may be achieved by such algae by a number of different methods, such as:

- being less pallatable, so grazing losses are lower;
- being physically stronger or more streamlined, so scouring losses during high flows are lower; or
- being adapted to photosynthesise at lower light intensities, so self-shading does not become limiting until higher standing crops are reached.

All of these mechanisms can work to produce greater algal problems in rivers as phosphorus concentrations increase from natural/background levels to 200-300 μg 1^{-1} and probably beyond

While emphasis is often placed on the Monod equation, the Droop equation often better describes algal growth rates in culture and natural systems (e.g. Hecky and Kilham 1988), since algae are able to accumulate nutrients internally when external nutrient levels are higher than those strictly required for spontaneous growth. This intracellular nutrient store can then be utilised when external nutrient availability becomes growth-limiting. This is an important issue, since this 'luxury uptake' increases the importance of phosphorus at times in the year when concentrations are too high to be limiting the growth of any algal species. If concentrations subsequently decline to levels that are potentially growth limiting (perhaps due to increase spring flows), algal species with high *Ks* values can produce and maintain high standing crops despite low external phosphorus availability.

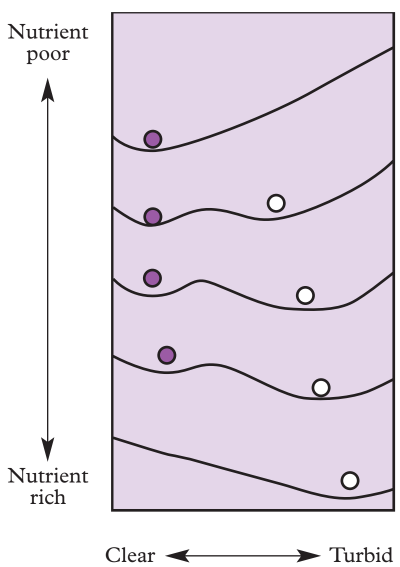
For algae such as *Cladophora*, both intracellular and extracellular nutrient concentrations are critical to understanding growth (Auer and Canale 1982a, b, Auer *et al.* 1982). Canale *et al.* (1982) and Canale and Auer (1982) discuss the seasonal and spatial variations in growth kinetics, and the development of a model for studying growth control strategies. Despite the fact that intracellular P concentrations are critical to understanding the growth dynamics of *Cladophora*, there is often a close relationship between extracellular and intracellular phosphorus concentration. For instance, Wong and Clark (1976) reported a correlation coefficient (r^2) of 0.76 between the two concentrations. Thus, Painter and Jackson (1989) were able to simplify the *Cladophora* model of Canale *et al.* (1982) and Canale and Auer (1982) by simulating internal phosphorus concentrations using temperature, Secchi depth and SRP concentration.

Box 4. The lake theory of alternative stable states.

There is now a general acceptance of the theory of 'alternative stable states' in lakes, based on a natural clearwater state dominated by submerged higher plants and a disturbed turbid state dominated by phytoplankton (e.g. Timms and Moss 1984, Scheffer *et al.* 1992, Moss 1997). These two states have both been observed in a stable condition at a wide range of total phosphorus concentrations, with various positive feedback mechanisms preventing a shift from one state to the other.

The clearwater, higher plant-dominated state is maintained by a range of biological processes, including phytoplankton grazing by a range of zooplankton harbouring in the beds of higher plants, and inhibition of phosphorus release from the sediment by the dense plant cover (inhibiting physical resuspension and desorption, the latter through plant uptake). Other processes that are likely to be important are the stripping of phosphorus from the water column by the shoots of higher plants, (particularly apparent with charophyte beds), and allelopathy (whereby higher plants exude chemicals that inhibit algal growth). The phytoplankton-dominated state is largely maintained by high turbidities preventing sufficient light reaching the sediment surface, from where submerged higher plants must develop. This is exacerbated by the presence of benthic algal mats and changes in sediment composition that inhibit higher plant establishment. Without submerged plant cover, the zooplankton suffers heavy predation and cannot suppress phytoplankton populations. Turbidity levels and zooplankton predation are typically exacerbated by the balance of the fish community, which in lowland areas is often dominated by bottom-feeding fish species that agitate and resuspend the sediment, and by small zooplanktivorous size classes.

The competitive balance between higher plants and algae is evidently highly complex and can be modified by encouragement or discouragement of a range of mechanisms (through techniques such as the manipulation of fish populations and the artificial reestablishment of higher plants). However, the likelihood of inducing a switch from one stable state to the other is fundamentally dictated by phosphorus availability in the water column. An empirical model has been proposed (illustrated below) concerning the probability of a lake existing in either of the two states, with the probability associated with the higher plant-dominated state increasing as phosphorus availability declines. The higher plant-dominated state is the only possible state at very low phosphorus concentrations, whilst the same is true of the phytoplankton-dominated state at very high concentrations.



Minimal model of the stability properties of the two alternative lake states (after Scheffer and Beets 1994). As nutrient concentrations increase, the stability of the macrophyte-dominated state declines and the likelihood of a shift to the phytoplankton-dominated state increases. As nutrient levels are brought under control, the likelihood of inducing a shift back to the macrophyte-dominated state (with the added application of biomanipulation techniques as necessary) increases.

● Macrophyte-dominated

○ Phytoplankton-dominated

Shifts from the higher plant-dominated state to the phytoplankton-dominated state are often triggered by specific disturbance events, such as dredging or weed-cutting activity. The chances of such a shift occurring depend upon phosphorus availability across a range of concentrations up to and probably over 1 mg l^{-1} total phosphorus (Moss 1997).

Question 2. How easy is it to separate the ecological effects of phosphorus enrichment from other environmental changes?

There are numerous other environmental factors that influence the growth and composition of higher plant communities. Some of these are influences that are generally not altered by human activities (such as catchment geology and morphology), whilst others can be greatly modified by Man. Community composition can therefore be seen as strongly determined by fundamental, fixed factors, and modified to a greater or lesser extent by anthropogenic impacts on a range of secondary factors, one of which is phosphorus levels (Table 1).

Table 1. Modifiable environmental factors that confound the effects of phosphorus on submerged higher plants in rivers.

Environmental factor	Key mechanism of impact				
	Reduced flows	Channel modifications	Pt. source discharges	Diffuse pollution	Loss of tree cover
Substrate (siltation)	*	*	*	*	
Current velocity	*	*			
Organic status			*	*	
Turbidity		*	*	*	
External shading					*
Residence time	*	*			
Other trace nutrients			*	*	
Algal/higher plant grazing	*	*	*	*	

The effects of these factors on plant communities are outlined in Box 5, but the important point to bear in mind is that elevated phosphorus concentrations are rarely the only important anthropogenic influence on the plant community in a given river reach. Only when all other influencing factors can be held constant whilst phosphorus availability changes within ecologically relevant ranges can the effects of phosphorus be unequivocally observed. In real systems this is rarely the case, and the impact of phosphorus is difficult to separate from other types of impact. This must not be taken as a justification for ignoring the role of phosphorus, which can be thought of as setting the underlying potential for impact upon which other anthropogenic factors are superimposed.

Box 5. Confounding impacts on plant communities.

Higher plant species often have specific **particle size** preferences, generally ranging from coarse gravels to fine silts (many aquatic mosses prefer very large material, from cobbles up to bedrock). Whilst many tolerant species respond well to the siltation of coarser substrates, others do not. Species such as brook water-crowfoot (*Ranunculus penicillatus* subsp. *pseudofluitans*) have difficulty in changing their rooting depth (Haslam 1978) and may have problems with gaseous and chemical exchange as water flow through the root zone declines. These factors also critically affect the establishment and growth of new plants, either from seed or root fragments. Increased siltation may be brought about as much by reduced current velocities as increased sediment loads, which in turn may result from reduced river flows or modifications of the channel. Much of the inorganic silt load is derived from diffuse sources, although the contribution from point sources should not be overlooked.

Current velocity is also important in terms of preventing the accumulation of filamentous algal populations. Reduced velocities, particularly over the winter months when strong flushing flows should occur, allow greater retention of algal cells and consequently more potential for sizeable growths that can smother higher plants.

The **organic content** of the sediment seems to be important to submerged higher plants, with many species showing poorer growth in highly organic conditions (Barko and Smart 1986). Again, oxygen availability may be a problem, as well as ammonia toxicity and possible nutrient limitation caused by complexation with organic matter under certain circumstances. Sewage treatment works are inevitably a major source of particulate organic material to rivers, whilst considerable loads can be supplied by other point sources and livestock wastes. Approximately 1.6 tonnes of organic solids are produced per year for every 1000 people served by a STW with secondary treatment, much of which enters during low summer flows and is thus more likely to be incorporated into riverine sediments. The presence of artificially enhanced higher plant growth downstream of STWs greatly increases the rate of organic inputs to riverine sediments, by trapping fine organic particulates from the effluent and facilitating the incorporation of these and their own die-back material into the substrate (Chambers and Prepas 1994). In this way higher plants can contribute to their own eventual decline.

Increased turbidities, caused by elevated solids loads to the river or by destabilisation of the channel and/or its bed sediments (often by river engineering or boating traffic), can create poor light conditions in the water column and consequently reduced growths of submerged higher plants. Some species are better adapted to low light intensities than others, such that a shift in community composition might be observed before reduced overall growths. **Shading** from riparian trees causes a well-defined community shift from shade-intolerant species, such as *Ranunculus* spp., to shade-tolerant species, such as *Callitriche stagnalis* and *Potamogeton pectinatus.*

Water residence times are important in lowland rivers in that they dictate the standing stock of phytoplankton that can be achieved at any given growth rate. Reduced residence times, as a result of reduced flows or greater river impoundment, are likely to increase algal cell concentrations and reduce light availability to submerged higher plants.

There is some evidence to suggest that **trace nutrients** in sewage treatment works discharges may stimulate the growth of algae such as *Cladophora* in rivers. Such discharges contain a huge number of biologically active chemicals that are candidates for investigation, but Vitamin B12 and thiamine are suspected in particular (pers. comm. B.A. Whitton, Durham University).

Grazing of algal cells by a range of animal species is important in keeping planktonic, epiphytic and filamentous populations to acceptable sizes. Zooplankton are particularly important in sluggish lowland rivers, whilst scrapers such as gastropod molluscs assimilate large quantities of epiphytes in a range of river types. Crayfish have been found to be highly important grazers of *Cladophora* mats in one American study (Creed 1994), creating a ten-fold reduction in biomass. Impacts on grazing populations (through toxic contamination or habitat degradation, for instance) can therefore create algal problems in the absence of phosphorus enrichment.

Question 3. What is the evidence for ecological change in rivers in response to phosphorus enrichment?

The pattern of decline in submerged higher plant communities is well-documented in freshwater, particularly in relation to shallow lakes and sluggish lowland rivers (see references in Box 4 for example). An initial boost in higher plant productivity is followed by increased standing crops of algae (which may be planktonic, filamentous, epiphytic and/or benthic), which reduce the amount of light reaching submerged higher plants and produces a decline in those species requiring high light intensities. Species adapted to higher nutrient levels and low light intensities (such as *Potamogeton pectinatus*) gain dominance, but even these are lost as algal populations increase. The final stage is the loss of higher plants and complete dominance by algal species, but all steps in the process are detrimental to riverine communities and need to be prevented or reversed. Phosphorus is one important contributing factor in this process of decline, with the probability of adverse community shifts increasing as phosphorus levels increase.

Owing to the confounding factors discussed in Question 2, field studies unequivocally demonstrating the impact of phosphorus on higher plant communities are relatively rare. Numerous surveys of vegetation upstream and downstream of sewage treatment works have been undertaken, but changes in phosphorus levels occur in parallel with changes in other influential factors such as river flow, current velocity, water depth, turbidity, sediment silt levels, sediment organic carbon and trace nutrient concentrations. Evidence of improvements to higher plant communities once phosphorus has been stripped out of such effluents would be unequivocal, but phosphorus stripping of riverine effluents is a recent phenomenon and there are no long-term observations of its benefits in rivers. In addition, other impacting factors often prevent the restoration of the macrophyte community and therefore need to be addressed before ecological benefits can be observed (see Question 14).

Some field studies have been undertaken that seek to minimise the effect of confounding factors by judicious selection of study area and individual study sites, producing relatively homogeneous environmental conditions in all respects but phosphorus availability. This is crucial, since a random selection of sites across the country would undoubtedly lead to the conclusion that factors such as catchment geology and shading are primarily determining community composition. This is in no real doubt, but what we need to uncover is how the species distribution generated by such factors is adversely affected by artificial phosphorus enrichment.

Whilst no such studies are known from the UK - the extensive riverine plant surveys undertaken by the then Nature Conservancy Council (Holmes 1983) did not include measurement of phosphorus - a number of studies have been undertaken in Europe that have provided useful information (Carbiener *et al.* 1990, Grasmuck *et al.* 1995, Robach et al. 1996). Work in north-east France by Robach *et al.* (1996) has led to the identification of community change along a trophic gradient, which differs between acidic and calcareous rivers. The main determinants of community change within each subset of rivers were identified as water column SRP (sediment phosphorus was not measured) and ammoniacal nitrogen (Table 2), with characteristic SRP concentrations varying between trophic groups from 7 to 191 $\mu g\ l^{-1}$ (calcareous waters) and from 25 to 150 $\mu g\ l^{-1}$ (acidic waters). Given the typically high N:P ratios in rivers at these SRP concentrations (see Box 2), it is likely that ammoniacal nitrogen is merely intercorrelated with SRP rather than acting as a mechanism of community change.

Table 2. Physico-chemical characteristics of trophic groups of rivers in north-east France (after Robach *et al.* 1996).

River type	Trophic group	pH	Conductivity ($\mu S\ cm^{-1}$)	Hardness ($meq\ l^{-1}$)	Ammniacal nitrogen ($\mu\ N\ l^{-1}$)	SRP ($\mu\ P\ l^{-1}$)	Nitrate ($mg\ N\ l^{-1}$)
Acidic waters	A	6 (0.2)	59 (14)	0.3 (0.1)	49 (16)	25 (11)	0.6 (0.2)
	B	6.5 (0.2)	49 (5)	0.3 (0.1)	47 (6)	26 (13)	0.3 (0.2)
	C	6.9 (0.3)	74 (18)	0.5 (0.2)	111 (99)	96 (79)	0.5 (0.2)
	D	6.8 (0.3)	80 (21)	0.6 (0.3)	142 (72)	150 (66)	0.7 (0.3)
Calcareous waters	A	7.4 (0.1)	608 (115)	4.8 (1.4)	13.7 (7.3)	7.2 (1.7)	5.5 (1.4)
	B	7.5 (0.2)	736 (112)	4.7 (0.9)	22.2 (13.8)	13.0 (5.5)	5.1 (1.8)
	C	7.5 (0.1)	740 (99)	5.0 (0.7)	45.3 (27.8)	14.9 (6.8)	4.7 (2.1)
	D	7.6 (0.2)	657 (66)	3.9 (0.4)	33.8 (31.3)	29.4 (23.6)	2.9 (2.5)
	E	7.9 (0.2)	657 (63)	3.8 (0.5)	61.2 (40.0)	39.9 (33)	1.6 (1.1)
	F	7.9 (0.2)	508 (52)	3.2 (0.3)	255 (107)	101.5 (116)	2.5 (0.9)

Numbers are means with standard deviation in parenthesis.

The species associations generated by Robach *et al.* (1996) are shown in Table 3. Although such work is based upon correlations and not causal relationships, it is compelling and fits with types of change that might be expected over the range of SRP levels observed. Owing to the generally far lower land use intensities and human densities in much of France compared to the UK, SRP concentrations at many sites are much closer to (and in many cases equate to) natural levels. The highest trophic group in each of the two subsets of rivers is therefore considered highly enriched in this region of France. Mean SRP concentrations generally lie below 40 $\mu g\ l^{-1}$ in calcareous rivers of the area, with a range of plant community types associated with SRP levels down to less than 10 $\mu g\ l^{-1}$. The overall effect of increasing phosphorus levels appears to be the elimination of certain species adapted to very low nutrient status, but subsequently the addition of more and more mesotrophic and eutrophic species until even these begin to be eliminated.

In the highest trophic categories, the risks of extensive algal proliferations are greatly increased and would be exacerbated by further increases in SRP concentrations up to a point, resulting in declines in the dominance of higher plants. Such risks are inevitably compounded by other anthropogenic disturbances such as siltation and habitat degradation. It should be noted that aquatic mosses of acidic oligotrophic rivers have not been considered in the study but are thought to be highly sensitive to nutrient enrichment.

Many higher plant species tolerate a wide range of trophic conditions and are therefore of little value in detecting the more subtle effects of nutrient enrichment. Emphasis on the identification of sensitive species is therefore important in detecting lower level impacts. In the UK, a system of estimating trophic status has been produced using extensive field observations of plant communities in near-pristine and enriched conditions over a range of river types. Species are assigned a score (termed its Species Trophic Rank, Table 4) which indicates its sensitivity to enrichment, and the mean score (the Mean Trophic Rank, or MTR) of the plant community at a particular site indicates the degree of enrichment. The judged sensitivity of many bryophytes (mosses and liverworts) is particularly notable, along with a range of higher plants including floating club-rush (*Eleogiton fluitans*), bulbous rush (*Juncus bilbosus*), alternate-leaved water-milfoil (*Myriophyllum alterniflorum*) and a number of water-crowfoots (*Ranunculus* spp.).

Table 3. Plant species groups associated with different trophic states in selected acidic and calcareous rivers of north-east France (after Robach *et al.* 1996).

I = <10% cover, II = 10-25% cover, III = 25-50% cover, IV = 50-75% cover, V = 75-100% cover.

Species	Trophic group (acidic rivers)			
	A	B	C	D
Potamogeton polygonifolius	V	V		
Cardamine armara	I	II		
Glyceria fluitans	IV	V	V	V
Fontinalis antipyretica	I	II	II	III
Mentha aquatica	I	I	II	II
Sparganium emersum	I	III	IV	III
Sparganium erectum	IV	III	I	I
Veronica beccabunga	I		III	I
Callitriche stagnalis		IV	IV	III
Callitriche hamulata		III	V	V
Lemna minor		II	III	IV
Ranunculus peltatus		II	II	II
Callitriche platycarpa		III	III	II
Berula erecta		II	I	I
Potamogeton crispus			I	
Myriophyllum alterniflorum			II	
Potamogeton alpinus			I	
Potamogeton variifolius			I	
Phalaris arundinacea			V	V
Glyceria maxima			III	II
Elodea canadensis			III	I
Elodea nuttallii			I	III
Nasturtium officinale			III	III
Oenanthe fluviatilis			I	I
Potamogeton berchtoldii			I	I
Myosotis scorpioides				II
Callitriche obtusangula				V
Nitella flexilis				I

Species	Trophic group (calcareous rivers)					
	A	B	D	C	E	F
Potamogeton coloratus	V					
Batrachospermum monoliforme	II					
Juncus subnodulosus (submerged)	II					
Chara vulgaris	II					
Chara hispida	II			I		
Lamprocystis roseo persicina	II		I	I		
Berula erecta	V	V	III	V	III	I
Callitriche obtusangula	I	III	V	V	IV	III
Lemna trisulca		I	III	III	II	
Fontinalis antypyretica		I	II	I	II	
Elodea canadensis			III	IV	II	I
Sparganium emersum			II	II	II	IV
Lemna minor			III	II	V	V
Potamogeton friesii			II	II	II	II
Elodea nuttallii			II	I	IV	IV
Ranunculus circinatus				I		
Nasturtium officinale			V		III	II
Spirodela polyrhiza			I		II	IV
Azolla filliculoides			I		I	II
Groenlandia densa			II		II	
Potamogeton crispus			III		II	I
Myriophyllum verticillatum			I		I	
Zannichellia palustris			II		II	
Hottonia palustris			I			
Hippurus vulgaris			I			
Potamogeton pectinatus			II		IV	IV
Myriophyllum spicatum			II		IV	V
Potamogeton perfoliatus			I		I	III
Ceratophyllum demersum			I		V	V
Oenanthe fluviatilis					I	
Ranunculus trichophyllus					I	
Potamogeton pusillus					I	
Ranunculus fluitans					II	III
Potamogeton lucens						III
Potamogeton nodosus						III
Mentha aquatica (submerged)	I	I	I	I	I	
Veronica anagallis-aquatica	I		I	I	II	
Myosotis scorpioides	I		II	I	II	
Veronica beccabunga			I		I	I

Table 4. Sensitivity of aquatic plants to nutrient enrichment, as indicated by Species Trophic Rank (Environment Agency 1996).

Species	STR	Species	STR	Species	STR
Algae		**Higher plants**		**Higher plants**	
Batrachospermum sp(p)	6	**a) Dicotyledons**		**b) Monocotyledons**	
Hildenbrandia rivularis	6				
Lemanea fluviatilis	7	*Apium inundatum*	9	***Acorus calamus***	2
Vaucheria sp(p)	1	*A. nodiflorum*	4	***Alisma aplantago-aquatica***	3
Cladophora agg.	1	*Berula erecta*	5	***Alisma lanceolatum***	3
Enteromorpha sp(p)	1	*Callitriche hamulata*	9	*Butomus umbellatus*	5
Hydrodictyum reticulatum	3	*C. obtusangula*	5	*Carex acuta*	5
Stigeoclonium tenue	1	***Ceratophyllum demersum***	2	***C. acutiformis***	3
		Hippurus vulgaris	4	*C. riparia*	4
Liverworts		*Littorella uniflora*	8	***C. rostrata***	7
		Lotus pedunculatus	8	***C. vesicaria***	6
Chiloscyphus polyanthos	8	*Menyanthes trifoliata*	9	*Catabrosa aquatica*	5
Jungermannia atrovirens	8	*Montia fontana*	8	***Eleocharis palustris***	6
Marsupella emarginata	10	*Myriophyllum alterniflorum*	8	*Eleogiton fluitans*	10
Nardia compressa	10	***M. spicatum***	3	*Elodea canadensis*	5
Pellia endiviifolia	6	***Myriophyllum spp. indet.***	6	***E. nutallii***	3
P. epiphylla	7	***Nuphar lutea***	3	***Glyceria maxima***	3
Scapania undulata	9	***Nymphaea alba***	6	***Groenlandia densa***	3
		Nymphoides peltata	2	***Hydrocharis morsus-ranae***	6
Mosses		***Oenanthe crocata***	7	*Iris pseudacorus*	5
		O. fluviatilis	5	*Juncus bulbosus*	10
Amblystegium fluviatilis	5	*Polygonum amphibium*	4	***Lemna gibba***	2
A. riparium	1	*Potentilla erecta*	9	*L. minor*	4
Blindia acuta	10	*Ranunculus aquatilis*	5	***L. minuta/miniscula***	3
Brachythecium plumosum	9	*R. circinatus*	4	*L. trisulca*	4
B. rivulare	8	***R. flammula***	7	*Phragmites australis*	4
B. rutabulum	3	***R. fluitans***	7	***Potamogeton alpinus***	7
Bryum pseudotriquetrum	9	*R. omiophyllus*	8	*P. berchtoldii*	4
Calliergon cuspidatum	8	*R. peltatus*	4	***P. crispus***	3
Cinclidotus fontinaloides	5	*R. penicillatus pseudofluitans*	5	***P. friesii***	3
Dichodontium flavescens	9	***R. penicillatus penicillatus***	6	***P. gramineus***	7
D. pellucidum	9	*R. penicillatus vertumnus*	5	***P. lucens***	3
Dicranella palustris	10	***R. trichophyllus***	6	*P. natans*	5
Fontinalis antipyretica	5	***R. hederaceus***	6	*P. obtusifolia*	5
F. squamosa	8	***R. sceleratus***	2	***P. pectinatus***	1
Hygrohypnum luridum	9	***Ranunculus spp. indet.***	6	*P. perfoliatus*	4
H. ochraceum	9	***Rorippa amphibia***	3	*P. polygonifolius*	10
Hyocomium armoricum	10	*Rorippa nasturtium-aquaticum*	5	***P. praelongus***	6
Philonotis fontana	9	***Rumex hydrolapathum***	3	*P. pusillus*	4
Polytrichum commune	10	*Veronica anagallis-aquatica*	4	***P. trichoides***	2
Racomitrium aciculare	10	*V. catenata*	5	***Sagittaria sagittifolia***	3
Rhynchostegium riparioides	5	***V. scutellata***	7	***Schoenoplectus lacustris***	3
Sphagnum	10	*Viola palustris*	9	***Scirpus maritimus***	3
Thamnobryum alopecurum	7			***Sparganium emersum***	3
				S. erectum	3
Fern-allies				***Spirodela polyrhiza***	2
				Typha latifolia	2
Azolla filiculoides	3			***T. angustifolia***	2
Equisetum fluviatile	5			***Zannichellia palustris***	2
E. palustre	5				

STR - Species Trophic Rank
Species - Judged to be most sensitive to nutrient/organic enrichment (STRs of 8-10).
Species - Judged to be moderately sensitive to nutrient/organic enrichment (STRs of 6-7)
Species - Judged to be most tolerant of nutrient/organic enrichment (STRs of 1-3)

Question 4. *What levels of phosphorus might be expected in the absence of significant human impact and how do these compare with existing levels?*

In pristine rivers, annual loads of phosphorus to the river system are extremely low, since phosphorus is not abundantly available from the majority of natural geologies. The nutrient status of the watercourse is largely dependent upon nutrient retention in the system and subsequent spiralling downstream, as nutrients are continually taken up and released by the abiotic and biotic mechanisms described in Appendix B. Through the summer months, SRP levels in the water column are dictated by the concentrations in river baseflow, as modified by instream processes which typically result in some of this SRP being stripped out of the water column. The release of phosphorus from riverine sediments under pristine conditions mainly occurs during autumn flushing events, when large amounts of particulates are resuspended.

There is no argument that natural levels of SRP in upland UK rivers are very low (certainly below 20 $\mu g\ l^{-1}$), since there are plenty of examples where such concentrations can still be found. There is much more debate about what levels might naturally be expected in lowland river types, where human activities have intensified in the UK to the extent that unimpacted examples do not exist. However, there is no evidence to suspect that the natural situation differs from the model described above, with low external inputs and a focus on nutrient retention and spiralling. For instance, work by researchers of unpolluted calcareous streams (such as Robach *et al.* 1996 and Mulholland and Hill 1997) indicates that the very low natural concentrations of SRP in calcareous aquifers give rise to natural riverine concentrations of less than 10 $\mu g\ l^{-1}$. This is supported by observations of background SRP concentrations of less than 10 $\mu g\ l^{-1}$ in chalk aquifers of southern England (Mainstone *et al.* 1999a). Phosphorus accumulation within the system may result in slightly higher natural concentrations in the lower reaches of large rivers, due to internal cycling, but this is unlikely to produce levels greater than 30 μg SRP l^{-1}.

Whilst sandstone geologies are more susceptible to contamination of baseflow and run-off and may therefore have suffered enrichment earlier than chalk rivers in the UK, it is likely that natural concentrations would not be any greater. Clay-based catchments may produce somewhat higher natural concentrations of *total phosphorus* than sand- and chalk-based catchments, due to the dominance of run-off as a hydrological pathway, but much of the natural load will be in non-labile particulate form and will not be biologically available (at least in the short term).

Background levels are distinct from *natural* levels in that they admit a certain amount of anthropogenic impact, but at an intensity which is judged unlikely to produce harmful effects. Typically, background levels are estimated for a specified reference or baseline date, before most of the adverse ecological impacts were visible in UK surface waters. Restoring phosphorus concentrations to this baseline date is then assumed to eliminate any ecological problems relating to phosphorus. A range of baseline dates has been employed in different studies, but pre-Second World War (1930s) is the time most often used (prior to large-scale increases in loads from agricultural and domestic sources). The problem is that some rivers inevitably suffered enrichment problems at this time, such that the use of a reference date from this period on a particular catchment can produce estimates of phosphorus levels that are inappropriate.

Unfortunately, there are no recorded phosphorus concentrations in rivers from any candidate reference dates, for the estimation of either natural or background concentrations, and so the assessment of natural or background levels in an impacted catchment therefore has to rely on indirect methods. The estimation of reference levels of phosphorus (which may be natural or background depending on the policy adopted) is likely to be a cornerstone of the European strategy for controlling freshwater eutrophication and is an important component of the proposed EU Water Framework Directive. Available methodologies for estimating reference loads of phosphorus are discussed in Box 6, along with some estimated reference values from the literature.

Figure 1 provides estimates of existing total phosphorus loads to a range of UK rivers (produced by Parr *et al.* 1999), expressed per unit area of catchment. These figures would suggest that the upper estimates of background load given in the literature (Box 6) are somewhat suspect and would certainly not be applicable to many, if any, UK situations. It is unfortunate that loads for many rivers in Figure 1 can only be calculated in terms of SRP rather than total phosphorus, but even so it is clear that a large proportion of catchments (including lowland examples) have existing loads lying well below 1 kg $ha^{-1}\ yr^{-1}$, equivalent to and often less than the higher background figures quoted. Attributing so much of the existing load to background sources is clearly inappropriate, considering the large increases in phosphorus loads to rivers during the last 70 years.

Box 6. Estimating reference phosphorus loads.

Defining reference nutrient levels (which may be natural or background) as a tool for setting management targets will be one of the requirements of the revised Water Framework Directive. There are three basic methodologies for doing this:

- identifying and monitoring a reference network of waterbody types
- modelling
- expert judgement

Whilst reference networks are highly useful, they rely on the existence of near-pristine examples of all river types against which to compare impacted catchments. Anthropogenic pressure is intense in lowland England, but it is possible to use examples from similar river types in certain parts of Europe where there is much less anthropogenic pressure. Workers on the continent have identified what they judge to be 'quasi-pristine' examples of rivers, calculated the total phosphorus load in the river, then presented this as a function of catchment size (termed an export rate, in kg ha^{-1} yr^{-1}). Figures therefore include the contribution from the limited number of point sources as well as from diffuse sources in the catchment. Billen *et al.* (1991) reported export rates of 0.05 - 0.65 kg SRP ha^{-1} yr^{-1} for a range of French rivers, whilst Vighi and Chiaudani (1985) produced figures of 0.07 - 0.65 TP kg ha^{-1} yr^{-1} for a range of Italian lakes (median value 0.31 kg ha^{-1} yr^{-1}). The figures of Billen *et al.* are likely to be somewhat higher if expressed in terms of total phosphorus.

Hind-casting modelling is a much-used approach, whereby the current contributions from different types of source are estimated using export coefficients (calibrated against instream loads), and then historical information on factors such as livestock densities, fertiliser application rates and population sizes are substituted for current information to produce a revised load estimate for a specific reference date. The difference between the estimated existing and historical loads then provides an indication of the degree of modern anthropogenic enrichment. This has been performed by Johnes (1994) on a number of British catchments, producing export rates ranging from 0.18 to 2.63 kg ha^{-1} yr^{-1} for the year 1931. However, it is important to note that such export coefficient approaches should be calibrated against real data on instream loads, and that no such data exist for historical conditions.

The upper values of the ranges given by all of the above workers are very high to act as reference levels, which may be due to inappropriate selection of rivers currently judged to be in a quasi-pristine state, or (in the case of hind-casting) inappropriate assessment of historical loading rates, inappropriate selection of rivers that actually suffered from relatively high enrichment at the reference date chosen, or inappropriate selection of reference date. For instance, general background export coefficients of 0.2 kg P ha^{-1} yr^{-1} are used in Austria and Switzerland, with a lower value (0.1 kg P ha^{-1} yr^{-1}) for Finland, Norway and Sweden. (e.g. Morse *et al.* 1993). The issue is not easily resolved, but it may be that the use of a defined level of anthropogenic stress may be more suitable than the rather arbitrary use of a reference date against which to judge the level of existing nutrient enrichment.

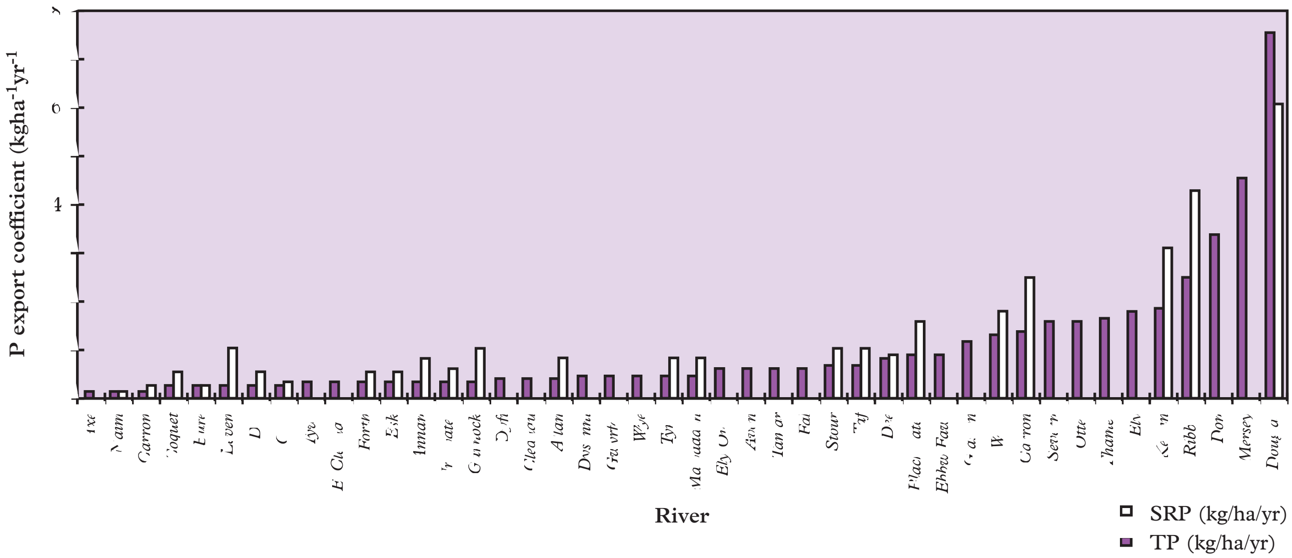


Figure 1. Phosphorus export rates for a range of UK rivers, calculated from instream loads and catchment area (information from Parr et al. 1999).

Background export rates can be crudely converted to phosphorus concentrations in the river by dividing the annual background load by the annual stream flow. Table 5 shows the results of applying a number of possible export rates to five rivers of varying characteristics. Export rates judged to be most relevant to different river types are shaded, producing mean natural concentrations below 30 µg l^{-1} total phosphorus for all rivers other than the Leam. The Leam is attributed with the highest potential values of natural export rate because it has a clay-based catchment which delivers much of the river flow as run-off. However, the calculated instream concentrations are probably over-estimated in this analysis because of the very low rainfall in this particular catchment, which provides little river flow with which to dilute the assumed natural load. In reality, clay-based catchments with very low rainfalls are likely to generate lower phosphorus loads than similar catchments with high rainfalls, so export rates in this exercise should really be revised downwards. Note that estimated instream concentrations are given in terms of total phosphorus, and that under background conditions a relatively small proportion of this would be SRP. Higher export rates are also shaded that yield riverine concentrations deemed unlikely to increase ecological risk greatly, as an indication of ecologically desirable background loads. No background rate is given for the Leam due to the over-estimation of natural rates discussed above - background levels would most appropriately lie below 0.1 mg l^{-1}.

Table 5. Estimated mean total phosphorus concentrations (µg l^{-1}) that would occur in selected UK rivers at a range of export rates.

	Afon Glaslyn @ Beddgelert	River Tees @ Middleton	River Otter @ Dotton	River Nadder @ Wilton	River Leam @ Princes Drive
NGR	SH 592478	NY 950250	SY 087885	SU 098308	SP 307654
Mean annual rainfall	3067 mm	1553 mm	985 mm	606 mm	659 mm
Mean annual runoff	2670 mm	1167 mm	483 mm	406 mm	189 mm
Catchment area	68.6 km^2	242.1 km^2	202.5 km^2	220.6 km^2	362 km^2
Surface geology	Igneous	Sandstone/ limestone/ millstone grit	Sandstone	Chalk/ greenstone	Clay
EC = 0.07 kg TP ha^{-1} yr^{-1}	2.6	6.0	14.5	17.2	37.0
EC = 0.1 kg TP ha^{-1} yr^{-1}	3.7	8.6	20.7	24.6	52.9
EC = 0.2 kg TP ha^{-1} yr^{-1}	7.5	17.1	41.4	49.3	105.8*
EC = 0.31 kg TP ha^{-1} yr^{-1}	11.6	26.6	64.2	76.4	164.0
EC = 0.65 kg TP ha^{-1} yr^{-1}	24.3	55.7	134.6	160.1	343.9

= most likely natural concentrations. EC = Export Coefficient. * See text.

= ecologically desirable background concentrations.

Inevitably this is not the whole story, since the delivery of loads to the river is not uniform throughout the year and varies between sources (see Question 7). Under background conditions, contamination of baseflow can be regarded as minimal (very low point source loads), with the majority of the load deriving from run-off components of river flow. This can be modelled by apportioning the load between baseflow and run-off components, to achieve an appropriately low phosphorus concentration in baseflow, and dividing the rest of the load through the year according to the seasonality of run-off. This has been undertaken for four rivers with contrasting surface geologies (Figure 2), with the separation of the annual hydrograph into baseflow and run-off components being performed by hydrological modelling procedures. For all surface geologies other than clay, growing season concentrations reflect those in the baseflow, with peak concentrations occurring at times when the flow contribution from run-off is greatest. This is a crude model (no account is taken of internal cycling or the fact that autumn flows often carry more phosphorus than spring flows), but it does give an indication of the importance of considering seasonality when attributing background loads to catchments.

It is enlightening to compare likely natural and background concentrations of SRP in UK rivers with existing levels. Figure 3 shows the extreme differences in existing SRP concentrations between coarse categories of river in England and Wales, based on catchment altitude and river size. The majority of rivers with high altitude catchments still maintain median concentrations of below 0.03 mg l^{-1} (with around half below 0.01 mg l^{-1}), although some sites exhibit concentrations an order of magnitude higher. Upland rivers are highly sensitive to small increases in phosphorus availability, so even enrichment of the order of 10 µg l^{-1} is of concern. There are therefore significant numbers of upland rivers exhibiting worryingly high phosphorus levels. The picture is similar for smaller rivers at intermediate altitudes, but is very different for lowland rivers where a massive range of ambient SRP concentrations is found. Very low concentrations still occur in some lowland rivers, particularly the smaller ones, but the majority of large lowland rivers exhibit concentrations of over 0.3 mg l^{-1}, with many exceeding median concentrations of 1 mg l^{-1}. This represents widespread and heavy enrichment.

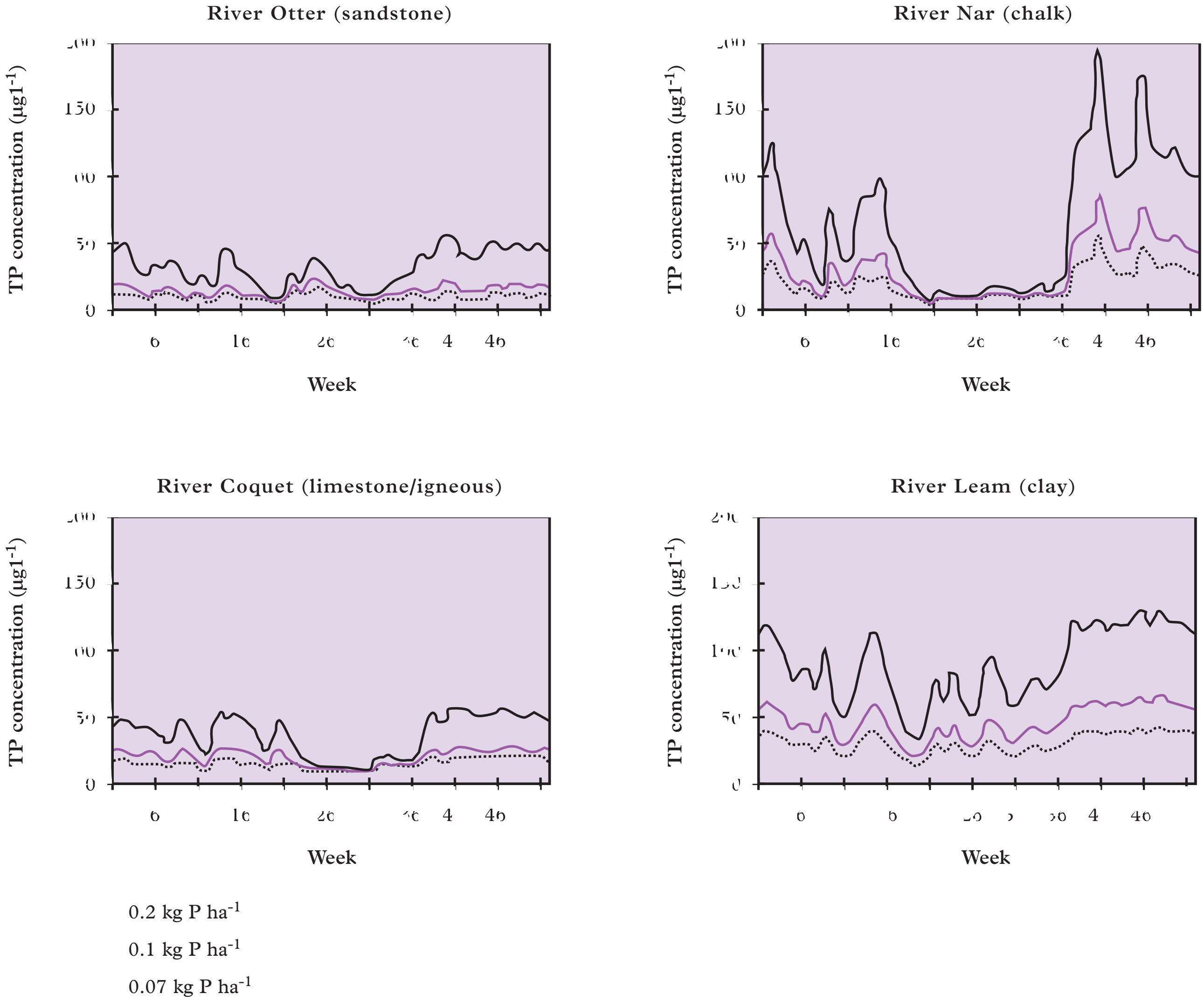


Figure 2. Modelled background phosphorus concentrations in a range of river types.

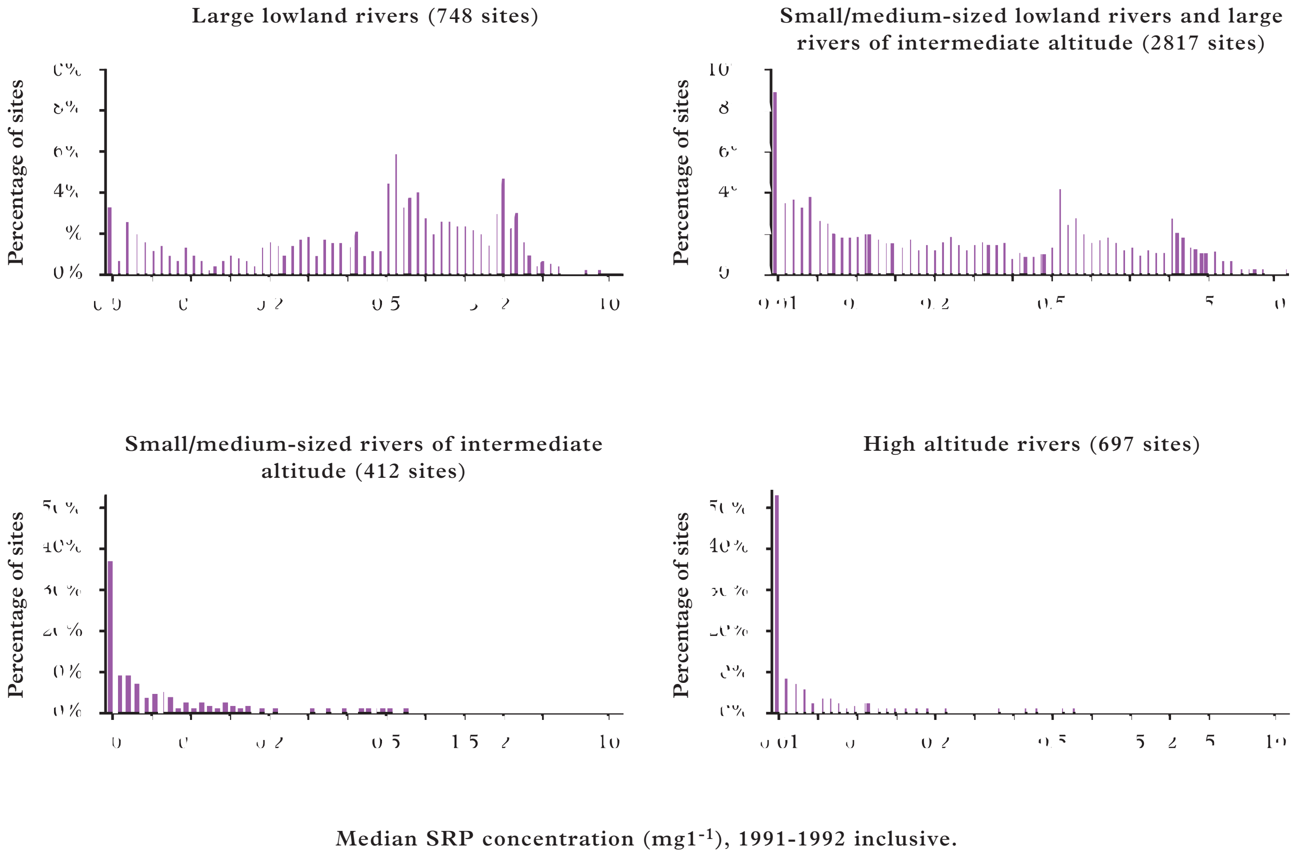


Figure 3. Ambient phosphorus concentrations in different types of river in England and Wales (after Mainstone* et al. *1995).

Note: the scale of the x-axes is non-linear, and values below the limit of detection have been set to 0.001 mg l^{-1}.

Question 5. What levels of phosphorus should we be aiming for in rivers?

To promote healthy riverine plant communities and the wide range of animal species dependent on them, phosphorus concentrations should be reduced to as near background levels as possible. The risk of adverse effects due to phosphorus declines as phosphorus concentrations approach background levels, such that any incremental reduction should be seen as a positive step towards trophic restoration. Given the sliding scale of ecological risk associated with riverine phosphorus concentrations, and the numerous confounding factors operating, it is unrealistic to expect to identify particular threshold concentrations of phosphorus that will automatically safeguard the plant and animal communities of different river types. However, it is clear that the level of risk changes most rapidly over the concentration range from natural conditions to around 200-300 µg l^{-1} (see previous sections). A pragmatic approach to setting targets is therefore required, involving the identification of phosphorus levels within this concentration range that are achievable and that approach those expected at low levels of anthropogenic input for the type of river in question.

The Environment Agency has recently released its revised national strategy for eutrophication control, within which a family of phosphorus targets is presented for rivers (Table 6). Target selection for any given river will depend upon site-specific considerations. A target may be chosen for a particular river based on historical conditions or on conditions in similar but less impacted examples of the river type (see Box 6), together with consideration of the feasibility of reducing phosphorus loads in the light of the nature of anthropogenic stresses. For the purposes of this document, the targets are tentatively linked to their likely generic suitability for different river types, as a guide to what might be appropriate in any given situation. Inevitably, where a river supplies a standing water requiring trophic restoration, riverine targets will need to consider the desired phosphorus concentrations in that standing water. The setting of interim targets should also be considered for highly enriched rivers (such as Hurst Haven on the Pevensey Levels, see Figure 4), to provide greater encouragement to restoration efforts and to assist in the reporting of real progress towards an ultimate goal.

Table 6. Target phosphorus concentrations for rivers in England and Wales (Environment Agency 2000), with suggested applications to different river types.

Target	Mean SRP (mg l^{-1})	Suggested application
1	0.002	Upland watercourses.
2	0.06	Mid-altitude watercourses on hard substrates. Lowland, small and medium-sized watercourses on chalk and sandstone.
3	0.1	Lowland large rivers on chalk and sandstone.
4	0.2	Lowland rivers on clay substrates and large alluvial river sections.

Water column concentrations are inevitably only one facet of riverine enrichment (although they are generally a useful indicator of enrichment in other environmental compartments) and greater attention needs to be focused on the status of the sediment in future. Sediment phosphorus targets for different river types, probably based upon the Equilibrium Phosphate Concentration (see Appendices A and B), ultimately need to be developed to provide a holistic framework for phosphorus control.

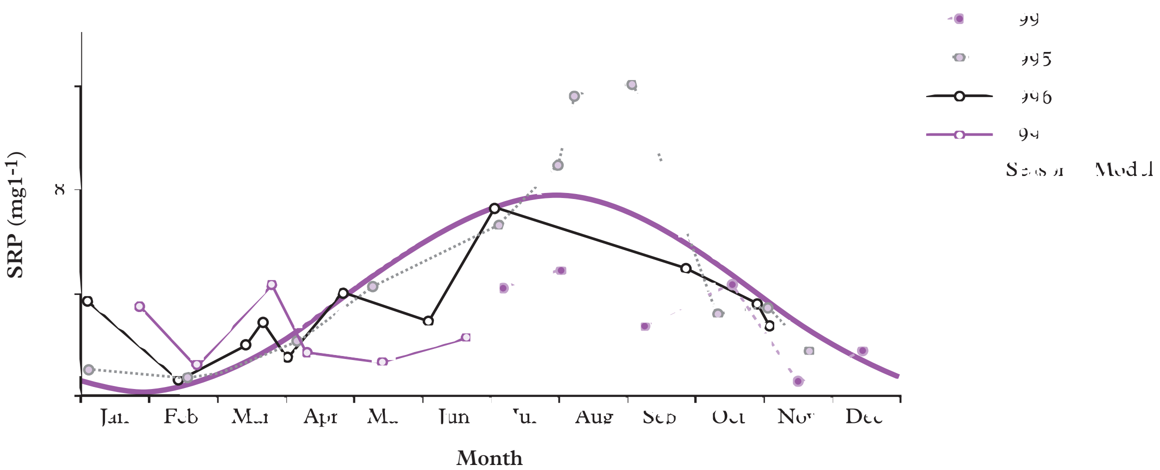


Figure 4. Phosphorus concentrations in Hurst Haven (Pevensey Levels) at New Bridge, a watercourse dominated by phosphorus loads from two major sewage treatment works.

Question 6. Can reducing phosphorus levels be damaging to existing wildlife?

Work in calcareous rivers (see Question 3) suggests that reducing ambient SRP concentrations in such situations to an annual mean as low as 40 µg l^{-1} would not result in the loss of higher plant species that thrive in eutrophic conditions. Even those species known to thrive in highly enriched conditions immediately below sewage treatment works discharges, such as *Potamogeton pectinatus*, are an important but balanced component of the plant community at these background nutrient levels. This is in agreement with the generally accepted opinion that there are no higher plant species in UK rivers that are dependent for their presence on high phosphorus concentrations. There is no reason to suspect that reductions to similar water column phosphorus concentrations in other lowland river types would result in the elimination of native higher plant species. It is likely that the plant community would focus much more strongly on riverine sediments as a phosphorus source as loads decline, eventually restoring a more natural nutrient cycling through the river system.

Unless phosphorus levels are driven down to ultra-low levels (probably less than 10 µg l^{-1}), the productivity of the macroinvertebrate and fish communities is much more dependent upon the physical quality of the habitat (including abiotic and vegetative habitats) than the nutrient status of the water column. Background levels of phosphorus would still permit adequate higher plant productivity and populations of benthic, epiphytic and planktonic algae for primary consumers, which then forms the platform for the rest of the food web.

Question 7. How important are different sources of phosphorus in the enrichment process?

Estimating the contribution of different sources to the total phosphorus load entering a receiving water (be it a river, lake or coastal water) is typically performed using annual estimates of total phosphorus. This is sensible for rapid evaluation, since there is great uncertainty in the estimation of phosphorus bioavailability and some difficulties in quantifying the seasonality of inputs. Whilst such estimates are generally adequate for lakes, where the whole of the phosphorus load is potentially relevant, they can be misleading for rivers, where much of the total load can be exported from the river soon after it has entered. For this reason, it is important to understand the nature and timing of different sources of phosphorus and how they are likely to impact upon the growth of higher plants and algae in the river.

Relatively simple methods of apportioning the total instream load between different sources are discussed in more detail in Box 7. The export coefficient approach described can be taken further in complex models such as HSPF and CREAMS (Mainstone *et al.* 1996), but these require detailed datasets and are expensive to run. GIS-based models of phosphorus export, such as MINDER for Rivers and AGNPS (Woodrow *et al.* 1994 and Morse *et al.* 1994 respectively), provide a compromise between complex models and simple spreadsheet calulations. Such models can tackle the issue of seasonality in non-point source loads by simply apportioning the estimated annual load though the year according to rainfall patterns, and can generate phosphorus concentrations in the river through the year and across the catchment. This specific consideration of non-point source loads is an important improvement on point source-based dilution models such as SIMCAT and QUASAR, providing a more realistic picture of the contribution of different sources to riverine phosphorus levels and giving a valuable assessment of the geographical distribution of diffuse loads.

In simple terms, the total load to the river can be broadly divided into point source inputs and diffuse inputs. Point sources are typically dominated by sewage treatment work (STW) effluents (although industrial effluents can be phosphorus-rich and should always be checked), whilst diffuse sources are dominated by agriculture (other diffuse sources include run-off from roads and urban areas, septic tanks and forestry practices). Diffuse agricultural sources contribute a substantial part of the annual load to rivers in all but the most urban catchments (some examples are provided in Table 7), but the ecological relevance to the river of much of the load from this source may be low. Since phosphorus sorbs strongly onto soil particles, most of the diffuse load enters the river during run-off events in autumn and winter, under conditions of high river flow. This means that a significant part of the load from this source will be immediately flushed out of the system along with a large proportion of the phosphorus accumulated in the river over the course of the summer.

Table 7. Examples of annual phosphorus budgets (in tonnes P per year).

	Upper reaches of Hampshire Avon (Parr *et al.* 1998)	Warwickshire Avon (Iversen *et al.* 1997)	Pevensey Levels (Parr and Mainstone 1997)	River Ant (Johnes *et al.* 1994)
Atmospheric/natural	12.5 (14.0%)	57.9 (5.5%)	0.6 (1.6%)	0.08 (1.6%)
Inorganic fertiliser	19.9 (22.4%)	209.5 (20.0%)	2.5 (7.4%)	1.04 (21.3%)
Livestock	18.7 (21.0%)	99.5 (9.5%)	2.4 (7.0%)	2.89 (59.3%)
STWs	35.5 (39.9%)	654.3 (62.6%)	28.7 (84.0%)	0.86 (17.6%)
Unsewered population	23.8 (2.3%)	-	-	-
Industry	2.5* (2.8%)	-	-	-
Total	89.1 (100%)	1045.0 (100%)	34.2 (100%)	4.87 (100.%
Catchment area (km^2)	1249	2892	56	49.3
P load exported to river ($kg\ ha^{-1}\ yr^{-1}$)	0.7	3.6	6.1	1.0

*Fish farming

Box 7. Methodologies for source apportionment.

There are two principal approaches to assessing the contribution of point sources and non-point sources to the total phosphorus load in a river, within which a number of different methodologies are available. Both approaches have merit, and the best strategy is generally to make assessments using a number of methodologies and then arrive at a consensus judgement. Mainstone *et al.* (1996) provide more detailed information.

1. Instream assessment methods

These involve the analysis of data on riverine phosphorus concentrations and river flow to produce either a quantitative division of the total load into point and non-point sources, or a qualitative understanding of this division through the interpretation of water quality/flow patterns. Key techniques are:

Comparison of total loads and point source loads. This additionally requires a reasonable knowledge of loads from all point source discharges in the catchment, either from direct monitoring or using indirect methods (see export coefficient methods below). The total instream load is estimated from flow and concentration data, and the non-point source contribution is estimated by the difference between the total instream load and the total point source load. Key pitfalls are failing to account for numerous small point sources, failing to produce an adequate estimate of total instream load (due to inadequate data or inappropriate analysis), and failing to account for instream loss/gain processes. Models such as SIMCAT and QUASAR essentially use this approach, but additionally allow a spatial analysis of the effect of point sources (see below).

Spatial analysis of instream phosphorus concentrations. This method does not involve the estimation of loads, but instead focuses on the longitudinal pattern of instream phosphorus concentration down the river in relation to known point source discharges. This analysis can often clearly show the dominant contribution of point sources to instream concentrations, particularly through the growing season when effluent dilution is at a minimum. Extra sampling sites may be necessary in one-off surveys to gain sufficient resolution of spatial patterns.

Temporal analysis of instream phosphorus concentrations and loads. Much information can be gleaned from the way in which phosphorus concentrations in the river vary with season and river flow, as long as these patterns are interpreted in the light of known phosphorus dynamics in river systems.

Separation of river hydrographs. This involves the division of the annual hydrograph into different flow components (essentially run-off, base-flow and perhaps effluent return), and apportioning the measured load in the river between the components in a way that mimics observed concentrations. This is a more involved process and requires computer automation, but is a worthwhile approach to use in tandem with other techniques.

2. Export coefficient approach

Export coefficients may be defined as standardised estimates of contaminant loading to a river, based on consideration of the size of the load potentially available for export to the river and the likely extent of on-land retention of that load prior to reaching the river. Export coefficents may be expressed in many different ways (such as the percentage of the load applied to land, a certain load per hectare of a given land use, a load per head of livestock or population) and are modified according to factors such as land characteristics, climate and effluent treatment procedures (depending on the source being considered). The following source categories are usually used.

- Sewage treatment works
- Direct industrial discharges
- Inorganic fertiliser
- Livestock
- Unsewered population
- Atmospheric loads

A critical step in generating phosphorus budgets from export coefficients is the calibration phase, whereby the total estimated load from all sources is compared with the calculated load in the river (from river flow and concentration data). Export coefficients generate crude measures of load, and extensive revision of the coefficients used for a particular catchment may be necessary following this comparison.

This is not to say that diffuse loads are unimportant to the river, since phosphorus-rich soil particles retained in the river system (in areas of sufficiently low energy to permit settlement) can supply plant growth in subsequent growing seasons, either directly via root uptake or via subsequent release (internal loading) to the water column. The scale of retention is greater in years of low winter flows, creating greater scope for impact in the following year. There is also potential for phosphorus applied to the land to leach into sub-surface drainage and groundwater where soils are heavily overloaded with phosphorus, particularly on sandy geologies but also where other geologies are heavily fissured or contain macropores. If this occurs, diffuse sources start to become a significant source of input throughout the year. Diffuse loads are also highly important to any lakes and wetlands fed by the river, in which case annual loads of total phosphorus are a more realistic reflection of their relative importance. It is therefore vital that diffuse sources are effectively controlled, but it is equally important to place their contribution to riverine eutrophication into context.

Point sources are more important than estimates of annual total phosphorus loads suggest, since they enter the river continually through the year and are at minimum dilution through the growing season when phosphorus concentrations in the water column are critical. In addition, the phosphorus load in STW effluents is highly bioavailable and can therefore have an immediate impact. Figure 5 provides a stylised illustration of the seasonality in point source and diffuse loads, and gives an indication of how the contribution from each type of source changes with flow through the year. Inevitably, there will be large variation about this general pattern, mainly depending upon the degree of urbanisation of the catchment. The potential contribution of point sources to the sedimentary phosphorus reservoir should also not be ignored, with inputs under low-flow conditions permitting enhanced rates of accumulation of the highly organic particulate load (particularly if higher plant abundance has been increased by artificial stimulation from the effluent).

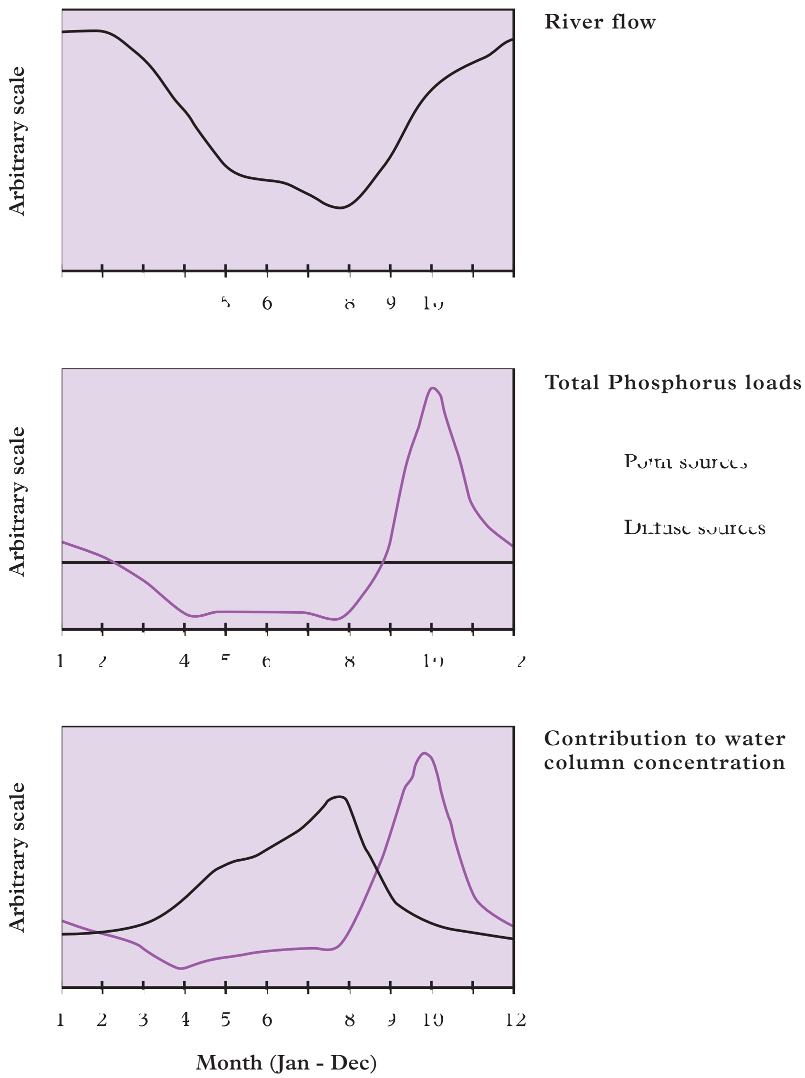


Figure 5. Typical seasonality in the contribution of point and diffuse sources to phosphorus concentrations in the river.

The different contributions from point and non-point sources can be observed in flow and concentration data from real rivers, such as the River Bourne in Hampshire (Figure 6). Concentrations are highest at low flows, primarily due to the lack of dilution offered to point source inputs. However, as flows in the Bourne increase to between 1 and 5 $m^3 s^{-1}$, diffuse inputs of phosphorus (including internal loading from sediments) increase but only so as to maintain instream SRP concentrations at about 0.1 mg l^{-1}. At extremely high flows (>6 $m^3 s^{-1}$), concentrations begin to rise again due to greater resuspension of sediment and/or increased surface runoff of phosphorus.

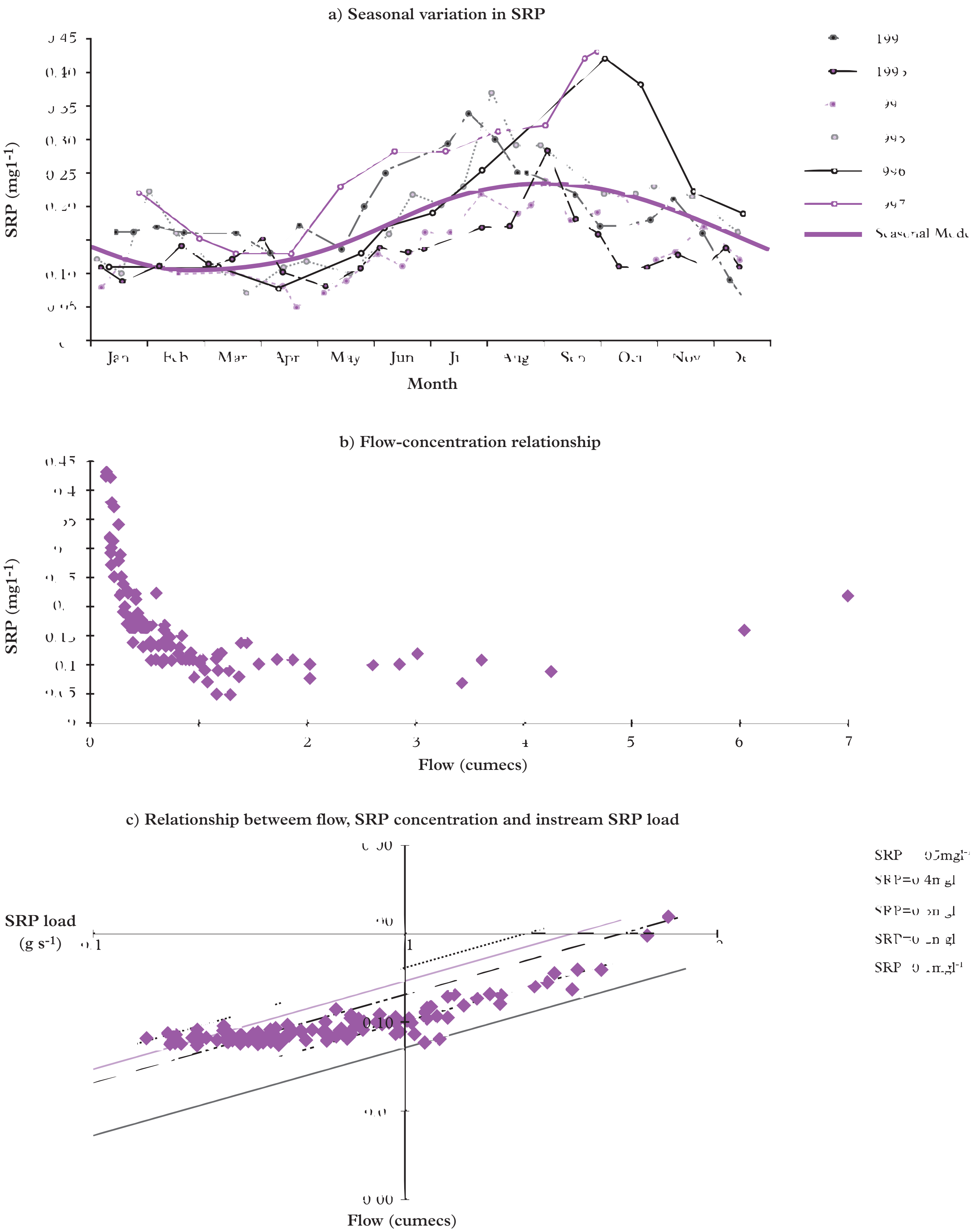


Figure 6. Phosphorus behaviour in the River Bourne, Hampshire.

Table 8 provides a rapid evaluation of the typical contribution of a STW effluent to the SRP concentration in a river immediately downstream of the discharge, taking into account the size of the discharge, the level of conventional effluent treatment employed and the river flow. The scale of the contribution to water column concentrations will inevitably decline with distance downstream as the processes of biological uptake, sorption and mineralisation strip the high concentrations of soluble phosphorus out of the water column or tie it up in colloids. This phosphorus then becomes part of the internal pool that spirals down the river along with any accumulated diffuse loads, continuing to contribute to the nutrient status of the system.

Table 8 Typical contribution of STWs to riverine concentrations of total phosphorus (µg l^{-1}) under different conditions of STW size, river flow and conventional treatment.

River flow ($m^3 s^{-1}$)	STW size (Pop. equiv).	Primary treatment	Secondary treatment
1	500 2,000 10,000 50,000	13.7 54.8 273.9 1359	11.1 44.5 222.6 1113
5	500 2,000 10,000 50,000	2.74 11.0 54.8 274.0	2.23 8.90 44.5 222.6
10	500 2,000 10,000 50,000	1.37 5.48 27.4 137.0	1.11 4.45 22.3 111.3
50	500 2,000 10,000 50,000	0.27 1.10 5.48 27.4	0.22 0.89 4.45 22.3

Question 8. How can phosphorus inputs be reduced cost-effectively?

If phosphorus concentrations in UK rivers are to be reduced to envisaged target levels, it is clear that an integrated approach is required to controlling loads, involving proactive action on both point and diffuse sources and the management of internal cycling of phosphorus where necessary. Within any given catchment, the importance attached to controlling point and diffuse sources will vary depending on population density, land use intensity and the nature of the river. However, there is no doubt that point sources are far easier to control than diffuse sources, and that, given the nature and timing of point source loads outlined above, a good return for the resources invested is likely to accrue from tackling point sources comprehensively. In any given situation, the dominant contribution to point source loads from STWs may be significantly augmented by industrial discharges (including those from fish and cress farms), which therefore need to be considered fully in any control programme (see Mainstone *et al.* 1996 for more detail). Diffuse sources generally attain their greatest importance in river reaches where the retention of particulates from run-off is highest (i.e. in sluggish, silty sections).

Question 9. How can diffuse sources be controlled?

Although the focus of this guidance is on tackling point sources, it is worth briefly discussing options for the control of diffuse loads of phosphorus. Whilst forestry, urban drainage and the unsewered population can be important in different situations, agriculture typically dominates the diffuse source contribution. A range of best management practices can be employed to reduce loads from livestock and arable agriculture (Mainstone *et al.* 1996). Agricultural controls can be divided into three main areas (Figure 7), comprising minimisation of inputs, retention of phosphorus in the soil, and run-off capture in buffer zones. Proper consideration of all three areas, with emphasis on input minimisation and sustainable soil management (including erosion prevention) is the key to successful diffuse source control. A heavy reliance on run-off amelioration by buffer zones, which can easily be circumvented by sub-surface hydrological pathways (enhanced by under-drainage systems), break-through surface run-off and artificial run-off pathways (paths, tracks and roads), does not constitute a comprehensive solution. However, judicious positioning, design and maintenance of buffer areas at key points within the catchment (not necessarily immediately adjacent to watercourses) is an important component of an integrated control strategy.

Phosphorus Application

P-test soil and animal excreta regularly
Base inputs on crop requirements and control soil P reserves
Maximise fertilising potential of animal excreta
Target applications at the crop root zone (band application, slurry injection)
Time application to maximise crop uptake
Do not apply to frozen or snow-covered ground or when soil is near field capacity
Control P in livestock feed

↓

Soil Conservation

Select cropping patterns appropriate to erosion risk
Leave sensitive soils under permanent cover
Minimise tillage but avoid compaction
Contour plough where feasible
Maintain/ increase soil organic content
Create run-off breaks of permanent vegetation
Delay tillage and grow spring-sown crops
Use cover crops where soil would otherwise be unstable
Where winter crops are grown, sow early
Establish tramlines after crop emergence
Do not overstock pasture relative to erosion risk
Control livestock access to water courses

↓

Offsite Retention

Lay to permanent vegetation
Target at focal ponts for surface run-off
Do not apply phsphorus within the zone
Maintain sward density
Avoid concentration of run-off and subsequent breakthrough

↓

River

Figure 7. Management practices to reduce diffuse loads of phosphorus to rivers (after Mainstone et al. *1996).*

Considerable change is required to current phosphorus application regimes in agriculture, and this issue has important links to the ultimate sustainability of phosphorus stripping programmes for point sources (Question 16). It is important to note that the concentrations of total and extractable phosphorus are very high in many agricultural soils in England and Wales, and higher than required to insure against crop growth limitations (Mainstone *et al.* 1996). This leads to unnecessarily high concentrations of phosphorus in run-off and the possibility of leaching into sub-surface drainage or groundwater, particularly on sandy geologies or other geologies with fissures and/or macropores. Recently revised guidance by MAFF (1998) advises farmers to limit phosphorus applications based on soil phosphorus reserves, which will hopefully help to reduce the potential for diffuse phosphorus losses. However, the guidance will not help to bring about a reduction in soil phosphorus levels in areas of intense slurry spreading activity, where sizable applications to land are still accepted by the guidance even where there is no nutritional requirement for phosphorus due to existing soil reserves.

Erosion control is key to reducing phosphorus loads from agricultural land, since the majority of the diffuse phosphorus load is typically associated with particulates in run-off. The importance of maximising soil stability cannot be overstressed, which may involve leaving critical areas of the catchment under permanent vegetation (pasture or woodland) or modifying tillage regimes. Run-off breaks in large sloping fields, which may take the form of hedges but could be grassed banks, are vital in preventing the gradual migration of fine particulates towards the river network (Parr *et al.* 1999). Artificial run-off pathways can greatly alter the classic perceptions of run-off patterns and can necessitate catchment walk-overs to ensure that the right areas of land within the catchment are being targeted for attention. New guidance on erosion control has recently been produced by MAFF (1999), which should help to reduce particulate loads to rivers if promoted properly.

The mechanisms for introducing desired changes into agricultural management regimes are varied, ranging from advice and education, through financial support to regulation. Recent local initiatives (see Mainstone 1999b) suggest that a great deal can be achieved by *proactively* raising awareness within the farming community, explaining the links between environmental problems in rivers and certain agricultural practices. Detailed explanation of the agroeconomic benefits of changing practices is equally important and is being built into new advice on best management practices from the Environment Agency. Nutrient management is one area of agricultural activity where both the farmer and the riverine environment can benefit greatly by modifying management regimes. However, there are changes required to modern agricultural regimes that are highly unlikely to be brought about by advice and education (such as the conversion/reversion of critical areas to permanent vegetation), and in such cases it is crucial that mechanisms are available to bring such changes about.

Agricultural grant aid schemes must be sufficiently flexible to incorporate the specific requirements of the aquatic environment - at present there is no grant aid available for specific measures to combat diffuse agricultural pollution. Recent reform of the EU Common Agricultural Policy, allowing environmental conditions to be attached to production subsidies, may provide useful leverage if implemented effectively in the UK. A range of possible regulatory scenarios also needs to be investigated, including various pieces of existing legislation (particularly Water Protection Zones under the 1991 Water Resources Act) and innovative approaches to bringing about the required changes in farming practice.

Question 10. What technologies are available for stripping phosphorus from point sources?

STW outfalls are the major point source inputs to rivers, the phosphorus originating primarily from human waste and detergents but also trade wastes and other ingressions to the sewerage system. Phosphorus concentrations in wastewater typically range from 6 to 15 mg l^{-1}, depending on the actual load and the degree of dilution by 'clean' water entering the sewer, either from ingression or from rainwater. Phosphorus is present in wastewater in three forms: orthophosphate, polyphosphates and organic phosphorus compounds. During conventional secondary treatment three main changes occur:

1. organic materials are decomposed and their phosphorus content is converted to orthophosphate;
2. inorganic phosphates are utilized in forming biological flocs;
3. most polyphosphates are converted to orthophosphates.

After secondary treatment, phosphorus is largely present as bioavailable orthophosphate, which reacts and precipitates out of solution in the presence of metal salts, can be taken up by micro-organisms or isolated from the waste stream by magnetic or ion exchange processes. A number of options therefore exist for stripping phosphorus from waste waters, within which lie a large number of variations. This document focuses on the two most widely used removal methods in the UK and overseas (chemical precipitation, by the addition of metal salts, and biological removal).

Details of chemical and biological removal processes are given in Box 8, whilst the advantages and disadvantages of each are shown in Table 9. In general terms, biological treatment is a more environmentally benign process in that sludge production is not increased (merely enriched) and there is no consumption/disposal of metal ions to consider. However, it cannot achieve the same phosphorus removal efficiencies as chemical treatment and is currently rather variable in performance without chemical supplements. This said, chemical treatment only achieves enhanced removal efficiencies (below 2 mg l^{-1}) at the expense of producing large amounts of extra sludge (Figure 8).

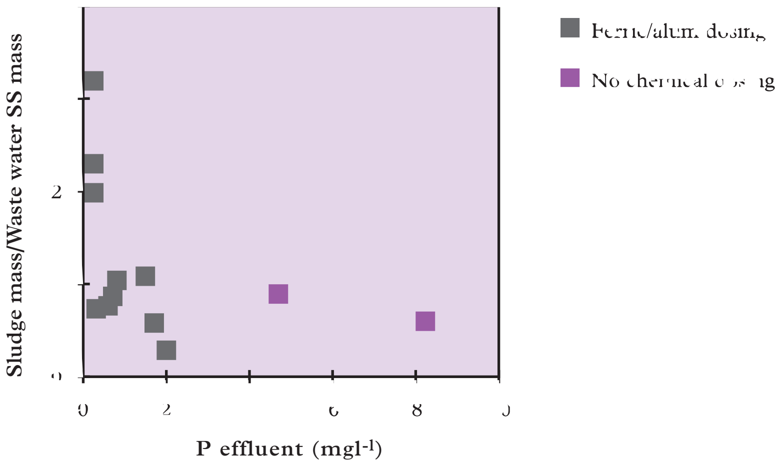


Figure 8. Relationship between sludge production rate and effluent P concentration (after USEPA 1987)

Ultimately, the choice between the two approaches is site- and cost-dependent (see later). Biological removal requires an activated sludge plant, which is costly to install if not already in place at the works. In general, activated sludge is only used at larger treatment works, and so these works are more amenable to biological removal (around 200 plants over 10 000 pe have activated sludge plants in the UK). Most smaller plants only have conventional secondary treatment, and so the only on-site treatment option is some form of chemical dosing. Of the chemical processes, calcium dosing to produce calcium phosphates is probably the best environmental option since the resultant sludge is of higher agricultural value (where dosing occurs within the secondary treatment plant) and phosphorus can also be recovered for agro-industrial applications (if dosed into the effluent after secondary treatment), particularly for use as inorganic fertiliser. However, the source of raw calcium also needs to be considered, and weighed against the fact that industrial by-products can be used as a source of iron salts. Calcium dosing and appropriate management of magnesium and ammonium concentrations can produce struvite (magnesium ammonium phosphates and potassium ammonium phosphates), another material suitable for recovery.

It should be noted that biological removal is complex and water companies are only likely to favour its installation where the STW is sufficiently large for labour to be available for monitoring its performance (generally above 50 000 pe). However, on-line colorimetric methods exist for monitoring phosphorus concentrations in real time after floc settlement, whereupon chemical salts can be automatically added as required to make up for the variable biological performance. In well-run modern plants, only occasional chemical additions may be required to keep effluent concentrations under 2 mg l^{-1} (CEEP 1998a). In addition, removal is generally more consistent in summer (due to greater consistency in influent wastewater), a time when phosphorus loads from STWs are most critical ecologically (see Question 7).

As mentioned above, the most promising process for recovery of a relatively clean product for use in industry is calcium phosphate formation. An important calcium-based technique is a Dutch process called the Crystalactor. After removing carbon dioxide by degassing, the effluent is dosed with lime to precipitate calcium phosphate, with sand particles acting as the seeding agent for pellet growth. The pellets can be dried to below 5 - 10% water and contain 5 - 15% phosphorus (compared to around 20% in rock phosphate). A few full-scale plants are in operation in the Netherlands, whilst operational plants based on similar processes or struvite formation exist in Japan (CEEP 1998a). Phosphorus recovery is inevitably more economically viable at the largest works, but it remains to be seen how small a works can be before the approach becomes impractical. Importantly, the cost of establishing phosphorus-stripping can be partially offset by the sale of recycled phosphorus to industry, who can be expected to pay a small premium for the product compared to rock phosphate due to its relative purity.

Finally, magnetic removal and ion exchange processes should be mentioned since these are potentially available for use on wastewater and are amenable to phosphorus recovery for industrial use. Whilst pilot plants have been established and both processes are worthy of further investigation, their application to wastewater may be too problematic (CEEP 1998a). They are certainly not available as operational processes are present; however, a test plant operating in the US has produced reductions in total phosphorus from around 4 mg l^{-1} to less than 0.1 mg l^{-1} (CEEP 1998b).

Box 8. The processes of biological and chemical phosphorus removal.

Biological phosphorus removal

Biological phosphorus removal can at present only be achieved with a modified activated sludge process or modified biological aerated filters, which incorporate anaerobic and aerobic zones. In conventional biological treatment, removal of phosphorus by micro-organism accounts for up to 20% of the influent phosphorus, with primary sedimentation accounting for a further 15%. However, when the method of phosphorus removal by luxury uptake is used, more than 90% removal can be achieved.

Luxury uptake of phosphorus relies upon one particular group of aerobic bacteria, *Acinetobacter spp*, and the provision of anaerobic and aerobic conditions. Under anaerobic conditions, *Acinetobacter* are able to store short-chain fatty acids (SCFAs) such as acetates, present in the wastewater as soluble BOD material. The SCFAs can only be stored by deriving energy from the hydrolysis of intracellular stored polyphosphates. This results in the release of phosphate into solution. Then, on entering the aerobic zone, the bacteria oxidise the stored SCFAs and simultaneously take up orthophosphate, resulting in the removal of phosphorus from the liquid.

The efficiency of phosphorus removal depends upon the sludge production rate, the ratio of SCFAs to phosphorus and the phosphorus content of the sludge. The latter relies on a number of factors including:

- plant design and operation;
- the percentage of phosphorus-storing bacteria;
- the removal of nitrates and oxygen in certain zones of the plant, which can inhibit the release of phosphorus back into solution.

Numerous processes based on the anaerobic/aerobic sequence have been developed to improve P removal efficiency and maximise cost-effectiveness. The performance of different types of plant is variable, but many are able to achieve effluent P standards of 1-2 mg l^{-1}. Results show that average effluent concentrations of <1 mg l^{-1} are achieved only when the influent concentration is low (<4 mg P l^{-1}). To meet an average value of 2 mg l^{-1} the influent concentration must be about 8 mg l^{-1} However, these values are averages which mask the variability in effluent quality which can occur. To reduce this variability, most works include sludge fermenters to produce the SCFAs which are not always present in the sewage at high enough concentrations, thereby maintaining P removal efficiency during wet weather conditions when BOD loadings are low. In a further attempt to maintain high P removal efficiencies, some biological treatment plants utilise supplemental chemical dosing. A key advantage to biological stripping is that sludge production is no greater than that produced from conventional activated sludge plants (with the exception of those processes that add supplementary chemicals).

Chemical phosphorus removal

Phosphorus can be removed by precipitation with ionic forms of aluminum, iron and calcium, including aluminum sulphate, sodium aluminate, calcium hydroxide, ferric/ferrous chloride and ferric/ferrous sulphate. Of these, the latter is the most widely used, simply on the basis of cost. All sewage treatment works can employ chemical precipitation to remove phosphorus to concentrations of 1^{-2} mg l^{-1} or less in the effluent, provided four process criteria are met.

1. There must be adequate wastewater aeration time or contact time in biological treatment processes to ensure conversion of polyphosphates to orthophosphates prior to precipitation.
2. The optimum dosing point must be selected. Dosing points are: a) pre-primary tank, b) addition to the activated sludge plant, c) after treatment processes but before the final settlement tank, and d) tertiary precipitation with addition just before a tertiary or membrane filter to achieve concentrations of 1 mg l^{-1} or less.
3. Optimum use must be made of chemical addition by the provision of adequate mixing and flocculation.
4. Finally, the sludge flocs containing the precipitated phosphorus must be removed either by settlement or by filtration.

Sludge floc removal is achieved by settlement tanks, sometimes in conjunction with tertiary filtration. Tertiary filtration using either sand or membrane filters is required to achieve P levels below 1 mg l^{-1}, with around 0.5 mg l^{-1} being the lowest practical value. Chemical phosphorus removal will generate extra sludge, the amount is dependent on:

- site-specific waste water characteristics - higher influent P concentrations will produce more sludge;
- dosing rates - to attain lower effluent P concentrations, greater dosing rates and increased sludge production are required;
- point of dosing - dosing to the primary tank produces more sludge compared to addition after secondary treatment;
- sludge handling methods at the plant - to prevent recycling of P;
- the type of conventional biological treatment - high-rate plants produce more biological sludge.

The amount of sludge produced can be anything up to two to three times higher than conventional sewage treatment, depending on the flocculant dosing rate. Large increases in sludge production occur as phosphorus concentrations are progressively lowered below 2.0 mg l^{-1}. Importantly, calcium salts are generally (and best) added after sludge settlement, such that a relatively clean phosphorus sludge is produced that is suitable for industrial application. Since dosing occurs at the tertiary stage, the volume and composition of sludge produced during secondary treatment is unaffected.

Table 9. Advantages and disadvantages of chemical and biological phosphorus stripping (after Day and Cooper 1992).

Advantages	Disadvantages
Chemical P removal	
○ Reliable, well-documented technique ○ Chemical costs can be reduced substantially if waste pickle[1] liquors (ferrous chloride or ferrous sulphate) are available and can be used ○ Controls are simple and straightforward - easy to maintain high P removal efficiency by controlling metal salt dosing rate. ○ Relatively easy and inexpensive to install at existing facilities ○ Sludge can be processed in the same manner as in non-P-removal systems ○ Primary clarifier metal addition can reduce organic load to secondary unit by 25-35%.	○ Chemical costs higher than for biological systems. ○ Significantly more sludge produced than waste water treatment process without metal addition; may overload existing sludge handling equipment; higher sludge treatment and disposal costs. ○ Sludge does not dewater as well or as easily as conventional STW sludges where metal salts are not added. ○ Requires tertiary filtration to remove P in suspended solids. ○ Coloured effluents if iron salts are used. ○ Toxicity problems if the process is handled inefficiently.
Biological P removal	
○ The amount of sludge generated is comparable to conventional activated sludge systems. ○ Can be installed at existing plug-flow[3] activated sludge plants with little or no equipment changes or additions, provided that the plant has sufficient capacity. ○ Existing sludge handling equipment can be used at retrofitted plants, provided phosphorus is not solubilised and returned to the plant. ○ Little or no chemical costs nor handling equipment, except for PhoStrip process[2], metal salt supplement or for effluent polishing. ○ With some processes, P removal can be achieved together with nitrogen removal at virtually no additional operating cost. ○ Better control of filamentous organisms is possible in some systems.	○ In all but the PhoStrip[2] system, P removal per formance is controlled by the BOD:P ratio of the wastewater ○ Highly efficient secondary clarifier performance is required to achieve an effluent concentration of 1 mg P l^{-1}. ○ Not easily retrofitted into fixed-film biological systems. ○ Potential for P release in sludge handling system. Recycle streams have low P content. ○ Standby chemical feed equipment may be required in case biological P removal efficiency falls. ○ Sludge is often poor-settling. ○ Requires increased retention time in activated sludge plants.

1 Pickle liquors - waste product from metal processing that contains iron salts.
2 The Phostrip process - commonly used biological phosphorus stripping process.
3 Plug-flow - whereby BOD loading is delivered to the plant in discrete plugs associated with domestic behaviour.

Question 11. How extensive is the use of phosphorus-stripping within the UK and other European countries?

In the UK, the majority of sewage treatment works incorporate primary (solids separation) and secondary (typically biological filtration) treatment. Whilst there are notable exceptions in the UK, such as the installation of P-stripping at all of the major STWs feeding Lough Neagh during the 1970s, the primary driver for the installation of P-stripping in the UK has until recently been the Urban Waste Water Treatment Directive (see Box 1). At present, this provides the only mechanism available by which the existing and future extent of phosphorus-stripping in different Member States can be easily compared.

'Sensitive areas' have to be identified by Member States under the Directive, which relate to waters that are, or are in danger of becoming, eutrophic. Within sensitive areas, 'appropriate' treatment for nitrogen and/or phosphorus removal has to be installed at all works serving more than 10 000 population equivalents (the issue is generally phosphorus in freshwater). In the first round of identifying 'sensitive areas', 37 sites (including 23 river stretches) were designated within the UK as requiring the installation of P-stripping, constituting a small proportion of the total sewage effluent load generated in the UK (some 5.2% - IEEP 1999). In some of the designated catchments all major works were already equipped with P-stripping. Further designations have been made, but the revised list still constitutes a small proportion of the total sewage effluent load.

The criteria for designating sensitive waters are set on a national basis so there is plenty of scope for interpretation. The approaches of other Member States vary, but all of those in north-west Europe have taken a much stricter stance towards phosphorus control. In Denmark, the Netherlands, Sweden and Finland, the whole territory has been designated as sensitive area, whilst the majority of Germany and a large proportion of France have also been designated (IEEP 1999). The result is that phosphorus removal will be undertaken at nearly all works in north-west Europe that are over 10 000 pe.

The approaches of most of these north-west European countries go considerably further than required by the Directive. Germany, Denmark, the Netherlands and Sweden have very strict controls on phosphorus loads in effluents and have spent considerable effort on removing phosphorus from smaller works. Germany currently has around 900 plants removing phosphorus, compared to 23 plants operating in the UK by 1997 (IEEP 1999). Since these countries have been actively seeking phosphorus removal for some years, existing plants tend to utilize chemical removal with iron salts. However, practices are changing as new information and technology comes to light; for instance, the policy in Denmark has changed from iron-dosing to biological treatment where possible.

Question 12. ***How expensive is phosphorus-stripping?***

The capital and operating costs of chemical treatment are site-specific, depending very much on the existing infrastructure. Indicative costs are provided in Table 10 for: 1) a works built recently to meet a high effluent quality standard; 2) an older works requiring new settlement tanks and extra capacity for sludge treatment. When considering older works, it is important to separate out upgrade costs that may be required whether phosphorus removal is installed or not, in order to comply with more stringent requirements on BOD and ammonia.

The costs for biological removal are again very site-specific, and the estimates given in Table 10 give only a crude indication. For a very modern activated sludge works that has spare capacity and fully nitrifies and denitrifies, the extra capital and operational costs would be relatively small. In contrast, an old, existing works that does not have an activated sludge plant would require almost complete replacement of secondary treatment. No cost estimates are available for works below 100 000 pe.

Table 10. Indicative costs of phosphorus removal at STWs, including necessary upgrades to enable the installation of removal processes.

STW size (population equivalents)	2,000	10,000	50,000	100,000	250,000
Chemical removal					
a) Modern works					
Capital (£k)	60	100	150	200	250
Operating (£/yr)	3,000	11,000	60,000	110,000	150,000
b) Older works					
Capital (£k)	100	500 - 1,000	750 - 3,000	1 000 - 5,000	1,250 - 6,500
Operating (£/yr)	3,000	11,000	60,000	110,000	150,000
Biological removal					
a) Modern works with spare capacity					
Capital (£k)	N/A	N/A	N/A	500	1,000
Operating (£/yr)	N/A	N/A	N/A	N/A	N/A
b) Older works (no activated sludge)					
Capital (£k)	N/A	N/A	N/A	30,000	50,000
Operating (£/yr)	N/A	N/A	N/A	N/A	N/A

N/A Costs not available.

The treatment of a number of very small works (chemical removal is the only option) is inevitably more problematical than treatment at a single larger works of the same overall size. Aggregation of smaller works by installing linking pipes and pumping effluent is technically feasible; however, the issue has already been addressed under AMP1 and AMP2 and so the most cost-effective aggregations have probably already been undertaken. This said, it is possible that the viability of aggregation may change when phosphorus removal is added into the equation.

In terms of the cost of different chemical removal options, ferrous sulphate is the cheapest material, costing £32.50 per tonne compared to £65 for ferric sulphate and about £100 for lime (calcium). Ferrous sulphate is generally favoured by the water industry since it is the cheapest material, but it has to be made up into a solution from crystals (unlike ferric sulphate which is supplied as a solution). Lime is provided as a powder, which has to be made up as a suspension prior to dosing. The quantity of lime required is independent of phosphorus concentration but dependent on alkalinity. A relatively large amount has to be added to raise the pH sufficiently for calcium hydroxide to precipitate (which co-precipitates phosphorus).

It is important to remember that conventional chemical precipitation using iron or aluminium is not compatible with the recovery of phosphorus for industrial use (CEEP 1998a), which might otherwise offset the cost of phosphorus removal from the waste stream.

Question 13. What water quality changes can be expected as a result of stripping?

The reductions in total phosphorus concentrations that can be expected immediately downstream of STW discharges are indicated in Table 11 for a range of STW sizes and river flows. As the majority of phosphorus in domestic effluents is bioavailable, similar reductions can be expected in SRP concentrations. Perhaps the most striking aspect of these figures is the important effect that relatively small works (2000 pe) can have on phosphorus concentrations in smaller rivers, indicating that a great deal of ecological benefit can accrue in headwater areas from bringing small works into phosphorus control programmes. The case for considering small works is even more apparent if their high densities in many catchments are considered, in combination having a considerable influence even on larger rivers. Inevitably, there are cost implications of treating large numbers of small works compared to smaller numbers of large works, but the contribution of smaller works is likely to be too significant to ignore in many instances.

Table 11. Reductions in the contribution of STW discharges to riverine phosphorus concentrations (µg l^{-1} total phosphorus) as a result of phosphorus stripping.

River flow ($m^3\ s^{-1}$)	STW size (PE)	Secondary treatment	P stripping to 2 mg l^{-1}	P stripping to 1 mg l^{-1}	P stripping to 0.5 mg l^{-1}
1	500	11.1	2.57	1.30	0.64
	2,000	44.5	10.3	5.21	2.57
	10,000	222.6	51.4	26.0	12.8
	50,000	1113	256.8	130.2	64.2
5	500	2.23	0.51	0.26	0.13
	2,000	8.90	2.05	1.04	0.51
	10,000	44.5	10.3	5.21	2.57
	50,000	222.6	51.4	26.0	12.8
10	500	1.11	0.26	0.13	0.06
	2,000	4.45	1.03	0.52	0.26
	10,000	22.3	5.14	2.61	1.28
	50,000	111.3	25.7	13.0	6.42
50	500	0.22	0.05	0.03	0.01
	2,000	0.89	0.21	0.10	0.05
	10,000	4.45	1.03	0.52	0.26
	50,000	22.3	5.14	2.61	1.28

When stripping with iron salts, overdosing can lead to significant amounts of iron in the final effluent, generating an orange discoloration that affects the aesthetic quality of the receiving river. With properly managed dosing this effect can be minimised. The use of aluminium salts carries a risk of significant quantities of aluminium in the final effluent, so this treatment method should be avoided to protect both aquatic life and human health.

Question 14. What ecological improvements can be expected following water quality improvements?

A reduction in water column phosphorus concentrations down to near-background levels can be expected to minimise the risks of dominance by tolerant higher plants and algae associated with elevated trophic status. These reduced risks will help to restore a proper balance in the plant community, and will consequently promote more diverse habitat opportunities for aquatic fauna. However, there may be a large reservoir of phosphorus in riverine sediments (especially if these are mainly silts), and diffuse sources of phosphorus will still be contributing to this. Other mechanisms of impact (as discussed in Question 2) may also constrain the recovery of the plant community. Time may be required to flush phosphorus from the river, and it is possible that dredging or jet-hosing of phosphorus-rich sediments will be needed in some situations to expedite the process (see Question 15). Catchment measures to reduce diffuse losses of phosphorus to the river will be required to prevent further accumulation in sediment. Even if phosphorus concentrations are restored to near background levels, measures to address factors such as physical degradation of the river channel (over-widening, overdeepening), siltation, turbidity and artificially low flows may be needed on certain river reaches.

If a programme of phosphorus removal is applied to STWs in a catchment and no ecological improvements are observed, there are three possible explanations:

1. water column concentrations of bioavailable phosphorus have not been reduced sufficiently to influence the growth of algal species suppressing higher plant growth;

2. there is significant residual enrichment of riverine substrates with phosphorus (particularly on river reaches with significant silt deposits), which is adversely affecting the plant community (perhaps through phosphorus release into the water column or through the competition between benthic algae and the germination of the seeds of higher plants);

3. environmental factors other than phosphorus enrichment are contributing to the observed impoverished plant community.

A lack of immediate ecological benefits should not be interpreted as a lack of progress towards ecological restoration. Where a river suffers from a number of physical and chemical impacts, tackling one aspect of one impact cannot be expected to solve all problems on its own, even if it does constitute one of the key ecological constraints. A long-term perspective and an integrated approach to river rehabilitation is required to bring about stable and lasting ecological benefits.

Question 15. Is internal cycling of phosphorus within the river likely to be a problem and how can it be dealt with?

In rivers where inputs have been high for a long period of time, a reservoir of phosphorus can accumulate in the bed sediments that can continue to contribute to the nutrient status of the river after inputs have been reduced. This phosphorus can be taken up by plants directly from the sediment (via the roots of higher plants or through uptake by benthic algae), or following release into the water column (via the shoots of rooted plants or through uptake by epiphytic or epilithic algae). Importantly, the lower the target concentration set for phosphorus, the more influential internal sources are likely to be. The internal phosphorus reservoir is most likely to cause problems in sluggish river reaches with silty bed sediments (i.e. depositional zones), which provide a trap for phosphorus-rich particulates and a large capacity for adsorbing soluble phosphorus from the water column. In addition, anoxic conditions can occur in this type of sediment, which enhances the release rate of phosphorus (in addition to having direct impacts on the establishment, growth and function of the roots of higher plants).

Depending on local circumstances, it may be appropriate to dredge the surface layers of sediments out of depositional reaches of the river, in order to reduce the size of the internal reservoir. In gravels silted up with phosphorus-enriched silt, it may be useful to artificially clean the substrate (through raking or jet-hosing). Such action should be decided after an assessment of the importance of internal loading to the river in question, which would sensibly be based on measurements of the EPC and redox potential of the sediment. It should be remembered that dredging can have detrimental effects on instream habitats and can also reduce the capacity of the river to influence its own structure and interact with its floodplain. In addition, downstream habitats may be severely affected by heavy loads of silt washed out of upstream areas. Care should therefore be taken in the design of dredging operations to minimise ecological impacts. Finally, it is important that phosphorus inputs to the river are tackled holistically so that further accumulation is avoided - both point sources and diffuse sources contribute to the internal reservoir and therefore need to be addressed.

Question 16. If more phosphorus is stripped out of effluents into sewage sludge, is there a risk of long-term accumulation of phosphorus in the catchment?

The Sludge (Use in Agriculture) Regulations 1989 stipulate that sludge should be used in a way that takes account of the nutrient needs of the crop whilst not impairing the quality of the soil, groundwaters and surface waters. The Code of Practice for Agricultural Use of Sewage Sludge stipulates a maximum sludge application rate to agricultural land based on nitrogen content, amounting to 250 kg ha^{-1} yr^{-1} total nitrogen (which is equivalent to around 10 tonnes dry solids). This nitrogen-based restriction is intended to reduce nitrate levels in drinking water supplies, rather than to reduce eutrophication risk. There are no stipulations for phosphorus, even though such nitrogen deliveries would typically provide 125 kg ha^{-1} yr^{-1} total phosphorus using conventional sludges. This is far in excess of the phosphorus requirements of crops (Table 12) and provides large amounts of phosphorus for long-term accumulation in the soil and for loss to receiving waters. On the basis of phosphorus requirements, conventional sewage sludge should be applied at about half the rate currently recommended on the basis of nitrogen, equivalent to around 5 tonnes dry solids ha^{-1} yr^{-1}. Even without considering phosphorus stripping, this clearly has major implications for sludge application programmes across England and Wales.

Table 12. Typical phosphate removal by crops.

Crop	Typical yield (t ha^{-1} yr^{-1})	Phosphate uptake (kg P ha^{-1})
Grass	40	56
Cereal grain	7.5	59
Cereal straw	4.9	7
Oilseed rape	3.5	56
Potatoes	50	50

The phosphorus content in sludge enriched with stripped phosphorus will vary with the phosphorus removal efficiency of the works and other site-related factors (such as sludge imports to the works), but will generally lie in the range 2 - 3.5% (by dry weight) compared to 0.6 - 1.8% in conventional sludges. As a very crude rule of thumb, therefore, 1 tonne dry weight of enriched sludge provides the same amount of phosphorus as 2 tonnes of conventional sludge. This suggests that application rates of enriched sludge should be around half that of conventional sludge to achieve the same phosphorus loading. Taken in combination with the environmental need to base acceptable sludge application rates on phosphorus rather than nitrogen, this would result in a further reduction in application rates, down to around 2.5 tonnes ha^{-1} yr^{-1}. The lower bioavailability of phosphorus produced by iron - stripping complicates the issue, providing less phosphorus for the following crop but more for long-term accumulation in the soil.

The phosphorus content of sludges where chemical removal is used will be somewhat lower than for biological removal (since chemical removal generates more sludge), which means that application rates would not need to be reduced so far. However, sludge volumes from chemical removal are higher, to a degree depending on the target phosphorus concentration in the STW effluent, so the overall effect on sludge application programmes (in terms of the amount of land required) will probably be similar.

It is clear then, that if phosphorus accumulation in catchment soils and enhanced diffuse losses of phosphorus to receiving waters are to be avoided, sludge spreading programmes will have to be heavily modified in the future even if the phosphorus content of sludge remains at present levels. The issue becomes more acute when phosphorus stripping is employed, unless phosphorus is recovered from the waste stream and reused in agrochemical or other industrial applications. It is vital that the enriched sludge is tested regularly for phosphorus content, with application rates calculated on the basis of:

- existing soil phosphorus reserves;
- phosphorus requirements of the following crop.

Applications should not result in soil phosphorus levels exceeding Index value 3, unless the requirements of the particular crop being grown are so high that growth limitation would occur (this is highly unlikely in most instances - Index value 2 is adequate for grass and cereal crops, whilst 3 is generally adequate for vegetables).

It is critical that the additional phosphorus in enriched sludge *replaces* an equivalent part of the existing phosphorus load to agricultural land, with less inorganic fertiliser being applied as a result. If this can be achieved by revised programmes of sludge application, there will be no effect of phosphorus stripping on catchment phosphorus reserves. Importantly, sewage sludge currently constitutes only 1% of the total amount of phosphorus applied to land each year. If all STWs were upgraded to remove phosphorus, this would only increase to around 2%, with the large majority of the total load being derived from inorganic fertilisers. Major changes in attitude are therefore required to the use of inorganic fertilisers in agriculture if the large phosphorus reserves present in UK soils are to be brought down to environmentally acceptable levels (Mainstone *et al.* 1996).

Eliminating the potential for phosphorus accumulation in the catchment through the recovery of phosphorus from the waste stream is a major consideration for the future (see Question 10). Recovery processes generate no extra phosphorus in sludge (typically operating on the supernatant from secondary treatment) and so have no impact on current sludge spreading operations. In fact, some recovery processes can act on the sludge itself, thereby reducing current phosphorus levels and perhaps making nitrogen-based application rates environmentally appropriate.

Phosphorus recovered from STWs is potentially highly attractive to industry compared to rock phosphate (the current raw material used), generally having lower concentrations of troublesome contaminants (particularly heavy metals). In scavenging heavy metals from the wastewater stream, the recovery process reduces the metals load from STW with no disbenefit to industry (recovered phosphorus still contains levels of metals one or two orders of magnitude lower than rock phosphate - CEEP 1998a).

In short, phosphorus recycling for industry has the potential to replace a non-renewable resource with a sustainable reclaimed resource, benefiting the water industry in economic and regulatory contexts, and reducing the mass-transfer of phosphorus into UK catchments (thereby tackling eutrophication problems at their true source). Active encouragement of this approach is likely to bring considerable environmental benefits.

Question 17. Will associated contaminants in enriched sludge further restrict its use in agriculture relative to conventional sludge?

Limits are set in the Code of Practice for Agricultural use of Sewage Sludge for zinc, copper, nickel, cadmium, lead, mercury, chromium, molybdenum, selenium, arsenic and fluoride, as Potentially Toxic Elements (PTEs). These limits are not normally a problem for sewage sludges unless there is a high industrial content to the wastewater. However, if chemical P removal is practiced, the PTE content of sludge may be increased due to contaminants in the flocculant. This should be considered when addressing which method of phosphorus stripping might be appropriate for a plant - biological methods do not carry the same risks.

Where iron salts are used, enriched sludges typically contain 6% w/w Fe, which would not result in greatly increased concentrations in many soils. There are no maximum permissible concentrations for iron in soils or sludge and so this would not restrict sludge use. Toxic effects are possible with aluminium salts (particularly on acid soils) and this method of dosing cannot therefore be recommended.

When chemical dosing, it should be noted that the use of iron salts results in phosphorus in sludge being less available to crop growth compared to conventional sludges. This paradoxically lessens the nutritive value of the enriched sludge in agriculture, such that it becomes less attractive to farmers. This could have consequences for maintaining and increasing the land area available for disposal. The use of calcium salts is a more attractive proposition agriculturally, since the calcium helps to regulate the bioavailability of phosphorus in the soil (Mainstone *et al.* 1996).

Question 18. How should decisions be made for a specific catchment/river?

The complex nature of competition within plant communities and the interaction of nutrient enrichment with many other anthropogenic impacts means that the ecological benefits accruing specifically from a nutrient reduction programme cannot be stated with any certainty. This makes the development of a business plan for investment a difficult process and requires that a more pragmatic, precautionary approach is taken to evaluating the need for investment in phosphorus removal.

The steps involved in developing a phosphorus control programme at a catchment level are outlined in Figure 9, along with references to where further guidance can be found in this document. In general, point sources (and in particular sewage treatment works), can be expected to be a high priority in control programmes even if their contribution to the annual phosphorus budget is relatively small, representing discrete and highly treatable sources that provide very bioavailable phosphorus to the water column at a time of minimum dilution and maximal plant activity. Diffuse loads need to be assessed in relation to their incorporation into riverine sediments and their subsequent utilisation by the plant community. In terms of control, diffuse loads need to be evaluated at sufficient resolution to identify high risk areas within the catchment, using modelling techniques but also including field investigations of run-off pathways and land management (in relation to factors such as the size of the soil phosphorus reserve and levels of erosion risk), so that resources invested in the promotion and implementation of best practices has greatest benefits.

Even the smaller point sources need to be considered for treatment since in combination they can have significant effects, particularly in headwater areas where relatively small loads are required to induce ecologically relevant enrichment. The largest works will not always be the most critical in relation to establishing phosphorus-stripping; position in the catchment is important, and it may be that removing phosphorus from smaller works upstream will have greater benefits to the river as a whole than treating a larger works in the lower reaches. When phasing phosphorus removal at a range of works within a catchment, it makes sense ecologically to focus on headwater areas and work downstream, assessing chemical and biological benefits along the way.

Table 13 gives a summary of the options for removing phosphorus from effluents, indicating the environmental desirability of each. The appropriate strategy for smaller point sources needs to be considered carefully in relation to local circumstances. There may be opportunities for transferring effluents from smaller works to larger works where phosphorus removal is more cost-effective and more environmentally desirable processes can be used (particularly in relation to recovery for agro-industrial reuse). However, these smaller works typically return waters to the river that have been abstracted within the catchment, such that transfer downstream to larger works can extend the zone of hydrological impact. One possibility for avoiding adverse effects is to pump stripped effluent back up the catchment, but the feasibility of such mitigation measures will vary greatly between works.

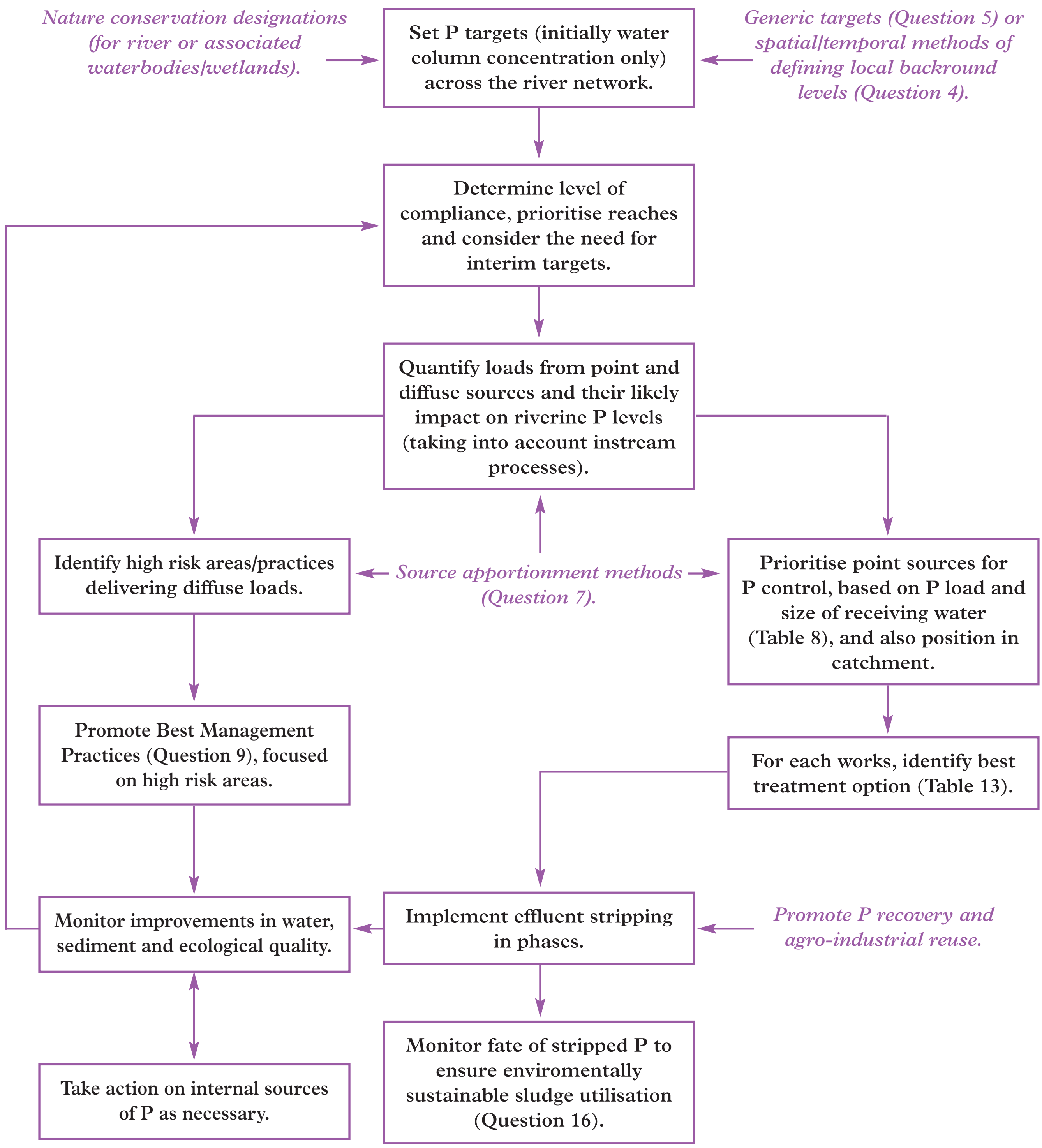


Figure 9. Process diagram for developing a phosphorus control strategy within a river catchment, with links to information in this document.

Table 13. Guide to the environmental desirability of different phosphorus stripping treatments.

Treatment type	Without P recovery	With P recovery
Biological treatment	8	10
Calcium phosphare/struvite recovery	N/A	10
Other novel P recovery techniques (e.g. ion exchange)	N/A	Evaluate method individually
Where the above are not feasible (due to works size/capacity constraints)		
Re-routing effluent to larger works where above options are in place or viable*	8	10
Calcium dosing	6	10
Iron dosing	4	Not possible
Aluminium dosing	0	Not possible

Numbers are subjecting ratings on a ten-point scale, with 10 representing the most desirable options.

* Care needs to be taken over potential hydrological effects associated with moving points of effluent discharge.

A case study of phosphorus stripping - The Great Ouse catchment

The upper reaches of the Great Ouse and its headwater tributaries (the Ivel and Ouzel) are highly nutrient enriched, with higher plant communities heavily impacted and displaying Mean Trophic Rank values of between 25 and 35 (Rose and Balbi 1997). SRP and Total Phosphorus levels are extremely high, with summer concentrations frequently reaching 2-3 mg l^{-1} at sites on the Ivel, Ouzel and the main Great Ouse. A trial programme of phosphorus stripping was undertaken at selected major STWs between June 1993 and December 1994 to assess the benefits to water quality. The effects on SRP concentrations in the river have been dramatic at a number of monitoring sites, compared to concentrations after stripping was discontinued (Figure 10). The effect is particularly apparent over the growing season, when the impact of STW discharges is most apparent due to low effluent dilution.

The very large summer peaks in SRP (combined with the fact that SRP constitutes the vast majority of phosphorus in the water column in these rivers) points to the importance of STWs as a phosphorus source, and this is supported by the observed impact of trial stripping at some of the major works (Cotton Valley and Bedford). The efficacy and duration of stripping varied between STWs, with Dunstable and Chalton effluents being stripped for a considerably shorter period and with significantly less effect in terms of load reduction. This is reflected in the greatly reduced benefits to downstream water quality compared to monitoring sites downstream of Cotton Valley and Bedford STWs. Small STWs have been estimated as contributing a considerable load, particularly on the Ivel where Chalton STW only accounts for a quarter of the SRP load from STWs. This also helps to explain the modest improvements made to SRP levels in the Ivel by stripping at Chalton, and highlights the need to look at the cumulative impact from minor works in addition to tackling the most obvious discharges.

Whilst SRP levels during the period of stripping are still much higher than desired, the considerable improvements to nutrient status generated by targeting the four largest works are extremely encouraging, particularly considering the long river stretches over which improvements have been observed. The targeting of smaller works and greater control of non-point sources may well bring SRP levels down to concentrations that would permit the recovery of higher plant communities, in addition to greatly reducing phosphorus loads to Grafham Water and other wetlands in the catchment (such as the Ouse Washes) which are suffering from enrichment problems (Mainstone *et al.* 1998). In addition, the efficiency of phosphorus removal can be improved compared to that observed in the trial at Dunstable and Chalton STWs. The efficiencies achieved at Cotton Valley and Bedford STWs approach the best achievable by current methodologies, where effluent concentrations fell to 0.68 and 0.95 mg l^{-1} respectively (producing associated reductions in SRP loads of 82.5 and 77.5%).

It is important to recognise that phosphorus stripping on this type of river may take some time to realise its full benefits, owing to the large phosphorus reservoir in riverine sediments. Whilst the immediate water quality benefits are very obvious, further benefit should accrue over time, particularly if progress is made in reducing diffuse loads.

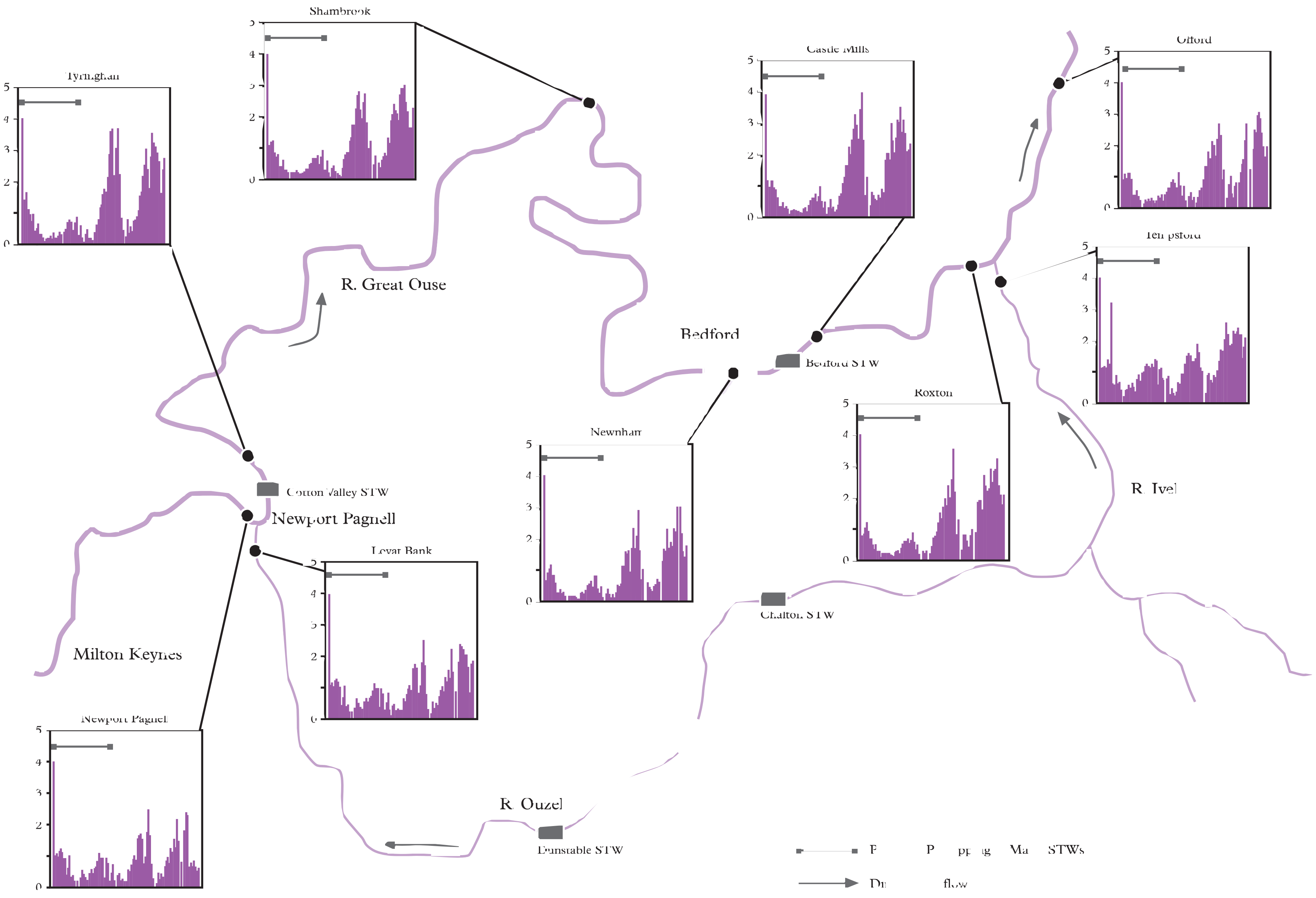


Figure 10. Effect on riverine SRP levels ($mg l^{-1}$) of phosphorus stripping at major sewage treatment works in the upper Great Ouse catchment (after Rose and Balbi 1997).

Appendix A - What are the main forms of phosphorus in rivers?

Phosphorus can exist in many forms, including inorganic soluble forms, organic bioavailable and non-bioavailable forms, and attached to particulates. This latter condition includes 'labile' phosphorus that is only loosely attached to particles, and firmly bound phosphorus that has been incorporated into the matrix of the particles. Phosphorus immediately available for plant growth (i.e. bioavailable phosphorus) essentially consists of inorganic soluble forms, organic forms of low molecular weight, and labile phosphorus that can rapidly desorb from particulates under certain conditions. Phosphorus in complex organic compounds will be released as the compounds are broken down by biological processes, whilst the long-term availability of phosphorus firmly bound to particulates is unclear.

Figure A1 shows the relationships between the analytical determinands used to measure phosphorus in aquatic systems. The most well-known parameter is Soluble Reactive Phosphorus (SRP), also known as Molybdate Reactive Phosphorus (MRP), Dissolved Reactive Phosphorus (DRP) or loosely as 'orthophosphate' (this latter term is actually only a theoretical parameter and cannot be measured analytically). SRP is a combination of many different forms of phosphorus, including inorganic phosphates (such as PO_4^{3-} and HPO_4^{2-}) and organic forms and inorganic polyphosphates that are hydrolysed during the analytical process. It is considered to be a reasonable approximation of bioavailable phosphorus, although the determinand Biologically Available Phosphorus (BAP) is measured by algal bioassay.

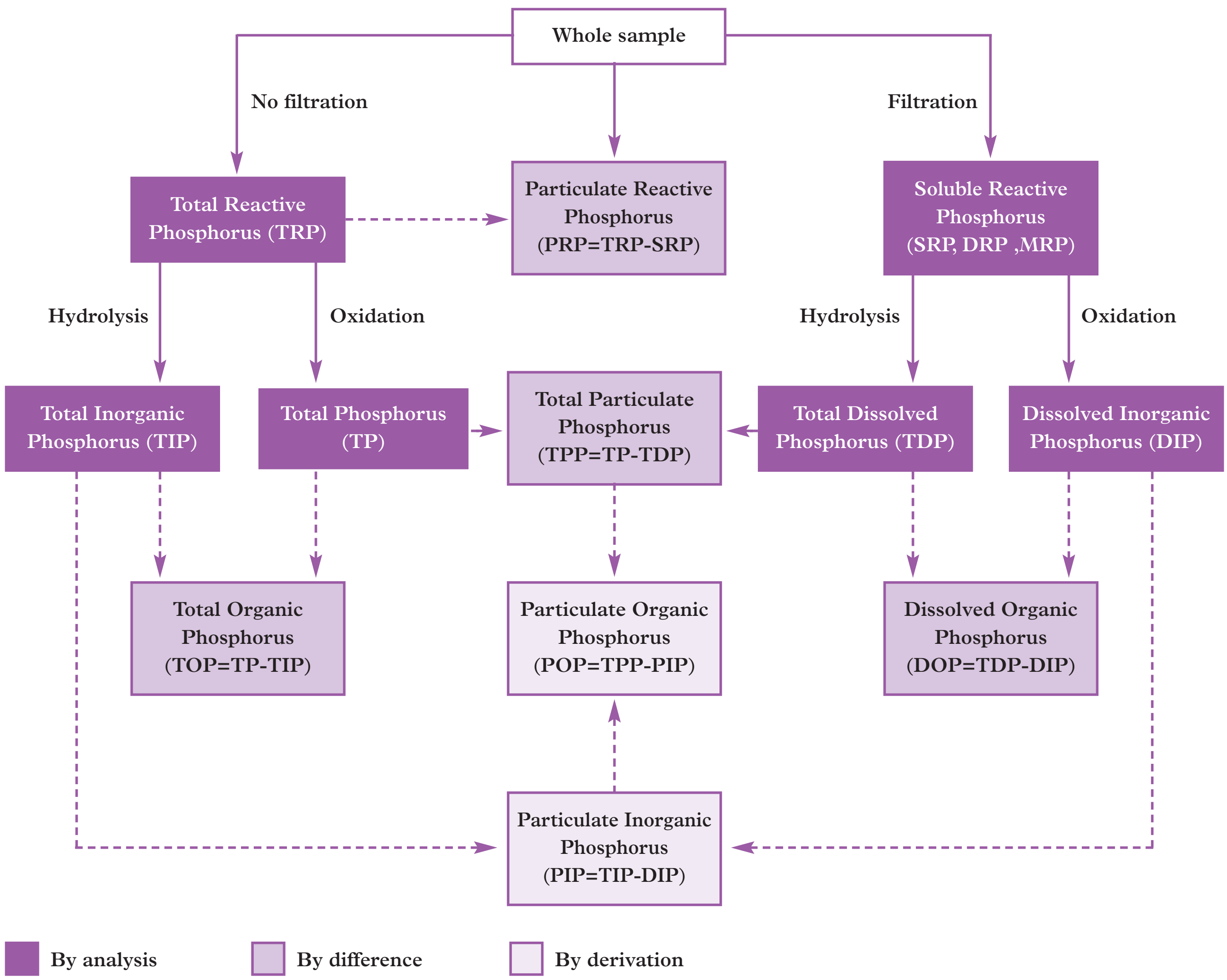


Figure A1. The relationship between different phosphorus determinands (modified from SCA 1981).

Total Reactive Phosphorus (TRP) is derived from the same analytical procedure as SRP but without first filtering the sample, thereby incorporating any labile phosphorus attached to particulates that desorbs during the analysis. The difference between SRP and TRP is usually small (e.g. Foster *et al.* 1996) but can be significant in certain situations. It is important to draw attention to the difference between these determinands, since the Environment Agency actually measures TRP and not the more commonly accepted SRP. To avoid further confusion within the Agency (who still commonly use the term SRP when reporting), the term SRP is adopted in this document when discussing Agency data; however, it should be noted that this is not the correct terminology and that the Agency should adopt the correct term in the future. The other common phosphorus determinand that is measured by the Agency at some riverine sites is Total Phosphorus, which includes all forms of phosphorus including many forms that are not immediately bioavailable. It may be taken as a measure of the longer-term potential for supplying phosphorus to plants, but in reality some of this phosphorus may never become bioavailable.

One last determinand that should be mentioned but does not feature in Figure A1 is the Equilibrium Phosphate Concentration (EPC), which is an important measure of the propensity of particulates to release soluble phosphorus into the water column or sediment pore water. It is defined as the SRP concentration in the water column (or pore water) that produces no net flux of dissolved phosphorus to or from the sediment particles. This determinand will be crucial in the future to our understanding of fluxes between the particulate and dissolved phases, and in particular the release of phosphorus from riverine bed sediments.

Appendix B - How does phosphorus behave in river systems?

Phosphorus is delivered to the river system from a range of sources, varying in its bioavailability from source to source. The load from point sources (which are dominated by sewage treatment works) is typically highly bioavailable and is delivered along with considerable loads of readily degradeable organic material. The delivery of diffuse loads is more complicated (Figure B1) and highly seasonal, but is largely dictated by the strong affinity of phosphorus for particulates. The majority of the annual load is therefore generally delivered in surface run-off attached to soil particles. However, much higher proportions of soluble phosphorus occur when livestock excreta (in forms such as slurry and 'dirty water') or soluble inorganic fertilisers are washed off the land soon after application.

Sub-surface drainage and leaching may be important pathways under certain conditions, particularly if the soil is overloaded with phosphorus. Sandy soils and underlying sandstone geology are particularly vulnerable since they have a very low adsorption capacity for phosphorus. Other soils and geologies are less vulnerable, but may be more at risk than supposed due to macropore and fissure flow within the soil/rock structure.

Once in the river, phosphorus is highly chemically and biologically active, undergoing numerous transformations and moving between the particulate and dissolved phases, between the sediment and water column, and between the biota and abiotic environment (Figure B2). Physical deposition and resuspension of particulates are obvious methods of phosphorus transfer between the water column and bed sediments, but direct adsorption/desorption processes between the two compartments are also important and will depend upon the EPC of the sediment, SRP levels in the overlying water, and current velocity (the latter dictating the sharpness of the diffusion gradient).

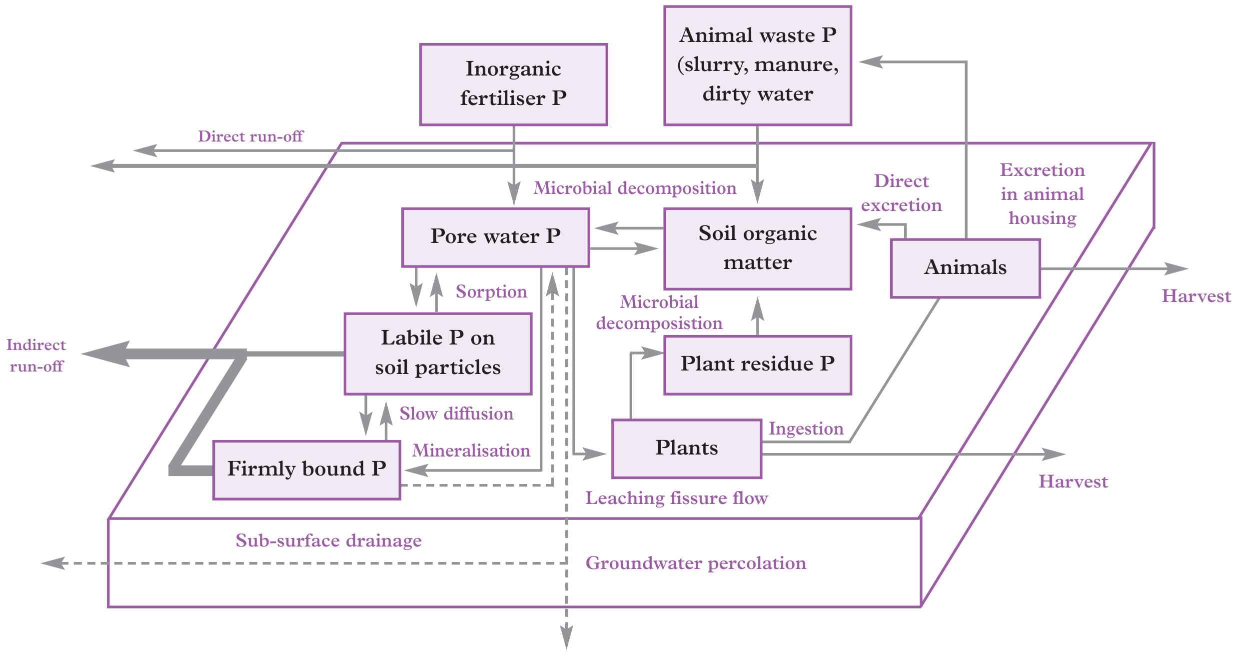


Figure B1. Phosphorus behaviour in soils and pathways to river (after Mainstone* et al. *1996). Width of line indicates importance of pathway, dotted lines indicate pathways that are usually minor but may be significant in certain situations.

Labile phosphorus attached to suspended particulates can rapidly desorb into the water column and become bioavailable, again depending upon the EPC of the particles and the SRP concentration in the water column. Firmly held phosphorus deep within the particle matrix can diffuse slowly into the water column, most likely to be an important mechanism for the river once particulates have settled as bed sediments. Soluble phosphorus can be incorporated into inorganic phosphate minerals by precipitation, particularly in association with calcium (in hardwater rivers), iron and aluminium (in softwater rivers). Precipitation of soluble phosphorus with calcium is particularly likely to occur below sewage treatment works in rivers with calcareous waters (e.g. House and Denison, 1997), where both calcium and soluble phosphorus concentrations are very high. Colloids of calcium phosphate minerals can be generated in the water column, whilst algal biofilms are thought to be involved in the coprecipitation of calcite and phosphorus onto bed sediments and plants (Hartley 1997).

Rooted aquatic plants are capable of deriving much, if not all, of their phosphorus requirements from the sediment, but there is considerable debate about the relative importance of root (via the sediment) and shoot (via the water column) uptake in real systems. Some studies have suggested that the uptake of phosphorus directly from the water column can be very important (Robach *et al.* 1995, 1996), particularly when SRP concentrations in the overlying water are higher than in sediment pore waters (Pelton *et al.* 1998). However, contrary to some beliefs, shoot uptake appears to have the potential to be important even at low water column concentrations of SRP (Pelton *et al.* 1998). Filamentous, epiphytic and planktonic algae generally take phosphorus directly from the water column by necessity, although benthic algae (including filamentous mats) will utilise both sources and epiphytic algae can derive some nutrition from the host plant. Microbial uptake from the water column and more particularly within the sediment can be substantial. Decay of plant shoots and the mineralisation of organic matter by the microbial community will lead to phosphorus release into both sediment pore waters and the water column, offset to varying degrees by uptake by higher plants and algae.

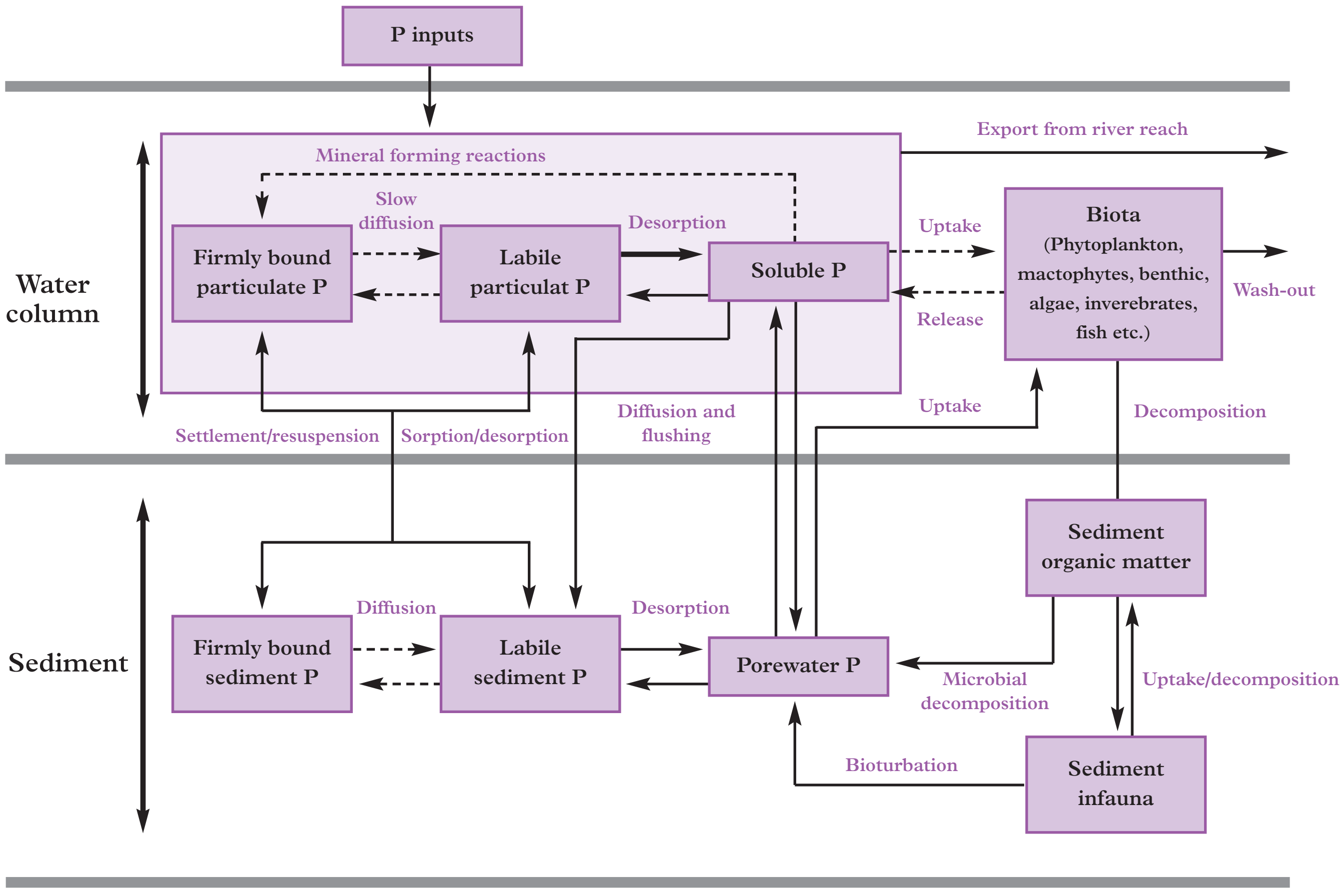


Figure B2. Phosphorus behaviour in rivers (after Mainstone* et al. *1996).
Width of line indicates importance of pathway, dotted lines indicate pathways that are usually minor or are of unknown importance.

The combination of all of these processes, in tandem with variations in river flow and other environmental factors (such as temperature), leads to a strong seasonality in phosphorus behaviour. Phosphorus will tend to be taken up and retained in the sediment and the biota (higher plants, algae and bacteria) through the summer months, whilst much of the accumulated load will be scoured and sorbed out during the high flows of autumn and winter (depending upon the strength of winter flows). Strong microbial activity in the spring can produce a significant flush of phosphorus from the sediment in advance of strong biological uptake through the growing season. Seasonal patterns in the phosphorus loads from different sources add a further layer of complexity (see Question 7).

Inevitably, the importance of different processes will vary greatly between rivers types. In very swift flowing river reaches, substrates will be coarse and areas of sediment deposition restricted, leading to limited accumulation of phosphorus within the sediment over the summer months. The high scouring velocities are unfavourable to plant growth and much water column SRP goes unutilised down the river. In sluggish river reaches, the fine sediments and low bed velocities create ideal conditions for the accumulation of phosphorus and the potential for subsequent biological utilisation. Populations of higher plants and planktonic, epiphytic, benthic and/or filamentous algae can strip SRP out of the water column to leave very low levels through the summer months, even though the river is highly enriched.

It quickly becomes clear that the monitoring of SRP alone is insufficient to fully understand the nutrient status of a river reach. The additional assessment of Total Phosphorus and the occasional monitoring of sediment EPC would provide a more meaningful (though by no means comprehensive) appraisal.

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This is one of a range of publications published by English Nature, Northminster House, Peterborough, PE1 1UA.
World Wide Website: http://www.english-nature.org.uk

ISBN 1 85716 505 5

Designed by Status Design & Advertising. Printed by Stanley L. Hunt (Printers) Ltd, 3m. Printed on Evolve Satin, 75% Recycled Paper, Elemental Chlorine Free.